

Experimental Investigations and Modeling of Mixed Thermoplastics Pyrolysis for Chemical Recycling

Zur Erlangung des akademischen Grades eines
DOKTORS DER INGENIEURWISSENSCHAFTEN (DR.-ING.)

von der KIT-Fakultät für Chemieingenieurwesen und Verfahrenstechnik des
Karlsruher Instituts für Technologie (KIT)
genehmigte

DISSERTATION

von

Niklas Netsch, M. Sc.
aus Bensheim

Tag der mündlichen Prüfung: 3. September 2026

Erstgutachter: Prof. Dr.-Ing. Dieter Stapf

Zweitgutachter: Prof. Dr. Reinhard Rauch



Except for Publication 1 (Netsch, Niklas; Zeller, Michael; Richter, Frank; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2024): Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Prediction and Pilot-Scale Validation. ACS Sustainable Resource Management, 1 (7), 1485-1492. DOI: 10.1021/acssusresmgt.4c00109; © 2024 American Chemical Society, reused with permission), this work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License (CC BY-SA 4.0):

<https://creativecommons.org/licenses/by-sa/4.0/>

Abstract

The global increase in plastic waste and its persistently low recycling rates pose an ecological and climate policy challenge. Chemical recycling of plastic waste is becoming increasingly important in the context of the EU's European Green Deal and Circular Economy Action Plan. It enables the use of heterogeneous, mechanically non-recyclable waste streams within a circular economy framework, thereby reducing environmental and climate impacts. Among thermochemical processes, pyrolysis is considered a promising option because of its high feedstock flexibility. However, its industrial implementation is limited by an insufficient process understanding, scale-up limitations, and a pyrolysis oil quality that does not meet common fossil-oriented specifications.

The objective of this dissertation is to investigate the fundamental influences of plastic composition as well as reactor parameters affecting the heat and mass transfer during the pyrolysis of thermoplastic mixtures. Four key evaluation criteria for plastic pyrolysis are examined in detail. These include decomposition kinetics, product yields, the composition of gaseous and condensable products, and the process energy demand.

The research approach combines thermal analysis methods, pyrolysis experiments in laboratory- and bench-scale reactors, and model-based calculations. The diversity of different polymer types in plastic waste is represented by considering the most produced thermoplastics: polyethylene (PE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET), polyamide 6 (PA6), and polyvinyl chloride (PVC). Thermogravimetry is used to characterize the decomposition mechanisms of the individual polymers and polymer mixtures. Endothermic and exothermic processes are determined using differential scanning calorimetry. A continuously operated screw reactor and a newly developed, semi-continuously operated stirred-tank reactor enable the comparison of both reactor systems. In addition to reference mixtures, a defined thermoplastic post-consumer waste is investigated. To estimate the energy demand, product yield, and product composition, a superposition-based model is applied. This model is based on linear combinations of the pyrolysis behavior of the individual polymers in the mixture. Detailed chemical analyses of the complex oil composition are performed using a novel two-dimensional gas chromatography method introduced within this work. Fundamental findings on decomposition kinetics and associated product formation in thermoplastic mixtures form the basis for investigating a temperature-staged pyrolysis concept. This concept specifically exploits kinetic differences between individual polymer types to optimize product yield and product quality in the chemical recycling of plastic waste.

The results reveal the dominant influence of feedstock composition on pyrolysis behavior. Pure polymers differ significantly in their decomposition mechanisms and product yields from one another. Polyolefins and styrene-based polymers react via radical mechanisms with high oil contents, while heteroatom-containing polymers such as PET, PA6, or PVC exhibit different reaction pathways.

Structure-dependent polymer-polymer interactions between intermediate pyrolysis products occur in complex polymer mixtures. These interactions are particularly pronounced for combinations of PVC, PA6, and PET. They lead to an accelerated decomposition reaction, increased gas and coke formation, and increased transfer of heteroatoms between the pyrolysis products. Differing polymer types only have a minor effect on the pyrolysis energy demand. Although intense interactions lead to its slight

increase, their effect is limited, causing an energy demand between 4 and 6% of the calorific value of the polymers.

The superposition approach enables reliable prediction of the energy demand, product yield, and product composition for non-interacting polymer blends consisting of polyolefins and PS. However, for more complex mixtures comprising the heteroatom-containing polymers PET, PA6, and PVC, the approach is not applicable, as interaction reactions alter the reaction mechanisms. Thus, the heteroatom-containing impurities in the pyrolysis products cannot be reliably predicted.

Besides the feedstock, the reactor type also has a major impact on the pyrolysis result. Differences in heat transfer, gas residence time distribution, and material mixing in pyrolysis reactors lead to varying product yields and compositions. Because of reactor-specific temperature gradients, the actual polymer temperature profile deviates significantly from the set reactor temperature. For example, the average polymer temperature during the reaction in the stirred tank reactor is up to 50 °C lower than the set reactor temperature of 500 °C. Compared to the stirred tank reactor, the longer gas residence time in the screw reactor promotes secondary cracking reactions. The secondary cracking increases the gas formation in the present investigations by up to 22 m.% and shifts the oil composition towards low-molecular-weight products. In complex mixtures, the feedstock-specific interactions overlap these reactor-specific effects. This hinders the comparability and scalability of pyrolysis results between different reactor systems. However, fundamental recommendations for process design can be derived from the results of this work. The proportion of heteroatom-containing polymers in the feedstock should be minimized to reduce heteroatom contamination in the product and thus the effort required for downstream oil treatment. Furthermore, continuous supply of feedstock, maximum efficiency in heat transfer, and short gas residence times are crucial for controlled process management.

The results of temperature-staged pyrolysis highlight the approach's potential for process optimization within the framework of chemical recycling. The concept enables the selective production of an aliphatic-rich oil fraction with significantly reduced heteroatom and aromatic content. It can therefore be used to improve the pyrolysis oil quality. However, there is an optimization conflict between achieving the maximum yield while maintaining a high quality of this oil fraction. Because of the reactor characteristics, the parameter optimization must be carried out on the pyrolysis system, as heat and mass transfer limitations impede direct scale-up from laboratory experiments. Finally, the approach requires further technoeconomic evaluation.

The findings on interaction effects, the scope of validity of superposition-based modeling, the interplay of feedstock- and reactor-specific impacts, and the suitability of the temperature-staged pyrolysis provide an important foundation for further investigations on the pyrolysis behavior of plastic mixtures.

Kurzfassung

Die weltweit steigende Menge an Kunststoffabfällen sowie anhaltend niedrige Recyclinganteile stellen eine ökologische und klimapolitische Herausforderung dar. Im Rahmen des „European Green Deal“ und des „Circular Economy Action Plans“ der EU gewinnt das chemische Recycling von Kunststoffabfällen zunehmend an Bedeutung. Es ermöglicht die Nutzung heterogener, mechanisch nicht recycelbarer Abfallströme in einer Kreislaufwirtschaft und trägt dadurch zur Reduktion von Umwelt- und Klimaauswirkungen bei. Unter den thermochemischen Verfahren gilt die Pyrolyse aufgrund ihrer hohen Einsatzstoffflexibilität als vielversprechend. Ihre industrielle Umsetzung ist jedoch durch unzureichendes Prozessverständnis, begrenzte Skalierbarkeit sowie eine Pyrolyseölqualität eingeschränkt, die nicht den Spezifikationen konventioneller fossiler Produkte entspricht.

Das Ziel dieser Dissertation besteht darin, die grundlegenden Einflüsse der Kunststoffzusammensetzung sowie der den Wärme- und Stofftransport beeinflussenden Reaktorparameter bei der Pyrolyse thermoplastischer Mischungen zu untersuchen. Der Fokus liegt dabei auf den vier zentralen Bewertungskriterien der Kunststoffpyrolyse. Zu diesen zählen die Zersetzungskinetik, die Produktausbeute, die Zusammensetzung der gasförmigen und kondensierbaren Produkte sowie der Energiebedarf des Prozesses.

Der Forschungsansatz basiert auf einer Kombination aus thermischen Analysemethoden, Pyrolyse-Experimenten im Labor und modellbasierten Berechnungen. Die Vielfalt der verschiedenen Polymertypen in Kunststoffabfällen wird durch die Berücksichtigung der meistproduzierten Thermoplaste abgebildet: Polyethylen (PE), Polypropylen (PP), Polystyrol (PS), Acryl-Butadien-Styrol (ABS), Polyethylenterephthalat (PET), Polyamid 6 (PA6) und Polyvinylchlorid (PVC). Zur Charakterisierung der Zersetzungsmechanismen der einzelnen Polymere und Polymermischungen wird Thermogravimetrie genutzt. Endotherme und exotherme Vorgänge werden mittels Differenzkalorimetrie ermittelt. Ein kontinuierlich betriebener Schneckenreaktor sowie ein neu entwickelter, semikontinuierlich betriebener Rührkesselreaktor ermöglichen den Vergleich beider Reaktorsysteme. Hierzu wird neben Referenzmischungen auch ein definierter thermoplastischer Post-Consumer-Abfallstrom verwendet. Zur Abschätzung des Energiebedarfs, der Produktausbeute und der Produktzusammensetzung wird ein superpositionsbasiertes Modell herangezogen. Dieses Modell basiert auf Linearkombinationen des Pyrolyseverhaltens der Einzelpolymere in der Mischung. Die detaillierte chemische Analyse der komplex zusammengesetzten Pyrolyseöle erfolgt mittels einer neu entwickelten zweidimensionalen Gaschromatographie-Methode. Die Erkenntnisse zur Zersetzungskinetik und der damit verbundenen Produktbildung in thermoplastischen Kunststoffmischungen bilden die Grundlage für die Untersuchung eines temperaturgestuften Pyrolysekonzepts. Dieses Konzept nutzt kinetische Unterschiede zwischen einzelnen Polymertypen gezielt aus, um die Produktausbeute und Produktqualität im chemischen Recycling von Kunststoffabfällen zu optimieren.

Die Ergebnisse zeigen den dominierenden Einfluss der Einsatzstoffzusammensetzung auf das Pyrolyseverhalten. Reine Polymere unterscheiden sich deutlich in ihren Zersetzungsmechanismen und Produktausbeuten. Polyolefine und styrolbasierte Polymere reagieren überwiegend über radikalische Mechanismen und führen zu hohen Ölanteilen, während heteroatomhaltige Polymere wie PET, PA6 oder PVC abweichende Reaktionspfade aufweisen. In Polymermischungen treten strukturabhängige Polymer-

Polymer-Wechselwirkungen zwischen intermediären Reaktionsprodukten auf. Diese sind besonders bei Kombinationen aus PVC, PA6 und PET ausgeprägt. Sie führen zu einer beschleunigten Zersetzungsreaktion, zu einer erhöhten Gas- und Koksbildung sowie zu einem verstärkten Heteroatomtransfer zwischen den Pyrolyseprodukten. Der Energiebedarf des Pyrolyseprozesses wird durch die verschiedenen Polymertypen nur in geringem Maße beeinflusst. Zwar führen intensive Interaktionen zu einer leichten Erhöhung des Energiebedarfs, ihr Einfluss bleibt jedoch begrenzt, da dieser zwischen 4 und 6 % des Heizwertes der eingesetzten Polymere liegt.

Der Superpositionsansatz ermöglicht eine zuverlässige Vorhersage des Energiebedarfs, der Produktausbeute und der Produktzusammensetzung für nicht interagierende Polymermischungen aus Polyolefinen und PS. Für komplexere Mischungen aus den heteroatomhaltigen Polymeren PET, PA6 und PVC ist der Ansatz jedoch nicht anwendbar, da Interaktionsreaktionen die Reaktionsmechanismen verändern. Heteroatomanteile in den Pyrolyseprodukten können daher nicht zuverlässig vorhergesagt werden.

Neben dem Einsatzstoff hat auch der Reaktortyp erheblichen Einfluss auf das Pyrolyseergebnis. Unterschiede im Wärmetransport, in der Gasverweilzeitverteilung und in der Materialdurchmischung der Pyrolysereaktoren führen zu variierenden Produktausbeuten und -zusammensetzungen. Aufgrund reaktorspezifischer Temperaturgradienten weicht die tatsächliche Polymertemperatur im zeitlichen Verlauf deutlich von der eingestellten Reaktortemperatur ab. So ist die mittlere Polymertemperatur während der Reaktion im Rührkesselreaktor beispielsweise bis zu 50 °C niedriger als die eingestellte Reaktortemperatur von 500 °C. Im Vergleich zum Rührkesselreaktor fördert die längere Gasverweilzeit im Schneckenreaktor sekundäre Spaltungsreaktionen. Diese erhöhen den Gasanteil in den vorliegenden Untersuchungen um bis zu 22 m.% und verschieben die Ölzusammensetzung in Richtung niedermolekularer Produkte. In komplexen Mischungen überlagern die einsatzstoffspezifischen Interaktionen diese reaktorspezifischen Effekte. Dadurch werden Vergleichbarkeit und Skalierbarkeit von Pyrolyseergebnissen zwischen unterschiedlichen Reaktorsystemen erschwert. Aus den Ergebnissen dieser Arbeit lassen sich jedoch grundlegende Empfehlungen für die Prozessauslegung ableiten. So sollte der Anteil heteroatomhaltiger Polymere im Einsatzstoff minimiert werden, um Heteroatomverunreinigungen im Produkt und damit den Aufwand für die nachgeschaltete Ölaufbereitung zu reduzieren. Eine kontinuierliche Beschickung mit Einsatzstoff, ein möglichst effizienter Wärmetransport und kurze Gasverweilzeiten sind entscheidend für eine kontrollierte Prozessführung.

Die Ergebnisse der temperaturgestuften Pyrolyse verdeutlichen das Potenzial zur Prozessoptimierung im Kontext des chemischen Recyclings. Das Konzept ermöglicht eine selektive Gewinnung einer aliphatenreichen Ölfraction mit deutlich reduziertem Heteroatom- und Aromatengehalt. Es kann somit zur Verbesserung der Pyrolyseölqualität beitragen. Dabei besteht jedoch ein Zielkonflikt zwischen einer möglichst hohen Ausbeute und der Qualität dieser Ölfraction. Die erforderliche Parameteroptimierung muss aufgrund der Reaktorcharakteristika am Pyrolysesystem selbst erfolgen, da Wärme- und Stofftransportlimitierungen eine direkte Hochskalierung von Laborexperimenten erschweren. Zusätzlich erfordert der Ansatz eine technoökonomische Bewertung.

Die gewonnenen Erkenntnisse zu Interaktionseffekten, zum Gültigkeitsbereich der superpositionsbasierten Modellierung, zum Zusammenspiel von stoff- und reaktorspezifischen Effekten sowie zur Eignung des temperaturgestuften Pyrolyseansatzes stellen eine wichtige Grundlage für weiterführende Untersuchungen zum Pyrolyseverhalten von Kunststoffmischungen dar.

Acknowledgements

This work was completed during my time as a research associate at the Institute for Technical Chemistry, and the thesis and three articles were finalized when I started my position at ARCUS Greencycling. I would like to sincerely thank everyone who accompanied and supported me throughout this intensive period.

I would like to begin by thanking my supervisor, Dieter Stapf, who laid the foundation for this dissertation. Over the past seven years, he has provided valuable advice and consistently supported me in all key decisions and milestones along the way. The funding he secured allowed me to devote the time and resources needed to complete this dissertation.

I would also like to express my gratitude to all my colleagues at the ITC for their support and the friendly atmosphere that enriched my time at KIT. Achieving the objectives of this research would have taken significantly longer or would not have been possible to the same extent without their involvement. Special thanks go to my two group leaders, Hans Leibold and Salar Tavakkol, who advised me during different phases of my affiliation at the institute and contributed significantly to my personal and professional development. Furthermore, I would like to thank all doctoral researchers at the ITC, but especially my closest companion, Michael Zeller. They were always willing to help when needed and motivated me to keep going during tough times. The same applies to all the students whose work I supervised. I greatly appreciated the focused yet friendly collaboration, which significantly strengthened my sense of responsibility.

Although they may not realize it, my friends have played a major role in the successful completion of this thesis. The time we spend together recharges my batteries, providing me with the energy I need to turn barriers into bridges and transform ideas into action.

My deepest gratitude belongs to my parents, Petra and Manfred Netsch, as well as my sister, Sabrina Schmitt. They were there for me from the very beginning, shaped my perspective on the world, provided unconditional love through every stage of my life, and always made me feel that I could achieve anything I aimed for. It is through this unwavering support that I gained the confidence and optimism with which I approach both my work and my life.

Finally, I would like to dedicate this work to Bianca Lachenmann for shaping and influencing my life so significantly. She is my anchor and my counterbalance, easing burdens in difficult times, offering comfort and reassurance, and motivating me whenever doubts arise. She understands me better than anyone else and gave me the strength to persevere throughout this dissertation.

Niklas Netsch

May 17, 2026, Karlsruhe, Germany

Table of Contents

Abstract	I
Kurzfassung	III
Table of Contents.....	VI
List of Figures	VIII
List of Tables.....	X
List of Symbols and Abbreviations	XI
1 Introduction	1
1.1 Problem Statement	1
1.2 Scope of Work	2
2 Literature Review.....	3
2.1 Fundamentals of Thermoplastics Pyrolysis	3
2.1.1 Primary Thermal Decomposition Mechanism	3
2.1.2 Secondary Reactions	7
2.1.3 Interaction Effects in Thermoplastic Mixtures	8
2.2 Mixed Plastic Waste Pyrolysis.....	9
2.2.1 Influence of Additives and Non-polymeric Components	9
2.2.2 Influence of Reactor Type and Process Conditions	10
2.3 Reintegration of Pyrolysis Products.....	15
2.3.1 Reintegration Options	15
2.3.2 Steam Cracker Route.....	16
3 Materials and Methods	17
3.1 Feedstocks	17
3.2 Pyrolysis Systems.....	19
3.2.1 Differential Scanning Calorimetry	19
3.2.2 Thermogravimetry	20
3.2.3 Screw Reactor Pyrolysis System	20
3.2.4 Stirred-Tank Reactor Pyrolysis System	21
3.3 Analytical Methods	24
3.3.1 Elemental Analysis	24
3.3.2 Calorimetry	24
3.3.3 Simulated Distillation.....	24
3.3.4 Nuclear Magnetic Resonance Spectroscopy	24
3.3.5 One-dimensional Gas Chromatography	24
3.3.6 Two-dimensional Gas Chromatography Development	25
3.4 Superposition-based Calculations	27

4 Results and Discussion	29
4.1 Feedstock Impact.....	29
4.1.1 Thermal Decomposition Kinetics	29
4.1.2 Product Yields and Product Compositions.....	33
4.1.3 Pyrolysis Energy Demand	38
4.2 Influence of Reactor Type and Design.....	39
4.2.1 Assessment of Reactor Characteristics	39
4.2.2 Interplay of Feedstock and Reactor-specific Effects	42
4.3 Process Optimization by Temperature-staged Pyrolysis.....	45
4.3.1 Thermogravimetry	45
4.3.2 Evaluation in the Stirred-Tank Reactor	47
5 Conclusion and Outlook	52
Appendix.....	54
References.....	55
Publications included in this Thesis.....	69
Complete List of Publications	70

List of Figures

Figure 1: Concept of carbon recovery in a circular economy for plastics	1
Figure 2: Radical chain scission mechanism of the primary thermal decomposition of PE (adapted from [30])	4
Figure 3: Depolymerization mechanism of PS decomposition (adapted from [37])	5
Figure 4: Thermochemical steps and influencing parameters during pyrolysis of mixed plastic waste	9
Figure 5: Schematic of the ASR pyrolysis system with material dosing section, electrically heated screw reactor, and two-stage condensation unit (adapted from Publication 4)	21
Figure 6: Schematic of the STR system including valve lock for material dosing, electrically heated stirred-tank reactor, and two-stage condensation unit (Publication 4)	22
Figure 7: Overview of the employed 2D-GC system (Publication 3)	25
Figure 8: Polymer group clustering and polymer interactions based on the decomposition kinetics of mixtures of PE, PP, PS, ABS, PVC, PET, and PA6 (adapted from [175])	30
Figure 9: Volatile formation of differently prepared samples of a 50/50 PET/PA6 mixture at a heating rate of 10 K·min ⁻¹ (adapted from Publication 2)	31
Figure 10: Experimentally determined and modeled volatile formation and formation rate of TG Mix 1 and 2 at a heating rate of 10 K·min ⁻¹ (adapted from Publication 2)	32
Figure 11: Product yields obtained by pyrolyzing pure thermoplastics and thermoplastic mixtures in the STR at 500 °C set temperature (adapted from Publication 4)	33
Figure 12: 2D-GC chromatogram of the pyrolysis oil generated from PCW pyrolysis in the STR system at 500 °C set temperature (Publication 4)	36
Figure 13: Experimentally determined and superposition-based calculated ED of different thermoplastic feedstocks in the ASR at 500 °C set temperature (adapted from Publication 1)	39
Figure 14: Time-dependent temperature profile of the reactor wall and the reaction zone during pyrolysis of LDPE, PS, PVC, and PCW in the STR system at 500 °C set temperature (Publication 4)	41
Figure 15: Mass balance comparison of STR and ASR experiments at 500 °C reactor set temperature with thermoplastics and plastic mixtures (Publication 4)	42

Figure 16: SimDist curves of pyrolysis oils obtained from STR and ASR experiments with various thermoplastic feedstocks, fossil naphtha [176] and VGO [177] (Publication 4)	44
Figure 17: Elemental composition of oils generated by pyrolysis of different thermoplastic feedstocks in the STR and ASR with a reactor wall temperature of 500 °C (Publication 4)	45
Figure 18: Three-staged TG experiments for individual polymers at isothermal segments for dechlorination at 300 °C, decomposition of aromatic-based and heteroatom-containing polymers at 370 °C, and polyolefin decomposition above 400 °C, including segments of constant heating rate at 10 K·min ⁻¹ (Publication 5) ...	46
Figure 19: Three-staged TG experiments with isothermal segments at 300 and 370 °C and a constant heating rate of 10 K·min ⁻¹ between the segments performed with ternary mixtures in the proportion of 30/30/40 wt.% and TG Mix 2 (Publication 5)	47
Figure 20: STR reaction zone and reactor wall temperature during temperature-staged pyrolysis of Mix C with isothermal segments at 400 and 430 °C. Gas sampling points are indicated by crosses along the x-axis (Publication 5)	48
Figure 21: Content of gas compounds sampled after 6, 30, 60, 96, and 120 min during staged pyrolysis experiments at 430 and 500 °C in the STR system (Publication 5)	49
Figure 22: NMR spectra of pyrolysis oils from temperature-staged experiments with Mix C at 400 and 500 °C (top) and 430 and 500 °C (bottom) (Publication 5)	51

List of Tables

Table 1: Qualitative comparison of characteristic parameters in different types of pyrolysis reactors	12
Table 2: Comparison of characteristic properties of fossil-based naphtha and common properties of pyrolysis oils stemming from mixed plastic waste [15,105,152].....	16
Table 3: Elemental composition, moisture, ash content, and HHV of the polymeric feedstocks employed for pyrolysis experiments [adapted from Publication 1].	18
Table 4: Polymer type-specific composition of the investigated thermoplastic reference mixtures and the PCW [Publications 1 and 2].....	19
Table 5: Polymer type-specific kinetic parameters of pure polymers derived by TG at constant heating rates between 2 and 40 K·min ⁻¹ [Publication 2]	29
Table 6: Normalized elemental composition of the oils obtained from pyrolysis of different thermoplastic feedstocks in the STR system [Publication 4].....	34
Table 7: Compound group analyses of oils from pyrolysis of pure polymers in the STR system at 500 °C set temperature [Publication 4].....	35
Table 8: Composition of pyrolysis gas obtained in STR experiments at 500 °C set temperature and corresponding superposition-based calculations [Publication 4]....	37
Table 9: Elemental analysis of the pyrolysis oils generated in temperature-staged pyrolysis experiments with isothermal segments at 400 and 430 °C and an isothermal reference experiment [Publication 5].....	50

List of Symbols and Abbreviations

Latin symbols

Symbol	Unit	Description
A_i	-	Peak area in 1D-GC of a compound i
c_i	$\text{mg}\cdot\text{ml}^{-1}$	Concentration of a compound i
c_p	$\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	Specific heat capacity
E_A	$\text{kJ}\cdot\text{mol}^{-1}$	Activation energy
$f(\alpha)$	-	Kinetic model function
h	$\text{J}\cdot\text{g}^{-1}$	Specific enthalpy
k_0	s^{-1}	Pre-exponential factor
m	g	Mass
n	-	Reaction order
R_i	$\text{ml}\cdot\text{mg}^{-1}$	Response factor
T	K	Temperature
t	s	Time
w_j	-	Reaction fraction of a decomposition stage j
x_i	-	Mass proportion of a polymer i in a mixture
y	-	Feedstock-related mass yield of a product fraction
z	-	Parameter of the product composition

Greek symbols

Symbol	Unit	Description
α	-	Conversion

Universal constants

Symbol	Unit	Description
R_{id}	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Universal gas constant

Indices

Index	Description
0	Start of the experiment
I	First decomposition stage of PA6 and PVC
II	Second decomposition stage of PA6 and PVC
III	Third decomposition stage of PA6 and PVC
∞	End of the experiment
exp	Experimentally determined value
i	Polymer type in the mixture
id	Ideal
j	Number of pseudo-reactions in the kinetic model
$melt$	Melt phase
$model$	Value calculated by using the kinetic model
NTP	Normal temperature and pressure (0 °C and 1 atm)
P	Product fraction
$postGT$	Polymer phase at a temperature above the glass transition
$preGT$	Polymer phase at a temperature below the glass transition
Py	Pyrolysis
R	Reaction
$solid$	Solid phase
$theo$	Theoretically expected value
v	Volatile product

Abbreviations

Symbol	Description
1D-GC	One-dimensional gas chromatography
2D-GC	Two-dimensional gas chromatography
ABS	Acrylonitrile butadiene styrene copolymer
ASR	Auger-type screw reactor
DSC	Differential scanning calorimetry
ED	Energy demand
EU	European Union
FCC	Fluid catalytic cracking
FID	Flame ionization detector
GRT	Gas residence time
GT	Glass transition temperature
HC	Hydrocarbon
HDPE	High-density polyethylene
HHV	Higher heating value
LDPE	Low-density polyethylene
MgOx	Magnesium oxalate dihydrate
MT	Melting temperature
NCD	Nitrogen chemiluminescence detector
NMR	Nuclear magnetic resonance spectroscopy
PA6	Polyamide 6
PCW	Post-consumer waste
PET	Polyethylene terephthalate
PFR	Plug flow reactor
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
qMS	Quadrupole mass spectrometer
RMSD	Root mean square deviation
SimDist	Simulated distillation
SPBM	Superposition-based modeling
SSL	Split/Splitless injector
STR	Stirred tank reactor
TCD	Thermal conductivity detector
TG	Thermogravimetry
TMS	Tetramethylsilane

1 Introduction

By 2050, global plastic consumption is predicted to double to approximately 7.7 Gt [1] compared to 2015, which will accelerate global problems, such as the consequences of climate change [2] or environmental pollution [3]. With the enactment of the *Green Deal*, the European Union (EU) has therefore committed to minimizing its plastic consumption and to promoting the collection and recycling of plastic waste [4]. The *Circular Economy Action Plan* provides the framework to transform linear value chains into a carbon-neutral circular economy [5]. Plastic recycling plays an essential role in this framework.

Worldwide, only 15% of plastic waste was collected for recycling in 2019, and only 9% was ultimately recycled [6]. The majority of waste is landfilled, incinerated, or mismanaged [6]. Although the recycling rate in some countries is slightly higher, only 35% of post-consumer plastic waste (PCW) was recovered in the EU in 2021, primarily via mechanical recycling processes [7]. Limitations in waste collection and sorting systems lead to heterogeneous waste compositions, which, combined with the technical limitations in mechanical processing, currently prevent reaching the ambitious recycling targets [8]. With the establishment of new recycling pathways based on chemical or thermochemical conversion, even plastics from hard-to-recycle waste fractions are accessible for recycling [9]. As shown in Figure 1, the implementation of an additional chemical recycling loop facilitates the carbon recovery for the synthesis of virgin polymers. Thus, complementary to mechanical recycling, chemical recycling technologies promote plastic circularity [10].

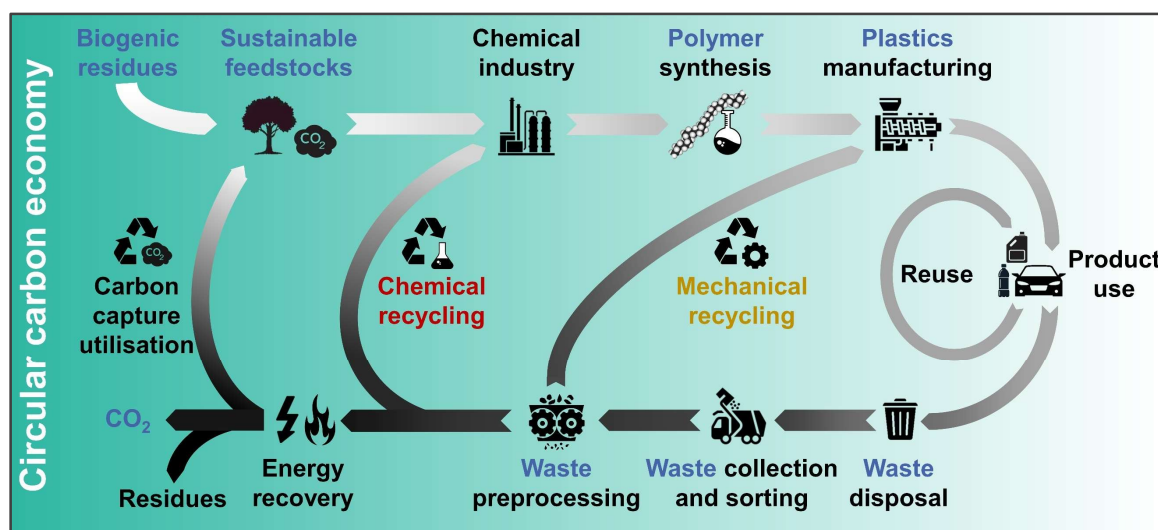


Figure 1: Concept of carbon recovery in a circular economy for plastics.

1.1 Problem Statement

Besides gasification, pyrolysis is a promising option for processing heterogeneous mixed plastic wastes [11]. However, plastic pyrolysis has been operated rarely on an industrial scale to date [12]. Several technical aspects pose challenges for the realization of plastic pyrolysis projects [13]. Firstly, the decomposition mechanisms comprise complex networks of elementary reactions that vary depending on the plastic type and process conditions [11]. Secondly, pyrolysis simulations are based on simplified assumptions. Therefore, process predictions mainly rely on elaborate experimental studies. These are often limited in transferability to large-scale applications, preventing reliable scale-up [14]. Finally, the organic products from waste pyrolysis do not meet the specifications required for reintegration into the petrochemical industry [15].

1.2 Scope of Work

This cumulative dissertation aims to investigate these technical aspects by examining fundamental effects in mixed thermoplastics pyrolysis. The dissertation is based on five scientific journal articles that contribute to answering the following main research questions:

- How do the decomposition reactions depend on the polymer type composition of thermoplastic mixtures?
- How do the reactor type and the process characteristics impact the pyrolysis behavior and the transferability of pyrolysis results?
- Can the targeted pyrolysis products be optimized through process parameter adjustment to meet (petro-)chemical specification requirements?

Four characteristics serve as evaluation criteria to address these questions. These are the decomposition kinetics, product fraction yields, the composition of gaseous and condensable product fractions, and the process energy demand (ED).

The amount of energy needed for plastic pyrolysis is of major concern in terms of the ecological footprint of potential recycling pathways. Therefore, *Publication 1* focuses on its determination for thermochemical conversion of mixed plastics by differential scanning calorimetry (DSC). Performing experiments at a bench-scale auger-type screw reactor (ASR), an application-oriented scale-up approach based on a linear superposition is investigated. The publication highlights the influence of the plastic mixture on the ED and provides a reliable database for future ED evaluations. It indicates polymer interactions during the pyrolysis of mixed plastics. In *Publication 2*, these interactions are examined in a thermogravimetric (TG) study on thermal decomposition kinetics in detail. Key effects with varying intensity are identified. These effects are assigned to specific polymer constellations. Based on these observations, the interactions are expected to impact the product yield and composition. Assessing the complex composition of pyrolysis oils is challenging. Therefore, *Publication 3* presents a novel analysis method by two-dimensional gas chromatography (2D-GC) for in-depth pyrolysis oil characterization. With this method, information on the influence of polymer types in the feedstock mixture on the oil composition is accessible. Thus, product yields and compositions are investigated in *Publication 3* and *Publication 4*. Besides the feedstock composition, the reactor type is decisive for the pyrolysis result because of its characteristic differences in design and process parameters. *Publication 4* compares experiments on a newly developed stirred tank reactor (STR) with the ASR experiments, both on a technical scale. The results emphasize the need for pyrolysis oil upgrading. To minimize oil upgrading, optimizing the pyrolysis process is essential. *Publication 5*, therefore, examines the potential process optimization via temperature-staged pyrolysis for improving the pyrolysis oil quality.

The work is structured in five main parts, including this introduction (Chapter 1). Chapter 2 summarizes the fundamentals of virgin polymer and plastic waste pyrolysis by presenting relevant literature. Along with the investigated plastics and analytical methods, the principles of the superposition are described in Chapter 3. Also, the reactors used for experiments are presented. The essential results of the published works are outlined in Chapter 4 and discussed in a broader context. Chapter 5 concludes with the key findings related to the previously highlighted scientific questions while also providing an outlook on future applications in chemical recycling of plastic waste via pyrolysis. The appendix contains all publications related to this dissertation in detail, as well as a comprehensive overview of the 2D-GC setup and method parameters.

2 Literature Review

This chapter summarizes the current scientific knowledge on the pyrolysis behavior of thermoplastics and plastic mixtures related to the engineering research questions addressed in this dissertation. Chapter 2.1 provides an overview of the primary reaction mechanisms of specific thermoplastics and potential secondary reactions of the resulting pyrolysis products. The current state of research on feedstock interactions is explained. The impact of process parameter variations and the underlying reactor technology on the pyrolysis behavior of plastic mixtures and plastic waste is outlined in Chapter 2.2. Finally, reintegration options for pyrolysis products are presented in Chapter 2.3. In this context, the feedstock specifications of subsequent processes considered for reintegration and the properties of pyrolysis products are critically compared.

2.1 Fundamentals of Thermoplastics Pyrolysis

The term pyrolysis is defined as the process of a feedstock's thermally induced decomposition reactions under an inert atmosphere and at elevated temperature above 300 °C [11]. It is occasionally also referred to as thermolysis [16]. In the case of plastics, macromolecules decompose into compounds of low molecular weight by covalent bond cleavage in the polymer backbone as a major initial step. The pyrolysis comprises several sub-steps, including the primary decomposition reaction mechanism and potential secondary reactions of the formed products in the hot reaction chamber [17,18]. As summarized by multiple authors, the thermochemical reaction is highly dependent on the reacting feedstock and the applied process parameters [19–21]. In the following, the focus is set on intermediate pyrolysis at temperatures ranging from 400 °C to 600 °C [16].

2.1.1 Primary Thermal Decomposition Mechanism

The primary decomposition mechanisms determine the emerging products, and consequently, the potential secondary reactions. The mechanisms are therefore decisive for the pyrolysis outcome. They consist of a multitude of elementary reactions that contribute to the cleavage of long-chain molecules into short-chain products [22]. Depending on their structure, the products are present as permanent gases, condensable compounds, or pyrolysis char. Compounds condensable at ambient conditions are referred to as pyrolysis oil, while char is often labeled as a solid residue, including other unreactive feedstock components such as metals or inorganic materials. The primary decomposition mechanisms of plastics differ fundamentally depending on the chemical structure of the polymer [22]. The mechanisms can be classified into three different categories: random chain scission, depolymerization, and side-group elimination [22]. They will be explained in detail and linked to the associated polymer types in the following. The decomposition mechanism of polyolefins is well described in the literature. In the 1950s, Wall and Straus already reported a radical chain scission mechanism at randomly positioned sites along the chain backbone for the thermal decomposition of polyolefins [23]. The mechanism was confirmed multiple times by experimental studies [24–32]. Bockhorn et al. illustrate the three-stage reaction process of PE in detail as shown in Figure 2 [30]. In an initiation phase, primary radicals are formed by the randomly distributed homolytic scission of carbon-carbon bonds. These primary radicals then undergo various consecutive reactions in the propagation phase. At high temperatures, the monomer ethene is formed by β -scission in the primary radical. At moderate temperatures, like in intermediate pyrolysis, intramolecular hydrogen transfer becomes dominant [30]. The intramolecular transfer is also known as a backbiting reaction [26]. A secondary radical is

formed, stabilizing the molecule [30]. This secondary radical can now either react via β -scission to form a new primary radical and an unsaturated linear HC, or an alkane and a secondary radical are generated via intermolecular hydrogen transfer [30]. The decomposition reaction ends with a second-order termination reaction [30]. This termination is performed by the recombination of secondary radicals forming linear saturated HCs [30]. Consequently, the pyrolysis of PE mainly produces linear HCs, which often contain unsaturated double bonds in the α - and α - ω -positions [30].

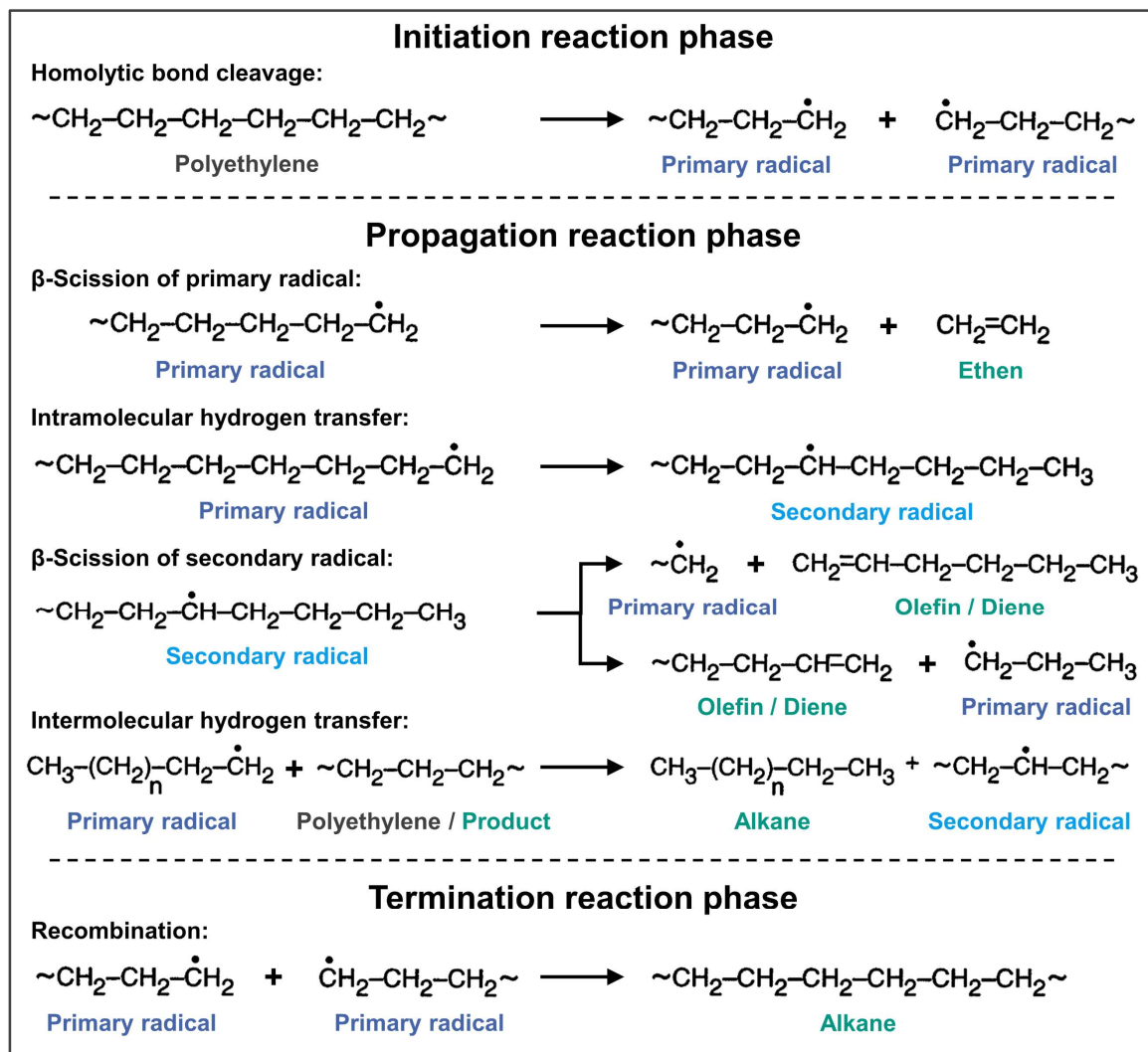


Figure 2: Radical chain scission mechanism of the primary thermal decomposition of PE (adapted from [30]).

The branches within the PE backbone influence its decomposition behavior. Westerhout et al. showed that low-density polyethylene (LDPE) decomposes with a higher conversion rate under identical conditions than high-density polyethylene (HDPE) [33]. LDPE features more branches than HDPE. Consequently, there are more tertiary carbon atoms in the polymer chain. Homolytic bond scissions at such tertiary carbon atoms in the backbone are favored as the resulting secondary primary radicals are more stable [33]. This accelerates the initiation reaction [33]. Moreover, secondary radicals at tertiary carbon atoms are stabilized, accelerating the propagation reactions [33]. This principle also applies to PP [33]. PP features a tertiary carbon atom at every second position of the carbon-carbon backbone by substituting a hydrogen atom with an alkyl group, compared to PE. The decomposition reactions are thus enhanced for PP compared to PE when similar conditions are applied [33]. The main PP pyrolysis products are branched saturated

and unsaturated HCs [30,34]. Compared to PE, the chain length distribution is shifted to lower molecular masses [30,34]. Propylene formation is also favored in the gas phase because of the preferred locations for bond scission caused by the alkyl groups [35].

Early research by Jellinek highlighted the similarity of PS decomposition to that of polyolefins [36]. The PS decomposition mechanism is also based on radical chain scission reactions and contains an initiation, propagation, and termination phase [36]. In contrast, the aromatic side group in the PS causes beneficial locations for carbon-carbon bond cleavages, which lead to a depolymerization mechanism [34]. Faravelli et al. summarized this depolymerization mechanism. Figure 3 illustrates this mechanism in detail by adapting their results [37].

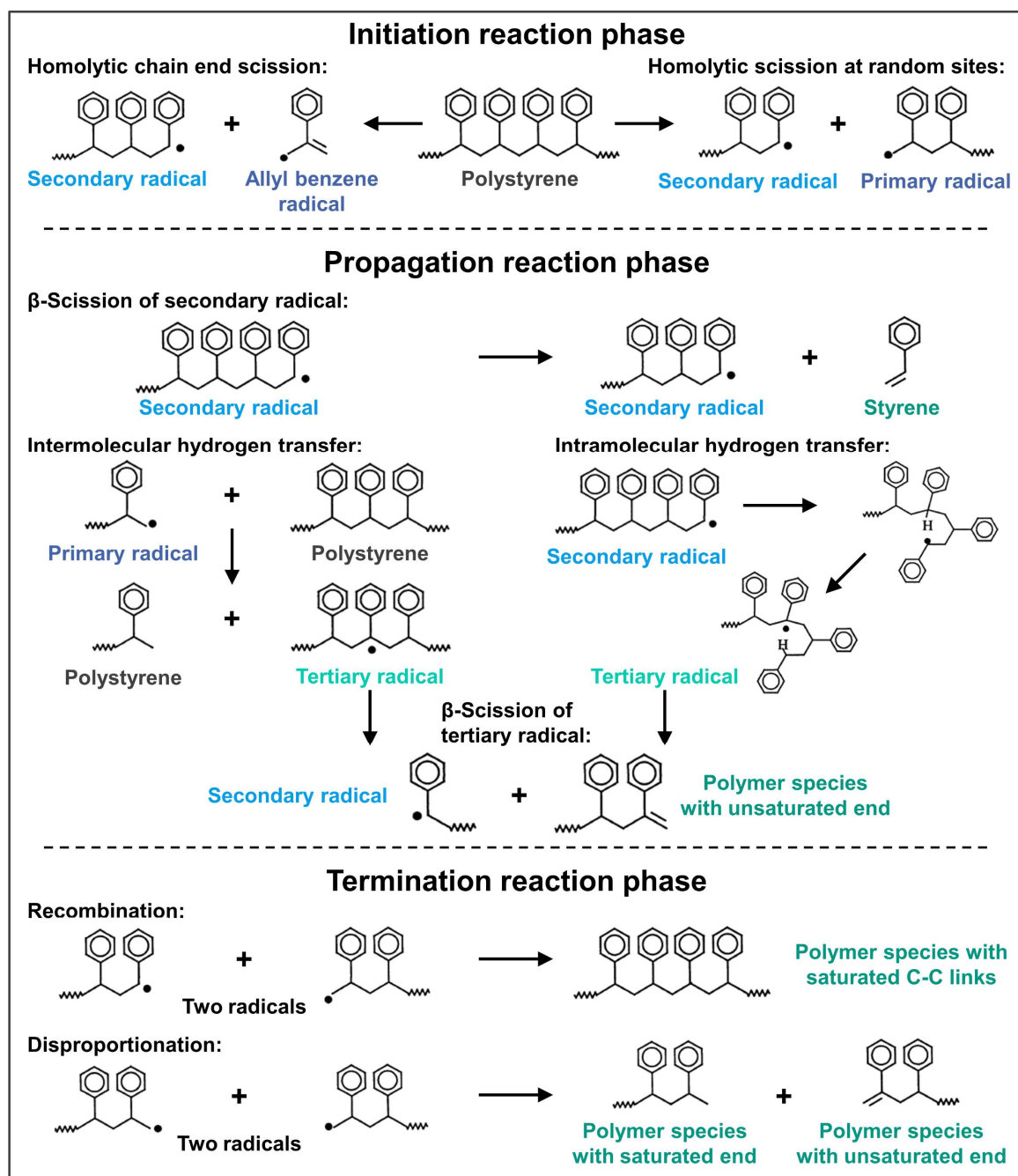


Figure 3: Depolymerization mechanism of PS decomposition (adapted from [37]).

Initiation reactions are apparent as chain scission, either randomly distributed over the chain backbone or at the chain end [37]. The second reaction becomes more important in the decomposition progression as a result of the decreasing polymer chain length [37].

Secondary benzyl radicals and allyl benzene radicals are formed [37]. The propagation phase is characterized by the competing reactions, either producing styrene monomer or “larger chain fragments”, as first described by Grassie and Kerr [38]. Various aspects, such as temperature or chain length of the PS, determine which reaction is favored [39]. For propagation, the secondary benzyl radicals undergo β -scission reactions, which can repeat multiple times and hence are called unzipping reactions [37]. The unzipping reactions result in the evolution of styrene monomers [37]. Competing reactions of intermolecular and intramolecular hydrogen abstraction are also possible [37]. In both cases, tertiary radicals are formed by the transfer of hydrogen between different molecules or in a single molecule by backbiting [37]. For intramolecular transfer, the 1,5-backbiting reactions are preferred due to steric reasons. The formed products can further react to a secondary benzyl radical and a PS polymer intermediate. This PS intermediate includes an unsaturated end and one monomer less in its chain [37]. Termination reactions include recombination or disproportionation of two radicals [37]. As unzipping reactions are generally dominant in PS decomposition, the reaction mechanism is referred to as depolymerization [34]. The main products of this mechanism are styrene monomer, monoaromatic structures, diphenyls, and styrene trimer. At higher temperatures, the yield of styrene monomer and monoaromatics is increased [37]. Compared to polyolefins, the decomposition of PS occurs at lower temperatures, as the aromatic side groups in the PS structure significantly stabilize the evolving radicals [33].

PVC is known to undergo a characteristic three-step decomposition process [40]. The PVC structure with its thermally labile carbon-chlorine bonds starts decomposing at low temperatures of about 250 °C [40]. Stromberg et al. described the first step as a side-group elimination mechanism of HCl [41]. The following decomposition steps of PVC were investigated extensively [42–46]. Marongiu et al. described the PVC radical mechanism in detail. As the first step, dechlorination is preferably initiated by homolytic carbon-chlorine bond cleavage [47]. A chlorine and a secondary carbon radical are formed [47]. The chlorine radicals abstract hydrogen from the PVC chain, which stabilizes by forming carbon-carbon double bonds [47]. With the propagation of this mechanism, the PVC structure transforms into a polyene chain [47]. These polyene chains perform either dealkylation or Diels-Alder condensation reactions, which represent the second step of the mechanism [45,47]. Benzene and alkyl aromatic structures evolve, while cross-linked polyene chains and polycondensed aromatic intermediates are apparent [47]. These intermediates decompose at temperatures above 350 °C [40]. Mainly mono- and diverse polyaromatic structures, as well as char, are formed in this third step of diverse and complex reactions [42–44,46].

The presence of heteroatoms, such as oxygen and nitrogen, in the polymer backbone has been shown to influence the primary decomposition behavior of the material significantly [53]. Marshall and Todd describe a radical decomposition mechanism for PET [54]. The initiation of this process can be triggered by either homolytic bond cleavage or by ionic processes resulting from beta-CH hydrogen transfer [55,56]. The homolytic bond rupture involves a competition between the processes of cleavage of the carbon-carbon and carbon-oxygen bonds [53]. This is attributable to the less stable carbon-oxygen bond and the possibility of aromatic resonance stabilization of the forming radicals [55]. Consequently, cleavage preferentially occurs at ester bonds. In a one-step decomposition occurring at approximately 350 °C, the predominant gaseous products are CO₂, CO, short-chain aliphatics, and acetaldehyde [57,58]. Aromatics, benzoic acid, and other oxygen-containing aromatic compounds have been detected in the condensate [58].

Furthermore, crosslinking reactions have been shown to result in the considerable formation of char as a solid product of PET pyrolysis [59].

Straus and Wall identified in the 1950s that PA6 does not decompose according to a random radical chain scission mechanism, but rather is influenced significantly by the amide bonds [60]. Experimental investigations and derived mechanisms were summarized by Levchik et al. [61]. According to the authors, different reaction pathways compete as dominant mechanisms [61]. Firstly, hydrolysis of the PA6 chains may occur, as hygroscopic PA6 often contains water if not dried before pyrolysis. In the absence of water, intramolecular back-biting reactions or intramolecular hydrogen transfer reactions, also called cis-elimination, are dominant [62]. The end-biting mechanism is characterized by cyclization because of the NH_2 -group reaction with a carbon atom of an amide group in the same polymer chain [62]. This reaction leads to the formation of ϵ -caprolactam or its oligomers [62]. Cis-elimination can also produce ϵ -caprolactam [63], but also generates unsaturated end chains in the aliphatic PA6 structures. They can further react to nitrile products [62]. Finally, homolytic bond cleavage of the carbon-carbon bond at the amide group enables a crosslinking reaction via carboimide, ultimately leading to the formation of a solid residue [62]. Bockhorn et al. produced over 90 wt.% of ϵ -caprolactam in the non-catalyzed thermal decomposition of PA6, which suggests that cis-elimination and the intramolecular backbiting mechanism are dominant [63]. This finding is confirmed by other authors [53,64].

As a copolymer, ABS exhibits a more complex degradation behavior compared to the previously discussed homopolymers. Due to the variability of the ABS terpolymer, no universally applicable decomposition mechanism has been formulated for it. A radical mechanism involving three phases of initiation, propagation, and termination for related butadiene-acrylonitrile and styrene-acrylonitrile copolymers is stated [48,49]. The thermal decomposition of ABS appears to follow a radical mechanism with a single stage of decomposition [50]. The condensable pyrolysis products mainly consist of styrene, its oligomers, monoaromatics, and aromatic nitriles [51]. Butadiene, acrylonitrile, and hydrogen cyanide have been detected in the gas phase [50,52].

2.1.2 Secondary Reactions

The pyrolysis products resulting from the primary decomposition mechanism of individual plastics undergo secondary reactions in the gas phase. The reactions are likely to occur due to the high reactivity of the primary pyrolysis products and the reaction-promoting conditions in the pyrolysis reactor [65]. These reactions overlap with the primary degradation reactions occurring in the polymer melt. Therefore, they may exert a strong influence on the product spectrum.

Dai et al. and Qin et al. summarize that secondary reactions in the pyrolysis of plastics tend to increase the gas yield and promote the formation of char and aromatic compounds [65,66]. They identify secondary cracking, dehydrogenation, aromatization, isomerization, alkylation, and repolymerization reactions as secondary reactions [65,66]. Gas phase reactions are favored by high temperatures but can also occur in intermediate pyrolysis depending on the choice of process parameters [17,65,67]. Various studies point to secondary cracking of long-chain aliphatic products of PE pyrolysis in the gas phase [67–69]. At the same time, pyrolysis products with unsaturated carbon-carbon bonds such as α -olefins, α - ω -dienes, or styrene, can repolymerize under pyrolysis conditions [17]. Lopez et al. suggest Diels-Alder reactions or unimolecular cyclization reactions as the reason for secondary aromatic formation [17]. For example, light olefins primarily undergo Diels-Alder reactions to form aromatics that cannot be explained by the primary decomposition mechanism [17]. Long-chain polyenes or monoaromatics with reactive substituents can

undergo further reactions to form (poly-)aromatic compounds [17]. The unsaturated bonds do not necessarily originate from the primary mechanism but may result from dehydrogenation, as Blazsó et al. illustrated [70]. Heteroatom-containing compounds may also undergo repolymerization by addition or condensation reactions [53,66]. The multitude of possible secondary gas-phase reactions thus increases the complexity of plastic pyrolysis.

2.1.3 Interaction Effects in Thermoplastic Mixtures

Reactions involving mixtures of different types of polymers can cause intermediate products of the primary decomposition mechanism to interact with each other [71]. Subsequently, various other secondary reactions may occur, or the severity of secondary reactions may change compared to the pure polymer pyrolysis behavior [18]. The potential interactions affect the decomposition kinetics and both the type and quantity of products. These interactions occur in particular when the respective polymer types in the mixture exhibit similar decomposition temperatures [72]. In general, they are highly dependent on the proportions of the respective polymer types in the mixture [72]. The intensity of interaction reactions as interfacial effects in the material system is also determined by the homogeneity of the polymers distributed in the feedstock [72].

For example, various authors have concluded that there are no or only negligible changes in the co-pyrolysis of PE, PP, and PS [33,73,74]. Wu et al. also found no significant changes in kinetics for mixtures of PE and PVC [75]. In the studies by Genuino et al., no change in yield and product composition was found for mixtures of PE, PS, and PP compared to pure polymer behavior [76].

However, several other experimental studies have contradicted these results. La Mantia et al. report that the reaction kinetics can be accelerated or delayed depending on the polymer combination due to interactions in the primary decomposition mechanism [71]. Slight accelerations are identified in mixed polyolefins [77–79]. The radicals formed in the PP initiation reaction act as an initiator for the decomposition of PE chains [79]. The decomposition of polyolefins is also reported to be accelerated in the presence of PS [80] and PET [81]. Also, initiation reactions of polymers with more stable radicals such as PS have decomposition-promoting effects on PP and PE chains [80]. In contrast, the reaction of polyolefins or PS is delayed in the presence of PVC and shifted to higher temperatures in TG curves [40]. These interaction reactions in mixed plastics also affect the product yields [40,76,82]. For example, interacting mixtures of PS, PE, PP, PET, and PVC produce more gas than expected from the pure polymer behavior [82]. In the presence of PET [76] and PVC [40], char formation is enhanced. In addition, Genuino et al. report increased formation of aromatic structures due to the interaction effects of PET with other polymers [76]. This observation is also evident for mixtures of LDPE and PP but to a lesser extent [79]. Some studies point to strong interaction reactions between PVC and PET in mixtures with [82–84] and without polyolefins [85]. Chlorinated HCs are increasingly produced and have been detected in both the gas [85] and oil phase [84]. Here, interactions between the HCl formed in the first decomposition step of PVC and other products appear to proceed [85]. As a result of interactions, the average molecular weight of the compounds in the oil phase also decreases in polyolefin-rich feedstocks [82].

Overall, these studies indicate that the interaction influence, both in terms of their form and intensity, is highly dependent on the types of polymers that are pyrolyzed together [82].

2.2 Mixed Plastic Waste Pyrolysis

Mixed plastic waste commonly exhibits a heterogeneous composition that undergoes complex reaction networks during pyrolysis [11]. Further effects superimpose the plastic-specific decomposition mechanisms, possible secondary reactions of primary products, and polymer-polymer interactions. These effects influence the pyrolysis behavior and depend on the waste composition and reaction conditions [86]. This chapter summarizes how the feedstock composition and reactor conditions affect the pyrolysis results. Figure 4 schematically illustrates these physical and thermochemical steps in plastic waste pyrolysis along with the possible influencing factors.

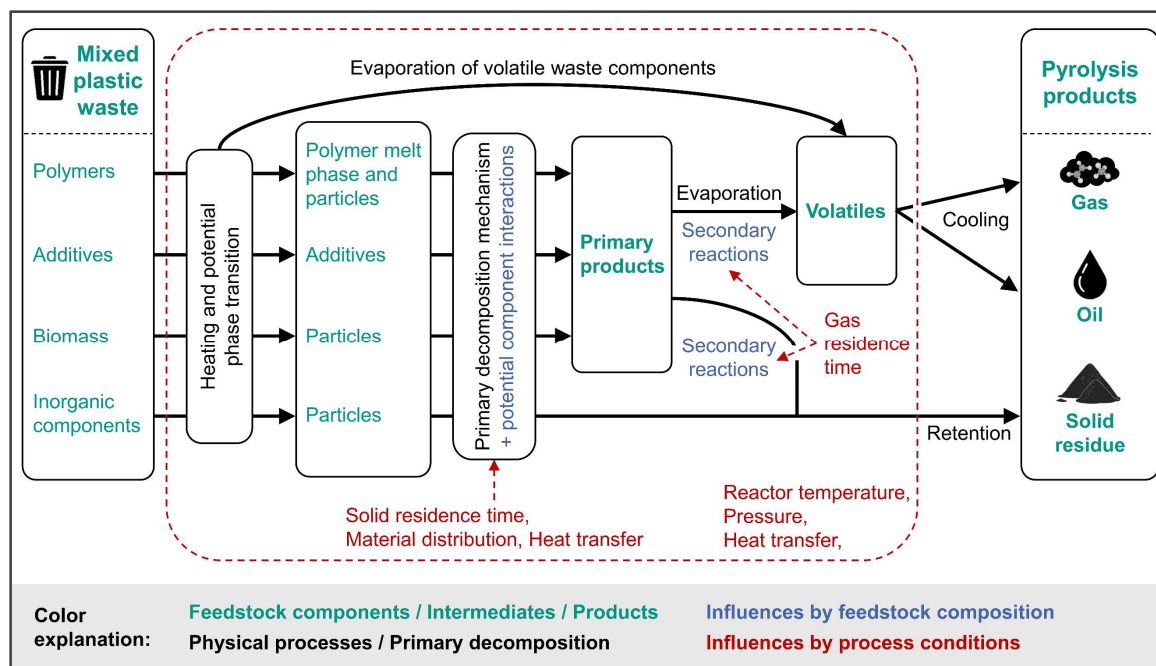


Figure 4: Thermochemical steps and influencing parameters during pyrolysis of mixed plastic waste.

2.2.1 Influence of Additives and Non-polymeric Components

The products in plastic waste are commonly functionalized to adjust thermal, mechanical, or other physical properties. Various additives, such as inorganic fillers, flame retardants, plasticizers, stabilizers like antioxidants, and colorants, are added to the polymers during the plastics compounding process [87]. Their presence leads to the formation of further additive-specific primary products or can even influence the primary decomposition mechanism of the polymers through interactions [86]. For example, Zhang et al. report both catalytic and inhibitory effects as well as altered heat transfer when Na_2SO_4 , CaCO_3 , and TiO_2 are blended in polyolefins [88]. Radhakrishnan et al. identified a catalytic effect of inorganic additives, for example, kaolin, talc, CaCO_3 , zinc, stearate, TiO_2 , and carbon black [89]. Conversely, investigated antioxidants and stabilizers inhibit the radical decomposition mechanism of polyolefin pyrolysis, thereby favoring high-boiling compounds [89]. Another study describes the influence of tetrabromobisphenol A, a common flame retardant [90]. Even though the polymer decomposition kinetics remain unaffected, brominated HCs are identified as products, and the formation of phenolic compounds is enhanced [90]. Ma et al. emphasize the problematic formation of brominated aromatic HCs and an increase in solid residues when brominated flame retardants are used [91]. Phosphorus-based flame retardants influence plastic pyrolysis, resulting in the formation of phosphorus-containing HCs in the gas and oil phases and

increased residue formation [92]. Kinetic studies of PVC with different plasticizers showed a significant influence on the polymer stability caused by inhibiting the dechlorination of PVC [93,94].

Biomass components are often found in PCW as part of multi-material composites or food impurities. Similar to plastic pyrolysis, biomass pyrolysis is complex, as the chemical structures are diverse [95]. The main products obtained are oxygenated aromatics, water, and char [95]. Zhao et al. conclude that a variety of interaction effects occur in primary decomposition, but also through secondary reactions, which depend strongly on the specific polymer-biomass combination [96]. Some plastic types, such as PVC, are reported to accelerate the thermal decomposition of cellulose-based biomass [97]. In general, biomass in plastic leads to an increase in oxygenated products and increased char formation compared to the pyrolysis of pure polymer fractions [96,98,99]. In addition, the carbon recycling rate is reduced by increased CO and CO₂ formation [100].

Inorganic components such as metals, glass, or salts also enter PCW via composite packaging, mechanical sorting errors, or food residues. They are mostly inert in intermediate pyrolysis and remain in the solid residue [15].

In general, these studies emphasize that the influence of additives and biomass must always be assessed in combination with the type of polymer, biomass, and additive, as well as their proportions. Possible effects can vary greatly depending on these variables. Often, undesired char formation is favored, and heteroatom contaminations migrate into the pyrolysis gas or pyrolysis oil, lowering their quality compared to pure polyolefinic pyrolysis products.

2.2.2 Influence of Reactor Type and Process Conditions

The conditions in the reactor system can decisively influence the physical processes and chemical reactions that comprise the thermochemical conversion, as shown in Figure 4. The following chapter describes the effects of the most important process parameters and summarizes their impact on the product spectrum in plastic pyrolysis.

Reactor system

Small reactor systems allow for defined reaction conditions. On a larger scale, however, relevant heat and mass transfer limitations prevail [65]. They are induced, for example, by the low thermal conductivity of plastics, endothermic processes during pyrolysis, remixing of material flows, or larger quantities of feedstock with limited heat-exchange surface area. The temperature profile of the polymers added at a temperature below that of the pyrolysis system is therefore not uniform and the reaction is not isothermal [101]. Consequently, the reactor-specific geometry and operating mode play an essential role as they are fundamental to the temporal and spatial characteristics of the polymer-specific temperature curve in pyrolysis systems above a certain scale [102]. However, the temperature profiles can often not be resolved because of technical limitations. Thus, they can only be approximated in technical scale pyrolysis reactors depending on the reactor geometry and operating mode.

The heating rate of polymers can only be adjusted to a limited extent in technical pyrolysis systems. It results indirectly from the temperature difference between the feedstock and the reactor [103]. Consequently, a high reactor temperature leads to a higher maximum achievable temperature of the polymers during pyrolysis [104]. Furthermore, it also leads to a higher time-averaged heating rate [104]. Yet, this time-averaged heating rate also depends on other factors such as the feeding procedure, the particle size of the polymers, or the homogenization of the material in the reactor, as these factors significantly determine the heat transfer to the polymer chains [104,105]. Under technical pyrolysis

conditions, the polymers therefore exhibit a temperature profile that varies over time. In reactors, this is usually superimposed by spatial material and temperature inhomogeneities. For example, particles larger than 4 mm can already exhibit significant temperature gradients within a single particle due to their low thermal conductivity of plastics [103].

The ideally mixed stirred tank reactor and the plug flow reactor (PFR) represent two contrasting approaches to describe chemical reactors [106]. The ideally stirred tank reactor is characterized by ideal mixing within the reaction zone. This results in a constant composition of reactants in the reaction zone and the absence of temperature gradients [106]. In contrast, the PFR represents an ideal reactor with spatially variable material composition and temperature gradients along one dimension [106]. Various reactor types are suitable for industrial-scale pyrolysis applications [21,65,104,105,107]. They can generally be classified according to these ideal reactor models, which they only approximate. The common reactor types, the STR, fixed-bed reactor, fluidized bed reactor, screw reactor, and rotary kiln reactor, are qualitatively compared in Table 1 based on their relevant characteristic features. While STRs and fluidized bed reactors represent more of a uniformly stirred tank, screw reactors and rotary kiln reactors reflect more of a plug flow approach.

These reactor types exhibit constructional and operational similarities. Accordingly, certain trends emerge for the reactor types in terms of specific parameters. For cost reasons, continuous operation is preferable to batch or semi-batch operation for industrial applications [105]. The same applies for economic reasons, in particular due to economies of scale, to reactors with larger feedstock capacities. In general, it has been shown that more intensive mixing of the feedstock and continuous feedstock addition result in a more homogeneous product composition over time [105]. Intense mixing, as in a stirred-tank reactor or a fluidized bed, is also often associated with better heat transfer within the reactor [21,65,105]. Thus, fixed-bed reactors generally exhibit the greatest inhomogeneity in terms of temperature and material distribution [104]. However, their design and scale-up are comparatively simple while featuring a low operation effort. This is in contrast to fluidized bed reactors. In these reactors, small particles are typically charged into a high mass of hot bed material, resulting in high heating rates [104]. However, the feedstock preparation effort is comparatively high [21]. In systems without agitators or screws, such as rotary kilns, the feedstock preparation effort is lower [104]. Despite many advantages, fluidized bed reactors are challenging to operate for plastic pyrolysis in the long term due to the restricted parameter window and recirculation of material flows [104]. They are susceptible to operational disruptions due to clogging or solidifying melt, which can lead to the collapse of fluidization in the fluidized bed [65,105]. Reactors such as the STR, screw reactor, and the rotary kiln reactor offer advantages here due to controlled conveying through the reaction zone [104]. This facilitates the defined adjustment of solid residence times.

These trends in the characteristics of reactors show that different types have different advantages and disadvantages. The choice of reactor type must therefore be adapted to the existing technical and economic framework constraints. Required feedstock capacity [104], feedstock composition [65,102], target product [102,104], or the option of integrating the process into a chemical complex site [66] can be a decisive factor.

Important characteristic factors that influence the polymer pyrolysis, such as the polymer temperature profile and the gas residence time (GRT) distribution of the pyrolysis vapor, are rarely or never determined and reported using a consistent methodology across experiments of different authors. Hence, literature data obtained with similar reactor types

are often overlaid by temperature differences which can lead to large fluctuations in the results. General statements about yields, product composition, and decomposition kinetics based solely on reactor type are thus difficult to formulate even when using similar polymer types. Maqsood et al. illustrate this finding with their literature study [69]. The authors state yields for pyrolysis oil and pyrolysis gas in an excessively broad range from 0 to 90 wt.% and 3 to 90 wt.%, respectively, for different reactor systems [69].

Table 1: Qualitative comparison of characteristic parameters in different types of pyrolysis reactors.

Parameter	Stirred tank reactor	Fluidized bed reactor	Fixed-bed reactor	Screw reactor	Rotary kiln
Feedstock pre-treatment effort	moderate	high	low	moderate	low
Maximum Capacity	low	high	high	moderate	high
Feeding procedure	semi-batch or batch	continuous	variable	continuous	continuous
Heat transfer	moderate	high	low	low	low
Material mixing	high	high	very low	low or moderate	low or moderate
GRT	variable	low	moderate	moderate	high

Pyrolysis temperature and heating rate

As described earlier, the pyrolysis result largely depends on the polymer temperature profile over time and thus mainly on the reactor temperature [65]. In small-scale experiments, such as TG, micro-pyrolyzers, or DSC, the sample quantity is small, and defined heating rates can be specified. This minimizes heat and mass transfer limitations, which is why the polymer temperature is assumed to correspond to the reactor temperature [108]. Even though heat and mass transfer limitations cannot be fully excluded from experimental procedures, the decomposition is the determining step in the pyrolysis process of such micro- and milligram-scale devices [86]. This enables the investigation of the influence of the polymer temperature and the heating rate on decomposition kinetics, product yields, and product composition.

The primary decomposition mechanisms of different types of plastic vary due to their different chemical structure. In most polymers, such as polyolefins, PS, or PET, significant decomposition rates are obtained above 350 °C [104]. PVC already decomposes at 250 °C due to the unstable carbon-chlorine bonds [40]. Experimental studies have shown that nearly isothermal pyrolysis conditions can be achieved, particularly in preheated micro-pyrolyzers with low feedstock mass [17,31,109,110]. Ceamanos et al. demonstrated accelerated reaction kinetics at higher pyrolysis temperatures for PE [31]. Encinar et al. confirmed this observation for various other plastics, such as PP, PS, and PET [109]. The pyrolysis temperature particularly affects the yield and composition of the valuable target fractions of pyrolysis gas and pyrolysis condensate. In general, Chang et al. conclude in their literature study that a higher pyrolysis temperature results in shifting yields from condensate to the gas fraction [20]. Other studies demonstrated this effect when examining mixed plastic waste [110]. With mixed plastics, which often contain high proportions of polyolefins, this shift is caused by the statistically distributed product composition of polyolefins shifting from high-molecular-weight to low-molecular-weight

compounds as the temperature rises [105]. As a result of more intensive and frequent primary cracking reactions, this leads to fewer wax-like products [105]. However, higher temperatures also increase the proportion of aromatics, as secondary reactions intensify [20]. Lopez et al. conclude from their studies on temperature dependence in a mixture of PE, PP, PS, PET, and PVC that the optimal pyrolysis temperature for producing a maximum amount of condensate with a low molecular weight distribution is obtained at approximately 500 °C [17].

The influence of the heating rate on the pyrolysis result is related to the influence of temperature. Dynamic TG tests performed at constant heating rates reveal that a higher heating rate results in a shorter reaction time for polymers at low reaction temperatures. Ceamanos et al. demonstrated this by investigating PE with varying heating rates between 5 to 50 K·min⁻¹ [31]. Similar results were obtained at heating rates of 100 to 300 K·min⁻¹ in the decomposition of PE, PP, and PVC [111]. The temperature profile over time, therefore, shifts to higher temperatures if the sample mass is low and inner heat gradients are negligible, which is why effects analogous to high pyrolysis temperatures are observed for high heating rates [101]. Accelerated pyrolysis reactions at higher heating rates and the associated apparent shift of the reaction to higher pyrolysis temperatures in TG curves are also verified for mixed plastics [101]. The analogy to the influence of temperature is also evident in the shift in product yields and the change in product composition. Chang et al. conclude that at low temperatures and moderate heating rates below 200 K·min⁻¹, predominantly pyrolysis oil is formed [20]. The investigations by Encinar et al. underline this conclusion, as increasing heating rates result in a higher gas yield at the expense of the oil yield when pyrolyzing PE, PP, PS, ABS, and PET [109]. The product composition changes accordingly with higher heating rates to condensates richer in aromatics and HCs with lower molecular weight [20]. However, this effect is less pronounced with increasing pyrolysis temperature [20].

The controlled setting of the temperature and heating rate in the reactor system allows for selective influencing of the pyrolysis process. As previously presented, the primary decomposition temperature is polymer-dependent. Thus, temperature staging can be used to optimize the yields and product composition in polymer mixtures or mixed plastic waste. The gradation is achieved by exposing the polymers to a defined pyrolysis temperature for a defined period of time. The temperature is then raised to a higher temperature and also maintained for a certain reaction time. The temperature staging is achieved either through continuous operation in a reactor system with different temperature zones [112] or through a time-dependent, stepwise increase in the reactor temperature [113,114]. Staged pyrolysis was investigated for the selective dechlorination of plastic mixtures by exploiting the rapid side chain elimination during the decomposition of PVC at 250 to 300 °C, producing mainly HCl [112,113,115,116]. Further studies on more complex plastic mixtures have demonstrated the effectiveness of deoxygenation [117], denitrogenation [118], and desulfurization [119] of pyrolysis condensates by temperature-staging. Alternatively, studies on plastic mixtures with high PS or PA6 content have shown that staged pyrolysis enables the production of pyrolysis oil fractions either rich in aliphatic compounds or enriched with styrene and caprolactam monomer [74,113,114,118]. This allows the selective separation of monomers of certain monomer-forming polymers in a mixture.

Solids residence time

Solids residence time refers to the period during which polymers and resulting solid (or non-volatile) intermediates from the primary decomposition mechanism remain in the reactor [20]. This residence time is important as it must be adjusted to the time needed for pyrolyzing the feedstock. Pyrolysis requires time for heating the feedstock and a reaction time depending on the primary decomposition kinetics. Thus, the solid residence time should exceed this time span to ensure complete conversion of the polymers or other organic waste components during pyrolytic processing [101,120].

Gas residence time

The GRT represents the time that volatile primary products remain in the hot reaction zone until they are cooled in the condensation unit [20]. This GRT is the decisive parameter for secondary reactions alongside the temperature of the gas phase [20,65]. Its impact has been experimentally investigated for polyolefins and plastic waste [17,121,122]. Dai et al. summarize that secondary reactions occur more intensely with longer GRTs [65]. As described in Chapter 2.1.2, this shifts the product distribution from pyrolysis oils to the gas while enhancing char formation.

Further affecting process parameters

Other process parameters that influence the pyrolysis result include the pressure and gas atmosphere of the pyrolysis system and feedstock morphology. For technical and economic reasons, pyrolysis plants are mainly operated at atmospheric pressure [20,105]. Pressure and temperature must be considered in combination, as the influence of pressure increases with decreasing temperature [20]. Pressure changes mainly affect phenomena occurring at the gas-liquid interface [105]. Particularly relevant are decomposition reactions, such as end-chain reactions by β -scission [105] and the evaporation behavior of primary products [123]. With increasing pressure, high-molecular-weight products tend to be retained in the liquid phase [123]. These molecules then undergo further cracking reactions [105]. The product spectrum shifts toward pyrolysis gas if the system pressure is increased [20,105]. Simultaneously, higher pressure leads to a denser gas phase, which enhances the probability of secondary reactions [123]. Consequently, the increased potential for crosslinking reactions in the melt and secondary reactions in the gas phase also favors the formation of char and aromatic compounds [123].

Nitrogen is favored as an inert gas for cost reasons [20]. When other inert gases like argon, helium, or CO₂ are applied, the pyrolysis results change. The flush gases affect the density of the gas phase, thereby promoting or inhibiting secondary reactions [20]. Nevertheless, this influence is considered of minor importance [20]. Switching the atmosphere to reactive gases such as hydrogen, steam, or recirculated pyrolysis gas can significantly influence the product spectrum. In the presence of hydrogen or steam, the formation of aromatics and char is inhibited while unsaturated HCs are reduced in favor of saturated alkanes [20,101]. Conversely, recirculating pyrolysis gas increases the aromatic content, caused by an extension of the GRT and the associated secondary reactions [101].

Several authors consistently report that particle size is a decisive parameter for heat transfer [20,104,124]. Bigger particles offer a reduced surface area and thus impair heat transfer. In combination with the low thermal conductivity of polymers, this results in a more pronounced inner-particle temperature gradient [109]. Similar to the heating rate, the temperature gradient affects the heating of the polymer chains in the particle core. As a result of the longer heating phase in the particle core, the reaction rate of the overall process decreases with larger particles [20,124]. However, this effect is considered rather weak in the range of commonly used particle sizes from 40 μm to 5 cm [104].

2.3 Reintegration of Pyrolysis Products

From a chemical recycling perspective, the reintegration of pyrolysis products into the (petro-)chemical value chains by replacing fossil feedstocks must satisfy certain prerequisites. These include technical feasibility, an ecological advantage over conventional fossil-based polymer production, and the economic viability of the process. Multiple case studies conducted life cycle assessments for plastic waste treatment, emphasizing the overall environmental superiority of the complementary use of mechanical and chemical recycling over incineration [125–131]. Economic viability depends heavily on the regulatory framework conditions and future scenarios of the energy mix and fossil raw materials [126,132–135]. Therefore, this chapter focuses on the technical aspects of potential integration routes for pyrolysis products. The technical specifications of the most important process routes are discussed in comparison with the properties of pyrolysis products.

2.3.1 Reintegration Options

Recycling via pyrolysis constitutes waste-to-polymer recycling in the narrow sense and, more broadly, recycling via the waste-to-chemicals pathway. These recycling pathways preclude the widely discussed use of pyrolysis products as fuel [86]. Consequently, solid residue and pyrolysis gas combustion can solely function as a by-product utilization to enhance efficiency. Several options are discussed for reintegrating pyrolysis oil into the chemical industry. The possibilities include further processing of pyrolysis oils into various basic chemicals or product fractions, such as naphtha or middle distillates [86,136]. The intermediates bridge the gap between polyolefin-rich mixed plastic waste and synthetic products of the chemical industry, closing the recycling loop. Multiple reintegration options discussed in the literature are presented below.

Reintegration options for pyrolysis oils from special, contamination-free, or low-contamination polymer fractions have been evaluated extensively [86,136–145]. The most elegant reintegration solution is the direct utilization of monomers and base chemicals produced during pyrolysis [86]. However, this option is only suitable for certain polymers with selective decomposition mechanisms, such as polystyrene [137,138] or PA6 and PET [86]. By adding catalysts with active acidic sites, high yields of ethylene and propylene can also be achieved for polyolefins in intermediate pyrolysis [86,136,139]. However, catalyst poisoning and its resulting deactivation prevent this option, even at low levels of heteroatom contamination in polyolefin waste [136]. The use of waxes primarily formed from PE decomposition as pharmaceutical white oils or lubricants is also discussed [140]. However, the wax fraction must first be processed using mild hydroprocessing [140].

The above-mentioned recycling pathways are therefore polymer-specific and depend on high-quality waste fractions. Lopez et al. compare further, more flexible integration options for polyolefin-based pyrolysis oils [136]. The integration of pyrolysis oils into fluid catalytic cracking (FCC) or hydrocracking plants is considered promising [141–143]. However, improving the pyrolysis oils by hydrogenation of the unsaturated bonds and reducing the aromatic content before cracker application is decisive [141].

The integration of mixed plastic pyrolysis oils in gasifiers offers certain benefits in this regard [144–146]. Contaminants can be removed during synthesis gas cleaning, avoiding the need for intensive pyrolysis oil upgrading [145].

Applying mixed plastics pyrolysis oils to steam crackers has been examined intensively [15,134,147–150]. This promising integration option will be discussed in more detail in the next chapter.

2.3.2 Steam Cracker Route

Steam crackers often employ naphtha to produce light olefins as target products, which are required, for example, for the synthesis of PE and PP [151]. In future scenarios, the process can also be supplied by mixed plastic pyrolysis oil, thereby enabling polymer-to-polymer recycling [134,147]. The feedstock specifications of steam crackers are stricter, but comparable to those of FCC or hydrocrackers [151]. Thus, they represent a benchmark regarding properties that pyrolysis oils must fulfill for successful reintegration into existing cracker facilities. An overview of critical specification parameters is provided in Table 2.

Table 2: Comparison of characteristic properties of fossil-based naphtha and common properties of pyrolysis oils stemming from mixed plastic waste [15,105,152].

Property	Fossil-based naphtha	Pyrolysis oil
Boiling Range ^[15]	35 – 200 °C	30 – 560 °C
Density (at 15 or 20 °C) ^[105,152]	< 0.9 g·ml ⁻¹	0.71 – 0.98 g·ml ⁻¹
Pour Point ^[105,152]	< -5 °C	-9 – 12 °C
Hydrocarbon composition		
Hydrogen-carbon ratio ^[152]	> 2 mol·mol ⁻¹	> 1.5 mol·mol ⁻¹
Olefins ^[15]	< 2 wt. %	29 – 32 wt. %
Aromatics ^[15]	< 12 wt. %	11 – 19 wt. %
Heteroatom contaminants		
Nitrogen ^[15,152]	100 ppm	> 300 ppm
Oxygen ^[15]	100 ppm	> 1250 ppm
Chlorine ^[15,152]	3 ppm	> 30 ppm

The conversion of the pyrolysis oil into a feedstock that meets specifications for steam crackers demands intensive post-processing [15,150]. This post-processing is referred to as oil upgrading in the following. Multiple authors specify the advantages of different upgrading steps. Distillation facilitates the separation of pyrolysis oils into product fractions with suitable boiling ranges [153,154]. Inorganic particles like metals or salts are removed by filtration [149]. Hydrotreatment, extraction, or adsorption processes enable the separation of heteroatom-containing HCs [15,134]. The energy-intensive post-processing reduces the overall carbon efficiency because of processing losses [134]. By integrating by-products into petrochemical clusters, this disadvantage is minimized [155].

Kusenberg et al. emphasize that the capacity of steam crackers exceeds the available waste quantities by magnitudes [134]. Pyrolysis oil distillation cuts will be blended with fossil or renewable naphtha from other sources, reducing the need for upgrading [134]. Determination of dilution factors enables oil integration even when certain oil properties do not meet the specification [15]. Nevertheless, high efficiency of every conversion step in the recycling loop is imperative. Optimizing the pyrolysis process to improve the oil quality is thus necessary for chemical plastic recycling. Table 2 emphasizes the objectives for oil improvements. Despite a high pyrolysis oil yield, the fraction of compounds in the desired boiling range has to be maximized. In addition, heteroatom content minimization, a shift of unsaturated compounds towards paraffins, suppression of aromatics formation, and removal of inorganic impurities must be achieved [15,150]. For this purpose, the application of active lime as a sorbent in the pyrolysis reactor is suggested to remove chlorine [134]. Dogu et al. highlight the importance of adjusting process parameters and implementing innovative pyrolysis process designs [86].

3 Materials and Methods

This chapter describes the thermoplastic feedstocks under investigation. The reactors used for pyrolysis experiments and the analyses applied to the gaseous and condensable products are introduced. Finally, the approach and objectives of the superposition model for calculating the decomposition kinetics, ED, and product yields are explained.

3.1 Feedstocks

The composition of plastic waste is diverse. Nevertheless, thermoplastics account for the majority of plastics produced in the EU [7]. Polyolefins in the form of LDPE, medium-density, and HDPE, as well as PP, represent the majority of these thermoplastics of about 51 wt.% [7]. In addition, increased amounts of PVC, PET, PS, polyamides, and copolymers based on styrene with nitrogen-containing components are produced [7]. These thermoplastic types account for 77 wt.% of the annual global production, not considering unspecified recyclates [7]. By reducing the variety of input materials to these plastic types, common waste streams stemming from lightweight packing sorting residues, shredder fractions from the automotive sector, or waste of electronic and electrical equipment can be reflected [120]. Meanwhile, nitrogen-, oxygen-, and chlorine-containing plastics are the sources of the most important contaminants in common waste fractions considered as feedstock for chemical recycling via pyrolysis [15]. Therefore, this dissertation focused on eight different types of thermoplastics. These plastics, namely Hostalen ACP 9255 Plus (HDPE), Lupolen 24020H (LDPE), Moplen HP 552H (PP), Styrolution 156F (PS), Sinkral F332 (ABS), and Alphalon 27 (PA6), were available as primary granulates with a particle size ranging from 2 to 5 mm. Plastipak Italia Preforme provided primary PET granulate. Primex P225-2, a virgin PVC, was available as a powder. Alongside polymers, plastic products contain additives such as fillers, plasticizers, stabilizers, or flame retardants [87]. These can significantly influence their pyrolysis behavior [88,90,156]. Thus, all polymers were free of additives to avoid interference with the pure or mixed plastic during pyrolysis. The virgin PVC powder was only used in laboratory-scale experiments, resulting from technical requirements regarding the particle size in the feedstock dosing systems. Therefore, PVC granulate from Inovyn was employed in the pilot-scale reactors. The granulate, used for window profile production, contained about 10 wt.% inorganic fillers and 2-3 wt.% of stabilizers. The manufacturer specified these fillers as CaCO_3 and TiO_2 . The plastics were characterized regarding their elemental composition, moisture and ash content, and higher heating value (HHV). The results listed are shown in Table 3.

The feedstock influence was examined using three reference mixtures each prepared from the polymers mentioned above. Also, a defined PCW was investigated. One reference mixture (Mix A) consisted of LDPE, PP, and PS. Mix A comprises only carbon and hydrogen. Two other reference mixtures reflected the composition of polyolefin-rich plastic waste with varying proportions of nitrogen-, oxygen-, and chlorine-containing polymers. These reference mixtures, Mix B and Mix C, contained ABS, PET, PA6, and PVC. The composition and the HHV of the mixtures are listed in Table 3. Furthermore, binary and tertiary mixtures in different proportions of the polymers were examined in TG (binary mixture: Polymer A/B = 75/25, 50/50, and 25/75; ternary mixture: Polymer A/B/C = 30/30/40). Two additional reference mixtures (TG Mix 1 and TG Mix 2) were used. The proportions of the polymers in all reference mixtures under investigation in this dissertation can be found in Table 4.

Table 3: Elemental composition, moisture, ash content, and HHV of the polymeric feedstocks employed for pyrolysis experiments [adapted from Publication 1].

Polymers	Composition / wt. %							HHV / MJ·kg ⁻¹
	Moisture	Ash	C	H	N	Cl	O ^a	
LDPE	< 0.01	< 0.01	85.8	14.2	< 0.2	0.0	0.0	46.3 ^b
HDPE	< 0.01	< 0.01	85.8	14.2	< 0.2	0.0	0.0	46.1 ^b
PP	< 0.01	< 0.01	85.8	14.2	< 0.2	0.0	0.0	46.1 ^b
PS	< 0.01	< 0.01	92.0	8.0	< 0.2	0.0	0.0	41.3 ^b
ABS	0.3	< 0.01	86.2	8.0	5.5	0.0	0.0	39.6 ^b
PET	0.2	< 0.01	63.3	4.4	< 0.2	0.0	32.1	22.9 ^b
PA6	1.2	< 0.01	63.6	9.8	12.6	0.0	12.7	31.2 ^b
Virgin PVC	0.1	< 0.01	39.6	5.6	< 0.2	54.7	0.3	20.3 ^c
PVC	0.2	10.6	36.2	4.9	< 0.2	47.9	0.0	18.3 ^c
Mix A ^d	< 0.01	< 0.01	87.6	12.4	< 0.2	0.0	0.0	44.8 ^c
Mix B ^d	0.0	0.2	83.5	13.4	0.3	1.0	1.6	44.5 ^c
Mix C ^d	0.1	0.5	80.6	11.6	0.9	2.4	3.9	41.1 ^c
PCW	0.0	2.2	80.0	12.3	0.8	1.4	3.2	41.2 ^b

^A calculated as the difference to 100 wt. %.

^B experimentally determined.

^C calculated from the elemental composition.

^D calculated from the proportion of individual polymers in the mixture.

The collection of packaging waste and consumer products allowed for the investigation of a well-defined PCW. This PCW is a non-representative waste stream as it was not derived from an established industrial collection system. It included products that are labeled according to the European identification system and was composed of the previously described plastic types [157]. Stick-on labels were removed manually. The waste was washed and dried to remove moisture or biomass contamination. After two-stage shredding (Untha RS30 and Retsch SM-200) and subsequent pelletizing (Amandus Kahl Type 14-175), cylindrical pellets with a diameter of 6 mm and a height of 5-15 mm were generated. Manual mixing ensured sufficient homogenization of the feedstock. Since the waste consisted of real end-of-life products, it also contained additives of unknown type and quantity. Dosing into the STR required additional compaction of the PCW. At temperatures of 200 °C, dimensionally stable extrudates with a diameter of 2-4 mm were produced using a laboratory extruder (HAAKE PolyLab Rheomex OS). Further information on PCW is provided in Table 3 and Table 4.

For characterizing the STR pyrolysis system, magnesium oxalate dihydrate (MgOx) was used. MgOx exhibits a defined decomposition mechanism. This mechanism follows a two-stage decomposition at temperatures of about 150 °C and above 450 °C, according to equations R1 and R2, respectively [158].

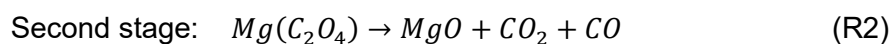
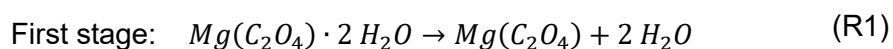


Table 4: Polymer type-specific composition of the investigated thermoplastic reference mixtures and the PCW [Publications 1 and 2].

Polymer	Proportion of polymer type in the mixture / wt. %					PCW
	Mix A	Mix B	Mix C	TG Mix 1	TG Mix 2	
LDPE	40.0	70.0	50.0	20.0	20.0	29.4
HDPE	-	-	-	20.0	20.0	17.1
PP	30.0	20.0	15.0	20.0	10.0	25.1
PS	30.0	2.0	10.0	20.0	10.0	4.2
ABS	-	-	5.0	20.0	10.0	3.8
PET	-	4.0	10.0	-	10.0	10.1
PA6	-	2.0	5.0	-	10.0	6.3
PVC	-	2.0	5.0	-	10.0	4.0

3.2 Pyrolysis Systems

In this work, experiments were conducted on four pyrolysis systems at different scales. Laboratory-scale reactors, such as TG or DSC, ensured experiments under well-controlled process conditions. The experiments in the STR and the bench-scale ASR system exhibit heat and mass transfer limitations, comparable to plants for industrial-scale chemical recycling of waste plastics. They approximate both fundamentally different reactor types of the ideal stirred tank reactor and the plug flow reactor. Therefore, the evaluation of the pyrolysis process in the different reactors enabled fundamental investigation of the influence of the feedstock and the impact of reactor design.

3.2.1 Differential Scanning Calorimetry

The DSC is a common method for the thermal analysis of polymers. DSC records the heat flux of a sample under a defined temperature program in an oven [159]. The heat flux is induced by a time-dependent temperature difference between an empty reference crucible and a crucible filled with the sample. The DSC enables the identification and quantification of exothermic and endothermic processes, such as phase changes or reactions, depending on the sample temperature [159]. The experiments were required as an experimental database for superposition-based ED modeling.

A 214 Polyma (Netzsch) was used to determine the enthalpy of fusion and the reaction enthalpy. The analysis was conducted in a nitrogen atmosphere and involved three cycles. Initially, the sample was heated and cooled twice between 30 and 300 °C at a rate of 10 K·min⁻¹ to eliminate thermal memory effects caused by polymer processing during production. In the case of PVC, the upper temperature was set to 200 °C to prevent early thermal decomposition. In the last cycle, the oven was heated to 550 °C. Each analysis used 10 mg of the sample prepared in aluminum crucibles with pierced lids. Following DIN EN ISO 11357, a linear baseline was applied for melting enthalpy determination [160]. A Bezier-curve baseline was used for the reaction enthalpy. The heat capacity of polymers and quartz sand, the moderator used in the ASR and STR systems, was examined using a Netzsch 204 F1 in an argon atmosphere. Temperature calibration and the heat capacity determination were performed using the sapphire method according to DIN 51007 [161]. Characteristic temperatures, such as the glass transition temperature (GT) or the melting temperature (MT), were defined according to DIN EN ISO 11357 [160,162]. Linear approximations allowed the simplification of the temperature-dependent curves in different regimes: below the GT, between the GT and the MT, plus above the MT.

3.2.2 Thermogravimetry

Monitoring the sample mass as a function of time or temperature enables the investigation of the decomposition behavior of thermoplastic feedstocks in the TG [159]. For the studies, a TG 209 F1 (Netzsch Group) with an automatic autosampler was used. Samples were heated at constant heating rates of 2, 5, 10, 20, and 40 K·min⁻¹ from 30 to 900 °C. An inert atmosphere was ensured by a nitrogen flow of 60 ml/min. Each polymer was measured at least twice after validating reproducibility by performing five measurements with a constant heating rate of 10 K·min⁻¹. The results of the individual measurements were averaged. This procedure was in accordance with DIN 51006 [163]. Following the ICTAC recommendations, it allowed for the determination of kinetic parameters [164]. With this methodology, a kinetic study of thermoplastic mixtures was enabled. The decomposition behavior of polymer mixtures was compared to model calculations. Also, temperature-staged pyrolysis experiments were performed. In these experiments, the temperature program was adjusted by implementing isothermal holding segments at 300 °C for 30 min and 370 °C for 60 min while maintaining the heating rate of 10 K·min⁻¹. Other experimental parameters were kept constant, ensuring comparability with the dynamic TG experiments. In all tests, 10 mg of the sample was placed in Al₂O₃ crucibles. Sample slices were cut from the primary granulate using a scalpel. The nonuniform particles weighed between 0.5 and 5 mg. The total sample mass only varied by a maximum of 0.1 mg. In addition to pure polymer experiments, binary and tertiary mixtures, as well as TG Mix 1 and TG Mix 2, were investigated. The individual polymer mass in the mixtures varied by 10-15 µg around the desired proportion. To evaluate the influence of the interface between different polymer types, samples with identical proportions but different levels of homogeneity were applied. Specific mixtures of pure polymer powders were prepared (LDPE/PP, LDPE/PS, PS/ABS, and PET/PA6). The powder mixtures exhibited more polymer interface available for interaction reactions. In addition, extrudates of these polymer combinations were produced using a Haake MiniLab 3 microextruder (Thermo Fisher Scientific). With the particle, the powder, and the extrudate samples, binary mixtures with different degrees of homogenization were compared. The samples reflected a regular polymer melt interface, a homogeneous mixture at macroscopic and at molecular levels, respectively. Additional tests were conducted with novel 3D-printed Al₂O₃ crucibles. The crucibles featured identical dimensions compared to the common crucibles but contained a wall that separated the polymers in different compartments. Each compartment was filled with particle slices of only one polymer type. This enabled the experimental validation of the superposition approach through comparative measurements without any polymer melt interface.

3.2.3 Screw Reactor Pyrolysis System

The ASR pyrolysis system was used for intermediate pyrolysis experiments on a pilot scale in continuous operation. It is characterized by high feedstock flexibility and offers accurate mass and energy balancing of the pyrolysis process. These advantages have been demonstrated in previous studies for a wide variety of feedstocks [120,139,165,166].

The system consisted of a dosing unit, an electrically heated screw reactor, and a downstream two-stage condensation unit for separating the pyrolysis oil and permanent gas. An integrated hot-gas filtration system was located in the freeboard of the screw reactor. The system is shown schematically in Figure 5. The nominal heating capacity of the ASR is 40 kW. The feedstock and quartz sand were supplied continuously via two separate hoppers, each equipped with a dosing screw. The sand served as an inert process moderator, improving the feedstock transfer through the reactor and the heat

transfer to the polymer. The feedstock and sand were added, applying a dosing rate of 1 and 4 kg·h⁻¹, respectively. The cold polymer-sand mixture fell into the reactor trough and was conveyed into the reactor. The reactor was heated to 500 °C. The screw rotated slowly at about 1 rpm. The reactor had a heated length of approximately 2 m with a freeboard volume of about 80 L. The screw featured a total length and a diameter of approximately 2.5 and 0.15 m. The solid residence time was set at 45 min to ensure sufficient reaction time for complete decomposition of the polymers in an inert atmosphere. This atmosphere was generated by flushing the reactor with 12 L_{NTP}·min⁻¹ nitrogen before and during the experiment. The sand and solid pyrolysis products are discharged at the end of the reactor. The volatile products evaporated, passed through the hot gas filtration system, and entered the two-stage condensation unit. In the first stage, consisting of two double-tube heat exchangers, the pyrolysis gas was cooled to 60 °C. A second stage, also containing two double-tube heat exchangers, further cooled the gas to approximately 0 °C. Electrostatic precipitators were installed at the end of both stages to remove droplets from the gas phase in the potentially oversaturated vapor. Condensing compounds were collected in flasks as pyrolysis oil. The physical properties and chemical composition of the permanent gas leaving the condensation unit were continuously analyzed.

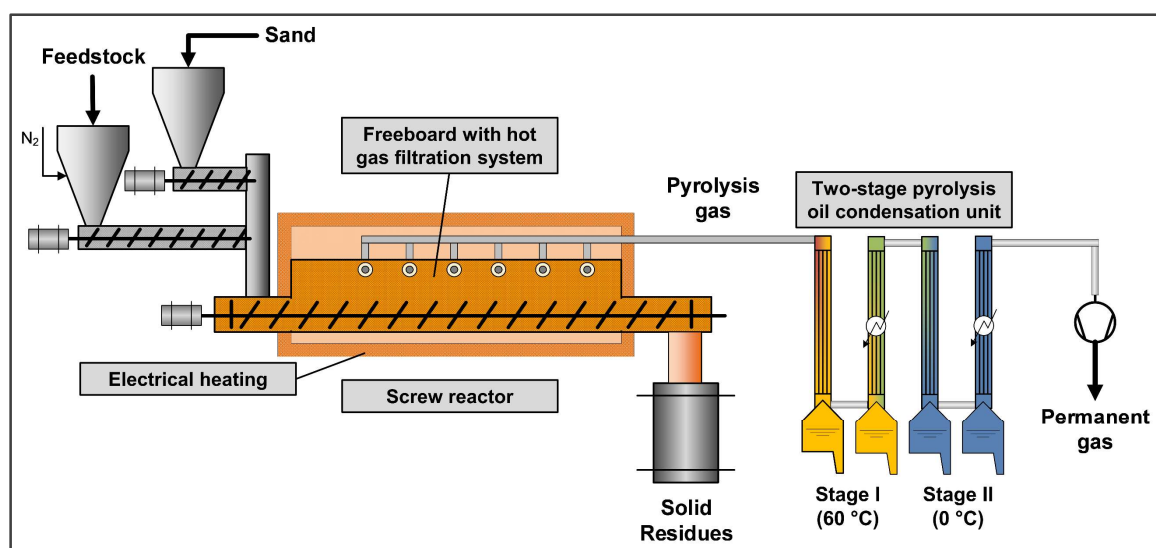


Figure 5: Schematic of the ASR pyrolysis system with material dosing section, electrically heated screw reactor, and two-stage condensation unit (adapted from Publication 4).

Determining the product yields of solid residue, pyrolysis oil, and permanent gas enabled the mass balancing of the test run. Together with the composition analyses, the mass balances were used to discuss the feedstock influence and the reactor impact. In addition, the feedstock-specific minimum pyrolysis ED was determined during steady-state operation by subtracting the characteristic values of a reference test without polymer addition. Thus, the experiments allowed the validation of the ED prediction based on DSC data.

3.2.4 Stirred-Tank Reactor Pyrolysis System

For the investigations of this dissertation, a pyrolysis system consisting of a STR was designed, constructed, commissioned, and characterized. The reactor recorded time-dependent variations in the pyrolysis conditions. This facilitated the assessment of technically relevant effects, such as heat-transfer limitations. With this system, the mass balance of pyrolysis experiments was evaluated, allowing comparisons to experiments at the ASR system regarding the impact of the reactor type.

In addition to the reactor vessel with its stirrer and agitator shaft, the STR system included a dosing unit consisting of a feedstock container and a valve lock as well as a downstream condensation unit. The main aggregates of the developed STR system are shown schematically in Figure 6.

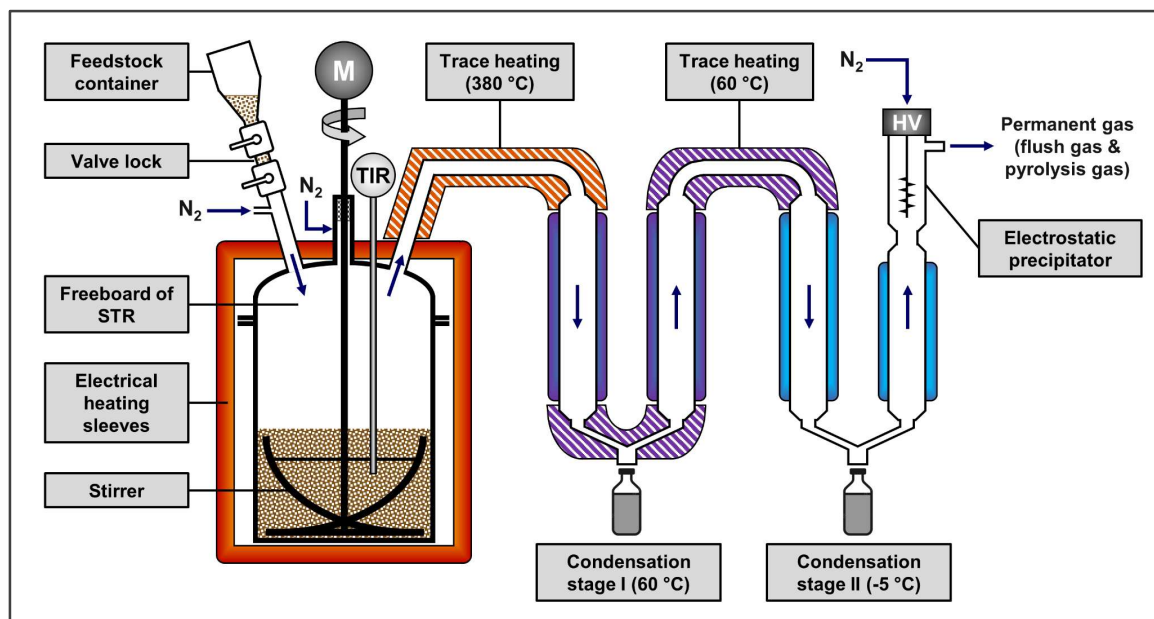


Figure 6: Schematic of the STR system including valve lock for material dosing, electrically heated stirred-tank reactor, and two-stage condensation unit (Publication 4).

The STR system comprised a cylindrical reactor vessel with a height of 30 cm, a diameter of 13.3 cm, and a total volume of 2.7 L. It was electrically heated by two heating sleeves of 1.25 kW each. Two thermocouples were located on the heated outer reactor wall to regulate the power input and maintain a constant wall temperature. Another thermocouple was placed inside the reactor system near the agitator shaft to monitor the temperature of the feedstock during the experiment. A tailored Paravisc-type impeller (EKATO GmbH) homogenized the feedstock mixture. It was driven by an electric motor having a maximum torque of 12 Nm. All experiments were conducted at a stirring speed of 50 rpm. The feedstock was stored in a feedstock container. By opening a valve lock comprising two ball valves and located underneath the container, feedstock was introduced into the reactor via a vertical fall neck. A nitrogen inlet was located at the fall neck. It served as the main flush gas inlet. Another inlet was located below the agitator shaft seal. This additional nitrogen flow prevented pyrolysis gases from flowing into the agitator shaft of the reactor system to avoid unwanted product deposition. A further nitrogen inlet at the head of the electrostatic precipitator of the condensation unit fulfilled the same function. The nitrogen for the main inlet, the agitator shaft flushing, and the precipitator was supplied by three mass flow controllers set to 2, 0.3, and 1 L_{NTP}·min⁻¹, respectively.

Evolving pyrolysis gas was flushed out of the reactor via an exhaust pipe and transferred into the first part of the two-stage condensation system. The exhaust pipe was equipped with a trace heating maintaining 380 °C. Each condensation system consisted of two vertical double-tube heat exchangers of each 1.5 m length. The condensers were connected by a Y-shaped pipe. Condensing products drained the exchangers and were collected in a glass flask at the bottom of the Y-pipe. The first stage was operated at 60 °C. The second stage was constructed in the identical design to the first stage, but was operated at a lower temperature of -5 °C. The electrostatic precipitator removed droplets in the potentially oversaturated gas comprised of nitrogen and pyrolysis products at 10 kV,

after the last condenser. The two-stage condensation unit is geometrically similar to the condensation system of the ASR pyrolysis plant. However, the lower purge gas and feedstock flow rates in the STR system result in lower gas velocities and longer residence times, which overall might intensify vapor condensation. In addition, the second condensation stage in the STR setup was operated at a temperature 5 °C lower than in the ASR system. Therefore, minor differences in condensation behavior between the two systems may occur. All connecting pipes were heated to prevent clogging by uncontrolled condensation of products. The permanent gas was analyzed by gas sensors for volume flow and gas density recording. Before transferring the gas to the flare, gas samples were withdrawn for offline gas analyses with an advanced GC.

Before the experiment, the reactor was cleaned and inerted with nitrogen. The feedstock was manually premixed, stored in the container, and also inerted. In all experiments, 2 kg of quartz sand was used as a moderator. The sand facilitated the mixing of the feedstock, which forms a highly viscous polymer melt and sticky intermediates while pyrolyzing [21]. The sand also served as a buffer for temperature variations caused by endothermic processes after feedstock addition, such as its heating, melting, reaction, or product evaporation. Before the start of the experiment, the reactor was inerted, filled with sand, and heated to the reactor set temperature. The valve lock enabled different feedstock dosing modes. Most of the experiments were conducted by semi-continuous feedstock dosing via alternating ball valve opening and closing. The feedstock was added in dosing cycles of five-minute intervals. Depending on the polymer density, the added feedstock mass ranged from 23 g (PCW) to 37 g (PVC) per cycle, corresponding to feed rates between 276 and 444 g·h⁻¹. A total mass of 250 g was dosed in each experiment conducted with LDPE, PP, PS, ABS, PA6, PVC, Mix A, Mix B, Mix C, and the PCW. This method minimized the temperature fluctuations in the reaction zone while the reactor wall was heated to 500 °C. Gas samples were usually taken after the fifth and eighth dosing cycles, which corresponded to 21 and 36 min after the first feedstock dosing.

For temperature-staged pyrolysis examination, the system was operated in batch mode. Mix C was used in these experiments. Both ball valves of the valve lock were opened simultaneously until 250 g of feedstock had fallen from the container into the reactor. For staged pyrolysis experiments, the reactor temperature was set to 370, 400, and 430 °C to investigate the temperature influence of the first pyrolysis stage. After 90 min (for 370 °C and 430 °C experiments) and 96 min (for 400 °C experiment), the reactor temperature was increased to the second stage set temperature of 500 °C with maximum heating power. Other parameters or aspects of the experimental procedure were maintained constant. After all experiments, the experimental settings were maintained for an additional 90 min to ensure complete conversion of the polymers. Also, sufficient time for product separation of the condensable products and flushing of the pyrolysis gas was guaranteed by the post-experimental delay. By weighing the residual mass in the reactor and the mass of the glass flasks, the yield of solid residue and pyrolysis oil was determined. With time-dependent resolution of the online gas sensors, the mass of pyrolysis gas was calculated.

Before pyrolysis experiments, the system was characterized and reliable mass balancing was validated using 150 g of MgOx under the same operating conditions as applied for polymer experiments. The decomposition products MgO, water, CO, and CO₂ were assumed to represent solid residue, condensable products, and pyrolysis gas, respectively.

3.3 Analytical Methods

A variety of analytical methods were used to characterize the feedstocks, the permanent gas, and the pyrolysis oil in detail. Alongside established methods, a novel 2D-GC method was developed within the frame of this dissertation.

3.3.1 Elemental Analysis

The elemental analysis was performed with the thermoplastic feedstocks and pyrolysis oils using a Truspec CHN Micro elemental analyzer (LECO Corporation), in accordance with DIN EN ISO 16948 [167]. This analyzer provided information on the proportions of carbon, hydrogen, and nitrogen in the sample. Additional analyses were conducted using a system comprising an AQF-2100 combustor (a1-EnviroScience GmbH) coupled with an Aquion ion chromatograph (Thermo Fisher Scientific GmbH), which enabled the analysis of the chlorine content. Furthermore, the ash content (600 °C for at least 5 hours) and the moisture (105 °C for at least 1 hour) of the polymers, as well as the PCW, were determined using a muffle oven. The water content of the pyrolysis oils was assessed by Karl Fischer titration using a 870 KF Titrino (Metrohm AG), in accordance with DIN 51777 [168].

3.3.2 Calorimetry

The HHV of the feedstocks and pyrolysis oils was determined in accordance with DIN 51900 using a C5000 calorimeter (IKA GmbH & Co. KG) [169]. The HHV was essential to reference the ED and to correct the elemental analysis when calculating the oxygen content in pyrolysis oils.

3.3.3 Simulated Distillation

Simulated Distillation (SimDist) was used to analyze the compound distribution in the pyrolysis oils concerning their boiling curves. It was performed following ASTM D 7169:2020 in a high-temperature GC setup [170]. The oven program covered a temperature range from 40 °C to 435 °C. The samples were diluted in C₂S to a concentration of approximately 10 mg·g⁻¹.

3.3.4 Nuclear Magnetic Resonance Spectroscopy

Additional nuclear magnetic resonance spectroscopy (NMR) analyses using a low-field Spinsolve MultiX benchtop device (Magritek) enabled quantitative analysis of the pyrolysis oils regarding the distribution of ¹H atoms across various functional groups. This allowed the distinction between saturated and unsaturated aliphatic structures, aromatic groups, and functional groups containing heteroatoms. The analysis was performed using a ¹H measurement with an 80 MHz permanent magnet. Samples were measured three times, with 16 scans and activated ¹³C-decoupling. The pulse angle was set to 90° and the repetition time to 15 s. The spectrum was referenced by adding 20 µL tetramethylsilane (TMS) to achieve a consistent chemical shift. The obtained spectrum was baseline-corrected using a polynomial algorithm. Liquid pyrolysis oils were analyzed neat, while wax-like pyrolysis oils were dissolved in deuterated chloroform to a concentration of approximately 50 mg·mL⁻¹.

3.3.5 One-dimensional Gas Chromatography

The pyrolysis gas was characterized offline using an advanced one-dimensional gas chromatography (1D-GC) system (Teckso GmbH) based on an 8890 GC (Agilent Technologies) and various detectors. The thermal conductivity detector (TCD), flame ionization detector (FID), and 5977C quadrupole mass spectrometer (qMS) (Agilent Technologies) enabled simultaneous identification and quantification of the compounds in the permanent gas. The TCD was installed subsequent to an external isothermal GC oven

and was used to analyze N_2 , O_2 , CO_2 , CO , and CH_4 . Applying helium as a carrier gas prevented the determination of H_2 . The qMS allowed for the identification of HCs in the range from C_2 to C_{10} . The compounds identified in the MS were quantified based on their FID signals. The quantification was performed using a three-point calibration with linear calibration curves including the zero point. With the integrated peak area A_i and the response factor R_i of a compound i , the concentration c_i in the pyrolysis gas was determined according to Equation (3.1).

$$c_i = \frac{A_i}{R_i} \quad (3.1)$$

With the concentration, the compound's proportion related to the total gas amount can be calculated. Zeller et al. provide a detailed overview of the measuring procedure and the hardware setup of the 1D-GC system [171].

3.3.6 Two-dimensional Gas Chromatography Development

A two-dimensional gas chromatography (2D-GC) method has been developed within this dissertation for the comprehensive and detailed analysis of the chemical composition of complex pyrolysis oils. The developed method is presented in Publication 3. The following chapter summarizes the methodology, including the obtainable insights and system limitations. The measurement system consisted of an 8890 GC, a 5977B qMS, and an 8255 nitrogen chemiluminescence detector (NCD) (all Agilent Technologies). A FID was installed upstream of the NCD. The schematic overview of the system configuration is shown in Figure 7.

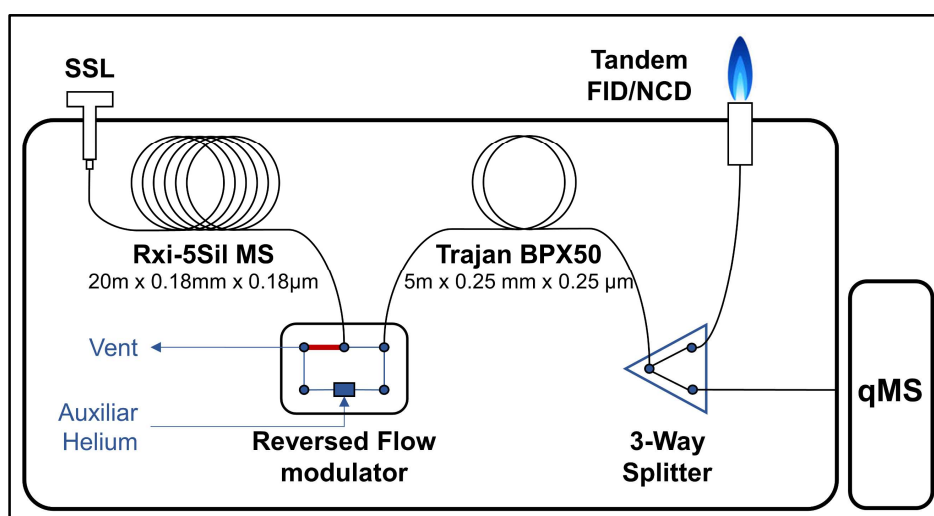


Figure 7: Overview of the employed 2D-GC system (Publication 3).

The pyrolysis oil sample was injected into a split/splitless injector (SSL) by a 7693A automated liquid sampler. The SSL was maintained at a temperature of 350 °C. The inlet pressure was set to 34.9 PSI. Helium was used as the carrier gas. The sample-carrier gas mixture entered the first separation column at a ratio of 20:1. The non-polar Rxi-5Sil MS (Restek GmbH) capillary column separated the analytes depending on their boiling behavior. The column flow rate was 0.5 mL·min⁻¹. A reversed flow modulator followed the first column. This modulator alternated between a 10-second modulation phase and a 0.36-second injection phase. This enabled the collection of analytes from the first column at short intervals and rapid reinjection into the second separation column. This second column was a mid-polar BPX50 (Trajan Scientific and Medical) capillary column. In the BPX50 column, the analytes that had been accumulated and refocused by the modulator were separated by their polarity. The flow rate of the column was set to 21 mL·min⁻¹. After

this column, a SilFlow GC 3-port splitter (Trajan Scientific and Medical) was installed. The splitter divided the analytes at a volumetric ratio of 1:10 between two connectors, leading to the qMS and the tandem FID/NCD system, respectively. The columns, modulator, and splitter were installed in the GC oven. During the measurement procedure, the oven was heated following a defined temperature program. Starting at 40 °C for 3 min, the temperature was increased at a rate of 3.5 K·min⁻¹ up to 315 °C. To ensure the complete removal of high-boiling components from the system, the maximum temperature was maintained for 39 min. The oven program is technically limited due to the columns' maximum temperature. Detailed information on the system settings, including the isothermally heated detectors, is listed in Appendix A.

The pyrolysis oil sample was dissolved in CHCl₃ before injection. The concentration varied between 70 and 100 mg·mL⁻¹ depending on the pyrolysis oil density. 1 µl of the sample was injected into the SSL. Comprehensive calibration was performed for reliable quantitative analyses. A total of 79 different reference substances were injected into the system. The triple measurement at five different concentration levels (1.0, 2.5, 5.0, 7.5, 10.0 mg·mL⁻¹) enabled a six-point calibration, taking the zero point into account. To address high styrene yields in PS-based pyrolysis oils, an additional calibration of styrene was performed at higher concentrations ranging from 10 to 70 mg·mL⁻¹. Analogously to the 1D-GC method, the compound concentration in the pyrolysis oil was calculated according to Equation (3.1, but based on the blob volume. The FID calibration exhibited high linearity with coefficients of determination of the response factors above 0.995. The accuracy of the 2D-GC main compound determination was high, with a relative statistical deviation of 1.2 %. Benzoic acid, a blob with pronounced tailing, exhibited a slightly higher statistical deviation of 2.5 %.

Evaluation of the developed method demonstrated improved separation performance compared to conventional 1D GC. Separating the pyrolysis oil into specific compounds by using two columns improved the separation of individual compounds, resulting in baseline-separated blobs. Consequently, the 2D-GC method achieved a significantly higher blob resolution than conventional 1D-GC. With this, errors caused by overlapping blobs in the complex plastic pyrolysis oil matrix during quantification were minimized. All the key products in the pyrolysis oil samples could be individually identified. Moreover, compounds with analogous chemical structures accumulated in similar retention time regions in the chromatogram. This enabled differentiation between various organic groups, such as aliphatics, monoaromatics, indenenes, naphthalenes, diphenyls, other aromatic compounds, and heteroatom-containing HCs. Grouping and integrating the blobs in these regions allowed for a quantitative, group-based evaluation of the pyrolysis oil. Technical limitations imposed by the GC temperature program resulted in high-boiling components being only partially detectable or not detected entirely. The systematic discrimination of compounds with a boiling point above 350 °C led to losses. These losses were verified by supplementary SimDist analyses, which revealed a comparable amount of a high boiling fraction in the vacuum gas oil (VGO) range above 350 °C. However, the compound-specific, group-based analyses covered 77 to 95 wt.% of the total pyrolysis mass for exemplary pyrolysis oils produced in the ASR system. Thus, an extensive characterization of the pyrolysis oils was provided. Especially, the chain length from C₆ to C₃₀ of pyrolysis oil, relevant for substituting the naphtha and middle distillate cut, was resolved in detail. The analysis was tailored to investigate pyrolysis oils of polyolefin-rich thermoplastic mixtures. The development was key to the comprehensive characterization of pyrolysis oil in this dissertation. It was complemented by the previously listed analytical methods, enabling a holistic evaluation of pyrolysis oils in the context of chemical recycling.

3.4 Superposition-based Calculations

Superposition-based modeling (SPBM) represents an empirical approach for predicting the pyrolysis behavior. The superposition principle describes the independent linear combination of properties in a mixture based on the proportions and properties of the individual components. Thus, SPBM enabled the prediction of key pyrolysis characteristics under the basic assumption that a polymer mixture reacts following the properties and decomposition mechanism of the pure polymers. Accordingly, the approach allowed for the assessment of interaction effects during the pyrolysis of plastic mixtures. Other authors successfully applied the principle to calculations of product yields, product composition, and pyrolysis ED of simple mixtures of polyolefins, polystyrene, and PET [76,121,172].

Calculation of Decomposition Kinetics

The SPBM was used to predict the decomposition kinetics of thermoplastic mixtures and to elucidate the occurring interaction effects. The model was based on the independent parallel reactions model of Zeller et al., adapted from Jomaa et al. [173,174]. It followed the Arrhenius approach. Introducing pseudo-reactions j simplified the complex reaction networks of numerous elementary reactions during the decomposition of the polymers i in the mixture. The time-dependent conversion $\alpha_{i,j}$ was calculated based on the kinetic triplet consisting of the activation energy $E_{A,i,j}$, the pre-exponential factor $k_{0,i,j}$, and the kinetic model $f(\alpha_{i,j})$.

$$\frac{d\alpha_{i,j}}{dt} = k_{0,i,j} \cdot f(\alpha_{i,j}) \exp\left(-\frac{E_{A,i,j}}{R_{id} \cdot T}\right) \quad (3.2)$$

The term for the kinetic model was further specified using an n^{th} -order model with the reaction order $n_{i,j}$ according to Equation (3.3).

$$f(\alpha_{i,j}) = (1 - \alpha_{i,j})^{n_{i,j}} \quad (3.3)$$

The number of pseudo-reactions was selected based on the decomposition stages of a polymer identified in TG experiments. For polymers with multiple decomposition stages, such as PVC or PA6, the reaction fraction $w_{i,j}$ specified the share of a pseudo-reaction to the total decomposition. The decomposition process of a polymer mixture was calculated using the sum of the pseudo-reactions and the mass fractions of the polymers x_i .

$$\frac{d\alpha_{i,j}}{dt} = \sum_i x_i \cdot \alpha_i(t) = \sum_i x_i \sum_j w_{i,j} \cdot k_{0,i,j} (1 - \alpha_{i,j})^{n_{i,j}} \exp\left(-\frac{E_{A,i,j}}{R_{id} \cdot T}\right) \quad (3.4)$$

The experiment and the model were linked by defining the conversion rate and determining the time-dependent mass loss in TG during decomposition. The definition involved the time-specific sample mass $m(t)$ as well as the mass at the start and at the end of the experiment m_0 and m_∞ , respectively.

$$\alpha_{i,j} = \frac{m_0 - m(t)}{m_0 - m_\infty} \quad (3.5)$$

According to Equation (3.6), the time-dependent mass of volatile products $m_v(t)$ was defined. It describes the formation of non-solid products, comprising pyrolysis gas and oil.

$$m_v(t) = 1 - \frac{m(t)}{m_0} \quad (3.6)$$

The root mean square deviation (RMSD) is used as a metric for the accuracy of the simulated decomposition curves. This metric can be calculated by processing the modeled and the experimentally determined mass loss for each datapoint z , as shown below.

$$RMSD = \sqrt{\frac{1}{Z} \sum_z (m_v(z)_{\text{exp}} - m_v(z)_{\text{model}})^2} \quad (3.7)$$

Calculation of Product Yields and Composition

The superposition-based approach was also applied to GC and elemental analyses of the gaseous and liquid pyrolysis products. The theoretical product yield $y_{theo,P}$ of a mixture's product fraction P was calculated by the mass fractions of the individual polymers and their respective experimentally determined yield $y_{exp,P,i}$.

$$y_{theo,P} = \sum_i x_i \cdot y_{exp,P,i} \quad (3.8)$$

The composition of the permanent gases and pyrolysis oil was analogously determined. The mass fraction of a compound, a compound group, or the contribution in the elemental analysis $z_{theo,P}$ was calculated for the respective product fraction. The polymer-specific yield of the corresponding product fraction and the corresponding experimentally determined result $z_{exp,P,i}$ in the pure polymer were considered accordingly.

$$z_{theo,P} = \sum_i x_i \cdot z_{exp,P,i} \cdot \left(\frac{x_i \cdot y_{exp,P,i}}{y_{theo,P}} \right) \quad (3.9)$$

Calculation of the Energy Demand

The minimum ED for the pyrolysis h_{py} of thermoplastic mixtures was calculated via SPBM. The calculation required DSC measurements of the pure substances. Physical and chemical processes were considered in the ED. However, plant-specific contributions, such as heat losses or the power required for periphery equipment, are neglected as they are not universally applicable to pyrolysis systems. Physical processes include the enthalpy h_{solid} for heating the solid polymer to its MT T_{melt} , the melting enthalpy h_f and the heating of the polymer melt h_{melt} to the pyrolysis temperature T_R . The reaction and evaporation of volatile products are summarized in the mathematical term of the reaction enthalpy h_R . The mass-weighted linear combination of the contributions of all polymers in the mixture allowed the minimum ED estimation.

$$h_{py} = \sum_i x_i \cdot h_{py,i} = \sum_i x_i \cdot (h_{solid,i} + h_{f,i} + h_{melt,i} + h_{R,i}) \quad (3.10)$$

The reaction enthalpy and melting enthalpy were directly determined using DSC data. The polymer-specific and temperature-dependent heat capacity was also ascertained using DSC. By linear approximation of heat capacity analysis results, the calculation of the heat capacity in different polymer regimes was possible. Depending on thermal properties such as the MT T_{Melt} or GT T_{GT} of the polymer, this resulted in fit parameters valid in different temperature ranges. The average specific heat capacity below and above the glass transition temperature, $c_{p,PreGT,i}$ and $c_{p,PostGT,i}$, as well as after melting, $c_{p,melt,i}$, covered the relevant ranges. These parameters were employed to calculate the missing contributions, considering the temperature of the introduced feedstock T_0 , as shown in Equations (3.11) and (3.12). This enabled the linkage of DSC data and SPBM to predict the minimum ED.

$$h_{solid,i} = \bar{c}_{p,preGT,i}(T_{GT,i} - T_0) + \bar{c}_{p,postGT,i}(T_{Melt,i} - T_{GT,i}) \quad (3.11)$$

$$h_{melt,i} = \bar{c}_{p,melt,i}(T_R - T_{melt,i}) \quad (3.12)$$

4 Results and Discussion

The following subchapters summarize the key findings of the publications relevant to this thesis.

4.1 Feedstock Impact

Chapter 2.1 emphasizes the composition of the feedstock as the decisive factor for the pyrolysis behavior of thermoplastic mixtures. This influence was systematically investigated by comparing the pyrolysis behavior of pure polymers and their mixtures by TG and experiments in the ASR and STR reactor. The results extracted from Publications 1, 2, and 4 are discussed in a common context to provide a comprehensive evaluation.

4.1.1 Thermal Decomposition Kinetics

Systematic TG tests were conducted to characterize the decomposition behavior concerning volatile products and solid residues, as well as the reaction kinetics of various mixtures. The results have been extracted from Publication 2.

The polymers under investigation decompose at different temperatures ranging from 250 °C to 500 °C. The PVC decomposition is in accordance with the reported three-stage mechanism [40]. PA6 shows minimal mass loss at temperatures below 250 °C, presumably resulting from water evaporating from the hygroscopic polymer. However, it subsequently decomposes in a single stage similar to the other thermoplastics. PVC and PET are the only polymers that form significant amounts of solid residue present as char. The different polymer types and their decomposition steps can be sorted based on their onset pyrolysis temperatures, i.e., the temperature at which initial mass loss occurs:

$$\text{PA6 I} < \text{PVC I} < \text{PVC II} < \text{PS} < \text{ABS} < \text{PET} < \text{PA6 II} < \text{PP} < \text{PVC III} < \text{LDPE} < \text{HDPE}$$

The decomposition steps are decisive for selecting the number of parallel reactions used when determining the kinetic parameters according to Equation 3.4. The kinetic parameters are summarized in Table 5. The data is valid for dynamic experiments performed with a constant heating rate from 2 K·min⁻¹ to 40 K·min⁻¹. With a maximum RMSD of 2.3, the simulated decomposition curves exhibit only minor deviations from the experimental results. Based on these data for the pure thermoplastics, the decomposition curves of mixtures can be simulated and compared with the experimental data.

Table 5: Polymer type-specific kinetic parameters of pure polymers derived by TG at constant heating rates between 2 and 40 K·min⁻¹ [Publication 2].

Polymer	Preexponential factor / s ⁻¹	Activation energy / kJ·mol ⁻¹	Reaction order / -	Reaction fraction / -
LDPE	$3.80 \cdot 10^{17}$	281	0.94	1.00
HDPE	$8.31 \cdot 10^{16}$	275	0.04	1.00
PP	$3.32 \cdot 10^{14}$	233	0.94	1.00
PS	$6.37 \cdot 10^{13}$	209	0.94	1.00
ABS	$1.22 \cdot 10^{14}$	217	1.08	1.00
PET	$1.46 \cdot 10^{13}$	209	0.93	0.99
PA6 I	$2.11 \cdot 10^8$	92	3.00	0.02
PA6 II	$3.02 \cdot 10^{12}$	203	0.93	0.98
PVC I	$1.35 \cdot 10^{13}$	164	0.94	0.53
PVC II	$2.98 \cdot 10^6$	103	0.92	0.16
PVC III	$1.89 \cdot 10^{16}$	257	1.97	0.31

In order to identify interaction effects and evaluate them quantitatively, the experimental results of mixtures were compared with the superposition-based decomposition curves of the modeled mixtures. Figure 8 shows the polymers clustered into three polymer groups according to their interaction possibilities and intensity.

Polymer **Group I** comprises LDPE, HDPE, PP, PS, and ABS. These polymers are all composed of a carbon-carbon backbone. The carbon-carbon bonds are thermally stable, which is why thermal decomposition only occurs at elevated temperatures. However, as described in Chapter 2.1.1, the onset pyrolysis temperatures vary depending on substituents that can stabilize the initial radical formation, such as phenyl or alkyl groups. In mixtures of Group I polymers, no or only minor differences in the decomposition kinetics compared to the pure polymer behavior are observed. If the onset temperatures only differ by 25 °C, as in mixtures of HDPE and LDPE or PS and ABS, significant interactions cannot be detected because of strongly overlapping decomposition curves. This overlapping effect hinders the identification of kinetic-relevant interactions. In contrast, when the onset temperature ranges differ greatly, the two decomposition steps of the respective polymers in the mixture can be clearly distinguished. The pyrolysis of PS and PE with a differing temperature range of about 60 °C represents such an example. The interactions lead to a slight shift of the decomposition of the polymer with the higher onset temperature toward lower temperatures when pyrolyzed with another Group I polymer. The radicals of the polymer that features a lower onset temperature may act as initiators for the decomposition reaction of the other polymer. This effect can be identified, for example, in mixtures of LDPE and PP or PS and PP. However, the acceleration effect on the overall kinetics is weak. Within Group I, none of the polymers showed an enhanced tendency to form char based on potential interaction effects. These observations are consistent with the studies described in Chapter 2.1.3.

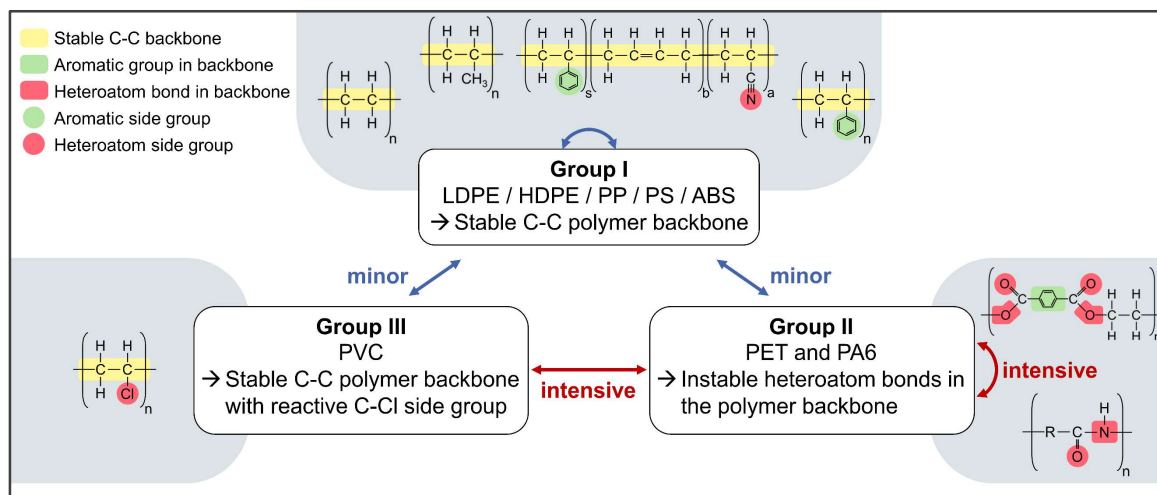


Figure 8: Polymer group clustering and polymer interactions based on the decomposition kinetics of mixtures of PE, PP, PS, ABS, PVC, PET, and PA6 (adapted from [175]).

By contrast, PET and PA6 mixtures which constitute polymer **Group II** exhibit intensive interactions. In Figure 9, their volatile formation curves are shown as a function of temperature. Both polymers consist of polymer backbones into which oxygen and nitrogen are bound in the form of ester and amide bonds. During co-pyrolysis, the decomposition reactions are significantly accelerated. Consequently, the decomposition temperature decreases by up to 60 °C compared to the pure polymer behavior. Given these interactions, accurate modeling of the decomposition curve is hampered because the superposition approach becomes invalid for these mixtures. However, the interactions hardly promote additional char formation.

The influence of the available interface for interactions is revealed by using samples of different homogeneity (particle, powder, extrudate) and samples in the compartmented crucibles. If intense interactions occur, they intensify with increasing polymer-polymer interface. The mixtures of PA6 and PET demonstrate this effect. Their time-dependent formation of volatiles during decomposition is depicted in Figure 9. In addition to the differently prepared samples, the superposition-based model results are shown. The curves for the compartmented crucibles and the modeled data closely resemble each other. This emphasizes the applicability and accuracy of the modeling approach within the framework of the underlying model assumptions. However, the occurrence of interactions means that the model cannot reproduce the experimentally determined curves of the mixtures with a common interface. The interactions greatly accelerate the decomposition reactions, significantly shifting the onset temperature to lower temperatures.

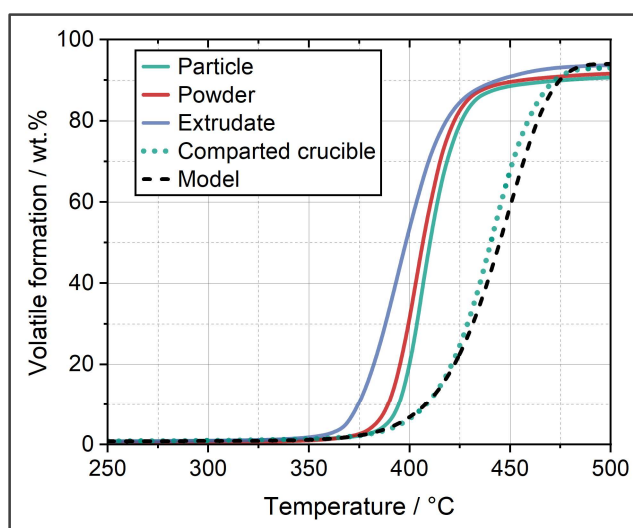


Figure 9: Volatile formation of differently prepared samples of a 50/50 PET/PA6 mixture at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ (adapted from Publication 2).

No significant changes in the decomposition kinetics are evident if just one polymer from Group II is pyrolyzed with polymers from Group I. Only PET/PS and PET/ABS mixtures show slight interaction effects, primarily affecting char formation. PS and ABS both contain phenyl groups, which, when in chemical contact with PET-derived char precursors, may lead to increased char formation. The additional char formation amounts to 2.3 wt.% for example, in a mixture of 75 % PET and 25 % PS. Thus, the superposition-based approach is not applicable for calculating the char formation of these polymer mixtures. This finding confirms the results of Genuino et al., who identified PET as main cause for increased char formation in mixed plastic waste [76]. However, the superposition approach can be used to model the overall reaction kinetics of mixtures containing polymers from Group I and Group II.

PVC forms a separate group (**Group III**) in Figure 8. During co-pyrolysis with polymers from Group I, generally no or only minor interactions are apparent. Polyene chains, formed as intermediate products in PVC pyrolysis, only marginally retard the decomposition of LDPE, HDPE, and PP. The pyrolysis of the polymer combinations PVC/PS or PVC/ABS is also affected by these polyene chains. The amount of char increases by 1.5 wt.% at maximum compared to the pure polymer behavior. As described in Chapter 2.1.1, pronounced styrene formation is reported during PS and ABS decomposition. The styrene may partially be incorporated into aromatic char precursors evolving during the PVC's third decomposition step. Other studies report similar results, including increased char formation in PVC and PS, and delayed reactions of polyolefins in mixtures with PVC [40].

In contrast, very strong interactions can be observed in mixtures of PVC and polymers from Group II. During the first step of PVC decomposition, the formation of volatile products increases significantly. The HCl produced during dechlorination at temperatures around 250 °C to 300 °C appears to catalyze the decomposition of the heteroatom-containing PET and PA6 backbone. Cao et al. formulated a simplified chemical mechanism to describe this acceleration for mixtures of PET and PVC [85]. This mechanism might also apply here or in a similar form, even when the experiments of Cao et al. were performed in the environment of ionic liquids. Detailed hypotheses of interaction mechanisms are discussed in the following chapter, relying on product yields and compound analyses.

A comparative study of TG Mix 1 (Group I polymers only) and TG Mix 2 (70 % Group I polymers and 30 % Group II and III) reveals that findings on interaction effects obtained from binary mixtures can be extended to more complex reference mixtures. Figure 10 depicts the volatile formation and the volatile formation rate of both mixtures. For TG Mix 1, the values calculated using the superposition model align well with the curves determined experimentally. The RMSD accounts for only 1.3 wt.%. This mixture consists of polymers from polymer Group I in equivalent proportions. These results confirm that polymers with a carbon-carbon backbone show hardly any interactions significantly affecting the reaction kinetics or the formation of solid residue, except in the presence of highly coke-forming polymers such as PVC or PET.

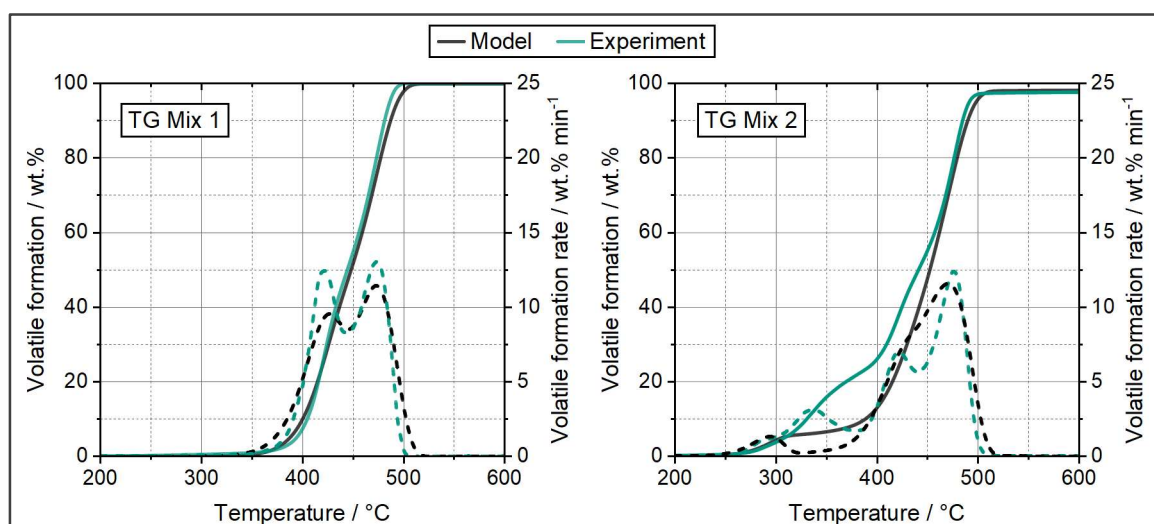


Figure 10: Experimentally determined and modeled volatile formation and formation rate of TG Mix 1 and 2 at a heating rate of 10 K·min⁻¹ (adapted from Publication 2).

The decomposition behavior of TG Mix 2 reflects the strong interaction effects of the polymers in Groups II and III, as described above. Increased formation of volatiles occurs during and briefly after the first PVC decomposition step. This phenomenon can be attributed to the intricate interactions between PVC, PET, and PA6. The generated char amount is also slightly higher than predicted by the comparative modeling calculations. Therefore, the RMSD of the heteroatom-containing polymer mixture TG Mix 2 amounts to 4.6 wt.%, which is significantly above the statistical margin of error. These findings demonstrate that the superposition method is not applicable for describing the decomposition kinetics of such polymer compositions. Significant interaction effects shift the decomposition curve to lower onset temperatures and cause an additional peak in the volatile formation rate at around 300 °C to 350 °C. Thus, the TG method allows the effective identification of interaction effects. However, more chemical product analyses are necessary to improve the assessment of the mechanisms of these interaction effects.

4.1.2 Product Yields and Product Compositions

The feedstock impact on the yields of generated product fractions was investigated using the STR system with a reactor wall set temperature of 500 °C. The results are extracted from Publication 4.

In preliminary tests with MgOx, the mass balance was almost closed, with a deviation of only 0.8 wt.%. Product yields of 47.5 wt.% pyrolysis gas, 22.3 wt.% pyrolysis oil, and 29.1 wt.% solid residue were obtained. High reproducibility was demonstrated by minor statistical deviations of up to 0.9 wt.%. Based on the well-defined decomposition mechanism of MgOx, theoretical yields of 48.5 wt.% for gaseous products (CO and CO₂) and 24.3 wt.% of condensable products (water) were expected. Consequently, the experimentally determined product yields exhibit a maximum deviation of 1.9 wt.%, which demonstrates the good agreement with the calculated values. These results emphasize the reliability and accuracy of the mass balancing in the developed STR pyrolysis system. Figure 11 depicts the yields of pyrolysis gas, pyrolysis oil, and remaining solid residue. The results demonstrate the considerable dependence of the pyrolysis on the polymer type. It is evident that both pure PP and pure PE result in comparable product yields of about 72 wt.%. The oil yields of PS and ABS at 98.5 wt.% and 91.2 wt.% are significantly higher. Moreover, gas formation is minimal during the pyrolysis of PS and ABS. The pyrolysis of PA6 predominantly yields condensable products. PVC exhibits a contrasting pyrolysis behavior. The PVC decomposition results in the release of 60 wt.% pyrolysis gas and only a minor amount of pyrolysis oil. The assessed yields are consistent with the current state of research, as outlined in Chapter 2.1. Dominant formation of char is only evident in PVC, among all the thermoplastics that were pyrolyzed. However, the char formation observed in this study significantly exceeds the amount previously determined for virgin PVC in TG analyses. Given the filler content of 10 wt.% in this PVC, the char content is about 13 wt.% higher than quantified via TG. Also, low char generation was observed for ABS and PA6, although the extent of char formation did not exceed 5 wt.%.

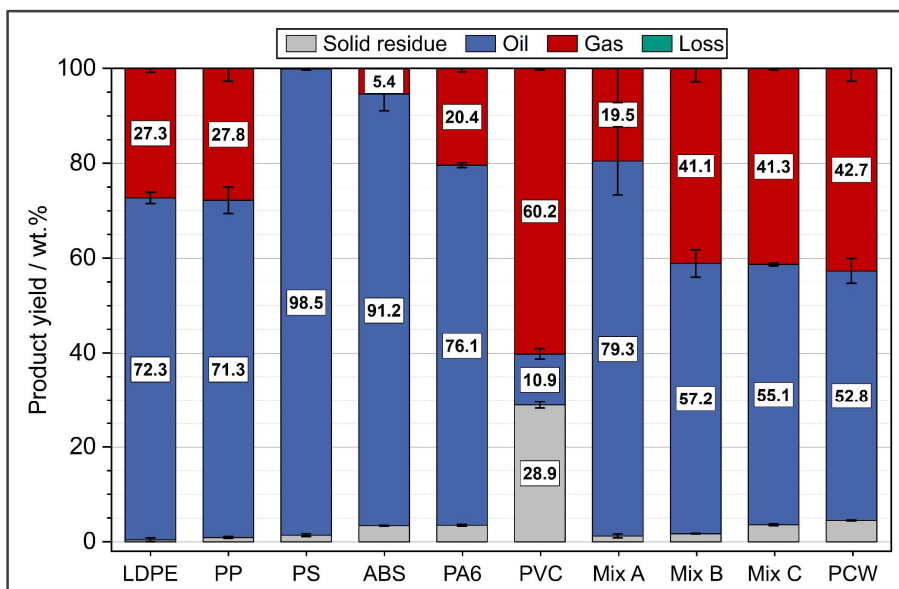


Figure 11: Product yields obtained by pyrolyzing pure thermoplastics and thermoplastic mixtures in the STR at 500 °C set temperature (adapted from Publication 4).

The elemental analyses highlight the differences in the composition of the pyrolysis oils. The results of the elemental analysis are shown in detail in Table 6. LDPE-, PP-, and PS-derived pyrolysis oils feature different hydrogen-to-carbon ratios corresponding to their specific chemical composition. The estimated hydrogen-to-carbon ratio is about 2.0, 1.8,

and 1.1 for pyrolysis oils generated from LDPE, PP, and PS, respectively. The carbon and hydrogen content in ABS and PVC pyrolysis oils is similar. Only PA6 pyrolysis oil features significantly a lower carbon proportion. The presence of nitrogen, oxygen, and chlorine in the respective pyrolysis oils generally reflects the elemental composition of the corresponding polymers. However, deviations, in particular the detection of chlorine in non-chlorinated systems and minor nitrogen signals in chlorine-containing systems, may be attributed to carryover effects from previous experiments. These artifacts most likely originate from difficult to avoid residual contamination in the multistage condensation system.

Table 6: Normalized elemental composition of the oils obtained from pyrolysis of different thermoplastic feedstocks in the STR system [Publication 4].

Oil	Elemental composition / wt.%				
	Carbon	Hydrogen	Nitrogen	Chlorine	Oxygen ^B
LDPE	85.6	14.4	< 0.2	0.0	0.0
PP	86.1	13.9	< 0.2	0.0	0.0
PS	91.5	8.3	0.2	0.0	0.0
ABS	86.7	8.4	4.7	0.2	0.0
PA6	62.3	10.0	11.0	0.6	16.1
PVC	85.8	9.7	0.9	3.6	0.0
Mix A	88.1	11.9	< 0.2	0.0	0.0
theo. ^B	87.9	12.0	0.1	0.0	0.0
Mix B	85.0	14.0	0.3	0.1	0.6
theo. ^B	84.7	13.8	0.2	0.0	1.3
Mix C	84.4	12.5	0.6	0.5	2.0
theo. ^B	83.5	12.2	0.9	0.1	3.3
PCW	82.6	13.6	0.4	0.5	2.9
theo. ^B	82.7	12.6	1.0	0.1	3.6

^A calculated as the difference to 100 wt. %.

^B theoretical results estimated based on superposition calculations.

The results of the 2D-GC compound group analysis are listed in Table 7. It further specifies main oil compounds of the LDPE, PP, PS, ABS, PA6, and PVC pyrolysis oil. The polymer-specific decomposition mechanisms of pure plastics are presented in the literature review in Chapter 2.1.1. From them, particular pyrolysis products can be expected. The 2D-GC results correspond to these expectations, showing similar main compounds and compound groups in comparable quantities. The analyses highlight the aliphatic character of the LDPE and PP pyrolysis oils. The linear compounds of LDPE and branched aliphatics generated from PP can be distinguished. PS pyrolysis oil consists largely of styrene and other monoaromatic or polyaromatic components. Styrene is the dominant compound in the oil obtained from PS and ABS with 61.8 wt.% and 31.0 wt.%, respectively. ϵ -Caprolactam is present in relevant quantities in the pyrolysis oil of PA6. Furthermore, about 42.0 wt.% of short-chain aliphatic nitriles and amides were quantified. Aromatic compounds, especially benzene, are predominantly detected in PVC pyrolysis oil. Only (1-chloroethyl)-benzene was identified as a chlorinated HC. Gas analyses of the pure plastics were also measured but are not explicitly presented below. They can be found in detail in Publication 4.

Table 7: Compound group analyses of oils from pyrolysis of pure polymers in the STR system at 500 °C set temperature [Publication 4].

Compound group	Content of compound group in the oil / wt.%					
	LDPE	PP	PS	ABS	PA6	PVC
Aliphatics	73.9	78.3	4.4	2.1	0.3	6.4
Monoaromatics	2.0	2.3	69.8	42.4	0.2	6.7
Indenes	0.1	0.0	0.1	0.2	0.1	1.2
Naphthalenes	0.1	0.0	0.1	0.7	0.1	1.2
Diphenyls	0.4	0.3	13.6	6.1	0.6	6.1
Other aromatic compounds	0.4	0.3	13.7	6.1	0.0	11.8
Heteroatom-containing HCs	0.0	0.1	0.8	28.7	67.7	11.0
Sum of identified compounds	76.9	81.3	102.5	86.3	69.0	44.4

Analogous to the decomposition kinetics, Mix A exhibits no interactions with a relevant effect on the product yields (cf. Figure 11). A comparison of superposition-based and experimentally determined results reveals only minor deviations of a maximum of 3 wt.%. These deviations fall within the margin of error (cf. Table 6). The same applies to the ratio of carbon and hydrogen, as well as the quantified compound groups. In addition to aromatics, only branched and unbranched aliphatics are detected. Applying Equation 3.8 to calculate the content of compound groups, the aliphatic and aromatic group proportions differ by only 0.9 and 1.7 wt.%, respectively. The findings of this study demonstrate that in simple mixtures of polyolefins and PS, interaction effects on the product yields and composition of the oils are negligible. Superposition-based modeling is thus valid when employed for such thermoplastic mixtures.

The pyrolysis of the heteroatom-containing polymer mixtures Mix B, Mix C, and the PCW presents a different situation. Although the composition of the polymers varies, an almost identical oil and gas yield is achieved (cf. Figure 11). The oil yield ranges from 53 wt.% to 57 wt.%, while the gas yield accounts for 41 wt.% to 43 wt.%. Analyses of the samples reveal a significantly higher solid residue content in Mix C and PCW at about 4 wt.%, compared to mixture B at 1.7 wt.%. The PET and PVC content have a significant influence on the amount of coke. Dominant interaction effects were already observed in the TG for a comparable mixture. The results were correlated with the values determined by superposition. A significant overestimation of the oil yield by 19 wt.% to 22 wt.% is observed for the calculation. Thus, the investigations indicate that the interactions cause a significant shift of the products from condensable to gaseous compounds. This observation is consistent with the findings of Genuino et al. In their study, the authors also observed a shift from oil to gas by 8 wt.% in the context of PET-induced interaction effects during pyrolysis [76]. In particular, the HCl produced in the first decomposition step of PVC probably interacts with the heteroatom-containing backbones of PET and PA6. Cao et al. stated that the HCl interacts with the ester fragments of the PET, producing chlorinated gaseous HCs [85]. This interaction partly explains the strong shift from condensable to gaseous compounds. It can be assumed that a similar effect of the released HCl will be observed when combining PVC and PA6. For example, the reaction mechanism of PA6 typically produces ϵ -caprolactam. This selective formation may change into decomposition to short-chain aliphatics, nitriles, CO, and CO₂. The elemental analysis of the condensates and the gas composition would have to show differences between the calculated and experimentally determined values in order to confirm this hypothesis.

In general, the oils produced by the pyrolysis of Mix B, Mix C, and PCW are complex mixtures of various organic compounds. The chromatogram of the PCW pyrolysis oil shown in *Figure 12* underlines this broad product spectrum. In addition to various aliphatic compounds, mono- and polyaromatics as well as heteroatom-containing HCs are present in relevant proportions. The most dominant compounds are highlighted in the chromatogram. These main compounds correspond to the polymer-specific composition of PCW and its main pyrolysis products which were described in detail in Chapter 2.1. Chlorine-containing polyaromatic structures could play an important role in the evaluation of the underestimated amount of chlorine in the condensate. These chlorine-containing polyaromatics are difficult to identify in 2D GC analysis because of their high boiling point and the reduced resolution of the qMS in this boiling range. The incorporation of chlorine into polyaromatic structures would thus explain the underestimation of the amount detected in the condensate. On the other hand, it also explains why only a fraction of the chlorinated HCs in the condensate is identified using the 2D-GC analysis.

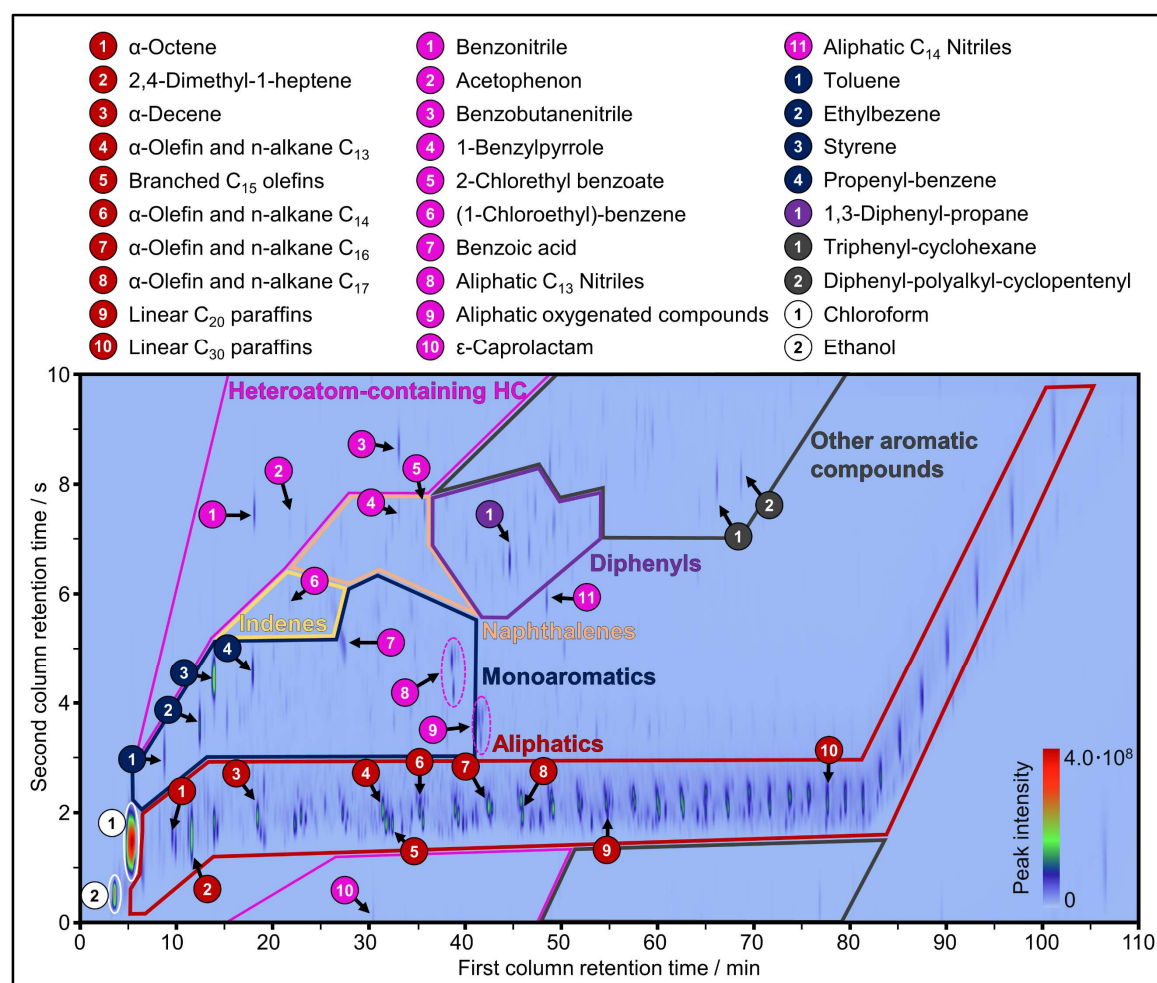


Figure 12: 2D-GC chromatogram of the pyrolysis oil generated from PCW pyrolysis in the STR system at 500 °C set temperature (Publication 4).

To evaluate the applicability of SPBM, the predicted elemental compositions of the pyrolysis oils are compared with the experimental data (cf. Table 6). The superposition model reflects the carbon and hydrogen well within the margin of error. However, the nitrogen and oxygen content of Mix C and PCW are overestimated by up to 0.6 wt.% and 1.3 wt.%. The chlorine content, on the other hand, is underestimated by up to 0.4 wt.%. This shows that chlorine is predominantly shifted to the oil fraction as a result of interaction effects. Nitrogen and oxygen might migrate to the gas phase predominantly.

The comparison of the superposition-based and experimentally determined gas composition of the thermoplastic mixtures is shown in Table 8. Mix A consists exclusively of aliphatic and aromatic hydrocarbons, reflecting its feedstock composition of LDPE, PP, and PS. In contrast, Mix B, Mix C, and PCW, derived from more complex feedstocks, exhibit significant formation of CO₂ and CO. With increasing polyolefin content, the gas composition shifts toward higher concentrations of light aliphatic hydrocarbons, while only minor amounts of aromatics are detected. In addition, heteroatom-containing gas species are present.

Table 8: Composition of pyrolysis gas obtained in STR experiments at 500 °C set temperature and corresponding superposition-based calculations [Publication 4].

Gas species in wt.%		Mix A		Mix B		Mix C		PCW	
		exp	theo	exp	theo	exp	theo	exp	theo
Light HCs (1 st row: saturated; 2 nd row: unsaturated)	CH ₄	3.7	4.2	3.7	4.0	3.3	3.7	4.9	3.8
	C ₂	7.2	8.9	7.2	8.6	6.1	7.7	5.2	7.8
		5.6	6.2	6.6	7.0	7.1	6.3	7.0	5.9
	C ₃	6.6	8.6	7.2	8.9	5.4	7.9	4.7	7.7
		19.1	18.4	12.8	14.5	9.8	12.9	10.3	14.8
	C ₄	3.9	5.8	5.1	6.7	4.0	5.9	3.0	5.4
		13.6	16.0	11.7	14.8	9.4	13.5	9.5	13.9
	C ₅	10.9	7.5	9.0	5.5	8.2	4.9	9.0	5.9
		11.0	10.7	7.9	10.7	7.7	9.6	7.2	9.6
	C ₆	1.7	1.0	3.6	1.1	2.3	0.9	2.4	0.9
		11.2	7.4	7.5	6.5	7.3	5.8	9.6	6.2
	C ₇ to C ₁₀	0.6	1.2	1.1	0.9	1.1	0.8	0.9	1.0
		2.4	1.9	2.1	1.5	2.2	2.4	3.4	1.5
Aromatics	Benzene	0.5	0.0	0.2	0.0	0.7	0.1	0.6	0.1
	Toluene	0.5	0.1	0.3	0.1	0.7	0.1	0.5	0.1
	Styrene	1.0	1.7	3.3	1.8	0.4	1.7	0.4	1.5
	Others	0.4	0.3	0.4	0.4	0.3	0.4	0.3	0.3
Heteroatom- containing gases	CO ₂	0.1	0.0	7.1	2.4	16.4	3.7	14.7	3.7
	CO	0.0	0.1	1.8	0.8	3.2	0.5	3.1	0.6
	Other O-HCs	0.0	0.0	1.0	0.0	1.5	0.1	3.1	0.6
	Acrylonitrile	0.0	0.0	0.0	0.0	1.1	0.4	0.5	0.3
	Other N-HCs	0.0	0.0	0.0	0.0	0.5	0.2	0.6	0.2
	HCl	-	0.0	-	3.8	-	11.4	-	8.6
	Other Cl-HCs	0.0	0.0	0.4	0.0	1.2	0.1	1.4	0.1

Compared to the SPBM results, slightly lower proportions of light olefins and aromatics are detected experimentally. The contents of CO, CO₂, and heteroatom-containing HCs are significantly higher than the modeled values. In addition, more C₆ gases are present. The gas analyses confirm enhanced nitrogen and oxygen migration into the gas phase, quantifying increased amounts of acrylonitrile, acetonitrile, and acetaldehyde. The interaction effects promote the formation of CO₂ and CO, which also explains the lower amount of oxygen in the oil. As larger amounts of heteroatom-containing compounds are present in the gas phase, the relative proportion of light olefins and aromatics decreases

accordingly. This supports the hypothesis that the heteroatom-containing bonds in the polymer backbone are involved in the interaction mechanisms present in Mix B, Mix C, and PCW. The HCl formed during the initial decomposition of PVC appears to be fundamental to the mechanistic shifts. However, HCl cannot be identified with a certain degree of accuracy using this gas analysis method, as the HCl peak exhibits severe peak tailing. This peak tailing impedes the identification of HCl in minor amounts and prevents its quantification. Overall, the results demonstrate that interaction effects in complex mixed thermoplastics lead to significant deviations from superposition-based predictions regarding product yields and the composition of the pyrolysis gas and pyrolysis oil.

4.1.3 Pyrolysis Energy Demand

The identified feedstock effects are evaluated for their impact on the ED of mixed thermoplastics pyrolysis. Laboratory-scale DSC experiments were performed to characterize endothermic and exothermic processes during the pyrolysis of pure thermoplastics. Additional ASR bench-scale tests were conducted to assess superposition-based ED calculations and the influence of polymer interactions in mixed plastics. The results are extracted from Publication 1.

The heat of fusion and the reaction enthalpy of the polymers were determined. The heat of fusion can vary from $0 \text{ J}\cdot\text{g}^{-1}$ for polymers without a melting transition to a maximum of $235 \text{ J}\cdot\text{g}^{-1}$ for HDPE. In comparison, the reaction enthalpy is significantly higher. It ranges from $232 \text{ J}\cdot\text{g}^{-1}$ for PET to $744 \text{ J}\cdot\text{g}^{-1}$ for PS. To describe the polymers' temperature-dependent heat capacity, the parameters of the linearization approach were determined and related to specific polymer phase transitions. The associated temperatures that define transitions between different polymer phases are also provided. These parameters are described in detail in Publication 1. The data form the basis for superposition-based ED modeling according to Equation (3.10).

The experimental results were obtained at a reactor temperature of $500 \text{ }^{\circ}\text{C}$ in the ASR system. These results are presented in Figure 13 alongside the superposition-based calculations for LDPE, PP, PS, and the plastic mixtures Mix A, Mix B, Mix C, and PCW. PS has a significantly lower pyrolysis ED than PP and LDPE, at $1575 \text{ J}\cdot\text{g}^{-1}$, $1976 \text{ J}\cdot\text{g}^{-1}$, and $2002 \text{ J}\cdot\text{g}^{-1}$, respectively. Considering the margin of error, SPBM provides consistent values. Thus, the methodology for determining the minimum pyrolysis ED of pure thermoplastics based on DSC data has been successfully validated.

The consistent results for Mix A demonstrate the methodology's transferability to mixtures without significant interaction effects. The interaction effects identified during the pyrolysis of the more complex polymer mixtures Mix B and Mix C exert a significant influence on the ED. The experimentally determined ED amounts to $2424 \text{ J}\cdot\text{g}^{-1}$ in maximum. These values exceed the modeled results for Mix B and Mix C by approximately $470 \text{ J}\cdot\text{g}^{-1}$ to $500 \text{ J}\cdot\text{g}^{-1}$.

The findings of Chapter 4.1.2 demonstrate enhanced cracking reactions in these mixtures and that the product distribution shifts towards gaseous products. For this shift, it is paramount that polymers perform increased fragmentation and thus chain scission. The additional scission reactions require supplementary energy. Thus, the additional ED can be attributed to the enhanced polymer cracking. Although interaction effects also occur in PCW, the modeling of the experimental value corresponds to the experimental result. Inert components such as ash and additives can be assumed to reduce the ED of the process because these components do not require additional energy for the melting phase transition or the pyrolysis reaction. In addition, lower heat capacities or evaporation at temperatures below the reaction temperature are also possible, reducing the overall ED and thereby compensating for its additional contribution resulting from interaction effects.

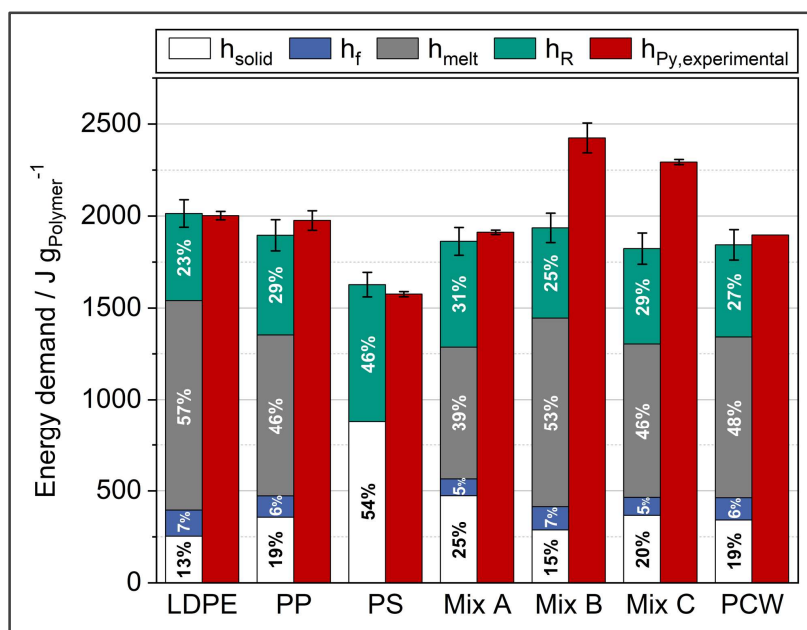


Figure 13: Experimentally determined and superposition-based calculated ED of different thermoplastic feedstocks in the ASR at 500 °C set temperature (adapted from Publication 1).

In general, the EDs determined are of a similar magnitude for all polymers. They also correlate with the calorific value of the input materials. The amount of all EDs examined is about 4-6 % of the calorific value of the input material. This general dependence is consistent with the results of other authors [120,172]. Superposition-based modeling also allows resolving the contribution of specific endothermic processes to the total ED. The pyrolysis reaction and the evaporation of resulting products account for only about 23 % to 46 % of the total ED. The vast majority of the energy is required to heat the polymer to the reaction temperature. In comparison, the heat of fusion is of minor importance. Because of similar material values, the share of individual polymers in the total ED of mixtures mainly depends on their mass fraction in the pyrolyzed mixture. The heating of the inert carrier material, which is not shown in Figure 13, also represents a significant proportion of the required process energy. It accounts for approximately $475 \text{ J} \cdot \text{g}_{\text{Sand}}^{-1}$.

4.2 Influence of Reactor Type and Design

Besides the influence of feedstocks, the reactor system has a significant impact on the pyrolysis results. This impact is exemplarily assessed for two common reactor types used in industrial applications, the STR and the ASR. Similar experiments were conducted after both reactor systems were characterized rigorously. The results presented below are adapted from Publication 4. Pyrolysis oil analyses obtained in ASR tests are extracted from Publication 3.

4.2.1 Assessment of Reactor Characteristics

The design and operational mode of pyrolysis systems determine the key parameters decisive for the decomposition behavior. In this context, the STR and ASR systems represent fundamentally different reactor concepts, corresponding to non-ideal representations of an ideal stirred tank reactor and a plug flow reactor. Due to differences in operation and design, both reactors are subject to heat and mass transfer limitations which result in variations in the prevailing temperature distribution, material homogeneity, and the GRT distribution. The crucial reactor characteristics are characterized in the following subchapters.

Material Mixing

Before the STR experiments, 2 kg of quartz sand are added to the reactor as a homogenizing agent to promote mixing. The feedstock is added semi-continuously in a high sand-to-feedstock ratio ranging from 54 to 87 depending on the polymer type. The reactor contents are continuously mixed by the impeller at a medium speed of 50 rpm. The speed is selected so that abrasion of the sand particles is minimized while achieving rapid mixing during polymer addition. Preliminary tests with polymer particles and silicone oils in a cold model support the assumption of rapid and homogeneous mixing. The homogeneous material distribution in the STR of less than 10 s was validated using an endoscope camera at ambient temperature.

In the ASR system, the sand-to-feedstock ratio is 4, which is significantly lower than in the STR reactor (about 54 to 87). The premixed sand-plastic mixture is continuously introduced and conveyed through the reactor at a constant speed. The screw rotates very slowly at approximately 1 rpm. As a result, no significant material mixing can be assumed. In addition, spatial material gradients are apparent, since the material position is linked to the solid residence time and consequently the reaction progress. Thus, only solid polymer granulate and sand are present at the inlet, while only solid residues and sand are contained in the material bed directly before discharge.

Polymer Temperature Profile

The addition of the polymer at room temperature and the endothermic processes during pyrolysis prevent isothermal process control in both reactors. The spatial and time-dependent temperature profile is therefore decisive for the pyrolysis behavior in the reactor systems and strongly dependent on their design and operation.

In the STR, a thermocouple allows for the monitoring of the temporal temperature curve in the homogeneously mixed sand-polymer bed inside the reaction zone. Figure 14 shows this curve for experiments with LDPE, PS, PVC, and PCW together with the reactor wall temperature. A time-averaged polymer temperature is shown as a dashed line.

The temperature declines periodically in all experiments. When feedstock is added, the rapid mixing in the system and the endothermic processes cause an almost instantaneous drop in temperature. It then rises again as a result of the additional heat input until the next addition of feedstock. Although the reactor temperature fluctuates by approximately 5 °C, deviations of up to 96 °C from the set temperature of 500 °C are recorded inside the reaction zone. Depending on the applied polymer type, the average temperature in the reaction zone ranges from 30 to 50 °C below the reactor set temperature. The system is therefore characterized by comparatively rapid heating to a reaction temperature that remains significantly lower than the reactor set temperature.

The complex trajectory of the reactor screw technically limits direct temperature measurement within the polymer-sand bed of the ASR system. A quantitative evaluation of the polymer temperature profiles is therefore not feasible. However, lower heating rates of the polymers can be assumed, as there is no rapid and intensive mixing. Nevertheless, several thermocouples positioned on the reactor wall below the material bed enable the monitoring of spatial temperature differences during stationary operation. At the thermocouple located 28 cm after the reactor inlet, temperature fluctuations of up to 10 °C are observed, regardless of the feedstock composition. Unlike in the STR system, the observed temperature fluctuations are not caused by feedstock addition but exhibit a regular frequency resulting from the binary control of the electrical reactor heating system. The fluctuations decrease significantly with increasing reactor length, clarifying that the majority of endothermic processes occur in the front section of the screw reactor.

Consequently, continuous feeding leads to more uniform heating with less temporal fluctuation compared to the STR reactor. Due to the larger reactor dimensions, a higher polymer temperature in the ASR is expected at the end of the process, although parts of the polymer react earlier due to the slower heating.

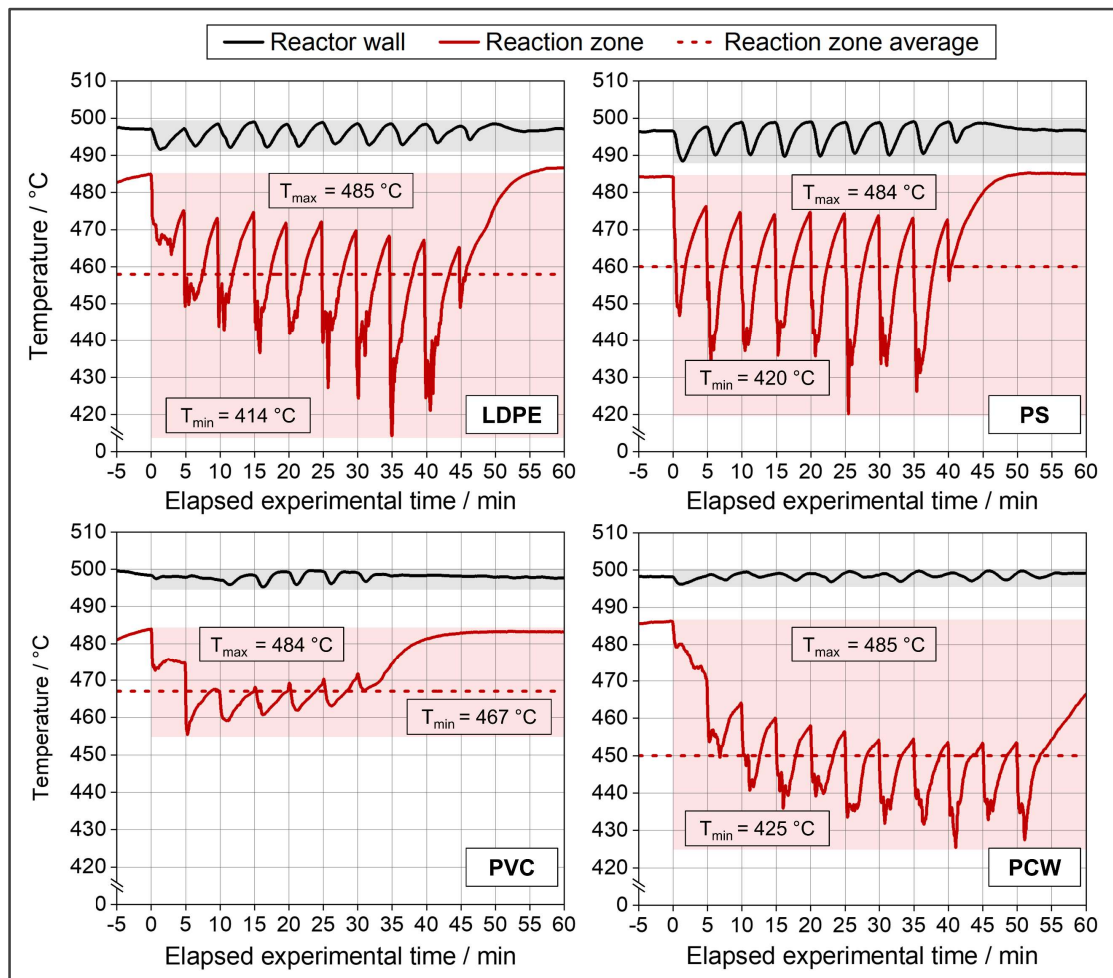


Figure 14: Time-dependent temperature profile of the reactor wall and the reaction zone during pyrolysis of LDPE, PS, PVC, and PCW in the STR system at 500 °C set temperature (Publication 4).

Gas Residence Time

The volume flow of product gas and flush gas, the freeboard volume, and the prevailing flow conditions are decisive parameters. These parameters determine the residence time distribution of volatile products in the gas phase.

The freeboard volume of the STR system only contains approximately 0.5 to 1 L. The purge gas volume flow is comparatively high at $2.3 \text{ L}_{\text{NTP}} \cdot \text{min}^{-1}$. In combination, this causes rapid flushing of volatile products in the gas phase. In the hot reactor, a minimum GRT of about 20 s was determined through experiments with alternating atmosphere exchange between N_2 and CO_2 . The distribution width in the hot reactor amounts to approximately 1 min, which indicates moderate gas remixing. In contrast, the ASR system features a freeboard of about 80 L and a purge gas volume flow of $12 \text{ L}_{\text{NTP}} \cdot \text{min}^{-1}$. The minimum GRT was determined in a similar way using pulses of CO_2 in an N_2 atmosphere. It amounts to about 30-50 s at a reactor temperature of 500 °C. However, the distribution width is around 5 min. This indicates pronounced non-ideal flow behavior including of gas phase backmixing in the ASR reactor, attributable to the prevailing laminar flow in combination with the limited number of localized nitrogen injection points.

The condensation systems of both reactors are similar in design and dimensions. Consequently, the GRT characteristics in this section are similar, with a minimum GRT of 1-2 min and a distribution width of about 100-120 s. The pipe sections downstream of the hot gas filtration system, including the condensation and gas measurement sections, are characterized by more plug-flow-like conditions and therefore reduced backmixing. However, a significantly longer residence time of volatile pyrolysis products within the hot reaction zone can be anticipated in the ASR compared to the STR.

4.2.2 Interplay of Feedstock and Reactor-specific Effects

The influence of feedstock on pyrolysis, examined in Chapter 4.1, is accompanied by reactor-specific effects. These reactor-specific effects and their interplay with the identified polymer interactions during the decomposition of thermoplastic blends are evaluated in the following. In addition to product yields, the composition of the pyrolysis gases and pyrolysis oils serve as the main criteria for this evaluation.

Figure 15 summarizes the mass balances of experiments with identical feedstocks in the STR and ASR at a reactor wall temperature of 500 °C. The amount of solid residue generated remains consistent across both reactor systems and their respective feedstocks. With less than 5 wt.%, its formation is of low importance to the mass balance. Applying the pure polymers LDPE, PP, and PS, the ASR produces less oil and more pyrolysis gas. The difference can amount to up to 24 wt.%. This trend continues for Mix A. A higher gas yield by about 14 wt.% is obtained in the ASR compared to the STR at the expense of oil yield when pyrolyzing Mix A.

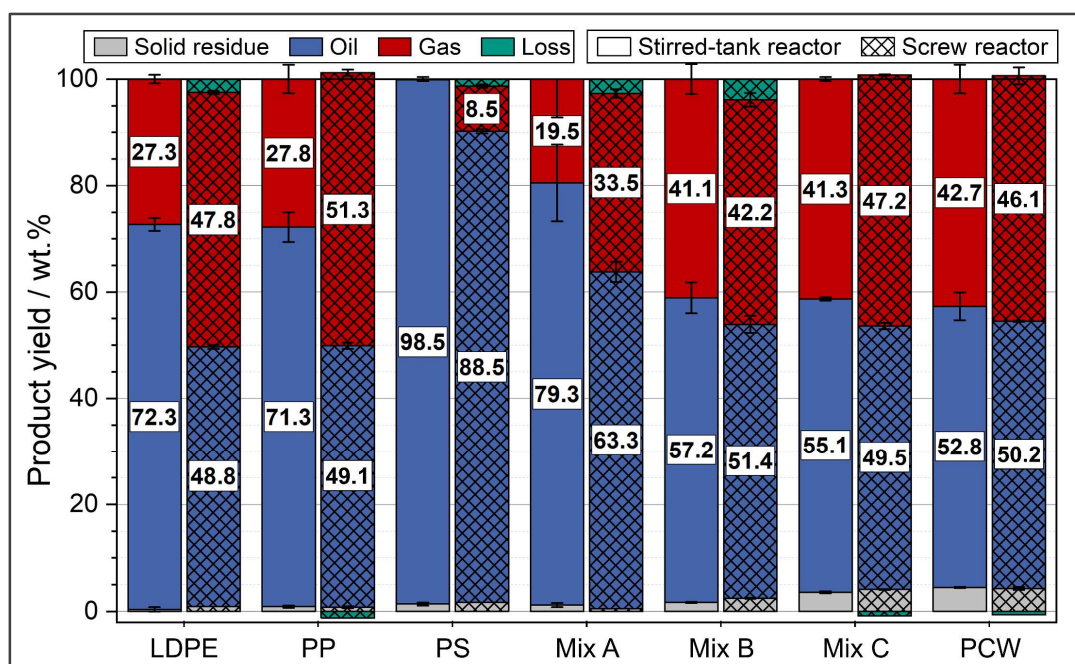


Figure 15: Mass balance comparison of STR and ASR experiments at 500 °C reactor set temperature with thermoplastics and plastic mixtures (Publication 4).

As no significant interaction effects arise in these pure thermoplastics and their polymer mixture, the product shift can only be attributed to the characteristics of the reactor system. This observation is justified by both the GRT and the polymer-specific temperature profile. In the ASR system, polymers experience a higher end temperature despite the presumed lower heating rate. This intensifies bond cleavages during primary cracking mechanisms. Additionally, the GRT is significantly higher in the ASR system, which promotes secondary reactions. In particular, secondary cracking appears to occur more prominently. Consequently, these two effects cause a shift in yield from pyrolysis oil to pyrolysis gas in

the ASR system. Significant interaction effects in the complex polymer blends Mix B, Mix C, and PCW are identified in TG experiments (cf. Figure 10) and mechanistically discussed in Chapter 4.1.24.1. The apparent shift from oil to gaseous products is significantly less pronounced in the ASR reactor in comparison to the pyrolysis in the STR for these mixtures. The ASR yields 5.8, 5.6, and 2.6 wt.% less oil than obtained in the STR for Mix B, Mix C, and PCW, respectively. The polymer interactions overlap the yield shifts induced by reactor-specific variations. The strong interaction effects appear to dominate this yield shift. Accordingly, the effect is weakened, and the product distribution for the three different feedstocks is evened out. The varying degrees of homogenization of the sand-polymer mixture in the reactors appear to play a minor role in this effect.

The results of the comparative gas analyses are presented in detail in Publication 4. The gases produced in the STR and ASR systems during the pyrolysis of LDPE, PP, PS, and Mix A are almost comparable. In the STR system, a slight shift toward lighter HCs is observed for LDPE and PP. Pyrolyzing PS and Mix A, slightly fewer aromatics are present in the gas produced by the STR. Although minor differences caused by slightly different condensation conditions in both systems cannot be excluded, the observed deviations are more likely attributable to differences in the effective temperature profile and the resulting decomposition pathways of the polymers.

However, for the other feedstock mixtures, a distinct difference in gas composition depending on the selected pyrolysis system is evident. For PCW, for example, the amount of CO₂ and CO released in the STR is reduced by 7.0 wt.% and 1.6 wt.% compared to the ASR system. A similar observation also applies to other gases containing oxygen, nitrogen, and chlorine. Their proportion in the gas composition is likewise decreased by a factor of around 2 to 3 in the ASR. At the same time, significantly more aliphatic HCs in the range of C₄ to C₇ are detected in the product gas from the ASR tests. The higher average pyrolysis temperature and longer GRT of the ASR system intensify the thermal decomposition. As a result, the gas yield is not only increased, but also a shift in the gas phase of complex mixtures occurs. Such a shift explains the higher proportions of C₄ to C₇ produced during pyrolysis in the ASR system. Since the formation of gaseous products from PET, PA6, and PVC is closely linked to interaction effects, they are less affected by the reactor type than the formed HCs. Their content dilutes the amounts of heteroatom-containing HCs as well as CO and CO₂ in the gas obtained from complex thermoplastic mixtures in the ASR system.

The SimDist curves of the oils reveal further details on the reactor influence. The results are shown in Figure 16. All pyrolysis oils exhibit a broad product distribution. The initial and final boiling points are at 50 °C and 650 °C. The PE oil exhibits the lowest proportion of naphtha cut, while the PS oil exhibits the highest. In contrast to the other oils, PS shows horizontal plateaus, which indicate the presence of major shares of specific chemical compounds. These plateaus are caused by styrene monomer and styrene oligomers. The oils from Mix B, Mix C, and PCW are similar to LDPE oil. A comparison of the oils from both reactor systems reveals a dramatic shift. The ASR oils have a significantly higher content in the naphtha cut and middle distillate range. For LDPE and PP, the naphtha cut content is increased by 32 and 36 wt.%, respectively, when the material is pyrolyzed in the ASR. For Mix B, Mix C, and PCW, this shift is even more pronounced by over 40 wt.%. In line with the shift in product yields toward gaseous products seen for the ASR, the SimDist curves also change. This shift is particularly evident for Group I polymers and for Mix A. The intensified primary and secondary cracking reactions promote the formation of compounds with a lower molecular weight. As a result, oils produced in the ASR contain a higher proportion of products corresponding to the naphtha and middle distillate range

compared to STR oils. In the case of PS, the shift of the horizontal plateau indicates a change in the distribution of styrene monomers and oligomers. More monoaromatics and styrene are produced in the ASR system. In contrast, the trimer content is reduced.

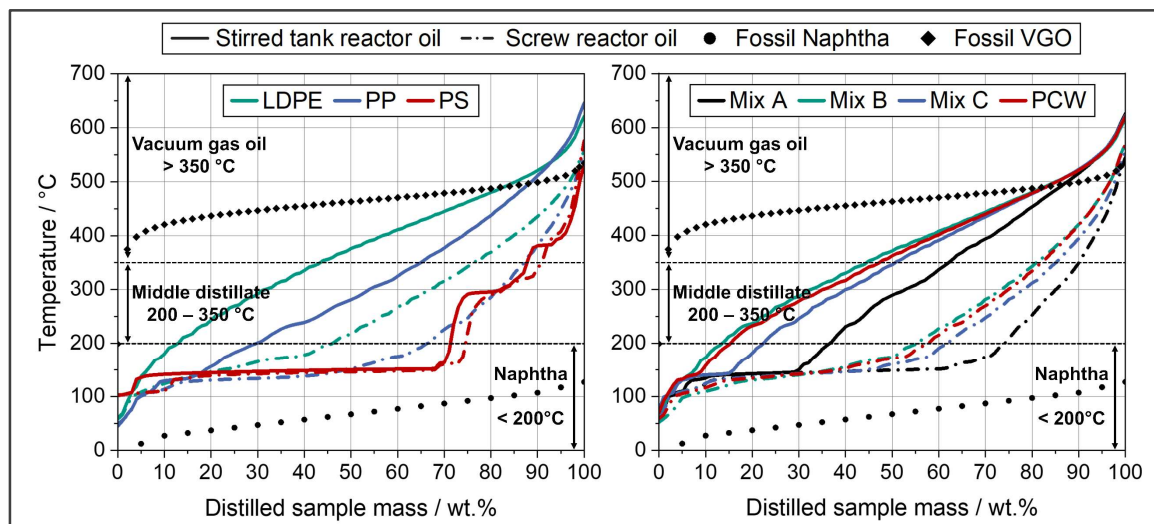


Figure 16: SimDist curves of pyrolysis oils obtained from STR and ASR experiments with various thermoplastic feedstocks, fossil naphtha [176] and VGO [177] (Publication 4).

The elemental analyses and 2D-GC analyses supplement the characterization of the oils. As illustrated in Figure 17, the carbon content in oils from the ASR system is higher, and the hydrogen content is lower. This effect is not as pronounced in pure polymers as it is in the reference mixture oils. The hydrogen-to-carbon ratio is calculated to 2.0, 1.8, and 2.0 for Mix B, Mix C, and the PCW produced at the STR, respectively. In comparison, the ratios for the corresponding oils from the ASR are 1.8, 1.6, and 1.7. The carbon-to-hydrogen ratios match the more frequent polymer backbone cleavages. They are consistent with the shifts in the mass balances and the SimDist curves. The ratios suggest more pronounced formation of unsaturated α -olefins and α - ω -dienes in the ASR, which is compatible with more intense cracking reactions. Furthermore, a higher GRT results in more secondary reactions and, thus, aromatics formation. The intensified formation of aromatics in the ASR system would also reduce the hydrogen-to-carbon ratio of the oils produced there. However, unlike the shift in molecular weight distribution toward lighter oil compounds, the increased aromatic formation cannot be confirmed by 2D-GC analysis.

The elemental analyses indicate no significant differences in nitrogen and chlorine content depending on the reactor system. However, the oxygen content in oils from the pyrolysis of Mix C and PCW is significantly lower when pyrolyzed in the ASR. The oxygen content in PCW oil from the ASR is 0.9 wt.%, but 2.9 wt.% in the STR. The 2D-GC analyses cannot confirm the increased content of O-containing HCs in Mix B, Mix C, and the PCW based on the quantified main compounds. Hence, the influence of the reactor on oxygen-containing components cannot be clarified conclusively with the applied analytical techniques. Measurement uncertainties in the challenging determination of oxygen by the elemental analysis as well as technical limitations of the 2D-GC analysis remain possible explanations.

The styrene content in oil from the STR system was determined to be 10 wt.% higher. At the same time, however, the proportion of other monomers, such as benzene or ethylbenzene, is increased by pyrolyzing in the ASR. However, the total amount of monoaromatic components remains constant in oils from both systems. The lower selectivity for styrene monomer can be attributed to the longer GRT and, thus, the enhanced secondary cracking reactions in the ASR.

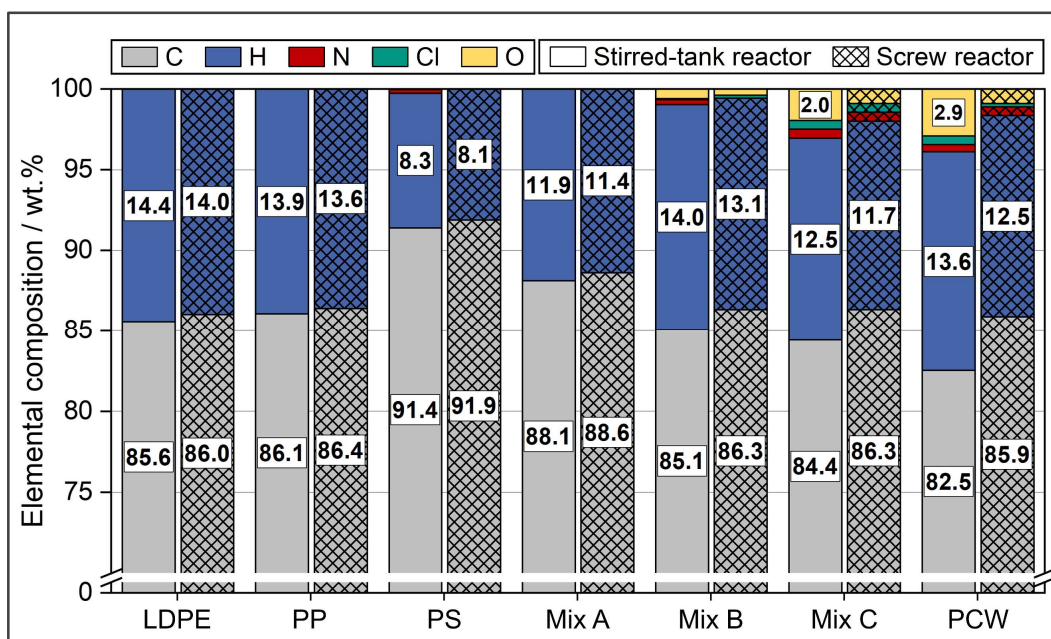


Figure 17: Elemental composition of oils from different thermoplastic feedstocks pyrolyzed in the STR and ASR with a reactor wall temperature of 500 °C (Publication 4).

The results highlight the considerable influence of the reactor system. While the ASR leads to a lower overall oil yield, it shifts the product distribution toward increased shares of naphtha and middle distillate fractions. At the same time, comparable or slightly lower proportions of heteroatom-containing compounds are obtained. However, this advantage in applications is accompanied by an increased olefin content and a higher proportion of aromatics. Consequently, the ASR oil cannot be regarded as generally superior in terms of suitability for cracker reintegration, since aromatics mainly dilute the potential monomer yield. The condensate produced fails to meet the requirements for potential reintegration pathways in chemical recycling outlined in Chapter 2.3. Thus, subsequent upgrading of the oils, their dilution in specification-compliant fossil products, or optimization of the pyrolysis process is essential.

4.3 Process Optimization by Temperature-staged Pyrolysis

As the decomposition kinetics of different types of thermoplastics vary, a temperature-staged pyrolysis approach was applied in the STR system to optimize the product yield and quality. The results displayed in this chapter have been excerpted from Publication 5.

4.3.1 Thermogravimetry

The investigation of the principal decomposition reaction rates is a prerequisite for experiments under technical conditions. In the dynamic TG tests conducted at a constant heating rate, the mass loss of PA6 I, PVC I, and PVC II occurs at significantly lower temperatures than the decomposition of the other polymers. This phenomenon is illustrated by temperature-staged TG experiments with pure polymers. The experimental results obtained from tests that incorporated two holding phases at temperatures of 300 °C and 370 °C are presented in Figure 18. A relevant volatile release in the initial holding phase at 300 °C is only observed for PVC. This step has previously been described by other authors as dehalogenation [113,115,116]. In the second isothermal segment, the plastics demonstrate varying degrees of volatile formation in accordance with the pyrolysis onset temperatures described in Chapter 4.1.1. PS almost completely reacts in the isothermal phase at 370 °C, while HDPE exhibits negligible decomposition reactions in the

form of released volatiles. The findings indicate that staged pyrolysis processes can be utilized to pyrolyze various polymers at distinct rates, thereby enabling their in-situ product separation. Furthermore, a significant divergence in reaction kinetics is observed between PS, ABS, PET, and PA6, as well as between polyolefins and the final stage of PVC decomposition. This phenomenon is reflected by a wider gap in the volatile formation curves of PA6 and PP. It is termed as “kinetic gap” in the following.

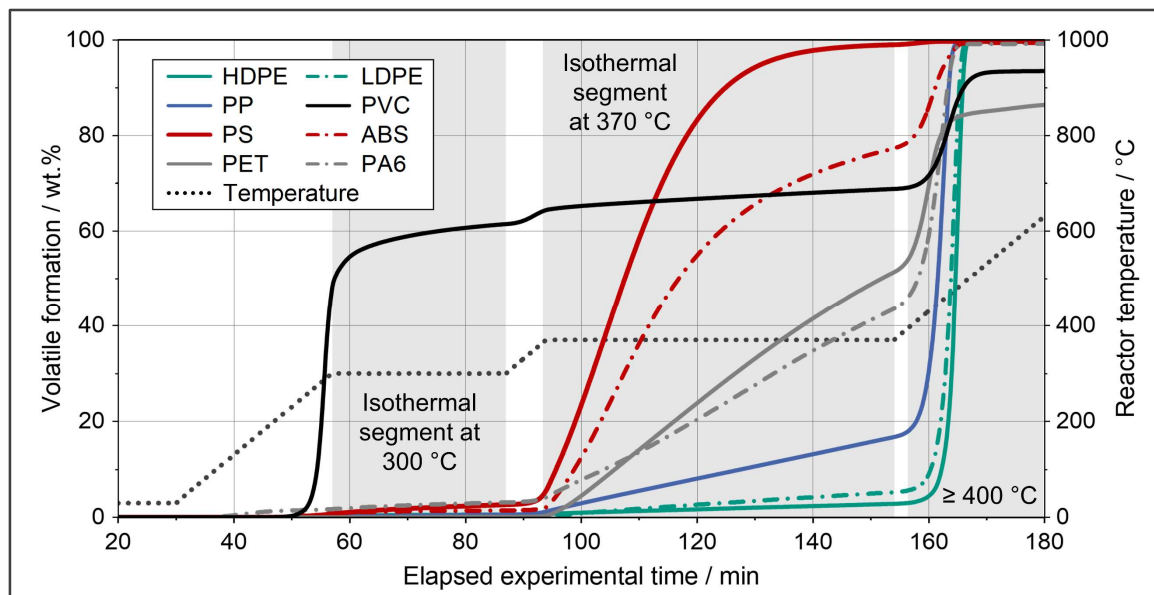


Figure 18: Three-staged TG experiments for individual polymers at isothermal segments for dechlorination at 300 °C, decomposition of aromatic-based and heteroatom-containing polymers at 370 °C, and polyolefin decomposition above 400 °C, including segments of constant heating rate at 10 K·min⁻¹ (Publication 5).

Further experiments reveal how the identified interaction effects between the polymers will affect the decomposition behavior in temperature-staged pyrolysis. Therefore, tests with different ternary plastic mixtures were carried out. The experiments confirm the interaction effects summarized in Chapter 4.1.1. In mixtures containing PP and PS, the decomposition of the PP chains is accelerated. Overall, the acceleration causes co-assembling of the compounds stemming from the aliphatic-forming polymers in the first stage. The kinetic gap becomes narrower, and the target product yield is reduced. The effect is less pronounced for other mixtures such as PP/LDPE/HDPE. In mixtures between PE and PS, no significant acceleration effect is apparent. These effects may be more pronounced in samples with more interaction interfaces [74]. Nevertheless, such interaction effects harm efficient optimization through selective product separation in the pyrolysis process.

More pronounced interaction effects occur in mixtures of PVC, PET, and PA6. The volatile formation curves in Figure 19 indicate their influence on pyrolysis behavior. In mixtures of PVC/PP with PET and PA6, significantly more volatile products are released in the segment at 300 °C than expected from their pure polymer behavior. This suggests that the HCl, produced during the PVC dechlorination step, causes partial co-decomposition of PET and PA6. This result is advantageous for temperature-staging, as the kinetic gap between PET, PA6, and PP is considerably extended in the presence of PVC. Consequently, oxygen- and nitrogen-containing products are expected to be reduced in the aliphatic-rich target product, improving its quality. Mixtures of PA6 and PET also exhibit a higher volatile formation rate at the 370 °C stage. Based on SPBM, 35.1 ± 0.7 wt.% of volatile products are expected for a PET/PA6/PP mixture. In the experiment, 55.8 ± 0.3 wt.% was determined. This interaction effect is also beneficial for optimizing the pyrolysis of mixed thermoplastics via temperature-staged pyrolysis.

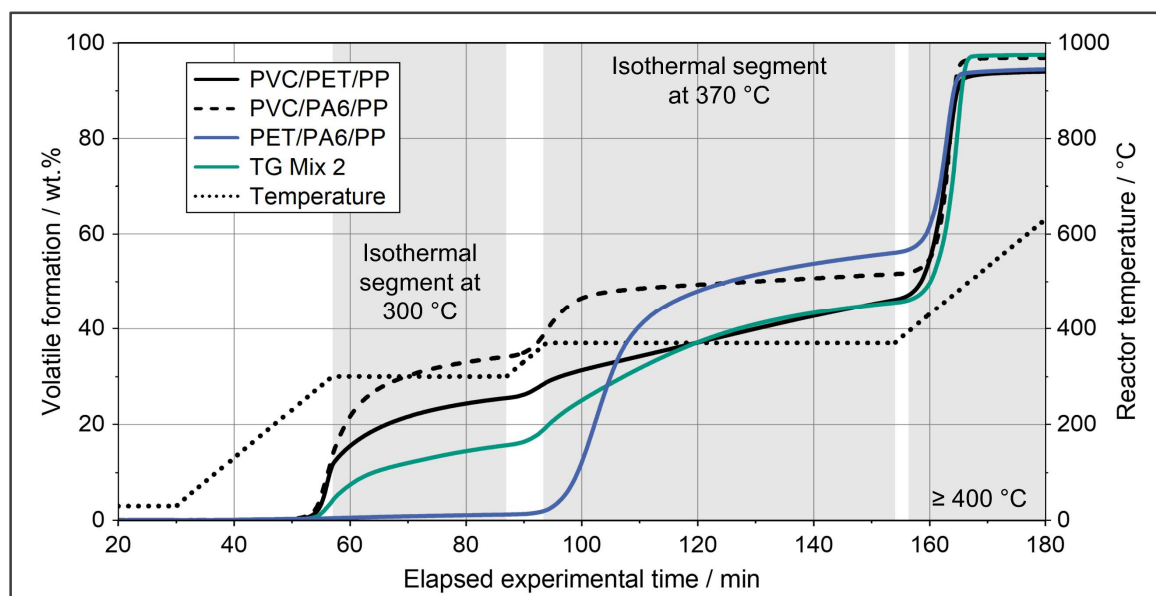


Figure 19: Three-staged TG experiments with isothermal segments at 300 and 370 °C and a constant heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ between the segments performed with ternary mixtures in the proportion of 30/30/40 wt.% and TG Mix 2 (Publication 5).

In combination with polyolefins, PVC additionally induces a slight delay in their decomposition reaction, which is accompanied by a minimal increase in the formation of char. However, this effect is rather weak and consequently will hardly impact tests conducted under technical conditions. Experiments with TG Mix 2 confirm that optimizing the pyrolysis of thermoplastic mixtures through temperature-staged pyrolysis is possible. Again, a strong interaction effect, attributed to PVC, PET, and PA6, is evident, leading to considerable mass losses of the feedstock at 300 and at 370 °C. TG Mix 2 contains 50 wt.% of polyolefins. After the 370 °C stage, this mixture has released $45 \pm 0.8 \text{ wt.}\%$ of volatile compounds. This represents about 8 wt.% more volatiles than expected based on superposition calculations. The remaining sample mass corresponds well to the polyolefin content. The interaction effects tend to widen the kinetic gap between the polymer types investigated, facilitating the application of temperature-graded pyrolysis. Nevertheless, the results also demonstrate that ideal, complete separation is not possible in this setup. Polyolefins, especially PP, begin to partially decompose at lower temperatures, while complete pyrolysis of the aromatic or heteroatom-containing polymers is not ensured at this stage.

4.3.2 Evaluation in the Stirred-Tank Reactor

Experiments with Mix C in the STR system were conducted to evaluate the temperature-staged pyrolysis concept under non-ideal technical pyrolysis conditions. As described in Chapter 4.2.1, the reactor exhibits heat transfer limitations due to the non-continuous addition of the feedstock. This causes two effects in the temperature profile of the added feedstock which are depicted in Figure 20. Firstly, the temperature in the reaction zone does not reach the target isothermal temperature in any of the staged tests as a result of the heating sleeves' control via the reactor wall temperature. At the 400 and 430 °C segments, the monitored temperature in the reactor accounts for about 395 and 420 °C. The subsequent set temperature of 500 °C in the second stage is also missed by 10 to 25 K. Secondly, the feedstock addition of 250 g causes a rapid temperature decline of about 140 °C. It takes approximately 30 min for the reaction zone to be heated back to the isothermal reaction temperature. Despite maximum heating power, the heating to the final pyrolysis stage at 500 °C also takes approximately 20 min.

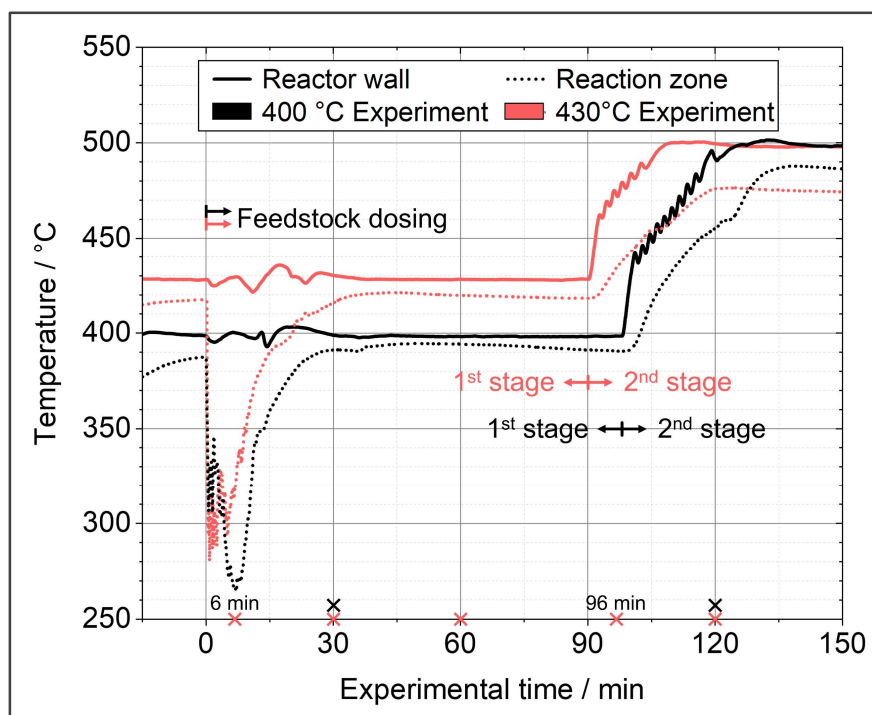


Figure 20: STR reaction zone and reactor wall temperature during temperature-staged pyrolysis of Mix C with isothermal segments at 400 and 430 °C. Gas sampling points are indicated by crosses along the x-axis (Publication 5).

The tests with an initial pyrolysis stage at 370 °C produce a negligible amount of condensate in the first stage. Given this low amount of oil, performing stage-specific mass balancing is not possible. Consequently, this experiment with an isothermal temperature at 370 °C behaves like an isothermal reference test. At 400 °C and 430 °C, evaluation of the mass balance and product compositions is feasible. In comparison to TG tests, the average polymer temperatures in STR tests are below the target set temperature of the isothermal stage. Consequently, the decomposition reaction is decelerated, and less product is generated in the holding phase.

The isothermal reference experiment yields 41.3 wt.% pyrolysis gas, 55.1 wt.% oil, and 3.6 wt.% solid residue. The amount of gas produced and the solid residue formed can only be recorded integrally in both staged experiments. For the 400 °C and 430 °C tests, these yields are 37.8 and 37.2 wt.%, respectively, and 5.2 wt.%. Both staged pyrolysis experiments thus produce slightly less pyrolysis gas and slightly more pyrolysis condensate. The lower yield for pyrolysis gas results from the lower average pyrolysis temperature in the staged experiments. The comparatively lower reaction rate during the staged tests further promotes the relevance of interaction effects in the melting phase. The investigations into the influence of feedstock in Chapter 4.1 have shown that increased coke formation occurs due to interactions between coke-forming polymers and non-coke-producing polymers. As a result, the solid residue increases slightly. Despite mass transport limitations in the condensers, the condensate yield can be evaluated specifically for each temperature stage. Overall, the tests conducted at 400 and 430 °C yielded a similar condensate fraction of 57.0 and 57.6 wt.%. However, the distribution between the first and second isothermal stages varies greatly. In accordance with the results of the kinetic analysis, a higher conversion rate is reached at the 430 °C stage. While only 2.9 wt.% of pyrolysis oil is produced at the 400 °C stage, 22.3 wt.% is obtained in the 430 °C test. Consequently, the higher pyrolysis temperature in the first stage leads to more intensive reactions and, thus, a higher oil yield.

Figure 21 reveals the impact of the isothermal temperature in the first stage on the time-dependent distribution of gaseous products. The figure shows the characteristic compounds in the gas product samples taken after 6, 30, 60, 96, and 120 minutes during the experiment at 430 °C. CO and CO₂, as well as acetaldehyde and heteroatom-containing trace gases, are particularly noticeable in the samples taken at sampling times of 6 and 30 min. Therefore, their formation at the beginning of the pyrolysis process during the 430 °C holding stage corresponds to the findings of the TG analysis. Following the temperature increase to 500 °C, these compounds are scarcely present. Chlorinated HCs can no longer be detected at this point.

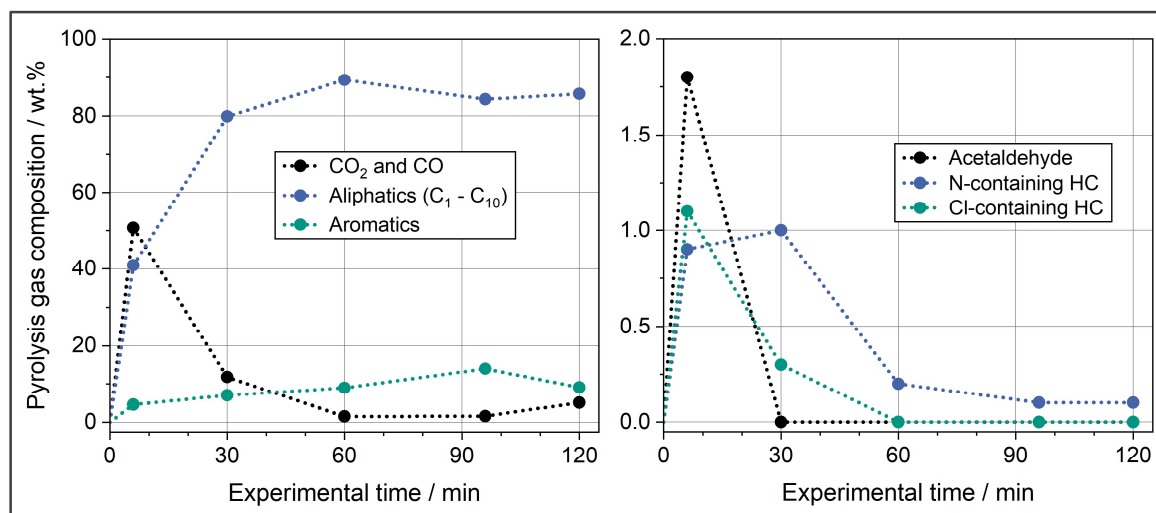


Figure 21: Content of gas compounds sampled after 6, 30, 60, 96, and 120 min during staged pyrolysis experiments at 430 and 500 °C in the STR system (Publication 5).

However, the formation of aromatic and aliphatic compounds differs. Aliphatics are only detectable in the gas sample withdrawn after 6 min. They account for under 40 wt.%. The aliphatics mainly consist of methane (5.3 wt.%) and ethene (29.8 wt.%). In the course of the experiment, the aliphatic HC concentration increases over time and stabilizes at around 85 to 90 wt.% after 60 min. The distribution of aliphatic HCs becomes broader, with branched C₃–C₆ compounds dominating the product distribution. The samples taken after 96 and 120 min also contain significant amounts of n-alkanes and α -olefins in the pyrolysis gas. This shows that gaseous HCs are first produced from PET, PVC, PA6, and ABS. PP decomposes already in the first pyrolysis stage, but in small quantities. PE decomposition begins after the reactor temperature has risen to 500 °C.

The aromatic compounds in the pyrolysis gas are mainly composed of benzene at the beginning. In the samples taken later, toluene dominates. Styrene is present in similar amounts in both samples, at 2.1 to 3.5 wt.%. In the case of aromatics, separation by temperature staging in the STR setup is only possible to a limited extent. Monoaromatics in particular exhibit boiling points that can lead to deposits in the gas sampling line and gas bags. These deposits lead to long-term outgassing. These mass transport limitations can lead to artifacts, reducing the effectiveness of product separation in staged pyrolysis processes. Nevertheless, the composition of the gas samples emphasizes the effectiveness of temperature-staged pyrolysis. Heteroatom-containing and aliphatic products in the gas phase are generated separately from each other by introducing an isothermal stage. For a pyrolysis system with spatially separated instead of temporally separated pyrolysis stages and with each stage featuring its own condensation system, an even sharper separation effect is expected.

The elemental analysis of the condensates supports the results of the gas analysis. The results are depicted in Table 9. The oil obtained during the 400 and 430 °C stages is enriched in nitrogen, chlorine, oxygen, and water. The oil produced at 500 °C corresponds to the pyrolysis temperature in both staged experiments and consequently contains high levels of carbon and hydrogen. The quality of these target product fractions is improved significantly compared to the reference experiments. Effective depletion of oil compounds, which are considered contaminants for reuse in chemical recycling, has been achieved. This is particularly the case for components containing O and Cl. However, complete dechlorination and denitrogenation are not achieved. This is in contrast to the experiments by Bockhorn et al. with simpler PVC mixtures [114].

Table 9: Elemental analysis of the pyrolysis oils generated in temperature-staged pyrolysis experiments with isothermal segments at 400 and 430 °C and an isothermal reference experiment [Publication 5].

Pyrolysis oil	Elemental composition / wt.%					
	C	H	N	Cl	Moisture	O ^A
Isothermal at 500 °C	84.4	12.5	0.6	0.5	0.0	2.0
Staged Pyrolysis						
400 °C (0 – 96 min)	60.7	11.7	1.3	7.0	15.0	4.8
500 °C (96 – 186 min)	85.6	13.7	0.2	0.2	0.0	0.3
Staged Pyrolysis						
430 °C (0 – 90 min)	82.8	11.7	1.0	1.7	1.7	1.0
500 °C (90 – 180 min)	86.8	12.6	0.3	0.2	0.0	0.0

^A calculated as the difference to 100 wt.%.

Figure 22 shows the results of the NMR analyses, which provide further information on the distribution of HCs in the oils. Aliphatic-bound protons prevail in both oil fractions obtained at the 500 °C stage. The presence of unsaturated C-C bonds and aromatic structures is also evident. This suggests that the oil primarily consists of decomposition products of PE and PP. The distribution of saturated and unsaturated aliphatics is not significantly affected by temperature staging. Secondary carbon atoms prevail, indicating a dominant presence of n-alkanes and α -olefins. Additional 2D-GC analyses support this finding. The peak intensity of protons bound to secondary carbon atoms is less pronounced in oils produced at 400 °C and 430 °C. In particular, aromatic components are detectable. At the same time, a broad peak is visible for the oil of the 400 °C stage in the carbonyl or carboxy group range, indicating PET decomposition products. The increased number of heteroatom-containing HCs in these samples is evident as peaks of aliphatic compounds near a non-aliphatic bond (range B). Compared to the oil generated at 430 °C, these trends are significantly more pronounced in the oil produced at 400 °C. This effect causes a lower oil yield of 2.9 wt.% in the experiment with a lower isothermal temperature. PP and PE undergo reduced decomposition at 400 °C, increasing the selectivity of the separation process.

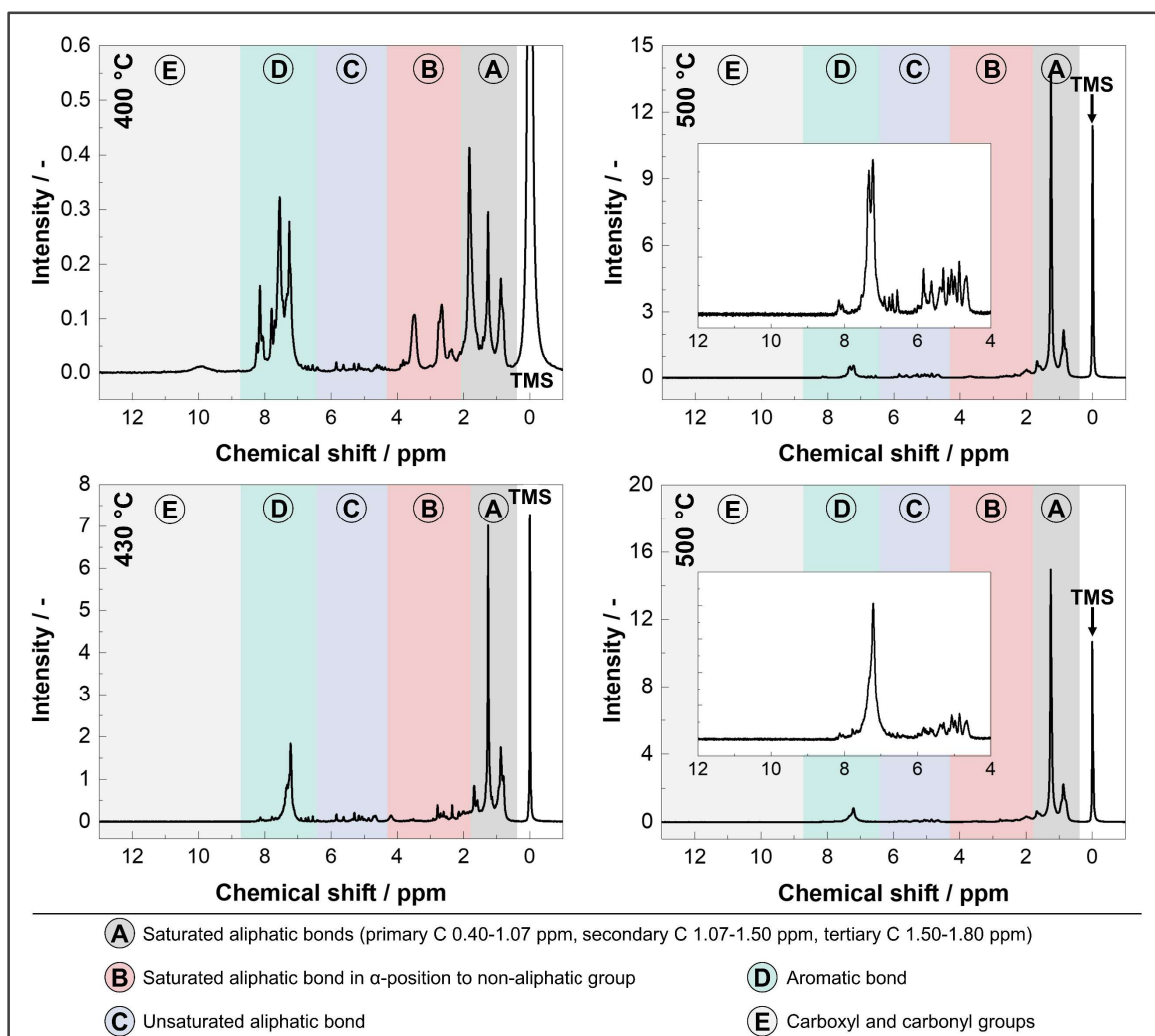


Figure 22: NMR spectra of pyrolysis oils from temperature-staged experiments with Mix C at 400 and 500 °C (top) and 430 and 500 °C (bottom) (Publication 5).

Overall, the mass balance and product analyses demonstrate that the selection of temperature and time of the isothermal segment is crucial for the efficiency of the staged pyrolysis process. However, laboratory-scale experiments can only be consulted for the correct parameter selection to a limited extent. Heat and mass transfer limitations in the reactor system prevent the transferability of the selection evaluated in laboratory experiments. At the same time, the results emphasize a discrepancy between maximum target product yield and target product quality. The interaction effects expand the kinetics gap for the mixtures investigated. However, it is not possible to completely separate the decomposition of polyolefins from aromatic-based and heteroatom-containing polymers. Choosing a high isothermal pyrolysis temperature causes a significant decomposition of PP and PE. The target product yield decreases. Using a low isothermal pyrolysis temperature in the first stage prevents the complete decomposition of PS, ABS, PET, PA6, and PVC during this stage. Some decomposition products are then transferred to the products of the second stage, reducing the target product quality. Thus, a conflicting interest between product quality and product yield arises when temperature-staged pyrolysis is applied to complex thermoplastic mixtures for producing a pyrolysis oil that exclusively consists of aliphatic compounds.

5 Conclusion and Outlook

The results presented in this cumulative dissertation clarify fundamental relationships between feedstock composition, reactor design, and key operational parameters in the pyrolysis of thermoplastic mixtures. For reintegration within a chemical recycling framework, particular emphasis is placed on the yield and composition of pyrolysis oils. A novel comprehensive 2D-GC method was successfully developed for the detailed characterization of pyrolysis oils, providing an extended analytical basis alongside established techniques. In addition, a STR pyrolysis system enabled a systematic comparison of pyrolysis behavior with the fundamentally different ASR concept. Finally, the experimental methods were complemented by SPBM, providing a consistent approach for evaluating and further developing plastic pyrolysis processes.

The feedstock composition is the dominant factor influencing pyrolysis behavior. It has a fundamental effect on reaction kinetics, product yield, and composition. Significant polymer-specific variations exist for pure polymers, with oil yields ranging from less than 11 wt.% for PVC to 72 wt.% for polyolefins and almost exclusive pyrolysis oil formation for styrene-based polymers in the STR experiments. Polymers with a stable carbon-carbon backbone, such as LDPE, HDPE, PP, PS, and ABS, are classified as Group I polymers and exhibit radical degradation mechanisms. Heteroatom-containing polymers, such as PET and PA6 (Group II) and PVC (Group III), follow different decomposition networks. In mixtures, polymers of Group I exhibit no or only minor interactions, enabling the applicability of SPBM to their decomposition behavior. In contrast, strong interactions occur between Group II and III polymers, underlining the importance of polymer structure. These interactions occur in the shared melt phase and intensify with increasing reaction interface, leading to accelerated decomposition kinetics and increased coke formation. Furthermore, more low-molecular-weight HCs are formed due to enhanced primary cracking.

These effects also play a dominant role in the overall pyrolysis behavior of complex, post-consumer-like mixtures. The pyrolysis ED varies between 1800 and 2450 J·g⁻¹ depending on the polymer type and increases in interacting mixtures by 400 to 500 J·g⁻¹ compared to SPBM results due to intensified cracking reactions. These interactions also strongly affect the presence of heteroatom-containing compounds in the oil, leading to increased chlorine and reduced oxygen content. These contaminations complicate the oil utilization in petrochemical processes. Furthermore, dominant interaction effects in these mixtures decrease the oil formation by up to 22 wt.%, leading to oil yields between 50 and 55 wt.% for the polyolefin-rich mixtures of this study. Detailed feedstock characterization by polymer type is therefore essential for industrial applications.

SPBM based on pure polymer behavior enables precise estimation of ED, product yields, and product compositions for simple mixtures of polyolefins and PS with good agreement to ASR and STR experiments. However, its applicability is limited to non-interacting polymer systems. In mixtures of Group II and III polymers, interactions cause systematic deviations in kinetics, yields, and product composition. In particular, heteroatom-containing impurities in pyrolysis oils cannot be reliably predicted. Nevertheless, SPBM remains a useful tool for the initial estimation of the pyrolysis behavior of thermoplastic mixtures.

Reactor design and operating conditions significantly influence the polymer decomposition through material mixing and heat and mass transfer, which determine the effective polymer temperature profile. This profile can deviate considerably from the operator-set reactor temperature. For example, the averaged polymer temperature in the STR decreases by up to 50 °C compared to the reactor wall, affecting the primary cracking mechanism. In

contrast, the GRT impacts secondary gas-phase reactions. Increased GRTs in technical pyrolysis reactors such as the ASR and STR systems promote secondary reactions. They result in higher gas yields of up to 24 wt.% and shift the oil composition toward low-boiling products. Overall, GRT-specific effects superimpose temperature-profile effects and contribute to shifts in thermoplastic pyrolysis behavior. In complex mixtures with polymer-polymer interactions, feedstock-specific effects dominate over reactor-specific effects.

Nevertheless, the overlap of reactor- and feedstock-related effects hinders the comparability and transferability of pyrolysis results across different studies. Process classification based solely on elemental feedstock composition, reactor type, and set temperature is insufficient for meaningful comparison of pyrolysis results. Scale-up and process evaluation therefore require detailed information on feedstock polymer types, reactor operating parameters, and reactor dimensions determining the polymer temperature profile caused by heat and mass transfer limitations, as well as the GRT distribution.

From a design perspective, several measures can improve the efficiency of industrial-scale chemical recycling by pyrolysis. Polymers containing heteroatoms should be minimized, as they cause contamination in the target product and increase the need for upgrading. Continuous feedstock supply and efficient heat and mass transfer ensure homogeneous reaction conditions. Higher average polymer temperature profiles reduce the condensate yield by promoting gas formation but increase the share of naphtha- and middle distillate-range HCs in the pyrolysis oil, while also favoring the formation of olefins and aromatics. The GRT distribution should be adjusted to control secondary reactions and minimize the formation of undesired by-products.

Temperature-staged pyrolysis is evaluated as a process optimization strategy for chemical recycling. It selectively exploits differences in polymer decomposition kinetics to improve pyrolysis oil quality. TG studies show that aromatic and heteroatom-containing polymers preferentially decompose below 370 °C, whereas polyolefins predominantly react above 370 °C. In technical reactors, the implementation requires adjustment of stage temperatures and the holding time of the isothermal stages due to heat and mass transport limitations. While the total oil yield remains largely unaffected, aliphatic compounds are partially recovered in the low-temperature fraction due to polyolefin decomposition kinetics. Meanwhile, heteroatoms and aromatics in the target product fraction are reduced by a factor of 0.5 to 0.33, resulting in an optimization conflict between product quality and the recoverable yield of the aliphatic-rich target fraction.

This work investigated the influence of feedstock composition using representative thermoplastic polymers commonly found in plastic waste. While SPBM allows reliable prediction of pyrolysis behavior for non-interacting polymer systems, its applicability remains limited for complex mixtures with pronounced polymer-polymer interactions. The proposed classification based on polymer backbone structure provides a first indication of expected interaction effects and may support the systematic extension of the experimental database to additional polymer types. Combined with predictive approaches that account for non-ideal reactor behavior, this can support the development of a robust process design tool for the targeted optimization and scale-up of pyrolysis reactors for chemical recycling of plastic waste.

Appendix

A. Setup and Parameters of the 2D-GC Method

This appendix provides additional information on the setup of the 2D-GC analysis. The information is listed in the following table. Further information can be found in Publication 3 and the corresponding supplementary information.

Table B.1: Overview of the hardware setup and the analysis parameters for 2D-GC:

SSL			
Split ratio of 20:1	Temperature:	Pressure:	Split flow: 10 ml/min
Injection by an Agilent 7693A ALS	350 °C	32.94 PSI	Purge flow: 3 ml/min
Agilent 8890 GC oven			
Temperature program:	First capillary column:	Second capillary column	
40 °C for 3 min	Restek Rxi-5Sil MS	Trajan BPX50	
Ramp of 3.5 K·min ⁻¹	20 m, 0.18 mm, 0.18 µm	5 m, 0.25 mm, 0.25 µm	
315 °C for 39 min	Column flow: 0.5 ml/min	Column flow: 21 ml/min	
Agilent reversed flow modulator and Trajan 3-port splitter			
Modulation phase: 10.0 s		Volumetric split ratio:	
Injection time: 0.36 s		10:1 (FID/NCD to qMS)	
FID			
Data rate: 100 Hz	Temperature:	Air flow: 400 ml/min	
	350 °C	H ₂ flow: 35 ml/min	
		Makeup flow: 20 ml/min	
Agilent 8255 NCD			
Data rate: 100 Hz	Base temperature: 350 °C	Oxidizer flow: 8 ml/min	
Pressure: 3 PSI	Burner temperature: 700 °C	Ozon flow: 37 ml/min	
Agilent 5977B qMS			
Scan Mode:	Temperatures	Vacuum by turbo pump	
Range: 30-300 u	Transfer line: 280 °C	Pressure not monitored	
Scan speed: 12,500 u·s ⁻¹	Ion source: 230 °C		
Cycle time: 40 ms	Quadrupole filter: 150 °C		

References

- [1] P. Stegmann, V. Daioglou, M. Londo, D.P. van Vuuren, M. Junginger, *Plastic futures and their CO₂ emissions*, *Nature* 612 (2022) 272–276. <https://doi.org/10.1038/s41586-022-05422-5>.
- [2] M. MacLeod, H.P.H. Arp, M.B. Tekman, A. Jahnke, *The global threat from plastic pollution*, *Science* 373 (2021) 61–65. <https://doi.org/10.1126/science.abg5433>.
- [3] H.V. Ford, N.H. Jones, A.J. Davies, B.J. Godley, J.R. Jambeck, I.E. Napper, C.C. Suckling, G.J. Williams, L.C. Woodall, H.J. Koldewey, *The fundamental links between climate change and marine plastic pollution*, *Science of The Total Environment* 806 (2022) 150392. <https://doi.org/10.1016/j.scitotenv.2021.150392>.
- [4] European Commission, *The European Green Deal*, Brussels (2019).
- [5] European Commission, *A New Circular Economy Action Plan: For a Cleaner and More Competitive Europe*, Brussels (2020).
- [6] OECD, *Global Plastics Outlook*, Paris (2022).
- [7] PlasticsEurope, *The Circular Economy for Plastics: A European Analysis*, Brussels (2024).
- [8] M. Klotz, M. Haupt, S. Hellweg, *Potentials and limits of mechanical plastic recycling*, *Journal of Industrial Ecology* 27 (2023) 1043–1059. <https://doi.org/10.1111/jiec.13393>.
- [9] K. van Geem, *Plastic waste recycling is gaining momentum*, *Science* 381 (2023) 607–608. <https://doi.org/10.1126/science.adj2807>.
- [10] A. Rahimi, J.M. García, *Chemical recycling of waste plastics for new materials production*, *Nature Reviews Chemistry* 1 (2017). <https://doi.org/10.1038/s41570-017-0046>.
- [11] K. Ragaert, L. Delva, K. van Geem, *Mechanical and chemical recycling of solid plastic waste*, *Waste Management* 69 (2017) 24–58. <https://doi.org/10.1016/j.wasman.2017.07.044>.
- [12] S. Kumagai, K. Fujiwara, T. Nishiyama, Y. Saito, T. Yoshioka, *Chemical Feedstock Recovery Through Plastic Pyrolysis: Challenges and Perspectives Toward a Circular Economy*, *ChemSusChem* 18 (2025) e2500210. <https://doi.org/10.1002/cssc.202500210>.
- [13] P. Biessey, J. Vogel, M. Seitz, P. Quicker, *Plastic Waste Utilization via Chemical Recycling: Approaches, Limitations, and the Challenges Ahead*, *Chemie Ingenieur Technik* 95 (2023) 1199–1214. <https://doi.org/10.1002/cite.202300042>.
- [14] S. Armenise, S. Wong, J.M. Ramírez-Velásquez, F. Launay, D. Wuebben, B.B. Nyakuma, J. Rams, M. Muñoz, *Application of computational approach in plastic pyrolysis kinetic modelling: a review*, *Reaction Kinetics, Mechanisms and Catalysis* 134 (2021) 591–614. <https://doi.org/10.1007/s11144-021-02093-7>.
- [15] M. Kusenberg, A. Eschenbacher, M.R. Djokic, A. Zayoud, K. Ragaert, S. de Meester, K. van Geem, *Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?*, *Waste Management* 138 (2022) 83–115. <https://doi.org/10.1016/j.wasman.2021.11.009>.
- [16] J. Scheirs, W. Kaminsky, *Feedstock Recycling and Pyrolysis of Waste Plastics*, Wiley, 2006.

- [17] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, *Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor*, Chemical Engineering Journal 173 (2011) 62–71. <https://doi.org/10.1016/j.cej.2011.07.037>.
- [18] E.A. Williams and P.T. Williams, *The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor*, Journal of Chemical Technology and Biotechnology 70 (1997) 9–20. [https://doi.org/10.1002/\(SICI\)1097-4660\(199709\)70:1%3C9::AID-JCTB700%3E3.0.CO;2-E](https://doi.org/10.1002/(SICI)1097-4660(199709)70:1%3C9::AID-JCTB700%3E3.0.CO;2-E).
- [19] M. Calero, R.R. Solís, M.J. Muñoz-Batista, A. Pérez, G. Blázquez, M. Ángeles Martín-Lara, *Oil and gas production from the pyrolytic transformation of recycled plastic waste: An integral study by polymer families*, Chemical Engineering Science 271 (2023) 118569. <https://doi.org/10.1016/j.ces.2023.118569>.
- [20] S.H. Chang, *Plastic waste as pyrolysis feedstock for plastic oil production: A review*, Science of The Total Environment 877 (2023) 162719. <https://doi.org/10.1016/j.scitotenv.2023.162719>.
- [21] F. Faisal, M.G. Rasul, M.I. Jahirul, D. Schaller, *Pyrolytic conversion of waste plastics to energy products: A review on yields, properties, and production costs*, Science of The Total Environment 861 (2023) 160721. <https://doi.org/10.1016/j.scitotenv.2022.160721>.
- [22] K. Pielichowski, J. Njuguna, T.M. Majka, *Mechanisms of thermal degradation of polymers*, in: K. Pielichowski, J. Njuguna, T.M. Majka (Eds.), Thermal Degradation of Polymeric Materials, Elsevier, 2023, pp. 9–11.
- [23] L.A. Wall, S. Straus, *Pyrolysis of polyolefins*, Journal of Polymer Science 44 (1960) 313–323. <https://doi.org/10.1002/pol.1960.1204414404>.
- [24] M. Seeger, H.-J. Cantow, *Thermische spaltungsmechanismen in homo- und copolymeren aus α -olefinen, 1. Grundlegende mechanismen und pyrolyse von linearem polyäthylen*, Die Makromolekulare Chemie 176 (1975) 1411–1425. <https://doi.org/10.1002/macp.1975.021760515>.
- [25] M. Seeger, H.-J. Cantow, *Thermische spaltungsmechanismen in homo- und copolymeren aus α -olefinen, 2. Polypropylene mit bekannter taktizität, polyisobutylene und poly(1-buten)*, Die Makromolekulare Chemie 176 (1975) 2059–2078. <https://doi.org/10.1002/macp.1975.021760714>.
- [26] R.P. Lattimer, *Pyrolysis field ionization mass spectrometry of polyolefins*, Journal of Analytical and Applied Pyrolysis 31 (1995) 203–225. [https://doi.org/10.1016/0165-2370\(94\)00824-K](https://doi.org/10.1016/0165-2370(94)00824-K).
- [27] J.A. Conesa, A. Marcilla, R. Font, J.A. Caballero, *Thermogravimetric studies on the thermal decomposition of polyethylene*, Journal of Analytical and Applied Pyrolysis 36 (1996) 1–15. [https://doi.org/10.1016/0165-2370\(95\)00917-5](https://doi.org/10.1016/0165-2370(95)00917-5).
- [28] E. Ranzi, M. Dente, T. Faravelli, G. Bozzano, S. Fabini, R. Nava, V. Cozzani, L. Tognotti, *Kinetic modeling of polyethylene and polypropylene thermal degradation*, Journal of Analytical and Applied Pyrolysis 40–41 (1997) 305–319. [https://doi.org/10.1016/S0165-2370\(97\)00032-6](https://doi.org/10.1016/S0165-2370(97)00032-6).
- [29] R.W.J. Westerhout, J.A.M. Kuipers, W.P.M. van Swaaij, *Experimental Determination of the Yield of Pyrolysis Products of Polyethene and Polypropene. Influence of Reaction Conditions*, Industrial & Engineering Chemistry Research 37 (1998) 841–847. <https://doi.org/10.1021/ie970384a>.

-
- [30] H. Bockhorn, A. Hornung, U. Hornung, D. Schawaller, *Kinetic study on the thermal degradation of polypropylene and polyethylene*, Journal of Analytical and Applied Pyrolysis 48 (1999) 93–109. [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4).
- [31] J. Ceamanos, J. Mastral, A. Millera, M. Aldea, *Kinetics of pyrolysis of high density polyethylene. Comparison of isothermal and dynamic experiments*, Journal of Analytical and Applied Pyrolysis 65 (2002) 93–110. [https://doi.org/10.1016/S0165-2370\(01\)00183-8](https://doi.org/10.1016/S0165-2370(01)00183-8).
- [32] R. Kumar and G. Madras, *Thermal degradation kinetics of isotactic and atactic polypropylene*, Journal of Applied Polymer Science 90 (2003) 2206–2213. <https://doi.org/10.1002/app.12880>.
- [33] R.W.J. Westerhout, J. Waanders, J.A.M. Kuipers, W.P.M. van Swaaij, *Kinetics of the Low-Temperature Pyrolysis of Polyethene, Polypropene, and Polystyrene Modeling, Experimental Determination, and Comparison with Literature Models and Data*, Industrial & Engineering Chemistry Research 36 (1997) 1955–1964. <https://doi.org/10.1021/ie960501m>.
- [34] D.G. Kulas, A. Zolghadr, D. Shonnard, *Micropyrolysis of Polyethylene and Polypropylene Prior to Bioconversion: The Effect of Reactor Temperature and Vapor Residence Time on Product Distribution*, ACS Sustainable Chemistry & Engineering 9 (2021) 14443–14450. <https://doi.org/10.1021/acssuschemeng.1c04705>.
- [35] S. Honus, S. Kumagai, G. Fedorko, V. Molnár, T. Yoshioka, *Pyrolysis gases produced from individual and mixed PE, PP, PS, PVC, and PET—Part I: Production and physical properties*, Fuel 221 (2018) 346–360. <https://doi.org/10.1016/j.fuel.2018.02.074>.
- [36] H.H.G. Jellinek, *Thermal degradation of polystyrene. Part II*, Journal of Polymer Science 4 (1949) 1–12. <https://doi.org/10.1002/pol.1949.120040101>.
- [37] T. Faravelli, M. Pincioli, F. Pisano, G. Bozzano, M. Dente, E. Ranzi, *Thermal degradation of polystyrene*, Journal of Analytical and Applied Pyrolysis 60 (2001) 103–121. [https://doi.org/10.1016/S0165-2370\(00\)00159-5](https://doi.org/10.1016/S0165-2370(00)00159-5).
- [38] N. Grassie, W.W. Kerr, *The thermal depolymerization of polystyrene. Part 1.-The reaction mechanism*, Transactions of the Faraday Society 53 (1957) 234–239. <https://doi.org/10.1039/TF9575300234>.
- [39] G. Audisio, F. Bertini, *Molecular weight and pyrolysis products distribution of polymers*, Journal of Analytical and Applied Pyrolysis 24 (1992) 61–74. [https://doi.org/10.1016/0165-2370\(92\)80005-7](https://doi.org/10.1016/0165-2370(92)80005-7).
- [40] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, *Thermal degradation of PVC: A review*, Waste Management 48 (2016) 300–314. <https://doi.org/10.1016/j.wasman.2015.11.041>.
- [41] R.R. Stromberg, S. Straus, B.G. Achhammer, *Thermal decomposition of poly(vinyl chloride)*, Journal of Polymer Science 35 (1959) 355–368. <https://doi.org/10.1002/pol.1959.1203512904>.
- [42] R.P. Lattimer, W.J. Kroenke, *The formation of volatile pyrolyzates from poly(vinyl chloride)*, Journal of Applied Polymer Science 25 (1980) 101–110. <https://doi.org/10.1002/app.1980.070250110>.
- [43] R.P. Lattimer, W.J. Kroenke, *Mechanisms of formation of volatile aromatic pyrolyzates from poly(vinyl chloride)*, Journal of Applied Polymer Science 27 (1982) 1355–1366. <https://doi.org/10.1002/app.1982.070270425>.
-

- [44] G. Montaudo and C. Puglisi, *Evolution of aromatics in the thermal degradation of poly(vinyl chloride): A mechanistic study*, Polymer Degradation and Stability 33 (1991) 229–262. [https://doi.org/10.1016/0141-3910\(91\)90019-N](https://doi.org/10.1016/0141-3910(91)90019-N).
- [45] H. Bockhorn, A. Hornung, U. Hornung, *Mechanisms and kinetics of thermal decomposition of plastics from isothermal and dynamic measurements*, Journal of Analytical and Applied Pyrolysis 50 (1999) 77–101. [https://doi.org/10.1016/S0165-2370\(99\)00026-1](https://doi.org/10.1016/S0165-2370(99)00026-1).
- [46] J. Yang, Y. Wu, J. Zhu, H. Yang, Y. Li, L. Jin, H. Hu, *Insight into the pyrolysis behavior of polyvinyl chloride using in situ pyrolysis time-of-flight mass spectrometry: Aromatization mechanism and Cl evolution*, Fuel 331 (2023) 125994. <https://doi.org/10.1016/j.fuel.2022.125994>.
- [47] A. Marongiu, T. Faravelli, G. Bozzano, M. Dente, E. Ranzi, *Thermal degradation of poly(vinyl chloride)*, Journal of Analytical and Applied Pyrolysis 70 (2003) 519–553. [https://doi.org/10.1016/S0165-2370\(03\)00024-X](https://doi.org/10.1016/S0165-2370(03)00024-X).
- [48] N. Grassie, D.R. Bain, *Thermal degradation of copolymers of styrene and acrylonitrile. I. Preliminary investigation of changes in molecular weight and the formation of volatile products*, Journal of Polymer Science Part A-1: Polymer Chemistry 8 (1970) 2653–2664. <https://doi.org/10.1002/pol.1970.150080930>.
- [49] N. Grassie, A. Heaney, *Thermal degradation of copolymers of butadiene and acrylonitrile*, European Polymer Journal 10 (1974) 415–424. [https://doi.org/10.1016/0014-3057\(74\)90206-7](https://doi.org/10.1016/0014-3057(74)90206-7).
- [50] M. Suzuki, C.A. Wilkie, *The thermal degradation of acrylonitrile-butadiene-styrene terpolymer as studied by TGA/FTIR*, Polymer Degradation and Stability 47 (1995) 217–221. [https://doi.org/10.1016/0141-3910\(94\)00122-O](https://doi.org/10.1016/0141-3910(94)00122-O).
- [51] K.-H. Lee, D.-H. Shin, Y.-H. Seo, *Thermal degradation of nitrogen-containing polymers, acrylonitrile-butadiene-styrene and styrene-acrylonitrile*, Korean Journal of Chemical Engineering 23 (2006) 224–229. <https://doi.org/10.1007/BF02705720>.
- [52] M. Di Cortemiglia, G. Camino, L. Costa, M. Guaita, *Thermal degradation of ABS*, Thermochimica Acta 93 (1985) 187–190. [https://doi.org/10.1016/0040-6031\(85\)85048-6](https://doi.org/10.1016/0040-6031(85)85048-6).
- [53] G. Wang, Z. Zhang, D. Xu, B. Xing, L. Zhu, S. Wang, *Insight into pyrolysis mechanism of plastic waste with C-O/C-N bonds in the backbone*, Science of The Total Environment 897 (2023) 165359. <https://doi.org/10.1016/j.scitotenv.2023.165359>.
- [54] I. Marshall, A. Todd, *The thermal degradation of polyethylene terephthalate*, Transactions of the Faraday Society 49 (1953) 67. <https://doi.org/10.1039/TF9534900067>.
- [55] I.C. McNeill, M. Bounekhel, *Thermal degradation studies of terephthalate polyesters: 1. Poly(alkylene terephthalates)*, Polymer Degradation and Stability 34 (1991) 187–204. [https://doi.org/10.1016/0141-3910\(91\)90119-C](https://doi.org/10.1016/0141-3910(91)90119-C).
- [56] G. Montaudo, C. Puglisi, F. Samperi, *Primary thermal degradation mechanisms of PET and PBT*, Polymer Degradation and Stability 42 (1993) 13–28. [https://doi.org/10.1016/0141-3910\(93\)90021-A](https://doi.org/10.1016/0141-3910(93)90021-A).
- [57] S.A. Jenekhe, J.W. Lin, B. Sun, *Kinetics of the thermal degradation of polyethylene terephthalate*, Thermochimica Acta 61 (1983) 287–299. [https://doi.org/10.1016/0040-6031\(83\)80283-4](https://doi.org/10.1016/0040-6031(83)80283-4).

-
- [58] T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, A. Okuwaki, *Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant*, *Polymer Degradation and Stability* 86 (2004) 499–504. <https://doi.org/10.1016/j.polymdegradstab.2004.06.001>.
- [59] J.W.F. Chia, O. Sawai, T. Nunoura, *Reaction pathway of poly(ethylene) terephthalate carbonization: Decomposition behavior based on carbonized product*, *Waste Management* 108 (2020) 62–69. <https://doi.org/10.1016/j.wasman.2020.04.035>.
- [60] S. Straus, L.A. Wall, *Pyrolysis of polyamides*, *Journal of Research of the National Institute of Standards* 60 (1958) 39–45.
- [61] S.V. Levchik, E.D. Weil, M. Lewin, *Thermal decomposition of aliphatic nylons*, *Polymer International* 48 (1999) 532–557. [https://doi.org/10.1002/\(SICI\)1097-0126\(199907\)48:7<532::AID-PI214>3.0.CO;2-R](https://doi.org/10.1002/(SICI)1097-0126(199907)48:7<532::AID-PI214>3.0.CO;2-R).
- [62] B.J. Holland, J.N. Hay, *Thermal degradation of nylon polymers*, *Polymer International* 49 (2000) 943–948. [https://doi.org/10.1002/\(SICI\)1097-0126\(199907\)48:7%3C532::AID-PI214%3E3.0.CO;2-R](https://doi.org/10.1002/(SICI)1097-0126(199907)48:7%3C532::AID-PI214%3E3.0.CO;2-R).
- [63] H. Bockhorn, A. Hornung, U. Hornung, J. Weichmann, *Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods*, *Thermochimica Acta* 337 (1999) 97–110. [https://doi.org/10.1016/S0040-6031\(99\)00151-3](https://doi.org/10.1016/S0040-6031(99)00151-3).
- [64] R. Lehrle, I. Parsons, M. Rollinson, *Thermal degradation mechanisms of nylon 6 deduced from kinetic studies by pyrolysis-g.c*, *Polymer Degradation and Stability* 67 (2000) 21–33. [https://doi.org/10.1016/S0141-3910\(99\)00112-3](https://doi.org/10.1016/S0141-3910(99)00112-3).
- [65] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei, R. Ruan, *Pyrolysis technology for plastic waste recycling: A state-of-the-art review*, *Progress in Energy and Combustion Science* 93 (2022) 101021. <https://doi.org/10.1016/j.pecs.2022.101021>.
- [66] Y. Qin, Z. Wang, F. Yang, D. Wang, W. Liu, D. Hanikai, J. Liu, J. Zhou, D. Liu, *Research progress on pyrolysis and resource utilisation of waste plastics: Methods, mechanisms, influencing factors, and future prospects*, *Journal of Analytical and Applied Pyrolysis* 193 (2026) 107459. <https://doi.org/10.1016/j.jaap.2025.107459>.
- [67] V. Cozzani, C. Nicolella, M. Rovatti, L. Tognotti, *Influence of Gas-Phase Reactions on the Product Yields Obtained in the Pyrolysis of Polyethylene*, *Industrial & Engineering Chemistry Research* 36 (1997) 342–348. <https://doi.org/10.1021/ie950779z>.
- [68] M.R. Del Hernández, A. Gómez, Á.N. García, J. Agulló, A. Marcilla, *Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE*, *Applied Catalysis A: General* 317 (2007) 183–194. <https://doi.org/10.1016/j.apcata.2006.10.017>.
- [69] T. Maqsood, J. Dai, Y. Zhang, M. Guang, B. Li, *Pyrolysis of plastic species: A review of resources and products*, *Journal of Analytical and Applied Pyrolysis* 159 (2021) 105295. <https://doi.org/10.1016/j.jaap.2021.105295>.
- [70] M. Blazsó, *Polyaromatization in common synthetic polymers at elevated temperatures*, *Journal of Analytical and Applied Pyrolysis* 25 (1993) 25–35. [https://doi.org/10.1016/0165-2370\(93\)80030-4](https://doi.org/10.1016/0165-2370(93)80030-4).
-

- [71] F.P. La Mantia, M. Morreale, L. Botta, M.C. Mistretta, M. Ceraulo, R. Scaffaro, *Degradation of polymer blends: A brief review*, *Polymer Degradation and Stability* 145 (2017) 79–92. <https://doi.org/10.1016/j.polymdegradstab.2017.07.011>.
- [72] R. Tuffi, S. D'Abramo, L.M. Cafiero, E. Trinca, S. Vecchio Cipriotti, *Thermal behavior and pyrolytic degradation kinetics of polymeric mixtures from waste packaging plastics*, *Express Polymer Letters* 12 (2018) 82–99. <https://doi.org/10.3144/expresspolymlett.2018.7>.
- [73] P. Costa, F. Pinto, A.M. Ramos, I. Gulyurtlu, I. Cabrita, M.S. Bernardo, *Study of the Pyrolysis Kinetics of a Mixture of Polyethylene, Polypropylene, and Polystyrene*, *Energy & Fuels* 24 (2010) 6239–6247. <https://doi.org/10.1021/ef101010n>.
- [74] T. Faravelli, G. Bozzano, M. Colombo, E. Ranzi, M. Dente, *Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures*, *Journal of Analytical and Applied Pyrolysis* 70 (2003) 761–777. [https://doi.org/10.1016/S0165-2370\(03\)00058-5](https://doi.org/10.1016/S0165-2370(03)00058-5).
- [75] J. Wu, T. Chen, X. Luo, D. Han, Z. Wang, J. Wu, *TG/FTIR analysis on co-pyrolysis behavior of PE, PVC and PS*, *Waste Management* 34 (2014) 676–682. <https://doi.org/10.1016/j.wasman.2013.12.005>.
- [76] H.C. Genuino, M. Pilar Ruiz, H.J. Heeres, S.R.A. Kersten, *Pyrolysis of mixed plastic waste: Predicting the product yields*, *Waste Management* 156 (2023) 208–215. <https://doi.org/10.1016/j.wasman.2022.11.040>.
- [77] A.C.K. Chowlu, P.K. Reddy, A.K. Ghoshal, *Pyrolytic decomposition and model-free kinetics analysis of mixture of polypropylene (PP) and low-density polyethylene (LDPE)*, *Thermochimica Acta* 485 (2009) 20–25. <https://doi.org/10.1016/j.tca.2008.12.004>.
- [78] S. Klaimy, J.F. Lamonier, M. Casetta, S. Heymans, S. Duquesne, *Recycling of plastic waste using flash pyrolysis – Effect of mixture composition*, *Polymer Degradation and Stability* 187 (2021) 109540. <https://doi.org/10.1016/j.polymdegradstab.2021.109540>.
- [79] X. Jing, Y. Zhao, H. Wen, Z. Xu, *Interactions between Low-Density Polyethylene (LDPE) and Polypropylene (PP) during the Mild Cracking of Polyolefin Mixtures in a Closed-Batch Reactor*, *Energy & Fuels* 27 (2013) 5841–5851. <https://doi.org/10.1021/ef401376m>.
- [80] G. Martínez-Narro, N.J. Royston, K.L. Billsborough, A.N. Phan, *Kinetic modelling of mixed plastic waste pyrolysis*, *Chemical Thermodynamics and Thermal Analysis* 9 (2023) 100105. <https://doi.org/10.1016/j.ctta.2023.100105>.
- [81] U. Hujuri, A.K. Ghoshal, S. Gumma, *Modeling pyrolysis kinetics of plastic mixtures*, *Polymer Degradation and Stability* 93 (2008) 1832–1837. <https://doi.org/10.1016/j.polymdegradstab.2008.07.006>.
- [82] P.T. Williams and E.A. Williams, *Interaction of Plastics in Mixed-Plastics Pyrolysis*, *Energy and Fuels* 13 (1999) 188–196. <https://doi.org/10.1021/ef980163x>.
- [83] R. Miranda, H. Pakdel, C. Roy, C. Vasile, *Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis*, *Polymer Degradation and Stability* 73 (2001) 47–67. [https://doi.org/10.1016/S0141-3910\(01\)00066-0](https://doi.org/10.1016/S0141-3910(01)00066-0).
- [84] M. Brebu, T. Bhaskar, K. Murai, A. Muto, Y. Sakata, M. Uddin, *The effect of PVC and/or PET on thermal degradation of polymer mixtures containing brominated ABS*, *Fuel* 83 (2004) 2021–2028. <https://doi.org/10.1016/j.fuel.2004.04.011>.

-
- [85] R. Cao, M.-Q. Zhang, Y. Jiao, Y. Li, B. Sun, D. Xiao, M. Wang, D. Ma, *Co-upcycling of polyvinyl chloride and polyesters*, *Nature Sustainability* 6 (2023) 1685–1692. <https://doi.org/10.1038/s41893-023-01234-1>.
- [86] O. Dogu, M. Pelucchi, R. van de Vijver, P.H. van Steenberge, D.R. D'hooge, A. Cuoci, M. Mehl, A. Frassoldati, T. Faravelli, K. van Geem, *The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions*, *Progress in Energy and Combustion Science* 84 (2021) 100901. <https://doi.org/10.1016/j.pecs.2020.100901>.
- [87] V. Marturano, P. Cerruti, V. Ambrogio, *Polymer additives*, *Physical Sciences Reviews* 2 (2017). <https://doi.org/10.1515/psr-2016-0130>.
- [88] L. Zhang, N. Zhou, L. Ke, Y. Zeng, Q. Wu, J. Zhang, R. Liao, L. Fan, K. Cobb, R. Ruan, Y. Liu, Y. Wang, *Understanding the role of plastic additives in the pyrolysis of plastic wastes: Impact of additives on product selectivity, kinetics, and mechanistic pathways*, *Chemical Engineering Journal* 514 (2025) 163194. <https://doi.org/10.1016/j.cej.2025.163194>.
- [89] H. Radhakrishnan, A.A.B.A. Mohammed, I. Coffman, X. Bai, *Influence of functional additives, fillers, and pigments on thermal and catalytic pyrolysis of polyethylene for waste plastic upcycling*, *Green Chemistry* 27 (2025) 5861–5882. <https://doi.org/10.1039/D5GC00688K>.
- [90] M.A. Charitopoulou, L. Papadopoulou, D.S. Achilias, *Effect of brominated flame retardant on the pyrolysis products of polymers originating in WEEE*, *Environmental Science and Pollution Research International* 29 (2022) 29570–29582. <https://doi.org/10.1007/s11356-021-15489-8>.
- [91] C. Ma, J. Yu, B. Wang, Z. Song, J. Xiang, S. Hu, S. Su, L. Sun, *Chemical recycling of brominated flame retarded plastics from e-waste for clean fuels production: A review*, *Renewable and Sustainable Energy Reviews* 61 (2016) 433–450. <https://doi.org/10.1016/j.rser.2016.04.020>.
- [92] B. Scharrel, *Phosphorus-based Flame Retardancy Mechanisms-Old Hat or a Starting Point for Future Development?*, *Materials* 3 (2010) 4710–4745. <https://doi.org/10.3390/ma3104710>.
- [93] Q. Wang, W. Wu, Y. Tang, J. Bian, S. Zhu, *Thermal Degradation Kinetics of Plasticized Poly (Vinyl Chloride) with Six Different Plasticizers*, *Journal of Macromolecular Science Part B* 56 (2017) 420–434. <https://doi.org/10.1080/00222348.2017.1316659>.
- [94] A. Jiménez, L. Torre, J. Kenny, *Thermal degradation of poly(vinyl chloride) plastisols based on low-migration polymeric plasticizers*, *Polymer Degradation and Stability* 73 (2001) 447–453. [https://doi.org/10.1016/S0141-3910\(01\)00128-8](https://doi.org/10.1016/S0141-3910(01)00128-8).
- [95] M. van de Velden, J. Baeyens, A. Brems, B. Janssens, R. Dewil, *Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction*, *Renewable Energy* 35 (2010) 232–242. <https://doi.org/10.1016/j.renene.2009.04.019>.
- [96] N. Zhao, S.S. Low, C.L. Law, T. Wu, C.H. Pang, *Co-pyrolysis of polymers: Recent advances, challenges and perspectives*, *Fuel Processing Technology* 274 (2025) 108239. <https://doi.org/10.1016/j.fuproc.2025.108239>.
- [97] L. Sørum, M. Grønli, J. Hustad, *Pyrolysis characteristics and kinetics of municipal solid wastes*, *Fuel* 80 (2001) 1217–1227. [https://doi.org/10.1016/S0016-2361\(00\)00218-0](https://doi.org/10.1016/S0016-2361(00)00218-0).
-

- [98] X. Zhang, H. Lei, S. Chen, J. Wu, *Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review*, *Green Chemistry* 18 (2016) 4145–4169. <https://doi.org/10.1039/C6GC00911E>.
- [99] M.H. Rahman, P.R. Bhoi, P.L. Menezes, *Pyrolysis of waste plastics into fuels and chemicals: A review*, *Renewable and Sustainable Energy Reviews* 188 (2023) 113799. <https://doi.org/10.1016/j.rser.2023.113799>.
- [100] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, *Pyrolysis of municipal plastic wastes: Influence of raw material composition*, *Waste Management* 30 (2010) 620–627. <https://doi.org/10.1016/j.wasman.2009.10.014>.
- [101] M.S. Abbas-Abadi, Y. Ureel, A. Eschenbacher, F.H. Vermeire, R.J. Varghese, J. Oenema, G.D. Stefanidis, K. van Geem, *Challenges and opportunities of light olefin production via thermal and catalytic pyrolysis of end-of-life polyolefins: Towards full recyclability*, *Progress in Energy and Combustion Science* 96 (2023) 101046. <https://doi.org/10.1016/j.pecs.2022.101046>.
- [102] M.J.B. Kabeyi, O.A. Olanrewaju, *Review and Design Overview of Plastic Waste-to-Pyrolysis Oil Conversion with Implications on the Energy Transition*, *Journal of Energy* 2023 (2023) 1–25. <https://doi.org/10.1155/2023/1821129>.
- [103] F. Zhang, S. Tavakkol, F.C.C. Galeazzo, D. Stapf, *Particle-resolved simulation of the pyrolysis process of a single plastic particle*, *Heat and Mass Transfer* 61 (2025). <https://doi.org/10.1007/s00231-024-03524-6>.
- [104] D. Chen, L. Yin, H. Wang, P. He, *Pyrolysis technologies for municipal solid waste: a review*, *Waste Management* 34 (2014) 2466–2486. <https://doi.org/10.1016/j.wasman.2014.08.004>.
- [105] M. Laghezza, S. Fiore, F. Berruti, *A review on the pyrolytic conversion of plastic waste into fuels and chemicals*, *Journal of Analytical and Applied Pyrolysis* 179 (2024) 106479. <https://doi.org/10.1016/j.jaap.2024.106479>.
- [106] H.S. Fogler (Ed.), *Elements of Chemical Reaction Engineering*, 5th ed., Pearson Education, Boston, 2016.
- [107] E. Giglio, A. Marino, P. Pizarro, J.M. Escola, M. Migliori, G. Giordano, D.P. Serrano, *Critical issues for the deployment of plastic waste pyrolysis*, *Catalysis Science & Technology* 13 (2023) 5799–5820. <https://doi.org/10.1039/d3cy00445g>.
- [108] M.P. Ruiz, D.M. Zairin, S.R. Kersten, *On the intrinsic reaction rate of polyethylene pyrolysis and its interplay with mass transfer*, *Chemical Engineering Journal* 469 (2023) 143886. <https://doi.org/10.1016/j.cej.2023.143886>.
- [109] J.M. Encinar and J.F. González, *Pyrolysis of synthetic polymers and plastic wastes. Kinetic study*, *Fuel Processing Technology* 89 (2008) 678–686. <https://doi.org/10.1016/j.fuproc.2007.12.011>.
- [110] J.M. Riesco-Avila, J.R. Vera-Rozo, D.A. Rodríguez-Valderrama, D.M. Pardo-Cely, B. Ramón-Valencia, *Effects of Heating Rate and Temperature on the Yield of Thermal Pyrolysis of a Random Waste Plastic Mixture*, *Sustainability* 14 (2022) 9026. <https://doi.org/10.3390/su14159026>.
- [111] F. Xu, B. Wang, D. Yang, J. Hao, Y. Qiao, Y. Tian, *Thermal degradation of typical plastics under high heating rate conditions by TG-FTIR: Pyrolysis behaviors and kinetic analysis*, *Energy Conversion and Management* 171 (2018) 1106–1115. <https://doi.org/10.1016/j.enconman.2018.06.047>.

-
- [112] K.-B. Park, M.-J. Choi, D.-Y. Chae, J. Jung, J.-S. Kim, *Separate two-step and continuous two-stage pyrolysis of a waste plastic mixture to produce a chlorine-depleted oil*, *Energy* 244 (2022) 122583. <https://doi.org/10.1016/j.energy.2021.122583>.
- [113] H. Bockhorn, A. Hornung, U. Hornung, P. Jakobströer, M. Kraus, *Dehydrochlorination of plastic mixtures*, *Journal of Analytical and Applied Pyrolysis* 49 (1999) 97–106. [https://doi.org/10.1016/S0165-2370\(98\)00124-7](https://doi.org/10.1016/S0165-2370(98)00124-7).
- [114] H. Bockhorn, A. Hornung, U. Hornung, *Stepwise pyrolysis for recycling of plastic mixtures*, *Macromolecular Symposium* 135 (1998) 35–41. <https://doi.org/10.1002/masy.19981350107>.
- [115] M. Fukushima, B. Wu, H. Ibe, K. Wakai, E. Sugiyama, H. Abe, K. Kitagawa, S. Tsuruga, K. Shimura, E. Ono, *Study on dechlorination technology for municipal waste plastics containing polyvinyl chloride and polyethylene terephthalate*, *Journal of Material Cycles and Waste Management* 12 (2010) 108–122. <https://doi.org/10.1007/s10163-010-0279-8>.
- [116] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, *Dechlorination of fuels in pyrolysis of PVC containing plastic wastes*, *Fuel Processing Technology* 92 (2011) 253–260. <https://doi.org/10.1016/j.fuproc.2010.05.008>.
- [117] N. Sophonrat, L. Sandström, I.N. Zaini, W. Yang, *Stepwise pyrolysis of mixed plastics and paper for separation of oxygenated and hydrocarbon condensates*, *Applied Energy* 229 (2018) 314–325. <https://doi.org/10.1016/j.apenergy.2018.08.006>.
- [118] T. Chang, C. Li, F. Fan, H. Wu, C. Wang, F. Yin, *Effects of temperature zones on pyrolysis products of mixed plastic waste*, *Journal of Material Cycles and Waste Management* 25 (2023) 430–440. <https://doi.org/10.1007/s10163-022-01549-9>.
- [119] G.-G. Choi, S.-J. Oh, J.-S. Kim, *Non-catalytic pyrolysis of scrap tires using a newly developed two-stage pyrolyzer for the production of a pyrolysis oil with a low sulfur content*, *Applied Energy* 170 (2016) 140–147. <https://doi.org/10.1016/j.apenergy.2016.02.119>.
- [120] M. Zeller, N. Netsch, F. Richter, H. Leibold, D. Stapf, *Chemical Recycling of Mixed Plastic Wastes by Pyrolysis – Pilot Scale Investigations*, *Chemie Ingenieur Technik* 93 (2021) 1763–1770. <https://doi.org/10.1002/cite.202100102>.
- [121] D. Sorino, P. de Vizia, M. Baldelli, L. Bartolucci, S. Cordiner, A. Falsetti, F. Lombardi, V. Mulone, *Pyrolysis of mixed contaminated plastic wastes: Assessing the influence of polymers composition, temperature and residence time*, *Waste Management* 201 (2025) 114793. <https://doi.org/10.1016/j.wasman.2025.114793>.
- [122] J.A. Onwudili, N. Insura, P.T. Williams, *Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time*, *Journal of Analytical and Applied Pyrolysis* 86 (2009) 293–303. <https://doi.org/10.1016/j.jaap.2009.07.008>.
- [123] M.S. Abbas-Abadi, M. Kusenbergh, A. Zayoud, M. Roosen, F. Vermeire, S. Madanikashani, M. Kuzmanović, B. Parvizi, U. Kresovic, S. de Meester, K. van Geem, *Thermal pyrolysis of waste versus virgin polyolefin feedstocks: The role of pressure, temperature and waste composition*, *Waste Management* 165 (2023) 108–118. <https://doi.org/10.1016/j.wasman.2023.04.029>.
-

- [124] M.S. Abbas-Abadi, M. Nekoomanesh Haghighi, H. Yeganeh, B. Bozorgi, *The effect of melt flow index, melt flow rate, and particle size on the thermal degradation of commercial high density polyethylene powder*, Journal of Thermal Analysis and Calorimetry 114 (2013) 1333–1339. <https://doi.org/10.1007/s10973-013-3133-0>.
- [125] A. Somoza-Tornos, A. Gonzalez-Garay, C. Pozo, M. Graells, A. Espuña, G. Guillén-Gosálbez, *Realizing the Potential High Benefits of Circular Economy in the Chemical Industry: Ethylene Monomer Recovery via Polyethylene Pyrolysis*, ACS Sustainable Chemistry & Engineering 8 (2020) 3561–3572. <https://doi.org/10.1021/acssuschemeng.9b04835>.
- [126] R. Volk, C. Stallkamp, J.J. Steins, S.P. Yogish, R.C. Müller, D. Stapf, F. Schultmann, *Techno-economic assessment and comparison of different plastic recycling pathways: A German case study*, Journal of Industrial Ecology 25 (2021) 1318–1337. <https://doi.org/10.1111/jiec.13145>.
- [127] F. Keller, R.L. Voss, R.P. Lee, B. Meyer, *Life cycle assessment of global warming potential of feedstock recycling technologies: Case study of waste gasification and pyrolysis in an integrated inventory model for waste treatment and chemical production in Germany*, Resources, Conservation and Recycling 179 (2022) 106106. <https://doi.org/10.1016/j.resconrec.2021.106106>.
- [128] M. Bachmann, C. Zibunas, J. Hartmann, V. Tulus, S. Suh, G. Guillén-Gosálbez, A. Bardow, *Towards circular plastics within planetary boundaries*, Nature Sustainability 6 (2023) 599–610. <https://doi.org/10.1038/s41893-022-01054-9>.
- [129] U.R. Gracida-Alvarez, P.T. Benavides, U. Lee, M. Wang, *Life-cycle analysis of recycling of post-use plastic to plastic via pyrolysis*, Journal of Cleaner Production 425 (2023) 138867. <https://doi.org/10.1016/j.jclepro.2023.138867>.
- [130] C. Stallkamp, M. Hennig, R. Volk, F. Richter, B. Bergfeldt, S. Tavakkol, F. Schultmann, D. Stapf, *Economic and environmental assessment of automotive plastic waste end-of-life options: Energy recovery versus chemical recycling*, Journal of Industrial Ecology 27 (2023) 1319–1334. <https://doi.org/10.1111/jiec.13416>.
- [131] M. Klotz, C. Oberschelp, C. Salah, L. Subal, S. Hellweg, *The role of chemical and solvent-based recycling within a sustainable circular economy for plastics*, Science of The Total Environment 906 (2024) 167586. <https://doi.org/10.1016/j.scitotenv.2023.167586>.
- [132] M. Solis and S. Silveira, *Technologies for chemical recycling of household plastics - A technical review and TRL assessment*, Waste Management 105 (2020) 128–138. <https://doi.org/10.1016/j.wasman.2020.01.038>.
- [133] C. Stallkamp, M. Hennig, R. Volk, D. Stapf, F. Schultmann, *Pyrolysis of mixed engineering plastics: Economic challenges for automotive plastic waste*, Waste Management 176 (2024) 105–116. <https://doi.org/10.1016/j.wasman.2024.01.035>.
- [134] M. Kusenberg, A. Eschenbacher, L. Delva, S. de Meester, E. Delikonstantis, G.D. Stefanidis, K. Ragaert, K. van Geem, *Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: The past, present and future*, Fuel Processing Technology 238 (2022) 107474. <https://doi.org/10.1016/j.fuproc.2022.107474>.
- [135] U. Arena, F. Parrillo, F. Ardolino, *An LCA answer to the mixed plastics waste dilemma: Energy recovery or chemical recycling?*, Waste Management 171 (2023) 662–675. <https://doi.org/10.1016/j.wasman.2023.10.011>.

- [136] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, *Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review*, Renewable and Sustainable Energy Reviews 73 (2017) 346–368. <https://doi.org/10.1016/j.rser.2017.01.142>.
- [137] M. Holtkamp, M. Renner, K. Matthiesen, M. Wald, G.A. Luinstra, P. Biessey, *Robust downstream technologies in polystyrene waste pyrolysis: Design and prospective life-cycle assessment of pyrolysis oil reintegration pathways*, Resources, Conservation and Recycling 205 (2024) 107558. <https://doi.org/10.1016/j.resconrec.2024.107558>.
- [138] N. Niessner, B. Wilhelmus, M. Verswyvel, T. Kolb, A. Schedl, H.-W. Schmidt, P. Schäfer, L. Hollerbach, K. Raulf, *Chemical Recycling of Polystyrene: From Post-Consumer Polystyrene Waste to High-Quality Polystyrene Products (Case Study)*, in: J. Mortier (Ed.), Industrial Arene Chemistry, Wiley, 2023, pp. 2163–2183.
- [139] N. Netsch, J. Vogt, F. Richter, G. Straczewski, G. Mannebach, V. Fraaije, S. Tavakkol, S. Mihan, D. Stapf, *Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis*, Chemie Ingenieur Technik 95 (2023) 1305–1313. <https://doi.org/10.1002/cite.202300078>.
- [140] P. Neuner, D. Graf, N. Netsch, M. Zeller, T.-C. Herrmann, D. Stapf, R. Rauch, *Chemical Conversion of Fischer–Tropsch Waxes and Plastic Waste Pyrolysis Condensate to Lubricating Oil and Potential Steam Cracker Feedstocks*, Reactions 3 (2022) 352–373. <https://doi.org/10.3390/reactions3030026>.
- [141] R. Palos, A. Gutiérrez, F.J. Vela, J.A. Maña, I. Hita, A. Asueta, S. Arnaiz, J.M. Arandes, J. Bilbao, *Assessing the potential of the recycled plastic slow pyrolysis for the production of streams attractive for refineries*, Journal of Analytical and Applied Pyrolysis 142 (2019) 104668. <https://doi.org/10.1016/j.jaap.2019.104668>.
- [142] E. Rodríguez, A. Gutiérrez, R. Palos, F.J. Vela, J.M. Arandes, J. Bilbao, *Fuel production by cracking of polyolefins pyrolysis waxes under fluid catalytic cracking (FCC) operating conditions*, Waste Management 93 (2019) 162–172. <https://doi.org/10.1016/j.wasman.2019.05.005>.
- [143] F. Knaus, H. Lutz, M. Büchele, A. Reichhold, A. Pazos-Costa, *Municipal plastic waste recycling in fluid catalytic cracking units: Production of petrochemicals and fuel in a fluid catalytic cracking pilot plant from biogenic and recycled feedstocks*, Chemical Engineering and Processing - Process Intensification 182 (2022) 109204. <https://doi.org/10.1016/j.cep.2022.109204>.
- [144] F. Weiland, M.S. Qureshi, J. Wennebro, C. Lindfors, T. Ohra-aho, H. Shafaghat, A.-C. Johansson, *Entrained Flow Gasification of Polypropylene Pyrolysis Oil*, Molecules 26 (2021) 7317. <https://doi.org/10.3390/molecules26237317>.
- [145] T.H. An, C.Y. Lee, U.M. Chung, T.W. Lee, M.J. Lee, S.M. Yoon, H.W. Ra, M.W. Seo, *Entrained-flow gasification characteristics of plastic waste pyrolysis oil*, Journal of Environmental Chemical Engineering 12 (2024) 114818. <https://doi.org/10.1016/j.jece.2024.114818>.
- [146] M. Hennig, T.M. Dreising, A. Reeves, T. Oehlcke, S. Tavakkol, R. Volk, F. Schultmann, D. Stapf, *Entrained-Flow Gasification for the Utilization of Pyrolysis Oil from Mixed Plastic Waste*, ACS Sustainable Chemistry and Engineering 13 (2025) 20638–20648. <https://doi.org/10.1021/acssuschemeng.5c03932>.

- [147] M. Kusenbergh, G.C. Fausson, H.D. Thi, M. Roosen, M. Grilc, A. Eschenbacher, S. de Meester, K. van Geem, *Maximizing olefin production via steam cracking of distilled pyrolysis oils from difficult-to-recycle municipal plastic waste and marine litter*, Science of The Total Environment 838 (2022) 156092. <https://doi.org/10.1016/j.scitotenv.2022.156092>.
- [148] M. Kusenbergh, S. de Langhe, B. Parvizi, A.J. Abdulrahman, R.J. Varghese, S.U. Aravindakshan, A. Kurkijärvi, A.M. Gandarillas, J. Jamieson, S. de Meester, K. van Geem, *Characterization and impact of oxygenates in post-consumer plastic waste-derived pyrolysis oils on steam cracking process efficiency*, Journal of Analytical and Applied Pyrolysis 181 (2024) 106571. <https://doi.org/10.1016/j.jaap.2024.106571>.
- [149] M. Kusenbergh, M. Roosen, A. Doktor, L. Casado, A. Jamil Abdulrahman, B. Parvizi, A. Eschenbacher, E. Biadi, N. Laudou, D. Jänsch, S. de Meester, K. van Geem, *Contaminant removal from plastic waste pyrolysis oil via depth filtration and the impact on chemical recycling: A simple solution with significant impact*, Chemical Engineering Journal 473 (2023) 145259. <https://doi.org/10.1016/j.cej.2023.145259>.
- [150] M. Kusenbergh, M. Roosen, A. Zayoud, M.R. Djokic, H. Dao Thi, S. de Meester, K. Ragaert, U. Kresovic, K. van Geem, *Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation*, Waste Management 141 (2022) 104–114. <https://doi.org/10.1016/j.wasman.2022.01.033>.
- [151] C.S. Hsu, P.R. Robinson, *Springer Handbook of Petroleum Technology*, Springer International Publishing, Cham, 2017.
- [152] A. Meiswinkel, H. Schmaderer, C. Delhomme-Neudecker, N. Schödel, A. Tota, G. Schmidt, *Plastic pyrolysis oils as feedstock for steam crackers: Opportunities and challenges*, in: DGMK Tagungsbericht K³/C³ - Kunststoff-Zirkularität durch chemisches Recycling, (2024) 31–39. Available online: https://dgmk.de/app/uploads/2024/09/DGMK_2024-02-.pdf (accessed 15 May 2026).
- [153] W. Zeb, M. Roosen, P. Knockaert, S. Janssens, D. Withoeck, M. Kusenbergh, J. Hogie, P. Billen, S. Tavernier, K. van Geem, S. de Meester, *Purification and characterisation of post-consumer plastic pyrolysis oil fractionated by vacuum distillation*, Journal of Cleaner Production 416 (2023) 137881. <https://doi.org/10.1016/j.jclepro.2023.137881>.
- [154] W. Zeb, T. de Somer, M. Roosen, P. Knockaert, M.S. Abbas-Abadi, U. Kresovic, J. Hogie, K. van Geem, S. de Meester, *Fractional distillation of waste plastic pyrolysis oil for isolating narrow hydrocarbons cuts*, Fuel 379 (2025) 133055. <https://doi.org/10.1016/j.fuel.2024.133055>.
- [155] H. Thunman, T. Berdugo Vilches, M. Seemann, J. Maric, I.C. Vela, S. Pissot, H.N. Nguyen, *Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery*, Sustainable Materials and Technologies 22 (2019) e00124. <https://doi.org/10.1016/j.susmat.2019.e00124>.
- [156] L. Saeed, A. Tohka, M. Haapala, R. Zevenhoven, *Slow pyrolysis of different PVC types in a bubbling fluidized bed: stabilizer effects*, Journal of Analytical and Applied Pyrolysis 72 (2004) 63–74. <https://doi.org/10.1016/j.jaap.2004.03.002>.

-
- [157] European Commission, *Establishing the identification system for packaging materials pursuant to European Parliament and Council Directive 94/62/EC on packaging and packaging waste*, Brussels (1997).
- [158] J.-J. Zhang, N. Ren, J.-H. Bai, *Non-isothermal Decomposition Reaction Kinetics of the Magnesium Oxalate Dihydrate*, Chinese Journal of Chemistry 24 (2006) 360–364. <https://doi.org/10.1002/cjoc.200690069>.
- [159] B. Wunderlich, *Thermal Analysis of Polymeric Materials*, 1st ed., Springer-Verlag, Berlin and Heidelberg (2005).
- [160] Deutsches Institut für Normung e.V., *Differential scanning calorimetry (DSC) - Part 3: Determination of temperature and enthalpy of melting and crystallization*, Berlin (2018).
- [161] Deutsches Institut für Normung e.V., *Thermal analysis (TA) - Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) - General principles*, Berlin (2019).
- [162] Deutsches Institut für Normung e.V., *Differential scanning calorimetry (DSC) - Part 2: Determination of glass transition temperature and step height*, Berlin (2014).
- [163] Deutsches Institut für Normung e.V., *Thermal analysis (TA) - Thermogravimetry (TG) - Principles*, Berlin (2005).
- [164] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, *ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*, Thermochimica Acta 520 (2011) 1–19. <https://doi.org/10.1016/j.tca.2011.03.034>.
- [165] N. Netsch, M. Simons, A. Feil, H. Leibold, F. Richter, J. Slama, S.P. Yogish, K. Greiff, D. Stapf, *Recycling of polystyrene-based external thermal insulation composite systems - Application of combined mechanical and chemical recycling*, Waste Management 150 (2022) 141–150. <https://doi.org/10.1016/j.wasman.2022.07.001>.
- [166] J. Vogt, A.D. Renno, M. Fuchs, T. Kurtz, N. Netsch, F. Richter, G. Straczewski, B. Bergfeldt, Y.C. Madriz-Diaz, A.d.L. Ribeiro, D. Ebert, S. Tavakkol, S. Raatz, D. Stapf, *Chemical recycling of refrigerator plastic waste by pyrolysis: Yields, product composition, and potential applications*, Fuel 400 (2025) 135776. <https://doi.org/10.1016/j.fuel.2025.135776>.
- [167] Deutsches Institut für Normung e.V., *Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen*, Berlin (2015).
- [168] Deutsches Institut für Normung e.V., *Petroleum Products - Determination of water content using titration according to Karl Fischer*, Berlin (2020).
- [169] Deutsches Institut für Normung e.V., *Testing of solid and liquid fuels - Determination of gross calorific value by the bomb calorimeter and calculation of net calorific value*, Berlin (2020).
- [170] ASTM International, *Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography*, West Conshohocken, PA, (2020).
- [171] M. Zeller, S. Tavakkol, D. Stapf, *Experimental and Analytical Tools for the Chemical Recycling of Engineering Plastics - A Multi-Scale Pyrolysis Study on Polydicyclopentadiene*, Macromolecular Rapid Communications 46 (2025) e2500161. <https://doi.org/10.1002/marc.202500161>.
-

- [172] L. Cafiero, D. Fabbri, E. Trinca, R. Tuffi, S. Vecchio Cipriotti, *Thermal and spectroscopic (TG/DSC–FTIR) characterization of mixed plastics for materials and energy recovery under pyrolytic conditions*, Journal of Thermal Analysis and Calorimetry 121 (2015) 1111–1119. <https://doi.org/10.1007/s10973-015-4799-2>.
- [173] M. Zeller, K. Garbev, L. Weigel, T. Saatzer, D. Merz, S. Tavakkol, D. Stapf, *Thermogravimetric studies, kinetic modeling and product analysis of the pyrolysis of model polymers for technical polyurethane applications*, Journal of Analytical and Applied Pyrolysis 171 (2023) 105976. <https://doi.org/10.1016/j.jaap.2023.105976>.
- [174] G. Jomaa, P. Goblet, C. Coquelet, V. Morlot, *Kinetic modeling of polyurethane pyrolysis using non-isothermal thermogravimetric analysis*, Thermochemica Acta 612 (2015) 10–18. <https://doi.org/10.1016/j.tca.2015.05.009>.
- [175] N. Netsch, L. Schröder, D. Merz, B. Zimmerlin, S. Tavakkol, D. Stapf, *Chemical Recycling of Thermoplastic Mixtures: Superposition Modeling and Experimental Validation*, 10th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng 2024), Sendai (2024). <https://doi.org/10.5445/IR/1000173749>.
- [176] L. dos S. Vargette, H. Mohamadzadeh Shirazi, O. Mynko, M. Kusenbergh, J. Jamieson, A.E. Muñoz Gandarillas, S. Ukkandath Aravindakshan, M.-F. Reyniers, K. van Geem, *Comprehensive Fouling Assessment in Steam Crackers: Fossil versus Renewable NEXBTL Naphtha*, Industrial & Engineering Chemistry Research 63 (2024) 111–120. <https://doi.org/10.1021/acs.iecr.3c02969>.
- [177] M. Espinosa-Peña, Y. Figueroa-Gómez, F. Jiménez-Cruz, *Simulated Distillation Yield Curves in Heavy Crude Oils: A Comparison of Precision between ASTM D-5307 and ASTM D-2892 Physical Distillation*, Energy & Fuels 18 (2004) 1832–1840. <https://doi.org/10.1021/ef049919k>.

Publications included in this Thesis

Publication 1:

Netsch, Niklas; Zeller, Michael; Richter, Frank; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2024): Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Prediction and Pilot-Scale Validation. ACS Sustainable Resource Management, 1 (7), 1485-1492. DOI: 10.1021/acssusresmgmt.4c00109

Publication 2:

Netsch, Niklas; Schröder, Lukas; Zeller, Michael; Neugber, Iuliiia; Merz, Daniela; Klein, Christopher; Tavakkol, Salar; Stapf, Dieter (2025): Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics. Journal of Thermal Analysis and Calorimetry, 150, 211-229. DOI: 10.1007/s10973-024-13630-6

Publication 3:

Netsch, Niklas; Weigel, Luca; Schmedding, Tim; Zeller, Michael; Bergfeldt, Britta; Straczewski, Grazyna; Tavakkol, Salar; Stapf, Dieter (2025): Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography. Fuel Processing Technology, 280, 108359. DOI: 10.1016/j.fuproc.2025.108359

Publication 4:

Netsch, Niklas; Tauber, Aljoscha; Keskin, Orhan; Bergfeldt, Britta; Wehner, Harald; Eidam, Dirk; Tavakkol, Salar; Stapf, Dieter (2026): Chemical recycling of mixed thermoplastics via pyrolysis: A comparative study of feedstock influence and reactor impact. Journal for Analytical and Applied Pyrolysis, 194, 107575. DOI: 10.1016/j.jaap.2025.107575

Publication 5:

Netsch, Niklas; Tauber, Aljoscha; Merz, Daniela; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2026): Optimizing product yield and composition in chemical recycling of mixed plastics by temperature-staged pyrolysis. Chemical Engineering Science, 327, 123622. DOI: 10.1016/j.ces.2026.123622

Complete List of Publications

as of May 19, 2026

2026

Journal Articles

Alsharqawi, Razan; Merz, Daniela; Kurtz, Tim; Zeller, Michael; **Netsch, Niklas**; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2026): Impact of brominated flame retardants on the chemical recycling of polystyrene via pyrolysis. Chemical Engineering Journal, 177409. DOI: <https://doi.org/10.1016/j.cej.2026.177409>

Zhang, Feichi; Li, Muhao; Ma, Xiaoyue; **Netsch, Niklas**; Tavakkol, Salar; Zirwes, Thorsten; Zhang Rui; Stapf, Dieter (2026): Assessment of the interplay between convective heat transfer and reaction kinetics during plastic pyrolysis. Particuology, 113, 180-188. DOI: 10.1016/j.partic.2026.03.019

Netsch, Niklas; Tauber, Aljoscha; Merz, Daniela; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2026): Optimizing product yield and composition in chemical recycling of mixed plastics by temperature-staged pyrolysis. Chemical Engineering Science, 327, 123622. DOI: 10.1016/j.ces.2026.123622

Netsch, Niklas; Tauber, Aljoscha; Keskin, Orhan; Bergfeldt, Britta; Wehner, Harald; Eidam, Dirk; Tavakkol, Salar; Stapf, Dieter (2026): Chemical recycling of mixed thermoplastics via pyrolysis: A comparative study of feedstock influence and reactor impact. Journal for Analytical and Applied Pyrolysis, 194, 107575. DOI: 10.1016/j.jaap.2025.107575

2025

Journal Articles

Zeller, Michael; Wattenberg, Lea; Shrestha, Pratistha; Hannemann, Aylin; Ankh-Erdene Erdenepurev, **Netsch, Niklas**; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2025): Characteristics of Polyurethane Pyrolysis – Experimental Investigations and Product Analyses for the Assessment of Chemical Recycling Potentials. Journal of Applied Polymer Science, e70032, 1-15. DOI: 10.1002/app.70032

Netsch, Niklas; Weigel, Luca; Schmedding, Tim; Zeller, Michael; Bergfeldt, Britta; Straczewski, Grazyna; Tavakkol, Salar; Stapf, Dieter (2025): Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography. Fuel Processing Technology, 280, 108359. DOI: 10.1016/j.fuproc.2025.108359

Vogt, Jonas; Renno, Axel; Fuchs, Margret; Kurtz, Tim; **Netsch, Niklas**; Richter, Frank; Straczewski, Grazyna; Bergfeldt, Britta; Madriz-Diaz, Yuleika Carolina; De Lima Ribeiro, Andréa; Ebert, Doreen; Tavakkol, Salar; Raatz, Simone; Stapf, Dieter (2025): Chemical recycling of refrigerator plastic waste by pyrolysis: Yields, product composition, and potential applications. Fuel, 400, 135776. DOI: 10.1016/j.fuel.2025.135776

Netsch, Niklas; Schröder, Lukas; Zeller, Michael; Neugber, Iuliia; Merz, Daniela; Klein, Christopher; Tavakkol, Salar; Stapf, Dieter (2025): Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics. *Journal of Thermal Analysis and Calorimetry*, 150, 211-229. DOI: 10.1007/s10973-024-13630-6

Conference Contributions

Zeller, Michael; **Netsch, Niklas**; Merz, Daniela; Tavakkol, Salar; Stapf, Dieter: Pyrolytic interactions of polyurethanes with thermoplastics: implications for chemical recycling. 13th International Freiberg Conference on Circular Carbon Technologies, September 2025, Prague, Czech Republic. DOI: 10.5445/IR/1000186034

Alsharqawi, Razan; Bergfeldt, Britta; Merz, Daniela; Richter, Frank; Straczewski, Grazyna; **Netsch, Niklas**; Tavakkol, Salar; Stapf, Dieter: Chemical recycling of flame-retarded plastics: Reducing the bromine content in the pyrolysis oil using calcium-based sorbents. 20th European Meeting on Fire Retardant Polymeric Materials, June 2025, Madrid, Spain. DOI: 10.5445/IR/1000182466

Alsharqawi, Razan; Merz, Daniela; Zeller, Michael; **Netsch, Niklas**; Kurtz, Tim; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter: Closing the loop: pyrolysis of flame-retarded (E)PS. Annual Meeting of the DECHEMA-Divisions „Hochtemperaturverfahrenstechnik“, „Abfallbehandlung und Wertstoffrückgewinnung“, and „Rohstoffe“, March 2025, Dresden, Germany. DOI: 10.5445/IR/1000186249

2024

Journal Articles

Netsch, Niklas; Zeller, Michael; Richter, Frank; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter (2024): Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Predictions and Pilot-Scale Validation. *ACS Sustainable Resource Management*, 1 (7), 1485-1492. DOI: 10.1021/acssusresmgmt.4c00109

Conference Contributions

Netsch, Niklas; Tauber, Aljoscha; Keskin, Orhan; Merz, Daniela; Bergfeldt, Britta; Tavakkol, Salar; Stapf, Dieter: Influencing the product quality in chemical recycling of mixed thermoplastics by temperature-staged pyrolysis. DGMK/ÖGEW/SCI-Conference “Energy and Material Flows in Sustainable Petrochemistry – Opportunities and Implications”, November 2024, Hamburg, Germany. DOI: 10.5445/IR/1000176788

Netsch, Niklas; Schmedding, Tim; Pöplow, Alexander; Zeller, Michael; Bergfeldt, Britta; Straczewski, Grazyna; Tavakkol, Salar; Stapf, Dieter: Advanced analytical methods for characterization of condensable pyrolysis products from plastic waste. KNT-Symposium “Chemical Engineering for a Sustainable World”, October 2024, Karlsruhe, Germany. DOI: 10.5445/IR/1000175260

Netsch, Niklas; Schröder, Lukas; Merz, Daniela; Zimmerlin, Bernd; Tavakkol, Salar; Stapf, Dieter: Chemical recycling of thermoplastic mixtures: superposition modeling and experimental validation. 10th International Conference on Engineering for Waste and Biomass Valorisation, August 2024, Sendai, Japan. DOI: 10.5445/IR/1000173749

Hennig, Malte; Pillich, Martin; **Netsch, Niklas**; Tavakkol, Salar; Bardow, Andre; Stapf, Dieter: Integration of mixed plastic waste pyrolysis into the chemical value chain via steam cracking and gasification. 10th International Conference on Engineering for Waste and Biomass Valorisation, August 2024, Sendai, Japan. DOI: 10.5445/IR/1000177247

Umemoto, Satoshi; **Netsch, Niklas**; Schröder, Lukas; Zeller, Michael; Tavakkol, Salar; Miura, Kouichi; Stapf, Dieter: Modification and application of DRCM (distributed reaction rate constant model) to plastic pyrolysis kinetics. 10th International Conference on Engineering for Waste and Biomass Valorisation, August 2024, Sendai, Japan.

2023

Journal Articles

Netsch, Niklas; Vogt, Jonas; Richter, Frank; Straczewski, Grazyna; Mannebach, Gerd; Fraaije, Volker; Tavakkol, Salar; Mihan, Shahram; Stapf, Dieter (2023): Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis. *Chemie Ingenieur Technik*, 95 (8), 1305-1313. DOI: 10.1002/cite.202300078

Conference Contributions

Zhang, Feichi; Cao, Jun; Zirwes, Thorsten; **Netsch, Niklas**; Tavakkol, Salar; Zhang, Rui; Bockhorn, Henning; Stapf, Dieter: Numerical simulation of thermal decomposition of polyethylene with a single-particle model. 14th International Conference on Computational Heat and Mass Transfer, September 2023, Düsseldorf, Germany. DOI: 10.5445/IR/1000164122

Netsch, Niklas; Tavakkol, Salar; Stapf, Dieter: Evaluating the technical integration of catalytic pyrolysis for polyolefin-rich waste recycling into light olefins. 11th International Freiberg Conference on Circular Carbon Technologies, September 2023, Rotterdam, Netherlands. DOI: 10.5445/IR/1000164079

Zhang, Feichi; Tavakkol, Salar; Zirwes, Thorsten; **Netsch, Niklas**; Zeller, Michael; Vogt, Jonas; Stapf, Dieter: Fundamental research on pyrolysis of plastic wastes via numerical simulation. Helmholtz Energy Conference, June 2023, Koblenz, Germany. DOI: 10.5445/IR/1000159548

2022

Journal Articles

Netsch, Niklas; Simons, Martin; Feil, Alexander; Leibold, Hans; Richter, Frank; Slama, Julia; Yogish, Savina Padumane; Greiff, Kathrin; Stapf, Dieter (2022): Recycling of polystyrene-based external thermal insulation composite systems – Application of combined mechanical and chemical recycling. *Waste Management*, 150, 141-150. DOI: 10.1016/j.wasman.2022.07.001

Neuner, Philipp; Graf, David; **Netsch, Niklas**; Zeller, Michael; Herrmann, Tom-Carlo; Stapf, Dieter; Rauch, Reinhard (2022): Chemical Conversion of Fischer-Tropsch Waxes and Plastic Waste Pyrolysis Condensate to Lubricating Oil and Potential Steam Cracker Feedstocks. *Reactions*, 3 (3), 352-373. DOI: 10.3390/reactions3030026

Conference Contributions

Netsch, Niklas; Richter, Frank; Fraaije, Volker; Mannebach, Gerd; Mihan, Shahram, Stapf, Dieter: Katalytische Pyrolyse polyolefinreicher Kunststoffabfälle. Annual Meeting of the ProcessNet-Divisions „Hochtemperaturverfahrenstechnik“, „Abfallbehandlung und Werkstoffrückgewinnung“ and „Rohstoffe“, June 2023, Bamberg, Germany. DOI: 10.5445/IR/1000148331

2021**Journal articles**

Zeller, Michael; **Netsch, Niklas**; Richter, Frank; Leibold, Hans; Stapf, Dieter (2021): Chemical Recycling of Mixed Plastic Waste by Pyrolysis – Pilot Scale Investigations. Chemie Ingenieur Technik, 93 (11), 1763-1770. DOI: 10.1002/cite.202100102

Conference contributions

Zeller, Michael; Leibold, Hans; **Netsch, Niklas**; Richter, Frank; Stapf, Dieter: Chemisches Recycling kunststoffhaltiger Abfälle – Das Potenzial der Pyrolyse. 33th Berliner Abfallwirtschaft- und Energiekonferenz, June 2021, Berlin, Germany. DOI: 10.5445/IR/1000126848

2020**Research Reports**

Bergs, Laura; Dobers, Kerstin; Feil, Alexander; Fricke, Claas; Hülsmann, Thomas; Koller, Michaela; Kopka, Jan-Philip; Mohmeyer, Stefanie, **Netsch, Niklas**; Ritthoff, Michael; Sartorius, Ingo; Simons, Martin; Stapf, Dieter; Walter, Gotthard; Wendler, Katja (2020): Schlussbericht zum BMBF-Verbundvorhaben “KUBA – Nachhaltige Wertschöpfungskette: Pilotfall Kunststoffe in Bauwirtschaft und Gebäuden“, Funding reference number BMBF 033R214 A-F. DOI: 10.2314/KXP:1767176708

Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Prediction and Pilot-Scale Validation

Niklas Netsch,* Michael Zeller, Frank Richter, Britta Bergfeldt, Salar Tavakkol,* and Dieter Stapf

Cite This: *ACS Sustainable Resour. Manage.* 2024, 1, 1485–1492

Read Online

ACCESS |



Metrics & More



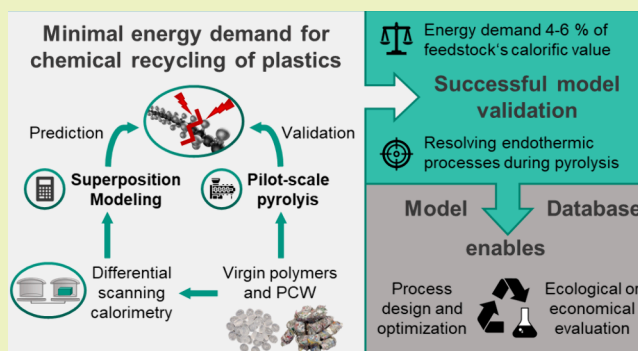
Article Recommendations



Supporting Information

ABSTRACT: Pyrolysis of plastic waste is a key technology for closing the anthropogenic carbon cycle. The energy demand (ED) of this endothermic process is a crucial factor to evaluate its benefits compared to established recycling pathways. The pyrolysis ED can be determined experimentally. However, this is elaborate and limited in transferability. Existing models cover virgin plastics or hydrocarbon thermoplastic mixtures on a laboratory scale. Here, a model for calculating the ED of thermoplastic mixtures based on the superposition of virgin polymer data is developed. The material data, such as heat capacity, phase transition enthalpy, and reaction enthalpy, are determined using differential scanning calorimetry. Pilot-scale experiments are performed in a 1 kg/h screw reactor. These experimental data are compared to model calculations. The feedstock-specific ED for pyrolysis is plastic-type independent. It amounts to approximately 4–6% of the feedstocks' net calorific value. The validation shows excellent accordance for virgin plastics and hydrocarbon plastics mixtures. The modeled ED of mixtures including heteroatoms is systematically underestimated, which indicates changes in the degradation mechanism. The model allows for resolving several phenomena contributing to the pyrolysis ED. The simple calculation of the ED with in-depth information on occurring phenomena enables more reliable process design, optimization, and evaluation.

KEYWORDS: plastic recycling, chemical recycling, pyrolysis, energy demand, thermal degradation, polymer decomposition, differential scanning calorimetry



INTRODUCTION

The transition from linear value chains to a circular carbon economy is a key element of climate neutrality.¹ Herein high-calorific waste plastics can substitute fossil feedstocks, e.g., naphtha, in chemical synthesis.² Different recycling technologies are considered to accomplish the recycling targets of industrialized nations.^{3–7} Complementary to mechanical recycling, various solvent-based and thermochemical processes are considered as chemical recycling options, often highlighting pyrolysis technologies as they recycle mixed plastic wastes to virgin polymers via the naphtha steam-cracking route.⁸

When the pyrolysis process is evaluated compared to existing waste treatment routes, the product yield and energy demand (ED) are crucial factors for cost estimations and assessments of potential environmental benefits of the endothermic pyrolytic process.⁹ Because the thermal decomposition mechanism of plastic waste highly depends on the feedstock composition, the ED must be obtained experimentally. Numerous studies have used differential scanning calorimetry (DSC) to determine the pyrolysis ED for various polymers on a laboratory scale.^{10–15} As shown in Table 1, the

energy needed for pyrolysis strongly depends on the polymer type and the evaluation methodology.

Most plastic waste considered for chemical recycling features a heterogeneous composition. This limits investigations on a laboratory scale, which is why elaborate measurements on a pilot-plant scale are required to obtain reliable data. Zeller et al. report an estimation for the ED of about 5% of the pyrolyzed feedstock's net calorific value, being in a range of 23–34 kJ/g.¹⁶ This ED is 2–5 times higher than the virgin polymer results for thermal decomposition shown in Table 1. This difference can be explained by the summation of the endothermic processes occurring during pyrolysis.¹⁶ However, such EDs representing a global value for the heating of solid plastics, followed by melting, heating of the plastic melt until

Received: March 19, 2024

Revised: June 27, 2024

Accepted: June 27, 2024

Published: July 16, 2024



Table 1. Pyrolysis Energy Demand of Different Polymer Types Differentiated According to Endothermic Processes via DSC

polymer type	physical or chemical phenomena	energy demand (J/g)	ref
PE	melting	75	12
		97	11
		218	15
	thermal decomposition	299	12
		365–575	10
		665	13
		920	15
		975	11
		1375	14
PP	melting	66	11
		80	15
	thermal decomposition	339–616	10
		632	13
		944	11
PS	thermal decomposition	1310	15
		690–732	10
		820	13
		855	11
ABS	thermal decomposition	1000	15
		647	11
PET	melting	35	11
		37	15
	thermal decomposition	217	11
		1800	15
PA6	thermal decomposition	787	13
PVC	thermal decomposition	170 (1st step), 540 (2nd step)	15

thermal decomposition, and product evaporation, prevent the differentiation of dominant endothermic phenomena. However, knowledge about the endothermic processes is fundamental to optimizing pyrolysis processes toward lower energy consumption. Cafiero et al. and Straka et al. present models for ED calculation assuming the superposition of individual components.^{11,17} Nevertheless, these studies only

cover polyolefins like polyethylene (PE) and polypropylene (PP) or polystyrene (PS), acrylonitrile butadiene styrene (ABS), and poly(ethylene terephthalate) (PET). Other important polymers of important waste streams,¹⁸ e.g., polyamide 6 (PA6) or poly(vinyl chloride) (PVC), are not investigated. Validations on a pilot scale are only performed to a limited extent.

Therefore, a data-driven model for predicting the ED for mixtures of low-density PE (LDPE), high-density PE (HDPE), PP, PS, ABS, PET, PA6, and PVC is presented. The model is based on the linear superposition of virgin polymer material data. Individual endothermic steps, namely, sensible heat of different phases, melting, pyrolytic reaction, and product evaporation, are resolved. To validate the model results, pilot-scale experiments are conducted for exemplary thermoplastics, thermoplastic mixtures, and post-consumer waste (PCW).

MATERIALS AND METHODS

Polymeric Feedstock. Different thermoplastics, namely, Hostalen ACP 9255 Plus (HDPE), Lupolen 24020H (LDPE), Moplen HP 552H (PP), Styrolution 156F (PS), Sinkral F332 (ABS), and Alphalon 27 (PA6), were used. PET was supplied by Plastikpak Italia Preforme. These polymers were acquired as white or transparent primary granules with a particle size of 2–5 mm. They are free of additives, such as inorganic fillers, UV stabilizers, colorants, or flame retardants. In pilot-scale tests, a PVC granulate manufactured by Inovyn was used. It contains approximately 10 wt % inorganic fillers (CaCO₃ and TiO₂), as well as 2–3 mol % stabilizers. An additive-free PVC powder, Primex P225-2 (virgin PVC), was investigated in DSC. The polymers were analyzed for their elemental composition, moisture, ash content, and higher heating value (HHV). Carbon, hydrogen, and nitrogen were determined according to DIN EN 15104 with a LECO elemental analyzer (Truspec CHN Micro). Chlorine was analyzed after combustion via ion chromatography according to DIN EN 14582 (AQF-2100 Combustion IC including an Aquion IC) from a1-envirosciences GmbH and Thermo Fisher Scientific GmbH. The detection limit of the chlorine measurement is 30 ppm. The analytical results including the lower heating value (LHV), which was calculated via the Boie formula from elemental analysis are shown in Table 2. Except for PCW, the HHV of the PVC-containing feedstocks was not determined experimentally due to potential corrosion.

Table 2. Elemental Composition, Moisture, Ash Content, and Calculated and Experimentally Determined Heating Values of the Investigated Feedstocks

polymer	composition (m.%)							heating value (MJ/kg)		
	C	H	N	Cl	moisture	ash	O ^a	LHV ^b	HHV ^b	HHV ^c
LDPE	85.8	14.2	<0.3	0.0	<0.01	<0.01	0.0	43.2	46.3	46.3
HDPE	85.8	14.2	<0.3	0.0	<0.01	<0.01	0.0	43.2	46.3	46.1
PP	85.8	14.2	<0.3	0.0	<0.01	<0.01	0.0	43.2	46.3	46.1
PS	92.0	8.0	<0.3	0.0	<0.01	<0.01	0.0	39.5	41.3	41.3
ABS	86.2	8.0	5.5	0.0	0.33	<0.01	0.0	37.9	39.6	39.6
PET	63.3	4.4	<0.3	0.0	0.19	<0.01	32.1	22.7	23.7	22.9
PA6	63.6	9.8	12.6	0.0	1.24	<0.01	12.7	30.8	33.0	31.2
PVC granulate	36.2	4.9	<0.3	47.9	0.16	10.6	0.3	17.2	18.3	
virgin PVC	39.6	5.6	<0.3	54.7	0.1	<0.01	0.0	19.0	20.3	
Mix 1 ^d	87.6	12.4	0.0	0.0	0.0	0.0	0.0	42.1	44.8	
Mix 2 ^d	83.5	13.4	0.3	1.0	0.0	0.2	1.6	41.5	44.5	
Mix 3 ^d	84.5	13.6	0.3	0.0	0.0	0.0	1.6	42.0	45.0	
Mix 4 ^d	80.6	11.6	0.9	2.4	0.1	0.5	3.9	38.6	41.1	
PCW	80.0	12.3	0.8	1.4	0.0	2.2	3.2	39.1	41.2	41.8

^aCalculated as a difference to 100 mol %. ^bCalculated from elemental analysis. ^cDetermined experimentally. ^dCalculated from a proportion of individual polymers in the mixture.

Four different mixtures of thermoplastics were prepared to validate the model on a pilot scale. These model mixtures represent thermoplastics-rich fractions of lightweight packaging waste of different quality. A simple mixture (Mix 1) of LDPE, PP, and PS was pyrolyzed. A more complex polyolefin-rich model mixture (Mix 2) consisted of nitrogen-, oxygen-, and chlorine-containing polymers. A similar mixture with reduced chlorine content (Mix 3) was also investigated. A fourth thermoplastic mixture with higher nitrogen, oxygen, and chlorine contents (Mix 4) was employed. After the polymers were weighed, the mixtures were homogenized by intensive manual mixing before being added to the feedstock hopper of the pyrolysis reactor. Additionally, PCW was pyrolyzed to evaluate the transferability of the additive-free model to functionalized plastic waste. This waste results from a collection of end-of-life packaging and consumer products with defined labeling according to the European identification system for packaging materials.¹⁹ The waste was washed and dried to avoid moisture or biomass contaminations. Stick-on labels were removed. Further pretreatment included a two-stage shredding (Untha RS30 and Retsch SM-2000) and subsequent pelletizing (Amandus Kahl Type 14-175) to cylindrical pellets of 6 mm diameter and 5–15 mm height. During the preparation steps, the PCW is mixed manually to promote additional homogenization of the PCW pellets. The respective material data are also listed in Table 2. The data of the model mixtures are calculated from the pure substances. Table 3 displays the detailed composition of the thermoplastic mixtures.

Laboratory-Scale Experiments. The material properties were determined using DSC for all polymers. The enthalpy of fusion and pyrolysis enthalpy were experimentally determined in a Netzsch 214 Polyma differential scanning calorimeter. Approximately 10 mg of material was weighed in aluminum crucibles with pierced lids. The samples were heated and cooled twice in a nitrogen atmosphere from 30 to 300 °C, for PVC up to 200 °C, with a heating rate of 10 K/min. The temperature program was chosen to ensure that no significant decomposition reactions occurred during the first heating phase. In the second heating cycle, the temperature was increased to 550 °C for determining the pyrolysis reaction enthalpy. Every polymer was measured twice, and the results were averaged. The heat capacity of the plastics and sand used in the pilot-scale tests was determined on a Netzsch DSC 204 F1 in an argon atmosphere with a heating rate of 10 K/min in the temperature range from −20 to +300 °C. The DSC calibration was carried out with indium, zinc, tin, bismuth, and lead according to DIN 51007.²⁰ The heat capacity was determined using the sapphire method, conforming to the DIN 51007 standard. By including the melting, glass transition (GT), and pyrolysis temperatures, the heat capacity of the various plastics can be derived. The temperatures are determined from characteristic points in the DSC curves according to DIN ISO 11357.²¹ The melting peak temperature in the DSC curve and the temperature associated with the inflection point of the GT are applied. Based on the DSC data, three options exist for determining the reaction temperature. These options open a potential range for the parameter choice.

Table 3. Composition of the Thermoplastic Mixtures Applied in Pilot-Scale Pyrolysis Experiments

polymer	share of polymer in the model and PCW mixture (m.%)				
	Mix 1	Mix 2	Mix 3	Mix 4	PCW
LDPE	40.0	70.0	71.96	50.0	29.4
HDPE					17.1
PP	30.0	20.0	20.0	15.0	25.1
PS	30.0	2.0	2.0	10.0	4.2
ABS				5.0	3.8
PET		4.0	4.0	10.0	10.1
PA6		2.0	2.0	5.0	6.3
PVC		2.0	0.04	5.0	4.0

First, the initial start of the polymer decomposition may be applied, which can be referred as the onset temperature of the reaction. Second, the peak temperature of the reaction can be selected. This parameter reflects the temperature with the highest reaction rate in DSC. Last, the temperature at which full conversion is reached may be used. This temperature reflects the temperature at which the DSC curve meets the baseline again and full conversion is reached. The selection of the reaction temperature is investigated in more detail in a sensitivity study (see the [Supporting Information](#)). The onset temperature is about 20 K lower than the DSC peak point used in this study, while the temperature of full conversion is about 20–30 K higher than the temperature used in the paper. The polymer is already decomposing during heating to the reactor temperature in the experiments. Using the onset temperature neglects further heating of unreacted molecules at higher temperatures during this heating process, therefore, it has not been chosen. In turn, implementing the temperature of full conversion in thermogravimetric analysis (TGA) would reflect additional heating of already decomposed molecules in the modeling. This selection increases the ED. Consequently, both options lead to a higher deviation from the real process. The enthalpy of the reaction, determined as the calibrated area under the DSC curve, remains unaffected. The values calculated with peak temperatures from DSC reflect an average value within this interval. Therefore, the DSC peak temperature selection appears to be a reasonable, average choice in the temperature parameter range to define the reaction temperature in the model as it represents a mean value between the three options.²¹

Between the characteristic temperatures, the heat capacity is linearly approximated as a function of the temperature. A linear baseline is used to calculate the enthalpy of fusion following DIN 11357.²¹ The baseline for determining the enthalpy required for polymer degradation and evaporation of the resulting products can be obtained in several ways.^{10,22} When a Bézier curve baseline was applied, an average value between those of the tangential and linear methods was determined.

Pilot-Scale Experiments. Pilot-scale experiments were carried out using an electrically heated screw reactor. The experimental setup and procedure are described in detail by Zeller et al. and Netsch et al. for the pyrolysis of contaminated plastic waste and polyolefin-rich plastic mixtures.^{16,23,24} The mass balance and ED were derived. The reactor temperature was set to 500 °C. This is necessary for the complete conversion of the polymer within the specified solid residence time of 30 min. To maximize the yield of condensable products, higher reactor temperatures are not desirable because they lead to increased gas formation. The reactor was operated with a feedstock input of 1 kg/h in a nitrogen atmosphere (12 L/min). Quartz sand was applied as the carrier material with a mass flow rate of approximately 4 kg/h. Feedstock and sand mass flow were determined before each test run since differences in the bulk density lead to deviations during material dosing. An ABB three-phase energy meter (type A43 313-100) recorded the electrical energy uptake of the reactor at 5 min intervals. The energy consumption of auxiliary equipment, including the condensation unit and the measurement and control unit, was counted separately. Startup and shutdown processes during the 5 h test runs were neglected so that approximately 3.5–4 h of continuous operation are included in the calculation of the ED. Each test was performed twice, and the determined values were averaged. Six experiments were conducted for Mix 2 to check reproducibility. Comparative experiments without feedstock addition were carried out for energy balancing, determining the required electrical energy consumption for sand and flush gas heating. The linearization of this basic ED depending on the supplied sand mass rate allowed flexible background demand adaption within the operating parameter window. Based on the energy difference of tests with and without feedstock, the feedstock-specific ED was calculated. The influence of the temperature, sand mass, and purge gas flow on the heat losses of the system was tested. Further information on the reactor setup can be found in the [Supporting Information](#).

THEORETICAL CALCULATIONS

The model determines the mass-specific ED based on a superposition approach. As proposed by Cafiero et al. and Netsch et al., this approach neglects any interaction of the polymers during thermal degradation.^{11,25} Reactor-specific heat losses are excluded, so calculated values represent the lower limit of the ED for the overall pyrolysis process. This minimal pyrolysis ED h_{py} of the entire pyrolysis process is calculated according to the mass fraction of each polymer in the mixture x_i following eq 1. The energy needed for solid polymer heating h_{solid} and for molten polymer heating h_{melt} is considered. Additionally, the equation comprises the feedstock-specific enthalpy of fusion h_f and the reaction enthalpy h_R , which includes the energy expended for product evaporation.

$$h_{py} = \sum_i x_i (h_{solid,i} + h_{f,i} + h_{melt,i} + h_{R,i}) \quad (1)$$

Initially, the energy for heating from ambient temperature T_a to the GT temperature T_g of the respective polymer i is calculated. In this temperature range, the specific heat capacity before GT $c_{p,preGT}$ is used. Between the state of GT and melting temperature T_m and from melting to reaction temperature T_R , the calculation is carried out analogously. The reaction temperature is defined as the degradation peak temperature. The sensible heat of the different heating stages is calculated according to eqs 2 and 3. The specific heat capacities before melting, $c_{p,postGT}$, and after melting, $c_{p,m}$, are also incorporated.

$$h_{f,i} = \int_{T_a}^{T_{g,i}} c_{p,preGT,i} dT + \int_{T_{g,i}}^{T_{m,i}} c_{p,postGT,i} dT \quad (2)$$

$$h_{R,i} = \int_{T_{m,i}}^{T_{R,i}} c_{p,m,i} dT \quad (3)$$

To linearize the temperature-dependent heat capacity, the DSC data are fitted following eq 4. The heat capacity for each polymer i in phase state j depends on the temperature T (°C) and the fit parameters A and B .

$$c_{p,j,i} = A_{i,j}T + B_{i,j} \quad (4)$$

Consequently, eqs 2 and 3 can be simplified by averaging the linearized heat capacities in the relevant temperature range, leading to eqs 5 and 6.

$$h_{solid,i} = \bar{c}_{p,preGT,i}(T_{g,i} - T_a) + \bar{c}_{p,postGT,i}(T_{m,i} - T_{g,i}) \quad (5)$$

$$h_{melt,i} = \bar{c}_{p,m,i}(T_{R,i} - T_{m,i}) \quad (6)$$

The enthalpy of phase transition is polymer-dependent. Thus, some terms are omitted for certain polymers. LDPE, HDPE, and PP show no GT in the relevant temperature range. In this case, eq 5 only consists of the postGT term while the preGT term is neglected. For PA6, a low GT temperature of about 50 °C is observed. The GT of PA6 is neglected, and only a postGT linearization of the specific heat capacity is considered from room temperature upward. ABS and PS lack a melting transition. Thus, the terms for sensible heat of ABS and PS melt, and their enthalpy of fusion are not considered. To linearize the heating process for different regimes, notional model limit temperatures for the different phases T_g^* and T_m^* are introduced. Those limit temperatures differ from the experimentally determined characteristic polymer temperatures. The integrated values for heat of fusion and the reaction enthalpy rely on a baseline similar to the linearized

heat capacities. Therefore, the notional limit temperatures reflect the intersection of the linearized heat capacities. The method for defining the model limit temperatures and deriving the linearized heat capacities is depicted for PET in Figure 1. The determination method of the melting and reaction enthalpy for PET is shown in Figure 2.

RESULTS AND DISCUSSION

Laboratory Experiments. With this study, heat capacities can be determined as a function of temperature for all polymers except PVC in the range of 50–300 °C. Table 3 presents the determined characteristic material data. Also, the linearized heat capacities and the model limit temperatures are shown. The GT and melt temperatures, heat of fusion, and heat capacities are consistent with the available literature data.²⁶ In some cases, the resulting limit temperatures used as model parameters deviate from the calculated DSC values to meet heat capacity intersections. For example, the melting transition for PET and PA6 is selected about 80 °C before the determined peak temperature. For LDPE, HDPE, and PP, the model limit temperature of the melting transition is about 10–20 K higher than their peak melting temperature. The use of these model parameters allows a closer replication of the linearized heat capacities because their intersection point reflects the baseline for determination of the heat of fusion more accurately. The two-stage decomposition mechanism of PVC hinders the determination of all material values. Up to approximately 180 °C, reproducible data for heat capacity is obtained. The degradation start of PVC prevents determination of the heat capacity above 180 °C and also integration of the reaction enthalpy. The heat capacity is therefore assumed to be constant (2000 J/g·K) from 180 °C onward. Following Stoliarov and Walters, the enthalpy of the reaction for the multistage PVC mechanism is estimated to be 700 J/g·K.¹⁵

The determined reaction temperature is compared to the results of TGA.²⁵ This comparison indicates close consistency between the peak temperature of the DSC and the peak temperature of the differential thermogravimetric curve of only a few Kelvin (see the Supporting Information).

The heat capacity of the quartz sand $c_{p,Sand}$ (in J/kg·K) used in pilot-scale tests can be approximated based on the DSC results in the temperature range of 0–500 °C according to eq 7. Additionally, eq 8 represents an approximation to material data from the VDI heat atlas for calculating the heat capacity of

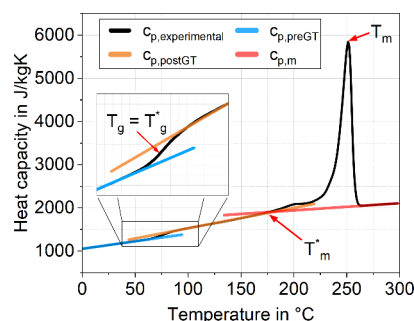


Figure 1. DSC data of PET marked with characteristic polymer temperatures (GT temperature T_g and melting temperature T_m), model limit temperatures (T_g^* and T_m^*), and linearized heat capacities before GT (blue), after GT (orange), and after melting (red).

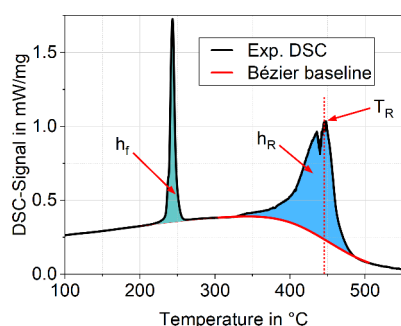


Figure 2. Integration of h_f and h_R and determination of T_R from the DSC data of PET with a Bézier baseline.

nitrogen from 0 to 600 °C.²⁷ The implementation is needed to match the model data to the experimental investigations in pilot scale.

$$c_{p,\text{Sand}} = 7 \times 10^{-12}T^5 - 8 \times 10^{-9}T^4 + 5 \times 10^{-6}T^3 - 0.0034T^2 + 1.8812T + 691.45 \quad (7)$$

$$c_{p,\text{N}_2} = 2 \times 10^{-15}T^5 - 3 \times 10^{-12}T^4 + 2 \times 10^{-9}T^3 + 7 \times 10^{-8}T^2 + 2 \times 10^{-6}T + 1.041 \quad (8)$$

The ED for thermal decomposition and melting of the polymers corresponds to the literature data summarized in Table 1. Because of the lower degree of crystallinity, the ED of the LDPE measured exhibits a lower heat of fusion than the HDPE, while both are in the range of the reported literature.^{12,15} The DSC data of PP and PET reveal slightly higher heat of fusion than those reported by Cafiero et al. and Stoliarov et al.^{11,15} The deviations may be caused by a different polymer configuration (e.g., degree of polymerization or additives). The measured ED for thermal decomposition of the polymers in this work, shown in Table 4, varies depending on the polymer type, as is evident for PE, PP, PS, and PET, for example. These results represent an average value in the stated range from the literature values in Table 4. Fewer comparative values are available for ABS and PA6. Still, the determined values are comparable, considering the influence of the evaluation methodology and differences in the structure and composition of the reported and used polymers.

Pilot-Scale Experiments. Pilot-scale pyrolysis experiments were carried out with pure LDPE, PP, PS, Mixes 1–4, and PCW to provide mass and energy balances. The mass balance

for each feedstock is shown in Figure 3. The product fractions deviate by max. 2 m.%, and a minor balance loss of max. 3.9 m. % for Mix 2 indicates a high reproducibility. The mass balances depend on the selected feedstocks. Generally, the pyrolysis gas and the condensates dominate the product yields. Increasing amounts of heteroatom-containing polymer mixtures such as PET and PVC lead to the formation of a solid residue. The residue reaches up to 4.3 and 4.1 m.% for additive-containing PCW and heteroatom-containing Mix 4, respectively.

Figure 4 shows the plastic-related ED for the pyrolysis at 500 °C. This universal plastic-specific ED excludes the sand's reactor-specific contribution as a carrier material. It ranges from 1575 to 2424 J/g of added feedstock. However, the energy required for heating the sand to a reactor temperature of 500 °C is also determined experimentally in pilot scale. It accounts for approximately 460–490 J/g_{Sand}. The ED for sand heating modeled based on the DSC results is 471 J/g_{Sand} according to formula (7). Detailed results, including the carrier material contribution, are summarized in the Supporting information. The energy balance also shows clear feedstock-dependent variations. Pyrolyzing PS requires a significantly lower ED compared to polyolefins. A mixture of LDPE, PP, and PS (Mix 1) exhibits an ED between the determined pure polymer values. Mix 2, Mix 3, and Mix 4 show significantly higher ED than Mix 1. The higher ED may result from the more complex composition incorporating heteroatom-containing polymers like PA6, PET, or PVC. For such thermoplastic blends, Netsch et al. report significant polymer interactions during pyrolysis.²⁴ These interactions lead to differing degradation mechanisms, which could explain the discrepancies between the model and experimentally determined ED. PCW features a lower ED compared to the polymer mixtures. This may be attributed to the additive content because inert fillers and other nonpyrolyzable components reduce the ED of PCW or have a catalytic effect. Another possible reason for these deviating results is secondary reactions of volatile products in the gas phase. The screw reactor exhibits longer gas residence times in the heated zone compared to DSC experiments with a virgin polymer. Consequently, additional secondary gas phase reactions may occur, leading to changes in the reaction mechanism and product distribution. This may also influence the measured ED.

The feedstock and sand dosage fluctuate depending on the conveying behavior. Therefore, the dosing rate represents the main influencing factor for deviating results of repeated experiments. Also, polymer experiments slightly lower the

Table 4. Model Data for Calculation of the ED of Phase Transition, Polymer Heating, and Pyrolytic Degradation Including Evaporation Experimentally Determined via DSC

polymer	phase transition			degradation reaction		linearized heat capacities A (J/g·K ²) and B (J/g·K)			limit temperatures for modeling	
	T_g (°C)	T_m (°C)	h_f (J/g)	T_R (°C)	h_R (J/g)	$c_{p,\text{preGT}}$	$c_{p,\text{postGT}}$	$c_{p,m}$	T_g^* (°C)	T_m^* (°C)
LDPE		112	142	478	473		$A = 4.376, B = 2106$	$A = 3.336, B = 2238$		125
HDPE		136	235	482	438		$A = 6.447, B = 1674$	$A = 3.250, B = 2191$		156
PP		164	116	459	542		$A = 5.992, B = 1636$	$A = 3.095, B = 2161$		180
PS	102			419	744	$A = 5.308, B = 1207$	$A = 2.762, B = 1668$		100	
ABS	109			422	739	$A = 3.695, B = 1359$	$A = 2.454, B = 1796$		105	
PET	73	251	56	443	232	$A = 3.468, B = 1058$	$A = 4.719, B = 1061$	$A = 1.659, B = 1615$	73	175
PA6		222	72	455	630		$A = 9.241, B = 1368$	$A = 2.424, B = 2444$		145
virgin PVC	87			256 (1st step), 470 (2nd step)		$A = 3.290, B = 890$	$A = 5.415, B = 988$	$A = 0, B = 2000$	87	180

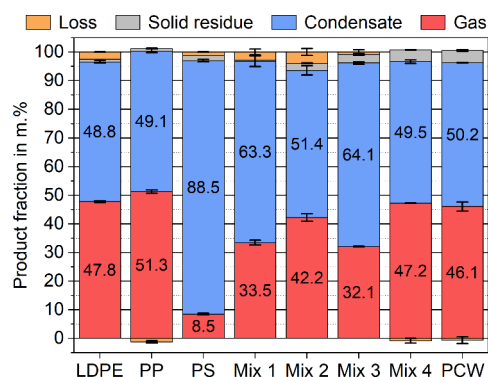


Figure 3. Average mass balance including standard deviation error bars of pilot-scale pyrolysis experiments at 500 °C with a feedstock dosing of 1 kg/h and a dwell time of 30 min.

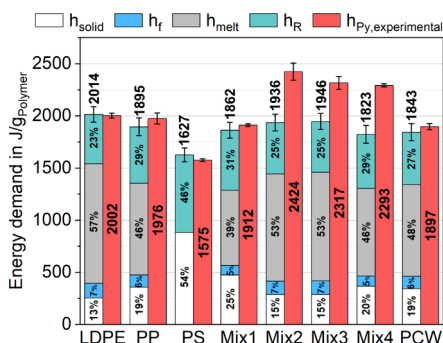


Figure 4. ED of the experimental measurements (red) and model calculations with subdivisions of heating of a solid polymer (white), heat of fusion (blue), heating of a polymer melt (grey), and reaction and product evaporation enthalpy (green).

reactor inlet temperature compared to the background measurement obtained with sand. This lower inlet temperature of up to 5 K reduces the heat emission to the environment, which is not compensable by background deduction. Nevertheless, the standard deviation of the ED for plastic pyrolysis accounts for only up to 81 J/g. Reducing the amount of sand as the carrier material favors the total ED of the pyrolysis process by minimizing the background ED.

Model Calculations. The model calculations are compared to the experimentally determined ED in Figure 4. The ED of the LDPE, PP, PS, and Mix 1 pyrolysis agrees with the model value within the range of measurement and model uncertainties. Different methods for selecting the reaction temperature influence the model results by less than 100 J/g_{Polymer}. For these feedstocks, the modeled ED for the pyrolysis deviates by less than about 5% of the experimental value. The results obtained with the more complex Mix 2, Mix 3, and Mix 4 significantly underestimate the ED, which cannot be explained by the experimental or modeling errors. The difference amounts to about 370–500 J/g. Additionally to the pyrolysis ED, the model calculates an ED for sand heating. These model results of the required energy for sand heating to 500 °C account for 471 J/g_{Sand} and are therefore similar to the experimental results (460–490 J/g_{Sand}). Thus, excellent accordance of the experimentally determined and modeled background ED for the reactor, flush gas, and carrier material heating is proven. Sand heating is well calculated compared to the experimental results. The model resolves the allocation of different pyrolysis phenomena that occur during polymer

pyrolysis. The sensible heat is indicated as a dominant endothermic share. The heat of the melt accounts for up to 57% of the pyrolysis enthalpy. Because PS does not exhibit a melting point, solid heating is decisive for its pyrolysis ED. The combined reaction and evaporation enthalpy is comparatively low at 23–46%.

The contribution of each polymer in the mixture to the pyrolysis ED is shown in Figure 5. Beyond their impact due to their high content in the mixture, the LDPE and HDPE contribute comparably higher values compared to other polymers as a result of their high heat capacity and heat of fusion. In contrast, PET has a lower melt and reaction enthalpy. The contribution of PET is therefore lower than its proportion in the mixtures. However, the material data are of similar magnitudes and only differ slightly for all investigated polymers. As a result, the mixture's polymer-specific ED correlates strongly with its polymer content.

The additional ED for heating up the sand and the flush gas in the presented pilot-scale pyrolysis is disadvantageous. With a sand-to-feedstock ratio of 4:1 the minimal ED for pyrolyzing the polymers increases by about 1800–2000 J/g_{Polymer}. Also, the reaction-related ED is low compared to the heating of the polymer to degradation temperature, which indicates potential opportunities for pyrolysis optimization to enhance the process efficiency. The carrier material should be minimized, and the effective heat recovery from hot products and sand should be implemented in comparable pyrolysis technologies. Also, a more efficient technology for preheating the polymer, e.g., in an extruder, may result in a more sustainable pyrolysis process.

The model predicts the energy requirement of Mixes 2–4 with less precision than that for the other feedstocks. The assumption of the PVC heating behavior is a potential source of this systematical underestimation. However, the PVC content in these mixtures is of max. 5 mol %. Therefore, the PVC material data cannot justify the significant difference between model calculations and experiments. The reason for the underestimation might be found in the model assumption itself. In thermoplastic mixtures, potential interactions occur during the degradation reaction. Degradation mechanisms that differ from pure plastic possibly might lead to a significant difference in the required ED depending on the types of reactions. For example, increased coke formation is observed in thermoplastic blends of polyolefins or PS with PVC or aromatic-containing polymers like PET.^{24,28} A systematic investigation of the degradation mechanisms and potential interactions in thermoplastic mixtures will thus be necessary to clarify the cause of the deviations.

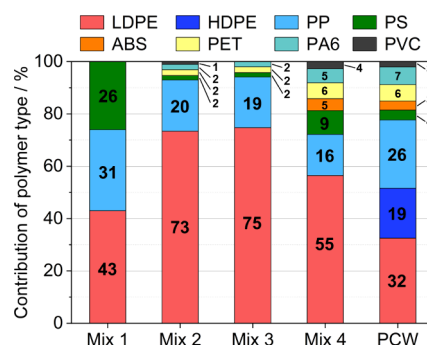


Figure 5. Calculated ED for pyrolysis of the model mixtures Mix 1–4 and die PCW specified by the contributing polymer type.

CONCLUSION

The model presented in this work enables ED calculation of the thermoplastics pyrolysis. The model results are validated in a pilot-scale screw reactor. The total ED for pyrolyzing the plastics is on the order of magnitude of 5% of the net calorific value of the polymeric feedstock, which is about 1575–2424 J/g_{Polymer}. The heating of the carrier material requires additional energy. As proven with pure substances or simple mixtures, a high agreement between the model and pilot-scale data is achieved. A systematic underestimation of the experimental data by the model predictions is evident when pyrolyzing heteroatom-containing polymer mixtures. The underestimation of the ED for pyrolyzing more complex mixtures by the model might be attributed to interactions of the polymers during the reaction. Additionally, the model provides detailed insight into dominant endothermic phenomena occurring in the pyrolysis process. The heating of the plastic and the carrier material are the main contributors to the ED.

Detailed investigations are required to better understand potential thermoplastic interactions, which may lead to differing degradation kinetics. The underestimation of the pyrolysis energy requirement is compensated for by this PCW by the present ash content and possible additives, which lower the ED. The transferability of the model based on the material data of additive-free polymers is validated by applying it to the pyrolysis of real PCW. The proven applicability to material systems comprising LDPE, HDPE, PP, PS, ABS, PET, PA6, and PVC enables the approximate calculation of the ED for future reactor designs or pyrolysis system evaluations. In the evaluation of such pyrolytic chemical recycling concepts, further energy requirements must be examined because the ED calculation of this work only covers the physical and chemical aspects of the thermochemical conversion process. For example, the energy required for heat losses, up- and downstream processes, and additional potential material pretreatment, e.g., shredding of the polymeric feedstock, needs to be considered. Depending on the reactor technology used, the ED contribution for reactor-specific accompanying materials must be calculated in the adaption to the pyrolysis system under evaluation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssusresmgmt.4c00109>.

Comparison of the detailed ED results in “experimental results of pilot-scale pyrolysis and model validation”, more information about the reactor setup and parameters given in “technical details of the screw reactor”, and sensitivity study’s in-depth results about the model reaction temperature selection provided in “sensitivity study on the parameter selection for model reaction temperature” (PDF)

AUTHOR INFORMATION

Corresponding Authors

Niklas Netsch – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*; orcid.org/0000-0002-2982-181X; Phone: +49 721 608 22869; Email: Niklas.Netsch@kit.edu

Salar Tavakkol – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*; orcid.org/0000-0001-5142-2439; Phone: +49 721 608 22898; Email: Salar.Tavakkol@kit.edu

Authors

Michael Zeller – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*

Frank Richter – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*

Britta Bergfeldt – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*

Dieter Stapf – *Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Baden-Württemberg 76131, Germany*; orcid.org/0000-0001-6499-062X

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acssusresmgmt.4c00109>

Author Contributions

N.N. conceptualized the study, performed the laboratory tests, contributed to the experimental work in pilot scale, and curated the data. He developed the theoretical model. The writing of the manuscript was performed by him. M.Z. gave support in the conceptualization stage and editing of the manuscript. F.R. contributed to the experimental conceptualization and performed investigations at the pilot scale pyrolysis reactor. B.B. was responsible for the feedstock analysis and reviewed the manuscript. S.T. and D.S. supported the work by supervising, reviewing the manuscript, and acquiring the necessary funding.

Funding

Funding of this work was provided by the German Helmholtz Association within the program “Materials and Technologies for the Energy Transition”, under the topic “Resource and Energy Efficiency”.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

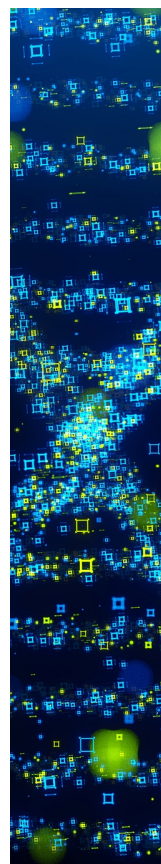
The authors thank Judith Jung from the Institute for Applied Materials of KIT for experimental support in determination of the heat capacities via DSC analyses. We gratefully acknowledge the support of LyondellBasell Industries, INEOS Styrolution, and INEOS Inovyn by providing the polymers.

ABBREVIATIONS

ABS, acrylonitrile butadiene styrene; DSC, differential scanning calorimetry; ED, energy demand; GT, glass transition; HDPE, high-density polyethylene; HHV, higher heating value; LDPE, low-density polyethylene; LHV, lower heating value; PA6, polyamide 6; PCW, post-consumer waste; PE, polyethylene; PET, poly(ethylene terephthalate); PP, polypropylene; PS, polystyrene; PVC, poly(vinyl chloride)

REFERENCES

- (1) Lee, R. P. Alternative carbon feedstock for the chemical industry? - Assessing the challenges posed by the human dimension in the carbon transition. *J. Clean. Prod.* **2019**, *219*, 786–796.
- (2) Keijer, T.; Bakker, V.; Slootweg, J. C. Circular chemistry to enable a circular economy. *Nat. Chem.* **2019**, *11* (3), 190–195.
- (3) European Commission. A European Strategy for Plastics in a Circular Economy. Published January 2018. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM%3A2018%3A28%3AFIN> (accessed 2023-12-08).
- (4) United States Environmental Protection Agency. National Recycling Strategy. Published November 2021. <https://www.epa.gov/system/files/documents/2021-11/final-national-recycling-strategy.pdf> (accessed 2023-12-08).
- (5) Ministry of the Environment, Government of Japan. Act of Promotion of Resource Circulation for Plastics. Published April 2022. https://www.env.go.jp/en/focus/jeq/issue/vol29/The%20Plastic%20Resource%20Circulation%20Act_0128%20final.pdf (accessed 2023-12-08).
- (6) Canadian Council of Ministers of the Environment. Canada-wide Action Plan on Zero Plastic Waste. Published November 2019. https://ccme.ca/en/res/1589_ccmecanada-wideactionplanonzeroplasticwaste_en-secured.pdf (accessed 2023-12-08).
- (7) Department of Agriculture, Water and the Environment, Australian Government. National Plastics Plan 2021. Updated October 2021. <https://www.dcceew.gov.au/sites/default/files/documents/national-plastics-plan-2021.pdf> (accessed 2023-12-08).
- (8) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste Manage.* **2017**, *69*, 24–58.
- (9) Quicker, P.; Seitz, M.; Vogel, J. Chemical Recycling: A critical assessment of potential process approaches. *Waste Manage. Res.* **2022**, *40* (10), 1494–1504.
- (10) Agarwal, G.; Lattimer, B. Method for measuring the standard heat of decomposition of materials. *Thermochim. Acta* **2012**, *545*, 34–47.
- (11) Cafiero, L.; Fabbri, D.; Trinca, E.; Tuffi, R.; Vecchio Cipriotti, S. Thermal and spectroscopic /TG(DSC-FTIR) characterization of mixed plastics for materials and energy recovery under pyrolytic conditions. *J. Therm. Anal. Calorim.* **2015**, *121* (3), 1111–1119.
- (12) Duque, J. V. F.; Martins, M. F.; Debenest, G.; Orlando, M. T. The influence of the recycling stress history on LDPE waste pyrolysis. *Polym. Test.* **2020**, *86*, 106460.
- (13) Frederick, W.; Mentzer, C. C. Determination of heats of volatilization for polymers by differential scanning calorimetry. *J. Appl. Polym. Sci.* **1975**, *19* (7), 1799–1804.
- (14) Khedri, S.; Elyasi, S. Determination of the heat of pyrolysis of HDPE via isothermal differential scanning calorimetry. *J. Therm. Anal. Calorim.* **2018**, *131* (2), 1509–1515.
- (15) Stoliarov, S. I.; Walters, R. N. Determination of the heats of gasification of polymers using differential scanning calorimetry. *Polym. Degrad. Stab.* **2008**, *93* (2), 422–427.
- (16) Zeller, M.; Netsch, N.; Richter, F.; Leibold, H.; Stapf, D. Chemical Recycling of Mixed Plastic Wastes by Pyrolysis - Pilot Scale Investigations. *Chem. Ing. Technol.* **2021**, *93* (11), 1763–1770.
- (17) Straka, P.; Bičáková, O.; Šupová, M. Thermal conversion of polyolefins/polystyrene ternary mixtures: Kinetics and pyrolysis on laboratory and commercial scales. *J. Anal. Appl. Pyrolysis* **2017**, *128*, 196–207.
- (18) Faraca, G.; Astrup, T. Plastic waste from recycling centers: Characterisation and evaluation of plastic recyclability. *Waste Manage.* **2019**, *95*, 388–398.
- (19) European Commission. Establishing the identification system for packaging materials pursuant to European Parliament and Council Directive 94/62/EC on Packaging and packaging waste. Published January 1997. <https://eur-lex.europa.eu/eli/dec/1997/129/oj> (accessed 2023-12-08).
- (20) Thermal analysis—Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)—general principles; Deutsches Institut für Normung: Berlin, 2019; DIN 51007.
- (21) Plastics—Differential scanning calorimetry (DSC); Deutsches Institut für Normung: Berlin, 2023; DIN EN ISO 11357.
- (22) Svoboda, R.; Málek, J. Importance of proper baseline identification for the subsequent kinetic analysis of derivative kinetic data. *J. Therm. Anal. Calorim.* **2016**, *124* (3), 1717–1725.
- (23) Netsch, N.; Simons, M.; Feil, A.; Leibold, H.; Richter, F.; Slama, J.; Yogish, S. P.; Greiff, K.; Stapf, D. Recycling of polystyrene-based external-thermal insulation composite systems - Application of combined mechanical and chemical recycling. *Waste Manage.* **2022**, *150*, 141–150.
- (24) Netsch, N.; Vogt, J.; Richter, F.; Straczewski, G.; Mannebach, G.; Fraaije, V.; Tavakkol, S.; Miha, S.; Stapf, D. Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis. *Chem. Ing. Technol.* **2023**, *95* (8), 1305–1313.
- (25) Netsch, N.; Schröder, L.; Zeller, M.; Neugber, I.; Merz, D.; Klein, C. O.; Tavakkol, S.; Stapf, D. Thermogravimetric Study on Thermal Degradation Kinetics and Polymer Interactions in Mixed Thermoplastics. *SSRN* **2024**. DOI: 10.2139/ssrn.4757121.
- (26) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley Interscience Publication, 1999.
- (27) VDI Gesellschaft Verfahrenstechnik und Chemieingenieurwesen. *VDI Heat Atlas*, 11th ed.; Springer Vieweg, 2013. DOI: 10.1007/978-3-540-77877-6.
- (28) Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H. Thermal degradation of PVC: A Review. *Waste Manage.* **2016**, *48*, 300–314.



CAS BIOFINDER DISCOVERY PLATFORM™

**STOP DIGGING
THROUGH DATA
—START MAKING
DISCOVERIES**CAS BioFinder helps you find the
right biological insights in seconds**Start your search****CAS**
A Division of the
American Chemical Society



Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics

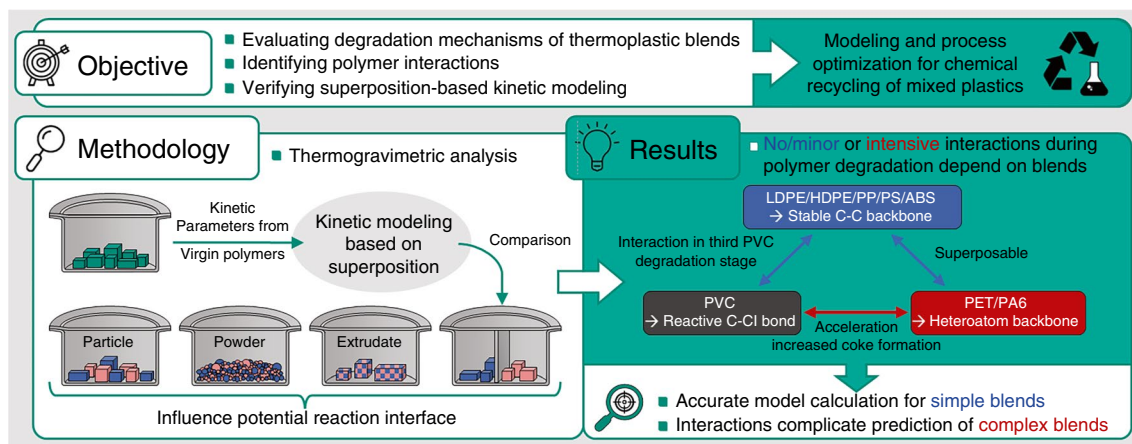
N. Netsch¹ · L. Schröder¹ · M. Zeller¹ · I. Neugber¹ · D. Merz¹ · C. O. Klein² · S. Tavakkol¹ · D. Stapf¹

Received: 2 May 2024 / Accepted: 31 August 2024 / Published online: 14 October 2024
 © The Author(s) 2024

Abstract

Potential interactions during thermal degradation of polymer blends significantly influence product yields and their composition. Therefore, chemical recycling of plastic waste requires fundamental understanding of feedstock dependency for effective process design. This study investigates the pyrolysis of polymer blends (HDPE, LDPE, PP, PS, ABS, PET, PA6, PVC) through thermogravimetric experiments at different heating rates. Sample homogeneity's impact on interactions is analyzed using particles, powder, coextruded blends, and samples in crucibles with separated compartments. A kinetic model is presented to support the experimental findings, assuming linear superposition of individual polymer kinetics. A proposed grouping of thermoplastics, reflecting their degradation behavior and potential interactions, correlates with the polymer structure. Observed interactions, particularly in blends of heteroatom-containing polymers (N, O, Cl), are accelerated reactions and coke formation. Hence, the model accurately predicts the degradation of heteroatom-free polymer mixtures but encounters challenges with more complex blends. This comprehensive study emphasizes the importance of feedstock composition for future pyrolytic polymer recycling.

Graphical abstract



Keywords Thermoplastics · Pyrolysis · Thermogravimetry · Thermal degradation · Kinetic modeling · Decomposition interaction

Abbreviations

ABS Acrylonitrile butadiene styrene
 HDPE High-density polyethylene
 LDPE Low-density polyethylene
 PA Polyamide

PE Polyethylene
 PET Polyethylene terephthalate
 PP Polypropylene
 PS Polystyrene
 PVC Polyvinyl chloride

Extended author information available on the last page of the article

RMSD Root mean square deviation
TG Thermogravimetry

Introduction

The transformation from linear value chains to a circular economy offers the advantage of growing independence from fossil raw materials and reduced CO₂ emissions [1]. The European Union has proclaimed carbon net zero as the main objective of future economic actions [2]. To reach this target, the production of polymers and the management of plastic waste have to become substantially resource-efficient [3, 4]. The recycling of plastic waste is preferable to its energetic use or landfilling to reduce the ecological footprint [5–8]. Mechanical plastics recycling is well established, leading to a global recycling rate of 24 mass% in 2014 [9]. Nevertheless, many plastic-rich waste fractions cannot be mechanically recycled, which is why chemical recycling is a useful complementary process [10]. Pyrolysis, the thermal degradation in inert atmosphere, gains focus as thermochemical recycling option [11].

Plastic wastes are heterogeneous mixtures of different types of plastic. Also, they may contain other adhesions such as biomass or inorganic components [12, 13]. Nevertheless, since a few thermoplastics dominate the plastic production these polymers are largely represented in the waste feedstocks relevant for the recycling via pyrolysis. These polymers are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), acrylonitrile butadiene styrene (ABS), and polyamide (PA) [14]. The pyrolysis of PE, PP, PS, and ABS follows complex single-step radical reaction mechanisms [15–18]. In these mechanisms, radicals are initially generated by homolytic bond cleavage, which proceeds to a preparation phase in which the radicals react with polymer chains and cause further cleavages. The mechanism terminates with the recombination of the radicals. Depending on the polymer type, the mechanisms favor bond cleavage at varying chain positions, which leads to significant different product compositions. PET and PA undergo single-step degradation initiated by ionic intramolecular transfer reactions [19–22]. Thermal degradation of all these polymers occurs at temperatures above 670 K, typically. Significant amounts of solid pyrolysis residue, considered as coke, are generated when pyrolyzing PET. The coke is formed during the degradation reaction while emitting oxygen-containing volatiles from the polymeric structure, e.g., CO₂ or carboxylic acids, resulting in polycyclic and polyaromatic structures. PVC degrades in a three-step radical chain scission with HCl formation in the first degradation step starting at approximately 520 K, already [23, 24]. The three-step mechanism results from the significant bond stability variations of the carbon–carbon

and chlorine–carbon bonds that build the polymeric PVC structure. This first step is followed by hydrocarbon volatilization and polyene intermediate formation. These unsaturated polyene chains ultimately degrade producing coke and volatile hydrocarbons with mostly aromatic structures. The coke is formed by cross-linking of the polyene chains.

Knowledge of the detailed degradation behavior enables process design and optimization. For pyrolysis, kinetic modeling is often based on experimental data and simplified model assumptions due to the complexity of degradation mechanisms. The pyrolysis kinetics are valid for the range of substances under investigation. For example, the multistage degradation of various polyurethanes can be represented with the *n*-th order model approach of Zeller et al. [25]. Also, Aboulkas et al. successfully applied this approach to HDPE, LDPE, and PP [26]. An application-oriented modeling technique to describe the degradation kinetics of mixtures based on the superposition of pure substance properties appears promising. Different authors negate significant mixing effects on the degradation products for various polymer blends. Mixtures of PE, PP, and PS can be described well via superposition according to Westerhout et al. [27]. This result is confirmed by Costa et al. and Faravelli et al. for PE-PP and PE-PS mixtures, respectively [28, 29]. Wu et al. proved that the degradation behavior of PVC-PE blends can be well represented with this linear superposition approach [30]. Even when Genuino et al. identified limitations by linear superposition of data, the approach was successfully applied for plastic mixtures of HDPE, LDPE, PP, PS, and PET to predict the product yields [31]. Interactions during co-pyrolysis are therefore often considered neglectable for specific blends.

Basically, when pyrolyzing plastic mixtures the resulting intermediates from one polymer can react with degradation intermediates of another one [32]. These interactions between polymer products may ultimately influence the product distribution, but also the degradation kinetics. In such cases, linear postponed approaches for degradation kinetics of mixtures are invalid [33]. When co-pyrolyzing polyolefins, slight acceleration in the thermal degradation compared to pure substances is reported [34, 35]. Genuino et al. found the formation of solid products increased beyond expectations when adding low amounts of PET to polyolefins and PS in a batch reactor [31]. This effect is confirmed by Hujuri et al. who additionally observed a synergistic effect as LDPE and PP degrade at lower temperatures when mixed with PET [36]. Therefore, they suggest an interaction term in superposition-based kinetic modeling. Contrary behavior is reported when pyrolyzing PVC in blends with PE, PP, and PS. Yu et al. summarized the degradation of polyolefins and PS being delayed because of PVC intermediates. Increased coke formation is observed [23], which is confirmed in vacuum pyrolysis in a batch reactor [37].

Miranda et al. also identified PVC and PS as responsible for interactions in the pyrolysis of their feedstocks. Therefore, Tuffi et al. proposed three criteria directly influencing potential interactions [38]. First, interaction is more present if polymers are pyrolyzed which feature similar onset temperatures of degradation. Second, the dependency of the polymer concentration is underlined. At last, the homogeneity of the blend emerges as a crucial factor for degradation kinetics. Faravelli et al. emphasized this factor of interfacial effects in the material system [29].

Concluding, a majority of the literature assumes interactions during the co-pyrolysis of mixed thermoplastics but conflicting degradation phenomena during thermoplastic co-pyrolysis are reported. Also, PA and ABS are rarely investigated in detailed mixed plastic studies. Most of the models published for the degradation kinetics are tailored for specific polymers or limited to only two or three polymers in the mixture. This systematic thermogravimetric investigation covers a broad polymer portfolio, namely LDPE, HDPE, PP, PS, ABS, PET, PA6, and PVC. Thus, this work aims to clarify the pyrolysis behavior of blends which include the major thermoplastics in plastic waste. Polymer interactions during degradation are investigated depending on the polymer type, its concentration, and the homogeneity of the sample mixture. The role of the interface available for interactions during the reactions is in focus. Differently prepared polymer samples allow a comparison of the interface influence based on spatial proximity. A superposition-based kinetic model is adapted by extending the kinetic modeling methodology of Zeller et al. from virgin plastics to thermoplastic blends [25]. In addition to the theoretical calculations based on a superposition approach, novel crucibles with divided compartments are used as defined control experiments. The applicability of this approach is validated by systematic comparison to the comprehensive experimental dataset.

Materials and experimental methods

In this study, eight thermoplastics were tested, namely Hostalen ACP 9255 Plus (HDPE), Lupolen 24020H (LDPE), Moplen HP 552H (PP), each from LyondellBasell industries, Styrolution 156F (PS) from INEOS Styrolution, Sinkral F332 (ABS) by Eni, and Alphalon 27 (PA6) by Grupa Azoty. PET is supplied by Plastikpak Italia Preforme. The thermoplastics were acquired as granules, except for Primex P2252 (PVC) which was delivered as powder by Mexichem. All polymers are free of additives, e.g., flame retardants, inorganic fillers, or UV stabilizers. The elemental analyses, ash and moisture content, higher heating values (HHV), and lower heating values (LHV) are listed in Table 1.

Thermogravimetry (TG) was carried out on a NETZSCH TG 209 F1 Libra equipped with an autosampler. The pyrolysis was performed from 303 to 1173 K and at constant heating rates of 2, 5, 10, 20, and 40 K min⁻¹ in nitrogen atmosphere. The nitrogen flow rate was set to 60 mL min⁻¹. Reproducibility could be confirmed in five tests per plastic type at 10 K min⁻¹. All other experiments were conducted twice and averaged. The samples were introduced in Al₂O₃ crucibles. The total sample mass accounts for 10 mg deviating only up to 0.1 mg. Following the ICTAC recommendations, the heating rate and sample mass were selected to prevent temperature errors [39]. Binary plastic blends were prepared with shares of 75/25 mass%, 50/50 mass%, and 25/75 mass%. Binary blends reach 28 plastic-type configurations by combining each of the eight polymers. The preparation of each component's sample mass only deviated 10–15 µg of the set value in the mixture. In the experiments, the heating rate was kept constant at 10 K min⁻¹.

The samples were added as small particles sliced from the primary granules using a scalpel. Therefore, the particle size was not uniform and varied in shape and mass between 0.5 and 5 mg of each particle slice. The influence on degradation

Table 1 Elemental analyses of the investigated polymers including heating values, moisture, and ash content

Polymer	Elemental analysis/mass%							Heating value/MJ kg ⁻¹		
	C	H	N	Cl	Moisture	Ash	O ^a	LHV ^b	HHV ^b	HHV ^c
LDPE	85.8	14.2	0.0	0.0	0.0	0.0	0.0	43.2	46.3	46.3
HDPE	85.8	14.2	0.0	0.0	0.0	0.0	0.0	43.2	46.3	46.1
PP	85.8	14.2	0.0	0.0	0.0	0.0	0.0	43.2	46.3	46.1
PS	92.0	8.0	0.0	0.0	0.0	0.0	0.0	39.5	41.3	41.3
ABS	86.2	8.0	5.5	0.0	0.3	0.0	0.0	37.9	39.6	39.6
PET	63.3	4.4	0.0	0.0	0.2	0.0	32.1	22.7	23.7	22.9
PA6	63.6	9.8	12.6	0.0	1.3	0.0	12.7	30.8	33.0	31.2
PVC	39.6	5.6	0.0	54.7	0.1	0.0	0.0	19.0	20.3	-

^a Calculated as difference to 100 mass%

^b Calculated from elemental analysis

^c Determined experimentally

interactions by the polymer arrangement within the mixture was tested. For this purpose, three different sample arrangements were compared: particles, powder, and coextruded samples. In any case, the sample preparation was performed by minimizing the energy input into the material to prevent the samples from aging, e.g., by thermal stress. The powders were obtained by crushing the granules to $< 500 \mu\text{m}$ in a rotor mill. Thermally induced degradation of the polymers was avoided by cooling the granulate and the rotor mill with liquid nitrogen [40, 41]. Powder samples were used in TG after manual mixing in the crucibles in the specific ratio. Powder experiments investigated homogeneous blends on a macroscopic level. Extrudate was generated by co-extruding the powder of pure plastics or premixed powder blends in a micro-extruder (Haake MiniLab 3 micro-compounder) by ThermoFisher Scientific. Coextruded samples represent a microscopic homogeneous mixture with maximum contact of the different polymer chains. Because of the varying melting and degradation temperatures and limited miscibility of the polymers, extruded samples were generated for pure LDPE, HDPE, PP, PS, ABS, PET, PA6, and 50/50 blends of LDPE/PP, LDPE/PS, PS/ABS, and PET/PA6. PVC powder could not be extruded because even at low temperatures visual changes of the polymer occurred. The dwell time in the extruder was set to 3 min. The extrusion temperature was selected as low as possible to prevent changes in the samples. The temperature it therefore adapted to the polymer properties. LDPE/PP was processed at 433 K and PET/PA6 at 523 K. Both other mixtures were extruded at 473 K. In contrast to extruded samples, control experiments with polymers were conducted avoiding any possible reaction interface. Crucibles of identical dimensions were used. These crucibles feature one additional wall that separates the sample into different compartments for each polymer of the mixture.

In addition to the binary mixtures, a particular blend of LDPE, HDPE, PP, PS, and ABS with 20 mass% each was tested (Mix 1). A blend of all thermoplastics (Mix 2) with 20 mass% LDPE and HDPE, and 10 mass% each of PP, PS, ABS, PET, PA 6, and PVC was also pyrolyzed under identical conditions.

Theory and calculations

Kinetic models describing the degradation of polymers can either use model-free approaches or model-based approaches. The model for predicting the reaction kinetics of thermoplastic mixtures is based on the independent parallel reactions model introduced by Jomaa et al. [42]. The model was refined by Zeller et al. [25]. Each independent reaction represents a pseudo-reaction j of polymer i , which describes a degradation stage of this polymer apparent in

the TG data. The reaction conversion α of the polymer is formulated following an Arrhenius approach. The time-dependent conversion rate of a pseudo-reaction is therefore described, as shown in Eq. 1. It includes the kinetic triplet of activation energy $E_{A,i,j}$, preexponential factor $k_{0,i,j}$, and kinetic model $f(\alpha_{i,j})$.

$$\frac{d\alpha_{i,j}}{dt} = k_{0,i,j} \cdot f(\alpha_{i,j}) \exp\left(-\frac{E_{A,i,j}}{RT}\right) \quad (1)$$

Several options are proposed for the kinetic model term [39, 43, 44]. In this work, a n -th order model is assumed. Therefore, a term for the reaction order $n_{i,j}$ is added as an additional parameter to the kinetic triplet, as shown in Eq. 2.

$$f(\alpha_{i,j}) = (1 - \alpha_{i,j})^{n_{i,j}} \quad (2)$$

Most of the thermoplastics investigated in this study include one pseudo-reaction due to the one-step degradation mechanism. PA6 and PVC are an exception. A low mass loss that precedes the degradation of PA6 results in the addition of a second pseudo-reaction. For PVC, three reactions are implemented because of the two-stage degradation with a split first degradation step [23]. Accordingly, the number of pseudo-reactions is adapted to polymer-specific experimental results. The number of pseudo-reactions is additionally validated by the conversion-dependent illustration of activation energy and the preexponential factor according to the model-free method of Kissinger–Akahira–Sunose (KAS). This method follows the recommendations of the ICTAC committee [39]. These plots can be found in the supplementary information. The share of multiple pseudo-reactions is considered by introducing the reaction fraction $q_{j,i}$ as following.

$$\frac{d\alpha_i}{dt} = \sum_j q_{j,i} \cdot k_{0,i,j} \cdot f(\alpha_{i,j}) \exp\left(-\frac{E_{A,i,j}}{RT}\right) \quad (3)$$

The time-dependent conversion $\alpha_i(t)$ is defined as a function of the mass at a specific time $m(t)$ of the experiment. The sample mass at the beginning m_0 and at the end m_∞ is also implemented according to formula 4. The kinetic parameters are calculated analogously to Zeller et al. using the pattern search algorithm in MATLAB [25].

$$\alpha_i(t) = \frac{m_0 - m(t)}{m_0 - m_\infty} \quad (4)$$

The volatile formation $m_v(t)$ represents the complement of the solid mass loss $m_s(t)$. In contrast to the conversion, these characteristic values also indicate the solid residue generated in the TG experiments. They are calculated as described in formula 5.

$$m_v(t) = 1 - m_s(t) = 1 - \frac{m(t)}{m_0} \quad (5)$$

The optimized determination of the kinetic parameters of the respective polymers follows the recommendations of the ICTAC kinetics committee [39]. It is based on the averaged datasets at different heating rates. The conversion rate of the degrading polymer mixtures α_{Mix} is calculated concerning the polymer mass fraction in the mixture x_i . Linear superposition of the individual polymer kinetics is used according to formula 6. The model is valid for non-isothermal experiments with a constant heating rate of 2 to 40 K min⁻¹.

$$\frac{d\alpha_{\text{Mix}}}{dt} = \sum_i (x_i a_i(t)) = \sum_i x_i \sum_j q_{ij} \cdot k_{0,ij} \cdot (1 - \alpha_{ij})^{n_{ij}} \exp\left(-\frac{E_{A,ij}}{RT}\right) \quad (6)$$

The pattern search algorithm in MATLAB [45] was applied to determine optimal kinetic parameters to fit the experimental data. The root mean square deviation (RMSD) is introduced as a metric to evaluate the model's accuracy by comparing the deviation of experimental and model results. The calculation of the RMSD of z datapoints from experimental mass loss $b_{\text{exp},k}$ and modeled mass loss $b_{\text{model},k}$ is described according to formula 7. In this study, the RMSD is determined for the mass loss in the temperature range of 313–1123 K with increments of 0.25 K.

$$\text{RMSD} = \sqrt{\frac{1}{z} \sum_k (b_{\text{exp},k} - b_{\text{model},k})^2} \quad (7)$$

Results and discussion

Pure polymers

Concerning the chemical recycling of plastics, the volatile pyrolysis products of condensed and permanent gases are of importance. Thus, instead of the mass loss curve, the temperature-related formation of volatiles is shown in Fig. 1. Volatile formation curves at a heating rate of 10 K min⁻¹ of the pure thermoplastics are displayed. However, these curves can be easily converted into mass loss curves using Eq. 5. The polymers heating rate-dependent onset temperature, respectively, for each degradation stage, can be sorted from low to high values as following:

$$\text{PA6 I} < \text{PVC I} < \text{PVC II} < \text{PS} < \text{ABS} < \text{PET} \\ < \text{PA6 II} < \text{PP} < \text{PVC III} < \text{LDPE} < \text{HDPE}$$

All polymers show a single-step degradation mechanism, except for PVC which features a three-step mechanism. Pyrolysis of PET and PVC leads to considerable coke formation of 12.0 mass% and 6.6 mass%, respectively. For ABS and PA6, minor solid amounts of 0.3 and 0.2 mass% are obtained. Coke formation of the other thermoplastics is neglectable since it accounts for less than 0.1 mass% in these investigations. In the variation of the heating rate from 2 to 40 K min⁻¹, no influence of the heating rate on the generated share of coke is identified.

The degradation shifts toward higher temperatures with increase in heating rates. This effect is often attributed to the phenomena of thermal lag. Thermal lag describes the delay of temperature measurement in the sample and the sensor due to thermal transport phenomena [46]. The effect is dependent on the device and the thermal properties of the sample, more precisely the thermal conductivity and heat capacity. Since the properties of the polymers are similar, the effect of thermal lag is comparable and mostly depends on the heating rate applied in the experiments. Because low heating rates are used, the time–temperature correlation is a more reasonable cause for the shift. At lower heating rates, the sample stays longer at a specific temperature. With the respective kinetic, the conversion is higher in the longer time interval. This results in the supposed shift of the curve to lower temperatures.

From the experimental dataset, kinetic parameters are derived according to the methodology of Zeller et al. [25]. The dataset including five heating rates was used for kinetic parameter determination with the pattern search algorithm. Table 2 lists the preexponential factor, activation energy, and reaction order. The reaction fraction of individual reactions in a multi-step degradation is also shown. The results match relevant literature [15, 22, 26, 47–51]. Except for the initial outgassing of PA6 and the third PVC stage, the reaction order varies between 0.9 and 1.1 for all polymers and degradation steps.

With the derived kinetic parameters, the degradation of pure plastics is modeled. In Fig. 1, experimental and modeled data are compared at a heating rate of 10 K min⁻¹. The data for the comparison at heating rates of 2, 5, 20, and 40 K min⁻¹ and the corresponding RMSD values can be found in the supplementary information. Additionally, the capability of model extrapolation was tested by comparing its results to data acquired in experiments with a heating rate of 100 K min⁻¹. Since the kinetic parameters are valid for a heating rate range from 2 to 40 K min⁻¹ differences are to be expected. The data and a summarizing figure are included in the supplementary information. For LDPE, PS, and ABS, the model shows a similar RMSD to the results in obtained at 2–40 K min⁻¹. For PET and PA6, the model

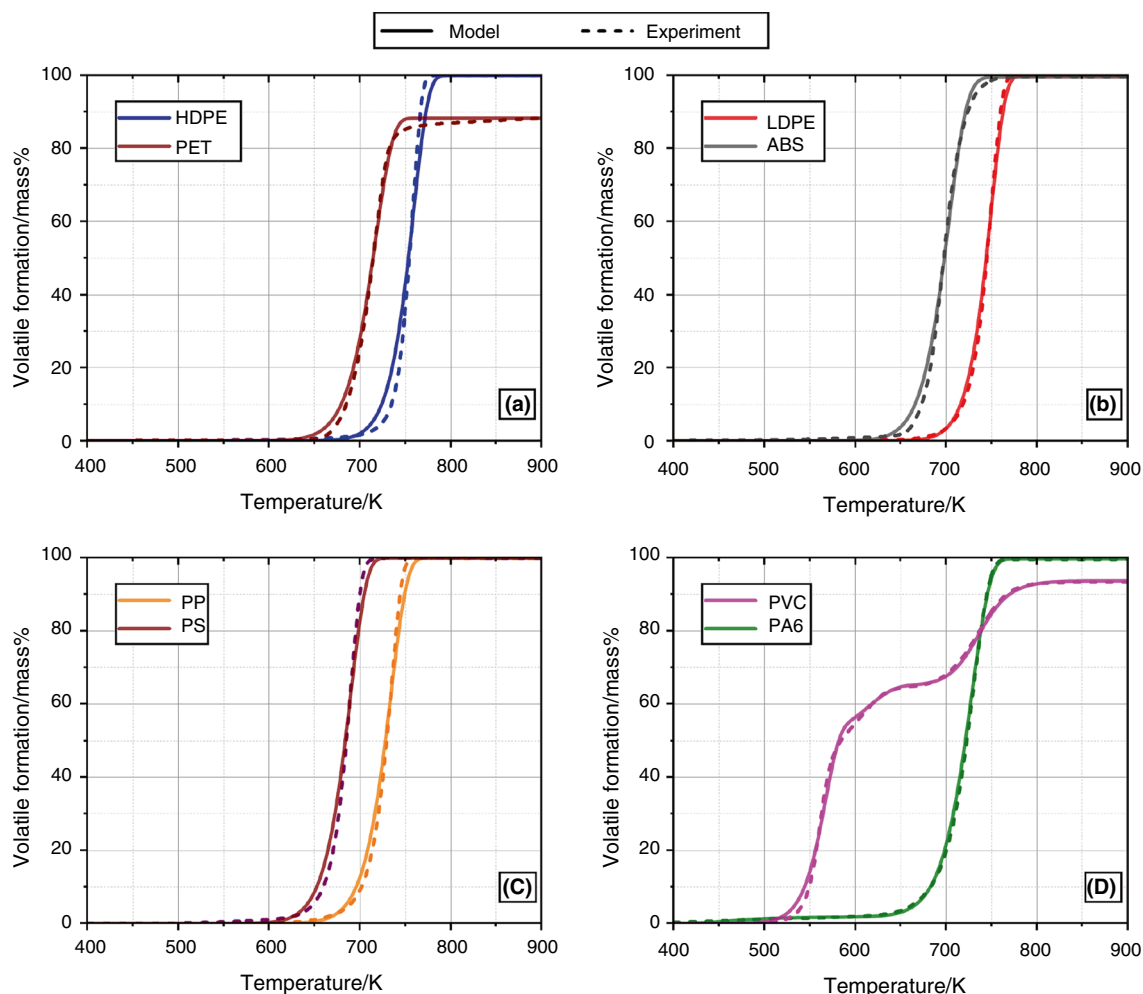


Fig. 1 Experimental and modeled volatile formation from particular sample of HDPE and PET **A**, LDPE and ABS **B**, PP and PS **C**, and PVC and PA6 **D** at a heating rate of 10 K min^{-1}

Table 2 Kinetic parameters derived from TG experiments of pure polymers at constant heating rates between 2 and 40 K min^{-1}

Polymer	Preexponential factor k_0/s^{-1}	Activation energy $E_A/\text{kJ}\cdot\text{mol}^{-1}$	Reaction order $n/$	Reaction fraction $q/$
LDPE	$3.80 \cdot 10^{17}$	281	0.94	1.00
HDPE	$8.31 \cdot 10^{16}$	275	0.94	1.00
PP	$3.32 \cdot 10^{14}$	233	0.94	1.00
PS	$6.37 \cdot 10^{13}$	209	0.94	1.00
ABS	$1.22 \cdot 10^{14}$	217	1.08	1.00
PET	$1.46 \cdot 10^{13}$	209	0.93	0.99
PA6 I	$2.11 \cdot 10^8$	92	3.00	0.02
PA6 II	$3.02 \cdot 10^{12}$	203	0.93	0.98
PVC I	$1.35 \cdot 10^{13}$	164	0.94	0.53
PVC II	$2.98 \cdot 10^6$	103	0.92	0.16
PVC III	$1.89 \cdot 10^{16}$	257	1.97	0.31

replicates the experimental results with minor deviations while PVC modeling exhibits more significant differences. These differences refer to the second degradation stage which compared to the first and third degradation stages of PVC is not replicated precisely. The model extrapolation to higher heating rates is therefore limited and depends on the polymer. In the heating rate validity range, the degradation of single-step pyrolyzing polymers is replicated well for the range of 10 to 90% of the conversion. The model accuracy is polymer dependent resulting in RMSD between 0.4 mass% (for PA6) and 2.2 mass% (HDPE). Most inaccuracies are present at the start and the end of the conversion, especially for HDPE, PET, ABS, and PS. The calculated initial mass loss of PA6 corresponds to the experimental data. For PVC, the first and the second degradation stages occur at temperatures between 520 and 620 K. Both, the first and the second stages overlap merging their transition. This effect is more pronounced in experiments than in the model and at lower heating rates. The RMSD for PVC is therefore

higher when comparing the model with experimental results with heating rates of 2 K min^{-1} (RMSD 1.7 mass%) and 40 K min^{-1} (RMSD 1.5 mass%) to the medium heating rate of 10 K min^{-1} (RMSD = 0.8). The third degradation step occurs at significantly higher temperatures over 700 K. This leads to a characteristic plateau at about 70 mass% mass loss independent of the heating rate. All stages are described well by the model. Consequently, this comparably straightforward model enables reliable simulation of pyrolytic mass loss in TG for all pure polymers in the validity range of heating rates over a broad range of the conversion process (approximately 10–90%). This may be explained by the underlying reaction mechanism. The radical degradation mechanisms require initiation reactions in the form of homolytic bond cleavage to generate the first radicals. The end of the mechanism is characterized by the recombination of radicals. In these phases, the reaction accelerates and slows down. In the conversion range of 10 to 90%, the reaction then reaches a stable level, as new radicals are generated, the main propagation phase takes place and free radicals recombine at the same time.

The influence of sample processing was investigated. Figure 2 exemplarily shows the comparison of different preprocessed LDPE and PET samples. Multiple tests with differently processed samples again emphasize the reproducibility of the experimental setup and no influence of the sample preparation with pure polymer experiments. The volatile formation curve and the final solid residue remain unchanged after shredding or extruding. The RMSD for differently prepared pure polymers is similar considering the margin of error. Short dwell time, cryo-cooling while shredding, and minimal extrusion temperatures prevent thermal degradation of the polymers or moisture-induced hydrolysis of PET during sample preparation [52]. Therefore, no influence of the sample preparation was present for LDPE and

PET. The same result was observed during testing HDPE, PP, PS, ABS, and PA6. Extrusion of PVC leads to significant changes in the polymer appearance which is why the experiments with extruded PVC are not conducted.

Binary polymer mixtures

The systematic study of binary mixtures reveals potential interaction effects during thermal degradation between the investigated polymers. To evaluate potential interaction, multiple criteria are considered. Interaction is proposed if the degradation of blends characterized by the volatile formation curve differs from model data and control experiments. For this purpose, the onset of the degradation mechanism, the completed conversion at characteristic temperatures, peak intensity, peaks in the differential volatile formation curves, or the solid residue mass is consulted.

The test matrix of 28 different polymer mixtures, each with three different mixing ratios, allows the polymers to be grouped. Three different groups for the investigated feedstocks are proposed. The groups are listed in Table 3. Polymers of the same group show similar behavior regarding interaction effects. In addition, exemplary mixtures with different sample homogeneity indicate influences of the polymer chain spatial proximity on the degradation.

Group I includes polymers with a chain backbone only composed of carbon–carbon bonds. This group consists of LDPE, HDPE, PP, PS, and ABS. Figure 3 shows exemplary curves of various binary blends within this group. As with the pure polymers, neglectable solid residue is formed in the mixtures of Group I. Similar to LDPE/PP blends, LDPE/HDPE, HDPE/PP, and PS/ABS also show a single-step degradation. The degradation occurs within the temperature range of the pure substance's degradation. It shifts with increase in concentration of the polymer toward its

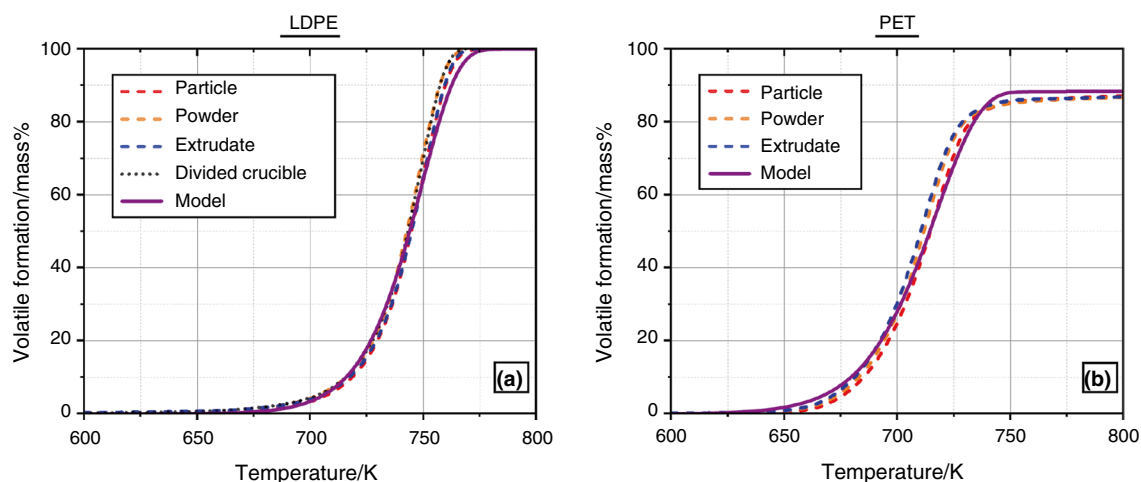


Fig. 2 Temperature-dependent volatile formation compared for differently prepared LDPE **A** and PET **B** samples at a heating rate of 10 K min^{-1}

Table 3 Proposed grouping of the investigated thermoplastics considering their degradation behavior and characteristic structure

	Polymers	Characteristic structure
Group I	LDPE, HDPE, PP, PS, ABS	Chain backbone of carbon–carbon bonds
Group II	PET, PA6	Chain backbone of carbon together with oxygen or nitrogen atoms
Group III	PVC	Carbon-containing chain backbone with multiple chlorine atoms as pendant groups

degradation curve. A mechanism with two strongly overlapping peaks can be assumed from the differential volatile formation curves in Fig. 3B. Those peaks serve as indicators of degradation stages. Multiple peaks emphasize the occurrence of multiple degradation stages which are also indicated by inflection points in the volatile formation curve. The RMSD of binary mixtures from polymers in Group I shows no or only minor deviations between the model and experimental results. Therefore, the model reproduces the curves in Fig. 3 well within the model deviations already evaluated with pure polymers.

The mixtures of HDPE/PS, HDPE/ABS, and LDPE/PS show a two-stage degradation with an inflection point. The temperature of the inflection point correlates closely with the mixing ratio. The volatile formation rate of these blends exhibits two different peaks correlating to each polymer as shown for LDPE/PS blends in Fig. 3. The first peak corresponds to the PS degradation, while the peak between 700 and 775 K can be attributed to LDPE. The onset of each polymer's degradation explains the partly varying shaped curves of the blends. If the onset temperature of the pure polymers is similar, as is the case with LDPE/PP, no stages emerge as a result of the proximity of differential TG peaks. Thus, inflection points in the volatile formation rate and an apparent two-stage mechanism only appear in plastic blends of polymers with a significant difference in the degradation onset temperature.

This result is confirmed by the data for LDPE/ABS, PP/PS, and PP/ABS. These blends show moderate differences in the onset temperature within polymer Group I. As depicted for PP/PS blends in Fig. 3, inflection points are only slightly pronounced and peaks in the volatile formation rate are overlapping. Nevertheless, two peaks corresponding to PS (650–725 K) and PP (700–760 K) are visible. In general, the inflection points indicate an independence of the individual polymer degradation within the mixture. In comparison with the superposition model, however, an acceleration of the polymer's degradation with a higher onset is evident, leading to slightly increased RMSD for LDPE/PP, LDPE/PS HDPE/PP, HDPE/PS, and PP/PS mixtures. Like with LDPE/PS, this acceleration is also more pronounced when the onset temperature varies significantly. This behavior can be attributed to the molecular structure and, thus, the degradation mechanisms. All polymers of Group I pyrolyze

via radical chain scission. This mechanism requires an initial reaction of homolytic bond cleavage. Aromatic or alkyl side groups stabilize these starting radicals, resulting in their formation at lower temperatures in PS, ABS, or PP than in HDPE or LDPE [16, 27]. Radicals from the earlier degrading component are present in the mixtures and may function as initial radicals for the degradation mechanism of the other component. The influence of the potential interaction interface on the degradation of LDPE/PS blends in a ratio of 50/50 is shown in Fig. 4. TG curves are shifted toward lower temperatures compared to samples of control experiments with the separated crucible compartments. This effect is indicated by the RMSD which is significantly lower for control experiments than for samples with a shared reaction room. The shift is comparable for all mixtures independently from sample preparation. With the mixing ratio of 50/50 mass%, this acceleration occurs at approximately 50% conversion rate. As a consequence, the model calculations are below the experimental results at the end of the degradation curve. However, the dependence of the TG curve on the onset temperature remains more pronounced than the sample preparation for Group I blends. Therefore, no clear dependency between the reaction acceleration and the proportions of the polymers in the mixture is evident. In conclusion, only minor interactions regarding the degradation kinetics were observed. These are characterized by a slight acceleration of the degradation reaction of the polymer with a higher onset temperature. Thus, the degradation is well described using the superposition model.

Group II is defined as consisting of polymers with additional heteroatoms in the chain backbone, like PET (oxygen) or PA6 (nitrogen). The volatile formation of these blends is shown in Fig. 5A. The blends exhibit differing degradation behavior compared to control experiments or linear postponed model results. The volatile formation in the temperature range from 695 to 775 K accounts for approx. 70 mass% in the model and the experiments with divided crucibles, while only 20% are formed below 629 K. In the particle, powder, and extruded samples, the volatile formation shifts to lower temperature exhibiting approx. 80 mass% of volatiles formed before reaching 695 K. This reaction acceleration of up to 60 K leads to a significant increase of the RMSD to 7.3 mass% to 11.6 mass%. Figure 5B shows a strong influence on the sample mixture intensity. The

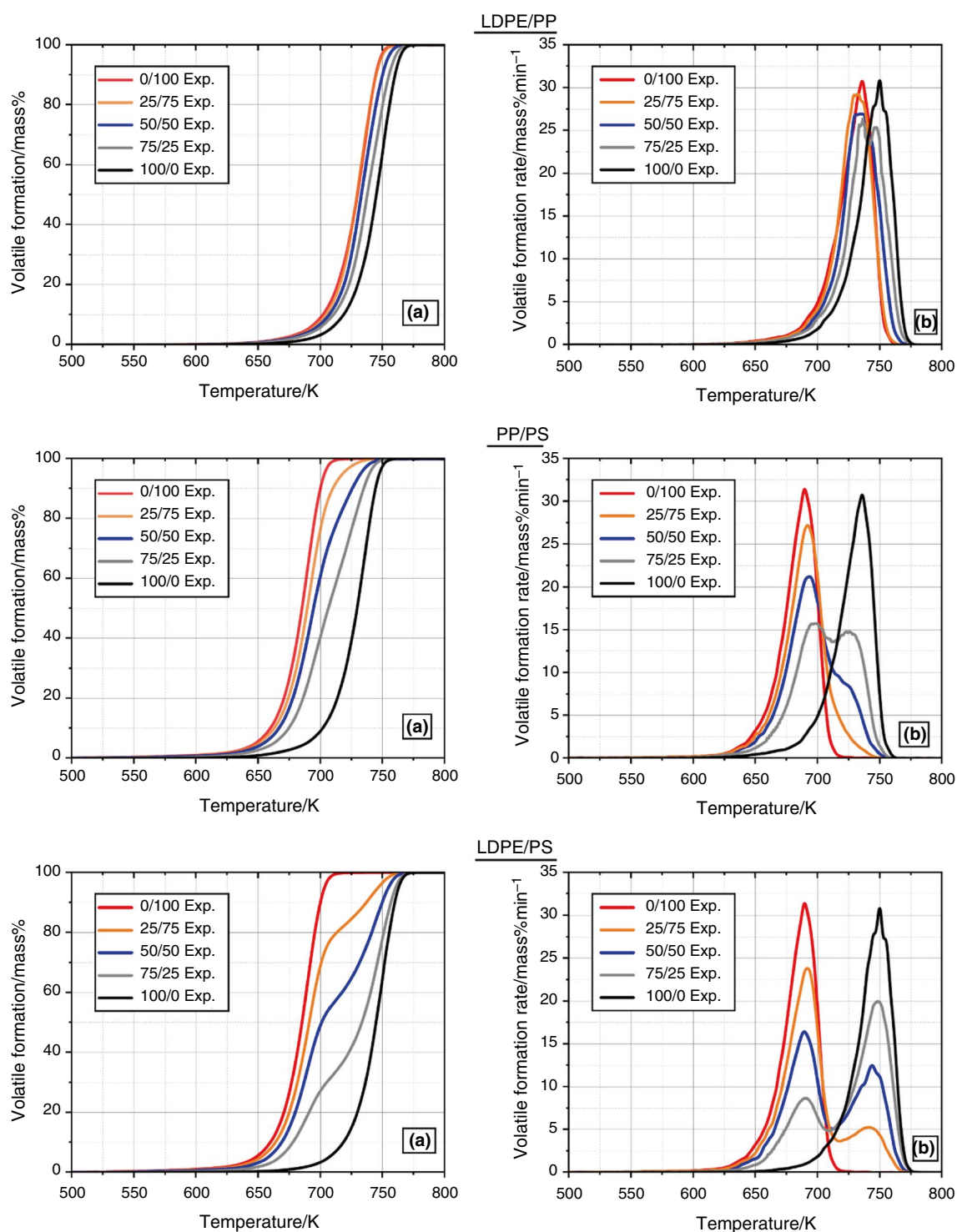


Fig. 3 Volatile formation **A** and its formation rate **B** of particular LDPE/PP, PP/PS, and LDPE/PS blends at mixing ratios 0/100, 25/75, 50/50, 75/25, and 100/0 mass% at a heating rate of 10 K min^{-1}

accelerated conversion is more pronounced for extrudates than for powders. In turn, the latter shows a stronger shift than the particles. Interactions of the polymers in the degradation intensify with increase in sample homogeneity and

thus the potential reaction interface of the polymers. Results of extruded, powdered, and particular blends of PA6 and PET differ significantly from the sample in separated crucible compartments of control experiments. This indicated

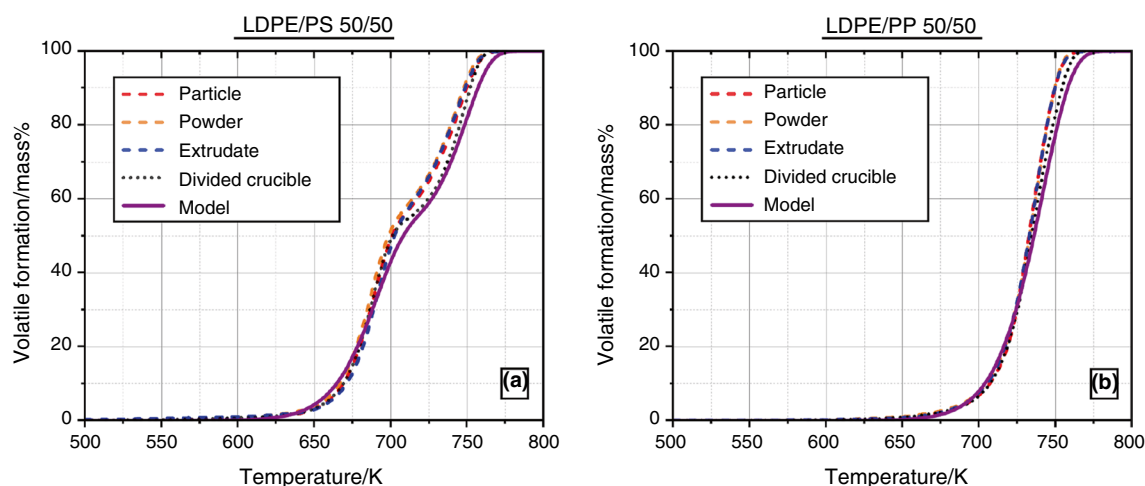


Fig. 4 Volatile formation in differently prepared LDPE/PS **A** and LDPE/PP **B** blend samples in the ratio of 50/50 mass% covering multiple homogeneity grades at a heating rate of 10 K min^{-1}

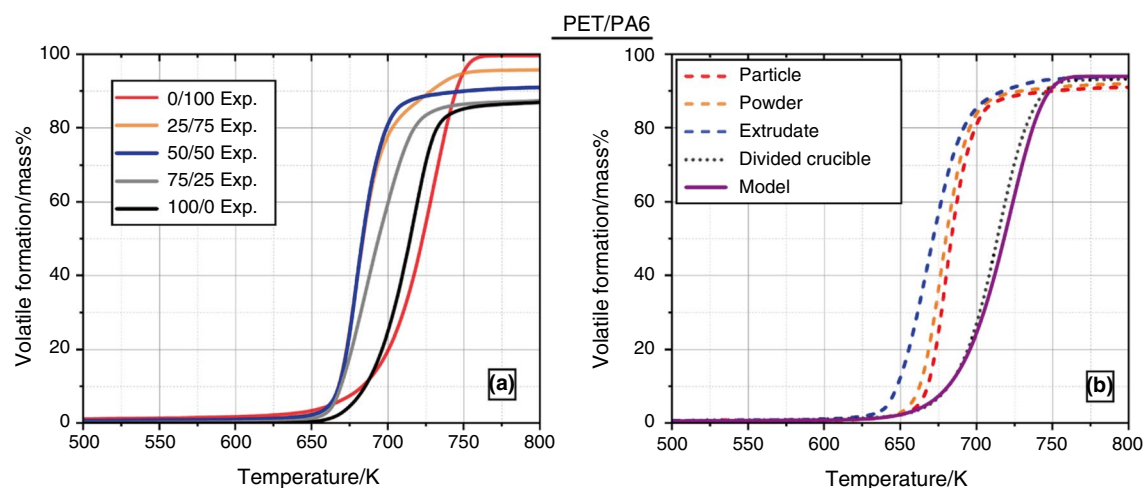


Fig. 5 Volatile formation from particular PET/PA6 mixtures in the ratio of 0/100, 25/75, 50/50, 75/25, and 100/0 mass% **A** and the comparison of the mixing intensity on 50/50 blends **B** at a heating rate of 10 K min^{-1}

significant interactions and changes in the degradation mechanism. The reaction mechanism of these polymers that involves intramolecular ionic transfer reactions resulting in carboxylic acids from PET degradation can therefore interfere with the mechanism of PA6 degradation [53]. Conversely, the presence of ϵ -caprolactam and the outgassing components of PA6 may accelerate PET degradation. As a result of the strong interactions, the superposition-based modeling of the degradation is not suitable for the mixture of PET/PA6. The data of the TG experiments only covering mass loss of the sample limit further analyses of the interaction and its mechanism.

Blends of PET/LDPE, PET/PS, and PA6/LDPE are exemplarily shown for blends of Group I and Group II in Fig. 6. Hardly any interactions occur in blends of PA6 and

Group I polymers. The RMSD between the experimental and modeled results of those polymers indicates high accuracy. The superposition approach is therefore considered to be valid. The selective degradation mechanism and degradation products of PA6 appear to only interact marginally with the radical mechanism of Group I polymers. For the volatile formation rate of PA6/LDPE blends in Fig. 6B, only one peak is detectable. This is attributed to the similar onset temperatures of both polymers. In blends with other Group I polymers, like HDPE or ABS two distinct overlapping peaks are noticeable. This reflects similar degradation behavior with a degradation onset dependency as identified for Group I blends.

With PET, which tends to form coke, different behavior is obtained. It degrades slightly faster in the presence of ABS

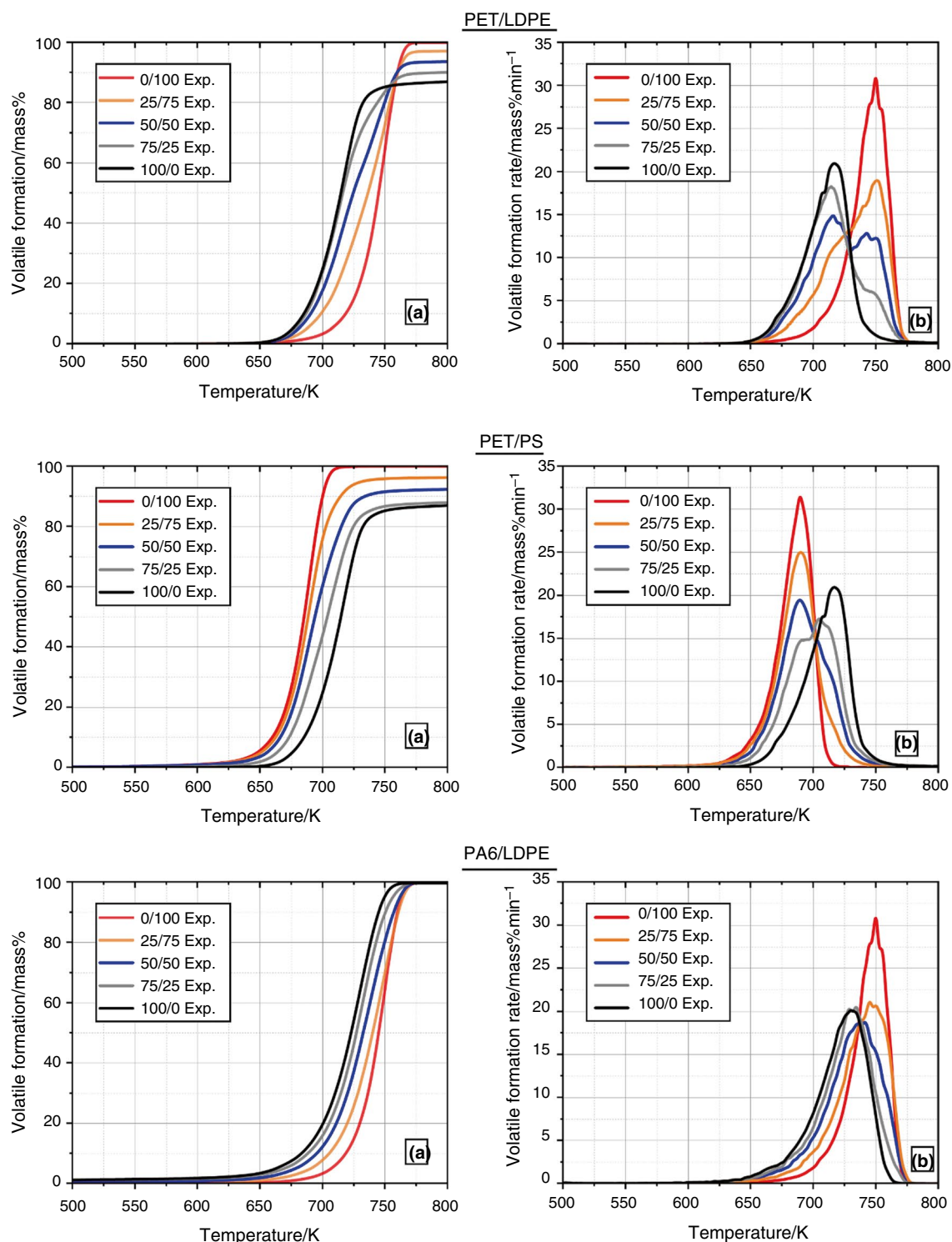


Fig. 6 Volatile formation **A** and its formation rate **B** from particular PET/LDPE, PET/PS, and PA6/LDPE blends in the ratio of 0/100, 25/75, 50/50, 75/25, and 100/0 mass% at a heating rate of 10 K min^{-1}

or PS. Both polymers have a lower onset of degradation. The solid residue mass is disproportionately increased in the blends as shown in Table 4. The coke formation tendency may be caused by coke precursors. These precursors usually

consist of unsaturated, cyclic compounds [54]. Styrene is the main product of PS and ABS [18, 55]. Presumably, the structure of styrene allows it to enhance interaction with the coke precursors formed in PET degradation. This may

lead to increased solid residue in blends of PET with PS and ABS. However, blends of PET with polyolefins differ from this observation. The somewhat earlier degradation of PET slightly accelerates the pyrolysis of LDPE, HDPE, and PP. The greater the onset temperature difference, the more pronounced becomes the effect. In contrast to PET blends with styrene-containing polymers, the residue mass corresponds approximately to the linear postponed value. The acceleration can be observed, especially with low PET contents.

The results shown in Fig. 7 indicate only a slight reaction kinetic-specific interaction between Group I polymers and PVC. Both, the first and second degradation stages of PVC remain unchanged as exemplarily described for PVC/LDPE and PVC/PS blends in the volatile formation curve. The modeled results represent the degradation of the first two stages accurately. Even though degradation curve modeling in this range appears correctly, the interaction effects emerge in the third degradation stage from 690 to 775 K. In this range, the degradation is delayed for both blends. Similar results were observed for other Group I polymers. The effect leads to slightly higher RMSD values for these binary mixtures, e.g., up to 3.8 mass% for LDPE/PVC or 3.7 mass% for PS/PVC.

Table 4 Comparison of solid residue mass of PET blends at 873 K determined experimentally with particle samples and calculated via superposition

Polymer blend/mass%		Experimental solid residue ^a mass%	Solid residue ¹⁾ by superposition/mass%
PET/LDPE	0/100	0.0 ± 0.07	0.0
	25/75	2.6 ^b	3.0
	50/50	5.9 ± 0.28	6.0
	75/25	9.2 ^b	9.0
	100/0	12.0 ± 0.29	12.0
PET/PS	0/100	0.0 ± 0.05	0.0
	25/75	3.5 ^b	3.0
	50/50	7.1 ± 0.31	6.0
	75/25	11.3 ^b	9.0
	100/0	12.0 ± 0.29	12.0
PET/ABS	0/100	0.3 ± 0.08	0.3
	25/75	3.8 ^b	3.2
	50/50	7.0 ± 0.05	6.2
	75/25	11.0 ± 0.10	9.1
	100/0	12.0 ± 0.29	12.0
PET/PVC	0/100	6.6 ± 0.38	6.6
	25/75	9.1 ^b	8.0
	50/50	10.0 ± 0.33	9.3
	75/25	11.2 ± 0.08	10.7
	100/0	12.0 ± 0.29	12.0

^aDetermined at 873 K with particular samples

^bStandard deviation not calculable

In addition to Fig. 7, the experimentally determined solid residue is compared to the amount of solid residue calculated via superposition in Table 5. For PVC/LDPE blends, the value matches. A significant increase of solid residue mass is evident for particle PVC/PS blends. Li et al. reported the degradation of the polyene chains to mono- or polyaromatic hydrocarbons and additionally coke in the third degradation stage of PVC. This coke is formed by restructuring the unsaturated polyene intermediates [54]. Styrene, with its aromatic ring and the allyl group bound to it, features a similar structure. Therefore, Dodson and McNeill conclude that the interaction of the PS degradation products with the PVC coke precursors leads to the delay in the third degradation step [56]. The reactive styrene is more likely to react with the polyenes to form coke in this stage than the long-chain paraffinic products of the polyolefins LDPE, HDPE, and PP. Nevertheless, also polyolefins share the effect of a minor reaction delay. The solid residue determined in ABS experiments supports this explanation. In ABS pyrolysis, styrene is also formed as main degradation product. ABS as a copolymer also contains acrylonitrile and butadiene structures. Therefore, a similar effect occurs as with PS, but to a reduced extent.

No dependence of the interactions on the potential polymer interface is identified by comparing particular and powder samples. It must be considered that PVC is only available as a powder for the experiments. The particular samples with PVC exhibit a more homogeneous blend as investigated for other blends. Therefore, differences are expected to be less prominent comparing these samples. Additionally, material homogenization processes such as diffusion may already occur before the effect becomes apparent at the end of the degradation reaction. Such processes could eliminate the influence of sample homogenization.

Distinct interactions become apparent in blends of PVC and the heteroatom-containing Group II polymers PET and PA6. The significant changes lead to high RMSD values, e.g., for PET/PVC of maximal 5.9 mass% and PA6/PVC of maximal 13.5 mass%. Consequently, the superposition approach is not valid for these binary mixtures. The characteristic three-stage mechanism of PVC is no longer visible. In contrast, the second degradation stage of PVC is more pronounced which is indicated by increasing volatile formation rates between 590 and 650 K in Fig. 8B. More sample reacts in this temperature range which shifts the typical plateau of PVC before the last degradation stage at about 690 K shown in Fig. 8A. This effect is underlined by the increased peak in the volatile formation rate at about 600 K. The rise from about 3 mass% min⁻¹ to a maximum of 7 mass% min⁻¹ is visible for all PVC/PET samples independently from the polymer proportions. In the volatile formation rate, elevated volatile formation rates in the temperature range of 600–675 K are present.

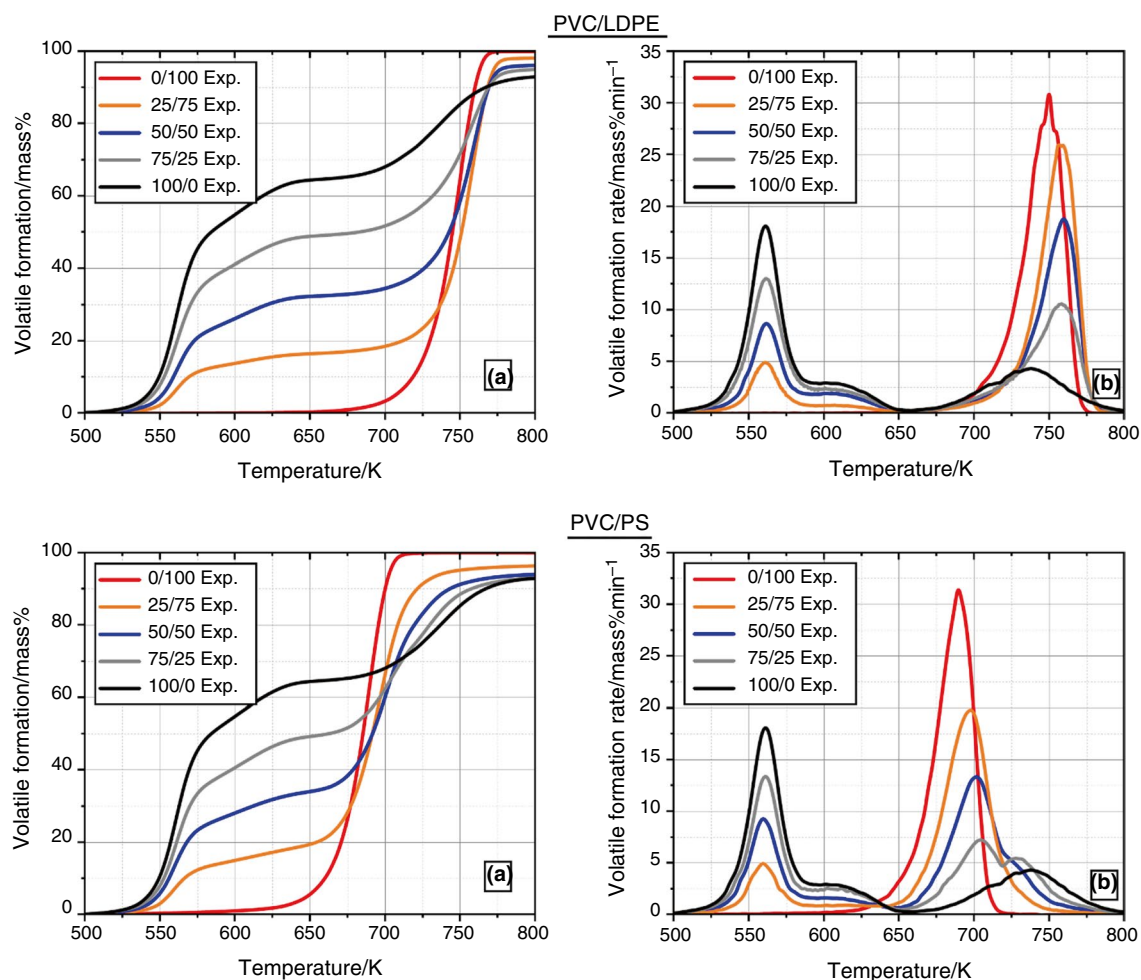


Fig. 7 Volatile formation **A** and its formation rate **B** from particular PVC/LDPE and PVC/PS blends in the ratio of 0/100, 25/75, 50/50, 75/25, and 100/0 mass% at a heating rate of 10 K min^{-1}

This confirms the conclusion of Chia et al. [57]. They report that HCl molecules formed in the primary degradation stage of PVC accelerate the degradation of PET. Considering the ionic degradation mechanism of PET and PA6, an interaction with HCl appears plausible. Yet, the start and end of the degradation of the mixtures remain predictable by model calculations. Solid residue formation increases disproportionately in the mixtures, similar to PS and PET blends. Intermediate products from polyene degradation and PET precursors may react to form new molecules, which form solid products as residues.

The volatile formation in Fig. 9 demonstrates deviating experimental results compared to modeled data and control experiments. While the RMSD of control experiments with model results is in the margin of error ($< 2 \text{ mass\%}$), the samples in a shared reaction room feature significant interactions. Strong acceleration of the reaction is evident. The volatile formation in the particle and powder samples of PVC/PET before 650 K accounts for approx. $50 \text{ mass\%}$, while it is

only $35 \text{ mass\%}$ in the model or the experiments with divided crucibles. Similar results are obtained with PA6/PVC blends. Approx. $60 \text{ mass\%}$ of volatiles are formed in the particle or powder samples. The experimental results with divided crucibles or the model results only show 35% of volatiles below 650 K . The acceleration in blends of Group II and PVC is slightly increased for the powders in comparison with the particle sample. Again, it has to be considered that PVC is provided as powder. Therefore, particular samples are assumed to vary less as the reaction interface is supposedly similar. In the case of PVC/PET, increased fluctuations in the individual measurements of powder and particle samples are observed. Therefore, a significant influence of the molecular proximity can neither be confirmed nor disproved for PVC/PET and PVC/PA6 blends in a ratio of $50/50 \text{ mass\%}$ at heating rates of 10 K min^{-1} within this study.

Table 5 Comparison of solid residue mass of PVC blends at 873 K determined experimentally with particle samples and calculated via superposition

Polymer blend/mass%		Experimental solid residue ^a mass%	Solid residue ^a by superposition/mass%
PVC/LDPE	0/100	0.0 ± 0.05	0.0
	25/75	1.8 ^b	1.7
	50/50	3.7 ± 0.15	3.3
	75/25	4.8 ± 0.10	5.0
	100/0	6.6 ± 0.38	6.6
PVC/PS	0/100	0.0 ± 0.04	0.0
	25/75	3.4 ^b	1.7
	50/50	5.7 ± 0.08	3.3
	75/25	6.6 ^b	5.0
	100/0	6.6 ± 0.38	6.6
PVC/ABS	0/100	0.3 ± 0.08	0.3
	25/75	2.7 ± 0.10	1.9
	50/50	4.4 ± 0.07	3.5
	75/25	6.1 ^b	5.0
	100/0	6.6 ± 0.38	6.6

^aDetermined at 873 K with particular samples^bStandard deviation not calculable

Complex polymer blends

The TG data of Mix 1 and Mix 2 allow validation of the effects found in the binary blend study in a more complex feedstock composition. As stated in Sect. “[Materials and experimental Methods](#)”, Mix 1 consists only of polymers from Group I. Those polymers show no significant interactions in binary mixtures. Therefore, their degradation in blends is assumed to be correctly modeled with the superposition approach. In contrast, Mix 2 contains all polymers investigated in this work. Significant deviations between the model and experiment are to be expected, considering the previously identified interactions of Group II polymers and PVC. A comparison of the modeled and the experimental volatile formation is shown in Fig. 10.

Both the experimental and modeled degradations of Mix 1 reveal similar results. The RMSD for the experiment of Mix 1 accounts for 1.3 mass%, indicating high modeling accuracy. The degradation starts at approximately 620 K

and ends at approximately 770 K. Minor differences in the degradation curves account for the uncertainties of different experiments and the model data. These results indicate that the model calculates reliable degradation kinetics in dynamic TG experiments for polymers in Group I. The effect of slightly accelerated polyolefin degradation induced by radicals of the PS or ABS degradation is visible. Nevertheless, neglectable polymer interaction in the degradation mechanism is identified for LDPE, HDPE, PP, PS, and ABS regarding the reaction kinetics. This validates the conclusions from the systematic study of binary mixtures.

The degradation modeling of Mix 2 needs to be evaluated at different curve sections. Comparable behavior is obtained at the beginning and the end of the degradation by experimental data and model calculations. The final degradation of the linear carbon backbone of polyolefin chains and the polyene intermediates of PVC is well described via superposition. The formation of solid residue in the experiment and the model is similar. The experiment reveals a somewhat higher solid residue in contrast to the model data. This effect was already observed with blends of PVC and PET with other polymers like PS. Between 590 and 670 K, a new peak in the volatile formation rate is present, leading to a significant acceleration of the volatile formation in the experiments. The third degradation section ranges from 670 to 725 K. This range possibly represents the degradation of PET, PA6, PS, and ABS. The RMSD for Mix 2 of 4.6 exceeds the margin of error and therefore indicates the significant interactions. Consequently, the model fails to represent the degradation correctly as a result of the interactions, for example, of the PVC intermediates with, PET or PA6. As expected, the superposition approach is inadequate for simulating the entire reaction process of such heteroatom-containing polymer blends. Nevertheless, the model correctly calculates the start and end of the degradation even for such a complex mixture with obvious interactions of polymers. Regarding the solid residue from the experiment, comparable but slightly lower coke formation is calculated. In general, the results of Mix 1 and Mix 2 confirm the transferability of the effects concluded from binary mixtures. A study on superposition-based modeling of pyrolysis energy demand shows comparable dependencies on the superposition approach toward comparable polymer mixtures [58].

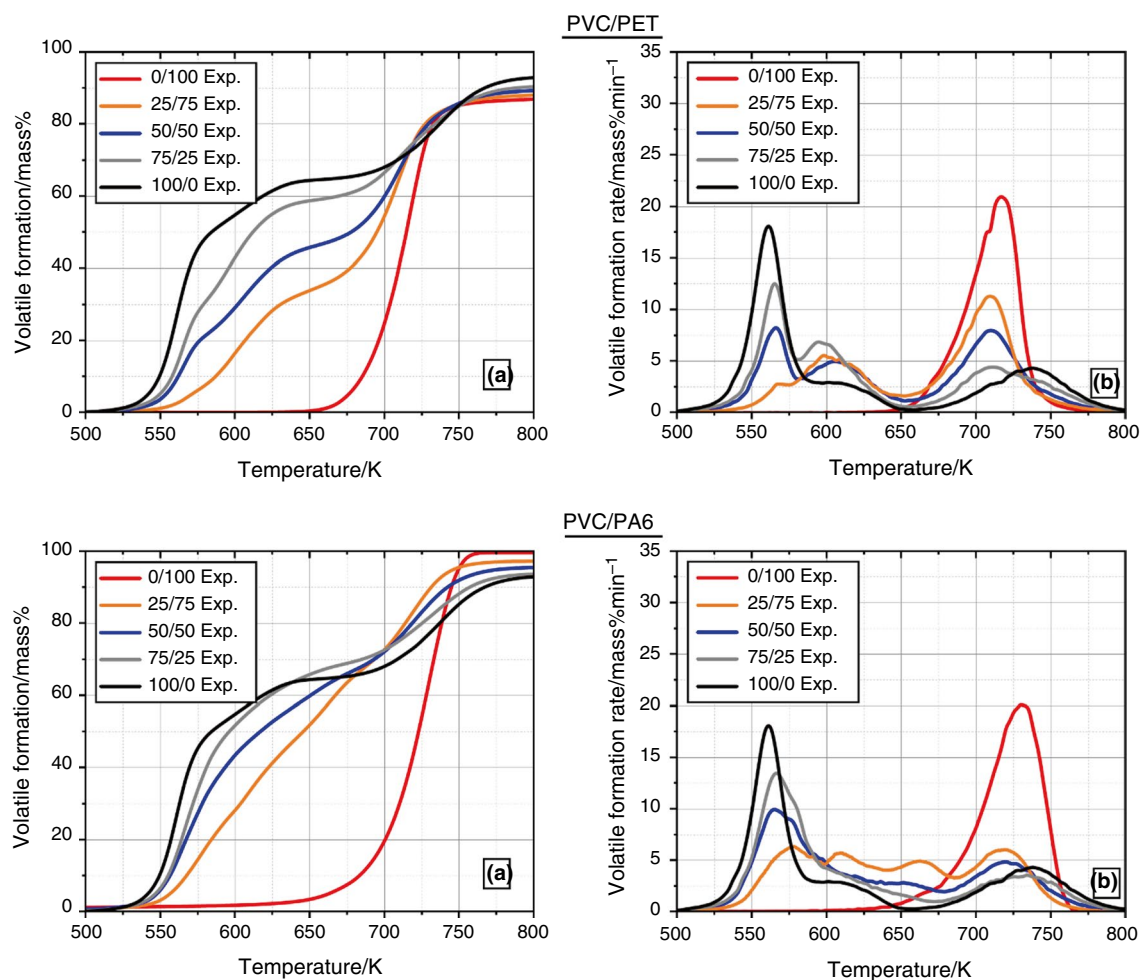


Fig. 8 Volatile formation **A** and its formation rate **B** from particular PVC/PET and PVC/PA6 blends in the ratio of 0/100, 25/75, 50/50, 75/25, and 100/0 mass% at a heating rate of 10 K min⁻¹

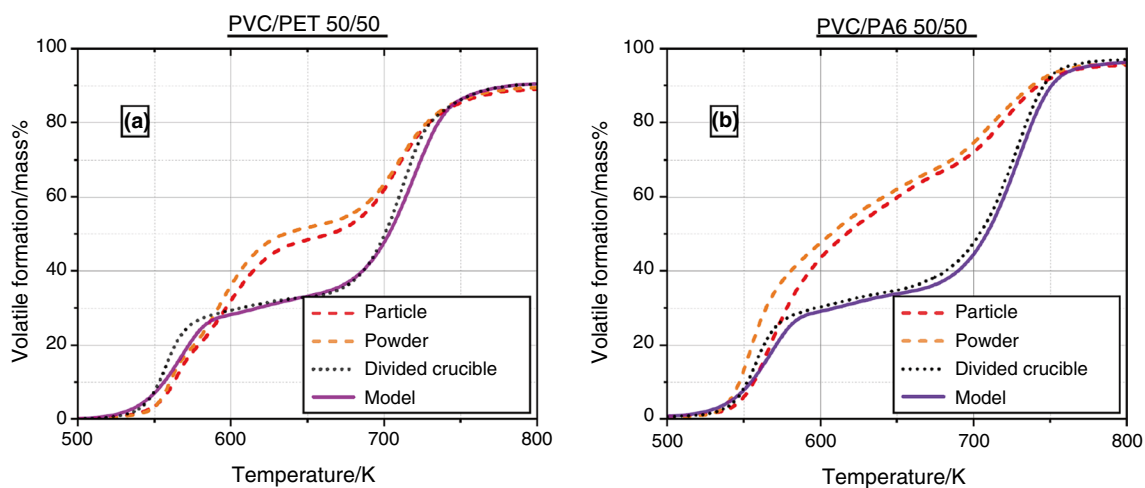


Fig. 9 Volatile formation of differently prepared PVC/PET **A** and PVC/PA6 **B** blend samples compared to modeled data in the ratio of 50/50 mass% at a heating rate of 10 K min⁻¹

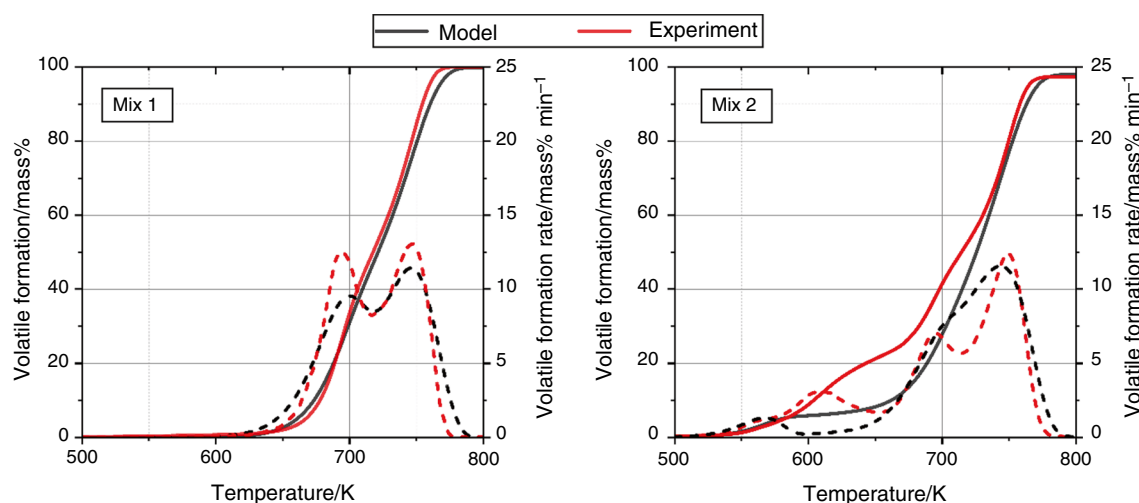


Fig. 10 Experimental and modeled volatile formation (continuous line) and volatile formation rate (dashed line) from the particular samples of Mix 1 and Mix 2 at a heating rate of 10 K min^{-1}

Conclusions

This systematic thermogravimetric study reveals different interaction effects and their significant dependency on the feedstock composition in the pyrolysis of mixed thermoplastics. From this, a grouping of thermoplastics depending on their chain structure is suggested. This chain structure, especially the type and location of heteroatoms, significantly influences the degradation mechanism. The interactions occur in the shared melt phase while degrading. Similar degradation mechanisms lead to comparable interaction effects of polymers in blends. The first group consisting of LDPE, HDPE, PP, PS, and ABS is characterized by a stable carbon–carbon chain backbone. In contrast, polymers in the second group contain heteroatoms in their main chain structure. Examples are the oxygenated ester bonds of PET and the nitrogen-containing peptide bonds of PA6. PVC represents an independent third group. Although PVC shares the carbon–carbon backbone of the first group polymers, the chlorine atoms exhibit electronegativity gradients of the bound side groups, leading to a differing degradation behavior. The observed polymer degradation interactions are group-dependent and lead to different effects of varying intensity. Increased coke formation and accelerated or delayed degradation reactions are observed in specific mixtures. Generally, the interactions are more pronounced with higher mixing homogeneity of the samples because of the increased potential interaction interface.

The evaluation of the model accuracy shows good accordance even though more complex polymer-specific models are expected to perform more precisely. The models' advantage mainly consists of the flexible adaptation to a multitude of thermoplastics while maintaining prediction quality. The

formation from thermoplastic blends of polymers featuring a carbon–carbon backbone is predicted well with the presented model. If heteroatom-containing polymers are present the occurring interactions change the degradation mechanisms.

Outlook

The study reveals further research demand for the characterization of interactions during the degradation of thermoplastic compounds. The precise identification of interaction reactions and reaction pathways requires comparative in-depth analyses of the resulting degradation products. For this purpose, experimental systems beyond thermogravimetry must be employed to overcome the methodological limitations of TG. Also, degradation intermediates and coke products should be analyzed in depth to characterize the interaction effects. Additional experimental methods (e.g., isothermal experiments) may contribute to evaluating the interaction dependencies in detail.

Various options for refining the superposition-based kinetic model are identified. In the case of interactions, a model adjustment in the form of an interaction term comparable to Hujuri et al. might be possible [36]. This model adjustment should allow for the simple implementation of further interaction effects. In addition, broadening the database by investigating further mixed plastic components, such as other polymer types, additives, or other waste components like biomass, would improve the prediction of complex plastic waste pyrolysis.

Supplementary Information

Two files provide more information on the comparison of the method of IPRM by Zeller et al. and the kinetic modeling of the virgin polymers by Kissinger–Akahira–Sunose method. File 1 shows activation energy and preexponential factor in dependence of the conversion rate of the pyrolysis reaction. File two provides the primary TG data which is the basis for the kinetic modeling. This SI file also shows eight additional figures that display the modeled and the primary experimental mass loss curves of each pure polymer (LDPE, HDPE, PP, PS, ABS, PET, PA6, and PVC) for different heating rates. Another file provides the data for the comparison of model results with experiments at 100 K min^{-1} . The fourth SI includes the RMSD values calculated for the entire experimental dataset and the corresponding model results generated in this study.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10973-024-13630-6>.

Author contributions N. Netsch was involved in conceptualization, experimental methodology, experimental investigation, methodology kinetic modeling, data curation, formal analysis, visualization, writing—original draft. L. Schröder helped in methodology kinetic modeling, modeling investigations, data curation, formal analysis, visualization. M. Zeller assisted in experimental methodology, kinetic modeling methodology, and review & editing. I. Neugber was involved in experimental investigation. D. Merz contributed to conceptualization, experimental methodology, resources, writing—review & editing. C. Klein helped in experimental methodology, resources. S. Tavakol was involved in funding acquisition, resources, supervision, writing—review & editing. D. Stapf was helped in funding acquisition, resources, supervision, writing—review & editing.

Funding Open Access funding enabled and organized by Projekt DEAL. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors and have therefore no relevant financial or nonfinancial interests to disclose.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Keijer T, Bakker V, Slootweg JV. Circular chemistry to enable a circular economy. *Nat Chem*. 2019. <https://doi.org/10.1038/s41557-019-0226-9>.
2. European Parliament and the Council. Establishing the framework for achieving climate neutrality and amending regulations (EC) No 401/2009 and (EU) 2018/1999 ("European Climate Law"), 2021. <https://eur-lex.europa.eu/eli/reg/2021/1119/oj>. Accessed 9 Aug 2024
3. Rahimi A, García JM. Chemical recycling of waste plastics for new materials production. *Nat Rev Chem*. 2017. <https://doi.org/10.1038/s41570-017-0046>.
4. Van Geem KM. Plastic waste recycling is gaining momentum. *Science*. 2023. <https://doi.org/10.1126/science.adj2807>.
5. Arena U, Ardolino F. Technical and environmental performances of alternative treatments for challenging plastics waste. *Resour Conserv Recycl*. 2022. <https://doi.org/10.1016/j.resconrec.2022.106379>.
6. Arena U, Parrillo F, Ardolino F. An LCA answer to the mixed plastics waste dilemma: energy recovery or chemical recycling? *Waste Manage*. 2023. <https://doi.org/10.1016/j.wasman.2023.10.011>.
7. Volk R, Stallkamp C, Steins JJ, Yogish SP, Müller RC, Stapf D, Schultmann D. Techno-economic assessment and comparison of different plastic recycling pathways: a German case study. *J Ind Ecol*. 2021. <https://doi.org/10.1111/jiec.13145>.
8. Keller F, Voss RL, Lee RP, Meyer B. Life cycle assessment of global warming potential of feedstock recycling technologies: case study of waste gasification and pyrolysis in an integrated inventory model for waste treatment and chemical production in Germany. *Resour Conserv Recycl*. 2022. <https://doi.org/10.1016/j.resconrec.2021.106106>.
9. Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Sci Adv*. 2017. <https://doi.org/10.1126/sciadv.1700782>.
10. Lase IS, Tonini D, Caro D, Albizzati PF, Cristóbal J, Roosen M, Kusenbergh M, Ragaert K, Van Geem KM, Dewulf J, De Meester S. How much can chemical recycling contribute to plastic waste recycling in Europe? An assessment using material flow analysis modeling. *Resour Conserv Recycl*. 2023. <https://doi.org/10.1016/j.resconrec.2023.106916>.
11. Ragaert K, Delva L, Van Geem KM. Mechanical and chemical recycling of solid plastic waste. *Waste Manage*. 2017. <https://doi.org/10.1016/j.wasman.2017.07.044>.
12. Lase IS, Bashirgonbadi A, Van Rhijn F, Dewulf J, Ragaert K, Delva L, Roosen M, Brandsma M, Langen M, De Meester S. Material flow analysis and recycling performance of an improved mechanical recycling process for post-consumer flexible plastics. *Waste Manage*. 2022. <https://doi.org/10.1016/j.wasman.2022.09.002>.
13. Brouwer MT, Van Thoden Velzen EU, Ragaert K, Ten Klooster R. Technical limits in circularity for plastic packages. *Sustainability*. 2020. <https://doi.org/10.3390/su122310021>.
14. PlasticsEurope, Plastics—The facts 2021. An analysis of European plastics production, demand and waste data, Brussels, 2022. <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/>. Accessed 9 Aug 2024
15. Bockhorn H, Hornung A, Hornung U, Schawaller U. Kinetic study on the thermal degradation of polypropylene and polyethylene. *J Anal Appl Pyrolysis*. 1999. [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4).
16. Faravelli T, Pincirolì M, Pisano F, Bozzano G, Dente M, Ranzi E. Thermal degradation of polystyrene. *J Anal Appl Pyrolysis*. 2001. [https://doi.org/10.1016/S0165-2370\(00\)00159-5](https://doi.org/10.1016/S0165-2370(00)00159-5).
17. Wall LA, Straus S. Pyrolysis of polyolefins. *J Polym Sci*. 1960. <https://doi.org/10.1002/pol.1960.1204414404>.
18. Suzuki M, Wilkie CA. The thermal degradation of acrylonitrile-butadiene-styrene terpolymer as studied by TGA/FTIR. *Polym Degrad Stab*. 1995. [https://doi.org/10.1016/0141-3910\(94\)00122-O](https://doi.org/10.1016/0141-3910(94)00122-O).

19. Jenekhe SA, Lin JW, Sun B. Kinetics of the thermal degradation of polyethylene terephthalate. *Thermochim Acta*. 1983. [https://doi.org/10.1016/0040-6031\(83\)80283-4](https://doi.org/10.1016/0040-6031(83)80283-4).
20. Montaudo G, Puglisi C, Samperi F. Primary thermal degradation mechanisms of PET and PBT. *Polym Degrad Stab*. 1993. [https://doi.org/10.1016/0141-3910\(93\)90021-A](https://doi.org/10.1016/0141-3910(93)90021-A).
21. Straus S, Wall LA. Pyrolysis of polyamides. *J Res Natl Inst Stand*. 1958;60:39–45.
22. Bockhorn H, Hornung A, Hornung U, Weichmann J. Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods. *Thermochim Acta*. 1999. [https://doi.org/10.1016/S0040-6031\(99\)00151-3](https://doi.org/10.1016/S0040-6031(99)00151-3).
23. Yu J, Sun L, Ma C, Qiao Y, Yao H. Thermal degradation of PVC: a review. *Waste Manage*. 2016. <https://doi.org/10.1016/j.wasman.2015.11.041>.
24. Marongiu A, Faravelli T, Bozzano G, Dente M, Ranzi E. Thermal degradation of poly(vinyl chloride). *J Anal Appl Pyrolysis*. 2003. [https://doi.org/10.1016/S0165-2370\(03\)00024-X](https://doi.org/10.1016/S0165-2370(03)00024-X).
25. Zeller M, Garbev K, Weigel L, Saatzer T, Merz D, Tavakkol S, Stapf D. Thermogravimetric studies, kinetic modeling and product analysis of the pyrolysis of model polymers for technical polyurethane applications. *J Anal Appl Pyrolysis*. 2023. <https://doi.org/10.1016/j.jaap.2023.105976>.
26. Aboulkas A, El Harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. *Energy Conv Manage*. 2010. <https://doi.org/10.1016/j.enconman.2009.12.017>.
27. Westerhout RWJ, Kuipers JAM, Van Swaaij WPN. Experimental determination of the yield of pyrolysis products of polyethene and polypropene: influence of reaction conditions. *Ind Eng Chem Res*. 1998. <https://doi.org/10.1021/ie970384a>.
28. Costa P, Pinto F, Ramos AM, Gulyurtlu I, Cabrita I, Bernardo MS. Study of the pyrolysis kinetics of a mixture of polyethylene, polypropylene, and polystyrene. *Energy Fuels*. 2010. <https://doi.org/10.1021/ef101010n>.
29. Faravelli T, Bozzano G, Colombo M, Ranzi E, Dente D. Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *J Anal Appl Pyrolysis*. 2003. [https://doi.org/10.1016/S0165-2370\(03\)00058-5](https://doi.org/10.1016/S0165-2370(03)00058-5).
30. Wu J, Chen T, Luo X, Han D, Wang Z, Wu J. TG/FTIR analysis on co-pyrolysis behavior of PE, PVC and PS. *Waste Manage*. 2014. <https://doi.org/10.1016/j.wasman.2013.12.005>.
31. Genuino HC, Pilar Ruiz M, Heeres HJ, Kersten SRA. Pyrolysis of mixed plastic waste: predicting the product yields. *Waste Manage*. 2023. <https://doi.org/10.1016/j.wasman.2022.11.040>.
32. La Mantia FP, Morreale M, Botta L, Mistretta MC, Ceraulo M, Scaffaro R. Degradation of polymer blends: a brief review. *Polym Degrad Stab*. 2017. <https://doi.org/10.1016/j.polymdegradstab.2017.07.011>.
33. Pek WK, Ghosh UK. Effect of binary mixture of waste plastics on the thermal behavior of pyrolysis process. *Environ Prog Sustain Energy*. 2015. <https://doi.org/10.1002/ep.12087>.
34. Chowlu ACK, Reddy PK, Ghoshal AK. Pyrolytic decomposition and model-free kinetics analysis of mixture of polypropylene (PP) and low-density polyethylene (LDPE). *Thermochim Acta*. 2009. <https://doi.org/10.1016/j.tca.2008.12.004>.
35. Klaimy S, Lamonier JF, Casetta M, Heymans S, Duquesne S. Recycling of plastic waste using flash pyrolysis—Effect of mixture composition. *Polym Degrad Stab*. 2021. <https://doi.org/10.1016/j.polymdegradstab.2021.109540>.
36. Hujuri U, Ghoshal AK, Gumma S. Modeling pyrolysis kinetics of plastic mixtures. *Polym Degrad Stab*. 2008. <https://doi.org/10.1016/j.polymdegradstab.2008.07.006>.
37. Miranda R, Pakdel H, Roy C, Vasile C. Vacuum pyrolysis of commingled plastics containing PVC II product analysis. *Polym Degrad Stab*. 2001. [https://doi.org/10.1016/S0141-3910\(01\)00066-0](https://doi.org/10.1016/S0141-3910(01)00066-0).
38. Tuffi R, D'Abramo S, Cafiero LM, Trinca E, Vecchio CS. Thermal behavior and pyrolytic degradation kinetics of polymeric mixtures from waste packaging plastics. *Express Polym Lett*. 2018. <https://doi.org/10.3144/expresspolymlett.2018.7>.
39. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta*. 2011. <https://doi.org/10.1016/j.tca.2011.03.034>.
40. Capone C, Di Landro L, Inzoli F, Penco M, Sartore L. Thermal and mechanical degradation during polymer extrusion processing. *Polym Eng Sci*. 2007. <https://doi.org/10.1002/pen.20882>.
41. Schweighuber A, Felgel-Farnholz A, Bögl T, Fischer J, Buchberger W. Investigations on the influence of multiple extrusion on the degradation of polyolefins. *Polym Degrad Stab*. 2021. <https://doi.org/10.1016/j.polymdegradstab.2021.109689>.
42. Jomaa G, Goblet P, Coquelet C, Morlot V. Kinetic modeling of polyurethane pyrolysis using non-isothermal thermogravimetric analysis. *Thermochim Acta*. 2015. <https://doi.org/10.1016/j.tca.2015.05.009>.
43. Gotor FJ, Criado JM, Malek J, Koga N. Kinetic analysis of solid-state reactions: the universality of master plots for analyzing isothermal and nonisothermal experiments. *J Phys Chem*. 2000;104:10777–82. <https://doi.org/10.1021/jp0022205>.
44. Criado JM. Kinetic analysis of DTG data from master curves. *Thermochim Acta*. 1978. [https://doi.org/10.1016/0040-6031\(78\)85151-X](https://doi.org/10.1016/0040-6031(78)85151-X).
45. The MathWorks Inc. Global optimization toolbox user's guide. 2023. <https://de.mathworks.com/help/gads/direct-search.html>. Accessed 9 Aug 2024.
46. Al-Salem SM, Antelava A, Constantinou A, Manos G, Dutta A. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *J Environ Manage*. 2017. <https://doi.org/10.1016/j.jenvman.2017.03.084>.
47. Encinar JM, González JF. Pyrolysis of synthetic polymers and plastic wastes: kinetic study. *Fuel Process Tech*. 2008. <https://doi.org/10.1016/j.fuproc.2007.12.011>.
48. Knümann R, Bockhorn H. Investigation of the kinetics of pyrolysis of PVC by TG-MS-Analysis. *Combust Sci Tech*. 1994. <https://doi.org/10.1080/00102209408951877>.
49. Marcilla A, Beltrán M. Thermogravimetric kinetic study of poly(vinyl chloride) pyrolysis. *Polym Degrad Stab*. 1995. [https://doi.org/10.1016/0141-3910\(95\)00050-V](https://doi.org/10.1016/0141-3910(95)00050-V).
50. Yang J, Miranda R, Roy C. Using the DTG curve fitting method to determine the apparent kinetic parameters of thermal decomposition of polymers. *Polym Degrad Stab*. 2001. [https://doi.org/10.1016/S0141-3910\(01\)00129-X](https://doi.org/10.1016/S0141-3910(01)00129-X).
51. Wu CH, Chang CY, Hor JL, Shih SM, Chen LW, Chang FW. On the thermal treatment of plastic mixtures of MSW: pyrolysis kinetics. *Waste Manage*. 1993. [https://doi.org/10.1016/0956-053X\(93\)90046-Y](https://doi.org/10.1016/0956-053X(93)90046-Y).
52. Nait-Ali LK, Colin X, Bergeret A. Kinetic analysis and modelling of PET macromolecular changes during its mechanical recycling by extrusion. *Polym Degrad Stab*. 2011. <https://doi.org/10.1016/j.polymdegradstab.2010.11.004>.
53. Lüderwald I, Aguilera C. Catalytic degradation of polymers, 2. Nylon 6. *Makromol Chem Rapid Commun*. 1982. <https://doi.org/10.1002/marc.1982.030030516>.
54. Li D, Lei S, Wang P, Zhong L, Ma W, Chen G. Study on the pyrolysis behaviors of mixed waste plastics. *Renew Energy*. 2021;173:662–74. <https://doi.org/10.1016/j.renene.2021.04.035>.
55. Faravelli T, Bozzano G, Scassa G, Perego M, Fabini S, Ranzi E, Dente M. Gas product distribution from polyethylene pyrolysis. *J Anal Appl Pyrolysis*. 1999. [https://doi.org/10.1016/S0165-2370\(99\)00032-7](https://doi.org/10.1016/S0165-2370(99)00032-7).

56. Dodson B, McNeill IC. Degradation of polymer mixtures: VI. Blends of poly (vinyl chloride) with polystyrene. *J Polym Sci Polym Chem*. 1976. <https://doi.org/10.1002/pol.1976.170140208>.
57. Chia JWF, Sawai O, Nunoura T. Reaction pathway of poly(ethylene) terephthalate carbonization: decomposition behavior based on carbonized product. *Waste Manage*. 2020. <https://doi.org/10.1016/j.wasman.2020.04.035>.
58. Netsch N, Zeller M, Richter F, Bergfeldt B, Tavakkol S, Stapf D. Energy demand for pyrolysis of mixed thermoplastics and waste plastics in chemical recycling: model prediction and pilot-scale validation. *ACS Sustain Resour Manage*. 2024. <https://doi.org/10.1021/acssusresmg.4c00109>.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Authors and Affiliations

N. Netsch¹  · L. Schröder¹ · M. Zeller¹  · I. Neugber¹ · D. Merz¹  · C. O. Klein²  · S. Tavakkol¹  · D. Stapf¹ 

✉ N. Netsch
Niklas.Netsch@kit.edu

S. Tavakkol
Salar.Tavakkol@kit.edu

² Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

¹ Institute for Technical Chemistry (ITC), Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany



Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography

Niklas Netsch^{*}, Luca Weigel, Tim Schmedding, Michael Zeller, Britta Bergfeldt, Grazyna Straczewski, Salar Tavakkol^{*}, Dieter Stapf

Institute for Technical Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Keywords:

Chemical recycling
Plastic pyrolysis
Thermoplastics
Pyrolysis oil
Two-dimensional gas chromatography
GC×GC
NMR

ABSTRACT

Pyrolysis oils are the crucial link between waste and chemicals in plastic recycling via pyrolysis. Oils from mixed plastic waste pyrolysis are complex mixtures of organic compounds typically containing impurities of nitrogen, oxygen, and chlorine. Therefore, their characterization is challenging. This study presents a tailored two-dimensional gas chromatography method supporting in-depth analysis of the chemical composition. It covers a boiling range from the naphtha cut to the middle distillate. These fractions represent the preferred feedstocks to be substituted by plastic pyrolysis oils in the future. The oil characterization is complemented by elemental analyses, nuclear magnetic resonance spectroscopy, and simulated distillation. The enhanced separation by two-dimensional chromatography results in significantly higher resolution than conventional one-dimensional methods. The most relevant oil compounds can be clustered, distinguished, and quantified based on compound grouping. Depending on the boiling range of the pyrolysis oils, 77 wt% to 96 wt% of the sample composition can be elucidated. Detecting main heteroatom-containing species such as benzoic acid, ϵ -caprolactam, acetophenone, and various aromatic nitriles provides detailed information for further pyrolysis oil utilization. The combination of the developed method with common analyses offers an advanced approach to evaluate the reintegration of contaminated mixed plastics oils into existing petrochemical value chains.

1. Introduction

Pyrolysis oils are essential in the pyrolytic recycling of plastic waste, linking waste management and the chemical industry in a circular economy framework [1,2]. Within this framework, chemical recycling provides complementary pathways for mechanically non-recyclable waste fractions. Fluctuating waste compositions and complex pyrolysis reaction mechanisms cause a versatile chemical composition of the pyrolysis oils [3]. This composition has a decisive influence on the feasibility of integration routes. Thus, a variety of fossil-based petrochemical product fractions can be substituted in a circular carbon economy [4]. Established petrochemical processes such as steam cracking, fluid catalytic cracking, hydrocracking, and gasification offer promising integration possibilities [5–7]. However, the properties of pyrolysis oils

must conform to fossil-based specifications of commonly used product fractions, e.g., naphtha, middle distillates, or vacuum gas oil (VGO) [8,9]. The strict specifications relate to the boiling behavior, as well as heteroatom impurities, e.g., sulfur, oxygen, nitrogen, and halogens, but also organic product components such as unsaturated hydrocarbons (HC) in the form of olefins, dienes, and aromatics [9]. However, plastic pyrolysis oils contain other compound groups in relevant quantities, extending the product spectrum to be investigated. As Kusenberg et al. conclude, comprehensive pyrolysis oil characterization requires complementary analytical methods [9]. Elemental analysis provides integral quantification of the content of carbon, hydrogen, and heteroatoms. Information on chemical structures in the pyrolysis oil, though, remains elusive [9]. This also applies, for example, to distillation or size exclusion chromatography [10,11]. Other analyses of physical and chemical

Abbreviations: ABS, Acrylonitrile butadiene styrene copolymer; GC×GC, Two-dimensional gas chromatography; FBP, Final boiling point; FID, Flame ionization detector; H/C, Hydrogen to carbon ratio; HC, Hydrocarbon; IBP, Initial boiling point; LDPE, Low-density polyethylene; MS, Mass spectrometer; NCD, Nitrogen chemiluminescence detector; NMR, Nuclear magnetic resonance spectroscopy; PA6, Polyamide 6; PCW, Post-consumer waste; PET, Polyethylene terephthalate; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl chloride; SSL, Split/Splitless injector; TMS, Tetramethylsilane; VGO, Vacuum gas oil.

^{*} Corresponding authors.

E-mail addresses: Niklas.Netsch@kit.edu (N. Netsch), Michael.Zeller@kit.edu (M. Zeller), Britta.Bergfeldt@kit.edu (B. Bergfeldt), Grazyna.Straczewski@kit.edu (G. Straczewski), Salar.Tavakkol@kit.edu (S. Tavakkol), Dieter.Stapf@kit.edu (D. Stapf).

<https://doi.org/10.1016/j.fuproc.2025.108359>

Received 9 September 2025; Received in revised form 19 October 2025; Accepted 30 October 2025

Available online 14 November 2025

0378-3820/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

properties, such as viscosity, density, ignition temperature, calorific value, and flash point, tend to play a subordinate role in the reintegration, as their relevance is mainly focused on certain technical applications [2].

Comprehensive spectroscopic and chromatographic analysis methods are therefore essential for structural information. Proton and carbon nuclear magnetic resonance spectroscopy (NMR) [12,13] and infrared spectroscopy [14,15] are often used to determine the chemical structure of pyrolysis products. They enable the integral identification and quantification of bond types occurring in the pyrolysis samples. This allows the detection of heteroatomic bonds and the differentiation between aromatic, paraffinic, or olefinic constitution. Potential applications include quality control based on product fingerprint comparisons, as shown by Diehl and Randel for diesel and gasoline [16]. However, the complexity and variety of chemical structures in pyrolysis oils, however, is higher than in diesel or gasoline fractions. This often impedes the identification of specific compounds in the mixture. Chromatographic techniques enable this determination. They are frequently performed as gas chromatography in combination with mass spectrometers (MS) or flame ionization detectors (FID). An MS setup is used in multiple studies for the identification of unknown compounds in the pyrolysis oil to optimize the pyrolysis process [17–20]. A FID setup allows for the quantification of main components in the pyrolysis oils, which is needed to evaluate chemical recycling pathways or optimize process parameters [21,22]. The complex matrix of the pyrolysis oils often causes co-elution, resulting in uncertainties that can be eliminated by the improved separation performance of two-dimensional gas chromatography (GC×GC) [23]. In addition, GC×GC enables a group-based evaluation of the chemical composition [9]. These advantages have already been successfully demonstrated for fossil-based petrochemical products, for example, polyaromatic HCs, crude oil fractions, VGO, or light and middle distillate [24–27]. The combination of a time-of-flight MS with a GC×GC setup can significantly enhance the characterization of pyrolysis oil derived from biomass [28]. In recent years, various GC×GC configurations were developed as advanced analytical options for plastic pyrolysis oil analysis. In high-temperature GC×GC, metallic columns are used, which allow resolution of the range of high-boiling waxes of polyethylene-based oils up to C₇₅ [29–32]. Most GC×GC applications are tailored to naphtha and middle distillate ranges (C₅ to approx. C₃₅) by implementing fused-silica columns for less wax-forming plastics [15,33–37]. In addition to FID and MS, GC×GC, coupled to sulfur or nitrogen chemiluminescence detectors (NCD), is popular to investigate corresponding heteroatom-containing HCs [32,34,38]. To gain qualitative information, investigations were performed for chlorinated HCs by high-resolution GC×GC–MS [39]. The application of micro pyrolyzers coupled to GC×GC for studies on the thermal degradation behavior of pure plastics and plastic waste is also established [23,40,41].

However, the reported methods focus on classifying paraffins, iso-paraffins, olefins, naphthenes, and aromatics (PIONA analysis) for narrow distillation cuts, for example, pyrolysis oil-derived naphtha or gasoline [34]. HCs containing heteroatoms are usually not covered or are only detected using complementary GC×GC analyses with element-specific detectors. Simplifying the calibration effort, the quantification of different oil components is performed on the principle of equal response factors. The structural differences between and within the compound groups comprised in the pyrolysis oil are expected to cause relevant deviations in the response factors. Using the conversion factors derived from only few specific standards may lead to systematic discrimination.

Therefore, this study presents a method on an advanced GC×GC–FID–MS–NCD system for the analysis of pyrolysis oils from different thermoplastic feedstocks. The comprehensive GC×GC technique performed in a single GC setup distinguishes heteroatom-containing functional groups and various condensed and non-condensed aromatic structures of aliphatic HCs in pyrolysis oils. This method is therefore an important supplement to common PIONA analyses, which focus on aromatic and

aliphatic components rather than resolving all constituents in contaminated pyrolysis oils. This enables the identification and quantification of paraffinic, aromatic, and heteroatom-containing components in the relevant naphtha and middle distillate cut range from C₆ to C₃₅. Additionally, comprehensive calibration of the main compounds and various representatives of all identified product groups is performed. Alongside the evaluation of the main products, this allows for a reliable compound group-based evaluation without the need to combine several element-specific methods. The GC×GC method was applied to various plastic-based pyrolysis oils, representing a broad spectrum of different compositions of mixed plastic waste. These oils were obtained from experiments already reported by Netsch et al. and conducted on a pilot-scale screw reactor with various pure thermoplastics, their blends, and post-consumer waste [42]. The results are evaluated considering additional elemental analyses, simulated distillation, and low-field NMR.

2. Materials and methods

2.1. Pyrolysis oil

This study examines various plastic pyrolysis oils to reflect the varying oil compositions. The investigated pyrolysis oils were obtained from a screw pyrolysis reactor at a reactor temperature of 500 °C. The electrically heated reactor was operated continuously with a feedstock addition of 1 kg/h in a nitrogen atmosphere for an experimental duration of 5 h. The feedstock residence time in the reactor was set to 30 min, ensuring complete conversion. The evolving volatiles exhibited a minimal gas residence time of about 40 s in the hot reactor zone. The gas residence time of molecules varied considerably, with a distribution width of around 300 s. The oils were separated from the permanent gas in a two-stage condensation unit after leaving the reactor. The stages were heated to 60 °C and cooled to 0 °C, respectively. The oils from both condensation stages were then reunited to obtain a representative full-range pyrolysis oil from the corresponding experiment. These full-range pyrolysis oils served as the basis for the performed analyses in this study.

Low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) were pyrolyzed. Additional pyrolysis oils derived from thermoplastic reference mixtures were analyzed. Oil obtained from the pyrolysis of a heteroatom-free mixture (Mix 1) comprised of 40 wt% LDPE, 30 wt% PP, and 30 wt% PS. Furthermore, pyrolysis oils from heteroatom-containing reference mixtures (Mix 2 and Mix 3) were investigated. These mixtures contained various amounts of polyethylene terephthalate (PET), acrylonitrile butadiene styrene copolymer (ABS), polyamide 6 (PA6), and polyvinyl chloride (PVC). Thus, Mix 2 and Mix 3 represent purely thermoplastic waste fractions with varying degrees of contamination covering the most important heteroatom-containing impurities such as oxygen, nitrogen, and chlorine. Moreover, the composition of a mixed thermoplastics pyrolysis oil from post-consumer waste (PCW) collection, similar to Mix 3, was examined. This waste comprises real products and contains potential additives like fillers, plasticizers, stabilizers, or flame retardants. The detailed feedstock composition of the mixtures is summarized in Table 2. Depending on the feedstock-specific condensate yield, between 2.4 and 4.4 kg of pyrolysis oil was produced per experiment. At least two tests were carried out for each input material. To rule out the influence of artifacts from previous tests, the condensate from the second test was analyzed. Further insights on experimental conditions, used feedstocks, and pyrolysis results are reported elsewhere [42].

2.2. Two-dimensional gas chromatography

A quantitative GC×GC–MS–FID–NCD method was developed. Quantification of main components and compound groups in the pyrolysis oils was performed with this method.

2.2.1. Hardware setup

The GC×GC system comprises an Agilent Technologies 8890 GC, a 5977B quadrupole MS, and an 8255 NCD. The NCD is installed in combination with an upstream FID. The setup has previously been used for qualitative analysis of pyrolysis oils from waste of electrical and electronic equipment [43] and was modified for the quantitative oil characterization. Fig. 1 shows a schematic diagram of the main components of the GC×GC system.

The split/splitless inlet (SSL) enables controlled evaporation of the injected sample at a constant temperature of 350 °C. The sample was injected into the SSL via an Agilent 7693A automatic liquid sampler. The inlet pressure was set to 34.9 PSI. The sample was introduced into the first column in split mode at a split ratio of 20:1. Helium was used as the carrier gas. The non-polar Restek Rxi-5Sil MS column with a length of 20 m, an inner diameter of 0.18 mm, and a film thickness of 0.18 µm performed the main separation. This column features a 1,4-bis(dimethylsiloxy)phenylene dimethylpolysiloxane phase. The resulting column flow rate was 0.5 mL/min. The analytes exiting the first column were transferred to the reversed flow modulator. The modulator alternates between a 10-s modulation period and a 0.36-s injection period. The analytes leaving the modulator were directed into the second separation column. A Trajan SGE BPX50 with a length of 5 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 µm was used as the second column. This column is coated with a phenyl polysilphenylene-siloxane phase. The mid-polar column features a significantly higher column flow of 21 mL/min than the first column. Finally, the analytes were divided by a Trajan SilFlow GC 3-port splitter. This enabled the analytes to be introduced into the MS and the FID/NCD in a volume flow ratio of 1 to 10. The columns, the modulator, and the splitter are located in the oven. The oven was heated to 40 °C with a holding time of 3 min at the start of the measurement. This was followed by heating to the maximum oven temperature of 315 °C at a constant heating rate of 3.5 K/min. The temperature program ends after an isothermal holding period at 315 °C for 39 min. The FID was heated to 350 °C. The NCD had a base temperature of 350 °C and a burner temperature of 700 °C. The NCD was run at a pressure of approx. 3 PSI. Both detectors were operated at a data rate of 100 Hz. The MS was connected to the three-way splitter via a 280 °C transfer line. The MS ion source and the quadrupole filter were heated to 230 °C and 150 °C, respectively. The MS operated in scan mode with a scan speed of 12,500 u/s in a mass range of 30 to 300 u. This resulted in a cycle time of approximately. 40 ms. All device components and analysis parameters are summarized in Table 1.

2.2.2. Sample preparation and calibration

The samples were dissolved in chloroform before injection. This involved adding 1 mL of sample per 10 mL of solution. The sample mass was weighed. The concentration of the pyrolysis oils depended on the oil density and ranged between 70 and 100 mg/mL. A sample volume of 1 µL was injected. The injection syringe was cleaned with solvent before and after each injection.

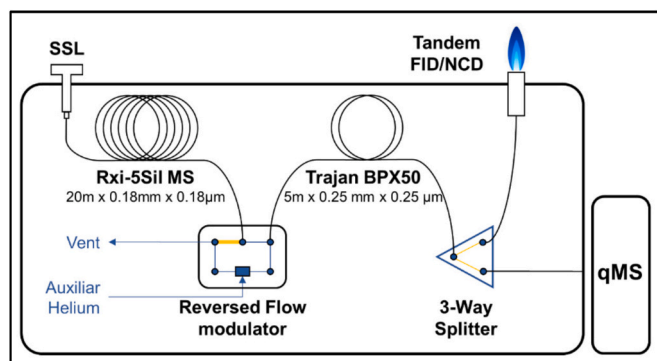


Fig. 1. Schematic overview of the employed GC×GC system.

Table 1

Overview on the hardware setup and the analysis parameters of the GC×GC method.

Split/Splitless Inlet			
Split mode (20:1)			
Injection with Agilent 7693A Automated Liquid Sampler	350 °C	32.94 PSI	Split flow 10 mL/min Purge flow 3 mL/min
Agilent 8890 GC oven			
Program: 40 °C for 3 min 40 to 315 °C at 3.5 K/min 315 °C for 39 min	First column: Rxi-5Sil MS (20 m, 0.18 mm, 0.18 µm) 0.5 mL/min	Second column: SGE Trajan BPX50 (5 m, 0.25 mm, 0.25 µm) 21 mL/min	
Agilent Reversed Flow Modulator and Trajan SilFlow 3-port Splitter			
Modulation period 10.0 s Modulation delay 0.01 min	Injection time 0.36 s	Split ratio (FID/NCD to MS) Approx. 10:1	
FID			
Data rate 100 Hz	350 °C	Air flow 400 mL/min Hydrogen flow 35 mL/min Makeup flow 20 mL/min (He)	
Agilent 8255 NCD			
Data rate 100 Hz	Base 350 °C Burner 700 °C	3 PSI	Oxidizer flow 8 mL/min Generator flow 37 mL/min (O ₃)
Agilent 5977B Quadrupole MS			
Scan mode: Range 30–300 u Scan speed 12,500 u/s Cycle time 40 ms	Transfer line 280 °C Ion source 230 °C Quadrupole 150 °C	Turbo pump vacuum not monitored	

Overall, 79 standards were calibrated. The calibration mixtures were prepared as a master batch of 10 mg/mL per standard in chloroform and then diluted to different concentrations. This allowed a five-point calibration with concentrations of 1.0, 2.5, 5.0, 7.5, and 10.0 mg/mL. As higher concentrations of styrene are expected in the analyzed samples, an additional calibration for high levels (10 to 70 mg/mL) was performed for this compound. An overview of the calibration mixtures and the included standards can be found in the supplementary information S1. Calibration curves were determined considering the zero point and all concentration levels. In GC×GC, blobs represent the peaks known from one-dimensional gas chromatography and can be quantified by their volume, which is proportional to the analyte mass. The concentration c_i of a component i in the pyrolysis oil was calculated using the component-specific response factor R_i and the blob volume measured in the sample V_i according to Formula 1.

$$c_i = \frac{V_i}{R_i} \quad (1)$$

The coefficient of determination was used as a criterion to assess the accuracy of the calibration lines. This coefficient was mostly higher than 0.995 except for hexylamine (0.993), benzoic acid, and some halogen-containing HCs. The determined response factors and the coefficient of determination of the calibration curves are included in the supplementary information S1. The response factor of compound groups was defined based on the individual response factor of the standards of the corresponding compound group. Supplementary information S2 contains the compound groups and their assumed response factors.

2.2.3. Data processing

The raw data from the GC×GC was analyzed using GC Image version 2021r3. The preprocessed FID data was converted into final quantitative results, conducting a customized VBA macro routine in MS Excel. The raw data processing included a phase shift of −3.1 s and a baseline correction. The phase shift corrected the time delay effects. Automatic peak integration and data smoothing were performed in hybrid detection mode to determine the blob volumes. Blobs with a minimum intensity of 100 and a signal-to-noise ratio of less than 450 were filtered out. The blobs were then matched with the standards known from the calibration using the retention times on the first and second dimensions. In addition, all blob volumes in predefined regions of the two-dimensional chromatogram were accumulated. These accumulated blob volumes were assigned to the respective compound groups defined in a template based on the retention times. Finally, the processed data was exported as a summary report. The summary report contains all identifiable and unidentified blobs including their retention times and blob volumes. The volumes of the defined compound groups are also listed. An Excel macro calculated the mass fractions of the identified components in the sample, considering the individual pyrolysis oil concentration in each sample. For this, the identified components were compared with the calibration database. Corresponding response factors were assigned. In addition, the correctness of the assignment was checked by verifying the retention times of the standard and the component to be quantified. The compound groups were calculated similarly. This involved linking the accumulated blob volumes of regions with the assumed response factors of the compound groups. To minimize errors in the group evaluation caused by varying response factors within the group, volumes of already identified and quantified blobs were subtracted from the group volume. The residual group volume consisted solely of the volumes of unidentified blobs within the respective retention window. This residual volume was then used to calculate the residual mass of the group, applying the corresponding group response factor. Finally, the masses of the components previously determined individually were added to the respective groups. The sum of quantified compounds was then calculated.

For qualitative evaluations, MS and NCD data were processed using a baseline correction and a phase shift. In MS, the phase shift accounted −0.5 s. It varies from the FID phase shift because of the differing connector geometries of the splitter and the detectors. The peaks were integrated and then identified by comparing their spectrum with the NIST20 database. This enables the identification of the main components that had not been assigned by FID retention time comparison with calibration standards. Comparing the retention times of blobs in NCD and FID data supports and simplifies the identification of nitrogen-containing compounds.

2.3. Further analysis methods

Elemental analyses were performed with a LECO Truspec CHN Micro elemental analyzer according to DIN EN 15104 to determine the carbon, hydrogen, and nitrogen content. A combustion ion chromatography analyzer consisting of an AQF-2100 combustion system with an Aquion ion chromatograph from a1-environsciences GmbH and Thermo Fisher Scientific GmbH was used for the determination of the chlorine content. The calorific value of the oils was measured using a C5000 calorimeter from IKA GmbH & Co. KG following DIN 51900.

Simulated distillation was performed according to ASTM D 7169:2020 in a high-temperature setup. It provides information on the product distribution of the pyrolysis oils based on the boiling curve. The analyses were carried out at a gas chromatograph equipped with a polydimethylsiloxane column. The oven program starts at 40 °C and ends at 435 °C. Analogous to the oven program, the Inlet is heated from 50 °C to 425 °C with a heating rate of 15 K/min. Calibration was performed with a Polywax standard mix, which was extended by short-chain n-paraffins. The samples were dissolved in carbon disulfide to a

concentration of about 10 mg/g.

Additional NMR analyses were performed using a Magritek Spin-solve MultiX benchtop NMR. The pyrolysis oils were investigated by ¹H-NMR experiments with an 80 MHz permanent magnet. A sample volume of 430 µL was measured three times with 16 scans and a repetition time of 15 s at a pulse angle of 90° with activated ¹³C decoupling. Chemical shift referencing was performed by adding 20 µL of tetramethylsilane (TMS) before analyzing. This method allows for quantitative differentiation between protons bound in saturated and unsaturated aliphatic groups, aromatics, or heteroatom-containing functional groups. Data processing includes TMS-referencing and polynomial baseline correction. In case of LDPE pyrolysis oil, the wax-like product was analyzed after being dissolved in deuterated chloroform.

3. Results and discussion

3.1. Elemental analysis

The results of the elemental analysis are shown in Table 2. As expected, the pyrolysis oils from LDPE, PP, PS, and Mix A contain only carbon and hydrogen. The molar hydrogen to carbon ratio (H/C) in the LDPE and PP pyrolysis oils is around 2.0, indicating a paraffinic nature of the samples. Conversely, the H/C of approx. 1.1 in PS pyrolysis oil strongly hints at a predominant presence of aromatic structures.

The pyrolysis oil obtained from Mix 1 falls between these values, showing the dependence of the elemental composition on the feedstocks' polymer composition. In Mix 3, the higher share of PA6 and ABS leads to a higher nitrogen content in the pyrolysis oil. The elevated proportions of oxygen and chlorine compared to Mix 2 are caused by the higher fractions of PET, PA6, and PVC in the feedstock. The PCW has a similar elemental composition to Mix 3. Both feedstock mixtures include high amounts of polyethylene, 46.5 % and 50 %, respectively. Nevertheless, the share of PP is significantly higher in the PCW with 17.1 %, while the PS content is lower with only 3.8 %. This leads to a slightly higher H/C while the oxygen and nitrogen content remain almost unaffected. Although the proportion of PVC in the PCW is 4 % compared to 5 % in Mix 3, the chlorine content is about 0.3 % higher in Mix 3. A cause for this may be found in measurement uncertainties, but this result is to be further validated by complementary analyses. The elemental analysis reveals the strong influence of the feedstock on the oil composition. The results confirm the findings of Kusenberget al. on the importance of pyrolysis oil upgrading for subsequent processing steps in the recycling loop [9]. For example, reducing PVC in the feedstock to a practically

Table 2

Elemental Analysis, H/C, and the calorific value of the pyrolysis oils obtained from experiments with different plastic feedstocks in a screw reactor reported by Netsch et al. [42].

Feedstock	Elemental composition in wt%					H/C in mol/mol	Calorific value in MJ/kg
	C	H	N	Cl	O [*]		
LDPE	86.0	14.0	< 0.2	0.0	0.0	2.0	46.1
PP	86.4	13.6	< 0.2	0.0	0.0	1.9	45.8
PS	91.9	8.1	< 0.2	0.0	0.0	1.1	41.4
Mix 1 ^A	88.6	11.4	< 0.2	0.0	0.0	1.5	44.0
Mix 2 ^B	86.3	13.1	< 0.2	0.2	0.4	1.8	45.2
Mix 3 ^C	86.3	11.7	0.6	0.5	0.9	1.6	43.5
PCW ^D	85.9	12.5	0.5	0.2	0.9	1.7	44.3

^{*} Calculated as the difference to 100 %.

^A Contains 40 % LDPE, 30 % PP, 30 % PS.

^B Contains 70 % LDPE, 20 % PP, 4 % PET, 2 % PS, 2 % PA6, 2 % PVC.

^C Contains 50 % LDPE, 15 % PP, 10 % PET, 10 % PS, 5 % ABS, 5 % PA6, 5 % PVC.

^D Contains 29.4 % LDPE, 25.1 % PP, 17.1 % HDPE, 10.1 % PET, 6.3 % PA6, 4.2 % PS, 4.0 % PVC, and 3.8 % ABS.

undetectable content in realistic applications is required to achieve the chlorine content in oils approaching the specification limit of 3 ppm. Also, the product upgrading, for example in the form of hydrotreating, is crucial for nitrogen and oxygen compounds, as the limit of 100 ppm is exceeded by far in elemental composition.

3.2. Simulated distillation

The simulated distillation results are displayed in Fig. 2 along with the boiling ranges of the common petrochemical products naphtha, middle distillate, and VGO. Supplementary information S3 contains a list of determined shares of these boiling ranges for all pyrolysis oils.

All pyrolysis oils feature a distillation curve over a broad temperature range. These are characterized by the initial (IBP) and final boiling points (FBP). Both characteristic parameters differ slightly depending on the pyrolysis feedstock. PP oil exhibits the lowest IBP of about 50 °C, while PS has the highest at 103 °C. The FBP for all oil ranges from 545 °C (Mix 1) to 601 °C (Mix 3). The wide boiling range indicates the products' significantly broad molecular weight distribution. The LDPE pyrolysis oil reveals the smoothest curve, and thus the most even distribution across the various boiling cuts, which agrees with previously published results [29,44]. The boiling range up to 200 °C, corresponding to a naphtha cut, dominates the composition of all oils. The pyrolysis oil of LDPE exhibits the lowest content of naphtha at 41 wt%. PS, with its styrene-selective decomposition mechanism, contains the highest proportion of compounds in the naphtha range at 75 wt%, similar to Mix 1. Horizontal segments are recognizable in the PS and Mix 1 distillation curve. These segments indicate an increased concentration of certain components, presumably styrene and its oligomers, in the pyrolysis oil. The middle distillate and the VGO section are similar in all pyrolysis oils. The pyrolysis oils of the reference mixtures and the PCW behave similarly to LDPE, resulting from the high proportion of polyethylene in the feedstocks. With lower contents of PE in the feedstock, the curve shifts towards lower boiling ranges and therefore the naphtha and middle distillate cuts. However, mechanically non-recyclable waste fractions that appear promising for chemical recycling via pyrolysis mainly contain high polyethylene content. Therefore, pyrolysis processes must deal with such feedstocks. By optimizing reactor design and process parameters, the boiling range can be adjusted. For example, higher temperature in the pyrolysis of polyethylene shifts the product composition towards low-boiling compounds as reported in several studies [1]. Nevertheless, no pronounced horizontal lines are visible in den mixed

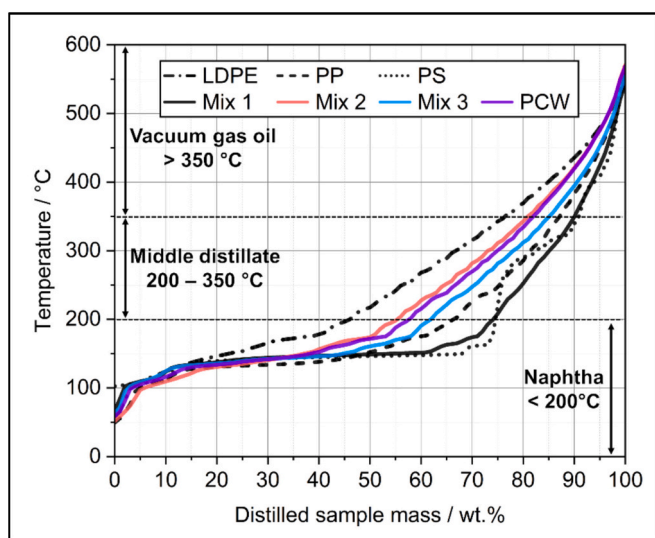


Fig. 2. Simulated distillation curve of the analyzed pyrolysis oils obtained from different thermoplastic feedstocks.

plastics pyrolysis oils, which indicates a broad product composition. Consequently, the oil of these feedstocks is not favorable for extracting specific base chemicals, as seen for the PS oil with its potential high styrene concentration. An in-depth analysis of the pyrolysis oil components is essential to further investigate the chemical structure of compounds incorporated in the oil. Therefore, NMR and GC×GC analysis are crucial.

3.3. Low-field NMR analysis

The results obtained from the NMR measurements of the pyrolysis oils allow qualitative comparison with the GC×GC analyses. They offer the advantage of analyzing the entire sample without limitations of physical properties, like the boiling behavior. The ^1H -spectra of the pyrolysis oils from LDPE, PP, PS, and PCW are shown in Fig. 3. The spectra of the reference mixtures are given in supplementary information S4. Different functional groups of the contained molecules were identified in the labeled chemical shift regions [45]. The peak integration in these regions allows a quantitative assessment of the ^1H -nuclei content of the respective groups. This enables a quantitative comparison of the pyrolysis oil composition. Additionally, Table 3 lists the entire quantitative results.

The LDPE and PP pyrolysis oils contain dominant signal intensities in the aliphatic range. The difference between the samples relates to the distribution of CH -, CH_2 -, and CH_3 -groups. While the proportion of CH_2 -groups prevails in LDPE, PP pyrolysis oil mainly contains CH - and CH_3 -groups. This demonstrates the difference in the decomposition behavior of the two polyolefins. While LDPE is known for its mainly long-chain unbranched n-alkanes, α -olefins, and α - ω -dienes, PP pyrolysis produces mainly branched saturated and unsaturated aliphatics [44]. The less frequently detected olefinic-bound protons confirm these findings in both pyrolysis oils. In PS oil, however, mainly aromatically bound protons are detected, representing the known product distribution of styrene, its oligomers, and other monoaromatic molecules [46]. The aliphatic and olefinic proton intensities are caused by substituents on aromatic compounds. After pyrolyzing the mixture of these polymers, Mix 1, aromatics, and various aliphatics are detected in the oil sample as expected.

In the pyrolysis oils of the other thermoplastic reference mixtures and the PCW, protons in carbonyl and carboxyl groups can be identified. However, the peaks are comparably weak because of the small number of protons bound in products with these functional groups. These molecules might form during pyrolysis, originating from PET degradation into benzoic acid or terephthalic acid [47]. The higher the PET content in the sample, the more pronounced the peak in this chemical shift range. Aliphatic components have the highest intensity in these samples as well. The proportion of protons in the range of 3.5 to 4.3 ppm is increased compared to LDPE, PP, PS, and Mix 1. This indicates an increased proportion of protons in the β -position to nitrogen-, chlorine-, or oxygen-containing groups [45]. The proportion of aromatic structures increases successively with the addition of PS, ABS, PET, and PVC, which is in line with the decomposition products of the pure substances. In addition to PS and PET, PVC also tends to form aromatic structures during pyrolysis. This primarily occurs in the final PVC pyrolysis stage of polyene chain degradation [48]. ABS polymer selectively forms styrene and other BTX aromatics [49] based on its copolymer structure, similar to PS. Thus, the proportion of aromatic structures increases successively with the addition of PS, ABS, PET, and PVC, which is consistent with reported degradation products of the pure polymers. The NMR analyses provide fast and general information that complements the elemental analysis, but lack details on the specific main compounds in the sample. Since ^1H -functional groups are determined instead of the existing compound groups, the comparison with GC×GC compound group results is limited. Also, heteroatom-containing impurities in the paraffinic and aromatic matrix are resolved poorly within the spectrum because of their lower concentration and, therefore, lower signal intensity.

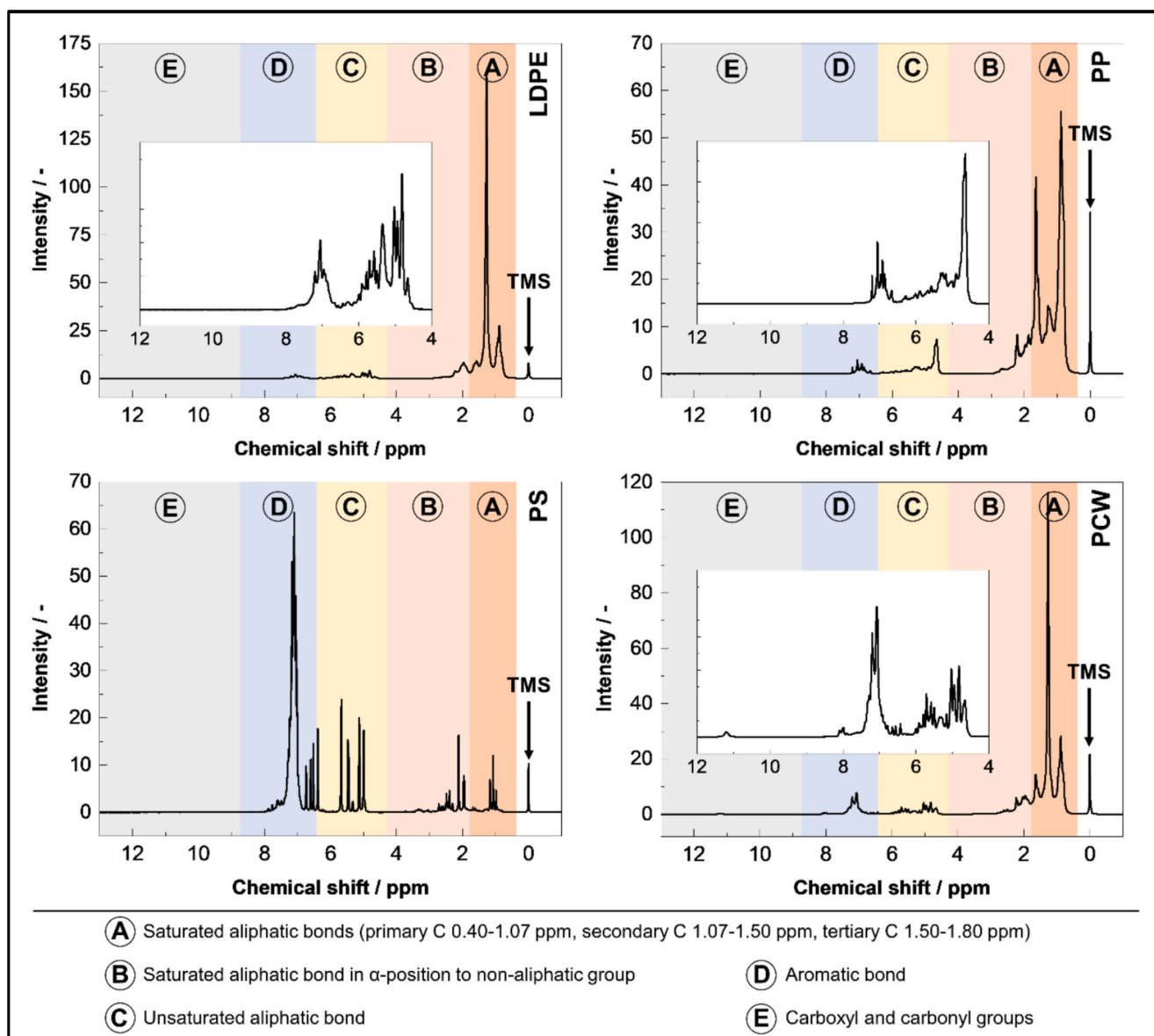


Fig. 3. Comparison of ^1H -NMR spectra of LDPE, PP, PS, and PCW pyrolysis oils.

3.4. Two-dimensional gas chromatography

Information about the molecular structure of the pyrolysis oil components is essential for subsequent processing and recycling. Therefore, in-depth GC $\times$ GC analyses supplement the elemental analysis and NMR.

3.4.1. Qualitative analysis and main compound quantification

The GC $\times$ GC chromatogram and the main components are exemplarily shown for the pyrolysis oil of LDPE, PS, and the PCW in Fig. 5, Fig. 6, and Fig. 6. Supplementary information S5 contains the chromatograms and Table S5.1, which lists the main compounds of the remaining pyrolysis oils under investigation in this study. The analytes are separated in the first dimension based on the molecular weight or boiling point of the compounds. In the second dimension, the polarity of the components is decisive. The comprehensive external calibration carried out in advance enables the quantification of a large proportion of these components.

In the pyrolysis oil of LDPE, mainly unbranched aliphatics with increasing chain length are recognized in Fig. 4 at a second-dimension retention time of about 2 s. α -Olefins dominate, but the corresponding

n-alkane and α - ω -diene can also be identified for each chain length. These structures form regular triplets. For the C_{10} triplet, α -decene, n-decane, and α - ω -decadiene with 2.1 wt%, 0.8 wt%, and 0.3 wt%, respectively, can be determined exemplarily. The proportions of triplets are almost constant and only decrease noticeably after reaching C_{25} . This decline can be attributed to the evaporation behavior of these HCs. The evaporation temperature of wax-like aliphatics exceeds the inlet temperature of the SSL. Therefore, a partial evaporation of such compounds is seen by a decreasing blob volume with increasing chain length from C_{25} upwards. Long-chain aliphatics are underestimated, which is in line with the comparatively high VGO Cut content of this pyrolysis oil. As expected, no heteroatom-containing compounds were detected. However, slightly increased levels of monoaromatics, naphthalene, and indene are recognizable. These products cannot be explained by the primary decomposition mechanism proposed by Bockhorn et al. [44]. The pyrolysis oils were generated in a pilot-scale screw pyrolysis reactor. Secondary reactions possibly cause alkyl-aromatics formation, which explains, for example, the toluene and xylene contents of 0.8 wt% each. However, styrene and α -methylstyrene are not common secondary reaction products of unsaturated gases. Before the LDPE experiments, the

Table 3

Proton quantification according to their functional groups and corresponding chemical shift from integrated low-field NMR analysis results.

Pyrolysis oil feedstock	¹ H-nuclei distribution according to chemical shift ranges in % (mol/mol)						
	Saturated aliphatic bonds			¹ H near a nonaliphatic bond ^D	Unsaturated aliphatic bonds ^E	¹ H in Aromatic bond ^F	¹ H in a carboxyl or carbonyl group ^G
	R-CH ₃ ^A	R ₂ -CH ₂ ^B	R ₃ -CH ^C				
LDPE	17.6	79.0 54.4	7.0	11.4	7.0	2.6	0.0
PP	38.0	75.8 17.2	20.6	13.3	8.5	2.4	0.0
PS	2.1	5.5 2.5	0.9	9.9	15.3	69.3	0.0
Mix 1	19.1	57.6 29.4	9.0	12.1	9.9	20.4	0.0
Mix 2	19.8	73.8 44.2	9.8	12.1	9.0	5.0	0.1
Mix 3	20.3	65.7 36.6	8.8	12.6	7.9	13.6	0.2
PCW	19.6	70.2 41.0	9.6	12.5	8.3	8.7	0.3

Spectrum was integrated in specific chemical shift areas of ^A 0.40–1.07 ppm, ^B 1.07–1.50 ppm, ^C 1.50–1.80 ppm, ^D 1.80–4.30 ppm, ^E 4.30–6.30 ppm, ^F 6.30–8.70 ppm, and ^G 8–70–13.00 ppm.

reactor was flushed using multiple polystyrene experiments. This flushing helped clean the condensers of viscous deposits before the experimental campaign. Some components may originate from these preliminary experiments as artifacts. The styrene component accounts for a small proportion of 0.70 wt%. Such artifacts are not detected in other pyrolysis oils generated in the later experiments.

The PP pyrolysis oil consists mainly of branched aliphatics as shown in the chromatogram in the supplementary information (S5). Compared to the LDPE sample, the majority of the components are detectable in the range up to C₂₀. The components 2,4-dimethylheptene, trimethylnonene, and isopentadecene stand out as main blobs. These are known to be primary decomposition products of PP pyrolysis [44]. A 2,4-dimethylheptene content of 7.2 wt% can be determined. The lower molecular weight of the aliphatics compared to the LDPE sample explains the results of the simulated distillation. The PP sample contains small amounts of alkyl aromatics. Only xylenes, toluene, benzene, and n-propylbenzene can be quantified. Secondary reactions of reactive gaseous components might cause their formation, since PP tends to selectively degrade into reactive compounds like propylene and other branched olefins.

In contrast to polyolefins, PS oil only contains aromatic structures, predominantly in the monoaromatic range. The chromatogram is shown in Fig. 5. The styrene monomer content is 52.5 wt%, which represents a low but reasonable value compared to other studies [46,50]. In addition, higher contents of ethylbenzene (7.1 wt%), α-methylstyrene (5.3 wt%), and toluene (4.6 wt%) are measured. Relevant quantities of diphenyls are identified, while further dimers are present in the chromatogram. The non-calibrated components, 1,2-diphenyl-isobutylene and 1,3-diphenyl-propane, are identified as main diphenyl compounds. The pronounced styrene trimer blob amounts to 0.88 wt%.

Mix 1 pyrolysis oil comprises the main components also present in LDPE, PP, and PS pyrolysis oil, but with minor intensities. The corresponding chromatogram to Mix 1 pyrolysis oil can be found in the supplementary information S5. Considerable amounts of previously unidentified structures are not detectable. Blobs in the range of retention times of 40 to 80 min and 3 to 4 s are recognizable. Monoaromatics with long-chain alkyl substituents might be found in this retention time range. However, the structures cannot be identified beyond doubt using MS because of low signal intensities. Supplementary information (S5) also contains the results for the pyrolysis oil from Mix 2. Branched and unbranched aliphatics dominate the composition of the pyrolysis oil Mix 2, as expected from the high LDPE and PP content in the feedstock. 6.2 wt% n-alkanes and 18.1 wt% α-olefins are determined in total. The

proportion of 2,4-dimethylheptene accounts for 1.5 wt%. Only a few aromatic structures are detectable. Toluene, styrene, xylenes, and benzene are present in increased quantities. Apart from styrene, these components are known from the PET and PVC product distribution reported in the literature [47,48]. The elemental analysis indicates oxygen- and chlorine-containing compounds in the oil. Benzoic acid (0.7 wt %), cyclopentanone, acetophenone, and benzaldehyde are identified as the main oxygen-carrying compounds. In addition, benzonitriles (0.2 wt %), ε-caprolactam (0.2 wt%), and ortho-toluidine are identified. These results align with the elemental analysis, which shows no nitrogen but features a detection limit of 0.2 wt% of total nitrogen in the oil sample. Using the quantified heteroatom-containing compounds in Table S5.1 of the supplementary information, a total nitrogen content of 0.06 wt% can be determined by GC×GC. The estimation relies on the respective molar masses and structural formulas of the products. Likewise, the GC×GC analysis provides an oxygen content in the oil of 0.20 wt%. A total chlorine estimation based on the GC×GC results in comparison to the elemental analysis is not feasible, as only one major compound could be specified in the pyrolysis oil of Mix 3 and the PCW with certainty. At retention times of 22 min and 5.8 s, 1-(chloroethyl)-benzene was found. Several other blobs of low intensity were identified, which might represent organochlorine HCs. For these blobs, the match factor of MS data is very low with the quadrupole MS. Wrong positive and false negative identifications of chlorinated compounds are therefore likely. This finding is also concluded by Jean et al., who investigated chlorinated HCs in pyrolysis oils using an advanced GC×GC setup [39]. They also highlight the distinct specification of chlorine compounds as challenging, even with their method specifically tailored for chlorinated compounds. Only a few organochloride structures could be ascertained by the Authors. They report significant misassignments by the algorithms.

Oxygen and chlorine content derived from the GC×GC analysis are below the values of the elemental analysis. GC×GC, therefore, provides further insights into the evaluation of low limits of heteroatom impurities in the sample. Nevertheless, blobs of heteroatom-containing components for low-boiling HCs may overlap with the solvent. Also, traces of heteroatom-containing HC structures may feature very low blob intensities. Thus, such chemical structures are not detectable, which explains the higher values of the elemental analysis. The feedstocks Mix 3 and PCW exhibit a similar plastic composition. The chromatogram depicted in Fig. 6 indicates the complex composition of the oil. Compared to Mix 2, both oils have a lower content of aliphatics, which is caused by the lower content of polyolefins in the pyrolysis

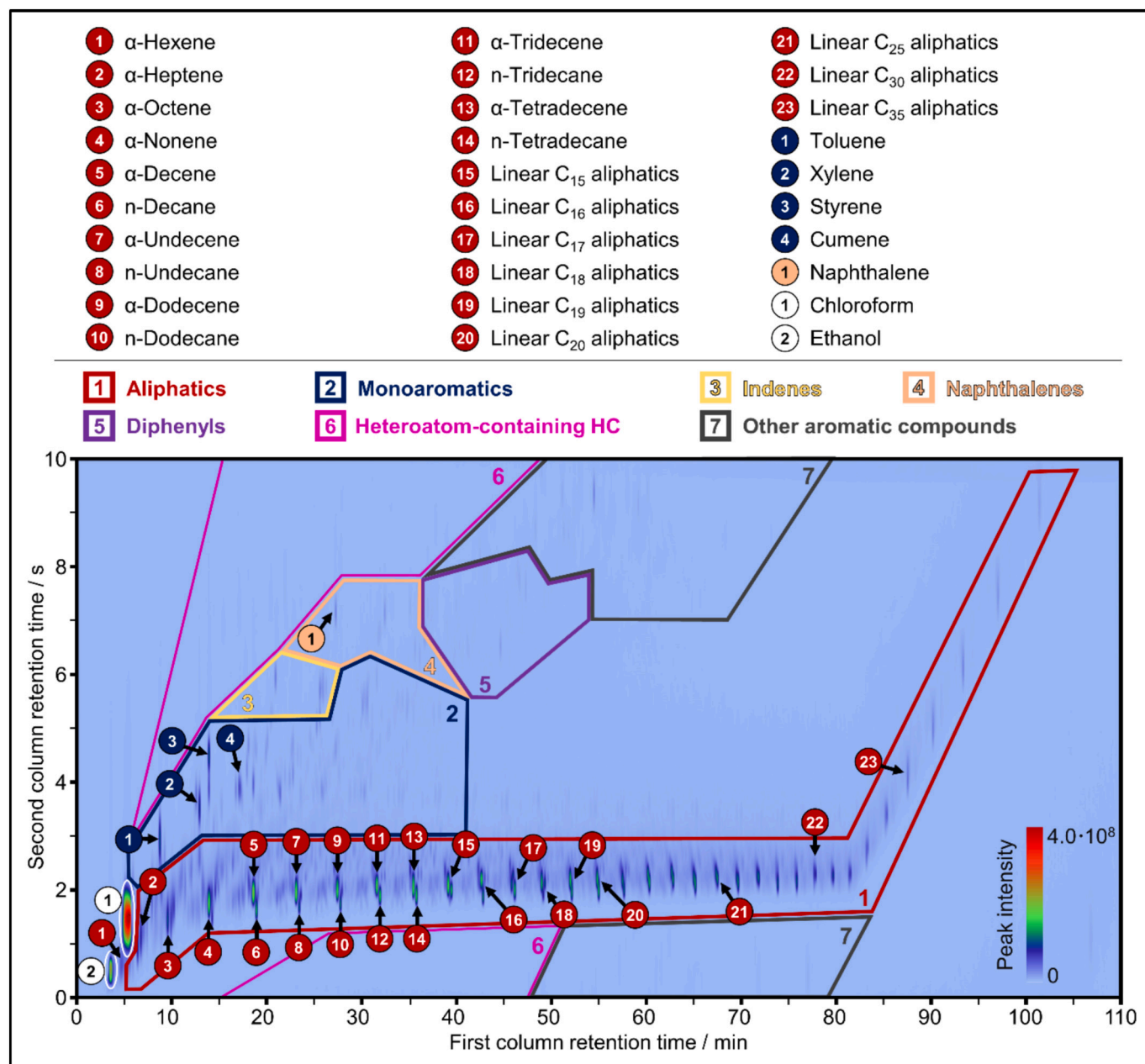


Fig. 4. GC×GC chromatogram of the LDPE pyrolysis oil analysis with labeled main compounds.

feedstock. Their feedstocks contain higher amounts of PA6, PET, PVC, PS, and ABS. In both pyrolysis oils, similar compositions can be found. However, less PS and ABS in PCW leads to a styrene content of only 3.7 wt% in PCW compared to 6.8 wt% in Mix 3. At the same time, the PP content in PCW is significantly higher. This leads to 1.9 wt% 2,4-dimethylheptene in the PCW pyrolysis oil compared to 1.0 wt% in Mix 2. The heteroatom-containing compounds already identified in the pyrolysis oil of Mix 2 are found in both mixtures. However, the proportion of benzoic acid is significantly higher in the pyrolysis oil of Mix 3 and the PCW, at 1.7 wt% and 1.5 wt%, respectively. More aromatic nitriles are also detected in the form of benzonitriles, o-toluidine, methyl benzonitrile, and 2-phenyl-butyronitrile. ε-Caprolactam appears in both pyrolysis oil samples in smaller quantities than in Mix 2, despite the higher PA6 content. The nitrogen and oxygen content, which can be estimated from the main compounds in the pyrolysis oil of the PCW, is 0.13 wt% and 0.42 wt%. For Mix 3, the contents are similar with 0.10 wt% and 0.46 wt%. These values fall below the detection limit or the respective results of

the total N and O content determined by elemental analysis. Missing calibrations of specific compounds pose a reason why not all of the identified heteroatom-containing HCs can be quantified. This applies to nitrogen in the form of methyl-benzonitrile or benzobutanenitrile, for example. However, other heteroatoms are likely also distributed among a large number of other HCs in quantities too low for identification. This assumption particularly concerns HCs that contain chlorine. Jean et al. identified up to 1800 chlorinated compounds in their experimental study [39]. Yang et al. detected various chlorine-containing light HCs and long-chain HCs in addition to chlorinated monoaromatics, such as 1-(chloroethyl)-benzene, which was also identified in this study [51]. Gui et al. describe that many polyaromatic compounds are formed during the pyrolysis of PVC [52]. In addition to monoaromatics, these condensed polyaromatics also contain one or more chlorine atoms. Additional chlorinated hydrocarbons that the primary PVC decomposition mechanism cannot explain were found to result from interactions between PVC and other polymers. Cao et al. encountered strong

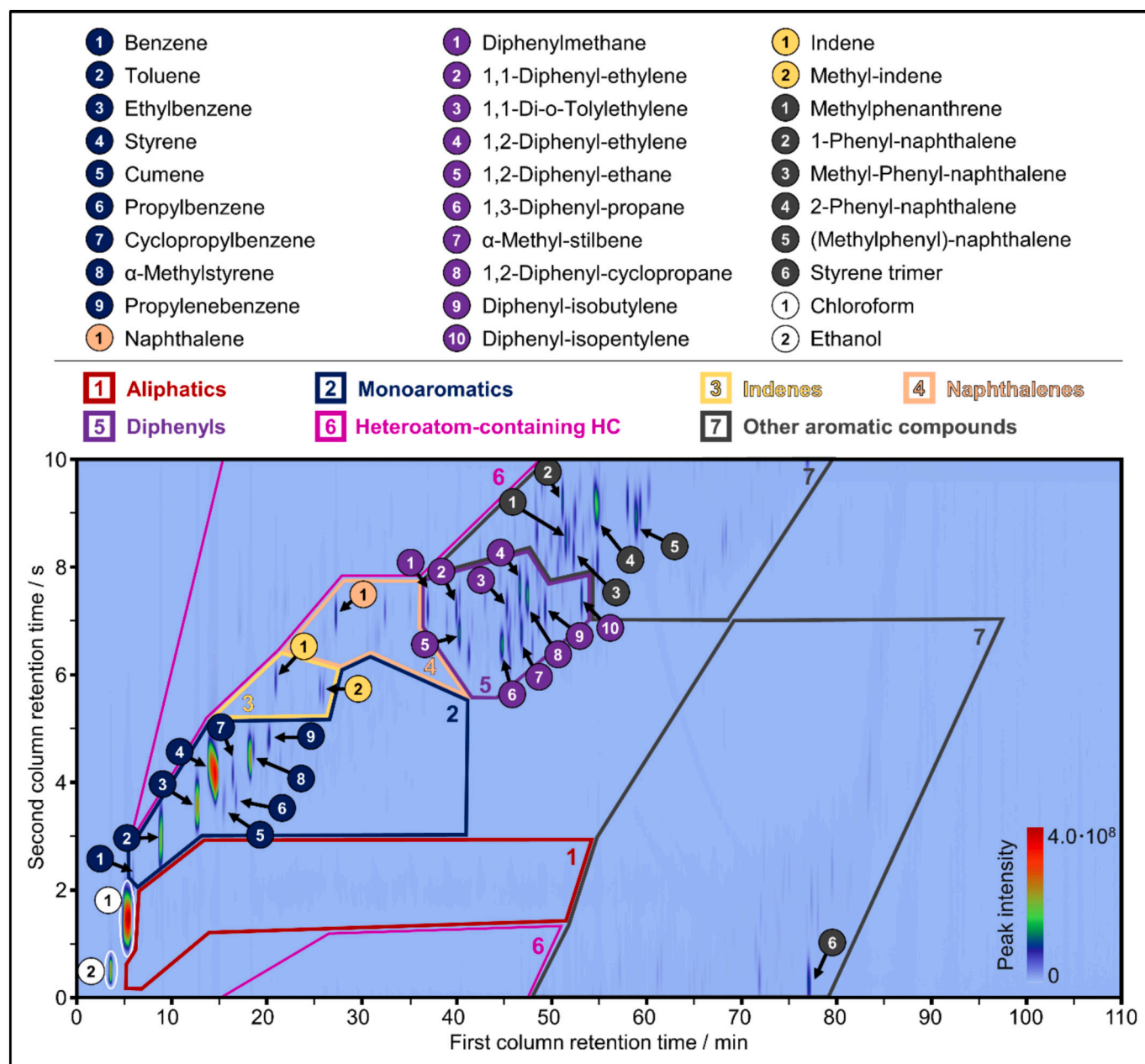


Fig. 5. GC×GC chromatogram of the PS pyrolysis oil analysis with labeled main compounds.

interactions between PVC and PET in their pyrolysis study [53]. These interactions, for example, lead to the formation of small amounts of chlorinated derivatives of terephthalic and benzoic acid. Such chlorinated terephthalic compounds fall into the temperature limitations of the GC×GC method. In general, other chemical compounds may be present in the oil that exceed the analyzable boiling range of this analytical method.

Neither cyclic nor linear silicon compounds were present in the pyrolysis oils obtained from LDPE, PP, PS, or the reference mixtures. As they are mainly introduced by additives or coatings, their absence is expected [9]. Despite the possible additives in the plastic products of the PCW, no silicone compounds were identified in this oil either.

As described above, the GC×GC parameters and operating principles set technical limits. The method allows measurements in the range from C_6 to C_{25} . It therefore covers the naphtha and middle distillate range almost entirely. For longer aliphatics from C_{25+} , complete evaporation is limited due to the maximum temperature of the columns of 315 °C and

the inlet temperature of 350 °C. Maintaining the column setup because of its high separation efficiency, increasing the oven temperature would irreversibly damage the columns. Increasing the inlet temperature can cause compound degradation during injection and leads to long-term accumulation of high boilers on the column. Therefore, this represents a recognizable upper limitation. Accordingly, partial quantification of the oil sample compounds in the VGO range is concluded. A second limit of the GC×GC analysis method is the low resolution of components with low retention times in the range from C_6 to C_7 . For example, blob overlapping of n-hexane and α -hexene occurs, leading to inaccuracies. Therefore, this blob is summarized as α -hexene due to its higher expected content in the product spectrum of LDPE. Other compounds, such as cyclohexanes, C_5 and C_6 isoaliphatics, or short-chain heteroatom-containing structures such as acetone, chlorobutanes, butanone, or ethyl acetate, also overlap in this range. Interference with the solvent blobs of chloroform or ethanol stabilizer contained in the solvent is possible.

This hypothesis was also verified experimentally with reference

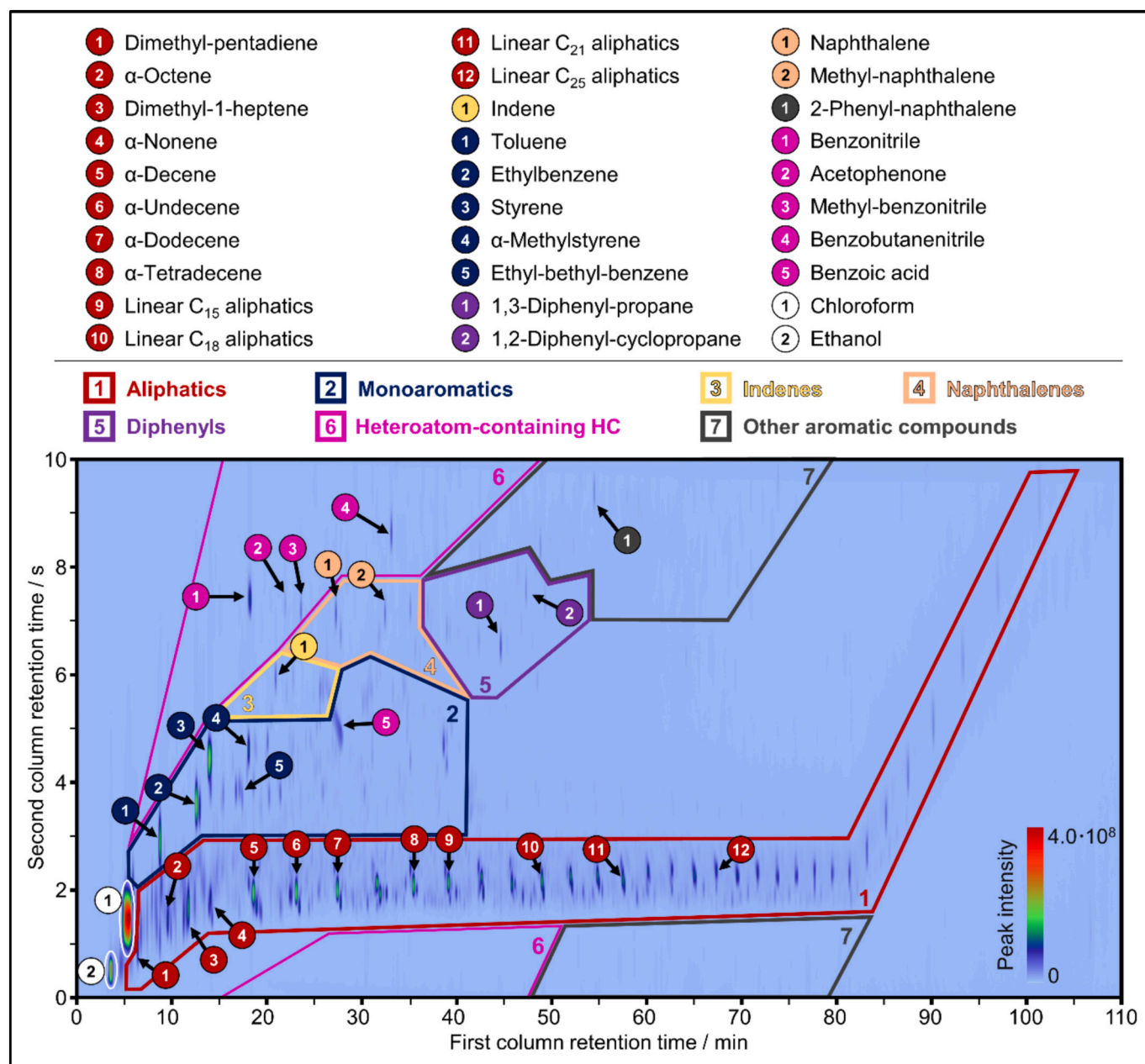


Fig. 6. GCxGC chromatogram of the PCW pyrolysis oil analysis with labeled main compounds.

standards for some of these components. The described method consequently only allows a reliable evaluation of benzene and aliphatics with a chain length of C₇ onwards. Furthermore, the effect concerning the second dimension may limit the analysis. Highly polar or large chemical structures, such as heteroatom-containing HCs or polycyclic aromatics, exhibit a higher retention time than monoaromatics or small-chain aliphatics. A retention time that exceeds the modulation time by far causes so-called wrap-around effects, which can inevitably represent a reason for overlapping peaks. However, this effect is only observed for a few oil components and in particular for high-boiling products due to the tailored development of the method, designed to minimize these effects. Wrap-around influence is therefore negligible. Consequently, the presented GCxGC technique allows excellent separation of complex pyrolysis oils. The strength of the method lies mainly in the separation of aromatic and aliphatic structures. The peak overlap in the study presented here is reduced to a minimum compared to one-dimensional gas chromatography. For example, the baseline-corrected evaluation of

styrene, o-xylene, and α-nonene is possible. In a one-dimensional configuration without a second column, these components feature similar retention times and would overlap, preventing reliable quantitative evaluation. With the separation in the second column, this effect is overcome. This advantage of the GCxGC configuration also applies to many other components, such as ε-caprolactam and C₁₂ aliphatics, or benzobutanenitrile and C₁₃ aliphatics.

The resolution in the aliphatic range is good enough to separate calibrated n-alkanes from α-olefins and dienes. N- and isoaliphatics, and olefins fall into a common retention time window, preventing automated evaluation of aliphatics. Thus, methods specially customized for their analysis are required, as presented by Abbas-Abadi et al. and Kusenberget al. for polyolefins [26,29,31]. The high-temperature GCxGC method developed by the authors enables a more precise resolution of alkanes, α-olefins, and α-ω-dienes, as well as the differentiation of branched and unbranched paraffines and naphthenes. Additionally, the high-temperature adaptations also allow for the measurement of

waxes with a chain length of up to C₇₅. However, this method accompanies a major disadvantage. It probably requires even higher modulation times for the separation of aromatics and heteroatom-containing HCs to avoid interference caused by wrap-around effects. Thus, we expect the method to be only advantageous for contamination-free, polyethylene-based pyrolysis oils. In contrast, the method presented in this study focuses on the analysis of pyrolysis oils from contaminated polyolefin-rich mixed plastics.

3.4.2. Quantitative compound group analysis

The quantitative analysis of the pyrolysis oil, categorized by compound group, is presented in Fig. 7. The full dataset is included in the supplementary information (Table S5.2). The method is designed so that compounds with similar chemical structures elute at similar retention times in both dimensions. This results in the accumulation of similar compounds in specific areas. Consequently, these compounds can be distinguished as compound groups quantitatively. Although aliphatic compounds cannot be differentiated by automated group evaluation, the group of aliphatics was further differentiated in more detail, considering the main compound-specific determination. As linear n-alkanes and α -olefins represent a major proportion of the aliphatic group, the component-specific quantification can be implemented in the group-based evaluation. This enables the aliphatic group to be differentiated in more detail into n-alkanes (chain lengths C₆–C₂₁, C₂₅, and C₃₀), α -olefins (chain lengths C₆–C₂₀), and other aliphatic compounds.

A strong influence of the feedstock is also evident in the group analysis. However, the group-based evaluation quantifies significant proportions of additional, non-calibrated compounds within respective compound groups. This capability constitutes the primary advantage of the novel GC $\times$ GC methodology. In contrast to most conventional one-dimensional methods, this approach captures the sample composition almost entirely. For example, paraffinic contents of 74 wt% for LDPE and 86 wt% for PP are detected. The sum of identified compounds serves as an indicator for the maximum analyzable share of pyrolysis products using the presented GC $\times$ GC method. The gap to a fully closed analysis stems primarily from the already discussed technical limitations at the boundaries of the boiling point range. Uncertainties arising from fluctuating response factors in a compound group appear to be of minor

influence. The relatively fine integration of blob volumes leads to minor errors in the group-based quantification, as seen in the heteroatom-containing HC group for LDPE, PP, and PS pyrolysis oils. However, this error can be estimated to be around 0.1 wt% in the final results.

The mass balance gap of 16 wt% in LDPE pyrolysis oil, when compared with 5 wt% for PP pyrolysis oil, is plausible considering results from simulated distillation. The highest share of the VGO cut is estimated for the LDPE sample with 33 wt%. Compounds of this cut feature a boiling point over 350 °C, which corresponds to the inlet temperature of the GC $\times$ GC system or even exceeds it. Consequently, compounds of this cut are only partly detectable in the GC $\times$ GC analysis of LDPE oil. Similarly, for PP, a VGO content of 17 wt% aligns with the compound group evaluation gap identified by GC $\times$ GC. In LDPE samples, the aromatic artifacts from cleaning cycles are also visible within the compound group results. The PS pyrolysis oil is composed predominantly of monoaromatics, diphenyls, and other aromatic compounds. The detected distributions are consistent with the data reported by Faravelli et al., indicating a composition of styrene, other monoaromatics, dimers, and trimers [46]. The low share of heteroatom-containing HCs in PS can be attributed to the tailing of the dominant styrene peak in the second dimension of the chromatogram. In Fig. 4, three low-intensity peaks are visible in this region, which are likely artifacts from previous experimental runs in the pilot plant. The pyrolysis oil from Mix 1, comprising LDPE, PP, and PS, consists of the corresponding product groups. High paraffinic and monoaromatic contents are detected. The minor content of heteroatom-containing HCs (0.4 wt %) results, analogously to PS, from the uncorrected tailing of the PS peak into this region. The pyrolysis oils from Mix 2, Mix 3, and PCW contain significant proportions of paraffinic compounds along with monoaromatics and heteroatom-containing HCs. While the results align with the main compound analysis, significantly higher levels of heteroatom-containing HCs are now detected. This confirms the prior hypothesis that additional traces of HCs with heteroatom-containing functional groups are present but not individually identifiable as discrete blobs.

These results highlight the benefit of group-based evaluation. A substantially higher proportion of the sample is characterized compared to the main compound analyses, enabling an almost complete mass balance of the composition. Associated uncertainties are also estimable.

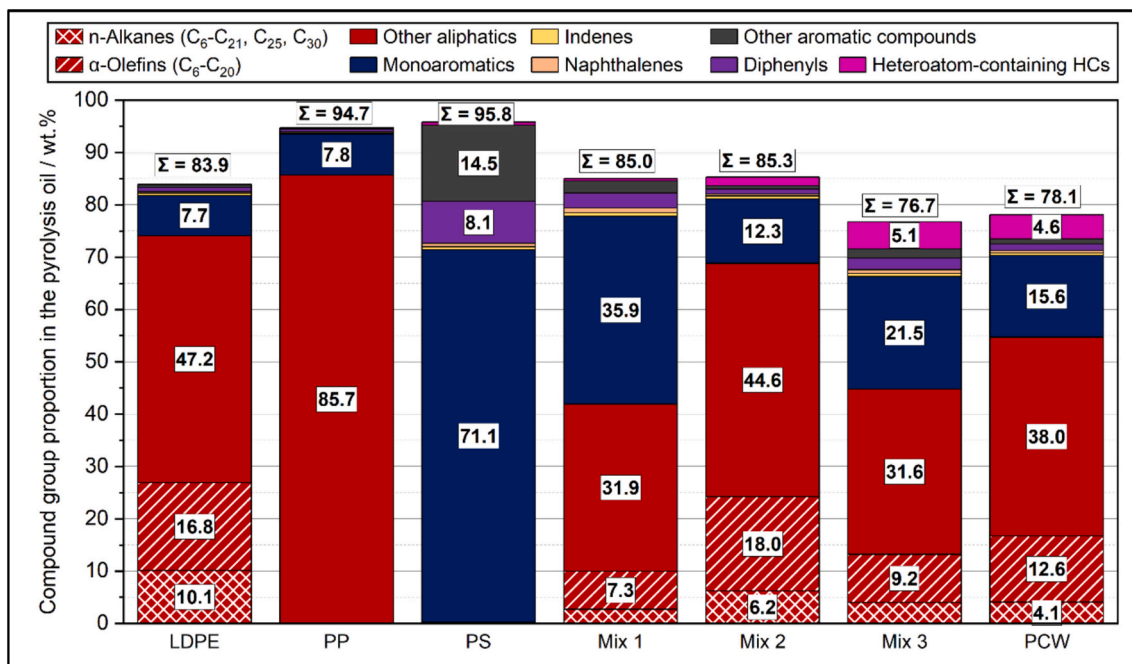


Fig. 7. Compound group-specific GC $\times$ GC results of the investigated pyrolysis oils stemming from different thermoplastic feedstocks pyrolyzed at 500 °C reactor set temperature in a screw reactor.

Errors originating from the integration methodology are considered relatively low in this approach. A key influencing factor is the boiling range of the pyrolysis oil under investigation. This is evidenced by higher losses in LDPE samples, likely due to high-boiling waxes and increased heteroatom content in the blends. The presence of heteroatoms promotes the formation of short-chain organic compounds, which may fall within the solvent range and are potentially discriminated because of reduced resolution in this range. Alternative solvents could potentially solve this issue. Commonly used solvents such as acetone, hexane, or isopropanol exhibit disadvantages, including overlap with other essential components or lower capability of solving all pyrolysis oil compounds. Therefore, carbon disulfide might be a potential solvent enhancing future analyses. Additionally, heteroatom-containing compounds may elute in other compound group retention time ranges. For benzoic acid, for example, the blob is quantifiable and was corrected by adding the volume to the group of heteroatom-containing HC and subtracting it from the monoaromatic range. Compounds of low content may not be unambiguously identified. In such cases, a compound group correction is not feasible. Furthermore, pyrolysis oil samples from PS and PCW demonstrate wrap-around effects in the second dimension, despite relatively long modulation times. Examples include ϵ -caprolactam and styrene trimers. Particularly in pure PS samples, higher amounts of additional high-boiling components with increased wrap-around are observed. Without group range adaptation for PS, these would be incorrectly attributed to the aliphatic region. Therefore, the compound group range is adjusted for pure PS pyrolysis oils. For predominantly olefinic mixtures, this error is negligible due to the minimal PS content. In addition to the identified compound groups, repeating blobs are observed in the retention time window of approximately 40 to 70 min (first dimension) and 3 to 4 s (second dimension) in the blends and PCW. These are presumed to be increasingly long, unbranched aliphatic chains with a single functional group, potentially amines, alcohols, or phenyl-alkanes. Such species may form via gas-phase reactions of reactive primary products. Reliable identification would require higher mass spectrometric resolution, achievable by broadening the scan range to higher mass fractions, e.g. to 400 or 450 u. However, this adaptation could presumably lower the resolution in the chromatogram because of the extended cycle time. Alternatively, the implementation of a more advanced MS type, like a time-of-flight MS, rather than a quadrupole MS, could overcome this problem.

The compound group evaluation matches the findings concluded from the NMR analyses. However, a quantitative comparison between the mass-related compound group-specific GC $\times$ GC results and the molar distribution of functional groups from the NMR analysis is challenging. Two aspects prevent this comparison. Firstly, the structures within a group in GC $\times$ GC are diverse. Saturated or unsaturated substituents of varying chain lengths are often found on aromatics. For example, benzene, but partly pentyl-benzene, can be identified within the monoaromatic group. Simplifying the compound groups to a specific molar distribution fails to account for the diversity of different molecules within the compound group and substantially distorts the result. Second, the GC $\times$ GC method determines between 76 wt% and 96 wt% of the total mass. NMR always detects all functional groups. Accordingly, almost the entire sample is detected in some oil. In the case of PS, a calculation would therefore be possible except for the problem mentioned above. With 25 wt% of compounds not detected in the GC $\times$ GC, as in the case of the oil from Mix 2 and Mix 3, a significant distortion is to be expected. Consequently, a quantitative comparison is not feasible. The first barrier, in particular, but also the second one, prevents reasonable calculations. While GC $\times$ GC analysis offers a much more detailed evaluation, the analysis is still elaborate. In contrast, NMR analyses on a benchtop device offer a limited level of detail but are highly valuable for screening experiments thanks to their robustness, comparatively short analysis time, and fast data evaluation.

3.4.3. Measurement uncertainties and technical limitations

The GC $\times$ GC method is subject to statistical and systematic errors. Statistical errors can be estimated based on the deviation of the double measurement of the pyrolysis oils. Apart from negligible retention time shifts, the chromatograms are identical. These shifts result from modulation and do not influence the measurement result. They are corrected during data processing. Corresponding chromatograms of each pyrolysis oil show identical blobs with hardly any variation in blob volume. For main compound analysis, the statistical error is evaluated based on multiple compounds in different samples, e.g., α -decene and linear C₂₀ aliphatics in LDPE pyrolysis oil, styrene and 1,3-diphenylpropane in PS pyrolysis oil, and benzoic acid, acetophenone, and benzonitrile in the PCW pyrolysis oil. The statistical error, which could be attributed to measurement inaccuracies, e.g., during sampling or sample preparation, is low. The standard deviations depend on the compound and the sample under investigation. It accounts for less than 2.5 % compared to the average compound concentration. The maximum deviation is found for benzoic acid, which is expected, as this compound features significant tailing. Blobs with uniform shape feature a standard deviation of less than 1.2 %. This result emphasizes the reproducibility of the main compound quantification results obtained with this GC $\times$ GC method.

However, for compound group quantification, further systematic errors are possible. Uncertainties may arise from the assumed response factors. The compound group response factors reflect a reasonable average of factors calibrated for compounds in the corresponding retention time range. Yet, they may deviate from the individual response factors of the unknown components within the group. Depending on the sample composition, this can lead to discrimination in the form of overestimation or underestimation of compound group proportions. Offsetting the quantified main components in the compound group range significantly reduces this influence. The offset reduces the impact of errors caused when calculating the mass-related share of the group with the associated response factor, since it reduces the unidentified compound group volume. Nevertheless, this systematic error is considered to be more significant for the measurement uncertainty of the compound group quantification than statistical error. Furthermore, the technical limitations (e.g., incomplete evaporation of high-boiling species and overlapping blobs in the boiling range of C₅–C₆ alkanes), which have already been discussed in the manuscript, are assumed to impact the quantitative compound group results more than the statistical errors. Therefore, when evaluating compound group quantification, it is important to consider the sum of all identified components and compare this with simulated distillation results. While the naphtha and middle distillate cut can be resolved well, the boiling range of VGO needs further analysis by high-temperature GC $\times$ GC.

4. Conclusion

The study highlights the importance of complementary analytical methods for the comprehensive characterization of pyrolysis oils from polyolefin-rich mixed plastics. In addition to commonly used elemental and one-dimensional gas chromatography, GC $\times$ GC methods must be employed for the holistic characterization of pyrolysis oils from thermoplastic feedstocks. Simulated distillation also provides key indicators for the subsequent reintegration of the condensable products into petrochemical processes.

A GC $\times$ GC method enabling the quantification of the most important main components, heteroatomic trace substances, and group-based evaluations has been developed. This method has been tailored to thermoplastic mixtures containing impurities of nitrogen, oxygen, and chlorine. It covers the most important HC groups forming in polyolefin and PS pyrolysis. Additionally, the extensive calibration and excellent blob separation enable the quantification of numerous heteroatom-containing products. The method allows for analyzing samples in a wide boiling range from naphtha to middle distillate, and with a complex composition of different compound groups. Furthermore, the

group-based evaluation enables a characterization of 77–95 wt% of the thermoplastics-based pyrolysis oils used in this study. The results are consistent with the decomposition mechanisms and product spectrum of thermoplastics reported in the literature. The identified products can be attributed to specific polymers in the mixture. Alongside benzoic acid, ϵ -caprolactam, acetophenone, and aromatic nitriles, benzaldehydes and both, conjugated and non-conjugated polyaromatics were identified as main impurities for further pyrolysis oil processing. Their proportion of up to 9 wt% emphasizes the importance of further detailed analysis of compound groups despite paraffinic species.

The results confirm the applicability of the GC×GC method to mixtures of heteroatomic thermoplastics such as PET, PA6, PVC, and ABS with up to 25 wt%. This feedstock classification applies to most waste fractions from packaging sorting residues, automotive shredder residues, or commercial waste collections discussed for chemical recycling [54]. Using this method instead of a combination of different GC×GC setups with different element-specific detectors enables detailed characterization at lower investment costs and with less time expenditure. The implementation of the NCD represents a supplementary quantification option for nitrogen-containing compounds for future method optimization. Thus, the level of detail and robustness of the results could be further enhanced.

The presence of heteroatoms and complex aromatic compounds in pyrolysis oil poses a challenge to processing it within established polymer or chemical production pathways [9]. Thus, the combined analyses enable the reliable evaluation of pyrolysis oils concerning their suitability for reintegration into various large-scale chemical plants, especially crackers. Furthermore, the GC×GC method offers the potential to relate specific problematic compounds in the oil to distinct polymers in the feedstock or feedstock interactions. Combining standard chemical analyses with the novel GC×GC method allows for improving pyrolysis plants in terms of scale-up, reactor design, and process conditions. Further parameters, such as viscosity and density, must be checked for compliance with common specifications through additional analyses. For this, it is crucial to interpret the compound group analysis in relation to the elemental analyses, including the derived heteroatom content and H/C. NMR Analysis or further GC methods tailored to PIONA analysis are needed, as they can resolve the content of saturated and unsaturated compounds in more detail.

However, the analyses reveal the importance of upgrading pyrolysis oil for its use as a substitute feedstock in the chemical industry, given that nitrogen, oxygen, and chlorine content significantly exceed specification limits [9]. Thus, further upgrading of pyrolysis oil or dilution with fossil naphtha is required before pyrolysis oils can be used as feedstock for steam crackers. Alternatively, pyrolysis oil components need further separation to enrich compound groups in product fractions that fit reintegration pathways. The presented GC×GC method also emerges as an advanced analysis for suitability tests of such upgraded and fractionated pyrolysis oils intended for closing the polymer-to-polymer recycling circle.

CRediT authorship contribution statement

Niklas Netsch: Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Luca Weigel:** Software, Methodology. **Tim Schmedding:** Methodology. **Michael Zeller:** Writing – review & editing, Methodology, Conceptualization. **Britta Bergfeldt:** Writing – review & editing, Resources, Formal analysis. **Grazyna Straczewski:** Writing – review & editing, Resources. **Salar Tavakkol:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Dieter Stapf:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Funding sources

Funding of this work was provided by the German Helmholtz

Association within the program Materials and Technologies for the Energy Transition (MTET).

Declaration of competing interest

The authors declare no competing financial interest.

Acknowledgment

The authors also gratefully acknowledge the support of Patrick Schieber and Aylin Hannemann in performing the supporting oil analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2025.108359>.

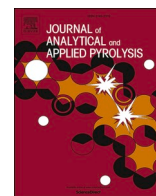
Data availability

Data will be made available on request.

References

- [1] M. Laghezza, S. Fiore, F. Berruti, A review on the pyrolytic conversion of plastic waste into fuels and chemicals, *J. Anal. Appl. Pyrolysis* 179 (2024) 106479, <https://doi.org/10.1016/j.jaap.2024.106479>.
- [2] S.H. Chang, Plastic waste as pyrolysis feedstock for plastic oil production: a review, *Sci. Total Environ.* 877 (2023) 162719, <https://doi.org/10.1016/j.scitotenv.2023.162719>.
- [3] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei, R. Ruan, Pyrolysis technology for plastic waste recycling: a state-of-the-art review, *Prog. Energy Combust. Sci.* 93 (2022) 101021, <https://doi.org/10.1016/j.pecs.2022.101021>.
- [4] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, *Renew. Sust. Energ. Rev.* 73 (2017) 346–368, <https://doi.org/10.1016/j.rser.2017.01.142>.
- [5] M. Kusenberg, A. Eschenbacher, L. Delva, S. de Meester, E. Delikonstantis, G. D. Stefanidis, K. Ragaert, K.M. van Geem, Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: the past, present and future, *Fuel Process. Technol.* 238 (2022) 107474, <https://doi.org/10.1016/j.fuproc.2022.107474>.
- [6] E. Rodríguez, A. Gutiérrez, R. Palos, F.J. Vela, J.M. Arandes, J. Bilbao, Fuel production by cracking of polyolefins pyrolysis waxes under fluid catalytic cracking (FCC) operating conditions, *Waste Manag.* 93 (2019) 162–172, <https://doi.org/10.1016/j.wasman.2019.05.005>.
- [7] R. Palos, A. Gutiérrez, F.J. Vela, J.A. Mañá, I. Hita, A. Asueta, S. Arnaiz, J. M. Arandes, J. Bilbao, Assessing the potential of the recycled plastic slow pyrolysis for the production of streams attractive for refineries, *J. Anal. Appl. Pyrolysis* 142 (2019) 104668, <https://doi.org/10.1016/j.jaap.2019.104668>.
- [8] C.S. Hsu, P.R. Robinson, *Springer Handbook of Petroleum Technology*, second ed., Springer International Publishing, Cham, 2017.
- [9] M. Kusenberg, A. Eschenbacher, M.R. Djokic, A. Zayoud, K. Ragaert, S. de Meester, K.M. van Geem, Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: to decontaminate or not to decontaminate? *Waste Manag.* 138 (2022) 83–115, <https://doi.org/10.1016/j.wasman.2021.11.009>.
- [10] E. Hoekstra, S.R. Kersten, A. Tudos, D. Meier, K.J. Hogendoorn, Possibilities and pitfalls in analyzing (upgraded) pyrolysis oil by size exclusion chromatography (SEC), *J. Anal. Appl. Pyrolysis* 91 (2011) 76–88, <https://doi.org/10.1016/j.jaap.2011.01.006>.
- [11] E.A. Williams, P.T. Williams, The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor, *J. Chem. Technol. Biotechnol.* 70 (1997) 9–20, [https://doi.org/10.1002/\(SICI\)1097-4660\(199709\)70:1<9::AID-JCTB700>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1097-4660(199709)70:1<9::AID-JCTB700>3.0.CO;2-E).
- [12] N. Hao, H. Ben, C.G. Yoo, S. Adhikari, A.J. Ragauskas, Review of NMR characterization of pyrolysis oils, *Energy Fuel* 30 (2016) 6863–6880, <https://doi.org/10.1021/acs.energyfuels.6b01002>.
- [13] U. Kumar, V. Gaikwad, M. Mayyas, M. Bucknall, V. Sahajwalla, Application of high-resolution NMR and GC-MS to study hydrocarbon oils derived from noncatalytic thermal transformation of e-waste plastics, *ACS Omega* 3 (2018) 9282–9289, <https://doi.org/10.1021/acsomega.8b01284>.
- [14] P.T. Williams, E.A. Williams, Interaction of plastics in mixed-plastics pyrolysis, *Energy Fuel* 13 (1999) 188–196, <https://doi.org/10.1021/ef980163x>.
- [15] R.L. Ware, S.M. Rowland, R.P. Rodgers, A.G. Marshall, Advanced Chemical characterization of pyrolysis oils from landfill waste, recycled plastics, and forestry residue, *Energy Fuel* 31 (2017) 8210–8216, <https://doi.org/10.1021/acs.energyfuels.7b00865>.

- [16] B. Diehl, G. Randel, Analysis of biodiesel, diesel and gasoline by NMR spectroscopy – a quick and robust alternative to NIR and GC, *Lipid Technol.* 19 (2007) 258–260, <https://doi.org/10.1002/lite.200700087>.
- [17] C. Mase, J.F. Maillard, B. Paupy, M. Farenc, C. Adam, M. Hubert-Roux, C. Afonso, P. Giusti, Molecular characterization of a mixed plastic pyrolysis oil from municipal wastes by direct infusion fourier transform ion cyclotron resonance mass spectrometry, *Energy Fuel* 35 (2021) 14828–14837, <https://doi.org/10.1021/acs.energyfuels.1c01678>.
- [18] T. Maqsood, J. Dai, Y. Zhang, M. Guang, B. Li, Pyrolysis of plastic species: a review of resources and products, *J. Anal. Appl. Pyrolysis* 159 (2021) 105295, <https://doi.org/10.1016/j.jaap.2021.105295>.
- [19] W. Kaminsky, J.-S. Kim, Pyrolysis of mixed plastics into aromatics, *J. Anal. Appl. Pyrolysis* 51 (1999) 127–134, [https://doi.org/10.1016/S0165-2370\(99\)00012-1](https://doi.org/10.1016/S0165-2370(99)00012-1).
- [20] N. Hassibi, Y. Quiring, V. Carré, F. Aubriet, L. Vernex-Loiset, G. Mauviel, V. Burklé-Vitzthum, Analysis and control of products obtained from pyrolysis of polypropylene using a reflux semi-batch reactor and GC-MS/FID and FT-ICR MS, *J. Anal. Appl. Pyrolysis* 169 (2023) 105826, <https://doi.org/10.1016/j.jaap.2022.105826>.
- [21] N. Netsch, M. Simons, A. Feil, H. Leibold, F. Richter, J. Slama, S.P. Yogish, K. Greiff, D. Stapf, Recycling of polystyrene-based external thermal insulation composite systems - application of combined mechanical and chemical recycling, *Waste Manag.* 150 (2022) 141–150, <https://doi.org/10.1016/j.wasman.2022.07.001>.
- [22] M.S. Abbas-Abadi, M.N. Haghighi, H. Yeganeh, Evaluation of pyrolysis product of virgin high density polyethylene degradation using different process parameters in a stirred reactor, *Fuel Process. Technol.* 109 (2013) 90–95, <https://doi.org/10.1016/j.fuproc.2012.09.042>.
- [23] B.A. Perez, J.V.J. Krishna, H.E. Toraman, Characterization of polyolefins-based pyrolysis oils: a comparison between one-dimensional gas chromatography and two-dimensional gas chromatography, *J. Chromatogr.* 1739 (2025) 465510, <https://doi.org/10.1016/j.chroma.2024.465510>.
- [24] T. Dutriez, M. Courtiade, D. Thiébaud, H. Dulot, M.-C. Hennion, Improved hydrocarbons analysis of heavy petroleum fractions by high temperature comprehensive two-dimensional gas chromatography, *Fuel* 89 (2010) 2338–2345, <https://doi.org/10.1016/j.fuel.2009.11.041>.
- [25] T. Dijkmans, K.M. van Geem, M.R. Djokic, G.B. Marin, Combined comprehensive two-dimensional gas chromatography analysis of polyaromatic hydrocarbons/polyaromatic sulfur-containing hydrocarbons (PAH/PASH) in complex matrices, *Ind. Eng. Chem. Res.* 53 (2014) 15436–15446, <https://doi.org/10.1021/ie5000888>.
- [26] M.R. Djokic, H. Muller, N.D. Ristic, A.R. Akhras, S.H. Symoens, G.B. Marin, K. M. van Geem, Combined characterization using HT-GC × GC-FID and FT-ICR MS: a pyrolysis fuel oil case study, *Fuel Process. Technol.* 182 (2018) 15–25, <https://doi.org/10.1016/j.fuproc.2018.10.007>.
- [27] M.E. Machado, Comprehensive two-dimensional gas chromatography for the analysis of nitrogen-containing compounds in fossil fuels: a review, *Talanta* 198 (2019) 263–276, <https://doi.org/10.1016/j.talanta.2019.02.031>.
- [28] T. Sfetsas, C. Michailof, A. Lappas, Q. Li, B. Kneale, Qualitative and quantitative analysis of pyrolysis oil by gas chromatography with flame ionization detection and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry, *J. Chromatogr. A* 1218 (2011) 3317–3325, <https://doi.org/10.1016/j.chroma.2010.10.034>.
- [29] M.S. Abbas-Abadi, M. Kusenber, A. Zayoud, M. Roosen, F. Vermeire, S. Madanikashani, M. Kuzmanović, B. Parvizi, U. Kresovic, S. de Meester, K.M. van Geem, Thermal pyrolysis of waste versus virgin polyolefin feedstocks: the role of pressure, temperature and waste composition, *Waste Manag.* 165 (2023) 108–118, <https://doi.org/10.1016/j.wasman.2023.04.029>.
- [30] H.E. Toraman, T. Dijkmans, M.R. Djokic, K.M. van Geem, G.B. Marin, Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors, *J. Chrom. A* 1359 (2014) 237–246, <https://doi.org/10.1016/j.chroma.2014.07.017>.
- [31] M.S. Abbas-Abadi, A. Zayoud, M. Kusenber, M. Roosen, F. Vermeire, P. Yazdani, J. van Waeyenberg, A. Eschenbacher, F.J.A. Hernandez, M. Kuzmanović, H. Dao Thi, U. Kresovic, B. Sels, P. van Puyvelde, S. de Meester, M. Saeys, K.M. van Geem, Thermochemical recycling of end-of-life and virgin HDPE: a pilot-scale study, *J. Anal. Appl. Pyrolysis* 166 (2022) 105614, <https://doi.org/10.1016/j.jaap.2022.105614>.
- [32] M. Kusenber, A. Zayoud, M. Roosen, H.D. Thi, M.S. Abbas-Abadi, A. Eschenbacher, U. Kresovic, S. de Meester, K.M. van Geem, A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition, *Fuel Process. Technol.* 227 (2022) 107090, <https://doi.org/10.1016/j.fuproc.2021.107090>.
- [33] R.L. Ware, S.M. Rowland, J. Lu, R.P. Rodgers, A.G. Marshall, Compositional and structural analysis of silica gel fractions from municipal waste pyrolysis oils, *Energy Fuel* 32 (2018) 7752–7761, <https://doi.org/10.1021/acs.energyfuels.8b00596>.
- [34] H. Dao Thi, M.R. Djokic, K.M. van Geem, Detailed group-type characterization of plastic-waste pyrolysis oils: by comprehensive two-dimensional gas chromatography including linear, branched, and di-olefins, *Separations* 8 (2021) 103, <https://doi.org/10.3390/separations8070103>.
- [35] M. Beccaria, M. Piparo, Y. Zou, P.-H. Stefanuto, G. Purcaro, A.L. Mendes Siqueira, A. Maniquet, P. Giusti, J.-F., Focant, Analysis of mixed plastic pyrolysis oil by comprehensive two-dimensional gas chromatography coupled with low- and high-resolution time-of-flight mass spectrometry with the support of soft ionization, *Talanta* 252 (2023) 123799, <https://doi.org/10.1016/j.talanta.2022.123799>.
- [36] H.C. Genuino, M.C.P. van Eijk, S.R.A. Kersten, M.P. Ruiz, Pyrolysis of real packaging plastic waste streams in a fluidized-bed pilot plant, *Energy Fuel* (2025), <https://doi.org/10.1021/acs.energyfuels.3c04114>.
- [37] E. Lazzari, M. Piparo, C. Mase, L. Levacher, P.-H. Stefanuto, G. Purcaro, J.-F. Focant, P. Giusti, Chemical elucidation of recycled plastic pyrolysis oils by means of GC×GC-PI-TOF-MS and GC-VUV, *J. Anal. Appl. Pyrolysis* 176 (2023) 106224, <https://doi.org/10.1016/j.jaap.2023.106224>.
- [38] A. Eschenbacher, R.J. Varghese, J. Weng, K.M. van Geem, Fast pyrolysis of polyurethanes and polyisocyanurate with and without flame retardant: Compounds of interest for chemical recycling, *J. Anal. Appl. Pyrolysis* 160 (2021) 105374, <https://doi.org/10.1016/j.jaap.2021.105374>.
- [39] A. Jean, B.C. Magalhaes, P. Pijcke, N. Verhoosel, T. Sanliturk, Y. Ureel, M. Kusenber, M. Ruitenbeek, G. Bellos, K.M. van Geem, M.N. Dunkle, Organochloride speciation in plastic pyrolysis oil by GC × GC coupled to high-resolution TOF-MS using scripting expressions, *Anal. Chem.* 97 (2025) 10680–10690, <https://doi.org/10.1021/acs.analchem.5c00546>.
- [40] B.A. Perez, H.E. Toraman, Investigating primary decomposition of polypropylene through detailed compositional analysis using two-dimensional gas chromatography and principal component analysis, *J. Anal. Appl. Pyrolysis* 177 (2024) 106376, <https://doi.org/10.1016/j.jaap.2024.106376>.
- [41] C. Kibuta, O. Akin, D. Withoeck, Q. He, M. Schmidt, R.J. Varghese, M. Schlummer, S. de Meester, F.D. Calik, M. Denton, A. Buettner, K.M. van Geem, Assessing the feasibility of ocean plastic waste as secondary feedstock for the production of base chemicals, *Waste Manag.* 195 (2025) 167–176, <https://doi.org/10.1016/j.wasman.2025.02.003>.
- [42] N. Netsch, M. Zeller, F. Richter, B. Bergfeldt, S. Tavakkol, D. Stapf, Energy demand for pyrolysis of mixed thermoplastics and waste plastics in chemical recycling: model prediction and pilot-scale validation, *ACS Sustain. Resour. Manag.* 1 (2024) 1485–1492, <https://doi.org/10.1021/acssusresmg.4c00109>.
- [43] J. Vogt, A.D. Renno, M. Fuchs, T. Kurtz, N. Netsch, F. Richter, G. Straczewski, B. Bergfeldt, Y.C. Madriz-Diaz, A.D.L. Ribeiro, D. Ebert, S. Tavakkol, S. Raatz, D. Stapf, Chemical recycling of refrigerator plastic waste by pyrolysis: yields, product composition, and potential applications, *Fuel* 400 (2025) 135776, <https://doi.org/10.1016/j.fuel.2025.135776>.
- [44] H. Bockhorn, A. Hornung, U. Hornung, D. Schwallier, Kinetic study on the thermal degradation of polypropylene and polyethylene, *J. Anal. Appl. Pyrolysis* 48 (1999) 93–109, [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4).
- [45] D.A. Skoog, F.J. Holler, S.R. Crouch, *Principles of Instrumental Analysis*, Sixth ed., Thomson Brooks/Cole, Belmont, 2007.
- [46] T. Faravelli, M. Pincioli, F. Pisano, G. Bozzano, M. Dente, E. Ranzi, Thermal degradation of polystyrene, *J. Anal. Appl. Pyrolysis* 60 (2001) 103–121, [https://doi.org/10.1016/S0165-2370\(00\)00159-5](https://doi.org/10.1016/S0165-2370(00)00159-5).
- [47] G. Montaudo, C. Puglisi, F. Samperi, Primary thermal degradation mechanisms of PET and PBT, *Polym. Degrad. Stab.* 42 (1993) 13–28, [https://doi.org/10.1016/0141-3910\(93\)90021-A](https://doi.org/10.1016/0141-3910(93)90021-A).
- [48] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, Thermal degradation of PVC: a review, *Waste Manag.* 48 (2016) 300–314, <https://doi.org/10.1016/j.wasman.2015.11.041>.
- [49] K.-H. Lee, D.-H. Shin, Y.-H. Seo, Thermal degradation of nitrogen-containing polymers, acrylonitrile-butadiene-styrene and styrene-acrylonitrile, *Korean J. Chem. Eng.* 23 (2006) 224–229, <https://doi.org/10.1007/BF02705720>.
- [50] M. Holtkamp, M. Renner, K. Matthiesen, M. Wald, G.A. Luinstra, P. Biessey, Robust downstream technologies in polystyrene waste pyrolysis: design and prospective life-cycle assessment of pyrolysis oil reintegration pathways, *Resour. Conserv. Recycl.* 205 (2024) 107558, <https://doi.org/10.1016/j.resconrec.2024.107558>.
- [51] J. Yang, Y. Wu, J. Zhu, H. Yang, Y. Li, L. Jin, H. Hu, Insight into the pyrolysis behavior of polyvinyl chloride using in situ pyrolysis time-of-flight mass spectrometry: Aromatization mechanism and Cl evolution, *Fuel* 331 (2023) 125994, <https://doi.org/10.1016/j.fuel.2022.125994>.
- [52] B. Gui, Y. Qiao, D. Wan, S. Liu, Z. Han, H. Yao, M. Xu, Nascent tar formation during polyvinylchloride (PVC) pyrolysis, *Proc. Combust. Inst.* 34 (2013) 2321–2329, <https://doi.org/10.1016/j.proci.2012.08.013>.
- [53] R. Cao, M.Q. Zhang, Y. Jiao, B. Sun, D. Xiao, M. Wang, D. Ma, Co-upcycling of polyvinyl chloride and polyesters, *Nat. Sustain.* 6 (2023) 1685–1692, <https://doi.org/10.1038/s41893-023-01234-1>.
- [54] M. Zeller, N. Netsch, F. Richter, H. Leibold, D. Stapf, Chemical recycling of mixed plastic wastes by pyrolysis – pilot scale investigations, *Chem. Ing. Tech.* 93 (2021) 1763–1770, <https://doi.org/10.1002/cite.202100102>.



Chemical recycling of mixed thermoplastics via pyrolysis: A comparative study of feedstock influence and reactor impact

Niklas Netsch^a, Aljoscha Tauber^a, Orhan Keskin^a, Britta Bergfeldt^a, Harald Wehner^b, Dirk Eidam^b, Salar Tavakkol^{a,*}, Dieter Stapf^a

^a Institute for Technical Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, Karlsruhe 76131, Germany

^b DHBW Karlsruhe, Erzbergerstraße 121, Karlsruhe 76133, Germany

ARTICLE INFO

Keywords:

Pyrolysis
Thermoplastics
Plastic waste
Chemical recycling
Stirred tank reactor
Screw reactor

ABSTRACT

Pyrolysis represents a promising solution for increasing plastic waste recycling rates in a circular economy. The thermal decomposition behavior of pure polymers is well investigated. However, the diverse composition and complex technical reactor conditions pose challenges for the pyrolysis of heterogeneous plastic waste. Therefore, this study examines the pyrolysis of virgin polymers, defined reference mixtures, and post-consumer waste in a scalable stirred tank reactor (STR) compared to an auger-type screw reactor (ASR) at pilot-scale. The results of the STR confirm that simple polymer blends of polyolefins and polystyrene degrade following the decomposition mechanisms of the pure polymer, while heteroatom-containing mixtures exhibit interaction effects. These interactions shift the products from the condensable to the gaseous fraction by up to 22 wt.%. Furthermore, product yields and compositions strongly depend on reactor design and process parameters. The gas residence time and the time-dependent polymer pyrolysis temperature are identified as the main influencing parameters. In this study, interaction effects between different polymers overlap the reactor-specific impact in complex feedstock mixtures, dominating the product yields. The condensate yield in the STR exceeds the results obtained in the ASR by 10–24 wt.% for LDPE, PP, PS, and a mixture of them. In contrast, the STR system yields only up to 6 wt.% more condensates than the ASR system for mixtures containing oxygen, nitrogen, and chlorine. The reactor type has a major impact on condensate quality. The H/C ratio, heteroatom content, and proportion of distillation cuts in the light and middle distillate range vary significantly.

1. Introduction

Growing plastic consumption and low global recycling rates require innovative technical solutions and a rethinking of plastic waste management [1]. By establishing a circular economy for plastic products, these challenges and several Sustainable Development Goals of the United Nations are being addressed [2]. Mechanical recycling is technically limited regarding the feedstock requirements and product quality. Consequently, heterogeneous waste fractions are mainly incinerated for energy recovery or landfilled [3]. Chemical recycling of plastic waste represents a promising option for the transformation to a closed-loop circular economy and for achieving higher recycling rates [4,5].

Robust thermochemical processes, such as pyrolysis or gasification, can help to fill the gap in material recycling of heterogeneous waste streams [6]. Pyrolysis offers multiple pathways to reintroduce its products into the petrochemical industry, substituting fossil-based feedstocks [7].

However, plastic pyrolysis strongly depends on the applied feedstock and the used reactor design. These dependencies often cause significant variance in experimentally determined product yields and compositions. Maqsood et al. and Soni et al. summarize numerous experimental studies on the pyrolysis of various polymers produced in different reactor technologies [8,9]. The reported yields of the generated product fractions, pyrolysis condensate, permanent gas, and solid residue, vary broadly. They conclude a yield range of 0–90, 3–90, and 0.5–78 wt.% for

Abbreviations: ABS, Acrylonitrile butadiene styrene; FID, Flame ionization detector; GC, Gas chromatograph; GRT, Gas residence time; H/C, Hydrogen to carbon ratio; HC, Hydrocarbon; HDPE, High-density polyethylene; LDPE, Low-density polyethylene; MgOx, Magnesium oxalate dihydrate; MS, Mass spectrometer; PA6, Polyamide 6; PCW, Post-consumer waste; PET, Polyethylene terephthalate; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl chloride; STR, Stirred tank reactor; TCD, Thermal conductivity detector; VGO, Vacuum gas oil.

* Corresponding author.

E-mail address: Salar.Tavakkol@kit.edu (S. Tavakkol).

<https://doi.org/10.1016/j.jaap.2025.107575>

Received 29 August 2025; Received in revised form 15 December 2025; Accepted 22 December 2025

Available online 23 December 2025

0165-2370/© 2025 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

these product fractions, respectively. The distinct pyrolysis mechanisms of the polymer types, consisting of countless elementary reactions, are decisive for the varying results in plastics pyrolysis. Interactions between intermediates of decomposing polymers further complicate the attribution of pyrolysis results to certain feedstock components [10,11].

Chang et al., Laghezza et al., and Faisal et al. confirm these results in their studies, whilst indicating a pronounced dependence of the resulting products on the pyrolysis temperature [12–14]. They conclude that, in general, reducing the reactor temperature leads to higher condensate yields. The formation of pyrolysis gas and solid residue, often obtained as coke, decreases accordingly. Honus et al. show that the feedstock and temperature dependency can also strongly influence the composition of the gaseous product [15]. The formation of CH₄, for example, increases as the temperature rises. Similar dependence can be observed in the pyrolysis condensate. Lopez et al. describe the shift towards aromatic products at higher reaction temperatures [7]. Moreover, reactions in the gas phase affect the pyrolysis. Secondary cracking reactions of aliphatic volatiles in the gas phase are reported for polyethylene [16]. The formation of polyaromatic components as a consequence of secondary gas phase reaction at high temperature is proven [17]. Therefore, the residence time of the volatile products at reaction temperature is another decisive factor influencing yields and composition. Overall, as the residence time of volatile products increases, secondary reactions such as secondary cracking, isomerization reactions, or aromatics and coke formation intensify similarly to rising pyrolysis temperatures [8,18].

Differences in the heat and mass transfer of technical pyrolysis systems often lead to variations of process parameters with insufficient or no experimental possibilities for detection and control [18]. For example, Dai et al. point out that even under seemingly isothermal reactor temperature, the polymers entering the reactor undergo an undefined heating process [18]. Depending on the heating, partial conversion by pyrolysis reactions occurs until the isothermal reactor temperature is reached. Therefore, the time-related temperature profile of the decomposing polymer can deviate considerably from the target pyrolysis temperature of the reactor. Inhomogeneous temperature distributions resulting from endothermic processes and heat transfer limitations are present in more complex technical reactor systems. The temperature gradients additionally enhance temperature deviations. Product backmixing in the polymer melt or within the gas phase, together with interfacial processes such as product evaporation, also prove challenges in characterizing and recording these effects. In this context, Hassibi et al. use the evaporation properties of the products to significantly influence the product yield and distribution using a reflux system while maintaining the constant feedstock and reactor temperature [19,20]. This multitude of parallel effects leads to a deficient database that complicates system evaluations [21], plant construction [14], or reactor upscaling [22] in the pyrolysis of plastic waste.

This study presents a comprehensive comparison of two common reactor types for different thermoplastic feedstocks. In preliminary tests, the STR and ASR systems are characterized in detail using analogous methods. This enables a technical comparison of fundamentally different reactor types under realistic, non-ideal conditions: a perfectly stirred reactor and a plug flow reactor. Reactor-dependent differences in the pyrolysis behavior are elucidated based on product yields and product composition. The reactor differences are attributed to specific design and operating characteristics. Defined pure thermoplastics, their mixtures, and a representative post-consumer waste (PCW) are investigated to reveal the feedstock influence. Calculations based on a linear superposition approach are performed for determining theoretical product yields and product compositions. The calculations allow for the identification of feedstock-specific interactions [11].

This study contributes to understanding the feedstock dependency of mixed thermoplastics pyrolysis and the importance of the reactor design and operation. The comparison highlights technical benefits and limitations for both reactor types. Furthermore, this work provides detailed data for process optimization and comparative process evaluation in the

chemical recycling of plastics via thermal pyrolysis.

2. Materials and methods

2.1. Feedstocks

Low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene copolymer (ABS), polyethylene terephthalate (PET), polyamide 6 (PA6), and polyvinyl chloride (PVC) were used in the pyrolysis experiments. Apart from PVC, the polymers were additive-free primary granules. This prevented the influence of additives, such as flame retardants, stabilizers, plasticizers, or fillers, focusing on the impact of polymers on the pyrolysis result. All thermoplastics, except for PET, were pyrolyzed as pure polymers to enable the deduction of results for mixtures from individual components. In addition, three different reference mixtures of these thermoplastics and a PCW, were pyrolyzed. PET was not pyrolyzed as a pure polymer, as the products caused rapid clogging of the reactor's exhaust piping and the condensers. Thus, PET was only used in the reference mixtures. The elemental analysis of the polymers and mixtures, as well as their moisture, ash, and polymer content, are listed in Table 1. The reference mixtures are referred to as Mix A, Mix B, and Mix C in the following. Mix A consists of 40 wt.% LDPE, 30 wt.% PP, and 30 wt.% PS. Mix B represents a less contaminated polyolefin-rich waste fraction, while Mix C is supposed to reflect a highly contaminated waste fraction. Compared to Mix B, it exhibits a higher proportion of nitrogen-, oxygen-, and chlorine-containing polymers, while reducing the polyolefin content. The PCW contained real plastic products that presumably incorporated few impurities and additives. The examined PCW originated from the same sample fraction as reported by Netsch et al. [23]. However, the PCW was additionally extruded for smooth feedstock dosing in the STR. The extrusion was performed in a single screw extruder type HAAKE PolyLab Rheomex OS (Thermo Fisher Scientific) at 200 °C. The nozzle temperature was set slightly higher at 225 °C. The mild temperature settings prevented feedstock alteration during the pre-treatment step, while ensuring form-stable extrudates with diameters ranging from 2 to 4 mm.

Magnesium oxalate dihydrate (MgOx) was used to validate the method of determining product fraction yields and deducting mass balances. MgOx features a defined two-stage decomposition mechanism [24]. This mechanism follows reaction Eq. R1 and reaction Eq. R2. Assuming complete decomposition, the product yields can be calculated from the reaction equations [24].

Table 1
Elemental Analysis of the pure polymers, reference mixtures, and the PCW [23].

Feedstock	Elemental composition in wt.%						
	C	H	N	Cl	Moisture	Ash	O ^A
LDPE	85.8	14.2	< 0.2	0.0	< 0.01	< 0.01	0.0
PP	85.8	14.2	< 0.2	0.0	< 0.01	< 0.01	0.0
PS	92.0	8.0	< 0.2	0.0	< 0.01	< 0.01	0.0
ABS	86.2	8.0	5.5	0.0	0.3	< 0.01	0.0
PET	63.3	4.4	< 0.2	0.0	0.2	< 0.01	32.1
PA6	63.6	9.8	12.6	0.0	1.2	< 0.01	12.7
PVC	36.2	4.9	< 0.2	47.9	0.2	10.6	0.2
Mix A ^{1,B}	87.6	12.4	< 0.2	0.0	0.0	0.0	0.0
Mix B ^{2,B}	83.5	13.4	0.3	1.0	0.0	0.2	1.6
Mix C ^{3,B}	80.6	11.6	0.9	2.4	0.1	0.5	3.9
PCW ^{4,B}	80.0	12.3	0.8	1.4	0.0	2.2	3.3

¹ contains 40 % LDPE, 30 % PP, 30 % PS.

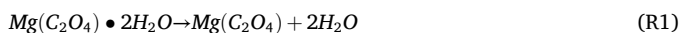
² contains 70 % LDPE, 20 % PP, 4 % PET, 2 % PS, 2 % PA6, 2 % PVC.

³ contains 50 % LDPE, 15 % PP, 10 % PET, 10 % PS, 5 % ABS, 5 % PA6, 5 % PVC.

⁴ contains 29.4 % LDPE, 25.1 % PP, 17.1 % HDPE, 10.1 % PET, 6.3 % PA6, 4.2 % PS, 4.0 % PVC, 3.8 % ABS.

^A calculated as the difference to 100 wt%.

^B calculated from the proportion of individual polymers in the mixture



2.2. Stirred tank reactor

The experiments were conducted in a scalable STR system. Fig. 1 schematically depicts this pyrolysis system. The detailed piping and instrumentation diagram and engineering drawings of reactor parts are provided in the [supplementary information](#) (S1). The cylindrical reactor featured a total volume of about 2.7 L. Two electrical heating sleeves with a power of 1.25 kW supplied the energy for the endothermic process by heating the outer reactor wall. Two thermocouples were arranged on the outer reactor wall to regulate the temperature of the reactor heating system, thereby ensuring a constant reactor wall temperature. Flange accesses were located on top of the reactor vessel. They were used for polymer addition, the installation of a thermocouple monitoring the inner reactor temperature, and a gas exhaust towards the condensation unit. The locations of thermocouples employed in this system can also be found in the [supplementary information](#) (S1). The reactor was equipped with a customized Paravisc-type impeller (Ekato GmbH). The stirrer was driven by an electric motor with a maximum torque of 12 Nm. The agitator shaft was flushed below the shaft seal via a nitrogen inlet. The polymer was added into a vertical fall neck equipped with a lock of two ball valves. A storage container was located above the second valve, and another nitrogen inlet was below the valve lock. It served as the primary flush gas inlet. Like the nitrogen inlet at the shaft flushing, a mass flow controller enabled a defined addition of Nitrogen. Together with the flush gas, product gases and volatile substances left the reactor through the exhaust pipe into the first condensation stage. This stage consisted of two vertically arranged double-tube heat exchangers of each 1.5 m length. At the bottom of the condensation stage, condensing products were collected in a glass flask. A second condensation stage of the same design followed, but concluded with an electrostatic precipitator. The condensing products in this stage were captured in an analogous arrangement to the first stage. The temperatures in both stages could be flexibly adjusted in the range of -25 – 100 °C using circulation thermostats. Demineralized water and a water-glycol mixture were used as heating and cooling media. Online gas sensors analyzed the remaining permanent gas before they were transferred to

the flare. Additionally, the permanent gas was sampled via gas bags for offline analyses in a gas chromatograph (GC).

The reactor was inerted with nitrogen before the experimental start. The feedstock was loaded into the storage container, flushed by nitrogen, and then placed on the upper part of the closed valve lock. The connection between the reactor and the first condensation stage was heated to a temperature of 380 °C with trace heaters to prevent blocking caused by condensing products. The condensation stages were heated and cooled to 60 and -5 °C, respectively. The connection between the two condensation stages and the section between both heat exchangers of the first condensation stage were heated to 60 °C with trace heaters. The main purge gas flow was set to $2 \text{ L}_{\text{NTP}}/\text{min}$ during operation (volume flow referenced to normal temperature and pressure). This setting enabled the defined transport of generated product gases through the condensation stages into the gas analysis. The purge gas flow of $0.3 \text{ L}_{\text{NTP}}/\text{min}$ ensured that no volatile products entered the agitator shaft sealing. The nitrogen flow at the electrostatic precipitator was $1 \text{ L}_{\text{NTP}}/\text{min}$ in experimental operation.

Ideally, the STR offers uniform polymer distribution. However, the semi-continuous feeding method with punctual injection hindered this. Time- and location-dependent fluctuations are expected but can be minimized by methodological adaptations and selecting optimal stirring parameters. At the start of the experiment, the reactor was filled with 2 kg of quartz sand. Applying quartz sand as a homogenizing agent accelerated the mixing of the highly viscous thermoplastic melt and sticky intermediates, which formed upon polymer addition [14]. Mixing effects dependent on the sand to polymer ratio and the selection of the optimal stirrer geometry were investigated in preliminary cold model tests. Sand, polymer, and silicon oil were used to reflect sand-polymer mixtures in the pyrolysis reactor. By applying the silicon oil with a dynamic viscosity of 97 and 970 Pa·s, the polymer melt could be simulated in the cold model operated at room temperature. The employed quartz sand featured a particle size of 1–4 mm. Before the experiment started, the stirrer speed was set to 50 rpm. Optimal stirring speed was verified visually using an endoscope camera in the STR system at ambient temperature. As reported by Abbas-Abadi et al., increasing the stirrer speed to 50 rpm led to more extensive mixing [26]. Higher speed further improved the mixing, but also caused intensive abrasion of the sand particles, leading to disadvantageous dust formation. In all experiments, the sand-filled reactor was preheated to a reactor wall temperature of

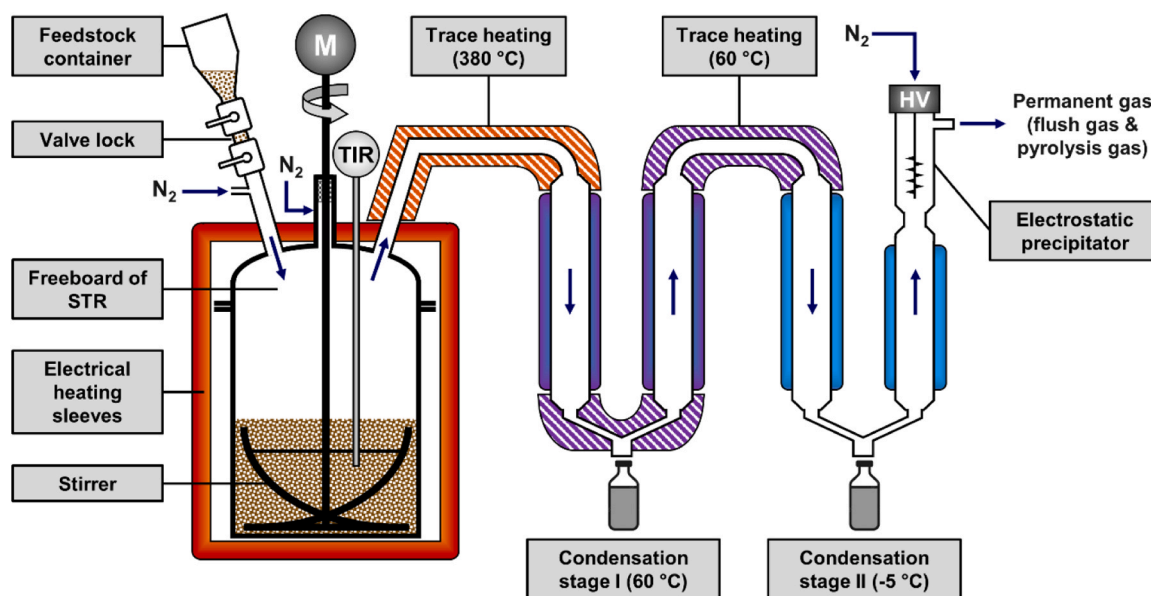


Fig. 1. Schematic illustration of the STR setup consisting of a feeding system, an externally heated sand stirred reactor with a thermocouple recording the internal reactor temperature, and a two-stage condensation system including an electrical precipitator.

500 °C before adding the feedstock. The temperature of 500 °C was chosen to meet optimal conditions of high condensate yields while minimizing the formation of waxes and coke [17,25].

Once the reactor temperature stabilized, the feedstock was introduced into the hot reactor in small batches at five-minute intervals by adjusting the position of the two ball valves. Premixing of Mix A, Mix B, and Mix C in the feedstock container ensured a constant feedstock composition in each feeding cycle. A total quantity of 250 g was added per experiment. Depending on the feedstock's density, between 23 (PCW) and 37 g (PVC) was introduced per feed cycle. This semi-continuous mode of operation was intended to ensure defined isothermal conditions and consistent product formation. The electrostatic precipitator removed condensate droplets from the gas flow at 10 kV. While simultaneously avoiding product build-up at cold spots, condensable products were separated from the permanent gas as effectively as possible in this setup. Gas samples for offline analyses were taken at specific times, usually after the fifth and eighth feeding cycle (21 and 36 min). The experimental settings were maintained for at least 1.5 h following the last material input. The delay time ensured a complete conversion, sufficient time for the product separation in the condensers, and the purging of all gases in the pyrolysis system [17]. After the experiment, the mixture of sand and the remaining solid pyrolysis product, the so-called solid residue, was weighed. The condensate flasks were also weighed before and after the test run.

2.3. Auger-type screw reactor

The ASR system operates on a pilot scale. Thus, it has significantly larger dimensions, with a screw length of 2.5 m and a freeboard volume of about 80 L. The system contains a feedstock dosing section, the screw reactor with an integrated hot gas filtration system, a two-stage condensation system, and a gas analysis section. A schematic overview of the ASR reactor is displayed in Fig. 2.

For comparison, the pyrolysis experiments were conducted at 500 °C reactor wall temperature. As with the STR system, the reactor was heated and flushed by nitrogen before feedstock addition. The pure polymers or polymer mixtures were introduced with a feeding rate of 1 kg/h. Also, quartz sand is used. The mass ratio of sand to polymer accounted for 4:1. The flush gas flow rate was set to 12 L_{NTP}/min. The polymer-sand mixture was fed continuously into the screw reactor, where it was forced through. During this transport in the reactor, the polymers heated up, melted, and pyrolyzed. The solid residence time was set to 45 min to ensure complete conversion. During transport

through the reactor, the polymer-sand mixture experienced minimal mixing compared to the STR system, as the screw rotation speed of about 1 rpm is low. Solid residues remained in the reactor and were moved to a storage container together with the sand. The pyrolysis gas, containing permanent gases and volatiles, evolved into the freeboard, passed the hot gas filtration system, and entered the two-stage condensation system. The condensation system operated at 60 and 0 °C. Trace heaters prevent the uncontrolled condensation of volatiles before they enter the condensation unit. The condensation system is technically similar to the STR in terms of dimensions and process parameters. Each condensation stage included an electrostatic precipitator at the outlet. The composition and properties of the permanent gas are analyzed online. More details on the reactor design are described elsewhere [23]. Reliable reactor comparisons are possible as a result of the similarity between the STR and ASR peripheries, identical analysis methods, and the application of the same feedstocks.

2.4. Reactor characteristics

The reactor design and the operational settings have a distinct influence on various pyrolysis process parameters. Consequently, the extensive characterization of the STR and ASR system was essential for comparing corresponding measurements. Special focus was set on the residence time of products in the reaction zone of the pyrolysis system and the time-dependent temperature distribution of the polymer during pyrolysis.

2.4.1. Gas residence time

The residence time of volatile products and permanent gases can significantly influence the yields and product composition, as sufficient residence time allows for isomerization reactions, aromatics formation, or secondary cracking of the primary pyrolysis products [17,26]. It is defined as the time required from the formation of these primary pyrolysis products in the reactor until the removal of condensables from the permanent gas in the condensation unit. In the following, it is further referred to as gas residence time (GRT). Two consecutive parts contribute to the GRT. Firstly, it includes the gas transport within the sand-melt system into the freeboard of the reactor. This mass transfer is challenging to investigate experimentally. Secondly, the mass transfer from the gas phase in the reactor freeboard to the condensation system inlet contributes to the GRT. This GRT is referred to as GRT in the hot reaction zone in the following. The GRT in the condensation system is also estimated, as it can impact the efficiency of the gas-liquid

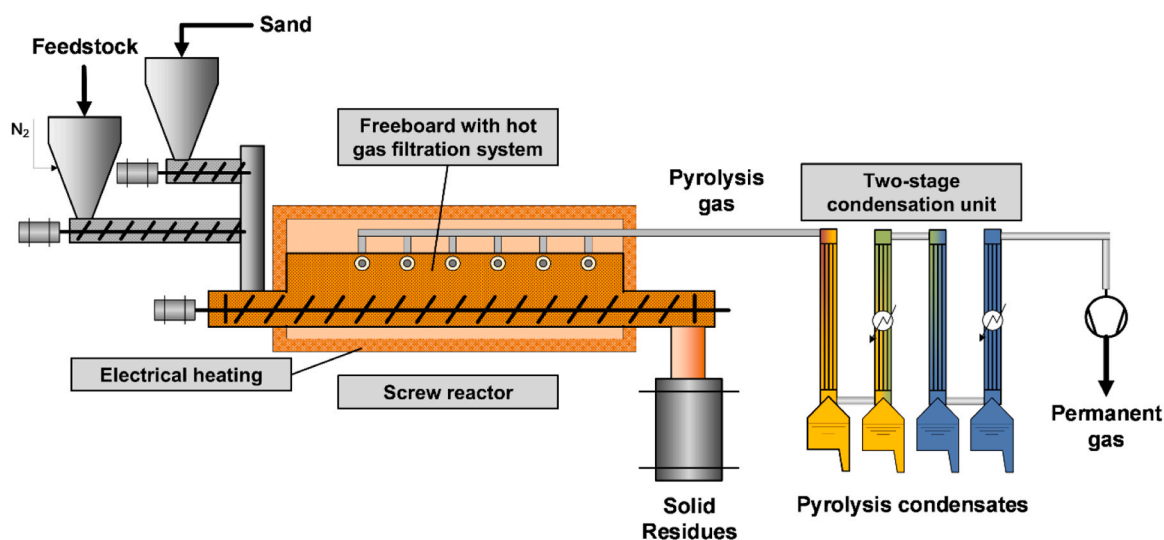


Fig. 2. Schematic illustration of the ASR system consisting of a feedstock and a sand dosing system, a screw reactor with integrated hot gas filtration, and a two-stage condensation system.

separation. This parameter covers the time required for the permanent gas to flow from the condensation inlet to the outlet of the electrical precipitator.

To estimate the GRT, CO₂ and N₂ were injected alternately into the sand-filled reactor until complete atmosphere replacement. The GRT estimation was conducted while no plastic was processed. Different insertion locations of the gases led to their detection with varying time delays. The inserts were located at the access flanges of the upper STR part, as well as directly before the first and after the last condenser. The density variations were recorded by a sensor to quantify the time delay. With the time delay varying between 5 s and 4 min, depending on the insert location, the GRT in the hot reaction zone can be ascertained. Because of back-mixing effects and inhomogeneous flow conditions, a residence time distribution evolved. The minimum GRT and its width characterize this GRT distribution. The minimum GRT represents the shortest period the gas molecules need from the reactor to the inlet of the condensation stage. The wider the distribution, the more pronounced the presence of back-mixing effects. With both characteristic parameters, the pyrolysis processes could be compared. These parameters depended mainly on the selected amount of flush gas and the reactor geometry. Also, the volume change of gases caused by different temperatures influenced the gas residence time. It was therefore determined for both reactor systems at operating conditions (500 °C) and at room temperature. The results of the gas residence time determination of the STR are listed in Table 2 in comparison with analogous measurements in the ASR described by Netsch et al. [23].

The minimum GRT at 2.3 L_{NTP}/min flush gas flow is approximately 17–20 s in the STR at both temperatures. The higher gas velocities in the hot reactor led to fast flushing, causing a narrower distribution of about 84 s. As a result of the higher reactor temperature and thus a temperature-induced increase in the flush gas volume flow in the reactor, the GRT width decreases significantly. In the STR, comparatively low freeboard volumes result in rapid flushing of the gas phase, with relatively little back-mixing. In comparison, the minimum GRT and the GRT distribution width are significantly higher in the ASR, with about 41 and 307 s, respectively. Therefore, secondary reactions of volatiles and gas molecules are expected to be more pronounced in the ASR pyrolysis system. The polymer-sand mixture is intensively mixed in the STR, and a large surface area of the polymer-sand bed is available in the ASR system. Therefore, the contribution of the mass transport from the sand-melt system to the freeboard is assumed to be comparatively negligible. Both reactor systems feature a condensation system of similar design. The minimum GRT accounts for about 1–2 min in both reactors. Comparable GRT distribution widths of about 100–120 s are estimated for the condensation systems, reflecting similar backmixing. The GRTs are therefore comparable, which implies a negligible impact on the efficiency of separating condensable and non-condensable products. This enables the comparison of the reactors for product yields and product compositions.

2.4.2. Temperature distribution

The temperature profile is an important characteristic of pyrolysis reactors. It is linked to temperature gradients and thus the feedstock heating. Besides the polymer-specific material properties (e.g., thermal conductivity, heat capacity, pyrolysis energy demand, particle size, and

particle density), the temperature distribution dominantly affects product yields through primary polymer decomposition and secondary reaction kinetics. Depending on the reaction speed and heating rate, the temperature of the pyrolyzing polymer can be significantly lower than the reactor set temperature. With the thermocouple in contact with the feedstock-sand mixture inside the STR system, the temperature of the polymeric feedstock was recorded over time. This allowed for comparison with the reactor wall temperature. Fig. 3 depicts this comparison in experiments with LDPE, PS, PVC, and PCW at a reactor wall temperature of 500 °C in the STR system. An average polymer temperature is also depicted as a dashed line. This temperature specifies the time-related average of the polymer temperature during its reaction, which can already start during the heating phase. Averaging is performed over the course of all 5 min feeding cycles. The semi-continuous dosing method with the feeding cycles is clearly visible in all curves. Because of varying polymer densities, the total feedstock mass of 250 g resulted in between seven and eleven dosing intervals for PVC and PCW, respectively. After each interval, the temperature of the polymer-sand bed in the hot reaction zone declined because of endothermic processes such as polymer heating, melt transition, and pyrolysis reaction. As this process continued, further energy was introduced through the heating sleeves, causing the temperature of the polymer-sand mixture to rise again. Therefore, the fluctuating polymer temperature varied on average by approximately 30–50 °C below the reactor wall temperature, depending on the feedstock. The maximal fluctuation accounted for LDPE up to 96 °C. In contrast, the reactor wall only experienced minor temperature fluctuations of 5 °C in maximum. In general, a rapid temperature acclimatization of the polymers is seen after dosing. The fast heating of the polymers is caused by the fast homogenization of the feedstock with the hot sand mixture in less than 10 s. Compared to PVC, LDPE, and PS represent polymers exhibiting higher pyrolysis energy demand. Consequently, PVC reveals the lowest deviation between internal temperature and wall temperature, LDPE and PS the highest. The PCW curve shows a progression between the previously mentioned examples.

Due to the complexity of the moving screw trajectory in the sand-polymer mixture, temperature monitoring within the polymer-sand bed was technically not feasible in the ASR system. Nevertheless, lower heating rates of the polymers can be assumed, as the polymer did not undergo fast and extensive mixing with hot sand particles as in the STR system. Several thermocouples located directly under the feedstock at the reactor wall allowed spatial temperature differences to be monitored during steady-state operation. The temperature measured by a thermocouple located 28 cm from the reactor inlet fluctuated by a maximum of 10 °C, independently of the feedstock composition. Standard deviations of 5.4, 2.8, 1.4, and 0.3 °C are recorded at reactor lengths of 28, 83, 139, and 193 cm, respectively. They emphasize that the majority of endothermic processes occur at the front of the reactor because of continuous feedstock transport from the inlet to the outlet. On the contrary, the continuous feeding method also leads to a more constant feedstock supply, which results in smoother reactor heating and less time-dependent fluctuations. Along with the significantly larger dimensions of the reactor, a higher polymer temperature is therefore expected at the end of the heating process than was observed with the STR. However, with a presumably slower heating rate in the ASR, parts of the polymer will have reacted before this end temperature is reached.

2.5. Analytical methods

The composition of the pyrolysis gas was determined by analyzing the gas bag samples with an advanced GC system. The system is based on an Agilent 8890 GC, which was customized with an additional isothermal oven by Teckso GmbH. Three detectors (thermal conductivity detector (TCD), flame ionization detector (FID), and Agilent 5977 C mass spectrometer (MS)) enabled the simultaneous identification and quantification of multiple gases. Details on the setup and the method parameters are summarized in the [supplementary information](#)

Table 2

Characteristic GRT distribution parameters of the investigated STR and ASR systems used for investigation.

Reactor	STR		ASR
Reactor temperature in °C	ambient	500	500
Minimum GRT in the hot reaction zone in s	17 ± 4	20 ± 3	41 ± 13
Width of GRT in the hot reaction zone in s	150 ± 13	84 ± 23	307 ± 21

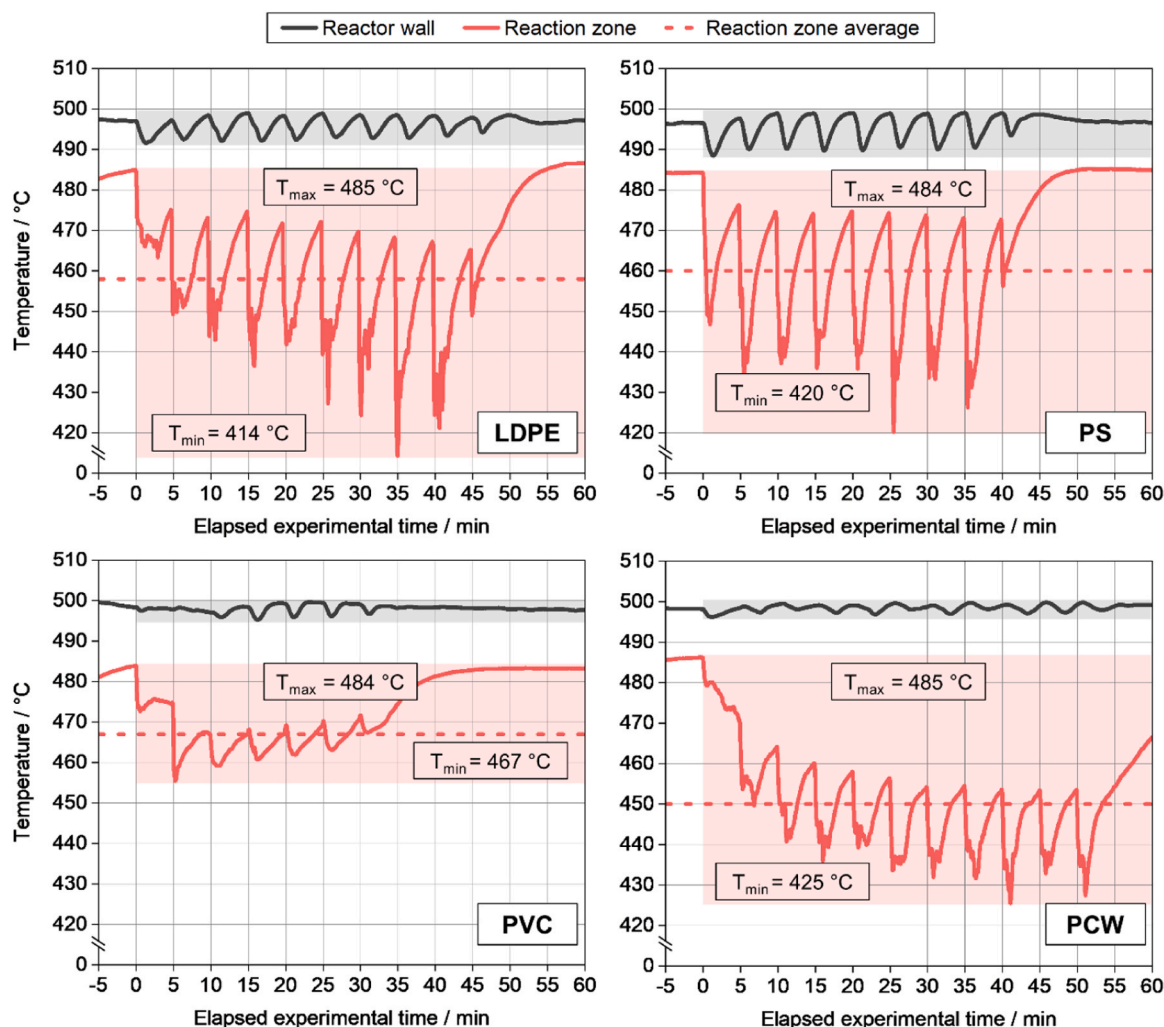


Fig. 3. Time-dependent temperature profile of the STR reactor wall and the internal temperature of the polymer-sand mixture for experiments with LDPE, PS, PVC, and PCW at 500 °C reactor wall temperature.

(S2). The TCD allowed for analyzing N_2 , O_2 , and main product gases such as CO_2 , CO , and CH_4 . The use of helium as the carrier gas prevented the quantification of H_2 . The MS enabled the identification of aliphatic and aromatic hydrocarbons (HC) ranging from C_2 to C_{10} , along with gaseous HCs comprising oxygen, nitrogen, and chlorine. These gases were quantified based on the FID signal. The sample was withdrawn from gas bags storing pyrolysis gas generated at the pyrolysis systems. Further details on the setup and mode of operation, such as the valve switching during the analytical procedure, are described in detail by Zeller et al. [27]. For quantification, the main gas species and expected trace gases were calibrated at least by a 3-point calibration, employing a linear calibration curve.

The condensate characterization required a variety of complementary analyses [28]. The elemental analysis for carbon, hydrogen, and nitrogen was carried out with a LECO Truspec CHN Micro elemental analyzer according to DIN EN 15104. An analyzer consisting of an AQF-2100 combustion system combined with an Aquion ion chromatograph (al-environsciences GmbH and Thermo Fisher Scientific GmbH) enabled the determination of the chlorine content. The water content in the condensates was measured based on DIN 51777 using Karl Fischer titration with a 870KF Titrino (Methrom). The calorific value of the condensates was determined using a C5000 calorimeter (IKA GmbH & Co. KG) according to DIN 51900. Simulated distillation performed under ASTM D 7169:2020 provided information on the product distribution of the condensates based on the boiling curve. In addition,

two-dimensional GC was performed to identify and quantify the main components of the condensate. The oils were analyzed by three parallel detectors: FID, MS, and a nitrogen-chemiluminescence detector. Details on the columns and parameters relevant to GC operation are described in the [supplementary information](#) (S2). The analysis system allowed the distinction between different product groups. Aliphatics, monoaromatics, indenenes, biphenyls, higher aromatic compounds, and heteroatom-containing HCs were distinguished. Further information on the development of this two-dimensional GC method and the data processing can be found elsewhere [28].

2.6. Calculations

The mass balance distinguished between the evolving product fractions: solid residue, condensate, and pyrolysis gas. The feedstock-related yield of the condensate y_{Cond} was determined by weighing the resulting condensate mass in the bottles of condensation stage 1 $m_{Cond,1}$ and stage 2 $m_{Cond,2}$ before and after the experiment according to formula 1.

$$y_{Cond} = \frac{(m_{Cond,1} - m_{Cond,1,Tare}) + (m_{Cond,2} - m_{Cond,2,Tare})}{m_{Feedstock}} \quad (1)$$

The yield of solid residue y_{Res} was calculated similarly using formula 2. Here, the weighed mass of sand and solid residue $m_{Sand+Res}$ after the test minus the initially added mass of quartz sand m_{Sand} was considered.

$$y_{Res} = \frac{(m_{Sand+Res} - m_{Sand})}{m_{Feedstock}} \quad (2)$$

By incinerating the remaining solid content in the reactor, the proportion of combustibles was determined. This value approximately corresponds to the content of coke y_{Coke} formed during pyrolysis. The coke yield was calculated from the mass before incineration $m_{Sand+Res,raw}$ and after incineration $m_{Sand+Res,incinerated}$ according to formula 3.

$$y_{Coke} = \frac{(m_{Sand+Res,raw} - m_{Sand+Res,incinerated})}{m_{Feedstock}} \quad (3)$$

The yield of pyrolysis gas $y_{Pyr,gas}$ was quantified following formula 4. This calculation required the total gas volume flow $\dot{V}_{Gas}$ and the gas density ρ_{Gas} to be integrated over the experimental phase. In addition, the purge gas mass $m_{Flushgas}$ had to be considered.

$$y_{Pyr,gas} = \frac{\left(\int_{Start}^{End} \dot{V}_{Gas} \rho_{Gas} \right) - m_{Flushgas}}{m_{Feedstock}} \quad (4)$$

According to Formula 5, the purge gas volume was calculated from the standard density of nitrogen $\rho_{Flushgas}$ and the purge gas volume flow $\dot{V}_{Flushgas}$ set at the mass flow controllers.

$$m_{Flushgas} = \dot{V}_{Flushgas} \rho_{Flushgas} \quad (5)$$

The pyrolysis gas composition was determined by integrating the individual peak areas of gases identified in the GC analysis. The calculation was based on the procedure described by Zeller et al. [27]. The concentration of each gas species c_i was calculated using its determined peak area A_i and the gas-specific response factor R_i as shown in formula 6 [27].

$$c_i = \frac{A_i}{R_i} \quad (6)$$

From the molar mass of the gas species M_i and the standard molar gas volume M_{Gas} , the volume fraction of the gas species in the product gas v_i was calculable according to formula 7 [27].

$$v_i = c_i \frac{M_{Gas}}{M_i} \quad (7)$$

The comprehensive gas characterization, with over 99 vol.% of determined compounds in all experiments (except for PVC), allowed the overall balance of the gas phase to be nearly closed. Therefore, the volume fractions were normalized to 100 vol.% except for the pure PVC pyrolysis gas. Quantification of HCl was not possible with the GC method. However, relevant quantities of HCl could be identified by MS in the PVC tests. Within this particular sample, HCl was assumed to account for the balance gap. HCl is therefore included in the normalization procedure as the difference from a completely closed balance. The pyrolysis gas density $\rho_{Pyr,gas}$ was calculated using the normalized volume fractions and the density of the gases ρ_i relying on the ideal gas law as defined in formula 8 [27]. This was required to determine the normalized mass fractions of the gases x_i for the pyrolysis gas composition according to formula 9 [27].

$$\rho_{Pyr,gas} = \sum_i (v_i \rho_i) \quad (8)$$

$$x_i = v_i \frac{\rho_i}{\rho_{Pyr,gas}} \quad (9)$$

In this study, a model approach was used to calculate product yields and composition for the pyrolysis of plastic mixtures. It was based on the linear combination of experimental values of the individual polymer components and has already been successfully applied for calculations of product yields [29], reaction kinetics [11], or the energy demand [23] in plastic pyrolysis. The theoretical values represent a reference value under an idealized assumption. The reaction mechanisms of the

polymers in the mixture are assumed to occur independently of each other, neglecting polymer-type-dependent interactions. This approach is referred to as the superposition assumption. The calculated yields y_{theo} for the product fraction were estimated from the proportions w_j of the pure substances j in the mixture and the respective product fractions during their pyrolysis y_j according to formula 10 [29].

$$y_{theo} = \sum_j (w_j y_j) \quad (10)$$

Model calculations of the composition of gases and condensates were carried out analogously. The content of a component $x_{i,theo}$ was calculated from the weight fraction in the pure polymer x_{ij} , considering the polymer proportion in the mixture and the normalized polymer-related yield of this product fraction as defined in formula 11 [29].

$$x_{i,theo} = \sum_j x_{ij} \cdot \left(\frac{w_j \cdot y_j}{\sum_j w_j \cdot y_j} \right) \quad (11)$$

3. Results

3.1. Stirred tank reactor

The experimental results for the pyrolysis of different feedstocks in the STR system include the yields of the product fractions and their respective chemical compositions. The product analyses focus on organic products, meaning pyrolysis oil and pyrolysis gas.

3.1.1. Product fraction yields

Experiments with MgOx were conducted for preliminary validation of the STR reactor setup. The results are averaged from three different experiments. The yields for pyrolysis gas, condensable products, and solid residue amount to 47.5, 22.3, and 29.1 wt.%, respectively. The statistical fluctuations of a maximum of 0.9 wt.% indicate excellent reproducibility. The mass balance closes up to 0.8 wt.%. Based on the stoichiometry of a complete thermal decomposition, the expected reaction products of MgOx account for 48.5 wt.% of gaseous products (carbon dioxide and carbon monoxide), 24.3 wt.% of water, and 27.2 wt.% of solid residue in the form of magnesium oxide. The experimental yields are consistent with the theoretically expected yields. The gas density sensor with its oscillating membrane proves to be unsuitable for tests with polyolefins and PVC. Therefore, no reliable density measurements are available for these tests. Consequently, the gas yield is assumed to represent the difference from a closed mass balance.

Fig. 4 shows an overview of the product yields obtained in pyrolysis experiments at 500 °C. The comprehensive data set, including all values, is listed in the [supplementary information](#) (S3). Pyrolyzing the polyolefins, LDPE and PP, mainly condensable products with 72.3 and 71.3 wt.% are formed. For PS and ABS, 98.5 and 91.2 wt.% of condensate are obtained, respectively, and almost no solid residue is formed. In the ABS experiments, 5.4 wt.% of pyrolysis gas is yielded. In these experiments, the balance loss is very low at 0.1 and 0.3 wt.%. With 76.1 wt.% PA6 pyrolysis mostly yields condensable products. The proportion of gas accounts for 20.4 wt.%. Both heteroatom-containing plastics, ABS and PA6, form solid residue with 3.5 wt.%. This solid residue is mainly comprised of coke. In the case of PVC, more pyrolysis gas with a yield of 60.2 wt.% is produced. Only a minor yield of condensable products is obtained. With 28.9 wt.%, a significant amount of solid residue remains in the reactor. This solid residue can be further specified by incineration. This residue is comprised by about 17 wt.% of coke and 12 wt.% of incombustibles.

The feedstocks Mix A, Mix B, Mix C, and PCW consist of over 70 wt.% of polyolefins. The additional proportion of PS in Mix A increases the condensate yield to 79.3 wt.%. However, this test also shows a higher experimental uncertainty of approximately 7.2 wt.% compared to the

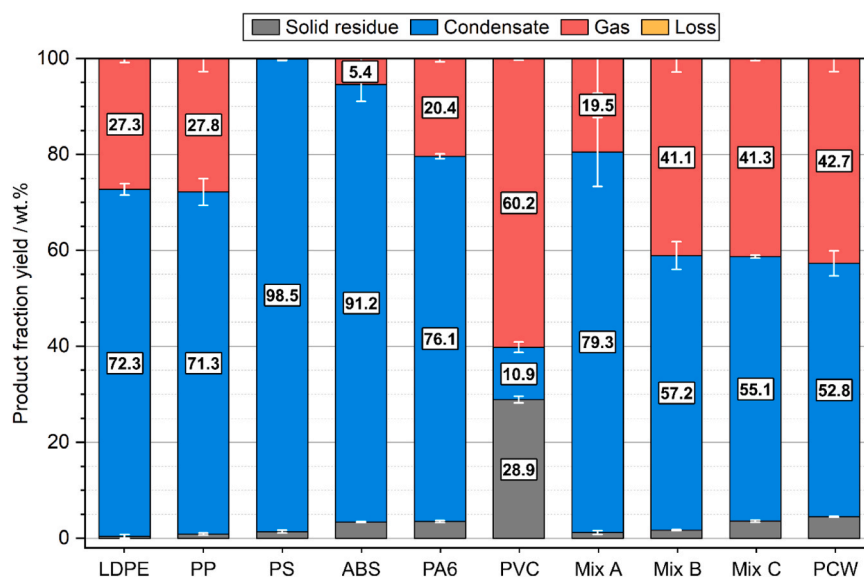


Fig. 4. Mass yields of the pyrolysis experiments with thermoplastics at 500 °C reactor wall temperature in the STR system.

other experiments. The gas yield accounts for 19.5 wt.%. Despite the different proportions of polyolefins, similar results are generated for the heteroatom-containing polymer blends Mix B and Mix C. The condensate yield amounts to 57.1 and 55.1 wt.%, respectively. Mix C generates slightly more solid residue (3.6 wt.%) than Mix B (1.7 wt.%), reflecting the higher PVC and PET content. The PCW exhibits a similar polymer composition to Mix C. The solid residue yield is slightly increased.

3.1.2. Gaseous product composition

The gas composition differs with the pyrolyzed feedstock. The gas analysis results of experiments with the pure thermoplastics are listed in Table 3. An aliphatic dominance is visible in the gas composition from LDPE pyrolysis experiments. The light HCs are distributed over a chain length range from C₁ to C₁₀, with a maximum at C₃ and C₄ HCs. At 9.0 and 8.4 wt.%, 1-butene and n-butane are the main gases alongside propane, propene, ethane, and ethene. Linear n-alkanes and α -olefins

also dominate in longer chain lengths. The gas composition in PP pyrolysis is similar to the LDPE results. However, a selectivity to propene (26.4 wt.%), iso-butenes (10.8 wt.%), and C₅ gases is detected. The C₅ gases are primarily composed of n-pentane (8.6 wt.%), 2-methyl-2-butene (3.9 wt.%), dimethyl-cyclo-propane (3.4 wt.%), and 2-pentenenes (2.2 wt.%). Elevated quantities of 2-methyl-pentenenes are also present (4.6 wt.%). In the polyolefin-based gases, the few aromatics, namely styrene and ethylbenzene, can probably be assumed to be artifacts from preliminary tests rather than having formed in the experiment. No heteroatom-containing HCs can be identified in the gas.

The composition of PS pyrolysis gas samples consists mainly of aromatics, as expected from other studies [15,30]. In addition to styrene (60.9 wt.%), toluene (9.8 wt.%), and benzene (4.7 wt.%), from Table 3, ethylbenzene (6.4 wt.%) and α -methylstyrene (1.4 wt.%) are quantified. Propylbenzene and cumene are also found in minor quantities. The low gas yield during PS pyrolysis complicates the gas analysis as the gas is

Table 3

Composition of pyrolysis gases generated in the experiments conducted with pure polymers in the STR at 500 °C wall temperature.

Gas species in wt.% ^A		LDPE	PP	PS	ABS	PA6	PVC
Light HCs (1st row: saturated; 2nd row: unsaturated)	CH ₄	4.3	4.0	0.0	2.7	4.2	0.7
	C ₂	9.7	7.8	0.3	2.7	4.0	0.5
		8.9	2.7	1.9	6.5	3.9	0.2
	C ₃	10.7	6.0	0.1	1.2	2.6	0.3
		12.4	26.4	2.1	4.7	4.9	0.2
	C ₄	8.8	1.8	0.1	0.6	1.8	0.2
		15.9	16.3	0.6	17.1	5.3	0.3
	C ₅	3.9	12.4	5.2	0.3	2.2	0.2
		12.4	8.6	0.1	4.0	6.6	0.2
	C ₆	1.3	0.6	0.0	0.5	0.3	0.1
Aromatics		6.5	8.5	0.0	1.5	2.4	0.2
	C ₇ to C ₁₀	0.8	1.7	0.5	0.0	0.2	0.1
		1.4	2.5	4.8	0.5	0.6	0.1
	Benzene	0.0	0.0	4.7	0.4	0.0	0.7
	Toluene	0.1	0.0	9.8	3.7	0.1	0.1
	Styrene	2.3	0.6	60.9	5.5	0.4	0.0
	Others aromatics	0.5	0.1	8.9	1.7	0.2	0.0
	CO ₂	0.0	0.0	0.0	3.3	47.3	10.7
	CO	0.1	0.0	0.0	0.2	9.3	0.2
	Other O-containing	0.0	0.0	0.0	0.0	0.9	0.2
Heteroatom-containing gases	HCN	0.0	0.0	0.0	1.0	0.0	0.0
	Acrylonitrile	0.0	0.0	0.0	35.9	0.3	0.0
	Other N-containing	0.0	0.0	0.0	6.0	2.5	0.0
	HCl	0.0	0.0	0.0	0.0	0.0	84.1
	Other Cl-containing	0.0	0.0	0.0	0.0	0.0	0.7

^A gas proportion related to the mass of entire permanent gas

diluted by a constant flow of flush gas. The concentration of some gas species reaches the limit for an adequate identification and quantification of the peaks. Also, the uncertainty and the influence of artifacts are higher compared to other gas samples of this study. The artifact impact is stronger because of the low amount of total gas. For example, the increased amounts of C₉ are presumably not formed as PS products but are rather attributed to artifacts of previous PP pyrolysis in the form of dimethyl-heptenes (4.0 wt.%) or the presence of 2-methylbutane (4.4 wt.%).

Similar gas species to PS experiments are obtained in the pyrolysis of the copolymer ABS. However, nitrogen-containing HCs and a relevant amount of HCN can be detected. The most prominent gases are acrylonitrile and acetonitrile with amounts of 35.9 and 6.0 wt.%, respectively. As a monomer in the ABS structure, acrylonitrile is expected, like the higher concentration of C₄ HCs. However, these C₄ HCs are mainly present in the form of butenes and not as butadiene, one monomer in the ABS structure.

Major amounts of CO₂ and CO form during PA6 pyrolysis. A few nitriles and multiple O-containing HC of low concentration are identified. The gas composition in PVC experiments is dominated by HCl and CO₂. HCl, as well as benzene and CH₄, which are also evident in the analysis, are known to be PVC's main decomposition components [31].

Table 4 lists the pyrolysis gas composition of the mixed plastics pyrolysis. Mix A only consists of aliphatic and aromatic hydrocarbons reflecting the feedstock composition, which comprises LDPE, PP, and PS. With Mix B, Mix C, and the PCW, gases generated from more complex feedstock compositions are analyzed. High amounts of CO₂ and CO are detectable. With more polyolefins in the mixtures, the gas composition shifts to higher concentrations of light aliphatic HCs. Only minor amounts of aromatics are detected. Heteroatom-containing gas species are identified. Reflecting the lower proportion of ABS, PA6, PET, and PVC in the feedstock, these values are significantly lower in Mix B than in Mix C or the PCW. Nevertheless, HCN is still present in Mix B with only 0.01 wt.%. For Mix C and PCW, the content of HCN amounts 0.06 and 0.03 wt.%, respectively. Chlorine- and oxygen-containing gases are

also increased in Mix C and Mix B.

3.1.3. Composition of condensable products

The elemental composition of the pyrolysis condensates obtained in the STR is displayed in Table 5. The full data set and corresponding superposition calculations of the elemental analysis can be found in the supplementary information (S5). All condensates produced with the STR system contain a high carbon and hydrogen content ranging from 62.3 to 91.5 wt.% and 8.3 to 14.4 wt.%, respectively. The heteroatom content and the calorific value are highly polymer-dependent. The calorific value of LDPE, PP, PS, and plastic mixtures pyrolysis oils ranges from 42.1 to 46.6 MJ/kg. These values fit into the general range of reported

Table 5

Normalized elemental composition and calorific value of the pyrolysis oils obtained from pyrolysis of the investigated thermoplastics and thermoplastic mixtures in the STR system and superposition-based calculations.

Condensate	Elemental composition in wt.%					Calorific Value in MJ/kg
	C	H	N	Cl	O ^A	
LDPE	85.6	14.4	< 0.2	0.0	0.0	46.6
PP	86.1	13.9	< 0.2	0.0	0.0	46.3
PS	91.5	8.3	0.2	0.0	0.0	42.1
ABS	86.7	8.4	4.7	0.2	0.0	40.0
PA6	62.3	10.0	11.0	0.6	16.1	31.8
PVC	85.8	9.7	0.9	3.6	0.0	^B
Mix A	88.1	11.9	< 0.2	0.0	0.0	45.4
theo. ^C	87.9	12.0	0.1	0.0	0.0	-
Mix B	85.0	14.0	0.3	0.1	0.6	45.8
theo. ^C	84.7	13.8	0.2	0.0	1.3	-
Mix C	84.4	12.5	0.6	0.5	2.0	43.7
theo. ^C	83.5	12.2	0.9	0.1	3.3	-
PCW	82.6	13.6	0.4	0.5	2.9	44.1
theo. ^C	82.7	12.6	1.0	0.1	3.6	-

^A calculated as the difference to 100 wt%.

^B analysis not conducted because of high chlorine content.

^C theoretical results estimated based on superposition calculations.

Table 4

Composition of pyrolysis gases obtained in STR experiments at 500 °C wall temperature and theoretical superposition-based calculations.

Gas species in wt.%		Mix A		Mix B		Mix C		PCW	
		exp.	theo.	exp.	theo.	exp.	theo.	exp.	theo.
Light HCs (1st row: saturated; 2nd row: unsaturated)	CH ₄	3.7		3.7		3.3		4.9	3.8
			4.2		4.0		3.7		
	C ₂	7.2	8.9	7.2	8.6	6.1	7.7	5.2	7.8
		5.6	6.2	6.6	7.0	7.1	6.3	7.0	5.9
	C ₃	6.6	8.6	7.2	8.9	5.4	7.9	4.7	7.7
		19.1	18.4	12.8	14.5	9.8	12.9	10.3	14.8
	C ₄	3.9	5.8	5.1	6.7	4.0	5.9	3.0	5.4
		13.6	16.0	11.7	14.8	9.4	13.5	9.5	13.9
	C ₅	10.9	7.5	9.0	5.5	8.2	4.9	9.0	5.9
		11.0	10.7	7.9	10.7	7.7	9.6	7.2	9.6
Aromatics	C ₆	1.7	1.0	3.6	1.1	2.3	0.9	2.4	0.9
		11.2	7.4	7.5	6.5	7.3	5.8	9.6	6.2
	C ₇ to C ₁₀	0.6	1.2	1.1	0.9	1.1	0.8	0.9	1.0
		2.4	1.9	2.1	1.5	2.2	1.4	3.4	1.5
	Benzene	0.5		0.2		0.7		0.6	0.1
			0.0		0.0		0.1		
	Toluene	0.5	0.1	0.3	0.1	0.7	0.1	0.5	0.1
	Styrene	1.0	1.7	3.3	1.8	0.4	1.7	0.4	1.5
	Others aromatics	0.4	0.3	0.4	0.4	0.3	0.4	0.3	0.3
Heteroatom-containing gases	CO ₂	0.1		7.1		16.4		14.7	3.7
			0.0		2.4		3.7		
	CO	0.0	0.1	1.8	0.8	3.2	0.5	3.1	0.6
	Other O-containing	0.0	0.0	1.0	0.0	1.5	0.1	0.8	0.1
	HCN	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
	Acrylonitrile	0.0	0.0	0.0	0.0	1.1	0.4	0.5	0.3
	Other N-containing	0.0	0.0	0.0	0.0	0.5	0.2	0.6	0.2
	HCl	-	0.0	-	3.8	-	11.4	-	8.6
	Other Cl-containing	0.0	0.0	0.4	0.0	1.2	0.1	1.4	0.1

^A gas proportion related to the total gas volume

data [12,13]. Chang et al. concluded a lower heating value of 45, 46, and 41–45 MJ/kg for PE, PP, and PS, respectively [12]. The calorific value of the mixed plastics corresponds well with the data summarized for the pyrolysis oil of mixed plastic waste [13]. They report a range of 40.5 to 45.6 MJ/kg [13].

In condensate of LDPE, PP, and PS experiments, no significant amounts of oxygen, nitrogen, or chlorine are detected. The polyolefins show a hydrogen/carbon ratio (H/C) of approximately 2.0. This finding is consistent with the expected aliphatic character of the LDPE and PP pyrolysis products. It corresponds to an H/C of about 1.8 and 2.0 for PP and PE reported by Calero et al. [25]. In contrast, an H/C of about 1.1 and 1.2 is calculated for the PS and ABS condensate, indicating mainly aromatic components. This value also corresponds to the H/C of 1.25 found in literature [25]. Nitrogen-containing compounds are also present in the ABS condensate. The highest content of HCs comprising nitrogen and oxygen is detected for the condensate generated from PA6. The condensate contains 16.1 wt.% of oxygen and 11.0 wt.% of nitrogen. This observation is consistent with the expected selective decomposition mechanism of PA6 to ϵ -caprolactam [32]. The low chlorine content in this sample may result from artifacts of previous PVC experiments. In PVC pyrolysis, a condensate with a high chlorine content of 3.6 wt.% chlorine is produced. Minor amounts of nitrogen artifacts from previous experiments also occur here. These artifacts complicate the interpretation of the results, but are hardly avoidable given the size and multistage setup of the pyrolysis condenser system in combination with the highly viscous condensates.

The condensate from Mix A contains only carbon and hydrogen as expected. The H/C is 1.6 and lies between the H/C of the condensate of individual polymers in the mixture. Mix B, Mix C, and PCW contain significant amounts of oxygen, nitrogen, and chlorine in addition to carbon and hydrogen. The nitrogen and chlorine content are significantly lower for Mix B (0.28–0.08 wt.%) than for Mix C (0.55 and 0.54 wt.%) and the PCW (0.43 and 0.53 wt.%). The oxygen content is also significantly lower for Mix B (0.6 wt.%) than for Mix C (2.0 wt.%) or the PCW (2.9 wt.%).

All condensates generated in the STR system are analyzed using the two-dimensional GC method. This allows for quantification of the main HC species and the compound groups. The results of the group evaluation are listed in Table 6. All chromatograms with indicated main compounds and the results of the main component quantification can be found in the supplementary information (S6).

Mostly linear aliphatic compounds are detected by two-dimensional GC in the LDPE condensate. These aliphatics are mostly comprised of unbranched n-alkanes and α -olefins. The condensable phase from PP pyrolysis, on the other hand, is composed of branched aliphatics. The most prominent component is 2,4-dimethylheptene at 3.7 wt.%. In both cases, the distribution extends over a broad chain length range, which is consistent with the results of the simulated distillation. Since the GC analysis method is technically limited for HCs with boiling points above 350 °C, a gap in the sum of quantifiable products prevents a complete analysis. This gap is not present for the PS condensate, as it mainly

contains products in the analyzable boiling range. Mainly monoaromatics, diphenyls, and other aromatic compounds are quantifiable. A styrene concentration of 61.8 wt.% is determined. In addition, 2.5 wt.% ethylbenzene and 2.3 wt.% each of toluene and α -methylstyrene are found. α -Methyl-stilbene and triphenyl-cyclohexane form a pronounced blob in the chromatogram. Furthermore, a blob with very low intensity is recognizable, which is identified via MS as benzaldehyde. Because of uncertainties in the quantification methodology, the sum of all compound groups is 102.5. This result indicates a nearly complete characterization of the compounds in the pyrolysis oil within typical method deviations [28].

Condensates of the other pure plastics consist of many HCs that contain nitrogen, oxygen, and chlorine. In the ABS condensate, almost all of the 28.7 wt.% of heteroatom-containing HCs are nitrogen-containing substances such as benzobutanenitrile, 1-benzylpyrrole, or phenyl-pentenitrile. Both aromatic and aliphatic nitriles are identified in relevant quantities. Fig. 5 shows the two-dimensional GC analysis of pyrolysis oil obtained by pyrolyzing ABS in the STR. HCs that have already been determined in the PS condensate are detected. The styrene concentration accounts for 31 wt.%. In addition, diphenyl-cyclopropane, α -methyl-stilbene, and triphenyl-cyclohexane are identified. ϵ -Caprolactam is also detected and is probably transferred to the condensate from previous PA6 experiments. It represents the main component in the PA6 condensate with approximately 42 wt.% of short-chain aliphatic nitriles, or short-chain and long-chain amides, are found in the PA6 condensate. Therefore, nitrogen- and oxygen-containing HCs can be detected exclusively. This requires fundamental adaptation of the compound group ranges, which are based on polyolefin-rich mixed plastic condensates.

However, for the PVC condensate, no group range adaptation is necessary. Increased concentrations of mono- as well as condensed and non-condensed polyaromatic compounds are detected. Only one prominent blob is recognizable, which can be specified as chlorine-containing HC. However, this blob, (1-chloroethyl)-benzene, emerges with high intensity. The analysis indicates small amounts of aliphatics. Palmitic acid and stearic acid, as well as smaller amounts of methyl palmitate and methyl stearate, are found. Small amounts of aliphatic HCs are detected. Benzobutanitrile and benzylpyrrole are found in the two-dimensional analysis of the PVC condensate, which can be attributed to the previous test with ABS, as already seen in the elemental analysis. However, due to the comparatively low condensate yield in the PVC test, their contribution to the composition is significantly higher than that of the PA6 artifacts in the ABS condensate.

The compound-group specific analysis for the mixtures is summarized in Table 7. The condensate of Mix A shows aromatic as well as branched and unbranched aliphatic components. Despite the blob of benzaldehydes, which also occurs in this mixture owing to the PS content, no heteroatom-containing HCs can be identified.

The two-dimensional GC chromatogram for the pyrolysis generated from the PCW is depicted in Fig. 6 as an example for the condensates of the mixed thermoplastic feedstocks. The condensates of Mix B, Mix C, and the PCW contain mostly aliphatics with 69.7, 52.6, and 56.2 wt.%, respectively. Nevertheless, monoaromatics and especially diphenyls and polyaromatic structures are also evident. The composition of the PCW condensate is similar to that of Mix C. At 3.5 wt.%, the heteroatom-containing HCs in the PCW condensate are slightly higher than in the condensate of Mix C. The previously determined main components of ABS, PA6, and PVC pyrolysis are detectable at lower intensities. In addition, benzoic acid is detected in the condensates from Mix B, Mix C, and PCW. The proportion of benzoic acid in the condensates amounts to 0.50 and 0.84 wt.% for the condensate from Mix B and Mix C. In the PCW, additional blobs are detectable as C₁₃ and C₁₄ nitriles, as well as aliphatic oxygenated compounds.

Table 6

Compound group-specific GC analyses of the pyrolysis oils obtained from pyrolysis of pure thermoplastics in the STR system.

Compound group	Content of compound group in the pyrolysis oil sample in wt.%					
	LDPE	PP	PS	ABS	PA6	PVC
Aliphatics	73.9	78.3	4.4	2.1	0.3	6.4
Monoaromatics	2.0	2.3	69.8	42.4	0.2	6.7
Indenes	0.1	0.0	0.1	0.2	0.1	1.2
Naphthalenes	0.1	0.0	0.1	0.7	0.1	1.2
Diphenyls	0.4	0.3	13.6	6.1	0.6	6.1
Other aromatic compounds	0.4	0.3	13.7	6.1	0.0	11.8
Heteroatom-containing HCs	0.0	0.1	0.8	28.7	67.7	11.0
Sum of identified compounds	76.9	81.3	102.5	86.3	69.0	44.4

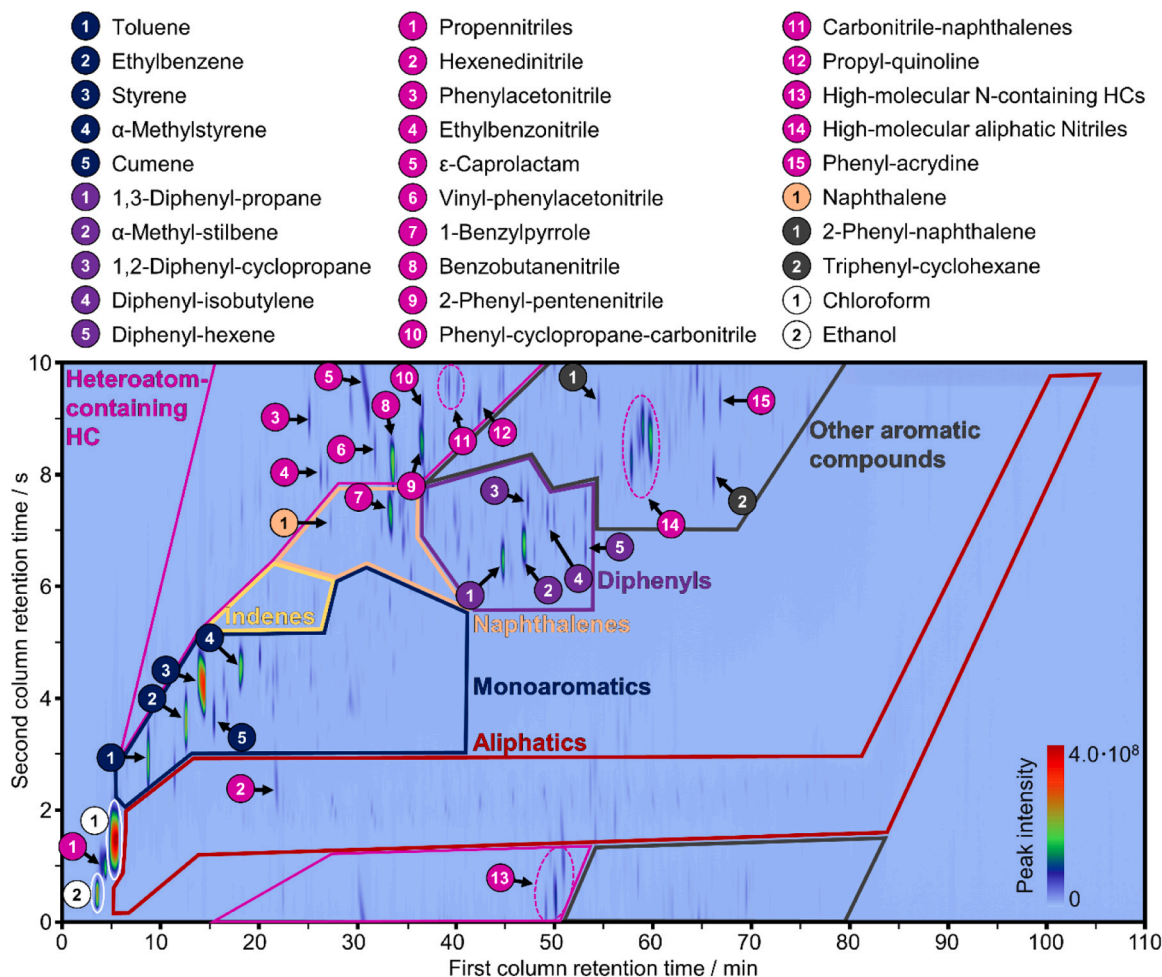


Fig. 5. Chromatogram of the condensate obtained during ABS pyrolysis in the STR system.

Table 7

Compound group-specific GC analyses of the pyrolysis oils obtained by pyrolysis in the STR system and the superposition-based calculated analysis for Mix A condensate.

Compound group	Content of compound group in the pyrolysis oil sample in wt. %				
	Mix A	Mix A (theo.) ¹	Mix B	Mix C	PCW
Aliphatics	50.2	49.3	69.7	52.6	56.2
Monoaromatics	25.5	27.2	3.3	13.5	6.1
Indenes	0.2	0.1	0.1	0.2	0.1
Naphthalenes	0.2	0.1	0.1	0.2	0.2
Diphenyls	3.8	5.2	1.0	1.8	1.1
Other aromatic compounds	3.6	5.3	1.2	1.4	0.9
Heteroatom-containing HCs	0.4	0.3	1.2	3.0	3.5
Sum of identified compounds	83.9	87.5	76.6	72.7	68.1

¹ superposition-based calculation considering polymer content in the feedstock and condensate yields.

3.2. Comparison of the STR and ASR pyrolysis system

The conducted investigations allow the comparison of the STR pyrolysis results with those of pyrolysis in the ASR system. The previously presented mass balances and product compositions of gas and condensate fractions of the STR system serve as comparison parameters to the ASR results.

3.2.1. Product yield comparison

In Fig. 7, the mass balances of pure thermoplastics and thermoplastic mixtures are compared to the available data from the ASR study [23]. As for the STR experiments, each feedstock was pyrolyzed at least twice in the ASR system. The condensate yields are significantly higher in the STR for LDPE, PP, and PS. Solid residues are negligible. In experiments with these pure polymers, the ASR yields less condensate of only 48.8, 49.1, and 88.5 wt.%, respectively. Consequently, it shows higher permanent gas yields.

Reactor-specific differences also emerge when comparing the mass balances for the thermoplastic mixtures. Compared to the STR, a lower condensate yield can be observed for pyrolyzing Mix A in the ASR system, as is the case when comparing the pure materials. Despite measurement inaccuracies of 1–3 wt.% of the condensate yields, this tendency is also identified for the yields of the mixtures Mix B, Mix C, and PCW. The condensate yield in the STR is 5.8, 5.6, and 2.6 wt.% higher, respectively. However, the trend is significantly less pronounced for the heteroatom-containing thermoplastic mixtures than for pure thermoplastics.

3.2.2. Comparison of gaseous products

The impact of reactor design is also evident when comparing the gas composition obtained in both reactor setups. The detailed results of the ASR experiments are provided in the [supplementary information \(S4\)](#). The gas from LDPE, PP, PS, and Mix A experiments shows similarity to the results of the ASR experiments. The HC distribution reveals a slight shift towards short-chain HCs at the STR for polyolefinic feedstocks. For the other feedstocks, lower aromatic contents can be quantified in the

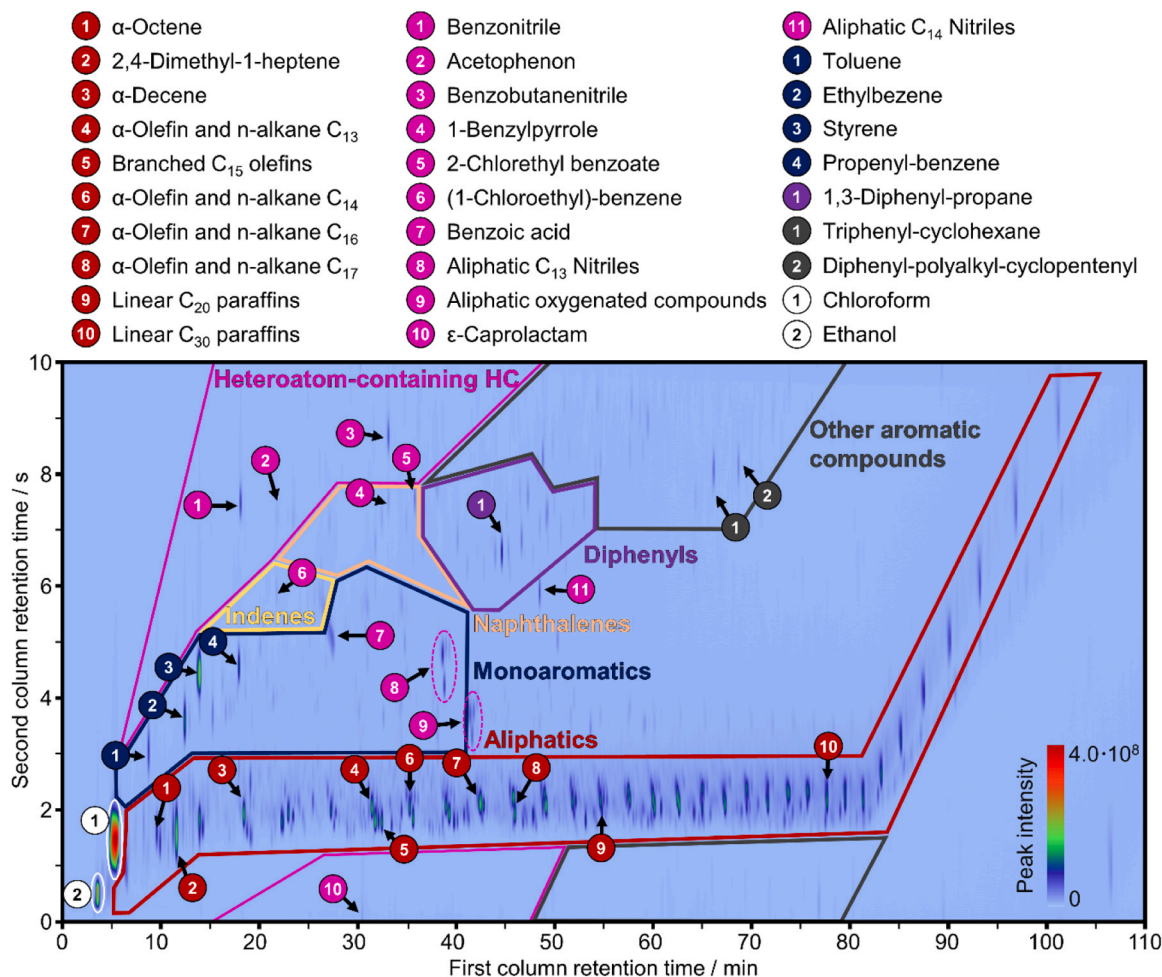


Fig. 6. Chromatogram of the condensate generated from PCW pyrolyzed in the STR system.

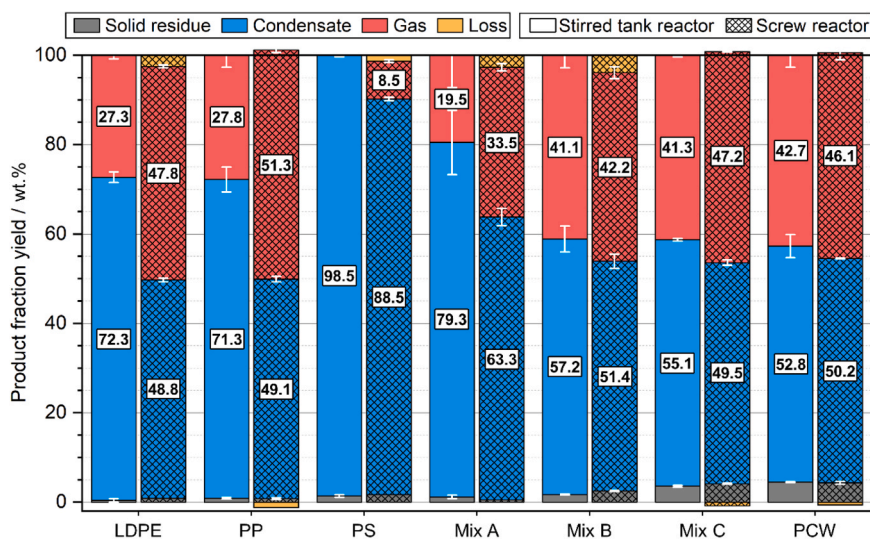


Fig. 7. Mass yields of the pyrolysis experiments with thermoplastics at 500 °C reactor wall temperature in the STR system (plain) compared to ASR results (shaded) [23].

product gas obtained from STR experiments.

Comparing the gas analyses of the heteroatom-containing feedstock experiments, less heteroatom-containing HCs are detected in the ASR than in the STR. For example, a lower concentration of CO₂ (4.4 and

7.7 wt.%) and CO (1.0 and 1.5 wt.%) is obtained in the ASR system for the pyrolysis of Mix B and the PCW, respectively. Comparisons regarding Mix C cannot be provided as comprehensive data for the pyrolysis of this feedstock in the ASR is missing.

3.2.3. Comparison of condensable products

The condensate analysis also reveals strong variations related to the reactor type. Fig. 8 depicts the condensates' elemental analyses obtained at the ASR in comparison to the results of the STR. The ASR condensate characterization is presented by Netsch et al. in a previous work [28]. The results are summarized in the [supplementary information](#) (S5) in detail. No significant differences are evident for the condensates obtained from LDPE, PP, PS, and Mix A, in contradiction to the heteroatom-containing polymer blends.

The carbon content in the condensates generated from Mix B, Mix C, and the PCW at the STR is significantly lower, while the hydrogen content is higher, resulting in a higher H/C in the condensates produced from Mix B, Mix C, and PCW of 2.0, 1.8, and 2.0, respectively. The H/C of the corresponding condensates obtained in the ASR are 1.8, 1.6, and 1.7. The comparison of the mixed plastic condensate for both reactors also reveals distinct contrasts relating to the oxygen content. In the condensates of the reference mixtures and the PCW that were produced in the STR, significantly higher oxygen and lower carbon content are determined. The increase in oxygen is less pronounced for Mix B. Mix C and the PCW condensate exhibit higher oxygen contents of 2.0 and 2.9 wt.% than the corresponding condensate from the ASR, accounting for 0.9 wt.% of oxygen, respectively. For nitrogen and chlorine, no significant trends are apparent for the three mixtures pyrolyzed in both reactor types.

The condensates obtained from the STR reactor were analyzed by two-dimensional gas chromatography and compared to the corresponding reported data by a previous study at the ASR system [28]. The detailed elemental compositions are provided in the [supplementary information](#) (S5). The same blobs can be seen in chromatograms of polyolefins and polystyrene condensate. However, the compound proportions shift slightly towards shorter retention times and thus molecules with low molecular weight. This observation is much more pronounced in condensate obtained from PS than from polyolefins. The two-dimensional GC analyses, cannot verify the increase in oxygen-containing species for the STR condensate from Mix B, Mix C, and the PCW.

While elemental and GC analyses provide a general overview of heteroatom impurities, they cannot reveal the entire condensate composition in terms of molecular weight distribution. In particular, the analysis of the boiling point distribution can serve as an indicator for this characteristic condensate property. Furthermore, it provides important key parameters for further utilization of the condensates in chemical processes. The condensate of the polyolefins, PS, and the mixtures pyrolyzed in the STR were analyzed. The results are shown in the diagrams

in Fig. 9. All condensates differ but cover a broad boiling range, including common petrochemical boiling cuts such as naphtha, middle distillate, and vacuum gas oil (VGO). The initial boiling point is at about 50 °C, and the final boiling point reaches 650 °C in maximum. The PE and the polymer mixtures' boiling curves exhibit the lowest proportion of naphtha cut. The PP curve shows a significantly lower boiling point in the range of 5 to 90 wt.% of distilled mass. In the styrene boiling curve, distinct horizontal lines at 145–150, 295, and 382 °C are visible. For Mix A, the styrene-indicating plateau remains visible. The distilled sample mass covered by the plateau accounts for about 20 wt.%. The rest of the curve is similar to that of LDPE and PP and extends over a broad boiling range. Condensate of Mix B and Mix C obtained from the STR system exhibits similar characteristics to LDPE condensate. This is expected from the LDPE content of 70 and 50 wt.%, respectively. Compared to condensate generated from Mix B, Mix C shifts slightly towards smaller molecular weights as a result of the lower LDPE content. The simulated distillation curve of the PCW condensate from the STR system differs minimally from these reference mixtures.

The simulated distillation curves of the condensate generated in the ASR system is also depicted in Fig. 9. For LDPE and PP, the curve is drastically shifted towards a lower boiling point compared to the STR results. Approximately 32 and 36 wt.% more naphtha-range product cuts are visible in the ASR condensate, respectively. The condensable product fraction from PS experiments in the ASR shows a similar proportion of the styrene-indicating horizontal plateau. Nevertheless, more compounds with boiling points below 140 °C are detected. Comparing Mix A, Mix B, Mix C, and the PCW condensate, the shift towards low-boiling products becomes even more significant.

4. Discussion

4.1. Feedstock influence

The results emphasize the feedstock influence in plastic pyrolysis. This influence on the pyrolysis behavior is discussed by highlighting the differences between pure polymers and examining mixed thermoplastics.

4.1.1. Pure polymer behavior

The preliminary validation of mass balancing with MgOX proves the reliability of the applied methodology and the generated data. The comparison of different plastic types pyrolyzed in the STR demonstrates the strong contrasts in their pyrolysis behavior.

The polyolefins pyrolyze following a statistically distributed radical

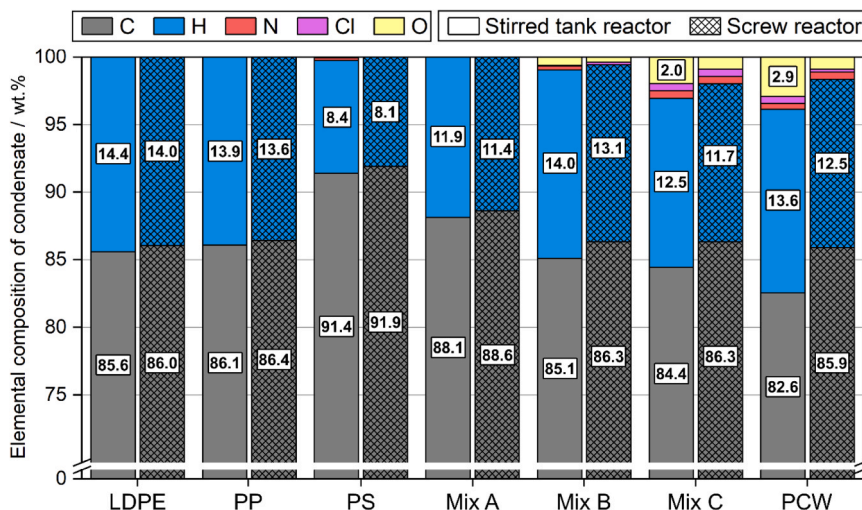


Fig. 8. Elemental composition of the pyrolysis condensate obtained at 500 °C reactor wall temperature in a STR (plain) and the ASR system (shaded; adapted from Netsch et al. [28]).

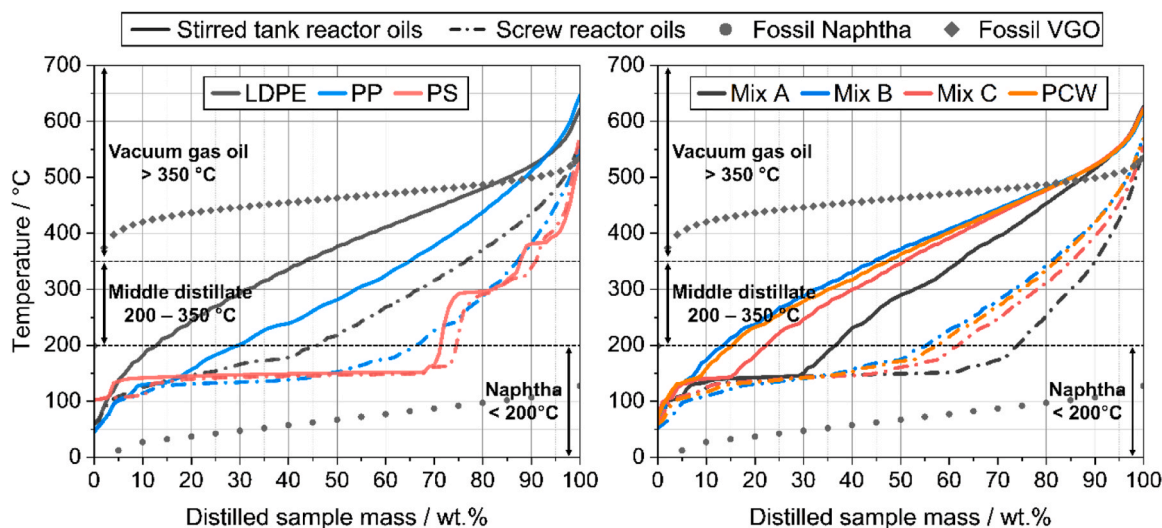


Fig. 9. Simulated distillation curves of the analyzed STR pyrolysis condensates compared to ASR results (adapted from Netsch et al. [28]) alongside fossil benchmark examples of naphtha (adapted from [33]) and VGO (adapted from [34]).

chain mechanism, leading to a broad product distribution of long-chain aliphatics [35]. The gas composition quantified for LDPE and PP pyrolysis meets the expectations drawn from reports by other authors [15, 17, 35]. An increased content of high-boiling gas species can be detected. However, other studies have not quantified components higher than C_4 in the pyrolysis gas [19, 20]. This difference could be caused by more efficient condensation systems in their reported experimental setups or in the lower resolution of their analyses. The number of potential HC configurations increases significantly with increasing chain length. Consequently, the respective concentrations become comparatively small. In these studies, pyrolysis gas is analyzed using a micro GC instead of a high-resolution GC system. Therefore, the combination of FID and MS in this study's GC method allows the identification and quantification of such less pronounced peaks over a broad range of chain lengths. The advantage of this system is also evident in the gas analyses of other experiments with different polymers. The results of the condensate analysis align with the product yields and the gaseous product. No heteroatoms are present, and the highest H/C is achieved in the LDPE and PP pyrolysis oil, making polyolefins the ideal feedstock for chemical recycling plants. Only unbranched α -olefins and n-alkanes dominate the composition of LDPE condensate, which extends over a broad boiling range. The simulated distillation curves depicted in Fig. 9 emphasize the broad molecular weight distribution of aliphatics in the PE condensate. This is consistent with the reported formation of waxes at lower pyrolysis temperatures [8, 35]. Following the decomposition mechanism of PP, the analyzed distribution is concentrated in the range of lower boiling temperatures.

The selective decomposition mechanism of PS feedstocks to styrene and its oligomers explains the high condensate yield [30]. The gaseous and condensable products confirm the presence of high amounts of PS monomer, its dimers, and its trimers. No specific dimer or trimer structure of PS can be found in the condensate. Rather, there are many different dimer- and trimer-like derivatives present. Nevertheless, condensed aromatic structures are found, giving examples of byproducts in the selective PS decomposition mechanism. The occurrence of benzaldehyde is not expected, given the chemical structure of PS. It is therefore attributed to impurities from the manufacturing process or to small amounts of additives in the polymer. The horizontal lines in the PS curve align with the presence of specific molecules of styrene, its dimers, and its trimers. The temperature of these horizontal lines of about 145–150, 295, and 382 °C corresponds to the monomer, dimer, and trimer evaporation temperatures.

ABS results are similar to PS pyrolysis yields and composition. The

additional butadiene and nitrile components in the co-polymer configuration of the ABS lead to the formation of pyrolysis gas [36], rich in butenes and acetonitrile and acrylonitrile. The presence of diphenyl-cyclopropane, α -methyl-stilbene, and triphenyl-cyclohexane also corresponds to the copolymer structure of ABS with aliphatic parts from butadiene and aromatic polymer parts. The chemical composition of the ABS condensate matches literature values for pyrolysis products of ABS [36]. The significant amounts of nitrogen in the condensate in the form of nitriles, quinolines, or pyrroles are expected to pose a problem in chemical recycling applications.

PA6 pyrolysis is reported to feature a selective decomposition mechanism to the monomer ϵ -caprolactam [32]. Because of its thermophysical properties, this monomer accumulates in the condensate. This explains the high condensate yield in PA6 pyrolysis determined in this study. With an ϵ -caprolactam content of approximately 42. wt.%, considerably less monomer is generated than compared to relevant studies in the literature [32]. The pronounced CO_2 formation during PA6 pyrolysis indicates a partial cleavage of the amide bonds of the PA6 backbone, resulting in the formation of other gas species. Consequently, HCs in the range of C_1 to C_6 are detectable in nearly evenly distributed amounts. This strengthens the assumption that under the experimental conditions, secondary cracking of ϵ -caprolactam occurs, reducing the overall monomer content. The absence of higher HCs strengthens the assumption of minor relevance of repolymerization reactions in the STR setup. These species are only expected if repolymerization or comparable addition reactions occur between unsaturated HCs of the gas phase.

The product yields of the PVC pyrolysis are consistent with a summary of PVC decomposition behavior by Yu et al. [31]. The reported two-stage PVC decomposition mechanism features preferential HCl formation in a first step and coke formation in a consecutive reaction of high-molecular polyene chains. Comparing the coke yield of 17.0 wt.% determined by incineration to the total amount of solid residue (28.9 wt. %), a difference is detectable. This difference is probably caused by the fillers contained in the PVC. The feedstock analysis reveals an ash content of about 12 wt.%. About 10.3 wt.% of this content are assigned to $CaCO_3$ and TiO_2 fillers by the manufacturer. TiO_2 is chemically stable in the relevant temperature range [37]. The composition of PVC pyrolysis gas includes high amounts of CO_2 and CO. CO_2 may only be formed via air exposure during pyrolysis or additives contained in the feedstock. Air entry can be excluded in this study, as the experimental methodology ensures a completely inert atmosphere in the reactor. Thus, their detection might also refer to the presence of fillers in PVC. The

decomposition of pure CaCO_3 to CO_2 and CaO starts at temperatures above 600 °C in an inert atmosphere [38]. However, Paydar et al. describe the decomposition of CaCO_3 happening at lower temperatures in the presence of HCl [39]. Therefore, interaction effects between filler and polymer emerge as a potential cause for the formation of CO_2 . Furthermore, oxygen-containing additives may also degrade during pyrolysis and release light oxygenated hydrocarbons. Other chlorine-containing HCs, such as chloromethane, chloroethane, chloroethene, chlorobutane, and dichlorocyclopropane, are identified in small quantities. The chlorine content in PVC condensate accounts for 3.6 wt.%. An experimental study with PVC in a furnace reactor revealed a significantly lower chlorine content in the oil of 0.16 wt.% [25]. Also, the authors report an oxygen content of 31.3 wt.% [25]. This finding, together with the elemental analysis of their feedstock, strengthens the presumption of additives that are incorporated in the PVC used in their study. The PVC employed in this study features a significantly lower amount of oxygen, which might explain the differences from the reported data. The oxygen content can be attributed to the palmitic and stearic acids identified via two-dimensional GC. Most probably, palmitic and stearic acids are not formed during pyrolysis, but rather represent additives contained in the PVC that volatilize during the pyrolysis process. Unexpectedly, only one specific chlorine-containing HC can be detected in the PVC condensate by two-dimensional gas chromatography. Chlorine atoms may be distributed across numerous different molecules with low intensities or high boiling points, making them difficult to identify in GC. However, aliphatic compounds are present. The presence of aliphatics may indicate that the polyene chains, which are formed as intermediate products [31], may not completely form aromatic structures, but also pass into the liquid product as unsaturated aliphatics.

4.1.2. Pyrolysis of mixed plastics

The strong feedstock influence is evident in the pyrolysis of the polymer mixtures. The yields of product fractions reflect the proportions of the yields of the incorporated individual polymers. Interaction effects can be assessed by applying the superposition approach to calculate theoretical product yields and product composition.

The calculated product yields for Mix A amount for 79.9 wt.% of condensate and 19.3 wt.% of the pyrolysis gas. They are consistent with the experimental results. Consequently, interactions between LDPE, PP, and PS that significantly change the overall product yields are not evident. This aligns with expectations based on laboratory-scale kinetic studies [11]. Applying the superposition calculation approach to the gas analysis, a similar composition can be calculated compared to the experimental results. Only minor differences of 3 wt.% in maximum are determined. Theoretical calculation of the elemental analysis results for Mix A reveals consistent findings. The carbon and the hydrogen content amount to 87.9 and 12.0 wt.%. The two-dimensional GC analyses show aromatic as well as branched and unbranched aliphatic components reflecting the LDPE, PP, and PS content in the feedstock. The content of aliphatics and monoaromatics differs only slightly at 0.9 and 1.7 wt.%. Diphenyls and other aromatic components are slightly overestimated. Considering measurement inaccuracies, the calculated compound groups also correspond well to the experimentally determined values. The condensate composition from Mix A appears suitable for chemical recycling applications, given its low heteroatom content. However, they still contain a high level of aromatics as a result of the high PS content in the feedstock, which must be considered during downstream pyrolysis oil processing. Generally, the STR results emphasize the possibility of calculating the product yields, as well as gas and condensate compositions for mixtures of LDPE, PP, and PS.

This conclusion does not apply to mixtures containing heteroatoms. The pyrolysis of these feedstocks results in similar product distributions independent of the polymer proportions. The slight increase in solid residue of PCW pyrolysis compared to Mix C might also be attributed to the presence of inorganic components, such as fillers. This corresponds

with the determined ash contents of the feedstocks in Table 1. The species in the gaseous product fraction of the pyrolyzed plastic mixtures can be referred to the specific polymer types. The intensive CO_2 and CO formation is known from the PA6 and PVC pyrolysis. Also, PET decomposition is known for its formation of CO_2 and CO in high quantities [15]. Because of the low gas yield of PS and ABS, minor proportions of aromatics are detected in the gas phase.

The condensate produced from Mix B, Mix C, and the PCW mainly consists of aliphatics and exhibits a comparatively low aromatic content. This relates to the low proportion of PS, ABS, PVC, and PET compared to Mix A. Heteroatom-containing HCs are detected in the condensate product of Mix B, Mix C, and the PCW via two-dimensional GC. The detected nitrogen- and oxygen-containing HCs in the mixtures extend over a broad chain length range and are bound in aliphatic as well as aromatic structures. Additional blobs in the PCW condensate, detectable as C_{13} and C_{14} nitriles, cannot be assigned to specific polymers tested individually. Consequently, they are assumed to originate from additives or other waste components contained in the polymers of the PCW. For example, certain additives may evaporate directly, similar to palmitic acid and stearic acid in PVC, or pyrolyze, leading to the formation of such compounds. The minor differences between the distillation curves of Mix C and the PCW condensate show that additives that may be present in the feedstock appear to have minimal influence on the condensates' boiling behavior. This is in line with the GC analyses. The potential additive-related compounds were only identified as trace substances. The total amount of oxygen in Mix C and PCW condensate is quantified to 2.0 and 2.9 wt.% by elemental analysis. Alongside the nitrogen and chlorine content in the samples, a higher proportion than 3.0 and 3.5 wt.% of heteroatom-containing HCs is expected from the two-dimensional GC. The selective enrichment of oxygen in compounds of the HC with elevated evaporation temperature may be possible and explain this finding. Compounds that contain chlorine and nitrogen may accumulate in this high-boiling distillation cut. Further research on the chemical composition of the high-boiling compounds in the condensate is required for final clarification. Kusenberget al. provide a comprehensive overview of the nitrogen, chlorine, and oxygen content analyzed by various authors for different plastic mixtures [40]. Their review indicates the tendency that high amounts of a contaminant in the feedstock increase the corresponding content in the pyrolysis oil. They report a maximum content of 0.36 wt.% nitrogen, 3.8 wt.% oxygen, and 1.4 wt.% chlorine in the pyrolysis oils [40]. The results of this study correspond with the author's findings. From the elemental composition, high amounts of polyolefins in the pyrolyzed feedstock are advantageous, referring to the heteroatom content. On the other hand, the simulated distillation reveals a possible disadvantage of high LDPE content, as it shifts the condensate composition towards high-molecular-weight compounds under the experimental conditions conducted in the STR experiments. Generally, the determined levels of heteroatom content impair further reintroduction of the mixed plastic oils into petrochemical processes. Thus, subsequent upgrading of the condensates would be required.

4.1.3. Polymer interactions in mixed plastics

Superposition calculations reveal decisive interaction effects when coprocessing the heteroatom-containing polymer mixtures. To estimate yields for Mix B, Mix C, and the PCW by superposition PET data is missing. Therefore PET product yields determined by Genuino et al. [29] are used. Following the PET study, a yield of condensate, gas, and solid residue for PET of 55, 13, and 32 wt.% is assumed. Applying these assumptions for calculations, Mix B and Mix C result in a condensate yield of 70.8 and 71.1 wt.%, respectively. These yields are about 20 and 22 wt.% higher than the experimentally determined results, emphasizing the dominant product shift from condensable to gaseous products because of interactions. The theoretical condensate yield of the PCW (69.9 wt.%) is also overestimated by about 19 wt.%. Similar findings concerning the overestimation of condensate yields based on the

superposition approach are reported by Genuino et al. [29]. The authors attribute these results to the interaction effects of PET with other polymers, indicating an overestimation by up to 8 wt.% in their study. Further studies show that the interactions are also involved in the co-pyrolysis of the heteroatomic polymers PVC and PA6 [11]. The interactions are specified in more detail, for example, by Cao et al. for a defined feedstock system of PVC and PET [41]. In the proposed reaction mechanism, reactions occur between evolving HCl and the intermediates of PET decomposition, more specifically, the aromatic ester fragments. Gaseous chlorinated HCs, like ethylene dichloride or ethylene chloride, form instead of HCl. This mechanism explains the increased gas yields and the reduction of the condensate amount. Similar interaction effects for PVC and PA6 appear reasonable, but require further investigation. The comparison of experimental and calculated results for thermoplastic mixtures in this study cannot confirm an increased tendency towards coke formation, as found by Genuino et al. in a fixed-bed reactor. They attributed an increase in solid residue formation of up to 18 wt.% to the interaction effects of PET with other polymers. The discrepancy between the two studies highlights the need for fundamental research into the interaction effects regarding the dependence on feedstock composition and reactor characteristics.

For the superposition-based estimation of the gas composition from the heteroatom-containing feedstocks, literature data of the PET pyrolysis gas composition are required. Honus et al. provide comprehensive data on the PET pyrolysis gas composition [15]. The authors report a composition comprising 64 wt.% CO₂, 31 wt.% CO, 2.8 wt.% ethylene, 0.6 wt.% CH₄, 0.5 wt.% benzene, 0.5 wt.% toluene, 0.25 wt.% propene, 0.2 wt.% ethane, and 0.15 wt.% butene. With this data, the occurrence of interactions can be verified for Mix B, Mix C, and the PCW. The experimentally determined amounts in the gas composition of Mix B, Mix C, and PCW differ from the superposition-based calculations. Fewer aromatics and slightly fewer light olefins are included in the normalized composition. Approximately 1–3 wt.% more C₆ aliphatics are formed than could be predicted by superposition calculations. The experimentally determined amounts of heteroatom-containing HC, CO, and CO₂ in the gas composition exceed the calculated results by far. In particular for Mix C, which has the highest heteroatom content of all feedstocks, an additional 3.6, 12.3, and 11.0 wt.% of these gas species are determined. Therefore, oxygen-, nitrogen-, or chlorine-containing polymers appear to pursue new reaction pathways leading to more heteroatom-containing HCs, CO, CO₂, and C₆ aliphatics in the gas while diluting aromatic and aliphatic gas species. For example, the reaction mechanism of PA6 could change in a way that the usual highly selective ϵ -caprolactam formation changes into decomposition to short-chain aliphatics, nitriles, CO, and CO₂. Further mechanistic insights into such changes cannot be resolved with this experimental setup.

Consistent with the previous calculations, the superposition principle is only partially applicable to the elemental composition of the mixed plastic condensates. The carbon and hydrogen content represented within the measurement uncertainty, considering simplifications by using pure PET tests from the literature [25]. However, the chlorine content is underestimated (by 0.4 wt.%), while the oxygen and nitrogen content are slightly overestimated by up to 0.6 and 1.3 wt.% for Mix C and the PCW. As discussed in the previous section, interactions appear to have a major influence on the product composition. As described before, interactions leading to the release of low molecular weight chlorinated HCs are reported [41]. The underestimated chlorine content indicates that HCl from primary PVC decomposition may be integrated into higher boiling HC structures during reactions with the PET and PA6 intermediates. Chlorinated polyaromatic hydrocarbons could play a dominant role in this process. As a result of the increasing cleavage of heteroatom-containing polymer chains caused by the interaction with HCl, more gaseous nitrogen- and oxygen-containing HCs, such as acrylonitrile, acetonitrile, or acetaldehyde, seem to be formed. The more pronounced formation of CO₂ and CO would explain the reduced oxygen content in the condensates. Also, it would explain the underestimation

of chlorine-containing HC by 1.3 m.% in the gas superposition calculations and the overestimation of chlorine by 0.4 m.% in the condensate phase. With this data, significant interactions during the pyrolysis of Mix B, Mix C, and PCW assumed from the gas analysis, are confirmed. Unfortunately, the gas measurement method does not allow the HCl content in the mixed plastics to be recorded. A decreasing amount of HCl in the gas phase would offer an additional validation possibility for the assumed interaction effects. The superposition calculations for the compound group distribution of the heteroatom-containing feedstocks are impossible, as adequate data for the PET condensate is not accessible in the literature. However, based on previous observations, it cannot be assumed that the superposition approach is valid for calculating the composition of Mix B, Mix C, and PCW.

4.2. Reactor impact

The comparison of the pyrolysis results generated in the STR and the ASR system allows for evaluating the reactor impact. The reactor impact is underlined by significant differences in the obtained product yields. Compared to the STR, the mass balance shifts significantly in favor of the gaseous products. This shift is attributed to differing reactor characteristics caused by the reactor geometry and technical operation. The GRT is considerably lower in the STR system. The potential for secondary reactions is therefore reduced compared to the ASR system. Secondary cracking of volatiles in the gas phase is less likely to occur in the STR. Additionally, the shift from condensable to gaseous products may be attributed to the time-dependent variations of the polymer temperatures. In the STR, the polymer end temperature is assumed to be lower than in the ASR, which would reduce the intensity of cracking reactions. Nevertheless, the lower heating rate in the ASR probably causes the polymer to react already at lower temperatures. Accordingly, a product distribution shift caused by the time-dependent temperature profile of the reacting polymers cannot finally be clarified. However, the GRT comparison of both reactor systems provides a comprehensible explanation for the effect of shifting yields.

When comparing this effect for different feedstocks, the effect is significantly weaker for mixtures containing heteroatoms. As described in the previous section, strong interaction effects between the polymers are noticeable in these mixtures. These interaction effects appear to superimpose and dominate the specific plant characteristics, such as temperature distribution and GRT. Regardless of the reactor type and plant design, more even product yields are achieved for the heteroatom-containing mixtures. The feedstock-specific interactions appear to be decisive for the pyrolysis yields in the compared reactor systems.

In combination with the observed lower gas yields, the gas analyses indicate less pronounced thermal cracking reactions in the STR reactor. Secondary thermal cracking is presumably intensified in the ASR system with longer GRT in the hot reactor section. The total amount of products with boiling points ranging from C₄ to C₇ is therefore increased, which may cause a higher content of these products in both fractions. However, for the pyrolysis gas of Mix B and PCW, the heteroatom-containing HCs are more pronounced in the STR system. This might also be attributed to less intense primary and secondary cracking in this reactor. As seen before, fewer gaseous HCs are formed compared to the ASR. The formation of heteroatom-containing gas species like CO, CO₂, or light nitriles is presumably less influenced by temperature variations than HCs that evolve during the polyolefin decomposition mechanisms. As a result, the other heteroatom-containing gases are diluted to a lesser extent.

The condensate analyses indicate further effects depending on the reactor type. For LDPE, PP, PS, and Mix A, the elemental composition of the pyrolysis oils remains unaffected. This result is expected, as evolving products may change regarding the chain lengths or the distribution between styrene monomer, dimer, and trimer, but do not modify the fundamental structural nature of the evolving products.

For Mix B, Mix C, and the PCW, the H/C ratio differs slightly by up to

0.3. Given the mostly polyolefin-rich feedstock composition, this indicates fewer unsaturated bonds in the condensates of the mixed plastics in the STR. This may be caused by a lower tendency to form unsaturated organic compounds, resulting from less pronounced aromatic formation as a secondary reaction. More likely, primary and secondary cracking are intensified in the ASR system, reflecting the longer GRT and the presumably higher average polymer temperature. Regarding the heteroatom content in the condensate, no significant changes are evident when comparing the condensate of both reactors, except for oxygen. The condensates produced in the STR have a slightly higher oxygen content. This slight increase could be related to measurement uncertainties and is inconsistent with the identified effect of increased CO₂ and CO levels in the STR system. The two-dimensional GC analysis shows no significant variation in oxygen-containing structures, supporting the assumption that the oxygen difference observed in elemental analysis is attributable to measurement uncertainties. On the other hand, the technical limitations of the GC method may cause this result. High-boiling oxygen-containing compounds in the condensate may be discriminated in the two-dimensional GC method. Since the method does not cover any or only partial components with an elevated boiling temperature of over 350 °C, high-boiling compounds with oxygen-containing structures are presumably undetected. Terephthalic acid, a typical product of PET pyrolysis with a sublimation temperature of 405 °C, would be an example of this. A final clarification of the oxygenated HCs requires further investigations, such as a distillative separation combined with an analysis of the distillation fractions for possible heteroatom enrichments. The results will further support the evaluation of interaction effects in the mixed plastic pyrolysis. Nevertheless, upgrading the pyrolysis condensates from the mixed plastics is necessary independently of the reactor type, considering common specifications for petrochemical products [40].

The two-dimensional condensate analysis confirms the shift towards a condensate distribution with fewer high-boiling compounds in the ASR system. The distribution of products in LDPE and PP condensates is shifting toward shorter chain lengths. Nevertheless, it is still very broad. The styrene content in the PS condensate is about 10 wt.% higher in the STR system compared to the sample generated in the ASR system. In literature, higher styrene yields are linked with increased reactor temperatures [30], which contradicts the assumption of a presumably higher polymer end temperature in the ASR system. However, the longer GRT in the ASR may lead to more pronounced gas phase reactions, interfering with the selective PS decomposition mechanism. This would explain why the amount of other monoaromatic structures, such as ethylbenzene, toluene, or α -methylstyrene, is significantly higher in samples of the ASR system, while the styrene content is lower. The sum of monoaromatic structures remains nearly constant in both samples. These findings confirm the hypotheses that the ASR geometry and operation procedure lead to more intense secondary gas-phase cracking reactions.

The comparison of the simulated distillation confirms this hypothesis of enhanced cracking in the ASR. The intensified primary and secondary cracking reactions result in more unsaturated aliphatic compounds of shorter chain length, considering the mostly polyolefinic character of the mixtures. The unsaturated bond of the typically formed α -olefins and α - ω -dienes has a stronger influence on the elemental composition with decreasing chain length. Therefore, the differences in the H/C of the elemental analysis can be attributed to the significantly higher proportion of low-boiling HCs from pyrolysis in the ASR system. Consequently, the amount of compounds in the naphtha range obtained in the STR is lower for condensates of polyolefin-rich feedstocks.

5. Conclusion and outlook

This study provides a comprehensive overview of the feedstock influence and reactor-type dependent effects in the pyrolysis of thermoplastics at constant reactor temperature. The experimental

investigations reveal their impact on the product yields and product compositions.

Ranging from 10.9 to 98.5 wt.%, the oil yields obtained in the STR system differ greatly for the pyrolyzed pure polymers. This emphasizes the decisive feedstock dependency in plastic pyrolysis. The product composition is highly polymer-dependent, covering a wide spectrum of organic HCs. Moreover, the reactor type affects the yields and compositions of the pyrolysis products. Enhanced gas formation by up to 22 wt.% is evident for all pure thermoplastics in the ASR system compared to the STR. The pyrolysis gases produced from LDPE and PP, as well as Mix A, seem suitable for use in the chemical industry after appropriate separation into ethene, propene, aromatics, or liquified petroleum gas. Pyrolyzing the more complex mixtures in the STR, high amounts of heteroatom-containing gas species of up to 27 wt.% are formed.

Varying results in different reactors can be attributed to characteristic reactor properties. Despite the preheated sand bed and rapid homogenization in the STR, temperature differences between the reactor wall and the polymer of 96 °C are measured at maximum. These differences are highly time-dependent, resulting from the semi-continuous dosing method. Despite the time-dependent polymer temperature profile, the GRT distribution of primary products is a decisive parameter. With 40 s, the minimum GRT in the heavier ASR reactor is twice as high as compared to the STR. The backmixing in the considerably larger freeboard of the ASR also leads to a GRT distribution width of about 5 min. The distribution width in the gas phase of the STR accounts for only 84 s. This promotes secondary cracking in the gas phase of the ASR, associated with the increased gas yields. In line with this, simulated distillation analyses indicate increased fractions of naphtha and middle distillate-like product cuts in the condensate by approximately 36 wt.% for the PCW. The increased gas formation in the ASR has no or only minor influence on the heteroatom content in the condensates measured within this study. In addition, the *n*- and iso-aliphatic compounds are predominantly unsaturated, which complicates the further use of the pyrolysis oils from both reactors. As the composition of the product fractions determines their suitability for chemical recycling, further purification and upgrading of the products before introducing them into petrochemical processes is required. Because of the strong influence of the reactor type on the product composition, this effort for subsequent processing can vary depending on the pyrolysis technology.

However, the reactor-type influence is less pronounced for Mix B, Mix C, or the PCW, as interaction effects occur in these complex mixtures that comprise heteroatom-containing polymers. Consequently, the interactions between polymers during pyrolytic decomposition seem to dominate the reactor-type-related effects. They prevent superposition-based estimations regarding product yields of heteroatom-containing mixtures under the experimental conditions. As a result of these interactions, the condensate yield is overestimated by 19–22 wt.%. Analyses of the product composition hint at the hypothesis that interactions intensify the cracking of polymer chains into lighter heteroatom-containing HCs during co-pyrolysis of PVC, PA6, PET, and ABS. This also leads to an overestimation of oxygen and nitrogen content in the condensate by superposition estimations for complex mixtures by up to 1.3 wt.%. Thus, the calculation approach is not suitable for the estimation of heteroatom impurities in the pyrolysis oil when applied to mixed plastics comprising heteroatom-containing polymers. In contrast, the superposition-based calculation is valid for determining the product yields and compositions for simple polymer mixtures, only including PE, PP, and PS. Estimations regarding the product yields or the elemental analysis of the condensate only deviate by a maximum of 0.6 and 0.4 wt.%, respectively.

However, reactor-specific variations can complicate a general and exact calculation of yields, boiling cuts, or product compositions during reactor scale-up. Heat and mass transfer limitations, along with the endothermic nature of pyrolysis, cause different results in the reactors even with identical feedstocks and reactor wall temperatures. Therefore, specifying the reactor type and the set temperature is only a superficial

assessment criterion for comparing pyrolysis results. Thus, further pyrolysis studies on a technical scale should provide a detailed reactor and process parameter characterization. Additional method development for measuring the polymer temperature profile in complex reactor geometries is required.

Moreover, detailed investigations of the pyrolysis behavior of complex plastic mixtures and an extension to other polymers are essential for understanding mechanisms of identified interaction effects and, thus, the complex pyrolysis mechanism. These studies must also concentrate on the GRT influence on the pyrolysis of mixed plastics.

CRedit authorship contribution statement

Harald Wehner: Investigation. **Dirk Eidam:** Writing – review & editing, Resources. **Orhan Keskin:** Investigation. **Britta Bergfeldt:** Writing – review & editing, Resources, Formal analysis. **Salar Tavakkol:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Dieter Stapf:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Niklas Netsch:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Aljoscha Tauber:** Investigation, Data curation.

Funding

The study was funded by the German Helmholtz Association within the program „Materials and Technologies for the Energy Transition“.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Technical support in the construction of the system was provided by Frank Richter, Sebastian Finger, Benjamin Seith, and Jens Jehle. The authors also gratefully acknowledge the assistance of Patrick Schieber, Galina Schuler, Michael Zeller, Grazyna Straczewski, Ankh-Erdene Erdenepurev, and Aylin Hannemann in supporting the pyrolysis gas and condensate analysis. Monika Schleinkofer and Julia Podszuweit performed the elemental analysis. The authors thank Feichi Zhang and Yufei Cao for their support with the technical drawing of the stirrer used in the stirred tank reactor.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2025.107575](https://doi.org/10.1016/j.jaap.2025.107575).

Data availability

Data will be made available on request.

References

- [1] R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, *Sci. Adv.* 3 (2017) e1700782, <https://doi.org/10.1126/sciadv.1700782>.
- [2] F.D.B. de Sousa, The role of plastic concerning the sustainable development goals: The literature point of view, *Clean. Respons. Consum.* 3 (2021) 100020, <https://doi.org/10.1016/j.clrc.2021.100020>.
- [3] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste, *Angew. Chem. Int. Ed.* 59 (2020) 15402–15423, <https://doi.org/10.1002/anie.201915651>.
- [4] K.M. van Geem, Plastic waste recycling is gaining momentum, *Science* 381 (2023) 607–608, <https://doi.org/10.1126/science.adj2807>.
- [5] A. Rahimi, J.M. García, Chemical recycling of waste plastics for new materials production, *Nat. Rev. Chem.* 1 (2017), <https://doi.org/10.1038/s41570-017-0046>.
- [6] K. Ragaert, L. Delva, K. van Geem, Mechanical and chemical recycling of solid plastic waste, *Waste Manag.* 69 (2017) 24–58, <https://doi.org/10.1016/j.wasman.2017.07.044>.
- [7] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, *Renew. Sustain. Energy Rev.* 73 (2017) 346–368, <https://doi.org/10.1016/j.rser.2017.01.142>.
- [8] T. Maqsood, J. Dai, Y. Zhang, M. Guang, B. Li, Pyrolysis of plastic species: A review of resources and products, *J. Anal. Appl. Pyrolysis* 159 (2021) 105295, <https://doi.org/10.1016/j.jaap.2021.105295>.
- [9] V.K. Soni, G. Singh, B.K. Vijayan, A. Chopra, G.S. Kapur, S.S.V. Ramakumar, Thermochemical recycling of waste plastics by pyrolysis: a review, *Energy Fuels* 35 (2021) 12763–12808, <https://doi.org/10.1021/acs.energyfuels.1c01292>.
- [10] P.T. Williams, E.A. Williams, Interaction of plastics in mixed-plastics pyrolysis, *Energy Fuels* 13 (1999) 188–196, <https://doi.org/10.1021/ef980163x>.
- [11] N. Netsch, L. Schröder, M. Zeller, I. Neugber, D. Merz, C.O. Klein, S. Tavakkol, D. Stapf, Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics, *J. Therm. Anal. Calor.* 150 (2025) 211–229, <https://doi.org/10.1007/s10973-024-13630-6>.
- [12] S.H. Chang, Plastic waste as pyrolysis feedstock for plastic oil production: A review, *Sci. Total Environ.* 877 (2023) 162719, <https://doi.org/10.1016/j.scitotenv.2023.162719>.
- [13] M. Laghezza, S. Fiore, F. Berruti, A review on the pyrolytic conversion of plastic waste into fuels and chemicals, *J. Anal. Appl. Pyrolysis (J. Anal. Appl. Pyrolysis)* 179 (2024) 106479, <https://doi.org/10.1016/j.jaap.2024.106479>.
- [14] F. Faisal, M.G. Rasul, M.I. Jahirul, D. Schaller, Pyrolytic conversion of waste plastics to energy products: A review on yields, properties, and production costs, *Sci. Total Environ.* 861 (2023) 160721, <https://doi.org/10.1016/j.scitotenv.2022.160721>.
- [15] S. Honus, S. Kumagai, G. Fedorko, V. Molnár, T. Yoshioka, Pyrolysis gases produced from individual and mixed PE, PP, PS, PVC, and PET-Part I: production and physical properties, *Fuel* 221 (2018) 346–360, <https://doi.org/10.1016/j.fuel.2018.02.074>.
- [16] V. Cozzani, C. Nicoletta, M. Rovatti, L. Tognotti, Influence of gas-phase reactions on the product yields obtained in the pyrolysis of polyethylene, *Ind. Eng. Chem. Res.* 36 (1997) 342–348, <https://doi.org/10.1021/ie950779z>.
- [17] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor, *Chem. Eng. J.* 173 (2011) 62–71, <https://doi.org/10.1016/j.cej.2011.07.037>.
- [18] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei, R. Ruan, Pyrolysis technology for plastic waste recycling: a state-of-the-art review, *Prog. Energy Combust. Sci.* 93 (2022) 101021, <https://doi.org/10.1016/j.pecs.2022.101021>.
- [19] N. Hassibi, Y. Quiring, V. Carré, F. Aubriet, L. Vernex-Loiset, G. Mauviel, V. Burklé-Vitzthum, Analysis and control of products obtained from pyrolysis of polypropylene using a reflux semi-batch reactor and GC-MS/FID and FT-ICR MS, *J. Anal. Appl. Pyrolysis* 169 (2023) 105826, <https://doi.org/10.1016/j.jaap.2022.105826>.
- [20] N. Hassibi, Y.A. Vega-Bustos, M.H. Aissaoui, G. Mauviel, V. Burklé-Vitzthum, Thermochemical Recycling of Polystyrene by Pyrolysis: Importance of the Reflux to Maximize the Production of Styrene and BTEX, *Ind. Eng. Chem. Res.* 62 (2023) 13432–13439, <https://doi.org/10.1021/acs.iecr.3c01692>.
- [21] C. Stallkamp, M. Hennig, R. Volk, D. Stapf, F. Schultmann, Pyrolysis of mixed engineering plastics: Economic challenges for automotive plastic waste, *Waste Manag.* 176 (2024) 105–116, <https://doi.org/10.1016/j.wasman.2024.01.035>.
- [22] H.C. Genuino, M.C.P. van Eijk, S.R.A. Kersten, M.P. Ruiz, Pyrolysis of real packaging plastic waste streams in a fluidized-bed pilot plant, *Energy Fuels* (2024), <https://doi.org/10.1021/acs.energyfuels.3c04114>.
- [23] N. Netsch, M. Zeller, F. Richter, B. Bergfeldt, S. Tavakkol, D. Stapf, Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Prediction and Pilot-Scale Validation, *ACS Sustain. Resour. Manag.* 1 (2024) 1485–1492, <https://doi.org/10.1021/acssusresmg.4c00109>.
- [24] J.-J. Zhang, N. Ren, J.-H. Bai, Non-isothermal decomposition reaction kinetics of the magnesium oxalate dihydrate, *Chin. J. Chem.* 24 (2006) 360–364, <https://doi.org/10.1002/cjoc.200690069>.
- [25] M. Calero, R.R. Solís, M.J. Muñoz-Batista, A. Pérez, G. Blázquez, M. Ángeles Martín-Lara, Oil and gas production from the pyrolytic transformation of recycled plastic waste: an integral study by polymer families, *Chem. Eng. Sci.* 271 (2023) 118569, <https://doi.org/10.1016/j.ces.2023.118569>.
- [26] S.M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, A review on thermal and catalytic pyrolysis of plastic solid waste (PSW), *J. Environ. Manag.* 197 (2017) 177–198, <https://doi.org/10.1016/j.jenvman.2017.03.084>.
- [27] M. Zeller, S. Tavakkol, D. Stapf, Experimental and analytical tools for the chemical recycling of engineering plastics - A multi-scale pyrolysis study on polydicyclopentadiene, *Macromol. Rapid Commun.* (2025) e2500161, <https://doi.org/10.1002/marc.202500161>.
- [28] N. Netsch, L. Weigel, T. Schmedding, M. Zeller, B. Bergfeldt, G. Straczewski, S. Tavakkol, D. Stapf, Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography, *Fuel Process. Tech.* 280 (2025) 108359, <https://doi.org/10.1016/j.fuproc.2025.108359>.
- [29] H.C. Genuino, M. Pilar Ruiz, H.J. Heeres, S.R.A. Kersten, Pyrolysis of mixed plastic waste: Predicting the product yields, *Waste Manag.* 156 (2023) 208–215, <https://doi.org/10.1016/j.wasman.2022.11.040>.

- [30] T. Faravelli, M. Pincioli, F. Pisano, G. Bozzano, M. Dente, E. Ranzi, Thermal degradation of polystyrene, *J. Anal. Appl. Pyrolysis* 60 (2001) 103–121, [https://doi.org/10.1016/S0165-2370\(00\)00159-5](https://doi.org/10.1016/S0165-2370(00)00159-5).
- [31] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, Thermal degradation of PVC: A review, *Waste Manag.* 48 (2016) 300–314, <https://doi.org/10.1016/j.wasman.2015.11.041>.
- [32] H. Bockhorn, A. Hornung, U. Hornung, J. Weichmann, Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods, *Thermochim. Acta* 337 (1999) 97–110, [https://doi.org/10.1016/S0040-6031\(99\)00151-3](https://doi.org/10.1016/S0040-6031(99)00151-3).
- [33] L. dos S. Vargette, H. Mohamadzadeh Shirazi, O. Mynko, M. Kusenberg, J. Jamieson, A.E. Muñoz Gandarillas, S. Ukkandath Aravindakshan, M.-F. Reyniers, K.M. van Geem, Comprehensive fouling assessment in steam crackers: fossil versus Renewable NEXBTL Naphtha, *Ind. Eng. Chem. Res.* 63 (2024) 111–120, <https://doi.org/10.1021/acs.iecr.3c02969>.
- [34] M. Espinosa-Peña, Y. Figueroa-Gómez, F. Jiménez-Cruz, Simulated distillation yield curves in heavy crude oils: a comparison of precision between ASTM D-5307 and ASTM D-2892 physical distillation, *Energy Fuels* 18 (2004) 1832–1840, <https://doi.org/10.1021/ef049919k>.
- [35] H. Bockhorn, A. Hornung, U. Hornung, D. Schawaller, Kinetic study on the thermal degradation of polypropylene and polyethylene, *J. Anal. Appl. Pyrolysis* 48 (1999) 93–109, [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4).
- [36] K.-H. Lee, D.-H. Shin, Y.-H. Seo, Thermal degradation of nitrogen-containing polymers, acrylonitrile-butadiene-styrene and styrene-acrylonitrile, *Korean J. Chem. Eng.* 23 (2006) 224–229, <https://doi.org/10.1007/BF02705720>.
- [37] C. Perego, R. Revel, O. Durupthy, S. Cassaignon, J.-P. Jolivet, Thermal stability of TiO₂-anatase: Impact of nanoparticles morphology on kinetic phase transformation, *Solid State Sci.* 12 (2010) 989–995, <https://doi.org/10.1016/j.solidstatesciences.2009.07.021>.
- [38] V. Georgieva, L. Vlaev, K. Gyurova, Non-Isothermal Degradation Kinetics of CaCO₃ from Different Origin, *J. Chem.* (2013), <https://doi.org/10.1155/2013/872981>.
- [39] K. Paydar, A. Ebadi, A. Ahmadi, M. Manteghian, Investigation of the effect of temperature and grain size on the kinetic of hydrochloric acid and calcium carbonate reaction as a simulation of wellbore acidizing, *J. Chem. Pet. Eng.* (2023), <https://doi.org/10.22059/jchpe.2023.357815.1429>.
- [40] M. Kusenberg, A. Eschenbacher, M.R. Djokic, A. Zayoud, K. Ragaert, S. de Meester, K.M. van Geem, Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? *Waste Manag.* 138 (2022) 83–115, <https://doi.org/10.1016/j.wasman.2021.11.009>.
- [41] R. Cao, M.-Q. Zhang, Y. Jiao, Y. Li, B. Sun, D. Xiao, M. Wang, D. Ma, Co-upcycling of polyvinyl chloride and polyesters, *Nat. Sustain* 6 (2023) 1685–1692, <https://doi.org/10.1038/s41893-023-01234-1>.



Optimizing product yield and composition in chemical recycling of mixed plastics through temperature-staged pyrolysis

Niklas Netsch , Aljoscha Tauber , Daniela Merz, Britta Bergfeldt, Salar Tavakkol *, Dieter Stapf

Institute for Technical Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Keywords:

Chemical recycling
Mixed thermoplastics
Temperature-staged pyrolysis
Thermogravimetry
Stirred tank reactor
Process optimization

ABSTRACT

Chemical recycling of plastic waste via pyrolysis contributes to higher recycling rates in a circular economy. One important prerequisite is the conformity of pyrolysis products with defined chemical feedstock specifications. In the pyrolysis of mixed plastics, specification compliance is particularly hindered by the presence of aromatic compounds and heteroatom-containing species (e.g., Cl, N, O) in the pyrolysis oils. Temperature-staged pyrolysis facilitates oil decontamination, but scaling up this concept in pyrolysis processes poses challenges. Therefore, investigations in thermogravimetry (TG) and a scalable stirred-tank reactor (STR) system are performed. Under well-defined TG conditions, low temperature stages allow for dehalogenation and the selective decomposition of non-polyolefinic polymers. Polyolefins decompose mainly in a separate stage at higher temperatures above 400 °C. Polymer interaction effects significantly influence the decomposition kinetics and depend strongly on the polymer type in the mixture. The application in the STR system confirms technical feasibility, but also reveals scale-up engineering challenges through heat and mass transfer limitations. The heat transfer limitations reduce the polymer temperature during the two-staged STR process, requiring a higher first-stage set temperature than in TG. Compared to isothermal pyrolysis at 500 °C, the total heteroatom content in the oil produced in the second stage decreases. Toluene, benzoic acid, and ϵ -caprolactam content are reduced by a factor of 2–3 while aliphatic compounds are enriched. Staging also facilitates the separation of heteroatom-containing gases from the aliphatic-rich gas fraction. In contrast, elevating the first-stage pyrolysis temperature from 370 °C to 430 °C reduces the target product yield from 56 wt.% to 23 wt.%. However, the temperature elevation also results in a higher quality of the target product because of a reduced amount of incorporated non-aliphatic compounds. These findings highlight the trade-off between maximizing the yield and enhancing the quality of the aliphatic-rich target product fraction.

1. Introduction

The growing environmental burden of plastic waste and the need for efficient resource management have intensified research into improving the sustainability of plastic manufacturing and waste utilization (Keijer et al., 2019). Establishing a circular economy for plastic products appears to be key in this context (van Geem, 2023). To promote its progress, the European Union introduced strict recycling targets in 2021 (Parliament, 2018). At present, the mechanical recycling of most waste fractions is technically limited because of their heterogeneity and

existing contaminations (Ragaert et al., 2017). Chemical recycling processes offer an approach to raise recycling rates for polymeric materials (Johansen et al., 2022). In particular, thermochemical processes such as pyrolysis and gasification are promising because of their feedstock flexibility and the product reintegration into various established chemical industry processes (Rahimi and García, 2017). While gasification aims to recycle via C_1 -chemistry, pyrolysis allows substituting crude oil fractions or even direct monomer production for polymer synthesis at comparatively lower temperatures (Palos et al., 2019; Holtkamp et al., 2024).

Abbreviations: ABS, Acrylonitrile butadiene styrene; FID, Flame ionization detector; GC, Gas chromatography; GCxGC, Two-dimensional GC; HC, Hydrocarbon; HDPE, High-density polyethylene; LDPE, Low-density polyethylene; MS, Mass spectrometer; PA6, Polyamide 6; PET, Polyethylene terephthalate; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl chloride; STR, Stirred tank reactor; TCD, Thermal conductivity detector; TG, Thermogravimetry.

* Corresponding author.

E-mail address: Salar.Tavakkol@kit.edu (S. Tavakkol).

<https://doi.org/10.1016/j.ces.2026.123622>

Received 24 November 2025; Received in revised form 10 February 2026; Accepted 13 February 2026

Available online 15 February 2026

0009-2509/© 2026 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

In pyrolysis, product yields and composition strongly depend on the waste plastic feedstock (Laghezza et al., 2024). Thermoplastic polymers dominate the waste streams relevant for chemical recycling (Geyer et al., 2017). These are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyamide (PA), and polyvinyl chloride (PVC). Each of these polymers forms different pyrolysis products, as their reaction mechanisms depend on the molecular structure of the plastic type (Bockhorn et al., 1999; Bockhorn et al., 1999; Faravelli et al., 2001; Montaudo et al., 1993; Yu et al., 2016; Lee et al., 2006).

Enabling chemical recycling requires converting pyrolysis products into base chemicals for polymer synthesis. This conversion is enabled by reintegrating the generated pyrolysis products in cracking plants of the chemical industry. For successful reintegration, they must meet fossil-based feedstock specifications (Palos et al., 2019; Kusenberget al., 2022). Thus, such cracking plants represent the final gate in a waste-to-polymer or waste-to-chemicals recycling concept. Mixed waste streams, in particular, consist largely of PE and PP, which often results in the formation of aliphatic-rich pyrolysis products. Nevertheless, high dilution of pyrolysis oils with fossil-based feedstocks or upgrading are necessary, as heteroatom contaminations by oxygen-, nitrogen-, or chlorine-containing hydrocarbons (HC) reduce the pyrolysis product quality (Kusenberget al., 2022). A high aromatic content in the pyrolysis oil also hinders its application (Kusenberget al., 2022), except if the aromatic contents reach a level where direct monomer separation is beneficial (Holtkamp et al., 2024). Pyrolysis oils usually exhibit a high proportion of olefins, which hinders their reintegration (Kusenberget al., 2022).

Different techniques for improving the pyrolysis oil quality have been reported in the literature. The use of catalysts (Laghezza et al., 2024; Zhang et al., 2024) or solid sorbents (Cao et al., 2025) can shift the product composition or remove chlorine-based contaminants. Downstream oil upgrading via hydrotreating, filtration, solvent extraction, and distillative fractionation offers a promising approach to obtain specification-compliant pyrolysis products suitable for reintegration (Kusenberget al., 2022). Alternatively, thermochemical feedstock pretreatment, such as low-temperature torrefaction, improves the pyrolysis oil quality by reducing the heteroatom content in the pyrolyzed feedstock (Kumar et al., 2024). However, all of these strategies require additional reactors or separation systems, which increase investment costs and can introduce additional technical difficulties.

Yet the polymer-specific differences in the decomposition mechanism and, thus, the decomposition kinetics allow the direct, in-situ process optimization of plastic pyrolysis. In particular, thermoplastics that contain chlorine, oxygen, nitrogen, or aromatic groups in their polymeric structure decompose at lower temperatures than polyolefins (Netsch et al., 2025). Fig. 1 shows the temperature-dependent decomposition curves of the most commonly produced thermoplastics and the copolymer acrylonitrile butadiene styrene (ABS) (Netsch et al., 2026). The polymer-specific decomposition ranges are highlighted. PVC pyrolyzes according to a two-stage decomposition mechanism (Yu et al., 2016). In the first dehalogenation phase above approximately 230 °C, HCl is released, and polyene chains form (Yu et al., 2016). These polyene chains degrade slowly at elevated temperatures to form aromatic structures, unsaturated aliphatics, and 6.6 wt.% of coke (Yu et al., 2016; Netsch et al., 2025). All other thermoplastics each exhibit individual single-stage decomposition mechanisms, whereby the onset pyrolysis temperatures differ, and only PET exhibits relevant coke formation (Montaudo et al., 1993). Despite differing onset temperatures, the degradation ranges overlap, raising the need for more detailed investigation.

The concept of temperature-staged pyrolysis was already investigated for mixed plastics in the late 1990 s by Bockhorn et al., conducting experiments with defined mixtures of PE, PS, PA6, and PVC (Bockhorn et al., 1998; Bockhorn et al., 1999). The chlorine content could be significantly minimized in the target product by selective temperature staging. Furthermore, the temperature staging for model mixtures of

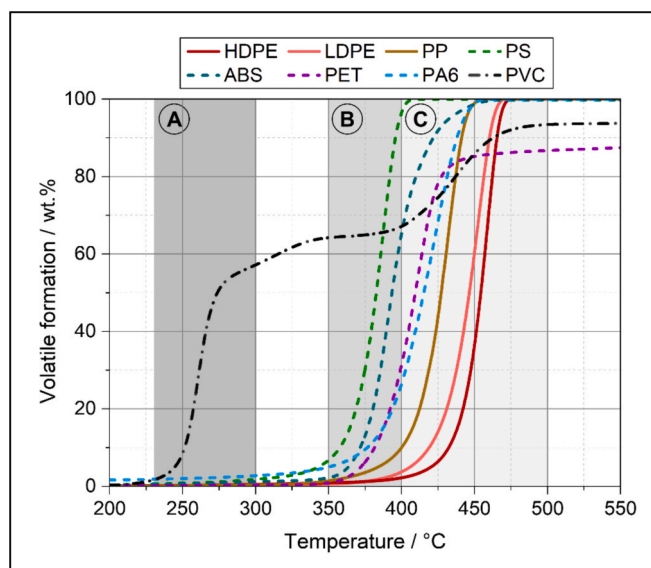


Fig. 1. TG experiments with different thermoplastics showing the main degradation ranges for PVC dehalogenation (A), PS, ABS, PET, and PA6 decomposition (B), and decomposition of polyolefins and PVC polyene chains (C) at a constant heating rate of 2 K/min (adapted from (Netsch et al., 2025)).

PVC, PS, PA6, and PE allowed the generation of a styrene- and caprolactam-rich pyrolysis oil separate from an aliphatic condensate. The concept was then transferred to plastic waste from electronic equipment (Bockhorn et al., 1999). At the same time, Faravelli et al. proved the styrene monomer enrichment by staged pyrolysis with PE and PS mixture in TG experiments (Faravelli et al., 2003). Also, they performed kinetic modeling of stepwise pyrolysis.

Further investigations of this pyrolysis concept were conducted by other authors (Korkmaz et al., 2009; Cheung et al., 2011; Oyedun et al., 2013; Choi et al., 2016; Oyedun et al., 2012; Fukushima et al., 2010; López et al., 2011; Lopez-Urionabarrenechea et al., 2012; Yuan et al., 2014; Yin et al., 2021; Park et al., 2018; Park et al., 2019; Park et al., 2022; Sophonrat et al., 2018; Chang et al., 2023). Other feedstocks were tested, such as cellulose-based composite packaging (Korkmaz et al., 2009), scrap tires (Cheung et al., 2011; Oyedun et al., 2013; Choi et al., 2016), and biomass (Oyedun et al., 2012). The focus in these studies was on separating the wax-like PE products from the aqueous phase and oxygen-containing aromatics from cellulose decomposition (Korkmaz et al., 2009), reducing the energy demand for the endothermic pyrolysis process (Korkmaz et al., 2009; Cheung et al., 2011; Oyedun et al., 2012), and the selective separation of sulfur from the generated pyrolysis oil (Choi et al., 2016). Other authors conducted further research with plastics, specifically investigating the dechlorination of plastic mixtures consisting of PE and PVC (Fukushima et al., 2010) and PE, PP, PS, PET, and PVC (López et al., 2011; Lopez-Urionabarrenechea et al., 2012). Lopez et al. emphasized the importance of reflecting the complex waste composition with the applied polymer mixture. Nevertheless, Lopez et al. excluded nitrogen-containing polymers from their study. With their more complex, oxygen-containing feedstock mixture, the application of a thermal (López et al., 2011) and catalytic (Lopez-Urionabarrenechea et al., 2012) second pyrolysis stage was compared. Other studies provided further insights into the fundamentals of the dechlorination step of PVC (Yuan et al., 2014; Yin et al., 2021) or confirmed the effectiveness of chlorine removal by temperature staging in bench-scale experiments with polyolefin-rich waste (Park et al., 2018; Park et al., 2019; Park et al., 2022).

Recent studies have investigated staged pyrolysis of mixed plastic waste, focusing on deoxygenation, dechlorination, and selective product enrichment. Sophonrat et al. applied the staged pyrolysis concept to a

mixture of PE and PS contaminated with paper, PET, and PVC. In doing so, they were able to demonstrate deoxygenation of the wax-like product fraction and the separation of water from this target product (Sophonrat et al., 2018). Chang et al. investigated the concept of temperature staging with a mixture that also contains ABS in addition to PE, PP, PS, and PVC (Chang et al., 2023). As in previous studies, the focus lay on the dechlorination of the feedstock in a first stage. The enrichment of aromatic compounds for styrene monomer recovery and the production of an aliphatic-rich product fraction was pointed out. The fate of nitrogen-containing compounds played only a minor role in this study.

Interactions in polymer mixtures occurring during the reaction are considered to cause the shift in product composition. Possible interactions strongly depend on the polymer types and reaction conditions employed (Netsch et al., 2025, 2026; Williams and Williams, 1999). Thus, the type and content of different polymers in the feedstock are crucial for temperature-staged pyrolysis applications.

Reported investigations on uncatalyzed staged pyrolysis of thermoplastic mixtures are limited in the literature. These studies often refer to binary or ternary model mixtures and mostly aim at dehalogenation. Only a few of these studies examined real waste streams (Bockhorn et al., 1999; Park et al., 2022) or more complex feedstock mixtures that incorporate oxygen (López et al., 2011; Lopez-Uriónabarrenechea et al., 2012; Sophonrat et al., 2018). One study covers nitrogen-containing polymers (Chang et al., 2023) but lacks information on denitrogenation effectiveness by temperature-staged processing. Thus, it remains unclear whether temperature-staging represents an appropriate method for optimizing polyolefin-rich mixed plastics from a circular economy perspective. This optimization aims to enrich heteroatoms and aromatics in one oil fraction while producing a high-quality aliphatic product suitable for reintegration in the (petro-)chemical industry for cracker applications.

Therefore, this study extends the concept of temperature staging to a broader feedstock spectrum. The aim is to produce aliphatic-rich pyrolysis oils of low oxygen-, nitrogen-, and chlorine-containing HCs and aromatics content. These contaminations should be transferred to a product fraction produced in the first pyrolysis stage, generated at a lower temperature. Additionally, the concept of temperature staging is tested in two different process scales to investigate the temperature control and scale-up challenges. Therefore, pyrolysis experiments are performed in laboratory-scale TG experiments and under technical conditions in a STR. The TG experiments offer the advantage of well-controlled conditions for a reliable parameter study. They enable the evaluation of the pyrolysis behavior in defined thermoplastic mixtures, considering possible interactions and reaction mechanisms. The potential of a temperature staging approach for optimizing the products of mixed plastic pyrolysis is then assessed in the STR system, based on the product yield and the composition of the resulting gas and pyrolysis oil. Temperature control and heat transfer effects are revealed, addressing crucial engineering aspects in stepwise pyrolysis. Mixtures of the eight most common thermoplastics are tested (PlasticsEurope, 2024). With PET, PVC, ABS, and PA6, the most critical contaminations, oxygen, chlorine, and nitrogen are included to reflect the diversity of plastic waste compositions and the associated impurities in the pyrolysis products (Kusenbergh et al., 2022).

2. Materials and methods

2.1. Feedstock

Various thermoplastics were used as pure plastics and in defined thermoplastic mixtures. These included low-density polyethylene (LDPE, Lupolen 2420H by LyondellBasell), high-density polyethylene (HDPE, Hostalen ACP 9255 Plus by LyondellBasell), PP (Moplen HP 552H by LyondellBasell), PS (Ineos Styrolution 156F), PET (PKKPET by Plastipak Preforme), PA6 (Alphalon 27 by Grupa Azoty ATT Polymers), ABS (Sinkral F332 by Eni Versalis), and PVC. These materials were

already used for kinetic analysis via dynamic TG (Netsch et al., 2025). Except for PVC, the polymers were supplied as additive-free primary granulates with a particle size of 2–5 mm. Mexichem provided the PVC (Primex P-2252) as a powder. It is referred to as virgin PVC in this study. In addition to pure polymers, various mixtures of thermoplastics were applied in TG. For technical reasons, a different PVC was used in STR experiments. For technical reasons, a different PVC was used in STR experiments. The powder caused clogging during the feeding process in the STR experiments because of its small particle size. Therefore, it was necessary to switch to PVC granulate in these investigations. This PVC by INEOS Inovyn was available as granulate with a particle size of 3 mm, but contained about 10 wt.% inorganic fillers such as CaCO₃ and TiO₂, as well as 2–3 wt.%. The stabilizers are not specified in detail by the manufacturer. In the following, this PVC is referred to as PVC granulate. In these STR experiments, the PVC granulate is examined in combination with other thermoplastics as a mixture, which is referred to as STR Mix in this study. This mixture contains 50 wt.% LDPE, 15 wt.% PP, 10 wt.% each of PS and PET, and 5 wt.% each of PA6, ABS and PVC granulate. It has already been used in isothermal STR experiments. The feedstock composition, including elemental composition, ash, and moisture content, was determined in a previous study and is summarized in Table 1.

2.2. Thermogravimetry

TG analyses were performed with a NETZSCH TG 209 F1 Libra. An automatic sampler was used to load the microbalance with Al₂O₃ crucibles containing 10 mg of sample. Before loading, the samples were cut from the primary granulate with a scalpel. The total sample mass only deviated by up to 0.1 mg. In addition to the pure plastics, binary and ternary thermoplastic mixtures were investigated. In binary mixtures, equal amounts of the polymer types were employed. The ternary mixtures comprised 30 wt.% of the first and second polymer types, as well as 40 wt.% of the third polymer under investigation. Additionally, a complex mixture containing 20 wt.% each of LDPE and HDPE, as well as 10 wt.% each of PP, PS, ABS, PET, PA6, and PVC, was tested and labeled as TG Mix in the following. The polymer content deviation in the mixtures ranged from 10 to 15 µg at maximum. The experiments were conducted at least twice for each mixture. The oven temperature was programmed from 30 °C to 900 °C with simultaneous purging at 60 ml/min nitrogen. Within this program, isothermal segments were applied, pausing the dynamic heating rate of 10 K/min. The selection of the heating rate, the segment's hold time, and its isothermal temperature was based on the results of a previous study under dynamic TG conditions (Netsch et al., 2025). The heating rate of 10 K/min ensured well-controlled conditions without the influence of temperature gradients. Also, the reported polymer-specific decomposition onset temperatures, along with the associated decomposition kinetics, were considered (Netsch et al., 2025). The hold time varied between 0.5 h and 1 h for the

Table 1

Elemental composition as well as the moisture and ash content of the investigated feedstocks.

Feedstock	Composition in wt.%			Cl	Moisture	Ash	O ^A
	C	H	N				
LDPE	85.8	14.2	< 0.3	0.0	< 0.01	< 0.01	0.0
HDPE	85.8	14.2	< 0.3	0.0	< 0.01	< 0.01	0.0
PP	85.8	14.2	< 0.3	0.0	< 0.01	< 0.01	0.0
PS	92.0	8.0	< 0.3	0.0	< 0.01	< 0.01	0.0
ABS	86.2	8.0	5.5	0.0	0.3	< 0.01	0.0
PET	63.3	4.4	< 0.3	0.0	0.2	< 0.01	32.1
PA6	63.6	9.8	12.6	0.0	1.2	< 0.01	12.7
Virgin PVC	39.6	5.6	< 0.3	54.7	0.1	< 0.01	0.0
PVC granulate	36.2	4.9	< 0.3	47.9	0.2	10.6	0.2
STR Mix ^B	80.6	11.6	0.9	2.4	0.1	0.5	3.9

^A organic oxygen calculated as the difference to 100 wt.%.
^B calculated from the individual polymer content in the mixture.

selected isothermal temperatures of 300 °C and 370 °C, respectively. The lower temperature segments enabled the investigation of the dechlorination process induced by the first step of the two-step PVC pyrolysis reaction mechanism. The defined decomposition of PS, ABS, PET, and PA6 was assessed by implementing the segment at 370 °C. The pyrolysis of polyolefins and the polyene chains, formed during the PVC dichlorination, followed in the third pyrolysis stage. The temperature increase after the 370 °C segment marked the beginning of this third stage. The systematic TG study also involved other isothermal segment temperatures and deviating hold times. [Supplementary information S1](#) provides an overview of all experimental setups that were tested but not shown in the manuscript, including the applied polymer mixtures and temperature programs.

2.3. Stirred tank reactor

Complementing the experiments under well-controlled conditions in the TG, the STR system offered additional investigations, as technical process conditions prevail here. This includes reactor-design effects known from large-scale pyrolysis plants, such as relevant heat and mass transport limitations or product residence time distributions. The system is also characterized by high feedstock and process flexibility. It has been described in detail by Netsch et al. for experiments with various thermoplastics and post-consumer waste at a constant reactor temperature of 500 °C ([Netsch et al., 2026](#)). The reactor had a capacity of 2.7 L and was electrically heated by two heating sleeves with each 1.25 kW power. A customized impeller enabled fast homogenization of the reactor content. Quartz sand was used as a homogenization agent. Nitrogen was supplied at various points of the reactor system to ensure an inert atmosphere, transfer emerging volatile products to the condensation system, and avoid blockages on critical system parts. The condensation system consisted of two parts, each including two double-tube heat exchangers. The first and second parts were maintained at 60 °C and −5 °C, respectively. An electrostatic precipitator prevented the transfer of droplets in the potentially oversaturated aerosols from the last condensation stage to the downstream gas sampling and analysis section of the pyrolysis system. This section enabled gas sampling for offline analysis and online analysis of the gas volume flow throughout the experiment. As toxic, corrosive, carcinogenic, and environmentally harmful substances were expected to form during pyrolysis, the experiments were conducted following high health and safety measures. The mass balancing was performed using the methodology already applied and validated in isothermal tests on this pyrolysis system ([Netsch et al., 2026](#)). A feedstock mass of 0.25 kg was introduced to the reactor in batch operation. Two-staged pyrolysis at different temperatures of the first stage was investigated in the STR system. The reactor, containing 2 kg of quartz sand, was preheated to the first isothermal temperature and held for at least one hour after the introduction of the feedstock. This isothermal temperature was varied at 370 °C, 400 °C, and 430 °C to evaluate the influence of increasing this temperature, starting from the set parameter investigated in TG. Following this stage, the reactor set temperature was increased to the second pyrolysis stage temperature of 500 °C and maintained for an additional 90 min to ensure complete conversion. Thermocouples on the reactor wall and in the interior of the reaction mixture allowed recording of the temperature profile and thus resolving the temperature gradients occurring between the reactor wall and the reaction zone. The STR system is characterized by intense mixing in the reaction zone and a narrow gas residence time distribution with a minimum gas residence time of less than 20 s ([Netsch et al., 2026](#)). For comparison, unstaged isothermal pyrolysis experiments at a set temperature of 500 °C were conducted using the same reactor system. However, the experiments differed in the feedstock dosing procedure. The feedstock was introduced semi-continuously in small quantities of about 30 g into the preheated reactor at 500 °C to ensure stable temperature conditions.

2.4. Analytics

To evaluate the valuable organic products, they were characterized using comprehensive offline analysis methods. An advanced gas chromatography (GC) system was used for the pyrolysis gas characterization. This system comprises an Agilent 8890 GC combined with an isothermal oven, a thermal conductivity detector (TCD), a flame ionization detector (FID), and a mass spectrometer (MS).

Gas samples were taken at various times during the experiment and analyzed. The system enabled the quantification of N₂, O₂, CO₂, CO, and CH₄ using the TCD. Other HCs were identified with the MS and quantified using the FID signal after calibration. HCl causes no distinct peak in the measuring system, but only a broad increase in the baseline as a result of its strong tailing tendency. The peak can be clearly attributed to HCl using the MS. However, reliable peak integration is not possible, thus preventing quantitative evaluation of HCl. A mass-related composition of the permanent gases is calculated from the other quantified gases. The calculation is performed in the first step by determining the volume-related proportion of the respective component y_i , considering the molar volume V_m under standard conditions (0 °C, 1 atm), the quantified concentration c_i , and the molar mass M_i of the respective gas, following equation (1).

$$y_i = c_i \frac{V_m}{M_i} \quad (1)$$

The sum of the volume fractions is normalized to correct for measurement deviations. The mass fraction of a gas species related to the permanent gas $x_{i, \text{permanent gas}}$ is then calculated using the density of the permanent gas $\rho_{\text{permanent gas}}$ and the gas species ρ_i , as shown in equation (2).

$$x_{i, \text{permanent gas}} = \frac{y_i}{\sum y_i} \cdot \frac{\rho_i}{\rho_{\text{permanent gas}}} \quad (2)$$

Finally, the purge gas in the form of nitrogen is excluded from the composition by subtracting its mass fraction $x_{\text{flush gas}}$ from the sum of mass fractions of all quantified gas species. The mass fraction related to the pyrolysis gas $x_{i, \text{Pygas}}$ is calculated as described in equation (3). Further details on the GC system and the calibration methodology are provided elsewhere ([Chang et al., 2023](#)).

$$x_{i, \text{Pygas}} = \frac{x_{i, \text{permanent gas}}}{\sum_i (x_{i, \text{permanent gas}}) - x_{\text{flush gas}}} \quad (3)$$

Elemental analysis, determination of water content, spectroscopy, and GC analysis are performed for pyrolysis condensate characterization. A micro elemental analyzer type LECO Truspec CHN was used for elemental analysis. The measurement uncertainty of the elemental analysis differs regarding the sample type and the determined element. For the polymers, a maximum uncertainty of less than 0.46 wt.% for carbon, 0.13 wt.% for hydrogen (0.47 wt.% in case of PVC), 0.05 wt.% for nitrogen, 0.01 wt.% for moisture, and 0.04 wt.% for ash determination were ascertained. For chlorine, the uncertainty accounted for 0.41 wt.% and 0.16 wt.% in the case of virgin PVC and PVC granulate, respectively. Elemental analyses of pyrolysis oils exhibit maximum uncertainties of 1.00 wt.% for carbon, 1.02 wt.% for hydrogen, 0.07 wt.% for nitrogen and chlorine, and 0.11 wt.% for moisture.

Karl Fischer titration was conducted with a Methohm 870 KF Titrino following DIN 51777. ¹H NMR analyses were carried out using an 80 MHz Magritek Spinsolve MultiX benchtop nuclear magnetic resonance (NMR) spectrometer. The NMR analyses indicate the distribution of differently bound ¹H-nuclei, also referred to as protons. This allows the examination of condensates from different stages regarding their share of aromatic bonds as well as saturated and unsaturated C-C bonds. The condensates were measured with a two-dimensional GC (GCxGC) method. All setups and methods are already described in detail by Netsch et al. ([Netsch et al., 2025](#)).

3. Results and discussion

3.1. Thermogravimetric analyses

3.1.1. Virgin polymers

The decomposition behavior of the polymers is characterized under well-controlled TG conditions. The time- and temperature-dependent sample mass change is recorded to resolve the progression of the pyrolysis reaction by the formation of gaseous and condensable products. TG experiments with virgin polymers exhibit the conversion rate of individual polymers in the selected isothermal segments. These segments are set to 300 °C and 370 °C. The temperatures were maintained for 30 min and 60 min, respectively. The results are shown in Fig. 2.

A significant mass loss during the 300 °C stage is only evident for PVC. The decomposition of PVC starts even before reaching the isothermal temperature. At the end of the segment, about 61.4 ± 0.1 wt.% of volatiles are released. The results emphasize the dichlorination reactions occurring in PVC at low temperatures below 300 °C (Yu et al., 2016). In the second stage, the reactions of PVC pyrolysis slow down, leading to a minor volatile release of only 7.3 ± 0.1 wt.%. As the temperature rises, the polyene chains pyrolyze at temperatures above 400 °C. This results in the additional release of volatile products and coke formation. The coke amounts to 6.2 ± 0.1 wt.%. In the second stage, at 370 °C, the non-polyolefinic thermoplastics degrade according to the kinetics that were characterized in the dynamic experiments shown in Fig. 1. While HDPE only degrades to approximately 3 wt.% until the end of the second isothermal segment, the decomposition of PS, ABS, PET, and PA6 is pronounced. The PS decomposition results in nearly complete conversion at the end of the stage. Here, the formation of volatiles from ABS, PET, PA6, and PP pyrolysis reaches 77.3 ± 0.1 wt.%, 51.1 ± 0.3 wt.%, 43.6 ± 1.8 wt.%, and 16.8 ± 0.1 wt.%, respectively. This partial decomposition reflects their slower pyrolysis kinetics at 370 °C compared to PS. Only for PET and PVC, significant coke formation can be detected at the end of the experiment. The coke amounts to 12.9 ± 0.2 wt.% in the case of PET. PP features a partial decomposition in this stage.

These TG results show remarkably different reaction rates, depending on the polymer type in the sample. Applying a higher temperature or extending the hold time raises the conversion rate of all thermoplastics. A distinct temperature cutoff for separating the pyrolysis of aromatic or heteroatom-containing polymers from the pyrolysis of polyolefins cannot be identified. The overlapping of decomposition ranges, especially for PP and PS, leads to a transitional effect. Instead of a clear separation, this suggests an enrichment or depletion of specific decomposition products by temperature-staging. Nevertheless, a temperature

range between 370 °C and 400 °C may offer the possibility of partially separating the polyolefin decomposition from the decomposition of other polymers. In the following, this temperature range between 370 °C and 400 °C is referred to as the kinetic gap and will be focused on.

3.1.2. Polymer mixtures

Some authors report polymer interaction effects that occur during pyrolysis (Netsch et al., 2025; Williams and Williams, 1999; Cao et al., 2023; Jing et al., 2013). These effects depend on the polymers that interact in the feedstock and can vary in intensity. In particular, the impact of interactions on the reaction rate is relevant for the application of temperature-staged pyrolysis. Possible deceleration or acceleration during the co-pyrolysis of polymers could limit or extend the kinetic gap between polyolefins and other thermoplastics. To evaluate such effects, the complexity of the feedstock mixture is increased through experiments performed with binary and ternary mixtures, and the TG Mix. Fig. 3 shows the TG result of a ternary mixture of polyolefins in a three-staged pyrolysis with isothermal segments at 300 °C and 370 °C. A mixture of PP, LDPE, and HDPE was tested in a proportion of 30 wt.%, 30 wt.%, and 40 wt.%, respectively. No volatile formation and only minor decomposition occur in the ternary polyolefin blend at both temperature stages. Approximately 10.9 ± 0.1 wt.% of volatiles are released from the sample by the end of the 370 °C stage. A comparison of the calculated and the experimental TG curves of this mixture can be found in the supplementary information in Fig. S1.1. These results rely on the determination according to the proportions of the polymers in the mixture. Based on the pure polymer results, only 7.8 ± 0.1 wt.% of released volatiles is calculated. Compared to the experimental results, this value is about 3.0 wt.% lower, indicating a slight acceleration. The slight acceleration may be attributed to interactions as reported by Jing et al. (Jing et al., 2013). Radicals formed during the PP pyrolysis may also serve as initiation radicals in the radical decomposition mechanism of PE (Bockhorn et al., 1999). Nevertheless, the absolute impact is low as the majority of the pyrolysis products are formed at higher temperatures. No or only minor deviations comparable to those of the polyolefinic ternary mixture are observed for other mixtures of polyolefins with PET, PA6, or ABS. This isothermal TG result confirms the absence of significant interactions in these samples, as reported in a previous TG study under dynamic parameter conditions (Netsch et al., 2025).

Exemplary results of PS blended with PET, PA6, PP, and HDPE are depicted in Fig. 3, too. For mixtures of PS and polyolefins, no considerable interactions were found based on the theoretical calculations of pure polymer decomposition, which confirms findings of blends comprised of PS and both PE types from other authors (Faravelli et al., 2003; Westerhout et al., 1997). The mixtures of PS/PET/HDPE and PS/

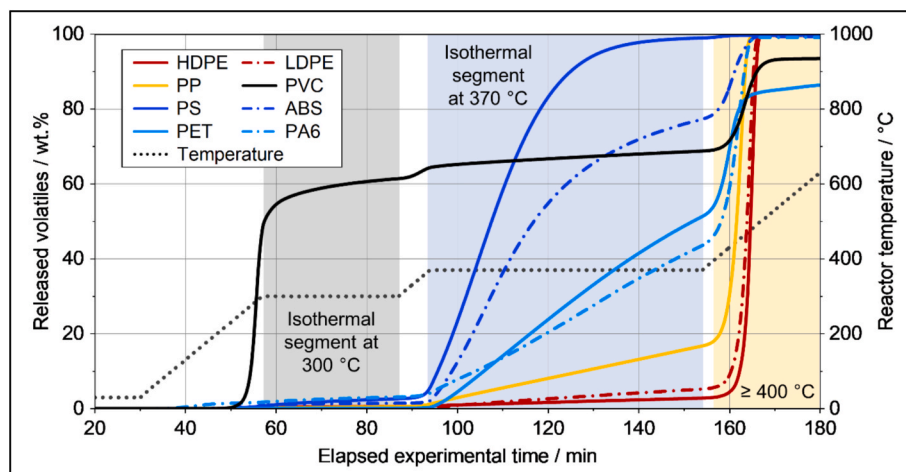


Fig. 2. Individual three-staged TG experiments conducted for virgin polymers at isothermal segments for PVC dichlorination at 300 °C (grey), decomposition of aromatic-based and heteroatom-containing polymers at 370 °C (blue), and polyolefin decomposition above 400 °C (yellow).

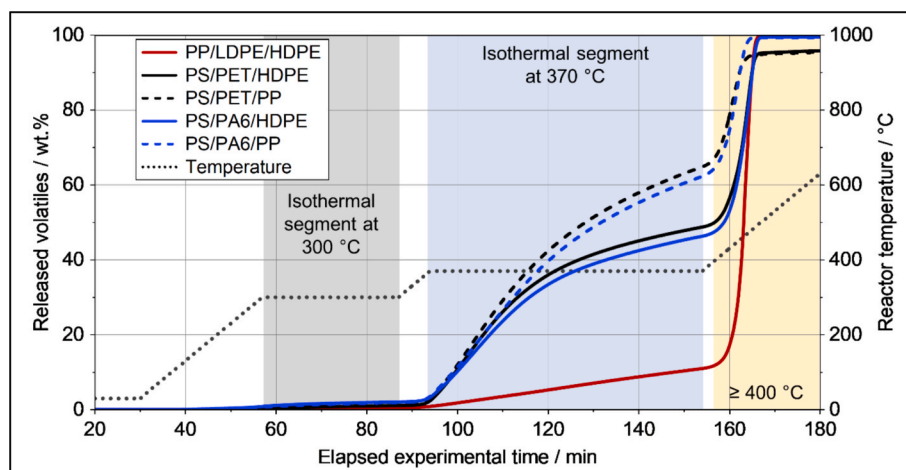


Fig. 3. Three-staged TG experiments with isothermal segments at 300 °C for 0.5 h (blue) and 370 °C for 1 h (blue) performed with ternary mixtures in the proportion of 30/30/40 wt. %.

PA6/HDPE release 47.9 ± 1.2 wt.% and 46.5 ± 0.3 wt.% of volatiles by the end of the second stage. From pure polymer decomposition, a volatile formation of 46.1 ± 0.2 wt.% and 43.9 ± 0.6 wt.% would be expected. The calculated and the experimental TG curves are depicted in Fig. S1.2 in the supplementary information. The similar values emphasize that interactions only play a minor role in these blends. In contrast, the reaction of a mixture containing PS and PP is accelerated compared to the values calculated from the individual polymer behavior. For PS/PET/PP and PS/PA6/PP, about 62.9 ± 2.7 and 62.3 ± 2.5 wt.% of volatiles are formed after the 370 °C stage, compared to the calculated volatile formation of 51.7 ± 0.2 and 49.4 ± 0.6 wt.%, respectively. The calculated decomposition results are compared to the experimental values in Fig. S1.3 in the supplementary information.

The radicals formed in the initiation step of the pyrolysis of PP and PS provide starting radicals for the other polymer. This effect is very pronounced in PS/PP blends, as already described by Kruse et al. (Kruse et al., 2005). It is also observed in the co-pyrolysis of PE and PS (Costa et al., 2010). The data under comparative experimental conditions for both mixtures of this study suggest, though, that the accelerating effect is less pronounced in PS/PE blends than in PS/PP blends. The similar pyrolysis set temperatures of PS and PP, which are based on more stable radicals in the initiation phase of decomposition, might explain this. The positive inductive effects of the phenyl or methyl substituents in PS and PP are a potential cause for this effect. Additionally, Faravelli et al. point

out that this effect in polyolefins and PS strongly depends on the mixture of polymers in the reactor system (Faravelli et al., 2003). Yet it can be assumed that the polyolefin chains decompose more intensely in the first stage. This effect of accelerated polyolefin decomposition in the presence of PS is disadvantageous, as it narrows the kinetic gap between PS and polyolefins. This would complicate the enrichment of aliphatic target products or the depletion of contaminants upon implementation of the temperature-staged pyrolysis concept.

The most intensive interactions are found in mixtures of PET, PA6, and PVC. To illustrate this, the decomposition of the TG Mix and exemplary ternary mixtures are shown in Fig. 4. Ternary mixtures with 30/30/40 wt.% proportions of PVC/PET/PP, PVC/PA6/PP, and PET/PA6/PP reveal different effects important for temperature staging. If a mixture contains at least two of the polymers PVC, PET, and PA6, a distinct acceleration of the decomposition occurs, as already described by dynamic TG tests with binary mixtures (Netsch et al., 2025). This acceleration enhances the volatile formation during the first stage of dechlorination. It is more pronounced for blends of PVC with PA6 than with PET. The underlying mechanisms for the co-pyrolysis of PVC with PET are mechanistically explained by Cao et al (Cao et al., 2023). According to the authors, the formation of hydrogen chloride at the initial PVC decomposition stage promotes the C-O bond cleavage in the polyester group of the PET polymer backbone. A detailed mechanistic description of the interactions between PVC and PA6 blends has yet to

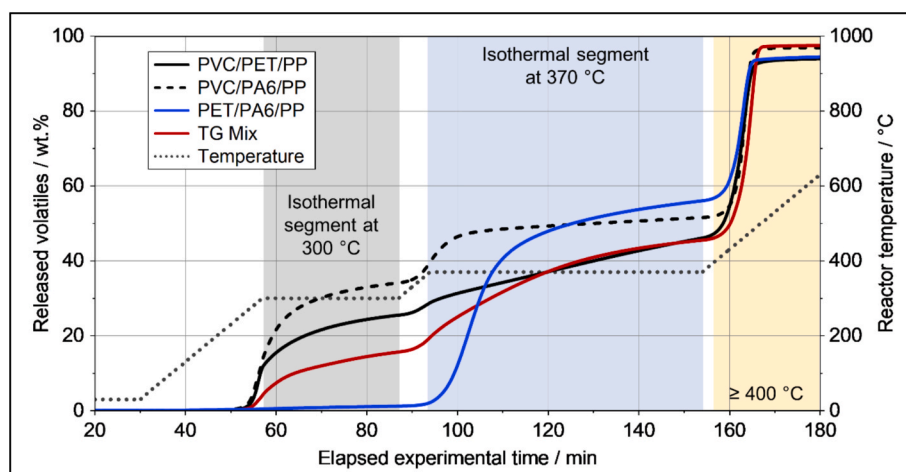


Fig. 4. Staged TG experiments with isothermal segments at 300 °C for 0.5 h (grey) and 370 °C for 1 h (blue) performed with ternary thermoplastic mixtures in the proportion of 30/30/40 wt. % and the TG Mix.

be provided. In the PET and PA6 mixture with PP, no volatile formation is evident in the first stage of 300 °C, but about 55.8 ± 0.3 wt.% of the blend pyrolyzes into volatile HCs in the second stage. From pure polymer decomposition, only 35.1 ± 0.7 wt.% of released products are expected. This finding emphasizes that PET and PA6 can interact during pyrolysis, causing faster decomposition. The entire calculated TG curve is shown in Fig. S1.4 in the [supplementary information](#).

Furthermore, the pyrolysis at temperatures above 400 °C exhibits a minor shift of the degradation curve towards higher temperatures when using PVC and polyolefin blends. The high-temperature decomposition of polyene chains formed as intermediates during PVC decomposition slightly delays the polyolefin pyrolysis during the co-pyrolysis (Yu et al., 2016). Together, both effects broaden the kinetic gap, facilitating the separation of the non-aliphatic and aliphatic pyrolysis products by temperature staging. Nevertheless, the interaction of PVC and polyolefins also leads to slightly lower aliphatic product yields because of the intensified coke formation (Yu et al., 2016).

In the complex TG Mix, the described interaction effects overlap simultaneously. During the dechlorination phase of PVC at 300 °C, twice the proportion of volatiles is released in comparison to the expected behavior from pure polymer decomposition. By the end of this stage, 15.7 ± 0.0 wt.% of volatiles are formed. Only 7.0 ± 0.0 wt.% was expected, emphasizing the decomposition interactions of PVC with PET and PA6. The calculated decomposition curve of the TG Mix is depicted in Fig. S1.5 in the [supplementary information](#) in detail. The proportion of pyrolysis products formed within the second stage is also increased by approximately 8 wt.% and amounts to 45.0 ± 0.8 wt.%. This corresponds to the polyolefin content of 50 wt.%. Based on the TG results, nearly complete decomposition can be assumed under the conditions applied. In conclusion, the TG results provide precise information on the interaction effects that can be attributed to specific polymer combinations. They explain how the decomposition kinetics of mixed thermoplastics are affected, whether they are accelerated or slowed down, and what impact this has on temperature-staged pyrolysis. In the TG Mix, some interactions are favorable due to the accelerated decomposition of the heteroatom-containing polymers as seen in PA6, PET, and PVC mixtures. The decomposition of the polyolefins differs depending on the mixture. PS accelerates, and PVC slightly inhibits their pyrolysis.

The yield and quality of the targeted product, the aliphatic-rich oil fraction, from the final pyrolysis stage are crucial for optimization of process parameters. Hypothetically, low temperature and hold time of the second decomposition stage (here at 370 °C) are beneficial for maximum pyrolysis condensate yield in the second stage, as minor amounts of polyolefins already decompose in the second stage. As the yield of the aliphatic-rich fraction increases, a higher conversion efficiency into the targeted product is achieved. Simultaneously, more pyrolysis products from the decomposition of PS, ABS, PET, and PA6 end up in this product, presumably reducing its quality. Consequently, the selectivity to aliphatic compounds in the products of the last stage is lower. With this, TG results imply that a simultaneous improvement in conversion efficiency and conversion selectivity is not possible. The selection of optimal parameters for temperature-staged pyrolysis thus depends on whether the objective is to maximize the target product yield or to achieve a high target product quality. Nevertheless, temperature-staged pyrolysis in complex mixtures can be assessed as a technically feasible option for improving the pyrolysis product under TG conditions from a kinetic point of view. However, temperature staging can only enable selective product enrichment or depletion rather than perfect separation. Based on these results, the scale-up of the concept was investigated employing a STR system, since additional tests under realistic pyrolysis conditions, along with further comprehensive product analyses, are required.

3.2. Stirred tank reactor

The well-defined set parameters from TG experiments might need

adjustment in application to technical reactors to achieve a similar product separation effect. The application was examined in the scalable STR system. These experiments enabled mass balancing and in-depth chemical product analyses. Since an aliphatic-rich pyrolysis oil is the targeted product, only a two-staged pyrolysis is performed in contrast to the TG experiments. The first stage should ensure complete dichlorination and the removal of heteroatoms and aromatic compounds in one step. From the second stage, the aliphatic-rich product fractions are obtained. Based on previous studies with the STR system, a constant pyrolysis temperature in the reaction zone cannot be assumed for batch operation with 250 g feedstock, due to heat and mass transfer limitations (Netsch et al., 2026). However, the temporal progression of the effective temperature in the STR mix is decisive for its kinetics and, therefore, the result of the temperature staging. Fig. 5 displays the time–temperature dependence of the reactor wall and the reaction zone during the experiments. After feedstock dosing, a significant temperature decline of about 140 °C was recorded in the reaction zone in both experiments. The reactor wall temperature remained stable, only varying approximately 5 °C. During the hold time of the isothermal segment, the reaction temperature increased to its set temperature in 20 min. The isothermal segment in the experiment was maintained at a higher temperature of 430 °C for 90 min. To compensate for the previously discussed drop at the 400 °C stage, the increase in reactor temperature started after 96 min. In both experiments, the internal reactor temperature followed the reactor wall temperature slowly until a stable internal temperature was reached. This temperature was approximately 10 to 25 K below the specified reactor wall temperature of 500 °C.

In the reference experiment, the feedstock was introduced semi-continuously in small portions (approximately 30 g) to maintain a stable pyrolysis temperature, whereas a single-step addition was used in the staged experiments to precisely control reaction time and temperature. The total feedstock mass is identical in both cases. The difference in dosing strategy exhibits only minor effects on the polymer temperature profile. The time-dependent polymer temperature profile mainly depends on the temperature program, rather than on the initial temperature decline upon feedstock addition. Therefore, the staged and reference experiments are comparable for assessing product distribution and reaction kinetics.

The results demonstrate how temperature gradients in the technical system and endothermic processes such as feedstock heating, phase transitions, or reaction enthalpy influence the time-dependent polymer temperature during plastics pyrolysis. This temperature is decisive for

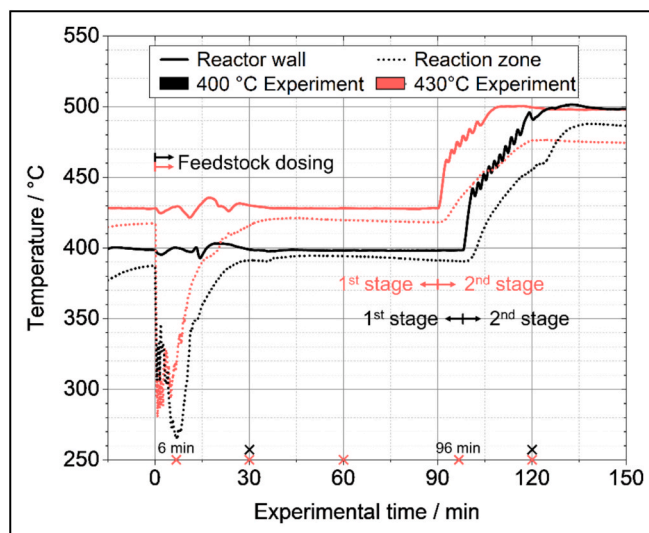


Fig. 5. STR reaction zone and reactor wall temperature during the temperature-staged pyrolysis of the STR Mix with isothermal segments at 400 °C and 430 °C, including gas sampling marked with a cross on the x-axis.

the reaction kinetics. Higher stage set temperature and longer hold time of the isothermal segments must thus be applied in the STR system to achieve comparable reaction conditions in both systems.

3.2.1. Mass balance

The mass balance provides information on the yields of the product fractions, which are referred to as pyrolysis gas, pyrolysis oil, and solid residue in the following. Generating a high oil yield is required to optimize the recycling process for pyrolysis condensate utilization. At the same time, this condensate phase ideally contains no heteroatoms and is rich in saturated aliphatic compounds. For this purpose, oxygen-, nitrogen-, chlorine-, and aromatic-containing products should be predominantly transferred to the gas phase or enriched in the separately collected condensate of the first stage of the pyrolysis process. On the one hand, both effects lead to a depletion in the target product. On the other hand, it would inevitably reduce the condensate yield. As already concluded from TG results, the general optimization task aims to simultaneously improve the product composition while maintaining the highest possible condensate yield. Table 2 shows the condensate yields obtained in the STR Mix two-stage pyrolysis experiments compared to an experiment at a constant temperature of 500 °C (Netsch et al., 2026). For technical reasons, only the condensate yield can be distinguished by the respective stages. Pyrolysis gas and solid residue are calculated for the entire experiment. Furthermore, an experiment not listed in Table 2 with an isothermal segment at 370 °C for 90 min was performed. This experiment showed no relevant condensate formation during the first stage. Only slight PVC dehalogenation was observed in this 370 °C test run, and low amounts of gases were detected. Insufficient condensate mass for further condensate analysis was obtained during the primary pyrolysis stage of the 370 °C experiment. Therefore, this experiment was neglected for evaluating the mass balance and product compositions.

All pyrolysis experiments of the STR Mix exhibit a similar mass balance. The gas yield of the staged pyrolysis results is slightly lower with 4 wt.% compared to the reference experiment at 500 °C under semi-continuous feedstock dosing. Accordingly, the yield of the solid fraction and the collected pyrolysis oil increase by approximately 1.5 wt.% and 2–2.5 wt.%, respectively. The polymers that predominantly decompose at lower temperatures, such as PS, ABS, PET, PA6, or PVC, are pyrolyzed in the first stage. This temperature was about 70–100 °C lower compared to the unstaged reference experiment at 500 °C. With a lower pyrolysis temperature, reduced formation of pyrolysis gas is reported (Calero et al., 2023; Chang, 2023). Thus, a shift in product distribution towards high-molecular products, and consequently from the gas phase to the condensate phase, is expected for the staged pyrolysis experiments. The mass balance results agree with the reported finding (Calero et al., 2023; Chang, 2023). Conversely, pronounced solid residue formation is commonly reported for increasing pyrolysis temperatures (Maqsood et al., 2021). However, an elevated solids residue yield during co-pyrolysis of mixed plastics results from interactions between coke-forming polymers and non-coke-forming polymers (Netsch et al., 2025; Williams and Williams, 1999). Such interactions may cause coke

formation by incorporating products of non-coke-generating polymers into polyaromatic coke precursors. Slower reaction kinetics as a consequence of the lower pyrolysis temperature lead to more time for interactions in the melt phase of the molten polymer mixture, which may explain the slight increase observed in this study.

The comparison of the pyrolysis oil yield of the different stages reveals significant differences, as indicated in Table 2. Increasing the hold temperature from 400 °C to 430 °C results in an increase in the condensate yield in the first stage by about 20 wt.%. The temperature increase accelerates the decomposition reactions, resulting in a higher feedstock conversion. The higher condensate yield during the 430 °C stage reduces the yield of the target product, but might improve the pyrolysis oil quality by enhanced conversion of PS and the heteroatom-containing polymers. Based on the condensate yield of 2.9 wt.% in the first stage of the 400 °C test, only partial pyrolysis can be expected for these polymer types in the thermoplastic mixture.

3.2.2. Gas product composition

The gas analyses support assessing the efficiency of the staged pyrolysis setup in the STR. The gas composition is measured at defined times during both staged pyrolysis experiments, as shown in Fig. 4. In the test with a 400 °C stage, samples are taken after 30 and 120 min, while in the test at 430 °C, samples are collected after 6, 30, 60, 96, and 120 min. The samples provide information about compositional changes in the gas during the reaction progress. Fig. 6 presents different gaseous product groups in the staged test at 430 °C as a function of the sampling time. These products are characteristic pyrolysis products of the individual thermoplastic polymer types in the mixture. The chromatograms and their corresponding quantitative gas compositions can be found in Supplementary Information S2. The gas composition of the temperature staging experiments at 400 °C confirms the observations seen in the more frequently sampled test at 430 °C holding temperature.

Aliphatic products, aromatics, CO₂, and CO dominate the integral gas composition. However, the gas analysis reveals distinct shifts in the gas composition depending on the sampling time. The CO₂ and CO contents decrease rapidly during the experiment and reach a stable level of 2 wt.% by the end of the isothermal segment of the staged pyrolysis. At the same time, the aliphatic content increases during the experiment and amounts to approximately 90 wt.% after 60 min. Only a few aliphatics are present in high amounts in the gas sample collected after 6 min, with 29.8 wt.% ethene and 5.3 wt.% methane. In the sample obtained after 30 min, this distribution becomes significantly broader. Branched C₃-, C₄-, C₅- and C₆-HCs dominate. This trend continues up to the gas sample taken at 60 min. Once the temperature is increased to 500 °C, higher proportions of methane, ethene, and ethane are recorded in the pyrolysis gas, broadening the distribution. Among the aliphatic components, n-alkanes and α-olefins appear in addition to the branched HCs after 60 min. The content of aromatics increases from 4.6 wt.% (6 min) to 14.0 wt.% (96 min) during the test. This maximum is reached following the end of the isothermal segment at 430 °C. At 120 min, the aromatic content has already declined. At 6 min, more benzene and hardly any toluene are detected. The toluene content then increases steadily to the sample withdrawn at 96 min. About 7 wt.% of toluene is detected before decreasing again. The styrene content remains almost constant at 2.1 to 3.5 wt.% over the entire test. Minor amounts of chlorine-, nitrogen-, and oxygen-containing HCs are also identified in the pyrolysis gas. HCl, as the main gaseous decomposition product of PVC, is identified in the sample taken after 6 min. Because of the pronounced peak tailing, it cannot be accurately quantified using the GC system. Therefore, HCl is missing in the normalized composition. The oxygen- and nitrogen-containing HCs consist of acetaldehydes, acrylonitrile, and HCN. Low amounts of acetonitrile and methacrylonitrile are also detected. While high quantities of acetaldehyde are only present in the sample at 6 min, the proportion of nitrogen-containing HCs only decreases slowly with the progression of the isothermal segment. Thus, after an initial 1.0 wt.% of nitrogen-containing HCs, only 0.1 wt.% can

Table 2

Mass balance of the staged pyrolysis experiments of the STR Mix with an end temperature of 500 °C compared to the pyrolysis at 500 °C in the STR.

Experiment	Product fraction yields in wt.%		
	Gas	Oil	Solid Residue
Isothermal 500 °C (Netsch et al., 2026)	41.3	55.1	3.6
Two-stage pyrolysis (400 °C for 96 min, 500 °C for 90 min)	37.8	57.0	5.2
		1st stage: 2.9	
		2nd stage: 54.1	
Two-stage pyrolysis (430 °C for 90 min, 500 °C for 90 min)	37.2	57.6	5.2
		1st stage: 22.3	
		2nd stage: 35.3	

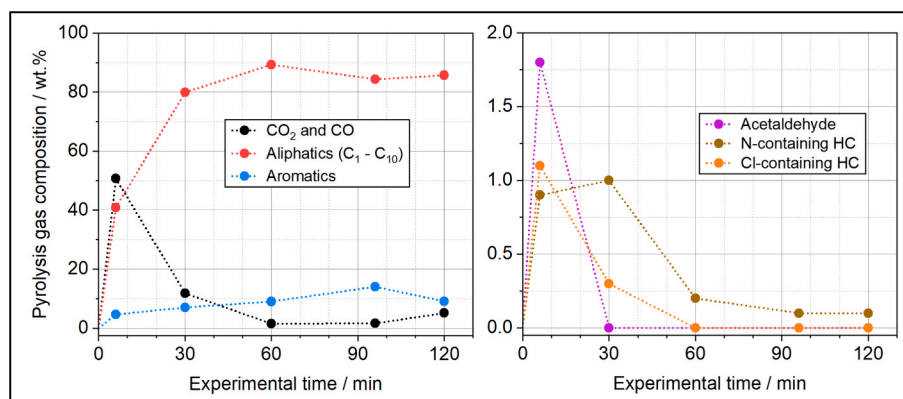


Fig. 6. Content of characteristic gas compounds sampled after 6, 30, 60, 96, and 120 min in the two-staged pyrolysis at 430 °C and 500 °C in the STR system.

be determined after the isothermal segment of the experiment. The chlorine-containing HCs are comprised of chloromethanes, chloroethanes, vinyl chlorides, 1,2-dichloroethanes, and chlorobutanes. These components are present in the 6 min gas sample predominantly. In the last gas sample of the isothermal segment (after 60 min), no more chlorine-containing HCs are detectable.

The gas analyses support the hypothesis that temperature-staged pyrolysis enables the separation of polymer-specific pyrolysis products. The typical gaseous PVC products are only recognizable at the start of the pyrolysis. With CO₂, CO, acetaldehyde, and ethylene, the results indicate an almost complete dichlorination of PVC and rapid decomposition of PET at the start of the experiment. Previously discussed interaction effects between PVC and PET may strongly accelerate the PET pyrolysis in the STR (Cao et al., 2023). Along with a high pentane content, the nitrile compounds indicate that PA6 and ABS also decompose at 430 °C during the isothermal segment. From 96 min on, more unbranched HCs are released beside the branched HCs. In the gas sample withdrawn after 60 min, the aliphatic C₄-C₁₀ HCs consist of about 55 wt.% linear and 45 wt.% branched molecules. In samples taken at 96 min and 120 min, the proportion of branched C₄-C₁₀ HCs declines to 40 wt.% and 27 wt.%, while the share of corresponding linear HCs rises to 60 wt.% and 73 wt.%, respectively. Thus, polyethylene appears to react in relevant quantities in the second stage, as assumed from the TG results. The TG results already identified the separation of PS and PP via temperature grading as the greatest engineering challenge. Relevant proportions of branched PP products are already apparent in the gas sample during the isothermal segment at 430 °C. This demonstrates that the decomposition of PS and PP is difficult to separate via temperature staging in the technical system. Their kinetics in the applied temperature range of 430 °C exhibit only slight reaction rate differences. The interactions between PS and polyolefins may further contribute to this effect. As a result, heteroatom-containing compounds can be efficiently enriched in the gas product during an isothermal pyrolysis stage. This applies to CO₂, CO, chlorine-, oxygen-, and nitrogen-containing HCs. The holding time of 90 min provides enough reaction time for their almost complete decomposition under the pyrolysis conditions. Nevertheless, an enrichment of aromatics in the first temperature stage can only be realized to a limited extent in the investigated pyrolysis system. Lowering the temperature delays all decomposition reactions, causing heteroatom-containing HCs formation for a longer experimental time. The gas analyses of the samples with a 400 °C step confirm this with higher quantities of heteroatom-containing HCs even after 30 min. In particular, nitrogen-containing HCs and aromatics from PS and ABS are present in the gas phase of the second stage in this test run. Although lowering the temperature would increase their yield in the second stage and above, more undesired HCs can be detected. Thus, the separation efficiency for gaseous species is reduced by lower temperatures.

3.2.3. Condensable pyrolysis products

The elemental composition reveals the mitigation of heteroatom-containing HCs into the condensable product fraction. Therefore, it allows for evaluating the potential enrichment of these oil species in the product obtained during the first isothermal pyrolysis stage. Table 3 lists the elemental analysis of the organic condensate obtained in the staged pyrolysis experiments.

The elemental analysis proves the enrichment of oxygen-, nitrogen-, and chlorine-containing HCs in the pyrolysis oil of the first pyrolysis stage. These chemical elements exceed the content of the pyrolysis oil in the isothermal reference test significantly. The water content in the condensate is also high in both condensate fractions. A comparison of the pyrolysis oil obtained in the first stage at the 400 °C and 430 °C experiments shows a higher carbon and hydrogen content than in the 430 °C condensate. This result supports the conclusion from the mass balance that relevant polyolefin decomposition occurs at the second pyrolysis stage. For the condensate fraction produced after the temperature increase, the heteroatom content is correspondingly lower.

Both pyrolysis oils that were obtained in the second stage at 500 °C exhibit a superior composition compared to the unstaged reference test at 500 °C. The comparison of both oils obtained from the staged experiments exhibits similar values with approximately 0.2–0.3 wt.% of nitrogen, chlorine, and oxygen. Some of the differences are already in the range of the measurement uncertainties of the analysis and close to the detection limit. The complete removal of chlorine-containing HCs, as reported by Bockhorn et al., could not be achieved with this setup (Bockhorn et al., 1998).

The analyses of the chemical composition support the findings deduced from elemental analyses. The comparison of the NMR results for the pyrolysis oils of different stages is shown in Fig. 7. The quantitative evaluation and the results of the isothermal reference experiment at 500 °C are shown in the supplementary information S3 according to the methodology of Netsch et al. (Netsch et al., 2026). Major differences

Table 3

Elemental composition of the condensate obtained from staged pyrolysis experiments and isothermal experiments at 500 °C with the STR Mix in the STR system.

Condensate	Elemental composition in wt.%				Moisture	O ^A
	C	H	N	Cl		
Isothermal 500 °C (Netsch et al., 2026)	84.4	12.5	0.6	0.5	0.0	2.0
Staged Pyrolysis						
400 °C (0 - 96 min)	60.7	11.7	1.3	7.0	15.0	4.8
500 °C (96 - 186 min)	85.6	13.7	0.2	0.2	0.0	0.3
Staged Pyrolysis						
430 °C (0 - 90 min)	82.8	11.7	1.0	1.7	1.7	1.0
500 °C (90 - 180 min)	86.8	12.6	0.3	0.2	0.0	0.0

^A organic oxygen calculated as the difference to 100 wt.%.

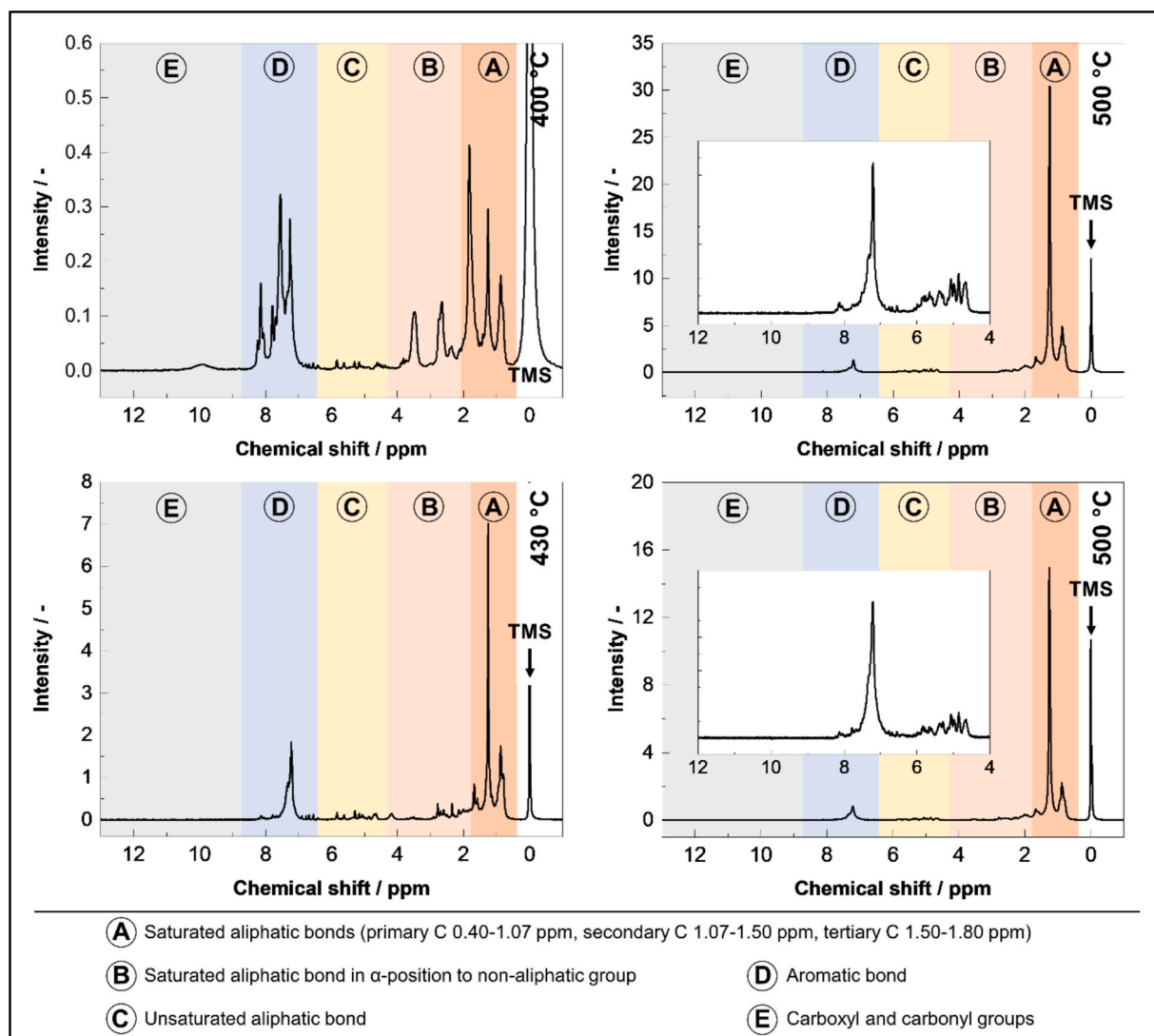


Fig. 7. NMR spectra of the pyrolysis oils obtained from the STR Mix pyrolyzed in two-staged experiments at temperature stages of 400 °C and 500 °C (top), and 430 °C and 500 °C (bottom). TMS indicates the chemical shift reference set to zero.

in the chemical composition of the condensate fractions are evident when comparing the first stage of the 400 °C experiment and the experiment at 430 °C. The condensate obtained in the first stage of the 400 °C test run requires dilution in deuterated chloroform. This preparation causes significantly lower signal intensities for this sample. Similar to the condensate of the 430 °C experiment, however, it exhibits more aromatic compounds and more protons close to a non-aliphatic functional group compared to the 430 °C product. The proportion of saturated aliphatic bonds is comparatively low. More aliphatic compounds are present in the 430 °C condensate than in the 400 °C condensate. This also reflects the higher carbon content determined in the elemental analysis for the 430 °C condensate compared to the 400 °C condensate. Consequently, the hypothesis of a substantial conversion of the polyolefinic components of the STR mix during the isothermal segment of the staged 430 °C pyrolysis is confirmed.

Carboxyl or carbonyl groups are detected in the 400 °C sample as a distinct peak at a chemical shift of 10 ppm. They reflect the high oxygen content indicated in the elemental analysis. Nevertheless, this peak is not visible in the 430 °C stage or the reference condensate obtained during the reference experiment under isothermal pyrolysis at 500 °C. The two condensate fractions collected in the second part of the staged pyrolysis are similar to each other but differ from the condensates produced in the respective experiment. Aromatic components are still

present, but in lower proportions of 6.3 mol.% and 9.4 mol.%. The aliphatic-bound protons dominate with 80.8 and 77.0 mol.%. The ratio between saturated and unsaturated aliphatic-bound protons remains almost constant. No significant but only minor differences are detected via NMR between the oils of the respective 500 °C samples and the reference.

Additional GCxGC analyses were performed to quantify the shift of main HCs in both pyrolysis oils obtained during the 430 °C staged experiment. The condensate generated during the 400 °C experiment contains a high amount of water, preventing its analysis in the sensitive GCxGC system. The chromatograms indicate a complex composition of a multitude of different HC species. Different HCs that represent typical decomposition compounds of specific polymers serve as indicators to evaluate the separation of condensable species during the temperature-staged pyrolysis. 2,4-Dimethylheptene from PP, linear n-alkanes and α -olefins from PE, toluene as PS, ABS, and PET products, ϵ -caprolactam from PA6, and benzoic acid from PET are focused on. In the 430 °C stage, the condensate contains 1.7 wt.% of toluene, 1.0 wt.% of benzoic acid, and 1.1 wt.% of ϵ -caprolactam. These results exceed the concentrations found in the pyrolysis oil obtained after temperature increase (0.6 wt.%, 0.4 wt.%, and 0.5 wt.%, respectively). This emphasizes the predominant decomposition of the PS, ABS, PA6, and PET during the first stage, even though the elemental analysis does not reveal a distinct trend. Also, the

intensity of diphenyls and other monoaromatics is increased compared to the product generated at elevated pyrolysis temperatures of this test run. Consistent with the gas analyses, a partial degradation of PP is also verified by the GCxGC analyses. A concentration of 1.8 wt.% 2,4-Dimethylheptene is detected in the pyrolysis product at the 430 °C stage. The targeted product contains only 1.0 wt.% of 2,4-dimethylheptene, emphasizing the disadvantageous shift from PP products to the first stage. This shift might also be attributed to the PS-PP-specific interactions that were identified in TG. Nevertheless, the target product of the second pyrolysis stage includes a total amount of 13.6 wt.% of quantified n-alkanes and α -olefins in the range from C₇ to C₂₀. In the pyrolysis oil of the first stage, only 5.2 wt.% is detectable. This finding underlines the general feasibility of temperature staging to improve the quality of the pyrolysis oil and gas by depletion of heteroatom-containing compounds and aromatics.

In the STR system, the selective product enrichment by staged pyrolysis was less pronounced for the pyrolysis oil than for the gas. In particular, mass transport phenomena might cause this finding. While gases are quickly conveyed to the downstream sampling system by continuous nitrogen purging, condensable products must first perform a phase transition and drain into the collecting tanks. This represents an additional mass transport for condensable products and a potential source for artifact effects. The condensable products need more time to be collected than the flushing of pyrolysis gas. This causes a time delay for their collection, leading to a potential carryover of condensable products generated during the first stage to the oil collected at the elevated temperatures. Such a carryover of condensable product can be neglected for well-controlled laboratory-scale experiments. It poses a technical challenge in real plastic pyrolysis applications and might weaken the temperature stage separation effect in this study. This challenge might be overcome by a continuously operated cascade system of two reactors pyrolyzing at different temperatures. In such a cascade process, with each reactor having its own condensation unit, independence in the gas–liquid separation of the volatile products is achieved through spatial separation. Nevertheless, further investigation into the separation of pyrolysis oil and permanent gas in plastic pyrolysis condensation systems is generally necessary for the optimization of chemical recycling of plastics.

4. Conclusion

The results demonstrate the technical feasibility of the temperature-staged pyrolysis concept for selective product enrichment. Associated engineering challenges are also highlighted. TG experiments identified temperature ranges that enable partial separation of thermoplastics based on their distinct decomposition kinetics. However, interactions between polymers in mixed feedstocks can accelerate or delay their decomposition. For instance, interactions involving PVC, PA6, and PET accelerate low-temperature decomposition, while PS narrows the kinetic gap between low- and high-temperature stages by accelerating polyolefin decomposition. Although selective decomposition of aromatic and heteroatom-containing polymers around 370 °C is possible under TG conditions, partial conversion of polyolefins, particularly PP, cannot be fully avoided.

The staged pyrolysis concept was further validated in STR experiments. Compared to TG, stage temperatures and holding times must be adapted to account for heat and mass transfer limitations, batch operation, and time-dependent polymer temperature profiles. As a result, polymer temperatures remain below the reactor set temperature, requiring higher or prolonged operating conditions to achieve comparable separation effects. While variations in the first-stage temperature (400–430 °C) had little influence on the overall mass balance, they strongly affected the proportion of generated pyrolysis oil in each temperature stage. Higher first-stage temperatures enabled a pronounced reduction of heteroatoms and aromatics in the oil, as well as a targeted enrichment of aliphatic HCs in the oil obtained during the second stage.

The results demonstrate the key aspect of the optimization regarding the generation of an aliphatic-rich pyrolysis oil. Finding a balance between achieving maximum target product yield and improving the product quality is essential. Higher temperatures or longer holding times will cause complete decomposition of PS and ABS in the first isothermal stage. Polyolefins, especially PP, will pyrolyze more intensively. This would improve the oil quality but reduce the yield of the aliphatic-rich target product. On the contrary, the decomposition of polyolefins during the first pyrolysis stage is avoided by lower temperatures, but is also associated with a lower partial conversion of the non-polyolefinic thermoplastics. Establishing a clear priority between product yield and oil quality in plastic pyrolysis is only feasible to a limited extent. While industrial operation generally favors yield maximization due to its direct impact on revenues, heterogeneous and contaminated plastic waste streams inherently constrain yield improvements and necessitate subsequent oil upgrading. As upgrading efforts strongly depend on feedstock composition and process-specific conditions, a universal prioritization between yield and quality is not applicable. Consequently, defining a case-specific trade-off between yield and quality requires a dedicated techno-economic assessment, for which this work provides the relevant parameters.

The effective enrichment of heteroatom-containing gas species emphasizes the importance of appropriate process and equipment design during scale-up of staged pyrolysis processes. Corrosion, acidification, and clogging from accumulating salts like ammonium chloride are particularly related to HCl release. As a result, robust downstream pyrolysis gas cleaning and neutralization must be addressed, even if such effects were not observed at the pilot scale.

This study estimated the content of unsaturated aliphatics in the pyrolysis oil using NMR analyses. The results indicate that temperature-staged pyrolysis cannot significantly reduce its olefin content. Consequently, other process adjustments must be investigated to minimize the olefin content for pyrolysis oil application. Also, this study investigated well-defined feedstocks. This enables a detailed evaluation of the relationship between the decomposition of individual polymers and the overall yields and product composition. However, this selection limits the study, as other polymer types and impurities, such as biomass, may exhibit different reaction kinetics, which further influence the complex overall reaction mechanisms (Burra and Gupta, 2018; Zhao et al., 2025). Additionally, waste plastic products are typically highly functionalized. Incorporated additives influence pyrolysis kinetics through their decomposition behavior or possible interaction effects (Zhang et al., 2025; Charitopoulou et al., 2022). Consequently, the staged pyrolysis of representative waste fractions should also be investigated for optimization of staged pyrolysis systems.

Funding sources

The study was funded by the German Helmholtz Association within the program, “Materials and Technologies for the Energy Transition”.

CRediT authorship contribution statement

Niklas Netsch: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Aljoscha Tauber:** Investigation, Data curation. **Daniela Merz:** Writing – review & editing, Resources, Methodology, Conceptualization. **Britta Bergfeldt:** Resources, Formal analysis. **Salar Tavakol:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Dieter Stapf:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Acknowledgment

-

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2026.123622>.

Data availability

Data will be made available on request.

References

- Keijer, T., Bakker, V., Sloopweg, J.C., 2019. Circular chemistry to enable a circular economy. *Nat. Chem.* 11, 190–195. <https://doi.org/10.1038/s41557-019-0226-9>.
- van Geem, K.M., 2023. Plastic waste recycling is gaining momentum. *Science* 381, 607–608. <https://doi.org/10.1126/science.adj2807>.
- European Parliament and the Council, Establishing the framework for achieving climate neutrality and amending Regulations (EC) No 401/2009 and (EU) 2018/1999 ("European Climate Law"), 2021.
- Ragaert, K., Delva, L., van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Manag.* 69, 24–58. <https://doi.org/10.1016/j.wasman.2017.07.044>.
- Johansen, M.R., Christensen, T.B., Ramos, T.M., Syberg, K., 2022. A review of the plastic value chain from a circular economy perspective. *J. Environ. Manage.* 302, 113975. <https://doi.org/10.1016/j.jenvman.2021.113975>.
- Rahimi, A., García, J.M., 2017. Chemical recycling of waste plastics for new materials production. *Nat. Rev. Chem.* 1. <https://doi.org/10.1038/s41570-017-0046>.
- Palos, R., Gutiérrez, A., Vela, F.J., Maña, J.A., Hita, I., Asueta, A., Arnaiz, S., Arandes, J. M., Bilbao, J., 2019. Assessing the potential of the recycled plastic slow pyrolysis for the production of streams attractive for refineries. *J. Anal. Appl. Pyrol.* 142, 104668. <https://doi.org/10.1016/j.jaap.2019.104668>.
- Holtkamp, M., Renner, M., Matthiesen, K., Wald, M., Luinstra, G.A., Biessey, P., 2024. Robust downstream technologies in polystyrene waste pyrolysis: Design and prospective life-cycle assessment of pyrolysis oil reintegration pathways. *Resour. Conserv. Recycl.* 205, 107558. <https://doi.org/10.1016/j.resconrec.2024.107558>.
- Laghezza, M., Fiore, S., Berruti, F., 2024. A review on the pyrolytic conversion of plastic waste into fuels and chemicals. *J. Anal. Appl. Pyrol.* 179, 106479. <https://doi.org/10.1016/j.jaap.2024.106479>.
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. <https://doi.org/10.1126/sciadv.1700782>.
- Bockhorn, H., Hornung, A., Hornung, U., Schwallier, D., 1999. Kinetic study on the thermal degradation of polypropylene and polyethylene. *J. Anal. Appl. Pyrol.* 48, 93–109. [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4).
- Bockhorn, H., Hornung, A., Hornung, U., Weichmann, J., 1999. Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods. *Thermochim. Acta* 337, 97–110. [https://doi.org/10.1016/S0040-6031\(99\)00151-3](https://doi.org/10.1016/S0040-6031(99)00151-3).
- Faravelli, T., Pincioli, M., Pisano, F., Bozzano, G., Dente, M., Ranzi, E., 2001. Thermal degradation of polystyrene. *J. Anal. Appl. Pyrol.* 60, 103–121. [https://doi.org/10.1016/S0165-2370\(00\)00159-5](https://doi.org/10.1016/S0165-2370(00)00159-5).
- Montaudou, G., Puglisi, C., Samperi, F., 1993. Primary thermal degradation mechanisms of PET and PBT. *Polym. Degrad. Stab.* 42, 13–28. [https://doi.org/10.1016/0141-3910\(93\)90021-A](https://doi.org/10.1016/0141-3910(93)90021-A).
- Yu, J., Sun, L., Ma, C., Qiao, Y., Yao, H., 2016. Thermal degradation of PVC: a review. *Waste Manag.* 48, 300–314. <https://doi.org/10.1016/j.wasman.2015.11.041>.
- Lee, K.-H., Shin, D.-H., Seo, Y.-H., 2006. Thermal degradation of nitrogen-containing polymers, acrylonitrile-butadiene-styrene and styrene-acrylonitrile. *Korean J. Chem. Eng.* 23, 224–229. <https://doi.org/10.1007/BF02705720>.
- Kusenberger, M., Eschenbacher, A., Djokic, M.R., Zayoud, A., Ragaert, K., de Meester, S., van Geem, K.M., 2022. Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: to decontaminate or not to decontaminate? *Waste Manag.* 138, 83–115. <https://doi.org/10.1016/j.wasman.2021.11.009>.
- Zhang, Y., Li, A., Zhang, Y.S., Xie, W., Liu, C., Peng, Y., Zhang, H., Kang, Y., Qu, B., Ji, G., 2024. In-situ catalytic pyrolysis of polyethylene to co-produce BTX aromatics and H₂ by Ni/ZSM-5 in the rotary reactor with solid heat carriers. *Fuel* 371, 131950. <https://doi.org/10.1016/j.fuel.2024.131950>.
- Cao, Y., Gao, R., Lei, J., Hou, Y., Xu, M., Cao, S., Chen, Z., Duan, Y., Du, H., 2025. Mechanistic insights into Cl transformation and calcium-based dechlorination during pyrolysis of waste plastics: Kinetics, product analysis and process optimization. *J. Environ. Chem. Eng.* 13, 119459. <https://doi.org/10.1016/j.jece.2025.119459>.
- Kumar, A., Kumari, L., Laghari, A.A., Rong, H., Jamro, I.A., Sajani, S., Aborisade, M.A., Rajput, G., Oba, B.T., Nkinahamira, F., Ndagijimana, P., Mehboob, G., Cui, B., Guo, D., 2024. Exploring the integrated potential of pyrolysis and low-temperature wet torrefaction for typical medical waste valorization: a multifaceted approach leveraging online TG-FTIR-MS, 2D-COS, iso-conversional kinetics, and reaction mechanisms. *Chem. Eng. J.* 499, 156464. <https://doi.org/10.1016/j.cej.2024.156464>.
- Netsch, N., Schröder, L., Zeller, M., Neugber, I., Merz, D., Klein, C.O., Tavakkol, S., Stapf, D., 2025. Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics. *J. Therm. Anal. Calorim.* 150, 211–229. <https://doi.org/10.1007/s10973-024-13630-6>.
- Bockhorn, H., Hornung, A., Hornung, U., 1998. Stepwise pyrolysis for raw material recovery from plastic waste. *J. Anal. Appl. Pyrol.* 46, 1–13. [https://doi.org/10.1016/S0165-2370\(98\)00066-7](https://doi.org/10.1016/S0165-2370(98)00066-7).
- Bockhorn, H., Hentschel, J., Hornung, A., Hornung, U., 1999. Environmental engineering: Stepwise pyrolysis of plastic waste. *Chem. Eng. Sci.* 54, 3043–3051. [https://doi.org/10.1016/S0009-2509\(98\)00385-6](https://doi.org/10.1016/S0009-2509(98)00385-6).
- Bockhorn, H., Hornung, A., Hornung, U., Jakobströer, P., Kraus, M., 1999. Dehydrochlorination of plastic mixtures. *J. Anal. Appl. Pyrol.* 49, 97–106. [https://doi.org/10.1016/S0165-2370\(98\)00124-7](https://doi.org/10.1016/S0165-2370(98)00124-7).
- Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., Dente, M., 2003. Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *J. Anal. Appl. Pyrol.* 70, 761–777. [https://doi.org/10.1016/S0165-2370\(03\)00058-5](https://doi.org/10.1016/S0165-2370(03)00058-5).
- Korkmaz, A., Yanik, J., Brebu, M., Vasile, C., 2009. Pyrolysis of the tetra pak. *Waste Manag.* 29, 761–777. [https://doi.org/10.1016/S0165-2370\(03\)00058-5](https://doi.org/10.1016/S0165-2370(03)00058-5).
- Cheung, W.Y., Lee, K.L., Lam, K.L., Chan, T.Y., Lee, C.W., Hui, C.-W., 2011. Operation strategy for multi-stage pyrolysis. *J. Anal. Appl. Pyrol.* 91, 165–182. <https://doi.org/10.1016/j.jaap.2011.02.004>.
- Netsch, N., Tauber, A., Keskin, O., Bergfeldt, B., Wehner, H., Eidam, D., Tavakkol, S., Stapf, D., 2026. Chemical Recycling of Mixed Thermoplastics via Pyrolysis: A Comparative Study of Feedstock Influence and Reactor Impact. *J. Anal. Appl. Pyrolysis* 194, 107575. <https://doi.org/10.1016/j.jaap.2025.107575>.
- Oyedun, A.O., Lam, K.L., Gebreegziabher, T., Hui, C.W., 2013. Optimization of multi-stage pyrolysis. *Appl. Therm. Eng.* 61, 123–127. <https://doi.org/10.1016/j.applthermaleng.2013.03.043>.
- Choi, G.G., Oh, S.J., Kim, J.S., 2016. Non-catalytic pyrolysis of scrap tires using a newly developed two-stage pyrolyzer for the production of a pyrolysis oil with a low sulfur content. *Appl. Energy* 170, 140–147. <https://doi.org/10.1016/j.apenergy.2016.02.119>.
- Oyedun, A.O., Lam, K.L., Hui, C.W., 2012. Charcoal Production via Multistage Pyrolysis. *Chin. J. Chem. Eng.* 20, 455–460. [https://doi.org/10.1016/S1004-9541\(11\)60206-1](https://doi.org/10.1016/S1004-9541(11)60206-1).
- Fukushima, M., Wu, B., Ibe, H., Wakai, K., Sugiyama, E., Abe, H., Kitagawa, K., Tsuruga, S., Shiruma, K., Ono, E., 2010. Study on dechlorination technology for municipal waste plastics containing polyvinyl chloride and polyethylene terephthalate. *J. Mater. Cycles Waste Manage.* 12, 108–122. <https://doi.org/10.1007/s10163-010-0279-8>.
- López, A., de Marco, I., Caballero, B.M., Laregoiti, M.F., Adrados, A., 2011. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. *Fuel Process. Technol.* 92, 253–260. <https://doi.org/10.1016/j.fuproc.2010.05.008>.
- Lopez-Uribebarrenechea, A., de Marco, I., Caballero, B.M., Laregoiti, M.F., Andrades, A., 2012. Catalytic stepwise pyrolysis of packaging plastic waste. *J. Anal. Appl. Pyrol.* 96, 54–62. <https://doi.org/10.1016/j.jaap.2012.03.004>.
- Yuan, G., Chen, D., Yin, L., Wang, Z., Zhao, L., Wang, J.Y., 2014. High efficiency chlorine removal from polyvinyl chloride (PVC) pyrolysis with a gas-liquid fluidized bed reactor. *Waste Manag.* 34, 1045–1050. <https://doi.org/10.1016/j.wasman.2013.08.021>.
- Yin, F., Zhuang, Q., Chang, T., Zhang, C., Sun, H., Sun, Q., Wang, C., Li, L., 2021. Study on pyrolysis characteristics and kinetics of mixed plastic waste. *J. Mater. Cycles Waste Manage.* 23, 1984–1994. <https://doi.org/10.1007/s10163-021-01271-y>.
- Park, K.-B., Oh, S.-J., Guzelciftci, B., Kim, J.-S., 2018. Production of clean oil with low levels of chlorine and olefins in a continuous two-stage pyrolysis of a mixture of waste low-density polyethylene and polyvinyl chloride. *Energy* 157, 402–411. <https://doi.org/10.1016/j.energy.2018.05.182>.
- Park, K.-B., Jeong, Y.-S., Guzelciftci, B., Kim, J.-S., 2019. Characteristics of a new type continuous two-stage pyrolysis of waste polyethylene. *Energy* 166, 343–351. <https://doi.org/10.1016/j.energy.2018.10.078>.
- Park, K.-B., Choi, M.-J., Chae, D.-Y., Jung, J., Kim, J.-S., 2022. Separate two-step and continuous two-stage pyrolysis of a waste plastic mixture to produce a chlorine-depleted oil. *Energy* 244, 122583. <https://doi.org/10.1016/j.energy.2021.122583>.
- N. Sophonrat, L. Sandström, I.N. Zaini, W. Yang, Stepwise pyrolysis of mixed plastics and paper for separation of oxygenated and hydrocarbon condensates, 229 (2018) 314–325. <https://doi.org/10.1016/j.apenergy.2018.08.006>.
- Chang, T., Li, C., Fan, F., Wu, H., Wang, C., Yin, F., 2023. Effects of temperature zones on pyrolysis products of mixed plastic waste. *J. Mater. Cycles Waste Manage.* 25, 430–440. <https://doi.org/10.1007/s10163-022-01549-9>.
- Williams, P.T., Williams, E.A., 1999. Interaction of Plastics in Mixed-Plastics Pyrolysis. *Energy Fuels* 13, 188–196. <https://doi.org/10.1021/ef980163x>.
- PlasticsEurope, The Circular Economy for Plastics: A European Analysis, Brussels, 2024.
- Netsch, N., Weigel, L., Schmedding, T., Zeller, M., Bergfeldt, B., Straczewski, G., Tavakkol, S., Stapf, D., 2025. Chemical Characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography. *Fuel Process. Technol.* 280, 108359. <https://doi.org/10.1016/j.fuproc.2025.108359>.
- Cao, R., Zhang, M.-Q., Jiao, Y., Li, Y., Sun, B., Xiao, D., Wang, M., Ma, D., 2023. Coprocessing of polyvinyl chloride and polyesters. *Nat. Sustain* 6, 1685–1692. <https://doi.org/10.1038/s41893-023-01234-1>.
- Jing, X., Zhao, Y., Wen, H., Xu, Z., 2013. Interactions between Low-Density Polyethylene (LDPE) and Polypropylene (PP) during the Mild Cracking of Polyolefin Mixtures in a Closed-batch Reactor. *Energy Fuels* 27, 5841–5851. <https://doi.org/10.1021/ef401376m>.

- Westerhout, R.W.J., Waanders, J., Kuipers, J.A.M., van Swaaij, W.P.M., 1997. Kinetics of the Low-Temperature Pyrolysis of Polyethylene, Polypropylene, and Polystyrene Modeling, Experimental Determination, and Comparison with Literature Models and Data. *Ind. Eng. Chem. Res.* 36, 1955–1964. <https://doi.org/10.1021/ie960501m>.
- Kruse, T.M., Levine, S.E., Wong, H.-W., Duoss, E., Lebovitz, A.H., Torkelson, J.M., Broadbelt, L.J., 2005. Binary mixture pyrolysis of polypropylene and polystyrene: a modeling and experimental study. *J. Anal. Appl. Pyrol.* 73, 342–354. <https://doi.org/10.1016/j.jaap.2005.03.006>.
- Costa, P., Pinto, F., Ramos, A.M., Gulyurtlu, I., Cabrita, I., Bernardo, M.S., 2010. Study of the Pyrolysis Kinetics of a Mixture of Polyethylene, Polypropylene, and Polystyrene. *Energy Fuels* 24, 6239–6247. <https://doi.org/10.1021/ef101010n>.
- Calero, M., Solís, R.R., Muñoz-Batista, M.J., Pérez, A., Blázquez, G., Ángeles Martín-Lara, M., 2023. Oil and gas production from the pyrolytic transformation of recycled plastic waste: an integral study by polymer families. *Chem. Eng. Sci.* 271, 118569. <https://doi.org/10.1016/j.ces.2023.118569>.
- Chang, S.H., 2023. Plastic waste as pyrolysis feedstock for plastic oil production: a review. *Sci. Total Environ.* 877, 162719. <https://doi.org/10.1016/j.scitotenv.2023.162719>.
- Maqsood, T., Dai, J., Zhang, Y., Guang, M., Li, B., 2021. Pyrolysis of plastic species: a review of resources and products. *J. Anal. Appl. Pyrol.* 159, 105295. <https://doi.org/10.1016/j.jaap.2021.105295>.
- Burra, K.G., Gupta, A.K., 2018. Kinetics of synergistic effects in co-pyrolysis of biomass with plastic wastes. *Appl. Energy* 220, 408–418. <https://doi.org/10.1016/j.apenergy.2018.03.117>.
- Zhao, N., Low, S.S., Law, C.L., Wu, T., Pang, C.H., 2025. Co-pyrolysis of polymers: recent advances, challenges and perspectives. *Fuel Process. Tech.* 274, 108239. <https://doi.org/10.1016/j.fuproc.2025.108239>.
- Zhang, L., Zhou, N., Ke, L., Zeng, Y., Wu, Q., Zhang, J., Liao, R., Fan, L., Cobb, K., Ruan, R., Liu, Y., Wang, Y., 2025. Understanding the role of plastic additives in the pyrolysis of plastic wastes: Impact of additives on product selectivity, kinetics, and mechanistic pathways. *Chem. Eng. J.* 514, 163194. <https://doi.org/10.1016/j.cej.2025.163194>.
- Charitopoulou, M.A., Papadopoulou, L., Achilias, D.S., 2022. Effect of brominated flame retardant on the pyrolysis products of polymers originating in WEEE. *Environ. Sci. Pollut. Res. Int.* 29, 29570–29582. <https://doi.org/10.1007/s11356-021-15489-8>.

Verification of the contribution from the co-authors

Title: **Energy Demand for Pyrolysis of Mixed Thermoplastics and Waste Plastics in Chemical Recycling: Model Prediction and Pilot-Scale Validation**

Journal: ACS Sustainable Resource Management

Authors: Niklas Netsch, Michael Zeller, Frank Richter, Britta Bergfeldt, Salar Tavakkol, Dieter Stapf

DOI: 10.1021/acssusresmgt.4c00109

Position in the dissertation:

The content of this paper has been included in chapters 3.1, 3.2.1, 3.2.3, 3.4, and 4.1.3.

Author contribution:

Niklas Netsch: Conceptualization (85%), Methodology, Investigations (80%), Analysis (90%), Data Curation, Visualization, Writing – Original Draft

Michael Zeller: Conceptualization (10%), Review (25%)

Frank Richter: Conceptualization (5%), Investigations (20%)

Britta Bergfeldt: Analysis (10%), Resources (10%), Review (25%)

Salar Tavakkol: Resources (45%), Supervision (50%), Review (25%)

Dieter Stapf: Resources (45%), Supervision (50%), Review (25%)

Signature of the authors:

<i>Author</i>	<i>Date</i>	<i>Signature</i>
Niklas Netsch		
Michael Zeller		
Frank Richter		
Britta Bergfeldt		
Salar Tavakkol		
Dieter Stapf		

Title: **Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics**

Journal: Journal of Thermal Analysis and Calorimetry

Authors: Niklas Netsch, Lukas Schröder, Michael Zeller, Iuliia Neugber, Daniela Merz, Christopher Klein, Salar Tavakkol, Dieter Stapf

DOI: 10.1007/s10973-024-13630-6

Position in the dissertation:

The content of this paper has been included in chapters 3.1, 3.2.2, 3.4, and 4.1.1.

Author contribution:

Niklas Netsch: Conceptualization (80%), Methodology (50%), Investigations (60%), Analysis (50%), Data Curation (50%), Visualization (80%), Writing – Original Draft

Lukas Schröder: Methodology (20%), Software (80%), Investigations (30%), Analysis (50%), Data Curation (50%), Visualization (20%)

Michael Zeller: Methodology (10%), Software (20%), Review (25%)

Iuliia Neugber: Investigations (10 %)

Daniela Merz: Conceptualization (20%), Methodology (10%), Resources (30%), Review (25%)

Christopher Klein: Methodology (10%), Resources (10%)

Salar Tavakkol: Resources (30%), Supervision (50%), Review (25%)

Dieter Stapf: Resources (30%), Supervision (50%), Review (25%)

Signature of the authors:

<i>Author</i>	<i>Date</i>	<i>Signature</i>
Niklas Netsch		
Lukas Schröder		
Michael Zeller		
Iuliia Neugber		
Daniela Merz		
Christopher Klein		
Salar Tavakkol		
Dieter Stapf		

Title: **Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography**

Journal: Fuel Processing Technology

Authors: Niklas Netsch, Luca Weigel, Tim Schmedding, Michael Zeller, Britta Bergfeldt, Grazyna Straczewski, Salar Tavakkol, Dieter Stapf

DOI: 10.1016/j.fuproc.2025.108359

Position in the dissertation:

The content of this paper has been included in chapters 3.3 and 4.2.2.

Author contribution:

Niklas Netsch: Conceptualization (80%), Methodology (70%), Investigation, Data Curation, Analysis (90%), Software (50%), Validation, Visualization, Writing – Original Draft

Luca Weigel: Methodology (10%), Software (50%)

Tim Schmedding: Methodology (10%)

Michael Zeller: Conceptualization (20%), Methodology (10%), Review (20%)

Britta Bergfeldt: Analysis (10%), Resources (10%), Review (20%)

Grazyna Straczewski: Resources (30%), Review (20%)

Salar Tavakkol: Resources (30%), Supervision (50%), Review (20%)

Dieter Stapf: Resources (30%), Supervision (50%), Review (20%)

Signature of the authors:

<i>Author</i>	<i>Date</i>	<i>Signature</i>
Niklas Netsch		
Luca Weigel		
Tim Schmedding		
Michael Zeller		
Britta Bergfeldt		
Grazyna Straczewski		
Salar Tavakkol		
Dieter Stapf		

Title: **Chemical Recycling of Mixed Thermoplastics via Pyrolysis: A Comparative Study of Feedstock Influence and Reactor Impact**

Journal: Journal for Analytical and Applied Pyrolysis

Authors: Niklas Netsch, Aljoscha Tauber, Orhan Keskin, Britta Bergfeldt, Harald Wehner, Dirk Eidam, Salar Tavakkol, Dieter Stapf

DOI: 10.1016/j.jaap.2025.107575

Position in the dissertation:

The content of this paper has been included in chapters 3.1, 3.2.3, 3.2.4, 3.3, 3.4, 4.1.2, 4.2.1, and 4.2.2.

Author contribution:

Niklas Netsch: Conceptualization, Methodology, Investigation (20%), Data Curation (80%), Analysis (90%), Validation, Visualization, Writing – Original Draft

Aljoscha Tauber: Investigation (70%), Data Curation (20%)

Orhan Keskin: Investigation (5%)

Britta Bergfeldt: Analysis (10%), Resources (5%), Review (10%)

Harald Wehner: Investigation (5%)

Dirk Eidam: Resources (5%), Review & Editing (10%)

Salar Tavakkol: Resources (45%), Supervision (50%), Review (40%)

Dieter Stapf: Resources (45%), Supervision (50%), Review (40%)

Signature of the authors:

<i>Author</i>	<i>Date</i>	<i>Signature</i>
Niklas Netsch		
Aljoscha Tauber		
Orhan Keskin		
Britta Bergfeldt		
Harald Wehner		
Dirk Eidam		
Salar Tavakkol		
Dieter Stapf		

Title: **Optimizing product yield and composition in chemical recycling of mixed plastics through temperature-staged pyrolysis**

Journal: Chemical Engineering Science

Authors: Niklas Netsch, Aljoscha Tauber, Daniela Merz, Britta Bergfeldt, Salar Tavakkol, Dieter Stapf

DOI: 10.1016/j.ces.2026.123622

Position in the dissertation:

The content of this paper has been included in chapters 3.1, 3.2.2, 3.2.4, 3.3, and 4.3.

Author contribution:

Niklas Netsch: Conceptualization (90%), Methodology (90%), Investigation (50%), Data Curation (80%), Analysis (90%), Validation, Visualization, Writing – Original Draft

Aljoscha Tauber: Investigation (50%), Data Curation (20%)

Daniela Merz: Conceptualization (10%), Methodology (10%), Resources (10%), Review (30%)

Britta Bergfeldt: Analysis (10%), Resources (10%), Review (10%)

Salar Tavakkol: Resources (40%), Supervision (50%), Review (30%)

Dieter Stapf: Resources (40%), Supervision (50%), Review (30%)

Signature of the authors:

<i>Author</i>	<i>Date</i>	<i>Signature</i>
Niklas Netsch		
Aljoscha Tauber		
Daniela Merz		
Britta Bergfeldt		
Salar Tavakkol		
Dieter Stapf		
