

ENVIRONMENTAL PERFORMANCE OF PYROLYSIS- BASED CHEMICAL RECYCLING: EFFECTS OF FEEDSTOCK COMPOSITION AND PYROLYSIS OIL UTILIZATION

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Abstract

The transition towards a sustainable and climate-neutral plastics economy requires the development of recycling technologies capable of recovering valuable resources from mixed plastic waste (MPW) that cannot be effectively processed by conventional mechanical recycling. Pyrolysis-based chemical recycling has emerged as a promising complementary technology by converting heterogeneous plastic waste into secondary chemical feedstocks suitable for the production of new chemicals and plastics. However, the environmental performance of pyrolysis strongly depends on feedstock characteristics, process configuration, and the integration of downstream utilization pathways, while these interdependencies have only been investigated to a limited extent. This thesis therefore evaluates the influence of waste composition on the climate change impact of pyrolysis-based chemical recycling, investigates the effect of pyrolysis oil composition on downstream conversion routes, and assesses its potential to reduce climate change impact relative to waste incineration with energy recovery.

The study combines experimental pyrolysis data from the literature, obtained using well-defined model feedstocks and two different reactor technologies, with process modeling of downstream conversion pathways to generate consistent mass and energy balances and life cycle inventories. The environmental assessment is performed using life cycle assessment (LCA) methodology for seven representative feedstocks ranging from virgin polyolefins to heterogeneous post-consumer plastic waste. Two waste-to-chemicals pathways are investigated: pyrolysis followed by upgrading and steam cracking for the production of base chemicals, and pyrolysis followed by entrained-flow gasification (EFG) for syngas production suitable for methanol or Oxo synthesis.

The results demonstrate that feedstock composition is the dominant factor governing the environmental performance of pyrolysis-based chemical recycling. Heteroatom-free polymers such as polyethylene, polypropylene, and polystyrene consistently achieve high pyrolysis oil yields and consequently provide greater reductions in climate change impact through increased recovery of valuable chemical products. In contrast, feedstocks containing polymers such as polyethylene terephthalate, polyamide, and polyvinyl chloride exhibit lower product yields due to reduced carbon recovery in pyrolysis oil.

Across all analyzed feedstocks, carbon content correlates with higher pyrolysis oil yields, carbon recycling efficiency, and climate change impact reduction potential, defined as the difference in net climate change impact between the respective chemical recycling route and conventional energy recovery. This relationship reflects the central role of carbon recovery during pyrolysis, which links feedstock composition to downstream product yields and ultimately to environmental performance. Consequently, heteroatom-containing feedstocks such as MPW exhibit a lower climate change impact reduction potential due to their lower carbon content. Nevertheless, even these feedstocks achieve lower climate change impacts than conventional energy recovery within the investigated scenarios.

Pyrolysis contributes the largest share of total process burdens, primarily because carbon lost to pyrolysis gas and residues is emitted as CO₂ during their treatment. Consequently, maximizing carbon recovery through appropriate feedstock selection and reactor design is key to achieving high climate change impact reduction potential. The remaining burdens can be reduced through efficient utilization of pyrolysis side products, particularly by material utilization of pyrolysis gas in EFG or, to a lesser extent, by energy recovery. Flaring of pyrolysis gas should be avoided due to the high associated climate change impacts.

The comparison of downstream utilization pathways reveals that steam cracking and EFG exhibit comparable performance in terms of climate change impact for most feedstocks. Although pyrolysis oil composition influences the preferred downstream utilization pathway, boundary conditions such as low-carbon hydrogen availability, opportunities for heat integration, and specifically the substituted syngas production route – based on heavy fuel oil or natural gas – have a greater influence on environmental performance.

A comparison of perspectives in LCA yielded seemingly contradictory conclusions regarding the environmental performance of pyrolysis-based chemical recycling. While the input-based waste management perspective consistently indicates environmental benefits in comparison to energy recovery, the product-based perspective only identifies advantages for heteroatom-free feedstocks with high yields in pyrolysis. The contradiction can be resolved in a combined system-wide perspective assessment, attributing the differences to diverging system boundaries and the underlying background system. The combined perspective results support the preferability of pyrolysis-based chemical recycling over energy recovery. Additionally, the combined perspective highlights that the environmental performance of pyrolysis-based chemical recycling cannot be evaluated in isolation but must be assessed within the broader context of the surrounding waste management and chemical production systems.

Overall, carbon recovery of pyrolysis represents the key process variable governing the environmental performance of pyrolysis-based chemical recycling. Feedstock composition, reactor design, and process integration influence climate change impacts primarily through their influence on carbon recovery, while the overall environmental benefit depends on the surrounding waste management and chemical production systems.

Kurzfassung

Der Wandel hin zu einer nachhaltigen und klimaneutralen Kunststoffwirtschaft erfordert Recyclingtechnologien, die auch gemischte Kunststoffabfälle (Mixed Plastic Waste, MPW) verwerten können, welche für das konventionelle mechanische Recycling ungeeignet sind. Das pyrolysebasierte chemische Recycling stellt hierfür einen vielversprechenden ergänzenden Ansatz dar, indem heterogene Kunststoffabfälle in Sekundärrohstoffe für die Produktion neuer Chemikalien und Kunststoffe umgewandelt werden. Die Umweltwirkung dieses Verfahrens hängt jedoch maßgeblich von der Zusammensetzung des Feedstocks, der Prozessführung sowie der Einbindung nachgeschalteter Verwertungsprozesse ab. Diese Zusammenhänge wurden bislang nur unzureichend untersucht. Ziel dieser Arbeit ist es daher, den Einfluss der Abfallzusammensetzung auf den Climate Change Impact des pyrolysebasierten chemischen Recyclings zu bewerten, den Einfluss der Zusammensetzung von Pyrolyseölen auf nachgeschaltete Konversionsprozesse zu untersuchen sowie das Potenzial des pyrolysebasierten chemischen Recyclings zur Verringerung des Climate Change Impacts gegenüber der energetischen Verwertung zu bewerten.

Hierzu werden Daten von Pyrolyseexperimenten aus der Literatur für definierte Modellfeedstocks und zwei unterschiedliche Reaktortechnologien mit der Prozessmodellierung nachgeschalteter Konversionspfade kombiniert, um konsistente Stoff- und Energiebilanzen sowie Life Cycle Inventories für die Ökobilanzierung zu erstellen. Die Umweltbewertung erfolgt anhand eines Life Cycle Assessments (LCA) für sieben repräsentative Feedstocks, die von reinen Polyolefinen bis hin zu heterogenen Post-Consumer-Kunststoffabfällen reichen. Untersucht werden zwei Prozessketten des chemischen Recyclings: die Pyrolyse mit anschließender Aufbereitung des Pyrolyseöls und Steamcracken zur Herstellung von Basischemikalien sowie die Pyrolyse mit nachgeschalteter Flugstromvergasung (Entrained-Flow Gasification, EFG) zur Erzeugung von Synthesegas für die Methanol- oder Oxosynthese.

Die Ergebnisse zeigen, dass die Zusammensetzung des Feedstocks die maßgebliche Einflussgröße auf den Climate Change Impact des pyrolysebasierten chemischen Recyclings ist. Heteroatomfreie Polymere wie Polyethylen, Polypropylen und Polystyrol erreichen hohe Pyrolyseölausbeuten und ermöglichen dadurch eine stärkere Reduktion des Climate Change Impacts infolge einer höheren Rückgewinnung an chemischen Produkten. Feedstocks, die Polymere wie Polyethylenterephthalat, Polyamid oder Polyvinylchlorid enthalten, weisen dagegen aufgrund einer geringeren Kohlenstoffrückgewinnung im Pyrolyseöl niedrigere Produktausbeuten auf.

Für alle untersuchten Feedstocks zeigt sich ein Zusammenhang zwischen dem Kohlenstoffgehalt des Feedstocks sowie der Pyrolyseölausbeute, der Kohlenstoffrecyclingrate und dem Climate Change Impact Reduction Potential. Dieses ist als Differenz des Net Climate Change Impacts der energetischen Verwertung und der jeweiligen Route des chemischen Recyclings definiert. Diese Korrelation verdeutlicht die zentrale Bedeutung der Kohlenstoffrückgewinnung in der Pyrolyse, welche die Feedstockzusammensetzung mit den Produktausbeuten der nachgeschalteten

Prozesse und letztlich mit dem Climate Change Impact verbindet. Entsprechend weisen heteroatomhaltige Feedstocks wie MPW aufgrund ihres geringeren Kohlenstoffgehalts ein niedrigeres Climate Change Impact Reduction Potential auf. Dennoch schneiden auch diese Feedstocks innerhalb der untersuchten Szenarien besser ab als die energetische Verwertung.

Die Pyrolyse verursacht den größten Anteil an den gesamten Process Burdens, da der in Pyrolysegas und Pyrolyserückständen enthaltene Kohlenstoff bei deren Behandlung als CO₂ freigesetzt wird. Eine möglichst hohe Kohlenstoffrückgewinnung durch eine geeignete Wahl von Feedstock und Reaktortechnologie ist daher der wichtigste Hebel zur Erhöhung des Climate Change Impact Reduction Potentials. Die verbleibenden Process Burdens lassen sich durch eine effiziente Nutzung der Pyrolyse Nebenprodukte weiter verringern, insbesondere durch die stoffliche Nutzung des Pyrolysegases in der Flugstromvergasung oder – in geringerem Umfang – durch dessen energetische Nutzung. Ein Flaring des Pyrolysegases sollte aufgrund des damit verbundenen hohen Climate Change Impacts vermieden werden.

Der Vergleich der nachgeschalteten Verwertungsprozesse zeigt, dass Steamcracken und Flugstromvergasung für die meisten Feedstocks hinsichtlich ihres Climate Change Impacts vergleichbare Ergebnisse erzielen. Obwohl die Zusammensetzung des Pyrolyseöls den zu bevorzugenden Verwertungspfad beeinflusst, haben Randbedingungen wie die Verfügbarkeit kohlenstoffarmen Wasserstoffs, Möglichkeiten zur Abwärmenutzung sowie insbesondere der substituierte Prozess zur Synthesegaserzeugung auf Basis von Schweröl oder Erdgas einen größeren Einfluss auf den resultierenden Climate Change Impact.

Der Vergleich unterschiedlicher Betrachtungsperspektiven innerhalb der Ökobilanz führt zunächst zu scheinbar widersprüchlichen Aussagen hinsichtlich der Umweltwirkung des pyrolysebasierten chemischen Recyclings. Während die inputbasierte Perspektive der Abfallwirtschaft durchgängig Vorteile gegenüber der energetischen Verwertung zeigt, ergeben sich aus der produktbasierten Perspektive lediglich Vorteile für heteroatomfreie Feedstocks mit hohen Pyrolyseölausbeuten. Dieser scheinbare Widerspruch lässt sich durch eine kombinierte, systemweite Betrachtung auflösen, durch welche sich die Unterschiede auf verschiedene Systemgrenzen und das zugrunde liegende Background System zurückführen lassen. Die Ergebnisse dieser kombinierten Betrachtung bestätigen die Vorteilhaftigkeit des pyrolysebasierten chemischen Recyclings gegenüber der energetischen Verwertung für alle analysierten Feedstocks. Gleichzeitig wird deutlich, dass die Umweltwirkung des pyrolysebasierten chemischen Recyclings nicht isoliert bewertet werden kann, sondern stets im Zusammenhang mit dem jeweiligen Abfallwirtschaftssystem und der chemischen Industrie betrachtet werden muss.

Insgesamt erweist sich die Kohlenstoffrückgewinnung in der Pyrolyse als die entscheidende Prozessgröße für den Climate Change Impact des pyrolysebasierten chemischen Recyclings. Sie wird in erster Linie durch die Feedstockzusammensetzung, die Reaktorauslegung und die Prozessintegration beeinflusst. Der tatsächliche Umweltnutzen hängt jedoch maßgeblich von der Integration in die Abfallwirtschaft und die chemische Industrie ab.

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Declaration on the use of AI tools

In the preparation of this dissertation, artificial intelligence (AI)-based tools were used solely as supportive instruments, in particular for linguistic revision, improving the clarity of selected text passages, and assisting in the identification of relevant scientific literature. The tools used include ChatGPT (OpenAI; used for text editing and literature review) and Perplexity (Perplexity AI; used for literature review).

I hereby declare that the conception of the research, the scientific reasoning, as well as the analysis and interpretation of the results were carried out independently by me. The aforementioned tools were used exclusively for language refinement and literature support and did not influence the scientific content, conclusions, or originality of this work. I, Malte Hennig, assume full responsibility for the content of this dissertation.

Karlsruhe, 23 September, 2026

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List of Abbreviations

Abbreviation	Meaning
ABS	Acrylonitrile butadiene styrene
AGO	Atmospheric gas oil
APW	Automotive plastic waste
ASR	Auger-type screw reactor
ASU	Air separation unit
BTX	Benzene, toluene, xylenes
CCI	Climate change impact
CCS	Carbon capture and storage
CF	Characterization factor
CGE	Cold gas efficiency
EFG	Entrained-flow gasification
ELV	End-of-life vehicle
EoL	End-of-life
EU	European Union
FCC	Fluid catalytic cracking
GHG	Greenhouse gas
HCR	Hydrocracker residue
HFO	Heavy fuel oil
IAM	Integrated assessment model
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LDPE	Low density polyethylene
LHV	Lower heating value
LPG	Liquefied petroleum gas
LWP	Lightweight packaging waste
MDI	Methylene diphenyl diisocyanate
MPW	Mixed plastic waste
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
NGL	Natural gas liquids
OECD	Organisation for Economic Cooperation and Development
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene terephthalate
PIONA	Paraffins, isoparaffins, olefins, naphthenes, aromatics
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl chloride
Pyr	Pyrolysis

RDF	Refuse-derived fuel
SAN	Styrene acrylonitrile
SC	Steam cracker
SimDist	Simulated distillation
SMR	Steam methane reforming
STR	Stirred-tank reactor
TDI	Toluene diisocyanate
TRL	Technology Readiness Level
VGO	Vacuum gas oil
WEEE	Waste electrical and electronic equipment
WGS	Water-gas shift

Nomenclature

Symbol	Unit	Meaning
a	kg/kg	Elemental mass fraction in pyrolysis gas
b	kg/kg	Mass fraction of gas species in pyrolysis gas
BF	depends on flow type	Biosphere flow
c	kg CO ₂ e/kg product	Product credit
$C-Eff$	-	Carbon recycling efficiency
$C-Yield$	-	Carbon yield
CCI	kg CO ₂ e/FU	Climate change impact per functional unit
e	kWh/kg	Specific electricity generation
HC	kmol/kmol	Hydrogen-to-carbon molar ratio
LHV	MJ/kg	Lower heating value
M	kg	Absolute mass
$\bar{M}$	kg/kmol	Molar mass
m	kg/kg	Specific mass flow
$\dot{m}$	kg/s	Mass flow
p	-	Product yield scaling factor
q	MJ/kg	Specific district heat generation
TF	depends on flow type	Technosphere flow
X	-	Carbon conversion efficiency
x	kg/kg	Mass fraction
y	kg/kg	Specific yield
z	-	Product credit scaling factor
α	-	Hydrogen utilization efficiency
η	-	Energy efficiency
ν	-	Stoichiometric coefficient

Indices

ash
C
c
Cl
CO₂
el
excess
Feedstock
fuel
gross
H
H₂
HC
HT
i
input
j
k
m
material
max
N
n
naphtha
net
O
Off-gas
product
Py.
Py. gas
Py. oil
r
Res.
S
SC
th
total
Upgr.
Upgr. oil
z

Meaning

Ash
Carbon
Credit
Elemental chlorine
Carbon dioxide
Electrical
Excess hydrogen in pyrolysis oil upgrading
Feedstock
Fuel use
Gross
Elemental hydrogen
Molecular hydrogen
Hydrocracking
Hydrotreating
Pyrolysis product
Input-based
Element
Steam cracker product
Index of technosphere flow
Material use
maximum
Elemental nitrogen
Index of biosphere flow
Naphtha
Net
Elemental oxygen
Off-gas from pyrolysis oil upgrading
Product-based
Pyrolysis
Pyrolysis gas
Pyrolysis oil
Waste treatment route
Pyrolysis residue
Sulfur
Steam cracker
thermal
Total
Pyrolysis oil upgrading
Upgraded pyrolysis oil
Gas species in pyrolysis gas

1 Introduction

Plastics have become indispensable in modern society. Their versatile material properties, durability, and high availability have enabled widespread use across a broad range of applications, from low-cost packaging to high-performance materials in aerospace and automotive engineering.¹ However, this extensive use comes with significant environmental consequences. Plastics contribute to the triple planetary crisis of pollution, biodiversity loss, and climate change, which increasingly affect both ecosystems and human well-being worldwide.^{2–4}

Substantial amounts of plastic waste remain untreated, leaking into the environment and accumulating in marine ecosystems.^{5,6} There, wildlife is harmed through ingestion and entanglement.⁷ Due to their persistence, most types of plastics do not biodegrade but fragment into smaller particles, forming microplastics. These have been detected even in remote regions such as Antarctica and have recently been found in the human bloodstream, likely entering via the digestive system.^{8,9}

A complete phase-out of plastics is neither feasible nor desirable.^{1,6} Instead, their use must become more sustainable, following the 5R framework: rethink, refuse, reduce, reuse, and recycle.^{10,11} Plastics should therefore be applied only where necessary and designed in a way that enables material recovery at the end of their use phase.¹² These measures are essential for establishing a circular economy and preventing environmental leakage.¹³

With regard to sustainability, Bachmann et al. identify recycling as a key strategy for operating the plastics industry within planetary boundaries, provided that production volumes do not continue to grow indefinitely.¹⁴ They estimate that at least 70% of all plastics produced must be made from recycled plastic waste. However, conventional mechanical recycling alone is insufficient to achieve the required recycling rate.^{14,15}

One major limitation arises from mixed plastic waste (MPW) as mechanical recycling requires relatively pure, single-polymer streams to produce high-quality recyclates capable of substituting virgin plastics.¹⁶ Mixed or contaminated waste streams, in contrast, lead to inferior material properties and are therefore often unsuitable for this pathway.¹⁶

Chemical recycling technologies have emerged as promising approaches to address these limitations by targeting plastic waste streams that are inaccessible to mechanical recycling either due to their material properties or their commingling with other non-plastic and plastic materials. These include thermochemical processes such as pyrolysis and gasification as well as depolymerization through solvolysis. In contrast to mechanical recycling, chemical recycling technologies convert waste plastics into chemicals or feedstock that can then be utilized for the production of new plastics, rather than preserving the intact polymer chain.^{17–19} Therefore, in combination with mechanical recycling, chemical recycling is expected to increase overall recycling rates by utilizing waste plastics that are incinerated today.^{14,15,20,21}

The pyrolysis process thermally degrades waste plastics in the absence of oxygen to produce pyrolysis oil.^{17,18} It is among the most technologically mature chemical recycling technologies and is regarded as a key thermochemical recycling route for mixed plastic waste.^{19,22} Although pyrolysis can process MPW, its performance is sensitive to feedstock composition. Contaminants such as chlorine from polyvinyl chloride (PVC) may transfer into the pyrolysis oil or reduce product yields.^{23,24} This poses challenges for both recycling efficiency and the downstream utilization of pyrolysis oils.

For example, direct use of pyrolysis oils in naphtha steam cracking for monomer production is restricted because they typically do not meet stringent feedstock specifications. Upgrading is therefore required to enable their integration into steam crackers.^{24,25} A possible alternative route is the conversion of pyrolysis oils into synthesis gas (syngas) via entrained-flow gasification (EFG), which is less sensitive to contaminants and generally does not require extensive upgrading.^{26,27} Compared to steam cracking, this pathway has received significantly less attention in the literature.

In addition to technological aspects, numerous life cycle assessment (LCA) studies have compared the environmental performance of pyrolysis and incineration with energy recovery. However, the influence of feedstock composition has not yet been systematically investigated.^{28–30} This represents a critical gap, as pyrolysis is specifically intended to process MPW, which exhibits high variability in composition. Similarly, with few exceptions, the effect of pyrolysis oil composition on downstream utilization pathways has rarely been analyzed in a consistent framework.^{26,31} A better understanding of these relationships is essential for assessing the potential of pyrolysis-based recycling to reduce the climate change impact of current waste management systems.

Against this background, this thesis addresses the following research questions:

- How does waste composition influence the climate change impact of pyrolysis-based chemical recycling?
- How does pyrolysis oil composition affect downstream utilization pathways, specifically steam cracking and entrained-flow gasification?
- To what extent can pyrolysis-based recycling of MPW reduce the climate change impact relative to waste incineration with energy recovery?

Due to the limited availability of industrial-scale data for defined feedstock compositions, this work combines experimental data from literature – based on well-defined model feedstocks and two different pyrolysis reactor systems – with process modeling of downstream conversion routes. This approach enables the generation of consistent mass and energy balances and the compilation of life cycle inventory (LCI) data for subsequent LCA. The environmental performance of pyrolysis-based chemical recycling is evaluated across seven model feedstocks, ranging from virgin polymers such as polyethylene (PE) and polypropylene (PP) to mixed post-consumer plastic waste containing multiple different end-of-life (EoL) polymers. Particular

emphasis is placed on process integration, including downstream utilization of pyrolysis oils and the utilization of by-products such as pyrolysis gas.

This thesis is structured as follows: Chapter 2 provides the theoretical background and summarizes the state of knowledge. Chapter 3 defines the methodology, including system boundaries as well as goal and scope of the study. Chapter 4 describes the modeling approaches used to generate mass and energy balances. Chapter 5 presents the resulting inventories and mass balances, which form the basis for the climate change impact assessment in Chapter 6, including a discussion of the implications of different perspectives in LCA. Chapter 7 presents sensitivities and scenario variations, analyzing the influence of energy systems and process integration strategies and discusses study limitations. Finally, Chapter 8 summarizes the key findings and outlines directions for future research.

2 Theoretical background

This chapter establishes the theoretical foundation for evaluating pyrolysis-based chemical recycling of MPW as a pathway toward a more circular and climate-neutral carbon economy. Section 2.1 outlines the role of plastics in the global economy and their associated environmental impacts across the life cycle, thereby motivating the need for improved EoL management strategies. Then, current waste management systems are examined (cf. Section 2.2), with particular emphasis on the limitations of the German waste management system. Section 2.3 introduces the pyrolysis of plastics, and summarizes the effects of feedstock composition and reaction conditions on pyrolysis products in detail. The utilization of pyrolysis oils in steam cracking and EFG is explored in Section 2.4, followed by the analysis of suitable feedstocks for pyrolysis-based chemical recycling (cf. Section 2.5). Finally, LCA is presented as the methodological framework used to evaluate the environmental performance of the processes analyzed in this work (cf. Section 2.6).

2.1 Life cycle emissions of plastics

The use of plastics causes environmental impacts across the entire life cycle – from the sourcing of raw materials and production of base chemicals (monomers), to polymerization, product formulation, use phase and final EoL treatment.³² The following sections summarize how each of these phases contributes to the carbon footprint of plastics.

2.1.1 Production of plastics

From a greenhouse gas (GHG) perspective, plastics production accounted for approximately 60% of total life-cycle emissions in 2015.³² However, the climate change impact varies significantly between different types of plastics.

In general, plastics can be categorized into three groups: thermoplastics, elastomers, and thermosets. While elastomers are primarily used in tires and other rubber products, thermosets – and especially thermoplastics – are applied across a much broader range of applications and account for the majority of global plastic production by volume (> 90%).^{6,33,34}

Within the thermoplastic and thermoset market, the most important thermoplastics are polyethylene (PE, 26.9%), polypropylene (PP, 19.3%), polyvinyl chloride (PVC, 12.9%), polyethylene terephthalate (PET, 6.2%), and polystyrene (PS, 5.3%). Other thermoplastics account for a further 7.1%. Among thermosets, polyurethane (PUR) represents 5.5%, while all remaining thermosets contribute another 5.5%. The remaining market share consists of recycled plastics (8.3%) and bio-based plastics (2.0%).³³ Due to differences in chemical composition and synthesis

pathways, the climate change impact of polymer production varies considerably, ranging from 1.95 kg CO₂e/kg polymer for PE to 4.90 kg CO₂e/kg polymer for PUR.³²

Despite the wide variety of plastics, most are derived – either directly or via intermediate synthesis steps – from a limited number of base chemicals, namely ethylene, propylene, butadiene, benzene, toluene, xylene, hydrogen, and carbon monoxide, as summarized in Table 1.³⁵ These substances are therefore often referred to as base chemicals.³⁶

Table 1: Overview of monomers and base chemicals used for the synthesis of the most important plastic types.

Plastic type	Monomer(s)	Base chemical precursors
PE	Ethylene (C ₂ H ₄)	Ethylene (C ₂ H ₄)
PP	Propylene (C ₃ H ₆)	Propylene (C ₃ H ₆)
PVC	Vinyl chloride (C ₂ H ₃ Cl)	Ethylene (C ₂ H ₄)
PET	Terephthalic acid Ethylene glycol	p-Xylene (C ₈ H ₁₀) Ethylene (C ₂ H ₄)
PS	Styrene (C ₈ H ₈)	Benzene (C ₆ H ₆) Ethylene (C ₂ H ₄)
Polyamide (PA)	ε-Caprolactam ^a	Benzene (C ₆ H ₆)
Polycarbonate (PC)	Bisphenol A Phosgene (COCl ₂)	Benzene (C ₆ H ₆) Carbon monoxide (CO)
Acrylonitrile butadiene styrene (ABS), Styrene acrylonitrile (SAN)	Styrene (C ₈ H ₈) Butadiene (C ₄ H ₆) Acrylonitrile (CH ₂ CHCN)	Styrene (C ₈ H ₈) Butadiene (C ₄ H ₆) Propylene (C ₃ H ₆) Ammonia (NH ₃)
PUR	Toluene diisocyanate (TDI) Methylene diphenyl diisocyanate (MDI) Polyol ^b	Toluene (C ₇ H ₈) Benzene (C ₆ H ₆) Hydrogen (H ₂) Carbon monoxide (CO)

The base chemicals are primarily produced from fossil resources, mainly crude oil and natural gas. They can be further classified into olefins (ethylene, propylene, butadiene) and aromatics (benzene, toluene, xylenes, collectively referred to as BTX). Hydrogen and carbon monoxide are used either individually or in mixtures of varying ratios, known as synthesis gas (syngas), depending on the specific application. Only a limited number of industrial processes are relevant for the production of these base chemicals. Steam cracking is the dominant process for olefin production. Aromatics are obtained either through extraction from the liquid product of steam cracking or are recovered as co-product during gasoline production via catalytic reforming.^{35,37} Syngas can be generated from a variety of feedstocks through different processes, such as steam-methane-reforming (SMR) of natural gas or partial oxidation of high-boiling residual oils such as vacuum gas oil (VGO) and even coal in an entrained-flow gasifier (EFG).^{38,39} Together,

^a Only PA6 is synthesized from caprolactam. Other polyamides as PA66 or PA612 are synthesized from different monomers.

^b PUR can be synthesized from different polyols which are almost always synthesized from one of the base chemicals

these processes form the backbone of the chemical industry and are fundamental to plastic production. At the same time, these processes are among the largest contributors to GHG emissions within the chemical industry.^{32,36}

2.1.2 Compounding and product formulation

In addition to polymer production, plastics are compounded with additives such as fillers, stabilizers, and fibers to tailor their properties for specific applications. Subsequently, they are processed into their final shapes through techniques such as injection molding, blow molding, and extrusion. These steps contribute significantly to the wide variety of different plastic products.⁴⁰

The compounding and product formulation stage accounts for 30% of the global climate change impact of plastics and varies between 0.81 kg CO₂e/kg polymer (PET) and 2.70 kg CO₂e / kg polymer (textile fibers based on polyesters, polyamides and acrylics).³² Despite its substantial contribution to the overall life cycle impact, compounding and product formulation are excluded from the scope of this work due to the vast diversity of plastic products and processing techniques.

2.1.3 End-of-life treatment

The EoL stage marks the final phase of a product's life cycle. For plastic products, EoL treatment accounts for 10% of the total GHG life cycle emissions based on current EoL practices.³² EoL treatment can be classified into five categories. Recycling, incineration, and landfilling represent controlled waste management options. In contrast, mismanaged waste – such as open dumping and incineration without emission control – and littering constitute uncontrolled forms of waste management or, effectively, the absence of proper EoL treatment.⁶

According to the OECD, 353 Mt of plastic waste were generated globally in 2019.⁶ Landfilling was the most common treatment method, accounting for approximately 46% of all plastic waste, while 17% was incinerated and 15% was collected for recycling. The remaining 22% was mismanaged or littered.⁶ Other studies show similar distributions among these treatment pathways.^{5,32} A significant portion of mismanaged plastic waste ultimately reaches the oceans, with estimated annual releases of 5 – 12 Mt.^{6,41}

The prevalence of different EoL treatment strategies varies globally and depends on several factors, including the availability of waste management infrastructure, economic constraints, the stringency of environmental regulations, and their enforcement.⁴² Leakage of plastic waste into the environment is particularly pronounced in emerging economies, which account for 18 of the 20 top polluting countries worldwide.^{6,41} However, countries with high per-capita plastic waste generation and dense coastal populations may also contribute substantially to marine pollution, even if their share of mismanaged plastic waste is comparatively low.⁴¹

In terms of GHG emissions, Zheng et al. showed that landfilling, including open dumping, produces the lowest GHG emissions among all waste treatment options, despite handling the largest share of plastic waste.³² Historically, landfilling and dumping have also been the dominant EoL treatment pathways: Of the 8300 Mt of plastics that have been produced until 2015, 4900 Mt are estimated to have been discarded (landfilled), 800 Mt were incinerated and only 600 Mt were recycled, while 2600 Mt are estimated to be in use today.⁵ Nevertheless, landfilling – even in regulated sanitary landfills – is widely considered unsustainable due to the potential release of toxic substances and microplastics through leaching, limited landfill capacities, and the loss of valuable materials.^{6,43–45}

Due to these shortcomings, several European Union (EU) member states, including Germany, the Netherlands, Belgium, Denmark, and Sweden, have banned the landfilling of combustible waste and implemented legislation mandating its recycling or recovery prior to disposal.⁴⁶ To guide waste management policy, best practices have been formalized in the waste hierarchy (cf. Figure 1), which prioritizes waste prevention as the most desirable option, followed by preparation for re-use, recycling, and recovery (including energy recovery). Disposal remains the least preferred option.⁴⁷

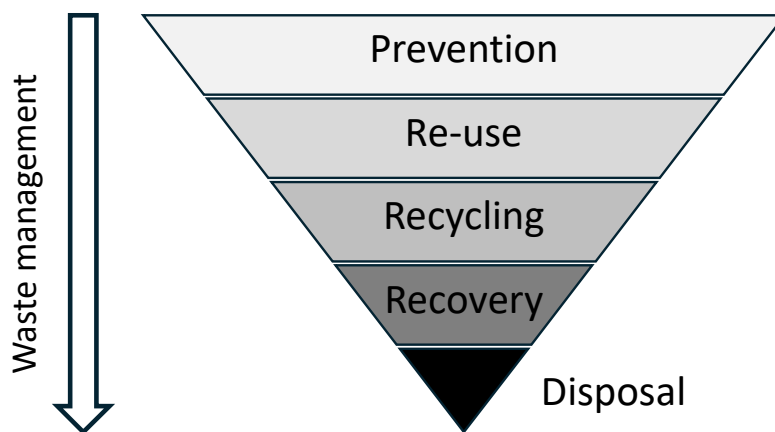


Figure 1: Waste hierarchy according to the EU Waste Framework Directive.⁴⁷

To further promote recycling and recovery, additional EU legislation reinforces these goals. The Waste Framework Directive mandates the separate collection of plastic waste; the Packaging and Packaging Waste Directive sets minimum recycling quotas for plastic and other packaging materials; and the Landfill Directive aims to largely phase out landfilling by 2035, unless already prohibited at the national level.^{47–49} Accordingly, the only waste treatment options remaining for the treatment of plastic waste in Europe and especially in Germany are recycling and incineration with energy recovery. However, a shift toward energy recovery as the predominant EoL option would lead to a significant increase in waste treatment-related GHG emissions due to the complete conversion of carbon contained in plastic waste to CO₂. Recycling therefore represents a key enabling technology for minimizing the climate change impact of waste treatment. In addition, recycling reduces the life cycle impact of plastics production by substituting production from primary, fossil resources.^{14,15,20}

2.2 Plastic waste management in Germany

In 2023, 6.3 Mt of plastic waste were treated within the German waste management sector.⁵⁰ Post-consumer waste accounted for 88% of the total plastic waste, while the remaining 12% originated from post-industrial waste and side products from plastics production and processing.^{50,51} Overall, 43% of plastic waste was recycled, 57% was directed to energy recovery, and less than 1% was disposed of via landfilling.⁵⁰

The majority of recycled plastics originates from separately collected waste fractions. These include lightweight packaging waste (LWP, 23%), PET bottle collection (12%), separately collected plastic packaging waste from industry and businesses (23%), and other dedicated collection schemes, e.g., for PVC window frames or agricultural films (5%), all of which fall under post-consumer waste. In addition, 27% of recycled plastics are derived from post-industrial waste and side products from plastics production and processing.

In contrast, plastic waste collected together with other waste streams – such as municipal solid waste (MSW) or mixed commercial waste – is significantly less likely to be recycled. Despite accounting for 48% of total waste plastics (post-consumer and post-industrial combined), these mixed fractions contribute only 10% to total recycled plastics.⁵⁰ This low recycling yield can be attributed to technical limitations and the greater effort required to generate clean waste fractions suitable for mechanical recycling from those types of waste.

Furthermore, recyclate quality from post-consumer plastic waste tends to fluctuate more strongly than that produced from post-industrial waste. As post-industrial waste is typically available as clean, well-sorted material, it enables the production of more consistent recyclates. This explains the substantially higher recycling rate of post-industrial waste (92%) compared to post-consumer waste (35%).^{50,52}

In line with EU legislation and its implementation into German law through the Kreislaufwirtschaftsgesetz (KrWG, engl. Waste Management Act), the Verpackungsgesetz (Verpackungsg, engl. Packaging Act), and the Gewerbeabfallverordnung (GewAbfV, engl. Commercial Waste Ordinance) waste must be treated according to the waste hierarchy, and certain waste streams – including plastics – must be collected separately.^{53–55} However, mixed waste fractions still arise when separate collection is not feasible due to technical or economic constraints.⁵⁵ For the recovery of plastics from these mixed waste fractions, dedicated sorting plants are required to separate plastics from other waste materials.^{56,57}

2.2.1 Sorting of plastic waste

The recovery of plastics from mixed waste streams is primarily driven by regulatory recycling targets and economic considerations.^{52,58} As requirements for recycling rates, sorting quotas, and waste composition vary across waste streams, different configurations of sorting facilities have evolved.⁵⁷

LWP represents the largest plastic-containing waste stream collected from private households, accounting for 20% of the overall plastic waste.⁵⁰ The waste composition depends on multiple factors including the collection scheme, and seasonality in addition to sociocultural factors affecting the quality of waste separation.⁵⁹ Sorting of LWP is regulated by recycling targets defined in the VerpackungsG, setting material-specific targets for different packaging materials. For plastics, a utilization rate of 90% must be met and a minimum of 70% must be treated targeting material recovery.⁵⁴

The sorting process for LWP comprises a sequence of mechanical and sensor-based separation steps, resulting in 16 to 20 sorting fractions, depending on the plant configurations.^{60–62} These fractions include:

- Plastics:
 - o Single plastics (PET, PE, PP, PS)
 - o Mixed plastics (films, mixed polyolefins (MPO), mixed rigid plastics, flexible plastics, black plastics, etc.)
- Metals:
 - o Ferrous metals
 - o Non-ferrous metals
- Paper and cardboard
- Liquid packaging cartons
- Sorting residues

Non-binding quality specifications for these fractions are defined by the dual system operator, such as “Der Grüne Punkt”. Acceptable contamination levels^c range from 2 wt.% for high-quality fractions (e.g., PET bottles) up to 30 wt.% for lower-quality fractions (e.g., rigid plastics quality grade 2).^{63,64} Single-polymer target fractions (e.g., PE, PP, PET, PS) are typically directed to mechanical recycling. In contrast, sorting residues are often processed into refuse-derived fuel (RDF) and subsequently utilized in energy recovery.^{61,65} Mixed plastic fractions may be partially recycled; however, this is frequently associated with reduced material quality, leading to downcycling. A substantial share of these fractions is therefore also directed to energy recovery.^{61,65,66} Although higher purities of sorted fractions are technically achievable, they are generally not realized due to limited economic incentives, the need for high throughputs, and a decline in overall material recovery at higher purity levels.^{61,62,64} As a result, sorting efficiencies for target polymers often remain well below 50%, with significant portions ending up in mixed plastic sorting fractions or sorting residues.^{61,64}

Mixed commercial waste contains a comparable share of waste plastics (21%) to LWP but contributes only 5% to total recycled plastics. Consequently, 89% of plastics in mixed commercial

^c Contaminants being materials other than the specified fraction, e.g., polymers other than the specified polymer for single polymer fractions or non-plastic materials as, e.g., glass or metal for mixed plastic fractions.

waste are incinerated. This is largely due to comparatively low recycling targets 30% across all material types and their limited enforcement in practice. In addition, economic constraints arising from the low quality of non-separately collected waste fractions lead sorting plants to prioritize the production of RDF over the maximization of recycling.^{52,67} As a result, only 11% of the input to commercial waste sorting plants is recycled. The recycled fraction consists primarily of metals (35%) and minerals or fines (31%), while plastics account for only 4%.⁶⁷

A significant share of plastic waste is not collected separately for recycling and remains embedded in MSW streams, which are typically directed to energy recovery.⁵⁰ Furthermore, plastics contained in complex product streams such as waste electrical and electronic equipment (WEEE) and end-of-life vehicles (ELVs) are subject to substantial technical and structural barriers to recycling, including heterogeneous material compositions, contamination, and insufficient collection and sorting efficiencies.⁶⁸ As a result, only a limited fraction of these plastics is currently recycled, while the majority remains unavailable for high-quality recycling within existing waste management systems.

2.2.2 Energy recovery

Overall, 3.6 Mt of plastic waste were incinerated across all types of thermal waste treatment plants in Germany.⁵⁰ The largest share, 2.3 Mt, was treated in municipal solid waste incineration (MSWI) plants, while 1.4 Mt were incinerated as part of RDF in the cement industry or in dedicated RDF power plants.⁵⁰ Consequently, the incineration of plastic waste in MSWI plants alone resulted in emissions of approximately 9 Mt of fossil-based CO₂.⁶⁹

The majority of German MSWI plants operate as combined heat and power plants, producing both electricity and district heat, thereby enabling energy recovery from waste. The average net electrical efficiency is 14.3%, while the net thermal efficiency reaches 39.1%.⁶⁹ Across all waste types, MSWI and RDF power plants in Germany generated 10.35 TWh of electricity, 13.39 TWh of process steam, and 11.18 TWh of district heat. This corresponds to 3.2% of Germany's net electricity production and 18.2% of net heat generation in 2022.^{69,70}

MSWI and RDF power plants are largely based on similar technologies, with grate incineration being the dominant process.^{69,71} Accordingly, this work focuses on grate-based MSWI systems. A typical plant consists of several process units, as illustrated in Figure 2.

Waste is delivered to the plant and stored in a bunker, where it is homogenized through mixing. Using an overhead crane system, which also serves for mixing, the waste is fed onto the grate in the combustion chamber.⁷¹ There, it is mixed with air and incinerated. At the end of the grate, the remaining bottom ash (slag) is discharged.⁷¹ The mineral fraction can be utilized as secondary construction material in road or landfill construction or is landfilled, while metals are recovered for recycling.^{71,72}

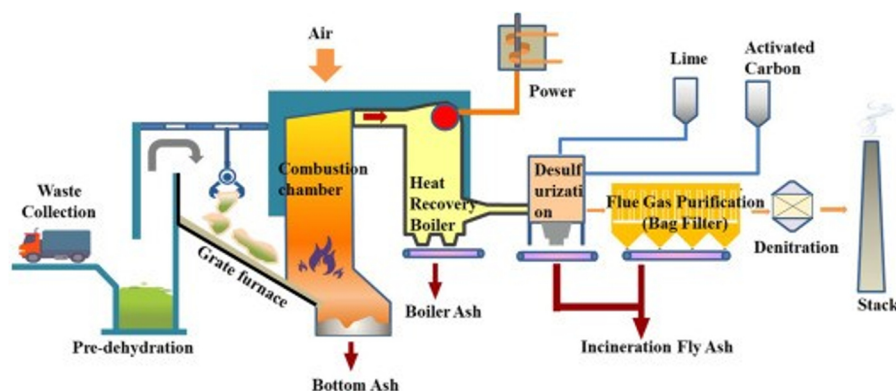


Figure 2: Process scheme of an MSWI plant. Reprinted from Tong and Qing with permission from Elsevier.⁷³

After heat recovery in the boiler, the cooled flue gas is directed to flue gas cleaning for the removal of pollutants, such as sulfur oxides, nitrogen oxides, and particulate matter.⁷¹ Strict emission limits for hazardous substances, including dioxins and heavy metals, have led to the implementation of a wide range of technologies for emission control.⁷¹ Nevertheless, CO₂ from the incineration of waste plastics and other carbonaceous materials is released to the atmosphere, as carbon capture and storage (CCS) technologies for removal of CO₂ from flue gas are not yet established at scale.^{74,75}

2.2.3 Mechanical recycling

Mechanical recycling reprocesses the suitable sorting fractions of LWP into regranulates that can substitute virgin plastic materials. As the process involves remelting, it is limited to thermoplastic polymers, primarily PET, PE, PP, and PS.⁷⁶

The production of high-quality recyclates requires a high-purity input material, i.e., feedstock largely free from non-polymer substances and cross-polymer contamination.⁷⁶ Post-industrial waste can typically be collected as clean, single-polymer fractions without contaminations from the use-phase. Consequently, it can be recycled more efficiently and yields higher-quality recyclates compared to post-consumer waste.^{16,50,52} In contrast, post-consumer waste pre-concentrates obtained from sorting mixed waste streams (cf. Section 2.2.1) require further processing to reduce contaminant levels.^{77,78} This is achieved through a series of treatment steps, including size reduction, washing, drying, sink-float separation, and melt filtration during final extrusion to produce regranulates.^{16,76,77,79}

However, recyclates from mechanical recycling generally exhibit inferior mechanical properties compared to virgin materials.⁷⁹ This deterioration results from polymer degradation during the product's lifetime (e.g., exposure to heat, oxidation, light, mechanical stress) as well as thermo-mechanical degradation during the recycling process itself.¹⁶ Both mechanisms alter the polymer structure, affecting the mechanical and rheological properties.^{16,79} In addition, residual contaminants can further reduce material quality. Due to immiscibility, even polymer impurities are

problematic, as most polymer mixtures form heterogeneous polymer blends rather than homogeneous single-phase systems.^{16,79}

To improve recyclate performance, a wide range of additives is employed, including compatibilizers, stabilizers, chain extenders, fillers, and fibres.^{16,79} In addition, recyclates are often blended with virgin materials to partially substitute primary plastics while maintaining desired mechanical properties.⁷⁹

Beyond single-polymer recycling, mechanical recycling of MPO from the float fraction of sink-float separation is also practiced.^{16,79} While recycling these fractions requires less intensive feedstock preparation and is therefore more cost-effective, the resulting recyclates exhibit limited mechanical performance and are unsuitable for demanding applications in terms of mechanical strength.^{16,79} Consequently, such recyclates are primarily used as substitutes for wood or concrete in applications including outdoor furniture, decking, or gutters.^{16,50}

Overall, it is estimated that 1.8 Mt of recyclates are suitable for substitution of virgin plastics, of which 51% originate from post-industrial waste and 49% from post-consumer waste. An additional 0.7 Mt of recyclates – entirely derived from post-consumer plastic waste – substitute other materials, resulting in an overall recycling rate of 38.4% in 2023.⁵¹

2.2.4 Chemical recycling

Chemical recycling technologies are in development to target plastic waste fractions that are not suitable for mechanical recycling.²³ Accordingly, they are discussed as an additional pathway to increase recycling rates by redirecting plastic waste that is currently treated via energy recovery. In this context, mixed plastic fractions originating from waste sorting are of particular interest (cf. Section 2.4).

Chemical recycling encompasses all processes that recover value from plastic waste by breaking down polymer chains into molecular fragments that can serve as feedstock for the chemical industry.⁷⁶ While numerous specialized processes exist, chemical recycling can broadly be divided into two main categories: solvolysis and thermochemical processes.^{76,77,80,81} Compared to mechanical recycling, these technologies exhibit lower technology readiness levels (TRL) and have not yet been widely established at industrial scale.^{19,21,82} Accordingly, in 2023, only 7 kt of plastic waste were treated via chemical recycling in Germany.⁵⁰

2.2.4.1 Solvolysis

Solvolysis processes use chemical reagents such as water, methanol or glycols to depolymerize condensation polymers.^{77,82} For example, the hydrolysis of PET reverses the condensation reaction, yielding terephthalic acid and ethylene glycol under elevated temperature and pressure.^{77,83}

Solvolysis is polymer-specific, and reaction conditions depend on the polymer, reagent, catalysts, and desired products.^{81,82} Therefore, solvolysis is best suited to waste streams containing high shares of the target polymer and is less suitable for MPW.^{82,84}

Solvent-based dissolution processes, although frequently associated with chemical recycling, are more accurately classified as physical recycling, as the polymer chains remain intact.⁷⁷ Dissolution relies on polymer solubility rather than chemical reactivity and is applicable to a wide range of polymers, including polyolefins.^{80,81,85} Like solvolysis, dissolution requires well-sorted waste streams, as solvent selection depends on both the target polymer and the presence of contaminants.⁸⁵ For this reason, solvolysis and dissolution are not considered further in the context of this thesis.

2.2.4.2 Thermochemical recycling processes

Thermochemical recycling processes break down the polymer structure through the application of heat. Two main process categories are distinguished: pyrolysis and gasification.^{17,80,81} Pyrolysis involves decomposition of plastics in the absence of oxygen, whereas gasification operates under sub-stoichiometric conditions, resulting in partial oxidation of the feedstock.⁸⁶ Both process types have been extensively researched in the past; however, their large-scale commercialization was primarily limited to energy recovery applications.⁸⁷

With increasing attention to environmental concerns, particularly GHG emissions, pyrolysis and gasification have regained interest due to their ability to process complex waste streams, including MPW. A growing number of industrial projects have been implemented or announced in recent years, with the majority focusing on pyrolysis for the treatment of MPW.^{82,88–90}

In contrast to direct gasification of MPW, pyrolysis produces liquid intermediates (pyrolysis oils) that can be more readily integrated into existing petrochemical infrastructure. These intermediates enable the production of key base chemicals such as light olefins, aromatics, and syngas – either via steam cracking or via EFG.

Hence, this thesis focuses on pyrolysis as the primary waste conversion technology, while gasification is considered in the context of downstream utilization of pyrolysis products. However, despite its ability to process MPW, the performance of pyrolysis-based processes – and the subsequent utilization of their products – is sensitive to waste composition and reaction conditions.^{91–93} Accordingly, the following sections outline the governing principles of pyrolysis (cf. Section 2.3) and the integration of pyrolysis oils into existing petrochemical processes (cf. Section 2.4).

2.3 Pyrolysis of plastics

In pyrolysis processes, polymeric materials such as plastics (synthetic polymers) or biomass (natural polymers) are thermally decomposed in the absence of oxygen.^{17,86} During this process, polymer chains break down into smaller molecular fragments, leading to the formation of a wide range of primary and secondary pyrolysis products.^{91–93}

Three main product fractions can be distinguished: pyrolysis condensates, pyrolysis gas and pyrolysis residue.⁸⁶ Pyrolysis condensates comprise all products that are liquid at room temperature as well as wax-like substances that melt upon heating, commonly referred to as pyrolysis waxes.¹⁷ Both aqueous and non-aqueous condensates may form, although non-aqueous fractions dominate in plastic pyrolysis. Aqueous condensate typically occurs as minor by-product, depending on feedstock composition and moisture content.⁹⁴

Pyrolysis gas refers to the fraction that remains non-condensable at room temperature.⁸⁶ It mainly consists of light hydrocarbons such as methane, ethane, ethylene, propane, propylene, as well as permanent gases (CO₂, CO, H₂) and water vapor.^{17,94}

The pyrolysis residue contains three main components: minerals, metals and carbonaceous material.^{94,95} The mineral fraction originates from inorganic fillers within the plastic or from external contaminants adhering to the waste.^{86,94} Metals present in the pyrolysis residue follow the same origin. The carbonaceous fraction, in contrast, is formed during pyrolysis and consists primarily of char rich in elemental carbon.^{86,95} In addition, carbon used as pigment in plastics may contribute to this fraction.^{95,96}

The detailed composition and distribution of pyrolysis products depend strongly on reaction conditions and feedstock composition, and therefore vary with the characteristics of MPW.^{17,86,94} Sections 2.3.1 provides an overview of the reaction mechanisms of different plastics, followed by a discussion of the influence of reaction conditions and feedstock composition on pyrolysis products in Section 2.3.2.

2.3.1 Reaction mechanisms

In general, two types of pyrolysis processes can be distinguished. Thermal pyrolysis relies solely on polymer degradation driven by thermal energy, whereas catalytic pyrolysis additionally employs catalysts to control the conversion process and influence product distribution.^{17,18,95} Catalytic approaches are widely applied in the conversion of polyolefinic plastic waste.⁹⁷ However, in the case of MPW, catalysts are prone to deactivation and poisoning, for example by chlorine or nitrogen present in the feedstock.^{16,97} For this reason, this thesis focuses exclusively on thermal pyrolysis.

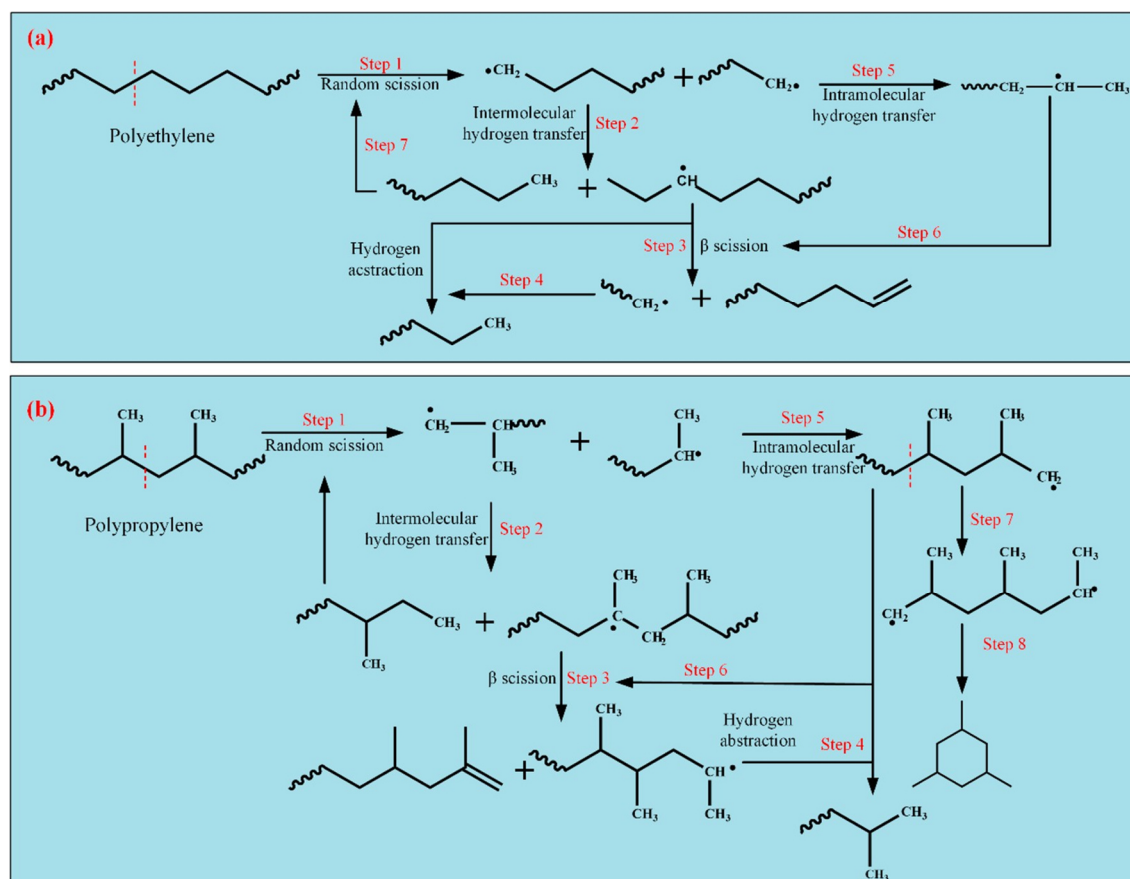


Figure 3: Primary degradation reaction mechanisms of PE (a) and PP (b). Reprinted with permission from Zhang et al.⁹⁸ Copyright 2022, American Chemical Society.

Reaction mechanisms in thermal pyrolysis vary significantly depending on the polymer type. PE, which has a simple molecular structure, undergoes random chain scission, as the carbon-carbon bonds in the polymer backbone are chemically similar and no substituents are present.⁹⁸ This results in the formation of linear hydrocarbon radicals of stochastic length, which undergo further reactions to yield linear alkanes and alkenes as primary products (cf. Figure 3).⁹⁸

The degradation of PP generally follows a similar initial pathway, also involving random chain scission.^{98,99} However, the presence of methyl groups on every second carbon atom of the carbon backbone stabilizes tertiary radicals relative to secondary radicals. As a result, the formation of propene oligomers, e.g., C₆ (dimer), C₉ (trimer), and C₁₂ hydrocarbons, is favored over products with other chain lengths.^{99,100} Consequently, primary pyrolysis products of PP mainly consist of iso-alkanes and -alkenes with characteristic chain lengths.^{99,100}

For PS, this tendency is even more pronounced.⁹⁹ Similar to PP, every second carbon atom of the backbone is substituted, but in this case with a phenyl group. Due to greater steric hindrance of the phenyl group, depolymerization reactions are favored, leading predominantly to styrene monomers and their oligomers. As a result, the product spectrum is dominated by aromatic compounds.¹⁰¹ PS is therefore one of the few polymers for which pyrolysis effectively reverses the polymerization reaction.⁸⁶

In contrast to PE, PP, and PS, the initial degradation step of PVC does not involve cleavage of the carbon backbone. Instead, thermal degradation begins with the release of hydrogen chloride (HCl) at temperatures below 320 °C, forming conjugated double bonds along the carbon backbone.^{102–104} Once dehydrochlorination has progressed, radical chain reactions break down the carbon backbone, forming polyene-like fragments.^{102,104} These intermediates undergo further cyclization and aromatization reactions, ultimately forming polyaromatic structures and char.^{103,104} As a consequence, the pyrolysis products of PVC differ substantially from the original polymer structure.

For polymers containing heteroatoms such as oxygen (O) or nitrogen (N) within the backbone, reaction pathways become more complex. In addition to C-C bond scission, cleavage of C-O and C-N bonds occurs, and the number of possible reaction pathways increases with the presence of additional functional groups within the polymer structure.^{84,105,106}

In polymer mixtures, interactions between degradation pathways can further influence product formation. Netsch et al. reported that mixtures of PE, PP, PS, and ABS exhibit largely additive behavior, indicating minimal interaction effects. In contrast, mixtures containing PET and PA6 show significant interactions, particularly when combined with aromatic-ring containing polymers such as PS and ABS.⁹³ In these mixtures, PVC further promotes char formation.⁹³ Accordingly, complex mixtures containing all of the analyzed polymers did not exhibit additive behavior due to these interactions, preventing the use of superposition to predict pyrolysis product yields.⁹³

Secondary reactions of primary products introduce an additional level of complexity, further influencing the final product distribution.¹⁰⁶ As a result, the pyrolysis of MPW represents a highly complex system that depends on multiple interacting variables.

2.3.2 Effects of feedstock and process conditions

The distribution and composition of pyrolysis products are governed by feedstock composition, reaction conditions, reactor design, and their interactions.^{17,18} Although a wide range of modeling approaches exists for specific systems and operating conditions, no universally applicable model is currently available that simultaneously accounts for these factors to reliably predict product yields and compositions.^{107,108} Nevertheless, general trends can be derived from extensive experimental studies.

Besides feedstock composition and the associated reaction mechanisms (cf. Section 2.3.1), reaction temperature is a key process parameter.¹⁷ Higher temperatures accelerate reaction kinetics and promote bond cleavage, shifting the pyrolysis product distribution toward lighter hydrocarbons and increasing pyrolysis gas yields.^{17,109,110} At the same time, cyclization and dehydrogenation reactions are enhanced, leading to higher aromatic content in the liquid products.^{109,110} As aromatic hydrocarbons can undergo secondary condensation reactions to

form polycyclic aromatic hydrocarbons, which act as precursors for coke formation, high temperatures also favor the formation of carbonaceous residue.^{17,110}

Primary reactions occur predominantly in the molten polymer phase, whereas secondary reactions take place after volatilization and are therefore governed by gas-phase conditions.¹⁸ Gas residence time is thus an important parameter influencing product composition.^{17,18} Longer gas residence times promote secondary cracking reactions, increasing the fraction of lighter hydrocarbons and facilitating isomerization.¹⁷ Parameters such as feedstock feeding rate, reactor volume, gas-phase mixing behavior, and the use of carrier or flush gases determine gas-phase residence time and therefore represent key design variables.¹⁸

The design of plastic pyrolysis reactors involves balancing multiple, partly conflicting requirements. Reactors must provide sufficient control over reaction conditions, enable high throughput, and remain robust toward variations in feedstock composition and the presence of contaminants. As a result, a variety of reactor concepts has been developed.¹⁶

Rotary kilns, stirred-tank reactors (STR), and auger-type screw reactors (ASR) are generally robust with respect to feedstock variability.^{18,19} However, they offer limited control over gas-phase residence time and product removal and they face challenges related to heat transfer and heat supply for the endothermic pyrolysis process.¹¹¹ The use of heat carriers such as quartz sand can improve heat transfer in ASR and STR systems, although overall scalability remains limited.⁹⁴

Fluidized-bed reactors, by contrast, provide excellent heat and mass transfer due to intense mixing and enable operation at high throughputs. Their application to plastic waste is limited by feedstock heterogeneity and the melting behavior of plastics, which can lead to particle agglomeration and defluidization, thereby affecting operational stability.^{16–18}

Liquid-phase processes, often referred to as liquefaction, involve pyrolysis in a hot hydrocarbon medium, which ensures efficient heat transfer.¹⁹ These systems typically use recycle loops, which limit control of residence time. Despite these differences, several reactor concepts have reached industrial relevance, and it remains unclear which design will prove most suitable for large-scale deployment under realistic waste conditions.⁸²

The relative importance of feedstock composition and reactor effects under comparable conditions is not yet fully understood, as systematic comparative studies are limited. Netsch et al. addressed this gap by investigating the interplay between feedstock composition and reactor behavior.^{91–93,112} To ensure comparability, experiments were carried out in both ASR and an STR systems using identical feedstocks and reactor set temperatures. As this thesis builds on these data, their results are discussed in more detail.

Netsch et al. investigated seven model feedstocks, including three virgin single polymers (LDPE, PP, and PS) and four mixtures of these polymers with varying amounts of heteroatom-containing plastics such as PET, PA, and PVC. These feedstocks represent compositions typical of plastic

packaging waste (cf. Section 2.5). The first mixture consisted of LDPE, PP, and PS (Mix AR^d) and yielded predominantly aromatic a pyrolysis oil. Two additional mixtures included heteroatom-containing polymers at medium (Mix MH^e) and high (Mix HH^f) concentrations. A final feedstock, a synthetic mixture of post-consumer plastics (S-PCW), was used to approximate real waste streams, as the other feedstocks consisted of virgin polymers. Detailed compositions are provided in Appendix A.

Figure 4 compares product yields obtained in STR and ASR systems for equal reactor set temperatures. Differences are most pronounced for LDPE, PP, and Mix AR.⁹¹ The higher pyrolysis oil yields observed in the STR fall within typical ranges reported in the literature, whereas ASR yields are comparatively lower.^{17,24} These differences are due to variations in heating rate and gas residence time. In the ASR system, longer gas-phase residence time promotes secondary cracking, resulting in higher gas yields and lower pyrolysis oil yields.¹⁸ For PS, this effect is less pronounced due to its inherently higher liquid yield arising from its depolymerization mechanism (cf. Section 2.3.1).

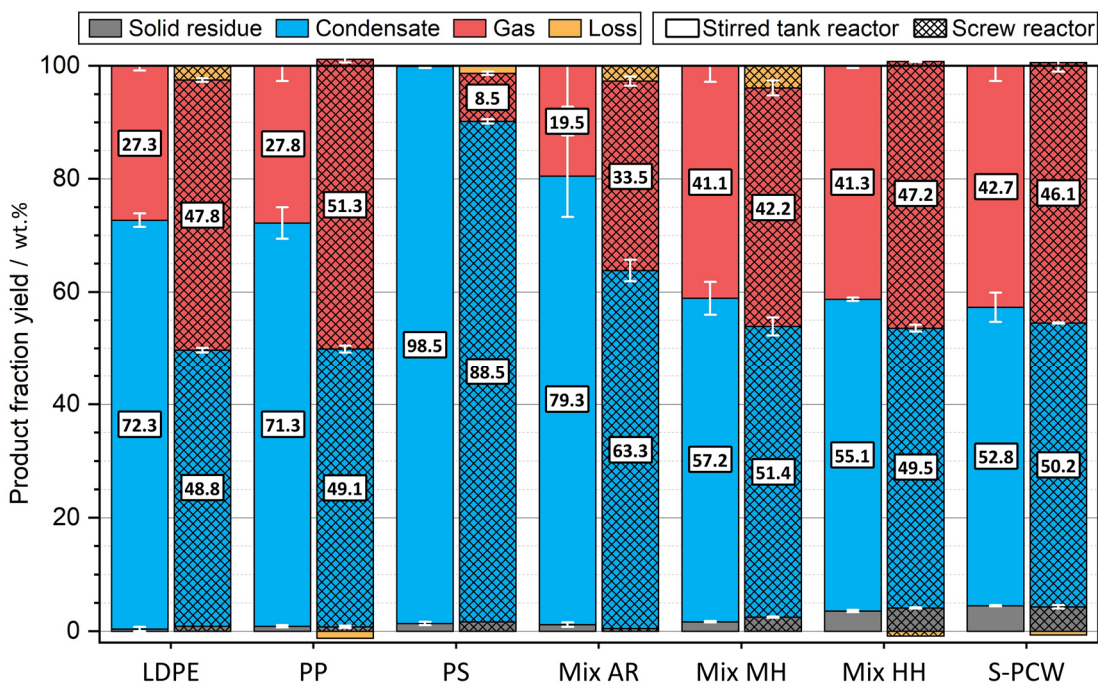


Figure 4: Comparison of product yields obtained with the STR and ASR experimental setups for identical feedstocks and reactor set temperatures. Reprinted from Netsch et al.⁹¹, used under CC-BY 4.0 license.

For mixtures containing heteroatom-bearing polymers (Mix MH, Mix HH, S-PCW), reactor effects are less pronounced, leading to similar pyrolysis oil yields in both systems. However, these yields

^d **AR**: Feedstock mixture designed to produce an **AR**omatic-rich pyrolysis oil.

^e **MH**: Feedstock mixture with **M**edium level of **H**eteroatom-containing polymers.

^f **HH**: Feedstock mixture with **H**igh level of **H**eteroatom-containing polymers.

are lower than expected based on superposition of single-polymer behavior. This deviation is attributed to interactions between degradation pathways, which alter product distribution and composition. Similar trends have been reported in other studies on mixed plastic feedstocks.^{93,110,113}

Product composition is more strongly influenced by feedstock composition than by reactor design. Elemental analysis of pyrolysis oils reveals clear differences between feedstocks (cf. Figure 5). Pyrolysis of LDPE and PP yield liquid hydrocarbons containing only carbon and hydrogen, with H/C ratios close to 2. PS and Mix AR also consist of C and H but exhibit lower H/C ratios of approximately 1.1 and 1.6, respectively.

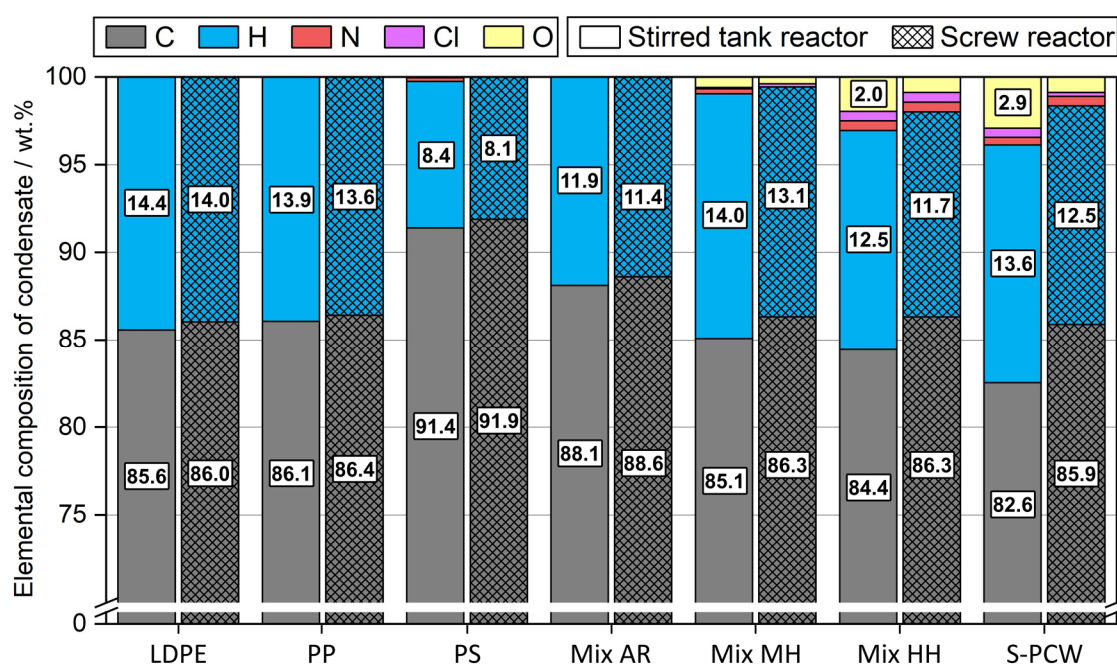


Figure 5: Pyrolysis oil composition of model feedstocks obtained with the ASR and STR experimental setups. Reprinted from Netsch et al.⁹¹, used under CC-BY 4.0 license.

Oils derived from heteroatom-containing feedstocks show a broader H/C range (1.6 – 2.0) and contain oxygen (up to 3%), nitrogen (up to 0.6%), and chlorine (up to 0.6%). Comparable ranges have been reported in the literature, although exact compositions depend on feedstock and operating conditions.^{24,114,115}

Simulated distillation (SimDist) analysis reveals that all pyrolysis oils exhibit broad boiling ranges between approximately 50 °C and 650 °C (cf. Figure 6). Nevertheless, distinct differences between feedstocks are apparent. LDPE tends to form wax-like products, whereas PP produces lighter hydrocarbons, resulting in a lower boiling curve.⁹⁸ PS shows a step-like boiling curve profile due to its depolymerization into styrene monomers and oligomers. The effects of reactor type are also evident: oils from ASR are generally lighter than those from STR, reflecting enhanced secondary cracking. Ultimately, feedstock composition remains the dominant factor shaping boiling point distributions.

Differences between feedstocks are also observed regarding the PIONA composition, i.e., the molecular composition in terms of paraffins, isoparaffins, olefins, naphthenes, and aromatics. GC $\times$ GC chromatograms displayed in Figure 7 show that LDPE and PP pyrolysis oils are dominated by aliphatic hydrocarbons, while PS yields predominantly aromatic compounds, following their respective degradation mechanisms. Oils derived from mixed plastics feedstocks, such as S-PCW, exhibit a combination of these features along with heteroatom-containing compounds, resulting in significantly higher compositional complexity.

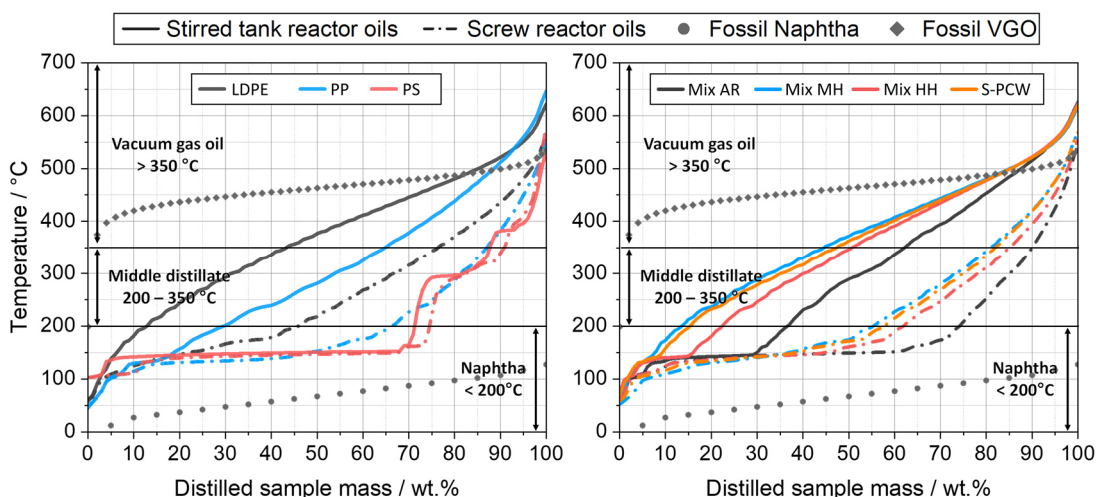


Figure 6: Boiling point distributions of pyrolysis oils from model feedstocks obtained with the ASR and STR experimental setups. Reprinted from Netsch et al.⁹¹, used under CC-BY 4.0 license.

In real waste streams, additional components further increase system complexity. Biomass fractions produce oxygenated compounds that may interact with plastic-derived intermediates.¹⁸ Inorganic constituents such as metals and minerals can exhibit catalytic activity, altering reaction pathways and product distributions.¹⁷ They may also act as sorbents, capturing volatile species such as chlorine and reducing their transfer into the liquid phase.^{16,116}

In summary, pyrolysis product distribution and composition are determined by the interplay of feedstock composition, reaction conditions, and reactor design. While general trends – such as the influence of temperature and residence time – are well established, feedstock-specific interactions play a critical role, particularly in mixed plastic systems. The presence of heteroatom-containing polymers introduces additional complexity, affecting both product yields and chemical composition. Pyrolysis oils should therefore be regarded as highly variable intermediates, whose properties depend strongly on process conditions and feedstock composition, with direct implications for downstream utilization.

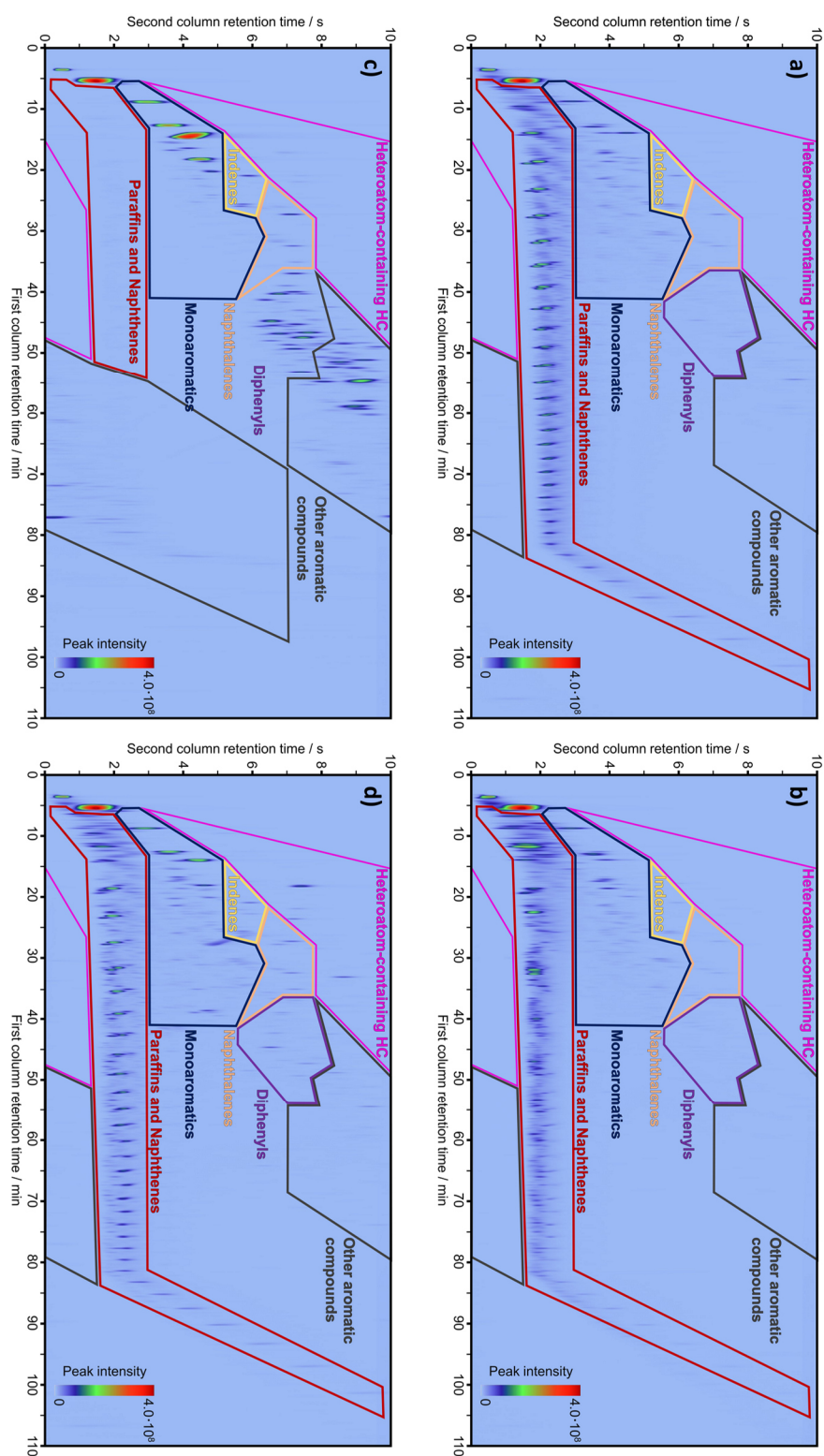


Figure 7: PIONA analysis of pyrolysis oils from model feedstocks obtained with the STR system for LDPE (a), PP (b), PS (c), and S-PCW (d) using GC x GC. Adapted from Netsch et al.⁹², used under CC-BY 4.0 license.

2.4 Processes for pyrolysis oil utilization

The large-scale implementation of chemical recycling requires the integration of pyrolysis processes into existing chemical industry infrastructure.^{16,23,117} Although the range of products in organic chemistry is vast, most synthesis routes are based on a limited set of fundamental base chemicals, including carbon monoxide, hydrogen, light olefins (ethylene, propylene, butenes, and butadiene), and aromatic compounds (benzene, toluene, and xylenes, cf. Section 2.1.1). These base chemicals are produced through a small number of large-scale industrial processes. Hydrogen is primarily generated via steam reforming of natural gas, while carbon monoxide is obtained from the partial oxidation of hydrocarbons including natural gas, heavy fuel oil, and coal. Olefins are mainly produced through steam cracking, whereas aromatics are derived from processes such as steam cracking, fluid catalytic cracking (FCC), and catalytic reforming.^{37,38,118}

The integration of plastic pyrolysis oils into refinery complexes is generally considered feasible.¹¹⁹ As a large share of the refinery's product slate consists of fuels rather than product streams intended for material use, the utilization of pyrolysis oils in this context would most likely be regarded as a form of energy recovery rather than recycling.^{119,120} Accordingly, this route is outside the scope of this thesis.

The direct recovery of value-added products from plastic pyrolysis oils – especially those derived from MPW – is economically not feasible due to their complex and heterogeneous composition. An exception is provided by polymers that undergo depolymerization during pyrolysis, such as polystyrene, which may allow direct monomer recovery.^{121,122} In most cases, further processing within established industrial pathways is required.

Integrating pyrolysis oils as alternative feedstocks into established processes such as steam cracking or gasification, enables the use of existing industrial assets and reduces the need for entirely new process chains.^{23,117,119} This approach facilitates the substitution of fossil feedstocks while leveraging the current chemical industry landscape, thereby contributing to closing the carbon cycle.

Among the available options, steam cracking and partial oxidation are particularly relevant, as they represent the principal industrial routes for producing olefins and synthesis gas, respectively. In steam crackers, pyrolysis oil can substitute conventional naphtha, enabling the production of light olefins as key monomers for virgin plastics. Likewise, replacing heavy hydrocarbon feedstocks in EFG provides a suitable pathway for converting pyrolysis oils into syngas, which serves as a flexible intermediate for the production of a wide range of base and specialty chemicals.¹²³

By contrast, processes such as catalytic reforming and FCC are primarily operated for fuel production, with the generation of base chemicals occurring only as a secondary objective under standard operating conditions.³⁷ Accordingly, this thesis focuses on the utilization of pyrolysis oils in steam cracking and partial oxidation via EFG.

2.4.1 Steam cracking

Steam cracking is the most important industrial process for the production of light olefins, in particular ethylene and propylene, which serve as the monomers for the two most widely produced polymers PE and PP.¹²⁴ Large-scale installations reach ethylene production capacities exceeding 1.5 Mt per year.^{118,125} Similar to pyrolysis, steam cracking proceeds via radical chain reactions and operates at temperature of approximately 800 °C.¹¹⁸

The hydrocarbon feedstock is first vaporized and diluted with steam before passing through fired reactor coils, where thermal cracking produces a complex mixture of light olefins, aromatic compounds, and heavier hydrocarbons (cf. Figure 8). Rapid quenching suppresses secondary reactions, after which the condensed liquid phase is separated into pyrolysis gasoline – used for the recovery of BTX aromatics – and pyrolysis fuel oil. The remaining gaseous stream is processed through a series of cryogenic distillation steps. Ethylene, propylene, butenes, and butadienes are recovered in dedicated C2, C3 and C4 splitting columns, while remaining gas components are recycled. Hydrogen and methane from the demethanizer are typically used as fuel gas, supplying the process heat required for steam cracking.^{118,126}

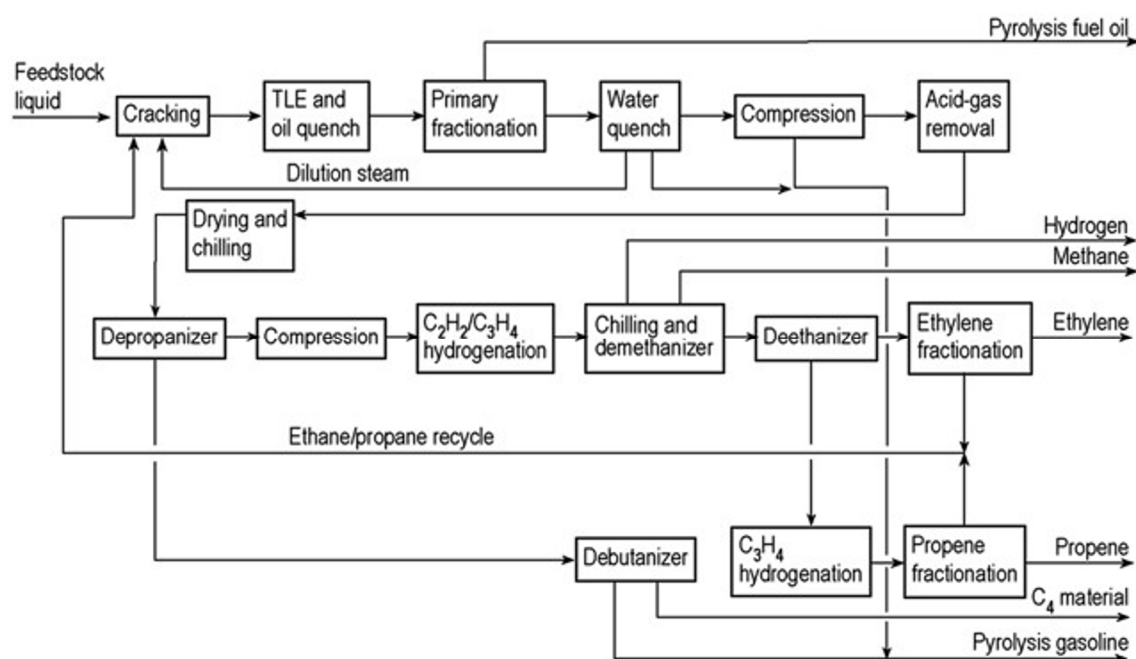


Figure 8: Process scheme of naphtha steam cracking for the production of light olefins and aromatics. Reprinted with permission from Zimmermann and Walzl.¹¹⁸ Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA.

A wide range of hydrocarbon feedstocks can be processed in steam crackers, including ethane, liquefied petroleum gas (LPG), natural gas liquids (NGL), naphtha, and gasoil. Product yields and distributions depend strongly on feedstock composition, and steam crackers are therefore optimized for specific feedstocks or feedstock ranges, depending on regional availability and economic considerations.¹²⁴ In the United States and the Middle East, lighter feedstocks such as

ethane and NGL dominate, whereas European steam crackers – particularly in Germany – primarily operate on naphtha.¹²⁴

Steam cracker operation requires strict feedstock specifications. Contaminants such as chlorine, nitrogen, oxygen, and metals must not exceed concentrations in the ppm to ppb range, depending on the respective contaminant, due to their detrimental effects on equipment and process performance.^{24,25} Additional requirements concern feedstock boiling range and PIONA composition.²⁴

Replacing conventional naphtha with plastic-derived pyrolysis oils is therefore challenging. Full substitution is currently not feasible due to the limited availability of pyrolysis oils relative to the large feedstock demand of steam crackers.²⁴ Even partial substitution is constrained, as untreated pyrolysis oils generally do not meet the required feedstock specifications, even when blended with naphtha.^{24,25} Consequently, upgrading of pyrolysis oils is necessary prior to their use in steam cracking.

Several upgrading strategies have been investigated to improve pyrolysis oil quality. Filtration reduces particulate matter and metals.¹²⁷ Distillation enables the removal of heavy fractions and the production of cuts within suitable boiling ranges, while partially retaining contaminants in the residue.¹²⁸ Adsorptive processes, for example using activated carbon, can reduce certain heteroatom-containing compounds.¹²⁹ More extensive upgrading is achieved through hydrotreating and hydrocracking, which remove heteroatoms, saturate unsaturated compounds, and adjust the boiling range.^{130–133} As these processes are well established in conventional refining, they are expected to play a key role in enabling the integration of plastic-derived pyrolysis oils into steam cracking.²⁴

Most studies on steam cracking of pyrolysis oils have focused on untreated feeds and report deviations in product yields compared to naphtha-based operation, including both increases and decreases.^{115,134} More recent work has demonstrated, for the first time, the feasibility of the complete process chain – from pyrolysis and subsequent upgrading to steam cracking – at laboratory scale for a MPW feedstock.¹³⁰

Reliable prediction of product yields for different pyrolysis oil feedstocks remains challenging. Detailed process models that consistently represent both upgrading and subsequent steam cracking of pyrolysis oils are not yet available and require a broader experimental database for validation.

In this thesis, data from conventional naphtha steam cracking are therefore used and complemented by assumptions regarding the upgrading process. Despite these limitations, available experimental evidence supports the technical feasibility of integrating plastic-derived pyrolysis oils into steam cracking as partial substitutes for fossil-based feedstocks.

2.4.2 Entrained-flow gasification

The EFG process is designed for the conversion of low-value, complex hydrocarbon feedstocks, such as heavy refinery residues, into syngas.³⁸ This syngas can subsequently be utilized for the production of hydrogen, methanol, or a range of chemical intermediates, including higher alcohols derived from Oxo synthesis gas with tailored H_2/CO ratios.³⁸

As pyrolysis oils are similarly complex as conventional EFG feedstocks, their integration is expected to be less demanding than in steam cracking. High operating temperatures and the complete conversion of the feedstock to synthesis gas reduce constraints related to boiling range, molecular composition, and PIONA distribution. In addition, EFG exhibits a high tolerance toward heteroatoms and metals, eliminating the need for extensive upgrading prior to conversion.¹²³

Although global syngas production is dominated by natural gas reforming, particularly via SMR, a substantial capacity for the gasification of heavy hydrocarbon feedstocks remains available.¹³⁵ In Germany alone, existing EFG plants provide a feedstock conversion capacity on the order of 2 Mt per year.¹³⁶

Despite this industrial relevance, research on the utilization of plastic-derived pyrolysis oils in EFG remains limited. Most studies focus either on the direct gasification of plastic waste or on the integration of pyrolysis oils into steam cracking processes.¹³⁷ Nevertheless, recent large-scale experiments at the Carbon Cycle Lab of the Karlsruhe Institute of Technology (KIT) have demonstrated the technical feasibility of converting plastic-waste-derived pyrolysis oils into synthesis gas using EFG, providing an important proof of concept for this pathway.¹³⁸

In contrast to steam cracking and upgrading, process models for EFG are more readily available. Following from high process temperatures, chemical equilibrium-based approaches can be applied to derive product yields independently of detailed reaction kinetics.²⁷ As a result, these models are less dependent on extensive experimental datasets. This thesis therefore adopts a process-modeling approach for the assessment of pyrolysis oil utilization in EFG. A more detailed description of the gasification process and its integration with downstream synthesis is provided in the following sections.

2.4.2.1 Principles of entrained-flow gasification

EFG reactors were originally developed for the conversion of high boiling refinery residues and coal. They operate at elevated pressures (up to 80 bar) and temperatures exceeding 1300 °C, producing a high-quality, tar free syngas.³⁹ The carbon-rich feedstock is converted into syngas using a gasifying agent that supplies the oxygen required for partial oxidation and supports fuel atomization.³⁹ For chemical applications, pure oxygen (O_2), steam, or mixtures of both are commonly used.^{39,139} After gasification, the raw syngas is cooled to recover process heat and subsequently conditioned to meet the specifications of downstream syntheses (cf. Figure 9).

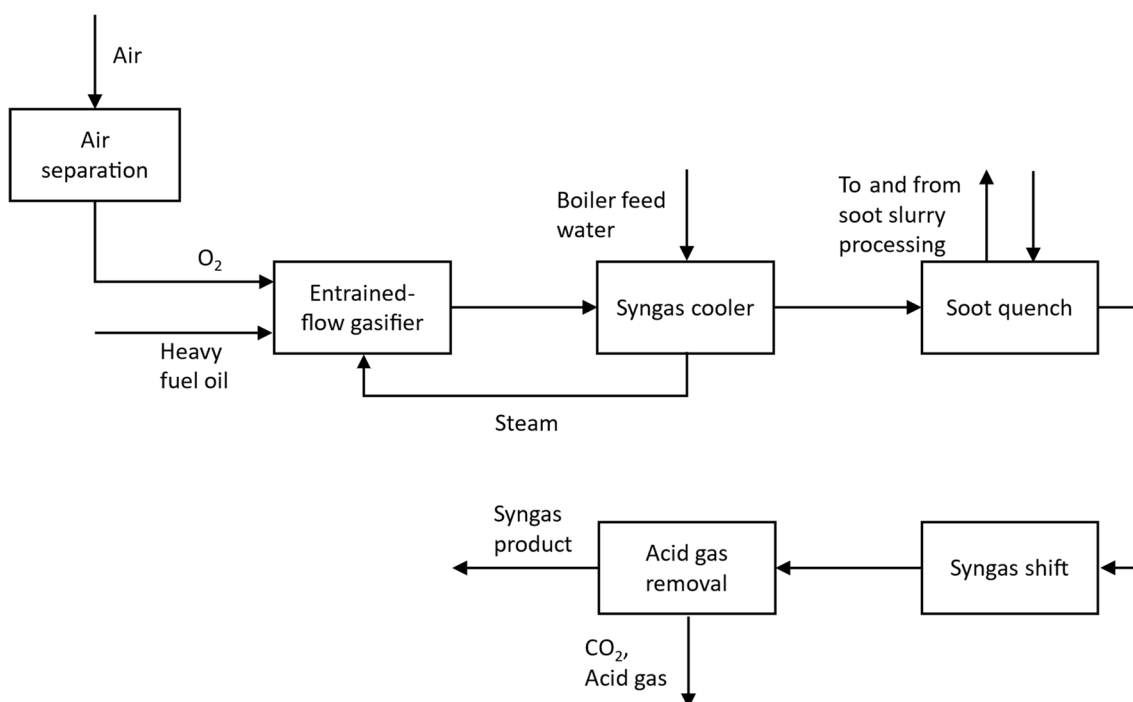


Figure 9: Process scheme of heavy fuel oil-based EFG based on Higman and Häussinger et al.^{38,39}

The resulting syngas primarily consists of carbon monoxide (CO) and hydrogen (H₂), accompanied by carbon dioxide (CO₂), water (H₂O), and methane (CH₄). Additional by-products may include light hydrocarbons, tar (condensable hydrocarbons including polyaromatic compounds), hydrogen sulfide (H₂S), soot, and trace species.^{39,137,139} The composition depends on feedstock characteristics, operating conditions (e.g., temperature and pressure), and the ratio of feedstock to gasifying agents.^{39,137,139}

Gasification involves a sequence of coupled physical and chemical processes, including drying, devolatilization (pyrolysis), and a network of homogeneous and heterogeneous reactions such as cracking, reforming, combustion, gasification, and water-gas shift (WGS) reaction.^{39,139} The governing reactions are summarized in Table 2. Owing to the high operating temperatures in EFG, the resulting syngas composition approaches chemical equilibrium.³⁹

Tars, defined as condensable hydrocarbons, result from incomplete fuel conversion and can cause fouling and operational issues in downstream equipment. Their formation decreases with increasing temperature and with the addition of steam as a gasifying agent, which promotes cracking and reforming reactions (cf. Table 2).^{139,140} Secondary and tertiary tars, i.e., polyaromatic hydrocarbons formed from secondary reactions, require temperatures above 1250 °C for effective thermal cracking.^{137,141–143}

High operating temperatures are therefore desirable to achieve high fuel conversion and minimize methane and tar formation. At the same time, excessively high temperatures reduce overall syngas yield due to increased oxygen demand and enhanced oxidation.¹⁴⁰ Process

conditions must therefore be carefully optimized with respect to both feedstock characteristics and the intended application of the syngas.

The raw syngas produced in EFG requires further conditioning and clean-up prior to use in downstream synthesis processes (cf. Section 2.4.2.2). The H_2/CO ratio can be adjusted via the WGS reaction in a dedicated CO-conversion stage (cf. Table 2). Unwanted components such as H_2S and CO_2 are removed using physical or chemical scrubbing processes, depending on process requirements.^{144,145}

Table 2: Overview of the governing exothermic and endothermic reactions involved in gasification.^{39,139,146}

Reaction type	Reaction	Reaction enthalpy, MJ/kmol
Exothermic reactions		
Combustion	$C + \frac{1}{2} O_2 \rightarrow CO$	-111
	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	-283
	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	-242
Homogeneous water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41
Heterogeneous methanation reaction	$C + 2 H_2 \leftrightarrow CH_4$	-75
Endothermic reactions		
Boudouard reaction	$C + CO_2 \leftrightarrow 2 CO$	172
Heterogeneous water-gas reaction	$C + H_2O \leftrightarrow CO + H_2$	131
Steam methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3 H_2$	206
Cracking	$C_n H_m \rightarrow C_x H_y + C_{n-x} H_{m-y}$	> 0

The syngas composition can therefore be controlled through temperature and the ratio of feedstock to gasifying agents, which shift the equilibrium between exothermic and endothermic reactions.^{39,139} Efficient gasification is characterized by high fuel conversion, high syngas yield including a high syngas lower heating value (LHV), and low tar content, the latter particularly important for downstream synthesis processes.^{139,147}

Operation under elevated pressure is advantageous for downstream utilization, as it reduces or eliminates the need for syngas compression. However, higher pressures favor methane formation. To suppress methane formation, temperatures above 1300 °C are typically required.³⁹

To evaluate gasification performance, cold gas efficiency (CGE) is commonly used alongside syngas yield. CGE quantifies the fraction of the feedstock's chemical energy retained in the product syngas, based on the respective LHV.^{39,148} It is defined as:

$$CGE = \frac{\text{chemical energy of syngas}}{\text{chemical energy of fuel}} \quad (2.1)$$

CGE can be calculated from syngas yield and composition. Since syngas composition can be approximated by minimizing Gibbs free energy, syngas yields can be estimated using flowsheet modeling.²⁷ This approach enables the evaluation of how variations in pyrolysis oil composition affect syngas yield and process efficiency and is therefore applied in this thesis.

2.4.2.2 Integration of gasification into chemical value chains

For the utilization of syngas, H₂/CO ratio and the pressure at which the syngas is supplied to downstream processes are key parameters. In industry, syngas serves as an important feedstock for the synthesis of base chemicals such as methanol, as well as specialty chemicals, including aldehydes and oxo alcohols. It is also used for the production of synthetic fuels and lubricants via Fischer-Tropsch synthesis. In addition, its individual components can be utilized separately: hydrogen is widely used in ammonia synthesis and petroleum refining, while carbon monoxide is applied in the production of chemicals such as formic acid, acetic acid, and phosgene. Table 3 summarizes the required H₂/CO ratios and operating pressures for selected industrial processes.

Among the various syngas applications, methanol synthesis is of particular relevance in this thesis for three main reasons. First, methanol represents the largest syngas-based chemical product, with a global production volume of 111 Mt in 2022.¹⁴⁹ Approximately 70% of this methanol is used in the manufacture of other chemicals and plastics.¹⁵⁰ Second, despite the increasing use of natural gas as feedstock, a significant share – around one third – is still based on gasification of coal or heavy fuel oil.^{150,151} Third, methanol is considered a key intermediate in the transition of the chemical industry towards more sustainable feedstocks, as it enables alternative production routes to olefins and aromatics via methanol-to-olefins (MtO) and methanol-to-aromatics (MtA) processes.^{151,152}

A second syngas configuration of interest is Oxo syngas which is used, e.g., in the synthesis of higher alcohols and aldehydes. If pyrolysis oils behave similarly to conventional EFG feedstocks, the resulting raw syngas composition is already close to that required for Oxo syntheses.³⁹ This reduces the need for adjustment of the H_2/CO ratio via WGS and, in turn, limits carbon losses in the form of CO_2 .

Table 3: Industrial applications of syngas, carbon monoxide, and hydrogen for the chemical synthesis of important chemical intermediates.

Application	Reaction	H_2/CO ratio	Reaction pressure	Source
Methanation / Synthetic natural gas (SNG)	$CO + 3 H_2 \rightarrow CH_4 + H_2O$	3	10 – 70 bar	153–155
Methanol	$CO + 2 H_2 \rightarrow CH_3OH$	2	50 – 100 bar	39,156
Fischer-Tropsch fuels	$n CO + 2n H_2 \rightarrow C_nH_n + H_2O$	2	20 – 40 bar	153,157
Butanal (Hydroformylation / Oxo synthesis)	$CO + H_2 + C_3H_6 \rightarrow C_3H_7CHO$	1	40 – 60 bar	158
Ammonia	$3 H_2 + N_2 \rightarrow 2 NH_3$	∞	80 – 300 bar	155
Formic acid ^g	$CO + H_2O \rightarrow HCOOH$	0	40 bar	159
Acetic acid	$CH_3OH + CO \rightarrow CH_3COOH$	0	30 – 60 bar	160
Phosgene	$CO + Cl_2 \rightarrow COCl_2$	0	1 – 2 bar	161

^g Multi step synthesis: Carbonylation of methanol followed by hydrolysis, yielding formic acid and recovering methanol

2.5 Feedstock availability and characteristics

The preceding sections on plastic pyrolysis and the utilization of pyrolysis products highlight that an ideal feedstock should yield large amounts of pyrolysis oil with sufficient quality for downstream material use, such as steam cracking or EFG. Among the most widely used plastics, PP and PE exhibit the most favorable characteristics. Both provide high pyrolysis oil yields and produce predominantly linear hydrocarbons, resulting in high H/C ratios. In contrast, PS typically achieves even higher pyrolysis oil yields but produces a pyrolysis oil rich in aromatics.^{92,162} While this is advantageous for direct styrene recovery, it leads to lower H/C ratios and reduces suitability for steam cracking or EFG.^{24,92,122}

Other polymers, including PET, PA, and PVC, present additional challenges. These include lower pyrolysis oil yields (especially for PET and PVC), higher heteroatom content in the resulting oils, and increased aromaticity (notably for PET and PVC).^{24,91} Consequently, these materials are less suitable as primary feedstocks. From a process perspective, an optimal feedstock would therefore consist predominantly of PE and PP, with only minor fractions of non-polyolefin materials.

In practice, however, the availability of such feedstocks is limited. Clean PE and PP waste streams should be preferentially directed to mechanical recycling due to their superior environmental performance.^{20,21} Mixed waste streams, such as MSW and commercial waste, contain significant amounts of plastics – including polyolefins – but are rarely sorted to the degree required for high-quality recycling and are often contaminated with non-plastic materials (cf. Section 2.2.1).⁵⁰

LWP sorting provides an intermediate case. While several fractions remain difficult to recycle mechanically, they still contain substantial shares of polyolefins.¹⁶³ Relevant examples include plastic films (DSD 310^h), mixed polyolefins (MPO; DSD 323 and DSD 323-2), and mixed plastics (DSD 350).⁶³ These fractions are also available in considerable quantities. Picuno et al. estimate that mixed plastic fractions (including DSD 323 and DSD 350) account for approximately 19% of LWP, while plastic films contribute a further 14%.⁶¹

A key challenge lies in the variability of these fractions. Sorting specifications typically define material classes based on broad categories (e.g., plastics vs. non-plastics) rather than specific polymer compositions. As a result, the composition of a given sorting fraction can vary significantly, both within a single facility and across different sorting plants.¹⁶⁴ This variability is reflected in the data summarized in Table 4, which show wide ranges in polymer composition for comparable waste fractions.

Data on elemental composition are more limited, particularly for datasets that simultaneously report polymer and elemental composition (cf. Table 4). Nevertheless, the available data suggests that fractions such as DSD 310 and DSD 323 generally contain lower levels of heteroatoms

^h DSD specifications published by *Der Grüne Punkt / Duales System Deutschland (DSD)* are the most commonly applied specifications.

than DSD 350. Independent of the specific fraction, however, the presence of heteroatoms is unavoidable due to the inclusion of non-polyolefin materials. Given the variability in polymer composition, similar fluctuations in elemental composition can be expected.

The utilization of such waste streams therefore requires strategies to manage these undesired components. This can be achieved through additional feedstock conditioning, which alters the composition prior to processing, or through process-based approaches. The latter include adapting pyrolysis conditions, upgrading pyrolysis oils, or selecting downstream conversion routes that are more tolerant to feedstock impurities (cf. Section 2.4).³⁰

Table 4: Waste composition of different LWP sorting fractions by plastic type.

Frac- tion	DSD 310			PE films		DSD 323	MPO rigids		DSD 350	
Source	<i>Frei- tag et al.¹⁶⁵</i>	<i>Lase et al.¹⁶³</i>	<i>Gen- uino et al.¹¹⁴</i>	<i>Kusen- berg et al.¹⁶⁶</i>	<i>Frei- tag et al.¹⁶⁵</i>	<i>Lase et al.¹⁶³</i>	<i>Kusen- berg et al.¹⁶⁶</i>	<i>Geier et al.¹⁶⁴</i>	<i>Gen- uino et al.¹¹⁴</i>	<i>Strien et al.¹⁶⁷</i>
Polymer composition, wt.%										
PE	90	76	71	97	66	35	53	18-70	24	28
PP	2	5	10	1	22	28	46	17-70	17	23
PS		n.a.	0		n.a.	n.a.		n.a.	4	3
PET	1	n.a.	2		3	n.a.		n.a.	8	12
PA	2	n.a.	n.a.		4	n.a.		n.a.	n.a.	n.a.
PVC	n.a.	n.a.	0		n.a.	n.a.		n.a.	0	< 1
Multi- layer films	n.a.	5	8	2	n.a.	7		n.a.	12	14
Other/ Resi- due	5	14	9		5	30	1	8-15	35	20
Elemental composition, wt.% (dry)										
C	n.a.	n.a.	74.7	83.4	n.a.	n.a.	84.7	n.a.	72.9	n.a.
H	n.a.	n.a.	10.7	13.7	n.a.	n.a.	14.1	n.a.	10.0	n.a.
N	n.a.	n.a.	0.4	0.2	n.a.	n.a.	0.2	n.a.	0.4	n.a.
S	n.a.	n.a.	< 0.2	< 0.1	n.a.	n.a.	< 0.1	n.a.	< 0.2	n.a.
O	n.a.	n.a.	7.7	1.6	n.a.	n.a.	0.3	n.a.	7.8	n.a.
Cl	n.a.	n.a.	0.6	0.2	n.a.	n.a.	0.4	n.a.	0.5	n.a.
Ash	n.a.	n.a.	6.3	0.9	n.a.	n.a.	0.3	n.a.	8.7	n.a.

Although a substantial body of literature addresses the pyrolysis of plastic waste with varying compositions, a systematic assessment of how feedstock composition influences the overall efficiency of pyrolysis-based chemical recycling – including downstream conversion – remains limited. This thesis addresses this gap by systematically evaluating the effect of feedstock composition across the entire process chain. Experimental data for well-defined model feedstocks are used in combination with LCA to quantify both the potentials and the limitations of their utilization.

2.6 Life cycle assessment of pyrolysis-based chemical recycling

LCA is a standardized methodology in industrial ecology used to quantify the environmental impacts associated with products and processes across their entire life cycle. This includes resource extraction, production, use, and EoL treatment, commonly referred to as cradle-to-grave approach. The fundamental principles of LCA are outlined in Section 2.6.1 followed by its application to chemical recycling in Section 2.6.2.

2.6.1 Fundamentals of life cycle assessment

The LCA methodology is standardized by the ISO norms DIN EN ISO 14040 and 14044, which define the framework and requirements for conducting LCA studies.^{168,169} The procedure consists of four interconnected phases: (1) goal and scope definition, (2) life cycle inventory (LCI) analysis, (3) life cycle impact assessment (LCIA), and (4) interpretation. The process is inherently iterative, as insights gained in later phases may require revisiting and refining assumptions made in earlier stages.

Different types of LCAs can be distinguished based on temporal scope and analytical perspective. Prospective LCAs assess future technologies and scenarios, whereas accounting LCAs evaluate existing systems.¹⁷⁰ With respect to system perspective, LCAs are commonly classified as attributional or consequential. Attributional LCAs describe the environmental burdens associated with a defined product system, while consequential LCAs evaluates the environmental consequences of changes within a broader system.¹⁷¹ The selected approach influences system boundaries, modeling choices, and data requirements and is therefore determined during the goal and scope definition.

The goal and scope definition establishes the overall framework of the study by specifying the research question, system boundaries, and functional unit (FU). The functional unit provides a quantitative reference for the system's function and ensures comparability of results.¹⁷² In waste management and chemical recycling, a common functional unit is the treatment of a defined amount of waste, for example 1 kg of MPW.²⁸ The chosen LCA perspective determines which processes are included within the system boundaries.

The LCI phase involves the collection and quantification of all relevant input and output flows associated with the system. This includes technosphere flows, representing exchanges between processes, and elementary flows, representing exchanges with the biosphere.¹⁷⁰ Processes are typically divided into foreground and background systems. Foreground processes are directly related to the system under study and are modeled in detail, often based on primary data or process simulations. Background processes represent external systems, such as energy supply, and can be modeled using data from LCA databases.¹⁷⁰ In prospective studies, such data may be

complemented or replaced by scenario-based data derived from integrated assessment models (IAMs).¹⁷³

In the LCIA phase, environmental impacts of the system are quantified by assigning elementary flows to a set of impact categories using characterization factors (CFs).¹⁷⁰ These categories represent different environmental problem areas and cause-effect pathways, such as climate change, acidification, and eutrophication. CFs express the relative contribution of a substance to a given impact category compared to a reference substance.¹⁷⁰ For example, within the Environmental Footprint (EF) 3.1 method, the climate change impact of methane is expressed relative to CO₂, with a CF of 36.8 over a 100-year time horizon.¹⁷⁴

The final phase, interpretation, evaluates the results in relation to the defined goal and scope.¹⁷² This includes assessing completeness, consistency, and plausibility of the results, as well as identifying key drivers and uncertainties. Sensitivity and scenario analyses are commonly applied to evaluate the robustness of results and to assess the influence of methodological choices and input parameters.¹⁶⁹

2.6.2 LCA of pyrolysis-based chemical recycling

LCA has been widely applied in recent years to evaluate the environmental performance of chemical recycling processes, particularly pyrolysis-based routes. Despite the large number of available studies, no clear consensus has emerged regarding their overall environmental performance. This lack of agreement can be attributed to differences in system boundaries and process definitions, variations in methodological approaches and assumptions, as well as variations differences in the investigated waste streams.^{28,172} As a result, direct comparison of individual studies and the derivation of general conclusions remain challenging.

Most studies assess chemical recycling in comparison to alternative waste treatment options, typically energy recovery and, in some cases, mechanical recycling. A review of 30 LCA studies by Zhang and Nakatani indicates that chemical recycling routes targeting monomer recovery outperform energy recovery in terms of climate change impact.²⁸ Comparisons with mechanical recycling, however, yield inconsistent results. While some studies report environmental benefits, others find inferior performance, depending on factors such as waste composition and the quality of the resulting secondary products.^{21,28,175–177}

Significant variations across studies also arise from differences in system configuration. These include feedstock composition, process design, and the choice of target products. Depending on the study, pyrolysis products may substitute fuels, refinery feedstocks, or base chemicals.^{21,31,176–178} Additional variability stems from the definition of functional units, which can be defined based on waste input, product output, or combined system-level functions, as shown by Keller et al. and Quicker et al.^{26,171,179,180} These methodological choices strongly influence both modeling approach and resulting environmental impacts.

A central methodological challenge in the LCA of chemical recycling is the treatment of multifunctionality. Since pyrolysis processes typically generate multiple products, allocation or system expansion approaches must be applied to account for co-products. The choice between these approaches can significantly affect the results and contributes to the variability observed across studies.¹⁸¹

Further uncertainty arises from limitations in data availability and quality. Only a small number of studies are based on experimentally validated pyrolysis data that are consistent with both total mass and elemental balances. This is largely due to confidentiality constraints and the scarcity of large-scale experimental data.^{29,181,182} Consequently, many studies rely on assumptions or simplified models, which introduce additional uncertainty.

Two aspects that remain insufficiently addressed in the literature are the influence of reactor design and the effect of feedstock composition.^{28,29} This gap is primarily due to the lack of comparable datasets, as experimental studies rarely investigate identical feedstocks across different reactor systems or systematically vary feedstock composition within a consistent process setup. In addition, the characterization of waste inputs is often limited, further complicating interpretation and comparison of results.¹⁷²

Downstream processing of pyrolysis oils has also received limited attention. While it is now widely recognized that pyrolysis oils require upgrading prior to their use in steam cracking, the impact of pyrolysis oil composition on subsequent conversion efficiency has not been systematically investigated. Moreover, different utilization pathways are rarely compared within a consistent framework. In particular, the use of pyrolysis oils in EFG has been only sparsely studied, with few contributions, such as those by Keller et al., addressing this pathway.^{26,171}

These limitations highlight the need for a more systematic and consistent assessment of pyrolysis-based chemical recycling processes. In particular, the influence of feedstock composition, reactor design, and downstream utilization pathways must be evaluated within a unified framework to enable meaningful comparison of results. The integration of experimentally validated process data with consistent system definitions is essential to reduce uncertainties and improve the robustness of LCA studies. This is especially relevant for assessing the role of chemical recycling within a circular economy, where both material efficiency and environmental performance must be considered simultaneously. This thesis addresses these challenges by providing a systematic analysis of feedstock composition and reactor effects, as well as their influence on the overall process chain of pyrolysis-based chemical recycling.

3 System definition and LCA framework

This thesis addresses three central research questions. First, how does the composition of MPW in terms of different plastics influence the climate change impacts of the pyrolysis process and the subsequent utilization of the resulting pyrolysis oils via upgrading and steam cracking (waste-to-monomers) and EFG (waste-to-syngas)? Second, how does the choice of reactor technology alter impacts and product yields of chemical recycling? Third, is the recycling of MPW via pyrolysis-based chemical recycling preferable to the established treatment route of energy recovery (waste-to-energy) with regard to climate change impact?

Addressing these questions requires the definition of the pyrolysis-based chemical recycling process routes to be studied and the establishment of an LCA framework for quantifying the associated climate change impacts (this chapter). Furthermore, representative pyrolysis experimental data must be identified. These data enable the assessment of the influence of both feedstock composition and reactor technology.

For the different process chains, modeling approaches are developed to calculate mass and energy balances of the respective process routes (cf. Chapter 4). Based on these models, feedstock- and process-specific LCIs for all foreground processes are generated. In addition, product yields and carbon recycling efficiencies are calculated (cf. Chapter 5).

On this basis, a comparative LCA of both the chemical recycling routes and the reference energy recovery route is conducted. This allows the assessment of the influence of feedstock composition, waste treatment technology, and reactor type on climate change impacts (cf. Chapter 6), followed by a discussion of sensitivities and study limitations (cf. Chapter 7).

The mass balancing, process modeling and assessment framework applied throughout this thesis builds upon methodologies previously developed and published in Hennig et al.¹⁷⁸ and Stallkamp, Hennig et al.¹⁸³ The present thesis adopts this framework as methodological foundation and systematically extends it to additional feedstocks and process integration scenarios.

3.1 Definition of process chains

As previously outlined, this thesis analyzes two different pyrolysis-based chemical recycling chains: the waste-to-monomers and waste-to-syngas process chains. In addition, the established waste-to-energy process route via incineration with energy recovery is considered as a benchmark. The following sections summarize the processes included within each process chain.

All process routes begin with the model feedstock as input. Preprocessing steps such as waste collection and waste sorting are excluded. This is because all model feedstocks are synthetic mixtures rather than actual waste streams (cf. Section 3.2).

3.1.1 Waste-to-monomers process route

The process chain starts with plastic pyrolysis, converting the feedstock into plastic pyrolysis oil (cf. Figure 10). For the pyrolysis process, it is assumed that the reactor is heated electrically, regardless of reactor type.

The pyrolysis side products – pyrolysis gas and pyrolysis residue – require further treatment. Prior to emission to the atmosphere, the pyrolysis gas is incinerated in a gas motor for the recovery of electricity and heat (base scenario; flows of excess electricity and district heat products not shown). The pyrolysis residue is sent to an MSWI plant for treatment, allowing the recovery of energy (cf. Section 3.1.3). The remaining bottom ash is sent to sanitary landfilling.

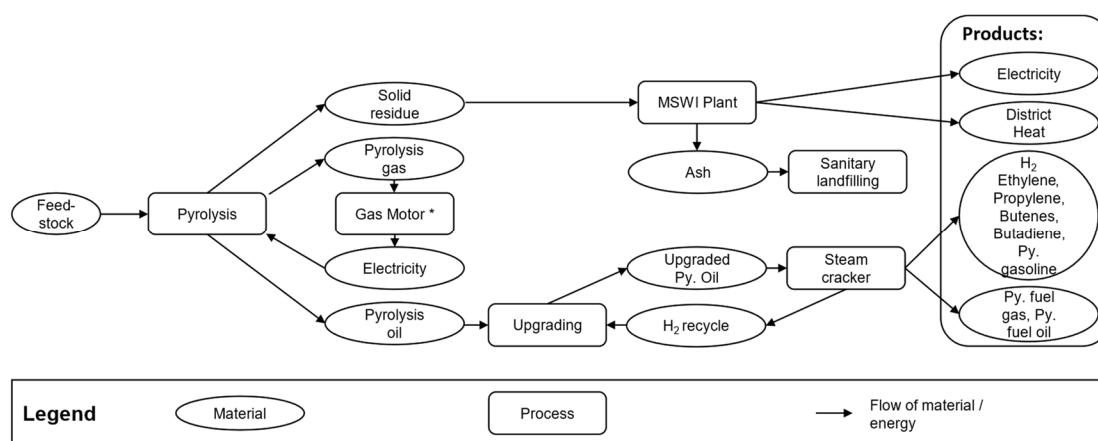


Figure 10: Block flow diagram of the waste-to-monomers process chain. (*) Excess electricity and district heat produced by the gas motor are not shown.

Following pyrolysis, the resulting pyrolysis oil must be upgraded to comply with steam cracker feedstock specifications. These specifications encompass parameters such as boiling range, content of heteroatoms and metals, and PIONA composition (cf. Section 2.4.1). The extent of upgrading depends on the specific pyrolysis oil. It is determined by the plastic waste feedstock and the pyrolysis process. In this study, it is represented by the share of heteroatoms and the molar H/C ratio in the pyrolysis oil.

Hydrogen for upgrading is supplied from refinery hydrogen in the base case. The upgraded pyrolysis oil is then processed in a steam cracker. This yields the target products olefins (ethylene, propylene, butenes, butadiene) and aromatics (benzene, toluene, xylenes) as main products for

material use. In addition, pyrolysis fuel oil and pyrolysis fuel gas are produced as fuel products.ⁱ Hydrogen is generated as a co-product. It can be recycled to the pyrolysis oil upgrading process, thereby reducing the overall hydrogen demand.

3.1.2 Waste-to-syngas process route

The pyrolysis step in the waste-to-syngas process route is identical to that in the waste-to-monomers route, including the treatment of pyrolysis side products. Instead of upgrading the pyrolysis oil to steam cracker feedstock, the pyrolysis oil is used directly in EFG. No prior upgrading is required (cf. Figure 11).

The pyrolysis oil is gasified in an entrained-flow gasifier using oxygen as the gasifying agent and high-pressure steam as a moderator. Oxygen is supplied by an air separation unit (ASU), while steam is generated using available high-temperature process heat. Excess heat enables the generation of district heat as a side product.

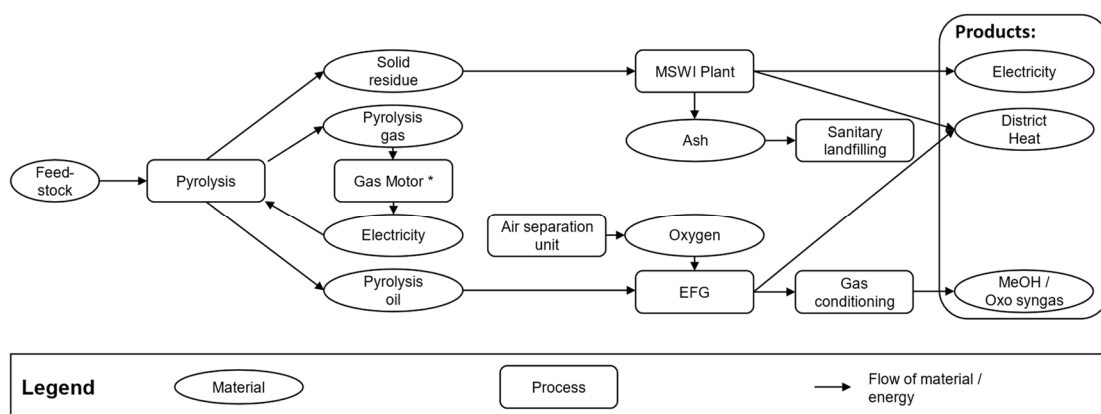


Figure 11: Block flow diagram of the waste-to-syngas process chain. (*) Excess electricity and district heat produced by the gas motor are not shown.

Following gasification, the raw syngas is conditioned to either MeOH syngas or Oxo syngas. These differ in their H_2/CO ratio, which is adjusted using a WGS stage. The syngas is then purified by removing undesirable components such as CO_2 using Rectisol scrubbing. This results in on-spec MeOH and Oxo syngas as target products for material use.

Based on current production volumes, the MeOH syngas configuration is treated as the base case, whereas the Oxo syngas configuration is evaluated as an alternative scenario (cf. Section 2.4.2.2).

ⁱ Material utilization for production of electrode material would also be possible but is not considered here

3.1.3 Waste-to-energy process route

Energy recovery through incineration of plastic waste in an MSWI plant serves as reference waste treatment method (cf. Figure 12). The incineration process enables the recovery of energy in the form of electricity and district heat. The flue gas undergoes treatment for the removal of airborne contaminants. The remaining bottom ash is sent to sanitary landfilling.

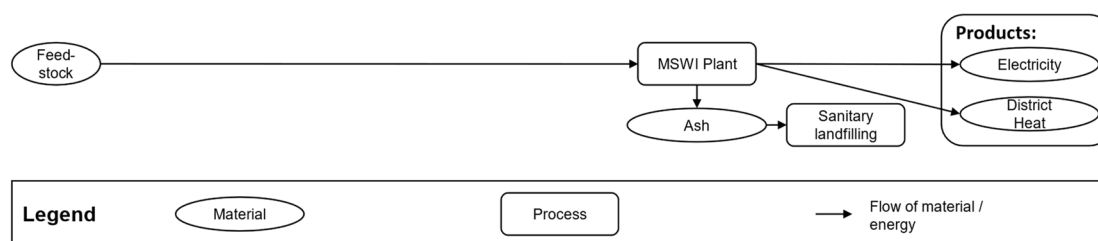


Figure 12: Block flow diagram of the waste-to-energy process chain.

3.2 Selection of pyrolysis experimental data

For the selection of model feedstocks required for a systematic analysis of the influence of different feedstock compositions on the pyrolysis process and the downstream utilization of pyrolysis oils, three criteria must be met. First, the feedstocks must be representative of those available for pyrolysis-based chemical recycling. Second, the resulting pyrolysis oils must cover a broad range of compositions to enable comparison of different utilization options. Third, datasets using identical feedstocks must be available for at least two reactor systems to allow the analysis of reactor effects.

Further requirements arise regarding the relevance, comparability, and completeness of datasets. These are necessary to attribute differences in calculated LCA impacts to feedstock composition rather than to differences in data acquisition or missing data. The experimental data should therefore be obtained from systems at high Technology Readiness Level (TRL) – preferably from TRL > 6, i.e. pre-industrial scale – to ensure that the data collected reflects industrial reality rather than laboratory effects and the comparison with established technologies is valid.^{184,185} In addition, identical experimental setups should be used when comparing different feedstocks to minimize the influence of factors other than feedstock composition, as variations in reactor type and process parameters, such as pyrolysis temperature, further affect pyrolysis behavior (cf. Section 2.3.2). Finally, the reported data must allow complete mass balancing of the pyrolysis experiments with respect to educts and products.

The dataset reported by Netsch et al., previously discussed in the context of feedstock composition and process conditions, comprises results from pyrolysis experiments on seven different feedstocks and two reactor setups across several publications.^{91,92,112} The feedstocks can be grouped into three categories: single virgin polymers (PE, PP, and PS), feedstock mixtures of virgin materials, and a synthetic post-consumer waste.

Netsch et al. designed the feedstock mixtures to represent the polymer composition of different plastic packaging waste fractions.¹¹² The mixture Mix AR^j consists of LDPE, PP, and PS and is thus free of heteroatoms and yields an aromatic-rich pyrolysis oil. In contrast, the mixtures Mix MH^k and Mix HH^l are made up from LDPE, PP, and PS and differing amounts of heteroatom-containing polymers such as PET, PA6, and PVC. Mix MH contains a share of 8% of heteroatom-containing polymers, while Mix HH contains 25%. Accordingly, levels of heteroatom-content of oxygen, nitrogen, and chlorine in the feedstock mixtures' elemental composition increase with increasing share of heteroatom-containing polymers (cf. Table 5).

The last feedstock is a synthetic post-consumer waste (S-PCW). It consists of cleaned EoL packaging waste that was manually sorted into individual polymers and subsequently remixed in a predefined ratio. This approach enables the inclusion of effects arising from compounded plastics in comparison to virgin materials. A full overview of the analyzed feedstocks in terms of polymer and elemental composition is given in Table 5.

Table 5: Definition of model feedstocks, including polymer composition, elemental composition, and lower heating value adapted from Netsch et al.^{91,92,112}

	Single polymers			Polymer mixtures			
<i>Model feedstock</i>	<i>LDPE</i>	<i>PP</i>	<i>PS</i>	<i>Mix AR</i>	<i>Mix MH</i>	<i>Mix HH</i>	<i>S-PCW</i>
Polymer composition, wt.%							
LDPE	100.0	-	-	40.0	70.0	50.0	29.4
HDPE	-	-	-				17.1
PP	-	100.0		30.0	20.0	15.0	25.1
PS	-	-	100.0	30.0	2.0	10.0	4.2
ABS	-	-	-	-	-	5.0	3.8
PET	-	-	-	-	4.0	10.0	10.1
PA6	-	-	-	-	2.0	5.0	6.3
PVC	-	-	-	-	2.0	5.0	4.0
Elemental composition, wt.%							
C	85.8	85.8	92.0	87.6	83.5	80.6	80.0
H	14.2	14.2	8.0	12.4	13.4	11.6	12.3
N	< 0.2	< 0.1	< 0.2	< 0.2	0.3	0.9	0.8
Cl	0.0	0.0	0.0	0.0	1.0	2.4	1.4
Moisture	< 0.01	< 0.01	< 0.01	0.0	0.0	0.1	0.0
Ash	< 0.01	< 0.01	< 0.01	0.0	0.2	0.5	2.2
O	0.0	0.0	0.0	0.0	1.6	3.9	3.3
Lower heating value, MJ/kg							
	43.2	43.2	39.5	42.1	41.5	38.6	39.1

^j **AR**: Feedstock mixture designed to produce an **AR**omatic-rich pyrolysis oil.

^k **MH**: Feedstock mixture with **M**edium level of **H**eteroatom-containing polymers.

^l **HH**: Feedstock mixture with **H**igh level of **H**eteroatom-containing polymers.

The comparison of the feedstock compositions used by Netsch et al. with those available for pyrolysis-based chemical recycling (cf. Section 2.5) shows that the relevant polymers identified in sorting analyses for the DSD 310, DSD 323, and DSD 350 fractions are represented in the model feedstocks. PE and PP, which constitute the largest shares in these sorting fractions, are included both as single virgin polymer feedstocks and as dominant components in all mixed feedstocks. Contaminants present in sorting fractions are represented by varying amounts of heteroatom-containing polymers in Mix MH and Mix HH.

The heteroatom content of the resulting pyrolysis oils ranges from zero to 3.8 wt.%, including O, N, and Cl (cf. Appendix A).^{91,92} The molar H/C ratio varies between 1.1 and 2.0 due to differences in PIONA composition, as shown by GC×GC chromatograms, implying different levels of aromaticity.^{91,92} Thus, the dataset covers both heteroatom-free and heteroatom-containing pyrolysis oils and includes a range of oils from aromatic to aliphatic character.

Data on pyrolysis product distribution as well as pyrolysis oil and gas composition are available for two reactor setups: an ASR and an STR. Thus, full balancing of the experiments is possible (cf. Section 4.1)^m. The reactor technologies used by Netsch et al., ASR and STR, are already applied in industry. Plastic Energy employs the STR concept, while ARCUS Greencycling Technologies uses the ASR concept.^{186,187} However, the experimental scale is significantly smaller than that of industrial systems. The ASR operates at a throughput of 1 kg/h, while the STR is conducted in batches of 0.25 kg, putting the ASR at a TRL of 6, while the STR can be categorized at TRL 5.

As the dataset of Netsch et al. fulfills all required criteria except for TRL, no other datasets of comparable quality and scope and higher TRL could be identified. Therefore, despite this limitation, the data of Netsch et al. are used as the basis for the pyrolysis modeling in this work.

3.3 Goal and scope definition for LCA

The LCA performed in this thesis follows the ISO standards ISO 14040 and ISO 14044.^{168,169} The methodology is used to analyze the influence of different feedstocks and pyrolysis reactors on the environmental impacts of chemical recycling via pyrolysis. In addition, results are compared to the established waste treatment method of energy recovery using the previously defined process chains and feedstocks (cf. Sections 3.1 and 3.2) and relative to the established conventional pathways for the production of the target products of chemical recycling, i.e., steam cracker products and syngas. Furthermore, the effect of differing pyrolysis oil compositions on downstream utilization is analyzed.

The contributions of individual subprocesses to the overall LCA results are also examined. This allows the identification of key process parameters that significantly influence the

^m Analysis of pyrolysis gas composition missing for Mix MH in ASR experiments.

environmental performance of the respective waste treatment processes. The assessment is limited to climate change impact. This restriction is due to limited data availability for additional impact categories, particularly for the pyrolysis process.

Figure 13 provides a graphical overview of the defined system boundaries. With the exception of landfilling of incineration ashes, all processes shown are treated as foreground processes and are modeled explicitly. The methods used to generate LCI data for these processes are described in Chapter 4.

Background processes are modeled using datasets from the ecoinvent 3.10 LCA database.¹⁸⁸ These include the selected reference processes representing the conventional production of products generated by waste treatment. As no corresponding dataset for syngas production from heavy fuel oil (HFO) is available, this process is modeled explicitly, using the same approach as for the gasification of pyrolysis oils. If available, datasets for Germany are used. Otherwise, data for Switzerland or Europe are applied. Table 6 summarizes the reference processes used for the generation of these products. A link to the corresponding ecoinvent datasets is provided in Appendix D.6.

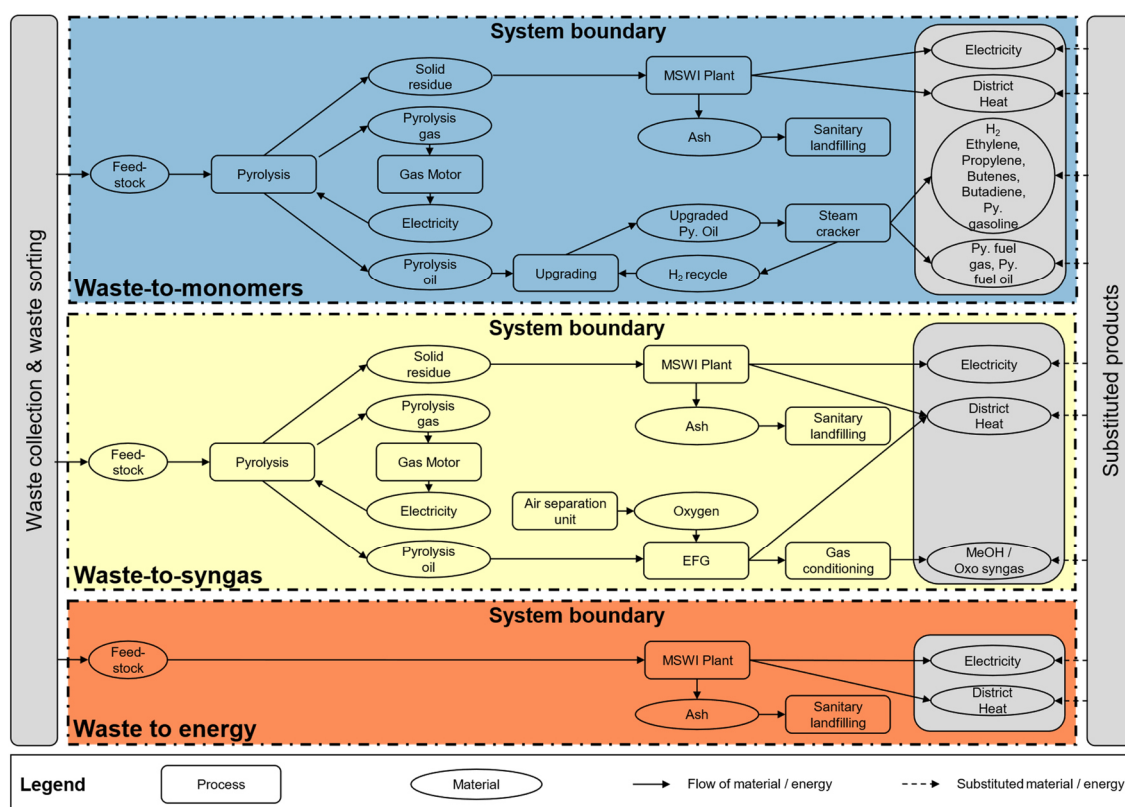


Figure 13: System boundaries of the waste-perspective LCA for pyrolysis-based chemical recycling via waste-to-syngas and waste-to-monomers with waste-to-energy as the reference waste treatment route. Adapted from Hennig et al.¹⁷⁸

Table 6: Overview of the reference processes for products generated by the waste treatment processes.

Product	Process	Feedstock
Electricity	German market mix	-
District heat	European market mix	Natural gas
Steam cracker products ⁿ	Steam cracking	Naphtha
MeOH syngas	EFG	HFO
Oxo syngas	EFG	HFO

The collection and sorting of waste are excluded from the system boundaries. This is because the study focuses on model feedstock composition rather than real waste streams. In addition, previous analyses have shown that sorting has only a limited impact on overall results, while impacts from waste collection would cancel out in comparison of different waste treatment routes due to equal contributions routes.^{171,183}

Contributions from infrastructure construction are also neglected. Most processes, except for pyrolysis, rely on existing infrastructure. Similarly, impacts from logistics, such as the transport of materials between process stages, are excluded due to their minor contribution in previous studies.¹⁸³ In all cases, a zero-burden approach is applied to the waste entering the system.¹⁸⁹

The assessment considers three perspectives for evaluating the environmental performance of the waste treatment pathways: a waste-centered perspective, a product-centered perspective, and a combined perspective. Accordingly, three different functional units are defined. This multi-perspective approach is required because direct comparisons of climate change impacts are only possible for systems providing identical functionality.

For the direct comparison of waste treatment routes, the waste-centered perspective is applied. Here, the functional unit is defined as the treatment of 1 kg of model feedstock. The comparison of different feedstocks is enabled through the product-centered perspective. In this case, the functional unit is defined as the production of 1 kg of syngas or 1 kg of steam cracker products.

Both the waste-centered and product-centered assessments use an avoided burden approach. This accounts for side products such as district heat by assuming substitution of equivalent products from conventional production, as defined by the reference processes.¹⁸⁹ Using cradle-to-gate system boundaries, the product-centered approach excludes waste treatment from the system boundary.

Finally, the combined perspective is used to evaluate the climate change impact reduction potential of the different waste treatment processes and their dependence on the selected reference processes. In this context, a combined input- and output-based functional unit, referred to as the product basket, is applied. This approach avoids the need for product credits.¹⁸⁹

ⁿ Steam cracker products include hydrogen, ethylene, propylene, butenes, butadiene, pyrolysis gasoline, pyrolysis fuel gas, and pyrolysis fuel oil

The system functionality is defined as the treatment of 1 kg of the respective feedstock combined with the simultaneous production of the maximum achievable product outputs for each process route. Accordingly, the functional unit differs for each feedstock. A detailed definition is provided in Appendix E.1.

Impacts are calculated using the Environmental Footprint method EF3.1 and the Activity Browser (v2.10.3) LCA calculation tool.^{174,190,191} The results are further analyzed through sensitivity and scenario analyses (cf. Chapter 7). These include variations in overall product yields, impacts of reference product generation, and changes in energy supply or process technology. Additional scenarios address process integration within the chemical recycling chain and utilization of pyrolysis side products.

4 Process modeling

The compilation of life cycle inventories (LCIs) for calculating climate change impacts requires consistent mass and energy balances for all processes within the defined process chains. Based on these balances, technosphere and biosphere flows can be derived. In addition, product yields as well as carbon recovery and recycling efficiency can be calculated.

The overall carbon recycling efficiency $C\text{-}Eff$ is defined for the full waste treatment process route as

$$C\text{-}Eff = \frac{\text{Carbon in products with material use}}{\text{Carbon in feedstock}} \quad (4.1)$$

Accordingly, carbon is considered recycled if it is contained in a product for material use that is identical to a conventionally produced product. Examples include carbon contained in steam cracker products for material use or in syngas.

In contrast, the process level carbon recovery is expressed as relative carbon yield $C\text{-}Yield$, defined as

$$C\text{-}Yield = \frac{\text{Carbon in target product}}{\text{Carbon in process input}} \quad (4.2)$$

Target products are those products of a subprocess that are either further processed in a subsequent conversion step or directly substitute a conventionally produced product. Consequently, the carbon yield also includes products used as fuels.

The following sections present the modeling approaches for all foreground processes.

4.1 Incineration with energy recovery

Incineration with energy recovery is used as the reference waste treatment route for comparison with the pyrolysis-based chemical recycling routes. The mass and energy balances are calculated using a simplified process scheme. This scheme considers only the amounts of CO_2 and bottom ash generated during combustion, as well as the electricity and district heat recovered.

Assuming complete combustion, the specific amounts of CO_2 $m_{\text{CO}_2,ER}$ and bottom ash $m_{\text{bottom ash},ER}$ can be calculated from the feedstock composition, i.e., the carbon mass fraction

$x_{C,Feedstock}$ and the ash mass fraction $x_{ash,Feedstock}$, and the molar masses of carbon $\bar{M}_C$ and CO_2 $\bar{M}_{\text{CO}_2}$:

$$m_{\text{CO}_2,ER} = x_{C,Feedstock} \frac{\bar{M}_{\text{CO}_2}}{\bar{M}_C} \quad (4.3)$$

$$m_{bottom\ ash,ER} = x_{ash,Feedstock} \quad (4.4)$$

The amounts of electricity and district heat recovered from incineration are estimated using average net efficiencies of German MSWI plants. This approach avoids the need to model the steam cycle and flue gas treatment explicitly, as both energy recovery and internal energy demands are already reflected in the net efficiencies.

According to the German association of thermal waste treatment plants (ITAD), the net electrical efficiency η_{el} of 14.3%, and the net thermal efficiency η_{th} is 39.1%.⁶⁹ Based on these values, the specific amount of electricity e_{ER} and the specific amount of district heat q_{ER} generated from energy recovery can be calculated from the waste's LHV:

$$e_{ER} = \eta_{el,ER} LHV \quad (4.5)$$

$$q_{ER} = \eta_{th,ER} LHV \quad (4.6)$$

4.2 Balancing of pyrolysis experiments

The experimental data reported by Netsch et al. are used for modeling the pyrolysis process of the different model feedstocks. As the balancing procedures for the two reactor types differ slightly, a generalized approach is first developed. This approach serves as a validity check for the reported data. Subsequently, reactor-specific corrections are applied to minimize errors arising from mass balance inconsistencies, e.g., the loss or an excess of carbon. These inconsistencies would otherwise propagate into the LCA results by distorting product yields.

Figure 14 illustrates the generalized pyrolysis process. The feedstock is fed into a pyrolysis reactor, where it decomposes into three product fractions: pyrolysis gas (*Py. gas*), pyrolysis residue (*Res*), and pyrolysis oil (*Py. oil*). The process is driven by an input of thermal or electrical energy $\dot{E}_{in}$ and releases waste heat $\dot{Q}_{off}$. The total mass balance is defined as

$$M_{Feedstock} = \sum_i M_i \quad (4.7)$$

where M represents the mass of the feedstock or pyrolysis product i .

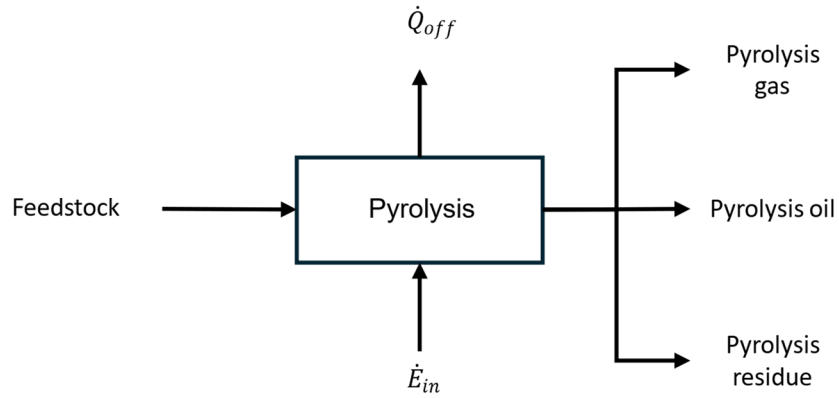


Figure 14: General pyrolysis process balancing scheme.

Introducing the pyrolysis product yields y_i defined as

$$y_{i,Pyr.} = \frac{M_i}{M_{Feedstock}} \quad (4.8)$$

the total mass balance can be rewritten as

$$\sum_i y_{i,Pyr.} = 1 \quad (4.9)$$

In addition to the total mass balance, elemental mass balances must be satisfied to ensure consistency of compositional data. These balances are defined as:

$$x_{j,Feedstock} = \sum_i y_{i,Pyr.} x_{j,i} \quad (4.10)$$

for all elements j . Here, x denotes the mass fraction of element j in the feedstock or product i . The relevant elements are those determined in the feedstock ultimate analysis, namely carbon (C), hydrogen (H), nitrogen (N), oxygen (O), sulfur (S), and chlorine (Cl). The parameter ash is determined from proximate analysis and represents all mineral and metallic components. These are assumed to be inert or unchanged during the experiment.

From equations (4.9) and (4.10), the total mass balance can also be expressed as

$$\sum_j x_{j,Feedstock} = \sum_i \sum_j y_{i,Pyr.} x_{j,i} = 1 \quad (4.11)$$

using the identity

$$\sum_j x_{j,i} = 1 \quad (4.12)$$

which holds for both the feedstock and all pyrolysis products.

In addition to feedstock composition, Netsch et al. report the elemental composition of the pyrolysis oil.⁹¹ The elemental composition of the gas-phase can be calculated from the composition of individual gas species, neglecting the nitrogen gas used for inertization and flushing. It is determined using the elemental mass fraction a_j of each gas species z and its mass fraction b in the gas-phase:

$$x_{j,Py.gas} = \sum_z a_{j,z} b_z \quad (4.13)$$

No elemental composition is reported for the pyrolysis residue. The residue consists of non-pyrolyzable inorganic material from the feedstock (minerals and metals) and a carbonaceous fraction formed during pyrolysis. Therefore, the elemental composition of the pyrolysis residue is approximated as

$$x_{ash,Res} = \frac{x_{ash,Feedstock} M_{Feedstock}}{M_{Res}} = \frac{x_{ash,Feedstock}}{y_{Res,Pyr.}} \quad (4.14)$$

and

$$x_{C,Res} = 1 - x_{ash,Res} \quad (4.15)$$

This assumption implies that the residue consists solely of ash and carbon, neglecting any other components that may be present.

The required energy input $\dot{E}_{in}$ could, in principle, be determined from an energy balance. In practice, this is difficult because detailed pyrolysis product compositions and thermodynamic data are often unavailable. Instead, the energy demand is estimated using the experimentally determined, feedstock-specific minimum energy demand $e_{Pyr,min}$.¹¹² This value was obtained by Netsch et al. using the ASR system. It includes contributions from polymer heating, melting, enthalpy of fusion, reaction enthalpy, and evaporation of pyrolysis products. Reactor waste heat $\dot{Q}_{off}$ is generally neglected.

Based on the experimental data, total and elemental mass balances can be established, and the energy demand can be estimated. This provides the required basis for deriving LCI data. In addition, the compositional data of pyrolysis gas and residue enable the calculation of their heating

values. These are required to assess their potential for energy recovery in subsequent side-product utilization (cf. Section 4.3).

4.2.1 Auger-type screw reactor

Netsch et al. conducted the experiments using an auger-type screw reactor (ASR) with the setup shown in Figure 15. The reactor was operated at a set temperature of 500 °C and a feedstock sample size of 5000 g.⁹¹ The feedstock was mixed with sand, which acts as a heat transfer medium, at a mass ratio of 4:1. The mixture was transported through the electrically heated reactor by a screw.

While the reactor was preheated to the set temperature, the sand was not preheated. Instead, it heated up together with the feedstock in the reactor's heating zone. Pyrolysis vapors were filtered in the reactor's freeboard and subsequently condensed in a series of condensers operating at 60 and 0 °C. The pyrolysis residue was collected together with the sand in a hopper at the end of the screw. Nitrogen was used as a flush gas to support the transport of pyrolysis vapors. Further details on the reactor setup are provided by Netsch et al.⁹¹ and Zeller et al.⁹⁴ All experimental data are summarized in Appendix A.

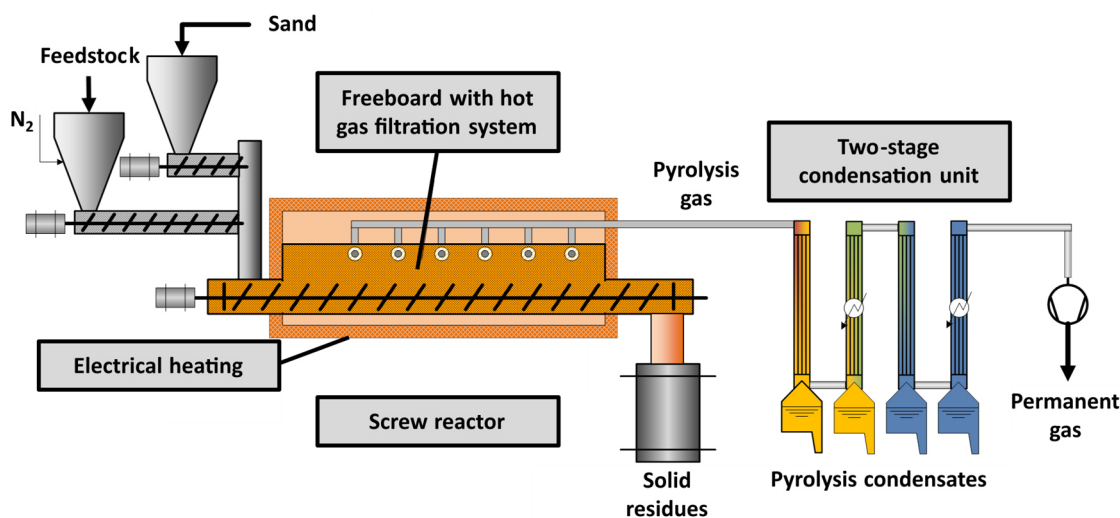


Figure 15: Experimental setup for plastic pyrolysis using an auger-type screw reactor. Adapted from Netsch et al.⁹¹, used under CC-BY 4.0 license.

The balancing of the ASR experiments shows generally good closure of the total mass balance. Errors range from -1 to 4 wt%, corresponding to a mass error between -60 and 195 g (cf. Figure 4, Figure 16, and Appendix B.1). Good closure is also observed for the elemental mass balances of C, H, and ash. In contrast, the elemental mass balances of N and Cl show significant deviations. Losses range up to 21 g for N and 90 g for Cl, corresponding to relative losses of 91% for N and 87% for Cl. The O balance shows a negative balance loss of up to -158 g, meaning that the O content in the pyrolysis products exceeds that in the feedstock. For Mix HH, this discrepancy can

be attributed to missing pyrolysis gas composition data. In this case, the gas composition from the corresponding STR experiment was used.

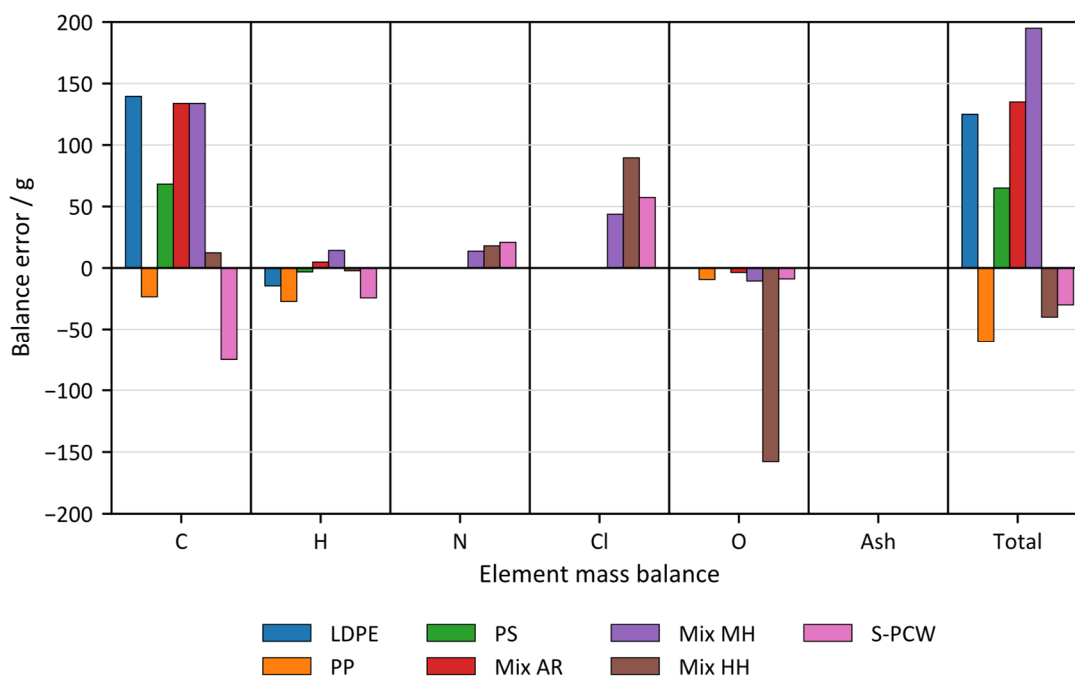


Figure 16: Absolute total mass and elemental mass balance errors of ASR experiments with 5000 g of model feedstock.

These errors arise from detection limits and limitations in identifying heteroatom-containing pyrolysis products. For N, only a limited number of N-containing compounds could be quantified in the gas-phase. In the pyrolysis oil, the detection limit for nitrogen prevented quantification below 2000 ppm.⁹¹ Despite low absolute errors, due to the low nitrogen content in the feedstocks, these limitations result in large relative deviations. For Cl, the main source of error is the uncertainty in quantifying hydrogen chloride (HCl), the primary decomposition product of PVC, in the pyrolysis gas (cf. Section 2.3.1).

The exceedance of the oxygen balance can be attributed to two factors. First, oxygen content in both feedstock and pyrolysis oil is determined by difference, which accumulates measurement inaccuracies in elemental analysis.⁹¹ Second, uncertainties arise from the characterization of pyrolysis gas. Not all gas components can be identified and quantified. Therefore, the gas composition is normalized, which leads to an overestimation of oxygen-containing species, mainly CO₂ and CO. As a result, uncertainties exist in both input and output quantities. This explains the larger deviations of the oxygen balance, despite the higher oxygen content compared to nitrogen and chlorine. In addition, dilution of the pyrolysis gas by N₂ flush gas complicates the quantification of low-concentration species.

For modeling the feedstock conversion in pyrolysis and generating the LCI data, minor adjustments are applied to improve mass balance closure. To ensure full closure of the total mass

balance, i.e., $\sum_i y_{i,pyr.} = 1$, the experimentally determined pyrolysis product distribution is slightly modified.

If $\sum_i y_{i,pyr.} < 1$, the balance loss is assigned to the pyrolysis residue fraction. This is justified by operational experience with the ASR, where not all residue and sand are always discharged from the reactor. If $\sum_i y_{i,pyr.} > 1$, all yields are normalized to avoid total yield exceeding 100%.

To address uncertainties in the chlorine balance, the balance loss is attributed to unquantified HCl in the pyrolysis gas. The gas composition is adjusted accordingly. This slightly affects the element balances of experiments involving heteroatom-containing feedstocks (Mix MH, Mix HH, and S-PCW), while other experiments remain unchanged (cf. Figure 17).

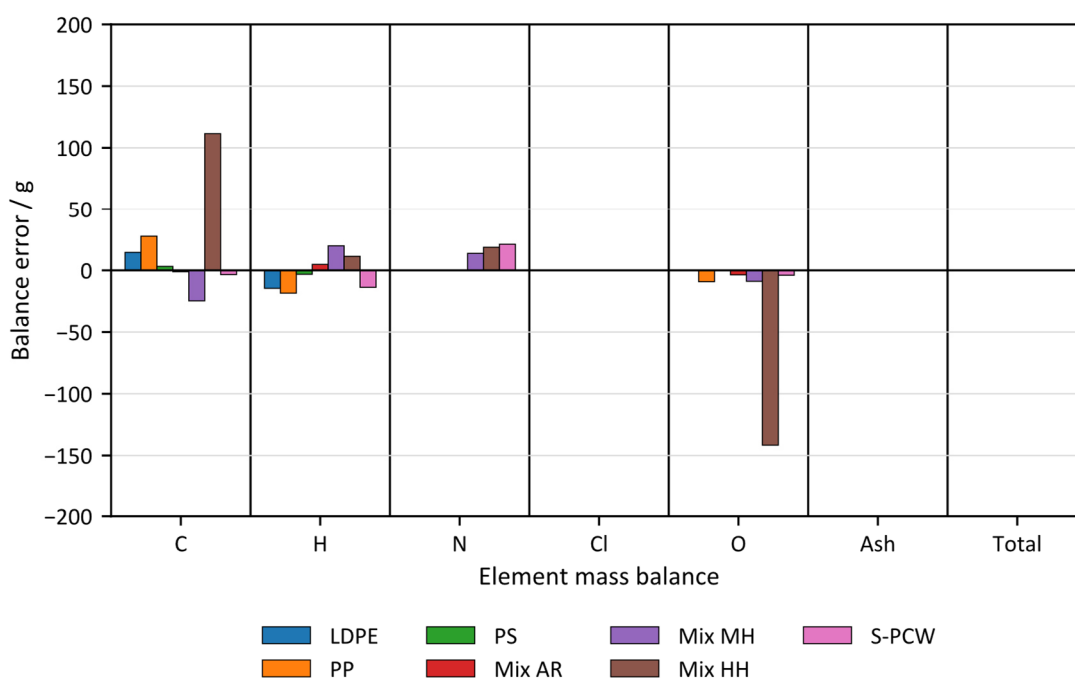


Figure 17: Absolute total mass and elemental mass balance errors of ASR experiments with 5000 g of model feedstock after correction of the pyrolysis data.

As a result, absolute and relative errors of most elemental mass balances are reduced. In particular, the carbon balance error falls within the range of -25 to 28 g, corresponding to $\pm 1\%$, except for Mix HH, where deviations remain due to the approximated gas composition. To avoid unaccounted carbon losses leading to an underestimation of climate change impact, in pyrolysis LCIs, any remaining carbon balance deficit is assumed to result in the equivalent emission of CO_2 .

The energy demand of the pyrolysis process is estimated based on the minimum energy demand measured by Netsch et al. during ASR experiments.¹¹² To account for additional energy requirements – such as heating the sand, auxiliary systems (e.g., pumps and cooling), and the

mechanical work required to drive the screw – the total electricity demand is assumed to be 200% of the reaction energy demand.

This assumption is consistent with values reported by ARCUS Greencycling Technologies for their thermally optimized double-screw reactor pyrolysis plant.¹⁹² The sensitivity of this assumption is evaluated in a dedicated sensitivity analysis (cf. Section 7.3). Complete LCIs are provided in Appendix D.

4.2.2 Stirred-tank reactor

For the experiments with the STR system, Netsch et al. used the reactor set-up shown in Figure 18. The electrically heated reactor consisted of a steel vessel filled with 2 kg of quartz sand. As in the ASR set-up, the sand improves heat transfer and mixing, supported by continuous stirring using an impeller. The experiments were conducted with a feedstock sample size of 250 g at a reactor wall temperature of 500 °C. Each experiment was performed in triplicate to ensure reproducibility.⁹¹

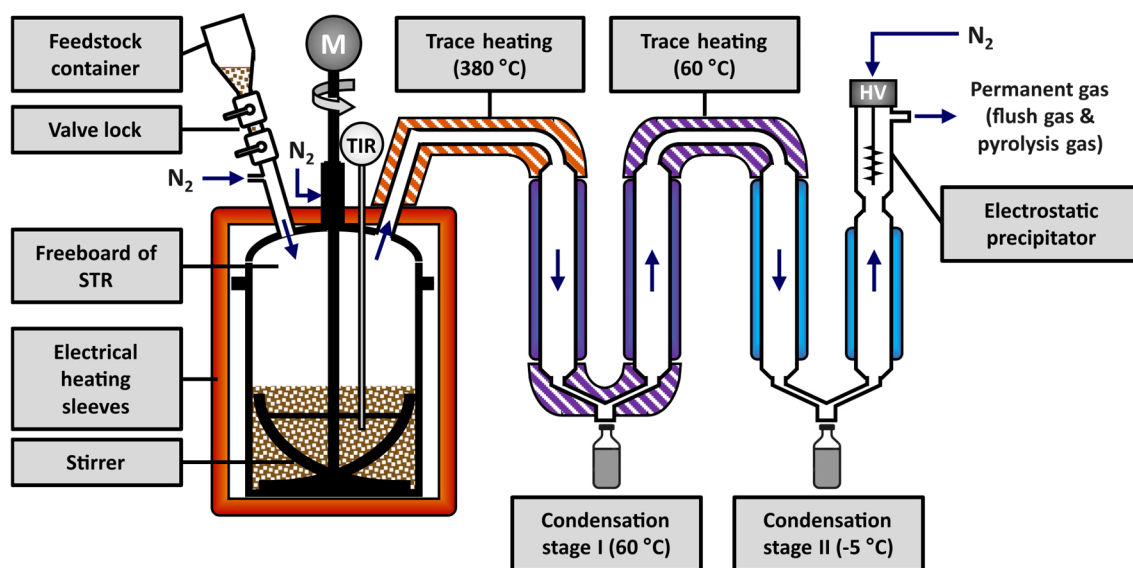


Figure 18: Experimental setup for plastic pyrolysis using a stirred-tank reactor. Adapted from Netsch et al.⁹¹, used under CC-BY 4.0 license.

The feedstock was added to the preheated vessel in five-minute intervals until the full sample was introduced. This approach was used to minimize the temperature drop in the sand bed caused by feedstock heating and the endothermic pyrolysis reaction.⁹¹ Nevertheless, temperature deviations of up to 96 °C below the reactor wall temperature were observed in the LDPE experiments. Across all experiments, the average deviation ranged between 30 and 50 °C.⁹¹

Pyrolysis oil was collected using two condensers operating at 60 and –5 °C, similar to the ASR setup. Nitrogen was used as a flush gas to transport pyrolysis vapors to the condensation unit.⁹¹ Further details on the experimental setup are provided by Netsch et al.⁹¹

A comparison of the total mass balances of the STR system with those of the ASR system shows perfect closure in all cases (cf. Figure 19 and Appendix B.1). However, this is a result of the method used to determine the pyrolysis gas yield. Netsch et al. calculated the gas yield by difference rather than by direct measurement.⁹¹ In addition, the repetitions of the STR experiments show greater variance than those of the ASR experiments. As a result, the calculated pyrolysis gas yields may be less accurate, since they depend on measurement uncertainties in the other product fractions.

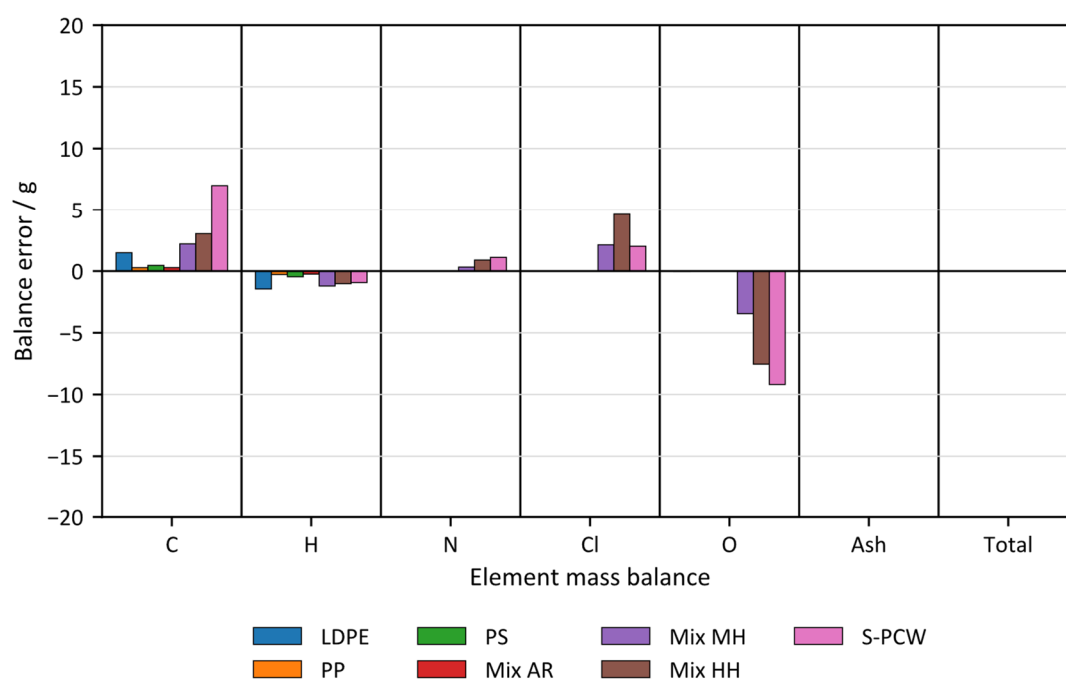


Figure 19: Absolute total mass and elemental mass balances errors of STR experiments with 250 g of model feedstock.

Despite the fully closed total mass balance, the elemental mass balances show trends similar to those observed for the ASR system with lower absolute errors due to the smaller sample size of STR experiments. The balances for C and H exhibit only small absolute and relative errors. In contrast, the balances for heteroatoms (N, Cl, and O) show larger deviations. The accuracy of the elemental mass balances generally decreases with increasing feedstock complexity, i.e., it is worst for the heteroatom-containing model feedstocks. This is likely due to the greater complexity of the resulting product mixtures, leading to greater difficulty in their reliable identification and quantification.

For the compilation of the STR LCI, the experimental data are adjusted in the same way as for the ASR system (cf. Figure 20). Since the total mass balance is already closed, the adjustments mainly improve the chlorine (Cl) element balance. After correction, the carbon mass balance errors range between < 1 and 9 g, corresponding to a relative error below 4%. While this

increases the error of the carbon balance slightly, the procedure for correcting the elemental mass balances is maintained for consistency with the ASR balances. Still, it is considered sufficiently accurate. Like in the ASR case, any remaining carbon loss is accounted for by assuming that it is emitted as CO₂.

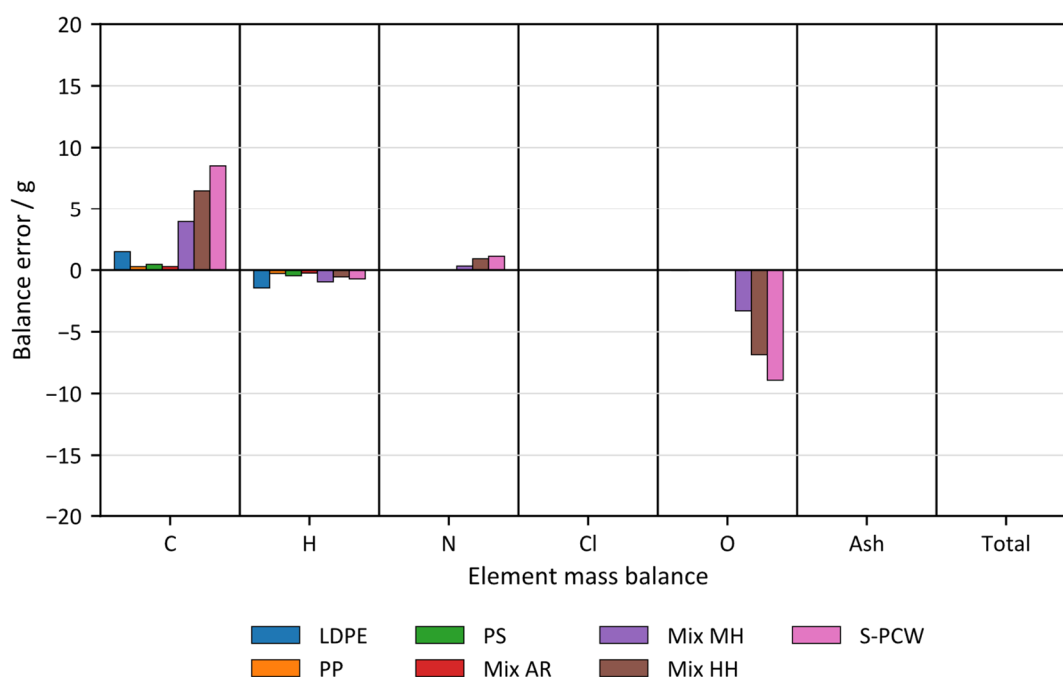


Figure 20: Absolute total mass and elemental mass balance errors of STR experiments with 250 g of model feedstock after correction of pyrolysis data.

The energy demand of the STR system was not measured experimentally. While the energy required for the pyrolysis reaction itself is expected to be comparable to that determined for the ASR system, the overall plant energy demand may differ. However, due to the lack of reliable data, the energy demand of the STR system is also estimated as 200% of the pyrolysis reaction energy demand.

4.3 Utilization of pyrolysis side products

Three scenarios are considered for the utilization of pyrolysis gas. The use of pyrolysis gas in a gas motor for the recovery of electricity and district heat serves as base case. Additionally, flaring of the pyrolysis gas and its use in EFG are evaluated as alternative utilization scenarios.

CO₂ emissions from pyrolysis gas combustion are calculated based on the gas compositions obtained from the balancing of the pyrolysis experiments. For electricity and district heat generation in the gas motor, an electrical efficiency of 34.5% and a thermal efficiency of 44.4%

are assumed. These values are based on efficiencies reported for conventional gas motors used in industrial combined heat and power (CHP) applications, as well as on the LHV of the pyrolysis gas.^{183,193}

Due to its carbon content, the pyrolysis residue cannot be landfilled. This restriction arises from regulatory limits for landfill disposal, which prohibit waste with a carbon content above 6 wt% and a heating value above 6 MJ/kg.¹⁹⁴ Therefore, the residue is treated in a conventional MSWI plant. Additionally, this allows the recovery of electricity and district heat. The incineration of pyrolysis residue is modeled in the same way as the incineration of the model feedstocks (cf. Section 4.1) based on the elemental composition of the respective pyrolysis residue.

4.4 Upgrading and steam cracking of pyrolysis oils

Steam cracker feedstocks must meet strict specifications regarding parameters such as boiling range, heteroatom content, and PIONA composition (cf. Section 2.4.1). Pyrolysis oils derived from mixed plastic feedstocks often deviate significantly from these specifications. As a result, further treatment is required.²⁴

Experimental data on the upgrading and subsequent steam cracking of pyrolysis oils from MPW are limited.¹⁹⁵ However, Yoon et al. and Neuner et al. demonstrated, as a proof of concept, that hydroprocessing can reduce heteroatom and olefin content. It can also lower the average boiling temperature.^{131,132}

The following sections describe the modeling approach used for upgrading pyrolysis oils and for their subsequent processing in a steam cracker.

4.4.1 Upgrading of pyrolysis oils

The upgrading of pyrolysis oil is based on established hydroprocessing methods for conventional petroleum fractions, such as desulfurization and denitrogenation via hydrotreating, followed by hydrocracking.³⁷ Typically, hydroprocessing consists of a hydrotreating reactor and a hydrocracking reactor, followed by a product recovery section. In the hydrotreating reactor, heteroatoms such as O, N, S, and Cl, as well as metals, are removed via hydrogenation. In addition, olefins are saturated. The subsequent hydrocracking reactor performs catalytic cracking of hydrocarbon chains, reducing their length and lowering the average boiling point. At the same time, aromatic compounds are saturated. The resulting product is then sent to the product recovery section, where light gases are separated from the liquid product and which is subsequently fractionated by distillation. Hydrogen is supplied in excess during hydroprocessing. To reduce overall hydrogen consumption, part of the hydrogen contained in the light gases is recovered and recycled to the process.³⁷

Since only limited data are available on the upgrading of plastic pyrolysis oils, the product yield, product distribution, and hydrogen demand are unknown. Therefore, the modeling approach

developed by Stallkamp et al. and Hennig et al. is applied to estimate product yields and hydrogen demand. Process energy demand is neglected, as the process is assumed to be exothermic, at least covering any thermal energy demands.^{178,183}

This approach is based on three main assumptions. First, all heteroatoms are completely removed during hydrotreating. Second, hydrocracking does not result in product loss, meaning that all carbon is recovered in the liquid product. Third, hydrogen demand can be estimated based on the composition of the raw pyrolysis oil and the targeted H/C ratio. The limitations arising from these assumptions are discussed in the context of sensitivity and scenario analyses (cf. Chapter 7).

Based on these assumptions, two variables are central to balancing the upgrading process: (1) the yield of upgraded pyrolysis oil $Y_{Upgr.oil}$ and (2) the specific total hydrogen demand $m_{H_2,total}$, defined as the hydrogen demand per unit mass of upgraded pyrolysis oil. Both variables can be derived from the total mass balance and the carbon and hydrogen element balances.

The yield of upgraded pyrolysis oil can be expressed as

$$Y_{Upgr.oil} = \left(\frac{HC_{Upgr.oil} \bar{M}_H}{\bar{M}_C} + 1 \right) x_{C,Py.oil} \quad (4.16)$$

This expression shows that the yield depends on the carbon content of the pyrolysis oil ($x_{C,Py.oil}$), the targeted molar H/C ratio of the upgraded pyrolysis oil $HC_{Upgr.oil}$, and the molar masses of carbon $\bar{M}_C$ and hydrogen $\bar{M}_H$. Assuming linear, saturated hydrocarbons, $HC_{Upgr.oil}$ is set to 2, similar to the molar H/C ratio of naphtha.^{115,118}

The specific total hydrogen demand $m_{H_2,total}$ is defined as

$$m_{H_2,total} = \frac{1}{\alpha_{H_2,Upgr.}} (m_{H_2,HT} + m_{H_2,HC}) \quad (4.17)$$

assuming a hydrogen utilization efficiency $\alpha_{H_2,Upgr.}$ of 70%.

The specific hydrogen demand for hydrotreating $m_{H_2,HT}$ is given by

$$m_{H_2,HT} = \sum_j x_{j,Py.oil} m_{H_2,j} \quad (4.18)$$

summing up the hydrogen demand $m_{H_2,j}$ for hydrogenating the respective mass fraction of the heteroatom $x_{j,Py.oil}$ in the pyrolysis oil.

The specific hydrogen demand for hydrocracking $m_{H_2,HC}$ is calculated as

$$m_{H_2,HC} = \left(\frac{HC_{Upgr.oil} \bar{M}_H}{\bar{M}_C} \right) x_{C,Py.oil} - x_{H,Py.oil} \quad (4.19)$$

This expression depends on the carbon and hydrogen content of the pyrolysis oil, as well as the targeted H/C ratio.

Detailed derivations of the equations for product yield and hydrogen demand are provided in Appendix B.2. The sensitivity of the yield and the targeted H/C ratio is analyzed in dedicated sensitivity analyses (cf. Section 7.4).

4.4.2 Steam cracking of upgraded pyrolysis oils

In line with the assumptions made by Stallkamp et al. and Hennig et al., the steam cracking of upgraded pyrolysis oils is modeled assuming properties similar to those of conventional naphtha.^{178,183} Accordingly, the mass and energy balances are based on those of naphtha steam cracking. Since all pyrolysis oils are assumed to have identical properties after upgrading, the resulting mass and energy balances are not specific to individual feedstocks. Instead, they are applied uniformly to all upgraded pyrolysis oils.

Steam cracking of naphtha produces a wide range of products. These are categorized into main products and additional products following the allocation approach recommended by PlasticsEurope.¹⁹⁶ The main products – hydrogen, ethylene, propylene, butenes, butadiene, and parts of the pyrolysis gasoline – are considered base chemicals. The additional products are used as fuels. Consequently, the carbon contained in the fraction of pyrolysis oil converted into fuel products is not considered recycled.⁴⁷

For the LCI, several parameters are required. These include the product yields $Y_{SC,k}$, the carbon yield of products with material use $X_{SC,material}$ and the carbon yield of products for fuel use $X_{SC,fuel}$. In addition, all technosphere and biosphere flows must be determined, including energy demand and CO₂ emissions (cf. Section 2.6.1).

The product yields of every steam cracker product k are taken directly from literature values for naphtha steam cracking, as summarized in Table 7. The carbon yields are calculated from the carbon mass balance of the steam cracker.

For the calculation of $X_{SC,material}$, only products classified as material use in Table 7 are considered. The carbon yield is then calculated based on the product yields $Y_{SC,k}$, their carbon content $x_{C,k}$ and the carbon content of naphtha $x_{C,Naphtha}$.

$$X_{SC,material} = \frac{\sum_k Y_{SC,k} x_{C,k}}{x_{C,naphtha}} \quad (4.20)$$

Table 7: Product distribution and product utilization in naphtha steam cracking based on Stallkamp et al.,¹⁸³ Zimmermann and Walzl,¹¹⁸ and Dellenbach and Fröhlich.¹⁹⁷

Steam cracker product	Product use	Steam cracker product yield $Y_{SC,k}$, wt.%
Hydrogen	Material	1
Ethylene	Material	30
Propylene	Material	15
Butenes	Material	5
Butadiene	Material	5
Pyrolysis gasoline [°]	Mixed	20
Fuel oil	Fuel	4
Fuel gas for export	Fuel	3
Fuel gas burnt in furnace	Fuel	17

In the case of pyrolysis gasoline, the content of benzene, toluene, and xylene are counted as material use, while the remainder is assigned to fuel use.

The carbon yield of fuel products $X_{SC,fuel}$ is calculated analogously, considering only products classified as fuel use. The resulting carbon distribution for steam cracking of naphtha is shown in Appendix B.3 and is assumed to be valid for the steam cracking of upgraded pyrolysis oil as well.

Technosphere and biosphere flows for the steam cracking process are derived from ecoinvent datasets of steam cracker products.^{197–204} These datasets already contain the required flows. However, they are product-based, meaning that they use 1 kg of a given steam cracker product as the functional unit. To obtain input-based technosphere and biosphere flows, the allocation rules and overall product distribution must be considered. While the allocation rules are provided in the datasets, the overall product distribution is not explicitly documented. Therefore, the product distribution given in Table 7 is applied.

The input-based technosphere flows $TF_{SC,input,m}$ are calculated by weighting the product-based technosphere flows $TF_{SC,product,k,m}$ with the corresponding yields $Y_{SC,k}$. Feedstock-related flows, such as naphtha input, are excluded.

$$TF_{SC,input,m} = \sum_k Y_{SC,k} TF_{SC,product,k,m} \quad (4.21)$$

The input-based biosphere flows $BF_{SC,input,n}$ are calculated analogously for all biosphere flows n . Due to the confidentiality of the underlying datasets, the reconstructed input-based dataset cannot be provided.

[°] Including benzene, toluene, and xylene for material use

To assess the sensitivity of the steam cracking model to variations in product distribution, two additional scenarios are considered. These represent alternative yield structures that may arise if upgraded pyrolysis oils behave differently from naphtha. The scenarios are based on steam cracking of two high-boiling fossil feedstocks: atmospheric gas oil (AGO) and hydrocracker residue (HCR). The development of these datasets is described in Appendix B.3.

4.5 Entrained-flow gasification of pyrolysis oils

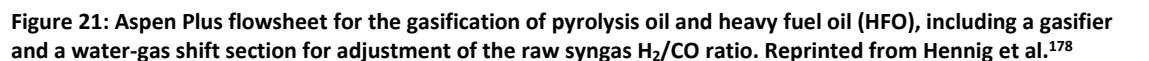
The EFG of pyrolysis oil is modeled using the process simulation software Aspen Plus V14 (version 40.0.0.359).²⁰⁵ The overall process model is split into two sections: The first comprises the gasification reactor, high-temperature heat recovery, and the subsequent adjustment of the H_2/CO ratio required for either MeOH or Oxo syngas in a WGS stage. The second represents the downstream syngas cleaning process for the removal of undesired gas components. The following sections describe the development of the gasification (cf. Section 4.5.1) and gas cleaning models (cf. Section 4.5.2). A comprehensive model description and validation against industrial EFG data are provided in Appendix B.4. Model calculations are performed in the MeOH syngas configuration for all pyrolysis oils, with HFO as reference feedstock for conventional EFG syngas generation, and bitumen used for model validation. Calculations in the Oxo syngas configuration are carried out only for selected pyrolysis oils for the assessment of different syngas configurations.

4.5.1 Gasifier model

The gasifier model shown in Figure 21 is based on a Texaco-type entrained-flow reactor employing a refractory-lined reaction chamber combined with a syngas cooler for recovery of high-temperature heat for steam generation.³⁹ As near-complete gasifier feedstock conversion is desired and the formation of tar and methane must be minimal, EFG-type gasifiers are typically operated at temperatures between 1250 and 1450 °C, ensuring the generation of a high-quality syngas.^{38,39} At such temperatures, the raw syngas composition approaches chemical equilibrium.^{39,206} Accordingly, in the model a chemical equilibrium-based approach is used to determine the gas-phase composition by minimization of the total Gibbs free energy.

Overall, the Peng-Robinson equation of state with the Boston-Mathias alpha function is used for the calculation of thermodynamic properties, which is suitable for nonpolar and mildly polar mixtures such as CO_2 , H_2S , CO , and H_2 .²⁰⁵ Pressure drops and heat losses are neglected unless stated otherwise.

The model calculations require the determination of the oxygen-to-fuel ratio and steam-to-fuel ratio for the maximization of the syngas yield. The optimal settings are determined via process optimization for a minimum reactor temperature of 1350 °C (cf. Appendix B.4.1.3). Full carbon conversion to syngas species (CO , CO_2 , CH_4) is permitted, provided that no soot formation is predicted by equilibrium calculations; therefore, no inert carbon fraction is defined ex ante.


$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} > 2 \quad (4.22)$$

A simplified heat integration is performed based on pinch analysis to determine minimum heating and cooling requirements according to Yang et al.²⁰⁷ Any surplus heat available above 150 °C is assumed to be convertible to district heat (cf. Appendix B.4.3). Electricity generation from excess heat via a steam cycle is not considered. Water scrubbing for the removal of trace components (e.g., HCN, HCl, NH₃) as well as dissolution of syngas components in the aqueous condensate phase are neglected. Despite these simplifications, the model shows close agreement with industrial data from EFG in terms of syngas composition and carbon-to-syngas conversion. Previously conducted sensitivity analyses regarding reaction temperature and carbon conversion confirmed the robustness of the modeling approach.¹⁷⁸

4.5.2 Gas cleaning model

The raw syngas is conditioned to meet the composition requirements of downstream MeOH or Oxo synthesis. This requires removal of CO₂ and elimination of impurities that act as catalyst poisons. In gasification-based applications, physical absorption processes using methanol as solvent are widely applied for syngas purification, commonly known as the Rectisol process, licensed by Linde and Lurgi/Air Liquide.^{144,208} In this work, Rectisol scrubbing is chosen as technology for gas cleaning, following the modeling approach reported by Gatti et al.¹⁴⁵

The process configuration allows selective CO₂ desorption (cf. Appendix B.4.2), provided that the CO₂ partial pressure in the raw syngas is sufficiently high. In the case of MeOH syngas production, separate recovery of CO₂ and a concentrated sour gas stream suitable for sulfur recovery from H₂S is therefore feasible. In contrast, for Oxo syngas production, the CO₂ desorption columns are bypassed due to the lower CO₂ loading of the raw syngas, which prevents selective desorption.

In contrast to the gasifier model, thermodynamic properties in the Rectisol section are calculated using the PC-SAFT equation of state to include liquid-phase molecular interactions.^{145,209} These are described using activity coefficients reported by Gatti et al.¹⁴⁵

5 Product yields and carbon recovery

Following the model development for balancing the different process routes, this chapter presents the results of the mass and energy balances developed for modeling and assessing the pyrolysis-based chemical recycling routes and the reference waste treatment process of energy recovery. Product yields and energy efficiencies of the different process steps are analyzed with respect to the influence of feedstock composition. First, results for the reference waste treatment route – incineration with energy recovery – are presented. Next, the results of the individual process steps of the pyrolysis-based chemical recycling routes are summarized. Finally, the results for the full process chains are analyzed.

5.1 Energy recovery

Energy recovery generates electricity and district heat as products. It is currently the dominant waste treatment technology for non-recyclable plastic waste. In the simplified energy recovery model used in this thesis (cf. Section 4.1), electricity and district heat are recovered with fixed electrical and thermal efficiencies of 14.3% and 39.1%, respectively, independent of feedstock composition. Consequently, the amounts of electricity and district heat recovered from incineration depend solely on the LHV of the model feedstocks. Accordingly, LDPE and PP yield the highest amounts of electricity and district heat per unit mass. These are followed by the PS-containing model feedstocks (PS and Mix AR), and finally by the heteroatom-containing model feedstocks (Mix MH, Mix HH, and S-PCW), as shown in Figure 22.

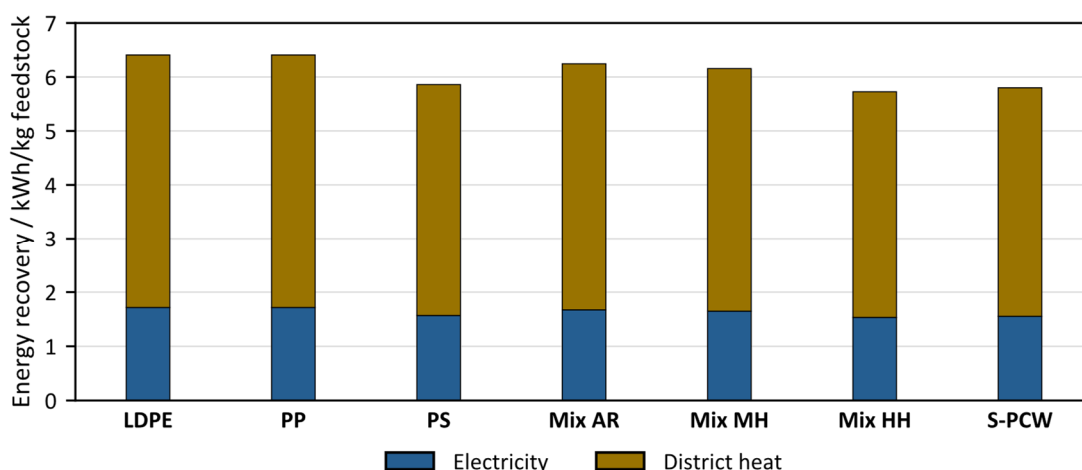


Figure 22: Recovery of electricity and heat from energy recovery of model feedstocks.

The heteroatom-free model feedstocks PS and Mix AR yield less energy than LDPE and PP. This is due to their lower molar H/C ratio and, consequently, lower LHV, despite the absence of heteroatoms. The heteroatom-containing model feedstocks (Mix MH, Mix HH, and S-PCW) yield the

lowest energy. This is because heteroatoms either contribute less to the LHV (nitrogen and sulfur) or reduce it (oxygen).

During incineration, all carbon is converted to CO₂ and released into the atmosphere. Therefore, mass-specific CO₂ emissions depend solely on the carbon content of the feedstock. As a result, PS exhibits the highest emissions, while S-PCW shows the lowest (cf. Figure 23).

When evaluated from an energy perspective, the results differ slightly. In this case, CO₂ emissions per unit of recovered energy are considered. Despite their higher carbon content, LDPE and PP exhibit lower energy-specific CO₂ emissions than the heteroatom-containing model feedstocks. Regardless of the feedstock, energy recovery does not result in carbon recycling, as no carbon from the feedstock is retained in material products.

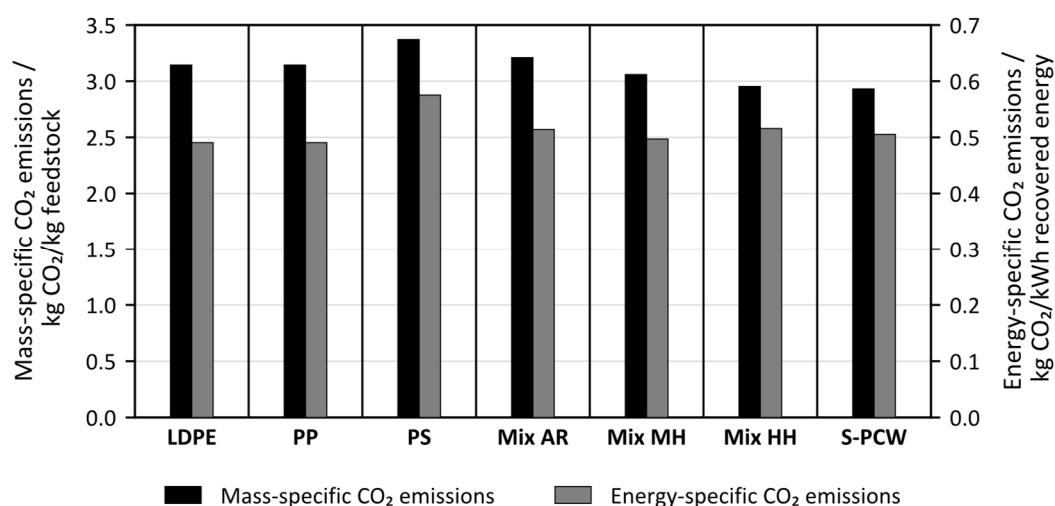


Figure 23: CO₂ emissions from energy recovery per kilogram of feedstock and per recovered energy.

As the LHV of plastic waste substantially exceeds that of MSW, electrical and thermal conversion efficiencies higher than the average values reported by the ITAD and used within this study can be expected, if waste plastics are incinerated by themselves.⁶⁹ This is because high-calorific, low-moisture fuels generally enable more efficient energy recovery than conventional MSW.²¹⁰ However, most MSWI plants are designed for a waste LHV in the range of 8.5 to 14 MJ/kg.⁷¹ Therefore, waste entering MSWI plants is mixed to homogenize its properties to compensate for increased heat flux, prevent excessive temperatures on the grate and in the boiler, and maintain plant throughput. (cf. Section 2.2.2).^{71,211} The higher LHV of plastic waste therefore does not necessarily translate into more efficient energy recovery but may reduce the input of auxiliary fuels that would otherwise be needed to incinerate low-calorific MSW. Accordingly, while the climate change impact of waste plastic incineration is underestimated using the average efficiencies of MSWI plants, in combination with the lower-calorific MSW that is incinerated alongside the waste plastics, it is considered representative of the current situation in Germany.

5.2 Pyrolysis yields of model feedstocks

In the pyrolysis-based chemical recycling process chains, the conversion of model feedstocks to pyrolysis oil represents the first process step. Using the balancing methodology outlined in Section 4.1, carbon yields and carbon distributions are calculated.

Figure 24 compares the calculated carbon distribution with the overall product distribution for each feedstock and reactor system. The influence of feedstock composition and reactor system on product distribution, as discussed by Netsch et al. (cf. Section 2.3.2), is clearly visible.⁹¹ Differences in pyrolysis oil yields between the reactor systems are primarily observed for the heteroatom-free model feedstocks (LDPE, PP, PS, Mix AR). For example, in the conversion of PP, the STR yields 71.3% pyrolysis oil whereas the ASR system reaches only 48.5%. The highest yields are achieved for PS, with 98.5% for the STR and 88.5% for the ASR. Netsch et al. attribute the lower pyrolysis oil yields of the ASR system to more pronounced cracking reactions, leading to an increase of pyrolysis gas yield at the cost of pyrolysis oil yield.⁹¹

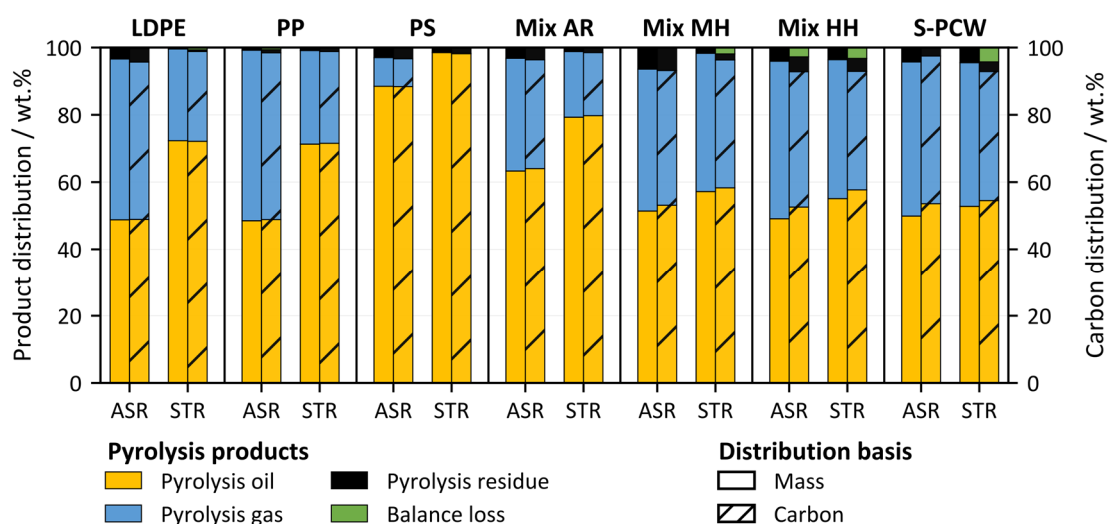


Figure 24: Product distribution and calculated carbon distribution of pyrolysis experiments by feedstock and reactor type, based on data from Netsch et al.^{91,112}

For the heteroatom-containing feedstocks, these differences decrease significantly. Pyrolysis oil yields are reduced for both reactor systems. For example, in the case of S-PCW, the STR yields 52.8% pyrolysis oil compared to 49.9% for the ASR. Netsch et al. attribute the similarity in yields for heteroatom-containing feedstocks to increased feedstock interactions.⁹¹ For the STR, this decrease in yield is already noticeable for Mix MH, which contains fewer heteroatoms than the other heteroatom-containing feedstocks. With increasing heteroatom content, yields decrease further, although only slightly for both reactor types. Even though S-PCW is the only feedstock consisting of EoL plastics, in contrast to the other model feedstocks composed of virgin polymers, no deviations attributable to the different material type can be observed.

At the same time, for most feedstocks, the carbon distribution closely follows the overall product distribution. Accordingly, the highest carbon recoveries, i.e., the share of carbon transferred to the pyrolysis oil, are achieved for PS, with 98.2% for the STR and 88.4% for the ASR. This indicates that the carbon content of the pyrolysis products is largely proportional to their mass yield. Thus, for the single-polymer feedstocks LDPE, PP, and PS, as well as Mix AR, the carbon fraction in each pyrolysis product closely matches its mass yield.

Again, for the heteroatom-containing feedstocks Mix MH, Mix HH, and S-PCW, the overall carbon recovery decreases in line with the pyrolysis oil yield. At the same time, a slight enrichment of carbon in the pyrolysis oil is observed. This is reflected by a higher share of carbon in the oil than its mass fraction. For S-PCW, for instance, 54% of the feedstock carbon is contained in the pyrolysis oil, while the oil mass fraction is only 50%.

This enrichment is accompanied by the removal of heteroatoms from the feedstock. During pyrolysis, 64 – 89% of heteroatoms by weight are transferred to the pyrolysis gas. By comparison, for the heteroatom-containing model feedstocks, only 53 – 58% of the carbon is recovered in the pyrolysis oil. Thus, heteroatom removal appears to be more selective than carbon recovery.

This behavior can be explained by the underlying pyrolysis mechanisms (cf. Section 2.3.1). For example, Cl is largely released into the gas phase as incondensable HCl.^{102–104} In contrast, N and O exhibit less selective behavior, forming a variety of heteroatom-containing condensable and incondensable compounds that partition between the pyrolysis gas and oil.^{91,106} Still, heteroatoms are preferentially released to the gas phase as low-molecular-weight, incondensable compounds containing heteroatoms, along with short-chain hydrocarbons. While the latter contribute to carbon loss, the former enhance heteroatom removal.

This effect is observed in both reactor systems, as shown in Figure 25, which summarizes carbon recovery in pyrolysis oil and heteroatom removal efficiency. Heteroatom removal efficiencies are generally higher in the ASR system. However, the removal efficiency decreases slightly with increasing heteroatom content as indicated by the higher removal efficiency for Mix MH compared to Mix HH. Still, the removal of heteroatoms occurs at the expense of lower carbon recovery for all model feedstocks.

Accordingly, pyrolysis in chemical recycling serves two purposes: (1) converting solid plastic waste feedstock into liquid, processable pyrolysis oil and (2) simultaneously remove heteroatoms as efficiently as possible. For heteroatom-free feedstocks, carbon losses during conversion to pyrolysis oil should be minimized, i.e., pyrolysis oil yield should be maximized. Consequently, the lower pyrolysis oil yield observed for the ASR system for heteroatom-free feedstocks can be interpreted as overcracking, resulting in reduced carbon yield and a lower H/C ratio of the pyrolysis oil (cf. Figure 25 and Appendix A). For heteroatom-containing feedstocks, both carbon recovery and heteroatom removal must be considered in parallel. However, it remains unclear whether these objectives can be optimized simultaneously or whether they represent competing process objectives.

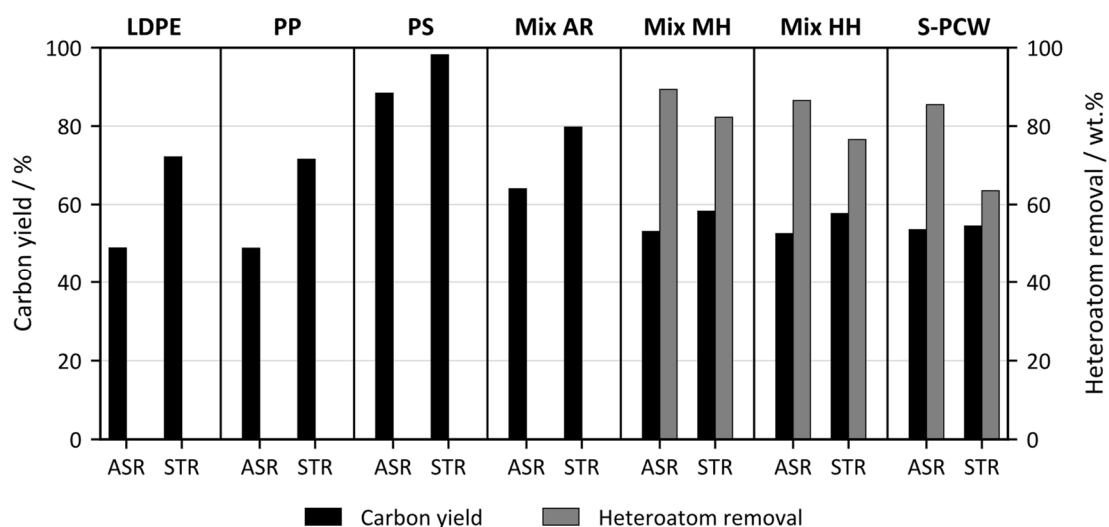


Figure 25: Carbon recovery in pyrolysis oil and heteroatom removal efficiency, based on data from Netsch et al.^{91,112}

In summary, the reactor concept and its inherent effects on reaction conditions mainly influence carbon recovery for heteroatom-free feedstocks. For heteroatom-containing feedstocks, only minor differences are observed. In these cases, interactions between different plastics seem to play a greater role than reactor effects. However, these interactions also limit the amount of carbon that can be recovered in the pyrolysis oil.

5.3 Upgrading and steam cracking

The conversion of raw pyrolysis oil in the waste-to-monomers process route consists of upgrading to steam cracker feedstock, followed by steam cracking. Figure 26 compares the product yields and hydrogen balance for pyrolysis oils derived from the model feedstocks using ASR and STR systems. The products are differentiated into steam cracker products for material and fuel use and hydrogen from steam cracking. The difference from 1 kg/kg corresponds to the combustion of fuel gas in the steam cracker furnaces (cf. Appendix B.3). As hydrogen is also required as input to pyrolysis oil upgrading, the hydrogen balance is further distinguished into hydrogen recycled to pyrolysis oil upgrading (stippled hatch), surplus hydrogen available as a product (no hatch), and – where the hydrogen generated by steam cracking is insufficient – hydrogen imported to satisfy the hydrogen demand of pyrolysis oil upgrading (cross-hatched).

For most pyrolysis oils, yields fall within a narrow range. Steam cracker product yields for material use lie between 0.64 and 0.68 kg/kg pyrolysis oil, while yields for fuel products range from 0.15 to 0.16 kg/kg. Higher yields are observed for pyrolysis oils derived from feedstocks with high PS content, namely PS and Mix AR. For PS, yields reach 0.71 kg/kg for material products and 0.17 kg/kg for fuel products. Additionally, pyrolysis oils derived from ASR achieve slightly higher yields than those from STR.

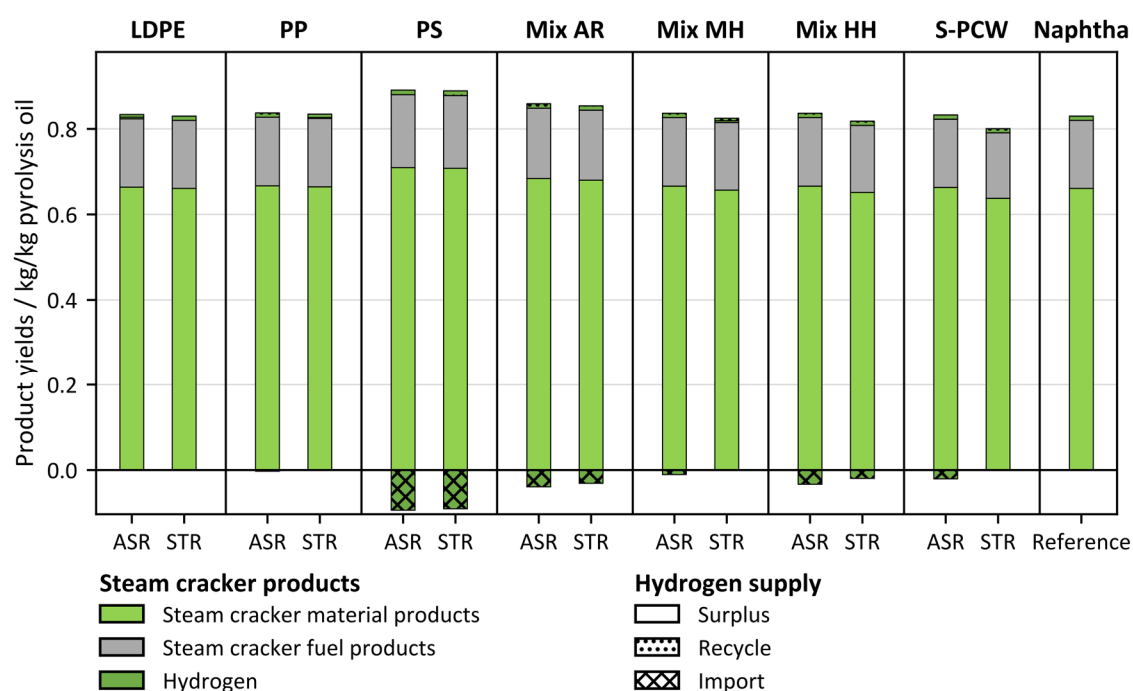


Figure 26: Product yields and hydrogen supply of upgrading and steam cracking for pyrolysis oils from model feedstocks.

H₂ produced from steam cracking is only a minor product and therefore largely recycled to the upgrading process. Only pyrolysis oils derived from LDPE, as well as from PP and Mix MH in the STR system, generate sufficient hydrogen to fully cover upgrading demand. In most cases, H₂ is therefore not available as an additional product.

Product yields correlate directly with the carbon content of the pyrolysis oils (cf. Figure 27, left), explaining the observed differences between pyrolysis oils from ASR and STR. This behavior results from two modeling assumptions (cf. Section 4.4): (1) no carbon loss during upgrading and (2) PIONA composition-independent steam cracking yields, representing a major simplification due to unavailability of applicable data. Consequently, higher carbon content in the raw pyrolysis oil directly translates into higher yields of steam cracker products for both material and fuel use. For the same reason, carbon recovery is identical for all pyrolysis oils, with 67.8% allocated to products with material use and 16.6% to products with fuel use.

For Mix AR and, more pronounced, for PS, product yields increase with hydrogen deficiency. H₂ addition during upgrading increases the mass of the pyrolysis oil, thereby increasing mass-based steam cracking yields.

H₂ demand, i.e. recycled and imported H₂, correlates with the molar H/C ratio of the pyrolysis oils (cf. Figure 27, right). Lower H/C ratios result in higher hydrogen demand. This demand is dominated by hydrogen deficiency rather than by heteroatom removal.

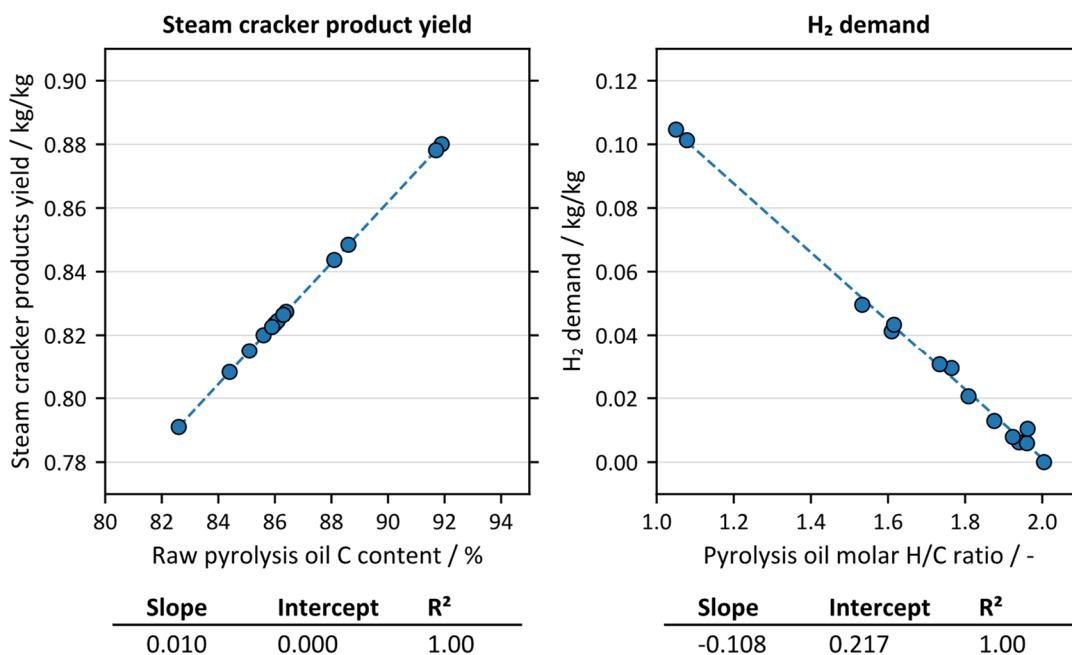


Figure 27: Correlation of steam cracker product yield (sum of material and fuel use products) with pyrolysis oil carbon content (left) and correlation of H₂ demand with pyrolysis oil molar H/C ratio (right).

Calculated H₂ demands range from less than 1% of the input pyrolysis oil mass for LDPE and PP-derived oils to 4% for oils derived from heteroatom-containing feedstocks such as Mix MH and Mix HH. These values are consistent with hydrogen requirements reported for conventional refinery hydroprocessing units but lower than those assumed by Steegborn et al.^{31,212}

For pyrolysis oils derived from Mix AR and especially PS, H₂ demand increases substantially. Up to 10% of the oil mass is required due to strong hydrogen deficiency, with H/C ratios below 1.6 (Mix AR) and 1.1 (PS). Accordingly, H₂ supply for upgrading in these cases largely depends on external sources rather than on internal recycling.

Recent work by Abdulrahman et al. provides initial experimental results on the steam cracking of hydrotreated pyrolysis oil fractions.¹³⁰ Yields of up to 77% steam cracker products for material use were derived from a blend of a hydrotreated diesel-range cut from pyrolysis of MPO, similar to the DSD 323 sorting fraction, with fossil naphtha. This is comparable to the yield of 76% assumed in this study. In addition, Abdulrahman et al. observed increased yields of ethylene and propylene in comparison to fossil naphtha.¹³⁰ For untreated pyrolysis oils, both higher and lower product yields have been reported relative to conventional naphtha.^{115,213}

Due to their exceptionally high aromatic content, PS-derived pyrolysis oils would require substantially more severe hydroprocessing conditions and hydrogen consumption than polyolefin-derived oils to achieve complete aromatic saturation.³⁷ Consequently, complete aromatic saturation is unlikely to represent a technologically and economically viable industrial upgrading strategy.

Validation of the calculated product yields and hydrogen demand remains limited due to the lack of experimental data. In addition, the modeling approach does not account for differences in PIONA composition of the upgraded pyrolysis oils. Accordingly, variations in product yields between different feedstocks, as well as deviations from the modeled values, are expected.^{214,215}

A sensitivity analysis was performed by varying the steam cracker product distribution based on steam cracking of high-boiling refinery cuts, namely AGO and HCR.¹¹⁸ Changes in product distribution primarily shift carbon between products for material and fuel use, while the amount of carbon converted to CO₂ remains largely unchanged (cf. Appendix B.3). Additional sensitivities regarding hydrogen demand and overall yield are discussed in Sections 7.4 and 7.5, addressing the potential loss of products associated with upgrading and steam cracking.

Based on this model and the underlying assumptions, a higher carbon content of pyrolysis oils leads to higher product yields in upgrading and steam cracking. This favors pyrolysis oils derived from LDPE, PP, PS, and Mix AR over those with higher heteroatom content. Also, pyrolysis oils from ASR perform better than pyrolysis oils from STR. At the same time, pyrolysis oils with low H/C ratios require significantly higher hydrogen input for upgrading.

5.4 Entrained-flow gasification

The second option analyzed within this work – the conversion of pyrolysis oils to syngas via EFG – does not require prior upgrading. Two configurations were modeled, differing in the syngas cleaning. The MeOH syngas configuration produces a hydrogen-rich syngas suitable for subsequent conversion to MeOH. The Oxo syngas configuration generates a syngas rich in CO for use in various specialty chemicals applications. Both process variants were modeled based on a thermodynamic flowsheet model described in Section 4.5.

5.4.1 MeOH syngas configuration

The conversion of pyrolysis oil into MeOH syngas shows only minor variations in product yields and side product generation across the different pyrolysis oils. MeOH syngas yields range from 1.37 to 1.51 kg/kg pyrolysis oil, while district heat generation ranges from 1.15 to 1.43 kWh_{th}/kg pyrolysis oil for PS and LDPE-derived pyrolysis oils, respectively (cf. Table 8, full table available in Appendix C.2).

The CGE varies between 81.7 and 82.3%, with a total variation between pyrolysis oils below 1%. In contrast, the carbon yield shows a wider variation, ranging from 54.4% (PS, ASR) to 64.4% (LDPE, STR). Differences between pyrolysis oils derived from the same feedstock using the ASR or STR are generally small. Compared to EFG of conventional HFO, pyrolysis oils from all model feedstocks achieve slightly higher MeOH syngas yields, with the exception of PS-derived oil.

Detailed analysis shows a correlation between specific syngas yield and pyrolysis oil LHV, with higher LHVs resulting in higher syngas yields (cf. Figure 28). Similarly, the carbon yield increases

with increasing molar H/C ratio. The CGE does not show a strong correlation with either parameter.

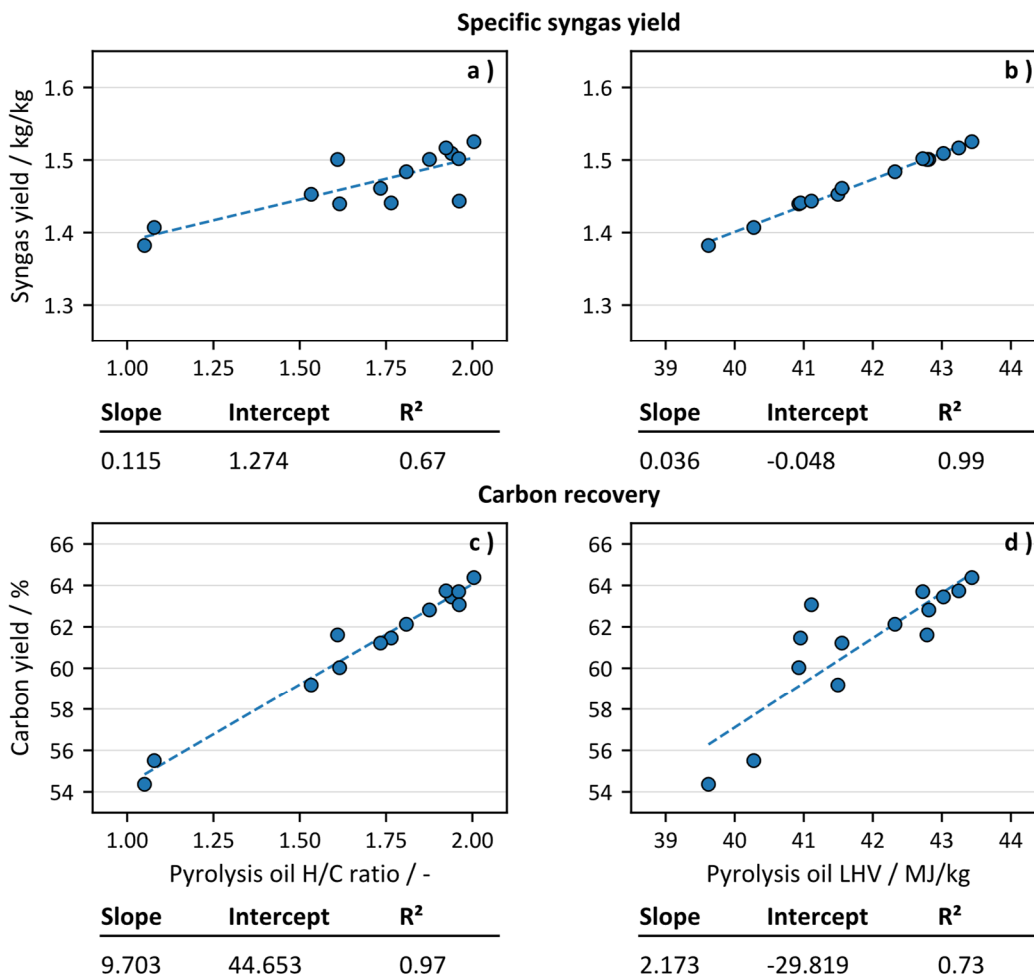


Figure 28: Correlations of EFG efficiency indicators with plastic pyrolysis oil parameters LHV and molar H/C ratio.

The increase in syngas yield with increasing LHV is consistent with literature. Gasification is an endothermic process, and the required energy is supplied by partial oxidation of the feedstock. A higher pyrolysis oil LHV therefore reduces the fraction of fuel that must be oxidized to provide the necessary reaction enthalpy, leaving more feedstock available for conversion into syngas.³⁹ The weaker correlations of CGE with both pyrolysis oil H/C ratio and LHV result from the narrow range of pyrolysis oil LHVs and optimization for maximum syngas yield rather than for maximum CGE, allowing greater variation.

The correlation between carbon yield and the molar H/C ratio results from the H₂/CO ratio required for downstream MeOH synthesis. As oils with lower H/C ratios produce more hydrogen-deficient syngas, the composition of raw syngas depends primarily on the elemental composition of the pyrolysis oil. In the WGS reactor, H₂ is generated at the expense of CO₂ formation

from CO to adjust the H₂/CO ratio. This leads to carbon losses and thus a lower carbon recovery from pyrolysis oils with lower H/C ratio.³⁹

In addition, the higher steam demand for the WGS reaction reduces the amount of district heat that can be recovered from the hot syngas in the syngas cooler. The higher syngas yields and CGEs compared to HFO gasification can be attributed to the lower carbon content and higher sulfur content of HFO, which reduce overall conversion efficiency.

Table 8: Process conditions, process efficiencies, and product yields for EFG of selected ASR and STR pyrolysis oils and HFO for MeOH syngas generation.

Model feedstock pyrolysis oil		PP		PS		S-PCW		HFO
	Reactor type	ASR	STR	ASR	STR	ASR	STR	Reference
Gasifier conditions								
Gasifier temperature	°C	1350	1350	1350	1350	1350	1350	1350
Oxygen input	kg O ₂ /kg feedstock	1.16	1.15	1.04	1.01	1.11	1.12	1.00
Steam input	kg H ₂ O/kg feedstock	0.20	0.23	0.34	0.39	0.18	0.18	0.34
Stoichio-metric ratio	-	0.34	0.34	0.34	0.33	0.34	0.34	0.32
Syngas product parameters								
SN MeOH syngas	-	2.02	2.02	2.02	2.02	2.02	2.02	2.02
LHV syngas	MJ/kg	23.4	23.4	23.4	23.4	23.4	23.3	23.2
Process efficiency parameters								
Specific syngas yield	kg syngas/kg fuel	1.49	1.50	1.37	1.40	1.44	1.43	1.40
Cold gas efficiency	%	82.1	82.1	81.7	81.8	82.2	81.9	80.8
Carbon yield ^P	%	62.8	63.7	54.4	55.5	58.4	60.2	60.2
Power demand and district heat generation								
District heat	kWh _{th} /kg feedstock	1.40	1.42	1.15	1.16	1.33	1.38	1.24
Power demand	kWh _{el} /kg feedstock	0.89	0.88	0.83	0.81	0.86	0.86	0.80

^p Including CO₂ contained in MeOH syngas

EFG of plastic-derived pyrolysis oils has been demonstrated experimentally at semi-industrial scale at the Karlsruhe Institute of Technology (KIT) in the Carbon Cycle Lab as a proof-of-concept, although detailed data are not yet available.¹³⁸ Weiland et al. conducted lab-scale EFG experiments using PP-derived pyrolysis oil.²¹⁶ They reported a lower carbon efficiency of 74% and a lower CGE of 60% in comparison to those calculated in this study. Nevertheless, they expect significantly higher yields and efficiencies at industrial scale, as represented by the present flow-sheet model.

Compared to the EFG model by Rößger et al., the calculated carbon recovery is slightly higher, which can be attributed to lower gasification temperatures and different assumptions regarding gas cleaning.²⁷ Together with validation against data from the industrial conversion of conventional EFG feedstocks, the model results are therefore considered feasible (cf. Appendix B.4.1.2).

Adjustment of the H_2/CO ratio via WGS leads to carbon losses through CO_2 formation. These losses could be avoided by importing H_2 instead of using WGS as MeOH synthesis from CO_2 is also possible.^{156,217} However, this option was not evaluated in this thesis, as large amounts of H_2 would be required to reach a stoichiometric number of 2 in MeOH syngas generation.

With respect to pyrolysis oil composition, a high molar H/C ratio combined with a high LHV is advantageous for EFG, as it leads to high syngas yields and carbon recoveries. Accordingly, pyrolysis oils derived from LDPE and PP are most suitable, followed by those from heteroatom-containing feedstocks such as Mix MH and Mix HH. In contrast, pyrolysis oils from Mix AR and especially PS are less favorable due to their low H/C ratios. This contrasts with the results for upgrading and steam cracking, as hydrogen deficient pyrolysis oils achieved higher yields due to the import of H_2 .

5.4.2 Oxo syngas configuration

In the generation of Oxo syngas, the initial gasification step is identical to the MeOH syngas configuration. However, subsequent gas conditioning differs due to the lower required H_2/CO ratio of 1 for Oxo syngas. Among all model feedstock pyrolysis oils, only LDPE-derived oils produce a raw syngas with an H_2/CO ratio greater than 1. In this case, gas conditioning would require the separation of H_2 to adjust the H_2/CO ratio. Therefore, this case would differ both in the actual process and in the assessment, as H_2 would form an additional side product. Thus, LDPE-derived oils are not considered in the analysis of the Oxo configuration.

Instead, three ASR-derived pyrolysis oils were selected for evaluation of the Oxo syngas configuration, representing the different types of model feedstocks analyzed. PP represents a heteroatom-free model feedstock with high H/C ratio, PS represents a heteroatom-free feedstock with a low H/C ratio, and S-PCW represents a model feedstock containing heteroatoms with a medium H/C ratio. The model results for EFG of these pyrolysis oils are summarized in Table 9 and compared to the results of the MeOH syngas configuration also included in Table 8.

Table 9: Process conditions, process efficiencies, and product yields for EFG of selected ASR pyrolysis oils and HFO for MeOH and Oxo syngas generation.

Model feedstock pyrolysis oil		PP		PS		S-PCW		HFO (reference feedstock)	
Syngas configuration		MeOH	Oxo	MeOH	Oxo	MeOH	Oxo	MeOH	Oxo
Gasifier conditions									
Gasifier temperature	°C	1350	1350	1350	1350	1350	1350	1350	1350
Oxygen input	kg O ₂ /kg feedstock	1.16	1.16	1.04	1.04	1.11	1.11	1.00	1.00
Steam input	kg H ₂ O/kg feedstock	0.20	0.20	0.34	0.34	0.18	0.18	0.34	0.34
Stoichiometric ratio	-	0.34	0.34	0.34	0.34	0.34	0.34	0.32	0.32
Syngas product parameters									
SN MeOH syngas	-	2.02		2.02		2.02		2.02	
H ₂ /CO ratio Oxo syngas	-	-	1.01	-	1.00	-	1.00	-	1.00
LHV syngas	MJ/kg	23.4	17.5	23.4	17.5	23.4	17.5	23.2	17.5
Process efficiency parameters									
Specific syngas yield	kg syngas/kg pyrolysis oil	1.49	2.06	1.37	1.90	1.44	2.00	1.40	1.94
Cold gas efficiency	%	82.1	84.9	81.7	84.6	82.2	85.1	80.8	83.6
Carbon yield ^a	%	62.8	95.1	54.4	82.6	61.2	93.0	60.2	91.4
Power demand and district heat generation									
District heat	kWh _{th} /kg feedstock	1.40	1.49	1.15	1.20	1.33	1.41	1.24	1.29
Power demand	kWh _{el} /kg feedstock	0.89	0.76	0.83	0.81	0.86	0.75	0.80	0.73

In comparison to the MeOH syngas configuration, the Oxo syngas configuration achieves significantly higher specific syngas yields and carbon recoveries. For PP, for example, the specific syngas yield increases from 1.49 kg / kg pyrolysis oil to 2.06 kg / kg pyrolysis oil, while the carbon recovery increases from 62.8% to 95.1%. CGE and district heat generation also increase slightly, while the electricity demand decreases.

The increase in carbon recovery results from the lower requirement for WGS due to the lower target H₂/CO ratio. Consequently, less CO₂ is formed, increasing overall carbon recovery. While

^a Including CO₂ for MeOH syngas configuration

the molar syngas yield remains nearly unchanged – since the WGS reaction is equimolar – the mass-specific syngas yield increases due to the higher CO content of the Oxo syngas.

Similarly, losses in CGE due to shifting are limited. Simultaneously, less process steam is required for WGS, allowing increased heat recovery and increased district heat generation. In addition, the reduced gas volumes and lower heat release from CO₂ absorption in the Rectisol scrubbing unit decrease electricity demand for cryogenic cooling and recycle gas compression, resulting in a lower overall electricity consumption.

With respect to pyrolysis oil composition, the same trends as observed for the MeOH syngas configuration apply to the Oxo syngas configuration: Pyrolysis oils with high molar H/C ratio and high LHV show more favorable process efficiencies than those with lower values.

Among the pyrolysis oil utilization options analyzed, the EFG Oxo syngas configuration achieves the highest carbon yield, while the MeOH configuration achieves the lowest.

5.5 Full pyrolysis-based chemical recycling process chains

This section summarizes product yields and carbon distributions across the complete, pyrolysis-based process chains. These include conversion of the model feedstocks in either the ASR or STR system, followed by conversion of the resulting pyrolysis oil in upgrading and steam cracking or via EFG.

The pyrolysis-based chemical recycling process chains achieve carbon recycling efficiencies between 31 and 66% relative to the carbon contained in the model feedstock (cf. Figure 29). Between 18% and 69% of the carbon is emitted as CO₂ along the process chain, while up to 16% is converted into fuel products. This fraction is neither converted to CO₂ within system boundaries nor considered recycled carbon due to its intended use as fuel. The resulting product yields depend on the model feedstock, the pyrolysis reactor system, and the chosen route for pyrolysis oil utilization, which are discussed for the representative feedstocks PP, PS, and S-PCW in further detail. A full overview is provided in Appendix C.

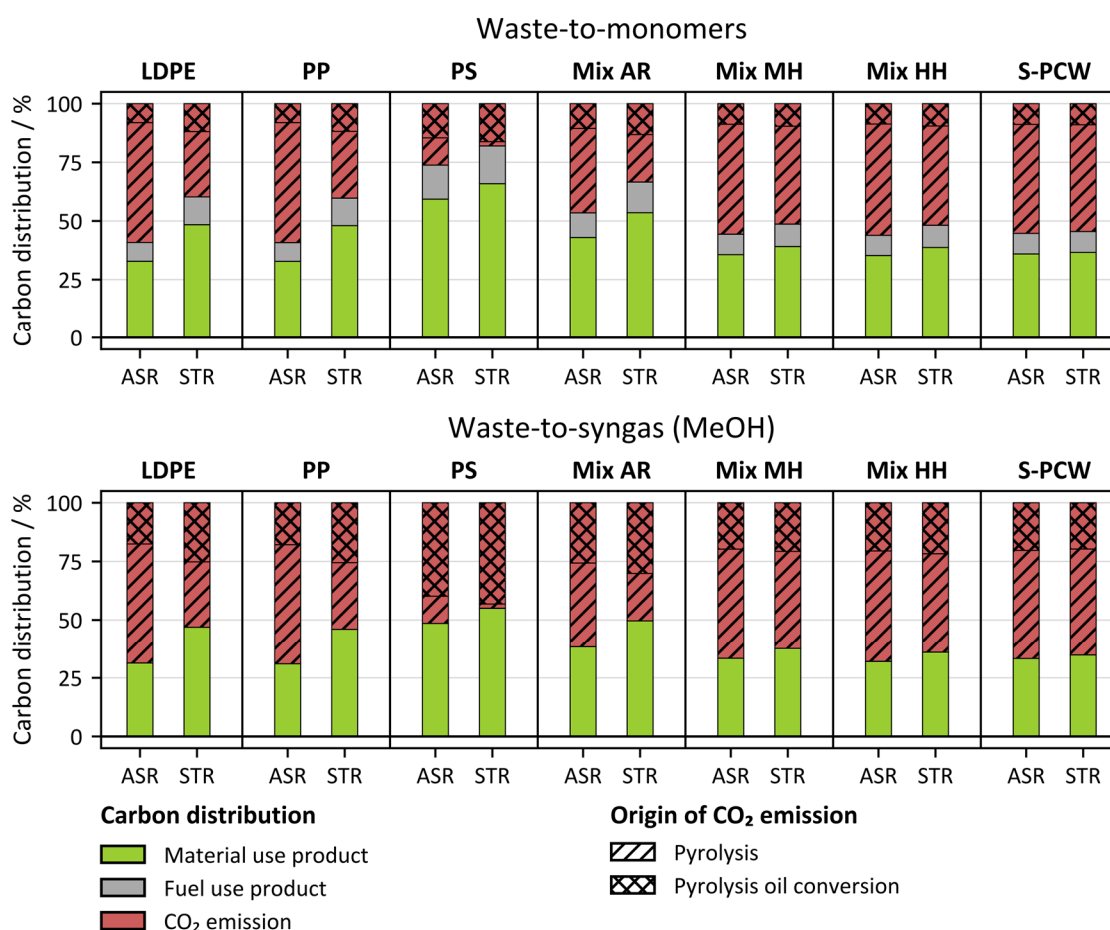


Figure 29: Carbon distribution of model feedstocks in the waste-to-monomers (top) and waste-to-syngas (MeOH configuration, bottom) process chain for ASR and STR pyrolysis.

The effect of the reactor system on pyrolysis oil yield and composition (cf. Section 5.1) is clearly reflected in the carbon distribution for PP recycling via the waste-to-monomers route (cf. Figure 30). Using the ASR system, the carbon recycling efficiency reaches 33%, with an additional 8% contained in fuel products. In contrast, the STR-based process achieves a carbon recycling efficiency of 48%, with an additional 12% in fuel products. The carbon loss of 51% during PP conversion in the ASR system, mainly attributed to overcracking, exceeds the losses associated with subsequent pyrolysis oil utilization, regardless of the utilization route (cf. Figure 29).

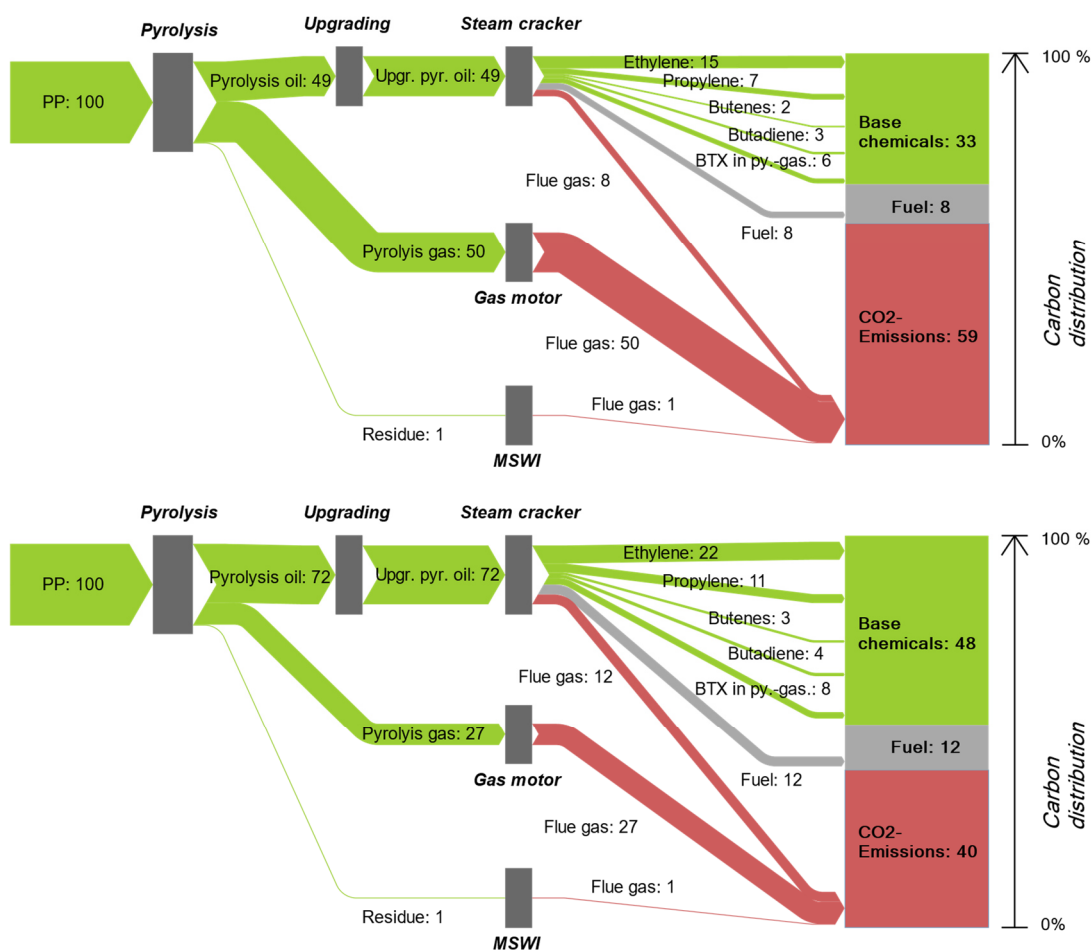


Figure 30: Carbon flows (% of feedstock carbon) in the waste-to-monomers process chain for PP. Top: ASR pyrolysis. Bottom: STR pyrolysis.

For PS, the difference between reactor systems decreases but remains visible (cf. Figure 31). The gap in carbon recycling efficiencies is reduced to 7%. For heteroatom-containing model feedstocks (Mix MH, Mix HH, S-PCW), the differences between reactor systems disappear entirely. Both systems achieve nearly identical carbon recycling efficiencies despite differences in heteroatom removal efficiency that were observed in the pyrolysis step (cf. Figure 29 and Figure 32). Thus, variations in pyrolysis oil composition between reactor systems do not translate into differences in the overall carbon recycling efficiencies, as the influence of the pyrolysis step dominates over that of subsequent pyrolysis oil conversion.

The comparison of utilization routes shows that EFG in the Oxo syngas configuration achieves the highest carbon recycling efficiency for PP in the ASR system, followed by upgrading and steam cracking (cf. Figure 33). EFG in the MeOH syngas configuration consistently results in the lowest carbon recycling efficiency, in line with the results presented in Sections 5.3 and 5.4. As differences in pyrolysis oil properties between ASR and STR are small for a given model feedstock, this ranking applies across all model feedstocks analyzed.

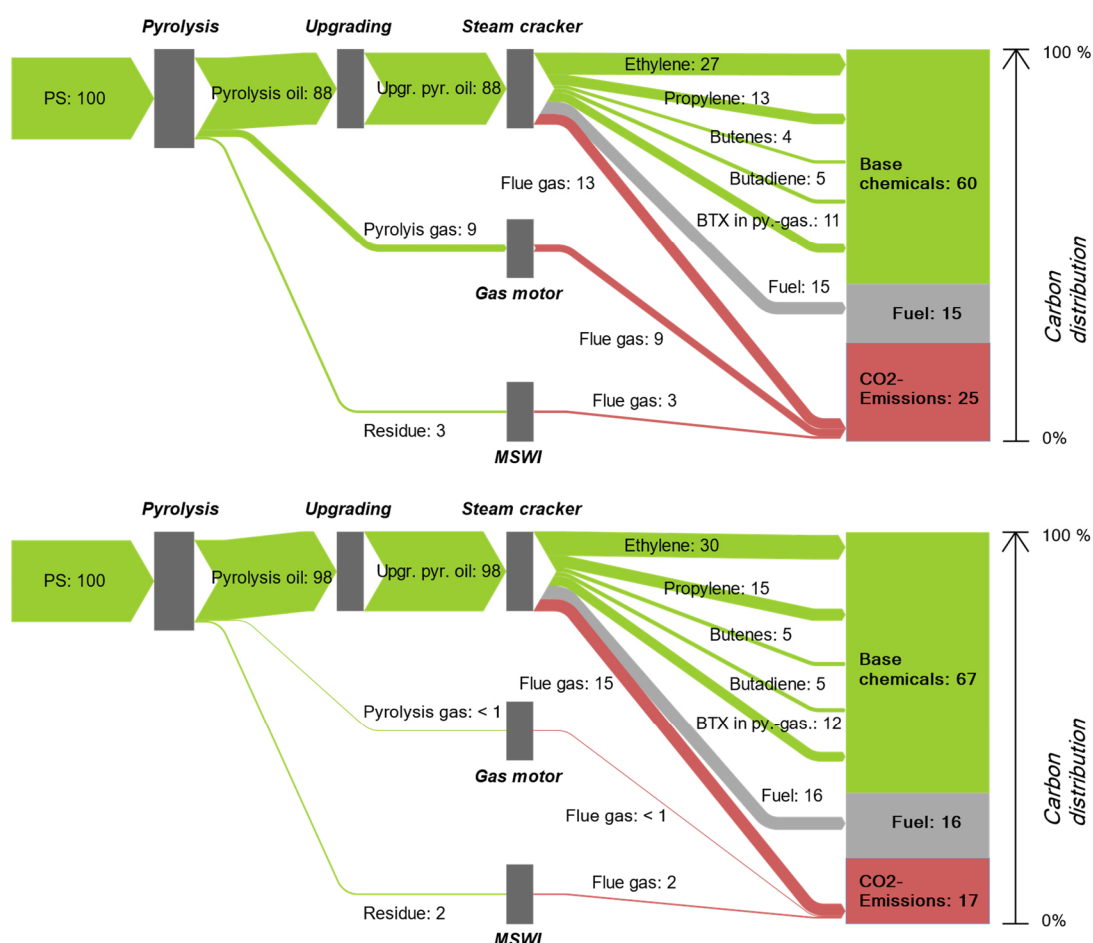


Figure 31: Carbon flows (% of feedstock carbon) in the waste-to-monomers process chain for PS. Top: ASR pyrolysis. Bottom: STR pyrolysis.

Across all cases, pyrolysis is the largest contributor to carbon loss within the process chain. Only in the cases of PS (for both reactor systems and all utilization routes) and for Mix AR in the STR system with EFG in the MeOH syngas configuration does carbon loss during downstream conversion exceed that of pyrolysis (cf. Figure 29). In all other cases, feedstock conversion to pyrolysis oil represents the primary source of carbon loss.

For clean feedstocks such as LDPE and PP, carbon loss can be minimized through appropriate selection of reactor concept and reaction conditions, as demonstrated by the comparison of ASR and STR systems. Overcracking should be avoided to limit the transfer of carbon into the pyrolysis gas product. Direct integration of pyrolysis with the gas separation train of a steam cracker

could enable recovery of valuable products, as proposed by Netsch et al. for catalytic pyrolysis of polyolefins.⁹⁷

For heteroatom-containing feedstocks, this approach would require extensive gas cleaning, as heteroatoms are preferentially transferred to the pyrolysis gas (cf. Sections 2.3.2 and 5.1). Consequently, significant amounts of non-hydrocarbon compounds such as CO₂, NH₃, and HCl would need to be removed.

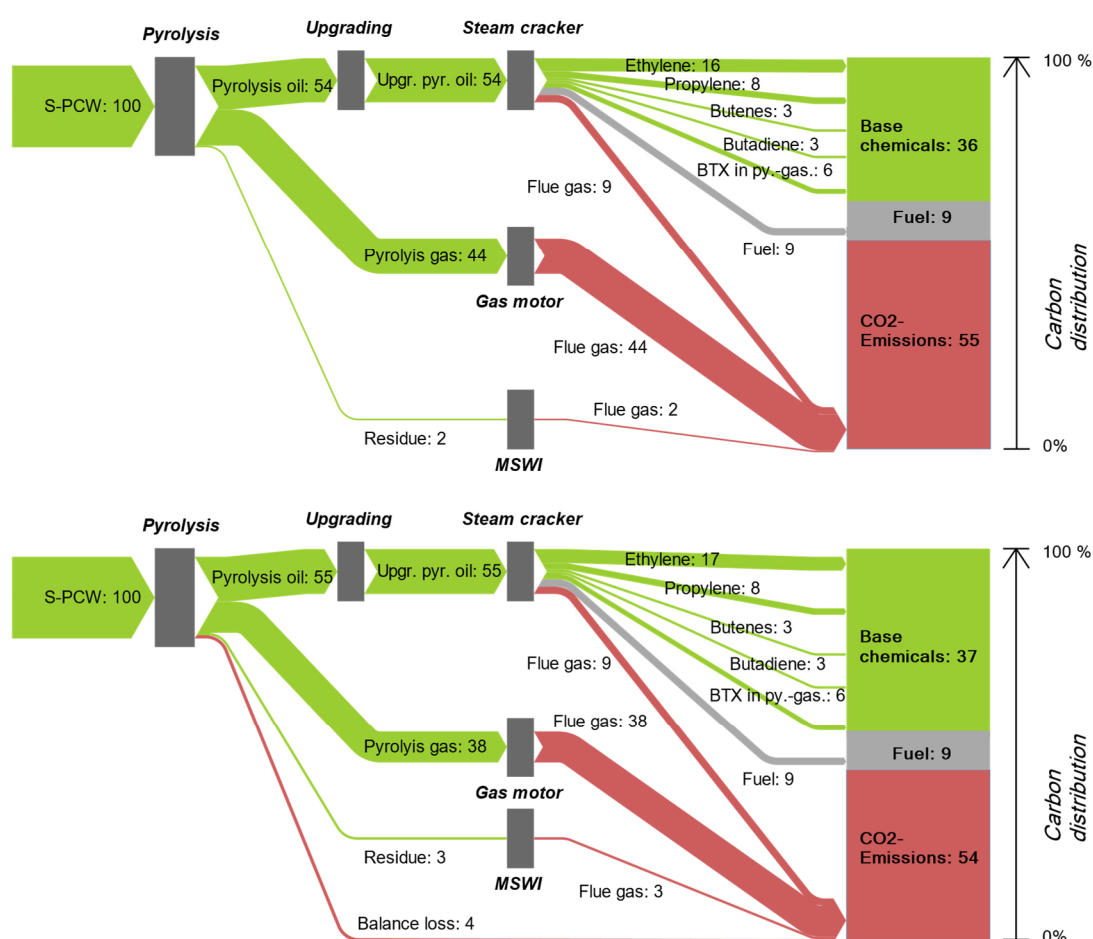


Figure 32: Carbon flows (% of feedstock carbon) in the waste-to-monomers process chain for S-PCW. Top: ASR pyrolysis. Bottom: STR pyrolysis.

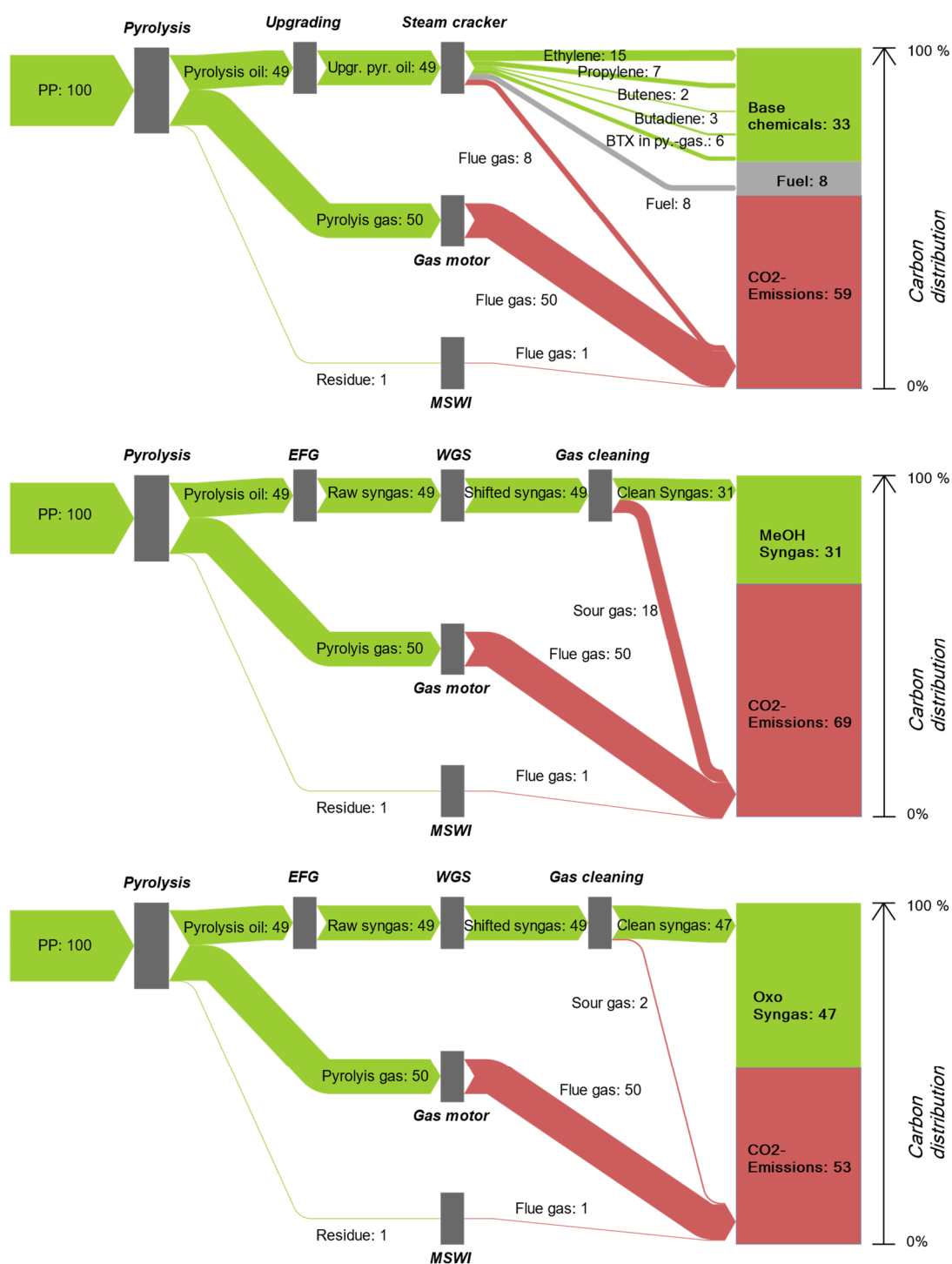


Figure 33: Carbon flows (% of feedstock carbon) for PP in the waste-to-monomers and waste-to-syngas process chains using ASR pyrolysis. Top: Waste-to-monomers. Middle: Waste-to-syngas (MeOH syngas configuration). Bottom: Waste-to-syngas (Oxo syngas configuration).

An alternative approach is the integration of pyrolysis gas into EFG, which is more tolerant toward such impurities. Figure 34 illustrates the potential of integrating pyrolysis gas from S-PCW conversion into the EFG MeOH syngas configuration. Compared to the base case without pyrolysis gas utilization, the carbon recycling increases substantially. A carbon recycling efficiency of 63% is achieved, compared to 33% without integration, corresponding to an increase of 91%.

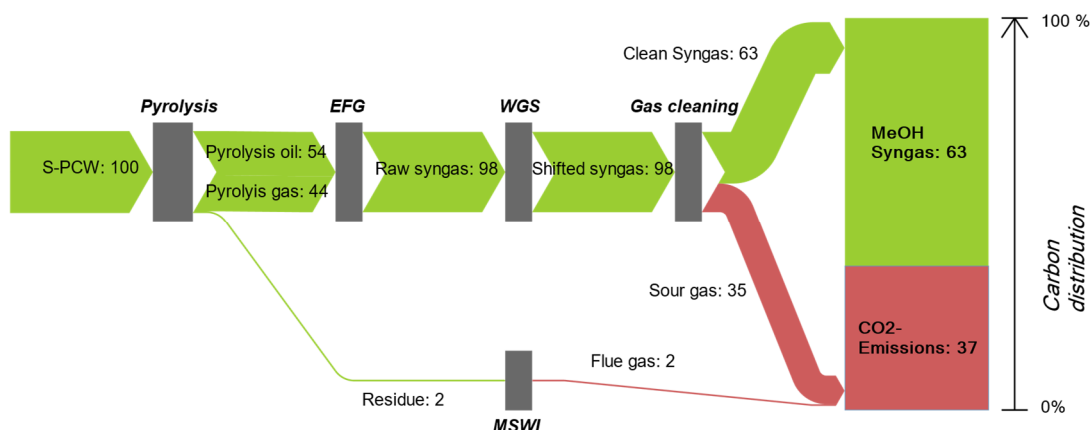


Figure 34: Carbon flows (% of feedstock carbon) in the waste-to-syngas process chain (MeOH syngas configuration) for S-PCW with utilization of pyrolysis gas in EFG. Reactor: ASR.

However, such integration requires process adaptations and is only feasible if the pyrolysis and gasification units are co-located, as long-distance transport of pyrolysis gas is not practical. Integration requires compression of pyrolysis gas from atmospheric pressure to gasifier conditions, which may lead to partial liquefaction of higher hydrocarbons, e.g., C₃ hydrocarbons and above. In addition, partial scrubbing may be required to remove corrosive components such as HCl. N₂ used for inertization of the pyrolysis process could also increase inert gas content in the product syngas. Accordingly, the carbon recycling efficiency calculated for this integration scenario should be considered a best-case estimate.

5.6 Influence of model feedstock composition

This section integrates the results across all process steps and discusses their implications for different feedstock compositions, including their relevance for real waste streams.

The carbon distributions and product yields determined for the different model feedstocks, reactor systems, and pyrolysis oil utilization routes reveal a broad range of achievable product yields and carbon recycling efficiencies. When product yields for steam cracker products and MeOH syngas are plotted against feedstock carbon content on an ash-free basis, thereby accounting for differences in polymer content between model feedstocks, a positive correlation is observed (cf. Figure 35, left). This trend reflects the higher availability of carbon for conversion into target products and is therefore expected. It is less pronounced for the ASR system than for the STR system.

A similar relationship is observed for the carbon recycling efficiency (cf. Figure 35, right). Recycled carbon increases with feedstock carbon content, again with a stronger correlation for STR-based process chains than for ASR-based ones. Despite normalization to feedstock carbon content, lower recycling rates are obtained for heteroatom-containing feedstocks, indicating less efficient carbon utilization compared to heteroatom-free feedstocks. In contrast, PS-containing feedstocks enable particularly high carbon utilization due to their high carbon content and consequently high pyrolysis oil yields.

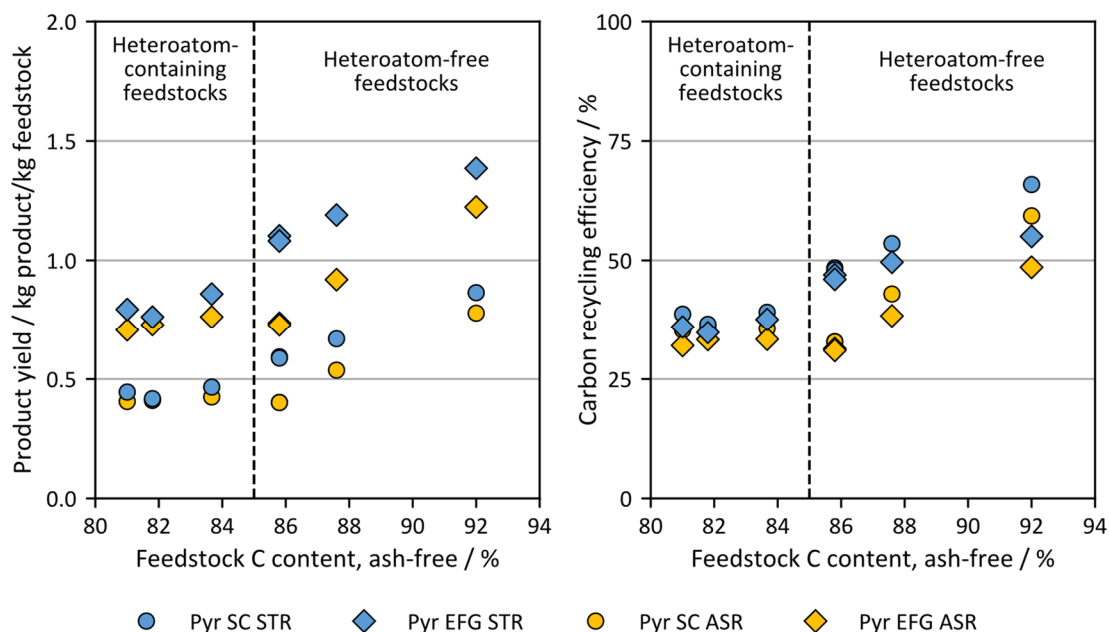


Figure 35: Correlation of product yield (left) and carbon recycling efficiency (right) with feedstock carbon content for the pyrolysis-based chemical recycling process chains. Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route.

These trends can be explained by the influence of feedstock composition on pyrolysis behavior (cf. Section 2.3.2). Heteroatom-containing polymers promote the formation of gaseous products, thereby reducing carbon recovery during pyrolysis. In contrast, for clean, polyolefin-rich feedstocks, carbon losses are primarily driven by overcracking, as observed in the ASR system. Feedstock composition therefore plays a significant role in determining the extent to which reactor effects influence overall process performance.

Relating these findings to real waste fractions highlights the relevance of feedstock composition. Feedstocks with high shares of polyolefins, such as the DSD 310 sorting fraction and, to a lesser extent, the DSD 323 fraction, are expected to enable high carbon recovery during pyrolysis. In contrast, fractions such as the DSD 350 fraction, which contain higher amounts of heteroatom-containing polymers (e.g., PET and PA), are expected to exhibit substantial carbon losses during pyrolysis. This behavior is consistent with the results obtained for the S-PCW model feedstock and is supported by experimental studies on comparable waste fractions.^{94,166,167}

Overall, the results indicate that carbon recovery during pyrolysis is the dominant factor determining the performance of the entire process chain in terms of recycled carbon. Differences in downstream utilization routes have a comparatively smaller influence, despite variations in product yields and hydrogen demand. While upgrading and steam cracking benefit from high carbon content in pyrolysis oils, EFG in the MeOH configuration favors oils with high molar H/C ratios and high LHVs.

The sensitivity of carbon recovery to feedstock composition further suggests that improving feedstock quality – for example through additional sorting – could enhance process performance. However, whether this leads to higher overall system-level carbon recycling compared to full utilization of MPW depends on the trade-off between improved conversion efficiency and carbon rejection during sorting.

6 Life cycle impact assessment

Building on the mass and energy balances presented in the previous chapter, the corresponding LCIs were implemented in the LCA software ActivityBrowser to quantify the climate change impacts of the different waste treatment routes. This chapter presents and discusses the results for the base scenario from three complementary perspectives: the waste perspective, the product perspective, and a system expansion-based perspective. Sensitivity analyses evaluating the influence of key modeling assumptions are presented in Chapter 7.

6.1 Input-based assessment

The input-based assessment allows direct comparison of different waste treatment routes for an identical system input, i.e., a single model feedstock. As the model feedstocks differ in composition, comparisons between feedstocks are not possible within this framework.

Figure 36 illustrates the avoided-burden approach applied in the waste-perspective LCA. The climate change impact of a given waste treatment route is determined by first summing all process burdens, represented by the *Burdens* bar. These include contributions from the individual process steps, such as pyrolysis, incineration of pyrolysis residues, and pyrolysis oil utilization.

Next, credits are deducted for electricity and hydrogen generated within the system boundaries of the foreground system. These internal energy flows reduce the demand for corresponding products from the background system and are referred to as *credit internal energy use* in the following analysis, yielding the gross climate change impact.

From the gross climate change impact, further credits are deducted for the substitution of conventionally produced products (e.g., steam cracker products). This results in the net climate change impact in accordance with the avoided-burden approach.¹⁸⁹

The stacked-bars representation on the right-hand side of Figure 36 summarizes the same information in a more compact form. Process burdens are shown as positive contributions, whereas credits are shown as negative contributions. Accordingly, the positive stacked-bar represents the *sum of all burdens*, the white diamond indicates the *gross climate change impact*, and the black dot represents the *net climate change impact*. Although less intuitive than the waterfall diagram, this representation facilitates side-by-side comparison of the different waste treatment routes.

While the net climate change impact is the primary performance indicator discussed in this chapter, the sum of all burdens and the gross climate change impact are also shown to distinguish the effects of internal process integration and product substitution on the overall results:

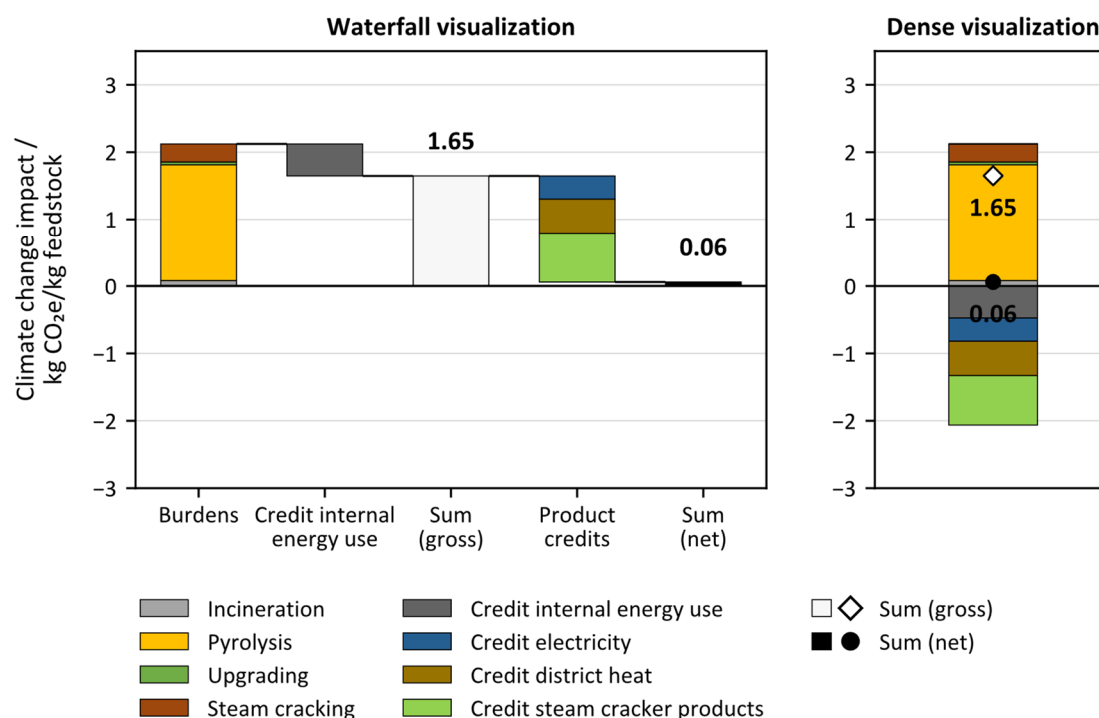


Figure 36: Input-based climate change impact of S-PCW recycling via the waste-to-monomers process chain with ASR pyrolysis. Left: Waterfall diagram. Right: Equivalent condensed representation using stacked bars with overlaid gross and net climate change impacts.

The *sum of all burdens*, indicated by the positive stacked bar, represents a scenario in which all electricity and hydrogen required by the recycling process are supplied by the background system, pyrolysis side products are incinerated without energy recovery, and no product substitution takes place. This metric therefore reflects only the process burdens of the respective recycling route and is independent of assumptions regarding product substitution.

The *gross climate change impact* additionally accounts for the energetic utilization of pyrolysis side products and – within the waste-to-monomers route – the recycling of hydrogen from steam cracking for pyrolysis oil upgrading. Consequently, it includes credits from the internal utilization of electricity and hydrogen generated within the process chain while remaining independent of assumptions regarding product substitution.

The *net climate change impact* further includes the product credits resulting from the avoided-burden approach, i.e., the substitution of conventionally produced products. It therefore reflects both the process burdens of the recycling route and the avoided climate change impacts associated with the substituted products.

The exemplary recycling route shown in Figure 36 is the conversion of S-PCW via the waste-to-monomers route with ASR pyrolysis. It results in a sum of all burdens of 2.12 kg CO₂e/kg S-PCW (cf. Figure 36). Pyrolysis is the dominant contributor, accounting for 1.73 kg CO₂e/kg S-PCW

(82% of the total process burdens), primarily due to the combustion of pyrolysis gas and the electricity demand for reactor heating. Upgrading and steam cracking of the resulting pyrolysis oil contribute a further 15%, with steam cracking alone accounting for 13%, while incineration of solid pyrolysis residues contributes the remaining 3%. Credits from the internal generation of electricity and H₂ reduce the process burdens by 23%, yielding a gross climate change impact of 1.65 kg CO₂e/kg S-PCW.

Product credits amount to 1.59 kg CO₂e/kg S-PCW, arising from the substitution of conventionally produced base chemicals, excess electricity, and district heat. Steam cracker products account for the largest share (46%), followed by district heat (32%) and electricity (22%). Overall, these credits largely offset the process burdens, resulting in a net climate change impact of 0.06 kg CO₂e/kg S-PCW.

Similar distributions of process burdens and credits are observed across the different model feedstocks and pyrolysis oil utilization routes (cf. Figure 37; full dataset in Appendix E.2). The only notable exceptions are the PS-rich model feedstocks (PS and Mix AR). In all other cases, pyrolysis is the dominant contributor to the process burdens, accounting for 58 – 87% of the sum of all burdens. This primarily results from carbon losses during pyrolysis, which ultimately lead to CO₂ emissions. Across all feedstocks, the contribution of pyrolysis is consistently higher for ASR than for STR, reflecting the lower carbon recovery of the ASR system (cf. Section 5.2).

Consequently, pyrolysis oil utilization contributes less to the sum of all process burdens than the pyrolysis step itself. For the waste-to-syngas route (MeOH syngas configuration), EFG accounts for 26% (LDPE and PP model feedstocks) to 30% (S-PCW) of the process burdens for the ASR system and 30% (S-PCW) to 44% (LDPE, PP) for the STR system, excluding PS and Mix AR. Differences between the MeOH and Oxo syngas configurations are discussed in Section 7.4.2.

In the waste-to-monomers route, upgrading and steam cracking together contribute 12% (LDPE) to 15% (S-PCW) of the process burdens for the ASR system and 14% (S-PCW) to 23% (PP) for the STR system. The different feedstocks defining the lower and upper ends of these ranges reflect the different carbon yields achieved by the two pyrolysis systems.

PS and Mix AR show higher contributions from pyrolysis oil utilization, consistent with the carbon flow analysis presented in Section 5.5. Similarly, the waste-to-syngas route in the MeOH syngas configuration exhibits higher process burdens than the waste-to-monomers route because of its lower overall carbon recovery, thereby increasing the relative contribution of the EFG step.

On the credit side, the main products (steam cracker products or MeOH syngas) dominate the overall product credits. Their share ranges from 46% (S-PCW) to 92% (PS) for the ASR system and 53% (S-PCW) to 99% (PS) for the STR system in the waste-to-monomers route. For the waste-to-syngas route, MeOH syngas accounts for 56% (S-PCW) to 85% (PS) for the ASR system and 64% (S-PCW) to 92% (PS) for the STR system, respectively. The remaining credits arise primarily from district heat, followed by electricity generation.

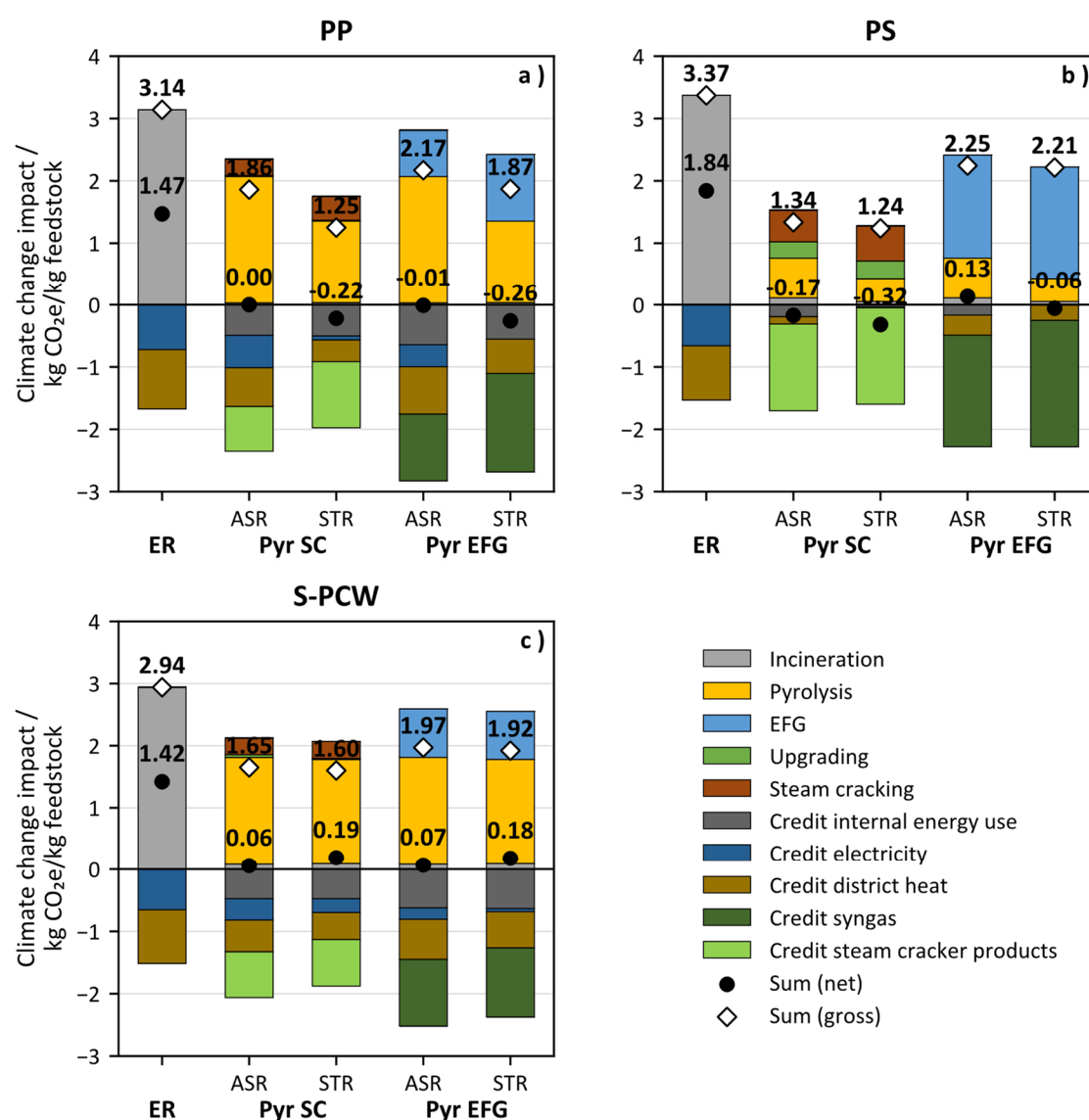


Figure 37: Comparison of input-based climate change impacts of the waste-to-energy, waste-to-monomers, and waste-to-syngas (MeOH configuration) routes using ASR and STR pyrolysis data for PP (a), PS (b), and S-PCW (c). ER: Waste-to-energy process route. Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route.

The share of product credits attributed to the main products increases with carbon recycling efficiency, whereas contributions from district heat and electricity decrease. This reflects the fact that these side products originate from incineration of pyrolysis gas and solid residues, both of which are associated with carbon losses. Consequently, PS exhibits the highest share of chemical product credits.

Despite the higher process burdens of the waste-to-syngas route, the greater product credits associated with MeOH syngas production from HFO largely compensate for these additional burdens. As a result, the net climate change impacts of the waste-to-syngas and waste-to-monomers routes differ by less than 0.1 kg CO₂e/kg model feedstock for all model feedstocks except

PS. For PS though, the waste-to-monomers route performs substantially better, reducing the net climate change impact by an additional 0.30 kg CO₂e/kg PS (ASR) and 0.26 kg CO₂e/kg PS (STR).

Compared to energy recovery, both chemical recycling routes consistently achieve lower net climate change impacts across all model feedstocks, pyrolysis oil utilization routes, and reactor systems. The largest reduction is obtained for PS processed via the waste-to-monomers route with STR pyrolysis (2.16 kg CO₂e/kg PS), whereas the smallest reduction is observed for Mix HH processed via the waste-to-syngas route with ASR pyrolysis (1.08 kg CO₂e/kg Mix HH).

The results of the input-based LCA can be summarized as follows:

- (1) In the base scenario, pyrolysis-based chemical recycling achieves lower net climate change impacts than energy recovery for all model feedstocks, independent of reactor technology and pyrolysis oil utilization route.
- (2) The waste-to-monomers and waste-to-syngas (MeOH syngas configuration) routes exhibit similar environmental performance. Only for PS does steam cracking outperform EFG by a notable margin.
- (3) Under the selected process conditions, the STR system consistently achieves lower net climate change impacts than the ASR, reflecting the higher carbon recovery already observed in the process balances.
- (4) Pyrolysis is the dominant contributor to the process burdens, primarily due to the combustion of pyrolysis gas and the electricity demand for reactor heating. Only at very high carbon recovery, as observed for PS, do downstream conversion processes contribute more to the process burdens than pyrolysis itself.
- (5) Product credits are dominated by the target products of chemical recycling. However, their contribution decreases with decreasing carbon recycling efficiency, increasing the relative importance of credits from electricity and district heat generated from pyrolysis side products.

Comparison with the literature shows good agreement with the present findings. Owing to differences in system boundaries, modeling approaches, and methodologies, only qualitative comparisons are possible. In a review of 30 LCA studies, Zhang et al. concluded that chemical recycling outperformed energy recovery with respect to climate change impact in most cases.²⁸ Schwartz et al. reported similar findings for LDPE and PP in a study that included both pyrolysis and gasification and highlighted the strong influence of waste composition on environmental performance.¹⁷⁵ Their study also found reduced performance for PS in gasification, consistent with the present results.

For the waste-to-monomers route, Gracida-Alvarez identified pyrolysis oil upgrading as only a minor contributor to the overall process burdens.¹⁹⁵ Likewise, for the utilization of pyrolysis oil from MSW in EFG, Keller et al. reported a lower climate change impact than energy recovery, consistent with the results for direct gasification of MPW published by Arena et al. and Voss et al.^{26,218,219}

Overall, the results obtained in this study are consistent with the current state of the literature. However, the environmental performance of chemical recycling remains sensitive to both process-related assumptions affecting the life cycle inventory, such as product yields and carbon distribution (cf. Chapter 5), and methodological choices in the LCA. The influence of these assumptions is therefore examined in Chapter 7 through a series of sensitivity analyses covering product yields, side-product utilization, and background processes.

6.2 Product-based assessment

While the input-based assessment evaluates the environmental performance of waste treatment, the product-based assessment focuses on the climate change impact associated with the target products relative to their conventional production. The objective is to evaluate how feedstock composition influences the climate change impact of these products using cradle-to-gate system boundaries. As the two pyrolysis-based chemical recycling routes produce different target products, the results are discussed separately in the following sections.

6.2.1 Steam cracker products

Steam cracking produces a product slate rather than a single product. For the present analysis, these outputs are collectively referred to as *steam cracker products*. These include ethylene, propylene, butenes, butadiene, and BTX contained in pyrolysis gasoline as products for material use, as well as the remaining pyrolysis gasoline, pyrolysis fuel oil, and pyrolysis fuel gas as products for fuel use.

Under the assumptions of the steam cracking model, the relative product distribution is fixed and corresponds to that of conventional naphtha steam cracking (cf. Section 4.4.2). Thus, the functional unit for the product-based assessment of the waste-to-monomers route is defined as 1 kg of steam cracker products. Hydrogen produced in excess of the upgrading demand, together with electricity and district heat, is treated as a side product and credited according to the avoided-burden approach. The environmental performance of the recycling route is therefore evaluated based on its net climate change impact relative to conventional naphtha steam cracking.

Figure 38 summarizes the climate change impacts associated with the production of 1 kg of steam cracker products from the different model feedstocks using ASR and STR technologies. In comparison to the input-based waste treatment, the sum of all burdens per functional unit is higher. This results from the product yield of the recycling process, which is always below 1 kg of steam cracker products per kilogram of feedstock. Consequently, more than 1 kg of feedstock is required to produce 1 kg of product, with the required feedstock input increasing as product yield decreases.

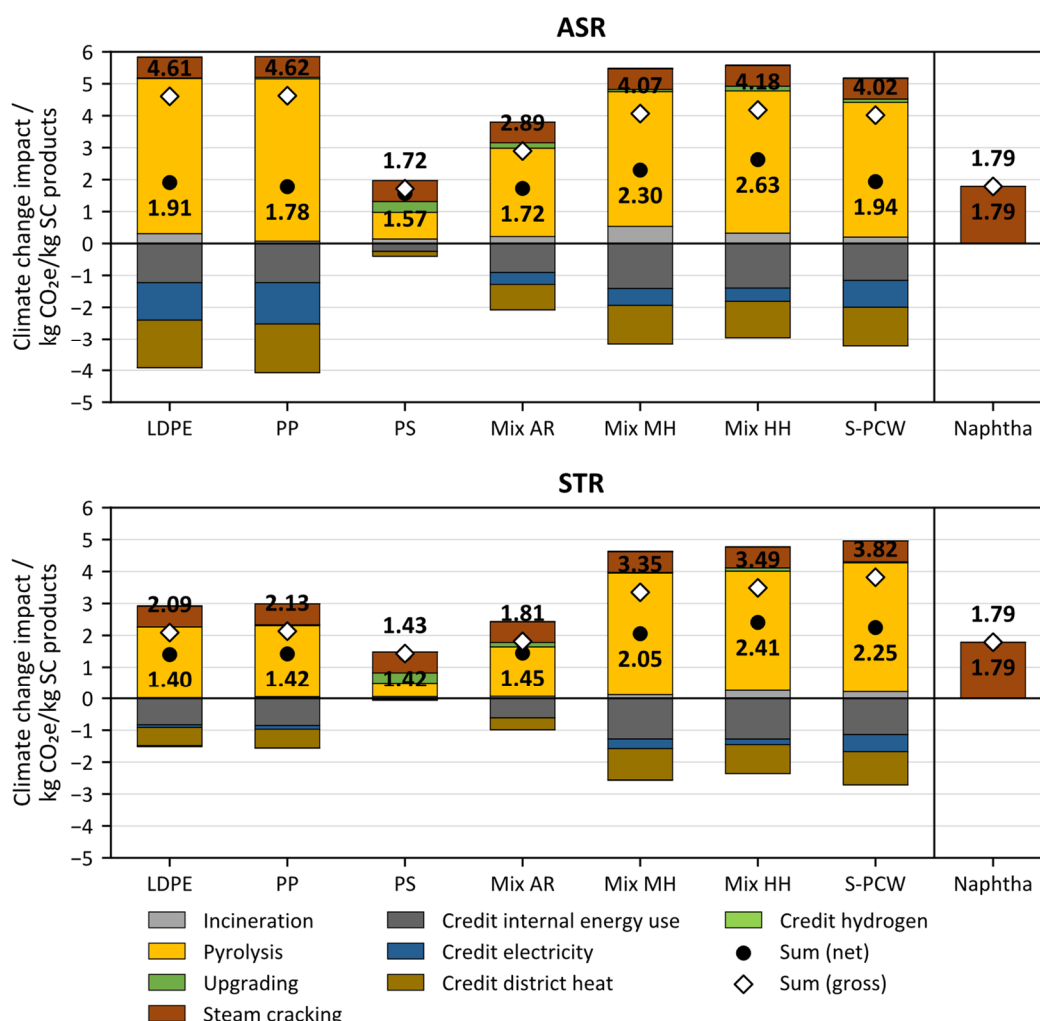


Figure 38: Climate change impacts of the production of 1 kg of steam cracker products from the model feedstocks with the ASR pyrolysis system (top) and the STR pyrolysis system (bottom). SC: Steam cracker.

At the same time, lower target product yields are associated with greater generation of side products. As a result, credits from electricity and district heat increase and partially offset the higher process burdens. This effect is particularly pronounced for the ASR system and reflects the lower carbon recovery previously observed for this reactor technology. Based on the net climate change impacts, only the heteroatom-free model feedstocks achieve lower net climate change impacts than conventional naphtha steam cracking. For the STR system, this applies to LDPE, PP, PS, and Mix AR, whereas for the ASR system only PP, PS, and Mix AR remain below the reference process.

Since the steam cracking process is assumed to be identical for upgraded pyrolysis oil and conventional naphtha, the differences between recycling-based and conventional production arise primarily from the upstream production of the steam cracking feedstock. Consequently, the higher net climate change impacts of the heteroatom-containing feedstocks reflect the greater

burdens associated with pyrolysis oil production from these feedstocks compared to the conventional production of naphtha, despite side product crediting.

Gracida-Alvarez et al. reported similar results, showing comparable net climate change impacts for conventional production of LDPE and HDPE plastics and their production based on chemical recycling of EoL LDPE and HDPE, corresponding to the heteroatom-free feedstocks considered here.¹⁹⁵ Additionally, they demonstrated that the net climate change impact depends on both the substitution rate of pyrolysis oil in steam cracking and the additional burdens associated with upgrading contaminated pyrolysis oils.¹⁹⁵

6.2.2 Syngas

The product-based assessment of the waste-to-syngas route in the MeOH syngas configuration shows trends similar to those observed for the waste-to-monomers route (cf. Figure 39). Only the heteroatom-free feedstocks (LDPE, PP, PS, Mix AR) using the STR pyrolysis system, together with PP using the ASR system, achieve net climate change impacts below those of conventionally produced MeOH syngas from HFO.

Although the flowsheet model predicts differences in the behavior of plastic pyrolysis oils and HFO in EFG, these differences result in only minor changes in the associated process burdens. Consequently, the higher climate change impacts of heteroatom-containing feedstocks are again primarily associated with the production of the pyrolysis oil rather than with its downstream conversion. This interpretation is supported by the background inventories from the ecoinvent database, which assign higher climate change impacts to naphtha production than to HFO production.^{220,221} A similar trend can be expected for Oxo syngas.

Overall, the product-based assessment indicates that pyrolysis-based chemical recycling can reduce the climate change impacts associated with the production of steam cracker products and MeOH syngas only for clean, heteroatom-free feedstocks. Heteroatom-containing feedstocks, on the other hand, consistently show higher impacts than the conventional production routes, resulting from the lower pyrolysis oil yield and thus higher process burdens of pyrolysis.

These findings contrast with the conclusions drawn from the input-based assessment, as the waste-perspective indicates clear benefits of chemical recycling regarding climate change impact for all feedstocks. The differences in the assessments result from different goal and scope definitions, as the input-based perspective evaluates the preferred waste treatment method whereas the product-based perspective evaluates the suitability of different feedstocks for product generation. Accordingly, underlying system boundaries differ, driven by the inclusion (input-based assessment) or exclusion (product-based assessment) of conventional waste treatment via energy recovery. Thus, the different conclusions obtained from the input- and product-based assessments are a direct consequence of their respective goal and scope definitions rather than inconsistencies in the underlying LCA model.

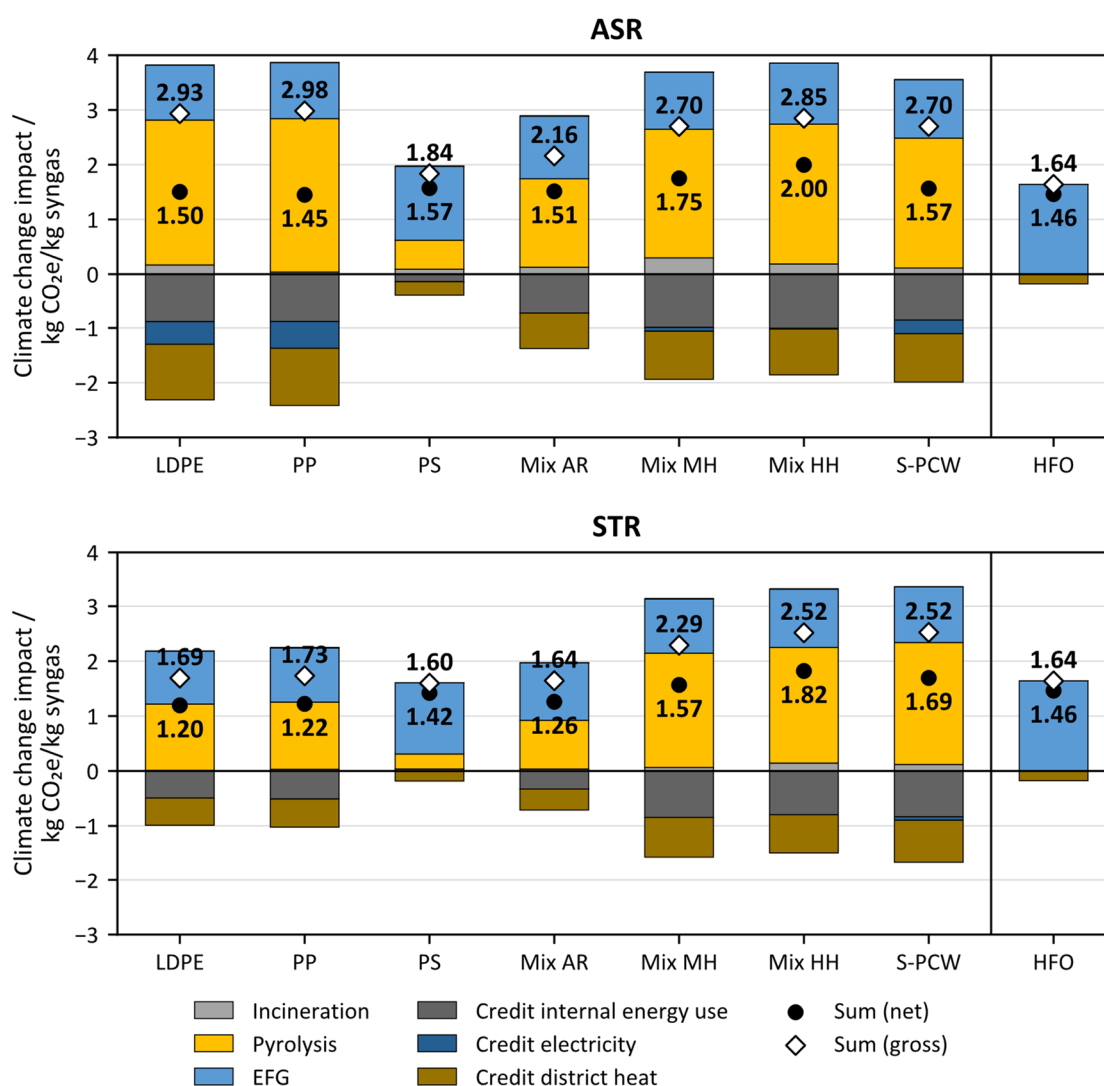


Figure 39: Climate change impacts of the production of 1 kg of MeOH syngas from the model feedstocks with the ASR pyrolysis system (top) and the STR pyrolysis system (bottom).

6.3 Combined perspective

The differing conclusions regarding the environmental performance of pyrolysis-based chemical recycling emphasize the need to combine the input- and product-based perspectives. Implementing pyrolysis-based chemical recycling diverts plastic waste from energy recovery and thereby affects both the waste management system, the energy system, and the chemical industry. As a result, both the products generated and the way they are produced change. To capture all relevant effects on environmental performance, changes in both sectors must therefore be considered from a combined, system-wide perspective. Furthermore, the combined perspective can be reformulated as a system optimization problem, as demonstrated by Meys

et al., Bachmann et al., and Keller et al., in their development of pathways toward a sustainable plastics economy.^{14,15,26,171}

Energy recovery represents the current standard for treating non-recyclable MPW, generating electricity and heat. Diverting this waste to chemical recycling reduces the supply of these energy carriers to the market. Assuming constant demand, this deficit must be compensated by alternative production routes. At the same time, chemical recycling generates different target products – monomers and base chemicals from steam cracking or MeOH syngas from EFG – which substitute fossil-based products while also altering the overall energy demand.

Based on the previously calculated product yields for each model feedstock and waste treatment route, a product basket can be defined. This basket includes the electricity and district heat generated through energy recovery, as well as the steam cracker products or MeOH syngas generated through chemical recycling.

This product basket is used as the functional unit for comparing waste treatment options. For each option, any products not generated in sufficient quantity must be supplied by predefined reference processes. The total climate change impact of the system is then calculated as the sum of the impacts from waste treatment and the impacts associated with producing the remaining products via reference processes. This ensures consistent system functionality across all scenarios.

Because each model feedstock yields different product quantities across the waste treatment routes, the corresponding product baskets differ. As a result, direct comparison between feedstocks is not possible within this framework unless a unified product basket is defined that includes all feedstocks and their corresponding outputs.

The difference in total climate change impact relative to energy recovery is defined as the climate change impact reduction potential of the respective waste treatment process. The calculated reduction potentials are consistent with those derived from the net climate change impacts in the input-based assessment, i.e., the differences of net climate change impacts. Thus, both approaches yield equivalent absolute results. However, as noted by Sanabria Garcia et al., this equivalence only holds when system boundaries are consistently defined and applied, and only for absolute – not relative – changes in climate change impact.¹⁸¹

As shown in Figure 40, chemical recycling of PP, LDPE, and S-PCW leads to a positive climate change impact reduction potential. The same applies to all other model feedstocks (full results in Appendix E.2). Thus, pyrolysis-based chemical recycling reduces the overall system climate change impact compared to energy recovery. The differences between reactor systems and feedstocks observed in the waste-perspective assessment are also reflected here (cf. Section 6.1). Differences between pyrolysis oil utilization routes remain small (within ± 0.1 kg CO₂e/kg feedstock), except for PS. These differences are negligible compared to the total system impacts, which are more than an order of magnitude larger.

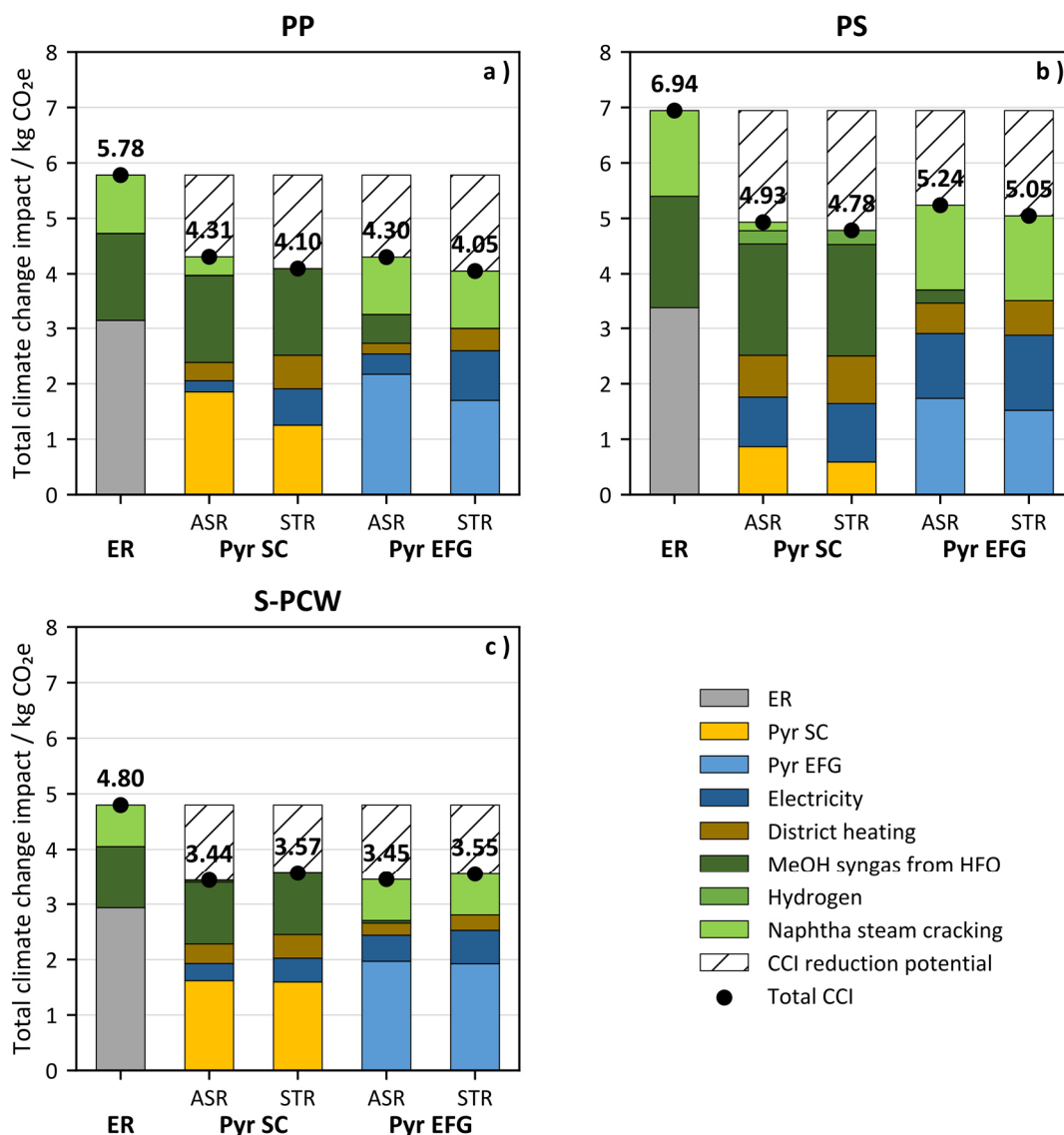


Figure 40: Total climate change impacts for the combined functional unit of waste treatment, base chemical production, and energy supply for PP (a), PS (b), and S-PCW (c). ER: Waste-to-energy process route. Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route. CCI: Climate change impact.

Figure 40 further shows that a significant share of total system climate change impact does not arise from the waste treatment itself, but from the reference processes reflecting current processes for the production of base chemicals. Reducing the climate change impact of the reference system can be achieved in two ways: (1) by lowering the impacts of waste treatment or (2) by reducing the impacts of the reference processes.

Chemical recycling affects both aspects simultaneously. On the one hand, the input-based assessment demonstrated reduced impacts from waste treatment for all feedstocks. On the other hand, the product-based assessment showed that only heteroatom-free feedstocks reduce the impacts associated with product generation. Despite these partially contrasting observations,

the combined perspective demonstrates that the net effect is a reduction in the system-wide total climate change impact for all model feedstocks.

The combined perspective highlights an additional key insight: achieving overall climate neutrality requires both waste treatment processes and reference production processes to reach near-zero emissions. Currently, all processes exhibit positive climate change impacts. These arise either from direct emissions, through the conversion of fossil carbon in plastics to CO₂, or from indirect emissions associated with energy consumption.

While energy-related emissions may be reduced through decarbonization of the energy system, carbon losses from material conversion are likely to persist. Therefore, achieving net-zero emissions may require the deployment of carbon removal technologies, either integrated into the process or applied externally. As current plastic waste is largely fossil-based, this must be combined with a transition from fossil-based plastics to bio-based carbon sources in the long term, also considering environmental effects beyond climate change.^{14,15}

7 Sensitivity and scenario analyses

LCA studies are sensitive to modeling decisions, including the choice of perspective, system boundaries, and process parameters.²⁸ While the influence of LCA perspective has already been discussed, this chapter correlates the climate change impact reduction potential previously calculated with the model feedstock composition (cf. Section 7.1), analyzes the influence of pyrolysis side product utilization (cf. Section 7.2), and pyrolysis energy demand (cf. Section 7.3), and assesses the effect of pyrolysis oil utilization options (cf. Section 7.4). Additionally, threshold values for product yields and product credits are determined to achieve a lower climate change impact than the reference waste treatment route, i.e., energy recovery (cf. Section 7.5). Finally, the influence of decarbonizing the energy system on chemical recycling is analyzed (cf. Section 7.6) and study limitations are discussed (cf. Section 7.7).

7.1 Influence of feedstock composition on climate change impact

The input-based assessment previously demonstrated that pyrolysis-based chemical recycling resulted in better environmental performance than energy recovery for all model feedstocks. In contrast, the product-based assessment concluded that only heteroatom-free feedstocks in distinct process configurations showed a lower climate change impact relative to the conventional process. Accordingly, the differing conclusions of the input- and product-based assessments raise the question of which feedstock properties govern the climate change impact reduction potential of pyrolysis-based chemical recycling.

When plotting the climate change impact reduction potential derived from the combined perspective assessment against feedstock carbon content on an ash-free basis as shown in Figure 41, a trend similar to that observed for carbon recycling efficiency emerges (cf. Section 5.6): Increasing feedstock carbon content leads to a higher climate change impact reduction potential, resulting from the higher carbon recovery in pyrolysis. Accordingly, feedstocks such as LDPE, PP, Mix AR, and PS show higher reduction potentials than model feedstocks with reduced carbon content following from their heteroatom content (Mix MH, Mix HH, and S-PCW).

The same relationship is found for both reactor systems and both process routes when limiting the scope of analysis to the pyrolysis process and excluding any credits from pyrolysis side product utilization, i.e., from internal energy utilization, excess electricity and district heat. Then, the burdens of pyrolysis correlate with both the carbon recovery in pyrolysis oil (cf. Figure 42, left) and feedstock carbon content (cf. Figure 42, right). Similarly, Jeswani et al. reported increasing burdens of pyrolysis with decreasing carbon recovery.¹⁷⁹

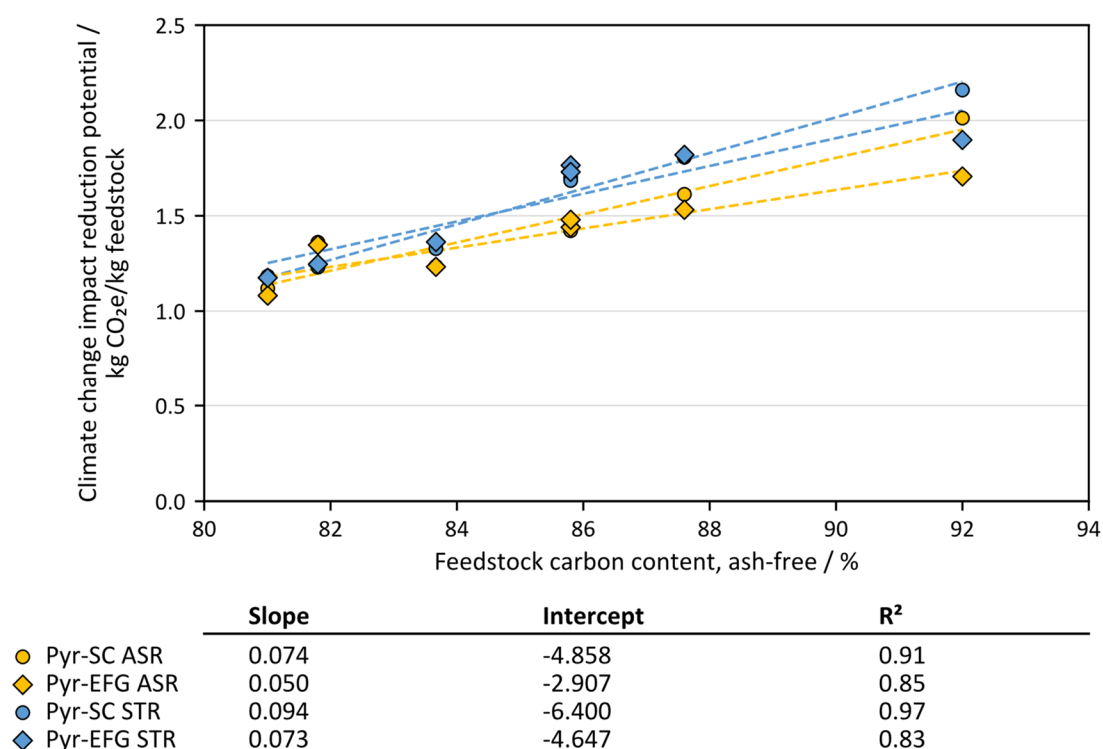


Figure 41: Correlation of climate change impact reduction potential with feedstock carbon content for pyrolysis-based chemical recycling process chains. Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route.

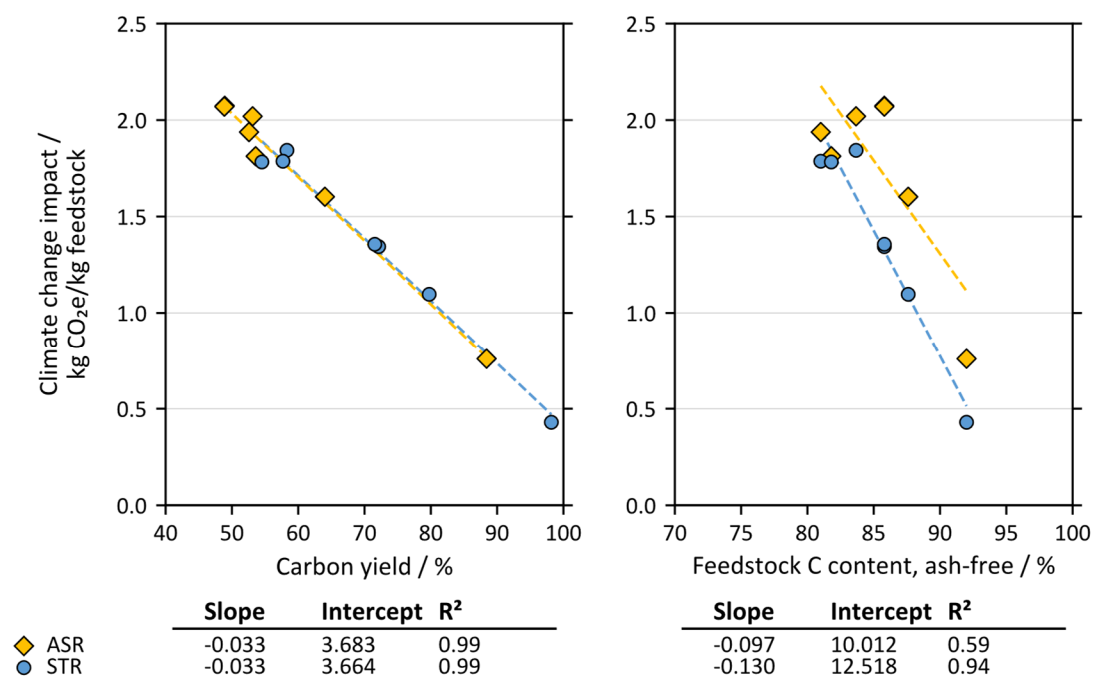


Figure 42: Correlation of pyrolysis process burdens with pyrolysis carbon recovery (left) and feedstock carbon content (right) for model feedstocks processed in the ASR and STR systems.

This demonstrates the same underlying relationship as observed previously, as a lower climate change impact of pyrolysis corresponds to a higher overall climate change impact reduction potential. Since the pyrolysis process was also shown to be the largest contributor to the sum of all process burdens of the entire process chain (cf. Section 6.1), the correlation of pyrolysis burdens with feedstock carbon content also explains the correlation of the climate change impact reduction potential with feedstock carbon content.

However, this correlation implies that improving carbon recovery through process optimization is likely constrained for heteroatom-containing feedstocks due to their lower carbon content. Thus, for feedstocks such as MPW, e.g., sorting fractions of LWP, a limited climate change impact reduction potential must be expected (cf. Section 5.6). Nevertheless, pyrolysis-based chemical recycling of the heteroatom-containing feedstocks outperformed energy recovery in terms of climate change impact.

This trend is consistent with previous studies, as similar conclusions were drawn by Krell et al.³⁰ Based on theoretical calculations, they concluded that the pyrolysis of MPO performed better than the pyrolysis of mixed plastic, and sorting residues on a mass-specific basis. If weighted with their yield in LWP sorting, however, they pointed out that due to their high share, the pyrolysis of sorting residues actually showed the highest potential to reduce climate change impact of all sorting fractions.

7.2 Influence of pyrolysis side product utilization

In addition to feedstock composition, the choice of reactor type influences the distribution of pyrolysis products by determining reaction conditions and thus affects the amount of side products formed requiring treatment for a given feedstock.

As shown in Figure 43 for selected model feedstocks, the influence of reactor type on process burdens is most pronounced for heteroatom-free feedstocks (LDPE and PP), less pronounced for PS and Mix AR, and nearly absent for heteroatom-containing feedstocks (Mix MH, Mix HH, and S-PCW). A comparison of contributions to the pyrolysis process burdens shows that the contribution of pyrolysis gas combustion significantly exceeds the impact of pyrolysis energy demand, regardless of reactor type. Only in the case of PS, following from a high pyrolysis oil yield and subsequently low gas yield, do energy-related impacts equal or exceed those from side product treatment.

Neglecting minor impacts due to differences in feedstock composition and energy demand, the previously introduced correlation of pyrolysis climate change impact and carbon recovery suggests that below a carbon recovery of approximately 80% in pyrolysis oil, CO₂ emissions from pyrolysis side product treatment dominate over pyrolysis energy demand as the main contributor to climate change impact (cf. Figure 44). Thus, reducing climate change impact primarily depends on improving carbon recovery in pyrolysis oil and efficient utilization of pyrolysis side products, while reducing energy demand plays a secondary role.

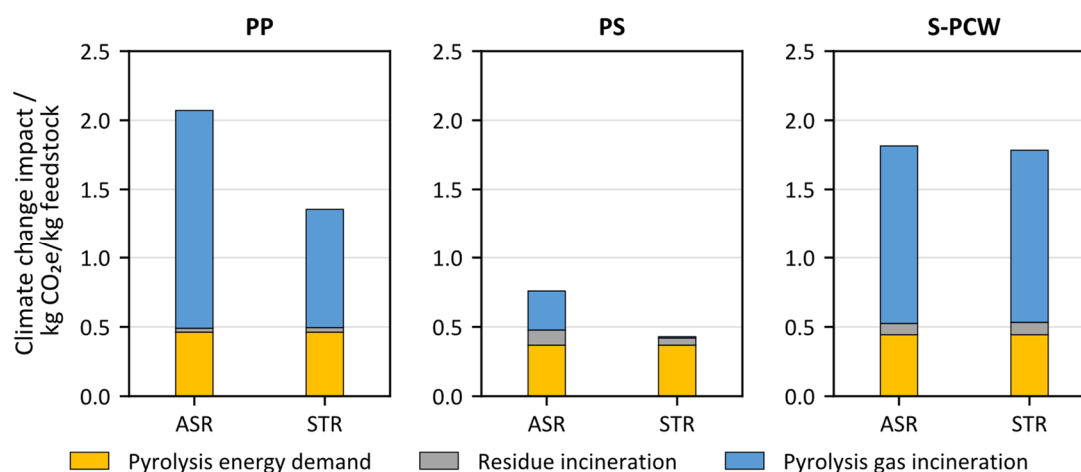


Figure 43: Pyrolysis process burdens including pyrolysis side product treatment for PP (left), PS (middle), and S-PCW (right).

Since complete avoidance of side product formation is unlikely – particularly for heteroatom-containing feedstocks – the utilization of pyrolysis side products becomes critical for reducing climate change impact. The impacts shown in Figure 43 represent a scenario in which pyrolysis gas is flared and pyrolysis residue is incinerated without energy recovery. Consequently, electricity is fully supplied from the grid, differing from the assumptions of the base case shown in Chapter 6. In cases with low carbon recovery in pyrolysis, this scenario leads to similar or even worse performance than energy recovery, if pyrolysis side products are not utilized at all. This is the case, regardless of pyrolysis oil utilization route, for the heteroatom-containing feedstocks Mix MH, Mix HH, and S-PCW, when using either the ASR or the STR system, as well as for LDPE and PP using the ASR system.

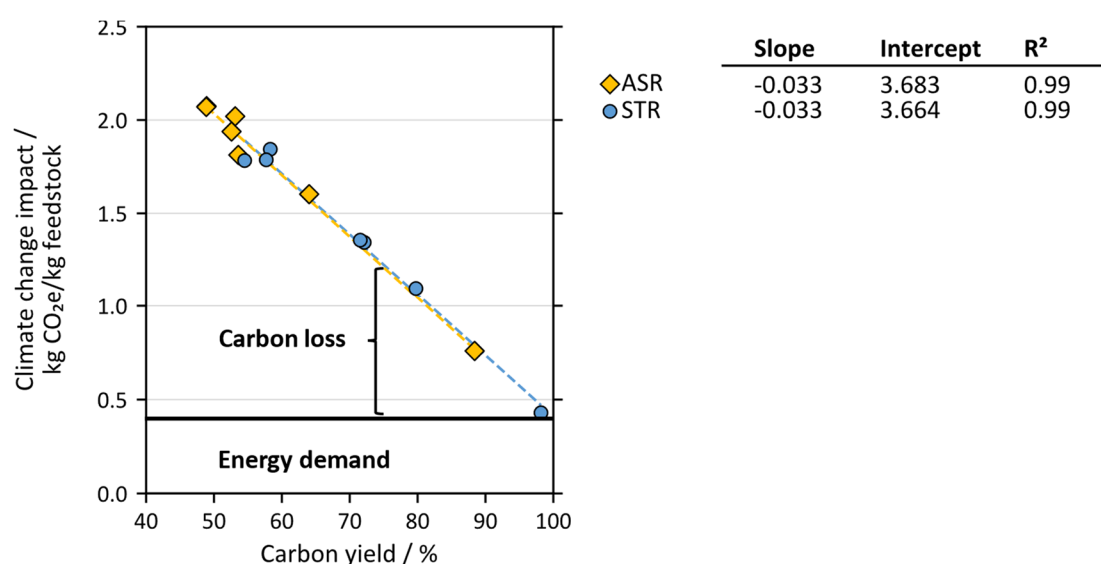


Figure 44: Distribution of pyrolysis process burdens from pyrolysis side product treatment and pyrolysis energy demand.

For the pyrolysis residue, alternative utilization options such as landfilling as form of CCS or use as a substitute fuel in cement kilns have been discussed.^{179,195} However, landfilling is currently not permitted in Germany due to restrictions regarding heating value and carbon content, and use in cement kilns may be limited by its chlorine content.¹⁹⁴ Therefore, treatment in MSWI, as modeled in this study, remains the most likely option. Due to the small quantities of residue, the resulting energy recovery and associated credits and their impact on the overall environmental performance are limited.

In contrast, energetic utilization of pyrolysis gas is more effective due to its higher quantity and energy content. Plastic Energy utilizes hot flue gas from pyrolysis gas combustion for reactor heating, eliminating the need for electric heating if the energy content of the pyrolysis gas is sufficiently high.²⁵ Arcus Greencycling targets electricity generation via a gas motor.¹⁹² For the model feedstocks analyzed, the electricity generated from pyrolysis gas would be sufficient to meet process demand in all cases except for pure PS, where gas production is insufficient.

While using a gas motor does not reduce direct emissions from pyrolysis or side product treatment, it reduces the sum of process burdens by substituting grid electricity. For PP, this results in a gross climate change impact of pyrolysis that is lower than the sum of pyrolysis process burdens by 0.46 kg CO₂e/kg PP, corresponding to decreases of 23% (ASR) and 35% (STR) (cf. Figure 45, left).

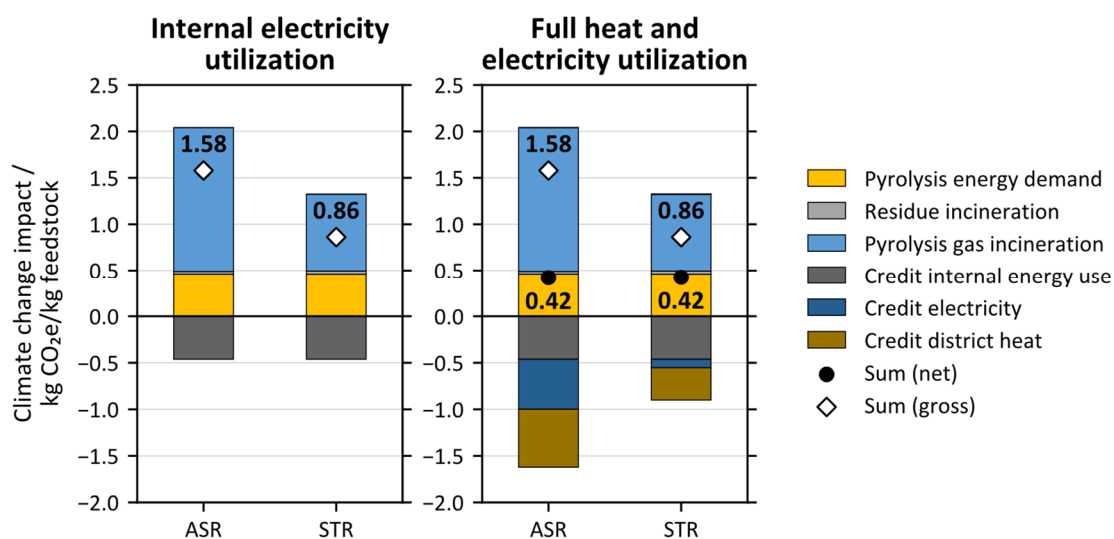


Figure 45: Climate change impact of PP pyrolysis with utilization of pyrolysis in a gas motor. Left: Coverage of internal electricity demand. Right: Full system integration with utilization of excess electricity and heat.

Further reductions are possible if combustion of pyrolysis gas in a gas motor is coupled with heat recovery for district heat generation.¹⁹³ This is assumed in the base scenario of this study. In the ASR case, these additional credits further reduce the gross climate change impact, offsetting the higher impacts caused by lower carbon recovery. Therefore, both reactor systems achieve identical net climate change impacts of pyrolysis of 0.42 kg CO₂e/kg PP (cf. Figure 45, right).

However, the STR system retains an advantage at the process chain level due to higher product yields and corresponding credits (cf. Section 6.1).

A second strategy to reduce carbon loss from pyrolysis is the material utilization of pyrolysis gas, e.g. in the EFG process. Thus, carbon that would otherwise be lost can be utilized. As shown in Figure 46, integrating pyrolysis gas from S-PCW into the EFG process reduces the net climate change impact by 0.49 kg CO₂e/kg S-PCW compared to the base case without integration. However, as discussed in Section 5.5, such integration requires co-location of pyrolysis and gasification units and may involve process adaptations that limit full utilization of pyrolysis gas. Furthermore, if both pyrolysis oil and pyrolysis gas are ultimately used as gasification feedstocks, direct gasification of plastic waste may represent a more efficient alternative by avoiding the intermediate pyrolysis step. Although such processes have been developed, they have not yet reached commercial maturity.⁸⁸

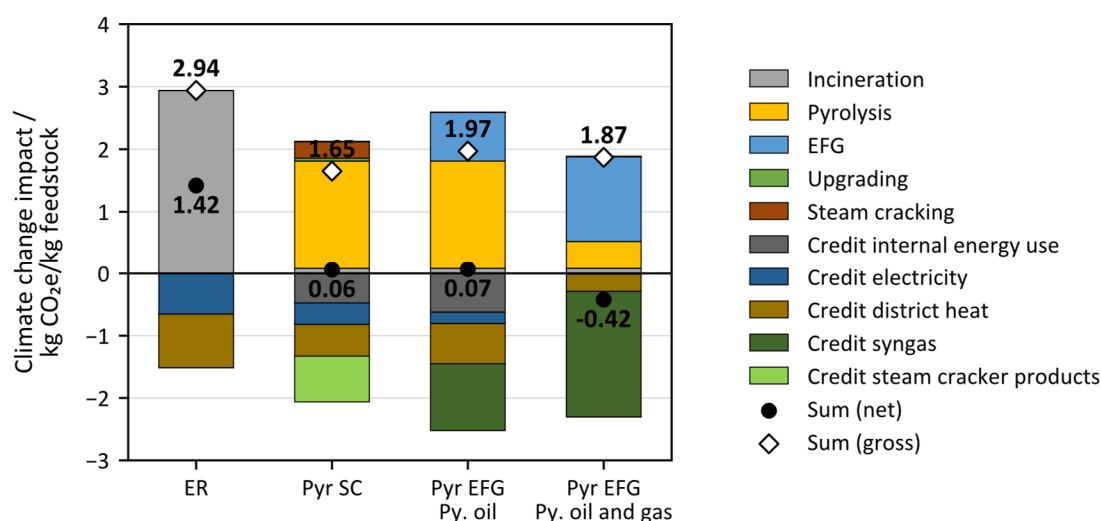


Figure 46: Climate change impact of integrating pyrolysis gas from conversion of S-PCW using the ASR system into EFG for the production of MeOH syngas. ER: Waste-to-energy process route. Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route.

This example demonstrates that material utilization of pyrolysis side products can be significantly more effective than their energetic use, as it reduces carbon losses from pyrolysis and increases production of target products. Similar concepts exist for the integration of pyrolysis gas into the cold part of the steam cracker, allowing direct recovery of monomers from pyrolysis gas, but have not been proven at larger scale.⁹⁷

7.3 Influence of pyrolysis energy demand

The energy demand of plastic pyrolysis has been widely debated, particularly in comparison to mechanical recycling.²²² While valid for high-quality recyclable plastics, this comparison is of

limited relevance for waste streams that cannot be mechanically recycled and are instead incinerated or downcycled, as highlighted by Schwarz et al.¹⁷⁵

Nevertheless, reliable data on pyrolysis energy demand – especially at industrial scale – are still limited. The values reported by Netsch et al. represent the minimum energy demand for heating, melting, reaction, and product evaporation, as they exclude heat losses and auxiliary energy consumption and are therefore independent of scale for the given product composition.¹¹² Accordingly, these values are used as the lower bound in the sensitivity analysis (50% of the base scenario).

Based on data from Arcus Greencycling, total electricity demand for PP conversion can be estimated at approximately 20% of the feedstock's heating value.¹⁹² This corresponds to roughly four times the minimum energy demand, or 200% of the base scenario, and is used as the upper bound. Comparable data for STR systems are not available, although a report of Plastic Energy suggests similar energy demand to the base case.²²³

The effect of changing energy demand depends on the utilization and availability of pyrolysis gas (cf. Figure 47). If sufficient pyrolysis gas is available for full coverage of pyrolysis electricity demand (e.g., PP in ASR), increasing energy demand reduces excess electricity available for export and thus lowers product credits. The gross impacts remain unchanged, since both pyrolysis burdens and credits for internal energy utilization increase by the same amount. If pyrolysis gas is insufficient, total process burdens, gross, and net impacts increase as electricity import from the grid increases.

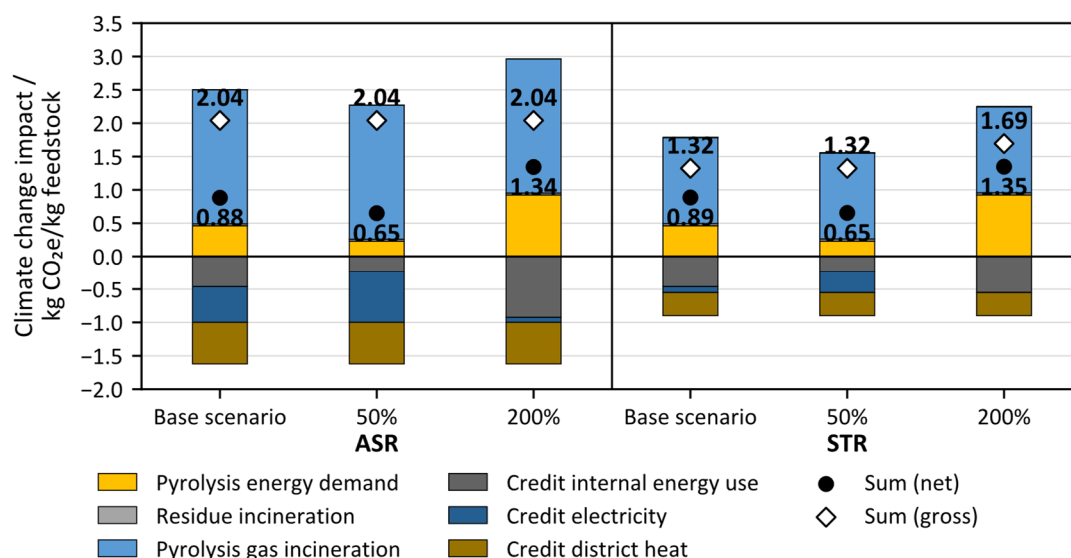


Figure 47: Influence of pyrolysis energy demand on climate change impact by halving or doubling electricity demand of the pyrolysis step for PP conversion in the ASR and STR system.

For the ASR system, reducing electricity demand decreases net climate change impact by up to 0.28 kg CO₂e/kg model feedstock, while increasing demand raises it by up to 0.57 kg CO₂e/kg.

Even at 200% of the base scenario, chemical recycling remains preferable to energy recovery, although the reduction potential decreases. Similar trends are expected for the STR system because identical energy demands are assumed in modeling. However, a combination of high energy demand and lack of energy recovery from pyrolysis gas can lead to worse performance than energy recovery, particularly for feedstocks with low carbon recovery.

Overall, these results confirm that carbon yield and the utilization of pyrolysis side products are the primary drivers of the climate change impact of pyrolysis. Improving carbon recovery reduces emissions from side product treatment and increases downstream product yields, thereby enhancing credits. Utilization of pyrolysis gas is therefore essential, particularly for feedstocks with limited carbon recovery due to heteroatom content, partially offsetting the burdens associated with carbon losses during pyrolysis. The influence of energy demand is secondary but becomes more relevant when energy recovery from pyrolysis gas is limited.

7.4 Pyrolysis oil utilization

With respect to the climate-optimal utilization of pyrolysis oil, no clear preference between upgrading and steam cracking on the one hand and EFG on the other hand could be established previously. Accordingly, key assumptions related to steam cracker product distribution, hydrogen demand and supply, and syngas composition are evaluated in this section. This enables identification of the factors that determine which pyrolysis oil utilization route is preferable.

7.4.1 Upgrading and steam cracking of pyrolysis oil

Based on the modeling assumptions applied in this thesis, the impact of pyrolysis oil upgrading is determined solely by hydrogen demand. This demand is calculated from the stoichiometric requirements for heteroatom removal and for adjusting the molar H/C ratio to 2 (cf. Section 4.4.1). Impacts from electricity consumption, catalysts, and other process elements are neglected due to a lack of data.

For pyrolysis oils derived from both ASR and STR systems, hydrogen consumption is dominated by saturation requirements rather than heteroatom removal. The only exception is S-PCW processed in the STR system. Consequently, the targeted H/C ratio has a strong influence on hydrogen demand. As shown in Figure 48a, increasing the target H/C ratio to 2.1 results in a 33% increase in hydrogen demand for S-PCW (ASR). However, this change has only a minor effect on the resulting net and gross climate change impacts.

In contrast, the hydrogen source has a much stronger influence. In the base scenario, refinery hydrogen is used. Substituting hydrogen from steam cracking leads to negligible changes, as both sources have similar impacts in the ecoinvent database (cf. Figure 48b). However, using hydrogen from SMR increases the upgrading impact approximately by a factor of four. The differences in impact can be attributed to the way that hydrogen is produced: refinery hydrogen

and steam cracking hydrogen can be considered as side products of other processes whereas hydrogen from SMR is produced on demand at the cost of high CO₂ emissions.³⁷

Although the overall effect on S-PCW remains limited, the impact becomes more significant for feedstocks requiring larger hydrogen inputs due to low H/C ratios. For example, in the case of PS processed in the ASR system, the net climate change impact increases by 0.68 kg CO₂e/kg PS, reducing the climate change impact reduction potential by 33%. Combined with increased hydrogen demand, this effect would be even more pronounced. Thus, the availability of low-impact hydrogen or the requirement to produce hydrogen via SMR to fulfill hydrogen demand can have a major impact on the process burdens of pyrolysis oil upgrading.

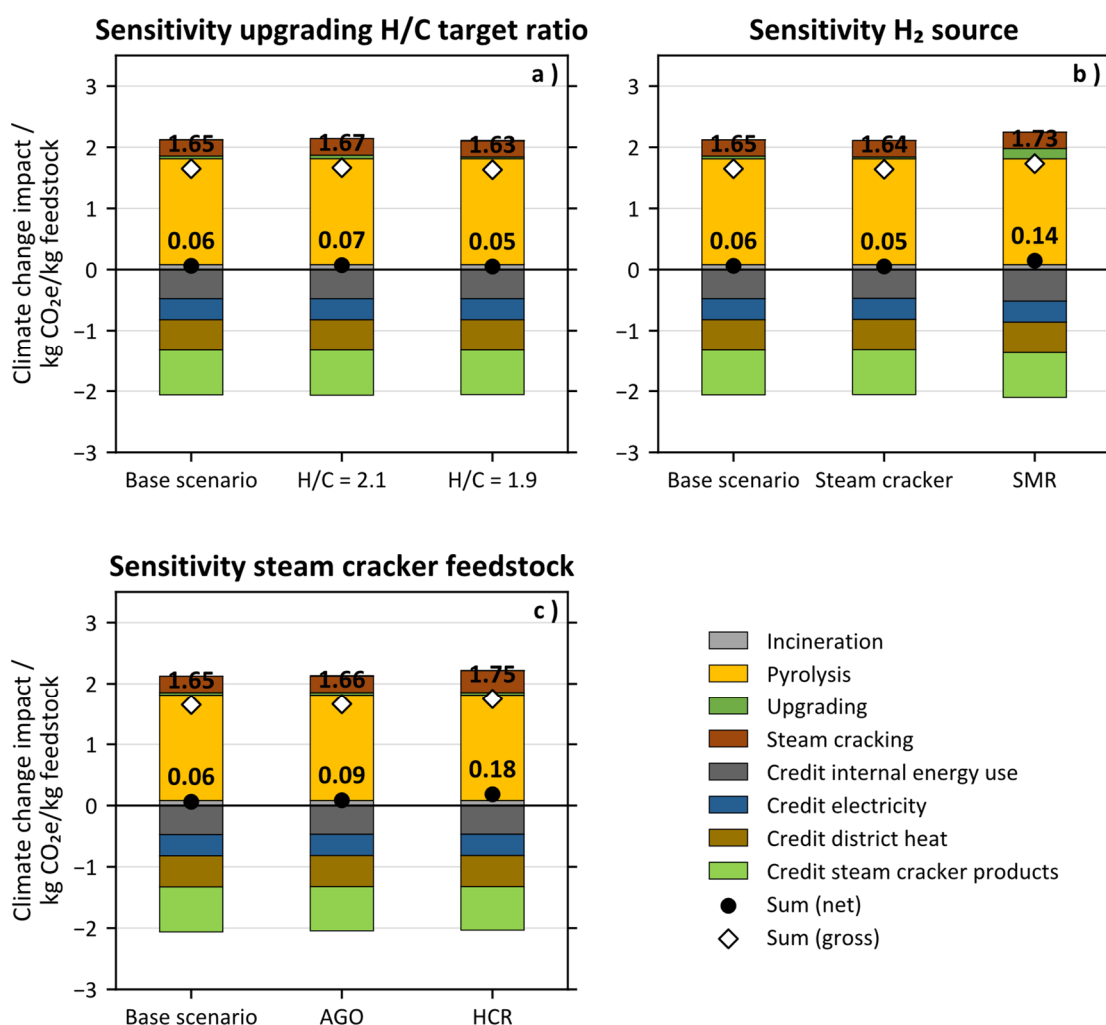


Figure 48: Influence of the target H/C ratio (a), hydrogen source for upgrading (b), and steam cracker product distribution (c) on the climate change impact of upgrading and steam cracking of pyrolysis oil from S-PCW produced in the ASR system.

For steam cracking of upgraded pyrolysis oils, experimental data are limited. Most available studies focus on untreated pyrolysis oils.^{115,213,224} However, it is well established that feedstock composition strongly influences steam cracker product yields.¹¹⁸ To assess this uncertainty,

alternative product distributions based on AGO and HCR were evaluated (cf. Appendix B.3). These high-boiling refinery fractions may resemble upgraded pyrolysis oils, given uncertainties regarding the extent to which upgrading reduces boiling range (cf. Section 2.3.2).

As shown in Figure 48c, shifting to AGO- or HCR-based product distributions increases the net climate change impact. This is caused by higher process impacts and reduced product credits. The increase is most pronounced for HCR but remains small in absolute terms (0.12 kg CO₂e/kg S-PCW). This limited effect can be explained by the relatively small change in total carbon recovery in steam cracker products despite a significant shift in product distribution. Since credits for all material-use products are identical, the reduction in credits results from a slight increase in carbon recovery in fuel products – receiving lower credits according to Plastics Europe allocation guidelines – and a small decrease in carbon recovery in material use products.¹⁹⁶ While these fuel products are primarily used as fuels as they are unsuitable for base chemical production, they are also valuable materials for electrode material production as they are rich in aromatics and free of sulfur and heavy metals.³⁷

In summary, the parameters analyzed here have a limited influence on the overall climate change impact of the waste-to-monomers route relative to upstream pyrolysis performance. However, their importance increases with higher pyrolysis oil yields. In addition, it remains uncertain whether upgraded pyrolysis oils can achieve the same product yields as conventional feedstocks. This uncertainty is addressed in a subsequent analysis of overall process yields (cf. Section 7.5).

7.4.2 EFG of pyrolysis oil

The second utilization option for pyrolysis oils analyzed in this thesis is their conversion to syngas. In contrast to the waste-to-monomers route, the results for the waste-to-syngas route are based on a thermodynamic flowsheet model rather than on a set of simplifying assumptions. This allows a more direct assessment of the influence of individual process parameters.

In gasification, two parameters primarily affect product yield, aside from design choices such as the selected syngas configuration: reactor temperature and gasifier feedstock conversion. These parameters were evaluated in previous work using the same flowsheet model.¹⁷⁸ The results indicate that the net climate change impact is not highly sensitive to variations of these parameters within typical operating ranges of an EFG plant.

This behavior can be explained by compensating effects within the system. For example, an increase in syngas yield resulting from a lower reactor temperature is accompanied by a decrease in recoverable district heat, and vice versa. As a result, the combined effect on process burdens and total credits remains small. Similarly, a 1% decrease in gasifier feedstock conversion does not lead to a proportional reduction in syngas yield, as the chemical equilibrium shifts according to Le Chatelier's principle, dampening the loss of product yield.

As discussed in Section 5.4, the choice of syngas configuration – MeOH syngas or Oxo syngas – has a strong influence on carbon recovery. For example, in the case of PP processed in the ASR system, the overall carbon recycling efficiency increases from 31% for MeOH syngas to 47% for Oxo syngas. For the STR system, this difference can be estimated at 47% versus 68%, based on the corresponding EFG carbon recovery data.

These differences are clearly reflected in the EFG process burdens (cf. Figure 49). The higher H_2/CO ratio required for MeOH syngas necessitates increased conversion of CO via the WGS reaction. The resulting CO_2 is separated from the syngas and emitted, decreasing carbon recovery and increasing process burdens and subsequently the gross climate change impact. In contrast, this effect is less pronounced in the Oxo syngas configuration, leading to higher carbon recovery and lower gross emissions. This behavior is observed consistently across the evaluated feedstocks PP, PS, and S-PCW.

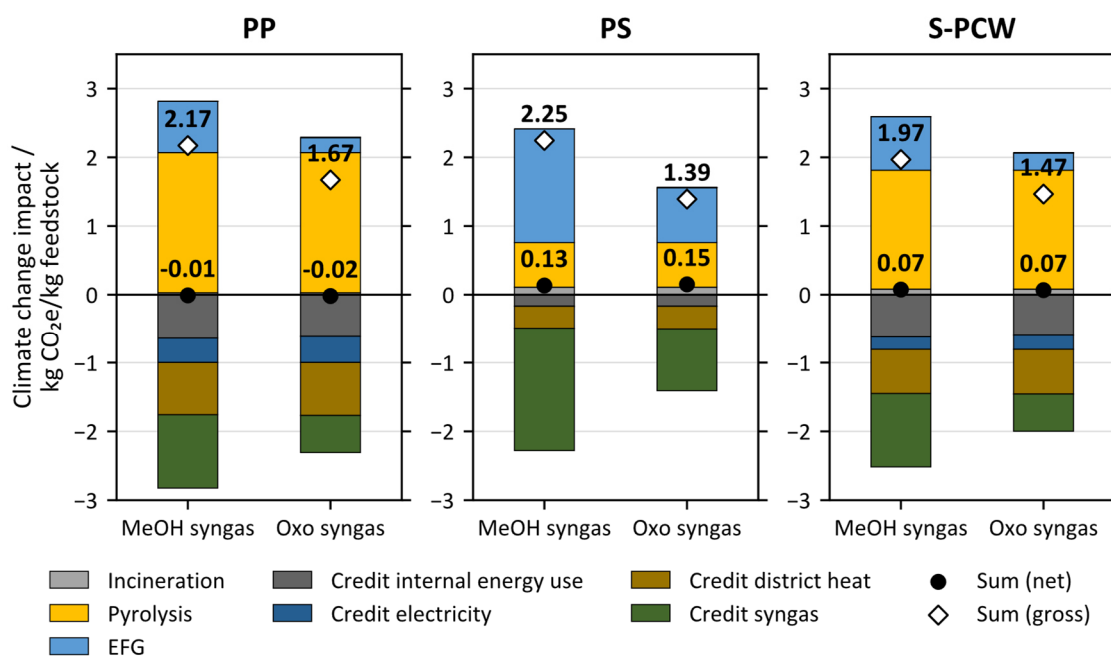


Figure 49: Influence of syngas composition on the climate change impact of EFG for pyrolysis oils from PP (left), PS (middle), and S-PCW (right) using the ASR system.

In contrast, these differences are not reflected in the net climate change impacts. This similarity arises from the reference process used for calculating product credits. HFO, commonly used as feedstock in EFG plants, exhibits properties similar to those of pyrolysis oils. Consequently, changes in process efficiency affect both the modeled system and the reference system in a similar manner. Lower process emissions in Oxo syngas production are therefore accompanied by reduced product credits, resulting in nearly identical net climate change impacts.

It can therefore be concluded that the choice of syngas configuration does not significantly influence the climate change impact reduction potential of the waste-to-syngas route – provided that HFO-derived syngas is the substituted reference. If syngas is derived from a feedstock with

higher H/C ratio than HFO such as natural gas, this is expected to change, as the hydrogen deficiency of the plastic pyrolysis oils becomes more pronounced.

If deficient hydrogen for adjusting the H_2/CO ratio of syngas was supplied from electrolysis instead of through WGS, this would decouple the H and C balances of the gasification process entirely, changing the picture altogether. Accordingly, the apparent decoupling between climate change impact and carbon recycling efficiency that is observed for the MeOH and Oxo syngas configurations is attributed to the chosen reference process for syngas generation. If hydrogen deficiency is resolved through feedstocks with more favorable H/C ratio or the import of hydrogen from electrolysis, the carbon efficiency of syngas generation and the resulting climate change impact will correlate again as observed for the pyrolysis process previously. Therefore, gasification processes that do not rely on WGS for adjusting of the syngas H_2/CO ratio will likely prove better in the long term as more carbon is retained in the target product.

7.4.3 Comparison of pyrolysis oil utilization options

In comparing utilization options for pyrolysis oil, the focus is placed solely on the conversion processes. The pyrolysis step itself does not influence downstream conversion beyond determining the composition of the resulting pyrolysis oil. Therefore, the comparison of pyrolysis oil conversion processes is conducted using 1 kg of pyrolysis oil as input, rather than relating results to the model feedstock.

As shown in Figure 50, conversion of pyrolysis oil via upgrading and steam cracking and via EFG in the MeOH syngas configuration results in very similar net climate change impacts. This is also the case for pyrolysis oils of differing composition arising from different feedstocks or reactor systems. Only pyrolysis oils derived from PS, and to a lesser extent from Mix AR, show more pronounced differences between the utilization options.

Analysis of the sources of process burdens reveals that, for both utilization routes, impacts are dominated by two main contributions. In the case of EFG, the largest share of burdens arises from direct CO_2 emissions, followed by electricity consumption. For upgrading and steam cracking, burdens similarly result from direct CO_2 emissions, while the second major contribution stems from hydrogen consumption. The latter is relevant only for pyrolysis oils with low H/C ratios or with significant heteroatom content (cf. Section 4.4).

For upgrading and steam cracking, correlations between hydrogen demand and molar H/C ratio, as well as between product yield and pyrolysis oil carbon content, were identified (cf. Section 5.3). These correlations are partly driven by the underlying modeling assumptions. For EFG, correlations between carbon recovery and syngas yield with pyrolysis oil H/C ratio and LHV were observed (cf. Section 5.4).

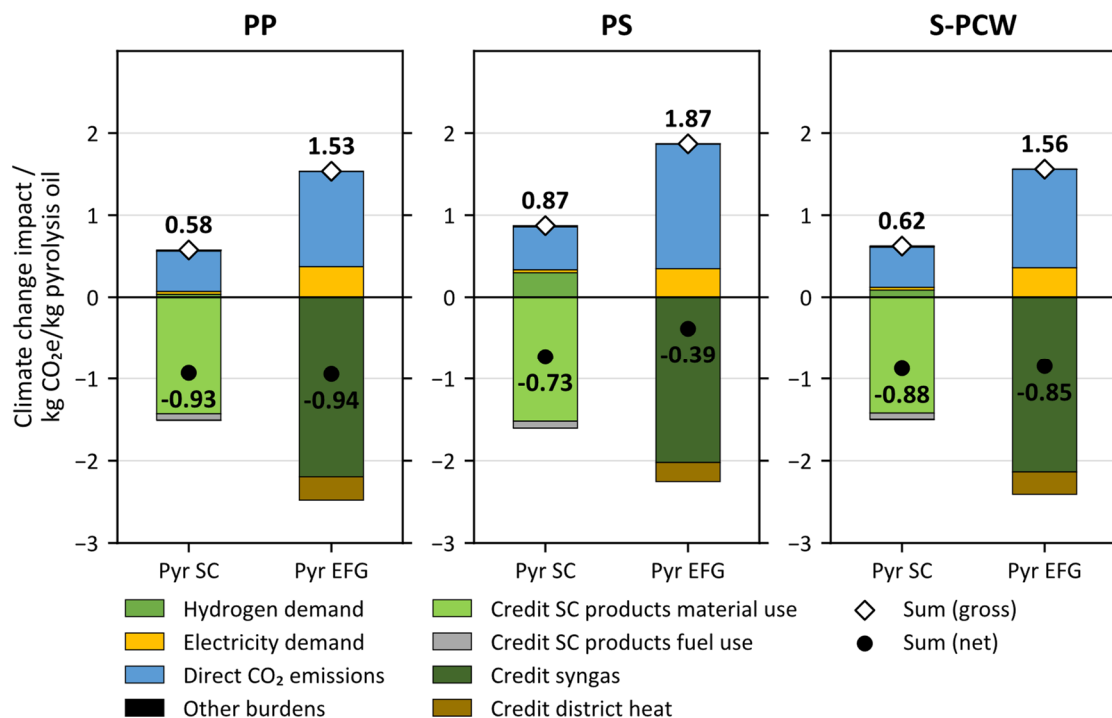


Figure 50: Climate change impacts of pyrolysis oil utilization via upgrading and steam cracking and via EFG (MeOH syngas configuration) for pyrolysis oils from PP (left), PS (middle), and S-PCW (right). Pyr SC: Waste-to-monomers process route. Pyr EFG: Waste-to-syngas process route. SC: steam cracker.

These relationships are also reflected in the gross and net climate change impacts of pyrolysis oil utilization, as shown in Figure 51. For both conversion pathways, gross climate change impact (i.e., total process burdens) increases with decreasing H/C ratio. At the same time, product credits for steam cracker products and MeOH syngas change to a lesser extent, resulting in an overall increase in net climate change impact with decreasing H/C ratio.

Based on the assumptions of the base scenario, EFG appears to be the preferable utilization route for pyrolysis oils with high H/C ratios when substituting syngas generated from HFO, whereas below an H/C ratio of approximately 1.8, upgrading and steam cracking become slightly more favorable (cf. Figure 51a). However, these differences are generally small, particularly in the region around $H/C \approx 2$. Additionally, they only become relevant when pyrolysis oil utilization is evaluated on its own, excluding the previous pyrolysis process.

Furthermore, altered boundary conditions can significantly change this relationship. In a scenario where hydrogen for upgrading is supplied via SMR and excess heat from EFG cannot be utilized, both the crossover point and the relative ranking of the utilization options shift (cf. Figure 51b). Under these conditions, upgrading and steam cracking become more favorable for pyrolysis oils with high H/C ratios, while EFG becomes preferable for oils with lower H/C ratios.

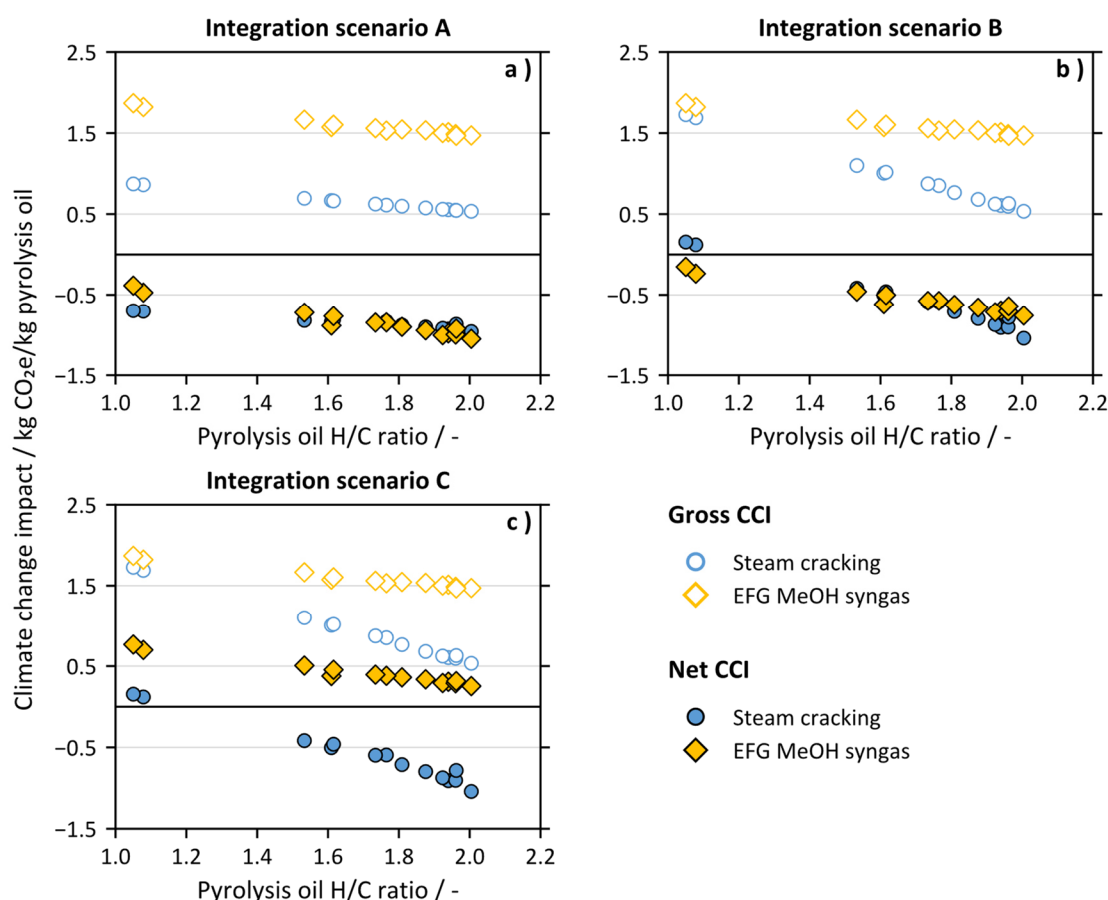


Figure 51: Dependence of the climate change impact of pyrolysis oil utilization on the pyrolysis oil H/C ratio for different integration scenarios. Scenario A: full utilization of all products, refinery H₂ for upgrading, MeOH syngas credits from HFO-based EFG (base scenario). Scenario B: utilization of main products only, SMR H₂ for upgrading, MeOH syngas credits from HFO-based EFG. Scenario C: utilization of main products only, SMR H₂ for upgrading, MeOH syngas credits from natural gas based partial oxidation.

At the same time, MeOH syngas can also be produced via partial oxidation (POx) of natural gas, which shows a 45% lower net climate change impact than HFO-based production^r. In this case, steam cracking of upgraded pyrolysis oils would always be the preferred pyrolysis oil utilization option (cf. Figure 51c). Consequently, substituting natural gas-based MeOH syngas would be detrimental, whereas substitution of HFO-based syngas can be beneficial.

Changes in overall yields will likely also affect the comparison of utilization routes. However, better process models and more experimental data are required especially regarding upgrading and steam cracking to validate current assumptions beyond the sensitivity analyses previously discussed.

While the climate change impact shows a dependency on pyrolysis oil composition, the results indicate that boundary conditions – particularly the reference process for syngas generation,

^r Calculated using the flowsheet model also used for modeling of EFG of pyrolysis oils and HFO.

energy integration of pyrolysis oil utilization and hydrogen supply for pyrolysis oil upgrading – are more decisive than intrinsic pyrolysis oil properties based on the current modeling strategy. Consequently, the selection of a pyrolysis oil utilization route should be guided primarily by system-level boundary conditions rather than by intrinsic process performance alone.

7.5 Variation of product yields and product credits

To achieve a positive climate change impact reduction potential of chemical recycling relative to energy recovery, the net climate change impact of the chemical recycling route must be lower than that of energy recovery. Consequently, the reduction potential is sensitive to changes in both process burdens and product credits.

As neither of the chemical recycling routes analyzed has yet been demonstrated at industrial scale and experimental data on pyrolysis oil utilization remain scarce, uncertainty persists regarding whether the yields calculated in this thesis can be realized. Since consistent thermodynamic models are only available for the conversion of pyrolysis oil via EFG, a parameter-based sensitivity analysis for pyrolysis, upgrading, and steam cracking is not feasible. Therefore, a model-independent sensitivity approach is applied, in which product yields and associated credits are varied independently of specific process assumptions, enabling the identification of robustness margins.

Process burdens are largely driven by carbon losses along the process chain. Accordingly, an increase in carbon losses relative to the base scenario leads to lower product yields, higher process burdens, and reduced product credits. In addition to process performance, the reduction potential depends on the climate change impact of the reference processes used for conventional product generation. Therefore, both product yield and product credit are varied in the following analysis.

Product yield is varied in the range from 0 to 100% of the base case. Any reduction in yield is assumed to result in the emission of the equivalent amount of carbon as CO₂ that would otherwise be bound in the product. Product credits are varied between 0 and 150% to account for changes in the environmental impact of reference processes. Credits from electricity and district heat generation are set to zero, as they strongly depend on process integration and are expected to change in the future (cf. Section 7.6). A detailed description of the calculation methodology is provided in Appendix E.3.

Figure 52 defines feasibility regions in which the respective chemical recycling route achieves a lower climate change impact than energy recovery. The black square indicates the base case in the three process routes evaluated. Chemical recycling is favorable to the right of the dashed line, which represents the threshold at which energy recovery performs better. From this representation, minimum product yields and minimum product credits (relative to the base case) can be derived that must be achieved to ensure a positive climate change impact reduction potential.

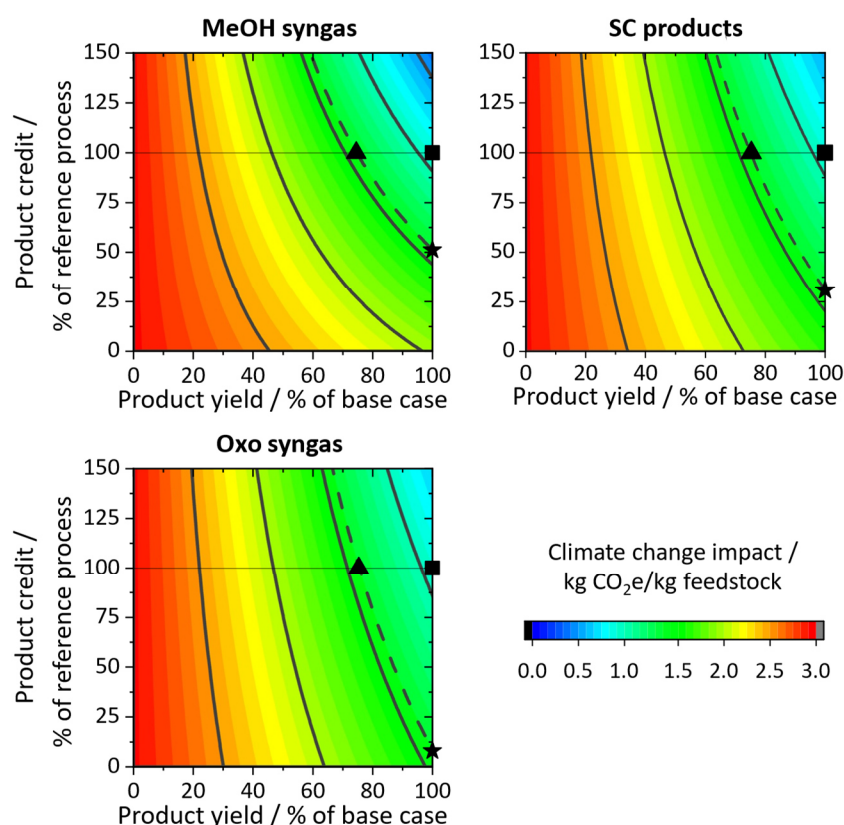


Figure 52: Sensitivity of the waste-to-syngas route in MeOH syngas configuration (top left), the waste-to-syngas route in Oxo syngas configuration (bottom left), and the waste-to-monomers route (top right) for chemical recycling of S-PCW with ASR pyrolysis to variations in overall product yield and product credit. Square: base scenario. Triangle: minimum product yield. Star: Minimum product credit.

For S-PCW processed in the ASR system, at least 75% (black triangle) of the base case steam cracker product yield must be achieved at full product credits, or alternatively, at least 31% (black star) of the base case product credit must be realized at full product yield to outperform energy recovery in the waste-to-monomers route. For the MeOH and Oxo syngas routes, the minimum product yields are also approximately 75%, while minimum product credits differ at 31% for MeOH syngas and only 8% for Oxo syngas. Minimum product yields and credits for all evaluated cases are summarized in Table 10.

Across all feedstocks and process chains, it is observed that minimum product yields and minimum product credits increase with decreasing carbon recycling efficiency. Accordingly, feedstocks and recycling routes with higher carbon recycling efficiencies are more likely to achieve a net climate benefit, as they provide greater flexibility with respect to variations in process performance and reference system conditions.

Table 10: Minimum product yields and product credits. Pyr SC: Waste-to-monomers. Pyr EFG MeOH: Waste-to-syngas in MeOH syngas configuration. Pyr EFG Oxo: Waste-to-syngas in Oxo syngas configuration. n.a.: not analyzed.

Feedstock		Pyr SC		Pyr EFG MeOH		Pyr EFG Oxo	
% of base case	Reactor	Minimum yield	Minimum credit	Minimum yield	Minimum credit	Minimum yield	Minimum credit
LDPE	ASR	83.0	53.1	81.3	64.1	n.a.	n.a.
	STR	55.8	-21.9	60.6	24.5	n.a.	n.a.
PP	ASR	83.3	53.9	82.2	65.9	83.2	37.3
	STR	56.3	-20.6	61.1	25.6	n.a.	n.a.
PS	ASR	50.6	-36.2	59.6	22.6	60.0	-49.3
	STR	49.7	-39.0	57.4	18.4	n.a.	n.a.
Mix AR	ASR	62.9	-2.5	63.7	30.4	n.a.	n.a.
	STR	52.7	-30.5	59.1	21.7	n.a.	n.a.
Mix MH	ASR	76.9	36.3	76.2	54.4	n.a.	n.a.
	STR	68.5	13.1	69.2	41.0	n.a.	n.a.
Mix HH	ASR	75.6	32.7	75.8	53.7	n.a.	n.a.
	STR	68.1	11.8	72.1	46.5	n.a.	n.a.
S-PCW	ASR	75.0	30.9	74.5	51.2	75.4	7.9
	STR	72.2	23.2	71.3	44.9	n.a.	n.a.

In extreme cases, such as PS recycling via the waste-to-syngas route in the Oxo syngas configuration and the waste-to-monomers route, the minimum required product credit drops below zero. In these cases, the amount of carbon retained in material products alone is sufficient to achieve a lower net climate change impact than energy recovery, despite the process burdens associated with recycling. Accordingly, achieving a positive climate change impact reduction potential no longer depends on product credits. Thus, regardless of the specific reference process selected, chemical recycling of the respective feedstock via the corresponding process route reduces the climate change impact of waste treatment and contributes to lowering the total climate change impact on the system level.

Regarding potential losses in upgrading and steam cracking that are not accounted for in the process model, these would likely not lead to inferior performance compared to energy recovery, provided that product yields remain above the calculated minimum thresholds. The conservative assumption to consider only credits from target products, neglecting generation of excess electricity and district heat, gives additional flexibility. However, such losses would reduce the achievable climate change impact reduction potential.

7.6 Impacts and credits of electricity and district heating

A significant share of the credits arises from the recovery of electricity and district heat. In the case of energy recovery, these constitute the primary products of the waste treatment process.

In contrast, within the chemical recycling pathways, electricity and district heat play a dual role. Electricity may either be supplied from the grid to operate the process, if not fully covered internally by energetic utilization of pyrolysis side products, or it may be exported to substitute grid electricity. District heat, by comparison, appears exclusively as a side product. Consequently, changes in the climate change impacts associated with conventional electricity and district heat generation directly affect both the net climate change impacts and the resulting reduction potentials.

As Germany and the EU pursue GHG emission reductions in line with the Paris Agreement, a continued decline in the climate change impact of electricity and district heat generation is expected.²²⁵ Historically, the climate change impact of electricity generation has decreased from 0.763 kg CO₂e/kWh_{el} in 1990 to 0.363 kg CO₂e/kWh_{el} in 2024.²²⁶ For district heat, the situation is more complex due to its decentralized and region-specific supply structures. Nevertheless, a similar downward trend is targeted.²²⁷

For the sensitivity analysis, the climate change impacts of electricity and district heat generation are varied between a reduction of 90% and an increase of 25% relative to the base values. The electricity mix is represented by the German market mix for 2021 as modeled in the ecoinvent database v3.10.²²⁸ District heat generation is approximated using a combined heat and power (CHP) plant fueled by natural gas as a proxy.²²⁹

For energy recovery, decreases in the credits for electricity and district heat lead to a significant increase in the resulting net climate change impact, as these products present the only source for product credits. For example, the net climate change impact of treating PP via energy recovery would rise from currently 1.47 kg CO₂e/kg PP to 2.98 kg CO₂e/kg PP, if credits decreased by 90%.

For the pyrolysis-based chemical recycling routes, effects differ depending on the feedstock and the process route. As electricity is sometimes available in excess while in other cases it is imported, the respective net climate change impact can both increase or decrease with decreasing credits for electricity generation. In contrast, net climate change impact of the chemical recycling routes always increases with decreasing credits for district heat generation.

As net climate change impacts of both treatment options change differently, the projection for one treatment option without showing the other does not lead to conclusive results. Therefore, Figure 53 shows the resulting climate change impact reduction potentials of the waste-to-monomers route – defined as the difference in net climate change impact between energy recovery and chemical recycling – for the model feedstocks PP, PS, and S-PCW. It becomes apparent that across the entire parameter range, chemical recycling remains the favorable option, as the reduction potential remains positive. This finding is consistent with results reported by Hermann et al.²³⁰

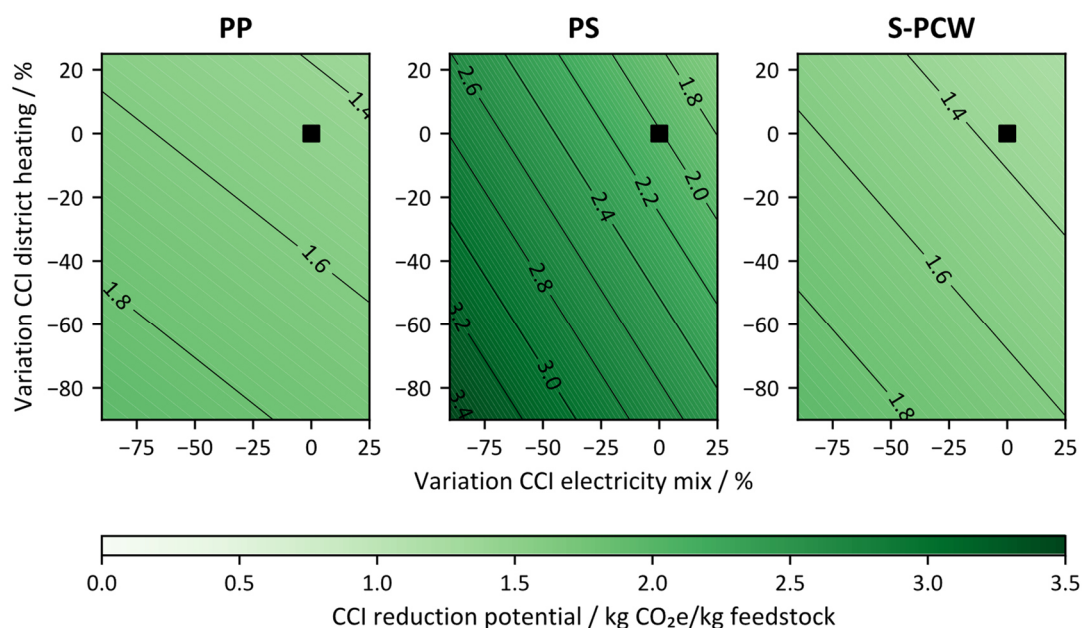


Figure 53: Climate change impact reduction potential of waste-to-monomers chemical recycling of PP (left), PS (middle), and S-PCW (right) based on ASR data for varying climate change impacts of electricity and district heat. Black square: Base case. CCI: Climate change impact.

A decrease in the climate change impact of electricity generation leads to an increase in the reduction potential. This effect is most pronounced for PS, as pyrolysis of PS relies more strongly on externally supplied electricity. Consequently, an electricity mix with lower carbon intensity reduces the climate change impact of chemical recycling.

For the other feedstocks, the effect is less pronounced due to higher internal electricity generation from pyrolysis side products. In cases with net electricity export, a decrease in the climate change impact of electricity generation may even increase the net climate change impact of chemical recycling. However, as 43% of product credits in energy recovery originate from electricity generation, the net climate change impact of energy recovery increases more strongly under these conditions. As a result, the overall climate change impact reduction potential of chemical recycling still increases with a decarbonized electricity mix.

A similar trend is observed for reductions in the climate change impact of district heat generation. Both chemical recycling and energy recovery produce district heat as a side product. However, energy recovery depends more strongly on district heat credits. Consequently, a decrease in the climate change impact of district heat generation reduces the net impacts of both systems, but increases the relative advantage of chemical recycling.

Overall, the defossilization of the electricity and heating sectors enhances the climate change impact reduction potential of pyrolysis-based chemical recycling. As a result, the minimum product yields and product credits required to outperform energy recovery decrease, expanding the feasibility space for implementing pyrolysis-based recycling technologies.

However, the projections do not consider a future equipment of MSWI plants with CCS technology in a fully decarbonized scenario as in this case both the burdens and the credits of energy recovery change. Likewise, burdens and credits of the pyrolysis-based chemical recycling routes change, if they are equipped with CO₂ mitigation technologies, e.g., by also using CCS or electrifying the steam cracking process.

7.7 Study limitations

Study limitations arise from the selection of chemical recycling routes, the underlying process modeling approaches used for compiling LCI data and from the LCA methodology itself. While the influence of key modeling assumptions has been addressed in the preceding sensitivity and scenario analyses, methodological limitations of the LCA – beyond the choice of perspective – have not yet been discussed.

A primary limitation of this study is the focus on only pyrolysis-based chemical recycling routes as other technologies and approaches are disregarded. Additionally, the restriction to climate change impact neglects effects that may occur for other impact categories, such as resource depletion, acidification, and eutrophication. Although the importance of climate change mitigation is widely emphasized in the literature, potential burden shifting cannot be excluded without a comprehensive multi-impact assessment.^{14,171,231} However, data availability for evaluating additional impact categories remains limited, particularly for the pyrolysis process itself.

Furthermore, waste collection and sorting are excluded from the system boundaries, as these steps are not relevant for the defined model feedstocks. In real waste management systems, however, these processes play a critical role in determining feedstock composition. While their absolute contribution to climate change impact is typically small, they become relevant in system-level assessments that evaluate changes in sorting strategies or waste management configurations.^{30,62} In such cases, inclusion of these processes would be necessary to ensure a consistent representation of all material flows.

At the process level, this study relies on model feedstocks rather than real waste fractions. Although the selected model feedstocks represent the most relevant polymer types and include a proxy for EoL plastic waste, additional contaminants commonly present in real waste – such as biomass residues, moisture, or adhering impurities – may affect process performance. These factors can affect pyrolysis behavior through additional feedstock interactions.⁶⁶ Moreover, the analysis is based on a single experimental dataset due to limitations in data availability and comparability, especially across feedstock composition and reactor type. The inclusion of additional datasets, particularly from industrial-scale operations, would significantly improve the robustness and reliability of the results.

Finally, this study focuses exclusively on environmental performance. A comprehensive assessment of chemical recycling technologies should also consider other dimensions of sustainability, including economic viability and social acceptance. Economic analyses are particularly relevant

both in the context of waste management systems and for integration into the future chemical industry. In addition, social factors may influence the implementation of chemical recycling technologies, as even technically mature solutions may face challenges related to public acceptance.

8 Conclusion and outlook

New approaches to waste management and resource use such as pyrolysis-based chemical recycling are required to transform the plastics industry into a sustainable industry, operating within planetary boundaries. As demonstrated in this thesis, pyrolysis can contribute to this transition by providing a pathway to recycle mixed plastic waste (MPW) that is currently directed to energy recovery. However, its actual potential to reduce climate change impacts depends on a multitude of factors and requires careful evaluation of the specific system context.

This thesis analyzed three research questions in particular:

- How does waste composition influence the climate change impact of pyrolysis-based chemical recycling?
- How does pyrolysis oil composition affect downstream utilization pathways?
- To what extent can pyrolysis-based recycling of MPW reduce the climate change impact relative to waste incineration with energy recovery?

By employing Life Cycle Assessment (LCA) methodology on the basis of pyrolysis experimental data from literature and model development for downstream processes, two pyrolysis-based process chains were analyzed: (1) pyrolysis with subsequent steam cracking of upgraded pyrolysis oils for the recovery of steam cracker products, i.e., ethylene, propylene, butenes, butadiene, and BTX aromatics, and (2) pyrolysis followed by entrained-flow gasification (EFG) of pyrolysis oils for the generation of syngas suitable for methanol (MeOH) or Oxo synthesis.

Feedstock composition, i.e., the types of polymers present in the waste, proved to be the most influential factor affecting process performance. Heteroatom-free feedstocks such as PE, PP, and PS consistently showed high product yields, resulting in lower direct process emissions and higher credits for chemical recycling products. In contrast, heteroatom-containing feedstocks – mixtures of polyolefins with PET, PA6, and PVC – exhibited significantly lower product yields. Nevertheless, within the analyzed scenarios, their recycling via pyrolysis still achieved a reduction in climate change impact compared to energy recovery.

For all waste-to-chemicals value chains and feedstocks, clear correlations between feedstock carbon content, product yield, and climate change impact reduction potential, i.e., the difference between net climate change impact of energy recovery and pyrolysis-based chemical recycling, were observed. Higher carbon content consistently led to higher pyrolysis oil yields and subsequently to higher target product yields, resulting in a greater overall climate change impact reduction potential. As this correlation was also reflected in the carbon recycling efficiency – thus accounting for differences in carbon availability – these results indicate that heteroatom-containing feedstocks inherently perform worse than heteroatom-free feedstocks.

This behavior was attributed to interactions during pyrolysis, which promote the formation of pyrolysis gas and thus increase carbon losses.

For heteroatom-free feedstocks, reactor technology also had a pronounced influence on overall process performance. When feedstock interactions were negligible, clear differences between the stirred-tank reactor (STR) and the Auger-type screw reactor (ASR) were observed. The ASR system, characterized by more intense cracking, produced higher yields of pyrolysis gas. Although this resulted in a narrower boiling point distribution of the pyrolysis oil, the associated carbon losses due to overcracking led to significantly lower overall performance. For mixed plastic feedstocks, however, this effect diminished, as feedstock interactions became the dominant factor.

These findings imply that the primary optimization objective for the pyrolysis step is the maximization of carbon retention in the pyrolysis oil. Carbon losses at this stage cannot be compensated in downstream processes. For clean feedstocks, reactor selection and operating conditions are therefore critical, as they largely determine carbon recovery. For heteroatom-containing MPW, greater emphasis must be placed on mitigating interaction effects that lead to additional carbon losses, independent of reactor type.

For utilization of the resulting pyrolysis oils, pyrolysis oil conversion via steam cracking and EFG showed largely comparable results in terms of the overall net climate change impact. In most cases, differences between the two routes – waste-to-monomers or waste-to-syngas – were small. Only for highly aromatic pyrolysis oils, such as those derived from PS, did steam cracking show a clear advantage. This can be explained by the losses associated with adjusting the H_2/CO ratio in the gasification route, whereas in steam cracking the low H/C ratio can be compensated by external hydrogen supply without rejecting carbon as CO_2 . However, the full hydrogenation of highly aromatic pyrolysis oils will likely not be economical due to the high consumption of externally supplied hydrogen.

When focusing on pyrolysis oil utilization only, nevertheless a correlation between the performance of pyrolysis oil utilization and the molar H/C ratio of the oils was identified. Pyrolysis oils with higher H/C ratios, such as those derived from LDPE and PP, showed better performance regarding net climate change impact. While this trend is partly influenced by assumptions in the modeling of upgrading and steam cracking, the results indicate that boundary conditions play a more decisive role than composition alone. For example, the availability of low-impact hydrogen for upgrading or the possibility of fully utilizing excess heat for district heating can have a stronger influence on process performance than the intrinsic properties of the pyrolysis oil.

For the waste-to-syngas route, the substitution of heavy fuel oil (HFO)-based syngas is decisive. The substitution of syngas from feedstocks with more favorable H/C ratio such as natural gas penalizes the hydrogen deficiency of plastic pyrolysis oil in the production of MeOH syngas. Thus, while being a niche application in comparison to MeOH, the production of Oxo syngas likely proves more beneficial in the long term due to its higher carbon recycling efficiency and

therefore lower process burdens. Only in the case of HFO as gasification feedstock, both syngas configurations show equal performance.

As the carbon loss to pyrolysis side products was identified as the largest contributor to process burdens of the pyrolysis-based chemical recycling process chain, efficient utilization of pyrolysis gas is essential to limit process impacts, particularly for feedstocks with high gas yields. While in the base scenario energetic utilization of pyrolysis gas significantly reduces the burdens of pyrolysis by generating electricity and district heat, even greater potential lies in the material utilization of pyrolysis gas, for example through integration into EFG. This approach increases overall product yield and carbon recycling efficiencies while reducing process emissions by avoiding direct CO₂ release. However, it requires co-location of pyrolysis and gasification facilities and may involve additional technical challenges, such as pyrolysis gas compression. Flaring of pyrolysis gas without energy recovery, however, can lead to worse performance in plastic waste treatment than energy recovery and must therefore be avoided.

The assessment from the input-based, waste management perspective was complemented by an output-based, product perspective for a comparison of waste as a feedstock to the conventional, fossil fuel-based production routes. This led to contradicting results in comparison to the input-based perspective. While the latter showed benefits of pyrolysis-based chemical recycling for all feedstocks and all pyrolysis oil utilization options, the product-perspective concluded that only for heteroatom-free feedstocks with high yields in pyrolysis, the pyrolysis-based process chain for the production of steam cracker products or syngas performed better than the conventional reference process.

By combining the input perspective with the output perspective in a combined, system-wide assessment, this contradiction can be resolved. As the results prove a strong dependence on the chosen reference processes, the contradiction can be attributed to different system boundaries and the avoided burden approach in the input- or output-based assessment, resulting from the two perspectives. The environmental performance of chemical recycling is therefore influenced not only by the efficiency of the recycling process itself but also by the characteristics of the background system, determining the performance of pyrolysis-based chemical recycling relative to energy recovery.

Overall, the results demonstrate that the environmental performance of pyrolysis-based chemical recycling is governed by both individual process efficiencies and by system-level interactions between feedstock composition, process integration, and substitution effects. Consequently, the isolated assessment of individual technologies is insufficient and must always be considered within a broader system context.

Yet several important research questions remain open. First, the scalability of the investigated processes remains uncertain. Current industrial pyrolysis plants have limited capacities, resulting in a low availability of pyrolysis oil. For a relevant increase in recycling of currently hard-to-recycle waste plastics, significantly larger installations are required. Further, validation of model-based results for downstream processes of pyrolysis oil utilization are needed. This applies

particularly to upgrading pyrolysis oils and their subsequent steam cracking, where current results rely heavily on assumptions. Additionally, combined approaches to pyrolysis oil utilization that include fractionation of the pyrolysis oil should be investigated further. Thus, the utilization of tailored pyrolysis oil cuts may improve overall recycling efficiency, e.g., through utilizing the naphtha-boiling range in steam cracking, high boiling fractions in deep catalytic cracking (DCC), and residues in entrained-flow gasification.

Second, the effects of adapting plastic waste sorting require closer investigation. As the results indicate that recycling performance decreases with increasing feedstock contamination, one potential approach is the implementation of an additional sorting step to reduce contaminants in pyrolysis feedstocks. This approach, however, introduces two key considerations. On the one hand, it must be assessed whether the improved feedstock still requires treatment via pyrolysis or whether it becomes suitable for mechanical recycling, which may represent the preferable option. On the other hand, the overall system-level impact must be evaluated. An additional sorting step does not necessarily lead to a lower climate change impact of waste treatment. Even if feedstock quality is improved, the combination of processing the upgraded fraction via pyrolysis while directing the remaining residues to energy recovery may result in a higher overall impact than treating the entire waste fraction via pyrolysis. This outcome will strongly depend on the sorting efficiency and the distribution of materials between the resulting fractions.

Third, future technological developments in both waste management and the chemical industry need to be considered. The implementation of CCS, electrification of processes such as steam cracking, integration of green hydrogen and the transition to alternative feedstocks (e.g., biomass or CO₂-based routes) may significantly alter both recycling processes and their reference systems. These developments must be evaluated within a dynamic system framework that captures interactions between evolving technologies.

While pyrolysis-based chemical recycling can play an important role in this transition, particularly for waste streams that are currently not accessible to established recycling technologies, reducing plastic waste generation and increasing recycling rates remain essential prerequisites for achieving a sustainable and climate-neutral plastics economy.

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Appendices

A Data from model feedstock pyrolysis experiments

Table A-1: Definition of model feedstocks, polymer compositions, and elemental compositions, and lower heating values adapted from Netsch et al.^{91,92,112}

<i>Model feedstock</i>	Single polymers			Polymer mixtures			
	<i>LDPE</i>	<i>PP</i>	<i>PS</i>	<i>Mix AR</i>	<i>Mix MH</i>	<i>Mix HH</i>	<i>S-PCW</i>
<i>Polymer composition, wt.%</i>							
LDPE	100.0	-	-	40.0	70.0	50.0	29.4
HDPE	-	-	-				17.1
PP	-	100.0		30.0	20.0	15.0	25.1
PS	-	-	100.0	30.0	2.0	10.0	4.2
ABS	-	-	-	-	-	5.0	3.8
PET	-	-	-	-	4.0	10.0	10.1
PA6	-	-	-	-	2.0	5.0	6.3
PVC	-	-	-	-	2.0	5.0	4.0
<i>Elemental composition, wt.%</i>							
C	85.8	85.8	92.0	87.6	83.5	80.6	80.0
H	14.2	14.2	8.0	12.4	13.4	11.6	12.3
N	< 0.2	< 0.1	< 0.2	< 0.2	0.3	0.9	0.8
Cl	0.0	0.0	0.0	0.0	1.0	2.4	1.4
Moisture	< 0.01	< 0.01	< 0.01	0.0	0.0	0.1	0.0
Ash	< 0.01	< 0.01	< 0.01	0.0	0.2	0.5	2.2
O	0.0	0.0	0.0	0.0	1.6	3.9	3.3
<i>Lower heating value, MJ/kg</i>							
	43.2	43.2	39.5	42.1	41.5	38.6	39.1

Table A-2: Pyrolysis product distribution of model feedstock in ASR and STR adapted from Netsch et al.^{91,92}

	Single polymers						Polymer mixtures							
	LDPE		PP		PS		Mix AR		Mix MH		Mix HH		S-PCW	
Reactor	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR
Pyrolysis product yields, wt.%														
Solid residue	0.9	0.4	0.8	0.9	1.7	1.4	0.5	1.2	2.5	1.7	4.1	3.6	4.3	4.5
Condensate	48.8	72.3	49.1	71.3	88.5	98.5	63.3	79.3	51.4	57.2	49.5	55.1	50.2	52.8
Gas	47.8	27.3	51.3	27.8	0.1	8.5	33.5	19.5	42.2	41.1	47.2	41.3	46.1	42.7
Loss	2.5	-	-1.2	-	1.3	-	2.7	-	3.9	-	-0.8	-	-0.6	-

Table A-3: Elemental composition, HHV and molar H/C ratio of pyrolysis oils from pyrolysis of model feedstocks in ASR and STR adapted from Netsch et al.^{91,92}

	Single polymers						Polymer mixtures							
	LDPE		PP		PS		Mix AR		Mix MH		Mix HH		S-PCW	
Reactor	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR
Elemental composition, wt.%														
C	86.0	85.6	86.4	86.1	91.9	91.5	88.6	88.1	86.3	85.0	86.3	84.4	85.9	82.6
H	14.0	14.4	13.6	13.9	8.1	8.3	11.4	11.9	13.1	14.0	11.7	12.5	12.5	13.6
N	0.0	< 0.2	< 0.2	< 0.2	< 0.2	0.2	< 0.2	< 0.2	< 0.2	0.3	0.6	0.6	0.5	0.4
S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.6	0.6	0.2	0.5
O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.6	0.9	0.9	0.9	2.9
HHV, MJ/kg	46.1	46.6	45.8	46.3	41.4	42.1	44.0	45.4	45.2	45.8	43.5	43.7	44.3	44.1
H/C, -	2.0	2.0	1.9	1.9	1.1	1.1	1.5	1.6	1.8	2.0	1.6	1.8	1.7	2.0

Table A-4: Pyrolysis gas composition of model feedstock experiments in ASR experiments adapted from Netsch et al.^{91,92}

Single polymers					Polymer mixtures			
		LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Detected component	Representative component for balancing	Pyrolysis gas composition, wt.%						
CH ₄	CH ₄	5.6	5.3	5.8	4.7	6.3	n.a.	5.1
C ₂ saturated	C ₂ H ₆	16.8	7.6	6.9	6.7	9.0	n.a.	8.3
C ₂ unsaturated	C ₂ H ₄		4.6		8.2	9.2	n.a.	9.4
C ₃ saturated	C ₃ H ₈	4.1	3.9	0.2	3.2	5.4	n.a.	4.5
C ₃ unsaturated	C ₃ H ₆	13.6	24.2	2.2	16.5	14.3	n.a.	14.2
C ₄ saturated	C ₄ H ₁₀	2.9	1.0	0.0	1.4	2.4	n.a.	1.7
C ₄ unsaturated	C ₄ H ₈	15.5	17.2	0.9	15.2	14.6	n.a.	13.5
C ₅ saturated	C ₅ H ₁₂	1.3	10.5	0.0	4.5	5.2	n.a.	3.5
C ₅ unsaturated	C ₅ H ₁₀	16.4	8.9	0.5	12.9	9.3	n.a.	9.6
C ₆ saturated	C ₆ H ₁₄	0.2	0.7	0.0	1.2	2.0	n.a.	2.0
C ₆ unsaturated	C ₆ H ₁₂	13.1	10.3	0.2	13.2	11.0	n.a.	9.6
C ₇ to C ₁₀ saturated	C ₈ H ₁₈	1.1	0.3	0.0	1.3	0.8	n.a.	0.7
C ₇ to C ₁₀ unsaturated	C ₈ H ₁₆	5.9	4.4	0.3	4.8	3.0	n.a.	3.8
Benzene	Benzene	0.9	0.1	7.7	0.7	0.8	n.a.	1.2
Toluene	Toluene	1.2	0.3	47.0	2.6	0.6	n.a.	0.8
Styrene	Styrene	1.0	0.0	19.1	1.8	0.1	n.a.	0.6
Other aromatics	Xylene	0.4	0.2	9.2	0.8	0.2	n.a.	0.5
CO ₂	CO ₂	0.0	0.5	0.0	0.3	4.4	n.a.	7.7
CO	CO	0.0	0.0	0.0	0.0	1.0	n.a.	1.5
Other O-containing	Acetaldehyde	0.0	0.0	0.0	0.0	0.1	n.a.	0.3
HCN	HCN	0.0	0.0	0.0	0.0	0.0	n.a.	0.0
Acrylonitrile	Acrylonitrile	0.0	0.0	0.0	0.0	0.1	n.a.	0.3
Other N-containing	Acetonitrile	0.0	0.0	0.0	0.0	0.1	n.a.	0.6
HCl	HCl	0.0	0.0	0.0	0.0	*	n.a.	*
Other Cl-containing	Chloroethane	0.0	0.0	0.0	0.0	0.1	n.a.	0.6

* Detected but quantitative information unavailable

Table A-5: Pyrolysis gas composition of model feedstock experiments in STR experiments adapted from Netsch et al.⁹¹

		Single polymers			Polymer mixtures			
		LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Detected component	Representative component for balancing	Pyrolysis gas composition, wt.%						
CH ₄	CH ₄	4.3	4.0	0.0	3.7	3.7	3.3	4.9
C ₂ saturated	C ₂ H ₆	9.7	7.8	0.3	7.2	7.2	6.1	5.2
C ₂ unsaturated	C ₂ H ₄	8.9	2.7	1.9	5.6	6.6	7.1	7.0
C ₃ saturated	C ₃ H ₈	10.7	6.0	0.1	6.6	7.2	5.4	4.7
C ₃ unsaturated	C ₃ H ₆	12.4	26.4	2.1	19.1	12.8	9.8	10.3
C ₄ saturated	C ₄ H ₁₀	8.8	1.8	0.1	3.9	5.1	4.0	3.0
C ₄ unsaturated	C ₄ H ₈	15.9	16.3	0.6	13.6	11.7	9.4	9.5
C ₅ saturated	C ₅ H ₁₂	3.9	12.4	5.2	10.9	9.0	8.2	9.0
C ₅ unsaturated	C ₅ H ₁₀	12.4	8.6	0.1	11.0	7.9	7.7	7.2
C ₆ saturated	C ₆ H ₁₄	1.3	0.6	0.0	1.7	3.6	2.3	2.4
C ₆ unsaturated	C ₆ H ₁₂	6.5	8.5	0.0	11.2	7.5	7.3	9.6
C ₇ to C ₁₀ saturated	C ₈ H ₁₈	0.8	1.7	0.5	0.6	1.1	1.1	0.9
C ₇ to C ₁₀ unsaturated	C ₈ H ₁₆	1.4	2.5	4.8	2.4	2.1	2.2	3.4
Benzene	Benzene	0.0	0.0	4.7	0.5	0.2	0.7	0.6
Toluene	Toluene	0.1	0.0	9.8	1.0	0.3	0.7	0.5
Styrene	Styrene	2.3	0.6	60.9	0.4	3.3	0.4	0.4
Other aromatics	Xylene	0.5	0.1	8.9	0.1	0.4	0.3	0.3
CO ₂	CO ₂	0.0	0.0	0.0	0.0	7.1	16.4	14.7
CO	CO	0.1	0.0	0.0	0.0	1.8	3.2	3.1
Other O-containing	Acetaldehyde	0.0	0.0	0.0	0.0	1.0	1.5	0.8
HCN	HCN	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Acrylonitrile	Acrylonitrile	0.0	0.0	0.0	0.0	0.0	1.1	0.5
Other N-containing	Acetonitrile	0.0	0.0	0.0	0.0	0.0	0.5	0.6
HCl	HCl	0.0	0.0	0.0	0.0	*	*	*
Other Cl-containing	Chloroethane	0.0	0.0	0.0	0.0	0.4	1.2	1.4

* Detected but quantitative information unavailable

B Model development for chemical recycling processes

This appendix provides additional in-depth information regarding balancing of the pyrolysis experiments and the model development of the different processes required for the conversion of pyrolysis oils to base chemicals that are not covered in detail in the main part of this work.

B.1 Relative balance errors of pyrolysis experiments

The following figures show the uncorrected and corrected relative total and elemental mass balances of the model feedstock pyrolysis experiments.

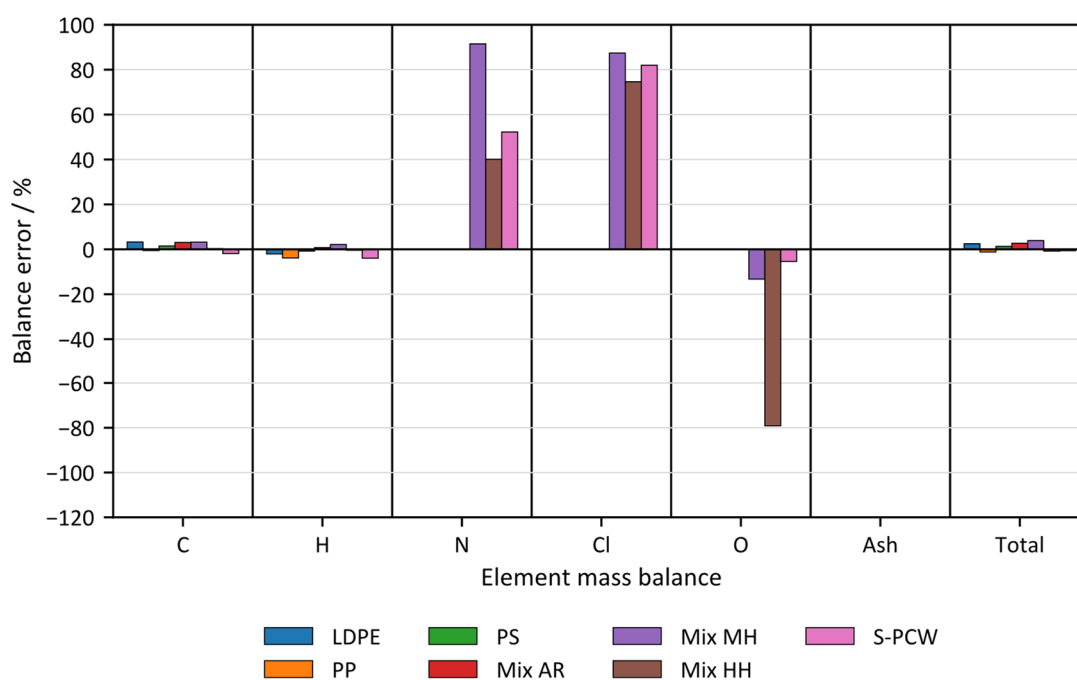


Figure B-1: Relative total mass and elemental mass balance errors of ASR experiments with model feedstocks.

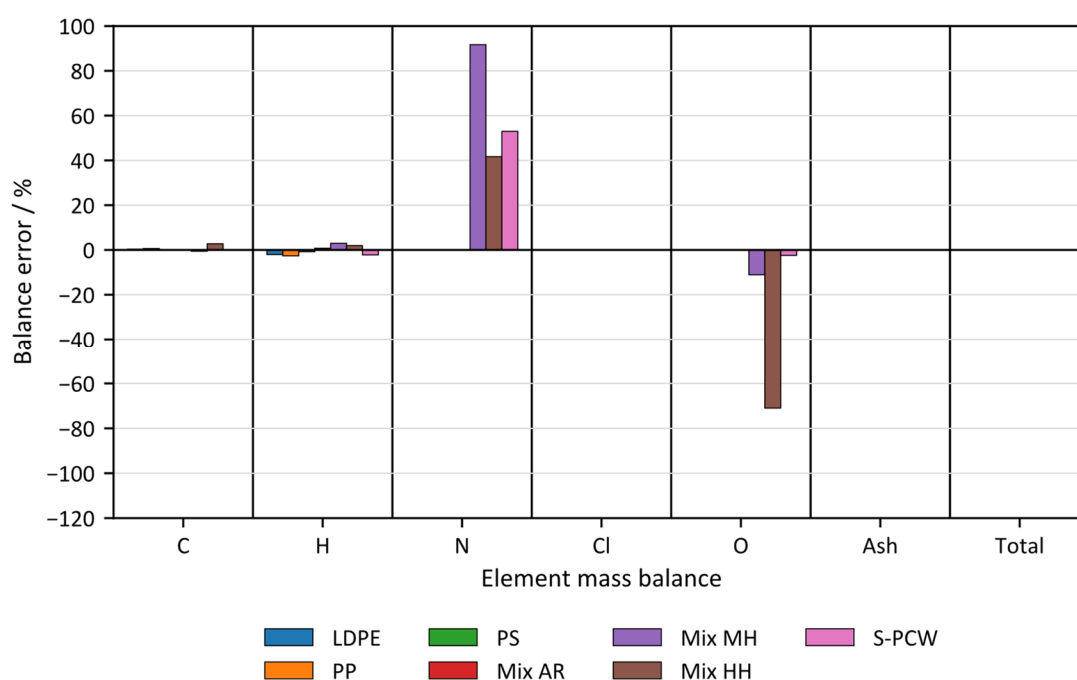


Figure B-2: Relative total mass and elemental mass balance errors of ASR experiments with model feedstocks after correction of pyrolysis data.

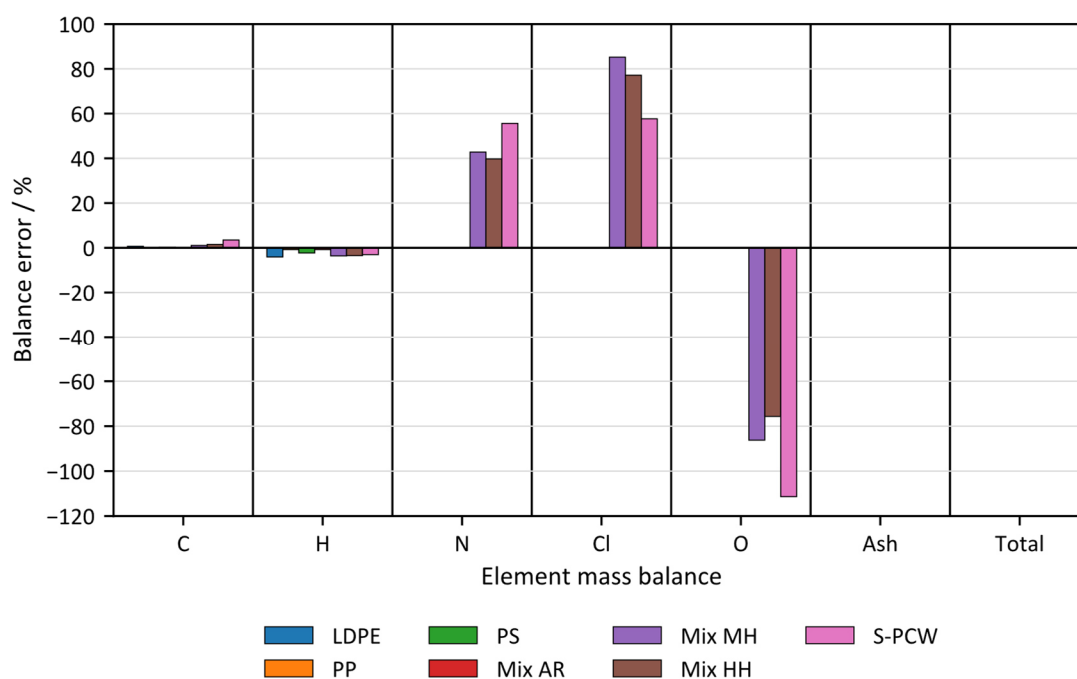


Figure B-3: Relative total mass and elemental mass balance errors of STR experiments with model feedstocks.

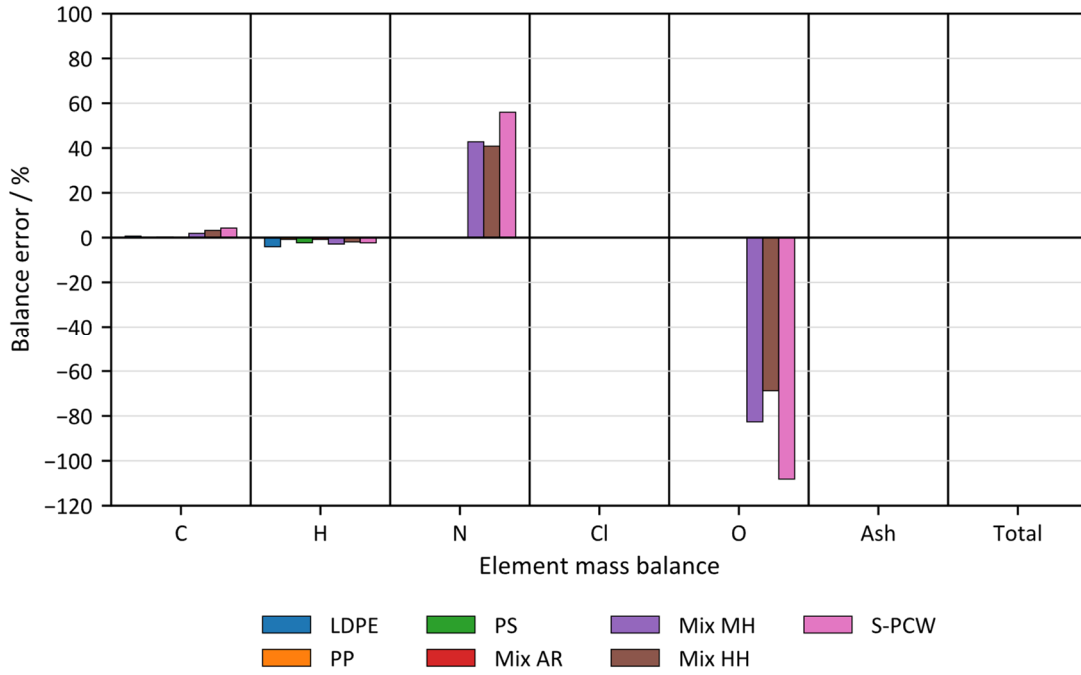


Figure B-4: Relative total mass and elemental mass balance errors of STR experiments with model feedstocks after correction of pyrolysis data.

B.2 Derivation of mass balances for pyrolysis oil upgrading

The target parameters yield of upgraded pyrolysis oil $Y_{Upgr.oil}$ and the specific total hydrogen demand $m_{H_2,total}$ can be derived from the upgrading process' total mass and elemental mass balances. The total mass balance links the mass flows of pyrolysis oil $\dot{m}_{Py.oil}$, upgraded pyrolysis oil $\dot{m}_{Upgr.oil}$, hydrogen $\dot{m}_{H_2,total}$, and off-gas $\dot{m}_{Off-gas}$:

$$\dot{m}_{Py.oil} + \dot{m}_{H_2,total} = \dot{m}_{Upgr.oil} + \dot{m}_{Off-gas} \quad (B.1)$$

Building on the previously stated assumptions, the off-gas does not contain any hydrocarbons as all carbon from the pyrolysis oil is contained in the liquid product from upgrading, the upgraded pyrolysis oil. Hence, the yield of upgraded pyrolysis oil can be calculated from the carbon elemental mass balance:

$$\dot{m}_{Py.oil} x_{C,Py.oil} = \dot{m}_{Upgr.oil} x_{C,Upgr.oil} \quad (B.2)$$

giving

$$Y_{Upgr.oil} = \frac{\dot{m}_{Upgr.oil}}{\dot{m}_{Py.oil}} = \frac{x_{C,Py.oil}}{x_{C,Upgr.oil}} \quad (B.3)$$

directly linking the yield of upgraded pyrolysis oil to the carbon content of the pyrolysis oil ($x_{C,Py.oil}$) and the carbon content of the upgraded pyrolysis oil ($x_{C,Upgr.oil}$). As the upgraded pyrolysis oil is free of any heteroatoms, the upgraded pyrolysis only contains carbon and hydrogen at the targeted H/C ratio ($HC_{Upgr.oil}$). Thus, it can be concluded that

$$1 = x_{C,Upgr.oil} + x_{H,Upgr.oil} \quad (B.4)$$

With the definition of the molar H/C ratio

$$HC_i = \frac{x_{H,i} \bar{M}_C}{x_{C,i} \bar{M}_H} \quad (B.5)$$

$x_{C,Upgr.oil}$ can be expressed solely depending on the targeted molar H/C ratio:

$$x_{C,Upgr.oil} = \frac{\bar{M}_C}{HC_{Upgr.oil} \bar{M}_H + \bar{M}_C} \quad (B.6)$$

Thus, the upgraded pyrolysis oil yield can be calculated by

$$Y_{Upgr.oil} = \left(\frac{HC_{Upgr.oil} \bar{M}_H}{\bar{M}_C} + 1 \right) x_{C,Py.oil} \quad (B.7)$$

The total hydrogen demand can be expressed as specific total hydrogen demand $m_{H_2,total}$:

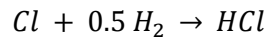
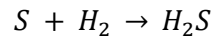
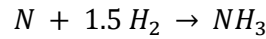
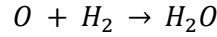
$$m_{H_2,total} = \frac{\dot{m}_{H_2,total}}{\dot{m}_{Py.oil}} \quad (B.8)$$

which in turn can be derived from the specific hydrogen consumption of hydrotreating $m_{H_2,HT}$ and hydrocracking $m_{H_2,HC}$, weighted with the hydrogen utilization efficiency $\alpha_{H_2,Upgr.}$, assumed to be 70% within the context of this work:

$$m_{H_2,total} = \frac{1}{\alpha_{H_2,Upgr.}} (m_{H_2,HT} + m_{H_2,HC}) \quad (B.9)$$

Thus, as a next step, the hydrogen demands of hydrotreating and hydrocracking need to be calculated.

For hydrotreating, it is assumed that the removal of O, N, S, and Cl follows a hydrogenation mechanism. Generally, the hydrotreating reaction schemes depend on how the heteroatoms are incorporated within the hydrocarbon chain. For simplicity, the following reactions are assumed within the context of upgrading of plastic pyrolysis oils, disregarding the exact incorporation of the respective heteroatom:



This simplification allows the definition of the stoichiometric coefficients $\nu_{HT,j}$ and the calculation of the specific stoichiometric hydrogen demand $m_{H_2,j}$ considering the respective molar masses $\bar{M}_j$ and assuming full conversion to the hydrogenated species:

$$m_{H_2,j} = \frac{\nu_{HT,j} \bar{M}_{H_2}}{\bar{M}_j} \quad (B.10)$$

The stoichiometric coefficients and the resulting specific stoichiometric hydrogen demand per each element are summarized in Table B-1.

Table B-1: Stoichiometric coefficients and specific stoichiometric hydrogen demand for hydrotreating of plastic pyrolysis oils.

Heteroatom j	$\bar{M}_j$, kg/mol	$\nu_{HT,j}$, mol/mol	$m_{H_2,j}$, kg/kg
O	0.01600	1	0.126
N	0.01401	1.5	0.216
S	0.03207	1	0.063
Cl	0.03545	0.5	0.028

The stoichiometric hydrogen demand $m_{H_2,HT}$ for full hydrotreating of all heteroatoms contained in a pyrolysis oil can then be calculated as the sum of the element-specific hydrogen demands and the mass fraction of the respective heteroatom $x_{j,Py.oil}$ in the pyrolysis oil:

$$m_{H_2,HT} = \sum_j x_{j,Py.oil} m_{H_2,j} \quad (B.11)$$

In hydrocracking, additional hydrogen is required for the increase of the H/C ratio by breaking down the hydrocarbon chains and saturating double bonds and aromatics. The calculatory hydrogen demand for hydrocracking $m_{H_2,HC}$ can be calculated from the hydrogen mass balance, given as:

$$\begin{aligned} \dot{m}_{Py.oil} x_{H,Py.oil} + \dot{m}_{H_2,total} \\ = \dot{m}_{Upgr.oil} x_{H,Upgr.oil} + \dot{m}_{Off-gas} x_{H,Off-gas} \end{aligned} \quad (B.12)$$

The total hydrogen demand depends on the hydrogen consumption of hydrotreating and hydrocracking and the excess hydrogen $\dot{m}_{H_2,excess}$ fed to the upgrading unit:

$$\dot{m}_{H_2,total} = \dot{m}_{H_2,HT} + \dot{m}_{H_2,HC} + \dot{m}_{H_2,excess} \quad (B.13)$$

Since the off-gas contains the hydrogen added for removal of the heteroatoms and the unused excess hydrogen, the overall hydrogen mass balance can be simplified, using

$$\dot{m}_{H_2,HT} + \dot{m}_{H_2,excess} = \dot{m}_{Off-gas} x_{H,Off-gas} \quad (B.14)$$

giving

$$\dot{m}_{Py.oil} x_{H,Py.oil} + \dot{m}_{H_2,HC} = \dot{m}_{Upgr.oil} x_{H,Upgr.oil} \quad (B.15)$$

and further, using the definition of the upgraded pyrolysis oil yield,

$$m_{H_2,HC} = Y_{Upgr.oil} x_{H,Upgr.oil} - x_{H,Py.oil} \quad (B.16)$$

With equations (B.6) and (B.7, this can be transferred to

$$m_{H_2,HC} = \left(\frac{HC_{Upgr.oil} \bar{M}_H}{\bar{M}_C} \right) x_{C,Py.oil} - x_{H,Py.oil} \quad (B.17)$$

enabling the calculation of the specific hydrogen demand for hydrocracking.

B.3 Steam cracker product distribution

For steam cracking of naphtha, the product distribution is derived as described in the main part. For steam cracking of AGO and HCR the reported product distributions of Zimmermann and Walzl used.¹¹⁸ All product distributions are shown in Figure B-5. Carbon distributions are calculated from the product compositions, summarized in Figure B-6. The inventory for steam cracking of AGO and HCR is derived from the naphtha steam cracking inventory and the energy balance provided by Zimmermann and Walzl.¹¹⁸ Additional fuel and steam input is considered by using refinery gas for firing and raising of steam (cf. Appendix D.2.5).

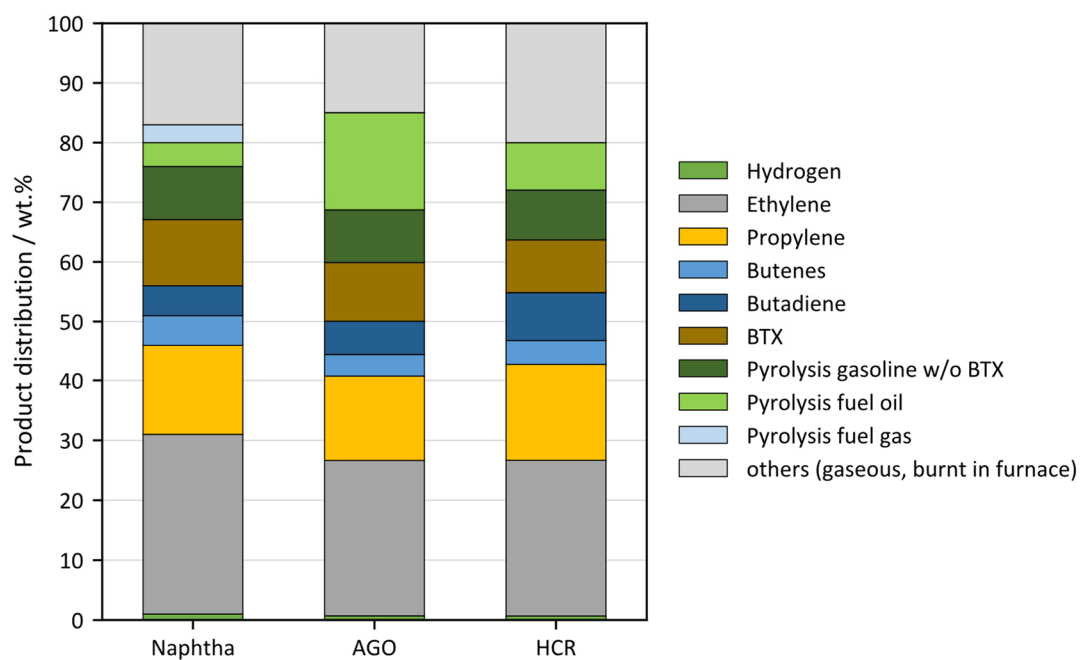


Figure B-5: Product distributions for steam cracking of naphtha, AGO, and HCR.

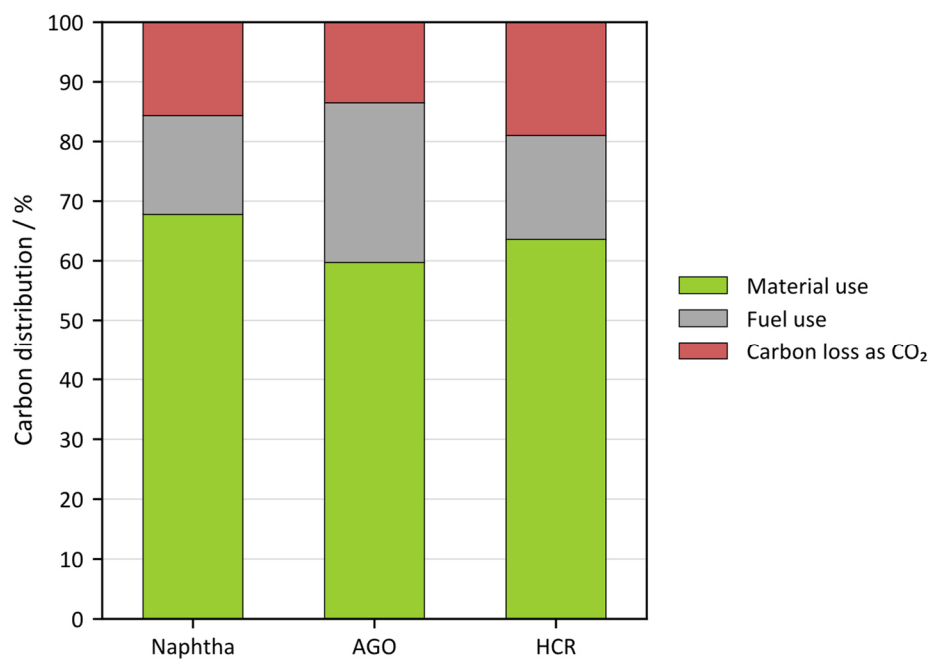


Figure B-6: Carbon distributions for steam cracking of naphtha, AGO, and HCR.

B.4 Entrained-flow gasification model

The EFG model applied in this thesis was originally developed for the utilization of pyrolysis oils derived from automotive plastic waste (APW), as published in Hennig et al.¹⁷⁸ This appendix provides a detailed description of the model structure and underlying assumptions. Additional analyses, in particular with regard to the effect of reactor temperature and carbon conversion, are reported in the original publication and are not repeated here.

B.4.1 Gasifying section

B.4.1.1 Model description and model parameters

The EFG model represents the conversion of pyrolysis oil and HFO into syngas, followed by its conditioning for downstream applications. The process is modeled at an industrial scale with a thermal input of 500 MW (LHV basis) and comprises two main steps: (i) gasification and (ii) adjustment of the syngas composition via the WGS reaction to meet the requirements of methanol or Oxo synthesis.

Prior to gasification, all feed streams are brought to operating conditions. Liquid fuels are pressurized to 6 MPa with the energy demand calculated in the calculator block FEEDPUMP assuming incompressible behavior with a density of 950 kg/m³, and are preheated from 25 °C to 150 °C using an average heat capacity of 2 kJ/kg/K. Oxygen from the ASU is compressed to 6 MPa in a multistage compressor with intercooling to 30 °C and fed directly to the gasifier. Water is pressurized, vaporized, and superheated to 450 °C prior to injection. The required oxygen- and steam-to-fuel ratios are determined through an internal optimization routine that maximizes specific syngas yield (cf. Section B.4.1.3).

The gasification process is modeled using a two-step approach. In the RYIELD reactor (DECOMP), the nonconventional feedstock is decomposed into its elemental constituents based on the ultimate analysis provided by the calculator block CHNSO. These elements are subsequently treated as conventional components. The gasification itself is modeled in a Gibbs equilibrium reactor (GASIFY), where the syngas composition is determined by minimization of Gibbs free energy. Similar modeling strategies have been previously used in the literature.^{27,232,233} The heat required for decomposition is calculated from the higher heating value of the fuel and coupled to the gasifier via the heat stream HEAT. Thermal losses are accounted for by assuming a heat loss of 1% of the higher heating value, calculated in the HEATL block.³⁹

The equilibrium of the water-gas shift (WGS) reaction is temperature dependent and shifts during cooling of the raw syngas. However, as temperature decreases, reaction kinetics become increasingly limited, such that the actual syngas composition no longer follows the equilibrium state. This freeze-in of composition is assumed to occur at a temperature of 1300 °C.^{39,206} To represent this effect, an additional equilibrium stage (WGSFREEZ) in combination with two

dummy heaters is introduced to determine the syngas composition at the freeze-in temperature.

Subsequently, the H_2/CO ratio is adjusted in the WGS section, which consists of an isothermal equilibrium reactor with a bypass stream. Due to insufficient steam content in the cooled raw syngas, additional steam is injected to achieve a water fraction of 40 mol%. The reactor operates under conditions representative of sour WGS at 240 °C, enabling near-complete conversion of CO to H_2 . In addition, COS hydrolysis is considered. The desired H_2/CO ratio is achieved via a design specification that controls the split between the syngas stream passing through the WGS reactor and the bypass stream. Target ratios are 2.15 for methanol synthesis and 1.0 for Oxo synthesis.

After the WGS stage, both syngas streams are recombined and cooled to 30 °C to enable phase separation. The aqueous phase is removed prior to gas cleaning. For simplification, complete separation of water and trace components is assumed, and the solubility of gaseous species such as CO_2 in the liquid phase is neglected.

B.4.1.2 Model validation

The gasifier model is validated against industrial data for EFG of bitumen reported by Häussinger et al.³⁸ As no detailed information on the steam input is available, validation is performed via regression by adjusting the steam feed to the gasification block such that the deviation between modeled and reported syngas compositions is minimized. Specifically, the steam input is varied until the molar fractions of the main syngas components (CO , H_2 , and CO_2) in the modeled stream RAW-SYN match the reference data as closely as possible. The resulting composition at minimum deviation is presented in Table B-2 and shows very good agreement for the major components.

Deviations are more pronounced for minor species in the sub-percent range. In particular, the lower methane content predicted by the model can be attributed to the equilibrium-based approach, which does not capture kinetic limitations of methane reforming reactions.³⁹ As a result, methane concentrations in the model are lower than those observed in industrial operation, where such kinetic constraints lead to incomplete conversion. The optimized operating conditions obtained from the regression – namely a steam-to-fuel ratio of 0.45 kg/kg and a gasification temperature of 1372 °C – are consistent with typical industrial values. Furthermore, the carbon-to-CO efficiency reaches 90.9% in the model, closely matching the reported value of 90.6% by Häussinger et al.³⁸

Overall, the comparison indicates that the model reproduces the main characteristics of industrial EFG of liquid hydrocarbon fuels with good accuracy, despite the simplifying assumptions of chemical equilibrium and complete carbon conversion. However, a dedicated validation for plastic-derived pyrolysis oils at industrial scale remains necessary to fully confirm the model's applicability to the systems investigated in this thesis.

Table B-2: Comparison of dry raw syngas composition from the industrial EFG shown in Häussinger et al.³⁸ (stream 4, dry) and the modeled process (stream RAW-SYN, dry). Reprinted from Hennig et al.¹⁷⁸

Composition (molar), dry mol%	Stream "RAW-SYN" in gasifier model	Stream 4 in Häussin- ger et al. ³⁸	Deviation, %
<i>H₂</i>	44.68	44.78	-0.2
<i>N₂</i>	0.14	0.12	16.7
<i>CO</i>	48.74	48.52	0.5
<i>Ar</i>	0.10	0.13	23.1
<i>CH₄</i>	0.09	0.29	-69.0
<i>CO₂</i>	4.73	4.64	1.9
<i>H₂S</i>	1.46	1.46	0.0
<i>COS</i>	0.06	0.07	-14.3
<i>O₂</i>	0.00	0.0	0.0

B.4.1.3 Determination of steam- and oxygen-to-fuel ratio for gasification

The gasification temperature is controlled via the oxygen-to-fuel and steam-to-fuel ratios. The influence of oxygen and steam input on gasifier performance is illustrated in Figure B-7, showing their effect on temperature, H_2/CO ratio, CGE, and specific molar syngas yield. For the production of synthesis gas as a chemical feedstock, maximizing the molar syngas yield – defined as the moles of H_2 and CO per unit mass of fuel – is the primary objective.³⁹ For varying combinations of oxygen- and steam-to-fuel ratios, characteristic iso-lines for these parameters can be identified. Notably, the iso-CGE lines shift towards lower oxygen input with increasing steam addition compared to iso-syngas-yield lines. This behavior is attributed to the endothermic nature of the water-gas shift reaction, which reduces CGE without affecting the molar syngas yield.

The optimal operating point is defined by an oxygen input that ensures complete fuel conversion while limiting excessive oxidation to CO_2 , combined with a steam input that suppresses methane formation via steam reforming.³⁹ Accordingly, the oxygen-to-fuel and steam-to-fuel ratios are determined through an internal optimization procedure that maximizes molar syngas yield subject to a constraint of a minimum gasifier temperature of 1350 ± 1 °C.

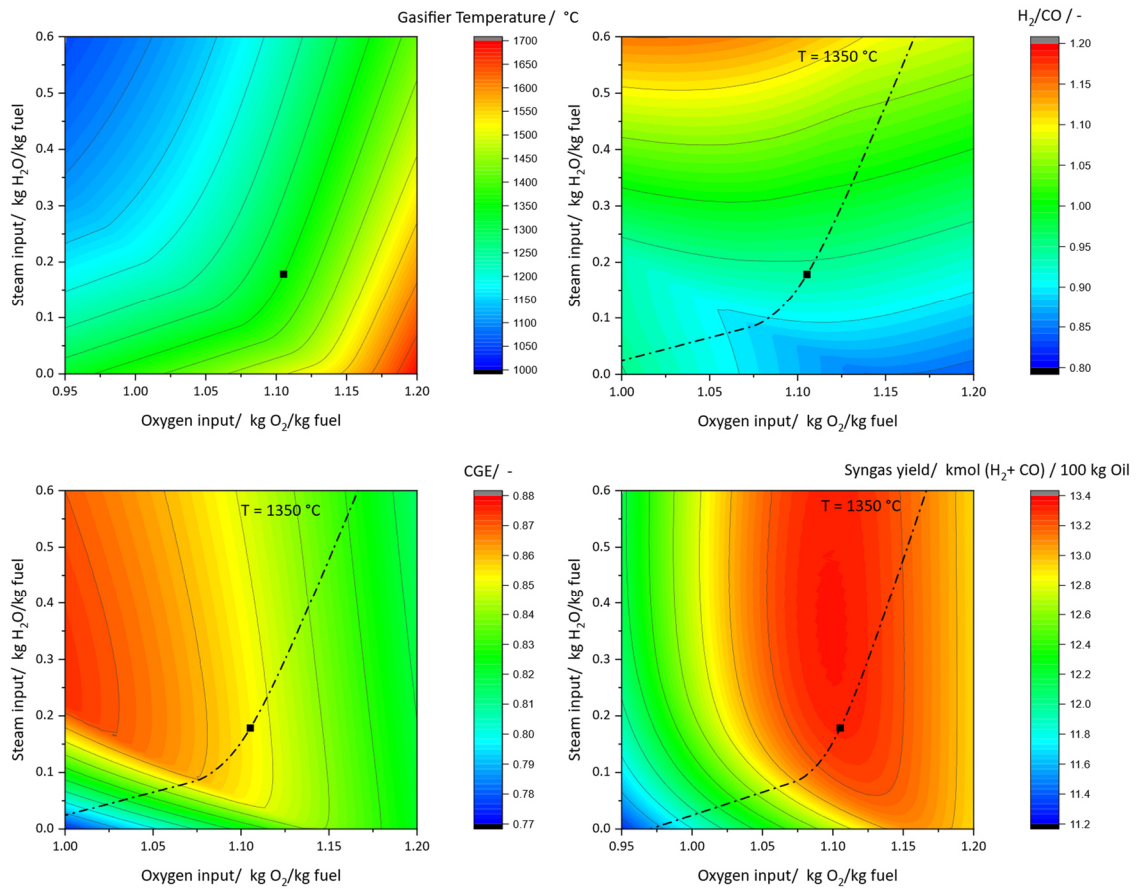


Figure B-7: Sensitivity of gasifier temperature (top left), H₂/CO ratio (top right), CGE (bottom left), and specific molar syngas yield (bottom right) to changes in oxygen-to-fuel and steam-to-fuel ratios for gasification of S-PCW pyrolysis oil from pyrolysis with ASR. Square: Optimal syngas yield for gasifier temperature T = 1350 °C.

B.4.2 Gas cleaning section

B.4.2.1 Model description and model parameters

Gas cleaning is performed by physical scrubbing using methanol. For methanol (MeOH) syngas, the process layout follows the concept presented by Gatti et al.¹⁴⁵ Due to differences in CO₂ partial pressure, two configurations are considered: a full scrubbing scheme for MeOH syngas and a simplified configuration for Oxo syngas, where CO₂ partial pressure is insufficient for selective recovery.

B.4.2.1.1 Scrubbing of MeOH syngas

The methanol scrubbing process for MeOH syngas is shown in Figure B-8. After removal of trace components in TRACECOM, the shifted syngas enters the absorber column (ABSORBER), where it is contacted in countercurrent with regenerated methanol (MEOH) at -50 °C. The solvent-to-gas ratio is controlled via a design specification to limit the CO₂ concentration in the clean syngas to 1.5 mol% at the column top. To remove the heat of absorption, a liquid side stream is withdrawn from the fourth stage, cooled to -30 °C, and returned to the fifth stage. A CO₂-rich, H₂S-

lean methanol stream is extracted from the eighth stage for selective CO₂ recovery, while the remaining solvent – containing both CO₂ and H₂S – is withdrawn from the column bottom. The split between these streams depends on the H₂S content of the feed gas.

Both methanol streams are flashed at 2 MPa (FLASH1, FLASH2) to recover dissolved CO and H₂, recompressed to 6 MPa, and recycled to the absorber. The CO₂-rich stream is subsequently used as solvent in the CO₂ desorption columns (CO₂DES1, CO₂DES2), operated at 0.6 MPa and 0.3 MPa, respectively (column specifications are given in Table B-3). Operating parameters – including side draw ratio, solvent split, and boil-up ratio in CO₂DES2 – are adjusted to ensure an H₂S concentration below 100 ppmv in the recovered CO₂ stream. Elevated H₂S levels in the feed gas reduce CO₂ recovery efficiency.

The H₂S-rich methanol stream is expanded to 0.12 MPa and regenerated in the column REGEN. Methanol losses are compensated by make-up solvent (MEOH-MUP), calculated in the MAKEUP block. The regenerated solvent is cooled to –50 °C and recycled to the absorber. For numerical stability, this recycle loop is not modeled explicitly.

Table B-3: Column configurations for absorption and desorption of CO₂ and H₂S. Reprinted from Hennig et al.¹⁷⁸

Column	ABSORBER	CO ₂ DES1	CO ₂ DES2	REGEN
Column specifications				
Stages	18	20	25	10
Reboiler	-	External	Internal	Internal
Condenser	-	-	-	Internal
Operating pressure, MPa	6	0.6	0.3	0.12
Liquid feeds				
	MEOH: 1	CO ₂ -rich methanol: 1	CO ₂ -rich methanol: 1	Internal condenser: 1
		H ₂ S-rich methanol: 16	H ₂ S-rich methanol: 20	H ₂ S-rich methanol: 2
		Side draw from CO ₂ DES2: 19		
Gaseous feeds				
	Syngas: 18	Recycle from external reboiler: 20	Internal reboiler: 25	Internal reboiler: 10
		Recycle from 0.2 MPa flash: 20		
Liquid withdrawals				
	Bottom: 18	Bottom: 20	Bottom: 25	Bottom: 10
	Side draw: 8		Side draw: 10	
Gaseous withdrawals				
	Clean syngas: 1	Raw CO ₂ : 1	Raw CO ₂ : 1	SOURGAS: 1

B.4.2.1.2 Scrubbing of Oxo syngas

Gas cleaning of the shifted Oxo syngas is based on a simplified version of the methanol scrubbing process described for MeOH syngas. The solvent-to-gas ratio is controlled via a design specification to limit the CO_2 concentration in the cleaned syngas to 1000 ppmv. Due to the lower CO_2 partial pressure in the Oxo syngas, selective CO_2 recovery is not feasible. Consequently, no side draw is taken from the absorber column (ABSORBER), and intermediate cooling for heat removal is not required. The solvent leaving the absorber bottom is therefore flashed directly to 0.3 MPa. The resulting vapor phase is recompressed and recycled to the absorber, while the liquid phase – containing absorbed CO_2 and H_2S – is sent to the regeneration column (REGEN).

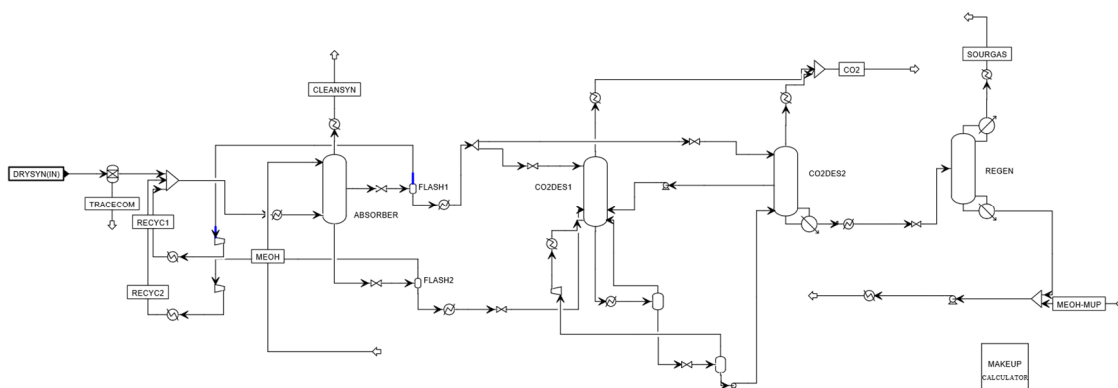


Figure B-8: MeOH scrubbing of dry syngas for removal of CO_2 and H_2S . In Oxo syngas configuration no side stream is drawn from absorber ABSORBER and CO_2 desorption columns CO2DES1 and CO2DES2 are bypassed. Reprinted from Hennig et al.¹⁷⁸

B.4.3 Heat integration

Pinch analysis is applied to estimate the minimum heating and cooling requirements without the need to design a complete heat exchanger network.²⁰⁷ Composite curves and utility composite curves are generated using Aspen Energy Analyzer, which directly extracts process data from the Aspen Plus flowsheet. The EFG process exhibits a net surplus of heat beyond the demand for steam generation in gasification, the WGS section, and the desorption columns of the gas cleaning unit. Heat available above 150 °C is assumed to be recoverable for district heating. At lower temperature levels, excess heat is removed using cold utilities as specified in Appendix D.5. The selection of appropriate cold utilities similarly follows the principles of pinch analysis, ensuring minimal temperature differences between process streams and utility levels.

C Product yields, process efficiencies and carbon distribution

C.1 Pyrolysis oil upgrading and steam cracking

Table C-1: Product yields and hydrogen balance of steam cracking and upgrading for model feedstock pyrolysis oils from ASR experiments.

<i>Model feedstock</i>	Single polymers				Polymer mixtures			Refer- ence
	<i>LDPE</i>	<i>PP</i>	<i>PS</i>	<i>Mix AR</i>	<i>Mix MH</i>	<i>Mix HH</i>	<i>S-PCW</i>	<i>Naphtha</i>
<i>Steam cracker products, kg/kg pyrolysis oil</i>								
Steam cracker material products	0.664	0.667	0.709	0.684	0.666	0.666	0.663	0.661
Steam cracker fuel products	0.160	0.160	0.171	0.165	0.160	0.160	0.160	0.159
Steam cracker hydrogen	0.010	0.010	0.011	0.010	0.010	0.010	0.010	0.010
<i>Hydrogen balance, kg/kg pyrolysis oil</i>								
Hydrogen recycle to upgrading	0.006	0.010	0.011	0.010	0.010	0.010	0.010	-
Excess hydrogen	0.004	-	-	-	-	-	-	0.01
Hydrogen import	-	0.003	0.094	0.039	0.011	0.033	0.021	-

Table C-2: Product yields and hydrogen balance of steam cracking and upgrading for model feedstock pyrolysis oils from STR experiments.

<i>Model feedstock</i>	Single polymers				Polymer mixtures			Refer- ence
	<i>LDPE</i>	<i>PP</i>	<i>PS</i>	<i>Mix AR</i>	<i>Mix MH</i>	<i>Mix HH</i>	<i>S-PCW</i>	<i>Naphtha</i>
<i>Steam cracker products, kg/kg pyrolysis oil</i>								
Steam cracker material products	0.661	0.665	0.708	0.680	0.657	0.652	0.638	0.661
Steam cracker fuel products	0.159	0.160	0.170	0.164	0.158	0.158	0.153	0.159
Steam cracker hydrogen	0.010	0.010	0.011	0.010	0.010	0.010	0.010	0.010
<i>Hydrogen balance, kg/kg pyrolysis oil</i>								
Hydrogen recycle to upgrading	-	0.008	0.011	0.010	0.006	0.010	0.010	-
Excess hydrogen	0.010	0.002	-	-	0.004	-	-	0.01
Hydrogen import	-	-	0.091	0.031	-	0.020	0.001	-

C.2 Entrained-flow gasification

Table C-3: Process conditions, process efficiencies, and product yields of EFG of pyrolysis oils from LDPE, PP, PS, and HFO as reference feedstock for MeOH syngas generation.

Model feedstock pyrolysis oil		LDPE		PP		PS		HFO
	Reactor type	ASR	STR	ASR	STR	ASR	STR	Reference
Gasifier conditions								
Gasifier temperature	°C	1350	1350	1350	1350	1350	1350	1350
Oxygen input	kg O ₂ /kg feedstock	1.16	1.16	1.16	1.15	1.04	1.01	1.00
Steam input	kg H ₂ O/kg feedstock	0.18	0.16	0.20	0.23	0.34	0.39	0.34
Stoichiometric ratio	-	0.34	0.34	0.34	0.34	0.34	0.33	0.32
Syngas product parameters								
SN MeOH syngas	-	2.02	2.02	2.02	2.02	2.02	2.02	2.02
LHV syngas	MJ/kg	23.4	23.4	23.4	23.4	23.4	23.4	23.2
Process efficiency parameters								
Specific syngas yield	kg syngas/kg fuel	1.50	1.51	1.49	1.50	1.37	1.40	1.40
Cold gas efficiency	%	82.1	82.3	82.1	82.1	81.7	81.8	80.8
Carbon yield ^s	%	63.4	64.4	62.8	63.7	54.4	55.5	60.2
Power demand and district heat generation								
District heat	kWh _{th} /kg feedstock	1.41	1.43	1.40	1.42	1.15	1.16	1.24
Power demand	kWh _{el} /kg feedstock	0.89	0.89	0.89	0.88	0.83	0.81	0.80

^s Including CO₂ contained in MeOH syngas

Table C-4: Process conditions, process efficiencies, and product yields of EFG of pyrolysis oils from Mix AR, Mix MH, Mix HH, and S-PCW for MeOH syngas generation.

Model feedstock pyrolysis oil		Mix AR		Mix MH		Mix HH		S-PCW	
	Reactor type	ASR	STR	ASR	STR	ASR	STR	ASR	STR
Gasifier conditions									
Gasifier temperature	°C	1350	1350	1350	1350	1350	1350	1350	1350
Oxygen input	kg O ₂ /kg feedstock	1.10	1.06	1.13	1.15	1.09	1.09	1.11	1.12
Steam input	kg H ₂ O/kg feedstock	0.21	0.31	0.18	0.18	0.21	0.19	0.18	0.18
Stoichiometric ratio	-	0.34	0.32	0.34	0.34	0.34	0.34	0.34	0.34
Syngas product parameters									
SN MeOH syngas	-	2.02	2.02	2.02	2.02	2.02	2.02	2.02	2.02
LHV syngas	MJ/kg	23.5	23.4	23.4	23.4	23.3	23.3	23.4	23.3
Process efficiency parameters									
Specific syngas yield	kg syngas/kg fuel	1.44	1.49	1.47	1.49	1.42	1.42	1.44	1.43
Cold gas efficiency	%	82.1	82.2	82.2	82.1	82.1	82.1	82.2	81.9
Carbon yield [†]	%	59.2	58.8	59.3	60.8	57.2	58.6	58.4	60.2
Power demand and district heat generation									
District heat	kWh _{th} /kg feedstock	1.30	1.31	1.37	1.42	1.31	1.33	1.33	1.38
Power demand	kWh _{el} /kg feedstock	0.86	0.84	0.87	0.88	0.85	0.84	0.86	0.86

[†] Including CO₂ contained in MeOH syngas

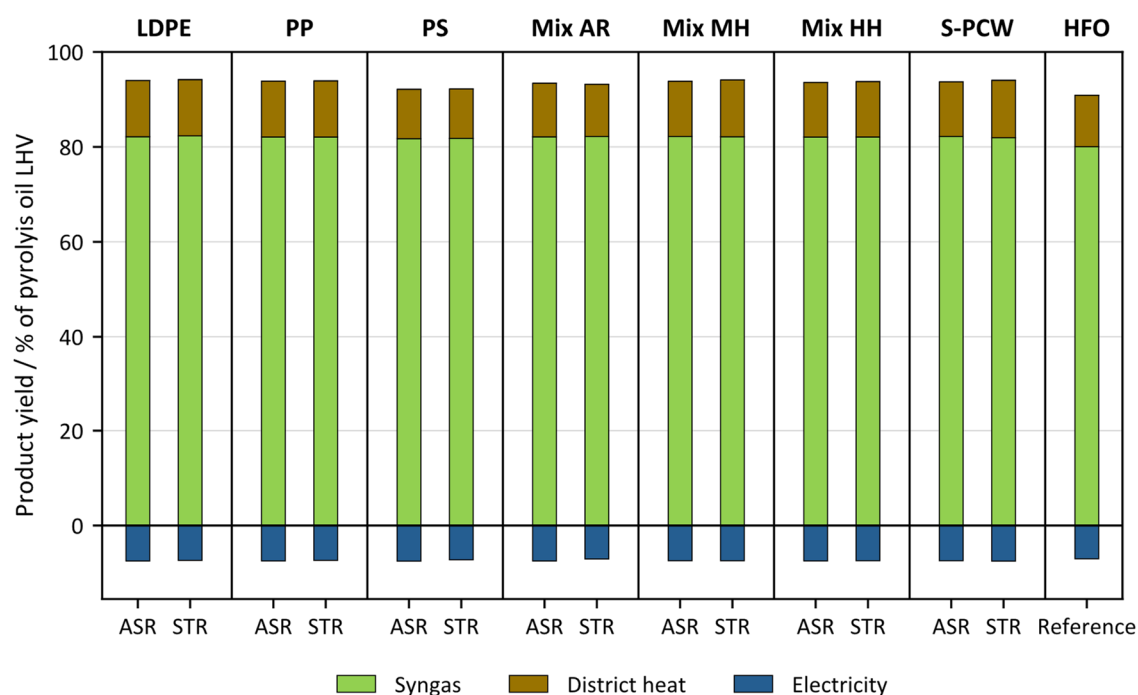


Figure C-1: Distribution of energy content of EFG products and electricity demand relative to pyrolysis oil LHV.

C.3 Carbon distributions of pyrolysis-based chemical recycling process chains

Table C-5: Carbon distribution for waste-to-monomers process chain using ASR or STR for feedstock conversion to pyrolysis oil.

	LDPE		PP		PS		Mix AR		Mix MH		Mix HH		S-PCW	
Reactor	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR	ASR	STR
Carbon distribution, %														
Material use	32.8	48.5	32.8	48.0	59.3	65.9	43.0	53.5	35.7	39.1	35.3	38.7	36.0	36.6
Fuel use	8.0	11.8	8.0	11.7	14.5	16.1	10.5	13.1	8.7	9.6	8.6	9.5	8.8	8.9
CO ₂ emissions	59.2	39.7	59.2	40.3	26.2	18.0	46.5	33.4	55.6	51.3	56.1	51.8	55.2	54.5

Table C-6: Carbon distribution for waste-to-syngas MeOH process chain using ASR or STR for feedstock conversion to pyrolysis oil.

	LDPE		PP		PS		Mix AR		Mix MH		Mix HH		S-PCW	
<i>Reactor</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
<i>Carbon distribution, %</i>														
Material use	31.4	47.0	31.0	46.0	48.6	55.0	38.4	49.6	33.4	37.6	32.0	36.0	33.3	34.8
Fuel use	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CO ₂ emissions	68.6	53.0	69.0	54.0	51.4	45.0	61.6	50.4	66.6	62.4	68.0	64.0	66.7	65.2

D Inventories

All inventories included in the appendix refer to the base scenario unless specified otherwise.

D.1 Waste-to-energy process route

The following tables summarize the inventories for the treatment of 1 kg of model feedstock in MSWI plants.

Table D-1: Inventory for energy recovery from LDPE in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE	3.1439	kg	CO ₂
			0	kg	Grate ashes
			1.7160	kWh	Electricity, medium voltage
			16.891	MJ	District heat

Table D-2: Inventory for energy recovery from PP in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP	3.1439	kg	CO ₂
			0	kg	Grate ashes
			1.7160	kWh	Electricity, medium voltage
			16.891	MJ	District heat

Table D-3: Inventory for energy recovery from PS in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS	3.3711	kg	CO ₂
			0	kg	Grate ashes
			1.5690	kWh	Electricity, medium voltage
			15.445	MJ	District heat

Table D-4: Inventory for energy recovery from Mix AR in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR	3.2098	kg	CO ₂
			0	kg	Grate ashes
			1.6723	kWh	Electricity, medium voltage
			16.461	MJ	District heat

Table D-5: Inventory for energy recovery from Mix MH in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH	3.0596	kg	CO ₂
			0.0020	kg	Grate ashes
			1.6485	kWh	Electricity, medium voltage
			16.227	MJ	District heat

Table D-6: Inventory for energy recovery from Mix HH in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH	2.9533	kg	CO ₂
			0.0050	kg	Grate ashes
			1.5333	kWh	Electricity, medium voltage
			15.093	MJ	District heat

Table D-7: Inventory for energy recovery from S-PCW in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW	2.9314	kg	CO ₂
			0.0220	kg	Grate ashes
			1.5531	kWh	Electricity, medium voltage
			15.288	MJ	District heat

D.2 Waste-to-monomers process route

The following subsections summarize inventories for the process involved in chemical recycling of the model feedstocks via the waste-to-monomers routes.

D.2.1 Pyrolysis

D.2.1.1 Pyrolysis with ASR system

Table D-8: Inventory for pyrolysis of LDPE.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE	0.48800	kg	Pyrolysis oil
1.1122	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.47800	kg	Pyrolysis gas
			0.03400	kg	Pyrolysis residue
			0	kg	CO ₂ release from carbon mass balance loss

Table D-9: Inventory for pyrolysis of PP.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP	0.48518	kg	Pyrolysis oil
1.0978	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.50692	kg	Pyrolysis gas
			0.00791	kg	Pyrolysis residue
			0.02031	kg	CO ₂ release from carbon mass balance loss

Table D-10: Inventory for pyrolysis of PS.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS	0.88500	kg	Pyrolysis oil
0.87500	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.08500	kg	Pyrolysis gas
			0.03000	kg	Pyrolysis residue
			0.00234	kg	CO ₂ release from carbon mass balance loss

Table D-11: Inventory for pyrolysis of Mix AR.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR	0.63300	kg	Pyrolysis oil
1.0622	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.33500	kg	Pyrolysis gas
			0.03200	kg	Pyrolysis residue
			0	kg	CO ₂ release from carbon mass balance loss

Table D-12: Inventory for pyrolysis of Mix MH.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH	0.51400	kg	Pyrolysis oil
1.3467	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.42200	kg	Pyrolysis gas
			0.06400	kg	Pyrolysis residue
			0	kg	CO ₂ release from carbon mass balance loss

Table D-13: Inventory for pyrolysis of Mix HH.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH	0.49107	kg	Pyrolysis oil
1.2739	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.46825	kg	Pyrolysis gas
			0.04067	kg	Pyrolysis residue
			0.08172	kg	CO ₂ release from carbon mass balance loss

Table D-14: Inventory for pyrolysis of S-PCW.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW	0.49901	kg	Pyrolysis oil
1.0539	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.45825	kg	Pyrolysis gas
			0.04274	kg	Pyrolysis residue
			0	kg	CO ₂ release from carbon mass balance loss

D.2.1.2 Pyrolysis with STR system

Table D-15: Inventory for pyrolysis of LDPE.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE	0.72300	kg	Pyrolysis oil
1.1122	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.27300	kg	Pyrolysis gas
			0.00400	kg	Pyrolysis residue
			0.02186	kg	CO ₂ release from carbon mass balance loss

Table D-16: Inventory for pyrolysis of PP.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP	0.71300	kg	Pyrolysis oil
1.0978	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.27800	kg	Pyrolysis gas
			0.00900	kg	Pyrolysis residue
			0.00406	kg	CO ₂ release from carbon mass balance loss

Table D-17: Inventory for pyrolysis of PS.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS	0.98500	kg	Pyrolysis oil
0.87500	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.00100	kg	Pyrolysis gas
			0.01400	kg	Pyrolysis residue
			0.00677	kg	CO ₂ release from carbon mass balance loss

Table D-18: Inventory for pyrolysis of Mix AR.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR	0.79300	kg	Pyrolysis oil
1.0622	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.19500	kg	Pyrolysis gas
			0.01200	kg	Pyrolysis residue
			0.00412	kg	CO ₂ release from carbon mass balance loss

Table D-19: Inventory for pyrolysis of Mix MH.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH	0.57200	kg	Pyrolysis oil
1.3467	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.41100	kg	Pyrolysis gas
			0.01700	kg	Pyrolysis residue
			0.05773	kg	CO ₂ release from carbon mass balance loss

Table D-20: Inventory for pyrolysis of Mix HH.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH	0.55100	kg	Pyrolysis oil
1.2739	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.41300	kg	Pyrolysis gas
			0.03600	kg	Pyrolysis residue
			0.09521	kg	CO ₂ release from carbon mass balance loss

Table D-21: Inventory for pyrolysis of S-PCW.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW	0.52800	kg	Pyrolysis oil
1.0539	kWh	Electricity, medium voltage	0	kg	Aqueous condensate
			0.42700	kg	Pyrolysis gas
			0.04500	kg	Pyrolysis residue
			0.12490	kg	CO ₂ release from carbon mass balance loss

D.2.2 Pyrolysis gas utilization in gas motor

Inventories include maximum recovery for electricity and heat in full integration scenario. For flaring of pyrolysis gas, inventories are identical with electricity and district heat output flows set to 0.

D.2.2.1 Pyrolysis gas from model feedstock pyrolysis in ASR system

Table D-22: Inventory for utilization of LDPE pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis gas	3.0770	kg	CO ₂
			4.6582	kWh	Electricity, medium voltage
			21.582	MJ	District heat

Table D-23: Inventory for utilization of PP pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis gas	3.0747	kg	CO ₂
			4.6592	kWh	Electricity, medium voltage
			21.586	MJ	District heat

Table D-24: Inventory for utilization of PS pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis gas	3.2783	kg	CO ₂
			4.2057	kWh	Electricity, medium voltage
			19.485	MJ	District heat

Table D-25: Inventory for utilization of Mix AR pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis gas	3.0997	kg	CO ₂
			4.6178	kWh	Electricity, medium voltage
			21.394	MJ	District heat

Table D-26: Inventory for utilization of Mix MH pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis gas	2.9033	kg	CO ₂
			4.3529	kWh	Electricity, medium voltage
			20.167	MJ	District heat

Table D-27: Inventory for utilization of Mix HH pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis gas	2.5372	kg	CO ₂
			3.5560	kWh	Electricity, medium voltage
			16.475	MJ	District heat

Table D-28: Inventory for utilization of S-PCW pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis gas	2.8090	kg	CO ₂
			4.1175	kWh	Electricity, medium voltage
			19.077	MJ	District heat

D.2.2.2 Pyrolysis gas from model feedstock pyrolysis in STR system

Table D-29: Inventory for utilization of LDPE pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis gas	3.0756	kg	CO ₂
			4.6968	kWh	Electricity, medium voltage
			21.760	MJ	District heat

Table D-30: Inventory for utilization of PP pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis gas	3.0842	kg	CO ₂
			4.6816	kWh	Electricity, medium voltage
			21.690	MJ	District heat

Table D-31: Inventory for utilization of PS pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis gas	3.3273	kg	CO ₂
			4.0791	kWh	Electricity, medium voltage
			18.899	MJ	District heat

Table D-32: Inventory for utilization of Mix AR pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis gas	3.0863	kg	CO ₂
			4.6616	kWh	Electricity, medium voltage
			21.597	MJ	District heat

Table D-33: Inventory for utilization of Mix MH pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis gas	2.8304	kg	CO ₂
			4.1489	kWh	Electricity, medium voltage
			19.222	MJ	District heat

Table D-34: Inventory for utilization of Mix HH pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis gas	2.5194	kg	CO ₂
			3.5312	kWh	Electricity, medium voltage
			16.360	MJ	District heat

Table D-35: Inventory for utilization of S-PCW pyrolysis gas in gas motor.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis gas	2.6326	kg	CO ₂
			3.7327	kWh	Electricity, medium voltage
			17.294	MJ	District heat

D.2.3 Pyrolysis residue utilization in MSWI

D.2.3.1 Pyrolysis residue utilization from model feedstock pyrolysis in ASR system

Table D-36: Inventory for energy recovery from LDPE pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-37: Inventory for energy recovery from PP pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-38: Inventory for energy recovery from PS pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-39: Inventory for energy recovery from Mix AR pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-40: Inventory for energy recovery from Mix MH pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis residue	3.5497	kg	CO ₂
			0.03125	kg	Grate ashes
			1.3391	kWh	Electricity, medium voltage
			13.182	MJ	District heat

Table D-41: Inventory for energy recovery from Mix HH pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis residue	3.2138	kg	CO ₂
			0.12293	kg	Grate ashes
			1.2124	kWh	Electricity, medium voltage
			11.934	MJ	District heat

Table D-42: Inventory for energy recovery from S-PCW pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis residue	1.7782	kg	CO ₂
			0.51470	kg	Grate ashes
			0.67085	kWh	Electricity, medium voltage
			6.6034	MJ	District heat

D.2.3.2 Pyrolysis residue utilization from model feedstock pyrolysis in STR system

Table D-43: Inventory for energy recovery from LDPE pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-44: Inventory for energy recovery from PP pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-45: Inventory for energy recovery from PS pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-46: Inventory for energy recovery from Mix AR pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis residue	3.6642	kg	CO ₂
			0	kg	Grate ashes
			1.3823	kWh	Electricity, medium voltage
			13.607	MJ	District heat

Table D-47: Inventory for energy recovery from Mix MH pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis residue	3.2331	kg	CO ₂
			0.11765	kg	Grate ashes
			1.2197	kWh	Electricity, medium voltage
			12.006	MJ	District heat

Table D-48: Inventory for energy recovery from Mix HH pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis residue	3.1553	kg	CO ₂
			0.13889	kg	Grate ashes
			1.1903	kWh	Electricity, medium voltage
			11.717	MJ	District heat

Table D-49: Inventory for energy recovery from S-PCW pyrolysis residue in MSWI.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis residue	1.8728	kg	CO ₂
			0.48889	kg	Grate ashes
			0.70653	kWh	Electricity, medium voltage
			6.9546	MJ	District heat

D.2.4 Pyrolysis oil upgrading

Hydrogen input in inventories for pyrolysis oil upgrading refers to total hydrogen input including hydrogen recycled from steam cracking and make-up hydrogen with a target H/C molar ratio of 2. Subsequent utilization of offgas and subsequent flue gas treatment are neglected.

D.2.4.1 Upgrading of pyrolysis oils from ASR system

Table D-50: Inventory for upgrading of LDPE pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis oil	1.0043	kg	Upgraded pyrolysis oil
0.0062	kg	Hydrogen			

Table D-51: Inventory for upgrading of PP pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis oil	1.0090	kg	Upgraded pyrolysis oil
0.01288	kg	Hydrogen			

Table D-52: Inventory for upgrading of PS pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis oil	1.0732	kg	Upgraded pyrolysis oil
0.10464	kg	Hydrogen			

Table D-53: Inventory for upgrading of Mix AR pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis oil	1.0347	kg	Upgraded pyrolysis oil
0.04958	kg	Hydrogen			

Table D-54: Inventory for upgrading of Mix MH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis oil	1.0078	kg	Upgraded pyrolysis oil
0.02058	kg	Hydrogen			

Table D-55: Inventory for upgrading of Mix HH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis oil	1.0078	kg	Upgraded pyrolysis oil
0.04331	kg	Hydrogen			

Table D-56: Inventory for upgrading of S-PCW pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis oil	1.0032	kg	Upgraded pyrolysis oil
0.03064	kg	Hydrogen			

D.2.4.2 Upgrading of pyrolysis oils from STR system

Table D-57: Inventory for upgrading of LDPE pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis oil	1	kg	Upgraded pyrolysis oil
0	kg	Hydrogen			

Table D-58: Inventory for upgrading of PP pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis oil	1.0055	kg	Upgraded pyrolysis oil
0.00787	kg	Hydrogen			

Table D-59: Inventory for upgrading of PS pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis oil	1.0709	kg	Upgraded pyrolysis oil
0.10130	kg	Hydrogen			

Table D-60: Inventory for upgrading of Mix AR pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis oil	1.0289	kg	Upgraded pyrolysis oil
0.04124	kg	Hydrogen			

Table D-61: Inventory for upgrading of Mix MH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis oil	0.99383	kg	Upgraded pyrolysis oil
0.005912	kg	Hydrogen			

Table D-62: Inventory for upgrading of Mix HH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis oil	0.98566	kg	Upgraded pyrolysis oil
0.029449	kg	Hydrogen			

Table D-63: Inventory for upgrading of S-PCW pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis oil	0.96464	kg	Upgraded pyrolysis oil
0.010422	kg	Hydrogen			

D.2.5 Steam cracking of pyrolysis oils

As all pyrolysis oils are assumed to be identical after upgrading the inventory for steam cracking is independent of the model feedstock. Due to the license agreement of the ecoinvent database, the reconstructed inventory for steam cracking of pyrolysis oil based on conventional naphtha steam cracking cannot be disclosed beyond the main products.

Table D-64: Inventory for steam cracking of upgraded pyrolysis oil based on naphtha steam cracking product distribution.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Upgraded pyrolysis oil	0.01	kg	Hydrogen
			0.30	kg	Ethylene
			0.15	kg	Propylene
			0.05	kg	Butene, mixed
			0.05	kg	Butadiene, crude
			0.20	kg	Pyrolysis gasoline
			0.04	kg	Pyrolysis fuel oil
			0.03	kg	Pyrolysis fuel gas
			0.48720	kg	CO ₂

Inventories for steam cracking of pyrolysis based on conventional steam cracking of AGO and HCR used in the context of the sensitivity analysis regarding steam cracking product distribution are likewise derived from the ecoinvent dataset for conventional naphtha steam cracking. Accordingly, these inventories are also limited to the main products.

Table D-65: Inventory for steam cracking of upgraded pyrolysis oil based on AGO steam cracking product distribution.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Upgraded pyrolysis oil	0.0071	kg	Hydrogen
0.019104	kg	Refinery gas	0.2593	kg	Ethylene
			0.1407	kg	Propylene
			0.0361	kg	Butene, mixed
			0.0573	kg	Butadiene, crude
			0.1868	kg	Pyrolysis gasoline
			0.1630	kg	Pyrolysis fuel oil
			0	kg	Pyrolysis fuel gas
			0.48059	kg	CO ₂

Table D-66: Inventory for steam cracking of upgraded pyrolysis oil based on HCR steam cracking product distribution.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Upgraded pyrolysis oil	0.0068	kg	Hydrogen
0.019104	kg	Refinery gas	0.2598	kg	Ethylene
			0.1602	kg	Propylene
			0.0414	kg	Butene, mixed
			0.0803	kg	Butadiene, crude
			0.1720	kg	Pyrolysis gasoline
			0.0795	kg	Pyrolysis fuel oil
			0	kg	Pyrolysis fuel gas
			0.48059	kg	CO ₂

D.3 Waste-to-syngas process route

Inventories for pyrolysis and utilization of pyrolysis side products are identical for the waste-to-monomers and waste-to-syngas process routes. Accordingly, for the waste-to-syngas process route, only inventories for EFG of pyrolysis oils from different model feedstocks are summarized.

D.3.1 EFG of pyrolysis oils from ASR system in MeOH syngas configuration

Table D-67: Inventory for MeOH syngas production by EFG from LDPE pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis oil	1.5091	kg	MeOH syngas
1.1704	kg	Oxygen	5.0906	MJ	District heat
0.78116	kg	Water, deionised	1.1328	kg	CO ₂
7.6938e-4	kg	Methanol	3.1811e-4	m ³	Waste water
0.17290	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.61222	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.067161	MJ	Cooling, low temperature (-25 °C)			
0.60580	MJ	Cooling, very low temperature (-55 °C)			

Table D-68: Inventory for MeOH syngas production by EFG from PP pyrolysis oil.

Input			Output		
Quantity	Unit	Flow	Quantity	Unit	Flow
1	kg	PP pyrolysis oil	1.5009	kg	MeOH syngas
1.1619	kg	Oxygen	5.0345	MJ	District heat
0.80357	kg	Water, deionised	1.1587	kg	CO ₂
7.5416e-4	kg	Methanol	3.1421e-4	m ³	Waste water
0.17212	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.59273	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.062323	MJ	Cooling, low temperature (-25 °C)			
0.60376	MJ	Cooling, very low temperature (-55 °C)			

Table D-69: Inventory for MeOH syngas production by EFG from PS pyrolysis oil.

Input			Output		
Quantity	Unit	Flow	Quantity	Unit	Flow
1	kg	PS pyrolysis oil	1.3822	kg	MeOH syngas
1.0450	kg	Oxygen	4.1225	MJ	District heat
1.0728	kg	Water, deionised	1.5184	kg	CO ₂
8.5061e-4	kg	Methanol	2.2543e-4	m ³	Waste water
0.16116	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.28226	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.032404	MJ	Cooling, low temperature (-25 °C)			
0.65097	MJ	Cooling, very low temperature (-55 °C)			

Table D-70: Inventory for MeOH syngas production by EFG from Mix AR pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis oil	1.4527	kg	MeOH syngas
1.1101	kg	Oxygen	4.6794	MJ	District heat
0.86953	kg	Water, deionised	1.3005	kg	CO ₂
8.1417e-4	kg	Methanol	2.3515e-4	m ³	Waste water
0.16700	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.30886	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.044910	MJ	Cooling, low temperature (-25 °C)			
0.63711	MJ	Cooling, very low temperature (-55 °C)			

Table D-71: Inventory for MeOH syngas production by EFG from Mix MH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis oil	1.4839	kg	MeOH syngas
1.1364	kg	Oxygen	4.9159	MJ	District heat
0.80415	kg	Water, deionised	1.1760	kg	CO ₂
7.6369e-4	kg	Methanol	2.8915e-4	m ³	Waste water
0.16905	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.50849	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.058840	MJ	Cooling, low temperature (-25 °C)			
0.60625	MJ	Cooling, very low temperature (-55 °C)			

Table D-72: Inventory for MeOH syngas production by EFG from Mix HH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis oil	1.4396	kg	MeOH syngas
1.0958	kg	Oxygen	4.7012	MJ	District heat
0.83943	kg	Water, deionised	1.2437	kg	CO ₂
7.7018e-4	kg	Methanol	2.6009e-4	m ³	Waste water
0.16442	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.37492	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.046795	MJ	Cooling, low temperature (-25 °C)			
0.61889	MJ	Cooling, very low temperature (-55 °C)			

Table D-73: Inventory for MeOH syngas production by EFG from S-PCW pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis oil	1.4610	kg	MeOH syngas
1.1118	kg	Oxygen	4.8159	MJ	District heat
0.79856	kg	Water, deionised	1.1977	kg	CO ₂
7.7107e-4	kg	Methanol	2.6004e-4	m ³	Waste water
0.16603	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.42141	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.053938	MJ	Cooling, low temperature (-25 °C)			
0.60865	MJ	Cooling, very low temperature (-55 °C)			

D.3.2 EFG of pyrolysis oils from ASR system in Oxo syngas configuration

Table D-74: Inventory for Oxo syngas production by EFG from PP pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PP pyrolysis oil	2.0753	kg	Oxo syngas
1.1619	kg	Oxygen	5.3774	MJ	District heat
0.19727	kg	Water, deionised	0.12918	kg	CO ₂
2.9667e-4	kg	Methanol	1.5598e-4	m ³	Waste water
0.14565	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.69584	MJ	Cooling, cooling water			
0.025380	MJ	Cooling, chilled water			
0.11232	MJ	Cooling, low temperature (-25 °C)			
0.18494	MJ	Cooling, very low temperature (-55 °C)			

Table D-75: Inventory for Oxo syngas production by EFG from PS pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	PS pyrolysis oil	1.9172	kg	Oxo syngas
1.0450	kg	Oxygen	4.3099	MJ	District heat
0.56047	kg	Water, deionised	0.55999	kg	CO ₂
9.1440e-4	kg	Methanol	1.2899e-4	m ³	Waste water
0.15023	kWh	Electricity, medium voltage	0	kg	Fly ashes
1.4167	MJ	Cooling, cooling water			
0.069589	MJ	Cooling, chilled water			
0.28067	MJ	Cooling, low temperature (-25 °C)			
0.45401	MJ	Cooling, very low temperature (-55 °C)			

Table D-76: Inventory for Oxo syngas production by EFG from S-PCW pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis oil	2.0231	kg	Oxo syngas
1.1118	kg	Oxygen	5.0646	MJ	District heat
0.17827	kg	Water, deionised	0.19067	kg	CO ₂
3.8056e-4	kg	Methanol	1.2725e-4	m ³	Waste water
0.14076	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.56394	MJ	Cooling, cooling water			
0.021441	MJ	Cooling, chilled water			
0.14318	MJ	Cooling, low temperature (-25 °C)			
0.21890	MJ	Cooling, very low temperature (-55 °C)			

D.3.3 EFG of pyrolysis oils from STR system in MeOH syngas configuration

Table D-77: Inventory for MeOH syngas production by EFG from LDPE pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	LDPE pyrolysis oil	1.5253	kg	MeOH syngas
1.1641	kg	Oxygen	5.1511	MJ	District heat
0.74525	kg	Water, deionised	1.0948	kg	CO ₂
7.5189e-4	kg	Methanol	2.9783e-4	m ³	Waste water
0.17180	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.58336	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.072554	MJ	Cooling, low temperature (-25 °C)			
0.59630	MJ	Cooling, very low temperature (-55 °C)			

Table D-78: Inventory for MeOH syngas production by EFG from PP pyrolysis oil.

Input			Output		
Quantity	Unit	Flow	Quantity	Unit	Flow
1	kg	PP pyrolysis oil	1.5167	kg	MeOH syngas
1.1565	kg	Oxygen	5.1163	MJ	District heat
0.80130	kg	Water, deionised	1.1274	kg	CO ₂
7.7140e-4	kg	Methanol	3.2204e-4	m ³	Waste water
0.17129	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.61873	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.066982	MJ	Cooling, low temperature (-25 °C)			
0.59596	MJ	Cooling, very low temperature (-55 °C)			

Table D-79: Inventory for MeOH syngas production by EFG from PS pyrolysis oil.

Input			Output		
Quantity	Unit	Flow	Quantity	Unit	Flow
1	kg	PS pyrolysis oil	1.4070	kg	MeOH syngas
1.0210	kg	Oxygen	4.1885	MJ	District heat
1.0805	kg	Water, deionised	1.4787	kg	CO ₂
8.0559e-4	kg	Methanol	2.2404e-4	m ³	Waste water
0.15813	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.15247	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.031904	MJ	Cooling, low temperature (-25 °C)			
0.64330	MJ	Cooling, very low temperature (-55 °C)			

Table D-80: Inventory for MeOH syngas production by EFG from Mix AR pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix AR pyrolysis oil	1.5007	kg	MeOH syngas
1.0703	kg	Oxygen	4.7083	MJ	District heat
0.94174	kg	Water, deionised	1.2203	kg	CO ₂
7.7935e-4	kg	Methanol	2.9949e-4	m ³	Waste water
0.16207	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.43692	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.056657	MJ	Cooling, low temperature (-25 °C)			
0.62276	MJ	Cooling, very low temperature (-55 °C)			

Table D-81: Inventory for MeOH syngas production by EFG from Mix MH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix MH pyrolysis oil	1.5019	kg	MeOH syngas
1.1572	kg	Oxygen	5.1060	MJ	District heat
0.75680	kg	Water, deionised	1.1136	kg	CO ₂
7.5803e-4	kg	Methanol	3.0679e-4	m ³	Waste water
0.17094	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.60046	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.066371	MJ	Cooling, low temperature (-25 °C)			
0.58951	MJ	Cooling, very low temperature (-55 °C)			

Table D-82: Inventory for MeOH syngas production by EFG from Mix HH pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	Mix HH pyrolysis oil	1.4408	kg	MeOH syngas
1.0957	kg	Oxygen	4.7800	MJ	District heat
0.79667	kg	Water, deionised	1.1728	kg	CO ₂
7.6196e-4	kg	Methanol	2.8673e-4	m ³	Waste water
0.16359	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.48032	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.053894	MJ	Cooling, low temperature (-25 °C)			
0.59769	MJ	Cooling, very low temperature (-55 °C)			

Table D-83: Inventory for MeOH syngas production by EFG from S-PCW pyrolysis oil.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	kg	S-PCW pyrolysis oil	1.4434	kg	MeOH syngas
1.1247	kg	Oxygen	4.9811	MJ	District heat
0.74604	kg	Water, deionised	1.1031	kg	CO ₂
7.5870e-4	kg	Methanol	3.3179e-4	m ³	Waste water
0.16626	kWh	Electricity, medium voltage	0	kg	Fly ashes
0.64685	MJ	Cooling, cooling water			
0	MJ	Cooling, chilled water			
0.060725	MJ	Cooling, low temperature (-25 °C)			
0.57716	MJ	Cooling, very low temperature (-55 °C)			

D.4 Reference processes for syngas production

Table D-84: Inventory (output-based) for MeOH syngas production from HFO by EFG.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
0.70466	kg	Heavy fuel oil	1	kg	MeOH syngas
0.70743	kg	Oxygen	3.1346	MJ	District heat
0.67131	kg	Water, deionised	0.86169	kg	CO ₂
7.1411e-4	kg	Methanol	1.9753e-4	m ³	Waste water
0.10803	kWh	Electricity, medium voltage	7.0466e-4	kg	Fly ashes
0.34734	MJ	Cooling, cooling water			
0.085683	MJ	Cooling, chilled water			
0.10133	MJ	Cooling, low temperature (-25 °C)			
0.38890	MJ	Cooling, very low temperature (-55 °C)			

Table D-85: Inventory (output-based) for Oxo syngas production from HFO by EFG.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
0.50853	kg	Heavy fuel oil	1	kg	Oxo syngas
0.51053	kg	Oxygen	2.3704	MJ	District heat
0.20346	kg	Water, deionised	0.12347	kg	CO ₂
2.6931e-4	kg	Methanol	7.8316e-5	m ³	Waste water
0.078728	kWh	Electricity, medium voltage	5.0853e-4	kg	Fly ashes
0.25513	MJ	Cooling, cooling water			
0.019542	MJ	Cooling, chilled water			
0.10436	MJ	Cooling, low temperature (-25 °C)			
0.13859	MJ	Cooling, very low temperature (-55 °C)			

Table D-86: Inventory (output-based) for MeOH syngas production from natural gas by partial oxidation (POx).

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
0.78732	m ³	Natural gas	1	kg	MeOH syngas
0.75953	kg	Oxygen	3.9067	MJ	District heat
0.15365	kg	Water, deionised	0.27078	kg	CO ₂
4.8626e-4	kg	Methanol	2.2493e-4	m ³	Waste water
0.0083818	kWh	Electricity, medium voltage	0	kg	Fly ashes
2.4330	MJ	Cooling, cooling water			
0.0078026	MJ	Cooling, chilled water			
0.25725	MJ	Cooling, low temperature (-25 °C)			
0.14959	MJ	Cooling, very low temperature (-55 °C)			

D.5 Utility processes

Table D-87: Inventory for cooling with cooling water.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	MJ	Heat rejected to cooling water	2.44e-6	kg	Residue from cooling towers
0.48757	kg	Water, softened			
9.5390e-3	kWh	Electricity, medium voltage			

Table D-88: Inventory for cooling with chilled water.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	MJ	Heat rejected to chilled water	1.2	MJ	Heat rejected to cooling water
5.556e-2	kWh	Electricity, medium voltage			

Table D-89: Inventory for low temperature cooling (-25 °C).

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	MJ	Heat rejected to low temperature cooling	1.403	MJ	Heat rejected to cooling water
0.11194	kWh	Electricity, medium voltage			

Table D-90: Inventory for very low temperature cooling (-55 °C).

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
1	MJ	Heat rejected to very low temperature cooling	1.3056	MJ	Heat rejected to low temperature cooling
0.084889	kWh	Electricity, medium voltage			

Table D-91: Inventory (output-based) for oxygen generation (gaseous) via air separation.

Input Quantity	Unit	Flow	Output Quantity	Unit	Flow
0.47	kWh	Electricity, medium voltage	1	kg	Oxygen

D.6 Background processes

Data for background processes is taken from ecoinvent v3.10 database. Flows from foreground processes are mapped to the respective processes shown in Table D-92.

Table D-92: Processes used for modeling of background processes.

Flow	Mapped process	Geography	Type	Source
District heating	market for heat, district or industrial, natural gas	Europe without Switzerland	Product (Credit)	229
Electricity, medium voltage	market for electricity, medium voltage	Germany	Product (Credit), Input	228
Hydrogen from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; hydrogen, gaseous, low pressure	Europe	Product (Credit), Calculation of steam cracking inventory	200
Ethylene from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; ethylene	Europe	Product (Credit), Calculation of steam cracking inventory	197
Propylene from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; propylene	Europe	Product (Credit), Calculation of steam cracking inventory	201
Butene, mixed, from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; butene, mixed	Europe	Product (Credit), Calculation of steam cracking inventory	199
Butadiene, crude, from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; butadiene, crude	Europe	Product (Credit), Calculation of steam cracking inventory	198
Pyrolysis gas, containing benzene, toluene and xylene from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; pyrolysis gas, containing benzene, toluene and xylene	Europe	Product (Credit), Calculation of steam cracking inventory	204
Pyrolysis fuel oil from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; pyrolysis fuel oil	Europe	Product (Credit), Calculation of steam cracking inventory	203

Table D-92 (continued): Processes used for modeling of background processes.

Flow	Mapped process	Geography	Type	Source
Pyrolysis fuel gas from steam cracking	unsaturated hydrocarbons production, steam cracking operation, average; pyrolysis fuel gas	Europe	Product (Credit), Calculation of steam cracking inventory	202
Heavy fuel oil	market for heavy fuel oil	Europe without Switzerland	Input	220
Natural gas	market for natural gas, high pressure	Germany	Input	234
Treatment of aqueous condensate	treatment of wastewater, average, wastewater treatment	Europe without Switzerland	Waste treatment	235
Treatment of grate ashes	market for average incineration residue	Switzerland	Waste treatment	236
Treatment of fly ashes	treatment of fly ash and scrubber sludge, hazardous waste incineration	Europe without Switzerland	Waste treatment	237
Treatment of wastewater from EFG	treatment of wastewater, average, wastewater treatment	Europe without Switzerland	Waste treatment	235
Treatment of residue from cooling tower	treatment of residue from cooling tower, sanitary landfill	Switzerland	Waste treatment	238
Hydrogen make-up	hydrogen production, gaseous, petroleum refinery operation	Europe without Switzerland	Input	239
Hydrogen make-up	Hydrogen production, steam methane reforming	Europe	Input	240
Water, deionised	water production, deionised	Europe without Switzerland	Input	241
Water, softened	water production, completely softened	Europe	Input	242
Methanol	market for methanol	Europe	Input	243

E Additional data and assumptions for LCA

E.1 Functional unit for system perspective LCA

The input and output values that make up the combined functional unit of the system perspective LCA are summarized in Table E-1. Values are derived from the maximum amount of product that can be derived from the treatment of 1 kg of model feedstock through either of the waste-treatment routes, i.e., waste-to-energy, waste-to-monomers, and waste-to-syngas in MeOH syngas configuration. For the pyrolysis-based chemical recycling route, the pyrolysis system with higher yield is chosen for the definition of maximum product yield. The consumption of a product defined as system output in the waste treatment process increases the overall required production of the respective product by the consumed amount. For example, even though no hydrogen may be defined as system output, the production of hydrogen is still required for upgrading of pyrolysis oil in the waste-to-monomers process route.

Table E-1: System inputs and outputs as functional unit for system perspective LCA.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
System input							
Feedstock input, kg	1	1	1	1	1	1	1
System output							
Electricity, kWh	1.716	1.716	1.569	1.672	1.648	1.533	1.553
District heat, MJ	16.89	16.89	15.44	16.46	16.23	15.09	15.29
Steam cracker products, kg	0.593	0.588	0.865	0.669	0.466	0.445	0.418
Hydrogen, kg	0.007	0.002	0	0	0.002	0	0
MeOH syngas, kg	1.103	1.081	1.386	1.190	0.859	0.794	0.762

E.2 Summary of LCA results

E.2.1 Input-based LCA

E.2.1.1 Waste-to-energy process route

Table E-2: Climate change impact in kg CO₂e/kg model feedstock for waste-to-energy process route for different model feedstocks.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	3.14	3.14	3.37	3.21	3.06	2.95	2.94
Credits							
<i>Electricity</i>	-0.72	-0.72	-0.66	-0.70	-0.69	-0.65	-0.65
<i>District heat</i>	-0.95	-0.95	-0.87	-0.93	-0.92	-0.85	-0.86
Total							
Sum (gross)	3.14	3.14	3.37	3.21	3.06	2.95	2.94
Sum (net)	1.47	1.47	1.84	1.58	1.45	1.46	1.42

E.2.1.2 Waste-to-monomers process route

Table E-3: Climate change impact in kg CO₂e/kg model feedstock for waste-to-monomers process route for different model feedstocks for pyrolysis with ASR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.13	0.03	0.11	0.12	0.23	0.13	0.08
<i>Pyrolysis</i>	1.95	2.04	0.65	1.49	1.79	1.81	1.73
<i>Upgrading</i>	0.01	0.02	0.27	0.09	0.03	0.06	0.04
<i>Steam cracking</i>	0.26	0.26	0.51	0.35	0.28	0.26	0.27
<i>Internal energy use</i>	-0.49	-0.49	-0.20	-0.49	-0.60	-0.57	-0.48
Credits							
<i>Steam cracker products</i>	-0.72	-0.72	-1.39	-0.96	-0.76	-0.73	-0.73
<i>Electricity</i>	-0.47	-0.52	0	-0.20	-0.23	-0.17	-0.35
<i>District heat</i>	-0.61	-0.62	-0.12	-0.43	-0.53	-0.46	-0.51
Total							
Sum (gross)	1.85	1.86	1.34	1.55	1.73	1.70	1.65
Sum (net)	0.05	0.00	-0.17	-0.03	0.22	0.34	0.06

Table E-4: Climate change impact in kg CO₂e/kg model feedstock for waste-to-monomers process route for different model feedstocks for pyrolysis with STR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.01	0.03	0.05	0.04	0.06	0.12	0.09
<i>Pyrolysis</i>	1.33	1.32	0.38	1.05	1.79	1.67	1.69
<i>Upgrading</i>	0	0.02	0.29	0.09	0.01	0.05	0.02
<i>Steam cracking</i>	0.39	0.38	0.56	0.44	0.30	0.29	0.27
<i>Internal energy use</i>	-0.49	-0.50	-0.04	-0.41	-0.60	-0.57	-0.48
Credits							
<i>Steam cracker products</i>	-1.08	-1.06	-1.55	-1.20	-0.84	-0.80	-0.75
<i>Electricity</i>	-0.05	-0.07	0	0	-0.14	-0.08	-0.22
<i>District heat</i>	-0.34	-0.35	-0.01	-0.25	-0.46	-0.41	-0.43
Total							
Sum (gross)	1.24	1.25	1.24	1.21	1.56	1.55	1.60
Sum (net)	-0.23	-0.22	-0.32	-0.23	0.12	0.28	0.19

E.2.1.3 Waste-to-syngas process route

Table E-5: Climate change impact in kg CO₂e/kg model feedstock for waste-to-syngas route in MeOH syngas configuration for different model feedstocks for pyrolysis with ASR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.13	0.03	0.11	0.12	0.23	0.13	0.08
<i>Pyrolysis</i>	1.95	2.04	0.65	1.49	1.79	1.81	1.73
<i>EFG</i>	0.74	0.75	1.65	1.05	0.79	0.79	0.78
<i>Internal energy use</i>	-0.65	-0.64	-0.17	-0.67	-0.76	-0.71	-0.62
Credits							
<i>MeOH syngas</i>	-1.08	-1.07	-1.79	-1.35	-1.12	-1.03	-1.07
<i>Electricity</i>	-0.31	-0.36	0	0	-0.05	-0.01	-0.18
<i>District heat</i>	-0.75	-0.76	-0.32	-0.60	-0.67	-0.59	-0.64
Total							
Sum (gross)	2.16	2.17	2.25	1.99	2.06	2.01	1.97
Sum (net)	0.03	-0.01	0.13	0.05	0.22	0.38	0.07

Table E-6: Climate change impact in kg CO₂e/kg model feedstock for waste-to-syngas route in MeOH syngas configuration for different model feedstocks for pyrolysis with STR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.01	0.03	0.05	0.04	0.06	0.12	0.09
<i>Pyrolysis</i>	1.33	1.32	0.38	1.05	1.79	1.67	1.69
<i>EFG</i>	1.06	1.07	1.79	1.25	0.85	0.84	0.77
<i>Internal energy use</i>	-0.54	-0.55	-0.01	-0.39	-0.73	-0.63	-0.63
Credits							
<i>MeOH syngas</i>	-1.61	-1.58	-2.03	-1.74	-1.26	-1.16	-1.11
<i>Electricity</i>	0	0	0	0	0	0	-0.05
<i>District heat</i>	-0.55	-0.55	-0.24	-0.46	-0.62	-0.55	-0.58
Total							
Sum (gross)	1.87	1.87	2.21	1.96	1.97	2.00	1.92
Sum (net)	-0.30	-0.26	-0.06	-0.24	0.09	0.28	0.18

Table E-7: Climate change impact in kg CO₂e/kg model feedstock for waste-to-syngas route in Oxo syngas configuration for different model feedstocks for pyrolysis with ASR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	n.a.	0.03	0.11	n.a.	n.a.	n.a.	0.08
<i>Pyrolysis</i>	n.a.	2.04	0.65	n.a.	n.a.	n.a.	1.73
<i>EFG</i>	n.a.	0.22	0.80	n.a.	n.a.	n.a.	0.25
<i>Internal energy use</i>	n.a.	-0.62	-0.17	n.a.	n.a.	n.a.	-0.60
Credits							
<i>Oxo syngas</i>	n.a.	-0.54	-0.91	n.a.	n.a.	n.a.	-0.54
<i>Electricity</i>	n.a.	-0.38	0	n.a.	n.a.	n.a.	-0.21
<i>District heat</i>	n.a.	-0.76	-0.33	n.a.	n.a.	n.a.	-0.65
Total							
Sum (gross)	n.a.	1.67	1.39	n.a.	n.a.	n.a.	1.47
Sum (net)	n.a.	-0.02	0.15	n.a.	n.a.	n.a.	0.07

E.2.2 Product-based LCA

E.2.2.1 Waste-to-monomers process route

Table E-8: Climate change impact in kg CO₂e/kg steam cracker products for waste-to-monomers process route for different model feedstocks for pyrolysis with ASR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.31	0.07	0.14	0.22	0.54	0.33	0.20
<i>Pyrolysis</i>	4.85	5.08	0.83	2.77	4.22	4.45	4.22
<i>Upgrading</i>	0.02	0.04	0.34	0.17	0.07	0.15	0.11
<i>Steam cracking</i>	0.65	0.65	0.65	0.65	0.65	0.65	0.65
<i>Internal energy use</i>	-1.23	-1.23	-0.25	-0.91	-1.41	-1.40	-1.16
Credits							
<i>Hydrogen</i>	-0.01	0	0	0	0	0	0
<i>Electricity</i>	-1.17	-1.29	0	-0.37	-0.53	-0.42	-0.84
<i>District heat</i>	-1.51	-1.55	-0.15	-0.80	-1.24	-1.14	-1.24
Total							
Sum (gross)	4.61	4.62	1.72	2.89	4.07	4.18	4.02
Sum (net)	1.91	1.78	1.57	1.72	2.30	2.63	1.94

Table E-9: Climate change impact in kg CO₂e/kg steam cracker products for waste-to-monomers process route for different model feedstocks for pyrolysis with STR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.02	0.06	0.06	0.07	0.12	0.26	0.20
<i>Pyrolysis</i>	2.24	2.25	0.44	1.57	3.84	3.75	4.22
<i>Upgrading</i>	0	0.03	0.33	0.14	0.02	0.10	0.11
<i>Steam cracking</i>	0.65	0.65	0.65	0.65	0.65	0.65	0.65
<i>Internal energy use</i>	-0.83	-0.86	-0.05	-0.62	-1.28	-1.28	-1.16
Credits							
<i>Hydrogen</i>	-0.03	-0.01	0	0	-0.01	0	0
<i>Electricity</i>	-0.08	-0.11	0	0	-0.30	-0.17	-0.84
<i>District heat</i>	-0.57	-0.59	-0.01	-0.37	-0.98	-0.91	-1.24
Total							
Sum (gross)	2.09	2.13	1.43	1.81	3.35	3.49	4.02
Sum (net)	1.40	1.42	1.42	1.45	2.05	2.41	1.94

E.2.2.2 Waste-to-syngas process route

Table E-10: Climate change impact in kg CO₂e/kg MeOH syngas for waste-to-syngas route for different model feedstocks for pyrolysis with ASR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.17	0.04	0.09	0.13	0.30	0.19	0.11
<i>Pyrolysis</i>	2.65	2.80	0.53	1.62	2.35	2.55	2.37
<i>EFG</i>	1.00	1.02	1.35	1.15	1.04	1.11	1.07
<i>Internal energy use</i>	-0.89	-0.88	-0.14	-0.73	-0.99	-1.01	-0.86
Credits							
<i>Electricity</i>	-0.41	-0.49	0	0	-0.07	-0.01	-0.25
<i>District heat</i>	-1.02	-1.04	-0.26	-0.65	-0.88	-0.84	-0.88
Total							
Sum (gross)	2.93	2.98	1.84	2.16	2.70	2.85	2.70
Sum (net)	1.50	1.45	1.57	1.51	1.75	2.00	1.57

Table E-11: Climate change impact in kg CO₂e/kg MeOH syngas for waste-to-syngas route for different model feedstocks for pyrolysis with STR system.

Model feedstock	LDPE	PP	PS	Mix AR	Mix MH	Mix HH	S-PCW
Process burdens							
<i>Incineration</i>	0.01	0.04	0.04	0.04	0.06	0.15	0.12
<i>Pyrolysis</i>	1.21	1.22	0.27	0.89	2.08	2.11	2.22
<i>EFG</i>	0.96	0.99	1.29	1.05	0.99	1.06	1.02
<i>Internal energy use</i>	-0.49	-0.51	-0.01	-0.33	-0.85	-0.80	-0.83
Credits							
<i>Electricity</i>	0	0	0	0	0	0	-0.07
<i>District heat</i>	-0.50	-0.51	-0.18	-0.38	-0.72	-0.70	-0.76
Total							
Sum (gross)	1.69	1.73	1.60	1.64	2.29	2.52	2.52
Sum (net)	1.20	1.22	1.42	1.26	1.57	1.82	1.69

E.2.3 System perspective LCA

Table E- 12: Climate change impact in kg CO₂e for combined functional unit of LDPE.

Process route	Waste-to-energy	Waste-to-monomers		Waste-to-syngas	
Reactor		ASR	STR	ASR	STR
Impacts of waste treatment					
<i>Treatment of LDPE</i>	3.14	1.85	1.24	2.16	1.67
Impacts of product generation from reference processes					
<i>Electricity</i>	0	0.25	0.67	0.42	0.92
<i>District heat</i>	0	0.34	0.61	0.20	0.40
<i>Steam cracker products</i>	1.06	0.34	0	1.06	1.06
<i>Hydrogen</i>	0.02	0.02	0	0.02	0.02
<i>MeOH syngas</i>	1.61	1.61	1.61	0.54	0
Total					
Total CCI	5.84	4.42	4.14	4.40	4.07
CCI reduction potential	0	1.42	1.70	1.44	1.76

Table E- 13: Climate change impact in kg CO₂e for combined functional unit of PP.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
<i>Impacts of waste treatment</i>					
<i>Treatment of PP</i>	3.14	1.85	1.25	2.17	1.70
<i>Impacts of product generation from reference processes</i>					
<i>Electricity</i>	0	0.20	0.66	0.37	0.90
<i>District heat</i>	0	0.33	0.61	0.19	0.40
<i>Steam cracker products</i>	1.05	0.33	0	1.05	1.05
<i>Hydrogen</i>	0.004	0.008	0	0.004	0.004
<i>MeOH syngas</i>	1.58	1.58	1.58	0.52	0
<i>Total</i>					
<i>Total CCI</i>	5.78	4.31	4.10	4.30	4.05
<i>CCI reduction potential</i>	0	1.47	1.69	1.48	1.73

Table E- 14: Climate change impact in kg CO₂e for combined functional unit of PS.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
<i>Impacts of waste treatment</i>					
<i>Treatment of PS</i>	3.37	0.87	0.59	1.74	1.52
<i>Impacts of product generation from reference processes</i>					
<i>Electricity</i>	0	0.89	1.05	1.17	1.35
<i>District heat</i>	0	0.75	0.86	0.55	0.63
<i>Steam cracker products</i>	1.55	0.15	0	1.55	1.55
<i>Hydrogen</i>	0	0.24	0.25	0	0
<i>MeOH syngas</i>	2.03	2.03	2.03	0.24	0
<i>Total</i>					
<i>Total CCI</i>	6.94	4.93	4.78	5.24	5.05
<i>CCI reduction potential</i>	0	2.01	2.16	1.71	1.90

Table E- 15: Climate change impact in kg CO₂e for combined functional unit of Mix AR.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
Impacts of waste treatment					
<i>Treatment of Mix AR</i>	3.21	1.48	1.06	1.98	1.62
Impacts of product generation from reference processes					
<i>Electricity</i>	0	0.50	0.79	0.71	1.04
<i>District heat</i>	0	0.50	0.68	0.33	0.47
<i>Steam cracker products</i>	1.20	0.24	0	1.20	1.20
<i>Hydrogen</i>	0	0.07	0.07	0	0
<i>MeOH syngas</i>	1.74	1.74	1.74	0.40	0
Total					
Total CCI	6.15	4.53	4.34	4.61	4.33
CCI reduction potential	0	1.61	1.81	1.53	1.82

Table E- 16: Climate change impact in kg CO₂e for combined functional unit of Mix MH.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
Impacts of waste treatment					
<i>Treatment of Mix MH</i>	3.06	1.71	1.56	2.06	1.91
Impacts of product generation from reference processes					
<i>Electricity</i>	0	0.47	0.55	0.64	0.75
<i>District heat</i>	0	0.39	0.46	0.24	0.29
<i>Steam cracker products</i>	0.83	0.07	0	0.83	0.83
<i>Hydrogen</i>	0.01	0.02	0	0.01	0.01
<i>MeOH syngas</i>	1.26	1.26	1.26	0.14	0
Total					
Total CCI	5.16	3.92	3.83	3.92	3.79
CCI reduction potential	0	1.24	1.33	1.23	1.36

Table E- 17: Climate change impact in kg CO₂e for combined functional unit of Mix HH.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
<i>Impacts of waste treatment</i>					
<i>Treatment of Mix HH</i>	2.95	1.65	1.52	2.01	1.90
<i>Impacts of product generation from reference processes</i>					
<i>Electricity</i>	0	0.48	0.57	0.64	0.75
<i>District heat</i>	0	0.39	0.45	0.26	0.30
<i>Steam cracker products</i>	0.80	0.07	0	0.80	0.80
<i>Hydrogen</i>	0	0.05	0.03	0	0
<i>MeOH syngas</i>	1.16	1.16	1.16	0.13	0
<i>Total</i>					
<i>Total CCI</i>	4.91	3.79	3.73	3.83	3.74
<i>CCI reduction potential</i>	0	1.12	1.33	1.08	1.17

Table E- 18: Climate change impact in kg CO₂e for combined functional unit of S-PCW.

Process route	Waste-to-en- ergy	Waste-to-monomers		Waste-to-syngas	
<i>Reactor</i>		<i>ASR</i>	<i>STR</i>	<i>ASR</i>	<i>STR</i>
<i>Impacts of waste treatment</i>					
<i>Treatment of Mix HH</i>	2.94	1.62	1.59	1.97	1.92
<i>Impacts of product generation from reference processes</i>					
<i>Electricity</i>	0	0.31	0.43	0.47	0.60
<i>District heat</i>	0	0.35	0.43	0.22	0.28
<i>Steam cracker products</i>	0.75	0.01	0	0.75	0.75
<i>Hydrogen</i>	0	0.03	0.001	0	0
<i>MeOH syngas</i>	1.11	1.11	1.11	0.05	0
<i>Total</i>					
<i>Total CCI</i>	4.80	3.44	3.57	3.45	3.55
<i>CCI reduction potential</i>	0	1.36	1.23	1.35	1.25

E.3 Sensitivity analysis of global yield on LCA results

The sensitivity of the net climate change impact $CCI_{net,r}$ for a given waste treatment route r is described by

$$CCI_{net,r} = CCI_{gross,r} + y_{max,r} \left((1 - p_r) x_{c,r} \bar{M}_{CO_2} \bar{M}_C - p_r z_r c_r \right) \quad (8.18)$$

The net climate change impact $CCI_{net,r}$ is determined by the achieved product yield p_r , expressed relative to the maximum yield $y_{max,r}$, and by the corresponding product credits c_r , which depend on the respective reference process for production of the substituted product. For evaluation of the sensitivity, p_r is varied within the interval $p_r \in [0, 1]$, while the scaling factor for product credits z_r is varied within $z_r \in [0, 1.5]$.

For $p_r < 1$, the fraction of carbon not converted into products is assumed to be fully oxidized and emitted as CO₂. The associated emissions are calculated based on the carbon content of the target product $x_{c,r}$. $CCI_{gross,r}$ denotes the gross climate change impact of the respective waste treatment route, i.e., all process-related emissions excluding any credits (cf. Figure 36 in the main part). Table E-19 summarizes the fixed parameters used in the sensitivity analysis shown in Figure 52.

Table E-19: Parameters for calculation of climate change impact for sensitivity analysis.

Waste treatment route r		Waste-to-MeOH-syngas MeOH syngas	Waste-to-Oxo-syngas Oxo syngas	Waste-to-monomers Monomers
$CCI_{gross,r}$	kg CO ₂ e/ kg waste	1.97	1.47	1.65
$y_{max,r}$	kg product/ kg waste	0.729	1.01	0.410
$x_{c,r}$	kg C/kg product	0.365	0.340	0.858
c_r	kg CO ₂ e/ kg product	1.463	0.536	1.787