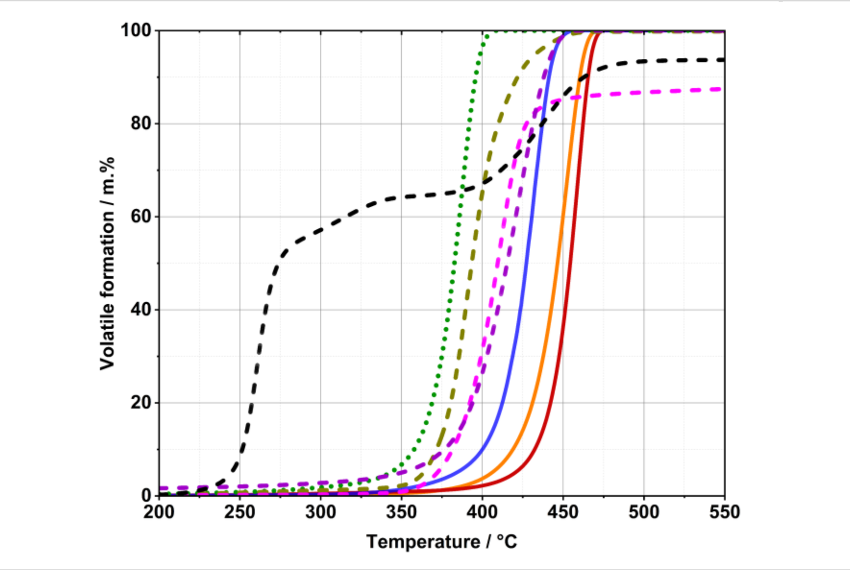
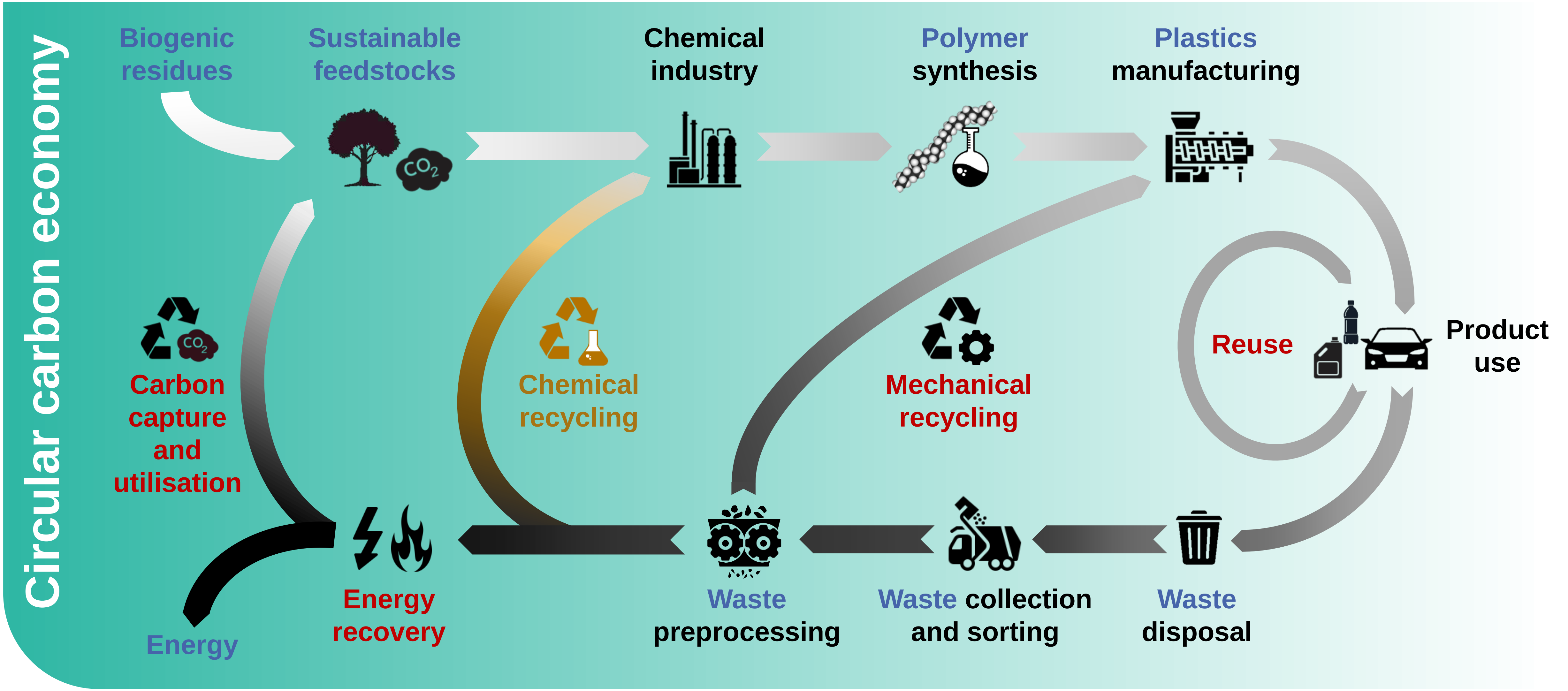
Influencing the Product Quality in Chemical Recycling of Mixed Thermoplastics by Temperature-staged Pyrolysis

DGMK-Conference: Energy and Material Flows in Sustainable Petrochemistry – Opportunities and Implications

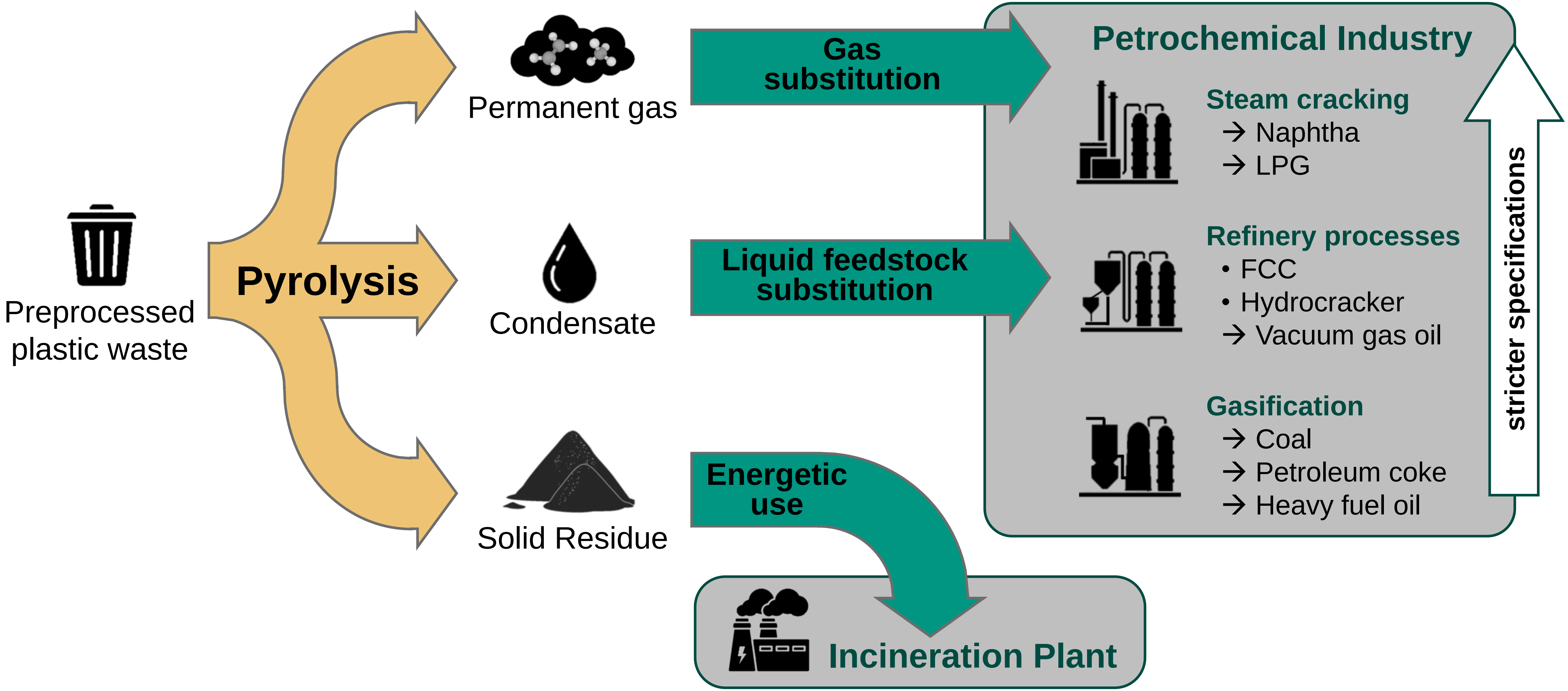
Niklas Netsch, Aljoscha Tauber, Orhan Keskin, Daniela Merz, Britta Bergfeldt, Salar Tavakkol, Dieter Stapf



Perspectives for the plastic lifecycle



Integrating pyrolysis as thermochemical recycling



Condensate requirements for re-integration

Karlsruhe Institute of Technology

Naphtha Steam Cracker specification [1]

Physical properties

Density
- Approx. 700 kg/m³

Boiling range
- Initial BP 35 °C
- Final BP 250 °C

Viscosity

Pourpoint

Storage stability

Chemical composition

Elemental limits
- Sulfur < 500 ppm
- Oxygen < 100 ppm
- Nitrogen < 100 ppm
- Chlorine < 3 ppm

Compound limits
- Paraffins > 65 %
- Olefins < 2 %
- Aromatics < 12 %

Metals
- Cu / Ni < 100 ppm
- Others < 1 ppm

Condensate composition

Products differ depending on application origin of waste fractions

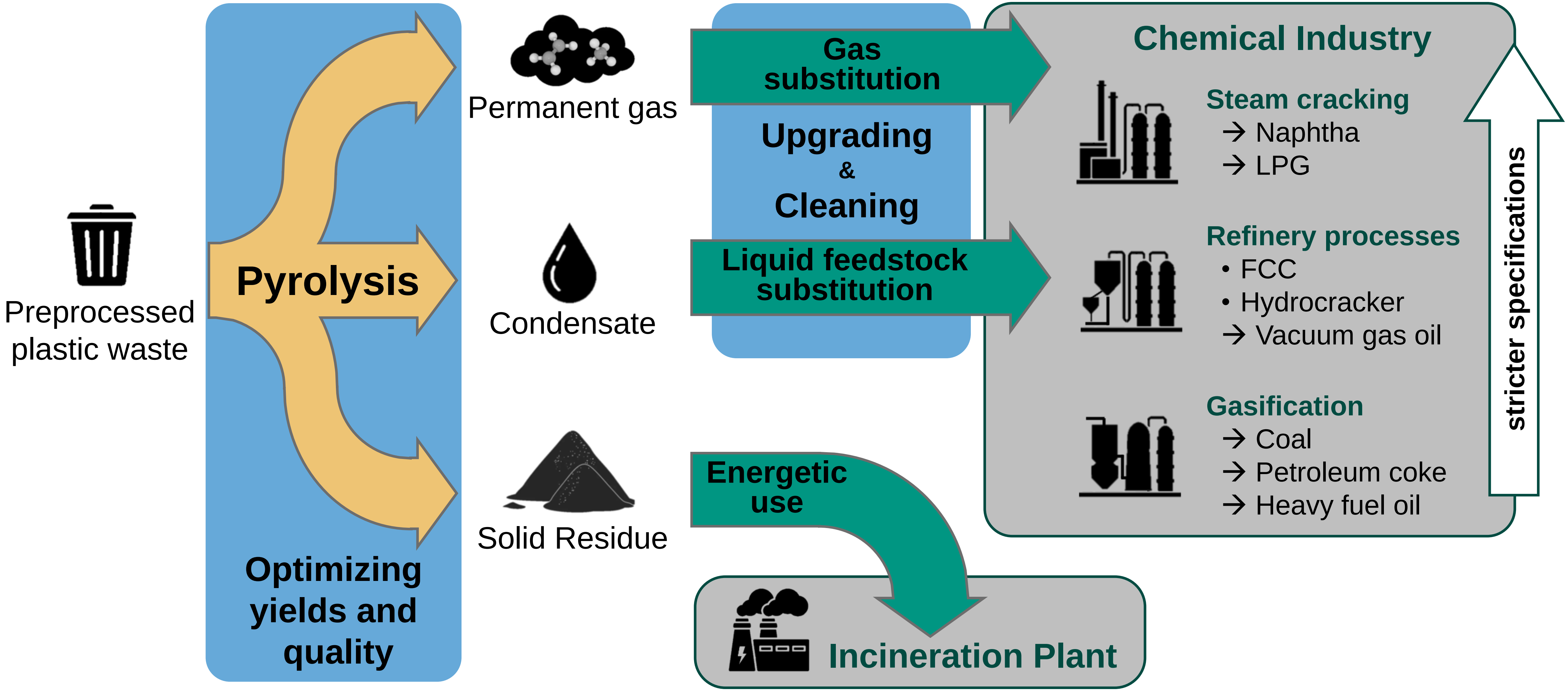
Packaging Automotive WEEE

Typical product properties [1,2]
- Occurance of waxy condensate
- Elemental limits far exceeded
  - → O > 1000 ppm
  - → N up to 25000 ppm
  - → Cl up to 4000 ppm
- High amount of aromatics and unsaturated hydrocarbons

[1] Kusenberg et al. 2022. *Waste Management*

[2] Zeller et al. 2021. *Chemie Ingenieur Technik*

Requirements on pyrolytic recycling process chains



Optimization options in plastic pyrolysis

Karlsruhe Institute of Technology

Feedstock restrictions

- Avoidance of non-plastic contaminations and heteroatom-containing polymers
- Restricted use of functionalized plastics

Relying on polyolefinic feedstocks

Parameter variations

- Process parameters adjustment

→ Reactor temperature
→ Reactor pressure
→ Gas residence times
…

Optimizing target product yields and quality

Process design

- Influencing pyrolysis by

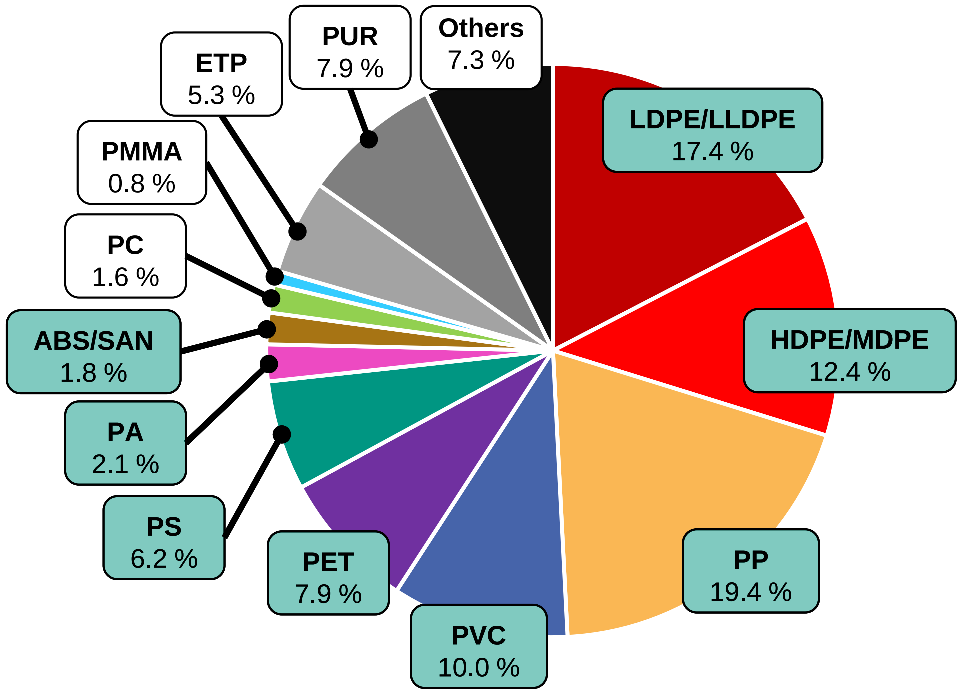
→ Catalyst / sorbent
→ Integrated gas filtration
→ Reflux of high boiling products
→ Temperature-staged pyrolysis

Optimizing target product yields and quality

Fundamentals of plastic pyrolysis

Karlsruhe Institute of Technology

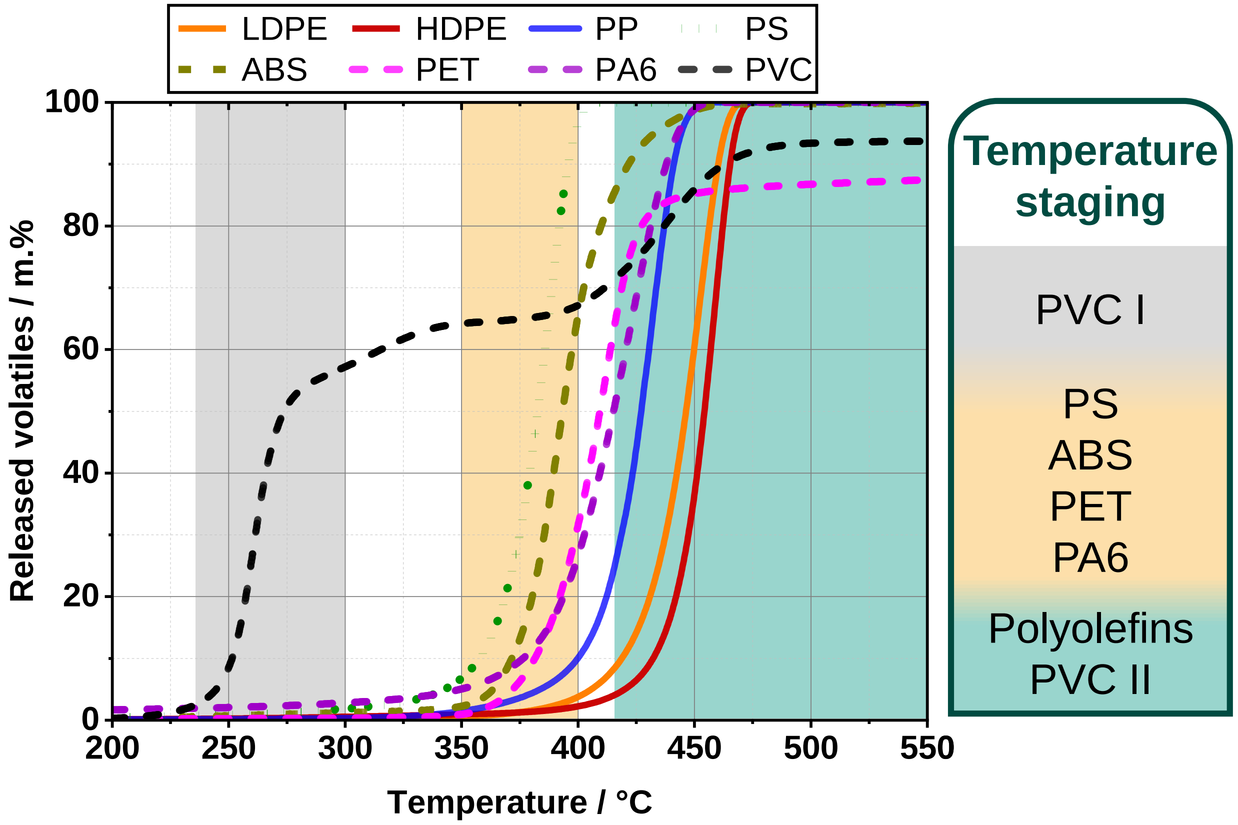
Plastics production (in $EU_{27+NO/CH/UK}$ 2019)



PlasticsEurope (2020)

→ Few plastic types dominate the market (75 m.%) and therefore plastic waste fractions

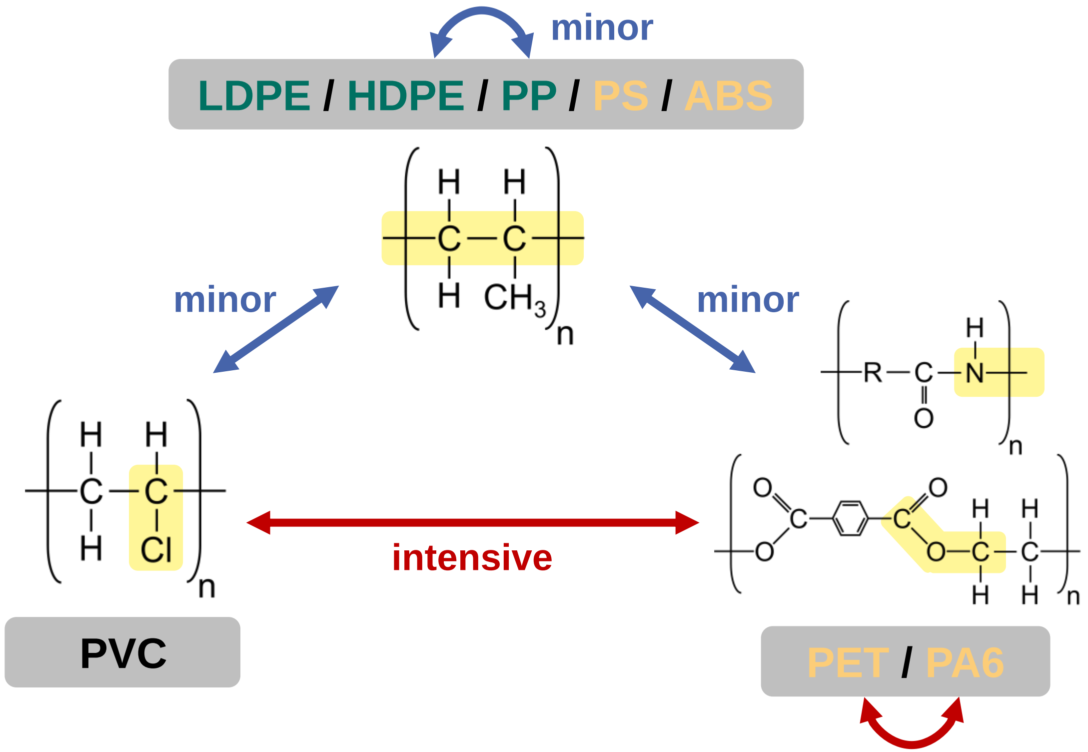
Degradation kinetics of thermoplastics



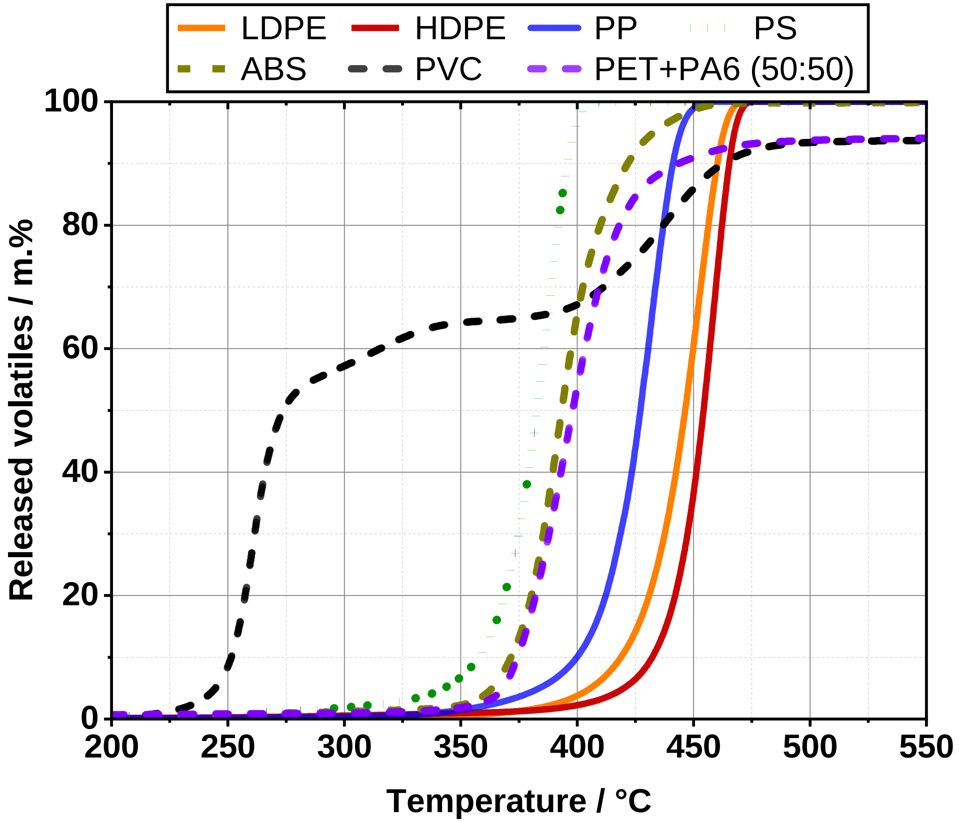
→ Reaction rate at specific temperatures differs by polymer type

Thermoplastic interactions during pyrolysis

- Polymer-dependent interactions
  → Heteroatoms and polymer backbone configuration
- **Minor** and **intensive** degradation interactions visible



Netsch et al. 2024. *Journal for Thermal Analysis and Calorimetry*



→ Accelerated PET and PA6 degradation may improve temperature staging effect

Temperature staging of thermoplastic mixtures

Retrospective view

Study of on stepwise pyrolysis via thermogravimetry and in a cascade reactor system of circulating steel spheres

Feedstocks

Mix A	Mix B
30% PE	20% PE
60% PS	60% PS
10% PVC	20% PA6

Bockhorn et al. 1998. *Journal of Analytical and Applied Pyrolysis*

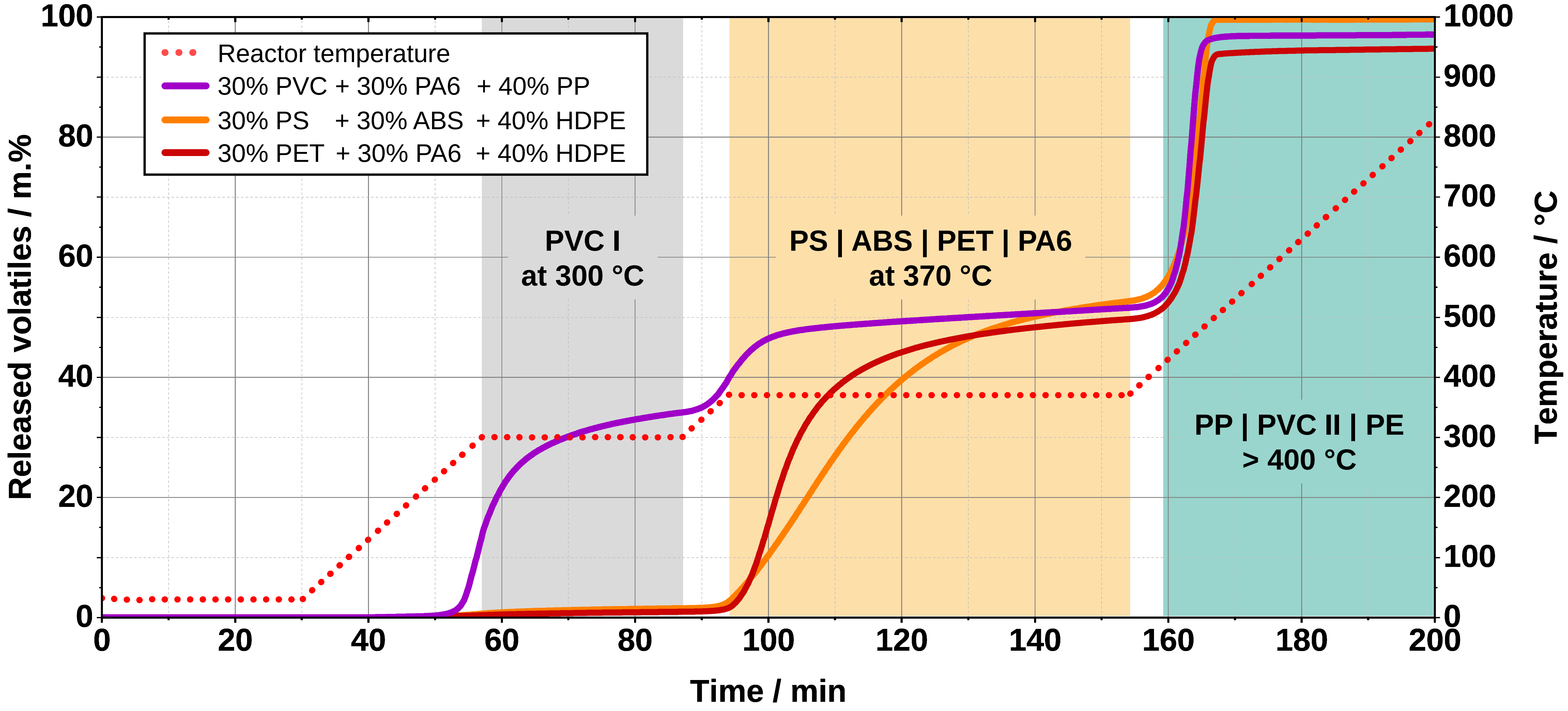
1st Reactor 330 °C → Dehydrochlorination of polymer melt (99.6 m.%)

Intermediate → **2nd Reactor** 380 °C → Styrene and ε-caprolactam enrichment in condensate

Intermediate → **3rd Reactor** 440 °C → Aliphatics enrichment in condensate

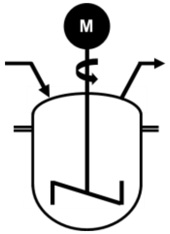
Minimizing Cl, N and O in condensate of heteroatom-containing polymer mixtures?

Two-staged thermogravimetry – ternary mixtures



Experimental setup

Stirred tank reactor



- Polymer mass: 250 g
- Quartz sand as homogenizing agent
  → Sand/Polymer ratio: 8:1
- Nitrogen atmosphere (2.3 l_N/min)
- Reactor featuring enforced mixing by helical impeller

Characteristics

Residence time

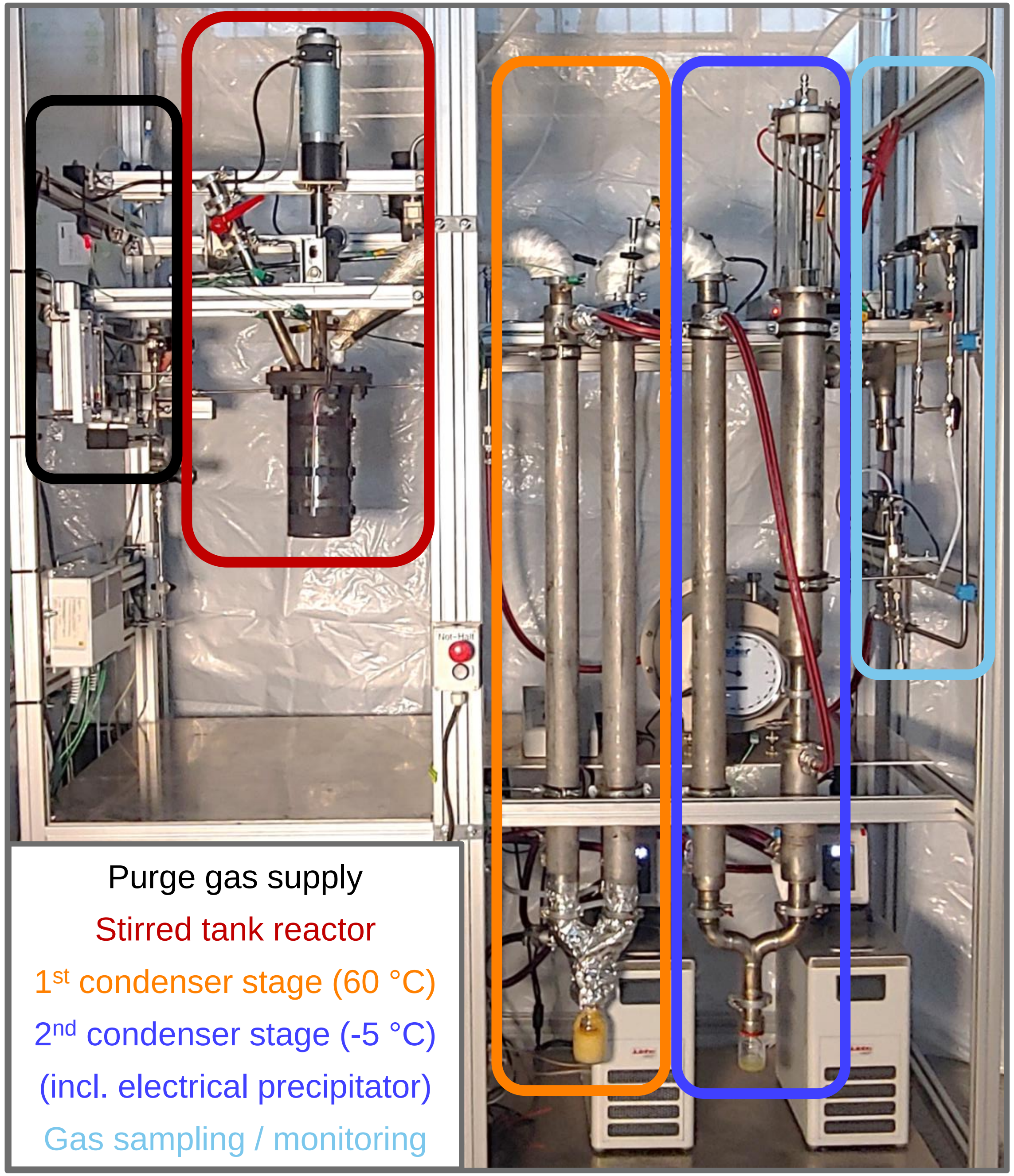
Secondary gas phase reactions minimized by low residence time

Spatial gradients

- Homogeneous material distribution
- Sand buffers temperature gradients

Validation

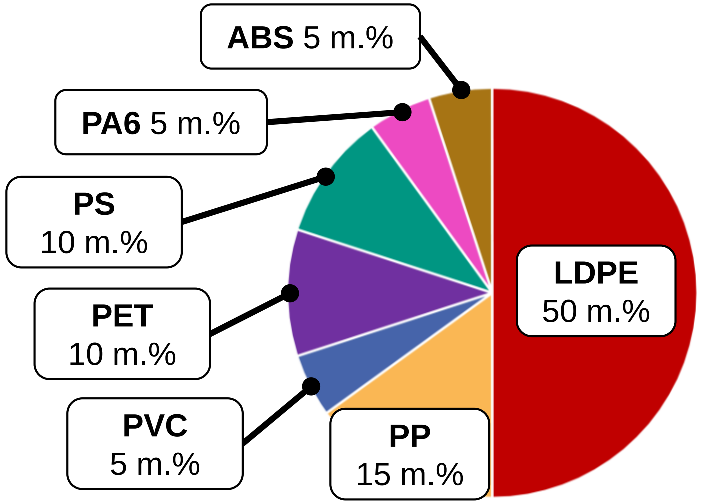
Reproducibility and accuracy validated with reference material



Feedstock and experimental procedure

Karlsruhe Institute of Technology

Feedstock characterization

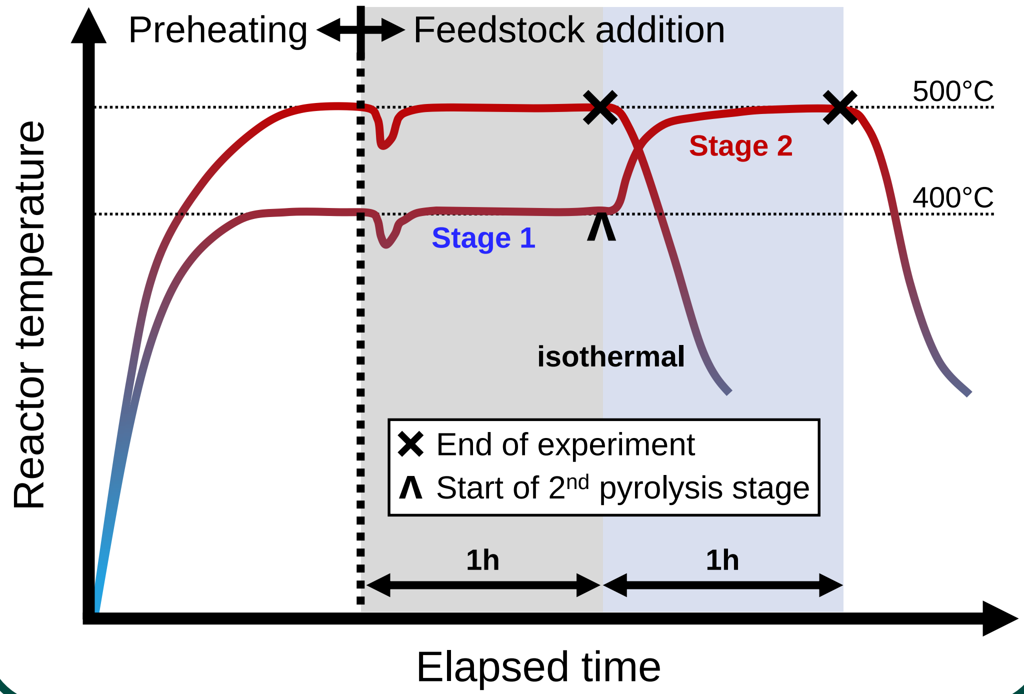


Thermoplastic mixture with high amount of N-, O- and Cl-containing polymers

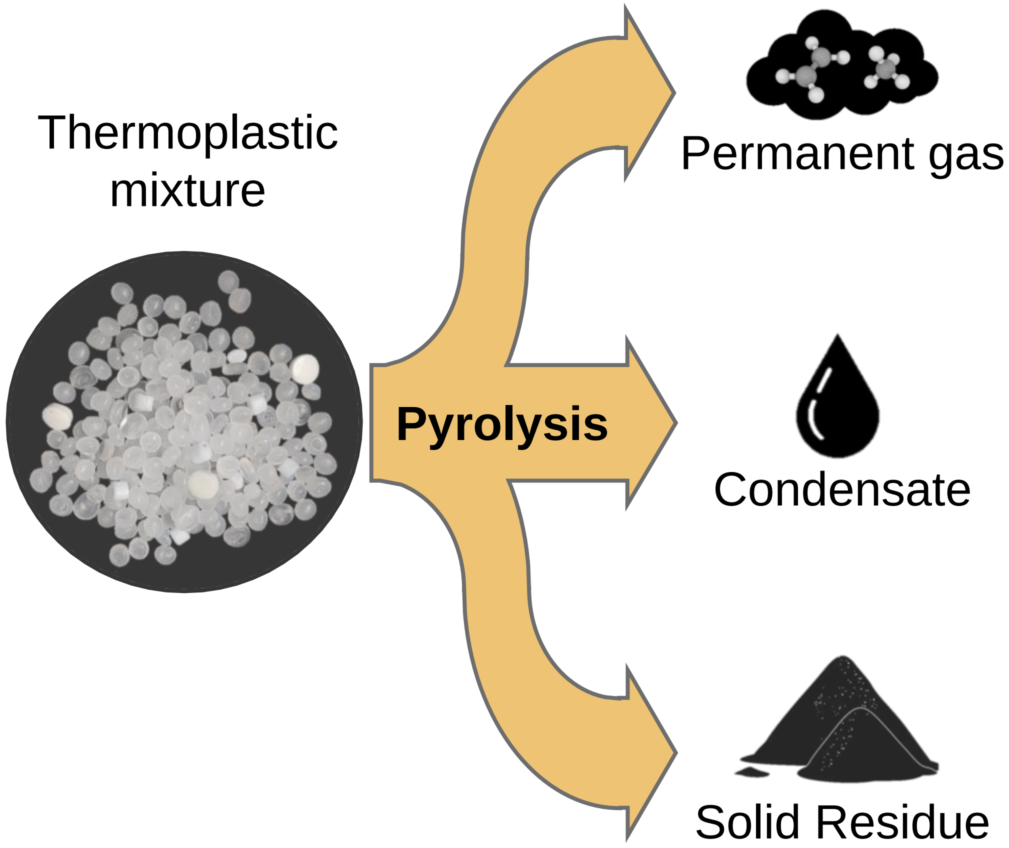
C	H	N	Cl	O	Moisture	Ash
80.6	11.6	0.9	2.4	3.9	0.1	0.5

Experimental procedure

- Two isothermal and one staged pyrolysis runs
- Preheating of quartz sand in reactor
- Immediate feedstock addition



Pyrolysis product yields



Mass balance in m.%

	Isothermal 500 °C	**Temperature-staged** pyrolysis **400 °C**	**500 °C**
	37.1 ± 0.8	**37.8**	
	 **C1 / C2: 59.5** ± 0.4	 **C1: 0.7** **C2: 2.2**	 **C1: 48.9** **C2: 5.2**
	3.4 ± 0.3	**5.2**	

Elemental analyses of condensable products

Karlsruhe Institute of Technology

Isothermal 500 °C

Condensate yield: 59.5 m.%
No aqueous phase obtained

C m.%	H m.%	N m.%	Cl m.%	O [1] m.%	H_2O m.%
82.1	13.3	0.4	0.5	2.7	1.0

[1] Difference to 100
[2] Sample not measurable

400 °C Stage

Condensate C1: 0.7 m.%

C m.%	H m.%	N m.%	Cl m.%	O [1] m.%	H_2O m.%
77.8	11.4	1.5	2.2	5.2	1.9

Condensate C2: 2.2 m.%

C m.%	H m.%	N m.%	Cl m.%	O [1] m.%	H_2O m.%
4.7	8.6	0.9	23.3	2.3	60.2

500 °C Stage

Condensate C1: 48.9 m.%

C m.%	H m.%	N m.%	Cl m.%	O [1] m.%	H_2O m.%
82.8	13.3	0.4	0.1	3.4	0.0

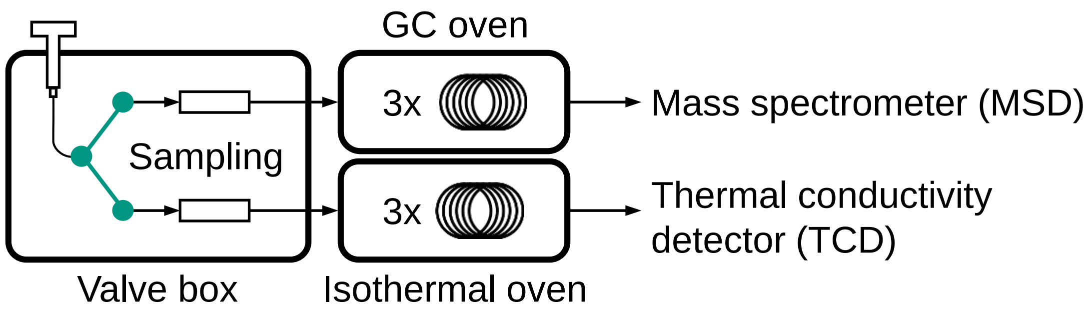
Condensate C2: [2] 5.2 m.%

C m.%	H m.%	N m.%	Cl m.%	O [1] m.%	H_2O m.%
n.a	n.a	n.a	1.1	-	0.0

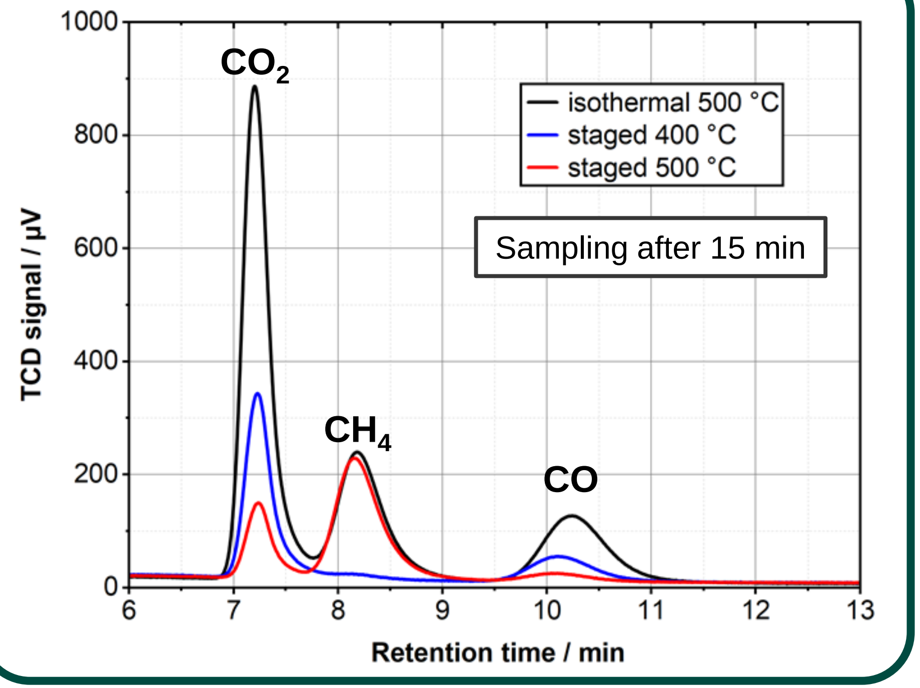
- **Selective N, O, and Cl enrichment in products of the 400 °C pyrolysis stage**
- **Low yields at 400°C stage reduce the condensate improvement effect of staged pyrolysis**
  → Optimization potential for parameter adjustment and condenser design

Analyses of gaseous products

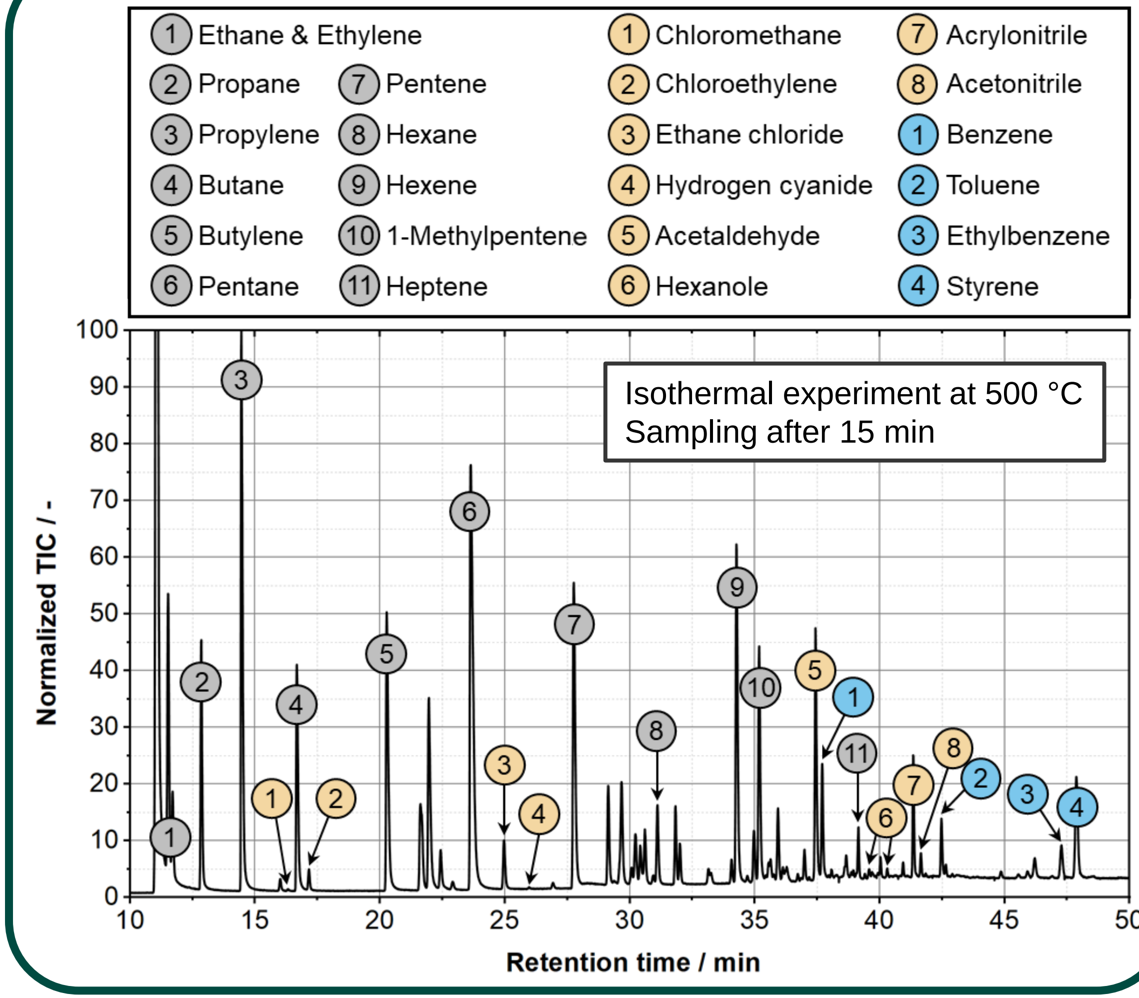
Karlsruhe Institute of Technology



TCD: Permanent gases



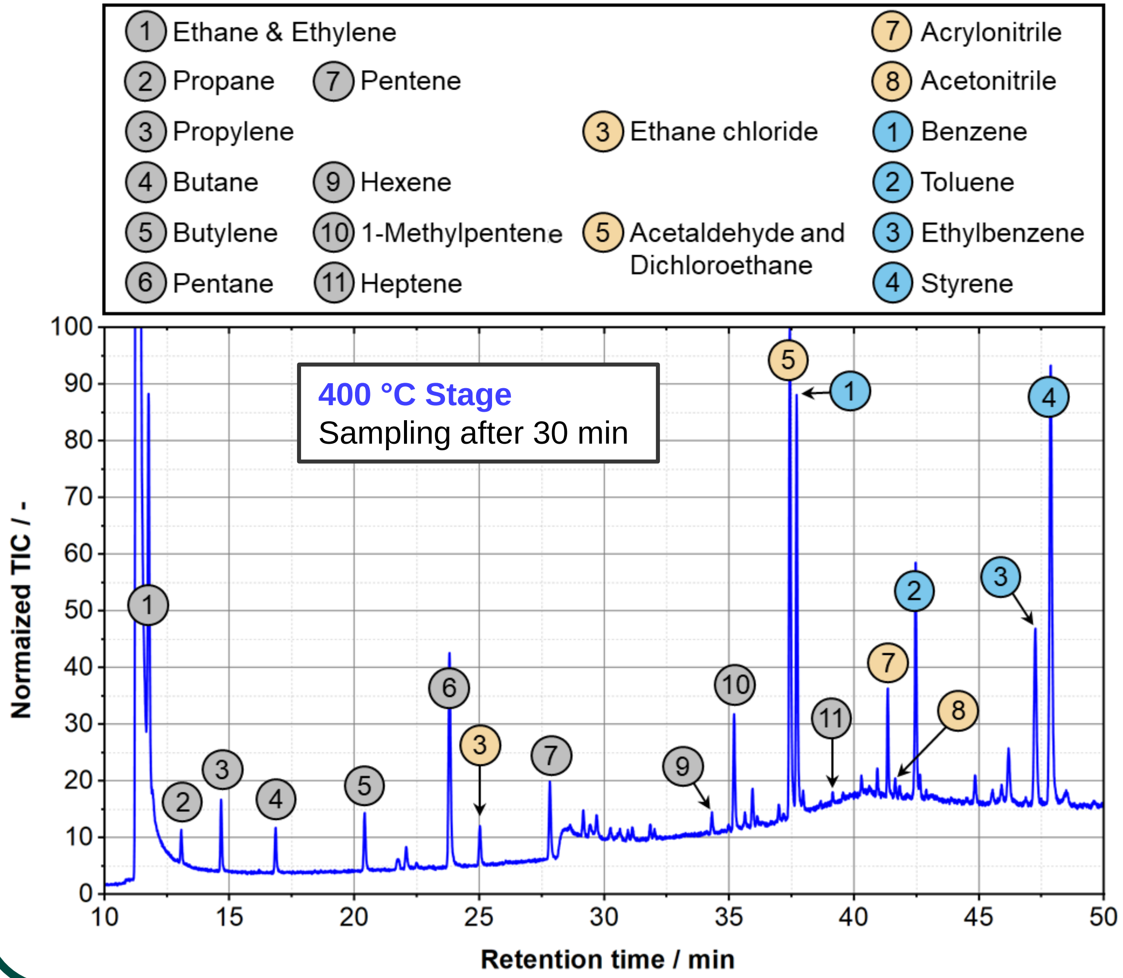
MSD: Organic gas compounds

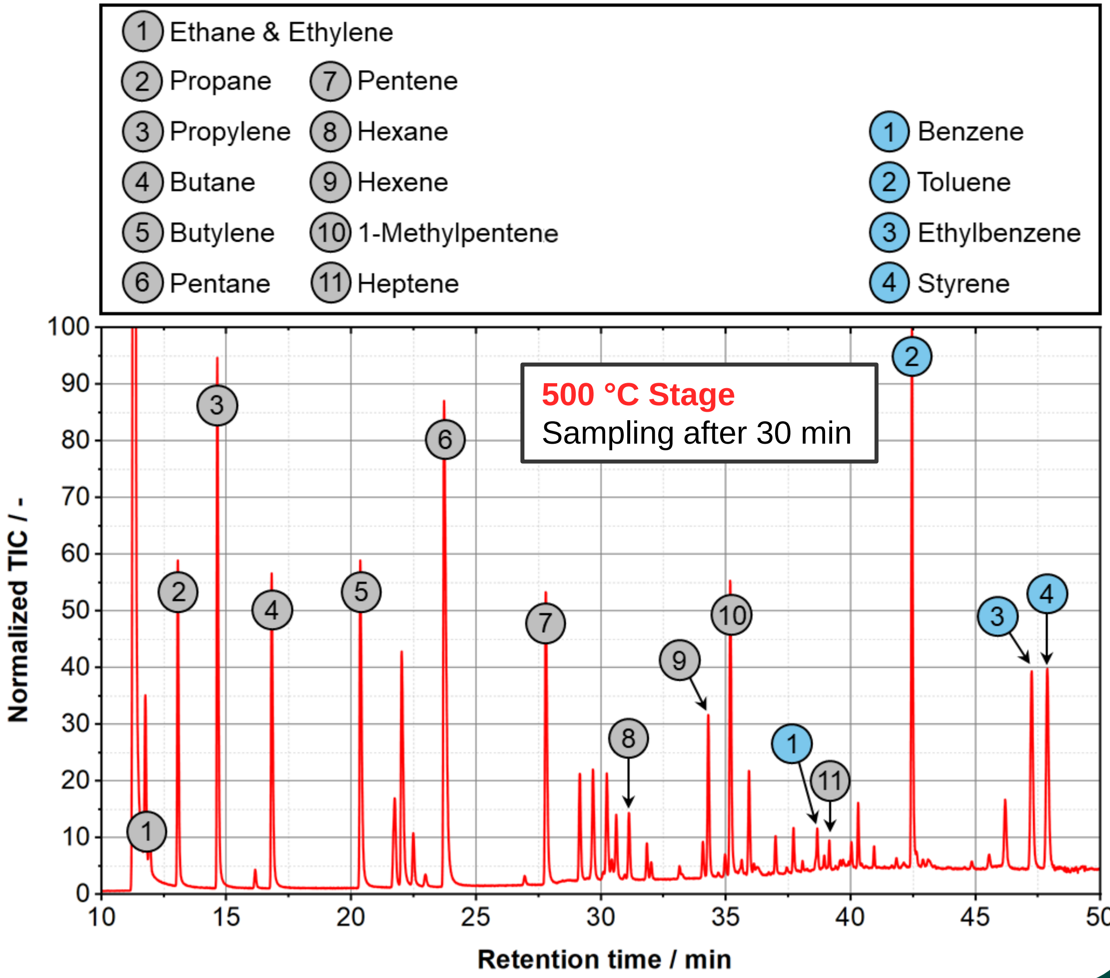


Analyses of gaseous products

Karlsruhe Institute of Technology

MSD: Organic gas compounds





Conclusion and Outlook

Karlsruhe Institute of Technology

Temperature-staged pyrolysis

Laboratory scale - Thermogravimetry

→ **Mechanism of complex mixtures evaluated**

→ **Synergistic effects by polymer interactions**

Technical scale - Stirred tank reactor

→ **Enrichment of heteroatom-containing compounds in gaseous and condensable products of 400 °C pyrolysis stage**

System-specific optimization

→ **Adjustment of reaction temperature and time in isothermal segments required**

Batch pyrolysis processes

- Adaptation of temperature program to reaction rate of polymers in waste

Promising option for discharging contaminants from target products

Continuous pyrolysis processes

- Implementing pretreatment pyrolysis

→ Feeding from high-temp. extruder

→ Feeding from screw reactor