

# Chemical Recycling of Mixed Plastic Wastes by Pyrolysis – Pilot Scale Investigations

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Chemical recycling of plastic wastes can be a useful complement to mechanical recycling to achieve the required plastics recycling rates and to establish a circular economy that is climate neutral and resource-efficient. Different mixed plastic wastes that are subject to future recycling efforts are studied under uniform conditions of intermediate pyrolysis characterized by a medium heating rate and pyrolysis temperature. Product distributions and selected product properties are determined, and process mass and energy balances are derived. Product yields and compositions are highly dependent on the waste pyrolyzed. The results show that pyrolysis is a suitable process to recover chemical feedstock from various complex mixed plastic wastes.

**Keywords:** Chemical recycling, Circular economy, Mixed plastic waste, Pyrolysis

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## 1 Introduction

European plastics converters' demand was 50.7 million tons in 2019 [1]. Packaging and construction are the largest end-use markets, followed by automotive and electrical, and electronic applications. The demand for common plastics and typical applications are listed in Tab. 1. Polyolefin plastics account for more than half of the demand.

In Germany, about 12 million tons of plastics were consumed in 2019 and about 6 million tons of plastic waste were collected. Depending on the application, utilization is reflected in the volume of waste quite differently. For typically short-life packaging plastics, more than 95 % of the consumed mass was recovered in waste. In the case of construction and automotive plastics with longer product life cycles, consumption and waste volume diverge significantly. Consequently, large amounts of plastics are still in use and will remain relevant for future recycling concepts.

In 2019, 47 % of the collected plastic wastes were fed to almost exclusively mechanical recycling processes. On an output basis, 32 % of the collected plastic wastes were available as recyclate for the production of new plastic products. In contrast, 53 % of the collected plastic wastes were directly used for energy recovery in waste incineration plants or utilized as refuse-derived fuel [2], resulting in the emission of carbon dioxide. The carbon contained in the plastic is no longer available for further material use. Chemical recycling of plastic waste needs to be established on scale and complementary to mechanical recycling to increase the amount of plastic material and thus carbon that is kept in cycle. Focus is to be put on mixed plastic wastes, unpurified and composite waste streams, and plastics that cannot be

recycled mechanically such as thermosets and elastomers. Furthermore, chemical recycling overcomes the quality issue of thermoplastic recyclates through enabling the production of virgin material from chemically recycled feedstocks.

Chemical recycling comprises solvolysis, pyrolysis, and gasification processes. The target products in each case are substances that can be reintegrated into existing process chains in the chemical industry. In solvolysis, plastic waste is decomposed into its monomeric components in a solvent. It can be applied to specific plastics, mainly polyethylene terephthalate, polyurethanes, and polyamide. Feedstock impurities and a high process-specific separation effort are hindrances [3]. In contrast, gasification can be applied to all kinds of waste. It refers to the partial oxidation of carbonaceous materials with air, oxygen, steam, or a mixture thereof [4]. The target product is synthesis gas with the main components carbon monoxide and hydrogen [3]. Chemical recycling by gasification at high temperatures replaces fossil feedstock for a broad spectrum of chemical products, but not specifically for monomer production.

In pyrolysis, feedstocks are decomposed in an inert atmosphere at elevated temperatures. It results in a broad distribution of solid, liquid, and gaseous products depending on

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the feedstock, process conditions, and specific technology. Liquid pyrolysis products can replace fossil hydrocarbon feedstock, specifically in monomer production [4]. Metallic and mineral contaminants are separated [3]. Heteroatoms in the products reduce product quality and have to be removed before downstream processing [4, 5]. Thus, first industrial pyrolysis processes for plastics currently target selected waste streams with low levels of impurities such as packaging waste polyolefins. For large-scale treatment of mixed plastic waste, the technologies are not yet fully developed [3, 4].

## 2 Pyrolysis of Plastics

Thermal degradation of plastics and thus generated products highly depends on the polymer type. Tab. 1 provides an

overview of common types of plastics, their demand in Europe, their application, their decomposition temperature, and their main pyrolysis products.

In addition to the decomposition temperature, the conversion and product yield depend on the residence time of the feedstock and the products. Basically, at higher temperatures, more short-chain products, gases, and coke are formed. At lower temperatures, more waxes and oily components are obtained [4]. According to Tab. 1, intermediate pyrolysis between 400 and 600 °C is suitable for the decomposition of common plastics. The target product here is mainly the condensed phase.

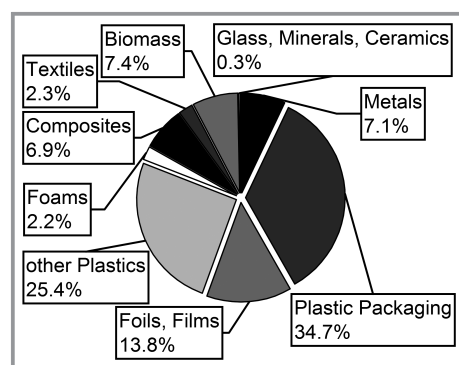
**Table 1.** Overview of common polymers with characteristic degradation properties and products.

Plastic	Applications	Demand in EU 28+NO+CH in 2019 [Mt]	Degradation Mechanism (inert atmosphere)	Degradation Temperature(s) [°C]	Characteristic Products	References
Polypropylene	Packaging, consumer goods, construction materials, ...	9.8	Single stage	> 370	Short chain alkanes and alkenes	[1, 6–9]
High density polyethylene	Consumer goods, construction materials, ...	6.3	Single stage	> 400	Paraffinic waxes, alkanes alkenes, dienes	[1, 6–13]
Low density polyethylene	Food packaging, consumer goods, films, general purpose containers, ...	8.8	Single stage	> 400	Paraffinic waxes, alkanes alkenes, dienes	[1, 6–9]
Polyethylene terephthalate	Bottles, packaging, ...	4.0	Single stage	> 300	CO, CO <sub>2</sub> , coke, benzoic acid, acetaldehyde, short chain aliphatics, benzene, toluene, formaldehyde, ...	[1, 14–19]
Polyvinyl chloride	Construction materials, electronics, ...	5.1	Two stage	250–350 dehydrochlorination, >350 further degradation	HCl, coke, aromatics	[1, 20, 21]
Polystyrene	Packaging, thermal insulation, electronics, ...	3.1	Single stage	> 300	Styrene, styrene oligomers, aromatics	[1, 9, 22–26]
Polyamide	Fibers, fabrics, technical components, ...	approx. 1	Single stage (PA6)	> 350 (PA 6)	CO <sub>2</sub> , H <sub>2</sub> O, coke, ε-caprolactam, nitriles, amines	[1, 27–30]
Styrene copolymers	Consumer goods, construction materials, ...	approx. 1	Single stage	> 340	Styrene, butadiene, acrylonitrile, aromatics, nitriles	[1, 31–33]
Polyurethane	Insulation, upholstery, mattresses, coatings, adhesives, ...	4.0	Two stage	Dependent on formulation	Isocyanates, amines, ethers, alcohols, CO <sub>2</sub> , HCN, NO <sub>x</sub> , coke	[1, 34–37]

### 3 Materials and Methods

#### 3.1 Investigated Waste Streams

The investigated feedstocks represent the most relevant mixed plastic waste streams in terms of emergence, composition, and volume [2]. Lightweight packaging sorting residues (LWP-SR), commercial waste from construction waste sorting (CW), external thermal insulation composite systems based on extruded polystyrene (ETICS), automotive shredder residue from the mechanical processing of shredder light fraction (ASR), and residue from the mechanical recycling of electrical and electronic waste (WEEE) were investigated. All wastes originate from state-of-the-art mechanical recycling facilities in Germany (LWP-SR, CW, ETICS, WEEE) and the Netherlands (ASR). Fig. 1 shows the composition of lightweight packaging sorting residue as received, obtained from a manual sorting analysis. The elemental composition, ash content, and lower calorific value of each feedstock are displayed in Tab. 2.



**Figure 1.** Macroscopic composition of a random sample of the lightweight packaging sorting residue as received, determined by manual sorting analysis.

All feedstocks were received in a lump size characteristic for the respective mechanical recycling processes for the plastic wastes. Thus, the conditioning effort varied for each feedstock.

Plastic parts that could not be shredded as well as macroscopic metallic and ceramic components were sorted out

manually from the lightweight packaging sorting residues. The WEEE and ETICS feedstocks were already crushed during the predeprocessing mechanical recycling. By means of a granulator (Retsch SM200), the feedstock materials LWP-SR, CW, and ASR were reduced to a particle size of maximum 6 mm. Following this shredding, the feedstocks were homogenized by extensive manual mixing. The ETICS feedstock has an unfavorable mass-to-volume ratio for use in the pyrolysis reactor and was therefore shrunk in an oven at 120 °C for 6 h to reduce the porosity of the material and to increase the bulk density. At this temperature, no significant chemical changes to the material are to be expected.

The shredded LWP-SR and WEEE were placed in an oven at 105 °C for at least 6 h to remove moisture.

It should be noted that the composition of the investigated waste streams is subject to regional, seasonal, technical, and random fluctuations.

#### 3.2 Pilot Scale Pyrolysis Experiments

##### 3.2.1 Pyrolysis Reactor

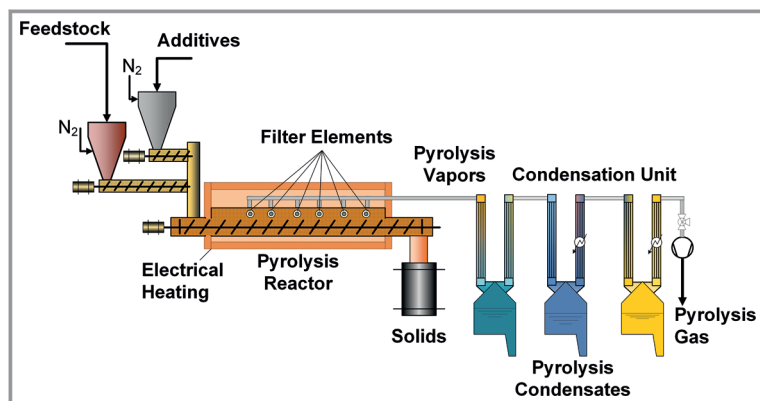
The pyrolysis experiments were carried out using the pilot scale screw reactor system at Institute for Technical Chemistry, KIT, previously described by Tomasi Morgano et al. [39,40]. Its components are shown schematically in Fig. 2.

Through two feed hoppers with screw feeders, the feedstocks and quartz sand are dosed into the reactor. For typical plastic waste, the throughput is around 1 kg h<sup>-1</sup> and the quartz sand throughput is around 4 kg h<sup>-1</sup>. This results in a maximum reactor filling degree of 30 %. The reactor walls forming a trough-type geometry are electrically heated over a length of 2 m. Multiple thermocouples along the reactor monitor the progression of temperature. The maximum deviation from setpoint temperature at the reactor bottom is less than 10 °C at all measuring points. The maximum reactor temperature is 550 °C. The screw has a diameter of 150 mm. At the end of the reactor, the solid pyrolysis residues are discharged into a char hopper. The pyrolysis gases and vapors are extracted from the reaction chamber via ceramic hot-gas filter elements and fed to the condensation unit which operates in two stages at 60 and 5 °C, respective-

**Table 2.** Elemental composition, ash content, and lower calorific value after preconditioning of the mixed plastic wastes.

Waste	Ash [wt %]	C [wt %]	H [wt %]	N [wt %]	S [wt %]	Halogens [wt %]	O <sup>a)</sup> [wt %]	Lower Calorific Value <sup>b)</sup> [MJ kg <sup>-1</sup> ]
LWP-SR	10.6	58.5	7.5	<1	0.1	2.0	21.3	25
CW	9.2	74.7	8.8	<1	<0.05	3.3	3.9	34
ETICS	6.7	79.4	7.1	<1	<0.05	0.1	6.7	34
ASR	13.5	68.0	8.6	1.8	0.2	0.9	6.9	31
WEEE	27.7	53.4	6.1	1.5	0.1	2.8	8.3	23

a) difference to 100 %, b) calculated from elemental analysis ( $H_i = 34.8c + 93.9h + 10.5s + 6.3n - 10.8o - 2.5w$ ) [38].



**Figure 2.** Screw pyrolysis reactor with feed system, hot-gas filtration, solids hopper, and condensation stages for the pyrolysis vapors.

ly. Each stage is equipped with a double-tube heat exchanger and an electrostatic precipitator. The reactor is continuously flushed with a nitrogen flow of approx.  $19 \text{ L min}^{-1}$  to rapidly discharge the pyrolysis gases and vapors and to supply the online analytic equipment continuously. For reasons of safety, the reactor is regulated to a slight negative pressure of approximately 1 mbar. The permanent pyrolysis gases pass through the online gas analysis system and are subsequently fed to a flare.

### 3.2.2 Experimental Procedure

A temperature of  $450^\circ\text{C}$  and a solids residence time of 30 min with a feedstock throughput of approx.  $1 \text{ kg h}^{-1}$  were defined as a uniform reference basis for the investigated feedstocks. Roughly 5 kg of feedstock was used per experiment. No additives were used. Quartz sand, which serves as a carrier and moderator medium for the plastics was assumed to be inert.

The reactor is preheated to the desired pyrolysis temperature before the start of the experiment and is continuously flushed with nitrogen. Sand is added to the plastic feedstock in a mass ratio of approximately 4 to 1. It serves as a carrier medium for the feedstock and supports heat transfer and material transport through the reactor. The feedstock experiences heating rates of at least several  $10^\circ\text{C min}^{-1}$  after introduction into the reactor. The residence time of 30 min is long enough that the feedstock completely pyrolyzes and no unreacted material is discharged at the end of the reactor. During the experiment, the permanent gas volume flow and the main gas species are measured continuously. The pyrolysis condensates are collected at the respective condensation stages, weighed after the end of each experiment, and subjected to further analyses. An aqueous and an oily condensate phase are distinguished based on phase separation. They are obtained manually with a separating funnel. The pyrolysis solids transferred to the char hopper are also weighed at the end of the experiment. Each experimental run is balanced fully from start to end point.

### 3.2.3 Analytical Methods

The permanent gas species  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{O}_2$  are analyzed online by infrared and paramagnetic detectors (Gasetm CX400, Siemens OXYMAT 6, Emerson X-Stream) to monitor the steady state of the pyrolysis process. A flame ionization detector (Siemens FIDAMAT 5E-E) is employed for the measurement of the total hydrocarbon content. Volumetric flow, lower calorific value and density are measured. Furthermore, gas is sampled for offline analyses in a gas chromatograph with a thermal conductivity detector and a flame ionization detector (GC-TCD/FID, Agilent 7890B, HP 5890 Series II). Pyrolysis gas species are identified and quantified with these GC analyses.

The liquid products are characterized through elemental analysis and Karl Fischer titration for the water content. The oily phase is analyzed by GC-FID (Agilent 7890B, HP 5890 Series II). Due to the multitude of liquid compounds, quantification in GC-FID is carried out for “indicator compounds”, namely *n*-alkanes and 1-alkenes with chain lengths  $\text{C}_5\text{--C}_{21}$  as well as the aromatic species benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, styrene, and phenol.

The volumetric flow and density of the gas fraction as well as the weights of the solid and liquid product fractions are used to calculate the mass balances.

The energy demand of the reactor is monitored continuously during the experiments. Energy demands determined for each experiment are corrected by the energy demand in operation with quartz sand only. The compensation of heat losses and energy expended for sand heating are thus excluded from the balance. The condensation unit is excluded from the energy balance as well. The energy demand determined in this manner thus solely reflects the energy to be expended for the processes of feedstock heating, melting, chemical reaction, evaporation, and superheating of gas species.

## 4 Results and Discussion

### 4.1 Mass Balances

The yields of the individual pyrolysis product fractions vary depending on the characteristic composition of the feedstock. Within a specific feedstock, it varies due to inhomogeneities impacting the feed as well as measurement uncertainties. The yield of pyrolysis solids is between 10 and 30%. This product fraction consists of coke and inert materials originating from functionalization of the plastics and contamination of the waste. Thus, the ash content of the feedstock must be considered when interpreting the solids yield.

Between 40 and 75 % of the feedstock mass pyrolyzed is found as oily condensate. The thermal insulation system feedstock shows the highest condensate yield, while the oily condensate yield from WEEE and lightweight packaging sorting residue is the lowest.

An aqueous phase with up to 5 % of the feedstock occurs as a second condensate phase. Since pyrolysis is carried out with dried feedstock, the introduction of chemically unbound water into the reactor as a source for the aqueous pyrolysis fraction is low. The aqueous condensate is thus attributed to oxygen-containing plastics or biomass contamination. The pyrolysis experiments with ASR and WEEE with an expected content of engineering plastics as well as LWP-SR with biomass contamination show an increased release of aqueous product and thus confirm this assumption.

The permanent gas fraction amounts to 13 to 30 % of the total mass.

Generally, the mass balances can be closed for these pilot scale experiments with real wastes. The deviations result from deposits in the reactor and the condensation unit, as well as measurement inaccuracies.

## 4.2 Energy Balances

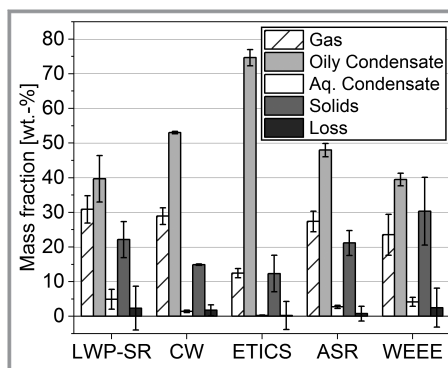
The experimental setup does not allow for the resolution of singular phase and material transformation processes. Since the feedstocks investigated are a mixture of plastics and other materials, detailed statements on the influence of the contained polymers in terms of energy demand cannot be made. Thus, the determined energy balances are of technical nature and relevant in applicative context.

The energy demands for heating, melting, pyrolysis, and evaporation determined in the pyrolysis experiments were normalized using the feedstock lower calorific value. They are 5.1 % for LWP-SR, 5.2 % for CW, 4.9 % for ETICS, 5.4 % for ASR, and 3.7 % for WEEE and are thus within a narrow range. In a technical process, heat losses and the energy demand of supporting infrastructure would add to these values.

## 4.3 Products Analysis

### 4.3.1 Gaseous Products

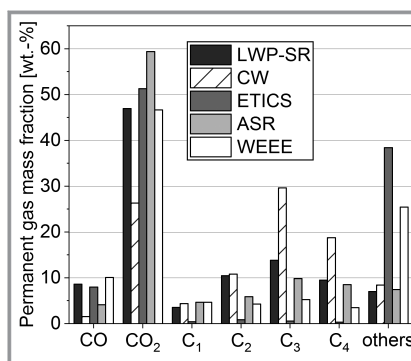
For all feedstocks, carbon monoxide and carbon dioxide are the main components of the pyrolysis gas. Around 60 % of the gas mass is attributable to these compounds. Only in the case of commercial waste carbon dioxide and carbon monoxide account for a significantly smaller proportion of the pyrolysis gas, at around 30 %. This is due to the relative purity of the feedstock and its low content of chemically bound oxygen. It should be noted, however, that very different amounts of permanent gas are formed depending on the feedstock as Fig. 3 shows.



**Figure 3.** Average mass balances for pyrolysis experiments with different feedstocks at 450 °C and 30 min solids residence time. Error bars show standard deviation. Average values and standard deviation were calculated from at least two experiments per feedstock.

During pyrolysis, gaseous hydrocarbons are formed. The distribution varies with the feedstock. The permanent gases from the pyrolysis of ETICS contain almost no short-chain hydrocarbons. For all other feedstocks, there is a maximum for propane and propene ( $C_3$ ) with varying intensity. The pyrolysis gases from commercial waste feedstock show an increased concentration of propene and butene as expected for polyolefin plastics.

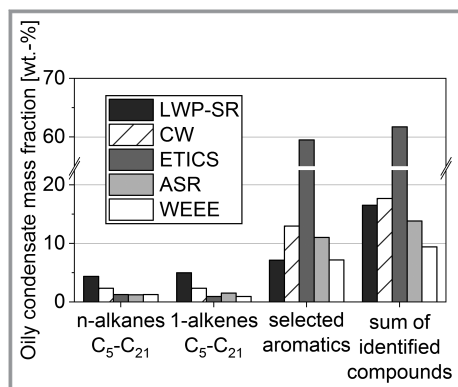
Unidentified gas components are reported as "others" in Fig. 4. Gases such as hydrogen chloride, halogenated hydrocarbons, and volatile nitrogen and sulfur compounds may be released from the input materials. Depending on the condensation step, there is an additional carry-over of condensables into the permanent gas phase.



**Figure 4.** Identified species in the pyrolysis gases for pyrolysis experiments with different feedstocks at 450 °C and 30 min solids residence time. Hydrocarbons are grouped by the number of carbon atoms in the molecule. Averaged from gas samples from multiple experiments per feedstock. Analysis by GC-FID/TCD.

### 4.3.2 Condensed Products

The results of the gas chromatographic analyses of the oily condensates are shown in Fig. 5. Although not all condensate components are covered, the analyses nevertheless



**Figure 5.** Identified species in the oily pyrolysis condensates for pyrolysis experiments with different feedstocks at 450 °C and 30 min solids residence time. Selected aromatics include benzene, toluene, ethyl benzene, *p*-xylene, *o*-xylene, styrene, and phenol.

show clear differences between the condensates from the different feedstocks.

In the condensate from the pyrolysis of LWP-SR, *n*-alkanes and 1-alkenes, as well as aromatic compounds, can be detected. In total, about 20 % of the condensate mass was identified.

In the pyrolysis condensate from the commercial waste, *n*-alkanes and 1-alkenes are present in approximately equal proportions. At about 13 % of the total condensate mass, the aromatics content is significantly higher than the identified aliphatic hydrocarbons. Styrene, ethylbenzene, and toluene are the most common compounds. As characteristic decomposition products of polystyrene, they indicate a presumably significant polystyrene content in the feedstock. A total of 18 % of the condensate mass can be assigned to a component. The amount of isomeric and longer-chain products is therefore also significant in the pyrolysis of commercial waste.

The polystyrene-based ETICS yields predominantly aromatic condensates. Styrene monomer is the main component, accounting for about 50 % of the condensate mass. The proportion of *n*-alkanes and 1-alkenes is low compared to the aromatic components.

In the condensates of the automotive shredder residue, likewise, only small proportions of the aliphatic indicator compounds are found. Toluene, ethylbenzene, styrene, and especially phenol were identified in larger amounts. The aromatic indicator compounds represent 11 % of the total condensate mass. In total, 14 % of the condensate mass can be attributed to a compound. The pyrolysis of the automotive shredder fraction thus yields a complex condensate. This is due to the feedstock composition including different types of plastics with a high degree of functionalization. The different engineering plastics are reflected in the complex condensate composition. The nitrogen content of 2.5 %, the halogen content of 0.4 %, and the sulfur content of 0.1 % in the oily condensate further hint at functionalized and engineering plastics in the feedstock.

The WEEE feedstock is also a mixture of functionalized engineering plastics. The concentrations of phenol, styrene, ethylbenzene, and toluene are significantly increased compared to the *n*-alkane and 1-alkene indicators. Overall, only 9 % of the total mass can be identified for the WEEE condensate, which indicates its complexity. The oily condensate contains 1.1 % of nitrogen which is likely originating from nitrogen-bearing plastics in the feedstock. The halogen content exceeds the analysis detection limit of 1.2 %, likely due to the degradation products of polyvinyl chloride and flame retardant additives. The condensate also contains 0.2 % of sulfur.

In general, non-negligible amounts of isomers, heteroatom-containing components, and species of higher molecular weight not covered by the conducted analyses are to be expected. A comprehensive elemental analysis was not performed. It can be assumed that pyrolysis product distributions and compositions obtained from the technical scale experiments shown here deviate from lab-scale experimental results to a certain degree due to secondary reactions such as isomerizations and recombinations.

#### 4.3.3 Solid Products

The pyrolysis solids consisting of coke and inert pyrolysis products are usually finely grained and homogeneously mixed with the added quartz sand. Due to the dilution of the pyrolysis solids with sand, detailed analyses are not easily performed. The solid residue contains metallic and ceramic components, e.g., from composite materials and polymer fillers. Fractionating and detailed examination of the received solid pyrolysis products was no subject of the analyses presented here.

#### 4.4 Carbon Yield

In the context of chemical recycling of plastic waste, closing the carbon loop is of particular interest. The carbon yield refers to the amount of carbon that can be recycled in relation to the feedstock carbon. Here, the carbon yields were determined only considering the carbon in the oily condensate. For this purpose, the carbon content of the condensates was determined via elemental analysis and combined with the oil yield. The carbon yields are 51.1 % for LWP-SR, 60.0 % for CW, 74.6 % for ETICS, 57.5 % for ASR, and 60.5 % for WEEE. For the employed experimental setup carbon balancing for the solid and gas phases is difficult due to heavy dilution with sand and nitrogen, preventing a comprehensive carbon balance. Depending on the location and detailed design of a large-scale pyrolysis plant, in addition to the carbon in the condensate phase, in particular, the carbon contained in the gas phase could also be partially recycled. Hence, the reported carbon yields are to be understood as minimum recycling rates. The value of oxidized carbonaceous species in the gas must be assessed individu-

ally. It should also be noted that no feedstock-dependent optimization was carried out regarding the pyrolysis parameters.

At least 50 % of the introduced carbon is recovered in the oily phase and is thus in principle available for reintroduction into a value chain. For ETICS, which contains almost solely polystyrene, about 75 % of the feedstock carbon is contained in the oily condensate. The potential for value chain reintegration of the pyrolysis products must be assessed individually for each waste type based on the specific composition.

## 5 Conclusions

Fundamental mass and energy balances for chemical recycling of mixed plastic wastes by pyrolysis were determined. Products for feedstock recycling can be obtained from all investigated plastic wastes. Product quality depends on the feedstock to a large extent. The energy demand for heating, melting, pyrolysis, and evaporation is about 5 % of the feedstock calorific value. Between 50 and 75 % of the feedstock carbon can be recovered in the condensate and potentially reintroduced in value chains in the chemical industry. Feedstock-dependent optimization of pyrolysis parameters as well as additive application for contaminant removal may further improve the oil product yield and quality to reduce product post-processing efforts. Heteroatom product distribution and removal is subject to further investigations.

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## Symbols used

$c$	[-]	carbon mass fraction
$h$	[-]	hydrogen mass fraction
$H_i$	[MJ kg <sup>-1</sup> ]	lower calorific value
$n$	[-]	nitrogen mass fraction
$o$	[-]	oxygen mass fraction
$s$	[-]	sulfur mass fraction
$w$	[-]	moisture mass fraction

## Abbreviations

ASR	automotive shredder residue
CH	Swiss Confederation
CW	commercial waste
EU	European Union
ETICS	external thermal insulation composite system
FID	flame ionization detector
GC	gas chromatograph
ITC	Institute for Technical Chemistry
KIT	Karlsruhe Institute of Technology
LWP-SR	lightweight packaging sorting residue
NO	Norway
PA 6	polyamide 6
TCD	thermal conductivity detector
WEEE	waste electrical and electronic equipment

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