

# Pyrolysis of Real Packaging Plastic Waste Streams in a Fluidized-Bed Pilot Plant

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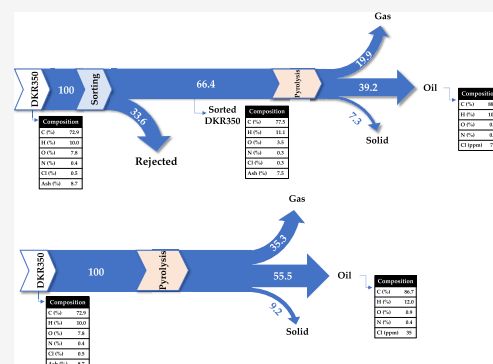
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**ABSTRACT:** Pyrolysis of different packaging plastics waste streams (DKR350) and films/foils (DKR310) was conducted at the pilot scale in a fluidized-bed reactor at 500 °C and 5 kg h<sup>-1</sup> with the aim to investigate the impact of sorting, the variability of the feedstock, and process parameters on the yield and quality of feedstocks and product oils. Sorting involved enriching the feedstock in polyolefins content, by mostly removing PET and clogged materials. The results indicated that sorting improved the quality of oil to a limited extent, compared to unsorted streams, as further processing will still be required before due to the presence of heteroatoms (e.g., O, Cl). With the reactor and conditions used, the effect of the variable composition of this type of feedstock (e.g., depending on the location or season) is very limited, as the yield and quality of the condensable product remain similar. Both the effect of temperature and residence time is relevant and comparable, as an increase in either of these parameters favor cracking and aromatization reactions in the gas phase, leading to less condensable product and lower aliphatics/aromatics ratios in their composition.



## 1. INTRODUCTION

Chemical recycling of plastics is essential to improve the circularity of the plastics and reduce landfilling or incineration alternatives. Specifically, pyrolysis is a chemical recycling technology that targets difficult-to-recycle and highly heterogeneous plastic waste, such as DKR350. DKR350 is a specific category of packaging plastic waste (the one that remains after all of the easily reusable plastics have been sorted out), which comprises mixed plastics, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), and others.<sup>1–4</sup> Aside from DKR350, DKR310 could also be a suitable feedstock for pyrolysis. DKR310 is a plastic waste stream rich in films and foils derived from packaging materials such as food packaging films and aluminum-coated plastic foils.<sup>5–8</sup> Indeed, it contains a large amount of plastic films in the form of bags, shrink-wrapping film, and labels. High potential is seen in DKR310 as feedstock for pyrolysis due to the challenges that the complex structure of multiple different material layers in the films and foils poses for mechanical recycling.<sup>8</sup> From a feedstock perspective, pyrolysis can readily accept films containing PE and PP at varying levels.

During pyrolysis, the quality of the condensable product (oil/wax) is significantly influenced by the characteristics of the plastic waste feedstock, including its composition and the presence of (elemental) contaminants and impurities.<sup>9,10</sup> Thus, industrial pyrolysis processes for plastics currently target

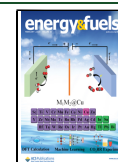
selected waste streams with low levels of impurities as feedstocks, such as packaging waste polyolefins. Sorting and washing have also been recognized as effective strategies to enhance the feedstock quality upstream, resulting in well-sorted, clean, and largely homogeneous feedstocks.<sup>11,12</sup> Sorting pretreatments involve the segregation and separation of plastic waste based on different attributes such as polymer type. By implementation of sorting techniques, it becomes possible to obtain less heterogeneous feedstocks with reduced levels of contaminants, leading to a more consistent and desirable composition of the feedstock for pyrolysis. The resulting oil is expected to exhibit improved properties and reduced levels of contaminants. Washing pretreatments, on the other hand, aim to remove surface contaminants, residual substances, and nonplastic materials from the plastic waste.<sup>13,14</sup> Various washing methods, such as mechanical washing, chemical treatment, and water-based processes, can effectively eliminate dirt, dust, and residual food particles and other impurities. The removal of these contaminants before pyrolysis could positively

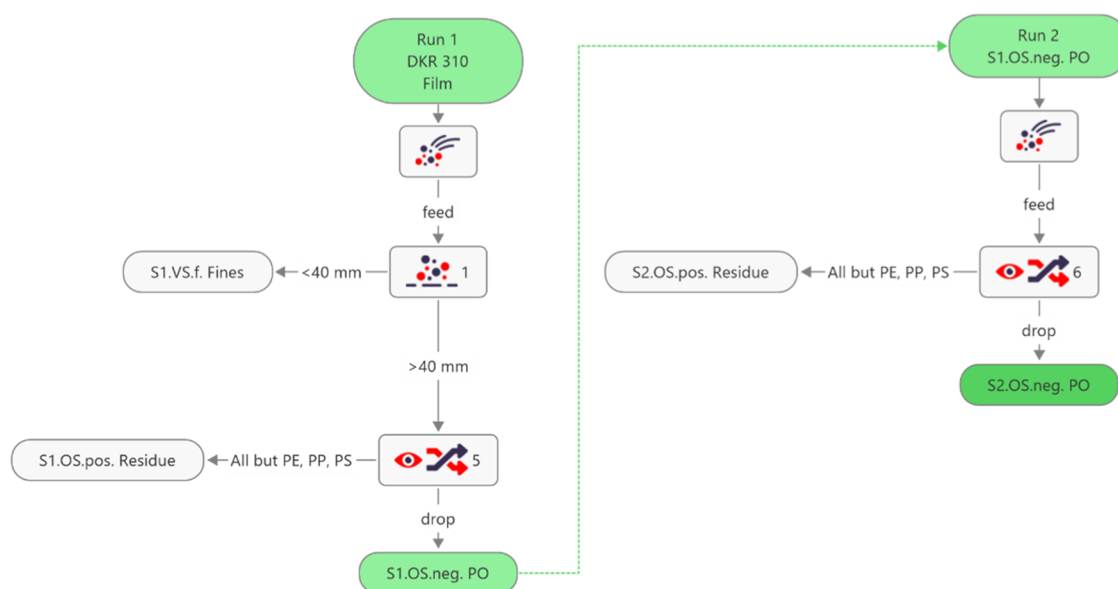
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**Figure 1.** Schematic of the sorting procedure applied in this work, which involves negative optical sorting on PE, PP, and PS and positive optical sorting to remove all but PE, PP, and PS.

influence the quality of the oil, though it barely affects the overall condensable yield.<sup>15</sup> Thus, understanding the impact of pretreatments such as sorting or washing on the quality of both feedstock and oil products at a large scale is of utmost importance for optimizing plastic waste recycling practices.

Upscaling pyrolysis enables the processing of larger quantities of these plastic waste streams and could serve as a crucial step in better assessing the technical and economic feasibility, as well as the environmental implications of plastic waste recycling.<sup>16</sup> We have previously reported laboratory-scale studies on pyrolysis of DKR350 streams, analyzing the effect of different washing pretreatments and the fate of contaminants, as well as the interaction among plastic components.<sup>15,17</sup> Building upon those results, we hereby present an experimental study on pyrolysis of real DKR350 and DKR310 streams at the pilot scale, focusing on the technical challenges of processing those complex streams at that scale, as well as on the effect of sorting pretreatment and the variability of the feedstock. As the composition of DKR is subject to seasonal, regional, technical, and other fluctuations, we evaluated how the variability of the feed could affect the quality and yields of the products. Finally, we discuss the main findings when comparing laboratory-scale and pilot-scale pyrolysis processing.

## 2. MATERIALS AND METHODS

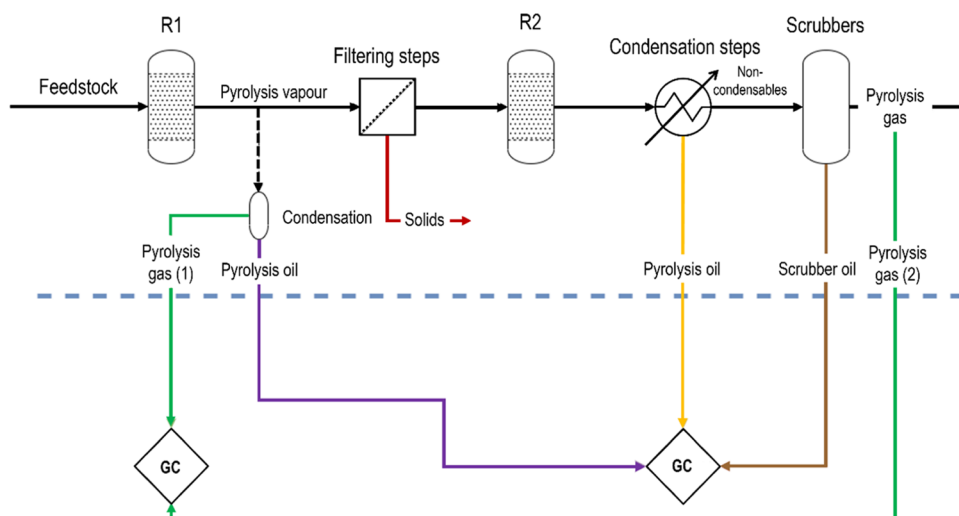
**2.1. Sorting and Conditioning of the Feedstocks.** Different source-separated and postconsumer-separated DKR350 and DKR310 waste streams were sourced from KSI plastic sorting facilities in Heerenveen, The Netherlands, before being transported to the Nationaal Testcentrum Circulaire Plastics (NTCP) sorting facilities.<sup>18</sup> The general methodology used at the NTCP involved sorting, characterization, and shredding. Two sorting protocols using an NIR optical sorter were developed and applied to DKR streams. The sorted materials were aimed to be rich in PE, PP, and PS. The schematic of the process is presented in Figure 1. The mass of DKR310 input material for sorting was 196.6 kg, whereas the mass of DKR350 input material was 314.0 kg. Typically, after loading to the dosing unit, the materials were transported to the vibrating screen to remove fines <40 mm in size mainly from surface contamination, as well as suspension magnet to remove metals. A two-step negative optical sorting was used to remove all (residues) but PE, PP, and PS.

After sorting, the materials were characterized for their material composition. Material characterization was systematically performed by manual sorting of approximately 25 kg in three batches, representative of the DKR materials, based on the different categories present. In case of doubt in categorizing a special piece of material, a laboratory NIR scanner and/or industrial NIR instrument was utilized. After categorization, the materials were weighed separately to determine the percent composition. All of the materials, including those used for materials composition characterization, were shredded by using a Shini granulator model SG-2336 to an average size of 20 mm. The flakes were then mixed together to further facilitate homogenization and then weighed. Thus, in total, four different streams of different compositions were produced: unsorted and sorted (A) DKR350 and unsorted and sorted DKR310.

The ash content of the different feedstocks was determined by the calcination of a representative sample of the feedstocks in air at 550 °C overnight.

Additionally, to study the effect of the variability of the feedstock, three additional DKR350 feedstocks were collected, sorted, and prepared as described above (flakes): (1) sorted DKR350 (B), (2) sorted DKR350 (C), and (3) sorted DKR350 (D). The sorting steps in this case included the use of a vibrating screen, positive optical sorting on PE, PP, and PS, and negative optical sorting to remove all but PE, PP, and PS.

**2.2. Flake Agglomeration and Characterization.** Following the shredding of all DKR materials to flakes, they were subsequently homogenized by extensive mixing. The flake materials as feedstock have an unfavorable mass-to-volume ratio for use in the pyrolysis reactor and were therefore shrunk by agglomeration, performed in TRH Recycling facility in Emmen, The Netherlands. Briefly, agglomeration was performed at about 170 °C to reduce the porosity of the material and increase the bulk density. At this temperature, no significant chemical changes to the materials are to be expected. The agglomerated feedstock described above were reduced into powders using a miller equipped with a sieve diameter of 1 mm. Dry ice was used to prevent thermal agglomeration of the flakes. Of each homogenized sample, the C, H, N, and S contents, the metal concentration, and the halogen concentration were determined using an elemental analyzer, X-ray fluorescence spectroscopy (XRF), and combustion ion chromatography (CIC). For XRF analysis, the samples were analyzed in a P1 cup with a 4 μm propylene film. Quantification was performed by using the Omnic software package from Malvern Panalytical. The data are semiquantitative but give the correct order of magnitude. The data provide the weight % of the



**Figure 2.** Flow diagram of the pilot pyrolysis plant setup used in this work.

detected elements (Na and higher). (Note that the chemical state cannot be measured by XRF, and it was assumed that the various elements are present as oxides.) The organic matrix is not measured via XRF but automatically calculated as a balance compound by Omnia Software. For XRF analysis of the solid product and ashes, a Bruker S8 Tiger 4 kW wavelength-dispersive XRF spectrometer was used. The powders were placed in a Chemplex funnel shape SpectroMicro sample cup. The samples were measured under a He atmosphere. A full scan was performed from 0.85 to 56.35 keV. Using the LiF200, Xs-SS, and PET crystal, the wavelengths were dispersed. A scintillation counter and proportional detector were used to detect the fluorescence photons. The results were produced using the internal calibration of Quan Express.

**2.3. Pilot-Scale Pyrolysis Experiments.** The pyrolysis experiments were carried out using a pilot-scale fluidized-bed reactor system from BioBTX B.V.<sup>19</sup> The components of the pilot plant are shown schematically in Figure 2, and the typical pyrolysis parameters are summarized in Table 1.

**Table 1. Typical Experimental Conditions Used in a Pilot-Scale Pyrolysis Plant**

process condition	value
reactor temperature (°C)	500
other vessels and lines temperature (°C)	500
time-on-stream (h)	5
feed rate (kg h <sup>-1</sup> )	5
amount of feedstock used (kg)	25
nitrogen flow over silo/screws (L h <sup>-1</sup> )	250
nitrogen flow fluidization gas (kg h <sup>-1</sup> )	2.5

The agglomerated DKR materials used as feedstocks were introduced into the pyrolysis reactor through two screw feeds. The feedstock was instantly heated after introduction into the fluidized-bed reactor. Sand was used as a heat carrier and medium for plastic pyrolysis and was assumed to be inert. The feedstock throughput of 5 kg h<sup>-1</sup> was used and defined as a uniform reference basis for the investigated feedstock. Thus, approximately 25 kg of feedstock was used per experiment. The reactor was continuously flushed with a N<sub>2</sub> flow of approximately 20 L min<sup>-1</sup> to rapidly discharge the pyrolysis gases and vapors and to supply the online analytic equipment continuously. Multiple thermocouples placed along the reactor monitor the progression of temperature. The maximum deviation from set point temperature at the reactor bottom is less than 10 °C at all measuring points. The maximum reactor temperature was recorded at 520 °C. Solid inerts fell under gravity and discharged into a catch

vessel. The second step was a cyclone, which was also operated at 520 °C and removed the finer particles and also being filtered in the catch vessel. The last gases or the last fines were removed by ceramic filter and was also operated at high temperature (520 °C), resulting in a clean gas stream. In the present work, pyrolysis experiments were run noncatalytically; thus, the reactor R2 was empty, and due to process design, it was not possible to bypass the reactor. During the experiment, the permanent gas volume flow and the main gas species are measured continuously. The pyrolysis gas was measured on a micro-GC, which can measure until C5 hydrocarbon. The liquid collected was then measured on a GC-FID. After the condensation step, the gas products were also measured by GC (Agilent Micro GC 990) to get more insights about the gases being converted. In the condensation system, the pyrolysis vapors were first cooled by a condenser and the liquid was collected in the condensation vessel, and the gases escaping from the heat exchangers were then collected in a heat exchanger then being washed by various scrubbers. The outlet temperature of the heat exchanger was about 80 °C to prevent wax formation. As scrubbing liquid, a clean biodiesel was used; therefore, two liquid streams were collected: (1) a heavy fraction of oil from the condenser and (2) a stream with lighter fractions in clean biodiesel. The light oil and biodiesel formed one phase mixture. The condensates were collected per hour (1st to 5th hour) and were all combined in one container. The pyrolysis condensates are collected at the respective condensation stages, weighed after each hour, and subjected to further analysis. The pyrolysis solid products (char from the catch vessels) are collected and also weighed at the end of the experiment. In the second set of experiments, the second reactor R2 was filled up with a noncatalytic material. Unsorted DKR350 and HDPE virgin polymer pellets were used for laboratory-scale pyrolysis for comparison of the effect of operational parameters, especially residence time. The coke yield is determined by measuring the gases released (CO and CO<sub>2</sub>) during combustion of the fluidized bed (R1) at 550 °C in air after the pyrolysis experiment.

**2.4. Pyrolysis Product Analysis.** The elemental composition of oil/wax and solid products was determined by using an elemental analyzer (Vario Micro Cube Elemental CHNS/O, Germany). All experiments were carried out in triplicate, and the average value is provided. Gas chromatography-mass spectroscopy (GC-MS) analyses were performed on a Hewlett-Packard (HP 6890 series GC system) GC instrument combined with a Quadrupole Hewlett-Packard 6890 mass selective detector. An Rtx-1701 capillary column (0.25 μm film thickness, 30 m × 0.25 mm i.d.) was used for separation. Helium was used as a carrier gas (2 mL min<sup>-1</sup>). The injector temperature was fixed at 280 °C. The following oven temperature profile was used: 40 °C for 5 min, from 40 to 250 °C at a rate of 5 °C min<sup>-1</sup>, and 250 °C for 10 min. Before analyses, the samples were diluted with THF

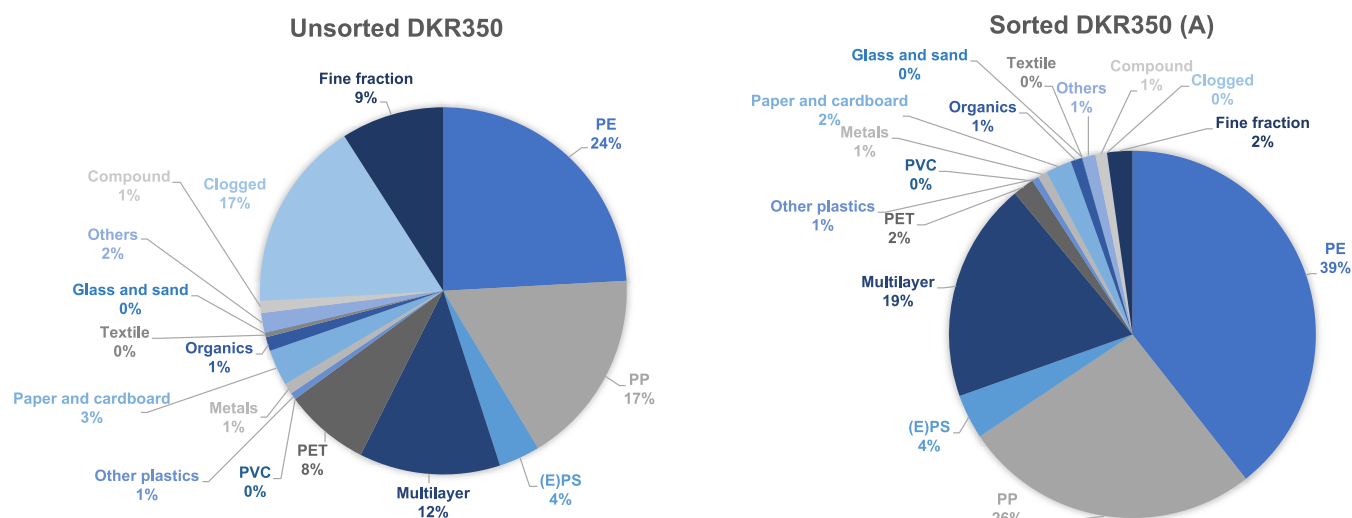


Figure 3. Composition (wt %) of unsorted (left) and sorted (right) DKR350 feeds.

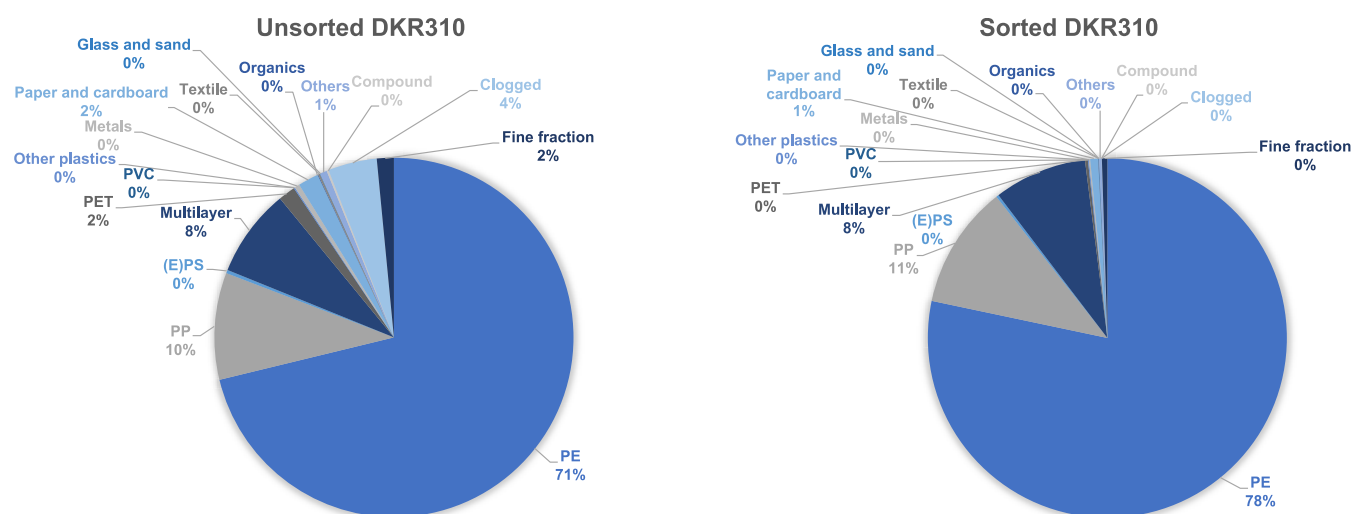


Figure 4. Composition (wt %) of unsorted (left) and sorted (right) DKR310 feeds.

(dilution factor of 10). GC  $\times$  GC/TOF-MS analysis was performed on a Agilent 7890B system equipped with a JEOL AccuTOF GCv 4G detector (detector temperature set at 280 °C) and two capillary columns (Restek Rtx-1701 capillary column, 30 m  $\times$  0.25 mm i.d. and 0.25  $\mu$ m film thickness) connected by a solid state modulator (Da Vinci DVLS GC<sup>2</sup>; modulation time of 6s) to a Rxi-5Sil MS column (1.2 m  $\times$  0.10 mm i.d. and 0.10  $\mu$ m film thickness). The injector temperature and volume used were 280 °C and 1  $\mu$ L, respectively. A split ratio of 1:50 and a column flow rate of 0.8 mL min<sup>-1</sup> were used. The oven temperature was set to 40 °C for 5 min and then increased to 250 °C at a heating rate of 3 °C min<sup>-1</sup>.

<sup>13</sup>C NMR spectra were acquired on a Bruker Ascend 400 spectrometer (400 MHz). A 90° pulse and an inverse-gated decoupling sequence with a relaxation delay of 10 s was applied. The sweep width was 225 ppm, and a total of 1024 scans were recorded. Samples were prepared by dissolving about 100 mg of oil/wax in deuterated chloroform (CDCl<sub>3</sub>, Sigma-Aldrich).

### 3. RESULTS AND DISCUSSION

As mentioned above, we have studied the effect of sorting, the flexibility of the process upon feedstock variability, and the effect of process conditions at the pilot scale, such as temperature and residence time.

#### 3.1. Effect of Sorting. 3.1.1. Feedstock Characterization.

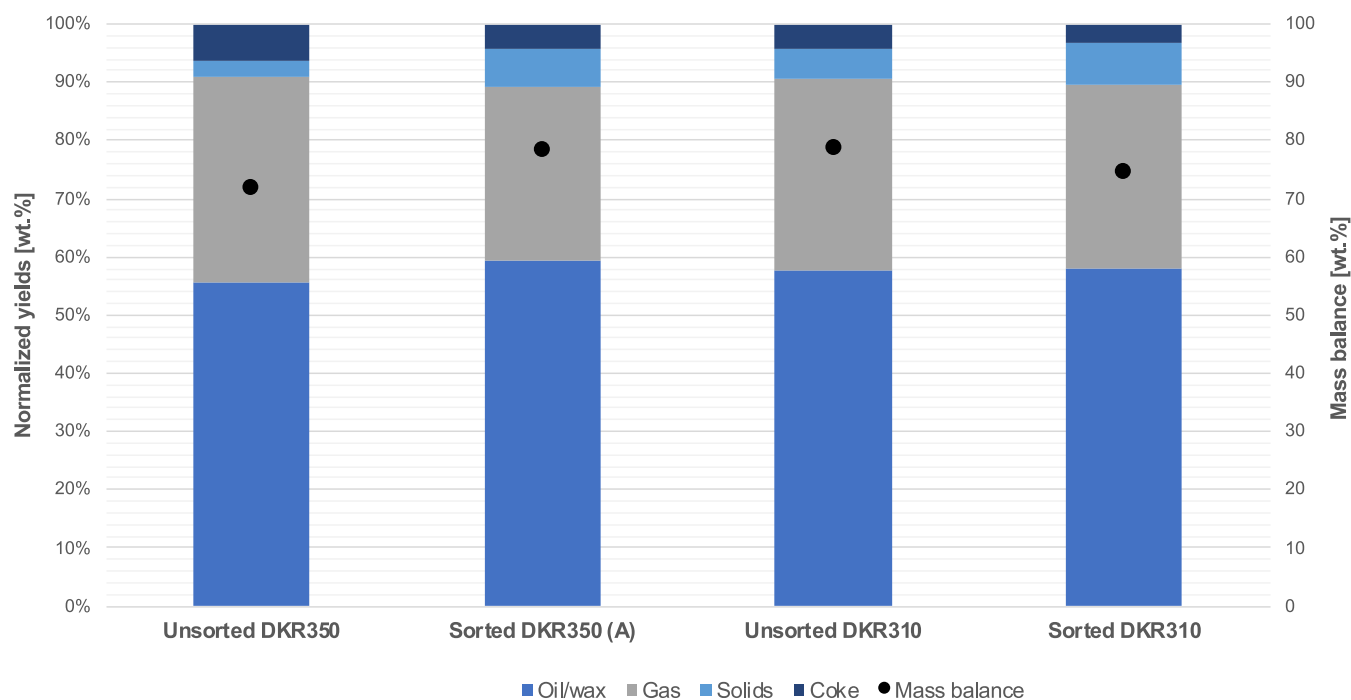
The composition of the feedstock used in the pyrolysis process plays a crucial role in determining the yields and composition of the resulting products. Thus, the production of high-quality oil may require effective pretreatments (e.g., washing and sorting) to enhance the feedstock quality and pyrolysis process efficiency. In this work, one stream of DKR350 and one of DKR310 were sorted following the procedure explained in Section 2, to enrich the stream in the polyolefin content (PE, PP, and PS). Figure 3 shows the composition of the DKR350 streams, before and after sorting, and Figure 4 shows the composition of the DKR310 streams, before and after sorting.

As can be seen, by sorting, mostly the fractions of PET and clogged materials were removed. The unsorted DKR350 feedstock contained 53 wt % PE, PP, and PS, and a PET content of 8 wt %. The content of multilayer materials was 12 wt %, which consist of a variety of different polymers and other materials, laminated or extruded together. Multilayer flexibles generally contain about 70 wt % combined PE and PP. By the sorting procedure in the DKR350 stream, the resulting amount of PE, PP, and PS increased to 83 wt %. In the case of the DKR310 stream, the amount of polyolefins (PE, PP, and PS)



Table 2. Elemental Composition and Ash Content (wt %) of the Feedstocks Used for Pilot-Scale Pyrolysis

DKR stream	ash content [wt %]	C [wt %]	H [wt %]	N [wt %]	S [wt %]	O [wt %]	Cl [wt %]
unsorted DKR350	8.7	72.9	10.0	0.4	<0.2	7.8	0.49
sorted DKR350 (A)	7.5	77.5	11.1	0.3	<0.2	3.5	0.29
unsorted DKR310	6.3	74.7	10.7	0.4	<0.2	7.7	0.59
sorted DKR310	6.6	76.9	11.8	0.3	<0.2	4.1	0.46
sorted DKR350 (B)	8.9	76.3	10.5	0.4	<0.2	3.6	0.31
sorted DKR350 (C)	7.8	77.2	11.8	0.3	<0.2	2.8	0.35
sorted DKR350 (D)	6.3	75.2	11.2	0.3	<0.2	6.8	0.38



**Figure 5.** Product yields (wt % based on feed intake) from pyrolysis of unsorted and sorted DKR350 and DKR310 streams. Pyrolysis conditions: 5 kg h<sup>-1</sup> and 500 °C.

increased from 87 to 95 wt % by the sorting procedure. These results indicate the high efficiency of the sorting method developed, which removed most nonpolyolefin plastics (lower PET) and paper, while black PET remained in the product stream. For example, sorting reduced the PET of DKR350 from 8 to 2 wt % and increased the multilayer flexibles levels, which contains mostly polyolefins, from 12 to 19 wt %. Additionally, by sorting, all of the clogged materials (17 wt %) were removed from DKR350.

All of the feedstocks were then analyzed by various analytical techniques. Table 2 shows that the ash content of these streams ranged from 6 to 9 wt % (determined by heating a representative sample at 550 °C in air overnight). The composition of ash can vary significantly based on the types of plastics present in the waste, with DKR310 having lower ash content than DKR350 as expected for films, which can then be related to the presence of inorganic additives, fillers, contaminants, and decomposition of plastic components, used in the rigid plastics (DKR350).

The presence of oxygen in feedstock could adversely affect the pyrolysis process, leading to reduced product condensable yield, altered composition (higher oxygenates), and lower energy efficiency.<sup>15,16,18</sup> Some plastics inherently contain oxygen-containing functional groups, such as carbonyl and hydroxyl. For example, PET and other plastics (EVOH, nylon)

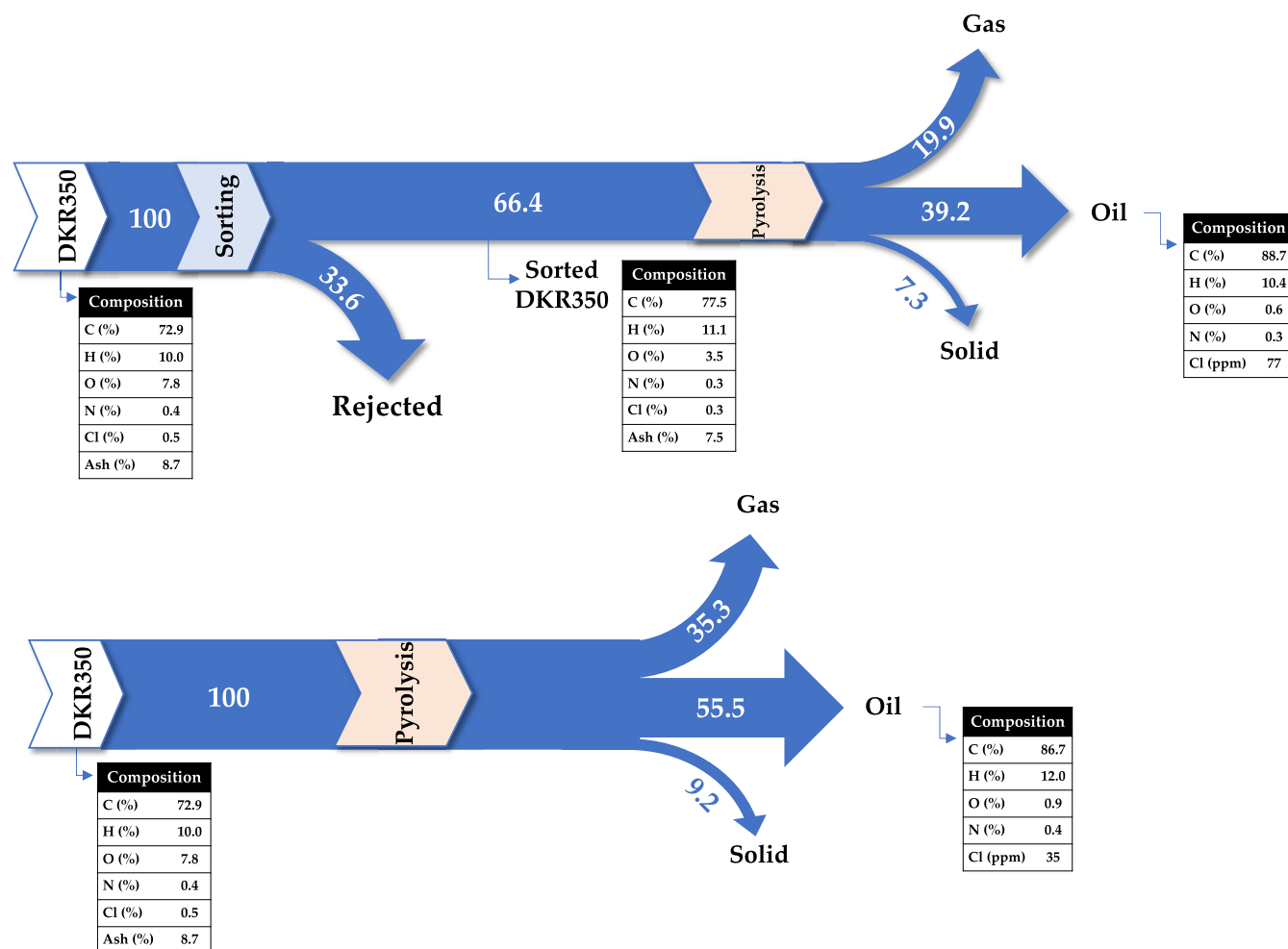
represent a family of contaminants that are problematic because they contain oxygen and more complex hydrogen-carbon structures. Indeed, the presence of oxygen in the feedstock results in oxygenated products, which reduces yield and negatively impact the quality of pyrolysis oil.<sup>15,16,18</sup> In this work, sorted DKR materials contained less oxygen than unsorted DKR materials, which was related to the lower PET.

Similar to oxygen, the presence of nitrogen (e.g., from polyamides and other synthetic polymers) introduces specific chemical reactivity and can affect the behavior of plastic waste during pyrolysis.<sup>20–23</sup> It is important to note, however, that these polymers are not expected to be present in significant amounts in household packaging waste streams. The N content is below 0.4 wt % in the feedstocks used in this work (Table 2).

Chlorine was also found in the waste streams (0.29–0.59 wt % Cl). Chlorine may originate from PVC, PVDC, and chlorinated additives.<sup>24–26</sup> PVC and PVDC films introduce chlorine atoms into the pyrolysis process, which can cause corrosion to equipment by HCl and catalytic effects and persist in the oil product as heteroatoms. Pyrolysis operators have limited cost-effective means of removing PVC/PVDC or circumventing the challenges that it poses. Unsorted DKR350 contains higher Cl content, suggesting that sorting lowers Cl levels. However, PVC/PVDC can be expected to be a very

**Table 3. Elemental Composition (CHNSO, wt %), Cl Content (\*in ppm), and Relative  $^{13}\text{C}$  NMR Area (%) in the Pyrolysis Oils Collected**

DKR stream	C	H	N	S	O	Cl*	relative $^{13}\text{C}$ NMR area (%)		
							aliphatic	aromatic	carbonyl
unsorted DKR350	86.7	12	0.4	0.018	0.9	35	55.9	43.7	0.4
sorted DKR350 (A)	88.7	10.4	0.3	0.014	0.6	77	64.7	35.3	0
unsorted DKR310	87.4	12.4	0.1	<LOD	0.1	21	73.3	26.7	0
sorted DKR310	89.7	9.5	0.3	0.007	0.5	18	73.8	26.2	0
sorted DKR350 (B)	86.6	12.3	0.4	0.024	0.6	28	70.9	29.1	0
sorted DKR350 (C)	86.8	12.2	0.4	0.017	0.6	17	68.9	31.1	0
sorted DKR350 (D)	88.8	10.4	0.3	0.013	0.5	33	68.7	31.3	0
sorted DKR350 (D) R2	89.5	9.7	0.3	0.013	0.5	19	70.8	29.2	0

**Figure 6.** Comparison of the mass balance overview of the integrated sorting and pyrolysis process (top) and the direct pyrolysis process (no sorting, bottom) of a DKR350 stream. Pyrolysis conditions:  $5 \text{ kg h}^{-1}$  and  $500 \text{ }^\circ\text{C}$ .

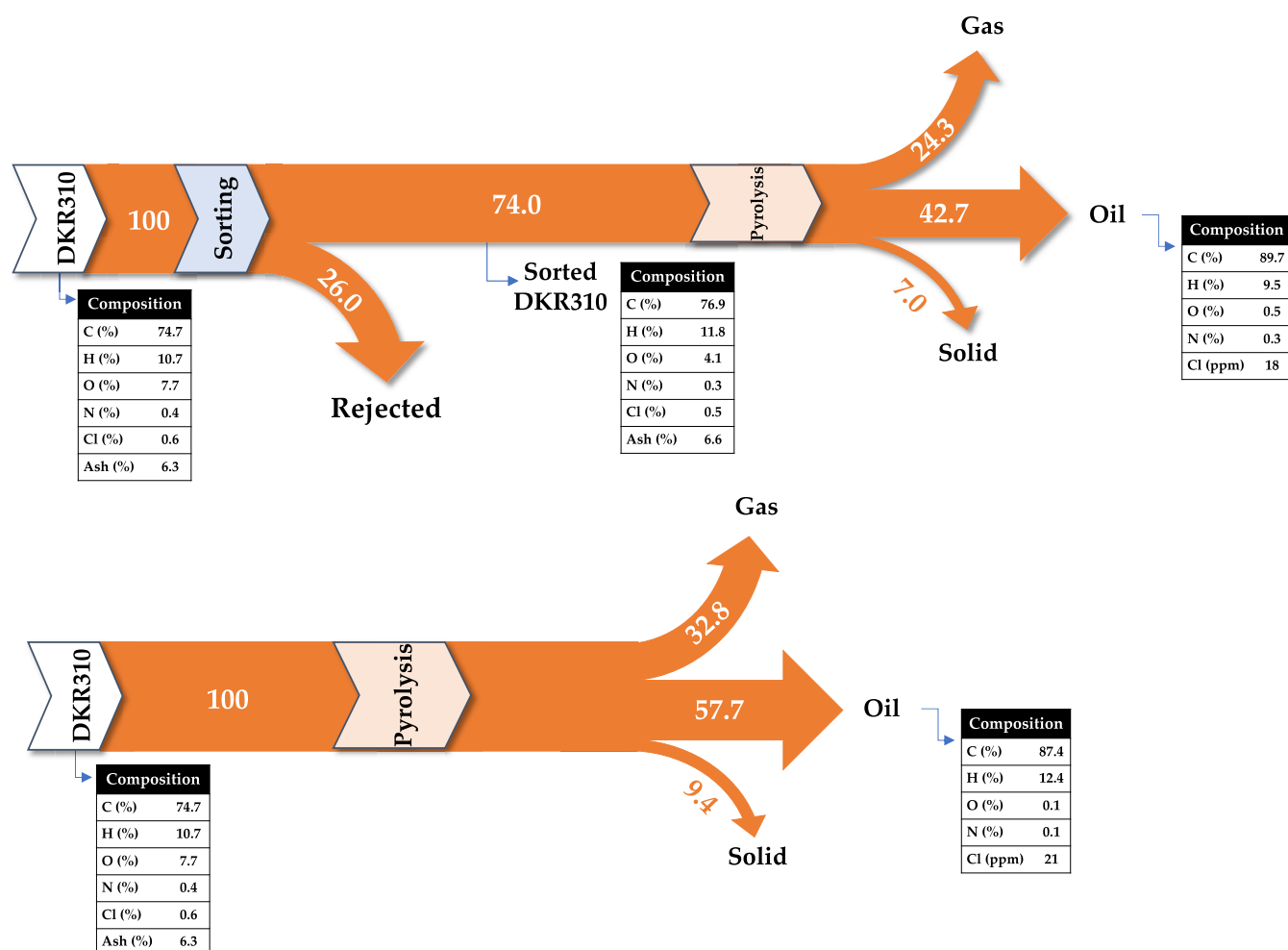
small portion of most postconsumer recycling streams, and it is expected that this is unlikely to change in the future.

The presence of other fractions such as metal, glass, dirt, and fine content can be problematic because these materials tend to be abrasive and can significantly damage equipment. These materials are generally nonreactive in pyrolysis operations and therefore do not present challenges to the chemistry of the product. The presence of Ca and Ti can be attributed to the inorganic additives present in rigids, thus higher in DKR350 (Supporting Information).

**3.1.2. Pyrolysis Product Yield and Composition.** The unsorted and sorted streams of DKR350 and DKR310 were

pyrolyzed in the pyrolysis pilot plant. The resulting product yields are shown in Figure 5.

The mass balance closure in these experiments was in the range of 72–78 wt %. We believe that the losses are mostly coming from the condensable product, accumulated in different parts of the setup, which are difficult to quantify. However, to avoid any favorable deviation in our analysis toward the condensable product, we have assumed an equivalent distribution of losses on the three product fractions (gas, solid, and condensable). The measured condensate (oil/wax) yields were in the range of 40–46 wt %, which are significantly lower than the ones obtained in the lab-scale



**Figure 7.** Comparison of the mass balance overview of the integrated sorting and pyrolysis process (top) and the direct pyrolysis process (no sorting, bottom) of a DKR310 stream. Pyrolysis conditions: 5 kg h<sup>-1</sup> and 500 °C.

experiments (~70%),<sup>15</sup> and the gas yields were 23–27 wt %, considerably higher than the ones obtained at the lab scale, from 7 to 14 wt %. For all experiments, CH<sub>4</sub>, CO, CO<sub>2</sub>, ethylene, ethane, propylene, propane, and some monoaromatics were the main components of the pyrolysis gas (Supporting Information). It should be noted, however, that different gases are formed, depending on the feedstock. The pyrolysis gases from DKR310 feedstock show an increased concentration of propylene and butene, as expected from polyolefins.

The yield of pyrolysis solids is between 2 and 5 wt %. The solid product fraction mostly consists of inert materials originating from the additives of the plastics and contamination of the waste. The coke yields vary also from feedstock. The yield of pyrolysis coke is between 2 and 5 wt %.

The condensable products were characterized using different techniques. The elemental composition of oil products from all these streams is summarized in Table 3 (a more detailed analysis on the elements present can be found in the Supporting Information). It can be observed that the oxygen concentration is low in all of the cases, below 1 wt %. The maximum allowable oxygen concentration in industrial steam cracker feedstocks is 100 ppm, which suggests that further processing of these oils would still be necessary.

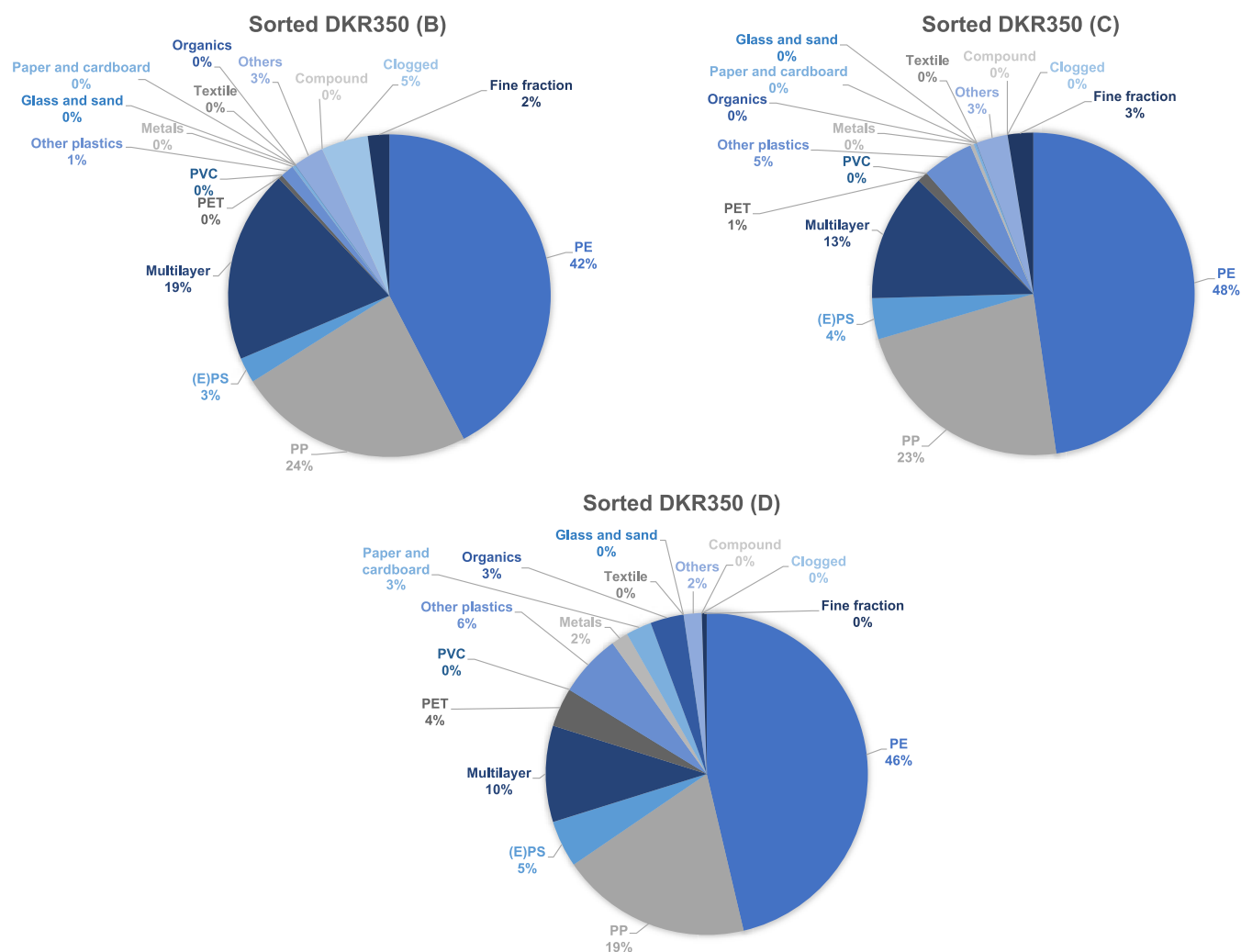
As mentioned above, the presence of chlorine in the condensable product is critical for further processing (e.g., in a

naphtha cracker, where the maximum allowable chlorine concentration is 10 ppm). In the oils obtained, the chlorine concentration is in the range 18–77 ppm, which makes further dechlorination still necessary. There is not a clear effect of sorting on the Cl concentration in the condensable products.

The results of the <sup>13</sup>C NMR analysis are also shown in Table 3. By sorting DKR350, the percentage of aromatic components in the condensable product decreases, which is in line with the removal of PET fraction in the feed (from 8 to 2 wt %), a known source of aromatics. In the case of DKR310, this effect is negligible as the concentration of the PET in the unsorted stream was already low (~2 wt %).

Figure 6 shows the comparison of the overall mass balance of the integrated sorting + pyrolysis process with the direct pyrolysis (no sorting) of the DKR350 stream. By sorting, ~34 wt % of the feed is rejected, and even though the pyrolysis condensable yield is slightly higher with the sorted stream (58 vs 55 wt %, Figure 5), the overall condensable yield with respect to the unsorted stream is much lower, 39 vs 55 wt %. With respect to the oil quality, sorting favors a slight reduction of O content in the oil and an increase in the aliphatic/aromatics ratio, from 1.3 to 1.8. Therefore, sorting slightly improves the quality of the oil but at the expense of discarding 34% of the DKR350 feed.

Figure 7 shows a similar overview of the mass balances for both processing alternatives for the DKR310 feed. In that case,



**Figure 8.** Composition (wt %) of three different sorted DKR350 feedstocks (B, C, and D samples).

the mass loss by sorting is lower, 26 wt %, but still significant, which makes that the oil yield respect to the unsorted feed drops from 58 to 43 wt % by sorting. Additionally, there is barely any improvement of the oil quality (almost no differences in O content or aliphatics/aromatics ratio, Table 3). Therefore, it seems that sorting does not have any benefit on the pyrolysis of this type of streams.

**3.2. Feedstock Variability.** **3.2.1. Feedstock Characterization.** This type of plastic waste stream has a diverse composition, depending on the season of the year and the location. To evaluate the robustness and flexibility of the pyrolysis approach for different compositions of the DKR350 feedstock, three different DKR350 streams (B–D) were sorted and pyrolyzed under the same conditions. The composition of these feedstocks is shown in Figure 8.

Results show a high amount of PE, PP, and multilayer flexibles and are comparable for the three streams, from 75 to 85 wt %.

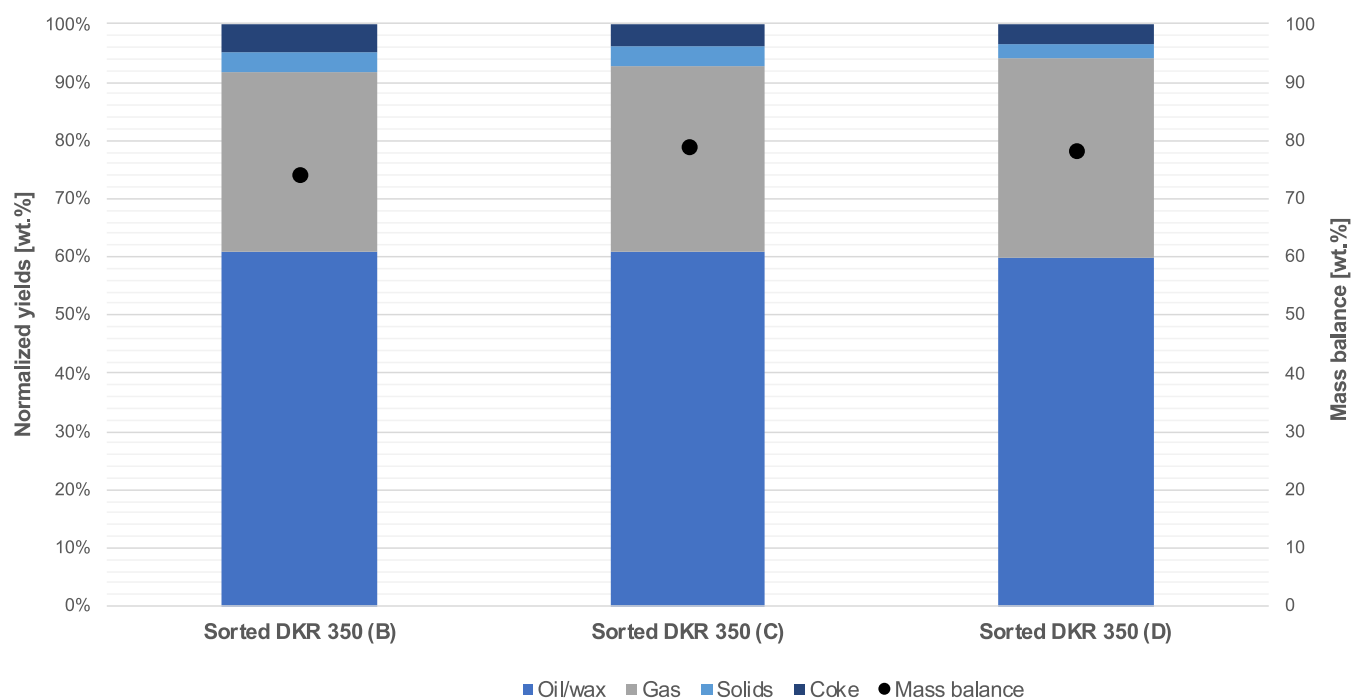
**3.2.2. Pyrolysis Product Yields.** Upon pyrolysis, the three different batches of DKR350 (B–D) led to similar condensable (~60 wt %) and gas (~32 wt %) yields, as shown in Figure 9, which were also similar to the ones obtained with the previous batch of sorted DRK350 (A, Figure 5), which was obtained by following a different sorting procedure. Besides, the composition of the oils obtained from

the three feeds is similar in terms of CHONS elements, Cl content (17–33 ppm), and aliphatics/aromatics ratios (2.2–2.4). Thus, the fluidized-bed reactor and the experimental conditions used can handle this type of streams despite differences in their composition and help minimize the impact or those in the product oil yield and composition.

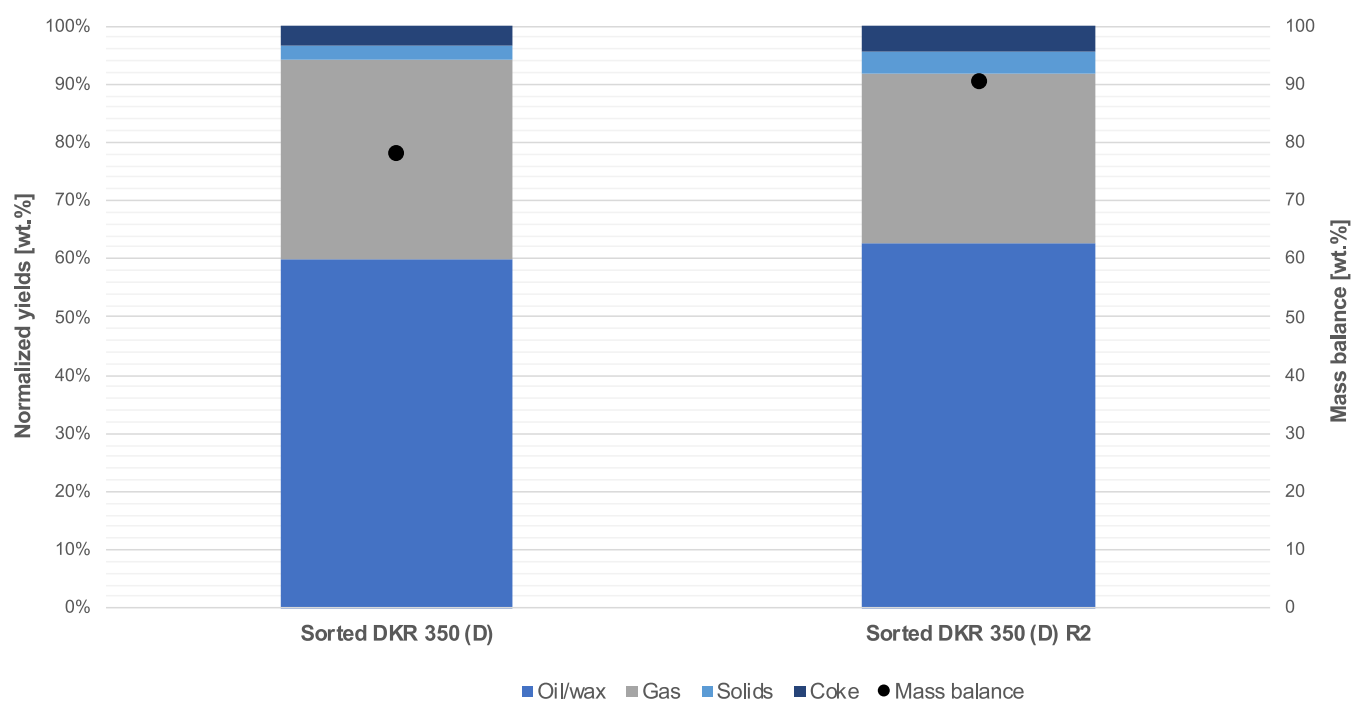
**3.3. Effect of Experimental Conditions.** **3.3.1. Effect of Residence Time.** One experiment was run in the pyrolysis pilot plant, where the vapor residence time was lowered. This was done by the addition of stones (inert) in the second empty reactor, which reduced the residence time by 33%, from 2.4 to 1.6 min. The pyrolysis product yields of this experiment, together with the ones of the experiment run with the same DKR350 feed and under the same conditions but at longer residence time, are shown in Figure 10. It can be observed that the condensable yield slightly increased (from 59 to 63 wt %), and the gas yield slightly decreased (from 35 to 30 wt %) with decreasing the residence time. Regarding oil composition, there is a slight decrease in the aliphatics/aromatics ratio by increasing the residence time from 2.4 to 2.2. These results seem to indicate that secondary cracking and aromatization reactions may take place in the gas phase, which is thus hindered by reducing the residence time.

In order to further investigate the effect of residence time, additional experiments were performed in the previously used





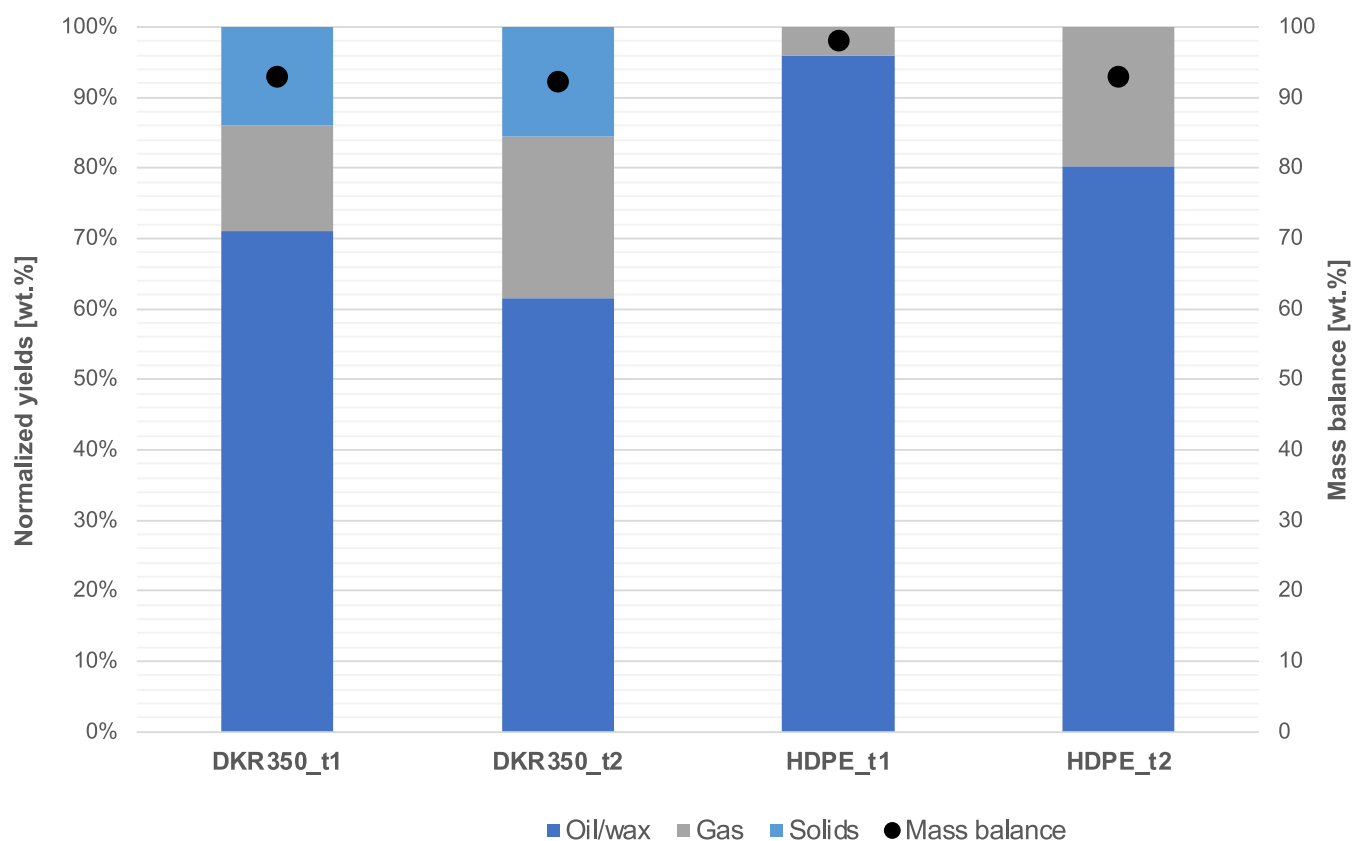
**Figure 9.** Product yields (wt % in terms of feed intake) from pyrolysis of different sorted DKR350 streams. Pyrolysis conditions: 5 kg h<sup>-1</sup> and 500 °C.



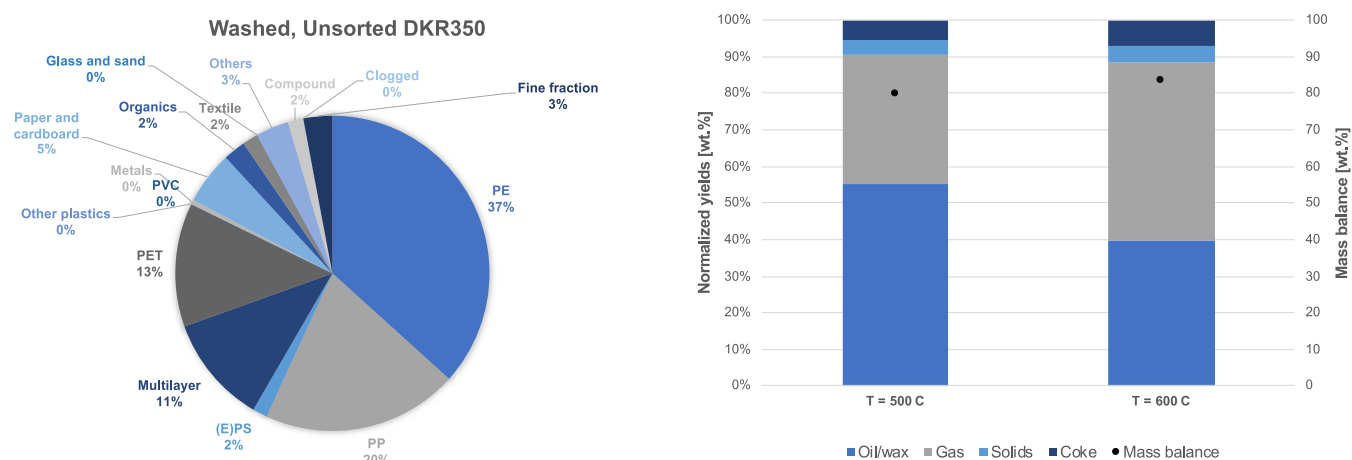
**Figure 10.** Product yields (wt % based on feed intake) from pyrolysis of a sorted DKR350 stream at two different times: 2.4 min (left bar) and 1.6 min (right bar, R2). Pyrolysis conditions: 5 kg h<sup>-1</sup> and 500 °C.

laboratory-scale batch reactor<sup>15,17</sup> at 500 °C, increasing the residence time by building a second reactor on top of the first one. Both DKR350 agglomerates and HDPE virgin pellets were used as feedstocks. The product yields are listed in Figure 11. It can be observed that for both feedstocks, the condensable yield decreased by increasing the residence time in the reactor. For DKR350, the oil/wax product decreased from 66 to 57 wt %, while the gas yield increased from 14 to 21 wt %. For HDPE, the condensable yield decreased from 93 to

74 wt %, at the expense of gas formation. More importantly, at the longer residence time, the condensable product was liquid oil instead of a mixture of oil and wax. Therefore, it can be concluded that cracking reactions occur in the gas phase, and thus, the residence time is a critical parameter affecting the product yields and composition. Apart from cracking reactions, the increase in residence time also favors aromatization reactions, as the aromatic percentage in the volatile (naphtha region) fraction of the oil (measured by GCxGC) increased



**Figure 11.** Product yields (wt % based on feed intake) from pyrolysis of DKR350 and HDPE at two different residence times (t1 and t2, t2 being 2 times t1). Pyrolysis conditions: lab-scale batch reactor, 100 g, and 500 °C.



**Figure 12.** Effect of temperature on pyrolysis at the pilot scale. (Left) Composition of the unsorted and washed DKR350 stream used as feedstock in these experiments. (Right) Product yields (wt % based on feed intake) from pyrolysis that stream at two different temperatures, 500 and 600 °C. Pyrolysis conditions: lab-scale batch reactor and 100 g. It is worth mentioning that due to the limited availability of the pilot plant, only the experiment at 500 °C was repeated twice, and the relative standard error in the oil yields was 5.5%.

from 21.1 to 34.7% for DRK350 and from 0 to 9.8% for HDPE, when increasing the residence time. This is in agreement with the trend observed in the pilot-scale experiments.

**3.3.2. Effect of Temperature.** The effect of temperature was also investigated at the pilot scale. For that, one DKR350 stream was pyrolyzed under the same conditions at two different temperatures, 500 and 600 °C. For these experiments, a different DKR350 stream was used (detailed composition in Figure 12). In this case, it went through a washing

pretreatment of cold + hot water + chemicals, similar to the one previously described.<sup>15</sup> No sorting was done in this stream, which has a high PET content of 13 wt %.

The results of the pyrolysis product yields are also shown in Figure 12. As expected, it can be concluded that temperature plays an important role in pyrolysis, favoring cracking reactions which led to higher gas yields (from 35 to 50 wt %) and lower condensable yields (from 55 to 40 wt %) when increasing from 500 to 600 °C. The effect of temperature is also significant in the oil composition. As observed in Table 4, the percentage of

**Table 4. Relative  $^{13}\text{C}$  NMR Area (%) in the Pyrolysis Oils Obtained at Two Different Temperatures**

pyrolysis temperature ( $^{\circ}\text{C}$ )	relative $^{13}\text{C}$ NMR area (%)		
	aliphatic	aromatic	carbonyl
500	52.8	47.1	0.2
600	39.4	60.6	0

aromatic components considerably increases with temperature, from 47% at 500  $^{\circ}\text{C}$  to 61% at 600  $^{\circ}\text{C}$ , which means that some aromatization reactions are taking place during pyrolysis in the pilot-scale experiments.

Pyrolysis could be a promising technology, flexible enough to recycle this type of complex packaging waste feedstocks. However, it still has some limitations that need to be overcome. Further research should be directed to design a proper pyrolysis reactor, able to deliver the amount of heat needed for the fast depolymerization reactions,<sup>27</sup> while optimizing the quality and yield of the condensable product and reducing the amount of contaminants in the product to minimize further processing steps.

## CONCLUSIONS

We show here an attempt to upscale thermal pyrolysis of real packaging plastic waste streams, DKR350 and DKR310, building upon our previous studies at the laboratory scale. Obviously, a direct comparison of both scales is not possible due to differences in reactors, batch vs continuous, heating rates, batch vs fluidized bed, and other parameters such as dimensions or residence times.

However, from a global perspective, we can conclude that operating conditions, such as temperature and residence time, are critical parameters that can allow us to control the yields and quality of our condensable products. For example, the condensable yields obtained at the pilot scale were significantly lower than at the lab scale, 45 vs 70 wt %, probably due to longer residence times in the pilot-scale reactor. This extended residence time was also responsible for aromatization reactions at the pilot scale, as shown in the composition of the oils produced.

Studies at pilot-scale encounter additional challenges related to operating larger and continuous systems as well as the need of supplementary sample preparation steps (production of flakes and further agglomeration). In general, the system and conditions used were capable of handling different streams and delivering products of relatively similar quality despite, e.g., mechanical sorting pretreatments or working with feedstocks of different composition.

Despite the efforts done in washing and sorting pretreatments, we have observed in both scales that the presence of heteroatoms (e.g., Cl) in the final condensable products poses a major challenge and limits their further processing (e.g., in a naphtha cracker), which thus would require the addition of extra post-treatment steps.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c04114>.

Elemental analyses of feedstocks and oils and the composition of the gas products (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Brouwer, M. T.; Smeding, I. W.; Thoden van Velzen, E. U. *Verkenning Effect Verschuiven Meetpunt Recycling Kunststoffverpakkingen*, 2019.
- (2) Brouwer, M. T.; Thoden van Velzen, E. U.; Augustinus, A.; Soethoudt, H.; De Meester, S.; Ragaert, K. Predictive Model for the Dutch Post-Consumer Plastic Packaging Recycling System and Implications for the Circular Economy. *Waste Manage.* **2018**, *71*, 62–85.
- (3) KIDV. 'Chemical Recycling of Plastic Packaging Materials'. Netherlands Institute for Sustainable Packaging, 2018.

- (4) Li, D.; Lei, S.; Wang, P.; Zhong, L.; Ma, W.; Chen, G. Study on the Pyrolysis Behaviors of Mixed Waste Plastics. *Renewable Energy* **2021**, *173*, 662–674.
- (5) CE Delft. *Monitoring Chemical Recycling*; Delft, 2022.
- (6) TNO. Marktverkenning mix kunststoffen en folies. <http://www.kidv.nl/7437>.
- (7) *Bevindingen pilots mix plastics (DKR350) (meermeterminderplastic.nl)*.
- (8) Gala, A.; Guerrero, M.; Serra, J. M. Characterization of Post-Consumer Plastic Film Waste from Mixed MSW in Spain: A Key Point for the Successful Implementation of Sustainable Plastic Waste Management Strategies. *Waste Manage.* **2020**, *111*, 22–33.
- (9) Kusenberg, M.; Roosen, M.; Zayoud, A.; Djokic, M. R.; Dao Thi, H.; De Meester, S.; Ragaert, K.; Kresovic, U.; Van Geem, K. M. Assessing the Feasibility of Chemical Recycling via Steam Cracking of Untreated Plastic Waste Pyrolysis Oils: Feedstock Impurities, Product Yields and Coke Formation. *Waste Manage.* **2022**, *141*, 104–114.
- (10) Kusenberg, M.; Zayoud, A.; Roosen, M.; Thi, H. D.; Abbas-Abadi, M. S.; Eschenbacher, A.; Kresovic, U.; De Meester, S.; Van Geem, K. M. A Comprehensive Experimental Investigation of Plastic Waste Pyrolysis Oil Quality and Its Dependence on the Plastic Waste Composition. *Fuel Process. Technol.* **2022**, *227*, No. 107090.
- (11) Lange, J.-P. Managing Plastic Waste—Sorting, Recycling, Disposal, and Product Redesign. *ACS Sustainable Chem. Eng.* **2021**, *9* (47), 15722–15738.
- (12) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and Chemical Recycling of Solid Plastic Waste. *Waste Manage.* **2017**, *69*, 24–58.
- (13) Stapf, D.; Seifert, H.; Wexler, M. *Energie Aus Abfall*; Thiel, S.; E Thomé-Kozmiensky, S.; Quicker, P.; Gosten, A., Eds.; Neuruppin, 2019; Vol. 16.
- (14) Kol, R.; Roosen, M.; Ügdüler, S.; Geem, K. M. Van.; Ragaert, K.; Achilias, D. S.; Meester, S. De.. Recent Advances in Pre-Treatment of Plastic Packaging Waste. In *Waste Material Recycling in the Circular Economy*; Achilias, D. S., Ed.; IntechOpen: Rijeka, 2021.
- (15) Genuino, H. C.; Ruiz, M. P.; Heeres, H. J.; Kersten, S. R. A. Pyrolysis of Mixed Plastic Waste (DKR-350): Effect of Washing Pre-Treatment and Fate of Chlorine. *Fuel Process. Technol.* **2022**, *233*, 107304.
- (16) Zeller, M.; Netsch, N.; Richter, F.; Leibold, H.; Stapf, D. Chemical Recycling of Mixed Plastic Wastes by Pyrolysis – Pilot Scale Investigations. *Chem. Ing. Tech.* **2021**, *93* (11), 1763–1770.
- (17) Genuino, H. C.; Pilar Ruiz, M.; Heeres, H. J.; Kersten, S. R. A. Pyrolysis of Mixed Plastic Waste: Predicting the Product Yields. *Waste Manage.* **2023**, *156*, 208–215.
- (18) NTCP. *National Test Centre Circular Plastics*.
- (19) BioBTX. <https://biobtx.com>. <https://biobtx.com>.
- (20) Guo, X.; Zhang, W.; Wang, L.; Hao, J. Comparative Study of Nitrogen Migration among the Products from Catalytic Pyrolysis and Gasification of Waste Rigid Polyurethane Foam. *J. Anal. Appl. Pyrolysis* **2016**, *120*, 144–153.
- (21) Ścierański, W. Migration of Sulfur and Nitrogen in the Pyrolysis Products of Waste and Contaminated Plastics. *Appl. Sci.* **2021**, *11* (10), No. 4374, DOI: 10.3390/app11104374.
- (22) Lee, K.-H.; Shin, D.-H.; Seo, Y.-H. Thermal Degradation of Nitrogen-Containing Polymers, Acrylonitrile-Butadiene-Styrene and Styrene-Acrylonitrile. *Korean J. Chem. Eng.* **2006**, *23* (2), 224–229.
- (23) Tiganis, B. E.; Burn, L. S.; Davis, P.; Hill, A. J. Thermal Degradation of Acrylonitrile-Butadiene-Styrene (ABS) Blends. *Polym. Degrad. Stab.* **2002**, *76* (3), 425–434.
- (24) Cueto, J.; Pérez-Martin, G.; Amodio, L.; Paniagua, M.; Morales, G.; Melero, J. A.; Serrano, D. P. Upgrading of Solid Recovered Fuel (SRF) by Dechlorination and Catalytic Pyrolysis over Nanocrystalline ZSM-5 Zeolite. *Chemosphere* **2023**, *339*, No. 139784.
- (25) Ferrari, D.; Radice, S.; Sciarrillo, V.; Marrani, A.; Ciolca, D.; Kounalis, K.; Jan Schenk, N.; Vries, T. PVDC Multilayer Films: Chemical Recycling by Means of Catalytic Conversion into Aromatics (BTX). *Sustainable Chem. Environ.* **2023**, *2*, No. 100010.
- (26) Xu, S.; Han, Z.; Yuan, K.; Qin, P.; Zhao, W.; Lin, T.; Zhou, T.; Huang, F. Upcycling Chlorinated Waste Plastics. *Nat. Rev. Methods Prim.* **2023**, *3* (1), No. 44.
- (27) Ruiz, M. P.; Zairin, D. M.; Kersten, S. R. A. On the Intrinsic Reaction Rate of Polyethylene Pyrolysis and Its Interplay with Mass Transfer. *Chem. Eng. J.* **2023**, *469*, No. 143886.