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Pyrolysis of mixed plastic waste (DKR-350): Effect of washing pre-treatment and fate of chlorine

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ABSTRACT

Pyrolysis of a post-consumer plastic waste stream (DKR-350) has been performed at a laboratory scale in a fixed-bed reactor at 500 °C. DKR-350 is a complex mixture of post-consumer plastics comprising polyethylene, polypropylene, polystyrene, polyethylene terephthalate, clogged materials, multilayer flexibles, together with considerable amounts of biogenic and inorganic residues and halogens. The influence of different washing procedures on feedstock composition and pyrolysis product yields was investigated. Washing effectively lowers the biogenic, inorganic and halogen contents in DKR-350, though does not affect the yield of the desired oil/wax (66 to 69 wt%). 27% of the oil/wax lies in the boiling point range of naphtha and gasoline (< 200 °C). During pyrolysis, the oxygen content of the oil/wax is reduced to 8–14 wt%, compared to 10–16 wt% in the feed. Chlorine analysis revealed that most of the chlorine present in the feed is removed by washing. Nevertheless, the concentration of chlorine in the oil/wax is still high (>150 ppm), showing the presence of recalcitrant organochlorides in the feed. Thus, post-treatment is still required to upgrade it to feedstock for the production of fuels and/or chemicals.

1. Introduction

Chemical recycling via pyrolysis is a promising alternative to convert plastic waste into oil and oil/wax products, which can be further processed in a steam or naphtha cracker or a refinery to produce chemicals or fuels [1–7]. One of the major challenges of processing plastic waste is the complexity of its composition. Mixed plastic streams from municipal wastes are extremely heterogeneous, typically containing mixed polyethylene, polypropylene and polystyrene (PE/PP/PS), and multilayer packaging and fiber-reinforced composites, which contain different polymers and thus can lead to completely different product spectra [8]. Indeed, mixed plastics are hard to separate, making pyrolysis more complicated as compared to high-purity individual plastics. Wenning et al. reported the pyrolysis of artificial mixtures of plastic waste comprising of PE, PP, PS, polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polyamide (PA), and found that depending on the composition of the plastic mixture and temperature, the product yield was in the range of 40–55 wt% oil/wax, 30–50 wt% gases, and 5–15 wt% solid (i.e., char) [9]. Donaj et al. also conducted a study on pyrolysis of polyolefin mixed plastics consisting of 46 wt% low-density polyethylene (LDPE), 30 wt% high-density polyethylene (HDPE), and 24 wt% PP in a

fluidized quartz-bed reactor at 650 °C, giving 48 wt% oil [10]. However, in a separate study using plastic mixtures of HDPE, LDPE, PP, PVC, PET, and PS, differences in product yields and composition were observed as compared to those expected from the pyrolysis of the individual plastics, implying that there are interactions of the main plastic types in plastic mixtures [2].

Another particularly relevant and interesting aspect in the area of mixed plastic waste pyrolysis is the presence of contaminants and additives in the feed. For example, organic and paper and cardboard-derived contaminants may be present in real plastic wastes, which arise from labels, caps, lids, food residues, etc., introducing unwanted heteroelements in the feeds [11–13]. Roosen et al. reported a detailed analysis of the composition of commonly generated plastic packaging waste streams in European sorting facilities, showing that such streams consist of mixtures of different polymers and contain various elements particularly metals (Ca, Al, Na, Zn, Fe) and halogens (Cl, F) [11]. Operational issues during pyrolysis caused by the presence of these heteroelements include corrosion of reactors by halogens and sulfur, deactivation of catalysts, and deposition and coking in the reactor due to the presence of metals [11].

Almost all plastic products contain additives to enhance polymer

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properties and to prolong their lifespan. The nature and purpose of the various plastics additives (e.g., protecting barrier for food packaging, namely polymeric, metallic or metal oxide films) have been studied and reported in the literature [14,15]. The general challenge that such additives pose can be addressed by removing them, for example, by solvent extraction, wherein the waste plastic is washed by an appropriate solvent or supercritical fluid [15]. The presence of inks or pigments, odoriferous constituents, and by-products can cause issues in the pyrolysis oil (or pyrolysis product) [11] because they will leave chemical constituents (or products) in the oily fraction that are harmful and for that reason should be removed. Thus, aside from effective and efficient sorting, removal of those contaminants in mixed plastic wastes (e.g., by optimization of the pre-treatment and washing procedure), it is key to obtain an appropriate feedstock for chemical recycling. Generally, plastic waste is washed using cold and/or hot water, with the assistance of detergents and/or caustic agents, which was also applied in this present work. This cleaning step is often integrated into the sorting chain, for example, after shredding and combined with a sink-float sorting step [7,16,17].

The most common packaging types that are sorted in European sorting facilities are defined according to the so-called Deutsche Kunststoff Recycling (DKR) as a minimum set of quality standards [18]. In the Netherlands, plastic packaging wastes are categorized into five groups, namely DKR-328 (PET), DKR-329 (PE), DKR-324 (PP), DKR-310 (foil), and DKR-350 (a mix of plastics that remains after these easily reusable plastics have been sorted out) [18,19]. The latter represents the largest stream from sorted PMD (plastic packaging, metal packaging, drinks cartons) waste, which is currently not recycled or has low recycling value, due to its high level of contaminants and variability in properties. To the best of our knowledge, no information in the literature regarding pyrolysis of DKR-350, including the effects of different washing procedures on composition and pyrolysis performance, is reported so far. This further underlines the validity and impact of our research goal, also considering the (expected) increase in the generation of this plastic waste stream.

The presence of PVC, with a high content of Cl (~56%), is one of the main issues in the pyrolysis of mixed plastic waste, as chlorinated compounds can be formed, which are detrimental when considering corrosion and environmental impact [20,21]. The presence of halogens, and chlorine in particular, which can come not only from PVC but also from inks (pigments), coatings and food, poses an important challenge in chemical recycling [22,23]. For example, aside from harmful dioxins, HCl could form, which is highly corrosive and can damage process and reactor equipment [11]. Moreover, the high chlorine content in the pyrolysis oil/wax products requires additional post-treatment before use as a petrochemical feedstock. A typical specification for such a liquid feed is a chlorine concentration below 10 ppm [11]. Indeed, the presence of chlorine in the mixed plastic waste is a real issue and underlines the need and urgency to study this aspect in detail.

In this context, this work provides first-of-a-kind data on the pyrolysis of various pre-treated DKR-350, essential to find a good balance between the degree of sorting and pre-treatment (washing) and downstream processing, to minimize cost and maximize product quality. First, the effect of different washing procedures to remove contaminants on the composition and pyrolysis performance of DKR-350 was studied. For this purpose, unwashed and washed DKR-350 streams were pyrolyzed in a fixed-bed reactor unit at laboratory-scale. The pyrolysis products were properly characterized in terms of yield and composition using various analytical techniques. Additionally, we analysed the fate of chlorine during pyrolysis of DKR-350, as chlorine is a detrimental contaminant that should be minimized in the oil/wax products. These parameters are an important input in the field of mixed plastic waste pyrolysis using real feedstocks particularly for further scale up of the process.

2. Materials and Methods

2.1. Characterization, washing, and drying of DKR-350 mixed plastic waste streams

A batch of post-consumer mixed plastic waste (PMD) was processed in KSI, a plastic sorting facility in Heerenveen, The Netherlands, before being transported to the Nationaal Testcentrum Circulare Plastics (NTCP) sorting and recycling plant in October 2020. NTCP determined the composition of the collected stream. The general methodology involved sorting, characterization, and washing. The specific waste stream types are summarized in Table S1 in terms of 25 categories. Manual separation of a total of 23.8 kg of DKR-350 stream based on these categories was systematically performed. In case of doubt in categorizing a special piece of material, a laboratory NIR scanner and/or industrial NIR instrument was utilized, which relies on a measurable difference in spectral signatures of different plastics. After categorization, the materials were weighed separately to determine the percent composition. The materials were then combined into a large bin and physically mixed. The mixed materials were shredded using a Shini granulator model SG-2336 to an average size of 12 mm. The flakes were then mixed all together to further facilitate homogenization and then weighed. The collected material was divided into four batches corresponding to the following washing procedures or absence thereof: (1) a hot water wash at 85 °C, (2) a cold water pre-wash followed by hot water wash, (3) a cold water pre-wash followed by hot water wash with detergent and NaOH, and (4) no wash. An industrial washing machine (Laundry Lion superior cleaning model LS 135) was used for washing. The amount of water (i.e., hot-water wash is 15 L), regular washing detergent (typically containing phenoxyalcohol, 50 g), and NaOH (1 wt % in the water medium) used in this work simulate a typical industrial washing process. To remove the residues, but retain the flakes in the washing process, nets were used (60 × 40 cm size, <10 mm holes). The washed flakes were dried in an oven at 95 °C overnight. The mass loss due to the removal of residues and moisture was quantified by weighing the streams before and after washing and drying.

2.2. Quantification of elemental composition and biomass residue analysis

Before elemental and biomass residue analyses, representative flakes (500 g) from each category described above were reduced into powders using a miller equipped with a sieve diameter of 1 mm. Dry ice was used to prevent the 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, inductively coupled plasma-optical emission chromatography (ICP-OES), X-ray fluorescence spectroscopy (XRF), and combustion ion chromatography (CIC).

2.2.1. X-Ray Fluorescence

For XRF analysis, the samples were analysed in a P1 cup with 4 µm propylene film. Quantification was performed using the Omnia software package from Malvern Panalytical. The data are semi-quantitative but give the correct order of magnitude. The data provide the weight % of the 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 balance compound by the Omnia Software. For XRF analysis of the solid product and ashes, 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 He atmosphere. A full scan was performed from 0.85 keV to 56.35 keV. Using the LiF200, Xs-S5 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 Quan Express.

2.2.2. Elemental analysis

For CHNS analysis, approximately 2–3 mg of sample is packed in a tin foil and subsequently analysed with a Vario EL Cube CHNS elemental analyzer. Calibration was performed with sulfanilamide. The procedure was repeated nine-fold.

2.2.3. Combustion Ion Chromatography

The Cl, F, and Br concentrations were determined by CIC measurements. Prior to analyses, the samples were pyrolyzed in an oxidizing atmosphere according to the method described in CMA/2/II/B.2, using ca. 1.0 g of sample. The resultant vapours are adsorbed in an aqueous solution and subsequently introduced into the IC system for analysis according to the CMA/2/I/C.3 method. The samples were analysed using 10 replicates at 20 mg sample amount (100 μL loop) and 10 replicates at 50 mg sample amount (15 L loop).

2.2.4. Biomass composition

Biomass compositional analysis of the samples (0.3 g) was performed by acid hydrolysis for three replicates on three representative samples via a two-step acid hydrolysis, following the NREL's LAP "Determination of Structural Carbohydrates and Lignin in Biomass" protocol. The procedure involved treatment of the sample with 72% sulfuric acid followed by autoclave incubation in 4% sulfuric acid in a sealed vessel to fractionate the biomass into forms that are more easily quantified. The concentration of glucose and glycerol (products of acid hydrolysis of cellulose and triglycerides, respectively) was determined by high-performance liquid chromatography (HPLC) using Agilent 1200 series instrument equipped with a refractive index detector at 60 °C with a dilute aqueous H_2SO_4 solution (5 mM) as the mobile phase at a flow rate of 0.55 mL min^{-1} . Samples were filtered (Whatman 0.2 μm filter) prior to HPLC analyses and calibration curves for the relevant components were established.

2.2.5. Ion Chromatography

The concentration of chloride anion in wastewater was measured using ion chromatography (IC), which was performed on a Metrohm 850 Professional IC operated on a Metrosep A Supp 16–150/4.0 column at 20 °C, running 7.5 $\text{mmol/L Na}_2\text{CO}_3$ + 0.75 mmol/L NaOH as mobile phase. Samples were filtered (Whatman 0.2 μm filter) prior to IC analyses and calibration curves for the relevant components were established.

2.3. Pyrolysis of DKR-350

2.3.1. Experimental pyrolysis set-up

A dedicated fixed-bed reactor unit (Fig. S1) was used to pyrolyze 60 g of dried DKR-350 mixed plastic waste. The unit consisted of a stainless-steel reactor (51 cm in length, 6 cm internal diameter) externally heated by insulated heating tapes. Heating was controlled by a programmable temperature controller which enabled the feeds (i.e., 60 g DKR-350) to be heated at a heating rate of 17 °C min^{-1} to the final pyrolysis temperature of 500 °C. The sample was held at 500 °C for 60 min to completion. Nitrogen was used as the carrier gas at a fixed metered flow rate of 5 NmL min^{-1} (200 NmL min^{-1} for 1 h for purging), which first passed through the pre-heater set at 500 °C before the fixed-bed reactor. The pyrolysis vapours then passed through a long cylindrical water-heated (or cooled in the case of PS as feed) tube at 90 °C to prevent clogging due to wax deposition. The oil and oil/wax product were trapped in a condenser cooled in an ice bath at about 10 °C. The gas effluent from the condenser system passed through a vessel containing about 2 kg of activated carbon pellets, to capture the remaining light components in the stream. The tubing, condenser, and activated carbon were weighed for mass balance calculations. Gas samples were collected using a syringe.

2.3.2. Analysis of pyrolysis products

2.3.2.1. Gas analysis. The gas samples were analysed for a range of gases using packed column gas chromatography. The non-condensable gases were analysed in the GC using the thermal conductivity detector (TCD) to determine the presence of CO_2 , CO, and H_2 . Gas standards with known concentrations were used to identify and quantify the gaseous components. The solid products (i.e., char, ash, residues) were also recovered and weighed. In addition to DKR-350 samples, virgin LDPE (from Sabic) in form of pellets (2–5 mm average diameter size) was also pyrolyzed individually (125 g). All pyrolysis experiments were done in duplicate and the average yields of products were reported.

2.3.2.2. Oil/wax analysis. - Elemental composition: The elemental composition of oil/wax and solid products was determined using an elemental analyzer (Vario Micro Cube Elemental CHNS/O, Germany). The oxygen content was determined by difference. All experiments were carried out in triplicate, and the average value is provided.

- Gas chromatography (GC): Gas chromatography-mass spectroscopy (GC-MS) analyses were performed on a Hewlett-Packard (HP 6890 series GC system, USA) GC combined with a Quadrupole Hewlett-Packard 6890 mass selective detector. A RTX-1701 capillary column (0.25 μm film thickness, 30 m \times 0.25 mm i.d.) was used for separation. Helium was used as a carrier gas (2 mL min^{-1}). The injector temperature was fixed at 280 °C. The following oven temperature profile was used: 40 °C for 5 min, from 40 °C to 250 °C at a rate of 5 °C min^{-1} , 250 °C for 10 min. Before analyses, the samples were diluted with THF (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 μm film thickness) connected by a solid state modulator (Da Vinci DVLS GC 2; modulation time of 6 s) to a Rxi-5Sil MS column (1.2 m \times 0.10 mm i.d. and 0.10 μm film thickness). The injector temperature and volume used were 280 °C and 1 μL , respectively. A split ratio of 1:50 and column flow rate of 0.8 mL min^{-1} 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^{-1} .

- Gel permeation chromatography (GPC): The average molecular weights (M_n and M_w) and polydispersity of the oil/wax were determined by gel permeation chromatography (GPC). A Hewlett Packard HP1100 (USA) combined with a GBC LC1240 RI detector was used. Three mixed-e columns (300 \times 7.5 mm PL gel, 3 μm) in series were applied for separation. Prior to GPC analysis, the sample was dissolved in THF (1 wt%) and filtered through a 0.45 μm PTFE syringe filter. Separation was achieved using THF as the mobile phase. Calibration was performed using polystyrene standards (580 to 19,720 Da) with a narrow molecular weight distribution. Data analysis was performed with PSS WinGPC UniChrom software (Massachusetts, USA).

- Nuclear magnetic resonance (NMR): ^{13}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 oil/wax in deuterated chloroform (CDCl_3 , Sigma-Aldrich). Heteronuclear single quantum correlation (HSQC) spectra were recorded on a Bruker NMR spectrometer (600 MHz, Germany). The following settings were used: a 11 ppm sweep width in the ^1H domain and a 220-ppm sweep width in the ^{13}C domain.

- Thermogravimetric analysis (TGA): TGA was used to get an indication of the simulated distillation curves of the oil/wax products. TGA curves were obtained using the TGA5500 thermogravimetric analyzer (TA Instruments). Analyses were performed using ~2 mg of oil/wax sample in Al pans sealed with pinhole lids, to obtain results similar to the actual simulated distillation results following the ASTM D86 standard method [24]. The pans were heated from 35 to 600 °C at a heating rate

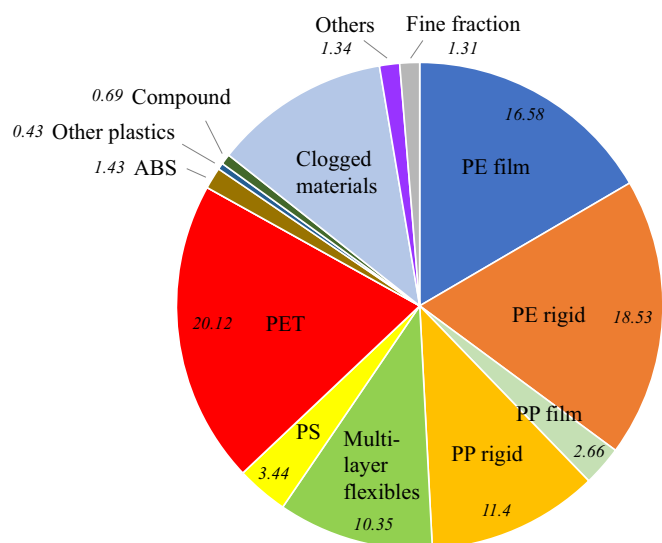


Fig. 1. Composition (wt%) of DKR-350 stream from sorted PMD waste (unwashed stream, which includes surface contamination and moisture). Details on the specific categories are given in Table S1.

of 10 °C min⁻¹, using 30 mL min⁻¹ of nitrogen as the purge gas.

3. Results and Discussion

3.1. Composition of DKR-350

A batch of DKR-350 (~20 kg) derived from PMD waste was characterized by manually separating it into the different categories (Table S1 in the Supporting Information). DKR-350 is a complex mixture of different plastics, as illustrated in Fig. 1. PE and PP (i.e., PE film, PE rigid, PP film, and PP rigid) were found to be the major constituents (about 50 wt%), followed by PET (all types) at 20 wt%. Only minor amounts of PS (3.4 wt%) and acrylonitrile butadiene styrene (ABS) (1.4 wt%) were present. Combined, they represent approximately 75 wt% of the total weight of DKR-350. Clogged materials (hard-to-separate plastic components) and multilayer (multimaterial) flexibles (paper and aluminum laminates) were also present in significant quantities (about 12 wt% and 10 wt%, respectively). Polylactic acid (PLA) and polyvinyl chloride (PVC) plastics were not detected. The remainder (3.8 wt%) is the catch-all category (“other plastics”, “compound”, “others”, and “fine fractions”), which consists of materials of different nature, hence difficult to classify and separate. Representative photographs of these categorized plastic constituents and other fractions of DKR-350 are also shown in Table S1.

3.2. Effect of washing on DKR-350 composition

After characterization of the composition of the DKR-350 stream, the separated fractions were combined, mixed thoroughly, shredded into flakes (12 mm sieve), further mixed, divided equally into four batches (to be used for different washing procedures), and finally washed and dried. Different washing procedures were applied, namely: (1) a hot-water wash at 85 °C (“hot water”), (2) a cold water pre-wash at 30 °C followed by a hot-water wash at 85 °C (“cold and hot water”), and (3) a cold water pre-wash at 30 °C followed by a hot-water wash at 85 °C with detergent and 1 wt% NaOH (“cold and hot water + chemicals”). The last batch (4) is “unwashed”, wherein the flakes were only dried at 95 °C. Table 1 summarizes the mass loss after washing and drying the flakes for each batch. Results show that the hot water wash removed a significant amount of material (6.43 wt%), which most likely comprises salts, soil, oils, metals, and/or biomass (food residues). The mass loss increased up

Table 1
Characterization of unwashed and washed DKR-350 mixed plastic waste streams.

DKR-350 stream	Mass loss ^a (wt %)	(ppmw) ^d											(wt%) ^e										
		C	H	N	S	O	Cl	F	Br	Ca	Ti	Al	Na	K	S	Mg	P	Fe	Si	Glucose	Glycerol	Moisture	Ash
Unwashed	-	73.31 ±1.60	10.07 ±0.49	0.55 ±0.14	-	16.07 ±1.80	1825	60	13	6030	4210	3180	2300	1040	798	789	496	1610	6070	1.47	2.18	1.56	7.53
Hot water	6.43	75.96 ±0.74	11.37 ±0.71	0.35 ±0.02	-	12.32 ±1.46	796	30	7	4260	4930	1020	104	970	138	567	127	1580	1040	0.59	0.89	0.45	4.1
Cold and hot water	11.31	77.91 ±0.5	11.38 ±0.07	0.39 ±0.07	-	10.31 ±0.47	627	31	7	3090	4030	1200	243	630	97	252	75	1070	1750	0.50	0.62	0.27	2.42
Cold and hot water + chemicals	11.71	77.23 ±1.30	11.57 ±0.77	0.22 ±0.04	-	10.98 ±2.00	681	33	7	4990	5020	1460	119	560	348	478	169	1240	1440	0.26	0.09	0.29	1.89

^a Mass loss (wt%, kg-scale): [(mass after characterization – mass after washing and drying) / (mass after characterization)] × 100%.

^b Elemental analysis on 10 representative samples. C (carbon), H (hydrogen), N (nitrogen), S (sulfur), and O (oxygen). %O = 100 – CHNS. “-” means below limit of detection (0.050 wt% for C, H and N, and 0.100 wt% for S). Average results and corresponding standard deviations are reported.

^c Cl and F by combustion ion chromatography (CIC), Br by inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray fluorescence spectroscopy for all other elements. Analysis on 10 representative samples.

^d By sulfuric acid hydrolysis followed by HPLC analysis on three representative samples. Glucose and glycerol are products of acid hydrolysis of cellulose and triglycerides, respectively.

^e Moisture and ash contents determined by heating 0.5–1.0 g sample in air overnight at 110 °C and 900 °C, respectively, performed on three representative samples.

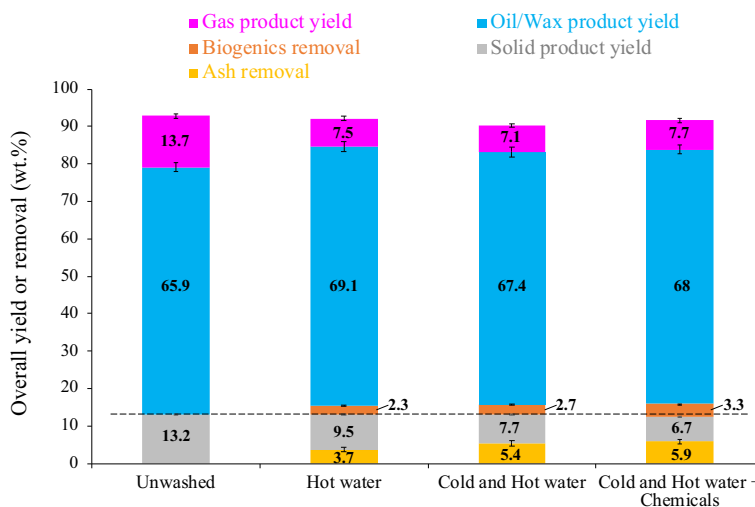


Fig. 2. Product yields (wt% relative to unwashed feed intake) from the fixed-bed pyrolysis of unwashed and washed DKR-350 feeds. For the washed samples, the levels of biogenics and ash removal by the washing step are also included. Conditions: 60 g flakes, 17 °C min⁻¹, 500 °C for 60 min, 5 mL min⁻¹ N₂. The experiments were run in duplicate, and the 95% confidence interval of the yields was below 3.6% in all cases.

to 11.31 wt% when using a combined cold water pre-wash followed by a hot water wash. Visual inspection of this stream showed that the flakes appear cleaner and hardly contain any attached residual materials compared to the hot water-washed stream. On the other hand, the use of chemicals in addition to the combined cold and hot water only had a minor influence on the mass loss (0.4 wt%), compared to the combined cold and hot water wash. However, the distinct smell was significantly reduced, suggesting that odoriferous components were effectively removed by using a regular detergent and a caustic soda wash.

For the subsequent compositional analyses of the various wash fractions, representative sample flakes (500 g) from the four DKR-350 streams were cryo-milled into a powder (≤ 1 mm) and subsequently analysed (Table 1). Sulfuric acid hydrolysis was performed to determine the amounts of biogenics (i.e., hydrolysable sugars, triglycerides) in the various DKR-350 fractions. The total concentration of glucose (a product from the hydrolysis of cellulose that is present in paper and cardboards) and glycerol (a product from the hydrolysis of triglycerides from fats, grease, and oils that may be derived from food residues) is much higher in the unwashed stream (3.65 wt%) as compared to the washed streams (0.35–1.48 wt%). Acid-soluble and acid-insoluble lignins were not found in all the samples, which is in agreement with the expected low amounts of lignin in residual paper and cardboards. The moisture content of all DKR-350 streams after drying at 95 °C was low (≤ 1.6 wt%).

Halogen analysis of the unwashed DKR-350 stream indicated that the concentrations of fluorine (60 ppm) and bromine (13 ppm) were significantly lower in comparison to the chlorine content (1825 ppm) (Table 1). As mentioned above, the presence of chlorinated compounds in the oil/wax stream produced in pyrolysis limits its application potential. The washing step(s) were shown to remove 59–70% of the Cl from the original DKR-350 material. One potential major source of chlorine are inorganic salts from food residues, and our results suggest that most of these salts are easily removed by washing. To prove this, samples of unwashed DKR-350 were treated with hot water (85 °C) and the wastewater collected was subsequently analysed for chloride by ion chromatography. Results showed that chlorides were indeed present, and the wastewater contained chloride anions corresponding to 1274 mg of chloride per kg of washed DKR-350. Chlorides were not detected in the wastewater of washed DKR-350 and therefore the remaining chlorines are likely chemically bound chlorines (organochlorines), potentially coming from additives including films, inks or pigments [11,14,15]. In addition, multilayer flexibles might contain small amounts of polyvinylidene chloride (PVDC) [25], which could

contribute to the chlorine content in all DKR-350 streams. These materials may vary greatly from one packaging type to another, and due to heterogeneity of DKR-350, some (small) differences in chlorine concentration can thus be observed among washed streams (Table 1). In terms of fluorine and bromine removal, washing removes about 50% Br and F, despite the low initial concentrations (60 and 13 ppm for F and Br, respectively). Although no threshold concentration is available for bromine in the oil product to be used a feedstock for steam cracker units, HBr could form, which is also problematic due to its corrosive nature.

Plastic wastes that contain high concentrations of metals are also undesired as pyrolysis feedstocks, as metals can cause deposition and promote coking in the reactor and pollute the products [11]. High levels of metals in the feed may also potentially increase char and non-condensable gas yields [26]. In this work, the concentration of metals in DKR-350 stream, in particular Ca, Al, Na, K, Ti, Fe, and semi-metal Si, were between 56 and 6070 ppm. They generally diminished in concentration upon washing (except for Ti), but were not quantitatively eliminated. This result suggests that some of the plastics in DKR-350 contain polymers with a relatively high intrinsic metal concentration, which cannot be fully removed by washing. Examples are TiO₂ (white pigment) and CaCO₃ (used to improve the mechanical properties and appearance of the plastic), which are known additives in the manufacture of different types of plastics [14,15]. Fe possibly originates from salts and biogenic sources, whereas both Fe and Al are known to be present in packaging components including labels, foils, lids, caps, and other debris such as metal particles, etc. Washing showed a significant impact on the concentrations of Na, Al, and Si. The abundance of Na and Si in the unwashed DKR-350 stream is likely attributed to the adsorbed salts from food residues, sand and glass debris, respectively. The maximum levels of reduction of Na, Al, and Si by washing were 95, 68, and 80% (Table 1).

In addition to these elements, pyrolysis of an oxygen-rich polymer feedstock can result in the production of certain organic acids, which can affect the reactor due to their corrosive nature, contaminate the pyrolysis products, and cause clogging of pipes and heat exchangers [11]. Moreover, oxygen present in the pyrolysis oil/wax lowers the heating value, causes thermal instability, and results in elevated soot levels, requiring energy-intensive cleaning [11]. Here, the principal source of oxygen content in DKR-350 streams is PET. The higher oxygen content of unwashed DKR-350 stream as compared to the washed streams is likely attributed to presence of biogenics, which is significantly reduced by, for example, a combination of cold and hot water

Table 2

Elemental analysis of the oil/wax products obtained from the pyrolysis of unwashed and different washed DKR-350 mixed plastic waste streams.^a

Element	DKR-350 pyrolysis feedstocks			
	Unwashed	Hot water	Cold and Hot water	Cold and Hot water + Chemicals
	wt%			
C	75.2 ± 0.7	80.7 ± 0.7	80.6 ± 0.4	80.9 ± 0.5
H	10.0 ± 0.5	11.4 ± 0.4	11.1 ± 0.6	10.9 ± 0.1
N	0.3 ± 0.01	0.2 ± 0.06	0.2 ± 0.03	0.2 ± 0.01
O ^b	14.5 ± 0.7	7.7 ± 1.0	8.2 ± 0.9	8.0 ± 0.4

^a Average of 10 representative measurements and corresponding standard deviations.

^b Obtained by difference.

wash. The % O removal from DKR-350 after washing is between 31 and 40%. Previously, Gala et al. performed immediate and elemental analysis of post-consumer plastic film wastes, obtaining oxygen concentration up to 6.1 wt%, albeit at higher ash content [27].

The unwashed DKR-350 stream had the highest ash content (7.5 wt%), attributed to the inorganics present in this stream (Table 1). The lower ash content of the washed streams thus implies that washing effectively lowers inorganic residues in the stream. X-ray fluorescence spectroscopy (XRF) analysis of these ashes shows that they are composed of metals in form of oxides and other materials such as SiO₂, which likely originate from glass and sand (Table S2).

3.3. Pyrolysis of the various DKR-350 feedstocks

3.3.1. Product yields

Pyrolysis of unwashed and washed and dried DKR-350 feeds was performed in a fixed-bed reactor heated to 500 °C. Fig. 2 shows the average product yields of combined oil and wax, solids, and non-condensable gaseous products obtained from the pyrolysis of the four different DKR-350 feeds. Typically, oil fractions dissolve in the waxes in the condenser giving a one-phase product. The melting point of oil/wax products ranged from 50 to 56 °C.

Unwashed DKR-350 feed produced oil/wax at 66 wt% yield and some gases (14 wt%) and solids (13 wt%), with a good mass balance

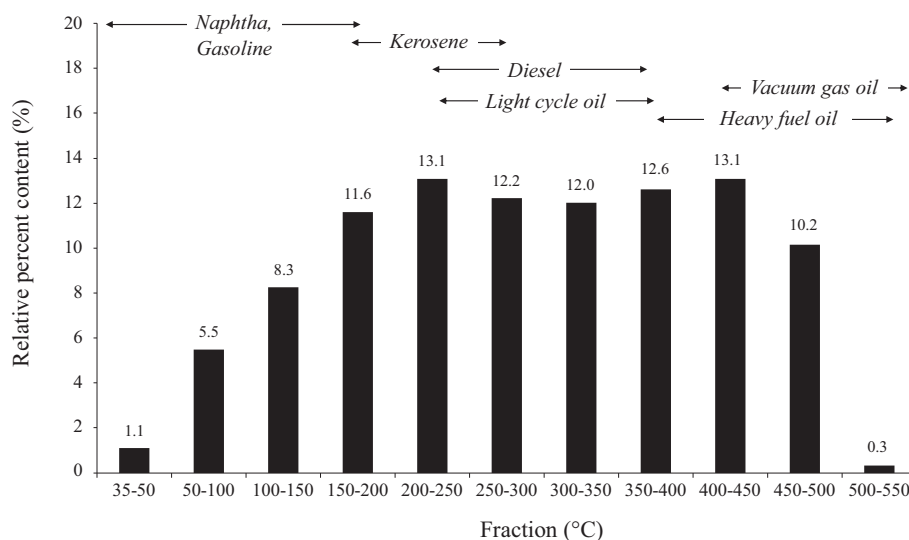


Fig. 3. TGA analysis of oil/wax product obtained from the pyrolysis of DKR-350 feed (washed with cold and hot water + chemicals), used as an indication of the simulated distillation analysis.

closure (93 wt%). The solid product consists of carbonaceous material, most likely from the PET and PS fraction, which are known to produce significant amounts of char [2], and inert materials (i.e., inorganics). As shown in Table 1, the ash content of the unwashed feed is 7.5 wt%; thus, about half of the solid product is presumably ash. Indeed, a detailed examination of the solid product by XRF indicates that it contains metallic and ceramic components, which most likely originate from polymer fillers, composite materials, etc. (Table S2).

The overall percentage of removal of biogenics and ashes due to the washing step(s) is also included in Fig. 2. Washing is also shown to effectively reduce the ash content in the feedstock, which is a fraction that ends up in the solid product during pyrolysis. In fact, the solid product yield for the unwashed feed closely matches the sum of the solid product yield and ash removal percentage for all washed feeds (see horizontal dashed line in Fig. 2).

Comparison between the product yields of unwashed and different washed feeds shows that, unlike the gaseous and solid products, the oil/wax yields are rather similar (66–69 wt%). This result suggests that washing effectively removes gas precursors from the feed without

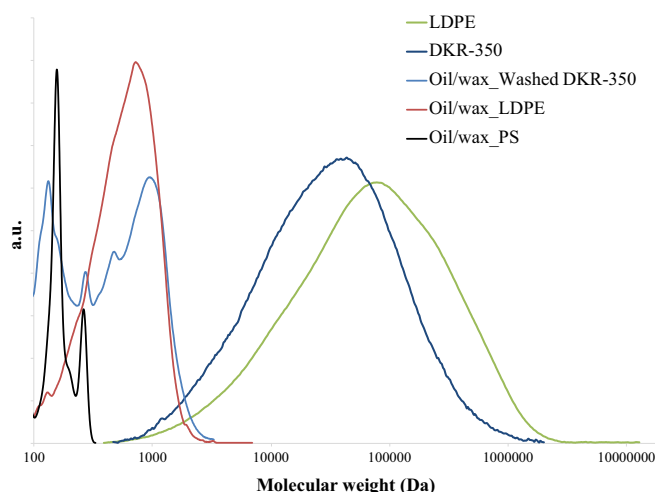


Fig. 4. GPC chromatograms of LDPE and DKR-350 feeds, and of oil/wax products derived from the pyrolysis of washed DKR-350 (washed with cold and hot water + chemicals), PS, and LDPE.

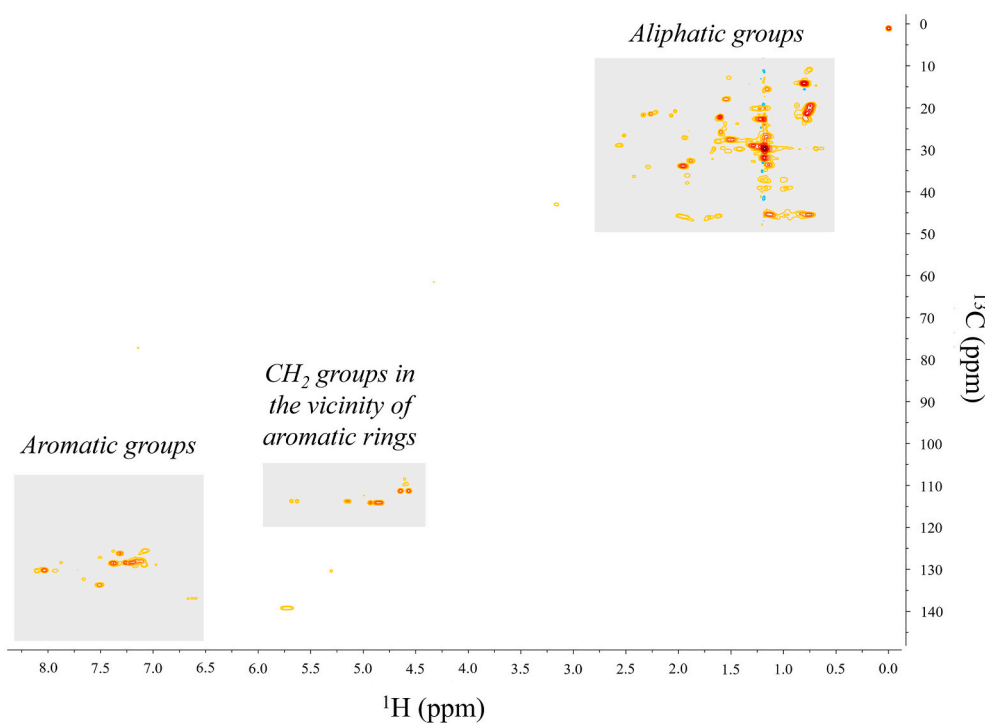


Fig. 5. 2D HSQC-NMR spectrum of oil/wax from the pyrolysis of DKR-350 feed (washed with cold and hot water + chemicals).

substantially affecting the oil/wax yields. Such gas precursors could be of biogenic origin (e.g., sugars, proteins, fatty acids). The higher levels of metals in the unwashed stream may also catalyse gas formation [26].

The evolved gases from the pyrolysis of DKR-350 feeds contain hydrocarbon gases (i.e., methane, ethane, ethylene, propane, propylene, propadiene, acetylene, n-butane, trans-2-butene, 1-butene, isobutylene, cis-2-butene, isopentane, trans-2-butene, pentane, methyl acetylene) and inorganic gases, such as H_2 , CO, and CO_2 (Table S3). The presence of oxygenated compounds (i.e., biogenics) and chemically bound oxygen in polymers (i.e., PET) in the feed can result in CO and CO_2 formation [26,28].

3.3.2. Characterization of the oil/wax products

The composition and relevant properties of oil/wax products were determined by various techniques: elemental analysis, simulated distillation with TGA, gel permeation chromatography (GPC), carbon and two-dimensional heteronuclear single-quantum correlation nuclear magnetic resonance spectroscopy (^{13}C NMR and 2D HSQC-NMR) and two-dimensional gas chromatography time-of-flight mass spectrometry (2D-GC ToF-MS).

3.3.2.1. Elemental analysis. Elemental analysis of the different oil/wax products (Table 2) shows a C content between 75.2 and 80.9%, H content between 10.0 and 11.4%, O content between 7.7 and 14.5%, and low levels of N, 0.18–0.28% (average from 3 representative samples). To compare the elemental composition of oil/wax with those of the starting material, a van Krevelen plot was constructed (Fig. S2). After pyrolysis, the O/C and H/C ratios for all DKR-350 feeds decreased. The lower oxygen concentration of oil/wax products compared to the starting materials implies that oxygen is transferred to the gaseous phase through CO and CO_2 formation (Table S3). Although some deoxygenation of the oil/wax in pyrolysis can be achieved by washing the feed (% O in the oil/wax product decreased from ~14% for the unwashed feedstock to ~8% for the washed feedstocks), still further processing of the oil/wax is required for certain applications, e.g., the maximum allowable oxygen concentration in industrial steam cracker feedstocks

lies at 100 ppm [29].

3.3.2.2. Boiling point distribution. In order to get an indication of the boiling point distribution of the oil/wax products from the pyrolysis of DKR-350 feeds, a simulated method of distillation was carried out by thermogravimetric analysis (TGA). This technique is common for a preliminary analysis of the boiling point distribution [24,30] of the oil/wax and thus could be relevant for an initial assessment of the compatibility of these products with the conventional feed of a refinery unit (i.e., FCC or hydrocracking). The boiling points of the majority of the components of the oil/wax for a representative product lie within the temperature range of ~200–450 °C (63%, Fig. 3). This is similar to the boiling point range of current transportation fuels and refinery streams, including kerosene (~150–275 °C) and diesel fuel (~200–350 °C) [31]. In comparison, the amounts of the fractions that correspond to naphtha oil (i.e., < 180 °C) and light and heavy gasoline (~30–180 °C) were relatively low (27%). Simulated distillation plots for the oil/wax from other DKR-350 feeds are presented in the Supporting Information for comparison (Fig. S3).

3.3.2.3. Molecular weight distribution. The molecular weight distribution of the oil/wax samples was determined by gel permeation chromatography (GPC). Fig. 4 shows the GPC chromatogram of the oil/wax product from pyrolysis of the DKR-350 sample washed with cold and hot water + chemicals, the GPC data for other DKR-350 oil/waxes are presented in Fig. S4. It shows a wide molecular weight (MW) distribution ($M_n = 246$, $M_w = 553$), with a polydispersity value of 2.25. Peaks appearing in the low MW region (~50–200 $g\ mol^{-1}$) represent the light fractions of the product. A proper comparison with the chromatograms of oil/wax from the individual polymers in DKR-350 shows that these low MW compounds mainly arise from the pyrolysis of PS (Fig. 4). Higher MW compounds (~300–500 $g\ mol^{-1}$) are also present, which can be attributed to various oligomeric products. Furthermore, higher MW compounds are also present as indicated by tailing in the chromatogram. These are mainly formed from the pyrolysis of the PE fraction in the feed, supported by the observation that LDPE pyrolysis mainly gives

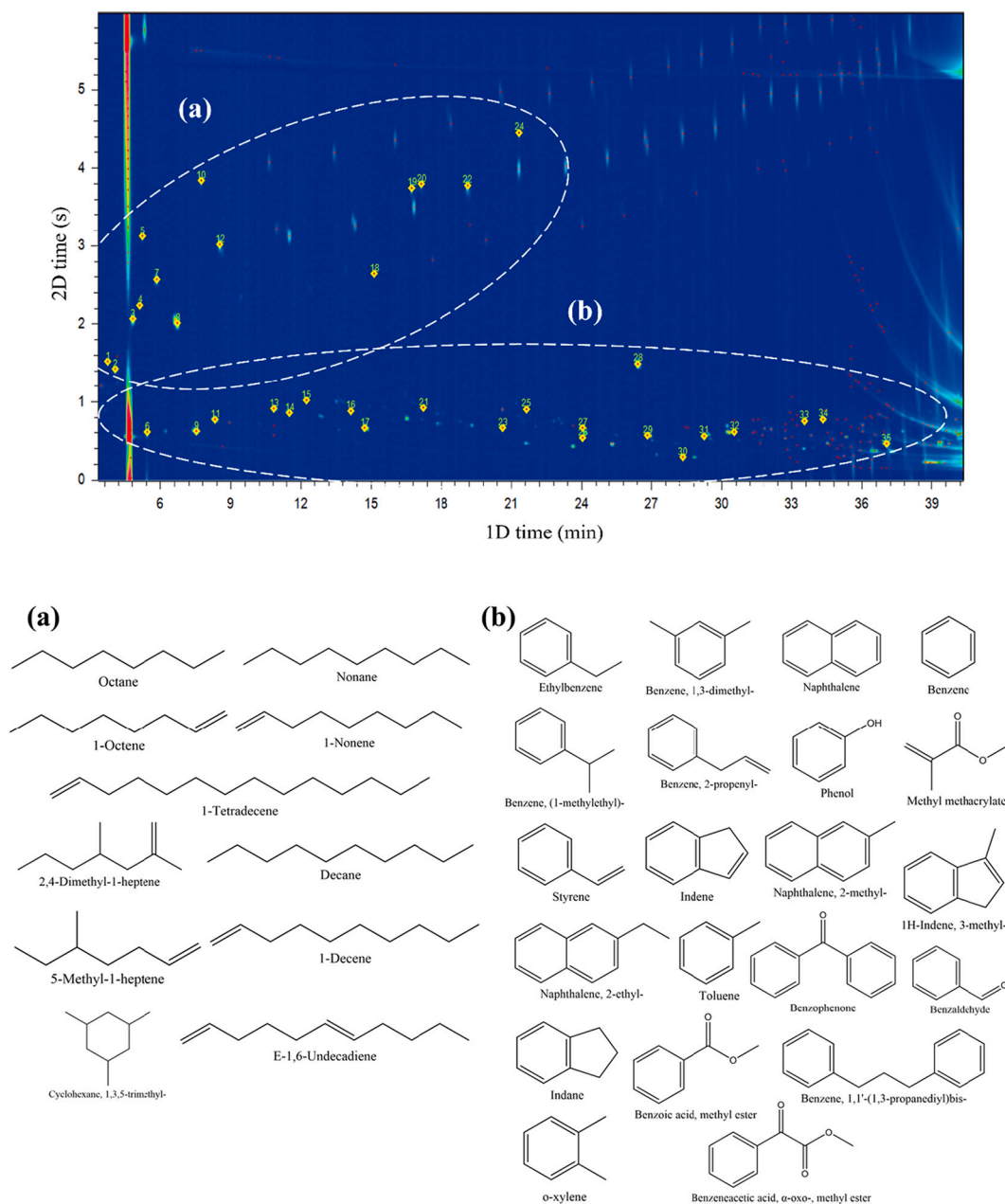


Fig. 6. 2D-GC ToF-MS chromatogram of oil/wax obtained from the pyrolysis of DKR-350 feed (washed with cold and hot water + chemicals) and the identified (a) aliphatic and (b) aromatic compounds.

waxy products with high molecular weight products (Fig. 4).

3.3.2.4. Hydrocarbon composition. The hydrocarbon composition of the oil/wax samples from DKR-350 pyrolysis was analysed using 1D (^{13}C) and 2D (^1H – ^{13}C HSQC) NMR spectroscopies. Using ^{13}C NMR spectroscopy, integration of the spectrum recorded for the oil/wax sample derived from DKR-350 washed with cold and hot water + chemicals gives an estimation of the content of various functional groups. The peaks in the range δ 166.5–95.8 ppm are associated with the presence of aromatic groups (27.5% of all the carbons in the spectrum) and those in the range of δ 55.2–0 ppm and δ 21.6–19.1 ppm are for aliphatic C–C (68.7% C) and methyl aromatic carbons (3.8% C). The 2D-HSQC NMR spectrum recorded for the same oil/wax sample is shown in Fig. 5, which confirms the 1D ^{13}C NMR data. Three relevant regions were assigned belonging to different C–H bonds, namely aromatic C–H bonds, CH_2 groups in the vicinity of the aromatic rings, and aliphatic C–H bonds.

This result confirms the presence of a higher proportion of longer-chain hydrocarbons in the oil/wax which are aliphatic in nature (more aliphatic-aliphatic than aliphatic-aromatic type of carbon).

Considering that DKR-350 has ~24% of aromatic polymers in its composition (PET, PS), we might conclude that the aromatics/aliphatics ratio (~1/3) from the feed is equal to the one in the pyrolysis oil/wax product. This result is additionally supported by the fact that the pyrolysis of LDPE under the same operating conditions gives an oil/wax composed of only aliphatic compounds (Fig. S5), where no aromatization products were observed.

In this present work, results of GPC and simulated distillation experiments indicate that the amount of light fraction in oil/wax products is significantly less than the heavy fraction. Nevertheless, additional semi-quantitative experiments using GC–MS and 2D-GC ToF-MS were performed to allow us to identify the main components present of this light fraction in the oil/wax (i.e., from pyrolysis of DKR-350 washed

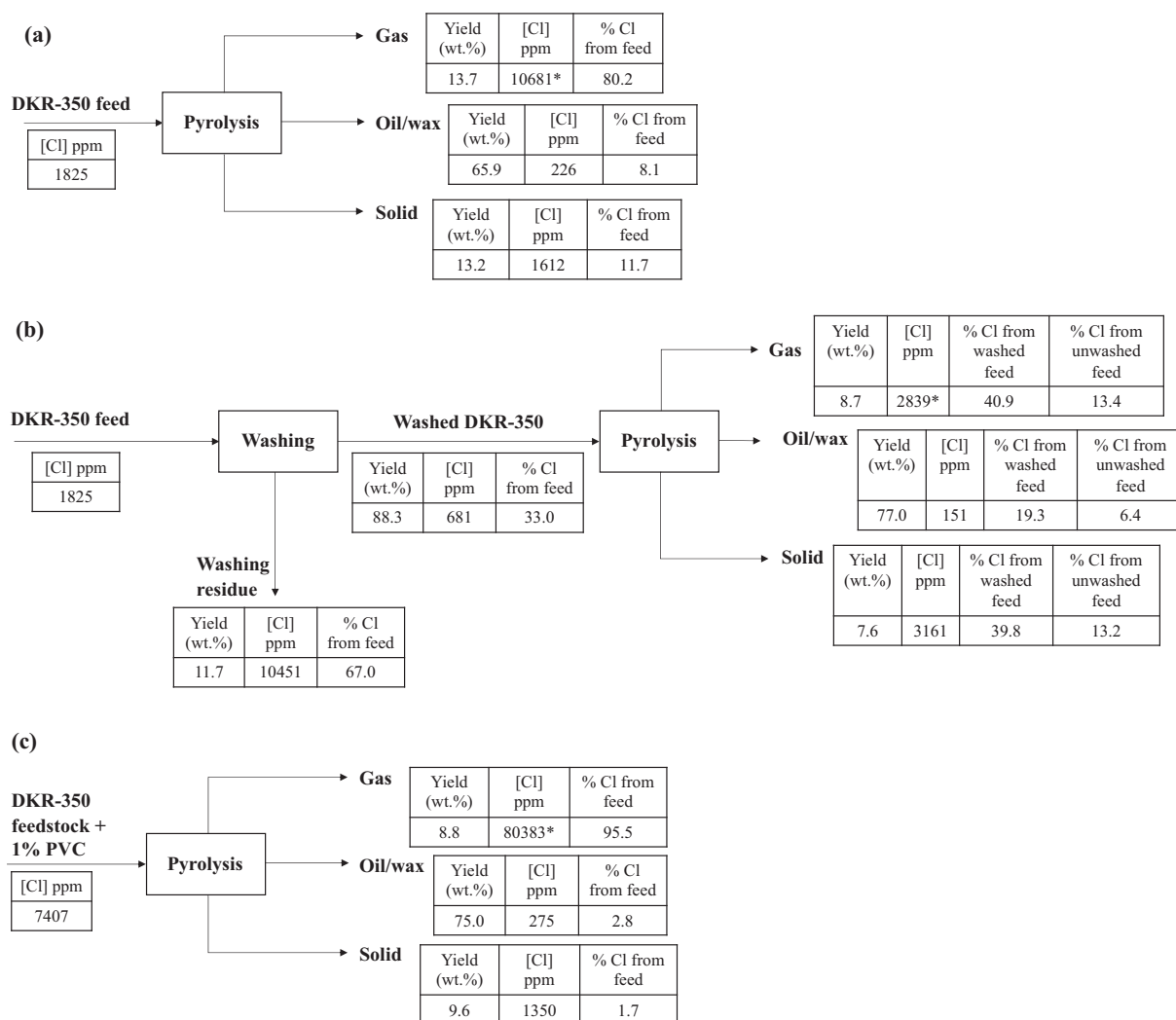


Fig. 7. Chlorine distribution in gas, oil/wax, and solid residue products from the pyrolysis of (a) unwashed, (b) washed DKR-350 feedstocks and (c) experiment of unwashed DKR-350 spiked with 1 wt% PVC. * [Cl] in gas phase is obtained by difference. These data are also tabulated in the Supporting Information (Table S4).



Scheme 1. Plausible steps for the formation of HCl and chlorinated hydrocarbons during (co-) pyrolysis of NaCl- and PVC-containing DKR-350 feeds.

cold and hot water + chemicals). GC-MS analysis indicates that alkanes and alkenes are present in the light fraction of oil/wax at approximately equal proportions (~30%, peak area). Moreover, the aromatic compounds in the light fraction of oil/wax are significant (~40%, peak area). Fig. 6 shows the identified peaks in 2D-GC ToF MS, which are essentially grouped into two, according to the distribution pattern—aliphatics (a) and aromatics (b). Aliphatic hydrocarbons consist predominantly of linear alkanes and alkenes (C₈-C₁₄) and some diolefin, branched olefins, and a cyclic alkane (e.g., 1,3,5-dimethyl cyclohexane). Branched isoolefins (e.g., 2,4-dimethyl-1-heptene, C₉-trimer) and diolefins can come from the PP fraction, whereas linear aliphatic hydrocarbons such as linear paraffins and olefins can result from the PE fraction in DKR-350 feed [26,29]. Identified aromatic compounds consist of monoaromatics, naphthoaromatics, diaromatics, and alkylated derivatives. Pyrolysis of other polymers also present in the original

DKR-350 feed such as PS and PET can result in these aromatic compounds in oil/wax product such as benzene, toluene, styrenes, and naphthenes [26,29,32]. Secondary reactions such as aromatization, isomerization, and recombination could have also occurred. Diolefins and naphthenes are typically less wanted as they are known precursors to coke formation in the subsequent processing of pyrolysis products (e.g., steam cracking), and therefore need to be reduced. Moreover, the presence of oxygen in the original feeds (e.g., biogenics, PET, multilayer flexibles) can consequently have caused the formation of oxygenated compounds in oil/wax (i.e., oxygenated compounds such as phenol, benzaldehyde, and esters), though this needs to be confirmed via GC analysis of these individual plastic components.

3.3.3. Fate of chlorine during DKR-350 pyrolysis

Aside from the hydrocarbon composition of the oil/wax products, the presence of other components, such as inorganics, chloride, or oxygen, will determine their suitability for further processing. In this work, we focused on the fate and distribution of chlorine in DKR-350 during the pyrolysis process. The concentration of chlorine in the feeds and oil/wax and solid products was measured using combustion ion chromatography, whereas the concentration of chlorine in the gas was obtained by difference. As shown in Fig. 7, most chlorines in the unwashed DKR-350 feed are removed in the gas stream during pyrolysis. Only 8.2% of the chlorines end up in oil/wax, compared to 11.7% in the solids, and

80.2% in the gas, suggesting that most chlorines (i.e., mostly as chloride salts) are likely eliminated as HCl (Scheme 1). The presence of HCl in the gas produced during pyrolysis of DKR350 was confirmed by flowing a sample of gas through a solution of NaOH and quantifying the chloride concentration of the resulting solution by ion chromatography.

After washing the DKR350, a significant amount of chlorine was removed (67%, as chlorides) from the feed whereas 33% of the chlorines remained (probably as organochlorines) (Fig. 7). The calculated amount of chlorine removed during washing matches with the amount of chlorine analysed in the wastewater (Section 3.2). Pyrolysis of this washed feed gave oil/wax with a comparable chlorine concentration (151 ppm) to the unwashed one (226 ppm). Additionally, a similar percentage of the chlorine feed (unwashed feed basis) ended up in the oil/wax product (8.1% for unwashed feed vs. 6.4% for washed feed). Most of the chlorine in the washed feed is distributed between the solid (39.8%) and gas phase (40.9%) products during pyrolysis. This difference in chlorine distribution can be attributed to the difference in the type of chlorine species present in the feeds. Nevertheless, the chlorine concentration in the oil/wax (151 ppm) is still relatively high as compared to the maximum allowable limit in refinery feeds (10 ppm), thus additional reduction is required before further processing.

Scheme 1 shows the plausible steps for the formation of HCl and chlorinated hydrocarbons during pyrolysis of chlorine-containing feedstocks. In reaction 1, NaCl can react with ROOH (e.g., from PET pyrolysis fragment) to give HCl and ROO-Na products [33]. When PVC is present in the feed, HCl is during thermal degradation, which can further react with alkenes to produce chlorinated organics (Scheme 1, reaction 2) [23,34]. In this work, the DKR-350 stream does not contain (separable) PVC components and therefore it can be assumed that the latter route does not occur to a significant extent.

Additionally, a pyrolysis experiment was then performed on a DKR-350 stream containing a known amount and type of chlorine species, that is, 1 wt% PVC (~7400 ppm Cl). The product yields and the fate of chlorine in this experiment are also shown in Fig. 7. Pyrolysis yielded 75 wt% oil/wax, 8.8 wt% gas, and 9.6 wt% solids. If all the chlorine in the oil/wax were formed from the degradation of PVC, then the chlorine content in the oil/wax of DKR-350 would be significantly lower than from the PVC-spiked experiment. Interestingly, 275 ppm Cl is present in the oil/wax (1350 ppm in solid product), which is again rather comparable to the chlorine concentration in the oil/wax from pyrolysis of a PVC-free DKR-350 feed, which is 226 ppm (1612 ppm in solid product). Thus, it implies that chlorines in PVC are predominantly eliminated as HCl during pyrolysis and do not react further to give organochlorines that end up in the oil/wax. The extent of organochlorine formation during pyrolysis seems thus independent from the amount of PVC present in DKR-350. Thermal degradation of PVC is thought to begin upon heating to ~200 °C, at which dechlorination occurs [23]. A second onset, affording HCl, tar, and a liquid fraction containing benzene as main side products, proceeds at temperatures about 360 °C [23]. A study by Miranda et al. showed that chlorine in PVC is completely removed at a temperature of 375 °C [35,36]. As such, mitigation of the formation of organochlorine components in the oil/wax consists of heating the plastic waste in the feeding system and recovering the HCl-rich gas before feeding the plastic melt to the reactor. Another approach involves the co-feeding of basic solids such as CaCO₃ to the reactor to trap and neutralize HCl, resulting in salt which is then removed together with the coke.

4. Conclusions

This first study on pyrolysis of DKR-350, a post-consumer mixed plastic waste stream, has provided useful information on the performance of this complex feedstock and the major challenges that need to be overcome before further development. After pyrolysis of unwashed and washed DKR-350 samples, it can be concluded that, while the washing procedure removed most of the ash and gas precursors, it did not significantly affect the oil/wax yield and composition. In all cases,

pyrolysis led to a high degree of cracking, i.e. a ~ 125 times reduction in molecular weight when going from the DKR-350 feed to the product. Interestingly, the aromatic/aliphatic ratio in the oil/wax is similar to the one present in the feedstock, indicating that aromatization products were not derived from the pyrolysis of the polyethylene and polypropylene fractions in the feed. This was also confirmed by pyrolysis experiments with LDPE, which under the conditions studied, did not yield any aromatic product.

However, despite a considerable reduction in molecular weight during pyrolysis, post-processing of the oil/wax product is still necessary before application, due to (1) its high molecular weight (only ~27% of the sample is in the boiling range of naphtha), (2) a high oxygen content (8–14%), and (3) a high chlorine content (>150 ppm).

A closer look at the fate of chlorine during pyrolysis of DKR-350 shows that the organochlorides present in the feedstock cannot be removed by washing to a large extent and end up in the oil/wax product. Most of the chlorides (salts) are removed by washing, leading to less HCl formation in the gas phase during pyrolysis. It seems that the presence of chloride salts (NaCl) in the feed is the most plausible cause of the formation of HCl when other sources of Cl (e.g., PVC) are not present in the feed.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2022.107304>.

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