Thermal pyrolysis of waste versus virgin polyolefin feedstocks: the role of pressure, temperature and waste composition

Mehrdad Seifali Abbas-Abadi[1], Marvin Kusenberg[1], Azd Zayoud[1], Martijn Roosen[2], Florence Vermeire[1], Sepehr Madanikashani[1,3], Maja Kuzmanović[1,4], Behzad Parvizi[1], Uros Kresovic[5], Steven De Meester[2], Kevin M. Van Geem[1,*]

[1] Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering & Architecture, Ghent University, B-9052 Zwijnaarde, Belgium;

[2] Laboratory for Circular Process Engineering (LCPE), Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, B-8500 Kortrijk, Belgium;

[3] Materials and Process Engineering (IMAP), Institute of Mechanics, Materials and Civil Engineering (iMMC), Université catholique de Louvain – Place Sainte Barbe 2, B-1348 Louvain-la-Neuve, Belgium;

[4] College of Polymer Science and Engineering, Sichuan University (Wangjiang campus), No.24 South Section 1, Yihuan Road, Chengdu, China, 610065;

[5] Indaver NV, Dijle 17 a, 2800, Mechelen, Belgium.

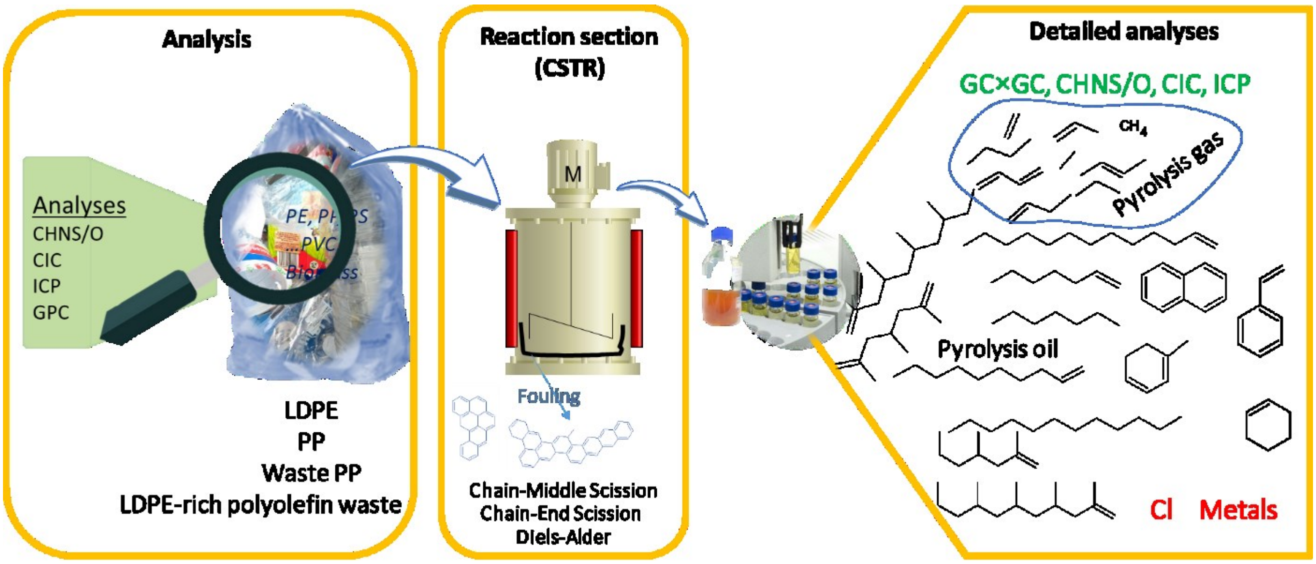
*Corresponding Author: Kevin.VanGeem@UGent.be

Abstract

Due to the complexity and diversity of polyolefinic plastic waste streams and the inherent non-selective nature of the pyrolysis chemistry, the chemical decomposition of plastic waste is still not fully understood. Accurate data of feedstock and products that also consider impurities is, in this context, quite scarce. Therefore this work focuses on the thermochemical recycling via pyrolysis of different virgin and contaminated waste-derived polyolefin feedstocks (i.e., low-density polyethylene (LDPE), polypropylene (PP) as main components), along with an investigation of the decomposition mechanisms based on the detailed composition of the pyrolysis oils. Crucial in this work is the detailed chemical analysis of the resulting pyrolysis oils by comprehensive two-dimensional gas chromatography (GC×GC) and ICP-OES, among others. Different feedstocks were pyrolyzed at a temperature range of 430-490 °C and at pressures between 0.1-2 bar in a continuous pilot-scale pyrolysis unit. At the lowest pressure, the pyrolysis oil yield of the studied polyolefins reached up to 95 wt.%. The pyrolysis oil consists of primarily α-olefins (37-42%) and n-paraffins (32-35%) for LDPE pyrolysis, while iso-olefins (mostly C_9 and C_{15}) and diolefins accounted for 84-91% of the PP-based pyrolysis oils. The post-consumer waste feedstocks led to significantly less pyrolysis oil yields and more char formation compared to their virgin equivalents. It was found that plastic aging, polyvinyl chloride (PVC) (3 wt.%), and metal contamination were the main causes of char formation during the pyrolysis of polyolefin waste (4.9 wt.%).

Keywords: Plastic Waste; Pyrolysis; Degradation Mechanism; Kinetic Study; comprehensive two-dimensional gas chromatography (GC×GC);

Graphical abstract



1. Introduction

Nowadays, plastic waste is an important global challenge that can endanger human civilization. Within the global production of plastics (~356 $Mt \cdot y^{-1}$), more than 50% is polyolefinic (Faraca and Astrup, 2019). Due to the substantial emission of greenhouse gases and the resulting climate changes, as well as due to disruption of ecosystems, plastic wastes should preferably not be incinerated, landfilled, or discarded into the environment (Cappucci et al., 2020; Nasri et al., 2022; Verma et al., 2016). To move to a circular economy and to achieve the waste-free environment from the sustainable development goals (SDGs) (Hák et al., 2016), efficient plastic waste recycling pathways are needed. Preferably, this should be closed-loop recycling, meaning that the recyclates can be used and then turned into a new product (or converted back to raw material) indefinitely without losing its properties during the recycling process (Jubinville et al., 2020; Lange, 2021; Vogt et al., 2021).

Over the last decades, mechanical recycling of plastics has been mostly implemented. Mechanical recycling begins with plastic sorting, and the next steps include washing, grinding, and granulating (extrusion) (Ragaert et al., 2017). The prepared raw materials are then used in various applications, potentially blended in different percentages with virgin plastics (Akash and Vasudevan, 2021; Briassoulis et al., 2013). Yet, mechanical recycling faces many challenges, such as the difficulty of dealing with the difference between polyolefin grades (melt flow index (MFI), flow rate ratio (FRR), and density) (Lase et al., 2022), various polymer alloys (Tonini et al., 2022), multilayer products (Salehi Morgani et al., 2021), plastic aging (Agboola et al., 2017), additives (Delva et al., 2018; Núñez et al., 2022), pigments (Antonopoulos et al., 2021), mineral fillers used (Eriksen et al., 2018), and contaminations (Abbas-Abadi et al., 2022b; Horodytska et al., 2018). The result is that recycled products often have a lower quality compared to virgin-based products (Mohammadi and Enayati, 2022), which is the reason why interest has been growing in the chemical recycling of plastics and, more specifically, for hydrocarbon-based polymers such as PE/PP in pyrolysis (Cao et al., 2022; Wan et al., 2022). This can be seen by the fact that the world's major petrochemical companies are trying to achieve high-value-added recycling strategies via the pyrolysis of polyolefins (Frediani and Frediani, 2021; Rodríguez et al., 2019). In this regard, several studies have already investigated the thermochemical conversion of polyolefins into light olefins that can be used as building blocks of virgin polymers (Eschenbacher et al., 2021; Eschenbacher et al., 2022).

If mechanical recycling of plastics is not feasible due to any reasons, chemical recycling can be an efficient alternative. Chemical recycling involves various techniques such as pyrolysis, solvolysis, and gasification. The efficiency of these methods depends on the polymer structure and its level of purity. Pyrolysis is widely recognized as a more productive method for recycling polyolefins, yielding more valuable products than other approaches (Kim et al., 2022; Park et al., 2022; Yang et al., 2022). Hence, thermal pyrolysis is mostly applied to produce pyrolysis oil from polyolefins at moderate pyrolysis temperatures (400-500 °C) (Kusenberg et al., 2022b; Kusenberg et al., 2022e). Pyrolysis oils can then subsequently be converted to light olefins, for instance, in a steam cracker. Elordi et al. (Elordi et al., 2011) performed thermal pyrolysis of PE in a conical spouted bed reactor (CSBR) at a temperature of 500-700 ºC. At 500 °C, the main product (67 wt.%) was wax, while with increasing temperature, the produced wax dropped sharply to 12 wt.% with an increase in lighter liquid products. At a temperature of 700 °C, gas (C_1-C_4), a light liquid (C_5-C_{11}), and a heavy liquid (C_{12}-C_{21}) were produced with yields of 40, 33, and 15 wt.%, respectively. Furthermore, the light olefins (C_2-C_4) and paraffins (C_1-C_4) produced were close to 38 and 2 wt.%, respectively. The effect of the total pressure was not studied.

The pressure has two competing effects during polyolefin pyrolysis. Firstly, an increased pressure leads to an increase of the boiling point of hydrocarbons (Avaullee et al., 1997) and consequently longer residence time of liquid pyrolysis products in the reactor. Secondly, it results in an increase in the concentration within the reactor atmosphere, causing more molecular collisions and intensification of bimolecular reactions. Increasing the residence time and the gas concentration simultaneously leads to the intensification of chain scission and Diels-Alder reactions (Abbas-Abadi et al., 2023; Cheng et al., 2020). Consequently, increasing the pressure should lead to lighter products with higher relative fractions of naphthenes and aromatics, along with more coke formation (Cheng et al., 2020). For example, for LDPE, a broad pressure range (1-51 bar) was investigated by Cheng et al. (Cheng et al., 2020), resulting in the production of more cyclic and nonlinear hydrocarbons. Yet, whereas these studies give a good first impression on the effect of certain parameters, they lack a clear deeper analysis of the process chemistry, the effective degradation mechanisms, and the influence of the feedstock structure on pyrolysis products.

Polyolefin pyrolysis has been studied by several people who studied the pyrolysis products under different process parameters as mentioned in the previous paragraphs. However, individual aspects that are influencing the pyrolysis yields such as structural parameters of polyolefins and their effect on the decomposition chemistry, as well as the role of contaminants has not yet been fully understood.

To close this important knowledge gap, in this paper, polyolefins, including virgin-grade PP and LDPE, end-of-life PP and LDPE-rich polyolefins were fully characterized using Gel permeation chromatography (GPC), inductively coupled plasma – optical emission spectrometry (ICP-OES), combustion ion chromatography (CIC) and CHNS/O. Consequently, the effect of temperature (430-490 °C) and pressure (0.1-2 bar) on the polyolefins pyrolysis has been studied experimentally in a continuous pilot-scale unit. Furthermore, the pyrolysis products were analysed by two-dimensional gas chromatography (GC×GC), ICP, CIC, and CHNS/O and optimized using Minitab software. The complete analysis of pyrolysis products and structural data of polyolefins has led to valuable information in the field of polyolefins pyrolysis. Detailed analysis of feedstocks and products led to the unraveling of valuable mechanisms in the field of PP pyrolysis, as well as the influence of contaminations such as PVC on secondary reactions and coke formation. Finally, the molar distribution of the products was studied to evaluate the influence of the scission of polyolefin chains. This work thus aims to help understand the challenges of industrialization of the polyolefin pyrolysis process, especially aiming towards increased yield of the plastic waste to olefins pathway.

2. Materials and Instruments

2.1. Materials

Materials used in this study were the injection grade of PP HE125MO (homopolymer) purchased from the Borealis group and the film grade of LDPE LD 150 Series grade (ExxonMobil). The PP and LDPE-rich polyolefin waste fractions were provided by ECO-oh! (Belgium).

The GC×GC analytical gases with a minimum purity of 99.999 %, including nitrogen, hydrogen, helium, air, oxygen, and carbon dioxide, were purchased from Air Liquide (Belgium). CS_2 (Sigma-Aldrich, Belgium), with a purity of over 99%, was applied in different ratios to dilute the pyrolysis oils before GC×GC analyses. 3-chlorothiophene (>96 %, Sigma-Aldrich, Belgium) was applied as a suitable internal standard in the GC×GC analyses.

2.2. Instruments and Methods

To pyrolyze polyolefins, a continuous pilot-scale unit was used which was characterized in earlier work (Zayoud et al., 2022). The unit consists of three main sections, namely, feeding (utilizing an extruder), a reaction section using a continuous stirred tank reactor (CSTR) of 5.7 L (1.5 gallons) volume (Parr reactor, Model: 4584, U.S.A), and finally a condensation section (Figure 1). The reactor conditions are controlled through a PC (Figure 1, 3) using SpecView software and a PID controller. The reactor is also equipped with three K-type thermocouples, a stirrer, shaft magnetic coupling, a manometer, and a pressure transducer. Furthermore, a flexible graphite gasket with a maximum operating temperature of 500 °C was applied in the Parr CSTR. A single-screw extruder (Model: LE25-30/CV, LabTech, Thailand) with a feeding rate range of 0.1–10 $kg \cdot h^{-1}$ and an operating temperature range of 140-260 °C, and motor speed range of 50-70 rpm was applied to achieve the desired feeding rate (Figure S1). The temperature of the condensers is controlled by using an external LAUDA cooler (Figure 1, 7) (RE 420 G, Germany). The outlet of the third condenser is connected to a three-way valve which directs the off-gasses either to a back-pressure regulator (Figure 1, 8) (EQUILIBAR, U.S.A) or a vacuum pump (Figure 1, 9) (KNF, SC 920G, Germany). Experiments were performed in a pressure range of 0.1- 20 bar using a vacuum pump in case of vacuum experiments or a back pressure regulator in case of pressurized experiments to control the reactor operating pressure. The stirrer speed in the CSTR was optimized and set at 500 rpm to provide uniform mass and heat transfer. Based on our previous work (Abbas-Abadi, 2021), the range of temperature (430-490 °C) and pressure (0.1-2 bar) was applied to obtain the maximum pyrolysis oil yield with minimum energy consumption for the virgin plastics. Furthermore, to study plastic aging and contamination, the pyrolysis of LDPE-rich polyolefin waste and waste PP was investigated at 450 °C and 1 bar as suitable application conditions in terms of energy consumption and maximum liquid production (Abbas-Abadi et al., 2022b).

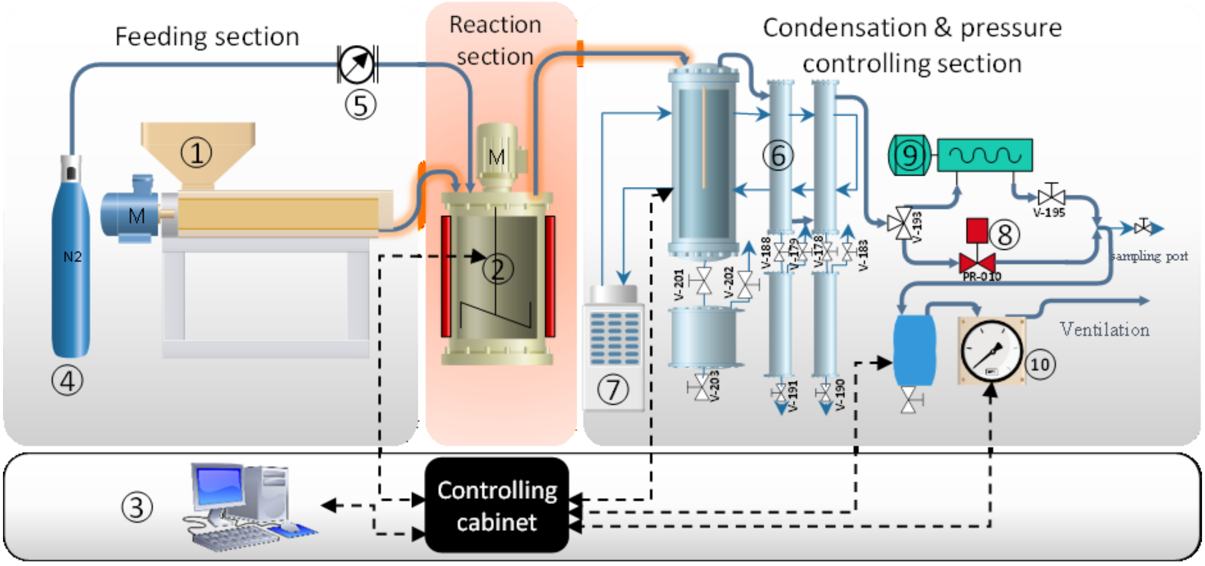


Figure 1. Pilot unit: (1) feeding system (extruder), (2) CSTR, (3) Control board, (4) Nitrogen, (5) The flow controller of nitrogen, (6) The condensation section, (7) Oil circulator, (8) back pressure (9) vacuum pump, (10) flowmeter.

The condensation section utilizes a LAUDA cooler (RE 420 G, Germany) to condense the evaporated products and collect the condensed products while the gaseous products were vented. The pyrolysis oils were in the form of semi-solid wax with varying viscosity depending on the pressure and temperature. Based on the optimization, the temperature of the first condenser was set to 40-85 °C to avoid condensed pyrolysis wax blocking the downstream tubes. In order to capture a maximum amount of condensable product, the temperature of the next condensers was set at 20 °C. A volumetric drum-type gas flowmeter (Ritter, TG3/1-1bar, Germany) was applied to measure the outlet gas flow. The remaining char residue, including coke and minerals, was collected after the experiment and weighed separately. All pipes and fittings (Swagelok, U.S.A.) were made of stainless steel 316.

2.3. Analytics

2.3.1. Comprehensive two-dimensional gas chromatography (GC×GC)

A comprehensive two-dimensional GC×GC was applied to characterize the detailed composition of the produced pyrolysis oils. An Mxt-1 column (60 m × 0.25 mm × 0.25 µm) and a ZB-35HT column (2.2 m × 0.18 mm × 0.18 µm), both temperature resistant up to >400 °C, were applied in the GC×GC instrument as the first and second columns, respectively (Interscience, Belgium). A cryogenic modulator (liquid CO_2) and the columns were placed in a single oven with a uniform temperature profile. The outlet of ZB-35HT column was connected to a quadrupole mass spectrometer (qMS) for qualitative analysis or to a flame ionization detector (FID) for quantitative analyses. The GC×GC performance is based on the boiling point and polarity separation in the first and second columns, respectively. In previous work, the performance of the GC×GC instrument has been thoroughly discussed (Abbas-Abadi et al., 2022b). A detailed overview of the used analysis method including heating ramps, modulation times and others can be found in Table S1 in the supporting information (SI).

2.3.2. Halogen analysis

According to the standard method of EN 14582, CIC was applied to analyze the halogen content of the polyolefin feedstocks. The ASTM standard D6470–99 was applied to analyze the halogen content of the pyrolysis oils. An ion chromatography setup (930 Compact IC Flex, Metrohm, Switzerland), equipped with a Metrosep A Supp 7-250/4.0 column (250 x 4.0 mm) and conductivity detector, was applied to measure the halogen concentrations in the final solution. Linear calibration curves using 5 standard solutions in the range of 0 and 50 ppmw of the analytes of interest were used to quantify the halogen concentration.

2.3.3. Metal analysis

The inductively coupled plasma–optical emission spectrometry (ICP-OES) on a Thermo Scientific iCAP 7200 model, equipped with Qtegra Software (Thermo Scientific iCAP 7000 Plus Series ICP-OES, Thermo Fisher Scientific Brand, USA) and a CETAC AXP 560 autosampler (Teledyne Technology, USA) were applied to analyze the metal content in plastic and pyrolysis oils. For the calibration ranging from 0.001 to 20 ppmw, standards were prepared using Certipur multi-element standard solutions (100 mg/l in 10 % nitric acid) containing Ca, Fe, K, Al, Pb, Cd, Ti, Co, Be, Cu, Mg, Sr, Li, Sb, Se, Tl, Zn, Ni, As, Mo, Mn, V, Hg, Cr, Na, and Si. An Anton Paar (Austria) Multiwave 5000 microwave oven equipped with a 20 SVT-rotor and PTFE-TFM digestion vessels was applied to digestive the studied samples (0.50 ± 0.05 g) before ICP-OES experiments. Subsequently, 10.0 ml of concentrated nitric acid (70 %, Sigma Aldrich) and 3.0 mL of distilled water were mixed with the weighed sample. In the microwave oven, the vessels were heated up with 20 min ramping time up to a temperature of 200 °C and 15 min heating time. By using the double-distilled water, the samples were diluted after digestion to a volume of 50 mL. By using the same procedure, the blank experiments were done without the addition of a sample. Afterwards, the samples were completely filtered using a syringe filter (0.45 μm syringe filter, polypropylene filter media, CHROMAFIL). The limit of detection (LOD) and the limit of quantification (LOQ) were quantified by multiplying the standard deviation of the blank by 3 and 10, respectively. The LOD and LOQ values for the different methods are given in the SI.

2.3.4. Gel Permeation Chromatography (GPC)

An Agilent 1260 Infinity II High-Temperature GPC automated system equipped with a high-sensitivity refractive index, viscometer, light scattering detectors, and autosampler (40-position carousel) was applied to analyze the molecular specification of the polyolefins. By using GPC, the number average molecular weight (Mn), weight average molecular weight (Mw), and polydispersity index (PDI: Mw/Mn) have been reported. In previous work, the performance of the GPC instrument has been thoroughly discussed (Abbas-Abadi et al., 2022b).

2.3.5. CHNS/O

A Flash EA2000 elemental analyzer (Interscience, Belgium) equipped with a thermal conductivity detector (TCD) was applied to perform the CHNS/O analysis of plastic feedstocks and pyrolysis oils. In the combustion mode, C/H/N/S elements were determined according to the ASTM D 5291 standard method, while according to the ASTM D 5622, a separate reactor was used to determine the oxygen content in the pyrolysis mode.

3. Results and Discussion

3.1. Feedstock characterization

The studied polyolefins include virgin LDPE, virgin and waste PP, along with LDPE-rich polyolefin waste. The latter consisted mostly of LDPE films and foils packaging and smaller amounts of rigid HDPE and PP, working as a good example for a waste LDPE fraction. Furthermore, as it was a real post-consumer plastic waste fraction, other plastics types (e.g., polystyrene (PS), PVC, polyethylene terephthalate (PET)), biomass and minerals were also present in small amounts (Kusenberg et al., 2022e). The detailed elemental analysis was performed by different instruments such as CHNS/O analyzer, ICP-OES, and CIC. It showed a H/C ratio of virgin polyolefins (LDPE and PP) of about 0.166, while lower ratios have been reported for PP waste (0.160), and LDPE-rich polyolefin waste (0.155). Virgin polyolefins had a higher H/C ratio compared to waste polyolefins, probably due to the presence of double bonds and aromatics in the waste plastics (Abbas-Abadi et al., 2022b). Contaminations (e.g., PVC, PET, PS, and biomass), plastic aging, environmental degradation, and even thermo-mechanical degradation (extrusion) are the main roots of the decreased H/C ratio in polyolefin (Abbas-Abadi, 2021; Muñoz-Batista et al., 2022). By using the CIC instrument, the measured chlorine content in the LDPE-rich polyolefin waste fraction was found to be in the order of 18,000 ppmw, which can be related to the presence of PVC or salts. Using ICP-OES analyses, a sodium content of 1452 ppmw was detected. A considerable share of this sodium is related to sodium stearate, while the salt content is negligible (Zabihzadeh Khajavi et al., 2019). Furthermore, the chlorine content of PVC is ~58 wt.%, and taking into account the mentioned considerations, the PVC content of LDPE-rich polyolefin waste is approximately still 3 wt.%. The nitrogen (0.4 wt.%) present mainly belongs to biomass, nitrogen-containing polymers such as polyamides and polyurethanes, and other additives. The oxygen in waste PP (0.6 wt.%) and LDPE-rich polyolefin waste (1.6 wt.%) can originate from different sources, e.g., additives in plastics (antioxidants), fillers such as calcium carbonate ($CaCO_3$), polymeric impurities (e.g., PET), paper, and a variety of organic contaminants. Various pigments (e.g., titanium oxide (TiO_2)), additives (e.g., antioxidant, metal stearate, and other stabilizers), and fillers (e.g., $CaCO_3$, talc, silica, mica, etc.), as well as environmental contaminants (soil, moisture and etc.), were the main source of other metal and non-metal contaminants (Kusenberg et al., 2022e). The full analysis results of the waste feedstocks incuding a large range of metals can be found in Table S2 in the SI. Some elements are more visible in plastic contamination due to calcium carbonate (a widely used filler), soil, and aluminum foils which are used in many commercial plastic products (Kleinhans et al., 2021; Roosen et al., 2020). Moreover, in Table S3 in the SI, further characteristics of the studied feedstocks are given, including molecular weight, molecular weight distribution, and density (ρ). Typically, with an increase of branching or tertiary carbon atoms, the density of polyolefins decreases, and consequently, polyolefins with lower density are prone to degrade at lower temperatures.

3.2. Influence of pressure, temperature, and contaminants on the pyrolysis products

The effect of temperature and pressure have been studied because they affect the composition of the pyrolysis oil. Also the influence of real-waste contaminants were studied and benchmarked against virgin material.

3.2.1. Pyrolysis mass balance

The pyrolysis products include pyrolysis oil (condensed hydrocarbons), gas (non-condensable products), and char (coke and minerals). As seen in Figure S2, the pyrolysis oil yields (virgin LDPE: 94.8-87.8 wt.%, virgin PP: 95.2-86.1 wt.%) decreased, while the amounts of gas (virgin LDPE: 4.9-11.6 wt.%, virgin PP: 4.6-13.4 wt.%) and char (virgin LDPE: 0.3-0.6 wt.%, virgin PP: 0.2-0.5 wt.%) increased with increasing pressure and temperature in the studied ranges. In the pyrolysis of polyolefins, any factor that leads to the intensification of chain scission reactions (temperature) and increasing the residence time (pressure) can increase the number of chain breaks and reduce the amount of liquid produced (Abbas-Abadi et al., 2022b). The detailed mass balances for every experiment are shown in Figure S2 in the SI. It is known that higher temperatures favor chain scissions over abstractions, resulting in lighter products, including more non-condensable gas. Furthermore, as the pressure increases, the residence time inside the reactor increases for the heavier products because it becomes more challenging to move from the liquid to the gas phase. This leads to more chain scissions and gas production. Moreover, in the lower temperature and pressure ranges, bimolecular and secondary reactions are not expected to be very effective as found in our previous study (Abbas-Abadi et al., 2022b). Coke formation in pyrolysis of virgin plastics was found to be less than 0.6 wt.%. However, with increasing temperature and pressure, coke formation increased. With the increase in gas production, which is mainly composed of light olefins and dienes, the necessary conditions are provided for intensifying Diels-Alder reactions and the formation of cyclic hydrocarbons. As the carbon number of olefins increases, their reactivity tends to decrease. Hence, light olefins have a higher tendency to participate in secondary reactions compared to heavier ones. In other words, more chain scissions indirectly lead to higher amounts of naphthenes and (poly)aromatics (Abbas-Abadi et al., 2022a; Abbas-Abadi et al., 2023; Green and Sadrameli, 2004). Furthermore, increasing the temperature and pressure affects the kinetics and the diffusion. The pressure as such plays a crucial role in increasing bimolecular reactions and intensifying coke formation.

In addition, contour plots were created to perform a complete evaluation of the carbon range of the pyrolysis products as function of pressure and temperature. The results of the studies, as shown in Figure 2 indicate almost the same trend for the pyrolysis products of LDPE and PP. As can be seen, with increasing temperature and pressure, the pyrolysis oil decreased step by step. In other words, pyrolysis products became lighter, and at the same time, the pyrolysis gas and coke increased. This was seen both for LDPE and for PP.

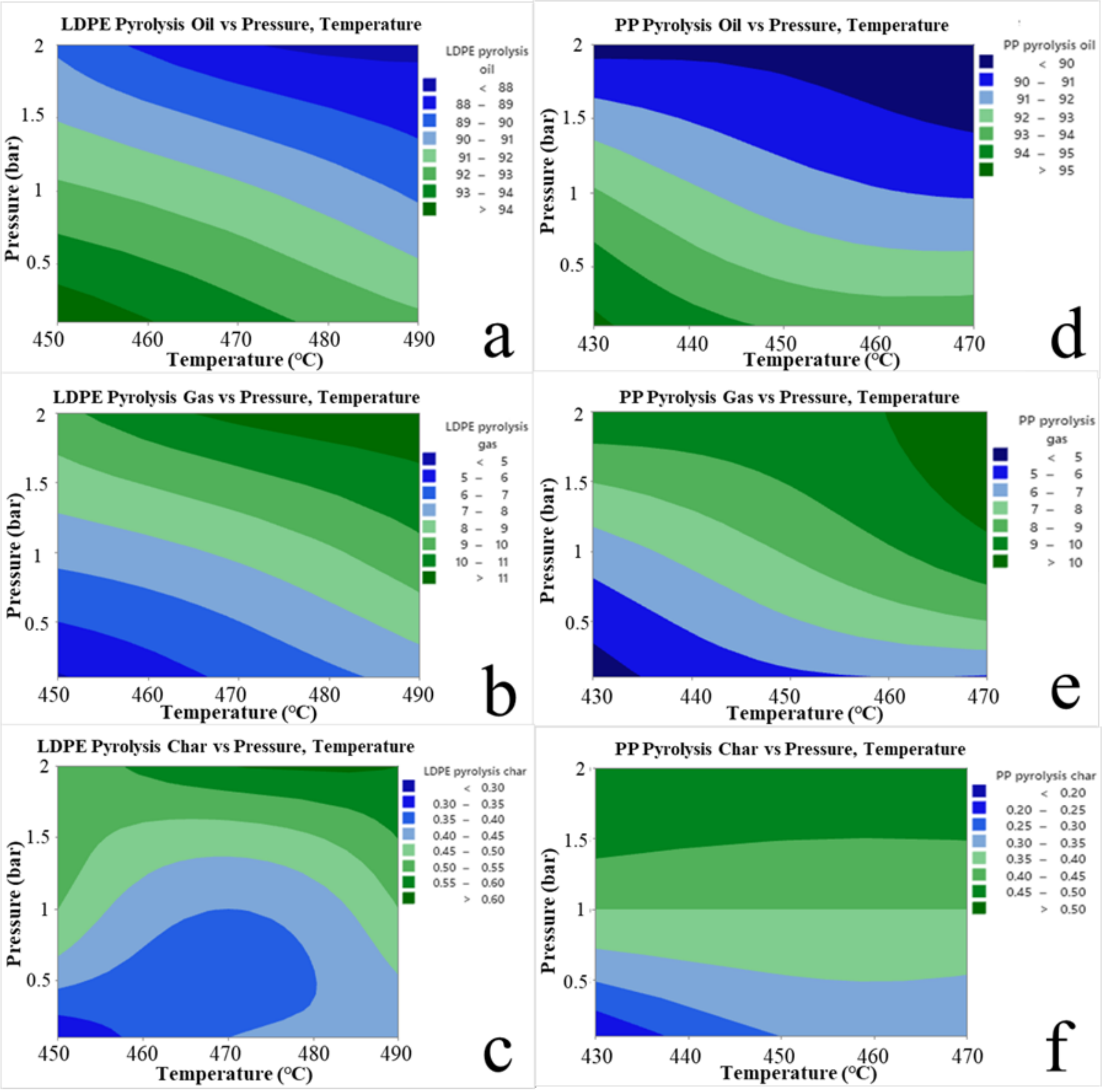


Figure 2. The contour plots of the yield (wt.%) of different pyrolysis products (oil, gas, and char) of virgin LDPE and PP based on temperature (°C) and pressure (bar).

Compared to virgin polymers, polyolefin waste materials are expected to have lower thermal stability because of an increased content of double bonds and oxygen due to aging effects and contamination. This has led to a higher number of chain scission compared to virgin plastic (Ammala et al., 2011). Furthermore, it is known that organic and inorganic contaminants might reduce the pyrolysis oil yield (Kusenberg et al., 2022e). Experiments with waste PP and LDPE-rich polyolefin waste at similar conditions (450 °C and 1 bar) show a significant reduction in pyrolysis oil yield to 85.7 wt% and 84.4 wt%, respectively.

Another important aspect of plastic waste pyrolysis is the tendency for char formation of a given feedstock. In fact, the char residue consists of two parts: coke and mineral compounds (Sharuddin et al., 2016). In the PP waste, considering the 6500 ppm of metallic and quasi-metallic elements that are present as oxides or chemical salts, such as $CaCO_3$, iron oxide, TiO_2, etc. (Kusenberg et al., 2022e), approximately 1.6 wt.% ± 0.2 of mineral compounds were present in the remaining char. Since the remaining char of PP waste was 2.8 wt.%, consequently, the coke formed was around 1.2 wt.% ± 0.2. Since PVC made up around 3 wt.% of the LDPE-rich polyolefin waste, a significant portion of the coke formation is associated with the remaining PVC substrate during degradation (Figure S3). In general, some MPO contaminations such as PVC and biomass release heterogeneous atoms as H_2O and HCl, leading to the formation of an unstable radical substrate during decomposition. Subsequently, the remaining substrate reacts with styrene and light olefins and results in the intensification of the coke formation (Abbas-Abadi et al., 2023; Abbas-Abadi et al., 2021). Hence, the measured char formation in LDPE-rich polyolefin waste pyrolysis (4.9 wt.%) compared to waste PP (2.8 wt.%) can be attributed to a combination of plastic aging (more double bonds), the presence of a PVC residue, and organic and mineral contaminations.

As the β-scission in the vicinity of tertiary carbon requires less energy, consequently, PP requires less energy than PE to crack, and hence degrades at lower temperatures (Aboulkas et al., 2010). The lower activation energy of PP degradation leads to the shorter residence time of PP chains in the semi-batch reactor compared to PE. Lower residence time inside the reactor and more steric hindrance in PP chains (due to methyl side groups) lead to the reduction of bimolecular and cyclic reactions, resulting in less coke formation in PP pyrolysis compared to LDPE pyrolysis. Furthermore, in the studied ranges, shorter residence times with lower selected temperature ranges for the PP pyrolysis have resulted in the production of (partially) more pyrolysis oil compared to LDPE.

3.2.2. The carbon molar distribution of pyrolysis products

Figure 3 (a, b) indicates the impact of pressure and temperature on the carbon mole (C·mol.%) distribution of virgin LDPE, LDPE-rich polyolefin waste and PP (virgin and waste) pyrolysis oils. The molar distribution of the pyrolysis oil can be a function of the products distribution depending on the number of chain scission reactions. In PP pyrolysis, the β-scission leads to primarily propylene oligomers, which can be clearly seen in Figure 3b.

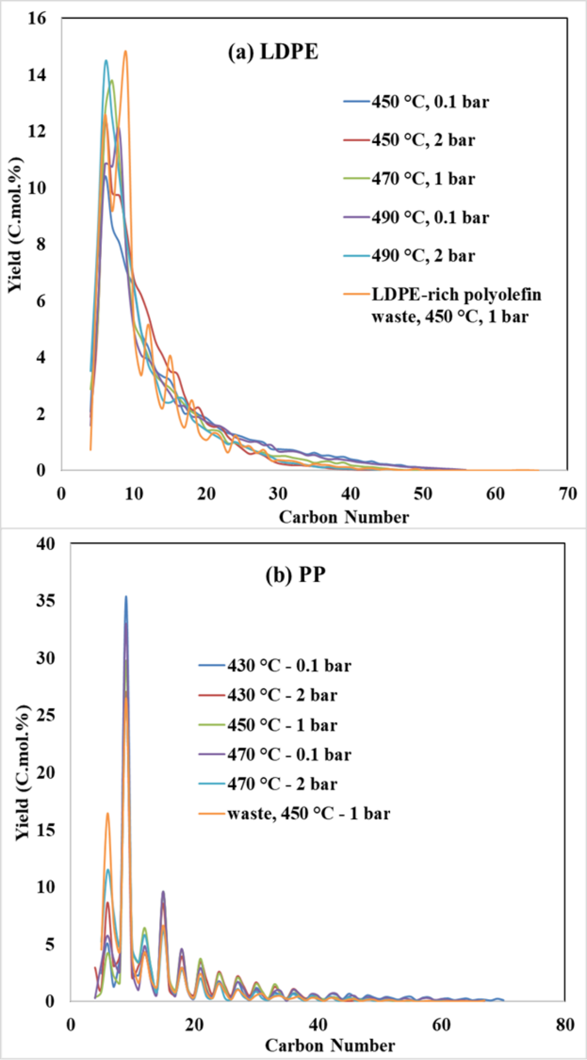


Figure 3. The carbon moles distribution of the pyrolysis oils of waste and virgin (a) LDPE and (b) PP under different pressure (bar) and temperature (°C) conditions.

C$_9$-hydrocarbons (26-35 C·mol.%) make up a significant portion of the pyrolysis oil, and in particular the propylene trimer. In contrast, the LDPE pyrolysis oil has a more uniform molar distribution. The results further indicate that the C$_6$-C$_9$ (41-53 C·mol.%) components had a major share in the LDPE pyrolysis oils. The LDPE-rich pyrolysis oil followed an intermediate trend between PE and PP pyrolysis. It contained small amounts of PP and the C$_6$-C$_9$ range accounted for the largest molar share of the products. In addition, the results indicate that the chain scission was intensified with increasing pressure and temperature, which resulted in lighter pyrolysis LDPE C$_{av}$ (average molecular weight): 20.5-14.7;

PP C_{av}: 26.8-19.9). Table 1 presents the distribution of pyrolysis products based on the number of carbon moles. Around 30-44 C·mol.% of LDPE pyrolysis products and 30-49 C·mol.% of PP pyrolysis products include C_1-C_5 which were increased by raising the temperature and pressure in the studied ranges. Furthermore, compounds in the C_6-C_{12} range accounted for ~38-41 C·mol.% and 31-40 C·mol.% of LDPE and PP pyrolysis products, respectively. Easier and faster rotation at the end of the chain raises the energy level at the end C-C bonds, and therefore chain-end scissions are more likely to occur compared to chain-middle scissions. Since light dienes and α-olefins are effective in the formation of naphthenes and (poly)aromatics (Abbas-Abadi et al., 2022b), consequently, the share of chain-end scission should be higher than the measured values. C_{21+} products, which were in the waxy hydrocarbons range, accounted for a smaller molar share of LDPE (6-14 C·mol.%) and PP (7-16 C·mol.%) pyrolysis products, although regarding their high molecular weight, they play a significant role in the physical properties of pyrolysis oils. Furthermore, the presence of double bonds and chain defects in the waste PP (C_{av}: 19.5) and LDPE-rich polyolefin waste (C_{av}: 15.9) has resulted in a lower thermal stability (Singh et al., 2019) and more chain scissions compared to virgin polyolefins.

Table 1. Hydrocarbon composition of the pyrolysis oils measured using GC×GC-FID.

Polymer type		T(°C)	P(bar)	C_1-C_5 (C·mol.%)	C_6-C_{12} (C·mol.%)	C_{13}-C_{21} (C·mol.%)	C_{21+} (C·mol.%)
LDPE	Virgin	450	0.1	30	41	15	14
	Virgin	450	2	39	40	12	9
	Virgin	470	1	38	41	12	9
	Virgin	490	0.1	37	38	13	12
	Virgin	490	2	44	40	10	6
	Waste	450	1	45	39	10	6
PP	Virgin	430	0.1	30	40	14	16
	Virgin	430	2	45	31	11	13
	Virgin	450	1	38	33	14	15
	Virgin	470	0.1	34	38	13	15
	Virgin	470	2	49	35	9	7
	Waste	450	1	47	36	9	8

3.2.3. Pyrolysis oil quality assessment

Ideally pyrolysis oils should consist mostly of paraffinic compounds if they would serve as feedstock for the petrochemical industry and in particular steam crackers. During the breaking down olefins and diolefins, there is a significantly greater likelihood of butadiene being generated as the primary substrate for Diels-Alder reactions compared to paraffins. This results in a substantial increase in the formation rate of (poly)aromatics. (Abbas-Abadi et al., 2023; Kusenberg et al., 2022b). To study the resulting pyrolysis products in detail, a GC×GC characterization was performed. As an example, Figure S4 in the SI shows GC×GC-FID chromatograms related to the pyrolysis oils of waste PP, LDPE-rich polyolefin waste and virgin LDPE. The detailed results of the pyrolysis oil analyses using GC×GC-FID are shown in Table 2. The hydrocarbon composition is structured along the respective hydrocarbon families paraffins, olefins, iso-olefins, isoparaffins, diolefins, naphthenes, aromatics (PIONA), total linear hydrocarbons, total non-linear hydrocarbons and total cyclic hydrocarbons. The results clearly show the effect of pressure and temperature on the different hydrocarbon types of pyrolysis oil.

Table 2. The different components of the polyolefin pyrolysis oils quantified using GC×GC-FID.

Polymer type		T(°C)	P (bar)	O (%)	P (%)	IO (%)	IP (%)	D (%)	N (%)	A (%)	L (%)	NL (%)	C (%)
LDPE	Virgin	450	0.1	40.7	34.6	4.0	2.6	12.9	4.9	0.3	88.2	6.6	5.2
	Virgin	450	2	37.9	33.8	6.0	2.9	8.7	8.5	2.2	80.4	8.9	10.7
	Virgin	470	1	40.7	32.1	5.2	4.0	10.3	5.5	2.2	83.1	9.2	7.7
	Virgin	490	0.1	41.9	33.4	3.5	2.3	12.3	5.8	0.8	87.6	5.8	6.6
	Virgin	490	2	37.6	33.5	4.3	3.4	8.3	9.1	3.8	79.4	7.7	12.9
LDPE-rich polyolefin	Waste	450	1	23.0	19.5	20.2	4.6	14.4	7.1	11.2	47.5	34.2	18.3
PP	Virgin	430	0.1	0.3	0.4	69.6	6.7	21.0	1.8	0.2	0.7	97.3	2.0
	Virgin	430	2	1.1	0.9	66.7	7.9	18.1	4.5	0.8	2.0	92.7	5.3
	Virgin	450	1	0.9	0.8	69.5	5	19.3	4.1	0.4	1.7	93.8	4.5
	Virgin	470	0.1	0.6	0.3	70.4	5.9	19.9	2.7	0.2	0.9	96.2	2.9
	Virgin	470	2	0.8	0.8	67.4	5.6	19.6	4.9	0.9	1.6	92.6	5.8
	Waste	450	1	0.9	1.3	68.3	4.8	18.6	5.2	0.9	2.2	91.7	6.1

O: Olefin; P: Paraffin; IO: Iso-olefin; IP: Isoparaffin; D: Diolefin; N: Naphthene; A: Aromatic; L: Linear hydrocarbons NL: Nonlinear hydrocarbons; C: Cyclic hydrocarbons.

The obvious difference between LDPE and PP pyrolysis products indicates how much the polyolefin structure can affect the composition of the pyrolysis oil. Olefins (37.6-41.9 wt.%) and paraffins (32.1-34.6 wt.%) were the main components of LDPE pyrolysis oils. Iso-olefins (66.7-70.4 wt.%) and diolefins (18.1-21.0 wt.%) accounted for about 90 wt.% of PP pyrolysis oils. However, to better evaluate the impact of pressure and temperature on the main pyrolysis oil components, the contour plots of α-olefin and n-paraffin for LDPE and iso-olefins and diolefins for PP are shown in Figure 4. According to the optimization findings, during LDPE pyrolysis, reducing pressure leads to an increase in linear products, whereas raising temperature results in more olefins being produced and a reduction in paraffins. Conversely, in the case of PP pyrolysis, lowering the pressure causes an increase in the amounts of isoolefin and diolefin, while raising the temperature results in an increase in isoolefin and a decrease in diolefin.

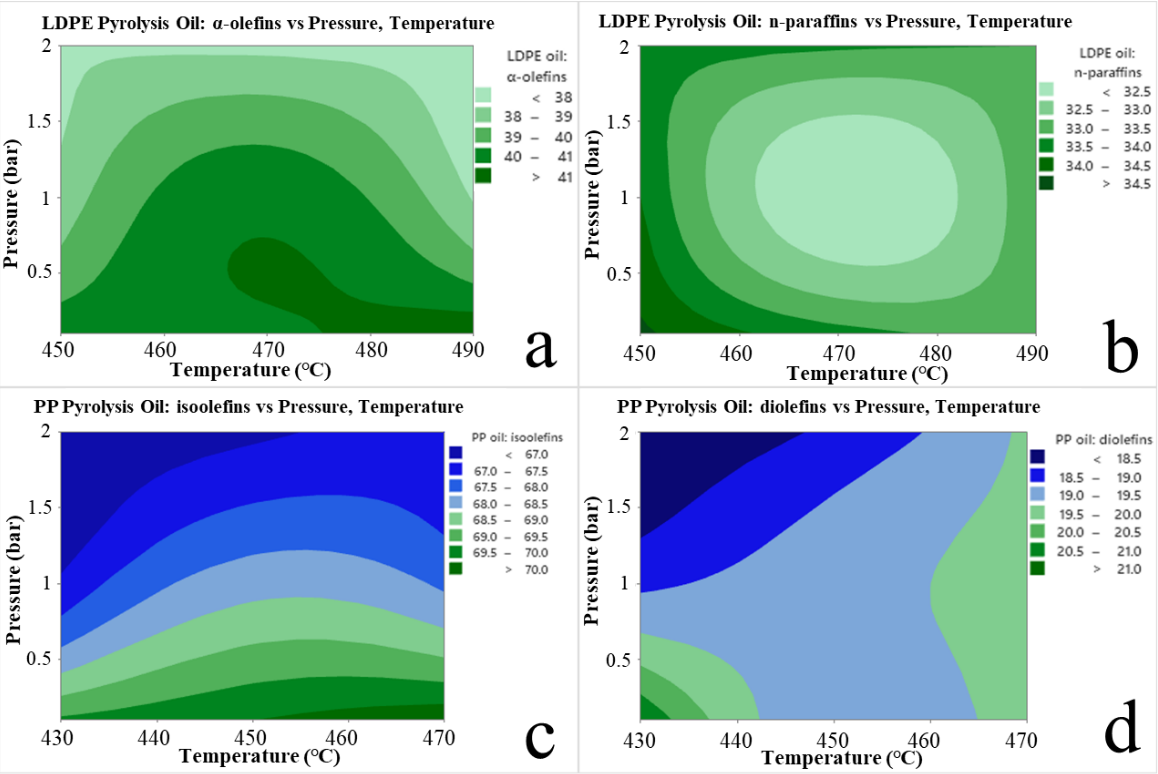


Figure 4. The contour plots of (a) LDPE α-olefins, (b) LDPE n-paraffins, (c) PP isoolefins and (d) PP diolefins based on temperature (°C) and pressure (bar).

In general, at a moderate range of temperature (400-500 °C) and pressure (0.1-2 bar), the impact of the polyolefin structure on the pyrolysis oil composition is stronger than the effect of process parameters investigated. This is due to the impact of chain scission and of the trade-off between unimolecular reactions and bi-molecular ones. Under the studied conditions, the results showed that with increasing pressure and temperature, the amount of linear components (L: 88.2-79.4%) in LDPE pyrolysis oil has decreased, while an increase in cyclic hydrocarbons (C: 5.2-12.9%) could be observed. In PP pyrolysis oil, C_{12} (15.7-18.9%) and C_{15} (6.9-9%) iso-olefins were the main products, which are the tetramer and pentamer of propylene, respectively. Furthermore, the tendency to undergo selective β-scission is clearly noticeable and propylene oligomers (C_{3n}) accounted for more than half of the products (as shown in Figure S5 (a) in the SI). β-scission of C_{3n+1} oligomers form diolefins and those are the largest group in the pyrolysis oil after iso-olefins. Given that the PP structure is 90-95% isotactic and the rest is atactic (Barabanov et al., 2021), the placement of even one methyl group in atactic form can lead to different stereo-isomers. This is why, for example, for each isoolefin and/or diolefin, several peaks were observed close to each other in the GC × GC chromatogram (see Figure S4 in the SI) (Kusenberg et al., 2022e). It can be seen that the pyrolysis oil of PP waste was different compared to virgin PP as the amount of linear and cyclic hydrocarbons was slightly higher. The higher content of linear hydrocarbons in PP waste (2.2%) compared to virgin PP (0.7-2.0%) can be associated with a small percentage of PE in PP waste due to imperfect sorting. The increase of double bonds due to aging can be an additional factor in intensifying secondary reactions and producing more cyclic products in waste PP pyrolysis oil (6.1%) compared to virgin PP pyrolysis oil (2.0-5.8%). As expected, LDPE-rich polyolefin waste pyrolysis oil consisted of a mix of linear (47.5%), nonlinear (34.2%), and cyclic (18.3%) hydrocarbons. Due to the large presence of LDPE in the feedstock, a significant portion of the products was α-olefins and n-paraffins which is in line with the virgin LDPE pyrolysis oil composition. However, because of the presence of PP in the waste fraction, iso-olefins and isoparaffins were also detected in the oil. The amount of naphthenes in the pyrolysis oil was approximately equal to that expected from the pyrolysis of virgin PE, while the aromatics content was higher. From the aromatic compounds measured in the oil, styrene was the major compound. Close to 3 wt.% of the pyrolysis oil was styrene. Given that styrene can not be formed from the pyrolysis of polyolefins and PVC, it is proven that seems that 3% of the initial feedstock was PS.

Furthermore, Figure 5 presents the distribution of α-olefins and n-paraffins hydrocarbons of LDPE pyrolysis oil next to the iso-olefins and diolefins of PP pyrolysis oil, based on the carbon number in the studied ranges of pressure and temperature.

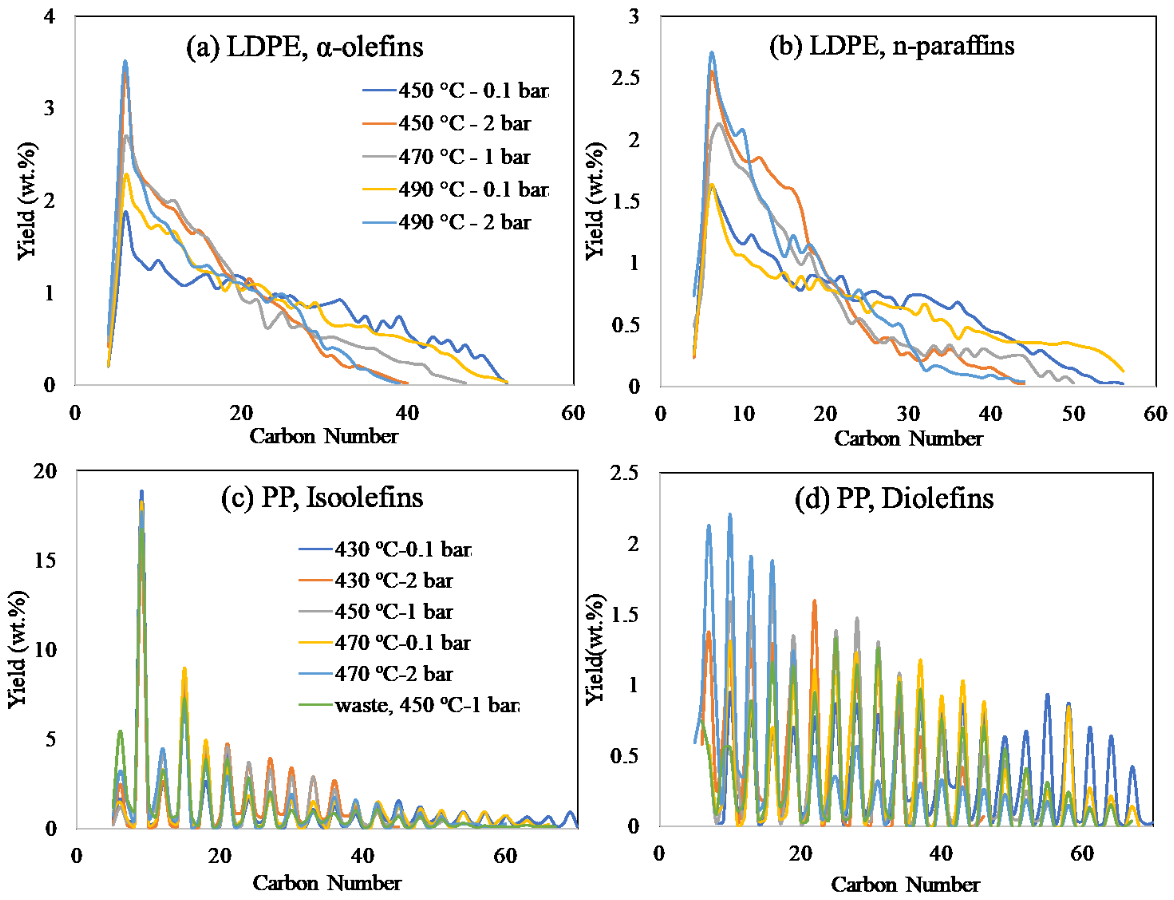


Figure 5. The yields of (a) LDPE α-olefins, (b) LDPE n-paraffins, (c) PP iso-olefins, and (d) PP diolefins versus carbon numbers.

Several conclusions can be drawn from these diagrams. In the virgin LDPE pyrolysis oil, the ratio of olefin/paraffin has decreased with increasing carbon number relatively. It seems that under random chain scission, mostly heavier radicals tend to form n-paraffins, while lighter radicals are prone to become α-olefins. In addition, the share of linear hydrocarbons has decreased with increasing pressure and temperature. As can be seen in Figure 5, for PP the iso-olefins and diolefins decreased with approximately a sinusoidal shape when the carbon number increases.

3.2.4. Elemental analysis of pyrolysis oil impurities

Since pyrolysis oil is preferably used for light olefin production in petrochemical plants such as steam crackers, a comprehensive study of pyrolysis oil quality is essential, with special emphasis on contaminants. It has been shown recently that contaminants are the main bottleneck for steam cracking of plastic waste pyrolysis oils (Kusenberg et al., 2022c; Kusenberg et al., 2022d; Pernusch et al., 2022). Negative effects of contaminants in steam cracking range from severe corrosion (e.g., chlorine, calcium), to increased coke formation (e.g., iron), fouling of heat exchanger surfaces (e.g., calcium, silicon), irreversible depletion of reactor materials (e.g., sodium, lead) to severe downstream catalyst poisoning (e.g., lead, arsenic) (Kusenberg et al., 2022b; Sundaram and Stancato, 2018). These negative effects need to be considered with pyrolysis oils from real post-consumer plastic waste, as industrial companies who operate large-scale steam crackers strictly require high-quality feedstocks with ultra-low contaminant levels to be acceptable in the long run (Baumgartner et al., 2004; Sundaram and Stancato, 2018). Obviously, if the injection of pyrolysis oils into a commercial steam cracker leads to process related issues such as increased coke formation and consequently to a reduced time-on-stream of a steam cracking furnace, the economic penalties of such technical issues are substantial. Practically, these considerations are the main reason why steam cracking of pyrolysis oils has not been performed on a larger scale to this day. Metal and non-metal contaminants detected in the waste-derived oils are given in Table 3. Furthermore, known maximum allowable concentrations for industrial steam crackers are included as reported by (Baumgartner et al., 2004; Sundaram and Stancato, 2018).

Table 3. Impurity concentrations in the pyrolysis oils of PP and LDPE-rich polyolefin wastes inclucing the maximum allowable concentrations of industrial steam crackers (Baumgartner et al., 2004; Sundaram and Stancato, 2018).

Element	PP waste (ppm)	LDPE-rich polyolefin waste (ppm)	Industrial limit (ppm)
F	78.2	86.5	n.a.
Cl	164.4	1191.7	3
Ca	179.7	152.2	0.5
Zn	24.3	35.4	n.a.
Fe	66.3	67	1
Al	36.3	48.3	n.a.
Na	50.1	82.1	0.125
Li	0.1	0.2	n.a.
Mg	5.6	13	n.a.
Sb	<LOD	2.2	n.a.
Mn	0.3	0.7	n.a.
Cr	0.9	2	n.a.
As	3.5	3.1	0.005
Si	7.3	26	0.5-1
Sr	0.3	0.7	n.a.
Cd	0.1	<LOD	n.a.
Pb	<LOD	0.9	0.05-0.1

It is important to note that feedstock specifications of industrial steam crackers are set for fossil-based fuels such as naphtha. As pyrolysis oils are synthetic fuels stemming from a highly diverse feedstock that is plastic waste, it is obvious that more and different contaminants will be introduced into commercial steam crackers. Thus, specification values do not exist for elements that are typically not present in fossil-based fuels, but that are very likely present in pyrolysis oils such as aluminium, magnesium or zinc. This important knowledge gap requires additional research in order to evaluate the steam cracking feasibility of pyrolysis oils with full certainty. If in doubt, it is likely that steam cracking operators will reject pyrolysis oils due to unknown effects of certain contaminants that have not been encountered with fossil-based fuels.

The results presented in Table 3 show that large amounts of the impurities that were detected in the waste feedstocks transferred to the pyrolysis oils. The large chlorine content especially in the LDPE-rich polyolefin waste pyrolysis oil (1191.7 ppmw) can be partly attributed to the dissolution of HCl in pyrolysis oil or the formation of halogen containing hydrocarbons. Compared to the industrial threshold value of 3 ppm, it is obvious that the pyrolysis oils would not be acceptable for industrial steam crackers but that severe upgrading is required with thermal dehalogenation of the waste fractions being the most promising pathway (López et al., 2011; Wang et al., 2021). In terms of metals, the most important elements are silicon, calcium, zinc, iron, aluminium and sodium, which were detected in substantial amounts in the pyrolysis oils. Furthermore, the total metal concentration in LDPE-rich polyolefin waste pyrolysis oil was higher than the one in PP waste pyrolysis oil. This can be explained by the larger share of plastic films present in the LDPE-rich waste compared to the PP waste which contained more rigid plastics. Film fractions are known to contain more metals due to the larger amounts of inks and pigments (Roosen et al., 2020). In terms of the steam cracking feasibility, it is clear that both real-waste pyrolysis oils will cause substantial technical issues if no thorough upgrading is performed. Potential demetallization steps are hydrodemetallization, filtration, or solvent-based demetallization steps as elaborated in our recent review paper (Kusenberg et al., 2022a). Furthermore, distillation of pyrolysis oils would be a viable and relatively simple treatment step to remove the heaviest fractions that likely contain the highest amounts of metals (Wiriyaumpaiwong and Jamradloedluk, 2017).

4. Conclusions

In this work the effect of pressure, temperature, molecular structure, and the presence of contaminations of different polyolefin feedstocks on the pyrolysis process were studied. We evaluated virgin and waste feedstocks, including LDPE and PP. GC×GC-FID, GC×GC–qMS, CIC, ICP-OES, CHNS/O, and GPC analyses were applied to characterize the polyolefin feedstocks and the corresponding produced pyrolysis oils. Especially the pressure had a substantial influence on the amount of pyrolysis oil produced and its composition. In general, as temperature and pressure increase, more chain scissions occur resulting in lighter products and higher concentrations of olefins and conjugated dienes. More linear olefins also implies the formation of more acromatics and other secondary products and intensifying coke formation. However, due to the high steric hindrance in the isoolefin products of PP pyrolysis, the possibility of Diels-Alder reactions and the formation of cyclic products is significantly reduced compared to PE pyrolysis.

The results obtained with the polyolefinic waste showed that at low pyrolysis temperatures (< 500 °C), most of the polyolefin feedstock is degraded. For PP, around 90% of the pyrolysis oil consists of nonlinear iso-olefins and diolefins. Furthermore, the majority of iso-olefins were propylene oligomers. C_9 and C_{15} were the main components of PP pyrolysis oils in the studied ranges.

Regarding the presence of double bonds (from aging and contaminating other plastics such as PVC, biomass, and PS) in the waste polyolefin feedstocks, pyrolysis resulted in a lower pyrolysis oil yield with lighter products including more naphthenes and (poly)aromatics. PVC and biomass residues clearly result in increased coke formation. Furthermore, the metal content in the pyrolysis oil in the ppmw range can accelerate the coke formation and catalyst deactivation. Hence it was clear that without thorough upgrading, the obtained waste-derived pyrolysis oils are not feasible for petrochemical processes such as steam cracking as the most important process for light olefins production. It can be concluded that further in-depth investigation of the polyolefins structure, existing contaminations, and effective degradation mechanisms in the polyolefins pyrolysis is essential to improve our fundamental understanding of the technology and how to further improve it towards large-scale industrial application.

In general, depending on the final application of pyrolysis oil, including steam cracking feedstocks (requiring minimum olefin and cyclic components), it is possible to significantly change the PIONA composition with structural (e.g., feedstock, contaminations) and process (e.g., pressure, temperature, reactor type, residence time) parameters. A proper understanding of chemistry and degradation mechanisms and contaminations can pave the way for industrialization. Finally, any step that is taken in the field of the chemical recycling of plastics and prevents plastics from being deposited in landfills, incinerated, or discarded in the environment or oceans, will definitely meet the sustainable development goals (SDGs).

Author Contributions

Authors	Conceptualization	Methodology	Software	Validation	Writing - Original Draft	Writing - Review & Editing	Supervision
Mehrdad Seifali Abbas-Abadi	*	*	*	*	*	*	
Marvin Kusenberg		*		*		*	
Azd Zayoud	*	*		*		*	
Martijn Roosen		*				*	
Florence Vermeire			*			*	
Sepehr Madanikashani			*			*	
Maja Kuzmanović						*	
Behzad Parvizi		*				*	
Uros Kresovic		*					
Steven De Meester		*		*		*	
Kevin M. Van Geem	*	*		*		*	*

Acknowledgments

The research leading to these results has also received funding from the Fund for Scientific Research Flanders (FWO) and innovation program/ERC grant agreement no.818607 (OPTIMA). This work was also performed in the framework of the Catalisti cluster SBO project WATCH (HBC.2019.0001 "Plastic waste to chemicals"), PSYCHE project (Interreg France-Wallonie-Vlaanderen) and P2PC (Plastics to Precious Chemicals) with the financial support of VLAIO (Flemish Agency for Innovation and Entrepreneurship).

Declaration of competing interest

The authors declare no conflict of interest.

5. References

Abbas-Abadi, M.S., 2021. The effect of process and structural parameters on the stability, thermo-mechanical and thermal degradation of polymers with hydrocarbon skeleton containing PE, PP, PS, PVC, NR, PBR and SBR. Journal of Thermal Analysis and Calorimetry 143, 2867-2882.

Abbas-Abadi, M.S., Kusenberg, M., Shirazi, H.M., Goshayeshi, B., Van Geem, K.M., 2022a. Towards full recyclability of end-of-life tires: Challenges and opportunities. Journal of Cleaner Production 374, 134036.

Abbas-Abadi, M.S., Ureel, Y., Eschenbacher, A., Vermeire, F.H., Varghese, R.J., Oenema, J., Stefanidis, G.D., Van Geem, K.M., 2023. Challenges and opportunities of light olefin production via thermal and catalytic pyrolysis of end-of-life polyolefins: Towards full recyclability. Progress in Energy and Combustion Science 96, 101046.

Abbas-Abadi, M.S., Van Geem, K.M., Fathi, M., Bazgir, H., Ghadiri, M., 2021. The pyrolysis of oak with polyethylene, polypropylene and polystyrene using fixed bed and stirred reactors and TGA instrument. Energy 232, 121085.

Abbas-Abadi, M.S., Zayoud, A., Kusenberg, M., Roosen, M., Vermeire, F., Yazdani, P., Van Waeyenberg, J., Eschenbacher, A., Hernandez, F.J.A., Kuzmanović, M., 2022b. Thermochemical recycling of end-of-life and virgin HDPE: A pilot-scale study. Journal of Analytical and Applied Pyrolysis, 105614.

Aboulkas, A., El harfi, K., El Bouadili, A., 2010. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Conversion and Management 51, 1363-1369.

Agboola, O., Sadiku, R., Mokrani, T., Amer, I., Imoru, O., 2017. Polyolefins and the environment, Polyolefin Fibres. Elsevier, pp. 89-133.

Akash, M., Vasudevan, A., 2021. Experimental analysis of recycled thermoplastic material. Materials Today: Proceedings 45, 6198-6203.

Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P., Wong, S., Yuan, Q., Yu, L., Patrick, C., Leong, K., 2011. An overview of degradable and biodegradable polyolefins. Progress in Polymer Science 36, 1015-1049.

Antonopoulos, I., Faraca, G., Tonini, D., 2021. Recycling of post-consumer plastic packaging waste in the EU: Recovery rates, material flows, and barriers. Waste Management 126, 694-705.

Avaullee, L., Trassy, L., Neau, E., Jaubert, J.N., 1997. Thermodynamic modeling for petroleum fluids I. Equation of state and group contribution for the estimation of thermodynamic parameters of heavy hydrocarbons. Fluid Phase Equilibria 139, 155-170.

Barabanov, A.A., Vereykina, V.V., Matsko, M.A., Zakharov, V.A., 2021. Propylene polymerization over titanium–magnesium catalysts: The effect of internal and external stereoregulating donors on the number of active centers with different stereospecificity and their reactivity in propagation reaction. Journal of Catalysis 404, 187-197.

Baumgartner, A.J., Blaschke, M.W., Coleman, S.T., Kohler, R., Paxson, T.E., 2004. Feedstock Contaminants in Ethylene Plants - an Update, AIChE Spring National Meeting, Ethylene Producers Conference, New Orleans, Louisiana.

Briassoulis, D., Hiskakis, M., Babou, E., 2013. Technical specifications for mechanical recycling of agricultural plastic waste. Waste management 33, 1516-1530.

Cao, R., Zhou, R., Liu, Y., Ma, D., Wang, J., Guan, Y., Yao, Q., Sun, M., 2022. Research on the pyrolysis characteristics and mechanisms of waste printed circuit boards at fast and slow heating rates. Waste Management 149, 134-145.

Cappucci, G.M., Avolio, R., Carfagna, C., Cocca, M., Gentile, G., Scarpellini, S., Spina, F., Tealdo, G., Errico, M.E., Ferrari, A.M., 2020. Environmental life cycle assessment of the recycling processes of waste plastics recovered by landfill mining. Waste Management 118, 68-78.

Cheng, L., Gu, J., Wang, Y., Zhang, J., Yuan, H., Chen, Y., 2020. Polyethylene high-pressure pyrolysis: Better product distribution and process mechanism analysis. Chemical Engineering Journal 385, 123866.

Delva, L., Hubo, S., Cardon, L., Ragaert, K., 2018. On the role of flame retardants in mechanical recycling of solid plastic waste. Waste Management 82, 198-206.

Elordi, G., Olazar, M., Lopez, G., Artetxe, M., Bilbao, J., 2011. Product yields and compositions in the continuous pyrolysis of high-density polyethylene in a conical spouted bed reactor. Industrial & engineering chemistry research 50, 6650-6659.

Eriksen, M.K., Pivnenko, K., Olsson, M.E., Astrup, T.F., 2018. Contamination in plastic recycling: Influence of metals on the quality of reprocessed plastic. Waste Management 79, 595-606.

Eschenbacher, A., Goodarzi, F., Varghese, R.J., Enemark-Rasmussen, K., Kegnæs, S., Abbas-Abadi, M.S., Van Geem, K.M., 2021. Boron-Modified Mesoporous ZSM-5 for the Conversion of Pyrolysis Vapors from LDPE and Mixed Polyolefins: Maximizing the C2–C4 Olefin Yield with Minimal Carbon Footprint. ACS Sustainable Chemistry & Engineering 9, 14618-14630.

Eschenbacher, A., Varghese, R.J., Delikonstantis, E., Mynko, O., Goodarzi, F., Enemark-Rasmussen, K., Oenema, J., Abbas-Abadi, M.S., Stefanidis, G.D., Van Geem, K.M., 2022. Highly selective conversion of mixed polyolefins to valuable base chemicals using phosphorus-modified and steam-treated mesoporous HZSM-5 zeolite with minimal carbon footprint. Applied Catalysis B: Environmental 309, 121251.

Faraca, G., Astrup, T., 2019. Plastic waste from recycling centres: Characterisation and evaluation of plastic recyclability. Waste Management 95, 388-398.

Frediani, P., Frediani, M., 2021. Mixed or Contaminated Waste Plastic Recycling through Microwave-Assisted Pyrolysis, Recent Perspectives in Pyrolysis Research. IntechOpen.

Green, A.E.S., Sadrameli, S.M., 2004. Analytical representations of experimental polyethylene pyrolysis yields. Journal of Analytical and Applied Pyrolysis 72, 329-335.

Hák, T., Janoušková, S., Moldan, B., 2016. Sustainable Development Goals: A need for relevant indicators. Ecological indicators 60, 565-573.

Horodytska, O., Valdés, F.J., Fullana, A., 2018. Plastic flexible films waste management – A state of art review. Waste Management 77, 413-425.

Jubinville, D., Esmizadeh, E., Saikrishnan, S., Tzoganakis, C., Mekonnen, T., 2020. A comprehensive review of global production and recycling methods of polyolefin (PO) based products and their post-recycling applications. Sustainable materials and technologies 25, e00188.

Kim, S., Kim, Y.T., Oh, L.S., Kim, H.J., Lee, J., 2022. Marine waste upcycling—Recovery of nylon monomers from fishing net waste using seashell waste-derived catalysts in a CO 2-mediated thermocatalytic process. Journal of Materials Chemistry A 10, 20024-20034.

Kleinhans, K., Hallemans, M., Huysveld, S., Thomassen, G., Ragaert, K., Van Geem, K.M., Roosen, M., Mys, N., Dewulf, J., De Meester, S., 2021. Development and application of a predictive modelling approach for household packaging waste flows in sorting facilities. Waste Management 120, 290-302.

Kusenberg, M., Eschenbacher, A., Delva, L., De Meester, S., Delikonstantis, E., Stefanidis, G.D., Ragaert, K., Van Geem, K.M., 2022a. Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: The past, present and future. Fuel Processing Technology 238, 107474.

Kusenberg, M., Eschenbacher, A., Djokic, M.R., Zayoud, A., Ragaert, K., De Meester, S., Van Geem, K.M., 2022b. Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? Waste Management 138, 83-115.

Kusenberg, M., Faussone, G.C., Thi, H.D., Roosen, M., Grilc, M., Eschenbacher, A., De Meester, S., Van Geem, K.M., 2022c. Maximizing olefin production via steam cracking of distilled pyrolysis oils from difficult-to-recycle municipal plastic waste and marine litter. Science of The Total Environment 838, 156092.

Kusenberg, M., Roosen, M., Zayoud, A., Djokic, M.R., Thi, H.D., De Meester, S., Ragaert, K., Kresovic, U., Van Geem, K.M., 2022d. Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: feedstock impurities, product yields and coke formation. Waste Management 141, 104-114.

Kusenberg, M., Zayoud, A., Roosen, M., Thi, H.D., Abbas-Abadi, M.S., Eschenbacher, A., Kresovic, U., De Meester, S., Van Geem, K.M., 2022e. A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition. Fuel Processing Technology 227, 107090.

Lange, J.-P., 2021. Managing plastic waste─ sorting, recycling, disposal, and product redesign. ACS Sustainable Chemistry & Engineering 9, 15722-15738.

Lase, I.S., Bashirgonbadi, A., van Rhijn, F., Dewulf, J., Ragaert, K., Delva, L., Roosen, M., Brandsma, M., Langen, M., De Meester, S., 2022. Material flow analysis and recycling performance of an improved mechanical recycling process for post-consumer flexible plastics. Waste Management 153, 249-263.

López, A., De Marco, I., Caballero, B., Laresgoiti, M., Adrados, A., 2011. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. Fuel Processing Technology 92, 253-260.

Mohammadi, S., Enayati, M., 2022. Dual catalytic activity of antimony (III) oxide: The polymerization catalyst for synthesis of polyethylene terephthalate also catalyze depolymerization. Polymer Degradation and Stability 206, 110180.

Muñoz-Batista, M.J., Blázquez, G., Franco, J.F., Calero, M., Martín-Lara, M.A., 2022. Recovery, separation and production of fuel, plastic and aluminum from the Tetra PAK waste to hydrothermal and pyrolysis processes. Waste Management 137, 179-189.

Nasri, Y., Benaniba, M.T., Bouquey, M., 2022. Elaboration and characterization of polymers used in flexible multilayer food packaging. Materials Today: Proceedings 53, 91-95.

Núñez, S.S., Moltó, J., Conesa, J.A., Fullana, A., 2022. Heavy metals, PAHs and POPs in recycled polyethylene samples of agricultural, post-commercial, post-industrial and post-consumer origin. Waste Management 144, 113-121.

Park, C., Lee, H., Lee, N., Ahn, B., Lee, J., 2022. Upcycling of abandoned banner via thermocatalytic process over a MnFeCoNiCu high-entropy alloy catalyst. Journal of Hazardous Materials 440, 129825.

Pernusch, D.C., Paulik, C., Mastalir, M., Hofer, W., 2022. Assessing the Downstream Contamination of Chemically Recycled Ethylene Feed Streams on the Kinetic Behavior of Ziegler-Natta Catalysts and Microstructural Properties of HDPE and LLDPE. Macromolecular Reaction Engineering 16, 2200042.

Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. Waste management 69, 24-58.

Rodríguez, E., Gutiérrez, A., Palos, R., Vela, F.J., Arandes, J.M., Bilbao, J., 2019. Fuel production by cracking of polyolefins pyrolysis waxes under fluid catalytic cracking (FCC) operating conditions. Waste Management 93, 162-172.

Roosen, M., Mys, N., Kusenberg, M., Billen, P., Dumoulin, A., Dewulf, J., Van Geem, K.M., Ragaert, K., De Meester, S., 2020. Detailed Analysis of the Composition of Selected Plastic Packaging Waste Products and Its Implications for Mechanical and Thermochemical Recycling. Environ Sci Technol 54, 13282-13293.

Salehi Morgani, M., Jalali Dil, E., Ajji, A., 2021. Effect of processing condition and antioxidants on visual properties of multilayer post-consumer recycled high density polyethylene films. Waste Management 126, 239-246.

Sharuddin, S.D.A., Abnisa, F., Daud, W.M.A.W., Aroua, M.K., 2016. A review on pyrolysis of plastic wastes. Energy conversion and management 115, 308-326.

Singh, R.K., Ruj, B., Sadhukhan, A.K., Gupta, P., 2019. Thermal degradation of waste plastics under non-sweeping atmosphere: Part 1: Effect of temperature, product optimization, and degradation mechanism. Journal of Environmental Management 239, 395-406.

Sundaram, K.M., Stancato, B., 2018. How much is too much? Feed contaminants and their consequences, AIChE Spring National Meeting, Ethylene Producers Conference, Orlando, Florida.

Tonini, D., Albizzati, P.F., Caro, D., De Meester, S., Garbarino, E., Blengini, G.A., 2022. Quality of recycling: Urgent and undefined. Waste Management 146, 11-19.

Verma, R., Vinoda, K., Papireddy, M., Gowda, A., 2016. Toxic pollutants from plastic waste-a review. Procedia Environmental Sciences 35, 701-708.

Vogt, B.D., Stokes, K.K., Kumar, S.K., 2021. Why is recycling of postconsumer plastics so challenging? ACS Applied Polymer Materials 3, 4325-4346.

Wan, K., Chen, H., Li, P., Duan, D., Niu, B., Zhang, Y., Long, D., 2022. Thermo-catalytic conversion of waste plastics into surrogate fuels over spherical activated carbon of long-life durability. Waste Management 148, 1-11.

Wang, Y., Wu, K., Liu, Q., Zhang, H., 2021. Low chlorine oil production through fast pyrolysis of mixed plastics combined with hydrothermal dechlorination pretreatment. Process Safety and Environmental Protection 149, 105-114.

Wiriyaumpaiwong, S., Jamradloedluk, J., 2017. Distillation of Pyrolytic Oil Obtained from Fast Pyrolysis of Plastic Wastes. Energy Procedia 138, 111-115.

Yang, W., Kim, K.-H., Lee, J., 2022. Upcycling of decommissioned wind turbine blades through pyrolysis. Journal of Cleaner Production 376, 134292.

Zabihzadeh Khajavi, M., Mohammadi, R., Ahmadi, S., Farhoodi, M., Abedi, A.S., 2019. Evaluating the potential of nanoparticles for controlling zinc stearate release from low-density polyethylene into food simulants. Packaging Technology and Science 32, 175-183.

Zayoud, A., Dao Thi, H., Kusenberg, M., Eschenbacher, A., Kresovic, U., Alderweireldt, N., Djokic, M., Van Geem, K.M., 2022. Pyrolysis of end-of-life polystyrene in a pilot-scale reactor: Maximizing styrene production. Waste Management 139, 85-95.