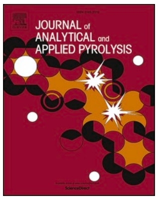
Journal of Analytical and Applied Pyrolysis 187 (2025) 106984

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



Microwave-assisted pyrolysis of waste LDPE: Unveiling the role of induced gas-solid thermal gradients on pyrolysis oil product distribution

Alejandro Fresneda-Cruz [a,*], Gonzalo Murillo-Ciordia [a], Monique B. Figueirêdo [a], Fabiola Tovar-Lasheras [a], Ahmad AL Farra [b], Jesús Arauzo [c], Ignacio Julian [a,*]

[a] *CIRCE - Technology Center for Energy Resources and Consumption, Parque Empresarial Dinamiza, Av. Ranillas 3D, 1st Floor, Zaragoza 50018, Spain*
[b] *TRTG-TotalEnergies Research & Technology Gonfreville, BP 27, Harfleur 76700, France*
[c] *Thermochemical Processes Group, Aragón Institute of Engineering Research (I3A), University of Zaragoza, Edificio I+D, Campus Rio Ebro, Zaragoza 50018, Spain*

ARTICLE INFO

Keywords:
Polyolefin waste valorization
Microwave-assisted pyrolysis
Pyrolysis oil
Hydrocarbon production, gas-solid phase reactions
Circular economy

ABSTRACT

Microwave-assisted heating plays an important role in minimizing the high energy consumption of traditional thermochemical recycling processes. Its application to plastic waste recycling routes enables a more efficient production of new renewable feedstocks for the petrochemical industry. This work presents the experimental assessment of low-density polyethylene (LDPE) waste recycling in a microwave-assisted pyrolysis (MAP) fixed bed reactor and the in-depth evaluation of the obtained pyrolysis oils in comparison with conventional plastic waste pyrolysis oils. The role of main process variables (temperature, nitrogen flow rate and susceptor-to-LDPE ratio) on the pyrolysis oil yield and composition was addressed. The maximum attained oil and wax yields were of 60–75 wt%. As a general trend, the microwave-assisted process led to a distinct chemo-selectivity compared to that of traditional LDPE pyrolysis, shifting the products distribution from saturated paraffins to olefinic species and longer molecular chains. Olefins content rose from 28 % under conventional pyrolysis to 75 % under MAP. The negligible content of aromatic compounds in MAP oils offers great potential to serve as a recycled feedstock for steam crackers. These findings are ascribed to gas-phase reactions quenching due to the microwave-induced thermal gradient between the selectively heated bed and the comparatively colder surrounding atmosphere. A statistical parametric analysis and regression model have been implemented to further evaluate the impact of each variable, and mechanistic considerations were considered on the experimental microwave-induced thermal gradients and fixed bed mass and heat transfer properties. By integrating real polyolefin waste streams as feedstocks for chemical building blocks through microwave-assisted pyrolysis, this study helps paving the way for a transition to circularity in petrochemical industries.

1. Introduction

Each year, near 380 million tons of plastics are produced by the global plastic industry [1]. Plastic materials are extensively used along core sectors which include urban and industrial applications, i.e in packaging and component materials [2]. Polyolefins represent the most prevalent type of polymer due to their wide array of applications and low cost, constituting 45–57 % of the total plastic production. The ubiquity of plastic waste, added to its global mismanagement, has already provoked major environmental issues due to accumulation in landfills and natural environments, as well as their inherent persistency to biodegradation [3]. To address these threats, the establishment of well-designed end-of-life paths and the development of circular value chains for plastics represent a viable solution to decrease dependence on limited fossil resources while mitigating environmental hazards and managing the generated waste through recycling [4]. Accordingly, plastics like PET and polyolefins (PP, LDPE, HDPE) can be recycled mechanically if well-sorted and homogenized [5]. Nonetheless, chemically recycling waste streams to obtain building blocks that can be used in the synthesis of new ("as-virgin") polymers, as well as many other products which nowadays rely on fossil sources, represents an important advance to fulfill the need for circular raw materials in petrochemical value chains and overcome the limitations of mechanical recycling [6–8]. In this context, thermochemical processes have emerged as promising solutions for the recycling of plastic waste streams: traditional thermolysis, catalytic pyrolysis, hydrocracking, solvolysis,

---

[*] Corresponding authors.
E-mail addresses: afresneda@fcirce.es (A. Fresneda-Cruz), iajulian@fcirce.es (I. Julian).

https://doi.org/10.1016/j.jaap.2025.106984
Received 29 October 2024; Received in revised form 20 January 2025; Accepted 24 January 2025

hydrogenolysis [9]. Among those, the pyrolysis of plastic waste has been identified as a major potential technology for the conversion of polymeric chains into smaller organic compounds via thermal cracking of long-chain hydrocarbons and rearrangement reactions through controlled heating [10]. As such, pyrolysis allows the transformation of plastic waste into a circular feedstock for petrochemical industries and plastic manufacturers [11–14]. Besides their large availability, polyolefins stand out for their negligible oxygen content and chemical homogeneity, which leads to hydrocarbon-rich sources that can be more easily integrated in traditional value chains.

The distribution of pyrolysis products is largely affected by the feedstock properties (polymer type, impurities, etc.), pyrolysis technology (e.g. slow pyrolysis, fast pyrolysis, flash pyrolysis, catalytic pyrolysis), reactor configuration and particle size. For instance, fixed bed and vacuum reactors have been preferentially chosen in lab scale research studies to conduct the slow pyrolysis of waste polyolefin blends at temperatures ranges of 500–900 °C and heating rates lower than 1 °C/s [15,16]. For the optimized production of pyrolysis oils enriched in hydrocarbons, faster heating rates of 10 – 200 ºC /s are generally reported. The optimal thermolytic conversion of waste PP, PE, PS and PET into pyrolysis oils has been generally set around a temperature of 450 °C, and the oil yields reported range from 60 – 84 wt% [17,18]. In the particular case of polyethylene, higher temperature ranges of 500 – 550 ºC are required to maximize pyrolysis oil yields due to the strength of C-C bonds [19]. Several reactors have been implemented to evaluate the process, namely: screw reactors [20], fluidized beds [21], and conical spouted bed reactors [22]. Recent studies have evaluated the catalytic pyrolysis of pure LDPE to achieve pyrolysis oil yields of 47 – 70 wt% in 5 L capacity batch reactors [23,24]. Dassi Djoukouo et al. reported the modelling of a conventional pyrolyser having waste LDPE mixed with other polyolefins such as PP and PS as feedstock; at operating temperatures of 450 ºC, light gasoline fraction yields of 6 – 12.4 wt% and heavier diesel fractions yields ranging from 43 – 64 wt% are reported [25], with similar properties to petrochemical naphtha [26].

The energy consumption of industrial conventional pyrolysis facilities has been reported in literature to range from 1.5 – 2.5 MJ/kg depending on the reactor design and temperature settings. Stallkamp et al. modelled the operational cost (OPEX) for the conversion of plastic waste into fuel range products; the reported OPEX for a pilot capacity of 0.1 ton/h was of 2.2 – 4 € per kilo of plastic waste, whilst in the case of upscaled industrial processes (0.5 – 10 ton/h) it has been quantified at 0.5–1.2 € per kg[27]. Due to the high energy consumption and operational costs, as well as the typical oil yields, properties, and difficulties to compete with petro-based oils, the deployment of conventional pyrolysis for LDPE recycling faces challenges in terms of techno-economic viability [28–30]. Hence, in the realm of sustainable waste management and resource recovery, the development of feasible recycling technologies represents the main target for industrial process development [31].

In this context, alternative heating methods such as ultrasound or microwaves have potential to increase the recycling efficiency [32,33]. These innovative technologies offer the possibility of directly electrifying the process, thereby reducing reliance on auxiliary fossil-based fuels like natural gas for heat supply. Despite the inherent losses in the conversion of electrical to thermal energy ascribed to microwave-assisted heating systems (typically, magnetrons have an energy conversion efficiency up to 75 % for a matched load under irradiation at 2.45 GHz), still this heating technology has been endorsed with energy savings up to 80 % over traditional convection methods for a number of thermochemical conversion processes [34–37]. Microwave-assisted pyrolysis (MAP) systems, in particular, present significant advantages due to their faster, volumetric, effective, and efficient heating, which ultimately enhances safety in the recycling process and improves process control [38]. Accordingly, reaction time reductions of 50 % and energy consumption savings of 40–53 % compared with electric heating have been reported for the pyrolysis of biomass and other waste types [39–41].

Besides energy savings, the distinctive dielectric heating mechanism employed in microwave-assisted systems sets them apart from conventional pyrolysis methods, which rely on conductive and convective heating mechanisms [42]. It is generally accepted that microwave heating influences certain chemical reactions in a catalytic sense due to the extremely rapid heating and overall finer process control [9,29,43]. Despite the promising prospects of MAP, microwave heating faces significant barriers that must be addressed, notably avoiding the generation of hotspots that causes thermal heterogeneity and achieving an accurate temperature measurement within the electromagnetic fields [44,45]. Furthermore, the efficient absorption and transmission of microwave power to transparent materials like plastic waste requires the use of microwave susceptors with precise dielectric properties, adding complexity to reactor design and material selection [46]. Overcoming these barriers requires interdisciplinary research efforts and innovative engineering solutions to ensure the reliability, scalability, and safety of microwave-assisted polyolefin recycling processes. The process variables that are reported to play a relevant role in MAP performance are temperature, residence time, feedstock composition, and catalyst use [47–49]. Pyrolysis temperature and susceptor-to-feedstock ratio are considered key to describe the thermal homogeneity and process performance.

Recent studies already showcased the thermochemical conversion of plastic waste into high-value organic products through microwave-assisted processes. Oil yields reported for the microwave assisted thermolysis of polyethylene in a variety of studies ranged 60–75 wt% at temperatures of 450 – 800 ºC [50,51]. In most MAP studies, the oil yield has been reported to decrease with the increase of microwave power and operational temperature/reaction time. Ding et al. reported the MAP process catalyzed by NiO/zeolite in a lab batch reactor, with 56.5 wt% oil yield achieved from LDPE and an increased selectivity to gasoline fractions, using silicon carbide as microwave susceptor [52]. Non-catalyzed MAP of LDPE was reported by Istoto et al. at 450 – 600 ºC obtaining gasoline and diesel range oils but no further data was reported regarding oil fraction yields [53]. Low pyrolysis oil yields have been reported at 500 – 2500 W of microwave power for the MAP of LDPE at scales of 15–20 g. Arshad et al. reported 16 wt% oil yields from MAP of LDPE [54], whereas the implementation of different microwave susceptors and catalysts was reported to increase the pyrolysis oil yield up to 32 – 80 wt% [55–58].

Few studies are found in literature addressing the impact of microwave heating on reaction mechanisms or hypothesizing about the effect of the gas-solid temperature gradient on the chemo-selective degradation of polyolefins in means of quenching of pyrolysis products [59,60]. To the best of the authors' knowledge, the two-fold effect of microwave-assisted fixed bed heating and pyrolysis vapours quenching on the composition of pyrolysis oils from real LPDE waste streams has not been yet reported. The current study dives into the different nature and chemical composition of LDPE pyrolysis oils obtained through MAP in comparison to that obtained under a conventional electrically heated pyrolysis (EHP) in a stirred tank reactor, and the new opportunities that this brings for integrating secondary feedstocks into petrochemical processes. Furthermore, it showcases the significant role that emerging technologies like microwaves could play in transitioning from a linear fossil economy to a circular one.

2. Materials and methods

2.1. Feedstock and materials

The residual low-density polyethylene (LDPE) pellets used in this research were provided directly by URBASER Urban Solid Waste Treatment facilities from Zaragoza. LDPE pellets were obtained from a solid waste sorting line in which metals and discarded impurities are physically separated from LDPE. The output is then subjected to a thermal treatment and pelletizing step to obtain a homogeneous plastic waste pellet with average size of about 2 mm (Figure S1). The supplier provided the pellet characterization by ^{13}C NMR (used to estimate LDPE, PP and PET contents) as well as the ashes content, which are discussed in detail in 3.1.

Due to the low capacity of LDPE to absorb microwave radiation, pyrolysis tests have been carried out in the presence of a susceptor material intimately mixed with the pellets to favour heat transfer. The LDPE-to-susceptor mass ratio was one of the variables assessed during this research study. Silicon carbide (SiC) was selected as microwave susceptor due to its high thermal conductivity, efficient heat absorption, excellent thermal stability, chemical resistance, and affordability [35, 36]. A black 200 micron SiC powder was provided by Superior Graphite Inc.

A series of external standards (Table S1) were purchased from Dr. Ehrenstorfer Reference Materials to perform the analytical quantification of pyrolysis products by external standard calibration curve method (see section S3).

A sample of pyrolysis oil from the degradation of the same waste LDPE feedstock was provided by URBASER pilot plant pyrolysis facilities for comparison purposes. This pyrolysis oil, named as “conventional oil” was produced via a conventional electrically heated CSTR reactor operating at *ca.* 425 ºC and slight overpressure, with a processing capacity of 100 kg/h.

2.2. *Microwave-assisted pyrolysis set-up and experimental procedure*

MAP tests were conducted in a multi-mode customized BP-211 microwave cavity (Microwave Research and Applications, Inc.). The microwave cavity features four independent 800 W magnetrons to deliver a maximum microwave power of 3200 W at 2450 MHz, as well as mode stirrers at the end of each BJ26 waveguide (L x W = 86 mm×43 mm) to maximize the electromagnetic field distribution along the time on stream (Fig. 1a) The microwave power input can be tuned by an electric power variator either manually or automatically through a temperature PID control loop. The sample is placed inside a vertical quartz tube reactor (28 mm ID) and temperature is monitored by a contactless infrared pyrometer (model CT 3 M IR) pointing to the center of the sample through a drilled hole at the lateral wall of the cavity. The pyrometer features a quartz-transparent wavelength spectral range centered in 2.3 µm. As a result, the temperature of the surface of the heated sample in contact with the inner reactor wall can be directly measured, without needing any further correlation. For the assessment of the fixed bed temperature gradient, a thermal imaging camera (model FLIR Bcam) was used for the measurement of the external quartz reactor surface temperature, which has been corrected to the real temperature inside the quartz reactor using an apparent material emissivity [61].

In a typical MAP experiment, 14 g of waste LDPE pellets are mixed with a specified amount of microwave susceptor (SiC, in this study) and the mixture is supported vertically by glass wool A fixed bed of pure SiC susceptor is placed in the system’ inlet to serve as a preheater for the nitrogen gas flow (Fig. 1b). The quartz reactor is placed inside the microwave cavity, and a flow of nitrogen gas is passed through the system to inertize and evacuate the pyrolysis vapors during each experiment. Initially, the temperature is set to 110 °C to remove moisture from the system for 10 minutes, and then the reaction temperature is set. Pyrolysis vapors pass through traced pipes to avoid condensation in the reactor cavity and are directed to a system of condensers for the collection of the pyrolysis oils.

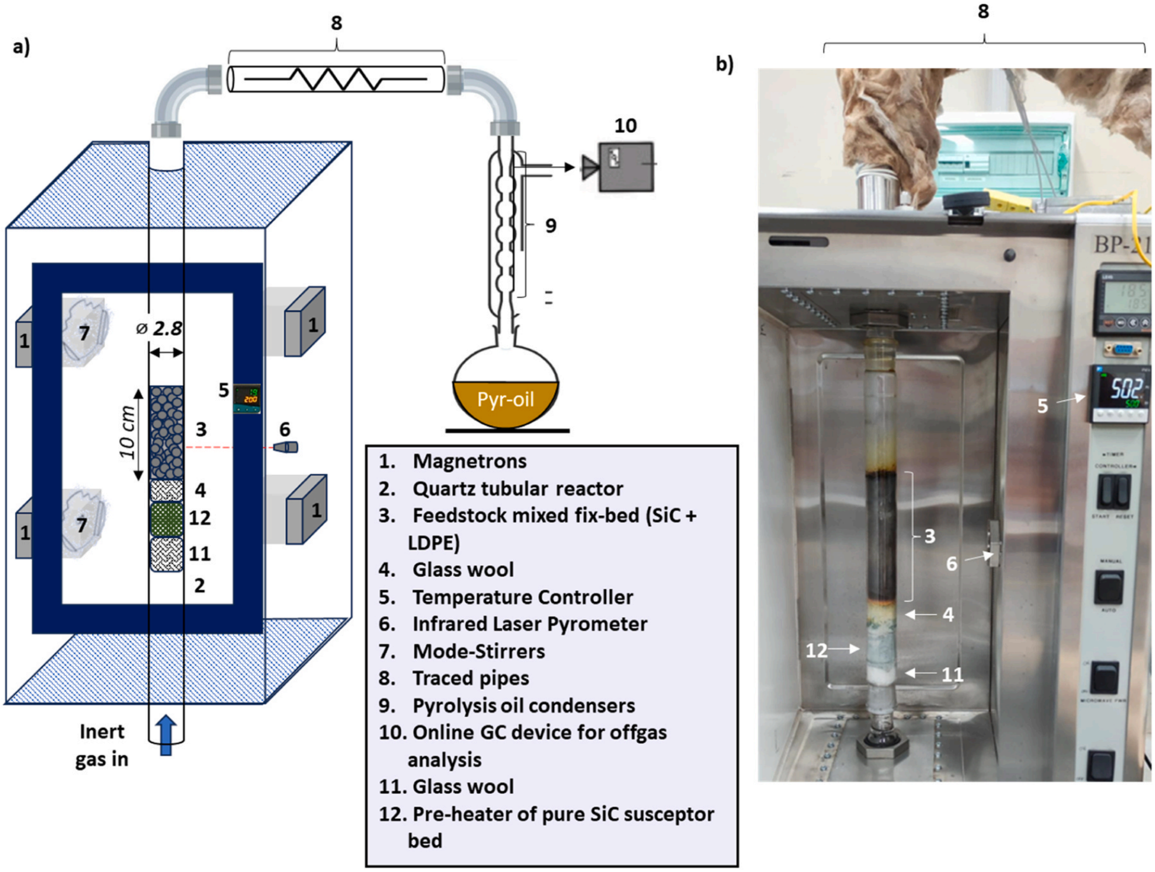


Fig. 1. a) Microwave-assisted pyrolysis experimental system scheme in a 3.2 kW multimode microwave cavity; b) configuration of a LDPE:SiC mixture fixed bed in a tubular quartz reactor.

2.3. Pyrolysis parametric analysis: design of experiments (DoE)

To assess the influence of main operation parameters on the performance of the MAP system for LDPE chemical recycling, a L8 Taguchi Design of experiments (DoE) approach using an orthogonal array was selected and designed to systematically capture the main effects of multiple process variables and their complex interactions with a minimum number of experimental runs [62].

Based in the existing literature, a pyrolysis temperature of 450 ºC [63,64] was chosen as the lower temperature value, while 0.1 L_{STP} /min refers to the lower nitrogen gas flow rate, which is related to the maximum residence time for the pyrolysis volatiles attainable by the MAP set-up used in this study. On the other hand, the susceptor-to-LDPE weight ratio plays a relevant role in the MAP performance, as it gives an indirect measure of the contact degree between the susceptor and waste plastic pellets. For this reason, a ratio of 5:1 was set as lower value in order to have an acceptable temperature distribution within the quartz reactor.

Additional experiments, particularly at the center of the design space, were required to enhance the precision of the multivariable regression model coefficients' estimation. The assessment of central points in the temperature, gas flow and susceptor-to-feedstock ranges improved the fitting of the regression model. Thus, four central-value experiments (tests 9–12) have been added to the original orthogonal array, totaling a set of 12 MAP experiments. The tested process conditions are listed in Table 1.

The properties of the obtained MAP oils have been compared with those supplied by URBASER, produced by the same LDPE feedstock and proprietary pyrolysis technology under conventional heating.

2.4. Characterization of pyrolysis oils by GC-MS analysis

GC-MS (gas chromatography coupled with mass spectroscopy, model Shimadzu GCMS-QP2010 SE) was used to identify the different compounds present in the obtained pyrolysis oils. The employed GC-MS characterization equipment features an automatic sampling injection system (AOC-20i Plus), a DB-5 molecular sieve column (30 m x 0.25 mm×0.25 μm) and a Quadrupolar QP2010 detector.

The sample preparation involved diluting the pyrolysis oils with toluene to 1 mg/mL. The injector temperature was set to 300 °C. 1 μL of each sample was injected into the column with a split ratio of 80. Pure helium was used and purged to keep the inert atmosphere and sweep the volatiles into the capillary column at a flow of 1 mL/min. The initial column temperature was set at 40 °C and kept constant for 5 min. The column was then heated up to 90 °C at a rate of 5 °C/min and ramped up to 40 °C/min until 170 °C were reached. Afterwards, a ramp of 5 °C/min was induced up to 270 °C. Finally, the column reached 310 °C by ramping up at 2 °C/min and the temperature was maintained for 20 min. The sample passed through the interface set at 300 °C where finally it reaches the MS detector (70 ev ionization, 230 °C) set at a sensitivity of 0.2 kV. Mass spectrometry detection was conducted in full-scan *m/z* mode range from 33 to 533. The total ion chromatogram (TIC) peaks were identified comparing the mass spectra data with NIST mass spectral library and a specific library of pyrolyzates mass spectra (PyGC-MS14B) and search engine (F-Search Ver.3.5) purchased from Shimadzu. A minimal match quality of 80 % was set for peak identification.

Bi-dimensional GC x GC characterization was carried out with an Agilent 7890 oven model to evaluate the oils' relative polarity and the various compound fractions present within the hydrocarbon mixture, particularly aromatics. Analytical parameters for the GCxGC method were based on the partner petrochemical industry internal big data analysis of typical petroleum refining products. Elemental analysis was also carried out by the industrial external labs to characterize the pyrolysis oils.

2.5. Characterization of pyrolysis oil by simulated distillation and thermogravimetric analysis

Pyrolysis oil molecular weight distribution was studied by simulated distillation (SIMDIST), where its weight loss curve was obtained and evaluated, providing insights into the boiling point (BP) distribution of the sample and allowing for the prediction of heavier hydrocarbons that are not volatilized at the GC-MS injector. This technique was used to quantify the average molecular weight of hydrocarbon chains present in the oil and to determine the polymer cracking degree achieved during MAP. SIMDIST studies were carried out with a Shimadzu simulated distillation system, Nexis GC-2030 high-performance capillary gas chromatograph complying with ASTDM D7169/D5307/D7500 standards. Raw data were post-treated by LabSolutions simulated distillation GC analysis software.

Thermogravimetric analysis (TGA) was also performed for the determination of pyrolysis oil thermal stability with a Mettler Toledo STA/SDTA 851e device. Analyses were conducted in atmospheric pressure conditions with air or nitrogen as a carrier gas at 50 mL/min flowrate. The heating rate was of 10 °C/min from 65 ºC up to 900 ºC, at which the temperature was held for 10 minutes. Air flow was used as carrier gas for the quantification of inorganic impurities in the LDPE pellets, whereas inert nitrogen flow was used for the rest of analysis with the product oils to assess their thermal profile.

2.6. Predictive model for oil yield assessment

A multivariable regression analysis [65] was implemented to develop a predictive model enabling the estimation of a key process output (in this study, overall MAP oil yield) based on input process parameters such as pyrolysis temperature, SiC-to-LDPE ratio and gas flow rate. Having these as model inputs, a quadratic fitting was implemented to establish the adjustment equation of each process output with the three defined independent variables (temperature, SiC-to-LDPE ratio and nitrogen flow rate). Eq. 1 shows the fitting equation model to predict the oil yield, in which inputs 1 to 3 represent "temperature (ºC)", "SiC-to-LDPE ratio (-)" and "nitrogen flow rate (L/min)", respectively, and P1 to P10 are the fitting parameters.

$$\begin{aligned}\text{Oil yield\%} = P1 \quad &+ P2\cdot input_1 + P3\cdot input_2 + P4\cdot input_3 + P5\cdot input_1^2 \\ &+ P6\cdot input_1\cdot input_2 + P7\cdot input_1\cdot input_3 + P8\cdot input_2^2 \\ &+ P9\cdot input_2\cdot input_3 + P10\cdot input_3^2\end{aligned} \tag{1}$$

In parallel, a parametric sensitivity study was conducted to quantify the impact of the process parameters in the pyrolysis oil yield model prediction. Similar analyses were described by Ge et al. [51]. A random forest regression model has been developed with 100 estimators and a random seed of 0 to evaluate the performance of the different parameters by the output mean square error.

The generated predictive models for all relevant outputs (oil yield and oil composition in terms of hydrocarbon chain length and

Table 1
Operating conditions for MAP experiments using LDPE waste as feedstock.

Test #	1	2	3	4	5	6	7	8	9	10	11	12
Temperature (ºC)	450	450	450	450	500	500	500	500	450	475	475	475
SiC-to-LDPE (wt/wt) ratio	5	5	10	10	10	10	5	5	7.5	7.5	7.5	7.5
Gas Flow (L/min)	0.1	1	0.1	1	0.1	1	1	0.1	0.1	0.5	1	0.1

saturation) were integrated into an interactive radar chart using the Ansys Workbench Software environment. A screenshot of the software output is depicted in the Supporting Information (Figure S4).

2.7. Characterization of pyrolysis non-condensable gases

The online analysis of non-condensable gases generated during pyrolysis was conducted using a MicroGC Agilent 990 equipped with two complementary channels for the identification and quantification of hydrogen (H_2), nitrogen (N_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and short-chain hydrocarbons: ethylene (C_2H_4), propylene (C_3H_6), ethane (C_2H_6) and propane (C_3H_8). Channel 1 was operated with helium (4.5 bar) using a 10 m Molesieve column, heated injector, and 3 min backflush, whilst Channel 2 was operated with argon (4.5 bar) using a 10 m CP-PoraPLOT Q column, heated injector, and 1 min backflush. Genie Filters were utilized to remove water and particles from samples before each injection. The GC device and data analysis was controlled by an OpenLab EXChrom Compact Station.

The MicroGC method used consisted of injector temperature set at 80 °C, with an automated auto-sampling each 3 minutes. Both chromatography columns were set to 50 °C. For quantitative analysis, peak areas were calibrated using the response factor provided by a standard gas mixture of known composition (60.28 mol% N_2, 5.05 mol% H_2, 4.94 mol% CO, 4.95 mol% CH_4, 4.95 mol% C_2H_6, 4.95 mol% C_3H_6, 4.96 mol% CO_2, 4.96 mol% C_2H_4, 4.96 mol% C_3H_8).

3. Results and discussion

3.1. Feedstock characterization

Several physio-chemical analyses were carried out to characterize the waste LDPE feedstock. Their chemical composition was characterized by ^{13}C NMR analysis prior to this work by the associated waste treatment company. Results indicated contents of 95.3 wt% polyethylene (PE), 3.5 wt% polypropylene (PP), and 1.2 wt% polyethylene terephthalate (PET) in the sorted waste LDPE pellets. ^{13}C NMR showed the presence of residual cellulose and polyamide. Importantly, this analysis didn't quantify any insoluble fillers and reticulated thermoset polymers that might be present in the LDPE waste pellets, since the sample was dissolved in trichloroethylene and filtered prior to the NMR analysis. Ash content was estimed by the supplier at 6.6 wt%.

The feedstock's thermal stability was also evaluated by TGA in N_2 atmosphere (Fig. 2). This characterization aimed at getting insights about the most suitable pyrolysis temperature range to be evaluated along the parametric study, as well as to confirm the LDPE content in the provided plastic waste pellets.

The initial weight loss of approximately 10 wt% at 200–400 ºC is ascribed to small impurities from PET, textiles and cardboard residues. A major decay occurs near 450 ºC, being related to the thermal decomposition of LDPE. A third minor devolatilization is detected at 600–650 ºC. Some authors have attributed this to the thermal decomposition of carbonates and pigments/dyes [66,67]. A remaining 12 wt% of residue is observed after 600 ºC, related to the presence of ashes (estimated at 6.6 wt% by the supplier) and char, the latter coming from thermally favored condensation reactions that are generally more prevalent with oxygenated compounds (in this case, the identified lignocellulosic, textile and PET residues) [68] In the view of this, the theoretical maximum obtainable yield to pyrolysis oils and gas should be understood as the one corresponding to the 78 wt% of the sample which is, in effect, LDPE. Importantly, the overall yields presented throughout this study refer to the absolute feedstock mass load, irrespective of the degree of impurities.

3.2. Characterization of hydrocarbons distribution and chemical functionalization of pyrolysis oils

Simulated distillation tests provided insights into the boiling point distribution of selected main pyrolysis oils obtained by MAP. Fig. 3a shows the boiling point profile of the MAP oils. Depending on the process conditions, a fraction of 64 – 79 wt% has been reported to have a BP lower than 510 ºC, related to <C38 hydrocarbon chains based on the model compounds used for calibration. It is then concluded that 21–36 wt% of the obtained MAP oils consists of >C38 hydrocarbon chain lengths that, hence, are not being properly detected and quantified by GC-MS analysis.

To better understand the differences between microwave-assisted and conventional electrically heated pyrolysis (EHP), the simulated distillation analyses of a MAP pyrolysis oil sample (450 ºC, 5:1 SiC-to-LDPE, 0.1 L/min), has been compared with the EHP oil sample provided by the industrial partner (see Fig. 3b).

The results show a 51 wt% fraction of hydrocarbon chains with lower boiling points (BP) than the upper diesel hydrocarbon length limit C20 (BP = 343 ºC) [69] for EHP oils, whereas a lower 31 wt% is reported for the selected MAP oil. Accordingly, 96 wt% of the EHP oil possesses a chain length suitable for detection and quantification by GC (<C38). In contrast, analogous results for the selected MAP oil indicate that only

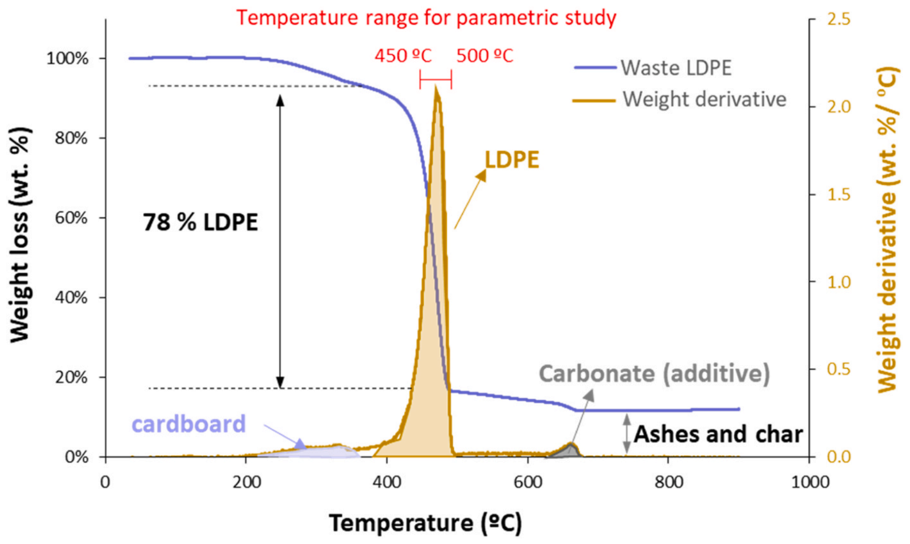


Fig. 2. LDPE pellets thermogravimetric curve (nitrogen atmosphere).

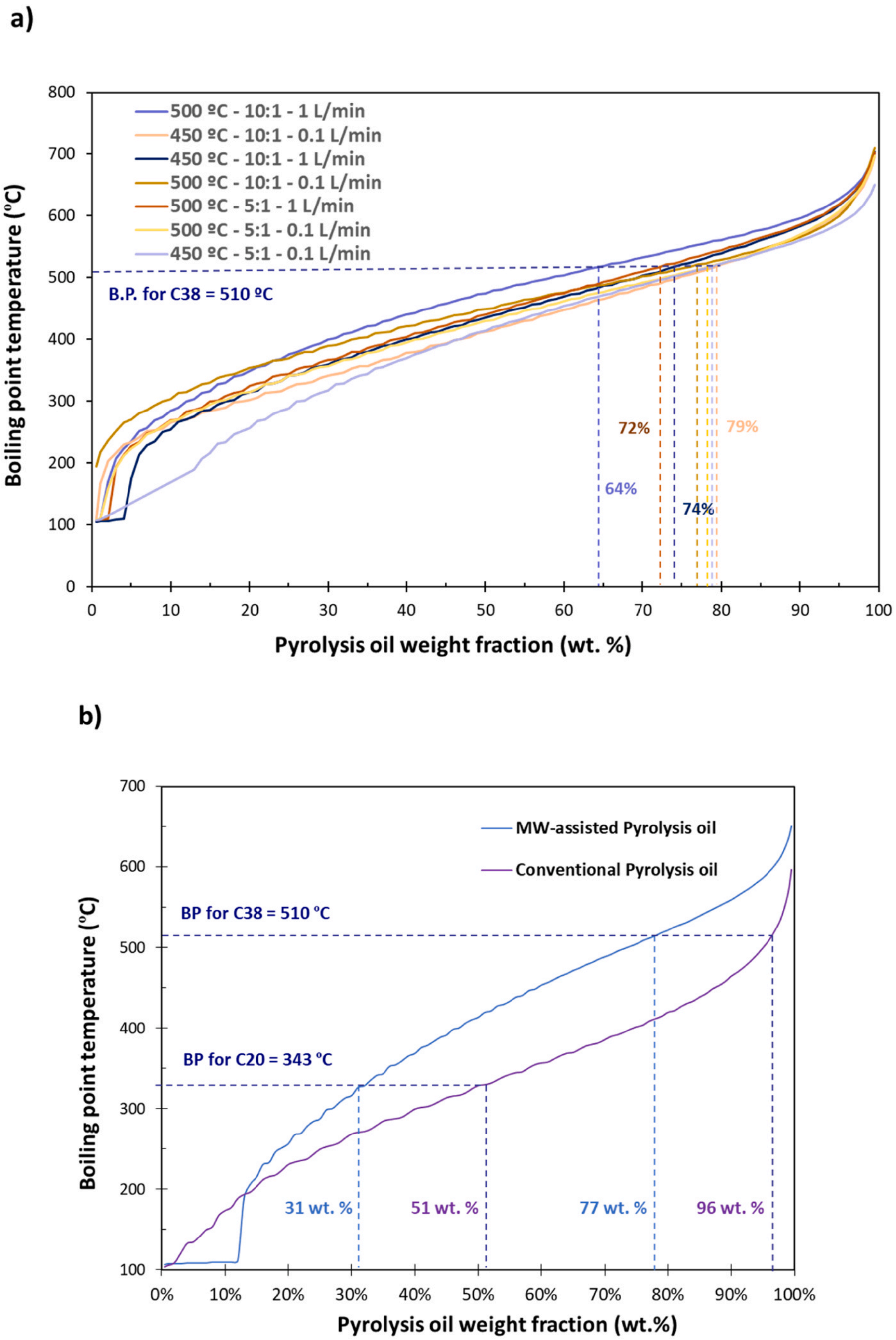


Fig. 3. a) Microwave-assisted pyrolysis oil simulated distillation analysis and b) boiling point profile comparison of MAP and EHP oils of waste LDPE.

77 wt% have been characterized by GC (next sections of this study). Results overall indicate a trade-off between the oil yield and the average hydrocarbon chain length obtained by MAP. Furthermore, TGA results corroborate that lower SiC-to-LDPE ratios are associated with low cracking yields during MAP, thus resulting in lower volatilities of the pyrolysis oils (Figure S2).

Overall, the results show that the obtained MAP oils are heavier, likely due to the very short residence times of the feedstock in the MW reactor system compared to the pilot stirred tank. Accordingly, the lab-scale system had operational limitations with respect to the residence times i.e. the minimum N2 flow of 0.1 L/min, as well as a limited packed bed length of 20 cm. While these were not sufficient to fully crack the LDPE waste pellets into low-medium hydrocarbon chains, it is expected that optimized systems can achieve improved results in terms of cracking with similar proportions of olefinic species.

Elemental analysis has been carried out for selected main MAP oils, showing negligible oxygen and nitrogen contents due to the minimum organic oxygenated impurities present in the waste LDPE (see 3.1). Alkanes are expressed by the general formula C_nH_{2n+2} and thus have a H/C ratio > 2, while unsaturated hydrocarbons are represented by the general formula C_nH_{2n} (for alkenes) and C_nH_{2n-2} (for dienes), thus having a < 2H/C ratio. The results are presented in Table 2 and show an overall H/C ratio lower than 2, suggesting the main presence of insaturated hydrocarbons in the oils, as it will be supported by GC-MS analyses in the next section.

Advanced characterization techniques were also performed to have a deeper understanding of the unsaturated nature of the obtained MAP oils and their further suitability to be integrated into petrochemical

Table 2
Pyrolysis oil samples elemental analysis.

Data	Elemental Analysis					
Pyrolysis conditions	**C%**	**H%**	**N%**	**S%**	**O%**	**H/C**
450 °C - 5:1–0.1 L/min	84.6	13.9	0.4	BDL	1.5	1.97
500 °C - 10:1–1 L/min	85.8	14.0	BDL	BDL	0.7	1.95
450 °C - 10:1–0.1 L/min	85.1	13.9	BDL	BDL	0.8	1.96
450 °C - 10:1–1 L/min	85.5	13.7	BDL	BDL	0.6	1.92
500 °C - 10:1–0.1 L/min	84.7	13.9	0.4	BDL	1.4	1.97
500 °C - 5:1–1 L/min	85.3	13.8	BDL	BDL	1.0	1.94
500 °C - 5:1–0.1 L/min	84.9	13.8	BDL	BDL	0.9	1.95

*BDL: Below detection Limit.

industrial processes, particularly steam cracking. A bi-dimensional GCxGC-MS analysis has been conducted to comprehensively evaluate the functional chemical groups present in the obtained oils, both in terms of molecular size and polarity.

Fig. 4 shows the results for a selected MAP oil (conditions: 450 °C, 5:1 SiC-to-LDPE, 0.1 L/min) and the EHP oil obtained by conventional heating (425 °C). It summarizes the overall distribution of chemical groups considering both the separation of the hydrocarbon chains by size (x-axis) and their relative polarity (y-axis).

Semi-quantitative results of GCxGC-MS analysis are reported in Table 3. It can be observed that a negligible content of aromatics, conjugated compounds and sulfur molecules have been detected in the obtained MAP oils. Accordingly, 97.3 wt% of the MAP oil sample consisted of unsaturated/saturated hydrocarbon chains (paraffins and isoparaffins, olefins and cycloalkenes) that might be suitable for upgrading

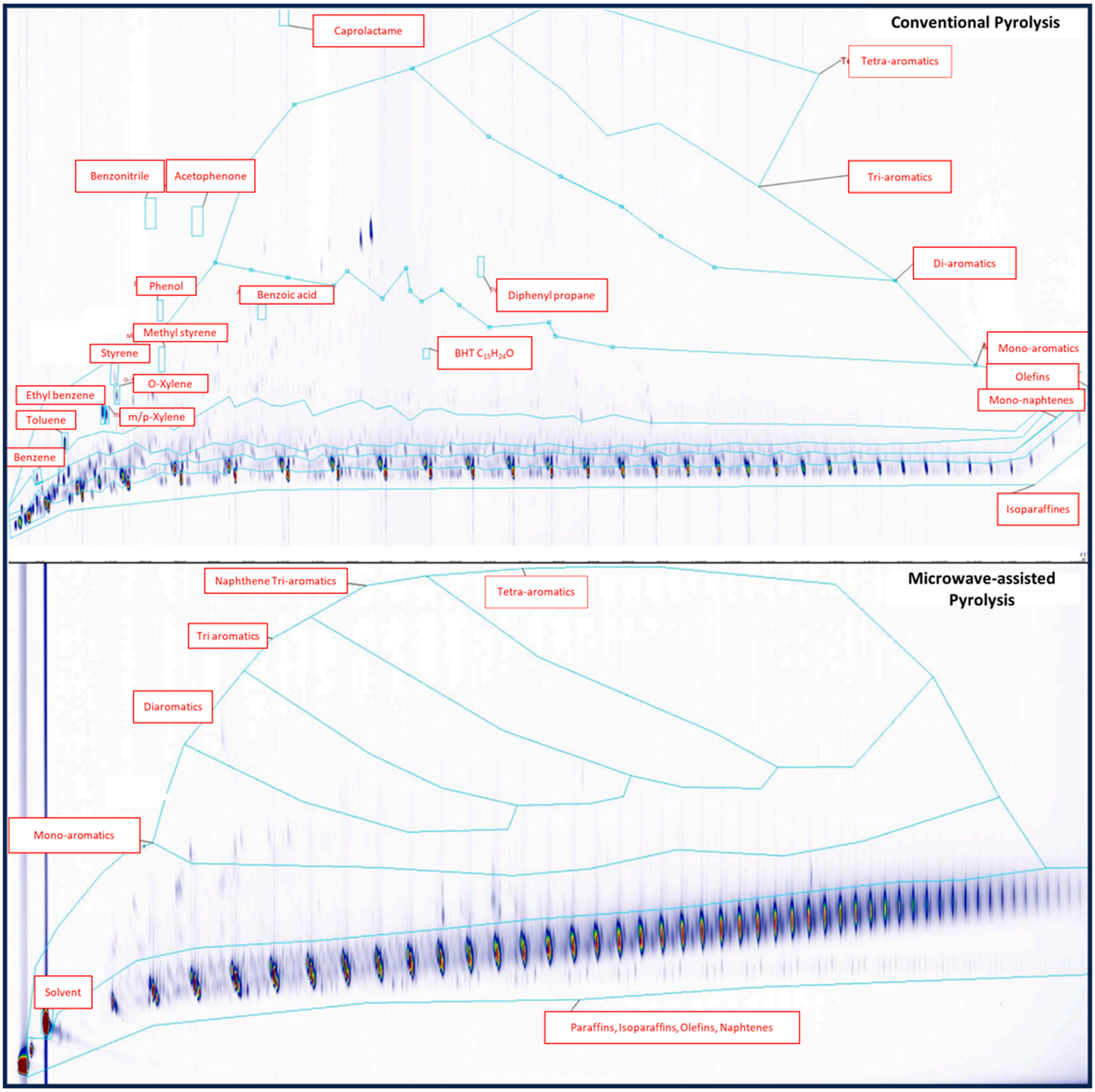
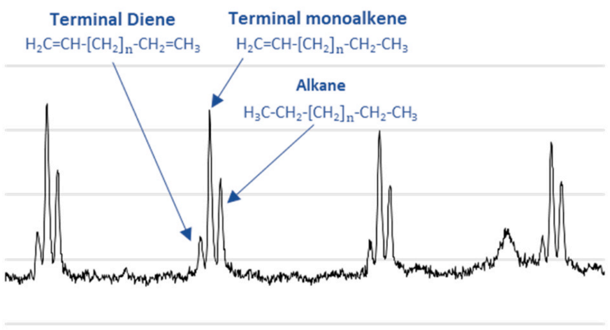


Fig. 4. GCxGC chromatogram for obtained microwave-assisted (upper) and conventional pyrolysis (bottom) oils.

Table 3
Semi-quantitative compound group distribution in produced pyrolysis oils.

Compound Group	MW-assisted Pyrolysis (wt%)	Conventional Pyrolysis (wt%)
Paraffins, isoparaffins, olefins + cycloalkenes	97.3	90.7
Mono Aromatics	1.9	7.3
Benzothiophenes & Diaromatics	0.6	1.72
Dibenzothiophenes & Triaromatics	0.0	0.1
Tetraromatics	0.0	0.02
Other molecules	0.0	0.1
TOTAL	100.0	100.0

steps via hydrotreatment to provide naphtha-like compounds as well as feedstock for steam crackers to boost the concentration of olefins. For instance, triggering compounds responsible for hindering the catalytical activity during hydrotreatment (e.g. molecules containing sulphur, nitrogen) and compounds that are undesired for steam cracking due to their coking tendency (e.g. aromatics) are either absent or, in the latter case, present in minimal amounts, i.e. < 3 wt%. On the other hand, the conventionally heated CSTR reactor produced a pyrolysis oil with higher aromatics content, as well as with traces of triggering compounds such as phenols and styrenes (9.3 wt%) that might negatively impact subsequent co-processing in steam crackers, for example. Overall, the absence of contaminants and undesirable compounds in MAP oils is beneficial for processing in traditional petrochemical processes. Hence, the produced MAP oils from LDPE waste offer great potential to serve as a renewable feedstock, ultimately increasing the share of secondary raw materials from waste streams in petrochemical production processes, which is well aligned with current policies that call for a shift to circular economy models in major industries [70–72].


a) Microwave-assisted pyrolysis

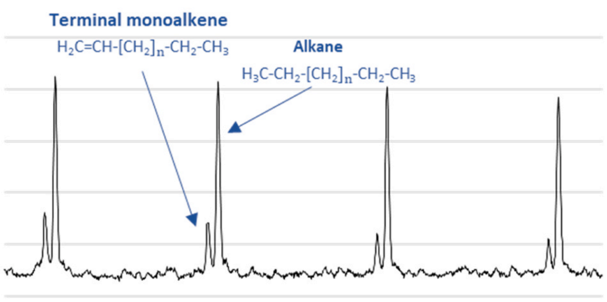

b) Conventional pyrolysis

Fig. 5. a) MAP oil chromatogram in comparison with b) a conventional pyrolysis oil (EHP).

3.3. *Impact of microwave heating to the chemical composition of pyrolysis oils*

Further evaluation of the MAP and EHP oils composition was conducted by GC-MS. Fig. 5 shows raw chromatogram sections from pyrolysis oils obtained under MAP and conventional heating, respectively.

In case of MAP-derived oils (Fig. 5a), the chromatograms typically show a sequence of peak triads, where each triad corresponds to a compound with a carbon number that is one unit higher than the previous triad. The most prominent and easily identifiable peak is associated with a terminal mono-alkene, preceded by a homologous di-unsaturated terminal diene, and followed by an n-alkane. This is in line with recent LDPE microwave-assisted pyrolysis studies [73,74].

In contrast, the chromatograms of EHP oils (Fig. 5b) show a sequence of just two peaks that correspond to the olefinic and paraffinic compounds, being the saturated paraffin compound the most prominent peak. Notably, no terminal di-unsaturated dienes were detected in this case.

Fig. 6 presents the hydrocarbon product distribution of all the 12 MAP oils obtained, based on carbon number, as well as the MAP oil yields. The quantification of each species was conducted using the calibration curves obtained for a series of representative paraffinic and olefinic model compounds (see Supplementary Information, section S3).

In all cases, the diesel range (C10-C20) species roughly represent 50 – 60 wt% of the detectable pyrolysis oil fraction, being the rest waxes (>C20). Overall, the obtained MAP yields range from 32 up to 75 wt%, depending on the operating conditions. These values are consistent with those already reported in similar studies using microwave irradiation as heating source [52,75,76]. It was observed that the maximum oil yields, specifically for lighter diesel fractions, are found for those experiments conducted at higher temperatures and SiC-to-LDPE ratio, e.g. 475 – 500 ºC and 7:5 – 10:1, respectively. This is aligned with the fact that these conditions should promote a more intense cracking degree. The lowest yields of fractions in the diesel range (C10-C20) were attained in the experiments carried out at the lower 5:1 SiC-to-LDPE ratio, which furthermore yielded the highest yield of heavier products (waxes) i.e. 21 – 25 wt%. Both low overall yield and high selectivity to waxes are undesirable. Thus, the use of low susceptor loadings in fixed bed MAP reactors has a negative impact on the polymer cracking rate of polyolefins to shorter molecules.

The product distribution based on the chemical nature of the obtained hydrocarbons, e.g. unsaturated (olefins and dienes) and saturated (paraffins), is illustrated in Fig. 7. For instance, the MAP oils exhibit a high content of unsaturated products, with mono-olefins and terminal dienes ranging from 65 – 77 wt%. The yields of paraffinic hydrocarbons were lower than 35 wt% in all cases, where the lowest yields, 23–24 wt %, were observed for the milder thermochemical cracking conditions (450 ºC, 5:1 SiC-to-LDPE ratio). The higher temperature and SiC-to-LDPE ratio, e.g. 500 ºC and 10:1, and low carrier gas flow, 0.1 L/min, has led to the highest MAP oil yield obtained (75 wt%), which is expected for harsher conditions and longer residence times for pyrolysis vapours along the fixed bed length, which is translated to > 90 % conversion of LDPE considering its content of 78 % in the plastic waste pellet used as feedstock.

A selected oil obtained from MAP (450 ºC, 5:1 SiC-to-LDPE, 0.1 L/min) was compared with the EHP oil in terms of product distribution (Fig. 8a). It can be observed that the oils obtained under conventional pyrolysis (EHP) show a higher cracking degree which leads to significantly lower hydrocarbon chain lengths, i.e. 20 wt% yield to C5 - C9 for EHP oil vs. negligible yield for MAP oil; 76 wt% yield to C5 – C19 for EHP vs. 45 wt% yield for MAP oil. Regarding the type of C-C bonds (Fig. 8b), MAP oils show a major presence of unsaturated compounds, i.e. 76 wt% vs. 19 wt% yields for the EHP oil. Besides the much higher paraffinic content of EHP oils, a significant fraction of aromatics (ca. 10 wt%) was observed in this case.

It is not obvious to address the causes of the large differences

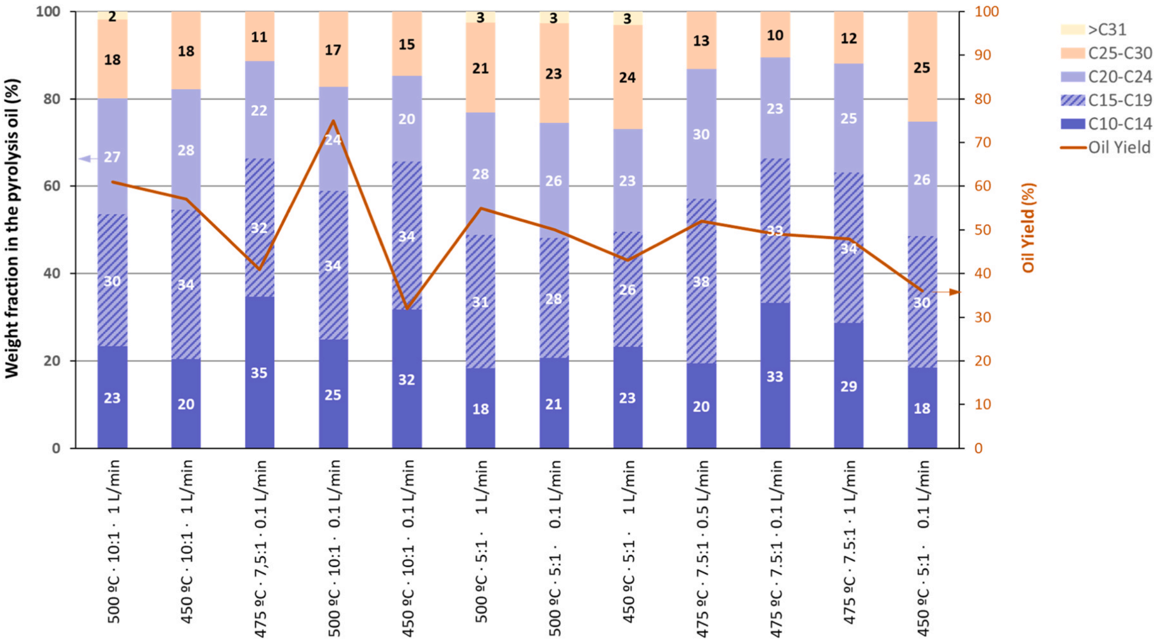


Fig. 6. Characterization and quantification of carbon chain length distribution in analyzed pyrolysis oil samples.

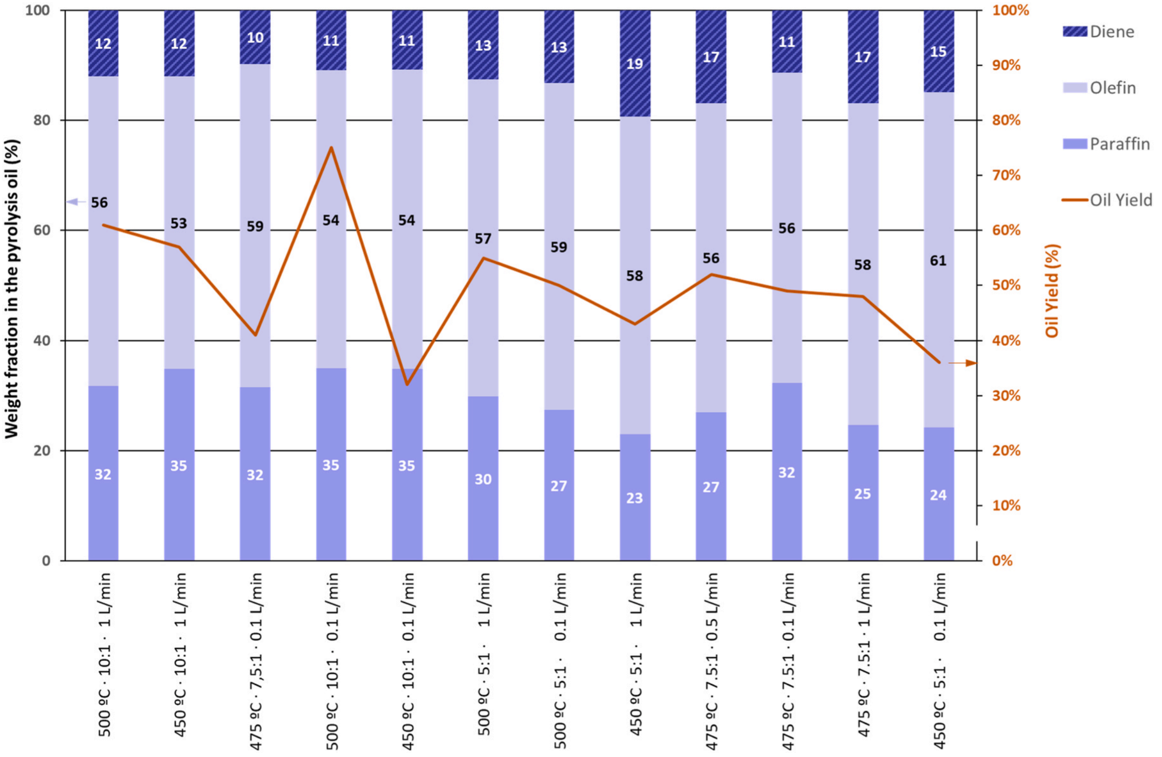


Fig. 7. Quantification of unsaturated/saturated compound distribution in analyzed pyrolysis oil samples.

observed between microwave-assisted and conventional pyrolysis oils. Beyond the different heating modes, the reactor type and production scale differ. Nonetheless, the quenching effect enabled by the microwave-heated fixed bed is considered a primary cause of said differences. Accordingly, the microwave-assisted heating of a fixed bed of susceptor particles leads to a high thermal gradient between the hot particle bed itself and the passing carrier gas flow [77]. The thermal gradient has been quantified via thermographic cameras and thermal profile image processing (Fig. 9).

It can be observed that the temperature gradient between the core of the fixed bed and the adjacent empty sections of the quartz reactor inside the microwave cavity reaches up to 500 ºC, being estimated at 225°C just 6 cm above the fixed bed edge. Such a major thermal gradient induces a quenching effect on the reaction intermediates produced in the fixed bed by MAP, where the thermolytic reaction of the polymer chains occurs. It is suggested that the longer residence times and the absence of this quenching effect in the case of conventionally heated pyrolysis led to greater cracking and thus the formation of more stable and overall

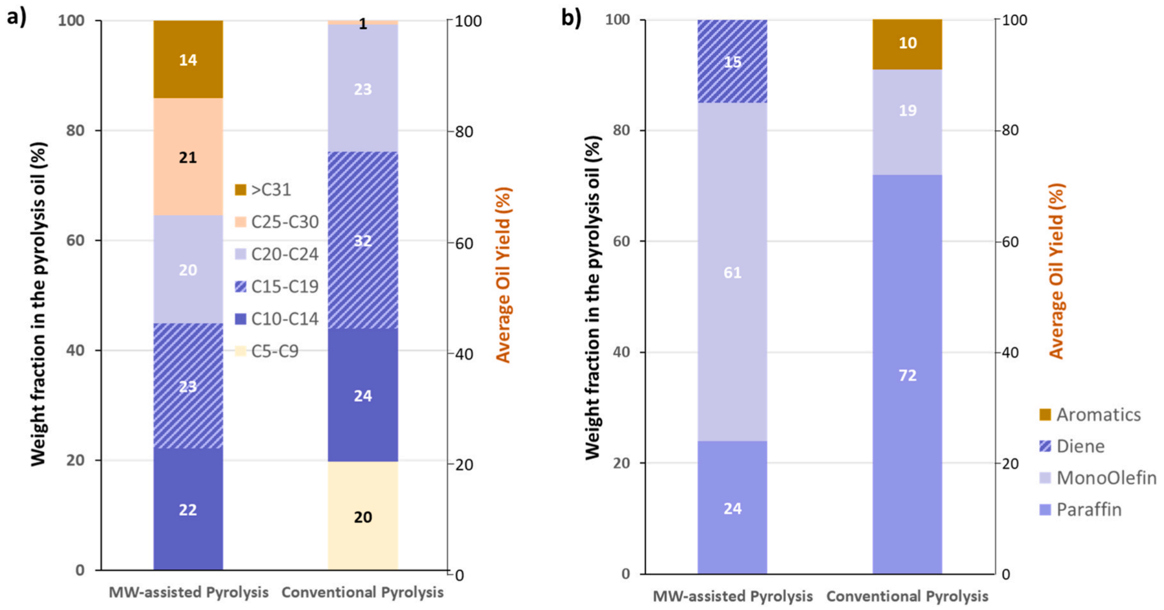


Fig. 8. a) carbon chain length distribution and b) chemical composition distribution of oils obtained through conventional heating (EHP) and microwave-assisted pyrolysis (MAP), quantified by GC-MS using an external standard calibration method.

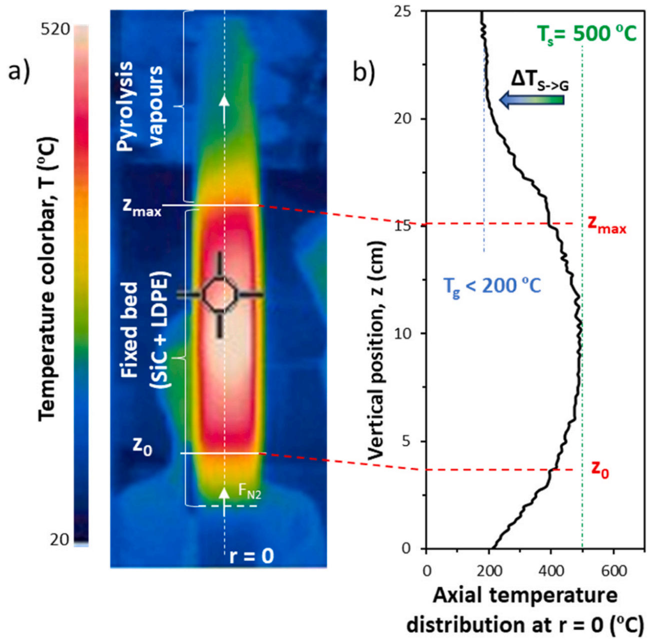


Fig. 9. Fixed bed thermal gradient and temperature profile.

shorter molecules (saturated paraffins and benzene rings) to the detriment of others with higher energy levels and lower stability (olefins).

3.4. Mechanistic considerations for the microwave-assisted pyrolysis of LDPE

The various analyses conducted in this work reflect an empirical relationship between the microwave-induced thermal gradient, the polyolefin cracking efficiency and pyrolysis oil yield, and the content of saturated/unsaturated products in the obtained pyrolysis oils. Since these are important correlations to consider for process optimization and upscaling, some fundamental considerations of reaction mechanisms and the product distribution observed using the microwave-assisted reactor of this study are discussed in this section.

Two distinguished mechanisms are currently accepted for polyolefin thermal cracking: *i)* Random scission of the melted macromolecules, yielding long chain hydrocarbons; *ii)* chain-end scission of oligomers. This is supported by several recent lumped kinetic models on polyethylene pyrolysis, which experimentally confirm that the initial scission mainly leads to waxes and that these evolve further towards higher paraffinic oil and light olefin gas fractions favoured by long times on stream [78–82]. These simplified models assess the role of temperature and residence time on the pyrolysis products distribution (typically categorized as waxes, liquids and gases), assuming first-order kinetics for every transformation among the sort of products. These studies agree on the fact that the most kinetically favoured step (lower activation energy) is the initial conversion of the feedstock into waxes, followed by the formation of oils out of such waxes. Interestingly, hydrocarbon waxes-to-light olefin steps have the most temperature-dependent kinetic constant, thus being drastically favoured at high temperatures [83]. This proves that the maximization of oil yield will ultimately depend on the careful selection of both process temperature and reaction time, apart from other considerations such as mass transfer limitations and volumetric temperature distribution.

After the initial primary scission steps, it is also widely accepted that radicals transfer from chain ends to internal positions, favouring depolymerization routes towards low molecular weight products such as alkenes, terminal dienes and paraffins [52,84–86] (Fig. 10, route A). As already discussed, high temperatures and residence times favour the formation of volatile products, but also subsequent secondary pathways, i.e. olefin isomerization, hydrogen transfer and termination steps [87, 88]. In contrast, the use of acid catalysts favours the formation of aromatic compounds and naphthenes by oligomerization, cyclization and dehydrogenation pathways [57,74,88–90] (Fig. 10, route B). It is also well-accepted in literature that low residence times and low concentrations of the olefin intermediates hinder end-chain scission routes, volatilisation and secondary reactions [91–93].

Due to its specific configuration, the fixed-bed MAP reactor used in this study induces notable thermal gradients and low residence time of volatile intermediates which impact the thermochemical depolymerization of LDPE. Heat and mass transfer processes are severely limited in fixed-bed reactor configuration, hindering intermolecular hydrogen transfer and radical rearrangement steps. In this way, recombination or

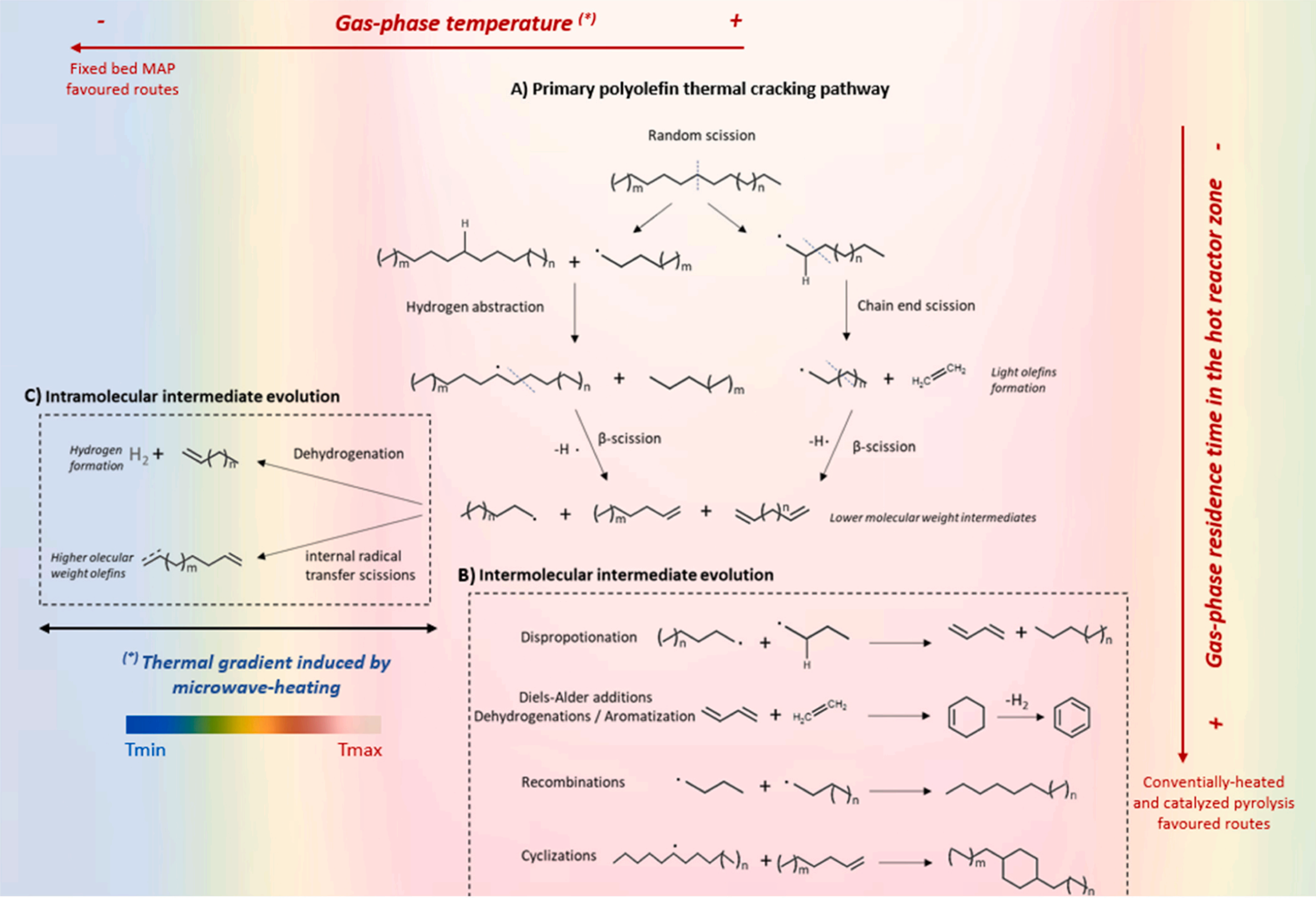


Fig. 10. Thermally induced reaction mechanisms during the pyrolysis of polyolefins. Re-elaborated from refs [52,80,90].

disproportion steps to form saturated hydrocarbon chains and conjugated alkenes or further aromatics are minimized. This is in line with the higher proportion of olefinic species observed in other MAP studies [94]. Fundamentally, overheated regions via hotspots and subsequent thermal gradients enabled by microwave-assisted heating would enhance random and chain-end scission, which are not effectively evolving through intermolecular secondary reactions due to the implied short residence times of the volatiles intermediates inside the fixed bed reactor body. This could explain the average distribution towards larger carbon lengths on the composition of obtained pyrolysis oils in a MAP fixed bed reactor. Most importantly, the very low residence times achieved in the MAP system, together with the thermal gradient, likely impact towards a kinetic control of rapid intramolecular propagation and termination mechanisms. The shorter reaction times of intermediates in microwave-heated systems [95] and the attained thermal gradients could kinetically favour faster intramolecular 1,x-radical transfer and β-scission mechanisms, besides suppressing the isomerization and rearrangement of terminal diolefins towards thermodynamically more stable internal olefins or conjugated systems (Fig. 10, route C). As a result of this, the maximization of the mono-olefins and terminal dienes yields has been experimentally observed within MAP oils. Thus, the immediate cold zone adjacent to the fixed bed body, caused by the microwave-assisted induced thermal gradient, shall be considered as a reaction quencher, unfavouring the secondary thermodynamic evolution of reaction intermediates towards more stable products i.e. paraffins, conjugated olefins and aromatics via bimolecular steps. For the conventional, pilot scale CSTR in which EHP oils were obtained, longer residence times are applied. In this case, recombination of radical intermediates by simultaneous isomerization, rearrangement, cyclisation or aromatization secondary reactions are expected to take place in a much higher extent, increasing the formation of paraffins and aromatic compounds.

Overall, the reported results support the hypothesis of chemoselectivity of MAP towards olefinic products due to the very short residence times applied and the limited convective heat and mass transfer rates.

3.5. Model results for oil yield prediction

Figure 11a summarizes the experimental MAP oil yields obtained at the different tested conditions, which served as input for the regression model detailed in 2.6. The dataset used for the model development includes process parameters and process outputs such as oil species grouped by saturation degree and chain length, as well as overall oil yields (Table S5). The nine fitting parameters that minimized the mean squared error of this quadratic regression model are shown in Eq. 2.

$$\begin{aligned} \mathit{Oil\ yield}\% = {} & 75.9394 + (-0.3276) * \mathit{input}_1 + 0.1846 * \mathit{input}_2 + 2.6697 \\ & * \mathit{input}_3 + 0.0003 * \mathit{input}_1^2 + 0.0004 * \mathit{input}_1 \\ & * \mathit{input}_2 + (-0.0046) * \mathit{input}_1 * \mathit{input}_3 + (-0.0242) \\ & * \mathit{input}_2^2 + (-0.0011) * \mathit{input}_2 * \mathit{input}_3 + (-0.3917) \\ & * \mathit{input}_3^2 \end{aligned} \tag{2}$$

Using the triad of independent variables (pyrolysis temperature, SiC-to-LDPE ratio and N_2 flow rate) as inputs in this equation, the predicted values of oil yield for each experimental condition were attained. Fig. 11b shows how predicted and experimental oil yields compare. Accordingly, the maximum deviation of the model prediction did not

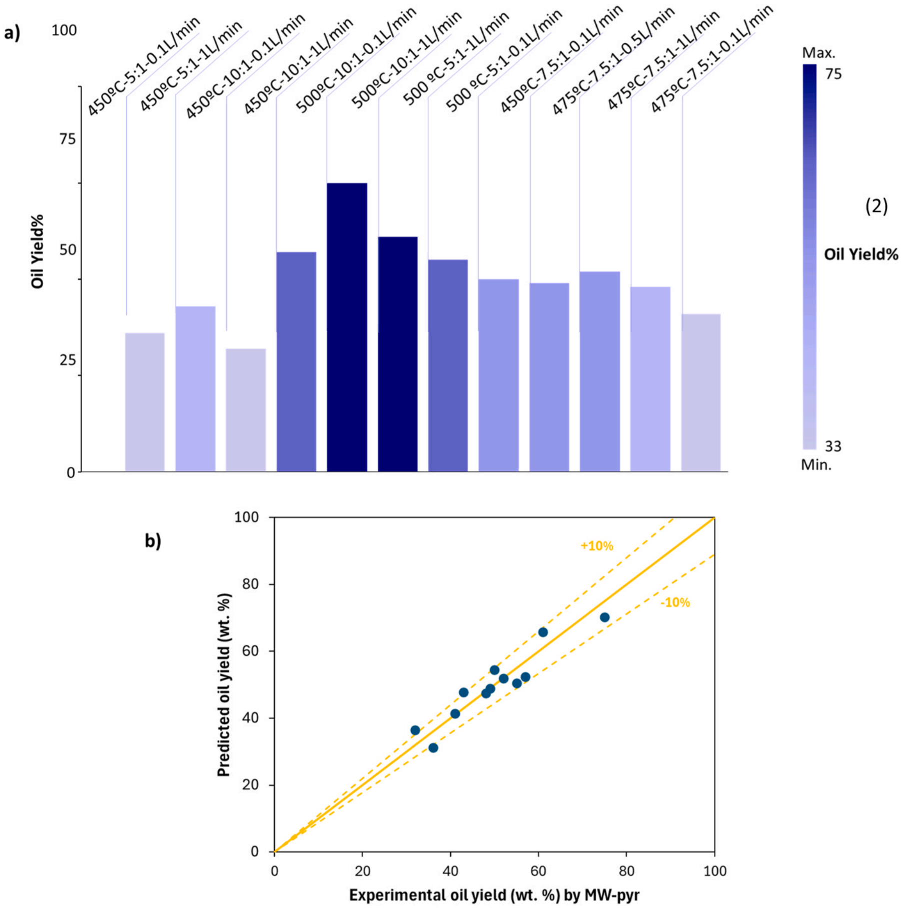


Fig. 11. a) Experimental MAP oil yields obtained at the different tested conditions; b) experimental vs. predicted oil yield values obtained using a 10-parameter multivariable quadratic regression model.

exceed 10 % along the full dataset. The predictability of oil productivity for the intermediate yield values is very good, while less accurate at the extrema. A table containing the specific pairs of experimental and predicted values for each run is showcased in the Supporting Information (Table S6).

In order to quantify the relative impact of each process variable, a sensitivity analysis was conducted based on the available experimental data. Results revealed that the SiC-to-LDPE ratio is the variable that has the highest impact on the overall oil productivity in a fixed bed reactor, followed by pyrolysis temperature and N_2 flow rate. Specifically, the normalized impact of the three variables was quantified to be 40.3, 34.2 and 25.6 %, respectively. This suggests that, in the specific case of the fixed-bed MAP reactor used in this study, the efficiency of the plastic-susceptor contact is more relevant to the process performance than the pyrolysis temperature and the gas-phase residence time. Similar studies that have recently applied analogous methodologies to assess the impact of various operating parameters on the pyrolysis performance confirm that the temperature is one of the most influential variables on the pyrolysis oil yield in batch reactors [96], while the susceptor/catalyst-to-feedstock ratio is the most influential variable in the case of fixed bed reactors [97].

In summary, the obtained model is able to predict the expected oil yield and composition by changing any (or a combination) of the three process variables defined in this study (temperature, SiC-to-LDPE ratio, N2 flow rate). This preliminary digital tool facilitates the prediction of the MAP oil yields and quality, potentially reducing the number of experiments. Nevertheless, further research is required to validate the model by expanding its database with additional experimental data within and beyond the current operating window limits, aiming to increase prediction accuracy and usability.

Microwave-assisted fixed bed pyrolysis reactors are shown to be a promising alternative for producing high yields of LDPE waste-derived pyrolysis oils enriched in olefins and with a reduced aromatic content compared to conventionally produced pyrolysis oils. However, from a practical standpoint, the strong influence of the SiC-to-LDPE ratio, i.e. susceptor amounts, on the process outputs presents a significant challenge for the upscaling of microwave-assisted plastic pyrolysis processes, given the lower efficiency of fixed bed reactors at industrial scales [98]. Microwave-assisted stirred reactors are currently under development to face such upscaling strategies [74], and ensuring the regeneration and reuse of susceptors is crucial for the cost-competitiveness and sustainability of the process.

3.6. Characterization of MW-pyrolysis non-condensable gases

The non-condensable gases produced during MAP were analysed by online micro-chromatography (as detailed in 2.7). Overall, their composition was found to be virtually insensitive within the range of experimental conditions studied, and the olefin/paraffin ratios for C2 and C3 fluctuate in accordance with those reported for oils. Fig. 12a shows the transient evolution of the pyrolysis gas phase composition measured at the exhaust pipe for a representative pyrolysis run carried out at 450 °C, 5:1 SiC-to-LDPE ratio and 1 L/min nitrogen gas flow. The maximum concentration was observed simultaneously for almost all non-condensable gases after 12 minutes on stream from the beginning of the trial (which includes sample heating from room temperature). This production peak of pyrolysis gases is linked to the highest transient conversion rate of LDPE to gas. A quantification of the gas composition

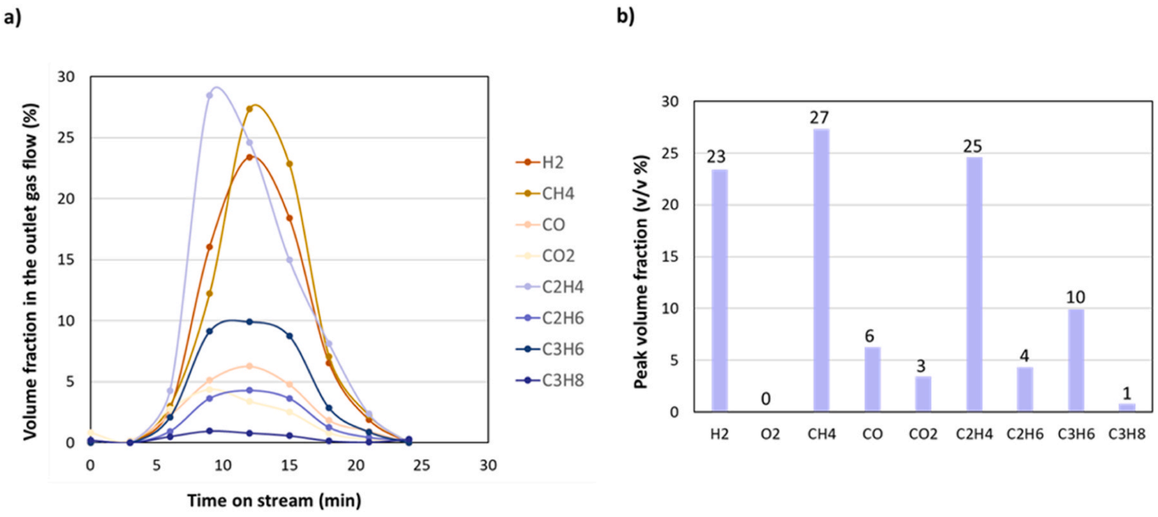


Fig. 12. a) Time evolution of reaction gas phase products in a typical MAP experiment; b) Non-condensable gases distribution at t = 12 min for 450 ºC, 5:1 SiC-to-LDPE ratio, 1 L/min gas flow experimental conditions.

in the non-condensable gas fraction is depicted in Fig. 12b. Accordingly, CH4, C_2H_4 and H_2 are the main species in the gas phase, with maximum volumetric concentrations of 27, 25 and 23 v/v %, respectively. The breakdown of polyethylene involves the cleavage of carbon-carbon bonds, with C_2H_4,CH_4 and H_2 being the most abundant gaseous products under typical decomposition conditions, due to the favourable lower activation energy of chain-end scission and dehydrogenation steps and their higher volatility [99,100]. Due to the anoxic nature of the pyrolysis process and the waste LDPE composition, the minor 6 and 3 v/v% concentrations of CO and CO_2, respectively, are related to the thermal degradation and volatilisation of the oxygenated impurities found in the residual LDPE pellets.

4. Conclusions

This work assessed the performance of a real LDPE-based waste pyrolysis process assisted by microwave heating from five different perspectives: 1) elucidating the role of key variables on the process performance (oil yields and chemical profile); 2) providing a thorough characterization of the pyrolysis oils properties; 3) evaluating the differences between oils obtained under microwave-assisted and conventionally heated pyrolysis systems; 4) developing a predictive tool that helps further optimizing the process and 5) unravelling the reaction mechanisms that explain the prevalence of mono-olefins and terminal diene species at the pyrolysis oils obtained via MAP.

In detail, a multimode microwave-cavity fixed-bed reactor system was employed to assess the impact of three key variables, namely temperature, SiC-to-LDPE ratio and nitrogen flow rate, on the pyrolysis oil yield and chemical composition. The observed MAP oil yields ranged from 32 to 75 wt%. The susceptor-to-LDPE ratio was found to be the most impactful variable on the overall process performance, followed by temperature and nitrogen flow rate (which is related to residence time). The MAP results were also compared with results obtained by processing the same waste LDPE feedstock in a conventional, electrically heated pyrolysis reactor (EHP). For the MAP system, lower cracking rates and significantly higher olefins production (ca. 76 wt%) than conventional pyrolysis (28 wt%) were observed. Accordingly, gasoline and diesel range hydrocarbon fractions (C5-C19) were the major fraction in the EHP oil, i.e. 76 wt%., whereas a high wax (>C25, 25 – 27 wt%) and olefin content (ca. 75 wt%) were observed in the MAP oils. Interestingly, relevant concentrations of terminal dienes (ca. 15 wt%) and a negligible aromatic content were systematically measured in all MAP oils, which, in contrast, were not observed under conventional heating. This trend was ascribed to the short gas-phase residence times and very fast quenching enabled by the existing thermal gradient between the heated bed and the comparatively colder surrounding atmosphere in the MAP reactor.

To serve as the base for further assessments and decrease the number of experiments, a predictive tool based on a quadratic regression model was developed to evaluate the impact of the process variables on the oil yield and composition for the fixed-bed MAP LDPE valorisation process. The model was able to predict the experimental overall oil yield with less than 10 % deviation within the framework of the evaluated operating window, which represents a promising starting point to pave the way for further studies and optimizations. In conclusion, this work showcases the potential of microwave-assisted pyrolysis to convert real LDPE waste streams into hydrocarbon oils enriched in olefinic species, with negligible aromatic content as well as negligible contents of undesired heteroatoms such as sulphur, nitrogen and oxygen. Due to the very fast quenching enabled by the use of microwaves, the process can be fine-tuned to ensure great controllability of the thermal pathways and thus of the oil yield and distribution. As shown in this study, this particular feature enabled achieving higher concentrations of valuable products such as olefins.

Author Statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

CRediT authorship contribution statement

Murillo-Ciordia Gonzalo: Validation, Investigation. **Fresneda-Cruz Alejandro:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Julian Ignacio:** Writing – review & editing, Conceptualization. **Farra Ahmad AL:** Writing – review & editing, Conceptualization. **Arauzo Jesús:** Writing – review & editing, Supervision. **Figueirêdo Monique B.:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Tovar-Lasheras Fabiola:** Software, Data curation.

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.

Acknowledgements

This work was performed in support of the European Union's Horizon Europe Research and Innovation PLASTICE Project under grant agreement n° 101058540. The authors acknowledge the support of Dr. Marta Guerrero and Dr. Alberto J. Gala from Urbaser waste managing facilities (Zaragoza) as well as of Dr. Ahmad Al-Farra and TotalEnergies facilities for the supply of LDPE feedstock and the characterization of the oil & waxes by SIM-DIST, EA and GCxGC, respectively, characterization of LDPE by NMR, as well as for the fruitful discussions kept. The authors would also like to acknowledge Pilar Tarifa from the Research Assistance Service (SAI) of the University of Zaragoza for her contribution with the thermogravimetric analysis presented in this study. The authors also want to thank Superior Graphite Inc. for their contribution with silicon carbide susceptor feedstocks.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2025.106984.

Data availability

Data will be made available on request.

References

[1] M. Chu, W. Tu, S. Yang, C. Zhang, Q. Li, Q. Zhang, J. Chen, Sustainable chemical upcycling of waste polyolefins by heterogeneous catalysis, SusMat 2 (2022) 161–185, https://doi.org/10.1002/sus2.55.

[2] M. Dokl, A. Copot, D. Krajnc, Y.V. Fan, A. Vujanović, K.B. Aviso, R.R. Tan, Z. Kravanja, L. Čuček, Global projections of plastic use, end-of-life fate and potential changes in consumption, reduction, recycling and replacement with bioplastics to 2050, Sustain. Prod. Consum. 51 (2024) 498–518, https://doi.org/10.1016/j.spc.2024.09.025.

[3] A. Milbrandt, K. Coney, A. Badgett, G.T. Beckham, Quantification and evaluation of plastic waste in the United States, Resour. Conserv. Recycl. 183 (2022) 106363, https://doi.org/10.1016/j.resconrec.2022.106363.

[4] X. Shi, Z. Chen, W. Wei, B.-J. Ni, Perspectives on sustainable plastic treatment: a shift from linear to circular economy, TrAC Trends Anal. Chem. 173 (2024) 117631, https://doi.org/10.1016/j.trac.2024.117631.

[5] P. Benyathiar, P. Kumar, G. Carpenter, J. Brace, D.K. Mishra, Polyethylene terephthalate (PET) bottle-to-bottle recycling for the beverage industry: a review, Polymers 14 (2022) 2366, https://doi.org/10.3390/polym14122366.

[6] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste, Angew. Chem. Int. Ed. 59 (2020) 15402–15423, https://doi.org/10.1002/anie.201915651.

[7] F. Zhang, F. Wang, X. Wei, Y. Yang, S. Xu, D. Deng, Y.-Z. Wang, From trash to treasure: chemical recycling and upcycling of commodity plastic waste to fuels, high-valued chemicals and advanced materials, J. Energy Chem. 69 (2022) 369–388, https://doi.org/10.1016/j.jechem.2021.12.052.

[8] A.J. Martín, C. Mondelli, S.D. Jaydev, J. Pérez-Ramírez, Catalytic processing of plastic waste on the rise, Chem 7 (2021) 1487–1533, https://doi.org/10.1016/j.chempr.2020.12.006.

[9] S.D. Anuar Sharuddin, F. Abnisa, W.M.A. Wan Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, Energy Convers. Manag. 115 (2016) 308–326, https://doi.org/10.1016/J.ENCONMAN.2016.02.037.

[10] Z. Yao, J. Tong, J. Jiang, A. Mohamed Abdel Sattar, J. Constantino Gomes da Silva, S. Kumar, X. Wang, M.S. Abd-Elhady, J. Liu, M. Jin, O. Tursunov, W. Qi, Pyrolysis-gasification conversion of waste pharmaceutical blisters: thermo-kinetic and thermodynamic study, fuel gas analysis and machine learning modeling, Chem. Eng. Sci. 300 (2024) 120583, https://doi.org/10.1016/j.ces.2024.120583.

[11] A. Vijayakumar, J. Sebastian, Pyrolysis process to produce fuel from different types of plastic – a review, IOP Conf. Ser. Mater. Sci. Eng. 396 (2018) 012062, https://doi.org/10.1088/1757-899X/396/1/012062.

[12] M. Sekar, V.K. Ponnusamy, A. Pugazhendhi, S. Nižetić, T.R. Praveenkumar, Production and utilization of pyrolysis oil from solidplastic wastes: a review on pyrolysis process and influence of reactors design, J. Environ. Manag. 302 (2022) 114046, https://doi.org/10.1016/j.jenvman.2021.114046.

[13] O.Y. Yansaneh, S.H. Zein, Recent advances on waste plastic thermal pyrolysis: a critical overview, Processes 10 (2022) 332, https://doi.org/10.3390/pr10020332.

[14] T. Maqsood, J. Dai, Y. Zhang, M. Guang, B. Li, Pyrolysis of plastic species: a review of resources and products, J. Anal. Appl. Pyrolysis 159 (2021) 105295, https://doi.org/10.1016/j.jaap.2021.105295.

[15] A. Matayeva, F. Basile, F. Cavani, D. Bianchi, S. Chiaberge, Chapter 12 - Development of upgraded bio-oil via liquefaction and pyrolysis, in: S. Albonetti, S. Perathoner, E.A. Quadrelli (Eds.), Stud. Surf. Sci. Catal., Elsevier, 2019: 231–256. https://doi.org/10.1016/B978-0-444-64127-4.00012-4.

[16] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor, Chem. Eng. J. 173 (2011) 62–71, https://doi.org/10.1016/j.cej.2011.07.037.

[17] R. Miandad, M.A. Barakat, A.S. Aburiazaiza, M. Rehan, I.M.I. Ismail, A.S. Nizami, Effect of plastic waste types on pyrolysis liquid oil, Int. Biodeterior. Biodegrad. 119 (2017) 239–252, https://doi.org/10.1016/j.ibiod.2016.09.017.

[18] N. Kiran Ciliz, E. Ekinci, C.E. Snape, Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene, Waste Manag 24 (2004) 173–181, https://doi.org/10.1016/j.wasman.2003.06.002.

[19] A. Marcilla, M.I. Beltrán, R. Navarro, Evolution of products during the degradation of polyethylene in a batch reactor, J. Anal. Appl. Pyrolysis 86 (2009) 14–21, https://doi.org/10.1016/j.jaap.2009.03.004.

[20] A.L. Figueiredo, A.S. Araujo, M. Linares, Á. Peral, R.A. García, D.P. Serrano, V. J. Fernandes, Catalytic cracking of LDPE over nanocrystalline HZSM-5 zeolite prepared by seed-assisted synthesis from an organic-template-free system, J. Anal. Appl. Pyrolysis 117 (2016) 132–140, https://doi.org/10.1016/j.jaap.2015.12.005.

[21] G. Luo, T. Suto, S. Yasu, K. Kato, Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed, Polym. Degrad. Stab. 70 (2000) 97–102, https://doi.org/10.1016/S0141-3910(00)00095-1.

[22] M. Arabiourrutia, G. Elordi, G. Lopez, E. Borsella, J. Bilbao, M. Olazar, Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor, J. Anal. Appl. Pyrolysis 94 (2012) 230–237, https://doi.org/10.1016/j.jaap.2011.12.012.

[23] J. Oufkir, R. Cherouaki, S. Zerraf, S. Belaaouad, Highly efficient conversion of plastic waste into fuel via thermal cracking: thermo-structural analysis of the pyrolysis reactor and characterization of the final product, Mater. Today Proc. (2024), https://doi.org/10.1016/j.matpr.2024.02.027.

[24] A. Chaudhary, J. Lakhani, P. Dalsaniya, P. Chaudhary, A. Trada, N.K. Shah, D. S. Upadhyay, Slow pyrolysis of low-density Poly-Ethylene (LDPE): a batch experiment and thermodynamic analysis, Energy 263 (2023) 125810, https://doi.org/10.1016/j.energy.2022.125810.

[25] N.H. Dassi Djoukouo, B.M.K. Djousse, H.G. Doukeng, D.A.M. Egbe, J.K. Tangka, M. Tchoffo, Design of a pyrolyser model for the conversion of thermoplastics into fuels, Heliyon 10 (2024) e26702, https://doi.org/10.1016/j.heliyon.2024.e26702.

[26] Z.T. Aung, C. Charoenphonphanich, H. Kosaka, Fuel characterization of waste plastic diesel from mixed waste plastic catalytic pyrolysis, in: Proceedings of the Ninth Int. Conf. Eng. Appl. Sci. Technol. ICEAST (2023) 213–216, https://doi.org/10.1109/ICEAST58324.2023.10157020.

[27] S.H. Zein, C.T. Grogan, O.Y. Yansaneh, A. Putranto, Pyrolysis of high-density polyethylene waste plastic to liquid fuels—modelling and economic analysis, Processes 10 (2022) 1503, https://doi.org/10.3390/pr10081503.

[28] T. Xayachak, N. Haque, R. Parthasarathy, S. King, N. Emami, D. Lau, B. K. Pramanik, Pyrolysis for plastic waste management: an engineering perspective, J. Environ. Chem. Eng. 10 (2022) 108865–1088615, https://doi.org/10.1016/J.JECE.2022.108865.

[29] B. Kunwar, H.N. Cheng, S.R. Chandrashekaran, B.K. Sharma, Plastics to fuel: a review, Renew. Sustain. Energy Rev. 54 (2016) 421–428, https://doi.org/10.1016/J.RSER.2015.10.015.

[30] F. Abnisa, Enhanced liquid fuel production from pyrolysis of plastic waste mixtures using a natural mineral catalyst, Energies 16 (2023), https://doi.org/10.3390/en16031224.

[31] D.G. Kulas, A. Zolghadr, U.S. Chaudhari, D.R. Shonnard, Economic and environmental analysis of plastics pyrolysis after secondary sortation of mixed plastic waste, J. Clean. Prod. 384 (2023) 135542, https://doi.org/10.1016/j.jclepro.2022.135542.

[32] P. Priecel, J.A. Lopez-Sanchez, Advantages and limitations of microwave reactors: from chemical synthesis to the catalytic valorization of biobased chemicals, ACS Sustain. Chem. Eng. 7 (2019) 3–21, https://doi.org/10.1021/acssuschemeng.8b03286.

[33] R. De La Cruz Iturbides, U. Jauregui Haza, I. Polaert, Recent technological innovations on continuous microwave assisted biomass pyrolysis and perspectives for industrial scale applications, Bioresour. Technol. Rep. 19 (2022) 101202, https://doi.org/10.1016/j.biteb.2022.101202.

[34] W. Wang, C. Zhao, J. Sun, X. Wang, X. Zhao, Y. Mao, X. Li, Z. Song, Quantitative measurement of energy utilization efficiency and study of influence factors in

typical microwave heating process, Energy 87 (2015) 678–685, https://doi.org/10.1016/j.energy.2015.05.036.

[35] A. Fresneda-Cruz, C. Chaine, M.B. Figueirêdo, G. Murillo-Ciordia, A. Sanz-Martinez, I. Julian, Potentials and limitations of microwave-assisted chemical recycling of fiber-reinforced composites from wind blades, Sustain. Energy Fuels 8 (2024) 4752–4766, https://doi.org/10.1039/D4SE00242C.

[36] Comparing Life Cycle energy and global warming potential of carbon fiber composite recycling technologies and waste management options, ACS Sustain. Chem. Eng. (n.d.). https://pubs-acs-org.cuarzo.unizar.es:9443/doi/10.1021/acssuschemeng.8b01026 (Accessed 7 December 2024). 2024.

[37] J. Asomaning, S. Haupt, M. Chae, D.C. Bressler, Recent developments in microwave-assisted thermal conversion of biomass for fuels and chemicals, Renew. Sustain. Energy Rev. 92 (2018) 642–657, https://doi.org/10.1016/j.rser.2018.04.084.

[38] C. Ludlow-Palafox, H.A. Chase, Microwave pyrolysis of plastic wastes, Feedstock Recycl. Pyrolysis Waste Plast. Convert. Waste Plast. Diesel Fuels (2006) 569–594, https://doi.org/10.1002/0470021543.ch21.

[39] X. Yang, L. Ke, Q. Wu, X. Cui, Q. Zhang, X. Tian, Y. Zeng, K. Cobb, Y. Liu, R. Ruan, Y. Wang, Microwave-assisted pyrolysis spent bleaching clay for aromatic bio-oil production: exploration of heating pathway based on microwave response characteristics of feedstock, J. Anal. Appl. Pyrolysis 167 (2022) 105685, https://doi.org/10.1016/j.jaap.2022.105685.

[40] S.Y. Foong, Y.H. Chan, P.N.Y. Yek, S.S.M. Lock, B.L.F. Chin, C.L. Yiin, J.C.-W. Lan, S.S. Lam, Microwave-assisted Pyrolysis in Biomass and Waste Valorisation: Insights Into the Life-cycle Assessment (Lca) and Techno-Economic Analysis (Tea), (2023). https://doi.org/10.2139/ssrn.4646091.

[41] S.K. Vyas, S. Maurya, R.K. Verma, V.P. Singh, Synthesis and simulation studies of a 10-kW 2.45-GHz CW magnetron, IEEE Trans. Plasma Sci. 43 (2015) 3615–3619, https://doi.org/10.1109/TPS.2015.2475182.

[42] M. Radoiu, A. Mello, Technical advances, barriers, and solutions in microwave—assisted technology for industrial processing, Chem. Eng. Res. Des. 181 (2022) 331–342, https://doi.org/10.1016/j.cherd.2022.03.029.

[43] Y. Peng, Y. Wang, L. Ke, L. Dai, Q. Wu, K. Cobb, Y. Zeng, R. Zou, Y. Liu, R. Ruan, A review on catalytic pyrolysis of plastic wastes to high-value products, Energy Convers. Manag. 254 (2022) 115243–1152413, https://doi.org/10.1016/J.ENCONMAN.2022.115243.

[44] M. Bartoli, M. Frediani, C. Briens, F. Berruti, L. Rosi, An overview of temperature issues in microwave-assisted pyrolysis, Processes 7 (2019) 658, https://doi.org/10.3390/pr7100658.

[45] A. Malhotra, W. Chen, H. Goyal, P.J. Plaza-Gonzalez, I. Julian, J.M. Catala-Civera, D.G. Vlachos, Temperature homogeneity under selective and localized microwave heating in structured flow reactors, Ind. Eng. Chem. Res. 60 (2021) 6835–6847, https://doi.org/10.1021/acs.iecr.0c05580.

[46] S.D. Malkina, A.I. Malkin, A.N. Korotkov, Permittivity measurement technique for solid and powder materials, in: Proceedings of the IEEE Twenty Third Int. Conf. Young Prof. Electron Devices Mater. EDM (2022) 84–87, https://doi.org/10.1109/EDM55285.2022.9855182.

[47] D.V. Suriapparao, R. Tejasvi, A review on role of process parameters on pyrolysis of biomass and plastics: present scope and future opportunities in conventional and microwave-assisted pyrolysis technologies, Process Saf. Environ. Prot. 162 (2022) 435–462, https://doi.org/10.1016/J.PSEP.2022.04.024.

[48] D.V. Suriapparao, R. Vinu, Effects of biomass particle size on slow pyrolysis kinetics and fast pyrolysis product distribution, Waste Biomass Valoriz. 9 (2018) 465–477, https://doi.org/10.1007/s12649-016-9815-7.

[49] S.R. Juliastuti, M.I. Hisbullah, M. Abdillah, High density Polyethylene plastic waste treatment with microwave heating pyrolysis method using coconut-shell activated carbon to produce alternative fuels, IOP Conf. Ser. Mater. Sci. Eng. 334 (2018) 012015, https://doi.org/10.1088/1757-899X/334/1/012015.

[50] Z. Liu, M. Xie, T. Zhou, J. Yang, Y. Yang, T. Liu, S. Dai, Q. Huang, Q. Cen, P. Xiao, B. Li, H. Du, A review on liquid fuel produced from microwave-assisted pyrolysis of plastic waste, Process Saf. Environ. Prot. 187 (2024) 833–844, https://doi.org/10.1016/j.psep.2024.05.035.

[51] S. Ge, Y. Shi, C. Xia, Z. Huang, M. Manzo, L. Cai, H. Ma, S. Zhang, J. Jiang, C. Sonne, S.S. Lam, Progress in pyrolysis conversion of waste into value-added liquid pyro-oil, with focus on heating source and machine learning analysis, Energy Convers. Manag. 245 (2021) 114638, https://doi.org/10.1016/j.enconman.2021.114638.

[52] K. Ding, S. Liu, Y. Huang, S. Liu, N. Zhou, P. Peng, Y. Wang, P. Chen, R. Ruan, Catalytic microwave-assisted pyrolysis of plastic waste over NiO and HY for gasoline-range hydrocarbons production, Energy Convers. Manag. 196 (2019) 1316–1325, https://doi.org/10.1016/j.enconman.2019.07.001.

[53] E.H. Istoto, Widayat, S. Saptadi, Production of fuels from HDPE and LDPE plastic waste via pyrolysis methods, E3S Web Conf. 125 (2019) 14011, https://doi.org/10.1051/e3sconf/201912514011.

[54] H. Arshad, S.A. Sulaiman, Z. Hussain, M.Y. Naz, M.N.Z. Moni, Effect of input power and process time on conversion of pure and mixed plastics into fuels through microwave-metal interaction pyrolysis, Waste Biomass Valoriz. 12 (2021) 3443–3457, https://doi.org/10.1007/s12649-020-01225-9.

[55] X. Zhang, H. Lei, G. Yadavalli, L. Zhu, Y. Wei, Y. Liu, Gasoline-range hydrocarbons produced from microwave-induced pyrolysis of low-density polyethylene over ZSM-5, Fuel 144 (2015) 33–42, https://doi.org/10.1016/j.fuel.2014.12.013.

[56] Y. Zhang, D. Duan, H. Lei, E. Villota, R. Ruan, Jet fuel production from waste plastics via catalytic pyrolysis with activated carbons, Appl. Energy 251 (2019) 113337, https://doi.org/10.1016/j.apenergy.2019.113337.

[57] L. Fan, P. Chen, Y. Zhang, S. Liu, Y. Liu, Y. Wang, L. Dai, R. Ruan, Fast microwave-assisted catalytic co-pyrolysis of lignin and low-density polyethylene with HZSM-5 and MgO for improved bio-oil yield and quality, Bioresour. Technol. 225 (2017) 199–205, https://doi.org/10.1016/j.biortech.2016.11.072.

[58] Y. Zhang, P. Chen, S. Liu, P. Peng, M. Min, Y. Cheng, E. Anderson, N. Zhou, L. Fan, C. Liu, G. Chen, Y. Liu, H. Lei, B. Li, R. Ruan, Effects of feedstock characteristics on microwave-assisted pyrolysis – a review, Bioresour. Technol. 230 (2017) 143–151, https://doi.org/10.1016/j.biortech.2017.01.046.

[59] J. Luo, S. Sun, X. Chen, J. Lin, R. Ma, R. Zhang, L. Fang, In-depth exploration of the energy utilization and pyrolysis mechanism of advanced continuous microwave pyrolysis, Appl. Energy 292 (2021) 116941–1169411, https://doi.org/10.1016/j.apenergy.2021.116941.

[60] L. Fan, L. Liu, Z. Xiao, Z. Su, P. Huang, H. Peng, S. Lv, H. Jiang, R. Ruan, P. Chen, W. Zhou, Comparative study of continuous-stirred and batch microwave pyrolysis of linear low-density polyethylene in the presence/absence of HZSM-5, Energy 228 (2021) 120612, https://doi.org/10.1016/j.energy.2021.120612.

[61] A. Ramirez, J.L. Hueso, R. Mallada, J. Santamaria, In situ temperature measurements in microwave-heated gas-solid catalytic systems. Detection of hot spots and solid-fluid temperature gradients in the ethylene epoxidation reaction, Chem. Eng. J. 316 (2017) 50–60, https://doi.org/10.1016/J.CEJ.2017.01.077.

[62] W.H. Yang, Y.S. Tarng, Design optimization of cutting parameters for turning operations based on the Taguchi method, J. Mater. Process. Technol. 84 (1998) 122–129, https://doi.org/10.1016/S0924-0136(98)00079-X.

[63] Y. Zhang, Z. Fu, W. Wang, G. Ji, M. Zhao, A. Li, Kinetics, product evolution, and mechanism for the pyrolysis of typical plastic waste, ACS Sustain. Chem. Eng. 10 (2022) 91–103, https://doi.org/10.1021/acssuschemeng.1c04915.

[64] K. Zheng, Y. Wu, Z. Hu, S. Wang, X. Jiao, J. Zhu, Y. Sun, Y. Xie, Progress and perspective for conversion of plastic wastes into valuable chemicals, Chem. Soc. Rev. 52 (2023) 8–29, https://doi.org/10.1039/D2CS00688J.

[65] M. Torres, A machine learning method for parameter estimation and sensitivity analysis, in: M. Paszynski, D. Kranzlmüller, V.V. Krzhizhanovskaya, J. J. Dongarra, P.M.A. Sloot (Eds.), Comput. Sci. – ICCS 2021, Springer International Publishing, Cham, 2021, pp. 330–343, https://doi.org/10.1007/978-3-030-77977-1_26.

[66] A.P. dos S. Pereira, M.H.P. da Silva, É .P. Lima, A. dos S. Paula, F.J. Tommasini, Processing and characterization of PET composites reinforced with geopolymer concrete waste, Mater. Res. 20 (2017) 411–420, https://doi.org/10.1590/1980-5373-MR-2017-0734.

[67] L.M. Alvarenga, T.P. Xavier, M.A.S. Barrozo, M.S. Bacelos, T.S. Lira, Determination of activation energy of pyrolysis of carton packaging wastes and its pure components using thermogravimetry, Waste Manag 53 (2016) 68–75, https://doi.org/10.1016/j.wasman.2016.04.015.

[68] A. Phounglamcheik, L. Wang, H. Romar, N. Kienzl, M. Broström, K. Ramser, Ø. Skreiberg, K. Umeki, Effects of pyrolysis conditions and feedstocks on the properties and gasification reactivity of charcoal from woodchips, Energy Fuels 34 (2020) 8353–8365, https://doi.org/10.1021/acs.energyfuels.0c00592.

[69] J.G. Speight, Chapter 9 - Chemical and physical properties of hydrocarbons, in: J. G. Speight (Ed.), Handb. Ind. Hydrocarb. Process., Gulf Professional Publishing, Boston, 2011, pp. 325–353, https://doi.org/10.1016/B978-0-7506-8632-7.10009-X.

[70] B. Erkmen, A. Ozdogan, A. Ezdesir, G. Celik, Can pyrolysis oil be used as a feedstock to close the gap in the circular economy of polyolefins? Polymers 15 (2023) 859, https://doi.org/10.3390/polym15040859.

[71] Z. Gholami, F. Gholami, Z. Tišler, M. Vakili, A review on the production of light olefins using steam cracking of hydrocarbons, Energies 14 (2021) 8190, https://doi.org/10.3390/en14238190.

[72] L. Li, H. Luo, Z. Shao, H. Zhou, J. Lu, J. Chen, C. Huang, S. Zhang, X. Liu, L. Xia, J. Li, H. Wang, Y. Sun, Converting plastic wastes to naphtha for closing the plastic loop, J. Am. Chem. Soc. 145 (2023) 1847–1854, https://doi.org/10.1021/jacs.2c11407.

[73] O.A. Attallah, P. Ferrero, M. Ljesevic, B. Loncarevic, I. Aleksic, B. Pantelic, G. Gojgic, R. Siaperas, E. Topakas, V. Beskoski, J. Nikodinovic-Runic, Micro-wave induced pyrolysis of low density polyethylene (LDPE) and biodegradation of resulting wax in soil and by defined microbial consortia is closing the loop towards LDPE upcycling, J. Environ. Chem. Eng. 12 (2024) 114269, https://doi.org/10.1016/j.jece.2024.114269.

[74] N. Zhou, L. Dai, Y. Lyu, H. Li, W. Deng, F. Guo, P. Chen, H. Lei, R. Ruan, Catalytic pyrolysis of plastic wastes in a continuous microwave assisted pyrolysis system for fuel production, Chem. Eng. J. 418 (2021) 129412, https://doi.org/10.1016/J.CEJ.2021.129412.

[75] Y. Cui, Y. Zhang, L. Cui, Q. Xiong, E. Mostafa, Microwave-assisted fluidized bed reactor pyrolysis of polypropylene plastic for pyrolysis gas production towards a sustainable development, Appl. Energy 342 (2023) 121099–1210919, https://doi.org/10.1016/J.APENERGY.2023.121099.

[76] Y. Zhang, C. Zhou, Y. Liu, T. Zhang, X. Li, L. Wang, J. Dai, J. Qu, C. Zhang, M. Yu, Y. Yuan, Y. Jin, H. Yu, J. Fu, Product characteristics and potential energy recovery for microwave assisted pyrolysis of waste printed circuit boards in a continuously operated auger pyrolyser, Energy 239 (2022) 122383–1223813, https://doi.org/10.1016/j.energy.2021.122383.

[77] H. Goyal, T.-Y. Chen, W. Chen, D.G. Vlachos, A review of microwave-assisted process intensified multiphase reactors, Chem. Eng. J. 430 (2022) 133183, https://doi.org/10.1016/j.cej.2021.133183.

[78] A. Locaspi, M. Pelucchi, M. Mehl, T. Faravelli, Towards a lumped approach for solid plastic waste gasification: polyethylene and polypropylene pyrolysis, Waste Manag 156 (2023) 107–117, https://doi.org/10.1016/j.wasman.2022.11.028.

[79] G. Jiang, R. Fenwick, J. Seville, H.B. Mahood, R.B. Thorpe, S. Bhattacharya, D.A. S. Monsalve, G.A. Leeke, Lumped kinetic modelling of polyolefin pyrolysis: a non-isothermal method to estimate rate constants, J. Anal. Appl. Pyrolysis 164 (2022) 105530, https://doi.org/10.1016/j.jaap.2022.105530.

[80] Z. Fu, Q. Sun, S. Yang, F. Hua, Y. Ji, Y. Cheng, Molecular-level kinetic modelling for the pyrolysis of high-density polyethylene in a two-stage process, J. Anal. Appl. Pyrolysis 178 (2024) 106428, https://doi.org/10.1016/j.jaap.2024.106428.

[81] A.E. Lechleitner, T. Schubert, W. Hofer, M. Lehner, Lumped kinetic modeling of polypropylene and polyethylene co-pyrolysis in tubular reactors, Processes 9 (2021) 34, https://doi.org/10.3390/pr9010034.

[82] S.-M. Lorbach, A.E. Lechleitner, F. Zapf, M. Lehner, Usefulness of lumped kinetic modeling, Chem. Bio Eng. 1 (2024) 623–632, https://doi.org/10.1021/cbe.4c00032.

[83] T. Schubert, A. Lechleitner, M. Lehner, W. Hofer, 4-Lump kinetic model of the co-pyrolysis of LDPE and a heavy petroleum fraction, Fuel 262 (2020) 116597, https://doi.org/10.1016/j.fuel.2019.116597.

[84] L.S. Diaz-Silvarrey, K. Zhang, A.N. Phan, Monomer recovery through advanced pyrolysis of waste high density polyethylene (HDPE), Green Chem. 20 (2018) 1813–1823, https://doi.org/10.1039/C7GC03662K.

[85] A. Witkowski, A.A. Stec, T.R. Hull, Thermal decomposition of polymeric materials, in: M.J. Hurley, D. Gottuk, J.R. Hall, K. Harada, E. Kuligowski, M. Puchovsky, J. Torero, J.M. Watts, C. Wieczorek (Eds.), SFPE Handb. Fire Prot. Eng., Springer New York, New York, NY, 2016, pp. 167–254, https://doi.org/10.1007/978-1-4939-2565-0_7.

[86] T. Ueno, E. Nakashima, K. Takeda, Quantitative analysis of random scission and chain-end scission in the thermal degradation of polyethylene, Polym. Degrad. Stab. 95 (2010) 1862–1869, https://doi.org/10.1016/j.polymdegradstab.2010.04.020.

[87] D.P. Serrano, J. Aguado, J.M. Escola, J.M. Rodríguez, G. San Miguel, An investigation into the catalytic cracking of LDPE using Py–GC/MS, J. Anal. Appl. Pyrolysis 74 (2005) 370–378, https://doi.org/10.1016/j.jaap.2004.11.026.

[88] N.H. Nazarloo, O. Zabihi, K. Shirvanimoghaddam, M. Ahmadi, P. Zamani, M. Naebe, Innovative Ex-Situ catalyst bed integration for LDPE plastic Pyrolysis: a thermodynamically closed system approach, Chem. Eng. J. 495 (2024) 153450, https://doi.org/10.1016/j.cej.2024.153450.

[89] I. Calinescu, G. Psenovschi, M. Cojocaru, C.G. Chisega-Negrila, C. Albulescu, M. Brebu, A. Trifan, N.D. Ignat, P. Chipurici, Catalytic pyrolysis of low-density polyethylene waste, Sustainability 16 (2024) 6788, https://doi.org/10.3390/su16166788.

[90] L. Dai, H. Zhao, N. Zhou, K. Cobb, P. Chen, Y. Cheng, H. Lei, R. Zou, Y. Wang, R. Ruan, Catalytic microwave-assisted pyrolysis of plastic waste to produce naphtha for a circular economy, Resour. Conserv. Recycl. 198 (2023) 107154, https://doi.org/10.1016/j.resconrec.2023.107154.

[91] K. Murata, Y. Hirano, Y. Sakata, Md.A. Uddin, Basic study on a continuous flow reactor for thermal degradation of polymers, J. Anal. Appl. Pyrolysis 65 (2002) 71–90, https://doi.org/10.1016/S0165-2370(01)00181-4.

[92] M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Olazar, Light olefins from HDPE cracking in a two-step thermal and catalytic process, Chem. Eng. J. 207–208 (2012) 27–34, https://doi.org/10.1016/j.cej.2012.06.105.

[93] M. Artetxe, G. Lopez, G. Elordi, M. Amutio, J. Bilbao, M. Olazar, Production of light Olefins from polyethylene in a two-step process: pyrolysis in a conical spouted bed and downstream high-temperature thermal cracking, Ind. Eng. Chem. Res. 51 (2012) 13915–13923, https://doi.org/10.1021/ie300178e.

[94] R.R. Mishra, P.H. Rana, P.A. Parikh, Microwave-assisted pyrolysis of low-density polyethylene (LDPE)to value-added products over HY, HZSM-5 and Hβ catalyst, Mater. Today Commun. 41 (2024) 110829, https://doi.org/10.1016/j.mtcomm.2024.110829.

[95] I.J. Siddique, A.A. Salema, E. Antunes, R. Vinu, Technical challenges in scaling up the microwave technology for biomass processing, Renew. Sustain. Energy Rev. 153 (2022) 111767, https://doi.org/10.1016/j.rser.2021.111767.

[96] N. Dutta, P. Mondal, A. Gupta, Optimization of process parameters using response surface methodology for maximum liquid yield during thermal pyrolysis of blend of virgin and waste high-density polyethylene, J. Mater. Cycles Waste Manag. 24 (2022) 1182–1193, https://doi.org/10.1007/s10163-022-01392-y.

[97] V. Balasundram, K.K. Zaman, N. Ibrahim, R.Md Kasmani, R. Isha, MohdK. Abd Hamid, H. Hasbullah, Optimizing the catalytic performance of Ni-Ce/HZSM-5 catalyst for enriched C6–C8 hydrocarbons in pyrolysis oil via response surface methodology, Biomass Convers. Biorefin. 13 (2023) 8603–8613, https://doi.org/10.1007/s13399-020-00873-0.

[98] I.A. Julian, A. Fresneda-Cruz, Scale-up of Microwave-assisted Heterogeneous Catalytic Processes, (2023). https://doi.org/10.1039/BK9781837670277-00368.

[99] Z. Zhang, W. Xu, Y. Zhu, S. Ma, Y. Li, J. Jiang, Z. Yang, W. Cheng, Z. Zhou, B. Sun, The decomposition mechanism of ethylene and modeling simulation during LDPE production: a comprehensive review and perspectives, J. Anal. Appl. Pyrolysis 175 (2023) 106199, https://doi.org/10.1016/j.jaap.2023.106199.

[100] S.M. Frolov, I.O. Shamshin, M.V. Kazachenko, V.S. Aksenov, I.V. Bilera, V. S. Ivanov, V.I. Zvegintsev, Polyethylene pyrolysis products: their detonability in air and applicability to solid-fuel detonation Ramjets, Energies 14 (2021) 820, https://doi.org/10.3390/en14040820.