https://doi.org/10.31436/iiumej.v27i3.3489

Pretreatment of Plastic Waste and Optimization of the Pyrolysis Process for Liquid Fuel Production

NORSYAMIRA LIYANA SULAIMAN, YUSILAWATI AHMAD NOR*

Department of Chemical Engineering and Sustainability, Kulliyyah of Engineering, International Islamic University Malaysia, P.O. Box 10, 50728 Kuala Lumpur, Malaysia.

**Corresponding author: yusilawati_ahmadnor@iium.edu.my*

(Received: 30 October 2024; Accepted: 21 June 2026; Published online*: 11 September 2026)*

ABSTRACT: This study investigates the conversion of polypropylene (PP), polyethylene terephthalate (PET), and high-density polyethylene (HDPE) into liquid fuel through pyrolysis, emphasizing the mechanistic effects of mechanical and chemical pretreatment. As global plastic waste generation reaches critical levels, sustainable upcycling technologies are urgently required to support the circular economy and mitigate escalating environmental contamination. Therefore, this study aimed to optimize pyrolysis parameters and maximize liquid-fuel yield by comparing untreated plastic feedstocks with ozonated, crushed, and combined ozonated-crushed samples. Pretreatment methods included ozonation and crushing, followed by pyrolysis under varying conditions of temperature (300 to 400 °C), heating rate (5 to 15 °C/min), holding time (1 to 3 h), and ozonation duration (0.5 to 1.5 h). For the first objective, the highest yield (46.6%) was achieved using ozone-treated PP at 400 °C, a heating rate of 5 °C/min, a holding time of 1 h, and an ozonation time of 1 h. Mechanistically, ozonation increased liquid-fuel yield by introducing oxygenated functional groups that facilitate chain scission at lower activation energies, whereas crushing plastic gave a lower liquid yield than ozonation by accelerating volatilization into non-condensable gases. Furthermore, FTIR analysis revealed that liquid fuel from treated plastics shared chemical similarities with diesel, gasoline, and kerosene, particularly in the C-H and aromatic C=C bands, although PP-derived fuels exhibited unique olefinic signatures. A Box-Behnken design and ANOVA were used to optimize the process conditions for the second objective. A maximum yield of 38.8% was achieved under the following conditions: 400 °C, a heating rate of 10 °C/min, a holding time of 2 h, and an ozonation time of 0.5 h. The PP-derived liquid fuel contained hydrocarbons similar to commercial fuels, indicating its potential as an alternative fuel source. This study concludes that chemical pretreatment significantly enhanced fuel yield and quality, making PP-derived liquid fuel a potential substitute for conventional petroleum fuels and thereby advancing the technological readiness of plastic-to-fuel biorefineries.

ABSTRAK: Kajian ini mengkaji penukaran polipropilena (PP), polietilena tereftalat (PET), dan polietilena berketumpatan tinggi (HDPE) kepada bahan api cecair melalui pirolisis, dengan penekanan terhadap kesan mekanistik prarawatan mekanikal dan kimia. Memandangkan penjanaan sisa plastik global telah mencapai tahap kritikal, teknologi kitar tinggi nilai sisa secara mampan amat diperlukan bagi menyokong ekonomi kitaran dan mengurangkan pencemaran alam sekitar yang semakin meningkat. Oleh itu, kajian ini bertujuan mengoptimum parameter pirolisis dan memaksimum hasil bahan api cecair dengan membanding bahan suapan plastik tanpa rawatan dengan sampel rawatan menggunakan ozon, dihancurkan, serta gabungan ozonasi dan penghancuran. Kaedah prarawatan melibatkan ozonasi dan penghancuran, diikuti oleh pirolisis pada keadaan suhu berbeza (300–400 °C), kadar pemanasan (5–15 °C/min), masa pegangan (1–3 jam), dan tempoh ozonasi (0.5–1.5 jam). Bagi objektif pertama, hasil tertinggi sebanyak 46.6% diperoleh daripada PP rawatan ozon pada suhu 400 °C, kadar pemanasan 5 °C/min, masa pegangan 1 jam, dan tempoh

ozonasi 1 jam. Secara mekanistik, ozonasi meningkatkan hasil bahan api cecair dengan memperkenal kumpulan oksigen yang memudahkan pemutusan rantai pada tenaga pengaktifan yang lebih rendah, manakala penghancuran plastik menghasilkan perolehan cecair lebih rendah berbanding ozonasi akibat pemeruapan yang dipercepatkan kepada gas tidak terkondensasi. Selain itu, analisis inframerah transformasi Fourier (FTIR) menunjukkan bahawa bahan api cecair daripada plastik terawat mempunyai persamaan kimia dengan diesel, petrol, dan kerosin, khususnya pada jalur C–H dan C=C aromatik, walaupun bahan api terbitan PP menunjukkan ciri olefin tersendiri. Reka bentuk Box-Behnken dan analisis varians (ANOVA) digunakan untuk mengoptimumkan keadaan proses bagi objektif kedua. Hasil maksimum sebanyak 38.8% dicapai pada suhu 400 °C, kadar pemanasan 10 °C/min, masa pegangan 2 jam, dan tempoh ozonasi 0.5 jam. Bahan api cecair terbitan PP mengandungi hidrokarbon serupa bahan api komersial, sekaligus menunjukkan potensinya sebagai sumber bahan api alternatif. Kajian ini menyimpulkan bahawa prarawatan kimia meningkatkan hasil dan kualiti bahan api dengan ketara, menjadikan bahan api cecair terbitan PP berpotensi sebagai pengganti kepada bahan api petroleum konvensional serta meningkatkan kesiapsiagaan teknologi biopenapisan plastik kepada bahan api.

KEYWORDS: *Plastic Wastes, Pyrolysis, Liquid Fuel, Pretreatment Methods, Ozonation*

1. INTRODUCTION

Plastic products significantly enhance human welfare and support innovations in healthcare, automotive technology, electronics, construction, and medical packaging. However, global plastic production, which amounts to approximately 413 million tonnes annually, has caused significant environmental issues, including land and marine pollution and risks to human health [1, 2]. Recent global projections indicate that, in 2025, approximately 130 million tonnes (Mt) of plastic is estimated to pollute the environment each year, affecting land, air, and water [2]. Without ambitious global intervention, this figure is projected to rise to 280 Mt by 2040, which is equivalent to dumping nearly one garbage truck worth of plastic waste every second. Furthermore, approximately 31.9% of this global volume is mismanaged, mainly due to the unchecked proliferation of single-use packaging [1, 2]. Traditional disposal methods, such as landfilling and incineration, exacerbate these problems by causing ecological degradation and emitting harmful greenhouse gases, necessitating sustainable, environmentally friendly solutions [3, 4].

In Malaysia, the plastic pollution crisis is particularly acute because of infrastructure limitations and high consumption rates. The nation's per capita plastic consumption is 16.78 kg, placing it among the highest consumers in the region. Annual post-consumer plastic waste generation increased from 1.07 million tonnes in 2016 to 1.4 million tonnes in 2019, with only 21% recycled and the remainder disposed of in landfills or incinerated. Malaysia currently operates 135 landfills, most of which are nearing full capacity and are potential sources of methane emissions [3]. If current trends continue, the world could be burdened with 12 billion metric tonnes of plastic waste by 2050 [5]. The slow decomposition of plastic over centuries poses a severe long-term environmental threat [5, 6]. Recognizing this unsustainable trajectory, the Malaysian government has mandated a paradigm shift through the Circular Economy Blueprint for Solid Waste (2025–2035) and the impending enforcement of Extended Producer Responsibility (EPR) regulations slated for 2026. These legislative frameworks demand robust technological solutions to reclaim the estimated 81% of material value that is currently lost during conventional plastic disposal [3, 7, 8, 9].

Plastic recycling faces challenges such as feedstock segregation, processing cost, contamination, and labor-intensive separation [4, 10]. Therefore, converting plastic waste into

fuel for the petrochemical industry, transportation, and heating applications has been explored as an alternative waste valorization route [6, 10, 11, 12]. Pyrolysis is an emerging thermochemical technology that converts low-value municipal plastic waste into higher-value char, tar, gas, and liquid fuel [6, 10, 12]. This process decomposes organic substances in the absence of oxygen, producing carbon-rich solids, liquid oil, and gases [6, 11]. Previous studies have documented the pyrolysis of various feedstocks, including LDPE, HDPE, PP, and PS, yielding approximately 50% carbon solid from the original organic material [13]. For example, LDPE can produce 10–15% gas, 45–50% liquid oil, and 35–40% solid residue, depending on operating conditions [6, 14]. Liquid fuels derived from plastic waste can be used in engines, power generators, and heating systems. Moreover, studies indicate that plastic waste pyrolysis can generate crude-oil-like products with properties comparable to standard crude oil [10, 11].

Although pyrolysis offers several benefits, it also presents energy-consumption challenges because conventional pyrolysis requires high temperatures (300–1000 °C), which can increase operating costs [6, 10, 12]. This process is also constrained by the low oil yield and poor oil quality, and it often requires extensive preprocessing of plastic waste [10, 15]. Furthermore, the liquid-fuel quality depends on the macromolecular structure of the feed plastics and the selected pyrolysis parameters [12, 16, 17]. Catalysts and pretreatment processes have shown promise for improving liquid-fuel yield and quality, but further work is needed to refine these methods [10, 15, 18]. Historically, pretreatment has been limited to methods such as mechanical sorting, thermal drying, and basic solvent extraction, which do little to fundamentally alter the thermodynamic energy barriers required for subsequent depolymerization [19].

Chemical pretreatment methods have also been explored to modify the molecular structure of plastics prior to pyrolysis. Among these methods, ozonation has gained attention due to its ability to induce oxidative degradation under relatively mild conditions. Ozonation breaks plastic molecules into smaller fragments through oxidative chain scission. During ozonation, reactive oxygen species attack the polymer backbone, targeting tertiary carbons and unsaturated bonds and forming unstable ozonides and hydroperoxides. These intermediate structures may have lower activation energies for thermal cracking than virgin polymer chains, theoretically allowing for higher liquid yields at lower pyrolysis temperatures [20]. Despite these promising attributes, the quantitative effects of ozonation pretreatment on pyrolysis performance across different plastic types have not yet been comprehensively investigated. A detailed comparison of the responses of various plastics such as polypropylene (PP), polyethylene terephthalate (PET), and high-density polyethylene (HDPE) to ozonation pretreatment is therefore needed to better understand its influence on fuel yield, product quality, and the formation of undesirable byproducts [10, 15]. By modifying the molecular structure of plastic waste prior to thermal conversion, ozonation pretreatment may further enhance the environmental and operational benefits of plastic waste pyrolysis.

To maximize fuel yield and quality, the pyrolysis conditions, including temperature, heating rate, and holding time, must be optimized [12, 21]. However, previous optimization studies on liquid-fuel yield have not fully considered the combined effects of pretreatment processes. Therefore, the full potential of combining optimum pyrolysis conditions with suitable pretreatment has yet to be exploited. Although statistical optimization techniques, such as Central Composite Design (CCD), are widely used in the literature, they frequently require testing at extreme axial points [21]. In thermochemical pyrolysis, subjecting polymers simultaneously to maximum temperatures, maximum holding times, and maximum heating rates can induce hazardous thermal runaway or secondary cracking that inadvertently favors non-condensable gas production over liquid fuels [10, 12]. Consequently, a Box-Behnken

https://doi.org/10.31436/iiumej.v27i3.3489

design (BBD) offers a suitable methodological alternative. BBD constructs a response surface using only the midpoints of the experimental cube and avoids extreme operational boundaries [21]. This ensures that the optimization process remains within a safe and energetically viable operating zone while requiring fewer experimental runs.

The aim of this research is to identify the optimal combinations of temperature, heating rate, holding time, and ozonation conditions for producing high-quality liquid fuel. Optimizing these parameters can make the pyrolysis process more economical, efficient, and sustainable. This study aims to increase liquid-fuel production from plastic waste while supporting environmental protection and resource conservation. This research can reduce costs, support sustainability, and make plastic-waste recycling more environmentally friendly through process optimization.

2. MATERIALS AND METHODS

This section defines the experimental techniques used in this study, including the project workflow, experimental design, materials and apparatus, and detailed analysis procedures.

2.1. Experimental Materials

In this study, polypropylene (PP), polyethylene terephthalate (PET), and high-density polyethylene (HDPE) plastic wastes were collected from households and areas surrounding the IIUM campus. Dichloromethane (DCM) (Sigma-Aldrich, >99% purity) was used for oil extraction. During pyrolysis, DCM was used to separate the liquid fuel (oil) from the carbon material produced. Scissors and knives were used to cut the plastic waste. Standard analytical laboratory equipment, including crucible boats, spatulas, sealer bags, centrifuge tubes, beakers, filter paper, conical flasks, weighing boats, micropipettes, and measuring cylinders, was used for sample preparation and measurement. The essential equipment included a laboratory-scale pyrolysis furnace, an analytical weighing scale, a Nano 15 ozone generator, a mechanical crusher (HITOP SY-20), and an FTIR instrument (Bruker INVENIO S). Safety equipment, including gloves, lab coats, and a ventilation system, was also used to ensure a safe working environment.

2.2. Experimental Procedures

2.2.1. Preparation of Plastic Waste and Pretreatment

Plastic waste was sorted, cleaned, and shredded into 1.25 cm by 1.25 cm pieces. Ozonation was performed on the sorted plastic waste at an ozone flow rate of 1 L/min for 1 h using the Nano 15 ozone generator to modify the plastic's molecular structure through oxidative degradation. For the optimization runs, ozonation time was varied as described in Section 2.2.3. Alternatively, the plastic waste was fed into the HITOP SY-20 crusher machine and crushed into smaller particles using a 3 mm × 6 mm mesh to increase the surface area available for treatment.

2.2.2. Plastic Waste Screening and Pretreatment Methods

PP, PET, and HDPE plastic wastes were each weighed at 5 g. In a nitrogen atmosphere (maintained via a continuous purge to ensure strictly non-oxidative conditions and prevent combustion), the pyrolysis process was carried out at 400 °C with a heating rate of 5 °C/min and a holding time of 1 h. To ensure experimental consistency and statistical reliability, all pyrolysis screening runs were performed in triplicate. Under identical conditions, the liquid-fuel yields were reported as the mean of the three replicates. All masses were measured with a

calibrated analytical balance (±0.001 g), and the same furnace temperature program, nitrogen flow, and extraction protocol were applied throughout to maintain experimental consistency. Solid products, mainly carbonaceous material, were collected, weighed, and placed in centrifuge tubes. Liquid fuel retained in the carbon material was extracted using DCM. The liquid fuel was separated from the carbon material by sonication and filtration using filter paper. The carbon material was dried overnight at 60 °C in an oven before weighing. The extracted liquid fuel was also weighed, and the experiment was repeated for each plastic waste type under different pretreatment conditions.

2.2.3. Optimization of Pyrolysis for Liquid Fuel Production

A Box-Behnken design, a response-surface methodology, was used to optimize the pyrolysis of ozone-treated PP plastic waste. The effects of temperature (300–400 °C), heating rate (5–15 °C/min), holding time (1–3 h), and ozonation time (0.5–1.5 h) on the liquid-fuel yield during macromolecular breakdown were investigated using four independent variables. As previously justified, the BBD approach was selected to construct a response-surface model without extrapolating into extreme and potentially hazardous axial permutations. The process variables were optimized, and liquid-fuel yield was maximized using 24 experimental runs, including the required center-point replications to estimate the system's pure error.

2.3. Experimental Analysis

FTIR analysis was performed to identify the functional groups present in the liquid fuel and provide insight into its molecular structure. Liquid fuel samples from PP plastic waste with different pretreatments (non-treated, ozone-treated, crushed, and crushed and ozone-treated) were analyzed. The FTIR instrument emitted infrared light across a standard mid-infrared range (4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}, with 32 scans accumulated per sample), and the liquid fuel absorbed specific frequencies associated with functional groups. The resulting absorption spectra were recorded and analyzed to identify characteristic functional-group peaks. The spectra were subsequently interpreted against published characterization of plastic-derived and conventional fuel components to assess the need for further upgrading.

3. Results and Discussion

3.1. Screening of Plastic Waste and Pretreatment Methods

The screening process involved pyrolyzing three types of plastic waste, PP, PET, and HDPE, under four pretreatment conditions: ozone-treated, crushed, ozone-treated-and-crushed, and untreated. Table 1 shows that liquid-fuel yield was highest for ozone-treated PP (46.6%), followed by PET (35.0%) and HDPE (8.2%). Promising results were also seen in the combined ozone-treated-and-crushed conditions, in which PP yielded 35.4%, PET yielded 32.4%, and HDPE yielded 5.4%. All plastic types showed lower liquid-fuel yields after crushing alone than after ozonation, with PP at 31.0%, PET at 24.0%, and HDPE at 3.2%. Non-treated plastics gave the lowest liquid-fuel yields, with 21.6% for PP, 17.2% for PET, and 2.2% for HDPE.

The results show that ozone treatment can efficiently enhance liquid-fuel production from plastic waste, especially PP, which exhibited the highest yield under all conditions. The ozone-treated PP yield of 46.6% is notable compared with previous studies on liquid-fuel conversion in the slow-pyrolysis process, which reported a maximum conversion rate of 50.1% even under highly optimized catalytic environments [18, 22, 23]. Although the yield was below the maximum values reported in some studies, the ozone pretreatment effect was large compared with untreated and other pretreated samples, indicating the potential of ozone pretreatment to improve the efficiency of liquid-fuel production from plastic waste.

Compared with alternative pretreatment strategies reported in the literature, such as dry washing, solvent extraction, or thermal drying, ozonation can alter the polymer's fundamental reaction kinetics rather than merely removing surface contaminants [10, 15, 20]. This distinction is evident from the present screening results, in which ozone pretreatment increased the PP liquid-fuel yield from 21.6% to 46.6%, representing a 25.0 percentage-point increase and a 2.16-fold improvement relative to untreated PP. By comparison, crushing alone increased the PP liquid-fuel yield to 31.0%, indicating that increased surface area and improved heat transfer contributed to conversion but did not achieve the same enhancement as chemical oxidation. Physical preprocessing methods, including washing, drying, crushing, and sieving, mainly improve feed cleanliness, moisture control, particle homogeneity, and thermal accessibility; however, they do not intentionally generate chemically weak sites along the polymer backbone [10, 12, 15].

The limited effect of cleaning-type pretreatment is also supported by previous PP pyrolysis work, in which washed and unwashed waste PP differed by only 1.85 percentage points in liquid yield at 300 °C (81.47 and 79.62 wt%, respectively) and 1.92 percentage points at 400 °C (80.55 and 78.70 wt%, respectively) [24]. In contrast, ozonation acts as an advanced oxidative preprocessing route. Ozone-derived reactive oxygen species preferentially attack tertiary carbon sites in PP, generating peroxy and hydroperoxide intermediates that undergo β-chain scission to form lower-molecular-weight fragments with olefinic and ketone end groups [20]. These oxidized defects facilitate thermal cracking initiation and are therefore consistent with lower effective thermal resistance to depolymerization than in untreated PP. Although activation energies were not directly measured in the present study, the substantial yield increase and the subsequent appearance of oxygenated FTIR bands support facilitated early-stage chain scission rather than a simple surface-area effect.

Solvent-based approaches should be interpreted differently because they are primarily separation or product-recovery methods rather than true depolymerization pretreatments. For example, sequential solvent extraction has been reported to recover 63–81% of pyrolytic oil trapped in crude char and to remove 64–86% of inorganic contaminants; however, this treatment does not chemically activate the polymer backbone before pyrolysis [15]. Selective dissolution can also improve polymer separation, but solvent cost, toxicity, and recovery requirements constrain its implementation [15]. Hydrogen-peroxide-based treatment may generate alkoxy, peroxy, and hydroxyl radical species that can promote PP chain fragmentation; nevertheless, it is a liquid-phase oxidation route that requires chemical storage, post-treatment separation, and drying [20]. Therefore, the present results indicate that ozonation is particularly advantageous as a gas-phase chemical preprocessing method because it introduces chain-scission-prone oxygenated sites without using an organic solvent, although safe ozone generation and off-gas destruction remain necessary.

The visual differences in Fig. 1 further support the influence of polymer structure and pretreatment on product distribution. The recovered product mixtures are consistent with the quantitative trend in Table 1, with PP producing the greatest condensable liquid fraction, followed by PET and HDPE. Fig. 1 therefore provides qualitative evidence of feedstock-dependent product distribution. To quantify these differences, the liquid-fuel yield was calculated as the mass of recovered liquid fuel relative to the initial mass of plastic feedstock, as expressed in Eq. (1). This calculation enables direct comparison of the liquid products obtained from PP, PET, and HDPE under the different pretreatment conditions. The following discussion relates these differences to the molecular structures and thermal-degradation behavior of the three polymers.

https://doi.org/10.31436/iiumej.v27i3.3489

$$Percentage\ of\ liquid\ fuel\ yield\ (\%) = \frac{Mass\ of\ liquid\ fuel\ (g)}{Initial\ mass\ of\ plastic\ (g)} \times 100\% \quad (1)$$

Table 1. Experimental results for different plastic types and pretreatment conditions. Values are means of three replicate runs

Type of plastic	Weight before pyrolysis (g)	Weight of carbon after pyrolysis (g)	Weight of carbon after oil extraction and drying (g)	Total mass of liquid fuel (g)	Liquid-fuel conversion yield (%)
No pretreatment					
PP	5.00	4.11	3.92	1.08	21.6
PET	5.00	4.23	4.14	0.86	17.2
HDPE	5.00	4.90	4.89	0.11	2.2
Ozone only					
PP	5.00	3.17	2.67	2.33	46.6
PET	5.00	3.53	3.25	1.75	35.0
HDPE	5.00	4.66	4.59	0.41	8.2
Crush only					
PP	5.00	3.75	3.45	1.55	31.0
PET	5.00	3.93	3.80	1.20	24.0
HDPE	5.00	4.87	4.84	0.16	3.2
Ozone and crush					
PP	5.00	3.62	3.23	1.77	35.4
PET	5.00	3.64	3.38	1.62	32.4
HDPE	5.00	4.78	4.73	0.27	5.4

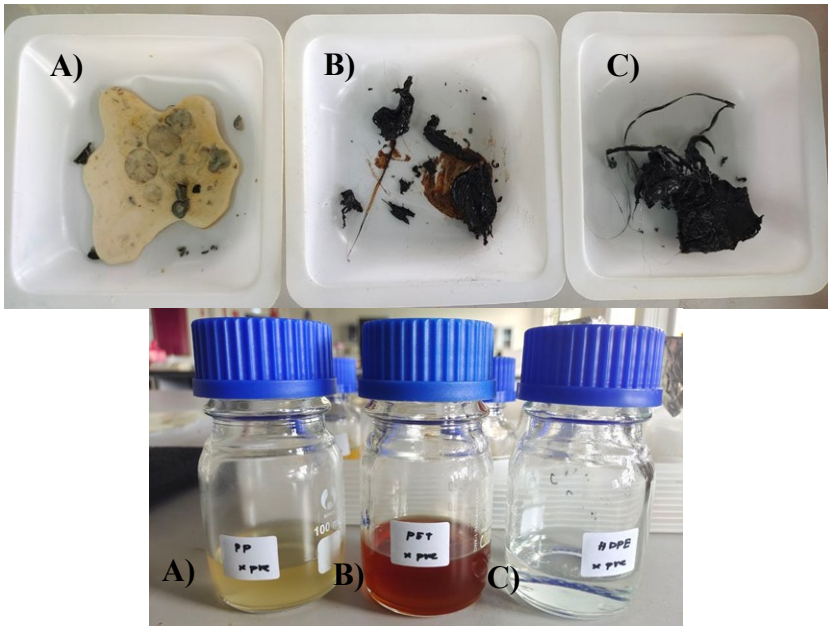

Figure 1. Mixtures of products from pyrolysis of several types of plastic waste. A: Polypropylene (PP). B: Polyethylene terephthalate (PET). C: High-density polyethylene (HDPE).

The higher liquid-fuel content from polypropylene (PP) is associated with its composition and molecular structure, which favor the formation of liquid-fuel products during pyrolysis [16, 17, 22]. The favorable decomposition characteristics of PP are related to its lower crystallinity and more amorphous structure, resulting in the thermal degradation of the shorter hydrocarbon chains. The relatively weak tertiary carbon-hydrogen bonds, which break down

more easily under pyrolytic conditions, explain the high liquid-fuel yield observed in this conversion. In essence, the tertiary carbons act as active sites where thermal cleavage initiates with a considerably lower activation energy than the primary or secondary carbons found in linear polyolefins [16, 22].

The high crystallinity and thermal stability of PET, in which ethylene terephthalate ($C_{10}H_8O_4$) repeating units are linked, mean that PET breakdown during pyrolysis produces more solid residue than liquid hydrocarbon products [12, 17]. The aromatic structure can promote gaseous by-product and solid-residue formation during pyrolysis, leading to a lower liquid-fuel yield. In contrast, HDPE consists of long chains of ethylene units $(C_2H_4)_n$ with a linear and highly crystalline structure due to the absence of side branches. Therefore, HDPE has higher thermal stability and greater potential for carbon-rich residue formation during pyrolysis, and it generally produces more solid residue than liquid hydrocarbons [11, 12, 17].

Crushing plastic before pyrolysis produces particles with a larger surface area, which facilitates heat transfer and more uniform thermal degradation. Nevertheless, this process can also decrease the liquid-fuel yield because of inherent factors in the pyrolysis process [10, 15]. These factors include the increased surface area, non-uniform pyrolysis, and shorter residence times of liquid intermediates in the reactor, resulting in a higher proportion of gaseous byproducts volatilizing before they can be effectively condensed into the target liquid phase. The present PP results support this interpretation: crushing improved conversion relative to untreated PP but did not reproduce the higher liquid yield achieved by ozone treatment, showing that physical size reduction and oxidative chain activation contribute differently to the overall product distribution.

3.2. Experimental Analysis

3.2.1. Chemical Composition

The liquid-fuel samples derived from PP plastic were characterized using Fourier-transform infrared spectroscopy (FTIR), as FTIR can identify specific molecular groups within the liquid fuel [24, 25]. Fig. 2 presents the FTIR spectra of liquid fuel produced from PP plastic under various pretreatment procedures, showing clear peaks associated with chemical changes induced by the pretreatment procedures.

The spectrum of the untreated sample is dominated by peaks for aliphatic hydrocarbons with C-H stretching bands at 2800–3000 cm^{-1} and C-C stretching at 1370 cm^{-1}, indicating the presence of long-chain hydrocarbons characteristic of PP-derived oil [24, 25]. However, the crushed-PP sample showed intensified peaks in this region, suggesting that hydrocarbons became more available because mechanical disruption exposed a larger surface area.

The spectrum of the ozone-treated PP shows strong peaks in the carbonyl (C=O) region (1700–1750 cm^{-1}) and hydroxyl (O-H) region (3200–3600 cm^{-1}) due to the oxidation of polymer chains. This spectroscopic evidence directly confirms the mechanistic hypothesis that ozone introduces reactive oxygen species onto the polyolefin backbone [20]. The combination of crushing and ozone treatment further intensified carbonyl and hydroxyl peaks, indicating stronger oxidative degradation when the two pretreatment methods were combined.

The FTIR results were interpreted by comparison with published characterization studies of plastic-derived liquid fuels. The strong aliphatic C-H stretching bands at approximately 2800–3000 cm^{-1} and the C-H deformation bands at 1460–1370 cm^{-1} indicate that the PP-derived oils were predominantly composed of hydrocarbons. Similar aliphatic hydrocarbon bands have been reported for liquid fuels produced from catalytic LDPE conversion, indicating that plastic-derived oils share important functional-group characteristics with conventional

fuels [26]. Therefore, the present results suggest chemical similarity with gasoline, kerosene, and diesel at the functional-group level, particularly in the aliphatic hydrocarbon region.

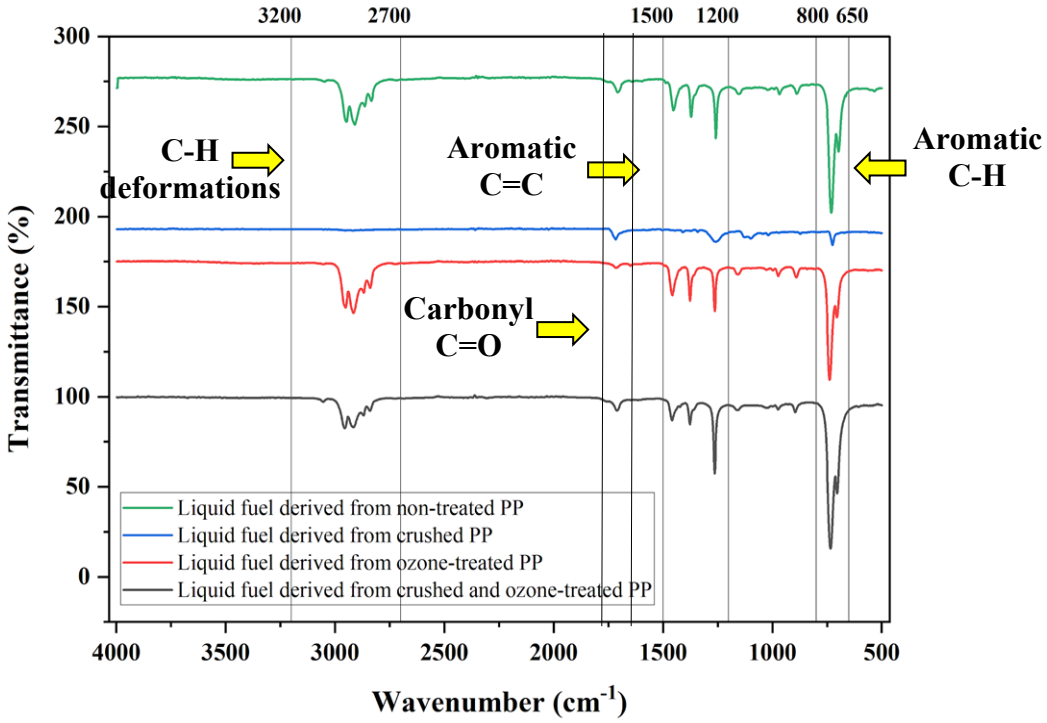

Figure 2. FTIR spectra of liquid fuel derived from PP plastic under four pretreatment conditions: non-treated, crushed, ozone-treated, and ozone-treated with crushing.

Nevertheless, similarity in the C-H region does not mean that PP-derived oil is chemically identical to commercial fuel. PP pyrolysis oil commonly contains paraffinic and olefinic hydrocarbons, while the amounts of unsaturated, aromatic, and oxygen-containing compounds depend on the feedstock composition and pyrolysis conditions [24, 25]. Consequently, differences are expected in the fingerprint region below 1500 cm^{-1}, where branched hydrocarbons, olefins, aromatics, and oxygenated compounds contribute differently to the spectral pattern. In the present study, the stronger carbonyl band at approximately 1700–1750 cm^{-1} and the broader hydroxyl band at approximately 3200–3600 cm^{-1} in the ozone-treated samples indicate that oxidation occurred before pyrolysis. This observation is consistent with the ozone-oxidation pathway of PP, in which tertiary-carbon sites form peroxy and hydroperoxide intermediates that promote chain shortening and oxygenated products [20].

In contrast, crushing mainly improves the physical accessibility of the plastic particles and is not expected to generate strong carbonyl or hydroxyl bands. Thus, the more intense C=O and O-H absorption bands in the ozone-treated oils provide spectroscopic evidence that ozonation modified the PP structure before pyrolysis. Although the oil contains hydrocarbon fractions within the ranges commonly associated with gasoline (C_4–C_{12}), kerosene (C_9–C_{16}) and diesel (C_{10}–C_{22}) [16, 24], further analysis using GC–MS, simulated distillation and standard fuel-property tests is required before confirming its suitability as a conventional fuel substitute.

3.3. Optimization of Pyrolysis for Liquid Fuel Formation

The Box-Behnken design was used to evaluate the effects of four process factors, namely temperature, heating rate, holding time, and ozonation time, on liquid-fuel yield [21]. The experimental design comprised 24 runs, as presented in Table 2. Temperature was investigated

https://doi.org/10.31436/iiumej.v27i3.3489

over the range of 300–400 °C, with a center point of 350 °C. The heating rate ranged from 5 to 15 °C/min, with a center point of 10 °C/min. Holding time and ozonation time were evaluated over the ranges of 1 to 3 h and 0.5 to 1.5 h, respectively, with center points of 2 h and 1 h. These operating ranges were selected to examine the combined effects of thermal severity and oxidative pretreatment on the formation of condensable liquid products.

According to Table 2, the highest liquid-fuel yield (38.8%) was obtained in Run 19 at 400 °C, a heating rate of 10 °C/min, a holding time of 2 h, and an ozonation time of 0.5 h. In contrast, Run 21 produced the lowest yield (7.4%) at 350 °C, a heating rate of 5 °C/min, a holding time of 2 h, and an ozonation time of 1.5 h. This variation confirms that liquid-fuel production was sensitive to the combined operating conditions. In particular, increasing temperature promotes polymer-chain cleavage and the formation of volatile compounds, which can subsequently condense into liquid products [6, 10, 12, 14]. However, in more severe thermal conditions, secondary cracking may convert condensable vapors into non-condensable gases, thereby reducing liquid-product recovery [6, 10, 12].

Table 2. Experimental design matrix and liquid-fuel yield responses obtained using the Box-Behnken design

Run	Factor 1: Temperature (°C) *A*	Factor 2: Heating rate (°C/min) *B*	Factor 3: Holding time (h) *C*	Factor 4: Ozonation time (h) *D*	Total mass of oil (g)	Response 1: Yield of oil (%) *R1*
1.	350	5	1	1	0.51	**10.2**
2.	300	5	2	1	0.75	**15.0**
3.	350	15	2	0.5	1.07	**21.4**
4.	300	10	2	0.5	1.04	**20.8**
5.	350	15	2	1.5	0.92	**18.4**
6.	400	10	3	1	1.85	**37.0**
7.	350	5	2	0.5	1.02	**20.4**
8.	350	10	3	1.5	1.23	**24.6**
9.	400	15	2	1	1.87	**37.4**
10.	400	10	1	1	1.27	**25.4**
11.	400	5	2	1	1.79	**35.8**
12.	300	10	3	1	1.03	**20.6**
13.	400	10	2	1.5	1.65	**33.0**
14.	300	15	2	1	0.83	**16.6**
15.	300	10	2	1.5	1.01	**20.2**
16.	350	5	3	1	1.10	**22.0**
17.	300	10	1	1	0.82	**16.4**
18.	350	10	1	0.5	0.67	**13.4**
19.	400	10	2	0.5	1.94	**38.8**
20.	350	10	1	1.5	0.59	**11.8**
21.	350	5	2	1.5	0.37	**7.4**
22.	350	15	3	1	1.22	**24.4**
23.	350	10	3	0.5	1.11	**22.2**
24.	350	15	1	1	0.56	**11.2**

The screening and optimization results should be interpreted in light of their different experimental conditions. During the screening stage, ozone-treated PP achieved the highest liquid-fuel yield of 46.6% at 400 °C, a heating rate of 5 °C/min, a holding time of 1 h, and an ozonation time of 1 h. In contrast, the Box-Behnken optimization identified a maximum yield of 38.8% at a moderate heating rate of 10 °C/min and a shorter ozonation time of 0.5 h. These findings indicate that liquid-fuel yield depends on the interaction between thermal conditions

https://doi.org/10.31436/iiumej.v27i3.3489

and pretreatment duration rather than on any single factor. Previous studies have similarly shown that temperature, heating rate, and residence time collectively influence polymer degradation, vapor-phase cracking, and the distribution of liquid, gas, and solid products during plastic pyrolysis [6, 10, 12, 14, 21]. Therefore, the selected operating conditions should balance sufficient thermal cracking for liquid formation against excessive thermal severity that may promote secondary cracking and gas production.

Moreover, liquid-fuel yield was evaluated as a function of the four process factors: temperature (A), heating rate (B), holding time (C), and ozonation time (D), using Design-Expert 13 software. A model was developed correlating the independent and dependent variables based on the observed responses. The model was statistically significant in affecting the response, as shown by analysis of variance (ANOVA), with an F-value of 8.52 and a p-value of 0.0004. This result implies that there is only a 0.04% probability that the observed response was attributed to noise. Meanwhile, p-values of 0.3606 and 0.2923 showed that the heating-rate (B) and ozonation-time (D) parameters were not significant, whereas temperature (A) and holding time (C) were significant in determining the response variable. This indicates that temperature and holding time are very important in determining the response variable. In contrast, changes in heating rate and ozonation time were less influential under these experimental conditions. From a mass and heat transfer perspective, the insignificance of the heating rate across the 5 to 15 °C/min range suggests that internal thermal gradients within the shredded polymer particles were already minimized at these modest ramp rates, allowing temperature and residence time to dictate the cracking kinetics. Furthermore, the lack of statistical significance for extending ozonation time from 0.5 to 1.5 h implies a rapid saturation of accessible oxidative surface sites on the PP matrix. Once these surface sites are fully saturated with hydroperoxides within the first 30 minutes, prolonged ozone exposure yields diminishing returns, a finding that has beneficial implications for minimizing energy consumption during industrial scale-up scenarios [20, 21].

Table 3. Analysis of variance (ANOVA) for liquid-fuel yield (R1)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1193.34	4	298.33	8.52	0.0004	significant
A-Temperature	797.07	1	797.07	22.77	0.0001	
B-Heating rate	30.72	1	30.72	0.8775	0.3606	
C-Holding time	324.48	1	324.48	9.27	0.0067	
D-Ozonation time	41.07	1	41.07	1.17	0.2923	
Residual	665.16	19	35.01			
Cor Total	1858.50	23				

Fig. 3 shows the response-surface plots generated using Design-Expert 13 software to illustrate the combined effects of temperature, heating rate, holding time, and ozonation time on liquid-fuel yield. Across the plotted factor combinations, liquid-fuel yield increased primarily with higher temperature and longer holding time, consistent with the ANOVA results showing that these two variables were significant model terms. Higher temperatures promoted polymer-chain cleavage and the formation of volatile products, whereas sufficient holding time allowed the thermal degradation process to proceed more completely and improved the recovery of condensable hydrocarbons [6, 10, 12, 14].

https://doi.org/10.31436/iiumej.v27i3.3489

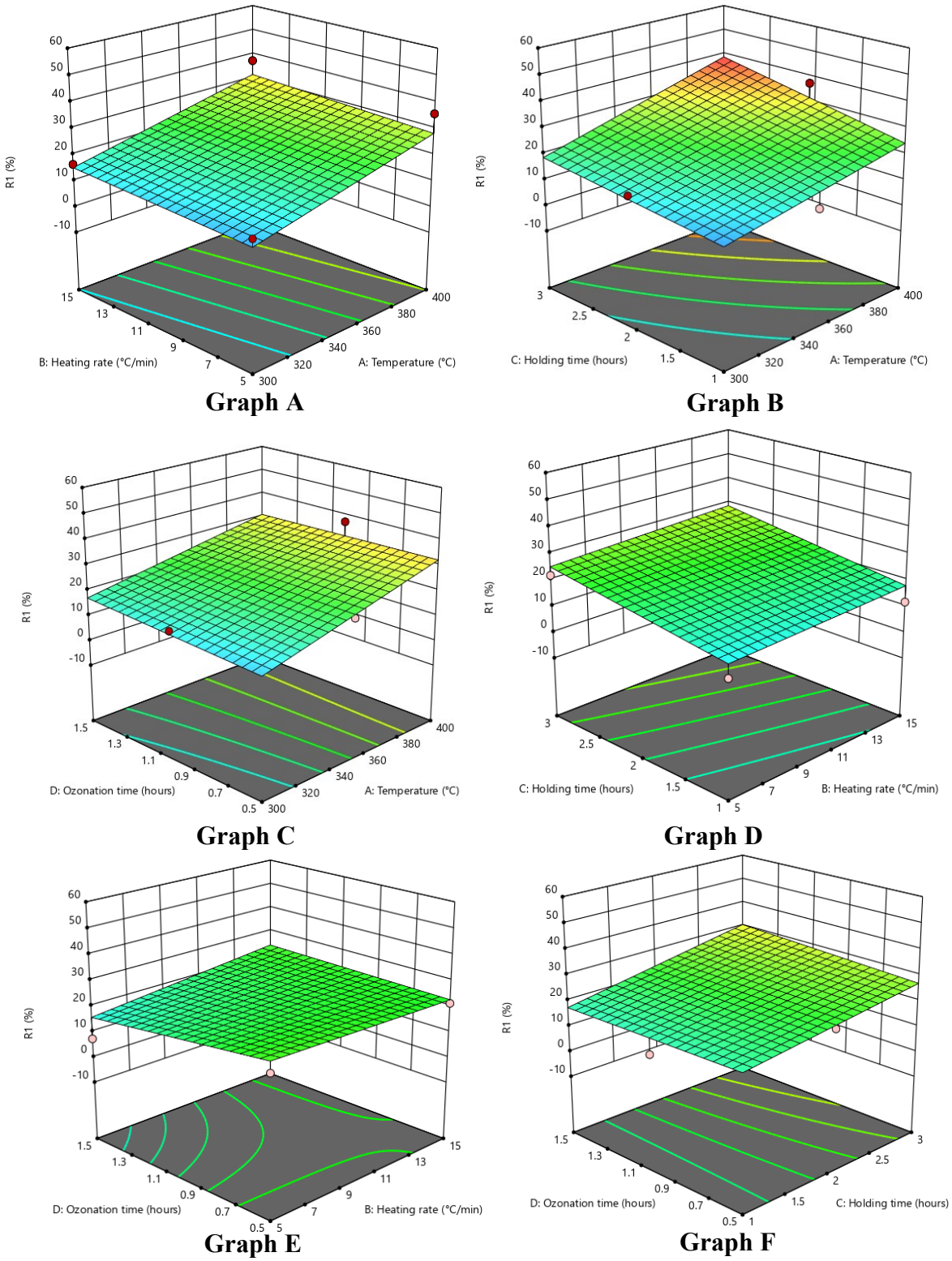

Figure 3. Three-dimensional response surfaces for liquid-fuel yield.

Graphs A–C demonstrate that temperature had the strongest positive influence on liquid-fuel yield within the investigated range. The effect of heating rates was comparatively limited, as reflected by its non-significant ANOVA result. Although moderate heating rates produced favorable yields in some combinations, the response surfaces indicate that temperature remained the dominant factor controlling liquid-fuel formation. This observation is consistent

with previous plastic-pyrolysis studies, which reported that temperature strongly affects the extent of polymer degradation and the distribution of liquid, gas, and solid products [6, 12, 14].

Graphs D–F further illustrate that holding time interacted with the remaining variables to influence liquid-fuel recovery. Longer holding times generally supported higher yields at elevated temperatures by allowing sufficient time for primary polymer cracking and vapor release. In contrast, ozonation time showed a comparatively weak effect within the tested range of 0.5–1.5 h, which agrees with its non-significant ANOVA result. This suggests that the accessible oxidative surface sites on the PP surface were substantially activated during the initial ozonation period, whereas prolonged ozone exposure provided limited additional benefit under the present experimental conditions [20, 21]. Overall, the response surfaces confirm that liquid-fuel yield optimization was governed mainly by temperature and holding time, while moderate heating rates and shorter ozonation durations were adequate for achieving favorable liquid-fuel production.

4. CONCLUSION

This study investigated the effects of pretreatment methods and pyrolysis parameters on liquid-fuel yield from polypropylene (PP), polyethylene terephthalate (PET), and high-density polyethylene (HDPE). Among the tested feedstocks and pretreatment conditions, ozone-treated PP produced the highest liquid-fuel yield (46.6%) at 400 °C, a heating rate of 5 °C/min, a holding time of 1 h, and an ozonation time of 1 h. This result demonstrates the engineering value of catalyst-free ozonation as a chemical pretreatment for improving PP conversion. Ozonation increased the PP liquid-fuel yield from 21.6% for untreated PP to 46.6%, whereas crushing alone produced a lower yield of 31.0%. This improvement is attributed to oxidative modification of the polymer backbone, whereby reactive oxygen intermediates promote chain scission and facilitate subsequent thermal degradation. Additionally, the optimization study identified a maximum liquid-fuel yield of 38.8% at 400 °C, a heating rate of 10 °C/min, a holding time of 2 h, and an ozonation time of 0.5 h. Analysis of variance (ANOVA) confirmed that extending ozonation beyond 0.5 h did not significantly improve the predicted liquid-fuel yield within the investigated operating range. This finding indicates that a shorter ozonation duration may reduce pretreatment time and energy demand while maintaining favorable liquid-fuel production under optimized pyrolysis conditions. Moreover, FTIR spectral analysis showed that the PP-derived oils contained hydrocarbon functional groups comparable with those reported for conventional fuels. However, the presence of oxygenated groups in the ozone-treated products indicates that further upgrading is required before use as a direct fuel substitute.

From an engineering perspective, integrating ozone pretreatment with process optimization provides a practical approach to improving liquid-fuel recovery from PP waste while avoiding catalyst use. Nevertheless, the findings are limited to laboratory-scale experiments using 5 g feed samples. In addition, the present response-surface analysis was based on a linear model, and FTIR provided only qualitative information on the chemical composition of the derived oils. Future work should therefore validate the optimized conditions at pilot scale, develop and validate an appropriate quadratic response-surface model, quantify fuel properties including calorific value, viscosity, density, flash point, sulfur content, oxygen content, and distillation range, and evaluate deoxygenation or other upgrading strategies. Complementary GC–MS analysis and techno-economic assessment should also be undertaken to determine the detailed hydrocarbon distribution, upgrading requirements, and commercial-scale feasibility of the proposed waste-to-fuel process. These outcomes would strengthen the

contribution of ozonation-assisted pyrolysis to sustainable plastic-waste management and circular-economy implementation in Malaysia.

ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to the Department of Chemical Engineering and Sustainability (CHES), Kulliyyah of Engineering, International Islamic University Malaysia (IIUM), for its assistance and for facilitating this work.

REFERENCES

[1] OECD. (2022). Global plastics outlook: Economic drivers, environmental impacts and policy options. OECD Publishing. https://doi.org/10.1787/de747aef-en

[2] The Pew Charitable Trusts. (2025). Breaking the plastic wave 2025: An assessment of the global system and strategies for transformative change. https://www.pew.org/en/research-and-analysis/reports/2025/12/breaking-the-plastic-wave-2025

[3] Chen, H. L., Nath, T. K., Chong, S., Foo, V., Gibbins, C., & Lechner, A. M. (2021). The plastic waste problem in Malaysia: Management, recycling and disposal of local and global plastic waste. SN Applied Sciences, 3, Article 437. https://doi.org/10.1007/s42452-021-04234-y

[4] Kumar, S., Singh, E., Mishra, R., Kumar, A., & Caucci, S. (2021). Utilization of plastic wastes for sustainable environmental management: A review. ChemSusChem, 14(19), 3985–4006. https://doi.org/10.1002/cssc.202101631

[5] Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science Advances, 3(7), e1700782. https://doi.org/10.1126/sciadv.1700782

[6] Anuar Sharuddin, S. D., Abnisa, F., Wan Daud, W. M. A., & Aroua, M. K. (2016). A review on pyrolysis of plastic wastes. Energy Conversion and Management, 115, 308–326. https://doi.org/10.1016/j.enconman.2016.02.037

[7] Nizami, A. S., Rehan, M., Waqas, M., Naqvi, M., Ouda, O. K. M., Shahzad, K., Miandad, R., Khan, M. Z., Syamsiro, M., Ismail, I. M. I., & Pant, D. (2017). Waste biorefineries: Enabling circular economies in developing countries. Bioresource Technology, 241, 1101–1117. https://doi.org/10.1016/j.biortech.2017.05.097

[8] World Bank Group. (2021). Market Study for Malaysia: Plastics circularity opportunities and barriers. https://www.worldbank.org/en/country/malaysia/publication/market-study-for-malaysia-plastics-circularity-opportunities-and-barriers

[9] BERNAMA. (2024). KPKT launches Circular Economy Blueprint, advancing solid waste management. https://www.bernama.com/tv/news.php?id=2326036

[10] Qureshi, M. S., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkkinen, H., Pohjakallio, M., & Laine-Ylijoki, J. (2020). Pyrolysis of plastic waste: Opportunities and challenges. Journal of Analytical and Applied Pyrolysis, 152, 104804. https://doi.org/10.1016/j.jaap.2020.104804

[11] Kunwar, B., Cheng, H. N., Chandrashekaran, S. R., & Sharma, B. K. (2016). Plastics to fuel: A review. Renewable and Sustainable Energy Reviews, 54, 421–428. https://doi.org/10.1016/j.rser.2015.10.015

[12] Singh, R. K., Balakrishnan, M., & Negi, R. K. (2022). A review on plastic pyrolysis: The current status, challenges, and future perspectives. Journal of Cleaner Production, 341, 130862. https://doi.org/10.1016/j.jclepro.2022.130862

[13] Dewangga, P. B., Rochmadi, & Purnomo, C. W. (2019). Pyrolysis of polystyrene plastic waste using bentonite catalyst. IOP Conference Series: Earth and Environmental Science, 399(1), 012110. https://doi.org/10.1088/1755-1315/399/1/012110

[14] Cahyono, M. S., & Fenti, U. I. (2017). Influence of heating rate and temperature on the yield and properties of pyrolysis oil obtained from waste plastic bag. Conserve: Journal of Energy and Environmental Studies, 1(1), 1–8. https://doi.org/10.30588/cjees.v1i1.248

[15] Belbessai, S., Azara, A., & Abatzoglou, N. (2022). Recent advances in the decontamination and upgrading of waste plastic pyrolysis products: An overview. Processes, 10(4), 733. https://doi.org/10.3390/pr10040733

[16] Das, N. C. (2025). Catalytic and noncatalytic pyrolysis of waste plastics: Comparative analysis of liquid products from polyethylene, polypropylene, and mixed plastics with diesel and petrol. Industrial & Engineering Chemistry Research, 64(6), 3240–3253. https://doi.org/10.1021/acs.iecr.4c04155

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

[18] Miandad, R., Rehan, M., Barakat, M. A., Aburiazaiza, A. S., Khan, H., Ismail, I. M. I., & Nizami, A. S. (2019). Catalytic pyrolysis of plastic waste: Moving toward pyrolysis based biorefineries. Frontiers in Energy Research, 7, 27. https://doi.org/10.3389/fenrg.2019.00027

[19] Lindberg, J., Ljungkvist Nordin, H., & Fråne, A. (2019). Sustainability assessment of pre-treatment methods for plastic waste from hospitals in Sweden (Report No. C 383). IVL Swedish Environmental Research Institute.

[20] García-López, E. I., Aoun, N., & Marcì, G. (2024). An overview of the sustainable depolymerization/degradation of polypropylene microplastics by advanced oxidation technologies. Molecules, 29(12), 2816. https://doi.org/10.3390/molecules29122816

[21] Faisal, F., Rasul, M. G., Chowdhury, A. A., & Jahirul, M. I. (2024). Optimisation of process parameters to maximise the oil yield from pyrolysis of mixed waste plastics. Sustainability, 16(7), 2619. https://doi.org/10.3390/su16072619

[22] Ahmad, I., Khan, M. I., Khan, H., Ishaq, M., Tariq, R., Gul, K., & Ahmad, W. (2015). Pyrolysis study of polypropylene and polyethylene into premium oil products. International Journal of Green Energy, 12(7), 663–671. https://doi.org/10.1080/15435075.2014.880146

[23] Muhammad, C., Onwudili, J. A., & Williams, P. T. (2015). Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis–catalysis reactor for fuel production. Energy & Fuels, 29(4), 2601–2609. https://doi.org/10.1021/ef502749h

[24] Uebe, J., Kryzevicius, Z., Majauskiene, R., Dulevicius, M., Kosychova, L., & Zukauskaite, A. (2022). Use of polypropylene pyrolysis oil in alternative fuel production. Waste Management & Research, 40(8), 1220–1230. https://doi.org/10.1177/0734242X211068243

[25] Ureel, Y., Chacón-Patiño, M. L., Kusenberg, M., Rodgers, R. P., Sabbe, M. K., & Van Geem, K. M. (2024). Characterization of PP and PE waste pyrolysis oils by ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry. Energy & Fuels, 38(12), 11148–11160. https://doi.org/10.1021/acs.energyfuels.4c01954

[26] Khan, M. S., Inamullah, Sohail, M., & Khattak, N. S. (2016). Conversion of mixed low-density polyethylene wastes into liquid fuel by novel CaO/SiO_2 catalyst. Journal of Polymers and the Environment, 24, 255–263. https://doi.org/10.1007/s10924-016-0768-5