

UPCYCLING OF PLASTIC WASTE FOR RESOURCE RECOVERY: UNVEILING THE TECHNICAL CHALLENGES AND STRATEGIES TOWARDS THE COMMERCIALIZATION OF PLASTIC-BASED CIRCULAR ECONOMY

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ABSTRACT

The study aimed to analyze the effects of different plastic wastes, including Polystyrene (PS), Polyethylene (PE), and Polypropylene (PP), and their 50:50 mixture on the yield and quality of liquid oil through pyrolysis. A small-scale batch pyrolysis reactor with the total capacity of 10kg was commissioned and operated at 550°C with a retention time of 90minutes. Results revealed that the highest feedstock conversion to liquid oil (51%) was recorded for PS compared to other types of plastic waste, whereas among mixed plastics, PE:PS produced the highest liquid oil yield (39%). The physicochemical analysis demonstrated that the obtained oils were predominantly aromatic compounds, with some alkanes and alkenes. Moreover, liquid oils from all types of plastic waste showed the density between 0.734 and 0.892g ml⁻¹, viscosity (1.99 to 3.1mm² s⁻¹), flash point (29 to 48°C), and high heating value (37.2 to 42.4MJ kg⁻¹). Based on the obtained results, an in-depth discussion has been conducted on the utilization of the produced liquid oil and gases in several energy-related applications, including transportation, heating, and electricity production, along with the applicability of the resultant char for several energy and environmental applications. Moreover, it has been emphasized that the key bottleneck in commercializing the plastic-based circular economy concept requires the continuous feedstock supply, characterization and pretreatment of feedstock to eliminate toxicity, approaches for reducing wax formation, technological advancements to enhance the quality and yield of pyrolysis, and detailed life cycle assessment to achieve maximum environmental and human health benefits.

1. INTRODUCTION

Plastic materials have been developed to meet human needs due to their properties such as lightweight, chemical stability, easy availability, and wide applicability in day-to-day life (Mishra et al., 2023). However, the exponential increase in global plastic production is driven by its durability and low cost also result in a monumental amount of plastic waste production (Yang et al., 2024). It has been reported that current global plastic waste production is about 1.7 to 1.9 billion metric tons per annum, which is expected to reach around 27 billion metric tons per annum by 2050

(Fayshal, 2024). Among the generated plastic waste, only 9% is recycled, 12% is incinerated, whereas the remaining major portion (79%) is landfilled without any material/resource recovery (Hou et al., 2021).

The substantial generation along with non-degradable nature, plastic waste can pose serious risk to the environment by remaining in landfills for decades, thus making space scarce for landfills, and may lead to soil and water pollution (Gebre et al., 2021). For example, single-use plastic bags takes an average of about 1,000 years to completely degrade and often end up in soil and water bodies



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(Dey et al., 2023). Hence, the production of anthropogenic plastic waste can lead to both ecological degradation and social impacts that urgently require serious action to prevent environmental degradation.

The current plastic waste management strategies include landfilling and recycling via incineration; however, the high space and resource requirements along with the release of toxic emissions hinders the effective implementation of these techniques (Yang et al., 2024). There is a dire need for such a strategy to deal the plastic waste according to environmental deliberations. Previous studies have shown that pyrolysis technology is a sustainable solution for recycling plastic waste, producing valuable products, including liquid oil, gases, and char (Gebre et al., 2021; Pan et al., 2024a). Pyrolysis is a thermochemical process carried out at elevated temperatures ranging from 400 to 900°C under oxygen-deficient conditions (Pan et al., 2024a). Elevated temperatures break down high-molecular chains into low-molecular products along with the production of liquid oil, solid residue, and gases (Mishra et al., 2023). For treatment of plastic waste, pyrolysis has been reported as a feasible and environmentally friendly technology (Putra et al., 2022). Moreover, pyrolysis technology is being employed not only to reduce plastic waste in landfills but also to recover energy and valuable products for wide range of applications (Sakthipriya, 2022).

Extensive research has been performed on pyrolysis using single type of plastic waste, including polyethylene (PE) (Al-Yaari & Dubdub, 2020), polypropylene (PP) (Xu et al., 2018), polystyrene (PS) (Chowlu et al., 2009), polyvinyl chloride (PVC) (Matsuzawa et al., 2004), and polycarbonate (PC) (Charde et al., 2018) under various parameters such as temperatures and heating rates. However, limited research has been reported on the pyrolysis of mixed plastic waste to recover liquid oil under various temperature protocols. Moreover, pyrolysis of single waste types such as PE generates olefins of various chain lengths and aromatic compounds, including toluene, styrene, and benzene. Hence, mixing various types of plastic waste such as PS, with these polyolefin feedstocks (PP and PE) accelerates pyrolysis and results in rapid decomposition, yielding high-oil products with shorter chain lengths.

Therefore, this study is designed to (i) assess the suitability of real plastic waste from the mixed municipal solid waste into liquid oil using pyrolysis technology along with the examination of individual and mixing at 50:50% of various types of plastic waste such as PS, PE, and PP on the quality and yield of produced liquid oil, (ii) characterization and evaluation of the pyrolysis-derived oil for resemblance with commercial fuel, (iii) integration of circular economy commercialization through highlighting the opportunities and approaches to cope with the challenges under the plastic based refinery concept for the effective management of plastic waste and encourage a shift to more sustainable consumption of derived oil as a source of clean energy.

2. MATERIAL AND METHODS

2.1 Feedstock collection and preparation

The real municipal plastic waste samples were collected from four waste transfer stations located in different

localities in Peshawar, Khyber-Pakhtunkhwa, Pakistan. The collected plastic wastes were categorized into PE, PS, and PP. Given the economic and market value of PET, this research considers only PE, PP, and PS. The selection of these plastic types was made based on the fact that these components reflect the major components of the waste stream of District Peshawar, Khyber-Pakhtunkhwa, Pakistan. Each type of plastic waste was weighed and crushed into fine pieces, approximately 1 to 2cm to obtain a homogeneous mixture. The crushed samples were washed to remove impurities and sundried to remove moisture. After drying, the feedstock was ready for pyrolysis.

2.2 Experimental setup

For pyrolysis, a small-scale batch pyrolysis reactor with a carrying capacity of 10kg, made of stainless steel was used to convert plastic waste into liquid oil. The schematic diagram of the pyrolysis reactor is shown in Figure 1, and the reactor's detailed features are listed in Table 1. The reactor was comprised of a reactor system, a cooling system, and a storage tank. For each pyrolysis reaction, 1kg of accurately weighed feedstock including PE, PS, and PP was individually loaded into the reactor (100%) and in a 50:50 mixture. The pyrolysis was carried out at 550°C with the heating rate of 10 to 15°C per minute and residence time of 90minutes. For temperature measurement, a thermostat was adjusted in conjunction with a temperature controller.

These pyrolysis conditions, with a temperature of 550°C and a residence time of 90minutes were based on the thermal stability and decomposition temperatures of various types of plastic waste under controlled conditions, as well as safety considerations reported in the literature (Miandad et al., 2017). As the temperature increased, the feedstock was broken down and converted into vapors, which were condensed into liquid after passing through the cooling system and subsequently collected in the collection tank. The char (remaining unburnt feedstock) was collected from the heating chamber after the reactor system was cooled to room temperature. Likewise, the mass balance of pyrolysis products after each experiment was determined by accurately weighing the obtained oil and char using a standard digital balance, while the remaining weight to make up 100% was assumed to be the gas product. Moreover, to eliminate interference from human or other factors and ensure the reproducibility of the experiment, each experimental trial was replicated three times, and the obtained average values are reported with their standard deviations.

2.3 Characterization of liquid oil

The pyrolysis-derived liquid oils were subjected to various characterizations using appropriate procedures based on ASTM standard methods. The liquid oil was characterized for density, viscosity, pour point, flash point, and high heating value (HHV), as well as by spectrometric analysis such as Fourier Transform Infrared (FT-IR) spectroscopy and Gas Chromatography coupled with Mass Spectrometry (GC-MS).

To measure the density of pyrolysis-derived liquid oils, a portable density meter (DMA35 from Anton Paar) was

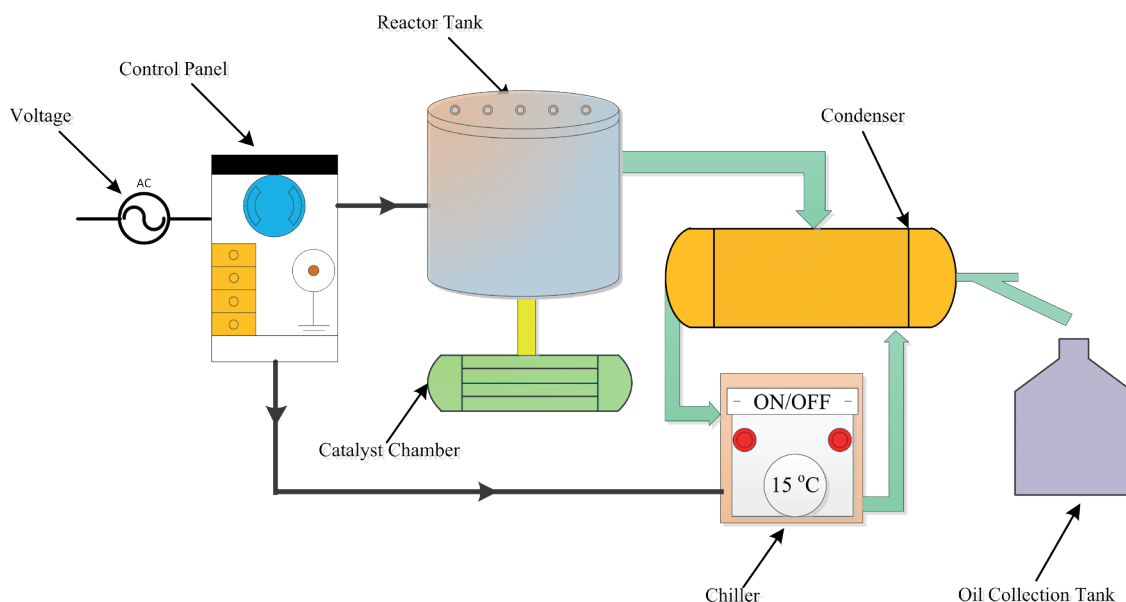


FIGURE 1: Schematic diagram of the small-scale batch pyrolysis reactor.

used. Prior to sample analysis, the density meter was calibrated with distilled water after rinsing with acetone and then allowed to dry completely. The variation in the viscosities of the derived liquid oils were determined using a hybrid rheometer (HR1 from TA Instruments) with a 40mm parallel-plate geometry. For viscosity analysis, a small amount of liquid oil was placed at the bottom of the horizontal plate and sandwiched between the upper 40mm plate. During analysis, the shear rate range and temperature of the rheometer were set to 1-500 $1/s^{-1}$ and 40°C, respectively.

Likewise, the AWD-12 pour point analyzer was used for determining the pour and freezing points. For analysis, the temperature range was kept at -10°C in one tank (left side tank), whereas in the right side tank, it was kept at -65°C. For each sample, the sampling tube was filled to the designated mark and first placed in the left tank until the temperature reached 0°C. Consequently, the sample was transferred to the right-side tank. The sample tube was periodically removed from the tank with the temperature reduced by 2°C to observe the liquid flow by holding the tube horizontally for 4 seconds. The procedure was repeat-

ed several times until the pour point and freezing points were achieved. Furthermore, the flash points of the liquid oil from various types of plastic waste and their mixtures were determined using a flash point analyzer (Automatic Pensky-Martens Closed Tester, Koehler, US) in accordance with ASTM D93. Likewise, the energy content of the pyrolysis-derived liquid oils was determined using a bomb calorimeter (Parr 6200 Calorimeter, US) to obtain high heating values (HHV) in accordance with ASTM D240.

The functional groups present in the derived liquid oils from all plastic types and their mixture (50:50) were investigated through FT-IR spectroscopy (Perkin Elmer's, UK). The analysis was carried out in the range of 500 to 4000 cm^{-1} with a minimum of 32 scans at an average IR signal at 4 cm^{-1} resolution. Moreover, the detailed composition of the liquid oils was analyzed by GC-MS (Hewlett-Packard HP7890, US) equipped with a 5975 quadrupole detector. The length of the GC capillary column was 30mm, whereas the diameter was 0.25mm, coated with a 0.25mm thick film of 5% phenyl-methylpolysiloxane. For the analysis, the initial temperature was set to 50°C for 2 minutes, then increased to 290°C at a rate of 5°C per minute and upon reaching 290°C, splitless injection was applied. Both the ion source and transfer line temperatures were 230 and 300°C, respectively. The resulting data were obtained in full-scan mode between m/z 33 and 533 with a solvent interval of 3 minutes. The obtained chromatographic peaks were identified using the NIST08 mass spectral data library against standard compounds.

3. RESULTS AND DISCUSSION

3.1 Effect of plastic waste on the yield of liquid oil

The results in Table 2 depict the end products from the pyrolysis of individual plastics and mixture of plastic waste types. The results showed that the highest conversion of the feedstock to liquid oil (51%) was recorded for PS com-

TABLE 1: Features of the pyrolysis reactor.

S. No	Reactor components	Features
1	Height of heating tank	609 mm
2	Diameter of heating tank	550 mm
3	Rated heating power	0.5kW
4	Reactor capacity for feedstock	10 kg
5	Length of condenser	609 mm
6	Diameter of condenser	305 mm
7	Heating rate	10 to 15°C min ⁻¹
8	Maximum temperature	550°C
9	Residence time	90 minutes

pared with other types of plastic waste. Similar results for the maximum liquid oil for PS compared with PP and PE have also been reported by Miandad et al. (2017). The maximum degradation and conversion to liquid oil in PS was due to its lower molecular complexity compared to other types of plastics (Liu et al., 2022). The thermal degradation of PS to oil comprises four steps: initiation, transfer, decomposition, and termination (Peng et al., 2022). Likewise, the lowest liquid oil content (21%) and the highest gas yield (68%) were recorded for PP (Table 2). Kiran et al. (2000) also observed low liquid oil yield with large amounts of gases from the pyrolysis of PP. The comparatively lower liquid oil yield from the pyrolysis of PP is due to differences in polymer structure, degradation pathways, and radical stability that affect the formation of condensable hydrocarbons and gases during thermal decomposition. Another key factor in the lower oil production from PP is the secondary cracking of the pyrolysis vapors. The less thermally stable aliphatic hydrocarbons produced during PP degradation further undergo thermal cracking at temperatures between 400 and 500°C, that results in the conversion of these intermediate liquid hydrocarbons into non-condensable gases, which reduces oil yield (Al-Salem et al., 2017).

The pyrolysis of mixed plastic waste also showed variation in the yields of pyrolysis products, especially the liquid oil. The results showed that the lowest oil yield (21%) was obtained when PE was mixed. Miandad et al. (2017) also reported that pyrolysis of mixed PE and PP yields lower oil and higher gas and char. Ciliz et al. (2004) also observed a similar trend of lower oil and higher gas yields from the pyrolysis of mixed PP and PE. Likewise, mixing PS with PP yield lower oil yield of 29% compared to the individual pyrolysis of PS (Table 2). The slight reduction in oil yield of mixed plastic waste compared to the individual plastics is attributed to the differences in thermal degradation mechanisms, radical interactions, and secondary cracking reactions occurring during co-pyrolysis of mixed plastic polymers. In addition, during pyrolysis of the mixed plastic, various polymers produce different radical species that interact with each other, and these cross-radical reactions promote secondary cracking, hydrogen transfer, and β -scission that convert the intermediate liquid hydrocarbons into gaseous products, including methane, propylene, and ethane, thereby slightly decreasing the oil yield as compared to the pyrolysis of single plastic waste (Lopez et al., 2018). However, compared with individual PE, the liquid oil yield increased when PS was mixed with PE at 50:50 ra-

tio. The results showed the maximum oil yield (39%) when PE was mixed with PS at 50:50% (Table 2). The production of free radicals from PS facilitates the conversion of PE into liquid oil instead of wax (Valizadeh et al., 2024). The comparatively high liquid oil yield due to the co-pyrolysis of PS with PE, as compared to the individual PE is mainly due to the synergistic interactions between the aromatic radicals from PS and aliphatic radicals from PE that enhance the stabilization of intermediate fragments and suppress excessive gas formation. Furthermore, the mixed pyrolysis of PS with PE changes the degradation pathway as depolymerization of PS results in the formation of styrene monomer and other aromatic radicals (Woo et al., 2000). These aromatic radicals are thermodynamically stabilized by resonance within the benzene ring, hence making them less susceptible to rapid fragmentation. Hence, during co-pyrolysis, these stabilized radicals interact with the reactive alkyl radicals produced from PE degradation, thereby suppressing excessive secondary cracking reactions and promoting the formation of larger condensable hydrocarbon molecules (Faravelli et al., 2003; Baeck et al., 2024).

3.2 Density (g ml⁻¹)

Density is a key physicochemical parameter that reflects the hydrocarbon distribution and molecular composition of oil produced by thermal degradation of various polymers during pyrolysis (Baskar et al., 2021). The density of pyrolysis oils varied with plastic waste type, depending on the polymer feedstock, pyrolysis temperature, and the presence of catalysts that affect cracking reactions and product composition (Sharuddin et al., 2016). Densities of the liquid oil produced from the pyrolysis of individual and mixed plastic waste were analyzed and found in the range between 0.734 to 0.892g ml⁻¹ (Table 3). The densities of PE, PS, and PP were 0.831g ml⁻¹, 0.892g ml⁻¹, and 0.786g ml⁻¹, respectively (Table 3). The findings of the current study are consistent with those of Syamsiro et al. (2014a), who reported the density of PE-derived oil of 0.854g ml⁻¹. Likewise, Mangesh et al. (2020) observed a density of 0.771g ml⁻¹ for PP-derived oil, however, the density of PS-derived oil (0.945g ml⁻¹) was slightly higher than the current study. During pyrolysis, PE primarily decomposes into long-chain aliphatic hydrocarbons, including olefins and paraffins that are structurally similar to those in the diesel and gasoline fractions, resulting in relatively low-density liquid fuels (Sharuddin et al., 2016). Likewise, the pyrolysis products of PP are branched alkanes and alkenes due to its methyl side

TABLE 2: Experimental scheme and pyrolysis yields of individual and mixed types of plastic waste.

S.No	Sample	Ratio	Feed Quantity (Kg)	Retention Time (minutes)	Temperature range	Liquid Oil (%)	Gases (%)	Char (%)
1	PE	100	1	90	550	25±0.16	31±0.03	44±0.11
2	PS	100	1	90	550	51±0.13	21±0.01	28±0.08
3	PP	100	1	90	550	21±0.17	68±0.03	11±0.10
4	PE:PS	50/50	1	90	550	39±0.12	45±0.04	16±0.16
5	PS:PP	50/50	1	90	550	29±0.18	59±0.03	12±0.12
6	PE:PP	50/50	1	90	550	21±0.10	61±0.05	18±0.13

groups, resulting in oils with densities ranging from 0.75 to 0.81 g cm⁻³, indicating the predominance of light hydrocarbon fractions compared to conventional petroleum fuels (Adoe et al., 2023). Conversely, during pyrolysis, the PS undergoes depolymerization reactions that primarily produce aromatic compounds, including toluene, ethylbenzene, and styrene, which have higher molecular density than aliphatic hydrocarbons (Miandad et al., 2017). Hence, pyrolysis oil derived from PS often exhibits higher density than other types of plastic waste due to the dominance of aromatic hydrocarbons in the liquid oil (Miandad et al., 2017). The liquid oil produced from the mixed pyrolysis of PE:PS, PE:PP, and PS:PP showed densities of 0.821 g ml⁻¹, 0.874 g ml⁻¹, and 0.734 g ml⁻¹ respectively (Table 3). Moreover, the density of liquid oil in the current study is similar to that of naturally produced commercial diesel ranging from 0.81 to 0.87 g ml⁻¹ (Arjhar et al., 2022). Panda et al. (2010) reported the density of 0.815 g ml⁻¹ for pyrolytic oil from LDPE and 0.778 g ml⁻¹ for liquid oil from PP. Research studies on the mixed plastic waste pyrolysis have demonstrated that the density of resulting oil depends on the composition of the mixing feedstock as well as process parameters, where the higher pyrolysis temperatures and catalytic cracking tend to produce lighter hydrocarbons that affect the density of the derived oil (Marwani & Trifarizy, 2024). The variations among the densities are linked to the degree of aromaticity, carbon chain length distribution, and cracking intensity during pyrolysis, which are determined by the type of plastic waste and hence collectively affect the physicochemical properties as well as the potential fuel applications of the produced oil (Sharuddin et al., 2016; Miandad et al., 2017).

3.3 Viscosity (mm² s⁻¹)

Viscosity of plastic waste-derived oil is another important physicochemical characteristic that defines the hydrocarbon composition and molecular weight distribution. It also represents the flow resistance of the fluids and thus directly related to pressure, temperature, and film formation (Yin et al., 2021). Moreover, viscosity also reveals and signifies the flow of fuel in automobile engines (Kass et al., 2022). Highly viscous fluids are often not recommended for engines because they cause mechanical inefficiency, whereas low-viscosity fuels burn faster in the engine and are also not recommended (Taylor, 2021). Furthermore, the high viscosity of fuel reduces its fluidity at low temperatures, thereby affecting fuel injector operation due to poor fuel spray atomization (Pham et al., 2020). The pyrolytic liquid oil in the current study showed the viscosity of

1.9 mm² s⁻¹ for PE, 3.1 mm² s⁻¹ for PS, and 2.1 mm² s⁻¹ for PP (Table 3). The oil derived from the pyrolysis of PE usually shows relatively moderate viscosities because during the thermal treatment, PE predominantly degrades into long-chain aliphatic hydrocarbons such as olefins and paraffin that result in the oil similar to diesel and exhibit the viscosities ranging between 1.8 and 4.1 mm² s⁻¹ depending on the extent of secondary cracking reactions during pyrolysis (Lopez et al., 2018). Likewise, the pyrolysis of PP result in the formation of branched alkanes and alkenes due to the methyl substituents in its polymer structure, which tend to generate lighter hydrocarbon fractions and hence show viscosities in the range of 1.5 to 3.0 mm² s⁻¹ (Miandad et al., 2016). However, the pyrolysis oil obtained from PS often exhibits higher viscosity due to the depolymerization of PS that results in aromatic compounds such as ethylbenzene, toluene, and styrene that possess stronger intermolecular interactions and higher molecular structure than aliphatic hydrocarbons. The PS-derived pyrolysis oils exhibited a viscosity range between 3 and 5 mm² s⁻¹ (Miandad et al., 2017).

Moreover, the mixed pyrolysis of PE:PS, PE:PP, and PS:PP revealed densities of 2.2, 2.3, and 2.1 mm² s⁻¹, respectively (Table 3). The oils from the pyrolysis of mixed plastic waste often represent intermediate viscosities because the liquid fraction comprised of the complex mixture of olefinic, aliphatic, and aromatic hydrocarbons originating from the various feedstocks. The reported viscosities from the pyrolysis of mixed plastic waste typically range from 1.2 to 4.0 mm² s⁻¹, depending on the process and pyrolysis temperature (Budsaereechai et al., 2019).

3.4 Flash point (°C)

Flash point is an important safety and fuel quality parameter that indicates the lowest temperature at which a liquid fuel can ignite when exposed to an external ignition source (Costa et al., 2024). Flash point is strongly influenced by the concentration of light volatile hydrocarbons produced during the thermal cracking of polymer chains. At higher temperatures, flash points are significant and are used to assess the hazardous potential of oil (Narayanasarma & Kuzhiveli, 2021). The pyrolytic oil of PE showed the flash points of 34°C, PP (44°C), and PS with the highest among all the individual plastic waste of 48°C (Table 3). Generally, plastic pyrolysis oils exhibit relatively low flash points compared to conventional diesel fuels because pyrolysis produce a significant fraction of low-boiling hydrocarbons, such as C5 to C10 alkanes and alkenes, that read-

TABLE 3: Properties of pyrolysis-derived liquid oil.

S. No	Properties	PE	PS	PP	PE:PS	PE:PP	PS:PP
1	Density (g ml ⁻¹)	0.831±0.13	0.892±0.33	0.786±0.21	0.821±0.16	0.874±0.03	0.734±0.08
2	Viscosity (mm ² s ⁻¹)	1.9±0.98	3.1±0.33	2.1±0.41	2.2±1.10	2.3±1.03	2.1±0.94
3	Flash point (°C)	34±2.31	48±2.76	44±3.07	32±1.87	31±2.53	29±3.02
4	Pour point	-12±1.03	-19±2.11	-15±1.01	-10±2.43	-13±1.05	-11±2.11
5	High heating value (MJ kg ⁻¹)	39.6±2.41	38.5±3.02	42.4±1.88	37.2±3.78	41.9±2.74	38.7±3.88

ily vaporize at lower temperatures (Sharuddin et al., 2016). For instance, the oils derived from the pyrolysis of PE have flash points in the range of 20 to 40°C, which can be attributed to the formation of light aliphatic hydrocarbons during the degradation of the long PE chain (Miandad et al., 2017). Likewise, the pyrolysis of PP produce branched alkanes and alkenes due to methyl substituents, result in liquid oils with flash points between 18 and 35°C, indicating a high proportion of volatile hydrocarbons in the derived oil (Syamsiro et al., 2014a). In contrast, the comparatively high flash point of PS-derived oil was due to the high aromatic compounds produced during the depolymerization of PS, which have higher boiling points and lower volatility than aliphatic hydrocarbons (Syamsiro et al., 2014b).

The pyrolysis of mixed plastic waste yielded lower flash points than those of liquid oil produced from individual plastic waste. It has been observed that the highest flash point of 32°C was for the liquid oil obtained from the mixture of PE and PS, while the flash points of PE:PP and PS:PP were 31 and 29°C, respectively (Table 3). The obtained results are in line with those of Palmay et al. (2022).

3.5 Pour point (°C)

Pour point is the property of liquid fuels that determines the minimum temperature at which liquid oil stops flowing when cooled without agitation (Verissimo et al., 2023). The quantity and amount of long-chain paraffines in petroleum fractions are measured through pour point (Elbanna et al., 2022). Fuels with high paraffin percentage usually have high wax content, which solidifies at low temperatures and creates difficulties in transportation and storage. Hence, it is an important attribute, especially in places where the temperature drops below freezing, as liquid fuel may clog the supply to the combustion chamber. The pour points of all oil samples were found between -10 and 19°C (Table 3). The pour point of liquid oil obtained from PE, PS, and PP was -12, -19, and -15°C, respectively, whereas the liquid obtained from the mixture of different plastic waste was -10, -13, and -11°C for PE:PS, PE:PP, and PS:PP respectively (Table 3). The current results are consistent with Soni et al. (2021), who also reported pour points for pyrolytic liquid oils in the range of gasoline and kerosene.

3.6 High heating value (MJ kg⁻¹)

High heating value (HHV) is an important characteristic that quantifies the upper limit of energy released during combustion of a fuel (Oyebanji et al., 2023). It is measured in units of energy per unit mass or volume of the fuel (Waqas et al., 2023). The higher HHV represents the higher energy content of the fuel (Miandad et al., 2017). The HHVs of the current study ranged between 37.2 and 42.4 MJ kg⁻¹ (Table 3 and Figure 2). The highest HHV (42.4 MJ kg⁻¹) was recorded for the pyrolytic oil obtained from PP, whereas for PE and PS, the HHVs were 39.6 and 38.5 MJ kg⁻¹ respectively (Figure 2). The results of the current study are consistent with those of Miandad et al. (2017) who evaluated the pyrolytic oil of PS and reported it as 39.3 MJ kg⁻¹. In addition, Syamsiro et al. (2014a) also reported 36.3 MJ kg⁻¹ for liquid oil produced from the pyrolysis of PS, with a slight variation relative to the current study. Moreover, the liquid oil pro-

duced from the mixed plastic waste of PE:PP showed the HHV of 41.9 MJ kg⁻¹, while HHVs for PS:PP and PE:PS were 38.7 and 37.2 MJ kg⁻¹ respectively that were close to the HHV of conventional diesel. Kasar et al. (2020) obtained similar HHV results for the pyrolytic oil and suggested that the liquid oil has a slightly lower HHV than diesel and hence can be used as fuel after mixing with kerosene oil.

3.7 Fourier transform infrared analysis

FT-IR analysis provides comprehensive data on different functional groups and the types of atomic linkages present in an organic compound. The polymers produced during pyrolysis are identified by their hydrocarbon composition, including alkenes, alkanes, aromatics, and aldehydes (Hasan et al., 2023). FTIR analysis was conducted to identify the functional groups present in the liquid oil obtained from the pyrolysis of plastic waste. The pyrolysis oils were analyzed over a wide range of 500 to 4000 cm⁻¹ and the spectra represent typical hydrocarbon vibrations in the derived oils. Based on absorption bands, the spectra are categorized into three wavenumber ranges including 3100 to 2800 cm⁻¹, 1700 to 1300 cm⁻¹, and 1000 to 600 cm⁻¹. The details of each spectrum are plotted in Figure 3.

The liquid obtained from the pyrolysis of PE revealed the presence of an aliphatic group at the start at 2924 and 2854 cm⁻¹. At 1456 cm⁻¹, 1377 cm⁻¹, CH₂ bending and C-H olefinic were observed (Figure 3a). Likewise, aromatic compounds were observed at a wavenumber of 696 cm⁻¹, corresponding to the aromatic group. Furthermore, the FTIR analysis of the pyrolysis of PS showed the presence of aliphatic groups, CH₂, and aromatic compounds (Figure 3b). A weak absorption band at 3082 cm⁻¹ was observed at the start followed by a medium absorption peak at 2924 and 2854 cm⁻¹, which can be attributed to CH₃ aliphatic functional group. In the middle of the graph, a medium peak was observed at a wavenumber of 1495 cm⁻¹ correspond to CH₂ group (Figure 3b). At the end, the aromatic and alkenic groups were observed at 696 and 775 cm⁻¹ respectively (Figure 3b). The current results are in agreement with the study conducted by Panda et al. (2012) who confirmed the presence of aromatic group at peaks at 1495 cm⁻¹ and 906 to 696 cm⁻¹. For PS-derived oil, the band at 1495 cm⁻¹

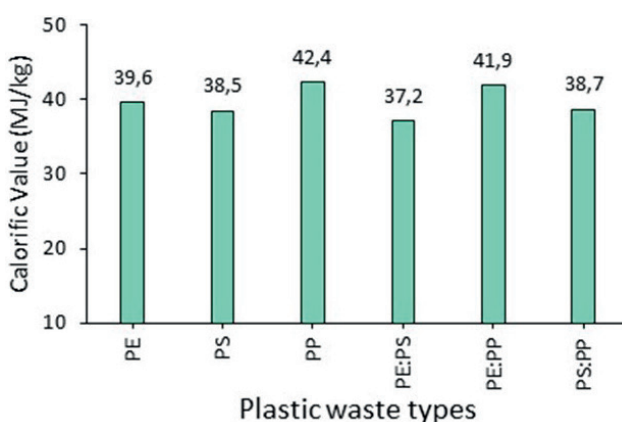


FIGURE 2: High heating value (MJ kg⁻¹) of thermal pyrolytic liquid oil.

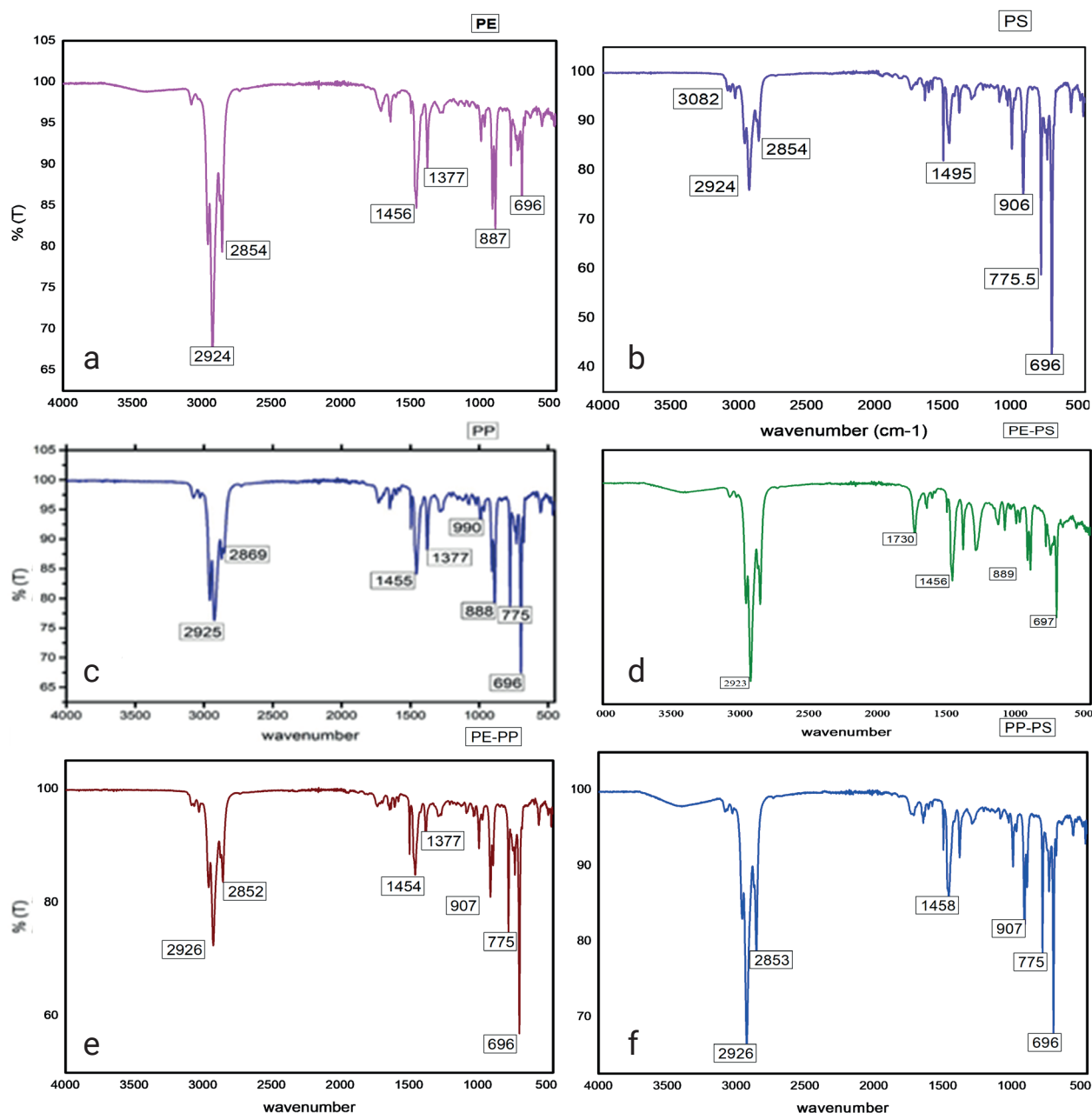


FIGURE 3: FT-IR spectra of liquid oils from the pyrolysis of individual and a mixture of different types of plastic waste.

corresponds to C–C stretching vibration and indicate the existence of aromatic group (Panda et al., 2012). The presence of C–H scissoring and bending vibrations at 145cm^{-1} further indicates the presence of a benzene derivative in the PS-based oil (Singh et al., 2020). Likewise, the two large absorption peaks centered around 2953 and 2868cm^{-1} , a weak peak at 1620cm^{-1} , and two medium peaks at 1456 and 1377cm^{-1} are visible in the spectra of the liquid product derived from PP (Figure 3c). Aliphatic C–H stretching (for CH_3 and CH_2), olefinic C=C stretching, CH_2 bending vibrations, and C–H scissoring and bending vibrations of alkanes respectively, correspond to these peaks. Olefinic C–H is visible as an ill-developed peak centered at 888cm^{-1} (Figure 3c).

FTIR analysis of the liquid oil obtained from the pyrolysis of mixed plastic waste of PE and PS showed strong

peaks at 2923 to 2862cm^{-1} , which can resemble aliphatic C–H stretching and reveal the presence of alkyne functional groups (Figure 3d). Similarly, weak peaks were also noticed at 1730cm^{-1} , 156cm^{-1} , 889cm^{-1} , and 697cm^{-1} , which showed the presence of C=C (Olefinic), CH_2 bending, and C–H (olefinic) functional groups (Figure 3d). The results revealed that the obtained liquid oils mostly comprised of aliphatic and some olefinic hydrocarbons. Likewise, the FTIR spectra of the mixture of PE and PP showed the presence of alkanes/aliphatic, olefinic, and aromatic groups (Figure 3e). The production of alkanes is observed at the start, followed by CH_2 bending and the formation of an olefinic group (Liu et al., 2023). Strong bonding at 2926cm^{-1} was observed at the start, corresponding to the presence of an alkanes group. At the end, a strong aromatic group was observed

at 696cm⁻¹, while a medium aromatic band was observed at 775cm⁻¹ (Figure 3e). For PP:PS, the major peaks at 2926 and 2853cm⁻¹ showed stretch single carbon and hydrogen bonding (C-H) and correspond to the alkanes (CH₃)/aliphatic functional group (figure 3f). Weak bonding at CH₂ bending at 1458cm⁻¹, while in the middle at 907cm⁻¹ (C-H) olefinic group, followed by aromatics and alkenes at the right side were observed at 775 and 696cm⁻¹, respectively (Figure 3f).

3.8 Gas chromatography mass spectrophotometry analysis

The GC-MS data revealed that pyrolysis of individual and mixed plastic waste produced a variety of chemicals (Hasan et al., 2023). The liquid oil comprised of different compounds of alkanes, olefins, and paraffins. Each liquid oil showed different composition and number of compounds, ranging from 32 to 43. Details and number of compounds in each liquid oil are given in Table 4. The identified compounds were grouped into six categories by carbon number: C6 to C10, C11 to C16, C17 to C20, and C21 to C30. However, compounds ranging from C1 to C4 to C5 to C6 were negligible and therefore they are not mentioned. Compounds with carbon numbers ranging from C7 to C10 were abundant in liquid oil obtained from PP, accounting for 83.2%, followed by liquid oil from PS and a mixture of PE and PP, at 78.1 and 69.8% respectively (Table 4). PE showed 61% of the carbon number in the C7 to C10 range, while 65.1% was found in a mixture of PE and PS. The least number of compounds in the range of C7 to C10 was noticed in the mixture of thermal liquid oil obtained from the mixture of PE and PP. Specifying the distribution of oil fractions obtained from the thermal pyrolysis of PP showed that more than 41% of oil is constituted by C7 to C10 hydrocarbon range products, representing the light naphtha range. Likewise, the liquid oil constituted 26.60% of hydrocarbons ranging from C11 to C16 representing the kerosene range (Table 4).

The oil fraction yielded by thermal pyrolysis of PE showed most hydrocarbons (29.7%) in the range of C11 to C16, representing the kerosene range, followed by hydrocarbons in the range of C17 to C20, which corresponds to the fuel oil range. The liquid oil obtained from the pyrolysis of PS also consists of styrene as a major component, and styrene was also observed as a dominant compound when PS was mixed with other plastic types. Such an observa-

tion of styrene as a major compound has been reported in the literature (Jaafar et al., 2022). The overall results show that hydrocarbons in the light naphtha C7 to 10 range were the major component (64.53%), followed by hydrocarbons (C11 to C16), with 26.6% products representing kerosene (Table 4). Moreover, the liquid oil also revealed significant quantities of other fractions, such as diesel and lubricant oil, which have potential uses, including as substitutes for conventional fuels in transport, refineries, and industry, and as chemical feedstocks (Zhang et al., 2022).

4. COMPARISON OF PLASTIC-BASED FUEL WITH COMMERCIAL FUEL

The properties of liquid oil obtained from the pyrolysis of plastic waste were assessed and compared with those of conventional fuels such as gasoline, diesel, and kerosene. The density and viscosity of liquid oil obtained from individual plastic and mixed pyrolytic liquid oil were found to fall within the ranges of conventional diesel, gasoline, and kerosene (Table 5). However, slight variations were observed in the flash points of the derived oils compared with those of conventional fuels. For instance, the flash point of conventional diesel ranges from 55 to 60°C, whereas the flash point of the derived oils from individual and mixed plastic waste ranges from 29 to 48°C. The lower flash point of pyrolysis oil is due to its high volatility and aromatic content, compared with conventional diesel (Miandad et al., 2017). Moreover, the obtained results were slightly lower than those for gasoline (37 to 42°C) and kerosene oil (38°C). The lower flash point of the pyrolysis-derived oil as compared to the conventional gasoline and kerosene oil is due to the high volatility and low boiling point hydrocarbons, including olefins, C5 to C9 fractions, and light aromatics, produced through random chain breaking and secondary cracking during pyrolysis that readily vaporize at lower temperatures (Sharuddin et al., 2016). Moreover, the composition of pyrolysis-derived oil, as well as the presence of unsaturated compounds, affects flammability and vapor pressure, thereby reducing the flash point compared to more refined, compositionally controlled fuels such as gasoline and kerosene (Al-Salem et al., 2017).

Pour points and HHVs were also observed within the ranges of conventional diesel and kerosene oil, while some of the liquid oils showed slightly lower HHVs (Table 5). The slightly lower HHV values of pyrolysis-derived oils com-

TABLE 4: Distribution of carbon number among different pyrolytic liquid oils.

Sample	Naphtha % (C6 to C10)	Kerosene % (C11 to C16)	Diesel % (C17 to C20)	Lub Oil % (C21 to C30)
PP	83.2	12.3	4.1	0.2
PS	78.1	15.6	6.0	0.3
PE	61.0	29.7	9.0	0.4
PE:PS	69.8	20.4	3.9	1.3
PP:PS	65.1	29.6	5.4	0.0
PE: PP	30.0	52.0	17.6	0.4
Mean	64.53	26.60	7.66	0.433

TABLE 5: Comparison of different plastic waste with conventional fuels.

Parameters	Density (g ml ⁻¹)	Viscosity (mm ² s ⁻¹)	Flash Point (°C)	Pour Point	HHV (MJ kg ⁻¹)	References
PE	0.831±0.13	1.9±0.98	34±2.31	-12±1.03	39.6±2.41	Current study
PS	0.892±0.33	3.1±0.33	48±2.76	-19±2.11	38.5±3.02	Current study
PP	0.786±0.21	2.1±2.76	44±3.07	-15±1.01	42.4±1.88	Current study
PE:PS	0.821±0.16	2.2±1.10	32±1.87	-10±2.43	37.2±3.78	Current study
PE: PP	0.874±0.03	2.3±1.03	31±2.53	-13±1.05	41.9±2.74	Current study
PS: PP	0.734±0.08	2.1±0.94	29±3.02	-11±2.11	38.7±3.88	Current study
Conventional diesel	0.815 to 0.870	2.0 to 5.0	55 to 60	Max 18	43.06	Syamsiro et al., 2014b; Kamal and Zainuri, 2015
Conventional gasoline	0.72 to 0.78	1.0 to 2.1	37 to 42	- 12	44	Lee et al., 2015
Kerosene oil	0.78 to 0.82	1.54 to 2.20	38	-18	43.4	Hakeem et al., 2018; Lee et al., 2015

pared to conventional fuels are due to their lower hydrogen-to-carbon (H/C) ratio and lower energy density which correspond to the presence of unsaturated hydrocarbons (olefins), oxygenated compounds, and light fractions (Sharuddin et al., 2016). Furthermore, incomplete cracking and the presence of various impurities and heteroatomic species in pyrolysis oil also reduce the HHV compared to refined fuels (Al-Salem et al., 2017).

Based on the obtained results and comparisons with the conventional fuels, several post-treatment technologies can enhance the fuel characteristics of the pyrolysis-derived oil, including hydrotreatment and catalytic upgrading, that will remove the impurities and enhance the saturation level, thereby increasing the overall stability and HHV. Moreover, fractional distillation to obtain fuel-range fractions, blending pyrolysis oil with conventional fuels, and optimizing pyrolysis conditions (residence time and temperature) could further improve the physicochemical properties and combustion performance of pyrolysis oil.

5. POTENTIAL APPLICATIONS OF PYROLYSIS-DERIVED PRODUCTS

5.1 Liquid oil

The liquid oil produced through pyrolysis of plastic waste is composed of numerous organic compounds, including naphthalene, olefins, and aromatic compounds similar to those found in petroleum products (Miandad et al., 2019). Moreover, it has been found that the HHV values of the obtained pyrolytic oil are slightly lower but close to those of conventional diesel, as observed in the current study, where HHV values ranged from 37.2 to 42.4 MJ kg⁻¹ (Figure 2 and Table 5). Hence, successful post-treatment could enhance the stability and HHV of pyrolysis-derived oil, thereby making them a viable alternative energy source. In this regard, Saptoadi & Pratama (2015) conducted an experiment on the pyrolysis of plastic waste and successfully utilized the liquid oil as an alternative to kerosene in kerosene stoves. Lee et al. (2015) and Rehan et al. (2016) also successfully reported the suitability of pyrolysis-derived liquid oil for use in diesel engine. However, as discussed above, to enhance engine performance and reduce vehicle emissions, several researchers blended pyrolysis-derived oil with conventional diesel at various ratios for utilizing as

transportation fuel. Various studies investigated blending pyrolytic liquid oil with diesel at ratios of 10%, 20%, 30%, and 40% to assess suitability for various types of diesel engines in terms of engine performance and exhaust emissions (Nileshkumar et al., 2015). Lee et al. (2015) and Nileshkumar et al. (2015) demonstrated that 80:20% blending ratio of pyrolysis-derived oil and conventional diesel yields engine performance comparable to that of conventional diesel. In addition to the direct application of pyrolysis oil, the produced aromatic compounds can also be used as raw materials in several chemical processes for polymerization (Miandad et al., 2019).

5.2 Gases

Various gases, including hydrogen, butane, methane, propene, ethene, and propane are produced during pyrolysis of several types of plastic waste (Kartik et al., 2022). However, the only hazardous chlorine gas is produced from the pyrolysis of polyvinyl chloride (PVC) (Li et al., 2023). It has been reported that increasing the pyrolysis temperature enhances gas production (Mlonka-Mędrala et al., 2021). It has been estimated that pyrolysis of 1 kg of plastic waste generates about 13 to 26.9% gas (w/w) (Chen et al., 2014). As like liquid oil, the pyrolysis-derived gases also possess high HHVs. In this regard, Miskolczi et al. (2009) reported that the gases produced from the pyrolysis of plastic waste possess the HHV of 45.9 to 46.6 MJ kg⁻¹. Jung et al. (2010) also reported that the gases produced from PE and PP have calorific values of 42 and 50 MJ kg⁻¹ respectively. The high HHV of the produced gases indicated their suitability for energy production. Moreover, the produced gases can be used in gas turbine to generate electricity and as heating source for boiler (Leme et al., 2018). Likewise, the recovery of isoprene and 1-butene through condensation from mixed gases can be used in tire production (Miandad et al., 2016). Moreover, ethane and propene gas can be used as chemical feedstock to produce polyolefins (Miandad et al., 2016).

5.3 Char

Char is produced as a by-product during pyrolysis and is essentially the unburnt feedstock plastic left over in the pyrolysis reactor (Dwivedi et al., 2019). However, compared with other pyrolysis products, such as liquid oils and

gases, the yield of char is very low, ranging from 1 to 1.3g from 1kg of plastic (Miandad et al., 2019). The produced char can be potentially used for several energy and environmental applications. The research by Syamsiro et al. (2014a) reported HHV of 23.04 and 36.29MJ kg⁻¹ for the char produced from pyrolysis of HDPE and PS respectively. Jamradloedluk and Lertsatitthanakorn (2014) successfully prepared pellets (1kg) by crushing the HDPE-derived char into powder and used them to heat 1 liter of water in 13 minutes. In addition to its energy applications, the obtained char can also be used for several environmental remediation strategies, such as adsorbing heavy metals and toxic gases from municipal and industrial wastewater (Li et al., 2021). However, to enhance adsorption capacity, several researchers have successfully activated char. For instance, Lopez et al. (2009) tested thermal activation of the pyrolysis-derived char at 900°C for 3 hours and found increases in BET surface area and pore volume of 44% and 55% respectively. Likewise, steam activation makes the produced char an environmentally friendly product by reducing its sulfur content. Bernardo (2011) studied activated charcoal for the adsorption of methylene blue dye and found significant adsorption results ranging from 3.59 to 22.2mg g⁻¹. Nevertheless, pyrolysis-derived char can also serve as suitable feedstock for the synthesis of activated carbon (Menya et al., 2020).

6. POTENTIAL OPPORTUNITIES FOR A PLASTIC-BASED CIRCULAR ECONOMY

Generally, there are two broad categories of plastic waste including post-consumer and post-industrial (Horodytska et al., 2019). The characteristics of these two plastic waste streams also differs. Consumer plastic waste is contaminated because it is mixed with other municipal solid waste, whereas post-industrial plastic waste is comparatively clean with a defined composition and consistent quality (Qureshi et al., 2020). This difference makes post-consumer plastic waste less suitable for recycling and usually leads to its disposal in landfills or incineration. On the other hand, it has been well understood that plastic materials are persistent and degrade slowly over time. In such situation, pyrolysis technology offers a sustainable option for valorizing plastic waste into liquid oil and other beneficial products (Fulgencio-Medrano et al., 2022). Moreover, pyrolysis can tolerate considerably higher levels of contaminants in feedstock, hence all types of plastic waste can be pyrolyzed, making it economically attractive by reducing pretreatment steps (Miandad et al., 2019).

Moreover, considerable engineering efforts have been made to design new reactors capable of treating various feedstocks and to optimize yield with minimal energy requirements (Waqas et al., 2018). Being a simple and one-step treatment process, pyrolysis has the potential to treat various types of plastic waste ranging from simple packaging waste to more complex and heterogeneous materials such as rubber, plastics from waste electrical and electronic equipment, and hospital waste that are contaminated with various toxic substances (Dogu et al., 2021). Furthermore, pyrolysis is also considered as a self-sus-

tainable technology because it produces hydrocarbon-rich gas with high HHV of 25 to 45MJ kg⁻¹, making it ideal for energy recovery (Oasmaa et al., 2019). Hence, the generated energy can be recirculated back into the process to meet its energy requirements, thereby making the process self-sustainable at commercial scale (Qureshi et al., 2020). Moreover, among the key advantages of pyrolysis technology is the minimal infrastructure requirement, as it can be installed in small, mobile units, making it easy to move to the feedstock-abundant site (Oasmaa et al., 2019). This approach reduces both the carbon footprint and transportation cost to treatment/recycling units. Furthermore, the oil and wax obtained from the pyrolysis of waste plastic are rich in hydrocarbons, making them an ideal raw material for a refinery process. In this regard, several studies have examined integrating pyrolysis with conventional refinery. The integrating approach shows that thermal technology for product recovery enables the completion of the loop of plastic waste circular economy. It has been estimated that by 2030, about one-third of the total plastic entering the global market could be manufactured from recycled plastics (Miandad et al., 2016). This estimate will bring an economic benefit of about 75USD per barrel in oil prices to the plastic and petrochemical industry, along with the dual benefit of fulfilling the regulatory framework for both consumer and industry plastic consumers.

7. TECHNICAL CHALLENGES AND APPRAISING OPTIONS TOWARDS THE COMMERCIALIZATION OF A PLASTIC-BASED CIRCULAR ECONOMY

7.1 Feedstock and process operation

The key consideration for an effective and economical plastic waste pyrolysis technology is the continuous supply chain of feedstock where the non-availability of continuous plastic waste feedstock has been reported as one of the main factors in the failure of plastic waste recycling initiatives (Bening et al., 2022). It has been reported that several countries import considerable amounts of plastic waste from other countries to ensure continuous feedstock supply (Nizami et al., 2017).

Moreover, the plastic waste collected from various waste streams is heterogeneous, originating from packaging materials to electrical and electronic equipments and containing a mix of polymers. Likewise, PVC and PET are rich in polyolefins, making them an ideal feedstock for pyrolysis due to their chemistry and synergistic effects (Qureshi et al., 2020). However, upon thermal degradation, PVC releases chlorine-containing compounds that have adverse effects, including equipment corrosion and oil halogenation. To overcome the problems associated with PVC, several steps have been taken including avoiding PVC in the feedstock and designing pyrolysis technology to tolerate high PVC concentrations (Al-Rumaihi et al., 2022). Avoiding PVC in the feedstock requires additional examination to separate it. However, PVC is not considered a major contributor to plastic waste, as it is primarily used in the construction sector and thus accounts for only a small por-

tion (Ciacci et al., 2017). On the other hand, PET is a major contributor to the plastic waste stream and is present in a wide range of materials.

Furthermore, pyrolysis is considered a high-energy-consuming technology that hinders its scalability for large-scale treatment of plastic waste. The energy supply in conventional pyrolysis is provided by electricity, auto-thermal heating, induction heating, and microwave-assisted heating. Except for auto-thermal heating, which partially uses heat generated from feedstock oxidation, all other energy supply pathways are energy-intensive (Pan et al., 2024a). However, the recent research trend is the utilization of solar energy to meet the energy demands of pyrolysis technology is receiving significant attention. The key benefits of using solar energy for pyrolysis include its renewable, clean, and abundant availability. However, appropriate reactor designs are critical for concentrating ambient solar energy to achieve high operating temperatures, high solar energy utilization, and high conversion efficiencies (Yadav and Banerjee, 2016). Recently, Pan et al. (2024a) designed a solar-driven pyrolysis reactor to address the energy and carbon-emissions challenges associated with heating. Using direct irradiated solar energy, they assess various operating and porous media parameters to determine the reactor's thermal performance. Their findings revealed that using SiC as a porous skeleton enhanced energy absorption up to 30% due to its high solar-absorbing capacity. They also reported that the simplified structure and integration with solar energy, enables the commercialization of solar-driven pyrolysis for large-scale treatment of plastic waste.

7.2 Toxicity and pretreatment of the feedstock

The heterogeneous nature of plastic waste from various sources may contain hazardous additives, halogens, and other toxic substances that necessitate appropriate characterization of the feedstock prior to pyrolysis (Kusenberget al., 2022). The characterization could enhance the overall treatment cost, however, it has the dual benefits of ensuring good quality of products along with operational safety because most of the toxic substances could escape from the recycling and hence pose serious threats to human and environmental health (Nizami et al., 2017). Furthermore, the variation in size and shape of plastic waste types also requires uniform size, achieved by crushing into small particles prior to pyrolysis (Miandad et al., 2019). Crushing and size reduction are beneficial, however, this step incurs an additional operational cost for the treatment technology (Nizami et al., 2017).

7.3 Wax formation and unstable nature of pyrolysis oil

Pyrolysis of plastic waste yields a variety of products mainly polyolefins and wax. Wax results from inefficient condensation during pyrolysis, which scales on the inner surfaces of the reactors and makes the recovery difficult (Miandad et al., 2019). Hence, the recovery systems must be designed to recover waxes produced during pyrolysis effectively. Kaminsky et al. (2004) developed an approach using heated impact precipitators in condensing tank to

keep waxes in liquid form during pyrolysis. Furthermore, stability of pyrolysis oils is the key property that determines the quality of the derived liquid oil (Qureshi et al., 2020). Generally, pyrolysis oils are thermodynamically unstable and tend to repolymerize. Thus, it requires post-treatments, including blending and dewaxing the liquid oil to maintain quality over an extended period (Butler et al., 2011).

However, the wax fraction is not only an undesirable residue but could also be a valuable intermediate (Brown et al., 2024). During pyrolysis, several conditions, such as short vapor residence time, result in high-molecular-weight wax fractions that comprise the major portion of the condensable products and a significant portion of the feedstock carbon. Such condensable products exhibit high energy density and molecular weight, making them valuable intermediates compared to raw plastic waste (Duque et al., 2023). In addition to high energy density, the semi-solid or liquid state of the wax also facilitates transportation, storage, and handling. Through technologies such as catalytic cracking, waxes could be readily upgraded to value-added olefins such as propylene and ethylene (Brown et al., 2024). However, rational care should be taken during the thermal upgrading of wax fractions due to the low volatility and high viscosity. Furthermore, from process engineering perspective, wax fractions enable a distributed pyrolysis approach to centralized upgrading facilities, thereby improving the logistical efficiency and overall process economics (Brown et al., 2024).

7.4 Life cycle assessment and kinetic models

The gases produced during the pyrolysis of certain types of plastic waste, such as PVC, are highly toxic and pose risks to human and environmental health (Moranda & Paladino, 2023). In this regard, pyrolysis emissions need to be refined to the greatest extent to maximize environmental and human health benefits (Tan et al., 2023). Likewise, significant efforts are needed to develop pyrolysis-derived oil to make it cleaner before its application to minimize environmental impacts (Miandad et al., 2019). Pyrolysis oil, being rich in aromatic compounds such as toluene, benzene, and styrene is attractive to the oil market hence, upon refining, these compounds can be sold (Lam et al., 2016). Though some of the aromatic hydrocarbons present in the pyrolysis oil are carcinogens and can cause serious human health impacts. Hence, extensive considerations are required to evaluate and minimize human health impacts (Tan et al., 2023). Furthermore, a detailed economic and environmental impact assessment of plastic-based refineries are also critical during design through specialized tools and techniques such as life cycle assessment (LCA) (Mannheim, 2021). The LCA study can fully analyze the refinery concept in terms of environmental impacts and all resultant products through a detailed materials and energy balance across all life stages, from raw feedstock collection/extraction, processing, manufacturing, product yield, and distribution. Such assessment helps to determine the sustainability of plastic-based circular economy, which is crucial for making the right decision (Schwarz et al., 2021).

Likewise, controlling the quality and yield of pyrolysis products is a key factor in estimating the economic benefit

of the pyrolysis technology. Several researchers have conducted detailed studies on the kinetic modeling of pyrolysis because it can provide reaction mechanisms for the pyrolysis of plastic waste (Pan et al., 2024b). In this regard, Wei and Kuo (1969) and Kuo and Wei (1969) developed a lumped reaction kinetic model that proposed dividing complex chemical constituents into several equivalent "lumps". These lumps can be modeled through various kinetic models used for various molecular compounds. Moreover, this kinetic model has been successfully applied to a range of complex reactions, including catalytic cracking and hydrocracking. Jiang et al. (2022) lumped a kinetic model of pyrolysis technology and distributed the products from plastic pyrolysis into oil, gas, and paraffin. As the current study focused on the yield and physicochemical characterization of individual mixed pyrolysis of various types of plastic waste, with no detailed kinetic modeling performed to elucidate the pyrolysis reaction pathways. Hence, given the complex reactions during thermal degradation, such as parallel and consecutive reactions, including depolymerization, β -scission, chain fragmentation, and secondary cracking, the application of advanced kinetic modeling is critical for future research on the pyrolysis of plastic waste. Furthermore, modeling such as lumped kinetic models and distributed activation energy models, would enable the quantitative description of the heterogeneous nature of plastic waste and product recovery. Moreover, the implementation of such models can provide critical insights into activation energies, reaction rates, and product-distribution mechanisms under varying thermal conditions, thereby improving the predictive capability of pyrolysis technology.

8. CONCLUSION AND OUTLOOKS

Pyrolysis of different types of plastic waste and their mixture at 50:50% ratio was carried out in a small-scale batch reactor. Among the plastic waste, the maximum liquid oil yield was recorded for PS, due to its lower molecular complexity compared to other types of plastic waste. The lowest oil yield with high gas content was observed for PP, that could be attributed to degradation pathways, secondary cracking of pyrolysis vapors, and radical stability that affect the formation of condensable hydrocarbons and gases during thermal degradation. The HHV ranged between 37.2 and 42.4 MJ kg⁻¹. However, the highest HHV was recorded for pyrolytic oil obtained from the pyrolysis of PP (42.4 MJ kg⁻¹), followed by PE and PS with HHVs of 39.6 and 38.5 MJ kg⁻¹ respectively. HHVs of liquid oil produced from mixed plastic waste of PE:PP were 41.9 MJ kg⁻¹, followed by PS:PP and PE:PS with HHV of 38.7 and 37.2 MJ kg⁻¹, respectively. The FTIR spectra revealed the presence of aliphatic group at 2924 and 2854 cm⁻¹. At 1456 cm⁻¹, 1377 cm⁻¹ CH₂ bending and C-H olefinic were observed. Aromatic compounds were observed at 696 cm⁻¹, corresponding to the aromatic group. Moreover, it was observed that hydrocarbons in the light naphtha range (C7 to C10) were the major component (64.53%), followed by hydrocarbons (C11 to C16), with 26.6% products representing kerosene. The comparison of pyrolysis-derived fuel with conventional fuel revealed that the density and viscosity of the in-

dividual plastic and mixed pyrolytic oil were found in the range of conventional fuel oil. However, slight variations were observed in the flash points and HHV of the derived oils compared with those of conventional fuels. Likewise, in-depth discussions have been made on the utilization of the produced gases for energy production, including in gas turbines for electricity generation and in boilers for heating, as well as on the applicability of the derived char for several energy and environmental applications. However, the presence of certain aromatic compounds in the pyrolysis-derived oil makes it unsuitable for direct use as fuel until upgradation, and various post-treatment methods, including distillation, refining, and/or blending with conventional fuel, are required to use the derived liquid oil as an energy source. It has been emphasized that valorizing plastic waste into a successful waste-to-energy concept requires overcoming several problems associated with continuous supply and the heterogeneous nature of the feedstock, appropriate characterization and pretreatment of the feedstock to reduce toxicity, and ensuring good quality products and operational safety. Likewise, approaches to reduce wax formation, technological advancements to enhance the quality and yield of pyrolysis, detailed life cycle assessment, and implementation of advanced kinetic modeling are critical for improving the capability of pyrolysis technology. Furthermore, there is also a dire need to create and expand the market for pyrolysis-derived products to attract the interest and funding of relevant stakeholders and make the concept of plastic waste as a resource more successful and practical.

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