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Liquid fuel production thermal degradation of mixed plastic waste

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Abstract

In this study, a mixture of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) was pyrolyzed at a temperature range of 350-400 °C for two hours to produce hydrocarbon liquid, which was then distilled at a temperature range of 150-275 °C to recover the target kerosene fraction. The resulting kerosene had a calorific value of 43150.1 MJ/Kg, a sulphur content of 0.01, a flash point of 121, a smoke point of 24.8, a specific gravity of 0.733, water content of 0.08, and a copper corrosion rating of 1a. The physicochemical properties were generally within acceptable limits for commercial Household Kerosene (HHK), although the water content, acid value, and API gravity were slightly outside the standard. This study, therefore, proffers a solution to the menace of environmental pollution and energy crisis, which has given rise to the prevalence of artisanal refining and adulteration, leading to disastrous consequences such as property damage and even death.

Keywords: Plastic; Pyrolysis; Kerosene; Recycling; Physico-chemical properties

1. Introduction

Plastic waste management has raised serious concern because of the attendant challenges associated with its management at the end of use (Bhosale *et al.,* [1], Dumbili and Henderson [2], Kehinde *et al.,* [3], Mihai *et al.,* [4], Hopewell *et al.,* [5]). Plastics are produced from fossil feedstock and have become a necessary part of our daily lives; consequently, their production has grown on a large scale globally (Thompson *et al.,* [6]). Over the years, plastics have experienced massive exponential growth in their production and consumption at a rate projected to triple by 2060 if the current trend in production and consumption is maintained. The annual global production of plastics doubled from 234 million metric tons in 2000 to 460 million metric tons in 2019 and is forecasted to rise to an estimated value of 1,231 metric tons in 2060 (OECD, [7]).

The steady growth in plastic production can be due to increased demand and consumption. OECD [7] stated that emerging economies such as in sub-Saharan Africa and Asia are expected to triple their plastic consumption against the countries that are members of the Organization for Economic Co-operation and Development (OECD). Nigeria, a consumer-driven nation, uses much plastic; therefore, it imports and internally produces large volumes of plastic polymers for different applications and sectors. Nigeria is ranked as the highest importer of plastics and plastic raw materials in Africa (Agberemi, [8]). Imported plastic in Nigeria is in the form of primary form, product and product components. Babayemi *et al.,* [9]) reported that between 1996-2014, approximately 23,165,700 tons. Of this amount, 14,200,000 tons were in primary form, 3,420,000 tons were in product form, and around 5,545,700 tons were imported

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as product components. Furthermore, during a six-year period, an estimated 194,000 tons of plastic toys were also imported. Statista reported that in 2015, the production volume of plastic in Nigeria reached around 411,000 metric tons. According to Jambeck *et al.,* [10], Nigeria contributes 0.13–0.34 million tonnes of plastic waste to the marine environment annually and is ranked ninth globally in marine plastic pollution. Nigeria generates 32,000,000 tons of municipal solid waste annually, about 13% of which is plastic. The production rate of plastic does not tally with the rate of its disposal at its end of life. The current practice of plastic management is more in the form of linear and far from circular. Statistically, considering that at its end of life, only 9% of plastic waste is recycled, 19% is incinerated, and approximately 50% goes to sanitary landfills. In comparison, the balance of 22% is disposed of in uncontrolled dumpsites, drainages, and surface water, burned in open pits or leaked into the environment (Jambeck *et al.,* [10]).

Plastic wastes predominantly accumulate in the Port Harcourt environment, both terrestrial and marine (Beloved [11]) and are persistent due to their low ability to degrade. Poor plastic waste management prompts severe threats to the environment. In the marine ecosystem, Plastic pollution represents one of the major perceived threats to biodiversity ranging from ingestion, creation of new habitats, entanglement, and possible transportation of invasive species and extinction of marine biodiversity. According to Gall and Thompson [12], entanglement and ingestion cause more destructive impacts on marine organisms and plastic is mostly the causative agent.

Burning of plastics has the disadvantage of causing air pollution due to the release of noxious fumes, dioxins, PAHs, VOCs, emission of greenhouse gases and other compounds associated with the process which have been banned through treaties like the Montreal Protocols and Stockholm Convention. (Pakpour *et al.,* [13] Nagy and Kuti [14]). Research has shown that plastics do not decompose, therefore when left in dumpsites or open dumps serves as a habitat for some pathogen, the leachate from it contaminates both surface and groundwater and sometimes animals visit these landfills and consumes the plastic. Plastic tends to cause bio-accumulation and bio magnifications of compounds across the food chain, leading to a global impact.

Energy demand has escalated far beyond what it was in the previous decade due to high technological advancement and population outbreak. Over the years, the household sector has consistently accounted for over half of the domestic energy consumption in Nigeria, followed by the transport and industrial sectors. Over 85% of the energy used in Nigeria is from non-renewable supplies such as crude oil, coal and natural gas, making Nigeria a country that solely depends on fossil fuels (Anowor *et al.,*[15]). The current structure of energy supply and consumption in the country needs to be more economically, environmentally and socially sustainable. Sustainable energy generation through the conversion of numerous plastic litter in constant generation through the pyrolysis process will serve as another alternative energy supply. Kerosene generation through the waste plastic pyrolysis process will provide an alternative to kerosene production through fossil fuel. Though low-income earners predominantly use kerosene in the country Nnaji et al., [16]: Dare et al., [17], the recent economic crisis is gradually eroding the middle-class group in the country, thereby increasing the dependency and demand on kerosene as an energy source.

Approximately 78% of the final energy consumption in Nigeria is from the residential sector for cooking and lighting. In the absence of kerosene, many residents of the country, especially the rural dwellers, have resorted to using firewood or charcoal; Nigeria consumes over 50 million metric tonnes of fuel-wood annually, leading to deforestation and several environmental issues like flooding and erosion (Sambo, [18]). Kerosene, unlike gasoline, is not highly regulated, causing an increase in its cost and leading to the upsurge of adulterated kerosene through artisanal refining in the Niger Delta region of the country leaving negative consequences Olusegun [19]: Oduwole [20].

Recycling plastic wastes through Pyrolysis has made it possible to recover enormous amounts of energy such as gasoline, and diesel (Sasse and Emig [21]). Kerosene produced from this process can be used independently or blended with ones obtained from fossils to reduce the quantity of the latter consumed directly and indirectly, aiding in the conservation of the resources. The exploration and production of fossil fuels contribute to climate change and global warming; the plastic polymer is one of the products that can be utilized as an alternative energy source, increasing its benefit and reducing its production cost. Waste plastic pyrolysis is an efficient, clean technology that, in addition to providing clean energy, will solve the numerous social, environmental and health problems associated with waste plastics and reduce kerosene scarcity. Finally, Pyrolysis is a promising technology for converting plastic waste into a valuable product such as oil, gas, char or chemicals which can be used as a heavy fuel oil substitute or as raw material by the petrochemical industry (Fivga and Dimitriou [22]).

Previous studies have shown that pyrolysis has excellent potential to produce fuels and other chemicals from plastics (Aida *et al*., [23], Kigozi [24], Paucar-Sánchez *et al.,* [25], Dobó *et al.,* [26], Sarker and Rashid [27], Nugroho and Saptoadi [28], although not much has been reported on the production of kerosene from waste plastic. Therefore, this study seeks to address this.

2. Material and method

2.1. Material

Waste plastics, pyrolysis equipment and ancillaries, shredder, condenser, weighing scale and beakers

2.2. Method

2.2.1. Feedstock preparation

Mixed plastics comprising HDPE, LDPE, PS, and PP were collected from the Port Harcourt dumpsite, shredded and weighed. A total of 7 kg of waste plastic were used as feedstock for the pyrolysis process.

2.2.2. Pyrolysis process

A fixed batch pyrolysis reactor was used to pyrolyze 7 kg of plastic at a temperature of 350- 450 °C and a residence time of 2:30 hrs. The pyrolysis was performed in triplicate. At the optimal temperature, the plastics undergo thermal decomposition, and the organic vapour is released and swept into the condenser; cool water was used for the condensation, and the organic vapour is condensed into a liquid. The liquid was collected with the non-condensable gas at the central collection tank.

The non-condensable gas was sent into the burner to supply heat for pyrolysis, while at the end of each batch, the reactor was allowed to cool, and the residue was removed and weighed. The recovered bio-oil was subjected to distillation, where the kerosene fraction was recovered.

2.2.3. Physicochemical property analysis

The physicochemical properties of the distilled product were evaluated as follows and compared with Nigerian Midstream and Downstream Petroleum Regulatory Authority (NMDPRA) standard for Household Kerosene (HHK):

- **Specific gravity/ API gravity:** To determine the density of a substance, we use specific gravity, which compares it to the density of water. On the other hand, API gravity is the inverse of specific gravity relative to water. The specific gravity of the recovered kerosene was measured with a hydrometer and found to be 0.77, within the acceptable range of 820 max for kerosene. Using the formula, we calculated the API gravity to be 52.27, higher than the maximum value of 41.06. The specific gravity indicates that the kerosene is lighter than water and can flow or spray easily for cooking and lighting.
- **Acid value:** The acid content in kerosene was determined by measuring the amount of potassium hydroxide needed for neutralization through potentiometry titration. High acid levels in kerosene can harm human health when used indoors for domestic purposes. The recovered kerosene had an acid value of 0.42 mg KOH/g higher than the 0.01mgKOH/g specified by the NMDPRA for kerosene, according to Sharma and Jain (2015), a good-quality oil should have a low acid value (< 0.1) to prevent the formation of gum, sludge, and corrosion.
- **Carbon residue:** To prevent the release of excessive carbon into the environment, it is necessary to test the capability of a specific hydrocarbon to produce coke. This is done by determining the amount of carbonaceous residue after the oil undergoes thermal decomposition. In this study, the kerosene had a carbon content of 0.05wt%.
- **Calorific value:** The heat released by kerosene during combustion is measured by its calorific value, also known as its heating value. The recovered kerosene had a calorific value of 43150.1MJ/kg, closely matching the value NMDPRA specified. As per Saptoadi and Pratama [29], the efficiency of the fuel is directly proportional to its calorific value, meaning that a higher calorific value indicates higher fuel efficiency. Therefore, the kerosene's high calorific value suggests that it is an efficient fuel source capable of providing the necessary energy for cooking or lighting.
- **Sulphur content:** The presence of Sulphur in kerosene is prohibited worldwide and heavily monitored to ensure that its presence is minimized. Like carbon found in kerosene or diesel, Sulphur has adverse effects on people and the environment. It can combine with water vapour in the atmosphere to create acid rain, as explained by Yin and Xia [30]. The kerosene from the mixed plastics has a sulphur content of 0.11, below the maximum limit of 0.15 set by NMDPRA.
- **Flash Point:** This property is crucial for safely handling and storing kerosene, as it eliminates potential hazards. The flash point is known as the lowest temperature at which the vapours of a liquid can ignite when exposed to an ignition source under controlled conditions. The recovered kerosene from the pyrolysis process has a

flash point value of 109.4 °F, which exceeds the minimum limit of 105 °F specified by NMDPRA, indicating that the kerosene is suitable for domestic use and poses no safety risks.

- **Smoke point:** The amount of smoke produced by fuel is determined by its aromatic composition, with more aromatic fuels producing smokier flames. The smoke point measures a liquid fuel's tendency to produce carbon particles or soot. In the case of kerosene, its smoke point was measured at 24.8, which exceeds the minimum value of 22 set by NMDPRA. This is expected given that the chemical characterization of the kerosene using GC-MS shows no presence of aromatic compounds.
- **Colour:** Kerosene is typically pale yellow and colourless, and its colour can identify any contaminants present. The recently recovered kerosene had a color reading of 24.2, which exceeds the maximum value of 20 set by NMDPRA for kerosene.
- **Water content:** Having water in the kerosene can negatively impact its performance. In the recovered kerosene, the water content is 0.08, exceeding the maximum standard of 0.05.
- **Copper corrosion:** Copper corrosion refers to the process by which copper or copper alloys deteriorate. The copper corrosion test is a technique used to measure the degree of corrosion in petroleum products. In this case, the kerosene had a corrosion rating of 1a which is within the maximum rating of 1b.

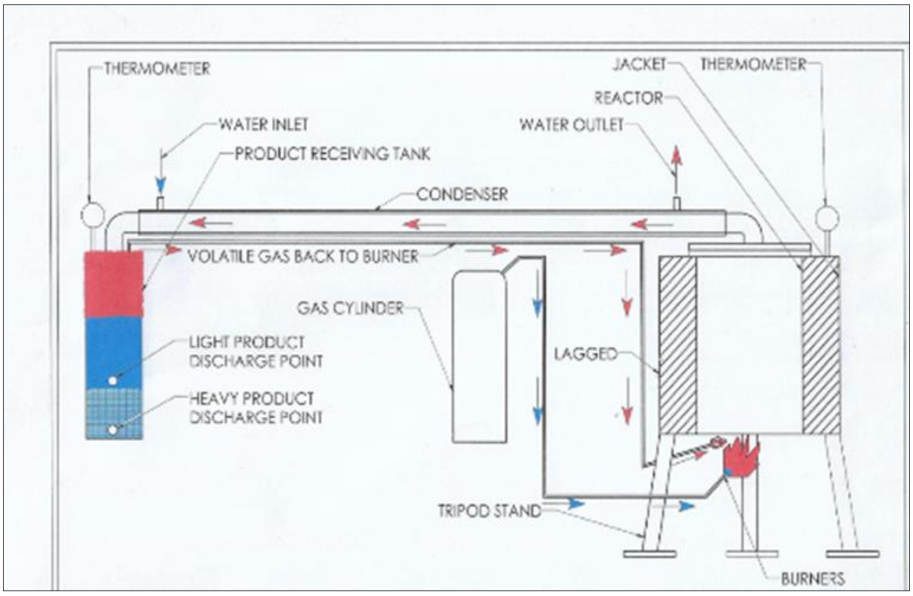

Figure 1 Schematic diagram of the Pyrolysis plant

Figure 2a, 2b. and 2c. The shredded mixed plastics before pyrolysis, generated bio-oil from pyrolysis and recovered kerosene after distillation

3. Results and Discussion

3.1. Mixed plastic waste distribution

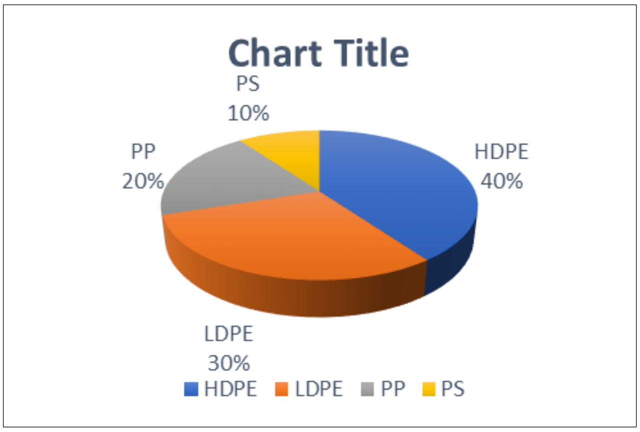

Figure 3 Distribution of the mixed plastic

Figure 3: shows the distribution of the plastics that comprised the 7 Kg of mixed plastic pyrolyzed; it includes: HDPE: 2.8 Kg, LDPE: 2.1 Kg, PP: 1.4 Kg, and PS: 0.7 Kg. The distribution is based on the availability of each group of waste plastic in the dumpsite. HDPE in the dumpsites are inform of bulky plastics and weighs more; they are primarily cosmetics, and drug containers, followed by LDPE, which are mostly disposable shopping bags and packaging, and sachet water liners; next to LDPE are PP plastics, and they consist of disposable plates and bulky bags such as jumbo bags, and finally, PS plastics that include: disposable cups, plates and packaging from furniture and electronic equipment used for protection against impact.

3.2. Product yield

The product yield from pyrolysis was determined using a calibrated scale for the solid or char and a measuring cylinder for the volume of the pyrolytic oil. The mass percentage of product composition was calculated for % conversion, % oil, % char and % gas according to the formula below (Mabood *et al.,* [31]).

Conversion of thermal cracking

$$\text{Conversion (wt.\%)} = \frac{\text{Mass of Mixed Plastic (MP)} - \text{Mass of residue}}{\text{Mass of Mixed plastic (MP)}} \times 100\% \ldots\ldots (1)$$

Liquid Yield

$$\text{Oil (wt.\%)} = \frac{\text{Mass of oil}}{\text{Mass of Mixed Plastic (MP)}} \times 100\% \ldots\ldots (2)$$

Residue (Char) Yield

$$\text{Residue (wt.\%)} = \frac{\text{Mass of residue}}{\text{Mass of Mixed Plastic (MP)}} \times 100\% \ldots\ldots (3)$$

Gas Yield

$$\text{Gas (wt.\%)} = 100\% - (\text{Oil} + \text{Residue}) \ldots\ldots\ldots\ldots\ldots (4)$$

Table 1 Percentage yield from the pyrolytic conversion of mixed plastics

Product	Yield (%)
Liquid	70.38
Solid	10.00
Gas	19.62

NB: Values are a replicate of 3 experiments

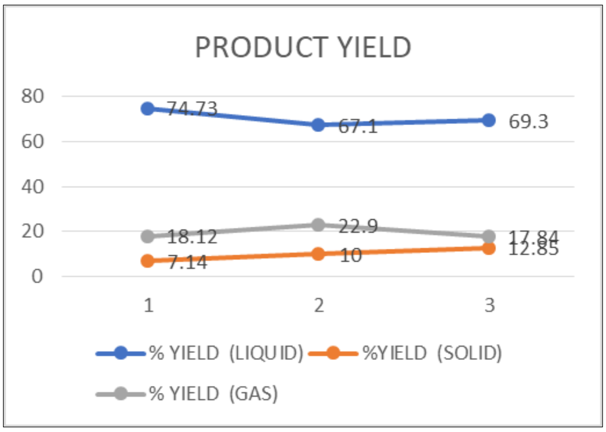

Figure 4 Product yield

The percentage yield of each of the pyrolysis products shows that there was more liquid yield for the triplicate process, followed by the gaseous yield and then the solid (Table 1 and Figure 4).

The distillation was carried out at a temperature range of 150 – 275 °C in a replicate of five separate experiments and from the result, an average of 257ML of kerosene was recovered from the process alongside other products. The yield corroborated that from the pyrolysis of mixed polypropylene and polystyrene as reported by Sarker and Rashid (2013).

3.3. Product characterization

Table 2 Physiochemical analysis of the distilled product

Parameter	Kerosene form mixed plastic	Nmdpra limit
Specific gravity	0.77	0.820 max
Acid value (mgKOH/g)	0.42	0.01
Carbon residue (wt. %)	0.05	-
Calorific Value (Mj/kg)	43150.1	45000
Sulphur content	0.01	0.015 max
Flash Point (^{o}F)	121	113 min
Smoke point(mm)	24.8	22 min
API gravity	52.27	41.060 max
Colour	24.2	+18min
Water content (wt. %)	0.08	0.05 max
Copper corrosion (2hr@100 ^{o}C)	1a	1b max

NB: The values reported are a replicate of 5 experiments

The physicochemical properties of the kerosene were assessed, and the values were compared with the limits set by the Nigerian Midstream and Downstream Petroleum Regulatory Authority (NMDPRA) standard for Household Kerosene (HHK).

Upon reviewing the physical and chemical characteristics of the distillate product, as displayed in Table 2, it is shown that the specific gravity falls within the permissible limit of NMDPRA and is similar to the values reported by Khan *et al.,* [32] for waste plastic pyrolytic oil. It also conforms to the range of values specified by Speight [33], Thahir *et al.,* [34] for kerosene. This means the recovered kerosene is very light, indicating a higher presence of aliphatic compounds. Specific gravity is one of the parameters used to establish the quality of the product. A high specific gravity means low kerosene consumption during burning, and less fuel will be consumed Ejilah *et al.,* [35]. However, the acid value showed 0.42 mgKOH/g, which is higher than the limit of 0.01 mgKOH/g. This can be attributed to the presence of naphthenic acids in the generated kerosene Mohamadbeigy *et al.,* [36]. The carbon residue value is 0.05wt%, which is small compared to those reported by Khan *et al.,* [32], Gaurh and Pramanik [37] but similar to the results presented by Desai [38]. This is preferable as high carbon content in fuels can negatively impact the environment. The calorific value of the recovered kerosene is 43150.1MJ/kg, closely matching the permissible limit. This value is higher than previous reports on waste plastic pyrolytic oil Sharuddin *et al.,* [39]. The reduced heating value of plastic kerosene compared to commercial kerosene can be attributed to the high percentage of unsaturated groups, which can lower the heating value Karisathan and Bhagavathi [40]. The sulphur content of the kerosene from mixed plastics is 0.01, slightly below the maximum limit of 0.015 set by NMDPRA. The mixed plastic kerosene flash point is above the minimum limit and can be used directly. A low flash point suggests that the kerosene contains more volatile materials, which can be rectified by removing the lighter fractions. The smoke point of the kerosene from mixed plastic is 24.8, within the permissible limit, and the API gravity is above the limit set by NMDPRA. However, it falls within the range of 52-40 specified for kerosene in the Handbook of Petroleum Product Analysis by Speight [33] but contrary to the result of Thahir *et al.,* [34], for kerosene from plastic. The water content of the kerosene from plastic is above the permissible limit for kerosene and in contrast to the result by Olalo [41] that reported the water content result for bio-liquid from mixed plastic as 1%, the high-water content can affect its performance and cause corrosion/wearing of storage tanks, including weakening the thread of the heating unit. Finally, the mixed plastic kerosene has low copper corrosion quality 1a and will not cause bright copper surfaces to tarnish or change colour after a very long period.

4. Conclusion

The result of this study shows 87% to 90% total conversion of waste plastic to fuel, which is significantly helpful as an energy source. Plastic pyrolysis is a highly efficient recycling procedure for managing waste plastics. The process itself is highly eco-friendly. There is no secondary waste or damage to human health and the environment. To a great extent, the process is self-sustaining because about 17% to 22% of gases generated during the pyrolysis process were used to support the energy needed. When distilled, the recovered oil gave, on average, of about 25% of kerosene; the remaining fractions were tested and are highly flammable. They can be used as unrefined fuel for generating heat for processes requiring non-refined fuel, such as the running of incinerators or even cement-making plants. The Kerosene physico-chemical properties were to some extent within the acceptable limits specified by NMDPRA, making it safe for utilization for cooking and lighting and making the process safe for reducing environmental pollution caused by plastic waste.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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