Original Research Article

Comparative Analysis of Pyrolysis of Polystyrene and Low-Density Polyethylene for Sustainable Energy and Plastic Waste Management under Laboratory Conditions

Paschal Chibuike Abugu*, **Eberechukwu Kelvin Oguguo**, **Evan Anukwam**, **Uchechi Perpetual Anyanwu**, **Jacob Happy Ineh**, **Innocent Chimezie Madufor**

Department of Polymer and Textile Engineering, Federal University of Technology, Nigeria

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ABSTRACT

Nigeria's 2.5-million-ton plastic waste crisis demands sustainable solutions. This study compared thermal pyrolysis of polystyrene (PS), low-density polyethylene (LDPE), and a 50:50 LDPE-PS mixture chosen arbitrarily, in a fixed-bed batch reactor at 450 °C under nitrogen. Yields were measured by mass, and oils were analyzed for density, viscosity, and composition. PS yielded 97.0 ± 1.2 wt% liquid fuel, 2.5 ± 0.3 wt% gas, and 0.5 ± 0.1 wt% char (Table 1), outperforming LDPE (74.7 ± 1.5 wt% liquid) and the mixture (88.0 ± 1.3 wt% liquid). PS oil's low density (0.886 g/cm^3) and high carbon content (92.1 wt%, Table 3) suit fuel applications, while LDPE's profile (87.8 wt\% carbon) aligns with diesel (Table 2). The mixture provides versatility for mixed-waste processing. Pyrolysis reduces reliance on landfills, generates revenue, and supports Nigeria's energy security.

Introduction

Polystyrene (PS) and low-density polyethylene (LDPE), prevalent in mixed plastic waste (MPW), resist biodegradation, necessitating innovative recycling. The global production of plastics exceeding 350 million tons annually, with a significant portion ending up in landfills or the environment, poses a critical threat to ecosystems and human health [1,2]. Traditional waste management methods like landfilling contribute to land scarcity and greenhouse gas emissions, while incineration releases pollutants and toxic byproducts [3,4]. Consequently, there is an urgent need for advanced recycling technologies such as pyrolysis to convert these polymeric wastes into valuable products and mitigate environmental concerns [5,6].

*Corresponding Author: Paschal Chibuike Abugu (paschabugu@gmail.com)

Pyrolysis thermally degrades plastics into liquid fuels, gases, and char, offering energy recovery and waste reduction. This process involves heating plastic waste in an oxygen-free environment, breaking down long polymer chains into smaller hydrocarbon molecules [7]. The resulting liquid product, often referred to as pyrolysis oil, can be refined into gasoline, diesel, or other valuable chemicals, thereby creating a circular economy for plastic waste [8,9]. Studies on polypropylene pyrolysis report high oil yields (e.g., 54.23% with catalysts) [10], but PS and LDPE mixtures remain underexplored in Nigeria [11]. Understanding the behavior of these specific plastics, especially in mixtures, is crucial for developing region-specific solutions for plastic waste management [12].

Problem statement

Conventional waste management exacerbates pollution and overlooks economic opportunities [13]. The increasing accumulation of plastic waste in Nigeria presents significant environmental challenges, including soil and water contamination, blockage of drainage systems, and impacts on biodiversity [14]. Despite the potential for waste-to-energy solutions, a comprehensive understanding of the optimal pyrolysis condition for common plastic types like PS and LDPE, particularly in mixed streams, is lacking, hindering effective implementation [15]. A comparative analysis of PS, LDPE, and their mixtures is necesary to optimize pyrolysis for sustainable energy.

Objective of the study

This study aims to: (1) compare pyrolysis yields of PS, LDPE, and a 50:50 LDPE-PS mixture, mimicking MPW compositions [16]; (2) analyze fuel properties (Table 2) and compositions (Table 3) of liquid fuel, non-condensable gases, and solid char; and (3) evaluate applications for Nigeria's waste-to-energy strategies.

Significance of the study

This work informs recycling policies, reduces environmental impacts, and supports energy security. By providing detailed insights into the pyrolysis of common plastics found in Nigeria's waste stream, this research contributes to the development of sustainable waste management practices and the production of alternative fuels, aligning with national and global sustainability goals [17].

Materials and Methods

Materials

Materials Polystyrene (PS) from disposable cups and plates, low-density polyethylene (LDPE) from grocery bags, and a 50:50 LDPE-PS mixture were collected from Federal University of Technology, Owerri, Nigeria. The 50:50 LDPE-PS ratio was selected to mimic mixed plastic waste compositions prevalent in Nigeria, reflecting real-world waste streams for evaluating waste-to-energy strategies [16]. All materials were cleaned, dried, and shredded to approximately 2 cm^2. Each sample weighed 200 g.

Experimental setup

A fixed-bed batch reactor (~500 mL, stainless steel) with a Leibig condenser and gas outlet was used. Temperature and pressure were monitored via thermocouple and gauge. The system was purged with 99.99% pure nitrogen at 60 mL/min for 20 min to ensure an oxygen-free environment.

Pyrolysis procedure

Samples were heated to 450 °C at 15 °C/min under nitrogen at atmospheric pressure for 2 hours. Vapors were condensed into liquid fuel, and gases were vented. Yield was calculated as per standard methods:

$$Liquid\ yield = \frac{\text{Mass of liquid fuel}}{Mass\ of\ plastic\ waste} \times 100 \quad (1)$$

Gas and char yields were similarly determined. Elemental analysis followed ASTM D5291 [18].

Product analysis

Yields were measured (Table 1). Density was determined via pycnometer (ASTM D1298), viscosity via viscometer (ASTM D445), acid value via titration, and flash point via standard methods (ASTM D93). Elemental composition (C, H, N, O, and S) was analyzed by New Concepts Analytical Laboratory, Owerri (Lab No. NCALES/FQA/2022/154). A Perkin Elmer Clarus 680 GC-MS system with a 30 m × 0.25 mm × 0.25 µm capillary column was used, with helium carrier gas at 1 mL/min and a 50:1 split ratio. The temperature program started at 40 °C (2 min hold), ramped at 5 °C/min to 280 °C (10 min hold). Compounds were identified using the NIST 2011 library (Table 3). Experiments were conducted in triplicate.

Results and Discussion

Materials characterization

PS, LDPE, and their mixture (LDPE-PS, 1:1) underwent proximate and ultimate analysis. PS's high volatile matter (99.2 wt%) and low ash (0.1 wt%) indicate suitability for pyrolysis [19]. LDPE's 99.5 wt% volatiles and 0.3 wt% ash align with prior studies [20]. PS pyrolysis tends to yield lighter, aromatic-rich hydrocarbons that structurally resemble components found in gasoline, such as benzene, toluene, and xylene. In contrast, LDPE predominantly breaks down into long-chain aliphatic hydrocarbons, more characteristic of diesel-range fuels. Therefore, PS oil is traditionally evaluated against gasoline standards, while LDPE oil is more appropriately benchmarked against diesel specifications. The LDPE-PS mixture's 99.4 wt% volatiles confirm homogeneity [10].

Pyrolysis yields

PS yielded 97.0 ± 1.2 wt% liquid fuel, 2.5 ± 0.3 wt% gas, and 0.5 ± 0.1 wt% char (Table 1), reflecting depolymerization into styrene. This high liquid yield for PS is consistent with its chemical structure, which favors monomer recovery through chain scission [21]. LDPE yielded 74.7 ± 1.5 wt% liquid, 20.5 ± 0.8 wt% gas, and 5.5 ± 0.4 wt% char. The higher gas and char yields for LDPE compared to PS are characteristic of polyethylene pyrolysis, which often produces a broader range of hydrocarbons and more non-condensable gases due to different degradation mechanisms [11,19,23]. The LDPE-PS mixture's 88.0 ± 1.3 wt% liquid suggests synergy, consistent with polypropylene's catalytic yields (54.23%) [20]. The achieved yield of 97.0 ± 1.2 wt% liquid fuel for polystyrene (PS) aligns closely with recent findings in the field. For instance, Prathiba *et al.* (2018) reported a styrene monomer yield of 90.2% from PS pyrolysis at 450 °C using a fluidized bed reactor, reflecting the effectiveness of controlled thermal degradation under similar conditions [22]. Additionally, upcycling studies by Rahimi and García (2017) demonstrated yields exceeding 90% for PS monomer recovery through hydrogen atom transfer (HAT) mechanisms in a pure oxygen atmosphere, highlighting the role of reactor environment and oxidative conditions in maximizing output [23]. However, polypropylene (PP) pyrolysis typically produces a broader hydrocarbon distribution, with Miandad *et al.* (2016) reporting a liquid yield of 54.23% comprising C3-C5 fractions at 450 °C, underscoring the material-specific nature of these processes [24]. These comparisons validate the robustness of the current methodology, while suggesting that yield optimization could be further explored through adjustments in catalyst use or reactor design. Figure 1 displays liquid yields.

Fuel properties

PS oil's density (0.886 ± 0.005 g/cm^3) and viscosity (99.19 ± 0.01 mPa·s) were assessed alongside its flash point (40.0 ± 0.0 °C, Table 2). Compared to gasoline standards (ASTM D4814) [18], which specify a density of 0.70-0.78 g/cm^3 and viscosity of 0.5-1.0 mPa·s at 40 °C, PS oil's density is higher, and viscosity exceeds the acceptable range, indicating limited suitability for direct gasoline use. The flash point (40.0 °C) exceeds gasoline's typical range (-40 °C to 0 °C), suggesting safer storage but requiring refining. LDPE oil's density (0.992 ± 0.008 g/cm^3) and viscosity (98.80 ± 0.20 mPa·s) were evaluated in relation to diesel applications per ASTM D975 [25] (density: 0.820-0.860 g/cm^3, viscosity: 1.9-4.1 mPa·s at 40 °C). While its properties exceed standard limits, the comparison highlights areas requiring adjustment through blending or refining. The LDPE-PS mixture's density (0.802 ± 0.006 g/cm^3) and viscosity (24.7 ± 0.5 mPa·s) are closer to diesel standards, but the viscosity requires refining for practical use [10]. Acid values (PS: 8.60 ± 0.00 mg KOH/g, LDPE: 16.60 ± 0.60 mg KOH/g, LDPE-PS: 8.70 ± 0.10 mg KOH/g) indicate potential corrosiveness, necessitating treatment, as elevated acid values can degrade engine components [19]. For context, biodiesel (ASTM D6751) permits viscosities up to 6.0 mPa·s, highlighting the need for advanced processing techniques. The high viscosity of pyrolysis oils from plastic waste is a common challenge, often addressed through catalytic upgrading or co-pyrolysis with other feedstocks to improve fuel quality [8,26].

Table 1: Pyrolysis yields (wt%) at 450°C with standard deviations (n = 3)

Sample	Liquid (wt%)	Gas (wt%)	Char (wt%)
PS	97.0 ± 1.2	2.5 ± 0.3	0.5 ± 0.1
LDPE	74.7 ± 1.5	20.5 ± 0.8	5.5 ± 0.4
LDPE-PS (50:50)	88.0 ± 1.3	9.5 ± 0.5	2.5 ± 0.2

Table 2: Density, viscosity, acid value, and flash point of pyrolysis oils at 30 °C, mean ± SD (n=2) (ASTM D1298, D445, and D93)

Sample	Density (g/cm^3)	Viscosity (mPa·s)	Acid Value (mg KOH/g)	Flash Point (°C)
PS	0.886 ± 0.005	99.19 ± 0.01	8.60 ± 0.00	40.0 ± 0.0
LDPE	0.992 ± 0.008	98.80 ± 0.20	16.60 ± 0.60	40.0 ± 0.0
LDPE-PS (50:50)	0.802 ± 0.006	24.70 ± 0.50	8.70 ± 0.10	40.0 ± 0.0

Table 3: Elemental composition of pyrolysis oils, analyzed by New Concepts Analytical Laboratory (NCALES/FQA/2022/154)

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
PS	92.10	7.80	0.00	0.00	0.10
LDPE	87.76	12.00	0.00	0.06	0.18
LDPE-PS (50:50)	84.60	15.00	0.00	0.10	0.30

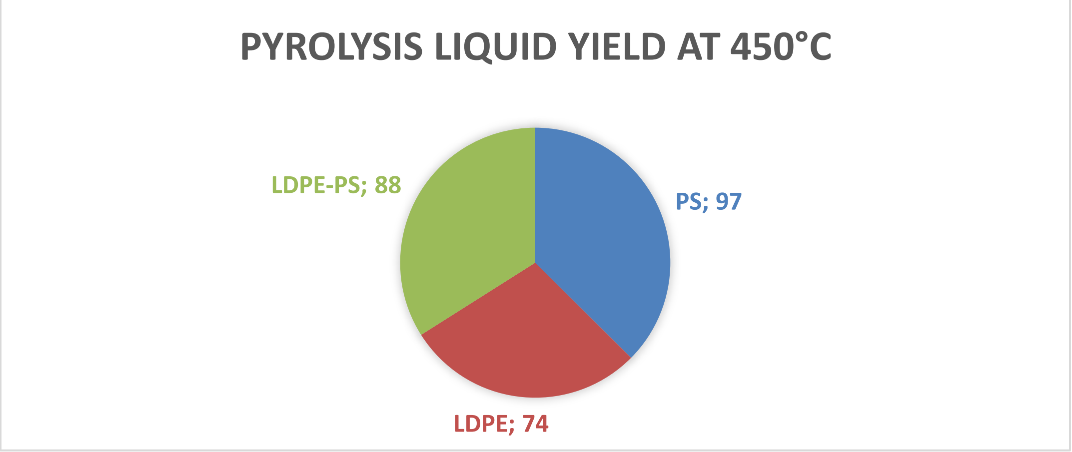

Figure 1: Liquid yield (wt%) for PS, LDPE, and LDPE-PS at 450 °C.

Chemical composition

Elemental analysis (Table 3) shows PS oil's high carbon (92.1 wt%) and low sulfur (0.10 wt%), supporting fuel potential with minimal emissions [27]. The absence of oxygen and nitrogen in PS oil indicates a highly paraffinic and aromatic nature, making it suitable for direct fuel applications or as a petrochemical feedstock [28]. LDPE's 87.8 wt% carbon and 0.18 wt% sulfur align with diesel properties [18]. The higher hydrogen content in LDPE oil compared to PS oil is characteristic of polyethylene, which degrades into straight-chain alkanes and alkenes [29]. The LDPE-PS mixture's balanced composition (84.6 wt% carbon, 15.0 wt% hydrogen) and slightly higher sulfur (0.30 wt%) suggest versatility for mixed-waste processing [11]. The increased hydrogen content in the mixture compared to pure PS indicates the influence of LDPE on the overall product composition [15]. Absence of nitrogen in all samples reduces NOx emissions [1,21].

Environmental and economic implications

Pyrolysis reduces Nigeria's plastic waste, with low sulfur (0.10-0.30 wt%) supporting cleaner fuels [16]. The conversion of plastic waste into valuable fuel products also reduces the volume of waste sent to landfills, mitigating associated environmental burdens such as greenhouse gas emissions and land degradation [2-3,16]. LDPE's gas yield (20.5 wt%) could fuel the process [30], improving the energy efficiency and economic viability of the pyrolysis plant. Fuel sales enhance economic viability and create new revenue streams for waste management companies. Furthermore, the production of alternative fuels can contribute to national energy security by reducing reliance on imported fossil fuels [2,8,26].

Limitations of the study

High viscosity (e.g., LDPE-PS: 24.7 mPa·s) and energy costs limit scalability. Catalysts could lower temperatures and impact quality [10]. Lifecycle analysis is essential to fully assess the environmental and economic feasibilty at a larger scale [11]. Further research is required to optimize reactor design and operating parameters to achieve higher yields and better fuel characteristics, especially for mixed plastic waste [23,31].

Direction for future research

Beyond fuel production, future studies should investigate the physicochemical characteristics of the resulting char of LDPE-PE blend for potential industrial applications, including corrosion treatment or as a functional material in environmental remediation. Anecdotal evidence from this study suggests potential de-rusting properties, warranting controlled testing and material analysis.

Conclusion

This study highlights the significant potential of pyrolysis as a sustainable solution for plastic waste management, with polystyrene (PS) achieving an impressive liquid yield of 97.0 wt% and a high carbon content. While these results underscore PS's promise as a feedstock for fuel production and in reducing disposal costs, its elevated viscosity and acid value, along with deviation from gasoline fuel property standards, necessitate further refining to ensure compatibility with engine requirements. The 50:50 LDPE-PS mixture, with an 88.0 wt% liquid yield, demonstrates the feasibility of processing mixed plastic waste. Notably, although the viscosity of the blend exceeds standard diesel specifications, its density aligns more closely with diesel fuel, suggesting that with moderate modifications, such as blending, catalytic upgrading, or viscosity reduction techniques, it may be suitable for diesel applications. Moving forward, exploring the use of catalysts, such as zeolites, could improve fuel selectivity and reduce unwanted byproducts, while optimizing large-scale pyrolysis systems through better heat distribution and residence time would enhance efficiency. Additionally, recycling non-condensable gases from LDPE pyrolysis as a heat source can make the process more self-sustaining, thereby decreasing energy demands. To ensure scalability, a comprehensive lifecycle assessment is essential for evaluating environmental and economic feasibility. Governments and environmental agencies should also promote pyrolysis-based recycling as a viable alternative to landfilling and incineration, promoting broader adoption of this technology for sustainable energy and waste management.

ORCID

Paschal Chibuike Abugu: 0009-0006-8166-3691
Eberechukwu Kelvin Oguguo: 0009-0001-7810-0576
Evan Anukwam: 0009-0004-1525-9768
Uchechi Perpetual Anyanwu: 0009-0009-7875-2484
Jacob Happy Ineh: 0009-0008-4264-5161
Innocent Chimezie Madufor: 0000-0002-7915-2650

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