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Enhancing Fuel Oil from Polyethylene Waste: A Comparative Study of Catalyst Efficiency in Thermal Pyrolysis

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ABSTRACT: The increasing accumulation of polyethylene (PE) plastic waste has become a pressing environmental concern, necessitating innovative recycling approaches. This study investigates the use of thermal pyrolysis as a method to convert PE waste into useful hydrocarbon products. Specifically, it aims to evaluate and compare the performance of different catalysts in enhancing pyrolysis efficiency and product quality. A total of 100 grams of PE pellets (2 cm size) were thermally decomposed using three catalysts—activated carbon, HZSM-5, and low-rank coal (LRC)—each at 10% weight ratio. The experiments were conducted across a range of temperatures (350–650°C) and durations (30–180 minutes), utilizing a pyrolysis system equipped with a furnace and fractional condensation setup. Analysis focused on product yield, API gravity, and calorific value, with results benchmarked against conventional fuel oil. Among the catalysts tested, LRC exhibited superior performance, achieving the highest yield of 61.10% at 650°C over 180 minutes. The resulting liquid fuel displayed physicochemical properties close to commercial gasoline. These findings demonstrate the potential of catalytic pyrolysis, particularly using LRC, as an effective strategy for PE waste valorization. The study emphasizes the critical role of catalyst selection in optimizing pyrolysis processes for sustainable plastic waste management and energy recovery.

Keywords: pyrolysis; polyethylene; catalyst; fuel; plastic waste

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1. Introduction

Plastic waste, particularly polyethylene (PE), poses a major environmental issue due to its persistence and increasing accumulation in land and marine ecosystems. With global plastic production exceeding 368 million metric tons in 2019, the challenge of managing plastic waste continues to grow (Kamaruddin et al., 2022). Among various treatment methods, thermal pyrolysis has emerged as a promising technique to convert PE waste into valuable hydrocarbon fuels, offering both an alternative energy source and a strategy to reduce plastic pollution(Alhazmi et al., 2021).

Pyrolysis involves decomposing plastics in the absence of oxygen, producing gases, liquid fuels, and char. Its efficiency depends on factors such as temperature, heating rate, and especially the use of catalysts (Setyoningrum et al., 2018). Compared to non-catalytic pyrolysis, catalytic pyrolysis enhances the yield and quality of liquid products, making the process more economically viable and environmentally friendly (Kurniawan et al., 2020).

Catalysts play a crucial role by lowering activation energy and improving fuel properties. Various types, such as zeolites (like ZSM-5) and metal oxides, have been investigated for their ability to influence the cracking of polymer chains and optimize hydrocarbon outputs. However, comprehensive comparisons of different catalysts under uniform conditions are still limited (Radhakrishnan et al., 2025).

This study aims to evaluate and compare the effectiveness of several catalysts—activated carbon, HZSM-5, and low-rank coal—in the pyrolysis of PE waste. By analyzing parameters such as product yield, heating value, and chemical composition using techniques like GC-MS, this research seeks to identify the most effective catalyst and provide insights for enhancing plastic waste conversion into alternative fuels.

2. Materials and Methods

2.1. Methods

This research used polyethylene plastic waste sourced from industrial byproducts, specifically in the form of pellets that measure ±2 cm and have a mass of 150g. The materials used as catalysts consist of activated carbon, HZSM-5, and low-rank coal (LRC), with the catalyst weight constituting 10% of the plastic weight. Additional variables employed include temperatures (350, 450, 550, and 650°C) and time (30, 60, 90, 120, 150 and 180min).

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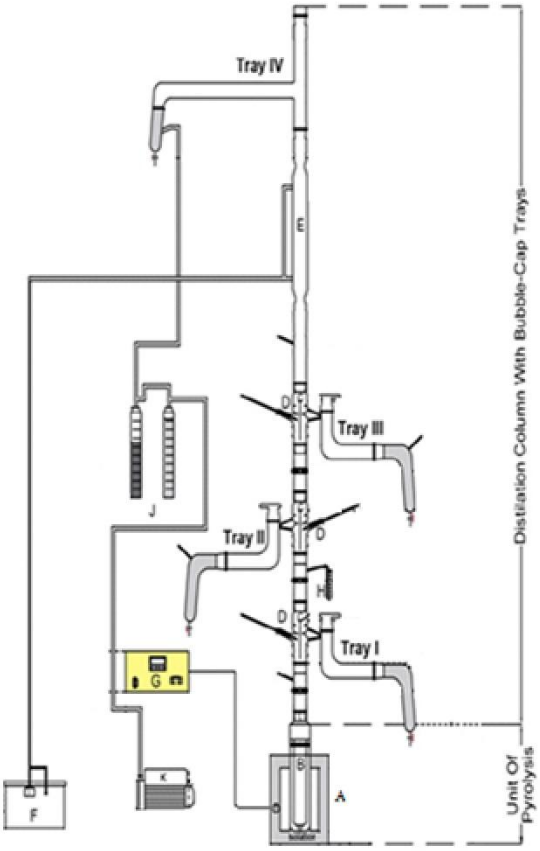


Figure 1. Schematic diagram of the pyrolysis and fractionation system equipped with four trays (Tray I–IV) for collecting pyrolysis oil fractions (Dhaniswara et al., 2025).

The experimental apparatus comprises several essential components. High-purity nitrogen gas is supplied from a gas cylinder (A. N_2 gas cylinder), with the flow precisely regulated using a control valve (B. N_2 gas valve). The gas enters a calcination reactor (C. Calcination reactor), which is housed inside a tube furnace (D. Furnace) capable of maintaining a uniform temperature profile. The sample, typically a catalyst (F. Catalyst), is placed inside a ceramic crucible boat (E. Crucible boat) and positioned in the center of the reactor. Temperature control and monitoring are handled via a digital furnace control panel (G. Furnace control panel). During the thermal treatment process, gases produced are directed out through a gas outlet tube (H. Gas outlet tube). Any condensable by-products, such as tar, are collected in an Erlenmeyer flask (I. Erlenmeyer flask) situated downstream. The exit gas (J. Exhaust gas) is released from the system, while the condensed tar (K. Collected tar) remains in the collection vessel for further analysis.

2.2. Materials

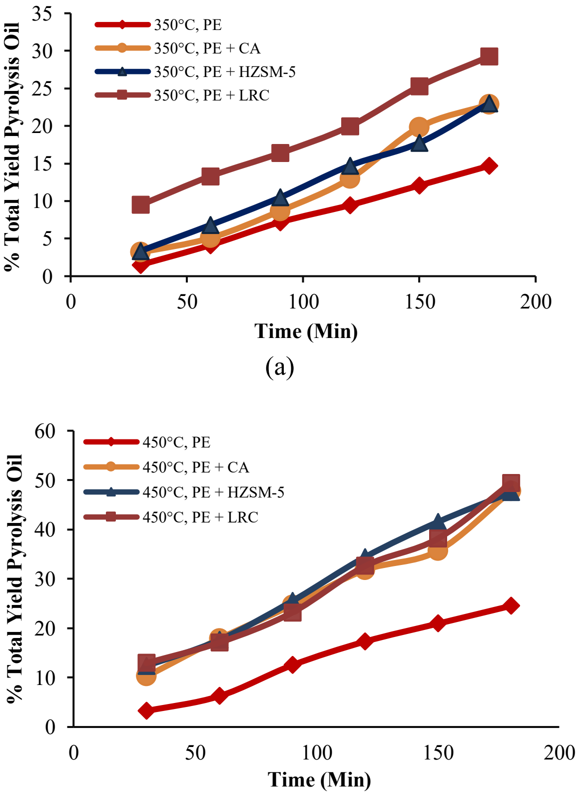
The prepared raw material weighs 150g. In the absence of a catalyst, the raw material is directly introduced into the glass reactor. Regardless, if a catalyst is used in the process, the raw material is mixed with it at a rate of 15g or 10% of catalyst's weight before it is put into the glass reactor. The glass reactor is equipped with a fractionation column and a condenser. The fractionation column has four trays that hold liquid products from pyrolysis, which are usually called bio-oil. Every 30 minutes, we assess the volume of the product exiting each tray. After being made in each tray, the bio-oil is tested for its total yield, °API gravity, calorific value, and GC-MS analysis. We conducted the investigation to characterize the bio-oil and compare it with fuel oil.

3. Results and Discussion

3.1. The Total Yield Comparison of Bio-Oil with and without Catalysts

The total yield of pyrolysis products in the form of liquid fuel, commonly known as bio-oil, varies greatly depending on the use of catalysts. Non-catalytic thermal pyrolysis of polyethylene generally produces a high proportion of waxy hydrocarbons and requires additional refining to obtain usable fuel oil. In contrast, catalytic pyrolysis increases cracking efficiency and modifies product distribution, leading to higher yields of desired liquid hydrocarbons.

Figure 2 shows the relationship between pyrolysis temperature, length of pyrolysis, and type of catalyst used. The higher the temperature and the longer the pyrolysis process, the higher the yield of liquid products (Sardi et al., 2023). This assumption is in line with the theory that the higher and longer the pyrolysis is carried out, the rawer materials will be degraded into liquid.



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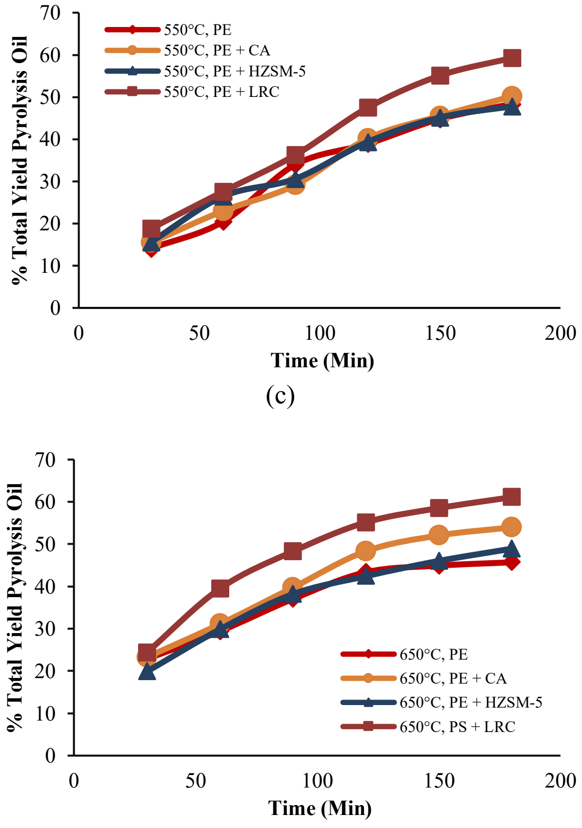

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Figure 2. Relationship Between Temperature and % Total Bio-Oil Yield at Variable Temperatures; (a) Temperature 350°C, (b) Temperature 450°C, (c) Temperature 550°C, (d) Temperature 650°C.

The pyrolysis of polyethylene non-catalyst yields a maximum total bio-oil output of 45.70% at a temperature of 650°C for a duration of 180 min, with the remainder consisting of gaseous hydrocarbons and solid wastes. The absence of a catalytic breaking mechanism results in the productions of long-chain hydrocarbons, which increase the viscosity and decrease the volatility of the resultant fuel oil. The co-pyrolysis of polyethylene and activated carbon yields a high surface area and enhances the thermal breakdown of the polyethylene chain (Wang et al., 2023).

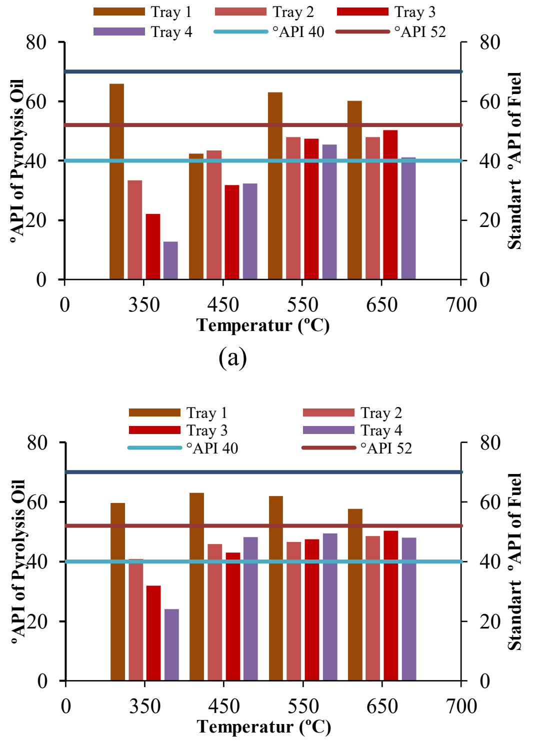
The co-pyrolysis of polyethylene and activated carbon results in a total bio-oil output of 53.97% at 450°C for 180 min, accompanied by a decrease in the gas and charcoal fractions. The porous architecture of activated carbon facilitates additional cracking processes, resulting in an increased yield of light hydrocarbons appropriate for fuel applications (Achmad et al., 2022).

The co-pyrolysis of polyethylene and HZSM-5 has pronounced acidity and shape-selective characteristics that considerably influence the outcome distribution. Catalytic pyrolysis utilizing HZSM-5 yields a total bio-oil of 48.92% at 650°C over 180 min, significantly enhancing the production of gasoline-range hydrocarbons. The pronounced selectivity of HZSM-5 towards aromatics and olefins yields a more refined fuel composition, hence diminishing the necessity for supplementary upgrading procedures.

The co-pyrolysis of polyethylene and low-rank coal (LRC) incorporates intrinsic mineral constituents that facilitate the degradation of polyethylene. The application of LRC in pyrolysis generally yields a total bio-oil output of 61.10% at 650°C over 180 minutes, enhancing the stability of hydrocarbon products. The catalytic activity of LRC is linked to its intrinsic oxygenated functional groups, which facilitate the degradation of polymer structures into smaller, more uniform hydrocarbon molecules (Xie et al., 2023). Comparative results indicate that all catalysts enhance liquid fuel yields compared to non-catalytic pyrolysis, with LRC demonstrating the greatest selectivity for refined fuel products. Additional modification of catalyst loading and process parameters is required to enhance fuel quality and economic feasibility.

3.2. °API Comparison Between Fuel Oil and Bio-Oil

Figure 3 presents the °API gravity of pyrolysis oil fractions collected from four trays at various temperatures (350–650°C), comparing the performance of different catalysts. Each subfigure corresponds to a specific condition: (a) non-catalytic, (b) with activated carbon, (c) with HZSM-5, and (d) with low-rank coal (LRC). °API gravity is an important parameter indicating the quality of fuel; higher API values correspond to lighter, more valuable fuel fractions. Across all conditions, an increase in reaction temperature generally leads to an improvement in the °API gravity, especially in the lighter fractions collected from trays 1 and 2.



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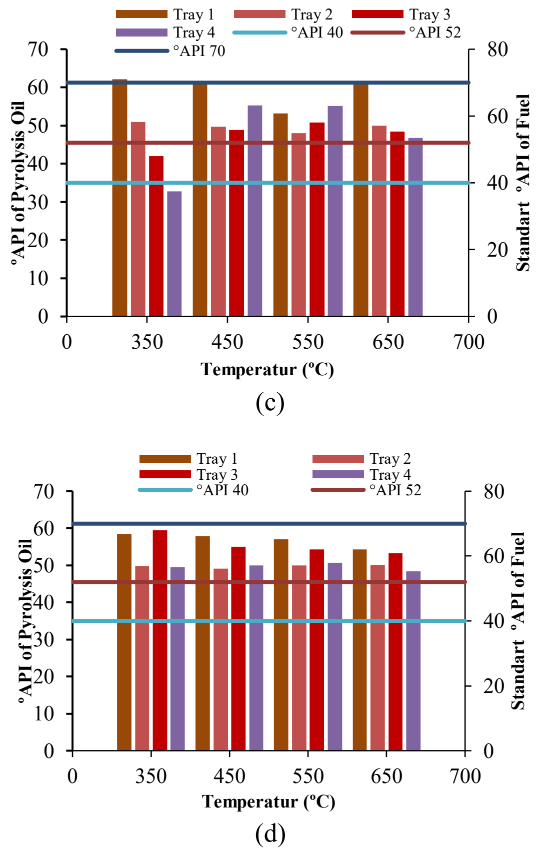

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Figure 3. Comparison between the °API of each bio-oil tray and the °API of fuel oil in the treatment of different samples; (a) PE without catalyst, (b) PE+CA, (c) PE+HZSM-5, (d) PE+LRC.

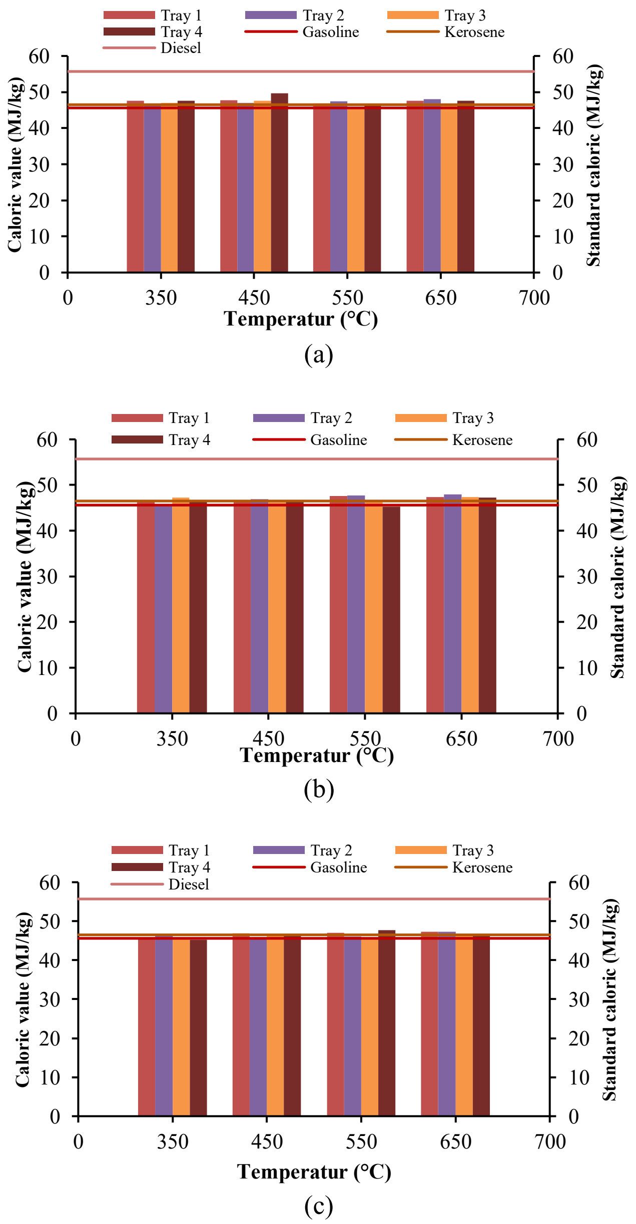
In the non-catalytic pyrolysis (Figure a), °API values remained relatively low, particularly in tray 3 and tray 4, suggesting the formation of heavier hydrocarbons. This indicates incomplete thermal cracking of polyethylene chains at lower temperatures and inefficient fuel conversion without catalytic assistance. While tray 1 displayed a slight increase in °API gravity at higher temperatures, the overall performance remained below desirable benchmarks (°API 40–52), limiting its potential for high-quality fuel production.

Using activated carbon as a catalyst (Figure b) resulted in moderate improvements in °API gravity, especially in trays 1 and 2, indicating enhanced cracking of PE chains into lighter hydrocarbons. However, trays 3 and 4 still produced lower °API values, implying the partial presence of heavier fractions. Compared to non-catalytic conditions, the activated carbon improved product quality but was less effective in producing uniform light fractions across all trays (Mufandi et al., 2023).

The most notable improvements were observed with HZSM-5 (Figure c) and LRC (Figure d). HZSM-5 promoted the formation of gasoline-range hydrocarbons, with °API values in trays 1 and 2 often exceeding 52 at higher temperatures, highlighting its strong acidity and shape-selective cracking ability. Meanwhile, LRC demonstrated the most consistent and balanced °API values across all trays, including tray 3 and tray 4, suggesting deeper cracking and better distribution of lighter fractions. The LRC catalyst effectively upgraded the pyrolysis oil into fuel with properties comparable to commercial gasoline, making it the most promising catalyst among those tested (Putra et al., 2023).

3.3. Comparison of the Calorific Values of Bio-Oil with Fuel Oil

Calorific value (CV) is an essential metric for evaluating the energy potential of pyrolysis oil. The calorific values of pyrolysis oil derived from various catalysts are compared to those of normal fossil fuel. In comparison, common fuels possess the following calorific value in The Handbook of Petroleum: Gasoline: 45.6 MJ/kg; Kerosene: 46.5 MJ/kg; Diesel: 55.7 MJ/kg.



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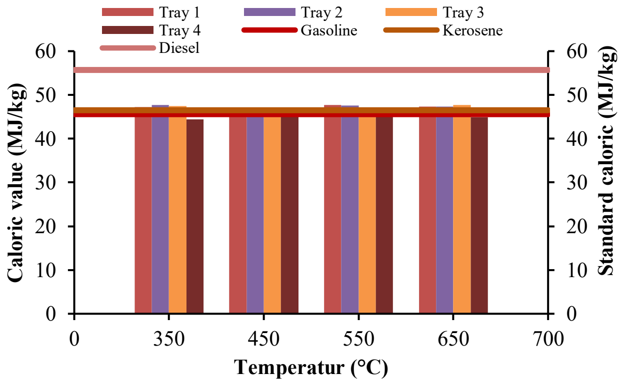

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Figure 4. Comparison of the calorific value of pyrolysis products (bio-oil) and fuel oil; (a) PE without catalyst, (b) PE+CA, (c) PE+HZSM-5, (d) PE+LRC.

Figure 4 shows the caloric value of pyrolysis products at different temperatures and catalyst changes, in comparison to the typical calorific values of common fuels like diesel, gasoline, and kerosene. The graph indicates that the calorific value from the pyrolysis results remains relatively stable despite the temperature rising from 350°C to 650°C. This indicates that although the hydrocarbon chain is disrupted at elevated temperatures, the composition of the final product is mostly unchanged regarding the energy that can be produced.

The comparison with fuel oil indicates that the horizontal line representing the conventional calorific values for diesel, gasoline, and kerosene reveals that pyrolysis products possess a marginally lower calorific value than diesel, although are comparable to gasoline and kerosene. This suggests that pyrolysis products could substitute fuel oil, particularly if the hydrocarbon makeup is improved (Natesakhawat et al., 2024).

The results indicate that pyrolysis oil derived from polyethylene had the potential to serve as an alternative fuel, exhibiting a calorific value comparable to that of traditional fossil fuels. Optimizing catalyst usage can enhance selectivity for light fractions, aligning their quality more closely with that of gasoline or diesel (Chen et al., 2023).

3.4. Bio-Oil Characteristics

The pyrolysis oil was analyzed using gas chromatography–mass spectrometry (GC–MS), and the major identified components are presented in Table 1. The dominant compound in the mixture was 1-decane ($C_{10}H_{22}$), comprising 34.64% of the total area, indicating a significant presence of straight-chain alkanes in the fuel product. This compound, along with 1-undecane (12.3%) and dodecane (2.41%), are saturated hydrocarbons commonly found in diesel and jet fuel ranges, suggesting the fuel's suitability for energy applications requiring medium-chain alkanes.

Tabel 1. Results of Bio-Oil GC-MS Analysis

No	Component	Formula	Mol Weight	% Area
1	1- Decana	$C_{10}H_{20}$	140	34.64
2	1-undecana	$C_{11}H_{22}$	154	12.3
3	Methyl cyclo octane	C_9H_{18}	126	6.15
4	1-Octena	C_8H_{16}	112	4.98
5	Dodecana	$C_{12}H_{26}$	170	2.41
6	5,7-dimethyl-1,6-octadiena	$C_{10}H_{18}$	138	2.19
7	4,8-dimethyl-1-nonanol	$C_{11}H_{24}O$	172	1.95
8	Other	-	-	35.38
	Total			100

In addition to straight-chain alkanes, the sample also contained cyclic and unsaturated hydrocarbons. Methyl cyclooctane accounted for 6.15%, representing the presence of cycloalkanes that may contribute to the stability and combustion characteristics of the pyrolysis oil. 1-octene (4.98%) and 5,7-dimethyl-1,6-octadiene (2.19%), as unsaturated hydrocarbons, indicate partial dehydrogenation during the pyrolysis process. These compounds are reactive intermediates and may be relevant for further upgrading processes or industrial chemical feedstock.

A small fraction of oxygenated compounds was also detected, notably 4,8-dimethyl-1-nonanol (1.95%), which may be the result of secondary reactions involving residual oxygen or trace impurities in the feedstock. While such compounds are generally undesirable in fuels due to their lower stability and energy content, their low concentration minimizes any negative impact on overall fuel performance (Yang et al., 2024).

The remaining 35.38% of the chromatogram is attributed to various minor compounds grouped as "Other." This includes a mixture of light and heavy hydrocarbons that were not individually identified but collectively contribute to the fuel’s calorific value and viscosity. Overall, the composition suggests that the pyrolysis oil is rich in medium-chain alkanes and has physical and chemical characteristics that make it a promising candidate for alternative fuel applications (Palanivelrajan & Feroskhan, 2023).

4. Conclusion

According to this research, pyrolyzing polyethylene using a catalyst improves the hydrocarbon cracking efficiency and yields higher-quality liquid fuel than pyrolyzing it without one. Low rank coal (LRC) catalysts have demonstrated superior efficacy in enhancing yield and generating fuel with elevated API gravity and calorific value comparable to diesel. GC-MS results indicate the prevalence of aliphatic hydrocarbons, specifically 1-decane and 1-undecane, which enhance fuel stability. Nonetheless, pyrolysis oil retains heavy fractions and oxygenated chemicals that necessitate additional purification to meet commercial fuel standards.

Pyrolysis oil derived from polyethylene possesses potential as a sustainable alternative fuel, particularly with further process optimization and purification. The appropriate catalyst enhances the quality of the end product, making it more akin to fossil fuels. Through further optimization, this technology can aid in addressing the issue of plastic waste while offering a more sustainable alternative energy source.

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Statement

During the preparation of this work, the author used ChatGPT for grammar check and editing. After using this tool/service, the author reviews and edits the content as necessary and takes full responsibility for the content of the publication.

CRediT authorship contribution statement

Trisna Kumala Dhaniswara: Writing – original draft, Investigation, Formal analysis, Data curation. **Mahfud Mahfud:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Juliastuti Sri Rachmania:** Supervision, Methodology, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data may be shared upon request

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