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Non-Catalytic Staged Thermal Pyrolysis of Polypropylene and High-Density Polyethylene for Fuel-Range Hydrocarbon Production

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Abstract

The conversion of waste plastics into liquid fuels via thermal pyrolysis presents a sustainable solution to both energy scarcity and plastic waste management. This study investigates the staged non-catalytic pyrolysis of polypropylene (PP), high-density polyethylene (HDPE), and their binary blends to evaluate liquid fuel yields, char formation, and the influence of feedstock composition on product distribution. Experiments were conducted in a 1.0 L semi-batch reactor at 450 °C (Stage A) with secondary cracking of waxes at 500 °C (Stage B). Product analysis via GC–FID quantified gasoline-, kerosene-, diesel-, and heavy-oil-like fractions. Results demonstrate that HDPE produces the highest liquid yield (39.05 g) with minimal char (0.77 g), whereas PP favors gas and char formation due to random chain scission. Binary blends exhibit synergistic behavior, where HDPE-rich mixtures (30% PP–70% HDPE) maximize liquid recovery (36.81 g) while moderating char formation, and PP-rich mixtures benefit from secondary cracking to enhance oil yield (25.1 g). Stage B pyrolysis substantially increased liquid fractions across all formulations, with negligible char generation. Fuel-range composition analysis revealed that PP favors lighter hydrocarbons (gasoline 32%), whereas HDPE yields heavier fractions (diesel 33.5%, heavy oil 26%), with intermediate profiles observed in blends. These findings highlight the tunable nature of co-pyrolysis for optimizing liquid fuel yield and quality, providing a viable route for converting heterogeneous plastic wastes into transportation and industrial fuels.

Keywords: Non-Catalytic; Thermal Pyrolysis; Fuel; Polyethylene; High-Density Polyethylene

1. Introduction

The increasing global demand for energy coupled with the escalating problem of plastic waste disposal has spurred significant interest in developing sustainable methods for converting waste plastics into valuable resources, particularly liquid fuels. This approach addresses both the environmental burden of plastic accumulation and the imperative to secure alternative energy sources amidst diminishing fossil fuel reserves [1]. On the other hand, worldwide plastic production increased from approximately 1.5 million tonnes in 1950 to around 400 million tonnes in 2020, reflecting a growth of nearly 266% over this 70-year period [2]. Pyrolysis, a thermochemical process involving the degradation of long-chain hydrocarbons into shorter-chain molecules at elevated temperatures in the absence of oxygen, offers a promising pathway for converting plastics like polypropylene and high-density polyethylene into liquid fuels [3, 4]. This method not only mitigates the environmental impact of plastic waste but also contributes to the circular economy by transforming a persistent pollutant into a usable energy commodity [5, 6]. Specifically, polypropylene and high-density polyethylene, two ubiquitous plastics, can be effectively depolymerized through pyrolysis to yield liquid hydrocarbons that exhibit fuel properties comparable to conventional diesel and gasoline [7, 8]. The resulting liquid products often possess high calorific values, making them suitable as transportation fuels or chemical feedstocks [9]. This process is

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particularly advantageous given the widespread use of these plastics, making their conversion to fuel a viable solution for both waste management and energy production [10, 11]. Further, the versatility of pyrolysis allows for the optimization of reaction conditions, such as temperature and heating rate, to tailor product yields and compositions, thereby maximizing the recovery of desired fuel fractions [12].

Park and Lee [13] focused on molecular weight effect by revealed that the thermal degradation behavior of PP critically depends on its molecular weight distribution, which influences product distribution in non-catalytic pyrolysis. Lower molecular weight PP yielded higher fractions of fuel-range hydrocarbons due to enhanced chain scission at lower temperatures, underscoring the need to tailor feedstock characteristics for optimized fuel production. Aremanda and Singhexplored [14] the pyrolysis of HDPE alone, affirming that non-catalytic thermal pyrolysis at 450–600 °C produces hydrocarbons in the diesel range, suitable for direct blending with diesel fuel. Their work underscored the minimal need for pretreatment and the adaptability of pyrolysis reactors to handle heterogeneous plastic feedstocks. Tsang et al. [2] highlighted the effect of PP molecular weight on thermal pyrolysis, showing that lower molecular weight PP favors higher yields of fuel-range hydrocarbons. The study demonstrated that precise control of feedstock properties can tailor product distribution in pyrolysis processes. Ghodke et al. [15] investigated the pyrolysis of HDPE, LDPE, PP, plastic mixtures, and household waste over a temperature range of 473–973 K. At 773 K, the process yielded liquids with weights of 64.6%, 62.2%, 63.1%, 68%, and 64.6%, respectively, comprising hydrocarbons ranging from C_8 to C_{20}. Analysis of the liquids' physical and chemical properties using various ASTM standards indicated that they closely resemble commercially available gaseous fuels. Wang et al. [16] reported that non-catalytic pyrolysis of PP in a double-fluidized-bed reactor could produce valuable liquid hydrocarbons such as benzene, toluene, and xylene (BTX) without catalytic assistance. Their kinetic studies underscored the pivotal role of temperature control in steering product selectivity and maximizing liquid yields. Dhaniswara et al. [16] investigated the non-catalytic pyrolysis of polypropylene and polyethylene using a reactor integrated with a fractionation column. Their study demonstrated that operating temperatures between 350–650 °C significantly affect liquid fuel yield and composition, with maximum liquid yields achieved at higher temperatures due to enhanced polymer chain scission. The produced liquid fractions contained C_1–C_{13} aromatic hydrocarbons with calorific values comparable to commercial fuels, underscoring the potential of pyrolysis as a sustainable fuel source.

In this study, the influence of feedstock composition on the staged non-catalytic thermal pyrolysis of polypropylene (PP), high-density polyethylene (HDPE), and their binary blends was evaluated, focusing on liquid fuel yield, char minimization, and elucidation of the synergistic effects governing the distribution of fuel-range hydrocarbons.

2. Materials and methods

2.1. Materials

Waste plastics consisting of PP and HDPE were used either as pure polymers or binary mixtures at weight ratios of 100% PP, 100% HDPE, 50% PP-50% HDPE, 30% PP-70% HDPE and 70% PP-30% HDPE.

2.2. Experimental setup

Pyrolysis experiments were carried out in a 1.0 L laboratory-scale semi-batch reactor system. The reactor was externally heated using a Glas-Col heating mantle with a maximum operating temperature of 1000 °C. Temperature monitoring and control were achieved with a thermocouple (0–1300 °C), ensuring accurate thermal regulation throughout the process. The evolved vapors were directed through a water-cooled condenser, where condensable fractions were collected in a receiver flask as shown in Figures 1 and 2. A circulating water pump maintained continuous coolant flow to ensure effective condensation. All experiments were conducted within a fume hood to maintain safe operating conditions. A high-precision analytical balance (AMPUT) and a digital stopwatch were employed for mass and time measurements, respectively. A schematic representation of the overall experimental setup is provided in Figure 3

2.3. Thermal pyrolysis process

For each run, 50 g of plastic feedstock was loaded into the reactor and heated to 450 °C. The condensable vapors were collected as liquid oil, while char was retained in the reactor. The mass of gaseous products was determined by material balance. To investigate secondary cracking, wax products obtained from stage A were reintroduced into the reactor and heated to 500 °C (stage B), yielding additional liquid hydrocarbons.

2.4. Experimental design

Five pyrolysis experiments were conducted using different feed compositions: (i) 100% PP, (ii) 100% HDPE, (iii) 50% PP–50% HDPE, (iv) 30% PP–70% HDPE, and (v) 70% PP–30% HDPE. Each experiment was carried out in two stages: primary pyrolysis (stage A) and secondary cracking of the resulting waxes (stage B). These two stages were designed to quantify the yields of liquid oil, solid char, and non-condensable gases.

2.5. Product analysis

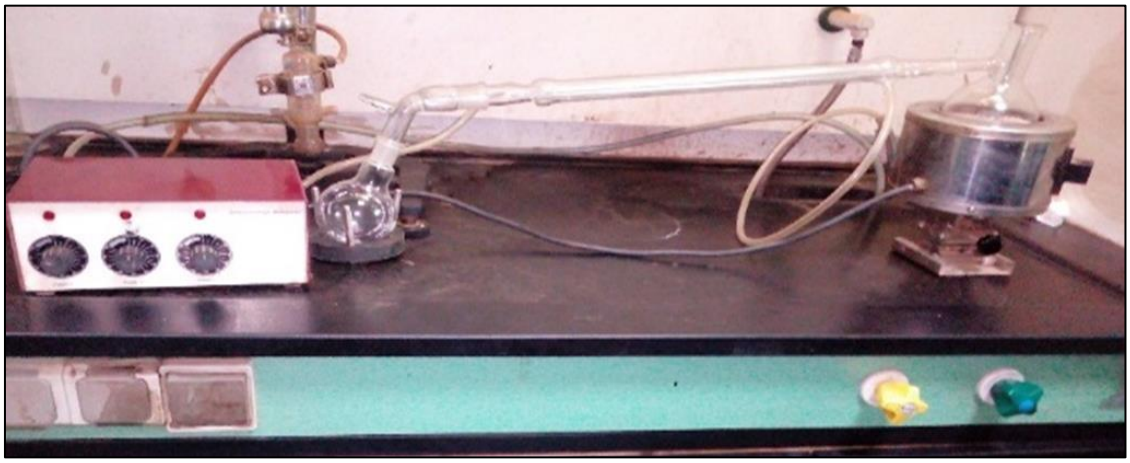


Figure 1 The non-catalytic thermal pyrolysis process.

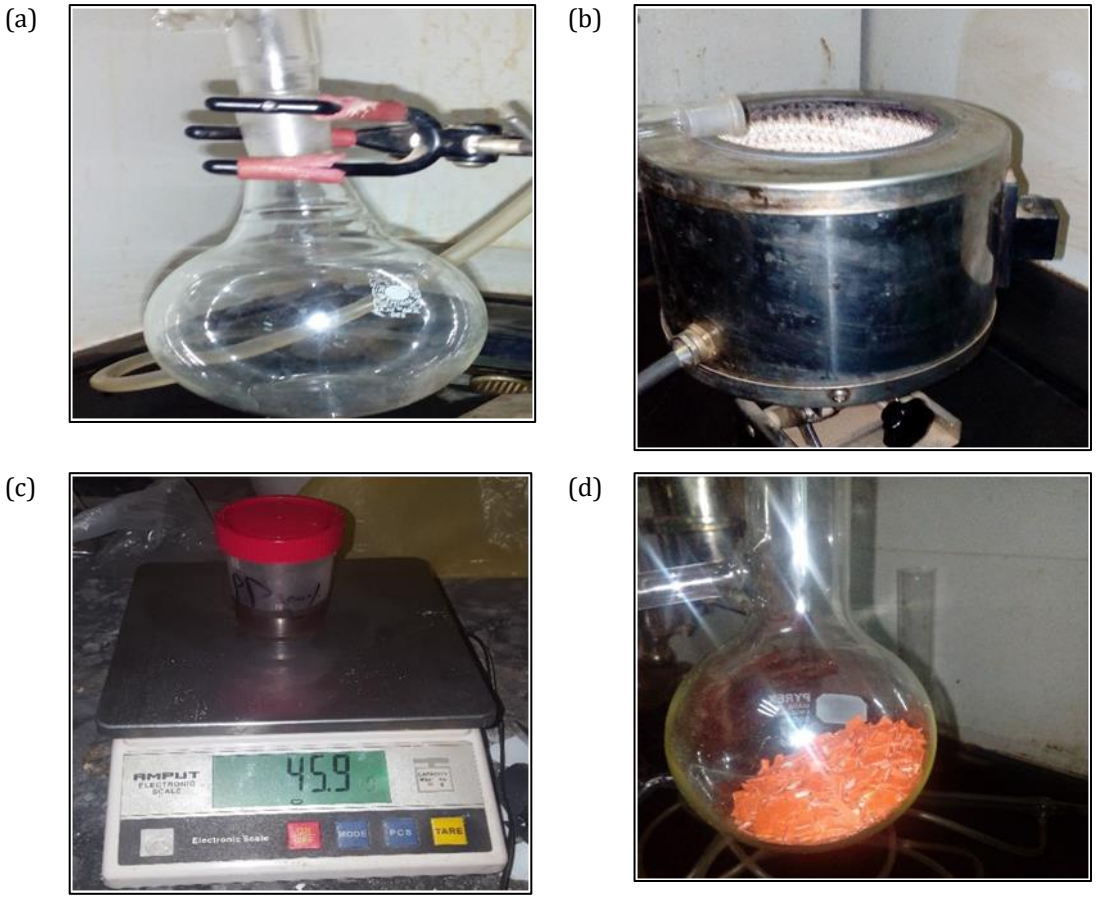


Figure 2 Experimental apparatus of the non-catalytic thermal pyrolysis process (a) receiving flask, (b) a heating mantle, (c) an analytical balance, (d) a flask containing PP and HPDE blend

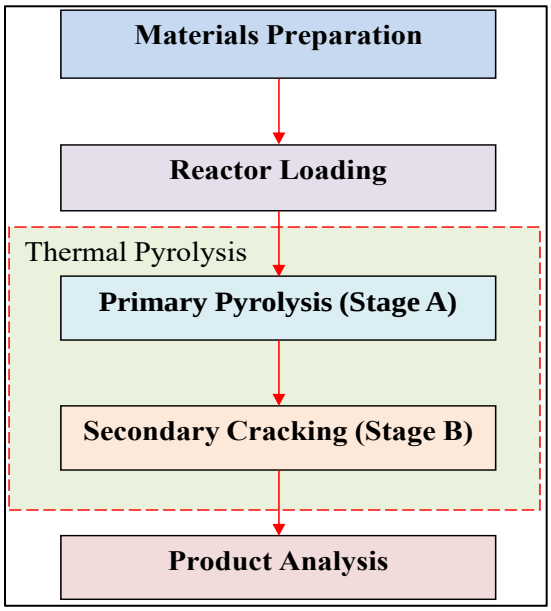


Figure 3 Schematic workflow of the thermal pyrolysis study

The chemical composition of the liquid pyrolysis products was determined using gas chromatography coupled with a flame ionization detector (GC–FID, Agilent Technologies). This analytical approach enabled the effective separation of hydrocarbon fractions and facilitated the quantitative assessment of fuel-range components, including gasoline-, kerosene-, diesel-, and heavy-oil-like fractions within the pyrolysis oil. Process simulation tools such as Aspen HYSYS have been successfully employed in modeling chemical reactions in continuous stirred tank reactors (CSTRs), providing valuable predictive insights for process optimization [17].

3. Results and discussion

The staged pyrolysis of PP, HDPE, and their blends revealed marked differences in degradation pathways and product selectivity. As shown in Table 1, pure PP produced comparatively low liquid hydrocarbons (32.3 g) with higher char (5.1 g) and non-condensable gases (12.6 g). This reflects PP's degradation mechanism, dominated by random chain scission of tertiary carbons, which favors gas formation. Increasing the proportion of PP in the feed not only raised the yields of char and gases but also reduced the reaction temperature, indicating enhanced cracking activity. In contrast, HDPE showed the most favorable performance, yielding the highest liquid fraction (39.05 g) with minimal char (0.77 g). This behavior arises from end-chain scission reactions, which promote the formation of long-chain hydrocarbons and waxes.

PP/HDPE blends demonstrated intermediate characteristics, with clear evidence of synergistic effects between PP- and HDPE-dominated pathways. The 70% HDPE–30% PP blend produced 36.8 g of wax with 2.86 g of char and subsequently generated 26.5 g of secondary liquid during Stage B pyrolysis as shown in Table 2. This formulation closely resembled the performance of pure HDPE, reinforcing the role of HDPE in maximizing liquid fuel recovery. Conversely, the 70% PP–30% HDPE mixture initially produced higher wax and char, yet secondary cracking improved the oil yield (25.1 g), demonstrating how HDPE moderates excessive gasification in PP-rich systems.

The second-stage pyrolysis experiments further confirmed that the primary waxes obtained in Stage A were efficiently converted into secondary liquids across all formulations. The 70% HDPE–30% PP blend was particularly notable, as it consistently maximized liquid output while minimizing solid residues. Taken together, these findings highlight that HDPE enhances liquid and wax recovery with increasing reaction temperature and duration, whereas PP promotes char and gas formation through intensified cracking. Optimizing the PP/HDPE ratio therefore provides a tunable route for selective product distribution, with the 70% HDPE–30% PP blend emerging as the most promising formulation for liquid fuel production.

(a)



(b)



(c)

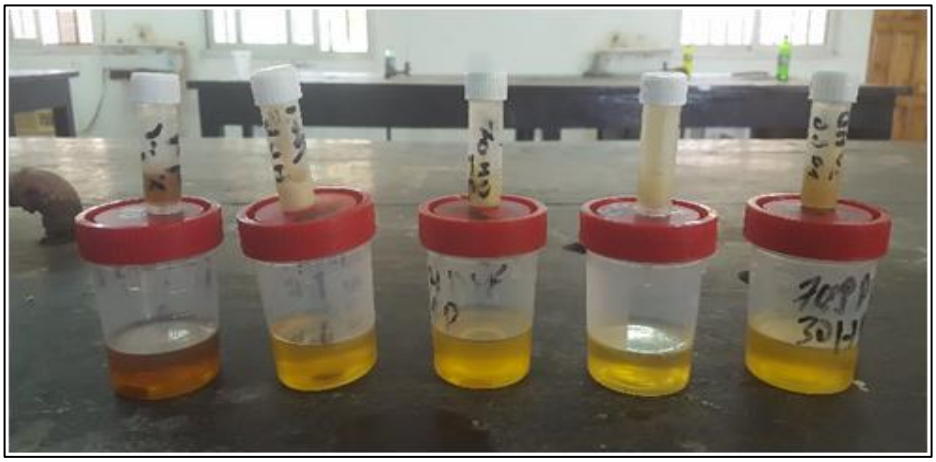


Figure 4 Non-catalytic thermal pyrolysis Products of PP, HDPE and their blends (a) wax formation after stage (A), (b) liquid formation after stage (B), (c) final products of PP and HPDE and their blends.

Table 1 Pyrolysis of PP, HDPE, and their mixtures (Stage A, 450 °C)

Run	Feed Composition (%)	Temperature (°C)	Reaction Time (min)	Final Composition (g)	Gases (g)	Char (g)
1	100% PP	364	23.56	32.30	12.60	5.10
2	100% HDPE	450	29.00	39.05	10.18	0.77
3	50% PP-50% HDPE	435	25.00	33.30	13.88	2.82
4	30% PP-70% HDPE	446	28.48	36.81	10.33	2.86
5	70% PP-30% HDPE	424	27.28	36.66	8.87	4.47

Table 2 Experimental results of thermal pyrolysis of PP, HDPE, and their blends (Stage B, 500 °C).

Run	Feed Composition (%)	Initial Amount (g)	Reaction Time (min)	Final Liquid (g)	Gases (g)
1	100% PP	27.70	16.37	23.20	4.50
2	100% HDPE	32.90	19.34	25.50	7.40
3	50% PP-50% HDPE	31.40	16.36	21.50	9.90
4	30% PP-70% HDPE	35.00	16.21	26.50	8.50
5	70% PP-30% HDPE	32.90	15.26	25.10	7.80

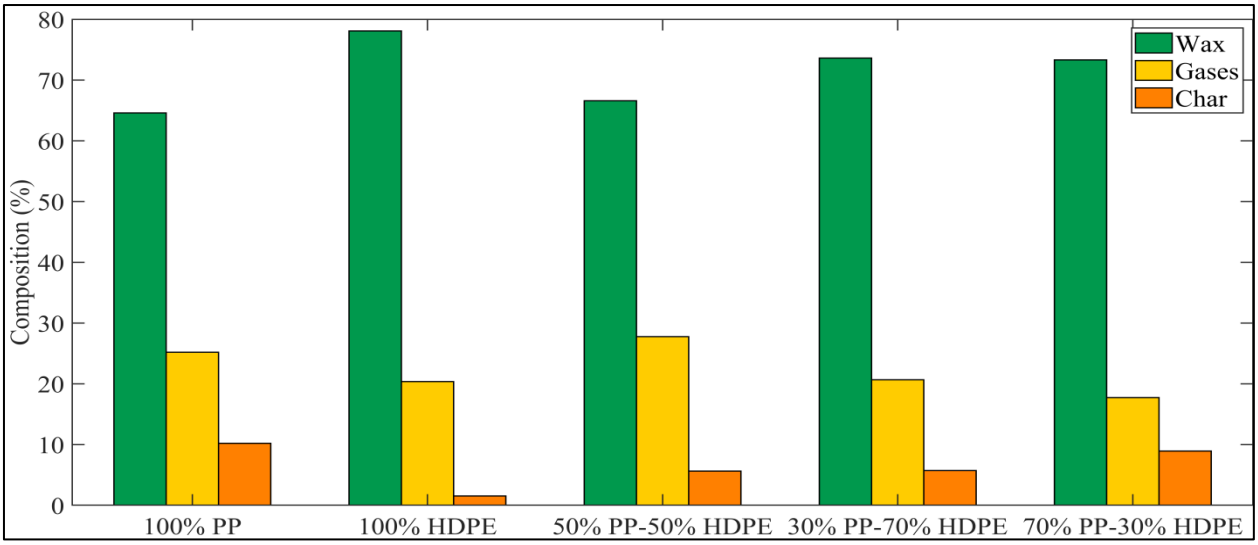


Figure 5 The GC–FID analysis of thermal pyrolysis for stage A.

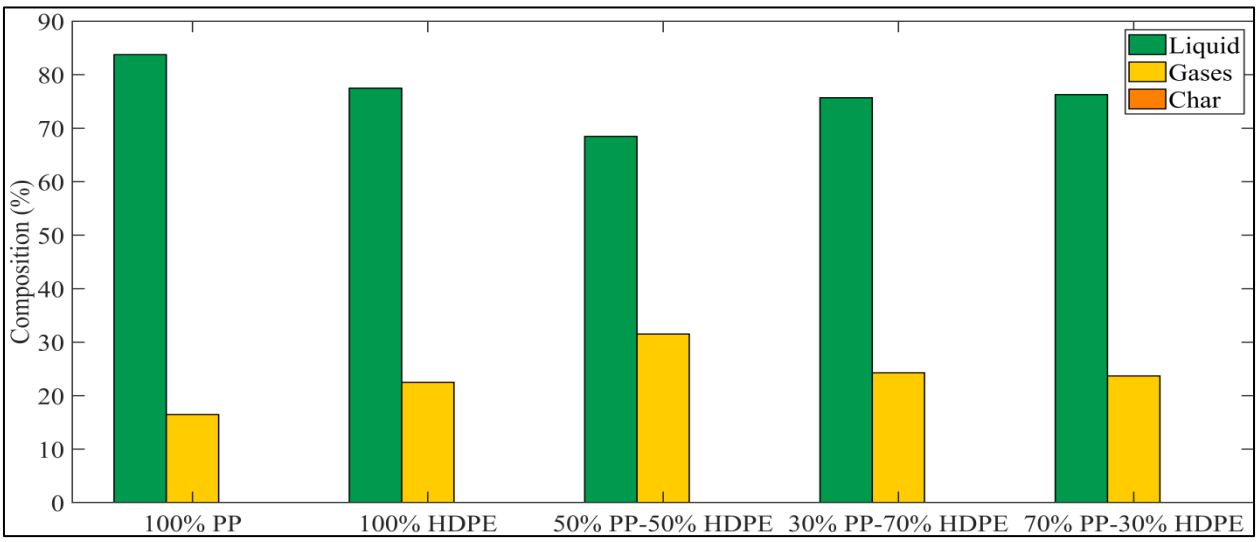


Figure 6 The GC–FID analysis of thermal pyrolysis for stage B.

The product distributions obtained from the thermal pyrolysis experiments are shown in Figure 5 (Stage A) and Figure 6 (Stage B). Distinct differences in yield profiles were observed between pure polymers and their binary blends, reflecting the intrinsic degradation mechanisms of PP and HDPE.

In Stage A (450 °C), wax was the dominant product across all feedstocks, with yields ranging from 64.6% to 78.1%. HDPE exhibited the highest wax recovery (78.1%) and the lowest char residue (1.54%), consistent with its linear structure that favors end-chain scission and the generation of long-chain hydrocarbons with limited secondary condensation. In contrast, PP produced lower wax (64.6%) and substantially higher char (10.2%), indicative of its random scission mechanism and the presence of tertiary carbons that accelerate chain branching, cyclization, and coke formation. Binary blends exhibited intermediate behaviors. The 50:50 PP/HDPE mixture yielded 66.6% wax and 5.64% char, while the 70% PP–30% HDPE blend produced elevated char (8.94%), resembling the PP-dominant pathway. Conversely, the 30% PP–70% HDPE blend produced a wax yield of 73.62% with reduced char (5.72%), underscoring the stabilizing influence of HDPE on suppressing coke formation. These observations highlight the synergistic effects of co-pyrolysis, whereby HDPE moderates the extensive gasification and char production associated with PP degradation.

In Stage B (500 °C), secondary pyrolysis of the wax fraction substantially enhanced liquid oil recovery, with all samples showing negligible char formation. For pure PP, the liquid yield increased markedly to 83.75%, with complete elimination of char, indicating that secondary cracking of the wax fraction favored volatilization over solid residue

formation. HDPE produced 77.5% liquid and 22.5% gases, confirming its sensitivity to thermal cracking into light hydrocarbons at elevated temperatures. Binary mixtures revealed more complex interactions. The 50:50 PP/HDPE blend yielded the lowest liquid fraction (68.47%) and the highest gas fraction (31.53%), suggesting competitive degradation pathways where PP promotes gas evolution while HDPE contributes to liquid stability. In contrast, asymmetric mixtures (30% PP–70% HDPE and 70% PP–30% HDPE) delivered balanced product distributions, with liquid yields of 75–76% and moderate gas generation (~24%). This indicates that mixed compositions benefit from partial synergism, with HDPE suppressing char formation and PP enhancing secondary cracking to lighter oils.

Overall, the staged thermal pyrolysis approach demonstrates that HDPE is inherently favorable for liquid fuel recovery due to its high wax and liquid yields with minimal char**,** while PP is more gas-prone and char-forming**,** requiring secondary cracking to maximize oil recovery. Binary blends offer tunable product distributions: HDPE-rich mixtures enhance liquid selectivity, while PP-rich mixtures benefit from secondary processing to convert wax into oils. These findings emphasize the significance of feedstock composition in optimizing pyrolysis outcomes for fuel applications, particularly when targeting high liquid recovery with reduced solid waste.

The compositional analysis of liquid fractions derived from the thermal pyrolysis of PP, HDPE, and their binary mixtures, as determined by GC–FID, provides critical insight into the distribution of fuel-range hydrocarbons as shown in Figure 7. The data reveal that the product spectrum is strongly dependent on the polymer feedstock composition, reflecting the intrinsic structural differences between PP and HDPE and their distinct degradation pathways.

For Pure PP exhibited the highest gasoline yield (32.0%), reflecting its lower thermal stability and higher tendency to undergo random chain scission, producing lighter hydrocarbons. In contrast, HDPE favored the formation of heavier fractions; with gasoline yield markedly lower (15.5%) and diesel and heavy oil fractions significantly higher ;33.5% and 26.0%, respectively.

This outcome is consistent with the more linear structure of HDPE, which promotes β-scission and the generation of longer hydrocarbon chains during pyrolysis. The co-pyrolysis of PP and HDPE produced intermediate product distributions, suggesting a synergistic effect between the two polymers. For instance, the 50% PP–50% HDPE blend resulted in a balanced fuel profile with 22.1% gasoline, 23.9% kerosene, 30.2% diesel, and 23.7% heavy oil. Notably, blends enriched with PP (70% PP–30% HDPE) shifted the product spectrum towards lighter fractions, yielding higher gasoline content (23.5%) compared to HDPE-dominant mixtures (30% PP–70% HDPE), which favored diesel and heavy oil production.

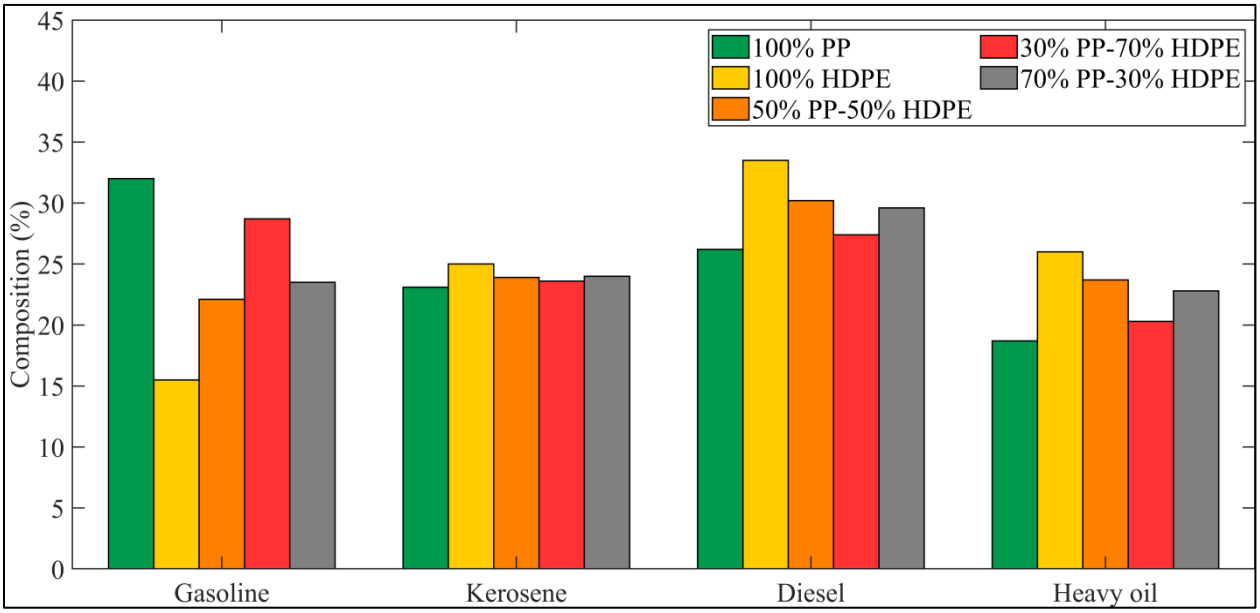


Figure 7 Fuel-range hydrocarbon distribution of liquid products from thermal pyrolysis of PP, HDPE and their blends by GC–FID analysis

These findings demonstrate that feedstock composition exerts a direct influence on the quality and distribution of liquid fuel products from thermal pyrolysis. Specifically, PP-rich systems enhance the generation of gasoline-range hydrocarbons, which are of high economic value due to their widespread use in spark-ignition engines. Conversely, HDPE contributes to heavier fractions, such as diesel and heavy oil, aligning with compression-ignition engine applications and industrial heating fuel demands. The tunability of fuel composition through blending thus represents a practical strategy for optimizing pyrolysis-derived fuels according to targeted applications.

4. Conclusion

The staged thermal pyrolysis of polypropylene, high-density polyethylene, and their binary blends demonstrates the critical influence of feedstock composition on product yield, distribution, and fuel quality. Pure HDPE exhibited superior liquid fuel recovery with minimal char formation due to its linear structure promoting end-chain scission, whereas pure PP favored gas and char production as a result of random chain scission of tertiary carbons. Binary blends revealed pronounced synergistic effects: HDPE-rich mixtures enhanced liquid fraction and suppressed char formation, while PP-rich mixtures benefitted from secondary cracking to convert waxes into additional liquid hydrocarbons. GC–FID analysis confirmed that PP promotes lighter, gasoline-range hydrocarbons, whereas HDPE favors diesel and heavy oil fractions, highlighting the tenability of fuel composition through feedstock blending. Overall, the 30% PP–70% HDPE blend emerged as the optimal formulation for maximizing liquid fuel yield and minimizing solid residues. These findings underscore the potential of feedstock-specific pyrolysis strategies for sustainable conversion of waste plastics into high-value liquid fuels, providing a scalable route to mitigate plastic pollution while contributing to alternative energy production.

Compliance with ethical standards

Disclosure of conflict of interest

The Authors declare NO Competing nor Conflicting Interest.

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