IJE TRANSACTIONS A: Basics Vol. 39, No. 10, (October 2026) 2395-2406

International Journal of Engineering

Journal Homepage: www.ije.ir

Valorization of Polypropylene Plastic Waste via Slow Pyrolysis: Pathways to Pyro-Oil Production

R. I. Mainil*[a], J. J. Panjaitan[a], A. W. Sari[b], A. Susilawati[b], A. K. Mainil[c], O. Farobie[d], A. Amrullah[e], A. Aziz[a]

[a] Thermal Engineering Laboratory, Department of Mechanical Engineering, Universitas Riau, Kampus Bina Widya, Jl. HR. Soebrantas Km 12.5, Pekanbaru 28293, Riau, Indonesia
[b]Department of Mechanical Engineering, Universitas Riau, Kampus Bina Widya, Jl. HR. Soebrantas Km 12.5, Pekanbaru 28293, Riau, Indonesia
[c] Department of Mechanical Engineering, Universitas Bengkulu, Bengkulu, 38371A, Indonesia
[d] Department of Mechanical and Biosystem Engineering, IPB University, IPB Darmaga Campus, Bogor, West Java 16002, Indonesia
[e] Department of Mechanical Engineering, Lambung Mangkurat University, Banjarmasin, South Kalimantan, Indonesia

PAPER INFO

Paper history:
Received 24 August 2025
Received in revised form 21 September 2025
Accepted 24 October 2025

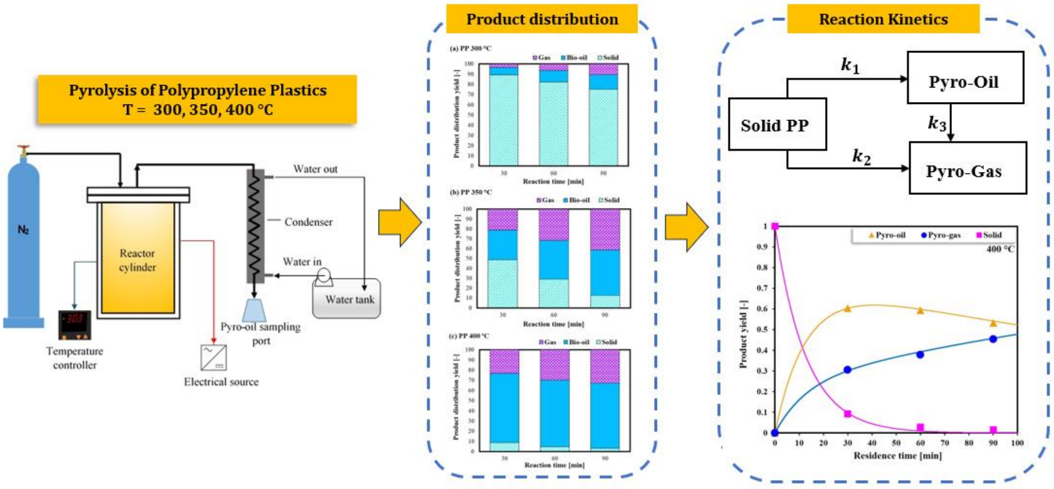
Keywords:
Energy
Pyro-Oil
Pyrolisis
Polypropylen
Kinetics

ABSTRACT

This research examines the pyrolysis of polypropylene (PP) plastic waste as a feasible method for pyro-oil generation. The primary objective is to convert non-biodegradable polymer waste into value-added liquid fuel while addressing environmental concerns associated with plastic pollution. The pyrolysis of PP was conducted in a batch reactor at regulated temperatures of 300, 350, and 400 °C with reaction times of 30, 60, and 90 minutes to examine the thermal degradation behavior, product distribution, and quality of the obtained pyro-oil. The highest pyro-oil yield of 68% was achieved at 400 °C, indicating optimal thermal cracking of polypropylene chains. Under these conditions, the pyro-oil exhibited a hydrocarbon content of 49.3%, emphasizing its viability as an alternative energy source. The calorific value of the pyro-oil ranged from 48 MJ kg^{-1} to nearly 49 MJ kg^{-1}. The possible reaction pathways were determined in this study, as indicated by the pre-exponential factor and activation energy derived from the Arrhenius equation. These findings demonstrate the feasibility of valorizing polypropylene waste through slow pyrolysis, offering a promising pathway for resource recovery, circular economy implementation, and reduction of the environmental impact of plastic waste.

doi: *10.5829/ije.2026.39.10a.04*

Graphical Abstract



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*Corresponding Author Email: rahmat.iman@lecturer.unri.ac.id (R. I. Mainil)

Please cite this article as: Mainil RI, Panjaitan JJ., Sari AW, Susilawati A, Mainil AK, Farobie O, Amrullah A, Aziz A. Vaorization of Polypropylene Plastic Waste via Sow Pyrolysis: Pathways to Pyro-Oil Production. International Journal of Engineering, Transactions A: Basics. 2026;39(10): 2395-406.

1. INTRODUCTION

Indonesia is currently faced with a critical challenge stemming from plastic waste generation. Daily, the country produces over 3.22 million metric tons of plastic waste, making it the second-largest contributor to global plastic waste, surpassed only by China (1). A substantial portion of this plastic waste, estimated between 0.48 and 1.29 million metric tons annually, is discharged into the marine environment, causing serious ecological degradation and disruption of marine ecosystems. The generation of plastic waste continues to escalate in line with global population growth. This trend is further driven by the increasing demand for plastics, which is due to their high versatility, low density, exceptional durability, resistance to corrosion, and overall cost-effectiveness (2-4).

The Indonesian authorities have set an ambitious goal to reduce plastic waste generation by 70% by 2025 (5), reflecting the urgent need for sustainable and effective waste management practices. Conventional landfilling presents numerous environmental and health concerns, including the extremely slow biodegradation of plastics, risks to terrestrial and aquatic organisms, and various forms of pollution (6). While recycling remains an important waste management strategy, it faces significant challenges such as high operational costs and the demand for a large labor force (7). Converting plastic waste into energy offers a promising alternative; however, direct incineration for thermal energy production has critical limitations, including greenhouse gas emissions that exacerbate climate change and the release of toxic pollutants (8).

Pyrolysis offers a viable alternative for the conversion of plastic waste. This thermochemical process operates under oxygen-deficient conditions, utilizing heat to decompose feedstocks into pyrolytic oil, solid residues, and gaseous products, generally observed in the temperature interval of 250–600 °C (9-12). Recent research has extensively investigated the production of pyro-oil from diverse plastic waste feedstocks via pyrolysis (13-15).

Polypropylene (PP) plays a significant role in the global plastic waste challenge, as it is the most extensively produced thermoplastic, accounting for approximately 17% of annual global plastic output, 18% of plastic packaging, and 24% of plastics found in municipal solid waste (16-18). Its chemical structure, characterized by a high volatile content, offers significant potential for conversion into fuel through pyrolysis (4).

Pasae et al. (19) investigated the pyrolysis of polypropylene (PP) plastic waste at temperatures ranging from 250 °C to 350 °C, with a constant holding time of 120 minutes. The highest oil yield of 62.56% was obtained at 350 °C. In a related study, Muchammad (20) pyrolyzed PP waste at three temperatures—250 °C, 300 °C, and 350 °C—yielding oil volumes of 420 mL, 480 mL, and 500 mL, respectively. Corresponding densities were 0.75 g/mL, 0.76 g/mL, and 0.77 g/mL, while calorific values were 39,221 kJ/kg, 38,870 kJ/kg, and 38,301 kJ/kg. The resulting pyrolysis oil exhibited an octane rating of 83.5 and a viscosity of 0.034 Poise.

Adoe et al. (21) employed a simple reactor for PP pyrolysis at a constant temperature of 250 °C, varying the reaction time between 1, 2, and 3 hours. The resulting pyrolysis oil demonstrated calorific values ranging from 10,296 to 11,670 cal/g, exceeding that of gasoline (8,356 cal/g). Its density (0.760–0.780 kg/L) was also higher than gasoline (0.680 kg/L), while the viscosity (0.65–0.78 cP) was comparable to that of gasoline (0.652 cP). Further studies have compared the pyrolysis conversion performance of PP with that of low-density polyethylene (LDPE) (22, 23), highlighting differences in product yield and composition between the two plastic types. To improve the efficiency of PP pyrolysis, several investigations have also examined the role of catalysts in enhancing conversion rates, optimizing product distribution, and reducing undesirable by-products (24, 25).

The ability to alter the solid structure of PP through thermal treatment is of significant importance. Based on analogous observations in plastics pyrolysis, the process can be generally described as follows: upon heating, the solid PP structure begins to break down, releasing oil and increasing the hydrocarbon content in the resulting pyrolysis oil. Chemically, pyrolysis oil consists of a complex mixture of various hydrocarbon compounds. Although several studies have explored how pyrolysis temperature affects the characteristics of products obtained from PP, research on the decomposition kinetics of PP into different products under varying temperatures and residence times remains limited. Therefore, this study aims to investigate the effects of temperature and reaction time on the decomposition behavior of PP plastic, with a particular focus on optimizing pyrolysis oil production.

2. MATERIALS AND METHODS

2. 1. Preparation of Feedstock

The PP plastics were obtain from waste collection of Mechanical Engineering Department of Riau University. The PP waste was crushed and screened to a particle size of 1 mm.

2. 2. Experimental Details

The experiment was conducted in a stainless-steel batch vessel equipped with an electric heater, condenser, thermocouple, and a temperature controller (Figure 1).

The reactor has an inner diameter (ID) of 0.15 m, OD of 0.16 m, and height of 0.36 m. An electric band heater

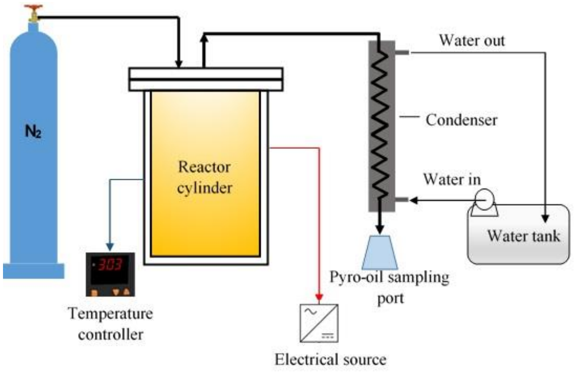


Figure 1. Schematic of experimental apparatus (pyrolisis reactor)

covers the outside of the vessel to heat and maintain a uniform temperature inside the reactor chamber during the experiments. The vessel was loaded with 500 g of PP plastics. Prior to experimental procedure, nitrogen was introduced into the reactor at 400 mL·min⁻¹ for 15 minutes to displace residual oxygen. The quality of the resulting pyro-oil is affected by the presence of oxygen in the reactor. Reduced oxygen levels improve pyrolysis efficiency, thereby increasing the production of condensable volatiles (26). The pyrolisis was conducted at temperatures of 300, 350, and 400 °C and was timed at different intervals of 30, 60, and 90 min. As pyrolysis progressed, the vapors were condensed and routed to a liquid sampling port for collection. The reactor was cooled after the reaction, and the formed char was subsequently collected and measured using a digital scale. All experiments were conducted in duplicate to ensure the accuracy. The yield of each product ($Y_{pyro-oil}$ and Y_{char}) was calculated as a ratio of product mass ($m_{pyro-oil}$ and m_{char}) to the original mass of feedstock ($m_{feedstock}$). The yield of non-condensable gases was quantified indirectly, calculated by difference between the initial feedstock and the combined yield of the collected liquid and solid, as expressed in Equations 1-3:

$$Y_{pyro-oil} = \frac{m_{pyro-oil}}{m_{feedstock}} \text{x } 100\ \% \qquad (1)$$

$$Y_{char} = \frac{m_{char}}{m_{feedstock}} \text{x } 100\ \% \qquad (2)$$

$$Y_{gas} = 100\ \% - \left(Y_{pyro-oil} + Y_{char}\right) \qquad (3)$$

2. 3. Product Characterization

Calorific value analysis of the pyro-oil was conducted using a Bomb Calorimeter (Shandong Co. Ltd, BCY-1A). The density of each liquid product was determined using a pycnometer based on a comparative mass-to-volume approach. Initially, the volume of the pycnometer was established by filling it with distilled water and recording the mass at a controlled temperature of 25 °C, at which the density of water is well defined. Using this reference, the actual volume of the pycnometer was calculated. Subsequently, the pycnometer was filled with the liquid sample, and the mass was measured. Sample density was calculated from the measured mass and the calibrated volume of the pycnometer. The density (ρ) was computed using the following equation (Equation 4):

$$\rho = \frac{\text{mass of pyro oil in picnometer}}{\text{volume of pyro oil in picnometer}} \qquad (4)$$

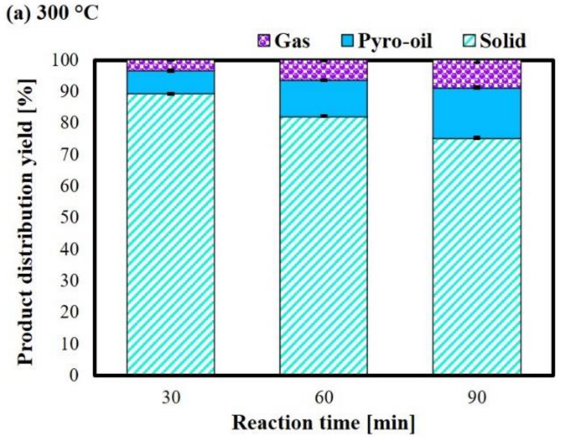
A GC-MS system equipped with an RTx-5MS capillary column was employed to analyze the composition of the pyro-oil. The gas chromatograph was initially held at 150 °C for 5 min, followed by a temperature increase of 10 °C per min until reaching 300 °C. The final temperature was then maintained at 300 °C for 26 min in the oven. To determine the pyro-oil components, the acquired mass spectra were compared against the NIST 2008 c2.0/X-Calibur data library, and compound identification was confirmed using standard reference solutions.

3. RESULTS AND DISCUSSION

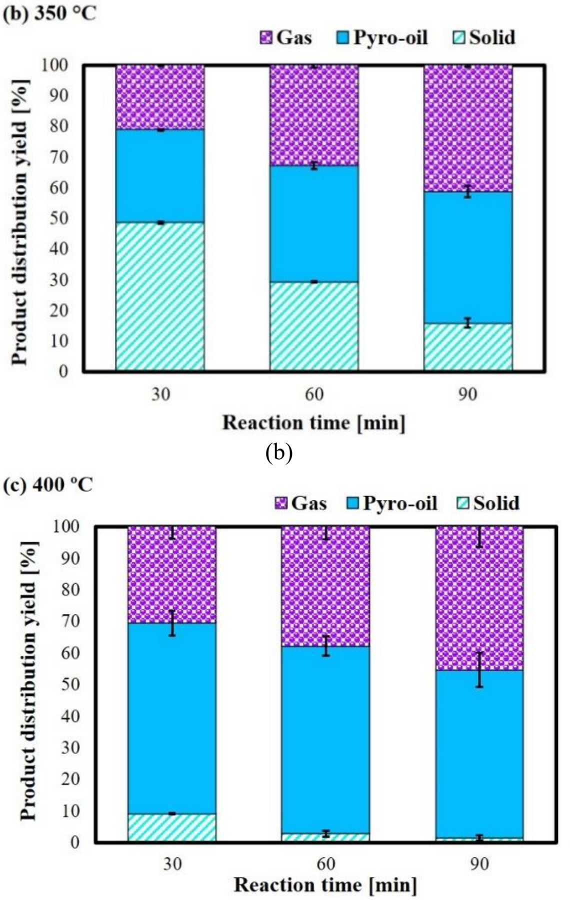
3. 1. Effect of Reaction Temperature and Time on Product Composition

To assess the effect of temperature variation and reaction time on pyrolysis product fractions of polypropylene (PP), a set of temperatures of 300, 350, and 400 °C and residence times of 30, 60, and 90 min were employed.

A clear pattern was observed, indicating a substantial rise in oil yield with increasing temperature between 300 and 400 °C (Figure 2). At elevated temperatures, the thermal degradation of PP is predominantly governed by random chain scission mechanisms, whereby the C–C bonds cleavage along the polymer chain is significantly accelerated. This enhanced rate of chain scission



(a)



(b)

(c)

Figure 2. Effect of temperature and reaction time on pyrolisis product of polypropylene plastic at (a) 300 °C, (b) 350 °C, and (c) 400 °C

facilitates the breakdown of long polymer chains into lower molecular weight hydrocarbon fragments. These smaller, more volatile compounds readily undergo vaporization under pyrolysis conditions and subsequently condense into liquid oil fractions upon cooling (27). Consequently, higher pyrolysis temperatures not only promote greater conversion efficiency but also favor the production of oil over solid residues. Conversely, char formation declined markedly with increasing temperature. At low temperatures, incomplete depolymerization leads to heavy residues and char due to insufficient energy for complete fragmentation. These findings are consistent with previous observations of products obtained from pyrolysis of PP (28-30).

Pyro-oil generation at 300 °C resulted in comparatively low yields, with values of 7.2%, 11.4%, and 16.09% obtained at reaction times of 30, 60, and 90 min, respectively, suggesting that pyrolysis of polypropylene was incomplete under these conditions. At a higher temperature of 350 °C, pyro-oil production increased significantly (30.20 %, 38.06 %, and 43.00 % at reaction times of 30, 60, and 90 min, respectively). This result indicates that higher temperatures favor full decomposition to volatiles rather than partial carbonization residues. Longer reaction times provide sufficient duration for heat transfer and thermal cracking reactions to proceed toward completion. Polypropylene chains require both adequate temperature and time to break down into smaller, volatile hydrocarbon fragments. However, a substantial increase in gas formation was also observed at this temperature, with gas yields reaching 41.10 % at a reaction time of 90 min. This behavior is attributed to the increased intensity of thermal cracking reactions under these conditions. Elevated temperatures provide sufficient energy not only to depolymerize polypropylene into liquid-range hydrocarbons but also to further break down these intermediates into lighter gaseous compounds. Moreover, extended residence times facilitate secondary cracking reactions, wherein the initially formed liquid products undergo additional thermal decomposition, thereby increasing gas yields. The greater generation and stability of free radicals at higher temperatures also promote extensive chain scission and fragmentation, favoring the formation of volatile gases (31). Consequently, the thermodynamic equilibrium of the pyrolysis process shifts toward the production of permanent gases as heavy and intermediate fractions continue to degrade with prolonged exposure.

Interestingly, at the highest temperature, char formation was suppressed by 9.21 %, 2.87 %, and 1.52 % at residence times of 30, 60, and 90 min. This was accompanied by a significant increase in bio-oil of 60.29 %, 59.33 %, and 53.18 % at reaction times of 30, 60, and 90 min. This phenomenon can be explained by temperature-dependent reaction pathways during polypropylene pyrolysis. At very high temperatures, thermal degradation is sufficiently intense to promote almost complete depolymerization of the polymer chains into volatile products, thereby minimizing the formation of thermally stable char residues. The elevated temperature favors rapid chain scission and volatilization without allowing sufficient time for cross-linking and aromatization reactions that typically stabilize carbonaceous char structures (32).

Although char formation decreased and pyro-oil yield increased markedly at 400 °C, the non-condensable gas fraction exhibited only slight variation compared to 350 °C. This outcome can be explained by the balance between vapor-phase reactions and reactor conditions. At elevated temperatures, primary chain scission generates a greater quantity of volatile hydrocarbons; however, under the residence times employed, these intermediates predominantly condense as liquid products rather than undergoing further secondary cracking into permanent gases. The slight increase in gas yield therefore indicates a kinetic limitation, wherein the rate of secondary cracking requiring higher activation energies and extended vapor-phase contact is insufficient to compete with rapid volatilization and condensation processes.

The results observed were compared to those of other studies as shown in Table 1.

3. 2. Effect of Reaction Temperature and Time on Pyro-oil Density

Pyro-oil produced from slow pyrolysis of polypropylene plastic was examined for physicochemical characteristics. Figure 3 illustrates the density of pyrolysis oil obtained from PP at temperatures of 300°C, 350°C, and 400°C with reaction times of 30, 60, and 90 min, compared to biodiesel as a reference. The results show that at 300°C, the oil density remains consistently at approximately 730 kg m^{-3} across all reaction times. Increasing the temperature to 350°C yields a slightly higher and stable density of around 740 kg m^{-3}, while at 400°C, the density further increases to approximately 760 kg m^{-3}.

Variation in reaction time within the studied range (30–90 min) does not significantly influence oil density at each temperature, suggesting that temperature is the key factor controlling pyrolysis oil density. When compared to biodiesel, which has a density of about 850 kg m^{-3}, the pyrolysis oils exhibit lower densities, indicating a prevalence of lighter hydrocarbon fractions in the oil products. The observed increase in density with temperature implies that higher pyrolysis temperatures favor secondary cracking reactions, leading to the formation of heavier hydrocarbon chains or aromatic compounds in the oil. This finding indicates that while pyrolysis oil derived from PP has potential as an alternative fuel source, its lower density relative to biodiesel may necessitate further upgrading or blending to meet standard fuel specifications, though its intermediate density profile suggests suitability as a feedstock for further refining into lighter fuel fractions or chemical intermediates.

3. 3. Effect of Reaction Temperature and Time on Calorific Value

The calorific value characteristics of pyro-oil from PP pyrolysis are shown in Figure 4. Overall, the data indicate a clear trend where increasing temperature results in higher calorific values. At 300°C, the calorific value ranges from approximately 44 MJ kg^{-1} at 30 min to about MJ kg^{-1} at 90 min, indicating a moderate increase with extended reaction time. At350°C, the calorific value is consistently higher, remaining around 47 MJ kg^{-1} across all reaction times with minimal variation, suggesting that reaction time has little influence at this temperature.

At 400°C, the highest calorific values are observed, ranging from approximately 48 MJ kg^{-1} at 30 min to nearly 49 MJ kg^{-1} at 90 min, demonstrating both the beneficial impact of elevated temperature and a slight increase with longer reaction time. This trend suggests

TABLE 1. Oil yields obtained from PP pyrolysis

Plastic type	Reactor	Catalyst	Temperature (°C)	Yield of pyrolysis product (wt%)			Reference
				Oil	Solid	Gas	
PP	Batch	-	400	60.29	9.21	30.5	This Study
PP	Batch	-	500	70	5.7	24.3	Eldahshory et al. (33)
PP	Batch	Kaolin	500	80.75	1.7	17.55	Eldahshory et al. (33)
PP	Micropyrolyzer	-	600	68	1.64	30.36	Supriyanto et al. (34)

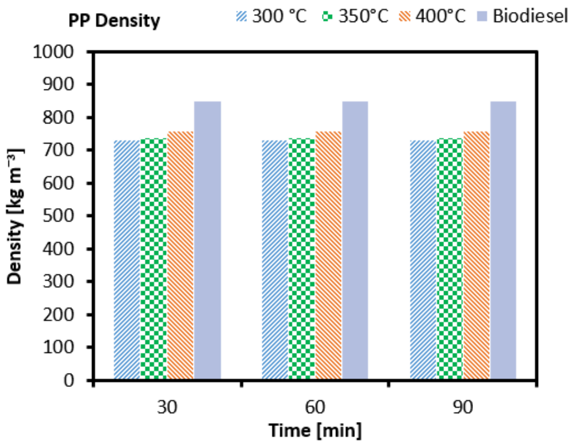


Figure 3. Density of pyro-oil compared to biodoesel

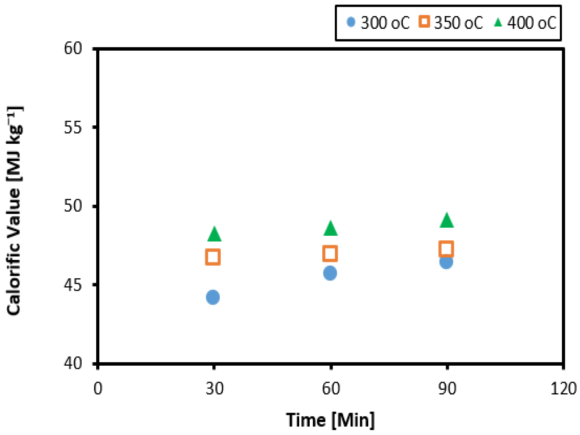


Figure 4. Calorific value of pyrolisis oil from PP

that higher temperatures favor the formation of oil with greater energy content, likely due to enhanced cracking and deoxygenation reactions producing hydrocarbons with higher heating values. Furthermore, the minimal influence of reaction time at 350°C demonstrates that temperature has a greater influence in determining calorific value than prolonged heating within the studied duration. These findings imply that conducting pyrolysis at 400°C is optimal for maximizing the energy density of PP-derived pyrolysis oil, enhancing its potential application as a fuel alternative. These findings are consistent with those reported in earlier studies (35, 36).

When compared to conventional diesel fuel, which typically has a calorific value in the range of 42–46 MJ kg^{-1} (37), the pyrolysis oil derived from PP in this study demonstrates comparable or even higher energy content. Notably, at 400°C, the calorific value of pyrolysis oil further increases, ranging from approximately 48 MJ kg^{-1} to nearly 49 MJ kg^{-1}, which is higher than the standard calorific value of diesel fuel. This indicates that PP-derived pyrolysis oil, especially at 400°C, possesses an energy density that exceeds that of conventional diesel, highlighting its potential as a high-energy alternative fuel. The elevated calorific values at higher temperatures suggest that increased thermal cracking enhances hydrocarbon quality by producing lighter and more energy-dense fractions. However, it is essential to consider that despite these promising calorific values, the direct utilization of pyrolysis oil as a diesel substitute may still require further upgrading to address issues such as viscosity, stability, and contaminant removal to meet fuel standards.

3. 4. Pyro-Oil Composition

The pyro-oil elucidated from pyrolysis of PP plastics was quantified through GC/MS analysis. The significant differences in pyro-oil composition derived from pyrolysis of polypropylene were observed across different temperatures, as presented in Table 2.

Hydrocarbon and alcohol were the two most prevalent compounds found in pyro-oil of polypropylene. The formation of hydrocarbons is predominantly driven by random chain scission and radical reactions in which the C–C bonds in the polypropylene backbone undergo homolytic cleavage, generating alkyl radicals. These radicals undergo β-scission, resulting in the generation of lower-molecular-weight hydrocarbons, primarily alkanes and alkenes (38). For example, the scission of a polypropylene chain can yield molecules such as propene, hexene, or nonane. The primary and secondary radicals generated may undergo recombination to form branched or cyclic hydrocarbons. Alternatively, disproportionation reactions can produce an alkane and an alkene pair (39). Alcohols are generated via side reactions involving oxygen-containing species or radical recombination with trace hydroxyl sources.

Figure 5 reveals that hydrocarbons constituted the major fraction across all temperatures. This trend suggests that at lower temperatures, PP primarily undergoes random β-scission, generating aliphatic and cyclic hydrocarbons as dominant products. However, with increasing temperature, these hydrocarbons are likely subjected to secondary cracking or oxidation reactions, reducing their relative abundance.

TABLE 2. Major chemical constituents of pyro-oil from PP pyrolysis

No	Compounds	R.Time	Temperature (°C)			Chemical Formula	Group
			300	350	400		
			% Area				
1	1,5-Hexadiene, 2,5-dimethyl (CAS)	3.096	1.01	na	na	C_8H_{14}	Hydrocarbon
2	Cyclopentane, 1,1,3,4-tetramethyl-, cis-(CAS)	3.67	1.49	1.22	na	C_9H_{18}	Hydrocarbon
3	DIMETHYL-2,3 HEPTENE-3	4.066	4.5	4.9	1.51	C_9H_{18}	Hydrocarbon
4	1-Undecene (CAS)	4.418	15.94	13.71	6.79	$C_{11}H_{22}$	Hydrocarbon
5	Cyclohexane, 1,2,3-trimethyl-(CAS)	4.727	2.88	2.66	2.46	C_9H_{18}	Hydrocarbon
6	3-Octene, 2,2-dimethyl-(CAS)	5.686	2.79	2.31	1.81	$C_{10}H_{20}$	Hydrocarbon
7	trans-3,8-undecadiene	6.444	1.21	1.18	na	$C_{11}H_{20}$	Hydrocarbon
8	NONANE, 2,6-DIMETHYL	11.078	1.57	1.27	na	$C_{11}H_{24}$	Hydrocarbon
9	DECANE, 4-METHYL-	11.296	1.72	1.38	na	$C_{11}H_{24}$	Hydrocarbon
10	2-DECENE, 2,4-DIMETHYL-	13.552	na	1.2	1.3	$C_{12}H_{24}$	Hydrocarbon
11	3-OCTADECENE	14.593	7.25	6.34	5.15	$C_{18}H_{36}$	Hydrocarbon
13	1-Tridecanol	16.665	1.31	na	na	$C_{13}H_{28}O$	Alcohol
14	(2,4,6-Trimethylcyclohexyl) methanol	17.748	1.9	1.42	2.05	$C_{10}H_{20}O$	Alcohol

15	3-DECENE, 2,2-DIMETHYL-, (E)-	22.677	1.86	2.06	1.73	$C_{12}H_{24}$	Hydrocarbon
16	Cyclohexane, eicosyl- (CAS)	23.592	1.94	1.95	1.62	$C_{26}H_{54}$	Hydrocarbon
17	1-Nonadecene (CAS)	23.91	11.08	10.71	9.39	$C_{19}H_{38}$	Hydrocarbon
18	Tridecanol (CAS)	24.181	5.98	5.79	4.77	$C_{13}H_{28}O$	Alcohol
19	1-Nonadecene (CAS)	24.524	8.89	8.66	7.4	$C_{19}H_{38}$	Hydrocarbon
20	1-Hexadecanol, 3,7,11,15-tetramethyl- (CAS)	25.358	1.16	1.25	1.23	$C_{20}H_{42}O$	Alcohol
21	hydroxymethylcyclododecane	26.314	1.72	2.09	2.73	$C_{13}H_{26}O$	Alcohol
22	2-Cyclohexylnonadecane	29.975	0.99	na	1.35	$C_{25}H_{50}$	Hydrocarbon
23	1-Hexadecanol, 3,7,11,15-tetramethyl- (CAS)	31.037	3.52	4.28	4.33	$C_{20}H_{42}O$	Alcohol
25	1-Hexadecanol, 3,7,11,15-tetramethyl- (CAS)	31.873	1.98	2.25	2.38	$C_{20}H_{42}O$	Alcohol
26	1-Eicosanol (CAS)	32.196	1.31	1.73	2.43	$C_{20}H_{42}O$	Alcohol
27	(2,4,6-Trimethylcyclohexyl) methanol	33.202	1.52	2.32	3.27	$C_{10}H_{20}O$	Alcohol
28	2-Cyclohexylnonadecane	36.267	na	na	1.84	$C_{25}H_{50}$	Hydrocarbon
29	1-Hentetracontanol (CAS)	37.225	2.91	na	na	$C_{41}H_{84}O$	Alcohol
33	11-Dodecen-1-ol, 2,4,6-trimethyl-, (R,R,R)- (CAS)	39.181	1.06	1.87	3.02	$C_{15}H_{30}O$	Alcohol
34	2-Cyclohexylnonadecane	41.853	na	na	1.22	$C_{25}H_{50}$	Hydrocarbon
35	Cyclohexane, 1,2,3,5-tetraisopropyl-	44.493	na	1.46	na	$C_{18}H_{36}$	Hydrocarbon
36	1-Hentetracontanol (CAS)	42.72	na	na	2.78	$C_{41}H_{84}O$	Alcohol
39	Cyclohexane, 1,2,3,5-tetraisopropyl-	44.526	na	na	2.7	C_6H_{12}	Hydrocarbon
40	Tetrapentacontane, 1,54	47.709	na	na	1.23	$C_{54}H_{11}$	Hydrocarbon
42	Cyclohexane, 1,2,3,5-tetraisopropyl-	49.369	na	na	1.79	C_6H_{12}	Hydrocarbon

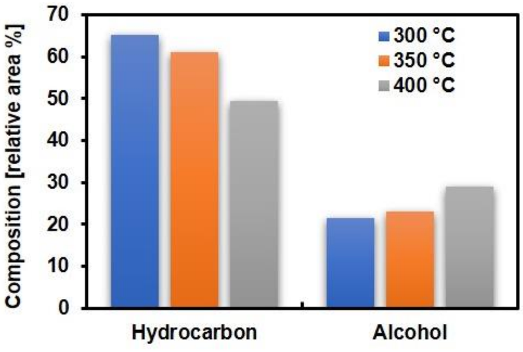


Figure 5. General composition of pyro-oil at different temperatures

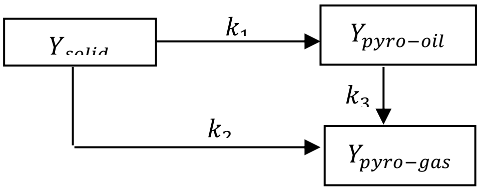
Interestingly, the alcohol content exhibits a marked increase with temperature, rising from 24.1% at 250 °C to 28.7% at 350 °C. This trend supports the hypothesis that alcohols are primarily formed through secondary radical recombination reactions, possibly involving hydrogen abstraction or hydroxylation of intermediate alkyl radicals. The increasing alcohol yield at elevated temperatures may also be ascribed to the decomposition of peroxides or hydroperoxides formed from trace oxygen or water contaminants during pyrolysis.

Overall, the data demonstrate that increasing pyrolysis temperature shifts the product distribution from hydrocarbons to more oxygenated species, particularly alcohols. This shift reflects the thermochemical transformation pathways of polypropylene, wherein radical-mediated reactions and oxidative fragmentations become more prominent with temperature.

3. 5. Reaction Kinetics of Polypropylene Degradation

A thorough understanding of reaction rate constants is essential for studying the decomposition behavior of plastics under thermochemical treatment. In many studies, plastic degradation has been described by first-order kinetics to determine the reaction rate constant. Safavi et al. (40) developed reaction models aimed at optimizing the plastic pyrolysis process. Three different lumped models, integrating both parallel and competing reaction pathways, were assessed against experimental results obtained across a wide range of temperatures. They explicitly applied a first-order kinetic model to determine activation energies for most plastics. The behavior of polypropylene under pyrolysis can be formulated by a model representing solid degradation as follows:

In this context, Y_{solid} represents the initial mass fraction of polypropylene in its solid form. The variable



Scheme 1. PP pyrolsis reaction kinetic model

$Y_{pyro-oil}$ and $Y_{pyro-gas}$ denote the fractions of the solid polymer that have been converted into pyrolytic oil and gas, respectively The proposed reaction pathway further indicates that a portion of the pyro-oil undergoes secondary conversion to gaseous products, while a fraction of the produced gas may subsequently condense and contribute to the formation of pyro-oil.

Assuming a first-order reaction, the rate of product change can be expressed using the following formula (Equations 5-7):

$$\frac{\mathrm{dY(solid)}}{\mathrm{dt}} = -(\mathrm{k}_1 + \mathrm{k}_2)[\mathrm{solid}] \quad (5)$$

$$\frac{\mathrm{dY(pyro-oil)}}{\mathrm{dt}} = \mathrm{k}_1[\mathrm{solid}] - \mathrm{k}_3[\mathrm{pyro-oil}] \quad (6)$$

$$\frac{\mathrm{dY(pyro-gas)}}{\mathrm{dt}} = \mathrm{k}_2[\mathrm{solid}] + (\mathrm{k}_3)[\mathrm{pyro-gas}] \quad (7)$$

where, k denotes the reaction rate constant [s^{-1}], t represents the reaction time [s], and Y(X) corresponds to the product yield.

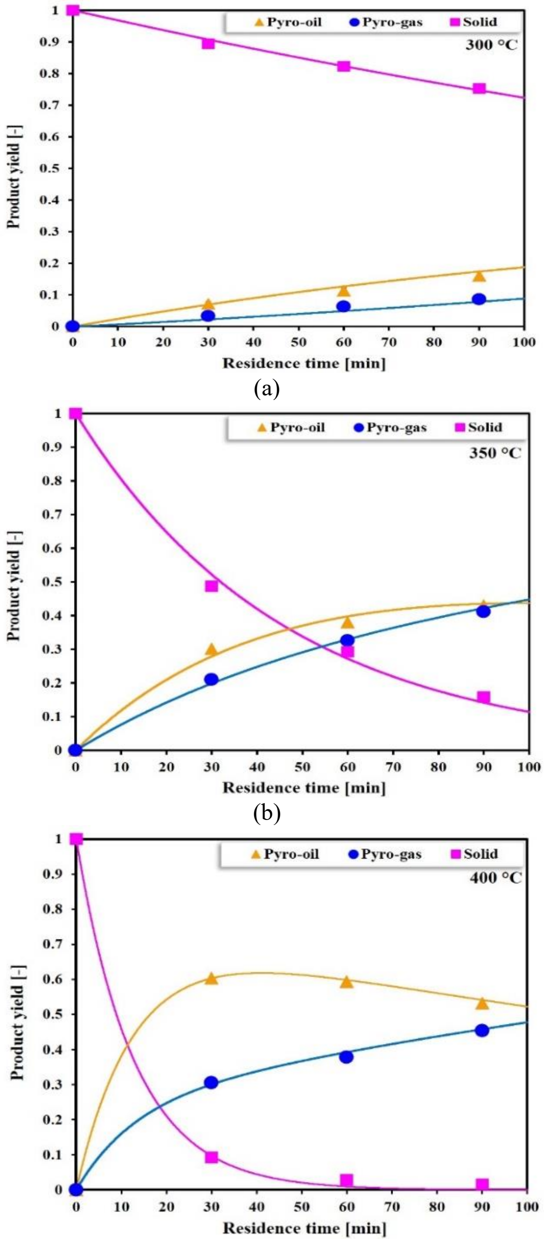
The rate constants were determined via non-linear regression using the least-squares-error (LSE) approach, a standard method that reduces the discrepancy between experimental data and model predictions to achieve optimal fitting. The fitting curve is presented in Figure 6, while the corresponding rate constant values are listed in Table 2.

Close correlation was observed between the experimental results and the calculated values. Figure 7 displays the parity plots for each product yield, confirming a strong correlation between the calculated and experimental results.

The Arrhenius formula (Equation 8) ws used to determined activation energy (E_a) and pre-exponential factor (A).

$$k = A\,e^{\left(\frac{-E_a}{RT}\right)} \quad (8)$$

where T is the reaction temperature [K], R is the universal gas constant [8.314 J/mol·K]. The Arrhenius plots provide valuable insight into the influence of temperature on the reaction rate constants during PP pyrolysis.



(a)

(b)

(c)

Figure 6. Curve fitting analysis of PP pyrolysis product yields at varying temperatures (a) 300 °C, (b) 350 °C, (c) 400 °C

The fitted activation energies and pre-exponential factors provide mechanistic insight into PP conversion pathways. The relatively high $\mathrm{E_a}$ for solid → pyro-oil (99 kJ·mol^{-1}) indicates that formation of stable liquid-range fragments requires substantial energetic input, whereas lower $\mathrm{E_a}$ values for secondary cracking reflect more facile fragmentation pathways.

Despite its potential as a renewable energy source, PP-derived pyro-oil cannot be utilized directly as a drop-in transportation fuel due to several limitations such as physicochemical properties and chemical impurities. To overcome these limitations, upgrading strategies are essential. Distillation can fractionate the oil into lighter and middle distillates, improving homogeneity.

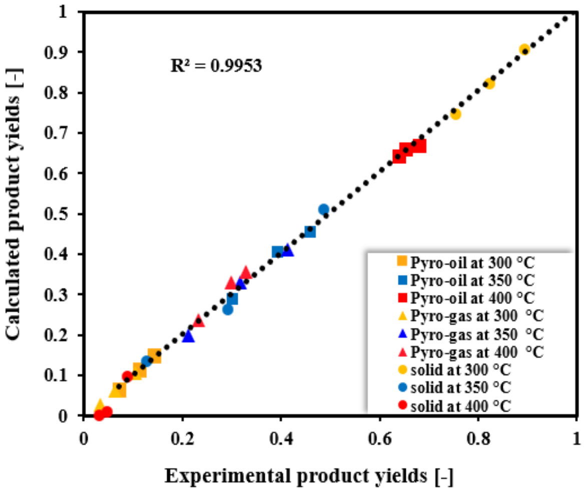


Figure 7. Parity plot of PP pyrolysis

Hydrotreating and hydrocracking effectively remove oxygenates and saturate olefins, producing stable paraffinic fuels with higher calorific value and improved cetane number. Alternatively, catalytic cracking or reforming can convert heavy fractions into lighter hydrocarbons or aromatic compounds suitable for gasoline or jet-fuel blending. Solvent extraction and adsorption methods may also be applied to reduce corrosive oxygenates and chlorinated compounds. In the short term, controlled blending with diesel or biodiesel could allow partial utilization.

These considerations highlight that, while PP pyro-oil shows promise as an energy carrier, its direct use is constrained by fuel property limitations. Consequently, coupling pyrolysis with appropriate upgrading steps is indispensable to realize its potential as a sustainable fuel alternative.

TABLE 2. Kinetic Parameters, Activation Energy, and Pre-Exponential Factor of Each Reaction of Polypropylene conversion via pyrolysis (Experimental Conditions: 300–400 °C, residence time 30-90 min)

kinetic parameter	Reaction	k [s^{-1}]			Activation energy, E_a [kJ mol^{-1}]	Pre-exponential factor, A [s^{-1}]
		300 °C	350°C	400°C		
k_1	solid → pyro-oil	2.5 x 10^{-3}	13.4 x 10^{-3}	5.60 x 10^{-2}	99.12	4.57 x 10^{4}
k_2	solid → pyro-gas	0.7 x 10^{-3}	8.3 x 10^{-3}	21.9 x 10^{-3}	111.85	2.18 x 10^{5}
k_3	pyro-oil → pyro-gas	2.9 x 10^{-3}	3.40 x 10^{-3}	3.70 x 10^{-3}	8.23	2.71 x 10^{-4}

4. CONCLUSION

These findings suggest that increasing the pyrolysis temperature significantly enhances the conversion efficiency of polypropylene by promoting extensive thermal degradation and reducing char formation, thereby maximizing pyro-oil yields. However, while moderate temperature increases (e.g., to 350°C) enhance both oil and gas production due to intensified cracking reactions, further temperature elevation results in a preferential formation of liquid hydrocarbons over gases, indicating an optimal temperature window where oil yield is maximized while gas formation slightly increases. Additionally, the suppression of char formation at higher temperatures highlights the importance of sufficient thermal energy to overcome cross-linking and aromatization pathways responsible for char stabilization. A first-order reaction with an Arrhenius-type rate constant was employed to elucidate the waste decomposition mechanism. Overall, these results indicate that both temperature and reaction time are critical parameters in steering product distribution toward desirable liquid fuels in polypropylene pyrolysis processes.

Acknowledgments

The authors gratefully acknowledge the Thermal Engineering Laboratory, Riau University for providing experimental apparatus, and the Directorate of Research and Community Service, Ministry of Higher Education, Science and Technology (DPPM, Kemendiktisaintek 2025) for funding this research [Grant no. 102/C3/DT.05.00/PL/2025, no. 19571/UN19.5.1.3/AL.04/2025].

Funding

This work was supported by Directorate of Research and Community Service, Ministry of Higher Education, Science and Technology (DPPM, Kemendiktisaintek 2025) [Grant no. 102/C3/DT.05.00/PL/2025, no. 19571/UN19.5.1.3/AL.04/2025].

Ethics Approval and Consent to Participate

This article does not involve any studies with human participants or animals performed by any of the authors. Therefore, ethics approval and consent to participate are not applicable.

Competing Interests

The author declares no financial or organizational conflicts of interest.

Data Availability

The data that support the findings of this study are available upon reasonable request.

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this manuscript, the author used ChatGPT exclusively for minor language editing to improve readability. After using this tool, the author carefully reviewed and edited the content as needed and takes full responsibility for the content of the published article.

Author(s) Biosketches

Rahmat Iman Mainil is an Associate Professor in Mechanical Engineering, Riau University with a focus on renewable energy systems, thermal management, and energy conversion technologies. His research interests include thermochemical conversion, photovoltaic–thermal systems, heat transfer, and sustainable energy applications.

Junior Jonathan Panjaitan is a former Mechanical Engineering student at Riau University.

Annisa Wulan Sari is a lecturer in the Department of Mechanical Engineering at Riau University. She is involved in several research projects related to energy conversion.

Anita Susilawati is an Associate Professor in Mechanical Engineering, Riau University specializing in manufacturing technology. Her research interests include advanced manufacturing processes, materials processing, and sustainable manufacturing systems.

Afdhal Kurniawan Mainil is an Associate Professor in Mechanical Engineering at the University of Bengkulu, Indonesia. His research interests include heat transfer, refrigeration and air-conditioning, and thermal systems, with contributions to international scientific publications.

Obie Farobie is a Lecturer and Researcher at IPB University. His research focuses on renewable energy, biomass conversion, and biofuel production, with publications in international journals.

Apip Amrullah is an Associate Professor in Lambung Mangkurat University specializing in biomass utilization and energy conversion. His work focuses on kinetic analysis and thermal processes for renewable energy applications.

Azridjal Aziz is a Professor of Mechanical Engineering, Riau University specializing in cooling and refrigeration systems, solar energy, and thermal systems. His research includes heat transfer, energy efficiency, and sustainable energy technologies.

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Persian Abstract

چکیده

این تحقیق، پیرولیز آهسته ضایعات پلاستیکی پلی‌پروپیلن (PP) را به عنوان یک روش عملی برای تولید پیرو–اویل بررسی می‌کند. هدف اصلی، تبدیل ضایعات پلیمری غیر قابل تجزیه زیستی به سوخت مایع با ارزش افزوده و در عین حال پرداختن به نگرانی‌های زیست‌محیطی مرتبط با آلودگی پلاستیک است. آزمایش‌های پیرولیز آهسته در یک راکتور ناپیوسته تحت دماهای تنظیم‌شده ۳۰۰، ۳۵۰ و ٤۰۰ درجه سانتیگراد با زمان‌های واکنش ۳۰، ٦۰ و ۹۰ دقیقه انجام شد تا رفتار تخریب حرارتی، توزیع محصول و کیفیت پیرو–اویل به‌دست‌آمده بررسی شود. بالاترین میزان تولید پیرو–اویل، معادل ٦۸ درصد، در دمای ٤۰۰ درجه سانتیگراد حاصل شد که نشان‌دهنده ترک‌خوردگی حرارتی بهینه زنجیره‌های پلی‌پروپیلن است. در این شرایط، پیرو–اویل محتوای هیدروکربنی ٤۹.۳ درصد را نشان داد که بر قابلیت آن به عنوان منبع جایگزین انرژی تأکید دارد. پیرو–اویل ارزش حرارتی در محدوده ٤۸ مگاژول بر کیلوگرم تا نزدیک به ٤۹ مگاژول بر کیلوگرم دارد. مسیرهای واکنش ممکن در این مطالعه تعیین شده‌اند، همانطور که توسط ضریب پیش نمایی و انرژی فعال‌سازی به‌دست‌آمده از معادله آرنیوس نشان داده شده است. این یافته‌ها امکان‌سنجی ارزش‌آفرینی ضایعات پلی‌پروپیلن از طریق پیرولیز آهسته را نشان می‌دهند و مسیری امیدوارکننده برای بازیابی منابع، اجرای اقتصاد چرخشی و کاهش اثرات زیست‌محیطی ضایعات پلاستیکی ارائه می‌دهند.