CATALYTIC PYROLYSIS OF POLYPROPYLENE WASTE

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This study investigates the catalytic pyrolysis of polypropylene waste from car dismantling using activated carbon and zeolite-type catalyst under controlled conditions. Original experiments evaluated the influence of catalyst type and loading on product yields, gas composition, and liquid hydrocarbon distribution. Results demonstrate enhanced production of light hydrocarbons (up to 88.72 wt.%) and gas analysis with high gross heating values exceeding 72,000 kJ/m³. The combined catalytic approach yielded superior selectivity compared to individual catalysts. This work provides new insights into optimizing pyrolysis processes for energy-dense, low-carbon fuels from plastic waste.

Keywords: polypropylene, pyrolysis, end-of-life vehicle, plastic waste, catalyst, activated carbon

1. Introduction

The global rise in plastic production and consumption has led to increasing concerns regarding plastic waste management. A significant and often overlooked source of plastic waste is the automotive sector, particularly from the dismantling of end-of-life vehicles (ELVs)**.** Among the polymers used in car interiors and structural components, polypropylene (PP) is one of the most abundant, commonly found in parts such as bumpers, dashboards, and door panels, having about 50% usage in the automotive interior, along with other thermoplastics [1]. While some high-quality PP can be mechanically recycled, the heterogeneity, contamination, and degradation of automotive plastic waste often limit its recyclability [2]. As a result, thermal recycling methods such as pyrolysis have gained attention as a more flexible and robust alternative.

Pyrolysis of PP involves thermal decomposition in an oxygen-free environment, typically between 300–700°C. The process yields three main product fractions: non-condensable gases, condensable liquids (pyrolysis oil), and solid

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residue (char) [3, 4]. Studies show that increasing temperature leads to greater gas production at the expense of liquids, with char formation typically around 15 wt.% [5, 6]. The liquid fraction from PP pyrolysis consists mainly of aliphatic hydrocarbons (C_5–C_{20}), while the gas fraction includes hydrogen, methane, ethane, ethylene, propane, propylene, and butanes [7].

The exact distribution depends on operating conditions, including residence time, heating rate, pyrolysis temperature, catalyst, etc. [8]. Sometimes, a distillation column is used to separate liquid products into several fractions [9].

Using a catalyst can significantly influence product distribution and improve the overall quality of the pyrolysis products. Catalysts with acidic active centres like zeolites tend to favor cracking and aromatization, producing more gases and aromatic oils [10-13]. Neutral or mildly basic materials such as activated carbon and metal oxides (e.g., CaO, MgO) can promote dehydrogenation and light hydrocarbon formation, promoting the gaseous fraction [14, 15]. The catalyst-to-polymer ratio, catalyst placement (e.g., mixed or layered), contact mode (in-situ or ex-situ), further impact reaction selectivity [16].

The gas phase from PP pyrolysis, particularly when enriched in C_1–C_4 hydrocarbons, can be used as a fuel for motogenerators, providing a decentralized energy solution with low sulfur emissions [17]. Meanwhile, the liquid fraction, if composed primarily of light paraffins and olefins, holds value for refinery integration [18].

This study examines the catalytic pyrolysis of polypropylene waste derived from automotive dismantling, with a focus on catalyst configurations to maximize gas yield and improve the quality of both the liquid and gaseous phases. The results aim to support the development of efficient, waste-to-fuel technologies and to identify practical pathways for integrating pyrolysis-derived products into existing energy and fuel systems.

2. Materials and Methods

2.1. Feedstock

The polypropylene (PP) feedstock used in this study was sourced from automotive dismantling operations, specifically from interior car components such as the car pole. The material was provided by SC Pieseauto Dez SRL, Constanța, Romania. No cleaning or washing was performed; the plastic was only manually cut into small pieces to facilitate uniform heating and contact with the catalyst during pyrolysis.

2.2. Catalysts

Two catalytic materials were employed in this study: activated carbon (AC) and a synthetic zeolite catalyst designated AMD4. The activated carbon, originating from coconut shell, 6*12 mesh, bought from Legend Inc. USA, was used at concentrations of 5 wt.%, 10 wt.%, and 20 wt.% relative to the polypropylene feedstock, with additional tests involving the reuse of spent AC recovered from previous runs. Zeolite AMD4, characterized by a surface area of 147.00 m^2/g, an acidity of 0.6300 mEq/g, and a porosity of 0.119 cm^3/g, was applied at a concentration of 20, 10, and 5 wt.%. One experimental configuration also combined 5 wt.% AC with AMD4 a 5 wt.% concentration.

In all cases, the catalytic material was dry-mixed with the PP waste prior to introduction into the pyrolysis reactor, ensuring homogeneous distribution throughout the feedstock.

2.3. Pyrolysis reactor and distillation system

The experiments were performed using a prototype laboratory-scale pyrolysis system equipped with a distillation column. The main pyrolysis reactor features are: supply flange, external temperature control, and a mechanical stirring system consisting of a variable-speed electric motor, sealing box, and stirrer [8].

The distillation column is composed of two sections and is equipped with a distillation head and a reflux divider, allowing manual control of the reflux ratio. Heating elements are mounted on the column walls to simulate adiabatic operation and maintain internal temperature gradients. The setup enables the collection of three distinct liquid fractions: naphtha, diesel, and a heavy fraction, with individual collection lines regulated by fine taps. The reactor has a total polymer processing capacity of up to 3000 g per batch. No inert atmosphere or nitrogen purge was employed during the process.

2.4. Pyrolysis conditions

Each pyrolysis experiment was carried out by heating the polypropylene–catalyst mixture to a final temperature of 420°C. Upon completion of pyrolysis, the resulting products were separated into three phases: liquid, solid, and gas. The liquid products, comprising two fractions (naphtha-range and heavy), were condensed and collected in separate Erlenmeyer flasks connected to different outlets along the distillation column. The solid residue, consisting of char and catalyst, was recovered directly from the reactor. Both the liquid fractions and the solid residue were measured gravimetrically using an analytical balance. The gas yield was collected in Tedlar gas bags and calculated by difference, subtracting the total mass of the recovered liquid and solid from the initial mass of the feedstock. The pyrolysis process diagram is described in Fig. 1.

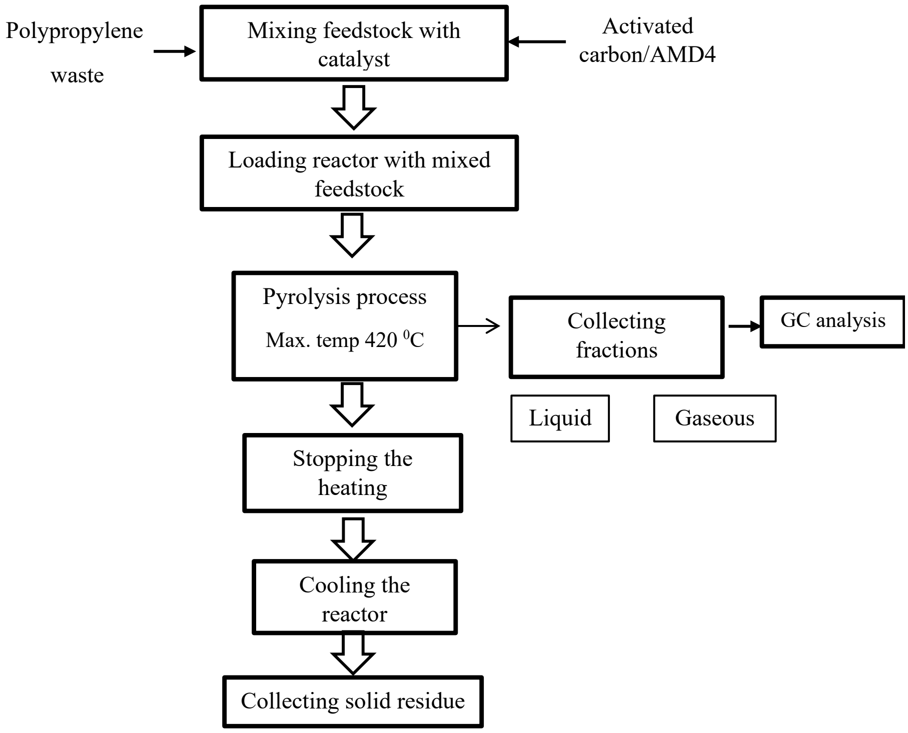

Fig. 1. The plastic waste pyrolysis process diagram.

2.5. Composition Analysis

The composition of the gaseous products was analyzed using a Buck Scientific 910 gas chromatograph (Buck Scientific Instruments, Norwalk, USA), equipped with two packed columns. A molecular sieve 13X column (6″ × 0.53 mm) was used for the separation of permanent gases such as N_2, O_2, CO, and CO_2, while a silica gel column (6″ × 0.53 mm) enabled the separation of light hydrocarbons including CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, n-C_4H_{10}, i-C_4H_{10}, C_4H_8, and i-C_4H_8. The system operated with helium and argon as carrier gases, maintained at a constant flow rate of 30 mL/min and a pressure of 84 psi. This configuration allowed accurate quantification of both inorganic and hydrocarbon gas species formed during the pyrolysis process.

The liquid products were analyzed using a second configuration of the Buck Scientific 910 gas chromatograph, equipped with a capillary column (MTX-1, 60 m length, 0.53 mm internal diameter). The GC oven was programmed to hold initially at 40 °C for 2.5 minutes, followed by a temperature ramp of 5 °C/min up to 315 °C, where it was maintained isothermally for 30 minutes. Detection was performed using both a Flame Ionization Detector (FID) and a Discharge Ionization Detector (DLCD), allowing for the identification of a wide range of hydrocarbon compounds. Liquid samples were introduced manually into the system using a 10 µL Hamilton microliter syringe.

2.6. Energy value of gases

For each compound present in the gaseous fraction, gross heating values were sourced from the literature [19] and shown in table 1. Based on these values and the volumetric composition of the gas mixtures (C_i), the gross heating value (GHV) of each sample—expressed in kJ/m³—can be calculated with equation (1):

$$GHV_{mixture} = \frac{\sum_1^n GHV_i \times C_i}{100} \ (kJ/m^3) \quad (1)$$

Table 1

Gross heating value and CO_2 emissions for gaseous fractions [19]

Component	Gross heating value, kJ/m³
H_2	12109
CO	12035
CH_4	37669
C_2H_6	66433
CO_2	0
C_2H_4	60769
C_3H_8	95830
C_3H_6	87037
i-C_4H_{10}	120160
n-C_4H_{10}	120160
1-C_4H_8	114646
2-C_4H_8	114646
C_5	148328
C_6	173888

3. Results and discussions

3.1. Product yields

The pyrolysis experiments using polypropylene (PP) waste from automotive dismantling produced three liquid fractions (light, diesel, and heavy), a solid residue, and a gaseous product. The influence of different catalytic systems on product distribution is summarized in Table 2.

Table 2

Product distribution from the pyrolysis of polypropylene waste with different catalysts

Exp.	Temperature, C		Results, % wt		
	Max. liquid yield	Depletion of liquid	solid	liquid	gas
AC_20	288	345	23.8	14.0	62.2
AC_10	298	347	24.2	16.3	59.5
AC_5	307	370	3.6	21.5	74.9
ACr_5	284	376	8.7	17.3	74.0
control	292	372	2.5	17.3	80.2

AMD4_5	287	367	1.8	12.5	85.7
AMD4+AC_5+5	294	372	1.4	15.4	83.1

The non-catalytic experiment (control) resulted in a gas yield of 80.2%, with a liquid yield of 17.3% and minimal solid residue (2.5%). This confirms the high thermal degradation efficiency of polypropylene under the applied conditions, favoring gas production in the absence of catalysts.

Introducing activated carbon influenced the product distribution markedly. At a low loading of 5% (AC_5), the gas yield decreased slightly to 74.9%, while the liquid yield increased to 21.5%, the highest among all experiments. Interestingly, the solid residue increased modestly to 3.6%. Increasing the AC content to 10% (AC_10) and 20% (AC_20) resulted in a reduced gas yield (59.5% and 62.2%, respectively) and increased solid formation (24.2% and 23.8%). The temperature at which maximum liquid formation occurred also shifted with catalyst loading. For AC_20 and AC_10, this point was observed at 288 °C and 298 °C, respectively, indicating early volatilization and catalytic cracking. In contrast, AC_5 reached peak liquid generation at 307 °C, suggesting a more balanced thermal-catalytic pathway that maximized liquid intermediates before overcracking. This shift in temperature behavior is further reinforced by the depletion temperature of the liquid phase, which increased progressively from 345 °C (AC_20) to 370 °C (AC_5), showing that lower catalyst amounts sustained volatile product release over a broader temperature window. This suggests that higher AC concentrations may lead to secondary condensation or coking reactions, reducing the conversion of solids into volatile products.

The test with recovered AC (ACr) produced 74.0% gas, similar to fresh AC at 5%, but with a higher solid residue (8.7%), indicating some loss of catalytic efficiency due to deactivation or surface changes after prior use. However, the liquid yield remained at 17.3%, comparable to the fresh catalyst. However, the thermal profile (with a maximum liquid yield at 284 °C and depletion at 376 °C) indicates that the recovered AC maintained sufficient activity to promote deep cracking, possibly due to the retention of porosity and active sites.

The zeolitic catalyst AMD4 at 5% of loading (AMD4_5) led to the highest gas yield among all setups, at 85.7%, with the lowest liquid and solid yields (12.5% and 1.8%, respectively). The rapid progression of the reaction is also reflected in the temperature of maximum liquid formation (287 °C), which occurred early and was followed by quick depletion at 367 °C. This implies that AMD4 strongly promotes gas-phase reforming reactions, limiting the accumulation of intermediate condensable products. This highlights AMD4 strong cracking ability and selectivity toward gaseous hydrocarbons. The combination of 5% AMD4 with 5% AC (AMD4+AC_5+5) maintained high gas production (83.1%) while improving the liquid yield to 15.4%. This experiment showed a balanced thermal window for condensable production, with maximum liquid yield occurring at 294 °C and depletion at 372 °C, indicating a prolonged volatilization process possibly due to the complementary activity of AC and AMD4.

Activated carbon promotes liquid production at lower loadings but can lead to increased char formation at higher concentrations. Zeolite AMD4, on the other hand, drives the system toward maximal gas generation with minimal residue. For applications prioritizing gaseous fuel production, the zeolite-based catalysts offer a promising route. Where valuable liquid intermediates are also desired, moderate AC loading or mixed catalytic systems can offer a better balance.

3.2 Gas composition

The gas phase resulting from the catalytic pyrolysis of polypropylene waste was analyzed using gas chromatography. The analysis revealed a complex mixture dominated by hydrogen (H_2), methane (CH_4), and light hydrocarbons, along with smaller amounts of CO, CO_2, and C_5+ compounds. The presence and proportion of these components varied significantly depending on the catalyst used and reaction configuration, as shown in Table 3.

The concentration of methane was highest at 31.53% for the sample with 20% catalyst (AC_20), indicating a strong tendency towards cracking reactions that favor saturated light hydrocarbons. As the AC concentration decreased to 10% (AC_10) and 5% (AC_5), the methane concentration decreased, 21.03% and 26.26% respectively, while the yields of unsaturated hydrocarbons such as ethylene and propene increased. Ethylene reached 3.69% in the AC_10 experiment, and propene increased to 12.37% in the same sample. This trend suggests that lower AC loadings are more favorable for dehydrogenation and olefin production, while higher loadings promote further cracking and hydrogenation, yielding more saturated compounds. The presence of C_{5+} compounds such as pentenes and hexenes also increased slightly with decreasing AC concentration, indicating less extensive cracking of larger molecules at lower catalyst amounts.

Table 3

The gas concentration of the gas fraction from the pyrolysis of polypropylene waste

Exp.	**Concentration, vol.%**												
	H_2	**CO**	**CH_4**	**C_2H_6**	**CO_2**	**C_2H_4**	**C_3H_8**	**C_3H_6**	**i-C_4H_{10}**	**n-C_4H_{10}**	**1-C_4H_8**	**2-C_4H_8**	**C_5**	**C_6**
AC_20	4.40	0.70	31.53	14.37	3.52	19.07	2.73	9.22	0.66	0.73	1.04	6.46	1.89	3.68
AC_10	4.31	0.27	21.03	18.78	1.03	20.22	3.69	12.37	0.55	0.86	1.35	7.12	3.70	4.72
AC_5	4.21	0.38	26.23	18.05	0.16	18.97	3.03	11.07	0.58	0.55	1.18	6.87	2.98	5.71
ACr	4.03	0.38	27.87	16.99	0.16	19.20	2.97	10.84	0.57	0.55	1.20	6.70	2.94	5.60

control	2.91	0.09	28.09	16.58	0.11	20.35	3.23	10.85	0.60	0.49	1.33	7.20	2.82	5.35
AMD4_5	4.3	0.0	29.8	17.5	0.2	18.1	3.3	9.1	0.7	0.6	1.1	5.7	2.9	6.6
AMD4 +AC_5+5	4.52	0.00	27.64	18.87	0.18	17.82	3.71	8.80	0.68	0.74	1.20	5.29	3.11	7.44

The experiment using recovered activated carbon (ACr) yielded a gas composition comparable to that of fresh AC at 5% loading, suggesting that the reused catalyst retains a significant portion of its activity. Methane concentration remained high (27.37%), and the propene level was similar to that in fresh catalyst runs. These results imply that recovered AC, though potentially partially deactivated, can still facilitate cracking reactions and olefin formation effectively.

The use of a zeolite-type catalyst (AMD4) led to a different distribution of gas products. The experiment AMD4_5 demonstrated a strong gasification performance, characterized by a significant methane yield of 29.8 vol%, indicating intense cracking activity and efficient C–C bond scission. Although the production of valuable light olefins such as ethylene (18.1 vol%) and propylene (9.1 vol%) was slightly lower compared to activated carbon-based systems, the composition points to effective conversion of the polymer matrix into light hydrocarbons and hydrogen-rich gas. The minimal CO (0.0 vol%) and low CO_2 (0.2 vol%) contents confirm the inert reaction atmosphere and lack of oxidative degradation. C_4–C_6+ compounds were present in moderate amounts, reflecting a balance between primary pyrolysis and secondary reactions like cracking and isomerization. Overall, AMD4_5 confirms that even a low concentration of AMD4 zeolite can promote pyrolysis catalytic cracking,

A combined catalyst system using both AMD4 and AC (AMD4+AC_5+5) provided a more balanced composition of gases. Methane (27.64 vol%) and ethylene (17.82 vol%) levels remained high, while propylene (8.80 vol%) and C_4–C_6+ compounds were moderately distributed, suggesting selective cracking and olefin formation with partial suppression of heavier hydrocarbon build-up. Notably, the absence of CO and the very low CO_2 content (0.18 vol%) further confirm that reactions proceeded under strict pyrolytic conditions without oxidation. Compared to the PP_AMD4_5 experiment, the addition of activated carbon appears to moderate excessive cracking while sustaining high gas yields and improving the selectivity toward hydrogen and light olefins, making this catalytic blend a promising route for promoting pyrolysis gas composition.

3.2 Liquid composition

The distribution of hydrocarbon fractions in the liquid products obtained from the catalytic pyrolysis of polypropylene waste is presented in Table 4. The composition was categorized into three distillation ranges: light (C_4–C_{13}), diesel (C_{14}–C_{19}), and heavy (C_{20}+) hydrocarbons.

Table 4

The liquid concentration of the liquid fraction from the pyrolysis of polypropylene waste

Exp.	C_4 - C_{13}, wt.%	C_{14} - C_{19}, wt.%	C_{20+}, wt.%
AC_20	83.76	13.13	3.06
AC_10	79.84	16.36	3.76
AC_5	82.03	14.70	3.27
ACr_5	80.96	15.26	3.78
control	83.96	12.79	3.24
AMD4_5	81.32	13.68	4.99
AMD4+AC_5+5	88.72	9.65	1.62

Across most experiments, the light fraction (C_4–C_{13}) dominated, accounting for 79.84–88.72 wt.% of the liquid yield. The control sample without a catalyst produced 83.96 wt.% of light compounds, suggesting that the thermal cracking of polypropylene alone generates a high proportion of lower molecular weight hydrocarbons. The use of activated carbon in different proportions (AC_5, AC_10, AC_20) resulted in broadly similar distributions, with light fractions ranging from 79.84 to 83.76 wt.% and moderate amounts of diesel-range compounds (13.13–16.36 wt.%) and heavy hydrocarbons (3.06–3.76 wt.%).

Notably, the combined use of AMD4 and activated carbon (AMD4+AC_5+5) significantly increased the proportion of light hydrocarbons to 88.72 wt.% while reducing the heavy fraction to only 1.62 wt.%. This shift indicates a more efficient cracking process and a higher selectivity towards lighter, more valuable products when both catalysts were employed. In contrast, the AMD4_5 sample alone produced a high proportion of heavy hydrocarbons (4.99 wt.%), suggesting a less selective conversion compared to the combined catalytic system.

Overall, these results demonstrate that the choice and combination of catalysts can influence the molecular weight distribution of the pyrolysis oil. The catalysts promoted fragmentation of polymer chains, favoring lighter hydrocarbon fractions suitable for use as fuels or chemical feedstocks. The AMD4+AC_5+5 configuration was particularly effective, achieving the highest selectivity towards light fractions among all tested conditions.

3.3. Heating value of gaseous products

The gross heating value (GHV) of the gaseous products obtained through pyrolysis exhibited notable variation depending on the type and composition of the catalysts employed in each experiment. As presented in Table 5, these differences reflect the influence of catalytic activity on the formation and distribution of energy-rich hydrocarbon gases, which ultimately determine the calorific potential of the resulting gas mixtures. The GHV varies, ranging from 49986 to 52442 kJ/kg. The lowest energy content was recorded for the AC_20 sample (49986 kJ/kg), suggesting that a high concentration of activated carbon (20%) might promote cracking pathways or secondary reactions that favor low-energy compounds.

Table 5

Gross heating value of gaseous products from plastic waste pyrolysis

Exp	$GHV_{mixture}$,	
	kJ/m³	kJ/kg
AC_20	63741.27	49986
AC_10	72642.82	51586
AC_5	71429.77	52230
ACr_5	70769.05	52265
control	71439.24	52347
AMD4_5	70589.90	52442
AMD4+CA_5+5	72235.60	52379

As the catalyst concentration decreased, the energy content of the resulting gas improved. The AC_10 and AC_5 samples reached 51586 and 52230 kJ/kg, respectively, indicating that a lower catalyst loading may optimize the distribution of light hydrocarbons that contribute more significantly to GHV. The ACr experiment, involving a reused catalyst, yielded 52265 kJ/kg—almost identical to the fresh AC 5% variant—showing that catalyst regeneration can preserve performance in terms of gas energy content.

The highest GHV was observed for the AMD4_5 sample (52442 kJ/kg), followed closely by the AMD4+AC_5+5 mixture (52379 kJ/kg), confirming that the AMD4 catalyst—alone or in combination with activated carbon—effectively enhances the production of energy-dense gases.

While activated carbon can influence the pyrolysis gas composition, its effectiveness depends heavily on concentration. Alternative catalysts like AMD4, and combinations appear more efficient in maximizing the heating value of the resulting gas, offering promising potential for energy recovery applications.

The calorific power of the pyrolysis-derived gases was compared with common commercial fuels, which are presented in Table 6.

Table 6

Calorific power and carbon intensity of commercial fuels

Fuel	GHV	
	kJ/m³	kJ/kg
propane	99000	50400
kerosene	37400	46200
diesel	38578	45600
natural gas	37285	52200

Notably, several experimental samples—including PP_AC_5, PP_ACr, PP_control, PP_AMD4_5, and AMD4+AC_5+5—exceeded the calorific value of natural gas, indicating that pyrolysis gases derived from polypropylene waste, especially under optimized catalytic conditions, can serve as potent fuel alternatives. The AMD4_5 sample exhibited the highest heating value at 52442 kJ/kg, outperforming even propane and closely matching the upper end of energy-dense commercial gases. This energetic potential underscores the viability of catalytic pyrolysis not only as a waste management solution but also as a potential source of producing high-calorific-value fuel gases. The data also suggest that the choice of catalyst—particularly the use of AMD4 or its combination with activated carbon—plays a critical role in enhancing the fuel quality of the gaseous product. Consequently, pyrolysis gas may serve as a promising substitute or supplement to traditional fossil fuels in applications requiring high energy density.

6. Conclusions

This research demonstrated that catalytic pyrolysis of polypropylene waste using activated carbon and AMD4 catalysts significantly enhances the yield and quality of valuable gas and liquid products. Original results include achieving gross heating values above 72,000 kJ/m³ in the gas fraction and concentrating desirable C_4–C_{13} hydrocarbons in the liquid phase up to 88.72 wt.% when combined catalytic systems were applied. The high-energy gas mixtures produced are particularly suitable for direct use in motogenerators, enabling efficient generation of electricity and heat from waste plastics. Overall, the study highlights a sustainable recycling strategy that transforms polypropylene waste into alternative fuels and chemical resources, supporting circular economy objectives and reducing environmental impact.

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