

# Oil production from thermal liquefaction of polyethylene in low-pressure superheated methanol

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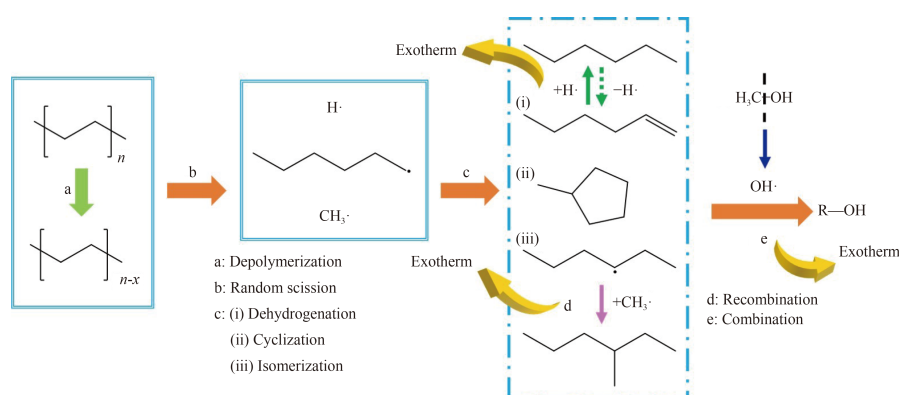
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**Abstract:** The improper disposal of plastic waste represents both the loss of valuable resources and significant environmental threat. To address this issue, this study investigates the thermal liquefaction of high-density polyethylene (HDPE) using low-pressure superheated

methanol. It systematically evaluates the effects of the reaction temperature and the ratio of reactant to methanol on the liquefaction efficiency and product characteristics. Results indicate that the complete conversion of HDPE could be achieved in low-pressure superheated state methanol (<0.5 MPa) at a minimum external heating temperature of 260 °C. Under this condition, the oil yield reached 77.1% with alkanes comprising 62.3% of the product alongside minor oxygenated compounds. As temperature increased, the average carbon number of hydrocarbons gradually decreased. Below 260 °C, the HDPE conversion decreased significantly, and the products were primarily waxy. At 290 °C, the proportion of gasoline-like fractions (C6–C12) increased markedly from 16.6% to 80.9%. Furthermore, reactant ratio plays a critical regulatory role; extremes in ratio—either too high or too low—diminish heat transfer efficiency and reduce conversion. Mechanistically, the liquefaction primarily involved the cleavage of secondary C–C bonds, where the resulting oligomers further cracked into free radicals to form diverse hydrocarbons through secondary reactions. This work demonstrates that low-pressure superheated methanol liquefaction is a mild, efficient, and pretreatment-free method to upcycle polyethylene into valuable fuels. Optimizing these process parameters can pave the way for industrial application, aiding in both plastic pollution management and sustainable resource recovery.

**Key words:** plastic waste; polyethylene; low-pressure superheated state methanol; thermal liquefaction; fuel oil



Over the past few decades, global plastic production has exceeded 8 billion tons<sup>[1–2]</sup>. Despite this massive output, waste management remains inefficient: only approximately 9% of plastic waste is recycled and 12% is incinerated, leaving the vast majority to accumulate in landfills or the

natural environment<sup>[3]</sup>. This mismanagement imposes severe negative impacts on global ecosystems<sup>[4–5]</sup>. Consequently, the development of efficient, environmentally friendly technologies for plastic recycling and circular utilization has become an urgent priority.

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Current plastic waste treatment technologies—including landfilling, mechanical recycling, incineration, pyrolysis, gasification, and hydrothermal methods—each face inherent limitations in practical application<sup>[6]</sup>. Landfilling is constrained by extensive land requirements, prolonged processing cycles and limited capacity. Mechanical recycling is hindered by complex separation requirements and low added-value of the products, often resulting in material degradation. While incineration reduces waste volume, it generates hazardous emissions, leading to secondary environmental pollution. Furthermore, pyrolysis and gasification typically necessitate energy-intensive consumption, which significantly increase the overall techno-economic burden of the process.

Solvothermal liquefaction presents a compelling alternative, as it facilitates the direct conversion of mixed and contaminated plastics without the need for intensive pretreatment. Characterized by relatively mild reaction conditions<sup>[7]</sup>, this technology demonstrates significant industrial potential and economic value<sup>[8]</sup>. In solvothermal liquefaction, besides conventional hydrothermal process (water as solvent)<sup>[9–10]</sup>, various organic solvents, such as alcohols, ketones, toluene, hydrocarbons, and other organic solvents have been adopted as the reaction media<sup>[11–14]</sup>. For instance, Saw et al.<sup>[15]</sup> utilized toluene to liquefy high-density polyethylene, yielding oil products with calorific values comparable to gasoline and diesel. Liu et al.<sup>[16]</sup> compared the thermal liquefaction behavior and oil quality of polyethylene in different solvents (water, ionic liquids, methanol, acetone), finding that oils obtained in organic solvents exhibited higher H/C ratios and lower O/C ratios. Lachos-perez et al.<sup>[17]</sup> investigated polyethylene liquefaction in superheated steam, demonstrating that its performance at 425 °C and moderate pressure rivals the performance of supercritical water.

As a polar protic solvent, methanol can reduce reaction activation energy by dissolving and stabilizing the reaction intermediates, thereby promoting plastic liquefaction and enhancing oil yields. It has been successfully applied in the liquefaction of nylon, fiber-reinforced resins, and carbon fiber-reinforced plastics<sup>[18–21]</sup>. As a typical thermoplastic polymer, polyethylene accounts for 36% of global plastic production<sup>[22–23]</sup>. Based on the finding of our research

group's prior work<sup>[19,24]</sup>, this study focuses on the liquefaction of high-density polyethylene (HDPE)—a material notably resistant to degradation. We systematically investigate the liquefaction characteristics of HDPE in a low-pressure superheated methanol system, where the methanol vapor pressure is below its critical pressure while the temperature exceeds the corresponding saturation temperature to validate the efficacy and versatility of this liquefaction approach.

## 1 Materials and method

### 1.1 Experimental materials

HDPE used in the experiment was purchased from the Maoming Branch of Sinopec Group. It has a particle size of 100 mesh (approximately 0.15 mm) and a density of 0.98 g/cm<sup>3</sup>. Its dry basis carbon, hydrogen, and oxygen contents are 85.05%, 13.40% and 1.56%, respectively, with a higher heating value (HHV) of 47.55 MJ/kg. Methanol (>99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All other chemical reagents with analytical grade were also purchased from Sinopharm Chemical Reagent Co., Ltd.

### 1.2 Solvothermal liquefaction

#### 1.2.1 Experimental procedure

The thermal liquefaction of HDPE was performed in a 100 mL Parr 4590 high-pressure reactor. The experimental workflow, illustrated in Figure 1, was conducted according to the following protocol.

(1) Reactor Charging and Pre-treatment: 4 g of HDPE powder was introduced into the reactor along with a specified volume of methanol. After sealing the vessel, the internal atmosphere was purged with argon to ensure an internal environment. Following a successful leak test, the heating system was activated with a heating rate of approximately 20 °C/min.

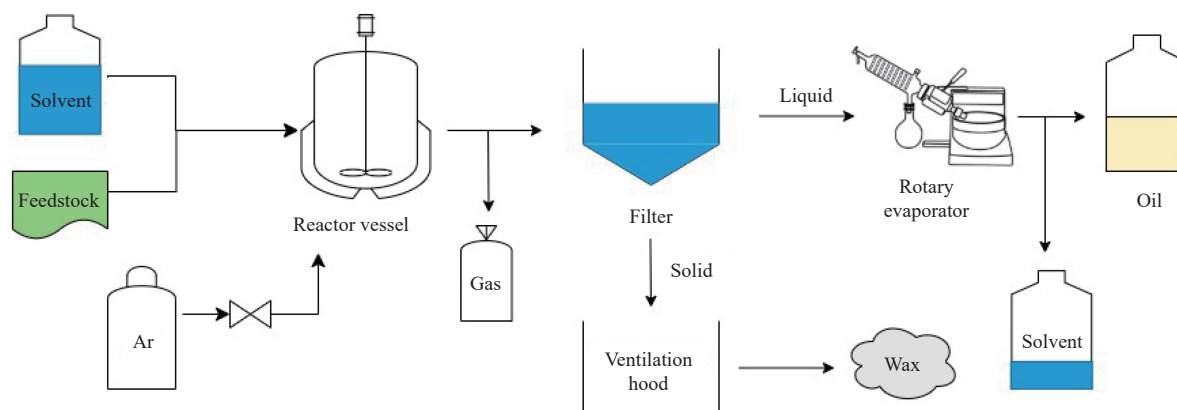


Fig. 1 Experimental procedure for polyethylene thermal liquefaction in methanol

Temperature and pressure data were monitored and recorded in real-time *via* a data acquisition system. Throughout the entire process, a constant stirring speed of 70 r/min was maintained.

(2) Reaction and Cooling: Upon reaching the target temperature, the heating was ceased automatically. Once the temperature begins to decline, the insulation jacket was removed, and the reactor was rapidly cooled to room temperature using forced-air cooling.

(3) Gas Collection: The vent valve was opened once the reactor reached ambient temperature. The total gas volume was measured using a wet gas flow meter, and samples were collected in gas bags for further analysis. Temperature and pressure acquisition were terminated at this moment.

(4) Product Collection: After the internal pressure returned to atmospheric levels, the reactor head was removed. The reaction products were removed and the interior of the reactor was thoroughly rinsed with methanol to ensure complete sample recovery. The resulting mixture was passed through a filter to separate the solid residues from the liquid phase.

(5) Oil and Solid Recovery: The filtrate was processed using a rotary evaporator at 70–75 °C to remove the methanol. The remaining liquid was defined as the “oil” product, which was subsequently weighed to calculate the oil yield. The solid residue was washed repeatedly with methanol and air-dried in a fume hood until a constant weight was achieved. The final mass was recorded to determine the solid yield.

The reaction temperature was set to 250, 255, 260, 270 and 290 °C to investigate the effect of reaction temperature, while the weight of HDPE was fixed at 4 g with a ratio of reactant to methanol of 0.8 g/mL. The reactant ratio (N/A, 1.33, 1.00, 0.80, 0.67, 0.50 and 0.40 g/mL) was adjusted by varying the methanol amount of 0, 3, 4, 5, 6, 8 and 10 mL, respectively, at a fixed reaction temperature of 270 °C and a constant HDPE weight of 4 g. N/A represents no methanol addition.

## 1.2.2 Product yield

Gas products and losses during the experiment are collectively categorized under the “Gas + Loss” term, with their mass percentage calculated using the difference method. The yield of each phase product is calculated according to the following formula<sup>[25]</sup>:

$$\text{Yield}_{\text{liquid}}(\%) = \frac{W_{\text{liquid}}}{W_{\text{plastic}}} \times 100\% \quad (1)$$

$$\text{Yield}_{\text{solid}}(\%) = \frac{W_{\text{solid}}}{W_{\text{plastic}}} \times 100\% \quad (2)$$

$$\text{Yield}_{\text{Gas + Loss}}(\%) = 100\% - \text{Yield}_{\text{liquid}} - \text{Yield}_{\text{solid}} \quad (3)$$

Among these,  $\text{Yield}_{\text{liquid}}$ ,  $\text{Yield}_{\text{solid}}$  and  $\text{Yield}_{\text{Gas + Loss}}$  represent respectively the oil yield, solid yield, and mass fraction of the “Gas + Loss” fraction in the product,  $W_{\text{liquid}}$ ,  $W_{\text{solid}}$  and  $W_{\text{plastic}}$  represent respectively the mass of oil, solid product, and plastic feedstock, respectively. Oil specifically

refers to liquid components at ambient temperature, and wax is not included in oil yield but classified into solid yield.

This paper defines the plastic conversion (CR) as the ratio of the mass of solid plastic converted into non-solid forms to its initial mass, expressed as<sup>[26]</sup>:

$$\text{CR}(\%) = \frac{W_{\text{plastic}} - W_{\text{solid}}}{W_{\text{plastic}}} \times 100\% \quad (4)$$

## 1.2.3 Product characterizing

The chemical composition of the oil was analyzed using an Agilent 7890A gas chromatograph coupled with a 5975C mass spectrometer (GC-MS). Separation was performed on a capillary column (15 m × 0.25 mm × 0.25 μm) with argon utilized as carrier gas. The initial oven temperature was set to 60 °C for 10 min, followed by a gradual increase from 60 to 300 °C at a heating rate of 5 °C/min. Mass spectrometry conditions employed an EI ion source at 150 °C. Preliminary compound identification was based on the NIST 11 mass spectrometry library, with peaks matching above 90% used for subsequent analysis. Following the method established in literature<sup>[17]</sup>, the relative content of each component was estimated using formula (5):

$$\text{Component X peak area}\% = \frac{\text{Peak area of component X}}{\sum \text{peak areas of component identified with a quality} > 90\%} \quad (5)$$

Nicolet iS50 Fourier Transform Infrared Spectrometer (FT-IR) was applied to characterize functional group of HDPE and products. Prior to test, samples and KBr were dried with an infrared lamp for about 2 h. 1–2 mg of sample and 200 mg of KBr was thoroughly ground and compressed into a transparent pellet. The pellets were then immediately scanned. All spectra underwent background subtraction and baseline correction for subsequent analysis.

Molecular weight and distribution were determined using a Waters 1525 gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive index detector and an Agilent PLgel 5 μm MIXED-C column (molecular weight range: 200–2000000 Da). Chloroform was used as the mobile phase at a flow rate of 1 mL/min. The system was calibrated using polystyrene/polymethyl methacrylate (PS/PMMA) standards.

## 2 Results and discussion

### 2.1 Effects of temperature and reactant ratio on liquefaction oil yield

#### 2.1.1 Effect of reaction temperature on the yield of liquefaction oil

Figure 2 illustrates the thermal liquefaction behavior of HDPE in low-pressure superheated methanol at various

target temperatures, including temperature-pressure curves, product appearance and distributions, and conversion. Temperature acceleration was commonly observed during the HDPE liquefaction process, where the final reaction temperatures significantly exceeded the pre-set target values. Specially, at target temperatures of 255, 260, 270 and 290 °C, the maximum heating rate reached 37.8 °C/min, with peak temperatures surpassing the target values by 140.3, 170.1, 172.1 and 174.1 °C, respectively. In contrast, no significant temperature overshoot was observed at the target of 250 °C after the setpoint was reached. Correlating these thermal profiles with product appearances, the significant temperature excursions were consistently associated with degrees of plastic depolymerization. At target temperatures of 250 and 255 °C, the products contained substantial amounts of waxy solids. Figure 2(c) displays the GPC elution curves for the raw HDPE and the solid products obtained at 255 °C. The molecular weight of the solid products at 255 °C was notably lower than that of the raw HDPE, indicating that partial depolymerization and chain scission occurred at this temperature; however, the degree of polymerization remained high enough to yield long-chain components that are solid at room temperature. At 250 °C, the molecular weight of the product remained comparable to the raw material, suggesting that the HDPE underwent only melting and re-solidification without substantial degradation.

Figure 2(b) illustrates the relationship between plastic conversion, oil yield, and target temperature. As the temperature increased, the conversion rose from 2% to 100%. Concurrently, the oil yield peaked at 77.1% at 260 °C before slightly decreasing to 69.3% at 290 °C. This suggests that while elevated temperatures promote liquefaction, it also facilitates the secondary cracking of liquid products into lighter oil components or gaseous components<sup>[25,27]</sup>. Notably, Irawan et al.<sup>[28]</sup> reported that HDPE is difficult to effectively convert into oil through non-catalytic pyrolysis at temperatures below 350 °C. Similarly, Saeung et al.<sup>[29]</sup> conducted MgO-catalyzed pyrolysis of HDPE and found that the HDPE was not fully converted even at 600 °C, yielding a wax content as high as 69%. In comparison, the low-pressure superheated methanol system achieved highly efficient HDPE conversion at lower external heating

temperatures and shorter reaction times, demonstrating a distinct technical advantage.

Under conditions of minimal external heat input, the occurrence of an intense “temperature surge” (or thermal runaway) appeared to be a prerequisite for the complete conversion of HDPE. The fundamental mechanism of HDPE liquefaction involved the scission of C–C bonds, a process that is inherently endothermic. Consequently, a system temperature significantly exceeded the set point can only occur when the internal heat released by the reaction outweighs the heat absorbed and loss<sup>[30–31]</sup>. The temperature overshoot observed in this study indicated the existence of a spontaneous exothermic process within the reaction system. Cheng et al.<sup>[32]</sup> observed that during high-pressure pyrolysis, pressure could induce liquid-liquid phase transitions, leading to the self-heating of long-chain hydrocarbons; furthermore, secondary reactions such as olefin polymerization and radical recombination are known to release significant latent heat. Zhang et al.<sup>[33–34]</sup> observed similar temperature excursions in the pressurized pyrolysis of polyethylene (PE), attributing to pressure-driven increases in phase transition temperatures and elevated intermediate concentrations that triggered exothermic reactions including radical polymerization and olefin hydrogenation.

In the present system, the application of pressure likely caused the intermediates to aggregate at the bottom of the reactor. This localized increased in concentration facilitates exothermic radical polymerization and hydrogenation reactions, with radicals potentially originating from both the polyethylene and the methanol solvent<sup>[6,17]</sup>. The magnitude of temperature surge served as an indicator of the heat released from these phase transitions and exothermic pathways. This internally generated heat further promoted the cracking of solid long-chain compounds into shorter-chain, non-solid fractions. The positive correlation observed between the magnitude of the temperature excursion and the HDPE conversion, indicating that this self-heating effect was a critical driver for the transformation of solids into liquid or gaseous products. Notably, at 255 °C, the moderate temperature overshoot was insufficient to achieve full degradation, resulting in a product dominated by high-molecular-weight waxy substances.

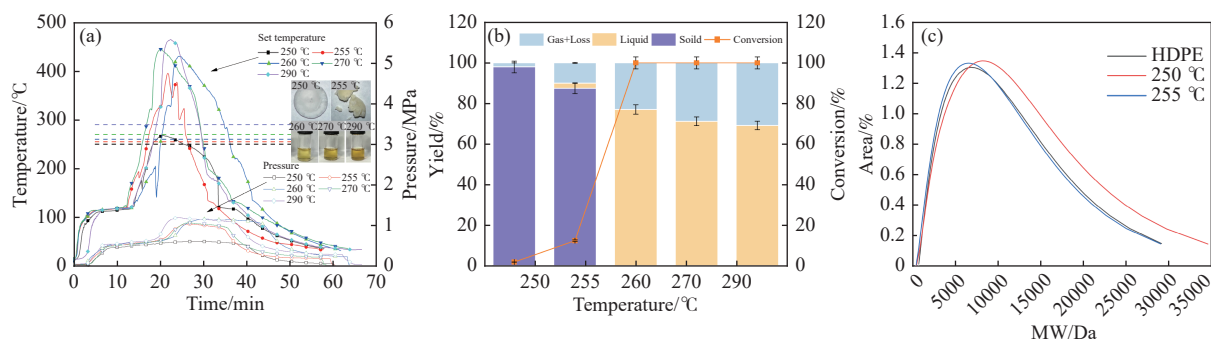


Fig. 2 (a) Temperature-pressure curve diagram; (b) Product distribution and polymer conversion at different temperatures; (c) GPC elution curve diagram

### 2.1.2 Effect of reactant to solvent ratio on oil yield

Figure 3(a) presents the temperature-pressure profiles at various reactant ratios. At ratios of N/A, 1.33, 1.00, 0.80, 0.67, 0.50 and 0.40 g/mL, the peak temperatures exceeded the set-point value by 58.3, 90.7, 161.4, 174.7, 49.1, 74.7 and 40.9 °C, respectively. This indicates that the reactant to solvent ratio exerted a profound influence on the thermal evolution of the reaction. Under these varied ratios, the peak pressures reached 0.0965, 0.7862, 0.8000, 1.0193, 0.6483, 0.9379 and 1.0897 MPa, corresponding to reactor peak temperatures of 328.3, 360.7, 431.4, 444.7, 319.1, 344.7 and 330.9 °C. By utilizing the Antoine equation to determine the saturated vapor temperatures at these peak pressures, the calculated degrees of superheat were 265.0, 233.1, 303.1, 307.1, 198.5, 210.4 and 190.7 °C, respectively. The influence of ratio on product distribution at 270 °C is presented in Figure 3(b). In the absence of solvent (N/A), the products consisted entirely of solids formed by the melting and subsequent solidification of the plastic, indicating that negligible liquefaction occurred. As the reactant to solvent ratio decreased from 0.80 g/mL to N/A, the HDPE conversion improved gradually, achieving complete conversion at 0.80 g/mL with the products consisting primarily liquid oil and a small gaseous fraction. However, further reducing the ratio to 0.40 g/mL resulted in a precipitous decline in conversion, with the HDPE remaining largely unreacted. A clear correlation was observed between the degree of superheating and liquefaction efficiency, with higher superheat levels yielding superior results. Consequently, 0.80 g/mL was identified as the optimal reactant ratio for achieving a high oil yield under an external heating temperature of 270 °C. Given that plastics are inherently poor thermal conductors, excessively high reactant ratio likely hinder the solvent's heat transfer efficiency, thereby failing to drive effective depolymerization. Conversely, an overly low ratio might result in the solvent absorbing and transferring a disproportionate amount of heat away from the polymer, reducing the effective energy available for cracking under constant external heating. It is important to note that factors such as reaction temperature, pressure, solvent filling rate,

and the ratio reactant to methanol are highly coupled during solvothermal liquefaction process. Future work must focus on decoupling these factors to reveal the underlying mechanisms governing product evolution and the complex coupling between heat transfer and chemical reaction kinetics.

## 2.2 Characteristics of oil from HDPE liquefaction

### 2.2.1 Effect of reaction temperature on the characteristics of oil components

The chemical composition of HDPE-derived oil is illustrated in Figure 4, where alkanes are identified as the predominant components. This could be attributed to two main factors. First, the molecular structure of HDPE is characterized by a scarcity of tertiary carbons. The liquefaction was therefore initiated by the cleavage of C–C bonds along the primary polymer backbone, which inherently favored the formation of alkanes. Second, the concentrations of alkanes and alkenes exhibited a distinct temperature dependence with an inverse correlation. This reciprocal trend suggests that these two components underwent interconversion *via* hydrogenation and dehydrogenation reactions during the liquefaction process. At a setpoint value of 260 °C, the alkane content reached 62.3%, whereas the alkene content was significantly lower at 18.8%. This indicates that a substantial number of alkenes or polyethylene precursors were consumed to produce alkanes under these specific conditions. As a result, the oil product is characterized by high paraffinicity and low unsaturation<sup>[35]</sup>.

Hydrocarbons are the predominant constituents of the HDPE liquefaction oil, while the oxygenate content remains minimal. This suggests that methanol participated only sparingly in the primary reaction. As reported by Su et al.<sup>[36]</sup> polyethylene (PE) lacked the reactive sites necessary for extensive chemical interaction; consequently, the process was driven primarily by thermal cracking rather than hydrolysis. This accounted for the high hydrocarbon content and low oxygenate levels in the HDPE liquefaction oil.

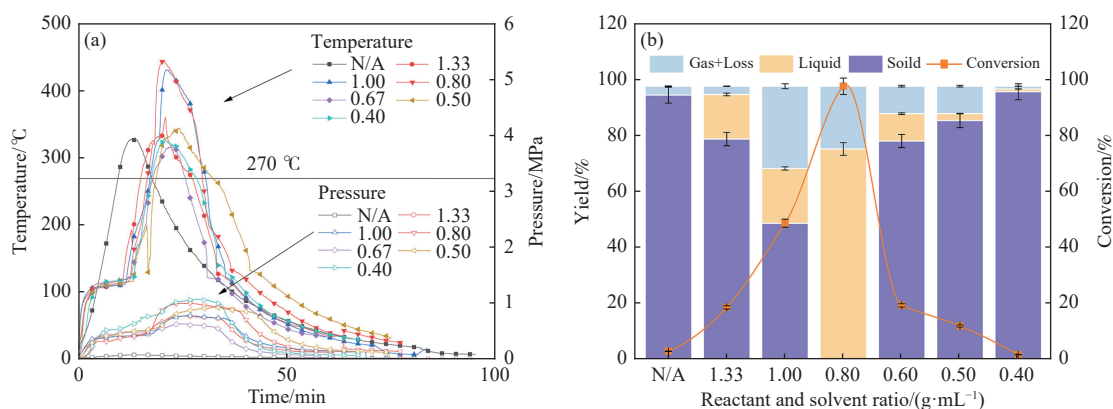


Fig. 3 Temperature-pressure curve and the effect of reactant ratio on product distribution and conversion

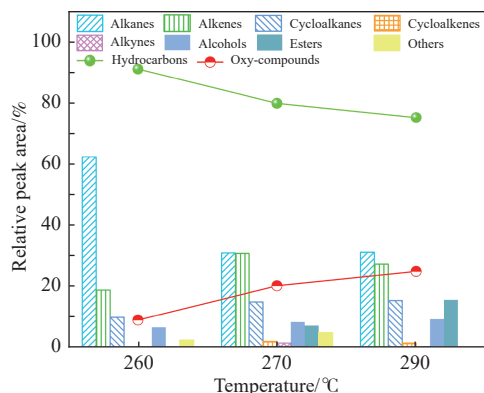


Fig. 4 Effect of setting reaction temperature on the distribution of oil components

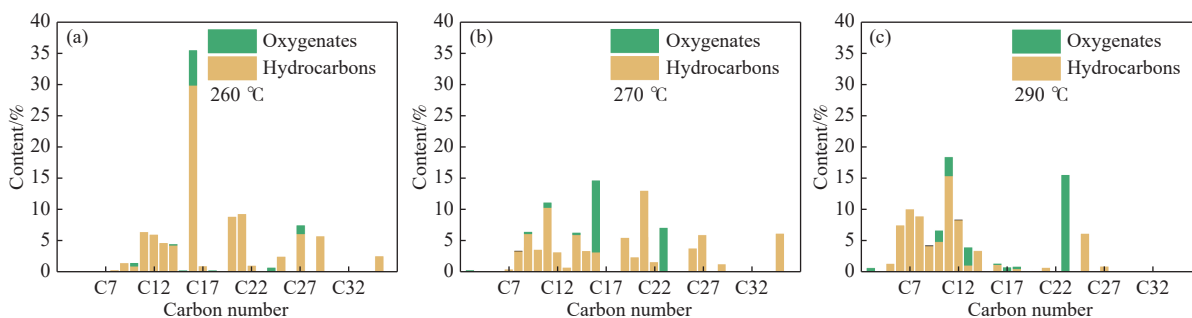
Among the oxygenates, alcohols and esters were the most abundant, indicating that alcoholysis occurred between the hydroxyl groups of methanol and the intermediates fragments generated from plastic cracking. Further, the relative concentration of oxygenated compounds increased with temperature, suggesting that higher temperature favored these alcoholysis reactions.

The carbon number distribution of the liquefaction oil at various target temperatures is illustrated in Figure 5. At target temperatures of 260 and 270 °C, the carbon numbers were primarily distributed within C8–C29, with a small fraction of hydrocarbon molecules containing up to 35 carbon atoms. Specifically, at 260 °C, C16 hydrocarbons represented the most abundant species. As the target temperature increased to 290 °C, the carbon number distribution shifted significantly to lower carbon numbers, ranging from C5 to C27. Within this range, hydrocarbons were predominantly concentrated between C5 and C16, while most oxygenated molecules consist of 23 carbon atoms. Overall, as the temperature rises, the carbon atom distribution became increasingly concentrated in the low range. This downward in the carbon number profile at 290 °C confirmed that higher reaction temperature effectively promoted further scission of the carbon chains.

The carbon number distribution of the hydrocarbon

compounds is categorized into specific ranges, as presented in Figure 5. As the target temperature increased from 260 to 290 °C, the gasoline-like fraction (C6–C12) rose significantly from 16.6% to 80.9%, while the diesel-like fraction (C13–C21) decreased from 63.7% to 9.7%. Simultaneously, the content of heavy hydrocarbons (C21+) followed a declining trend. These results indicate that an increase in temperature caused the carbon numbers of the hydrocarbons to concentrate within the C6–C12 range, which was accompanied by a reduction in the average molecular weight. This confirms that the elevated reaction temperatures facilitated the scission of C–C bonds in both HDPE and its intermediates, leading to the formation of shorter-chain hydrocarbons. In summary, the oil obtained from the low-pressure superheated methanol liquefaction of HDPE was characterized by high concentrations of gasoline and diesel fractions. Specifically, 260 °C was favorable for the production of diesel fractions, whereas 290 °C was conducive to the generation of gasoline fractions. Both products demonstrated significant potential for further upgrading into commercial fuels.

The elemental composition is presented in Figure 6. It is observed that the oils obtained from HDPE liquefaction at various reaction temperatures consistently exhibited high Higher Heating Values (HHV), ranging from 48.6 to 48.9 MJ/kg. These values were comparable to those of commercial gasoline and diesel, indicating substantial heat release during complete combustion when used as fuel. The carbon, hydrogen, and oxygen contents of the liquefaction oils were found to be 84.9%–85.3%, 14.0%–14.2% and 0.5%–0.6%, respectively. Compared to the raw feedstock, the hydrogen content in the oil increased slightly, while the oxygen slightly decreased. This suggests that the oxygen in the oil was more likely derived from the oxidized fractions of the original HDPE. Furthermore, the low-pressure superheated methanol liquefaction process facilitated the removal of oxygen elements from the HDPE. Additionally, methanol acted as a hydrogen donor in this process, thereby enhancing the hydrogen content of the resulting liquefaction oil<sup>[6]</sup>.



|        | C6–C12 | C13–C21 | C21+   |
|--------|--------|---------|--------|
| 260 °C | 16.61% | 63.72%  | 19.67% |
| 270 °C | 33.87% | 42.75%  | 23.38% |
| 290 °C | 80.93% | 9.73%   | 9.34%  |

Fig. 5 Effect of temperature on the product distribution with different carbon number in oil products and the percentage distribution across carbon number ranges

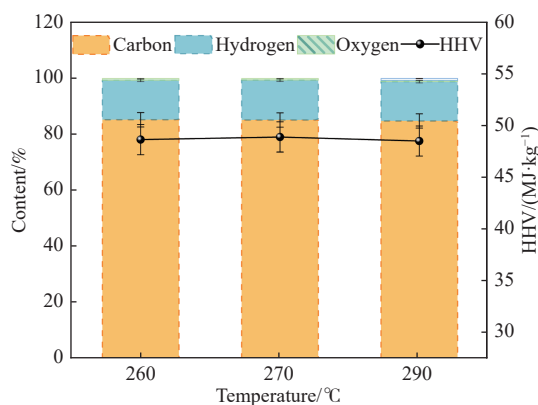


Fig. 6 Effect of setting reaction temperature on the element content and HHV of oils

### 2.2.2 Effect of reactant ratio on the characteristics of oil components

FT-IR spectroscopy was conducted to analyze the functional groups of the primary products obtained at various reactant ratio, and the results are illustrated in Figure 7. Data was illustrated according to [37]. HDPE exhibited alkane peaks only at  $2975\text{--}2800\text{ cm}^{-1}$  (C–H stretching vibration), approximately  $1465\text{ cm}^{-1}$  ( $\text{CH}_2$  bending vibration), and approximately  $720\text{ cm}^{-1}$  (rocking vibration of  $\geq 4\text{ CH}_2$  groups), confirming its long-chain saturated structure. Two critical alkene peaks at  $910\text{--}905\text{ cm}^{-1}$  (terminal alkene  $\text{--CH=CH}_2$  vibration) and  $980\text{--}965\text{ cm}^{-1}$  (trans-alkene vibration) were observed in the solid products. Simultaneously, an enhanced  $\text{CH}_3$  bending vibration was observed in the range of  $1853\text{--}1370\text{ cm}^{-1}$ , indicating that HDPE underwent chain scission to generate alkenes and short-chain alkanes. However, the persistence of  $720\text{ cm}^{-1}$  ( $\text{CH}_2$  rocking vibration) long-chain alongside the primary alkane peaks suggested that the chain scission was incomplete, leaving the products in a solid state. As the reactant concentration decreased, the intensities of the characteristic peaks at  $2975\text{--}2800\text{ cm}^{-1}$  (C–H stretching),  $1465\text{ cm}^{-1}$  ( $\text{CH}_2$  bending), and  $980\text{--}965\text{ cm}^{-1}$  (alkene) increased synchronously, signifying a deeper depolymerization degree. For the oil products, the alkene characteristic peaks ( $910\text{--}905$  and  $980\text{--}965\text{ cm}^{-1}$ ) and

significant  $\text{CH}_3$  vibrations ( $1853\text{--}1370\text{ cm}^{-1}$ ) were present. Long-chain peak at  $720\text{ cm}^{-1}$  completely disappeared. This confirms that the oil consisted of alkenes and alkanes with significantly lower molecular weights, demonstrating that pressurization effectively promoted deep depolymerization.

### 2.3 Mechanism of HDPE thermal liquefaction

HDPE is characterized by unbranched linear chains, and its degradation primarily involves the cleavage of C–C bonds at secondary carbon positions. The degradation process encompasses primary reactions, such as the depolymerization of macromolecules and the scission of C–C and C–H bonds, followed by secondary reactions of intermediates. These secondary processes included isomerization (yielding trans-olefins and iso-alkanes), recombination (resulting in broad product distributions), cyclization (forming cycloalkanes), dehydrogenation and hydrogenation. The latter explained the inverse correlation observed between alkane and alkene contents<sup>[34]</sup>. These secondary reactions occurred either through intramolecular interactions between different radicals on the same intermediate or *via* the intermolecular recombination of radicals from multiple intermediates<sup>[37–38]</sup>. Figure 8 illustrates the potential reaction pathways during the thermal liquefaction of HDPE. The polymer molecules first underwent depolymerization to form stable oligomers (Path a). Upon absorbing energy, these oligomers experience random scission of C–C and C–H bonds, generating various active radicals—primarily hydrogen radicals, methyl radicals, and alkyl radicals of varying lengths—to initiate secondary reactions (Path b). As shown in Path c, these radicals could undergo  $\beta$ -scission to yield olefins, cyclization to form cycloalkanes, or isomerization to generate alkyl radicals with diverse structures, which further recombined to produce hydrocarbons with complex carbon chain architectures. Notably, olefins could be further hydrogenated into saturated alkanes, while alkanes could also be converted back into olefins through dehydrogenation. Simultaneously, methanol acted as a source of hydroxyl groups, methyl groups, and hydrogen, participating in reactions with a portion of the generated hydrocarbons.

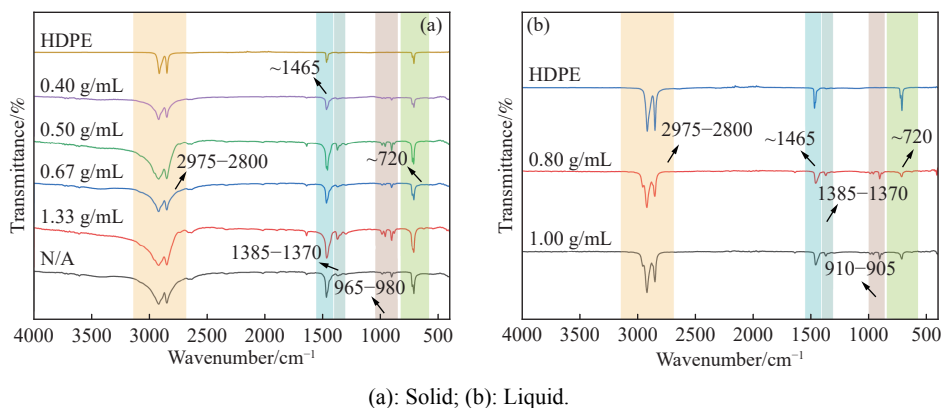


Fig. 7 Infrared spectra of products obtained under different reactant concentration

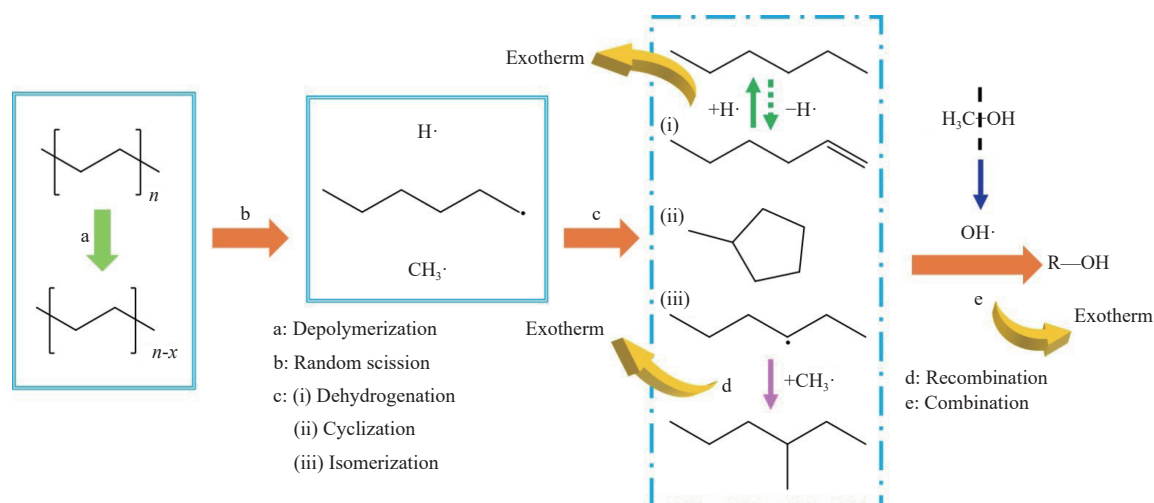


Fig. 8 Liquefaction reaction mechanism of HDPE in superheated methanol

### 3 Conclusions

This study investigated the thermal liquefaction of HDPE in a low-pressure superheated methanol system. It systematically analyzed the influences of reaction temperature and reactant dosage on the product distribution and characteristics. The main conclusions are listed as follows:

**Influence of Reaction Temperature:** Temperature exerted a decisive positive impact on the HDPE liquefaction. Below 260 °C, the conversion decreases significantly and the products were mainly solid. When the external temperature reached or exceeded 260 °C, complete conversion was achieved, yielding oil product. Furthermore, elevated temperatures favored the formation of alkenes and promoted the further scission of carbon chains.

**Optimal Reactant Dosage:** In the superheated methanol liquefaction of HDPE, the optimal reactant dosage at 270 °C was determined to be 0.80 g/mL. Deviations from this concentration (either excessively high or low) led to a decline in conversion, primarily due to the reduction in heat transfer efficiency.

**Liquefaction Mechanism:** The thermal liquefaction of HDPE was initiated by the preferential scission of secondary C–C bonds, which triggered the initial depolymerization. The resulting oligomers underwent further cracking to generate active free radicals; these intermediate species then participated in a suite of secondary reactions, including structural isomerization, cyclization, hydrogenation/dehydrogenation, and radical recombination, to form a diverse array of hydrocarbon products, such as alkenes, cycloalkanes, and iso-alkanes. Simultaneously, methanol served as a radical source, interacting with a portion of the nascent hydrocarbon fragments.

### Declaration of Competing Interest

The authors declare no conflict of interest.

### References

- ARMENISE S, SYIELUING W, RAMÍREZ-VELÁSQUEZ J M, et al. Plastic waste recycling via pyrolysis: A bibliometric survey and literature review[J]. J Anal Appl Pyrolysis, 2021, 158: 105265.
- LI Y Q, ZHAO Z G, LI T, et al. Influence of temperature, residence time, and solvent/feedstock mass ratio on overall product distribution and oil products quality in ethanol liquefaction of 230 polypropylene impact copolymer[J]. Fuel, 2022, 317: 123575.
- GEYER R, JAMBECK J R, LAW K L. Production, use, and fate of all plastics ever made[J]. Sci Adv, 2017, 3(7): e1700782.
- KWON G, CHO D W, PARK J, et al. A review of plastic pollution and their treatment technology: A circular economy platform by thermochemical pathway[J]. Chem Eng J, 2023, 464: 142771.
- SHEN M C, HUANG W, CHEN M, et al. (Micro)plastic crisis: Un-ignorable contribution to global greenhouse gas emissions and climate change[J]. J Clean Prod, 2020, 254: 120138.
- AZMAN D Q, DAUD W, PATAH M F A, et al. Plastic waste management through liquefaction in hydrogen donating solvents: A review[J]. J Environ Manage, 2024, 359: 120961.
- SERRANO D P, AGUADO J, VICENTE G, et al. Effects of hydrogen-donating solvents on the thermal degradation of HDPE[J]. J Anal Appl Pyrolysis, 2007, 78(1): 194–199.
- PEDERSEN T H, CONTI F. Improving the circular economy via hydrothermal processing of high-density waste plastics[J]. Waste Manage, 2017, 68: 24–31.
- BANIVAHEB S, GHALANDARI V, SMITH H, et al. SolvX: Solvothermal conversion of mixed waste plastics in supercritical toluene in presence of Pd/C catalyst[J]. J Environ Chem Eng, 2022, 10(6): 108622.
- AKIYA N, SAVAGE P E. Roles of water for chemical reactions in high-temperature water[J]. Chem Rev, 2002, 102(8): 2725–2750.
- HWANG G C, KIM K H, BAE S Y, et al. Degradation of

- high density polyethylene, polypropylene and their mixtures in supercritical acetone[J]. Korean J Chem Eng, 2001, 18(3): 396–401.
- [12] WANG Y M, ZHANG F S. Degradation of brominated flame retardant in computer housing plastic by supercritical fluids[J]. J Hazard Mater, 2012, 205: 156–163.
- [13] SHIN H-Y, BAE S-Y. Thermal decomposition of polystyrene in supercritical methanol[J]. J Appl Polym Sci, 2008, 108(6): 3467–3472.
- [14] HWANG G C, CHOI J H, BAE S Y, et al. Degradation of polystyrene in supercritical n-hexane[J]. Korean J Chem Eng, 2001, 18(6): 854–861.
- [15] SAW P A, MUHAMAD FAZLY A P, WAN DAUD W M A, et al. Thermochemical liquefaction of thermoplastic into fuel using toluene: Product distribution and behaviour[J]. Energy Convers Manage, 2025, 323: 119259.
- [16] LIU Y, AKULA K C, DANDAMUDI K P R, et al. Effective depolymerization of polyethylene plastic wastes under hydrothermal and solvothermal liquefaction conditions[J]. Chem Eng J, 2022, 446: 137238.
- [17] LACHOS-PEREZ D, JAN K, YU E, et al. Hydrothermal processing of polyethylene in superheated steam and supercritical water into fuels and chemicals[J]. Energy Convers Manage, 2025, 325: 119355.
- [18] MOHAMAD N, MOHAMAD YUSOF N N, YONG T L-K. Furfural production under subcritical alcohol conditions: Effect of reaction temperature, time, and types of alcohol[J]. J Jpn Inst Energy, 2017, 96(8): 279–284.
- [19] ZHAO P, YUAN Z, SONG X, et al. Product characteristics and synergy study on supercritical methanol liquefaction of lignocellulosic biomass and plastic[J]. ACS Sustainable Chem Eng, 2021, 9(50): 17103–17111.
- [20] OKAJIMA I, HIRAMATSU M, SHIMAMURA Y, et al. Chemical recycling of carbon fiber reinforced plastic using supercritical methanol[J]. J Supercrit Fluids, 2014, 91: 68–76.
- [21] GOTO M, SASAKI M, HIROSE T. Reactions of polymers in supercritical fluids for chemical recycling of waste plastics[J]. J Mater Sci, 2006, 41(5): 1509–1515.
- [22] ZHANG H, KONG D, WANG L, et al. Degradation of UV-pretreated polyolefins by latex clearing protein from *Streptomyces* sp. Strain K30[J]. Sci Total Environ, 2022, 806(Pt 4): 150779.
- [23] FAN Y V, JIANG P, TAN R R, et al. Forecasting plastic waste generation and interventions for environmental hazard mitigation[J]. J Hazard Mater, 2022, 424: 127330.
- [24] ZHAO P, FU B, ZHAO Q, et al. Thermal decomposition of plastics via low pressure and superheated solvent steam and its characteristics[J]. Chem Ind Eng Prog, 2024, 43(6): 3420–3429.
- [25] ZHAO B J, WANG H Y, HU Y L, et al. Hydrothermal Co-liquefaction of lignite and lignocellulosic biomass with the addition of formic acid: Study on product distribution, characteristics, and synergistic effects[J]. Ind Eng Chem Res, 2020, 59(50): 21663–21675.
- [26] FU B, GENG L, JIA G, et al. Effects of operating conditions on supercritical methanol liquefaction of polypropylene[J]. J Environ Chem Eng, 2023, 11(3): 110008.
- [27] PANG Y, ZHU X, SUN Y, et al. Research on co-gasification of polyethylene and cellulose via reactive molecular dynamics simulation[J]. J Energy Inst, 2023, 111: 101382.
- [28] IRAWAN A, KURNIAWAN T, NURKHOLIFAH N, et al. Pyrolysis of polyolefins into chemicals using low-cost natural zeolites[J]. Waste Biomass Valorization, 2023, 14(5): 1705–1719.
- [29] SAEAUNG K, PHUSUNTI N, PHETWAROTAI W, et al. Catalytic pyrolysis of petroleum-based and biodegradable plastic waste to obtain high-value chemicals[J]. Waste Manage, 2021, 127: 101–111.
- [30] MAZLOUM S, AWAD S, ALLAM N, et al. Modelling plastic heating and melting in a semi-batch pyrolysis reactor[J]. Appl Energy, 2021, 283: 116375.
- [31] HU Q, TANG Z Y, YAO D D, et al. Thermal behavior, kinetics and gas evolution characteristics for the co-pyrolysis of real-world plastic and tyre wastes[J]. J Clean Prod, 2020, 260: 121102.
- [32] CHENG L, ZHANG Y, WANG Y, et al. Pyrolysis of long chain hydrocarbon-based plastics via self-exothermic effects: The origin and influential factors of exothermic processes[J]. J Hazard Mater, 2022, 424: 127476.
- [33] ZHANG Y, CHEN X, CHENG L, et al. Conversion of polyethylene to high-yield fuel oil at low temperatures and atmospheric initial pressure[J]. Int J Environ Res Public Health, 2023, 20(5): 4048.
- [34] CHENG L, GU J, WANG Y, et al. Polyethylene high-pressure pyrolysis: Better product distribution and process mechanism analysis[J]. Chem Eng J, 2020, 385: 123866.
- [35] KUMARI A, KUMAR S. Pyrolytic degradation of polyethylene in autoclave under high pressure to obtain fuel[J]. J Anal Appl Pyrolysis, 2017, 124: 298–302.
- [36] SU X, ZHAO Y, ZHANG R, et al. Investigation on degradation of polyethylene to oils in supercritical water[J]. Fuel Process Technol, 2004, 85(8): 1249–1258.
- [37] ZHU M H, HU P. Instrumental Analysis[M]. 4th ed. Beijing: Higher Education Press, 2008: 304–305.
- [38] VICENTE G, AGUADO J, SERRANO D P, et al. HDPE chemical recycling promoted by phenol solvent[J]. J Anal Appl Pyrolysis, 2009, 85(1): 366–371.

## 低压过热态甲醇环境中聚乙烯液化油特性研究

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**摘要:** 塑料的不当处置导致资源浪费与环境污染, 塑料污染已成为全球性环境挑战。本研究以高密度聚乙烯(High-density polyethylene, HDPE)为原料, 甲醇为溶剂, 探究其在低压过热态甲醇环境下的热液化行为, 分析了反应温度与反应物浓度对 HDPE 液化效率及产物特性的影响规律。结果表明, 在低压(<0.5 MPa)过热态甲醇中, HDPE 可被高效液化, 其完全转化的最低外热源温度为 260 °C, 此时油产率达 77.1%。油相产物以烷烃为主, 含量达 62.3%, 含氧化合物较少, 且烃类平均碳原子数随热源温度的升高而减小。温度低于 260 °C 时, HDPE 转化率显著降低, 产物以蜡状固体为主; 而温度升至 290 °C 时, 油中类汽油馏分(C6-C12)占比从 16.6% 大幅提升至 80.9%。浓度对 HDPE 液化过程具有显著调控作用, 浓度过高或过低会因传热效率降低而导致转化率下降。HDPE 热液化始于仲碳 C-C 键断裂, 生成的低聚物进一步裂解为自由基, 并通过二次反应形成多样化烃类。本研究证实低压过热态甲醇热液化技术具有反应条件温和、无需预处理、产物品质高等优势, 为混合塑料回收提供了可行路径。未来通过进一步优化工艺参数, 有望推动其工业化应用, 助力塑料污染治理与资源循环利用。

**关键词:** 废塑料; 聚丙烯; 低压过热态甲醇; 热液化; 油

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