



MAXIMIZING LIQUID PRODUCT YIELD FROM PLASTIC WASTE PYROLYSIS THROUGH EXPERIMENTAL OPTIMIZATION OF PROCESS CONDITIONS

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Abstract. This study investigates the experimental optimization of plastic waste pyrolysis for maximizing liquid product yield using low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) as feedstocks and ZSM-5 as a catalyst. Pyrolysis experiments were carried out over a temperature range of 150-700 °C, while the ZSM-5 loading was varied from 1 to 10% relative to the mass of the plastic feedstock. The influence of temperature, polymer type, and catalyst concentration on the formation of liquid, gaseous, and solid products was systematically evaluated. The results showed that increasing the temperature up to 500 °C significantly enhanced the formation of condensable hydrocarbons, whereas further temperature increases promoted secondary cracking and increased gas formation. Under non-catalytic conditions, the liquid yields of LDPE, HDPE, and PP were 79.8, 76.5, and 82.3%, respectively. The optimum ZSM-5 loading was determined to be 5%, providing maximum liquid yields of 87.4% for LDPE, 84.6% for HDPE, and 89.5% for PP. These findings demonstrate that controlled catalytic pyrolysis can effectively enhance the conversion of polyolefin waste into valuable liquid hydrocarbons and may provide a promising approach for plastic waste valorization and alternative hydrocarbon feedstock production.

Keywords: plastic waste, pyrolysis, LDPE, HDPE, polypropylene, ZSM-5, liquid product, catalytic pyrolysis, process optimization.

Annotatsiya. Ushbu tadqiqotda past zichlikli polietilen (LDPE), yuqori zichlikli polietilen (HDPE) va polipropilen (PP) chiqindilarini piroliz qilish jarayonida suyuq mahsulot chiqishini maksimal darajada oshirish maqsadida tajriba sharoitlari optimallashtirildi. Katalizator sifatida ZSM-5 seolitidan foydalanildi. Piroliz jarayoni 150-700 °C harorat oralig‘ida olib borildi, ZSM-5 katalizatorining miqdori esa plastik xomashyo

massasiga nisbatan 1-10% oraliq‘ida o‘zgartirildi. Harorat, polimer turi va katalizator miqdorining suyuq, gazsimon hamda qattiq mahsulotlar hosil bo‘lishiga ta’siri tizimli ravishda o‘rganildi. Natijalar 500 °C gacha haroratning oshishi kondensatlanadigan uglevodorodlar hosil bo‘lishini sezilarli darajada kuchaytirishini, undan yuqori haroratlarda esa ikkilamchi kreking natijasida gaz mahsulotlari ulushi ortishini ko‘rsatdi. Katalizatorsiz sharoitda LDPE, HDPE va PP uchun suyuq mahsulot chiqishi mos ravishda 79,8, 76,5 va 82,3% ni tashkil etdi. ZSM-5 ning optimal miqdori 5% deb aniqlandi va bunda maksimal suyuq mahsulot chiqishi LDPE uchun 87,4%, HDPE uchun 84,6%, PP uchun esa 89,5% ga yetdi. Olingan natijalar katalitik piroliz poliolefin chiqindilarini qimmatli suyuq uglevodorodlarga samarali aylantirish imkonini berishini ko‘rsatdi.

Kalit so‘zlar: plastik chiqindilar, piroliz, LDPE, HDPE, polipropilen, ZSM-5, suyuq mahsulot, katalitik piroliz, jarayonni optimallashtirish.

Аннотация. В настоящем исследовании проведена экспериментальная оптимизация процесса пиролиза пластиковых отходов с целью максимального увеличения выхода жидких продуктов. В качестве исходного сырья использовали отходы полиэтилена низкой плотности (LDPE), полиэтилена высокой плотности (HDPE) и полипропилена (PP), а в качестве катализатора применяли цеолит ZSM-5. Пиролиз осуществляли в диапазоне температур 150-700 °C, при этом содержание катализатора ZSM-5 варьировали от 1 до 10% относительно массы пластикового сырья. Систематически исследовано влияние температуры, типа полимера и количества катализатора на распределение жидких, газообразных и твердых продуктов. Установлено, что повышение температуры до 500 °C способствует увеличению образования конденсируемых углеводородов, тогда как дальнейшее повышение температуры усиливает вторичный крекинг и образование газообразных продуктов. В некаталитических условиях выход жидких продуктов для LDPE, HDPE и PP составил соответственно 79,8, 76,5 и 82,3%. Оптимальное содержание ZSM-5 составило 5%, при котором максимальный выход жидкого продукта достиг 87,4% для LDPE, 84,6% для HDPE и 89,5% для PP. Полученные результаты показывают, что контролируемый каталитический пиролиз является эффективным способом переработки полиолефиновых отходов в ценные жидкие углеводороды.

Ключевые слова: пластиковые отходы, пиролиз, LDPE, HDPE, полипропилен, ZSM-5, жидкий продукт, каталитический пиролиз, оптимизация процесса.

INTRODUCTION. The rapid growth in plastic production and consumption has created one of the most serious solid-waste management challenges worldwide [1]. Plastics are widely used because of their low cost, low density, chemical resistance, durability, and versatility, however, these same characteristics also cause their long-term persistence in the environment [2]. According to the Organisation for Economic Co-operation and Development (OECD), global plastic production increased from 234 million tonnes in 2000 to approximately 460 million tonnes in 2019, while plastic waste generation more than doubled from 156 million tonnes to 353 million tonnes during the same period [3-4]. Of the

plastic waste generated in 2019, only approximately 9% was successfully recycled, whereas 19% was incinerated, nearly 50% was landfilled, and about 22% was mismanaged, including uncontrolled dumping, open burning, and leakage into terrestrial and aquatic environments [5].

More recent data indicate that the problem continues to intensify. The United Nations Environment Programme (UNEP) reported that approximately 400 million tonnes of plastic waste were generated globally in 2024, with plastic packaging accounting for about 50% of the total plastic waste stream [6]. Without substantial improvements in waste prevention, collection, reuse, and recycling, the OECD projects that global plastic waste generation could increase from 353 million tonnes in 2019 to approximately 1,014 million tonnes by 2060, representing almost a threefold increase [7]. Under the baseline scenario, only about 17% of plastic waste is expected to be recycled by 2060, while landfilling will continue to account for approximately half of global plastic waste [8]. These trends demonstrate the urgent need for alternative technologies capable of recovering both material and energy value from plastic waste that cannot be effectively processed through conventional mechanical recycling [9].

Among the available chemical recycling technologies, pyrolysis has attracted considerable attention because of its ability to convert plastic waste into liquid hydrocarbons, combustible gases, and carbonaceous residues in the absence of oxygen [10]. The process is particularly suitable for polyolefin-rich waste streams such as polyethylene (PE) and polypropylene (PP), which possess high hydrogen and carbon contents and can therefore generate substantial amounts of hydrocarbon-rich liquid products. Recent assessments indicate that plastic-waste pyrolysis can typically convert approximately 60-80 % of the feedstock into liquid products, while optimized fast-pyrolysis systems have achieved liquid yields approaching 85% at temperatures of approximately 450-600 °C. For polyethylene specifically, reported liquid yields are commonly in the range of 80-88% at temperatures between 350 and 500 °C, although the actual distribution of liquid, gas, wax, and solid fractions strongly depends on polymer composition and operating conditions [11].

Despite its considerable potential, obtaining a high liquid-product yield from plastic pyrolysis remains strongly dependent on the control of process parameters. Reaction temperature, residence time, heating rate, feedstock composition, particle size, reactor configuration, pressure, and condensation efficiency can significantly alter the extent of primary polymer degradation and secondary cracking reactions [12]. Temperature is particularly important because insufficient temperatures may result in incomplete decomposition and increased wax or solid formation, whereas excessively high temperatures promote secondary cracking of condensable hydrocarbons into permanent gases [13]. Experimental studies on mixed plastic waste have therefore frequently identified an intermediate temperature region as favorable for maximizing condensable products. For example, studies of mixed plastic pyrolysis have identified approximately 500 °C as an effective temperature for maximizing the liquid fraction, although the optimum value depends considerably on feedstock composition and reactor configuration [14].

The importance of simultaneous process optimization has also been demonstrated quantitatively. In a 2024 experimental study using a mixture of HDPE, PP, and PS, temperature was varied from 460 to 540 °C, residence time from 30 to 150 min, and feedstock particle size from 5 to 45 mm. Response surface methodology showed that temperature and residence time had the greatest influence on liquid production, followed by particle size. Under optimized conditions of 535.96 °C, 150 min residence time, and a particle size of 23.99 mm, a maximum liquid-oil yield of 75.14 % was obtained. Other experimental optimization studies reported even higher liquid fractions under specific feedstock and operating conditions, including liquid yields above 80-90 %, demonstrating that product distribution can be substantially shifted toward the liquid phase when the main operating parameters are appropriately controlled [15].

Therefore, the present study focuses on the experimental optimization of plastic-waste pyrolysis conditions with the primary objective of maximizing liquid-product yield. The influence of the main process parameters on the distribution of liquid, gaseous, and solid products is systematically evaluated to determine operating conditions favorable for enhanced production of pyrolysis oil. By increasing the conversion of waste plastics into recoverable liquid hydrocarbons, the study aims to contribute to the development of a more efficient waste-to-resource approach, reduce the amount of plastic directed to landfills or uncontrolled disposal, and provide a potential secondary hydrocarbon feedstock for subsequent fuel or petrochemical applications.

MATERIALS AND METHODS

Materials

Waste low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) were used as the raw materials for the pyrolysis experiments. Before use, the plastic wastes were cleaned to remove visible contaminants, dried, and reduced to suitable particle sizes to ensure more uniform heat transfer during thermal decomposition.

Commercial ZSM-5 zeolite was used as the catalyst. The amount of ZSM-5 was varied from 1 to 10 % relative to the mass of the plastic feedstock in order to evaluate the influence of catalyst loading on the distribution of pyrolysis products, with particular attention to maximizing the liquid fraction.

Preparation of Plastic Feedstock

LDPE, HDPE, and PP wastes were prepared prior to pyrolysis by removing foreign materials and surface impurities. The samples were subsequently dried and cut into smaller pieces to improve thermal contact and obtain reproducible experimental conditions.

The three polymer types were investigated under identical experimental conditions to evaluate differences in their thermal decomposition behavior and liquid-product formation. For catalytic experiments, the required amount of ZSM-5 corresponding to 1-10% of the plastic mass was introduced into the experimental system.

Pyrolysis Experiments

Pyrolysis experiments were performed over a temperature range of 150–700 °C under oxygen-limited conditions. The wide temperature interval was selected to investigate the

complete thermal behavior of LDPE, HDPE, and PP, including initial softening, thermal degradation, formation of condensable hydrocarbons, and secondary cracking at elevated temperatures.

For each experiment, a known mass of plastic feedstock was introduced into the pyrolysis reactor. The reactor was heated to the selected temperature, and the volatile products generated during polymer decomposition were transferred from the reaction zone to the condensation system.

At relatively low temperatures, polymer decomposition was limited and a substantial fraction of the feed remained undecomposed or was converted into wax-like products. With increasing temperature, thermal cracking became more intensive and the formation of volatile hydrocarbons increased. At higher temperatures, particularly toward the upper part of the investigated 150-700 °C range, secondary cracking of condensable hydrocarbons into lighter gaseous products was expected to become increasingly important.

Experiments were first carried out without catalyst to establish the thermal pyrolysis behavior of LDPE, HDPE, and PP. Catalytic pyrolysis experiments were subsequently conducted using ZSM-5 loadings ranging from 1 to 10%. All other operating parameters were maintained constant when evaluating the influence of catalyst concentration.

Catalytic Pyrolysis Using ZSM-5

The influence of ZSM-5 on plastic-waste conversion was investigated systematically by varying the catalyst loading within the range of - 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 % relative to the initial plastic mass.

The purpose of varying the catalyst loading was to determine the amount of ZSM-5 that provides the most favorable balance between polymer cracking and liquid-product formation. At low catalyst concentrations, the number of accessible catalytic active sites may be insufficient for effective conversion of pyrolysis vapors. Conversely, excessive catalyst loading can enhance secondary cracking reactions, resulting in increased formation of light gaseous hydrocarbons and a corresponding reduction in the recoverable liquid fraction.

Therefore, the catalyst-loading experiments were designed specifically to identify the ZSM-5 concentration that maximizes the yield of condensable liquid hydrocarbons.

Collection of Pyrolysis Products

The products obtained during pyrolysis were separated into three main fractions:

1. liquid product (pyrolysis oil);
2. non-condensable gaseous products;
3. solid residue.

The volatile products leaving the reactor were cooled in the condensation system. Condensable hydrocarbons were collected as the liquid fraction, while non-condensable gases passed through the condensation unit.

After completion of each experiment, the reactor was cooled and the remaining

For catalytic experiments, the initial mass of ZSM-5 was excluded from the mass of the solid pyrolysis residue when determining the actual solid-product yield.

Experimental Optimization

The experimental study was designed to determine the optimum conditions for maximizing the liquid-product yield from LDPE, HDPE, and PP pyrolysis. Two major operating variables were systematically evaluated:

- pyrolysis temperature: 150-700 °C;
- ZSM-5 catalyst loading: 1-10%.

The influence of temperature was evaluated by comparing the yields of liquid, gaseous, and solid products obtained at different thermal conditions. Subsequently, the effect of ZSM-5 concentration was examined to determine the catalyst loading that provided the maximum liquid-product yield.

The optimum condition was defined as the combination of pyrolysis temperature and catalyst loading at which the highest yield of condensable liquid product was obtained while minimizing excessive formation of non-condensable gases and solid residues.

RESULTS AND DISCUSSION

The experimental results obtained from the pyrolysis of LDPE, HDPE, and PP were evaluated to determine the influence of process temperature on the formation of liquid products. Particular attention was given to identifying the temperature range favorable for maximizing the condensable hydrocarbon fraction while limiting excessive gas formation and incomplete decomposition.

The effect of pyrolysis temperature on the liquid-product yield of LDPE, HDPE, and PP is presented in Table 1. These data were used to compare the thermal behavior of the three polymer types and to determine the most favorable temperature region for subsequent catalytic experiments with ZSM-5.

Table 1.

Effect of pyrolysis temperature on liquid product yield

Temperature, °C	LDPE liquid yield, %	HDPE liquid yield, %	PP liquid yield, %
150	2.4	1.8	3.1
250	8.7	6.5	10.2
350	36.8	31.4	41.7
400	58.6	53.9	62.8
450	72.4	68.7	75.9
500	79.8	76.5	82.3
550	75.6	72.1	77.8
600	68.2	65.4	70.3
650	59.7	57.2	61.8
700	50.8	48.6	53.1

The results presented in Table 1 show that pyrolysis temperature had a significant influence on the liquid-product yield of LDPE, HDPE, and PP. For all three polymers, the liquid fraction increased progressively with increasing temperature up to approximately 500 °C, indicating more effective thermal decomposition and conversion of the polymer chains into condensable hydrocarbons. Above this temperature, the liquid yield decreased, which can be attributed to intensified secondary cracking of heavier hydrocarbon vapors into lighter non-condensable gaseous products. Among the investigated polymers, PP showed the highest tendency toward liquid-product formation, followed by LDPE and HDPE. Based on these

observations, 500 °C was selected as the optimum temperature for further evaluation of product distribution, and the corresponding liquid, gas, and solid yields are presented in Table 2.

Table 2.

Product distribution at the optimum pyrolysis temperature of 500 °C

Plastic type	Liquid, %	Gas, %	Solid residue, %
LDPE	79.8	17.6	2.6
HDPE	76.5	20.4	3.1
PP	82.3	15.8	1.9

At 500 °C, PP produced the highest liquid yield (82.3 %), followed by LDPE (79.8 %) and HDPE (76.5 %). The corresponding gas and solid fractions remained comparatively low, confirming that this temperature favored the formation of condensable products. The effect of ZSM-5 catalyst loading on the liquid-product yield is presented in Table 3.

Table 3.

Effect of ZSM-5 catalyst loading on liquid product yield at 500 °C

ZSM-5 loading, %	LDPE, %	HDPE, %	PP, %
0	79.8	76.5	82.3
1	81.2	78.1	83.6
2	82.8	79.7	85.1
3	84.6	81.4	86.7
4	86.1	83.0	88.2
5	87.4	84.6	89.5
6	86.8	84.1	88.9
7	85.5	82.9	87.4
8	83.9	81.5	85.8
9	82.1	79.8	83.9
10	80.3	78.2	82.1

The results presented in Table 3 demonstrate that ZSM-5 loading strongly influenced the liquid-product yield of LDPE, HDPE, and PP during catalytic pyrolysis at 500 °C. For all three polymers, the liquid yield increased gradually as the catalyst concentration was raised from 1 to 5 %, indicating that the presence of ZSM-5 enhanced the conversion of polymer-derived intermediates into condensable hydrocarbon products.

For LDPE, the liquid-product yield increased from 79.8 % without catalyst to 87.4 % at 5 % ZSM-5. A similar tendency was observed for HDPE, where the yield increased from 76.5 to 84.6 %. These results suggest that moderate catalyst loading improved cracking efficiency and promoted the formation of hydrocarbons suitable for condensation.

PP exhibited the highest liquid-product yield among all investigated polymer types. Its liquid fraction increased from 82.3 % in non-catalytic pyrolysis to 89.5 % at 5 % ZSM-5, showing a particularly favorable response to catalytic treatment. This behavior may be associated with the branched molecular structure of PP, which facilitates thermal and catalytic chain scission.

Based on the experimental results, 5% ZSM-5 was identified as the optimum catalyst loading for maximizing liquid-product formation under the investigated conditions. The

optimum pyrolysis conditions and the corresponding improvements in liquid-product yield for LDPE, HDPE, and PP are summarized in Table 4.

Table 4.

Comparison of optimum pyrolysis conditions and product yields

Parameter	LDPE	HDPE	PP
Optimum temperature, °C	500	500	500
Optimum ZSM-5 loading, %	5	5	5
Liquid yield without catalyst, %	79.8	76.5	82.3
Maximum liquid yield with ZSM-5, %	87.4	84.6	89.5
Increase in liquid yield, percentage points	+7.6	+8.1	+7.2
Relative improvement, %	9.5	10.6	8.7
Best-performing polymer	-	-	PP

The results summarized in Table 4 confirm that the optimum conditions for maximizing liquid-product yield were 500 °C and 5 wt% ZSM-5 for all three polymers. Under these conditions, the liquid yield increased from 79.8 to 87.4 wt% for LDPE, from 76.5 to 84.6 wt% for HDPE, and from 82.3 to 89.5 wt% for PP, corresponding to relative improvements of 9.5%, 10.6%, and 8.7%, respectively. Although HDPE showed the greatest relative improvement after catalyst addition, PP achieved the highest absolute liquid-product yield, indicating its greater suitability for producing a high fraction of condensable hydrocarbons under the optimized pyrolysis conditions.

CONCLUSION

The present study demonstrated that the liquid-product yield from the pyrolysis of LDPE, HDPE, and PP can be significantly improved through optimization of process temperature and ZSM-5 catalyst loading. The experimental results showed that 500 °C was the most favorable temperature for maximizing the formation of condensable hydrocarbons, while temperatures above this value promoted secondary cracking and increased gas formation. Among the investigated polymers, PP exhibited the highest liquid-product yield under both thermal and catalytic conditions.

The addition of ZSM-5 enhanced liquid-product formation up to an optimum catalyst loading of 5%. Under these conditions, the maximum liquid yields reached 87.4% for LDPE, 84.6% for HDPE, and 89.5% for PP, compared with 79.8, 76.5, and 82.3%, respectively, in the absence of catalyst. Further increases in catalyst loading above 5 wt% resulted in a gradual reduction in liquid yield due to intensified secondary cracking of condensable hydrocarbons into lighter gaseous products.

Overall, the combination of 500 °C pyrolysis temperature and 5% ZSM-5 was identified as the optimum condition for maximizing liquid-product recovery from the investigated plastic wastes. The obtained results indicate that controlled catalytic pyrolysis can provide an effective route for converting polyolefin waste into valuable liquid hydrocarbon products and may contribute to the development of more efficient plastic-waste valorization and alternative hydrocarbon feedstock production technologies.

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