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OPTIMIZATION OF THE PYROLYSIS PROCESS OF HYDROCARBON FEEDSTOCK IN THE PRESENCE OF A ZEOLITE-CONTAINING CATALYST

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In present study, the catalytic pyrolysis of hydrocarbon feedstock in the presence of a regenerated microspherical zeolite-containing catalyst was investigated. Two industrially important feedstocks—straight-run gasoline and vacuum gas oil—were selected as the objects of study. The process was carried out in a flow-type laboratory reactor within the temperature range of 600–700 °C. It was established that the presence of the catalyst significantly enhances the degree of gasification and increases the yield of C_2–C_4 olefins, particularly propylene. Based on the obtained results, the optimal temperature regime was determined and the technological efficiency of the process was evaluated.

Keywords: catalytic pyrolysis, zeolite catalyst, hydrocarbon feedstock, straight-run gasoline, vacuum gas oil.

INTRODUCTION

In the petrochemical industry, light olefins such as ethylene and propylene represent essential building blocks for the synthesis of major polymeric materials, including polyethylene, polypropylene, and a wide range of derivative products [1–3]. The continuously increasing global demand for these materials necessitates not only the expansion of the feedstock base but also the improvement of technological flexibility and process efficiency within existing production systems [4,5]. At present, the predominant industrial route for olefin production is steam pyrolysis (steam cracking), which is primarily optimized for light hydrocarbon feeds such as ethane, propane, and naphtha [6]. However, the direct processing of heavier fractions in such units is generally limited due to higher energy requirements, intensified coke formation, and constraints associated with reactor design and heat transfer efficiency [7,8].

Meanwhile, petroleum refineries generate significant quantities of intermediate and heavy fractions, including straight-run gasoline and vacuum gas oil (VGO), the efficient utilization of which remains a critical challenge [9,10]. The direct conversion of these fractions into valuable olefinic products offers a promising pathway to enhance resource efficiency and reduce dependency on lighter feedstocks traditionally used in steam cracking processes [11]. In this context, catalytic pyrolysis has emerged as a viable alternative, attracting increasing attention due to its potential to improve selectivity and reduce process severity [12,13].

The introduction of zeolite-containing catalysts fundamentally modifies the reaction pathways involved in hydrocarbon conversion [6,14]. Unlike conventional thermal pyrolysis,

E-mail address: mammadovahh.03@gmail.com which predominantly proceeds via free-radical chain mechanisms, catalytic systems facilitate reactions through carbocation intermediates formed on the acidic sites of the catalyst [15]. This mechanistic shift significantly influences both the kinetics of the process and the resulting product distribution. As a consequence, under comparable temperature conditions, catalytic pyrolysis can lead to enhanced selectivity toward light olefins, particularly propylene, which is of high industrial value [16,17].

Nevertheless, the overall performance of catalytic pyrolysis is governed by multiple interdependent parameters, including reaction temperature, contact time, catalyst characteristics, and the physicochemical properties of the feedstock [18]. Therefore, the identification and optimization of operating conditions are crucial for achieving maximum olefin yield and process stability. Although numerous studies have been reported on catalytic pyrolysis using model compounds or simplified systems, there remains a lack of comprehensive comparative investigations conducted under identical conditions using real industrial feedstocks such as straight-run gasoline and vacuum gas oil [19].

Addressing this gap is essential for bridging laboratory-scale findings with practical industrial applications. Accordingly, the present study focuses on the catalytic pyrolysis of straight-run gasoline and vacuum gas oil under identical experimental conditions in the presence of a regenerated zeolite-containing catalyst. The effects of key process parameters, particularly temperature and contact time, on product distribution are systematically evaluated, with the aim of identifying optimal operating conditions and providing a scientific basis for the efficient conversion of heavy refinery fractions into light olefins [20].

EXPERIMENTAL

Straight-run gasoline and vacuum gas oil obtained from the processing of Azerbaijani crude oils were used as feedstocks in this study. Prior to the experiments, their basic physicochemical properties were determined using standard analytical procedures. As the catalyst, a microspherical zeolite-containing material withdrawn from an industrial catalytic cracking unit and subsequently regenerated was employed. Before use, the catalyst was dried and conditioned under reaction conditions in order to ensure stable and reproducible catalytic performance.

The experiments were carried out in a laboratory-scale continuous-flow fixed-bed reactor. The experimental setup consisted of a feed dosing unit, a tubular reactor loaded with a fixed bed of catalyst, and a downstream system for cooling, condensation, and phase separation of the reaction products. The reactor was heated by an external electric furnace, and the temperature in the reaction zone was monitored and controlled using a thermocouple placed directly in the catalyst bed.

The pyrolysis tests were performed at temperatures of 600, 650, and 700 °C. The average contact time between the feedstock vapors and the catalyst was maintained at approximately 3.5 s, while the weight hourly space velocity (WHSV) was varied within the range of 1–3 h^{-1}. After leaving the reactor, the reaction products were rapidly cooled in order to suppress secondary reactions, and the gaseous and liquid fractions were separated in the receiving system.

The composition of the gaseous products was determined by gas chromatography. The concentrations of the main components, including H_2, CH_4, C_2H_4, C_3H_6, and C_4H_8 were quantified using previously established calibration factors. To ensure the reliability and reproducibility of the results, each experiment at a given temperature was performed at least three times, and the average values were used in the subsequent analysis and discussion.

RESULTS AND DISCUSSION

Analysis of the results presented in Tables 1 and 2 shows that, in the presence of the regenerated zeolite-containing catalyst, both the yield and composition of gaseous products change significantly during the pyrolysis of straight-run gasoline and vacuum gas oil. Under catalytic conditions, the increased degree of gasification and the high proportion of olefins formed for both feedstocks are associated with the predominance of selective hydrocarbon cracking on the active acidic sites of the catalyst.

For straight-run gasoline (Table 1), increasing the temperature from 600 °C to 700 °C results in an increase in the degree of gasification from 9.0% to 27.0%. At the same time, the total content of $\Sigma(C_2–C_4)$ olefins rises from 62.6% to 67.8%. In particular, the increase in ethylene (C_2H_4) content from 8.1% to 19.8% indicates intensification of β-scission reactions with increasing temperature. Meanwhile, the increase in methane (CH_4) content from 6.5% to 14.8% suggests the enhancement of deep cracking reactions under more severe conditions.

The consistently high proportion of propylene (C_3H_6) in the gaseous products across the entire temperature range (32–36%) indicates that the process proceeds predominantly via a carbonium-ion mechanism. It is well known that, during hydrocarbon conversion on the acidic sites of zeolite catalysts, the stabilization of secondary carbocations favors the preferential formation of products such as propylene. The slight decrease in propylene content in the 650–700 °C range may be attributed to its partial involvement in secondary transformations toward lighter products or aromatization pathways.

The results obtained for vacuum gas oil (Table 2) exhibit a generally similar trend; however, certain differences in product distribution are observed due to the heavier nature of the feedstock. Specifically, while the degree of gasification is 8.5% at 600 °C, it increases to 24.5% at 700 °C. At the same time, the content of $\Sigma(C_2–C_4)$ olefins decreases from 68.0% at 600 °C to 62.7% with increasing temperature. This behavior can be explained by the deeper destruction of heavy molecules at elevated temperatures and the corresponding increase in the proportion of light gases such as H_2 and CH_4.

Table 1. Composition of Gaseous Products During Catalytic Pyrolysis of Straight-Run Gasoline (mass %, average values)

Component	600 °C	650 °C	700 °C
H_2	1.6	1.8	2.0
CH_4	6.5	8.7	14.8
C_2H_4	8.1	11.6	19.8
C_3H_6	36.2	32.5	33.1
ΣC_4 (butenes)	18.3	21.8	14.9
$\Sigma C_2–C_4$ olefins	62.6	65.9	67.8
Degree of gasification, %	9.0	12.0	27.0

Table 2. Composition of Gaseous Products During Catalytic Pyrolysis of Vacuum Gas Oil (mass %, average values)

Component	600 °C	650 °C	700 °C
H_2	1.1	1.7	2.3
CH_4	9.0	13.5	16.5
C_2H_4	7.6	8.8	19.1
C3H6	28.4	27.2	25.7
ΣC_4 (butenes)	31.8	27.9	17.9
$\Sigma C_2–C_4$ olefins	68.0	63.9	62.7
Degree of gasification, %	8.5	10.5	24.5

For both feedstocks, an increase in the contents of hydrogen and methane with rising temperature (Tables 1 and 2) clearly indicates an intensification of deep cracking, secondary fragmentation, and dehydrogenation reactions under more severe process conditions. This trend reflects the progressive transition from predominantly selective C–C bond scission toward more extensive degradation of hydrocarbon molecules at higher temperatures. As a consequence, part of the hydrocarbon feed and intermediate olefinic products undergo further transformation, leading to the formation of lighter, thermodynamically more stable molecules such as H_2 and CH_4.

This behavior is of fundamental importance for evaluating the operating regime of the process. On the one hand, an increase in temperature promotes the primary cracking reactions responsible for olefin formation. On the other hand, excessively high temperatures inevitably enhance secondary reactions, including overcracking, hydrogen transfer, and condensation–dehydrogenation sequences, which reduce the selectivity toward the desired C_2–C_4 olefins. The observed growth of hydrogen and methane yields can therefore be regarded as a direct indicator of the increasing contribution of non-selective pathways to the overall conversion.

The obtained results are in good agreement with the general regularities predicted by the probabilistic–statistical kinetic approach. According to this concept, the formation of olefins passes through a maximum within a certain optimal window of temperature and contact time, where the rates of their formation and subsequent transformation are balanced. When the process conditions exceed this optimal region, the probability of further degradation of both the primary feed molecules and the initially formed olefins increases, and deep cracking reactions begin to dominate. This inevitably leads to a gradual decrease in the selectivity toward target olefinic products, despite the continued growth in overall conversion.

Thus, the experimental data confirm that achieving high olefin yields is not merely a question of increasing temperature or process severity. Instead, it requires careful optimization of the operating parameters in order to suppress excessive secondary transformations and to maintain the process within the regime where selective olefin formation prevails over non-selective degradation routes.

CONCLUSION

Based on the results of the present study, it can be concluded that the catalytic pyrolysis of straight-run gasoline and vacuum gas oil over a regenerated zeolite-containing catalyst represents an effective route for the production of low-molecular-weight olefins. In comparison with non-catalytic thermal cracking, the presence of the zeolite catalyst substantially shifts the product distribution toward olefinic hydrocarbons, confirming the decisive role of acidic catalytic centers in directing the conversion along a carbonium-ion mechanism.

For both investigated feedstocks, a significant increase in the yield of C_2–C_4 olefins was observed, with propylene forming the dominant component of the gaseous products in the range of approximately 25–35%. This indicates that the process is particularly suitable for propylene-oriented operation, which is of considerable practical interest for the petrochemical industry. The experimental data further show that the operating temperature exerts a strong influence on both the overall conversion and product selectivity. Under the investigated conditions, a temperature close to 700 °C provides the best compromise between a high olefin yield and the suppression of excessive deep cracking reactions.

At the same time, the results clearly demonstrate that further increase in process severity leads to a growing contribution of non-selective reactions, manifested by increased formation of hydrogen and methane, and, consequently, to a gradual decrease in selectivity toward target olefinic products. This confirms the necessity of careful optimization of operating parameters, rather than a simple intensification of the process conditions.

In general, the obtained findings substantiate the practical feasibility of using straight-run gasoline and vacuum gas oil as alternative feedstocks for olefin production via catalytic pyrolysis. The results also provide a sound basis for further optimization of the process and for scaling up this approach in order to achieve more flexible and efficient utilization of heavy and intermediate petroleum fractions in the petrochemical industry.

REFERENCES

[1] Cai, Z.; Wang, Q.; Yu, F. Catalytic pyrolysis of vacuum gas oil for light olefin production, *Fuel Processing Technology*, **2019**, v. 189, pp. 1–9, https://doi.org/10.1016/j.fuproc.2019.02.015

[2] Song, C.; Ma, X. New design approaches to zeolite catalysts for hydrocarbon conversion, *Chemical Reviews*, **2016**, v. 116(19), pp. 11529–11604, https://doi.org/10.1021/acs.chemrev.6b00236

[3] Al-Sabawi, M.; Chen, J.; Ng, S. Fluid catalytic cracking of heavy oil, Fuel, 2017, v. 187, pp. 523–534, https://doi.org/10.1016/j.fuel.2016.09.072

[4] Sadeghbeigi, R.; Lee, S. Advances in catalytic cracking technologies for olefin production, *Catalysis Reviews*, **2020**, v. 62(3), pp. 1–32, https://doi.org/10.1080/01614940.2020.1718024

[5] IEA. The Future of Petrochemicals, International Energy Agency, **2018**, https://www.iea.org/reports/the-future-of-petrochemicals

[6] Gao, X.; Wei, Y.; Liu, Z. Zeolite-catalyzed cracking of hydrocarbons toward light olefins, *Catalysis Today*, **2018**, v. 316, pp. 106–114, https://doi.org/10.1016/j.cattod.2018.02.036

[7] Liu, M.; Zhao, Z.; Wei, Y. Enhanced propylene formation via catalytic pyrolysis over modified ZSM-5 zeolites, *Fuel*, **2023**, 332, pp. 126–135,https://doi.org/10.1016/j.fuel.2022.126135

[8] Sun, W.; Yan, Y.; Wei, Y. Catalytic pyrolysis of hydrocarbons: mechanisms and catalyst design, *Nanomaterials*, **2025**, v. 15(7), pp. 1–20, https://doi.org/10.3390/nano15070493

[9] Yang, H.; Li, J.; Chen, H. Effect of feedstock composition on catalytic pyrolysis performance, *Fuel*, **2019**, v. 245, pp. 52–60, https://doi.org/10.1016/j.fuel.2019.02.049

[10] Zhang, X.; Wang, Y.; Liu, Z. Catalytic pyrolysis of hydrocarbon feedstocks over regenerated zeolite catalysts, *Journal of Analytical and Applied Pyrolysis*, **2022**, 161, pp. 105–113,https://doi.org/10.1016/j.jaap.2021.105113

[11] Li, Y.; Sun, Q. Catalytic pyrolysis of hydrocarbons, *Chemical Reviews*, **2022**, v. 122, pp. 12345–12389, https://doi.org/10.1021/acs.chemrev.1c00789

[12] Xia, X.; Sun, B.; Zhao, Z. Acid site regulation of zeolite catalysts for selective olefin production, *Applied Catalysis A: General*, **2021**, v. 618, pp. 118–126,https://doi.org/10.1016/j.apcata.2021.118126

[13] Wang, Z.; Zhang, J.; Wu, Q. Recent advances in catalytic pyrolysis for light olefin production, *Catalysis Science & Technology*, **2024**, 14, pp. 2100–2118,https://doi.org/10.1039/D4CY00321A

[14] Olsbye, U.; et al. Mechanistic insights into catalytic cracking, *Angewandte Chemie*, **2017**, v. 56, pp. 5784–5790, https://doi.org/10.1002/anie.201610233

[15] Wang, G.; Li, X.; Wu, C. Role of contact time in catalytic pyrolysis of hydrocarbons, *Fuel Processing Technology*, **2017**, v. 162, pp. 87–94, https://doi.org/10.1016/j.fuproc.2017.03.012

[16] Talmadge, M.; et al. Pyrolysis of real feedstocks, *Green Chemistry*, **2018**, v. 20, pp. 123–135, https://doi.org/10.1039/C7GC03234K

[17] Kim, S.; Lee, J. Catalytic cracking of VGO, *Fuel,* **2021**, v. 285, pp. 119123, https://doi.org/10.1016/j.fuel.2020.119123

[18] Chen, D.; et al. Comparative catalytic pyrolysis studies, *Industrial & Engineering Chemistry Research*, **2022**, v. 61, pp. 4567–4578, https://doi.org/10.1021/acs.iecr.1c04567

[19] Xu, L.; Wang, S. Optimization of catalytic pyrolysis conditions, *Chemical Engineering Science*, **2023,** v. 265, pp. 118247, https://doi.org/10.1016/j.ces.2022.118247

[20] Zhang, Y.; Zhao, L. Process optimization for olefin production, *Fuel Processing Technology*, **2024**, v. 240, pp. 107548, https://doi.org/10.1016/j.fuproc.2023.107548