Available online at website: https://journal.bcrec.id/index.php/bcrec

Bulletin of Chemical Reaction Engineering & Catalysis, 20 (1) 2025, 129-142

Research Article

Y Zeolite-Based Catalyst for Palm Oil Cracking to Produce Gasoline

Arif Algifari[1*], I. G. B. N. Makertihartha[2], S. Subagjo[2], Heri Prabowo[1]

[1]Faculty of Engineering, Universitas Negeri Padang, Padang, 25131, Indonesia
[2]Departement of Chemical Engineering, Institut Teknologi Bandung, Bandung, 40132, Indonesia.

Received: 14th December 2024; Revised: 7th February 2025; Accepted: 10th February 2025
Available online: 14th February 2025; Published regularly: April 2025

Abstract

The increasing demand for oil fuel and the decline of crude oil reserves highlight the need for alternative energy sources. Palm oil, as a renewable resource, has potential for biofuel production through catalytic cracking. This study aims to develop and evaluate modified zeolite-based catalysts, particularly ZSM-5/HY, to produce palm oil-derived gasoline that meets European fuel standards. The research involved catalyst preparation, modification with ZSM-5 and phosphorus, and activity testing in a fixed-bed reactor. Gasoline yield and catalyst performance were analyzed using gas chromatography. The results showed nearly 100% conversion of palm oil under optimal conditions, with gasoline yield meeting European standard. The addition of ZSM-5 improved conversion and RON, while phosphorus modification reduced catalyst acidity, affecting yield and coke formation. This study concludes that modifying zeolite catalysts with ZSM-5 and phosphorus enables efficient palm oil-derived gasoline production with high RON and reduced aromatic content, contributing to sustainable energy solutions.

Keywords: Bio-gasoline; Catalytic cracking; Palm oil; Y Zeolite; ZSM-5; Phosphorous promotion

How to Cite: Algifari, A., Makertihartha, I. G. B. N., Subagjo, S., Prabowo, H. (2025). Y Zeolite-Based Catalyst for Palm Oil Cracking to Produce Gasoline. *Bulletin of Chemical Reaction Engineering & Catalysis*, 20 (1), 129-142. (doi: 10.9767/bcrec.20267)

Permalink/DOI: https://doi.org/10.9767/bcrec.20267

1. Introduction

The consumption of oil fuel in Indonesia in 2020 accounted for more than 32% of the total energy consumption [1]. The supply of oil fuel is highly needed, and to maintain the availability of domestic oil fuel, which is still imported [2], A study is needed regarding the reserves of crude oil that can meet the energy needs for the future. The reserves of crude oil in Indonesia are feared to be unable to meet the national energy needs in the long term as they are depleting every year. Estimates for the year 2025 still indicate a gap between the production of oil fuel in refineries, which is approximately 1,734 million barrels per day, while the consumption is around 2,197 million barrels per day [3]. The national oil fuel crisis feared to occur in the future can be mitigated considering Indonesia's wealth of renewable natural resources, namely vegetable oil, to produce biofuels. One of Indonesia's sources of vegetable oil comes from palm oil, with palm oil production approaching 40 million tons in 2018, and around 10 million tons of the total palm oil production being exported, meaning approximately 30 million tons are utilized for domestic purposes [4]. Until now, there are several processes for converting palm oil into fuel.

* Corresponding Author.
Email: a.algifari@ft.unp.ac.id (A. Algifari)

One of them is through cracking to produce gasoline fuel fractions. Palm oil contains palmitic acid $C_{16:0}$ and oleic acid $C_{18:1}$ [5]. Cracking oil with the assistance of acid catalysts yields hydrocarbon fractions ranging from C_5 to C_{12}, which are within the hydrocarbon range of gasoline fractions [6]. The process of refining palm oil into gasoline is crucial to develop because Indonesia is the world's largest producer of palm oil, and a portion of this production can be processed into gasoline.

The production of gasoline from palm oil begins with the formulation of cracking catalysts. Previous developments in cracking catalysts for palm oil have been based on ZSM-5 [6]. The gasoline fraction produced from this cracking process is predominantly aromatic. The utilization of ZSM-5 results in aromatics comprising 80-95% due to the strong acidity of the catalyst, pore structure, and zeolite framework [7]. The aromatic content, including benzene, indeed contributes to increasing the octane rating [8], but aromatics are carcinogenic in nature. Aromatics easily vaporize, and inhaling them can lead to health issues [9]. Method by EN 228:2012 gasoline fuel standard limits the aromatic content in gasoline to 35% (v/v) and benzene to 1% (v/v) [10]. In this context, the development of palm oil cracking catalysts capable of producing aromatic yields below the limits set for national gasoline fuel standards is necessary. The yield of cyclic hydrocarbons increases proportionally with residence time and temperature, while aromatic yield increases and the rate of coke formation from aromatic polymerization can be controlled by adjusting operating conditions to higher temperatures and extending residence time [11], So, the appropriate action to reduce aromatics is to lower the reaction temperature. However, this conflicts with reducing conversion because an increase in reactant conversion is proportional to the increase in temperature [6]. Furthermore, reducing aromatic content begins with the selection of cracking catalysts. Catalysts that aid in producing aromatics with lower content compared to ZSM-5 include zeolite Y [12], It also has the capability to promote isomerization reactions [13]. Isomerization reactions in cracking are influenced by the concentration and strength of Bronsted acids [14]. Based on the above study, the cracking catalyst used in this research is based on zeolite Y. The catalyst development involves adding phosphorus promoter and ZSM-5 as cracking catalyst additives.

The initial hypothesis is that strong catalyst acidity leads to over-cracking and excessive aromatic production. Considering the achievement of low aromatic content in the product, efforts to reduce catalyst acidity are necessary. The method employed is to add a phosphorus promoter to the cracking catalyst. Modifying the cracking catalyst by adding a phosphorus promoter can limit the amount of strong catalyst acid [15]. Therefore, phosphorus promotion can be said to reduce aromatic selectivity [16]. The addition of ZSM-5 in the cracking catalyst is based on increasing aromatic yield, thereby improving the octane number of the gasoline product. However, the amount of ZSM-5 added is limited to avoid exceeding gasoline quality standards. The addition of ZSM-5 to commercial FCC catalysts is typically around 5-10% [17] to increase the octane number. In this study, the addition of ZSM-5 is introduced as a few percent of the main catalyst mass.

2. Materials and Methods

The research process begins with a literature review to study literature related to palm oil cracking reactions, cracking catalysts, analysis methods, and research result processing methods. The next step is broadly divided into two groups of work: laboratory cracking operation studies aimed at learning the standard procedures for operating experimental equipment in the laboratory and producing catalysts according to the planned catalyst formulation in the research. Essentially, zeolite Y-based catalysts are already available in the laboratory. However, there are modifications to the cracking catalyst through the addition of ZSM-5 additive and phosphorus impregnation. After preparing the catalysts, the next step is to test the characteristics of the modified catalysts and the basic catalysts. The differences in the characteristics of each catalyst will be observed from the analysis results and described in the research findings. Catalyst characteristic tests are assisted by catalyst analysis instruments available in the laboratory, namely X-Ray Diffraction EDAX, Brunauer Emmett Teller, and NH_3-Temperature Programmed Desorption instruments.

The main process in this research is the catalyst activity testing in a fixed-bed reactor unit. The cracking experiments with the prepared catalysts yield several experimental data in the form of mass balance data of the palm oil cracking reaction. The collection of experimental data involves measuring some data during the cracking experiment process, followed by obtaining other important data that need to undergo analysis processes using analysis instruments, such as gas chromatography with Flame Ionization Detector (FID) simulation distillation (Agilent SimDis Technologies) for determining hydrocarbon fractions, gas chromatography with FID-Detailed Hydrocarbon Analysis DHA Agilent Technologies for determining hydrocarbon group fractions ranging from C_5 to C_{14}, and gas chromatography with FID-Shimadzu 2010 Plus for residual fatty acid analysis to calculate reaction conversion. The experimental results and analysis results obtained with the assistance of analysis

instruments are processed and correlated with each other. The analysis results of catalyst characteristics are correlated with the catalyst activity test results. For example, a catalyst with specifications consistent with its characteristics produces cracking reaction performance with certain conversion capabilities and selectivity towards specific products.

The crude palm oil is obtained from PT. Perkebunan Nusantara VII Unit Betung, South Sumatra, Indonesia (Table 1). The raw material is processed first before it can be used as cracking feedstock. The aim is to remove impurities such as water content and other impurities. The process involves degumming and filtration. The gum separation process is adjusted to the process conducted by Serrano *et al*. [18] The process involves using 50% citric acid form Merck at a concentration of 0.4% of the palm oil mass. Heating is carried out for 5-30 minutes at temperatures of 90-100 °C. Then, at the same temperature and stirring time, bleaching is performed based on adjustments from the study by Ifa *et al*. [19]. Bentonite is used as an adsorbent. The base material for the catalyst is HY. Zeolite Y is produced by Hitong Global Co. Ltd. in Tianjin City, China. The selection of zeolite Y is based on meeting the criteria for a cracking catalyst that is stable if the Si/Al molar ratio is greater than 5 and approaches equilibrium if it reaches 20 [20]. The additive for the cracking catalyst is ZSM-5, which is sourced from Gongyi City Meiqi Industry & Trade CO in Henan, China. The selection of ZSM-5 is based on its high Si/Al ratio, which is considered to have low acidity, meaning that an increase in the Si/Al molar ratio is proportional to a decrease in catalyst acidity [21].

2.1 Extrusion of Catalyst and Phosphorus Impregnation

The extrusion of catalyst involves the process of molding the catalyst into long cylindrical extrudates so that it can be used as a catalyst in fixed-bed reactors, thereby creating a bed void in the reactor bed [22]. Initially, the available zeolite catalyst is in powder form, so catalyst preparation is required to be able to use the extrusion method. Eight grams of zeolite powder, which includes 100% HY, 100% ZSM-5, or a mechanical mixture of HY and ZSM-5, is physically mixed with 1.5 grams of SiO_2 (Cab-O-Sil M5) and stirred for 60 minutes until the mixture becomes homogeneous. A total of 0.672 grams of $AlHO_2$ Katapal is mixed with 0.42 mL of HNO_3 low concentration form Merck. This mixture is then added to the mixture containing zeolite and SiO_2. The subsequent stirring is carried out for 30 minutes. Then, 12 mL of demineralized water is added until a paste is formed and ready for extrusion. The extruded catalyst is then dried at room temperature for 12 hours. The final step is the catalyst calcination at 550 °C for 6 hours. The impregnation method used is wet impregnation, following the method described by Hendrik *et al.* [16] and Corma *et al.* [23]. A total of 1 gram of zeolite powder is added to a solution containing 0.0317 grams of phosphoric acid. Impregnation is carried out by mechanical stirring for 1 hour. Then, the catalyst is dried at 120 °C for 2 hours and calcined at 500 °C for 1 hour.

Table 1. The composition of fatty acids in the palm oil feedstock as determined.

Fatty Acids	%Area
Myristic acid (C14:0)	1.07
Palmitic acid (C16:0)	44.16
Steatic acid (C18:0)	4.89
Oleic acid (C18:1)	49.99

2.2. Catalyst Activity Test

The catalyst activity test is conducted in a fixed-bed reactor unit made of quartz glass. The reactor has dimensions of 0.6 m in length, 0.015 m in internal diameter, and a reactor wall thickness of 2.5 mm. The reactor is positioned inside a heater as a controlled heat source regulated by a temperature control panel. The catalyst bed is positioned in the middle of the reactor, delimited by wire mesh and glass wool at the bottom of the bed, and glass wool and carborundum at the top of the bed. The operational sketch of the cracking reactor unit can be seen in Figure 1. A total of 1.5 grams of catalyst is required for each reaction at various temperature conditions ranging from 475 °C to 525 °C and a weight hourly space velocity

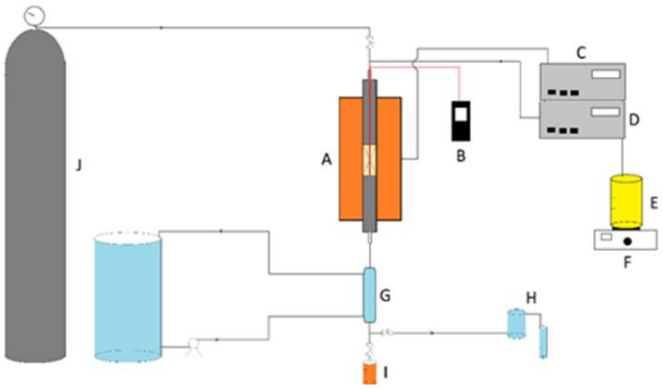


Figure 1. The cracking reactor unit schematic: (A) Tubular fixed bed reactor, (B) Thermocouple, (C) Heat controller, (D) Feed flow pump, (E) Feed, (F) Heater, (G) Condenser, (H) Gas volumeter, (I) Liquid product, (J) Inert gas.

(WHSV) of the feed ranging from 1.98/hour to 2.99/hour. The conversion of triglycerides is calculated with the assistance of Shimadzu 2010 Plus gas chromatography with Flame Ionization Detector analysis. The sample evaporation limit by GC is set at 350 °C, while triglycerides have a boiling point of >300 °C. Samples containing triglycerides must be in the form of methyl esters. Therefore, both reactant and product samples containing triglycerides need to be trans-esterified first to represent the fatty acids present in those triglycerides. The quantitative analysis results of gas chromatography are the peak area for each methyl ester, representing the concentration of each component. The triglyceride conversion calculation follows Equation (1), where A_{TG0} is the total peak area of methyl ester in the palm oil feed sample, while A_{TG} is the total peak area of methyl ester contained in the cracking products.

$$X_{TG} = \frac{A_{TG0} - A_{TG}}{A_{TG0}} \, x \, 100 \, \% \qquad (1)$$

The selectivity calculation is conducted based on the gasoline yield and the composition contained in the gasoline fraction. Instruments used for data collection on selectivity are the Shimadzu 2010 Plus GC and the Detailed Hydrocarbon Analysis GC. The Shimadzu 2010 Plus GC and the Simulation Distillation GC can analyze mass fractions of hydrocarbons based on their boiling point ranges. Based on this analysis range, gasoline fractions C_6-C_{12}, kerosene and diesel fractions C_{12}-C_{18}, classified as light cycle oil, and heavy fractions (C_{18}>) classified as heavy cycle oil, are obtained.

$$Y_{Gasoline} = \frac{A_{Gasoline\ fraction}}{A_{total\ organic\ liquid\ product}} \, x \, 100 \, \%) \qquad (2)$$

In the Gas Chromatography Simulated Distillation analysis, the peak area generated by the detector represents the hydrocarbon components in the sample based on the molar quantity, which is then converted by the GC software into mass percentages. This process is carried out by integrating the peak area of each component, referring to the molar mass and density of each hydrocarbon listed in the instrument's library. The total organic liquid product is obtained through direct weighing of the liquid product after the cracking reaction, separated from water and impurities using methods such as decantation or filtration. The gasoline fraction is calculated based on the mass percentage of the gasoline hydrocarbon range identified by GC SimDis, while the total organic liquid product is determined from the physical weighing results. Gasoline yield is calculated by comparing the gasoline fraction to the total organic liquid product using Equation (2).

3. Results and Discussion

3.1 Triglyceride Cracking Reaction Mechanism

During the catalytic cracking of triglycerides, the process initiates with the adsorption of triglyceride molecules onto the catalyst's surface, followed by their activation, which leads to the formation of active sites. Subsequently, bond cleavage occurs, breaking the ester bonds between the glycerol backbone and the fatty acid chains, resulting in the production of free fatty acids and glycerol. According to Simanda *et al.* [24], triglycerides initially decompose into oxygenated hydrocarbons such as fatty acids, ketones, aldehydes, and esters due to the breaking of C–O and C–C bonds through β-scission reactions, which are thermal processes [25]. The breaking of C–O and C–C bonds occurs through two reaction routes. The first route involves decarboxylation and decarbonylation accompanied by the breaking of C–C bonds in hydrocarbons. The second route involves the breaking of C–C bonds in hydrocarbons accompanied by decarboxylation and decarbonylation. The existence of these two routes depends on the presence or absence of double bonds in the oxygenated hydrocarbons. Decarboxylation and decarbonylation reactions occur first in saturated chain oxygenated hydrocarbons. For oxygenated hydrocarbons with double bonds, the bond breaking initially occurs at the double bonds themselves. Secondary reactions in the cracking reaction mechanism include ß-scission, hydrogen transfer, isomerization, cyclization, aromatization, and polymerization, which are a combination of thermal and catalytic processes [25]. These reactions are dominated by endothermic reactions except for some exothermic reactions, such as hydrogenation, n-paraffin isomerization, and olefin cyclization. The reactions in the cracking reaction mechanism are spontaneous and characterized by negative Gibbs energy [26].

According to Long [27] the formation reaction of fatty acids from triglycerides can occur through thermal cracking, which can be assisted by catalytic activity [25]. Triglyceride molecules are broken down into three fatty acid molecules with the assistance of Bronsted acid catalytic sites. The acid sites bond to the double-bonded oxygen on the triglyceride. Fatty acids undergo decarboxylation, where the carboxyl bond of the fatty acid is broken, forming either alkene or alkane and CO_2, and freeing itself from the Bronsted acid site $R - COOH \rightarrow R + CO_2$. Decarbonylation forms an aldehyde intermediate. Then, the aldehyde group is broken down to form either alkene or alkane, CO, and water. Hydrocarbons formed lacking two hydrogen atoms undergo hydrogenation to form alkane. Below is the decarbonylation reaction of fatty acids. $R - COOH \rightarrow R + CO + H_2O$. Dehydration reaction results in hydrocarbon

alkene or alkane and water $R - COOH \rightarrow R + 2H_2O$. Hydrocarbons formed lacking three hydrogen atoms and require hydrogenation to form alkane. Double bonds are more reactive, so cracking occurs first at these bonds rather than decarboxylation or decarbonylation reactions. Double bonds interact with Bronsted acid sites and then cleave the bond into carbene ions. This carbene ion acts like a reactive and short-lived free radical. One of the further reactions in the catalytic cracking mechanism is the isomerization of light paraffin and olefin. Olefins and paraffins undergo isomerization assisted by Bronsted acid sites [14]. The isomerization reaction mechanism starts with dehydrogenation by Bronsted acid sites at one of the hydrocarbon bonds, then ethyl shift or methyl shift occurs or the formation of dimethyl cyclopropane intermediates [7]. After the branch is formed, the previously extracted hydrogen is then returned to the carbon deficient in branch hydrogen. Paraffin and olefin undergo cyclization to form cyclo-paraffin and cyclo-olefin. Cyclo-paraffin and cyclo-olefin then form aromatics as a result of dehydrogenation reactions. The cyclization mechanism and straight-chain hydrocarbon are related to the Diels Alder reaction mechanism [28] and dehydrogenation and olefin cyclization [29,30]. Polymerization is an advanced stage of the aromatization reaction precisely when aromatic dehydrogenation occurs. Among aromatic compounds lacking hydrogen, they bond to each other to form polyaromatic compounds. If these reactions continue, coke is formed. Condensation reactions are the direct formation reactions of coke from oxygenates during deoxygenation [29,30]. Overall for triglyceride cracking reaction mechanism is as seen on Figure 2.

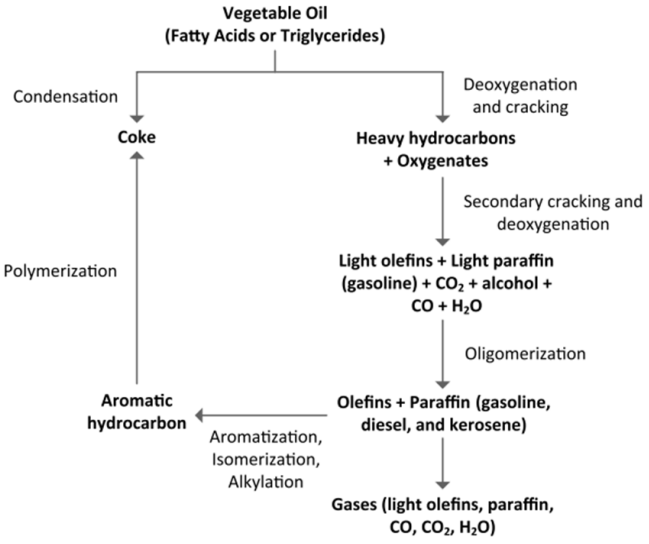


Figure 2. The mechanism of catalytic triglyceride cracking reaction [6,33].

3.2 Cracking Catalyst Characteristics

Testing and gathering data on the attributes of cracking catalysts have been meticulously undertaken, employing a combination of direct testing instruments and catalyst specification data analysis. Notably, examination of commercial zeolites' specifications revealed significant findings: the HY zeolite serving as the foundational component of the cracking catalyst exhibited a noteworthy specific surface area of 680 m^2/g, while the ZSM-5 counterpart demonstrated a slightly lower specific surface area of 450 m^2/g. Moreover, detailed characterization of the cracking catalysts using the Brunauer Emmett Teller instrument has yielded comprehensive insights into crucial parameters such as pore surface area, pore size, and pore volume of the zeolite catalyst, all of which are meticulously documented in Table 2.

The analysis conducted utilizing X-ray diffraction instruments has provided crucial insights into the structural characteristics of four distinct catalysts: HY zeolite, ZSM5-P, ZSM5/HY, and ZSM5/HY-P. The primary objective of this characterization process is to ascertain the degree of crystallinity exhibited by each catalyst. By scrutinizing the diffraction patterns obtained, discernible disparities in crystallinity levels among the zeolites become apparent, elucidating their unique structural properties. Notably, in composite zeolites like ZSM5/HY, the presence and dispersion of ZSM-5 within the Y zeolite matrix can be distinctly identified through the diffraction patterns. These XRD diffraction profiles, captured in Figure 3, serve as invaluable tools for comprehending the structural integrity and potential catalytic performance of the examined catalysts.

The crystallinity of ZSM-5 in the diffractogram can be identified at the 2 theta positions of 7.9°, 8.75°, and 23° [34]. Meanwhile, the crystallinity of Y zeolite can be identified at the 2 theta positions of 6.16°, 10.08°, and 20.24° [34]. As a comparison diffractogram, Figure 3 presents the standard diffractogram curves of Y zeolite and ZSM-5 obtained from XRD zeolite

Table 2. BET properties of cracking catalyst

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (cm^3/g)
HY	612.1	46.6	0.71
ZSM5/HY	578	45.9	0.66
ZSM5/HY-P	401.6	38.7	0.35
ZSM-5-P	303.5	38.5	0.29

patents. According to the reference, the crystal positions of Y zeolite are at 15.7°, and 23.7° [35], while for ZSM-5, they are around 21-23° [36].The dispersion of ZSM-5 in HY in the ZSM5/HY and ZSM5/HY-P catalysts can be identified in the diffractogram at the 2 theta positions of 7.9° and 8.75°. Based on Figure 3, the ZSM-5 diffractogram peaks in the ZSM5/HY and ZSM5/HY-P catalysts are marked with the notation 'X'. According to the XRD analysis results, the crystallinity levels of the HY, ZSM5/HY, ZSM5/HY-P, and ZSM-5-P catalysts are 77.4%, 76.6%, 69.1%, and 74.3%, respectively. The crystallinity of ZSM-5 in the composite catalysts can be determined by calculating the peak area ratio of the ZSM-5 sample to the standard ZSM-5 peak area. The crystallinity of ZSM-5 in the ZSM5/HY and ZSM5/HY-P catalysts is 12.79% and 10.09%, respectively. Based on the analysis of the crystallinity of each catalyst, there is a decrease in crystallinity influenced by phosphorus promotion. The cause can be identified in the mechanism of interaction between the catalyst acid sites and phosphoric acid as a phosphorus carrier compound that breaks the Si-O-Al bonds [16], thus disrupting the crystal system in the zeolite.

Phosphoric acid has the ability to break the Si–O–Al bonds in the aluminosilicate framework, such as in zeolite, due to its strong acidic nature. This process allows H^+ ions from the phosphoric acid to replace Si–O–Al bonds by directly bonding with Al ions in the zeolite framework, leading to a change in the framework structure. When phosphoric acid bonds with Al, one of the acidic centers in the aluminosilicate framework is lost, resulting in the formation of aluminosilicate-phosphate compounds such as $AlPO_4$. According to Agliullin [37], $AlPO_4$ compounds exhibit diffraction peaks at 2θ values of 6.5° and 8.1°, which are characteristic of the $AlPO_4$ crystal structure, and these peaks can be observed using X-ray diffraction (XRD) techniques. However, in Figure 3 of the diffractogram, the $AlPO_4$ diffraction peak overlaps with the zeolite Y peak at 2θ = 6.1°. This overlap indicates that phosphate compounds have been impregnated into the zeolite framework, as evidenced by the decrease in intensity of the zeolite Y peak at 6.1°. The decrease shows that the crystalline structure of zeolite Y has been altered due to the presence of phosphate compounds formed through impregnation, which affects the intensity of the diffraction peak that was previously dominant at 6.1°, characteristic of zeolite Y. As $AlPO_4$ forms, new diffraction peaks at 6.5° and 8.1° appear, indicating that the impregnation process successfully formed $AlPO_4$ bound to zeolite.

The next characteristic test of the catalyst is the assessment of acidity level using the Temperature Programmed Desorption instrument by adsorbing ammonia on the catalyst's acid sites. Figure 4 depicts the NH_3-TPD analysis results of the catalyst, illustrating the quantity of ammonia adsorption and desorption on the acid sites of the catalyst, thus providing an indication of the number of acid sites present. The acidity of the catalyst can be quantified by the area under the NH_3-TPD curve, representing the amount of ammonia adsorbed on the acid sites. The TPD analysis results, as shown in Figure 4, confirm that the number of acid sites in Y zeolite is greater than in ZSM-5, consistent with the findings of Wang *et al*. [34]. The initial hypothesis, which suggests that by analyzing the Si/Al ratio, the acidity of Y zeolite can be estimated to be greater than that of ZSM-5, is supported. Zeolites with lower Si/Al molar ratios tend to exhibit higher [21]. The acidity level of the ZSM5/HY catalyst is found to be between that of Y zeolite and ZSM-5.

3.3 The Influence of Product Yield on Catalyst Type

As an initial experiment, a comparison has been conducted on the use of four cracking catalysts for each activity test under conditions of 500 °C temperature, a Weight Hourly Space Velocity of 2.59/hour, and a time on stream of 1 hour. The activity of the catalysts was assessed based on conversion rates. Other test data obtained include product selectivity. The

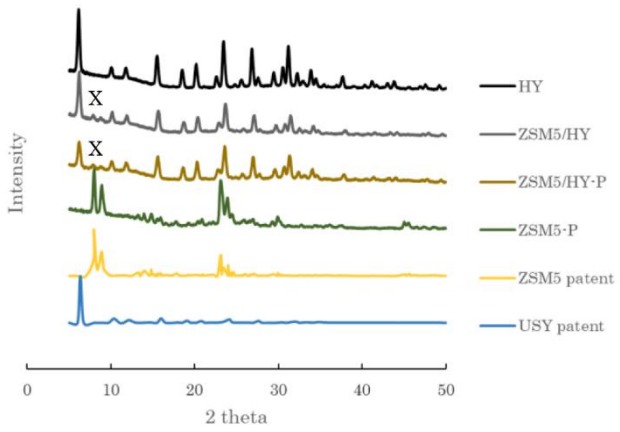


Figure 3. Diffractogram of cracking catalysts

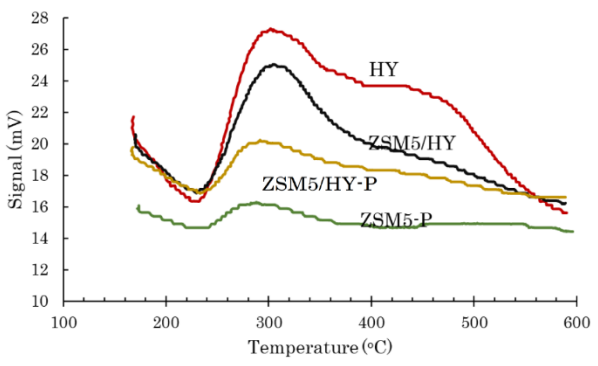


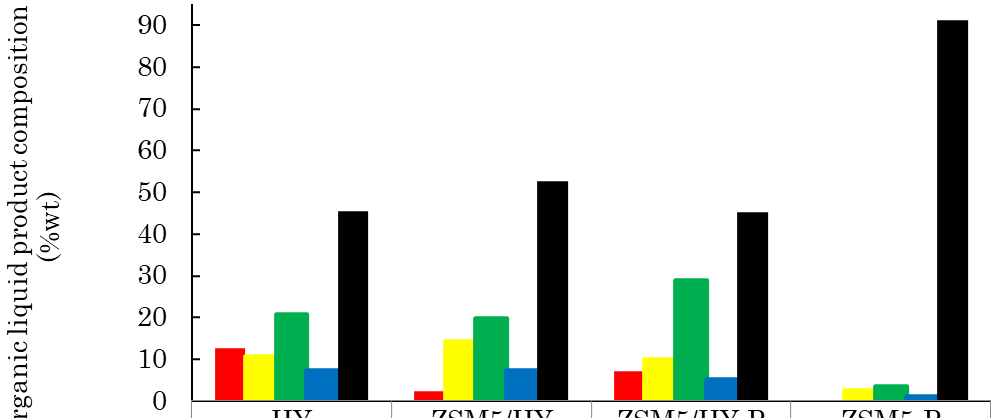
Figure 4. NH_3-TPD curve of the cracking catalyst

composition of liquid products is a crucial parameter, especially as it determines the quality of gasoline fuel and influences the fuel octane number. This composition is influenced by the catalyst in directing the reactions. Secondary reactions in the cracking reaction mechanism primarily involve the cyclization and aromatization of straight-chain hydrocarbons. As observed from the diagram in Figure 5, cracking assisted by Y zeolite is quite selective towards straight-chain hydrocarbon products and less selective towards aromatics compared to cracking using ZSM-5. A comparison of the liquid product yields from palm oil cracking reactions at a temperature of 500 °C and WHSV of 2.59/hour using HY, ZSM5/HY, ZSM5/HY-P, and ZSM5-P can be seen in the diagram in Figure 5. The mechanism of triglyceride cracking reaction is consecutive. Cyclization of straight-chain hydrocarbons occurs after the formation of straight-chain hydrocarbons from fatty acid deoxygenation reactions. The phenomenon of cyclization of straight-chain hydrocarbons is accompanied by dehydrogenation. Based on experimental results and comparison of four catalysts based on Y and ZSM-5 zeolites, it can be concluded that Y zeolite is less capable of dehydrogenating straight-chain hydrocarbons compared to ZSM-5. This is evidenced by the cracking products using Y zeolite containing fewer cyclic hydrocarbons compared to cracking products assisted by ZSM-5. The high yield of aromatics in cracking by ZSM-5 is attributed to shape selectivity, where the pore openings of ZSM-5 catalysts are of medium size [38], suitable for aromatic formation.

Shape selectivity in zeolites refers to the size of the catalyst's pore openings that selectively facilitate the formation of specific molecules within the catalyst pores. The yield of aromatic molecules is a function of the zeolite pore size [38]. The average pore sizes of HY Zeolite, ZSM5/HY, and ZSM-5-P are 46.6, 45.9, and 38.5 Å, respectively. From these three data points, it is inferred that Y zeolite has pore sizes above the medium pore size of ZSM-5 or falls into the macro pore size category. Both ZSM-5 and Y zeolite pores are suitable for accommodating triglyceride molecules, which have molecular sizes of 7-8 Å [39]. Aromatic molecules such as benzene, toluene, para-xylene, and naphthalene have respective sizes of 7.4, 8.7, 9.9, and 9.1 Å [38]. These molecular sizes are smaller than the catalyst pore openings, allowing aromatic molecules to form within the zeolite pores. The larger pore openings of Y zeolite result in lower yields of aromatics [38] and slightly promote the formation of straight-chain and branched hydrocarbons.

3.4 Results of Catalyst Activity Testing

The test outcomes underscore the distinct advantages of Y zeolite and ZSM-5, each contributing unique strengths to the cracking process. While Y zeolite demonstrates lower overall activity compared to ZSM-5, particularly evident in the conversion of triglycerides, its superiority lies in selectivity. Notably, the utilization of Y zeolite in palm oil cracking yields a higher volume of liquid products. However, it's worth noting that the organic liquid product from



	HY	ZSM5/HY	ZSM5/HY-P	ZSM5-P
N-Parafin	12.61	2.36	7.27	0.15
I-Parafin	10.63	14.28	9.92	2.42
Olefin	20.74	19.63	28.78	3.42
Naften	7.16	7.25	5.05	0.99
Aromatik	45.56	52.61	45.19	91.13

Figure 5. The yield of liquid hydrocarbon products for each catalyst (reaction conditions: T = 500 °C and WHSV = 2.59/hour)

Y zeolite cracking contains a higher proportion of light cycle oil, aligning with the hydrocarbon spectrum characteristic of kerosene and diesel [40]. Furthermore, Y zeolite exhibits a reduced tendency for coke formation compared to ZSM-5, enhancing its longevity and sustainability as a catalyst. These observations were made under controlled reaction conditions of 500 °C temperature and a WHSV of 2.59/hour, providing valuable insights into the performance and applicability of each catalyst in the palm oil cracking process.

The catalytic activity test (Table 3) showed that the combination of ZSM-5 and HY increased gasoline yield from 14.1% (HY) to 22.46%, with a significant rise in gas production from 44.22% to 65.09%, indicating more aggressive cracking activity due to smaller pore sizes. However, modification of this combination (ZSM5/HY-P) reduced gasoline yield to 14.31%, while gas yield remained high at 65.02%, and coke formation decreased from 1.28% to 0.74%, suggesting that the modification enhanced catalyst stability but did not significantly improve light product yields. The ZSM5-P catalyst exhibited the highest activity with 100% conversion and the highest gasoline yield of 24.42%, but it also resulted in higher coke formation (3.05%), indicating that although the modification improved cracking efficiency, there was a tendency for catalyst deactivation due to carbon deposition. Characterization results showed that the surface area of the catalysts followed the order HY > ZSM-5/HY > ZSM-5/HY-P > ZSM-5-P, with pore diameter and pore size inversely proportional to the surface area. According to Jae [38], in the cracking of aliphatic hydrocarbons, catalysts with macropores tend to produce lower aromatic yields, whereas ZSM-5, with its medium pore size, exhibits higher shape selectivity towards aromatic formation. Therefore, cracking with ZSM-5 is more selective for aromatics compared to Zeolite Y (HY), which has larger pores and tends to yield more non-aromatic products. As a result, the gasoline fraction produced, particularly when using ZSM-5-based catalysts, is predominantly composed of aromatic compounds, reflecting the shape-selective properties of ZSM-5 that favor aromatic hydrocarbon formation.

The gasoline yield from cracking with ZSM5-P is higher compared to cracking with Y zeolite, yet the aromatic content in the gasoline fraction remains high. The addition of phosphorus to the ZSM5/HY catalyst affects its activity, evidenced by the decrease in triglyceride conversion, aromatic yield, coke formation, and octane number. This decline in activity indicates that phosphorus in the zeolite catalyst helps reduce the concentration of acidic catalyst sites, as demonstrated in prior research by Hendrik *et al*. [16]. Similar studies by Istadi *et al*. [41], using HY as the base catalyst showed high conversion but decreased when impregnated with metals. Selectivity for the diesel fraction is relatively high, while light cycle oil containing kerosene and diesel dominates the cracking results in macro pores. In contrast, the aromatic fraction from ZSM-5 tends to distribute in the gasoline fraction. The addition of ZSM-5 enhances conversion and directs the reaction towards gasoline formation.

Cracking of palm oil using ZSM5/HY catalyst exhibits good activity with triglyceride conversion reaching approximately 99%. While the gasoline yield is not as high as when using ZSM-5, it is still greater than that obtained with zeolite Y. The ZSM5/HY catalyst also demonstrates good stability, operating for up to 8 hours without deactivation. Test results show that the ZSM5/HY catalyst produces liquid products with aromatic content below 50% by volume and benzene content below 5% by volume. Research Octane Number for the gasoline fraction ranges between 90-94. As the ZSM5/HY catalyst proves to be the best catalyst in this study, kinetic testing of palm oil cracking reaction for this catalyst is conducted as a further step in this research. The quality of the vegetable gasoline produced from palm oil approaches European fuel standards. However, the drawback of this vegetable gasoline is its olefin content exceeding 20% by volume. Table 4 presents a comparison of European standard gasoline composition with vegetable gasoline obtained from palm oil cracking using the ZSM5/HY catalyst according to the gasoline distillation method of ASTM D-86 [42].

Table 3. The catalyst activity test results (Temperature: 500 °C, Weight Hourly Space Velocity: 2.59 h^{-1}, and TOS: 1 hour)

Catalyst	Yields (%wt)						% Conversion
	Gasoline	LCO	HCO	OLP	Gas	Coke	
HY	14.1	34.75	4.21	53.07	44.22	1.41	98.71
ZSM5/HY	22.46	9.3	1.19	32.87	65.09	1.28	99.26
ZSM5/HY-P	14.31	13.31	5.25	32.88	65.02	0.74	98.64
ZSM5-P	24.42	4.76	0	29.19	67.74	3.05	100

3.5 Operation Condition Optimization

The optimized operating conditions for palm oil cracking with ZSM5/HY catalyst range from 475 °C to 525 °C and a WHSV of 1.98/h to 2.99/h. The process of optimizing the operating conditions for palm oil cracking involves comparing two fixed variables, namely temperature and WHSV, against the tested variables, which include conversion, yield, and RON. The desired test variables should maximize the objectives of the cracking reaction, while minimizing any variables that do not support these objectives.

The expected maximum values for the test variables are conversion, yield of liquid products, gasoline, and octane number. Meanwhile, the expected minimum values for the test variables are aromatic yield and benzene yield. Figure 6 depicts three-dimensional graphs showing the relationship between temperature and WHSV with the values of conversion, octane number, yield of liquid products, aromatics, and benzene. The magnitude of these variables is represented by surface contours, with higher values visualized in red and lower values in blue. Based on the correlation response in Figure 6, it can be observed that reaction conditions of 500-525 °C and WHSV 1.98-2.59/h produce better triglyceride conversion, exceeding 99%, and yield more than 20% wt of palm oil gasoline, with an octane number greater than 90. Additionally, aromatic and benzene yields are also maximized but still below 50 %wt OLP for aromatics and 5 %wt OLP for benzene. However, under these reaction conditions, the yield of liquid products decreases, especially at 525 °C and WHSV 1.98/h, due to excessively high reaction temperatures and prolonged residence times. In comparison, reaction conditions of 500 °C and WHSV 2.59/h are considered better for liquid product yield and thus can be deemed optimal for palm oil cracking with ZSM5/HY catalyst.

The next study focuses on time on stream. The results of catalyst activity testing with ZSM5/HY catalyst suggest deactivation for over 8 hours of operation. This is evident in Figure 7, where triglyceride conversion after 8 hours of operation is only 50.2%. Process optimization considerations aim for 100% reaction conversion. Decisions for further processing are based on this criterion. If the conversion is not 100%, feed recycling may be necessary, requiring additional utility process design to support this goal.

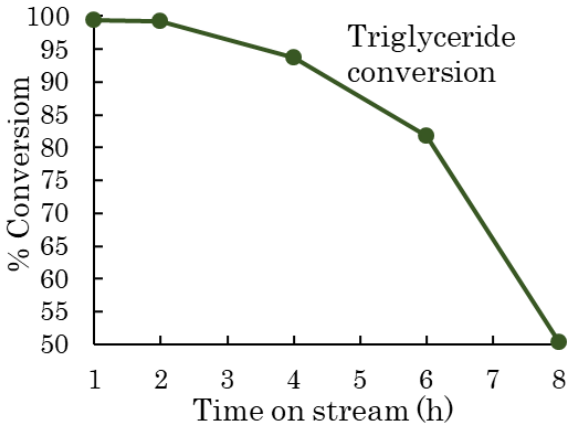


Figure 7. The triglyceride conversion during 8-hour time on stream period

Table 4. Comparison of European Standard Gasoline and bio-gasoline from cracking product.

Properties	Unit	European Standard EN 228:2012 [10]		Bio-gasoline
		Min	Max	Value
Research octane number	Ron 95	95		92
Oxidation stability	Minutes			n/a
Sulphur	%wt		10	0
Lead	gr/liter			0
Metal	mg/liter			0.13
Oxygen	%wt		2.7	0
Olefin	%-v/v		18	29.17
Aromatic	%-v/v		40	38.76
Benzene	%-v/v		1	2.7
Distillation:				
10% Vol vapour	^oC		60	80.95
50% Vol vapour	^oC	77	100	116.29
90% Vol vapour	^oC	130	175	121.04
Final boiling point	^oC		210	193.79
Residue	%vol		2	0
Density (15^oC)	kg/m^3	720	775	754.73

Additionally, considerations regarding product separation aspects are essential. If conversion approaches 100%, subsequent processes after the reactor only involve fractionation of light and heavy products, with no need for feed recycling utility. Figure 8 depicts the fluctuation profile of cracking yield influenced by time on stream. Based on the graph in Figure 7, it can be observed that palm oil conversion approaches 100% within the TOS range of 2 hours. For industrial process optimization considerations, to avoid feed recycling, commercial-scale palm oil cracking with ZSM5/HY catalyst is recommended for operation periods of 2 hours.

3.6 Effect of Reaction Temperature and Residence Time

Conversion and yield of cracking products as well as the octane number of gasoline are influenced by the reaction temperature. Reaction conditions at temperatures higher than 500 °C

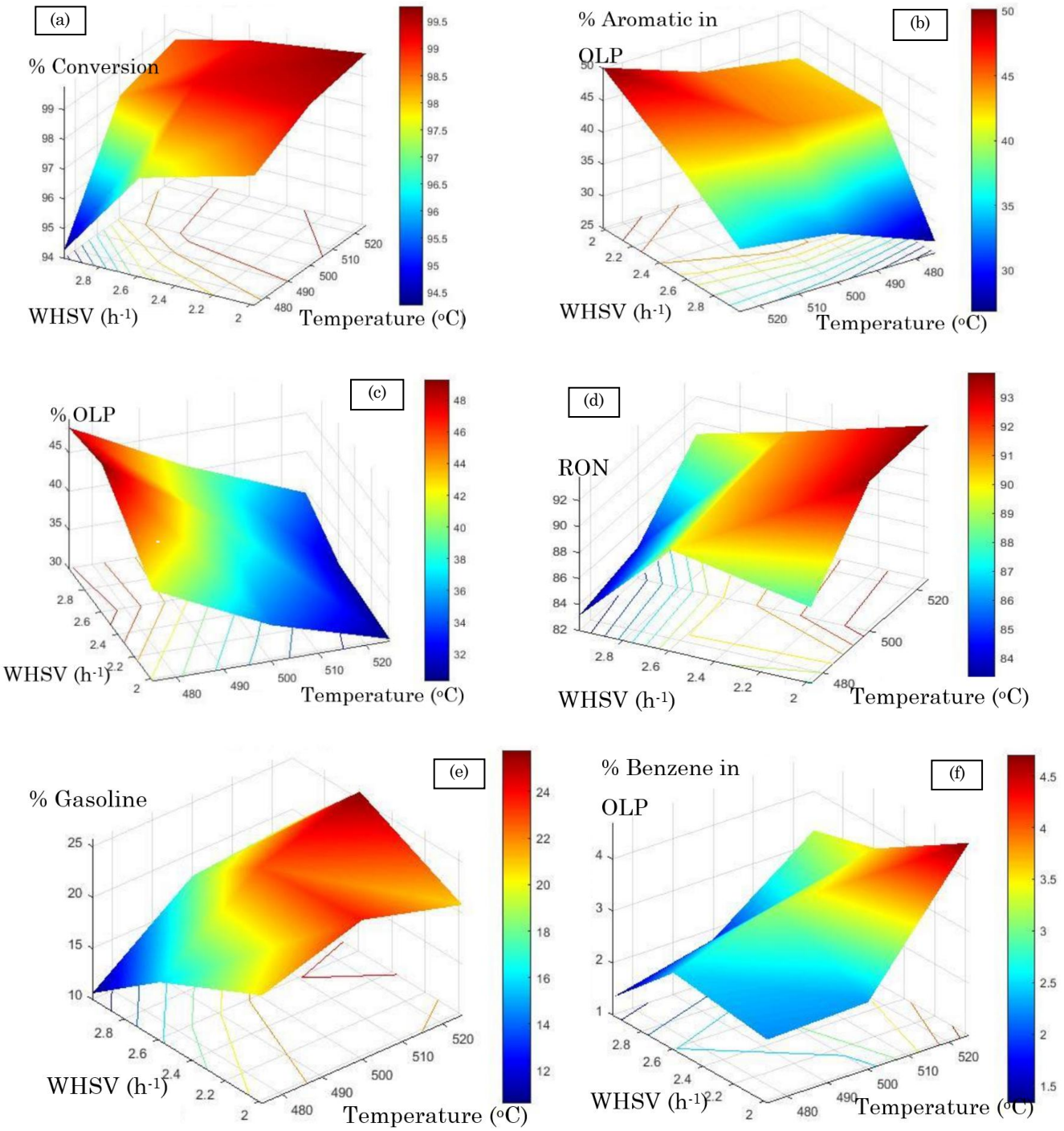


Figure 6. Correlation of operating conditions (Temperature and WHSV) with: (a) triglyceride conversion, (b) octane number, (c) organic liquid product, (d) Research Octane Number (RON), (e) gasoline yield, and (f) benzene yield.

result in a lower amount of liquid products and excess gas products due to over-cracking. Palm oil cracking reactions should ideally occur at temperatures above 450 °C. Reaction temperatures below 450 °C lead to a decrease in palm oil conversion. This is indicated in the study where at a reaction temperature of 450 °C, the cracking products contain fatty acids that solidify in the reactor outlet stream. Cracking reactions are complex processes. The reaction mechanism consists of fatty acid oxygenate formation, deoxygenation [43], cracking, hydrogenation, dehydrogenation [29,30,44], isomerization [14], cyclization [30], aromatization, and polymerization [31]. Some of these reactions are endothermic [26], while others are exothermic. Overall, cracking is classified as an endothermic reaction, with some secondary reactions being exothermic, such as olefin cyclization, isomerization, and hydrogenation. Figure 9 and Figure 10 depicts the relationship between reaction temperature, residence time and the liquid product composition at a WHSV of 2.59/hour.

The production of olefins and cyclic hydrocarbons rises in direct correlation with higher reaction temperatures. This increase in olefin yield occurs because less olefin is consumed in the cyclization reaction to form naphthenes, an exothermic process. Conversely, naphthene yield declines as temperature rises due to their consumption in dehydrogenation reactions that produce aromatics, an endothermic process. Similarly, the yields of n-paraffin and iso-paraffin hydrocarbons decrease with increasing temperatures, influenced by dehydrogenation reactions and the suppression of their formation, as these processes are exothermic.

The residence time of reactants plays a crucial role in palm oil conversion. Longer residence times lead to higher triglyceride conversion rates. Additionally, extending residence time enhances the octane number of gasoline products. However, prolonged residence time reduces liquid product yields while increasing gaseous products and cyclic hydrocarbons. Data on the influence of residence time on cracking product yields indicate that aromatics are the key component contributing to the rise in Research Octane Number (RON).

The temperature variable does not significantly affect the selectivity of hydrocarbon components, as indicated by a slightly increasing trend for olefins as the temperature rises. The variable affecting selectivity lies in the type of catalyst; between ZSM-5 and HY, they produce different hydrocarbon group compositions as representations of shape selectivity characteristics. HY is not entirely selective towards aromatics. Part of the zeolite Y activity involves isomerization and dehydrogenation reactions of paraffins to olefins [42,46]. Furthermore, the influence of residence time is a concern. After observing the cracking reaction mechanism, aromatization is a secondary reaction approaching the final reaction towards aromatic polymerization, meaning this product is formed later and requires more time in a series of cracking reaction mechanisms. The increasing trend in aromatic yield proportionate to the increase in residence time indicates that paraffins and olefins are continuously consumed due to dehydrogenation, resulting in aromatics when the reactant residence time is extended.

4. Conclusions

The developed catalyst for palm oil cracking is ZSM5/HY. Activity testing results under optimal reaction conditions yielded palm oil conversion approaching 100%, with gasoline yield approaching the quality of European gasoline. Catalyst durability is eight hours of reaction operation, but the optimal performance is within the first two hours. Shape selectivity factors make zeolite Y more selective in producing hydrocarbons in the LCO fraction, including

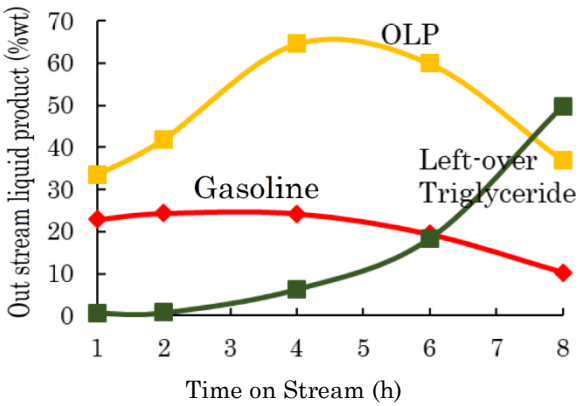


Figure 8. Outstream liquid product of cracking reaction during 8-hour time on stream

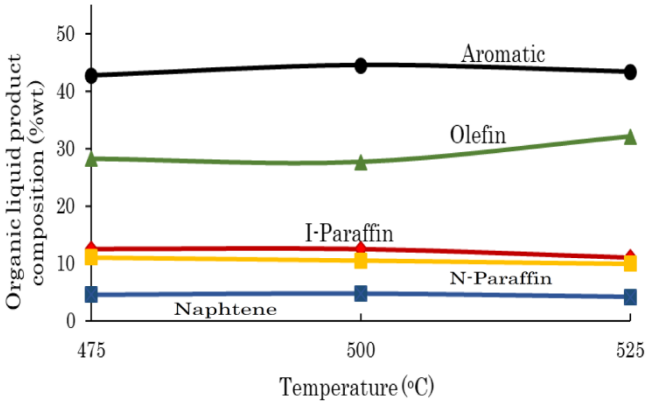


Figure 9. Effect of reaction temperature at a WHSV of 2.59/hour on the composition of organic liquid product.

kerosene and diesel. The addition of ZSM-5 to the cracking catalyst improves conversion, RON, and aromatic yield, thereby enhancing gasoline yield. Phosphorus promotion leads to decreased conversion, RON, reduced aromatic yield, and decreased coke yield. Increasing reaction temperature and residence time result in increased conversion and RON, but have minimal effect on hydrocarbon group composition changes, although this is influenced by residence time. Cracking with a zeolite Y-based catalyst in improving gasoline RON involves aromatic and olefin yield, with minimal iso-paraffin yield.

For future research, it is recommended to investigate methods to extend catalyst life beyond 8 hours, as prolonging catalyst longevity is crucial for industrial efficiency. Additionally, exploring the use of co-catalysts or process modifications to reduce olefin content while maintaining gasoline yield and octane number is suggested. High olefin content can affect fuel stability, making its reduction desirable without compromising the overall performance and quality of the produced gasoline.

Acknowledgements

The author expresses gratitude to Prof. IGBN Makertihartha and Prof. Subagjo for their guidance and for providing financial support for this research through the internal funding of the Laboratory of Chemical Reaction Engineering and Catalysis, Institut Teknologi Bandung.

CRediT Author Statement Author

Arif Algifari: writing for original draft and preparing the manuscript structure according to the journal template. IGBN Makertihartha and Subagjo: reviewing and refining the problem statement, background, data presentation and discussion in this research. Heri Prabowo: reviewing methodology section All authors have read and agreed to the published version of the manuscript.

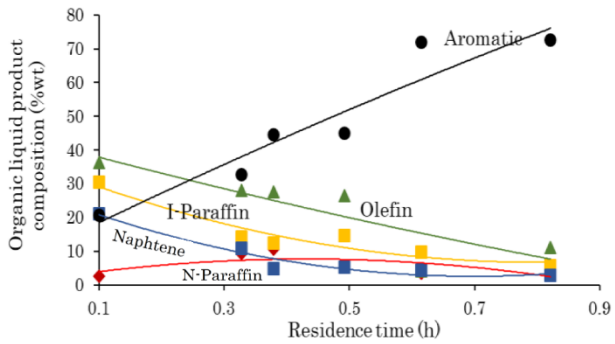


Figure 10. Effect of residence time at a temperature of 500 °C on the composition of organic liquid product

References

[1] Pambudi, N.A., Firdaus, R.A., Rizkiana, R., Ulfa, D.K., Salsabila, M.S., Suharno, Sukatiman (2023). Renewable Energy in Indonesia: Current Status, Potential, and Future Development. *Sustainability (Switzerland)*, 15(3). DOI: 10.3390/su15032342.

[2] Indupurnahayu, Setiawan, E.B., Agusinta, L., Suryawan, R.F., Ricardianto, P., Sari, M., Mulyono, S., Sakti, R.F.J. (2021). Changes in demand and supply of the crude oil market during the covid-19 pandemic and its effects on the natural gas market. *International Journal of Energy Economics and Policy*, 11(3), 1–6. DOI: 10.32479/ijeep.10671.

[3] Rahman, A., Dargusch, P., Wadley, D. (2021). The political economy of oil supply in Indonesia and the implications for renewable energy development. *Renewable and Sustainable Energy Reviews*, 144 (September 2020), 111027. DOI: 10.1016/j.rser.2021.111027.

[4] Betrix, B., Fajri, H.C., Rawung, S.S. (2022). Competitiveness of Indonesia's Crude Palm Oil (CPO) in International Markets: Based on Database 2018. *Journal of International Conference Proceedings*, 5(2), 106–115. DOI: 10.32535/jicp.v5i2.1677.

[5] de Almeida, E.S., da Silva Damaceno, D., Carvalho, L., Victor, P.A., Dos Passos, R.M., de Almeida Pontes, P.V., Cunha-Filho, M., Sampaio, K.A., Monteiro, S. (2021). Thermal and physical properties of crude palm oil with higher oleic content. *Applied Sciences (Switzerland)*, 11(15). DOI: 10.3390/app11157094.

[6] Makertihartha, I.G.B.N., Fitradi, R.B., Ramadhani, A.R., Laniwati, M., Muraza, O., Subagjo (2020). Biogasoline Production from Palm Oil: Optimization of Catalytic Cracking Parameters. *Arabian Journal for Science and Engineering*, 45(9), 7257–7266. DOI: 10.1007/s13369-020-04354-4.

[7] Wang, Y.L., Wang, X.X., Zhu, Y.A., Zhu, K.K., Chen, D., Zhou, X.G. (2020). Shape selectivity in acidic zeolite catalyzed 2-pentene skeletal isomerization from first principles. *Catalysis Today*, 347, 115–123. DOI: 10.1016/j.cattod.2018.06.009.

[8] Pazmiño-Viteri, K., Cabezas-Terán, K., Echeverría, D., Cabrera, M., Taco-Vásquez, S. (2024). Average Carbon Number Analysis and Relationship with Octane Number and PIONA Analysis of Premium and Regular Gasoline Expended in Ecuador. *Processes*, 12(8). DOI: 10.3390/pr12081706.

[9] Zheng, H., Kong, S., Yan, Y., Chen, N., Yao, L., Liu, X., Wu, F., Cheng, Y., Niu, Z., Zheng, S., Zeng, X., Yan, Q., Wu, J., Zheng, M., Liu, D., Zhao, D., Qi, S. (2020). Compositions, sources and health risks of ambient volatile organic compounds (VOCs) at a petrochemical industrial park along the Yangtze River. *Science of the Total Environment*, 703(2019), 135505. DOI: 10.1016/j.scitotenv.2019.135505.

[10] Abdellatief, T.M.M., Ershov, M.A., Kapustin, V.M., Ali Abdelkareem, M., Kamil, M., Olabi, A.G. (2021). Recent trends for introducing promising fuel components to enhance the anti-knock quality of gasoline: A systematic review. *Fuel*, 291 (January), 120112. DOI: 10.1016/j.fuel.2020.120112.

[11] Rezaei, P.S., Shafaghat, H., Daud, W.M.A.W. (2014). Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review. *Applied Catalysis A: General*, 469, 490–511. DOI: 10.1016/j.apcata.2013.09.036.

[12] Twaiq, F.A.A., Bhatia, S. (2001). Catalytic cracking of palm oil over zeolite catalysts : statistical approach. *IIUM Engineering Journal*, 2(1), 1–10. DOI: 10.31436/iiumej.v2i1.337.

[13] Liu, Y., Ding, G., Wang, H., Li, X., Zhang, J., Zhu, Y., Yang, Y., Li, Y. (2021). Highly selective glucose isomerization by HY zeolite in gamma-butyrolactone/H2O system over fixed bed reactor. *Catalysis Communications*, 156, 106324. DOI: 10.1016/j.catcom.2021.106324.

[14] Qian, E.W., Chen, N., Gong, S. (2014). Role of support in deoxygenation and isomerization of methyl stearate over nickel-molybdenum catalysts. *Journal of Molecular Catalysis A: Chemical*, 387, 76–85. DOI: 10.1016/j.molcata.2014.02.031.

[15] Xu, Y., Cui, S. (2018). A novel fluid catalytic cracking process for maximizing iso-paraffins: from fundamentals to commercialization. *Frontiers of Chemical Science and Engineering*, 12(1), 9–23. DOI: 10.1007/s11705-017-1696-1.

[16] Bij, H.E. Van Der, Weckhuysen, B.M. (2015). Phosphorus promotion and poisoning in zeolite-based materials: synthesis, characterisation and catalysis. *Chem. Soc. Rev.* 44, 7406-7428. DOI: 10.1039/C5CS00109A

[17] Farshi, A., Abri, H.R. (2012). The addition of ZSM-5 to a fluid catalytic cracking catalyst for increasing olefins in fluid catalytic cracking light gas. *Petroleum Science and Technology*, 30(12), 1285–1295. DOI: 10.1080/10916466.2010.497789.

[18] Serrano-Bermúdez, L.M., Monroy-Peña, C.A., Moreno, D., Abril, A., Imbachi Niño, A.D., Martínez Riascos, C.A., Buitrago Hurtado, G., Narváez Rincón, P.C. (2021). Kinetic models for degumming and bleaching of phospholipids from crude palm oil using citric acid and Super Flo B80® and Tonsil®. *Food and Bioproducts Processing*, 129, 75–83. DOI: 10.1016/j.fbp.2021.07.005.

[19] Ifa, L., Wiyani, L., Nurdjannah, N., Ghalib, A.M.T., Ramadhaniar, S., Kusuma, H.S. (2021). Analysis of bentonite performance on the quality of refined crude palm oil's color, free fatty acid and carotene: the effect of bentonite concentration and contact time. *Heliyon*, 7(6), e07230. DOI: 10.1016/j.heliyon.2021.e07230.

[20] Sousa-Aguiar, E.F., Trigueiro, F.E., Zotin, F.M.Z. (2013). The role of rare earth elements in zeolites and cracking catalysts. *Catalysis Today*, 218–219, 115–122. DOI: 10.1016/j.cattod.2013.06.021.

[21] Yan Gao, Binghui Zheng, Guang Wu, Fangwei Ma, C.L. (2016). Effect of the Si/Al ratio on the performance of hierarchical ZSM-5 zeolites for methanol aromatization. *RSC Advances,* 87. DOI: 10.1039/C6RA17084F

[22] Ravindran, K., Madhu, D.G. (2020). Impact of Shape and Size of Catalysts on the Physical Properties and Pressure Drop in Fixed Bed Catalytic Systems. *International Journal of Innovative Technology and Exploring Engineering*, 9(6), 1103–1109. DOI: 10.35940/ijitee.f4214.049620.

[23] Blasco, T., Corma, A., Martínez-Triguero, J. (2006). Hydrothermal stabilization of ZSM-5 catalytic-cracking additives by phosphorus addition. *Journal of Catalysis*, 237(2), 267–277. DOI: 10.1016/j.jcat.2005.11.011.

[24] Shimada, I., Kato, S., Hirazawa, N., Nakamura, Y., Ohta, H., Suzuki, K., Takatsuka, T. (2017). Deoxygenation of triglycerides by catalytic cracking with enhanced hydrogen transfer activity. *Industrial and Engineering Chemistry Research*, 56(1), 75–86. DOI: 10.1021/acs.iecr.6b03514.

[25] Shan Ahamed, T., Anto, S., Mathimani, T., Brindhadevi, K., Pugazhendhi, A. (2021). Upgrading of bio-oil from thermochemical conversion of various biomass – Mechanism, challenges and opportunities. *Fuel*, 287(August), 119329. DOI: 10.1016/j.fuel.2020.119329.

[26] Nazarova, G., Ivanchina, E., Ivashkina, E., Kiseleva, S., Stebeneva, V. (2015). Thermodynamic Analysis of Catalytic Cracking Reactions as the First Stage in the Development of Mathematical Description. *Procedia Chemistry*, 15, 342–349. DOI: 10.1016/j.proche.2015.10.054.

[27] Long, F., Zhang, X., Cao, X., Zhai, Q., Song, Y., Wang, F., Jiang, J., Xu, J. (2020). Mechanism investigation on the formation of olefins and paraffin from the thermochemical catalytic conversion of triglycerides catalyzed by alkali metal catalysts. *Fuel Processing Technology*, 200(December 2019), 106312. DOI: 10.1016/j.fuproc.2019.106312.

[28] Fluegel, L.L., Hoye, T.R. (2021). Hexadehydro-diels-alder reaction: Benzyne generation via cycloisomerization of tethered triynes. *Chemical Reviews*, 121(4), 2413–2444. DOI: 10.1021/acs.chemrev.0c00825.

[29] Bhasin, M.M., McCain, J.H., Vora, B. V., Imai, T., Pujadó, P.R. (2001). Dehydrogenation and oxydehydrogenation of paraffins to olefins. *Applied Catalysis A: General*, 221(1–2), 397–419. DOI: 10.1016/S0926-860X(01)00816-X.

[30] Zhang, Y., Wang, J., Guo, Y., Liu, S., Shen, X. (2024). Carbonyl Olefin Metathesis and Dehydrogenative Cyclization of Aromatic Ketones and gem-Difluoroalkenes. *Angewandte Chemie - International Edition*, 63(5) DOI: 10.1002/anie.202315269.

[31] Guisnet, M., Magnoux, P. (2001). Organic chemistry of coke formation. *Applied Catalysis A: General*, 212(1–2), 83–96. DOI: 10.1016/S0926-860X(00)00845-0.

[32] Anand, M., Sibi, M.G., Verma, D., Sinha, A.K. (2014). Anomalous hydrocracking of triglycerides over CoMo-catalyst-influence of reaction intermediates. *Journal of Chemical Sciences*, 126(2), 473–480. DOI: 10.1007/s12039-014-0587-y.

[33] Taufiqurrahmi, N., Bhatia, S. (2011). Catalytic cracking of edible and non-edible oils for the production of biofuels. *Energy and Environmental Science*, 4(4), 1087–1112. DOI: 10.1039/c0ee00460j.

[34] Wang, G. (2015). Zeolite – zeolite composite fabricated by polycrystalline Y zeolite crystals parasitizing ZSM-5 zeolite. *Material Research S,* 30(16), 2434-2446. DOI: 10.1557/jmr.2015.225

[35] Abdulridha, S., Jiao, Y., Xu, S., Zhang, R., Ren, Z., Garforth, A.A., Fan, X. (2021). A Comparative Study on Mesoporous Y Zeolites Prepared by Hard-Templating and Post-Synthetic Treatment Methods. *Applied Catalysis A: General*, 612(January), 117986. DOI: 10.1016/j.apcata.2020.117986.

[36] Annisa, W.W.A.N. (2017). Synthesis and Characterization of ZSM-5 Catalyst at Different Temperatures Synthesis and Characterization of ZSM-5 Catalyst at Different Temperatures. *Applied Catalysis A: General,* 612(January), 117986. DOI: 10.1088/1757-899X/214/1/012032

[37] Agliullin, M.R., Fayzullin, A. V., Fayzullina, Z.R., Kutepov, B.I. (2023). The Role of Intermediate Phases in the Crystallization of Aluminophosphate Sieves on Examples of AlPO-11 and AlPO-41. *Crystals*, 13(2). DOI: 10.3390/cryst13020227.

[38] Jae, J., Tompsett, G.A., Foster, A.J., Hammond, K.D., Auerbach, S.M., Lobo, R.F., Huber, G.W. (2011). Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *Journal of Catalysis*, 279(2), 257–268. DOI: 10.1016/j.jcat.2011.01.019.

[39] Uemura, Y., Sinnasami, R.A., Trinh, T.H., Onoe, K. (2020). Estimation of molecular size of triglyceride in a variety of solvents by using the intrinsic viscosity technique: An important index for transesterification of triglyceride in homogenous system. *IOP Conference Series: Earth and Environmental Science*, 460(1), 0–6. DOI: 10.1088/1755-1315/460/1/012011.

[40] Laredo, G.C., Vega Merino, P.M., Hernández, P.S. (2018). Light Cycle Oil Upgrading to High Quality Fuels and Petrochemicals: A Review. *Industrial and Engineering Chemistry Research*, 57(22), 7315–7321. DOI: 10.1021/acs.iecr.8b00248.

[41] Istadi, I., Riyanto, T., Buchori, L., Anggoro, D.D., Pakpahan, A.W.S., Pakpahan, A.J. (2021). Biofuels production from catalytic cracking of palm oil using modified hy zeolite catalysts over a continuous fixed bed catalytic reactor. *International Journal of Renewable Energy Development*, 10(1), 149–156. DOI: 10.14710/ijred.2021.33281.

[42] Al-Rubaye, A.H., Al-Robai, H.A., Jasim, D.J., Mohammed Al-Khafaj, H.A., Ameen, H.F.M., Al-Turaihi, A.S. (2024). Environmental Method of Distilling Gasoline Based on ASTM D86: A Comparative Study. *IOP Conference Series: Earth and Environmental Science*, 1371(2) DOI: 10.1088/1755-1315/1371/2/022021.

[43] Cheah, K.W., Yusup, S., Loy, A.C.M., How, B.S., Skoulou, V., Taylor, M.J. (2022). Recent advances in the catalytic deoxygenation of plant oils and prototypical fatty acid models compounds: Catalysis, process, and kinetics. *Molecular Catalysis*, 523(February), 111469. DOI: 10.1016/j.mcat.2021.111469.

[44] Ozawa, T., Kurahashi, T., Matsubara, S. (2011). Dehydrogenative diels-alder reaction. *Organic Letters*, 13(19), 5390–5393. DOI: 10.1021/ol202283d.

[45] Mostad, H.B., Riis, T.U., Ellestad, O.H. (1990). Shape selectivity in Y-zeolites. Catalytic cracking of decalin-isomers in fixed bed micro reactors. *Applied Catalysis*, 58(1), 105–117. DOI: 10.1016/S0166-9834(00)82281-2.