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# CATALYTIC CRACKING OF PALM OIL VIA HZSM-5 SYNTHESIS AND METAL IMPREGNATION

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Abstract- This study has investigated the successful synthesis of HZSM-5 zeolite. The synthesis was achieved by maintaining the temperature at 176 °C for 48 hours and performing an initial agitation for 5 h. Gel analysis verified the Si/Al ratio, the surface areas of HZSM-5 and M-HZSM-5, and the development of HZSM-5 and M-HZSM-5 crystal phases during synthesis process. Incipient wetness impregnation was used to make the M-HZSM-5 zeolites. Using atomic absorption spectrophotometry (AAS), the Si/Al ratio was determined to be in the range of 198 and 243. Brunauer-Emmett-Teller (BET) study revealed that the surface areas of HZSM-5 213.3524 m<sup>2</sup>/kg, Ni-HZSM-5 194.2372 m<sup>2</sup>/kg, Cu-HZSM-5 201.1762 m<sup>2</sup>/kg, and Zn-HZSM-5 192.9966 m<sup>2</sup>/g, respectively. The catalytic cracking of HZSM-5 was conducted in a fixed-bed microreactor. Subsequently, the products conducted investigation to analysis using GC-Flame Ionization Detector (GC-FID). The analysis results revealed that the primary fraction obtained was gasoline, by kerosene and diesel in descending order of quantity. The catalytic cracking process of palm oil in zeolite HZSM-5 instructs the formation of hydrocarbons C5-C18.

**Keywords:** Catalytic Cracking, HZSM-5 Zeolite, Impregnation, Palm Oil.

# **1. INTRODUCTION**

The conversion of dense hydrocarbons on catalysts in industrial settings is a multifaceted procedure where reactions occurring within the zeolite and matrix take place concurrently. Catalytic cracking processes have been developed since the Second World War. Nowadays, almost all materials produced are used in catalytic processes. Moreover, it is challenging to distinguish between thermal and catalytic cracking as they happen in conjunction. Approximately 80% of chemical industries rely on catalysts [1]. Catalysts can also be used to produce a new source of energy by cracking vegetable oil to yield petroleum-like fuels [2]. As the biggest palm oil producer, Indonesia has the potential to lead in the production of renewable fuels by catalyzing the cracking of palm oil. Zeolite is aluminosilicate crystalline, which is constructed from corner-sharing [SiO<sub>4</sub>] and [A<sub>1</sub>O<sub>4</sub>] tetrahedral. HZSM-5 is a zeolite widely used as an active component in cracking catalysts. HZSM-5 has a Si/Al ratio of 30-94 [3]. Some researchers synthesized catalytic process, such as Liu, et al., [4] compared the performance of nanoscale and microscale of HZSM-5, respectively.

Samples of zeolite were manufactured using a wellestablished hydrothermal method with n-butylamine as the starting material. After being washed three times in a 0.4 M-NH<sub>4</sub>NO<sub>3</sub> solution, drying at 120 °C for 12 hours, and calcining at 540 °C for three hours, the microscale NaZSM-5 was ready for use [5]. As a result, there were six times as many external acid sites per unit area in nanoscale HZSM-5 (NH) than there were in microscale HZSM-5 (MH). In contrast to microscale HZSM-5, nanoscale HZSM-5 displayed a significantly higher proportion of acidic on its surface, with percentages of 36% compared to 10%. In the measurements using modified Hammett indicators, nanoscale HZSM-5 indicated a higher concentration of acidic, quantified at 0.55 mmol/g, in comparison to microscale HZSM-5, which had a lower concentration of 0.3 mmol/g [6].

Yanan, et al., [7], conducted research on activitycatalytic cracking from ZSM-5 and Al-MCM-41. Zeolite HZSM-5 with a mole ratio of Si/Al 13 (HZSM-5/L), was synthesized by mixing Solution A and Solution B. NaOH, distilled water, TPAOH, and SiO2 were dissolved to create Solution A. NaOH, NaAlO2, distilled water, and SiO2 were dissolved to make Solution B. After 1 hour of constant stirring, solution A was added to solution B. Molar composition led to the formation of the gel. The following was varied and placed in a 120 mL. The synthesis process involved the use of a Teflon-lined stainless-steel autoclave, which was heated at 180 °C for a duration of 17 days [8]. The composition of the synthesis mixture was as follows: part of SiO<sub>2</sub>, 0.0075 parts of TPAOH (tetrapropylammonium hydroxide), 0.104 parts of Na<sub>2</sub>O, 0.032 parts of Al<sub>2</sub>O<sub>3</sub>, and a substantial amount of H<sub>2</sub>O, resulting in a solution with a pH of 14.

Recovering the final product (pH 12.5) required filtration, multiple washes in deionized water, and drying at 70 °C for 12 hours [9]. HZSM-5/H (Si/Al = 37) was synthesized by mixing tetrapropylammonium bromide (TPABr) + NH<sub>4</sub>F + distilled water + AlF<sub>3</sub>.3H<sub>2</sub>O + fumed silica (Merck). Molar composition: homogenous gel A mixture of SiO<sub>2</sub>:0.1 TPABr:0.56 + NH<sub>4</sub>F:0.065 + AlF3:8 H<sub>2</sub>O was heated in an oven at 200 °C for 48 hours in a stainless-steel autoclave with a Teflon lining. After crystallization, the pH settled at around 7. The end result was filtered for recovery, rinsed many times in deionized water, and dried at 70 °C for 24 hours [9, 10].

By synthesized Al-MCM-41 (Si/Al = 31) with fumed silica being dissolved in NaOH and sodium aluminate, and after mixing for 30 min, hex a decyl trimethyl ammonium chloride (CTACl) was added to the resultant solution. The result of ZSM-5/L is: micropore volume 0.14 cm<sup>3</sup>/g, the average size crystal 0.5  $\mu$ m, Na/Al = 0.5, surface area 333 m<sup>2</sup>/g. ZSM-5/H: micropore volume 0.18 cm3/g, average size crystal 20 µm, Na/Al 0.04, surface area 400 m<sup>2</sup>/g. Al-MCM-41: Na/Al= 0.55, surface area 992 m<sup>2</sup>/g, volume of pore 0.97 cm<sup>3</sup>/g, and particle diameters 3 nm [6-8]. HZSM-5 zeolite has a unique characteristic; the pore size of hydrocarbon molecule C is 0.54×0.57 nm (3D-structure), and has organophilic characteristics. Zeolite ZSM-5 is widely used for hydrocarbon catalytic cracking. Due to its simple microporous structure and extensive diffusion paths, however, traditional ZSM-5 zeolite tends to lose its activity quickly [11].

Various catalysts have been used in the cracking process to obtain biofuel, among other things. And zeolite of faujasite catalysts, the catalysts represent catalytic cracking, which is initially used at the cracking process of petroleum, then further developed at the cracking process of vegetable oil. Some catalysts are also used in the cracking process, including HZSM-5 and ultra stable *Y* Zeolite (USY). From the third catalyst, HZSM-5 zeolite (M-HZSM-5) was obtained with the biggest conversion and yield. While according to the catalytic conversion of palm oil base on a residue mixture of fatty acids by catalyst ZSM-5 in a reactor fixed-bed at atmospheric temperature resulted in a gasoline fraction of 44.4% weight at the rate of feed of  $3.66 \text{ h}^{-1}$  and temperature of  $440 \text{ }^{\circ}\text{C}$  [12].

Zeolites have demonstrated significant promise for utilization in catalytic cracking processes due to their notable characteristics, including a high surface area, substantial capacity, adsorption interconnecting microporous channels, and exceptional thermal and hydrothermal durability. Zeolites find extensive application in separation and catalytic technologies, especially within the hydrocarbon processing industry, the adsorptive properties of zeolites are of great significance. The phenomenon of adsorption of n-hexane, n-pentane, and n-heptane on MFI-type uniform size is being investigated, such as HZSM-5 has garnered considerable interest from researchers due to the intricate adsorption profiles observed within this system. Souza et al., [13] conducted the investigated of selective cracking

of liquid hydrocarbon mixture condensed (natural gasoline) utilizing zeolite of HZSM-5 as the catalyst. Catalytic cracking processes using a fixed bed reactor operate on flow rate and atmosphere. The HZSM-5 catalyst that was used in previous studies. The zeolite was subjected to activation at a temperature of 450 °C for a duration of 2 hours, flow rate range of 20 mL/min. The objective of the study was to investigate the impact of temperature and the ratio of catalyst to W/F on conversion and cracking of catalytic. Temperature at 350-450 °C and W/F 5-17 gcat h/mol. The result established that maximum selectivity and mass product every hour was obtained at a high temperature of 450 °C and a heavy ratio of catalyst with flow rate (W/F) (7, 2, 8  $g_{cat}$  h/mol) [14]. The highest level of selectivity for  $C_3H_6$  is achieved at a temperature of 350 °C and a catalyst loading of 7.0 grams per mole of reactant. The best conditions to produce maximum entirety are found 5.7 g/mol at 421 °C. The mass product of butene taken a fancy at high temperature of 450 °C by W/F 12.1 g<sub>cat</sub> h/mol, at a relatively low temperature of 350 °C, the highest level of selectivity was observed [15].

One alternative that can support the development of new and renewable energy is biofuels. Biofuels derived from biomass are still promising because they are inexpensive, abundant, and can be replenished over time [20]. Biofuels have advanced rapidly from the first to the third generation. The first generation of biofuels, produced by fermenting food ingredients such as sugar and flour, is less attractive because of the high costs of raw materials and the energy versus food issue. Among various method of cracking processes (i.e., catalytic cracking, thermal cracking, and hydrocracking), catalytic cracking offers numerous advantages [11]. Catalytic cracking is a conversion process that is applicable to a broad spectrum of feedstocks, chemical process in which intricate hydrocarbons are decomposed into less complex molecules, and it falls within the scope of this study. The fundamental principle underlying catalytic cracking has similarities to thermal cracking, it distinguishes itself through the utilization of a catalyst [1, 16]. It represents one of several practical applications within refineries where catalysts are employed to enhance both process efficiency and the variety of products produced. From these studies, the optimization of the process with a primary focus on maximizing mass fractions. The specific aim is to enhance the production of ethene, propene, and butanes [5].

# 2. CATALYST PREPARATION

Preparations of the M-HZSM-5 were intended with a Si/Al 94 ratio. Sodium silicate was used as a silicaalumina, aluminosilicate zeolite (ZSM-5). In order to achieve their aim, the experiments followed two procedures in the literature for HZSM-5 zeolite preparations: the first was US Patent No. 4.4891.199 in 1990, and the second was US Patent No. 4.341.748 in 1992. The process involved preparing a solution in a glass beaker with the following composition of solution A: Al<sub>2</sub>SO<sub>4</sub>.18H<sub>2</sub>O + H<sub>2</sub>SO<sub>4</sub> 98%; H<sub>2</sub>O. Subsequently, another solution, referred to as solution B, was prepared in a separate glass beaker with the following composition: 12.3 grams of  $Al_2(SO_4)_{3.1}8H_2O$ , 30 grams of  $H_2SO_4$  (98%), and 600 grams of  $H_2O$ . Solution B was then slowly added to Solution A, while stirring continuously to ensure the formation of a homogeneous mixture. This final mixture appeared as a white gel. It was allowed to stand for 1 h to achieve a smooth and uniform gel [1, 6, 17].

The gel with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 94 was subsequently placed into an autoclave. It was heated to 176 °C under a pressure of 10 bar and stirred at 100 rpm for a duration of 48 hours. Following this process, the crystals that developed were isolated through a filtration process, and the washing procedure entailed the use of distilled water until the pH of the resulting filtrate reached approximately pH 8. Following this, the obtained crystals were dried in an oven at 110 °C for a duration of 24 hours. In Figure 1 illustrates the synthesis scheme for the Na-Zeolite crystals obtained. The technique employed in this study include X-ray diffraction (XRD), Brunauer-Emmett Teller (BET) and absorption atomic spectroscopy (AAS) studies. The XRD examination was employed to ascertain the crystal structure and relative crystallinity of the zeolite. XRD characterization was carried out using a Phillips X-ray diffractometer. The initial 20 position was set at 5.0084, and the final position at 59.9864, with continuous scanning. The extension data of the specimen was established at a value of 10.00 mm, while the

temperature at which the measurement was conducted was -273.15 °C. Copper (Cu) was employed as the anodized material, and the diffractometer model utilized was XPert MPD.

### 2.1. H-Zeolite HZSM-5 Formation

Ion transfer of Na-Zeolite produced the H-Zeolite. The procedures were started by dissolving Na-Zeolite in a solution of ammonium chloride (NH<sub>4</sub>Cl) 1 M. The ratio of Na-zeolite to ammonium chloride was interval of 1:10. The operation process was reiterated three times. The produced H-Zeolite was then filtered, cleaned, and dried at 110 °C for 6 hours. H-Zeolite was then calcinated under an N<sub>2</sub> atmosphere at a temperature of 550 °C for 5 hours [13].

# 2.2. Catalyst Impregnation

Catalyst impregnation followed the procedure developed by Romero (1997). HZSM-5 was dissolved in each metallic solution as follows:  $CuSO_4.5H_2O$ , NiSO<sub>4</sub>.7H<sub>2</sub>O, and ZnSO<sub>4</sub>.7H<sub>2</sub>O. The mixture was kept at 25 °C. The solid material was subjected to a drying process at a temperature of 110 °C for a duration of 14 hours. Then, the solid was dried at 110 °C for 14 hours and calcinated at 500 °C for 4 h, then reduced with hydrogen at 450 °C for 3 h. The HZSM-5 catalyst obtained exhibits a powdery appearance, resembling a white form. In Figure 1, the equipment scheme was presented.



Figure 1. Flow chart of catalyst synthesis procedure, a) Na-Zeolite catalyst, b) Distorting catalyst Na-Zeolite to H-Zeolite, c) Impregnation procedure

### 2.3. Catalyst Cracking Process

The catalytic cracking processing, first, palm oil was fed to the fixed-bed microreactor at atmospheric pressure and heated temperature was set at 200 °C, pressure at 2 atm, and catalytic cracking was carried out for 120 min. Approximately 1 gram of catalyst was also fed to the reactor. Then, N<sub>2</sub> was flown to the reactor at a flow rate ranging from 100 to 160 mL.min<sup>-1</sup>. GC-FID analysis was engaged to conduct an analysis of the product, wherein the technique was utilized to separate and examine mixtures comprising volatile constituents, a PARAPLOT QO4 column. Typically, a variety of amplification ranges are offered, spanning from around 1 picoampere ( $p_A$ ) per millivolt (mV) at the uppermost output sensitivity to roughly 10 nanoampere ( $n_A$ ) per millivolt (mV) at the lowermost output sensitivity.

The carrier gas used in this study was high-purity hydrogen with a concentration of 99.995%. The flow rate of hydrogen-air mixture ranged from 30 to 450 mL/min. The visible scheme of catalytic cracking process was carried out in Figure 2, the equipment scheme was presented.



Figure 2. The illustration schematic of catalytic cracking process

A glass fixed-bed microreactor was used to process the palm oil. The thermocouple controls the temperature of the reactor. When the thermocouple reaches 200 °C, in catalytic cracking process; once the desired synthesis period has elapsed, the process is considered complete. After undergoing synthesis, the biofuel was separated into its light and heavy hydrocarbon components. To assess the catalytic product, the volatile component was calculated.

# **3. RESULTS AND DISCUSSION**

The results of the experiments are outlined in this section, which are broken down into various subheadings, including the characteristics of Si/Al ratio, composition of Ni, Cu and Zn in the catalysts, surface areas and pore size of the catalysts (i.e., AAS, XRD, GC-MS and Brunauer-Emmett-Teller (BET) method.

#### 3.1. Catalyst Characterization

The efficiency and quality of product from palm oil + HZSM-5 catalyst mixtures depend on surface areas and pore sizes of the catalysts [18]. Catalytic cracking stands as a fundamental process in numerous refineries, responsible for generating high-octane gasoline, light alkenes and aromatic middle distillates. This is achieved by giving lighter fractions as compared to thermal cracking. Hydrocarbon product can be controlled by using catalysts [3, 4]. HZSM-5 is a catalyst that finds widespread use as an active component in cracking catalysts.

These characteristics make HZSM-5 a catalyst that selectively forms hydrocarbons with a long-life catalyst, demonstrating durability under high-temperature and high-acidity conditions. In fact, ZSM-5 with different shapes like hollow, composite, and nanosheet structures can improve how well acid sites diffuse and how easy they are to reach. This leads to high catalytic activity. The results of the zeolite characterizations can be seen in Tables 1 and 2 used method US Patent 4.4891.199, at a Si/Al ratio of 198, various catalysts, including the addition of metal catalysts, resulted in only slight variations in the percentage of pore size and surface area values. In this case, the highest pore size value for the Ni/HZSM-5 catalyst exhibit observable activity with 5% nickel content, measuring 13.584 Å [18]. The highest surface area, however, was achieved with the unmodified HZSM-5 catalyst, measuring 149.9189 m²/g. While the Si/Al ratio is 243, we see that the highest pore size value was achieved with HZSM-5, measuring 13.255 Å. The highest surface area was associated with HZSM-5, registering at 213.3524 m<sup>2</sup>/g. These results highlight the effect of both composition of catalyst (Si/Al ratio) on pore size and surface area characteristics. This is because the material (palm oil) and HZSM-5 catalyst function as absorbents, increasing selectivity and catalytic activity in the direction of light alkenes. Through the adjustment of HZSM-5 properties via the interaction of compounds, it becomes possible to mitigate carbon deposit development due to excessive reaction of reactants [19].

Table 1. Characteristics of HZSM-5 catalyst with Si/Al 198

Catalyst	Surface Area (m <sup>2</sup> /kg)	Pore Size	Ni, Cu, Zn	Si/Al content (m/m)
HZSM-5	198	0	13.209	149.9189
Ni/HZSM-5 (Ni 5%)	198	4.98	13.584	149.9007
Cu/HZSM-5 (Cu 5%)	198	5	13.249	145.2944
Zn/HZSM-5 (Zn 5%)	198	4.20	13.390	142.5420

From Tables 1 and 2, the catalysts produced according with the standard of catalyst used for cracking size, which is a minimum of 8 Å. The synthesized catalysts surface areas are more than  $100 \text{ m}^2/\text{kg}$ ; thus, the synthesized catalysts can be used in the cracking process [20].

Catalyst	Surface Area (m <sup>2</sup> /kg)	Pore Size (Å)	Ni, Cu, Zn (%)	Si/Al content (m/m)
HZSM-5	243	0	13.255	213.3524
Ni/HZSM-5 (Ni 5%)	243	4.97	13.176	194.2372
Cu/HZSM-5 (Cu 5%)	243	4.98	13.249	201.1762
Zn/HZSM-5 (Zn 5%)	243	4.92	13.962	192.9966

Table 2. Characteristics of HZSM-5 catalyst with Si/Al 243

Absorption Atomic Spectroscopy (AAS) was employed to assess and determine the Si/Al ratio and the Ni, Cu, and Zn compositions of the catalysts. BET analysis was utilized to analyze the pore sizes and surface areas of the catalysts. ZSM-5 zeolite works well in a number of catalytic applications because it has good qualities like a high Brunauer-Emmett-Teller (BET) surface area, exceptional thermal and hydrothermal stability, a large amount and high of acid sites, and a distinctive channel structure [18]. Catalytic cracking of hydrocarbons holds great importance in industrial manufacturing. This process offers several advantages, including high cracking conversion efficiency, a propensity for selecting light alkenes, and reduced carbon deposition compared to thermal cracking. Most of the time, M-HZSM-5 is used for hydrocarbon catalytic cracking as a catalyst. This is due to its great thermal and hydrothermal stability as well as its exceptional acidity and porous structure [3, 21].



Figure 3. XRD pattern of HZSM-5 synthesize

Figure 3 shows that the XRD results indicate that the catalysts formed an amorphous structure. It can also be seen that there are intensities of HZSM-5. X-ray diffraction (XRD) analysis serves the dual purpose of identifying and quantitatively evaluating the crystal phase of ZSM-5. The results of the XRD analysis are portrayed in a diffractogram, which conveys information about the solidity of the material by examining the sharpness and location of distinct peaks. The information obtained through X-ray diffraction (XRD) consists of X-ray diffraction intensities paired with their corresponding  $2\theta$ angles, which are pivotal in identifying the crystal structure and composition of the materials being analyzed. The XRD pattern formed a peak with intensities at  $2\theta = 21^\circ$ ,  $23^\circ$ , which confirms that HZSM-5 was formed [22].







Figure 5. XRD pattern of Cu-HZSM-5 synthesize



Figure 6. XRD pattern of Zn-HZSM-5 synthesize

Figures 4-6 show the XRD results indicate that the catalysts formed an amorphous structure. It can also be seen that there are intensities of Ni, Cu, and Zn in the XRD spectra, which confirms that the active metals are present in zeolite after the impregnation process. Ni, Cu, and Zn, as transition metals, possess an unfilled delectron layer, a characteristic that facilitates the establishment of covalent bonds between catalysts and reactant molecules. This attribute contributes to excellent catalytic activity. Moreover, it offers a significantly higher cost-effectiveness in comparison to noble metals [23].

Consequently, metal-based catalysts have found commercial applications in various refinery processes, including hydrogenation. Furthermore, the metal group has demonstrated exceptional selectivity for monocyclic aromatic hydrocarbons, making it valuable in specific catalytic reactions where this selectivity is desired. The discovery revealed that when the active metal group was combined with HZSM-5, it produced a synergistic effect, resulting in the enhanced catalytic cracking of biomass, ultimately generating aromatic hydrocarbons at an accelerated rate. The XRD spectra show that the identification characteristic of HZSM-5 is that there are intensities at  $2\theta = 29.05^{\circ}$ ,  $47.8^{\circ}$  and  $56^{\circ}$ , which confirms that HZSM-5 was formed, influence the activity and stability of the catalyst [18].

The crystallization of the synthesized ZSM-5 appears to be quite successful, as indicated by the ZSM-5 diffractogram. The existence of well-defined peaks with distinct separation in the diffractogram suggests that the ZSM-5 crystals have formed well and exhibit a high degree of crystallinity. This is a positive indication of the quality and purity of the synthesized ZSM-5 material [24]. This suggests that the incorporation of the metalbased fraction onto HZSM-5 did not disrupt the fundamental molecular sieve structure. The molecular sieve's structure remained unchanged despite the introduction of metals [20, 25].

# 3.2. Product Analysis of Catalytic Cracking Process

Figure 7 shows the influence of active metal impregnation in the catalyst to surface area. Figure 7a illustrates how different catalysts have a notable impact on the surface area. Specifically, it shows that the specific surface area of impregnation process Ni-HZSM-5 had the highest initial value at 150 m<sup>2</sup>/kg, which slightly decreased to 145 m<sup>2</sup>/kg for Zn-HZSM-5. These findings suggest that the introduction of nickel did not damage the structural integrity of the HZSM-5 carrier. Instead, the Ni crystals formed upon loading and were deposited onto the HZSM-5 structure [2, 26].

However, this deposition led to a partial closure of the mesoporous structure within the catalyst. Those figures show that the addition of an active metal to the catalyst decreases the surface area but increases the active site of the catalyst. Hence, incorporating an active metal could potentially enhance both the yield and selectivity of the cracking products. Figure 7b it was also state that the specific surface area from impregnation process of HZSM-5 had the highest initial value from 180-215 m<sup>2</sup>/kg. The catalyst's extensive surface area plays a crucial role in influencing the reaction rate. Impregnation is typically characterized as the complete saturation of specific materials; its goal is to occupy the catalyst pores with active metal by submerging the catalyst in a solution containing the metal [27].

Based on Figure 8, the results of the effect of catalysts on pore size show that their size provides improved access to the size, thereby enhancing the diffusion rate as well as the overall catalytic performance. The average pore sizes for the HZSM-5, Ni-HZSM-5, Cu-HZSM-5, and Zn-HZSM-5 compositions were evaluated at 13.2 Å, 13.62 Å, 13.27 Å, and 13.41 Å, respectively. The HZSM-5 catalyst's acidic properties make it effective as an adsorbent. HZSM-5 possesses а diameter of approximately 5 Å and features a pore size measuring 0.54×0.56 nm. HZSM-5 with a size less than 2 nm falls into the category of microporous materials, endowing it with a substantial surface area [5, 6, 28].



Figure 7. The effect type of catalysts to surface area; a) 138-152 m<sup>2</sup>/kg; b) 180-215 m<sup>2</sup>/kg



Figure 8. The effect of catalysts to pore size a) 12.8-13.3 Å; b) 13-13.7 Å

The micro-sized variant of this catalyst is HZSM-5, known for its high selectivity. To assess the surface characteristics of the HZSM-5 catalyst impregnated with iron (Fe), copper (Cu), and nickel (Ni) metals, a surface analyzer was employed, utilizing the BET (Brunauer-Emmett-Teller) method. The BET method offers insights into a material's specific surface area, making it suitable for estimating the average size of particulate solids. It achieves this by measuring the pressure of nitrogen gas within the pores, which allows us to ascertain the catalyst's pore size and, consequently, its surface area. Catalytic activity, which depends on how reactants reach the active sites on the catalyst, can be quantified in relation to the total surface area [10, 29].



Figure 9. The effect of catalysts to yield and selectivity cracking product

According to Figure 9, the effectiveness of catalyst to yield and selectivity of gasoline product. The liquid product from the catalytic cracking process underwent analysis using GC-MS. Following the procedures outlined in US Patent 4.341.748, it was determined that the primary fraction consisted of gasoline, followed by kerosene and diesel as the subsequent fractions. Whereas the catalytic cracking products obtained from the US Patent 4.4891.199 method show that the dominant product fraction contains mainly kerosene, followed by diesel and a few gasolines [30]. The fractionation process takes place when the stream of cracked hydrocarbons is divided into separate fractions, each containing different products. Introducing an active metal into the catalyst is expected to enhance both the selectivity of the cracked products and yield product. In the case of catalytic cracking using zeolite HZSM-5, it was observed that the process generated hydrocarbons ranging from C<sub>5</sub> to C<sub>18</sub> in size. In cases of isomerization, domination-branched Three potential hydrocarbons arise. reactionspolymerization, cyclization, and aromatization-occur during the process, leading to catalyst deactivation. Consequently, a regeneration procedure is necessitated.

# 4. CONCLUSIONS

This study examines an analysis of a biofuel product through catalytic cracking of palm oil with the catalyst HZSM-5. HZSM-5 has the capacity to be employed for the conversion of gasoline, kerosene, and diesel fractions through catalytic cracking, showcasing its commercial potential, especially in the context of palm oil processing. HZSM-5 could be synthesized to convert and degrade palm oil into a fraction of a biofuel product. The products produced were mainly kerosene, followed by diesel and a few gasolines, respectively. Catalyst preparation is an important step in utilizing the product. The impregnation of an active metal into the catalyst decreases the area of surface and simultaneously increasing its active site of the catalyst.

Furthermore, the synthesis process confirmed the existence of HZSM-5 and M-HZSM-5 crystal phases, with metal (M) represents the incorporation of metals such as nickel (Ni), copper (Cu), and zinc (Zn). The analysis encompassed measurements of the surface areas of both HZSM-5 and M-HZSM-5, in addition to determining the Si/Al ratio. The findings found that gasoline made up the majority of the product, with kerosene and diesel coming in second and third. Notably, the catalytic cracking of palm oil utilizing zeolite HZSM-5 yielded hydrocarbons within from  $C_5$  to  $C_{18}$  range. The characteristics of the biofuels produced from this research would depend on various factors, including the feedstock (palm oil), the catalyst used (HZSM-5 and metalmodified), and the specific conditions of the catalytic cracking process. Which contained hydrocarbon molecules such as gasoline, kerosene, and diesel. These findings indicate that HZSM-5 could be an exceptionally promising catalyst for converting complex hydrocarbon molecules, offering a potential avenue for further industrial applications.

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# REFERENCES

[1] L.H. Chen, M.H. Sun, Z. Wang, W. Yang, Z. Xie, B.L. Su, "Hierarchically Structured Zeolites: From Design to Application", Chemical. Rev., Vol. 120, No. 1, pp. 194-294, 2020.

[2] W. Chen, D. Han, X. Sun, C. Li, "Studies on the Preliminary Cracking of Heavy Oils: Contributions of Various Factors", Fuel, Vol. 106, pp. 498-504, 2013.

[3] A. Eschenbacher, F. Goodarzi, A. Saraeian, S. Kegnæs, B.H. Shanks, A.D. Jensen, "Performance of Mesoporous HZSM-5 and Silicalite-1 Coated Mesoporous HZSM-5 Catalysts for Deoxygenation of Straw Fast Pyrolysis Vapors", Journal of Analytical and Applied Pyrolysis, Vol. 145, pp. 104712, 2020.

[4] J.F. Liu, Y. Liu, L.F. Peng, "Aromatization of Methane by Using Propane as Co-Reactant over Cobalt and Zinc-Impregnated HZSM-5 Catalysts", Journal of Molecular Catalysis A, Issue 1-2, Vol. 280, pp. 7-15, 2008.

[5] M. Irsyad, A. Amrizal, M.D Susila, A. Amrul, T.M. Fransisco, "Heat Transfer Characteristics of Coconut Oil as Phase Change Materials in Freezing Process", International Journal on Technical and Physical Problems of Engineering (IJTPE), Issue 50, Vol. 14, No. 1, pp. 29-33, March 2022.

[6] J. Zhang, R. Tang, Z. Shen, S. Liang, H. Zhong, "Catalytic Oligomerization of Ethylene over Nano-Sized HZSM-5", Journal Energy Inst., Vol. 93, pp. 2550-2557, 2020. [7] V. Balasundram, N. Ibrahim, R. Isha, M. Kamaruddin, A. Hamid, H. Hasbullah, "Catalytic Upgrading of Sugarcane Bagasse Pyrolysis Vapours over Rare Earth Metal (Ce) Loaded HZSM-5: Effect of Catalyst to Biomass Ratio on the Organic Compounds in Pyrolysis Oil", Applied Energy, Vol. 220, pp. 787-799, 2018.

[8] Y. Hu, J. Liu, J. Cheng, "Coupling Catalytic Hydrolysis and Oxidation of HCN over HZSM-5 Modified by Metal (Fe, Cu) Oxides", Applied Surface Science, Vol. 427, pp. 843-850, 2018.

[9] X. Huang, R. Wang, X. Pan, C. Wang, M. Fan, Y. Zhu, et al., "Catalyst Design Strategies Towards Highly Shape-Selective HZSM-5 for Para-Xylene Through Toluene Alkylation", Green Energy Environmental, Vol. 5, pp. 385-393, 2018.

[10] F.A. Twaiq, N. Asmawati, M. Zabidi, A. Rahman, S. Bhatia, "Catalytic Conversion of Palm Oil over Mesoporous Aluminosilicate MCM-41 for the Production of Liquid Hydrocarbon Fuels", Fuel Process Technology, Vol. 84, pp. 105-120, 2003.

[11] G. Liu, G. Zhao, F. Meng, S. Qu, L. Wang, X. Zhang, "Catalytic Cracking of Supercritical n-Dodecane over Wall-Coated HZSM-5 Zeolites with Micro and Nanocrystal Sizes", Energy and Fuels, Vol. 26, 1220-1229, 2012.

[12] Y. Huang, L. Wei, Z. Crandall, J. Julson, Z. Gu, "Combining Mo-Cu/HZSM-5 with a two-Stage Catalytic Pyrolysis System for Pine Sawdust Thermal Conversion", Fuel, Vol. 150, pp. 656-663, 2015.

[13] H.V. Bekkum, J.C. Jansen, E.M. Flasingen, "Studies in Surface, Science and Catalysis Introduction to Zeolite, Science and Practice", Elsevier, Vol. 163, New York, USA, 1991.

[14] A.M. Hashimov, N.M. Tabatabaei, U.F. Samedova, M.A. Nuriyev, M.N. Bayramov, A.O. Mehrabov, "Microwave Absorbing Property of Epoxy Resin Composites with Added Fe<sub>3</sub>O<sub>4</sub> Nanoparticles", International Journal on Technical and Physical Problems of Engineering (IJTPE), Issue 38, Vol. 11, No. 1, pp. 16-20, March 2019.

[15] M.J.B. Souza, F.A.N Fernandes, A.M.G. Pedrosa, A.S. Araujo, "Selective Cracking of Natural Gasoline over HZSM-5 Zeolite", Fuel Process Technology, Vol. 89, pp. 819-827, 2008.

[16] J. Li, G. Wang, C. Gao, X. Lv, Z. Wang, H. Liu, "Deoxy-Liquefaction of Laminaria Japonica to High-Quality Liquid Oil over Metal Modified ZSM-5 Catalysts Deoxy-Liquefaction of Laminaria Japonica to High-Quality Liquid Oil Over Metal Modified ZSM-5 Catalysts", Energy Fuels, Vol. 27, pp. 5207-5214, 2013.

[17] A. Zheng, Z. Zhao, S. Chang, Z. Huang, H. Wu, X. Wang, et al., "Effect of Crystal Size of ZSM-5 on the Aromatic Yield and Selectivity from Catalytic Fast Pyrolysis of Biomass", Journal of Molecular Catalysis A Chem, Vol. 383-384, pp. 23-30, 2014.

[18] Z. Zhang, B. Liu, F. Liu, Y. Zhao, T. Xiao, "Effect of Nickel Loading on the Performance of Nano- and Micro-Sized ZSM-5 Catalysts for Methanol to Hydrocarbon Conversion", Catalysis Today, Vol. 317, pp. 21-28, 2018.

[19] X. Yu, B. Liu, Y. Zhang, "Effect of Si/Al Ratio of High-Silica HZSM-5 Catalysts on the Prins Condensation of Isobutylene and Formaldehyde to Isoprene", Heliyon. Vol. 5, p. 01640, 2019.

[20] Y. Xu, J. Wang, Y. Suzuki, Z. Zhang, "Effect of Transition Metal Additives on the Catalytic Stability of Mo / HZSM-5 in the Methane Dehydroarom

atization under Periodic CH<sub>4</sub>-H<sub>2</sub> Switch Operation at 1073 K", Appl Catal A, Vol. 409-410, pp. 181-193, 2011. [21] J. Comparot, A. Faust, Y. Millot, T. Onfroy, P. Magnoux, J. Paillaud, et al., "High Catalytic Cracking Activity of Al-MCM-41 Type Materials Prepared from ZSM-5 Zeolite Crystals and Fumed Silica", Appl Catal A Gen, Vol. 344, 61-69, 2008.

[22] A.I. Zolotukhina, E.V. Romanova, T.A. Bugrova, A.S. Knyazev, G.V. Mamontov, "Influence of Impregnation Conditions on the Activity of CrOx / Al<sub>2</sub>O<sub>3</sub> Catalysts in Dehydrogenation of Isobutane in Fixed Bed Reactor", Arab J. Chem., Vol. 13, 9130-9138, 2020.

[23] C. Martinez, A. Corma, "Inorganic Molecular Sieves: Preparation, Modification and Industrial Application in Catalytic Processes", Coord Chem Rev, Vol. 255, pp. 1558-1580, 2011.

[24] F.A. Twaiq, A. Rahman, S. Bhatia, "Liquid Hydrocarbon Fuels from Palm Oil by Catalytic Cracking over Aluminosilicate Mesoporous Catalysts with Various Si/Al Ratios", Microporous Mesoporous Mater, Vol. 64, pp. 95-107, 2003.

[25] C. Liu, Y. Long, Z. Wang, "Optimization of Conditions for Preparation of ZSM-5@silicalite-1 Core-Shell Catalysts via Hydrothermal Synthesis", Chinese Journal Chem. Eng., Vol. 26, pp. 2070-2076, 2003.

[26] A. Okemoto, Y. Tsukano, A. Utsunomiya, K. Taniya, Y. Ichihashi, "Selective Catalytic Oxidation of Benzene over Cu/Ti/HZSM-5 under Low Oxygen Pressure for one Step Synthesis of Phenol", Journal Mol. Catal. a Chem., Vol. 411, pp. 372-376, 2016.

[27] V.D. Vu, M. Miyamoto, N. Nishiyama, Y. Egashira, K. Ueyama, "Selective Formation of Para-Xylene over H-ZSM-5 Coated with Polycrystalline Silicalite Crystals", Journal Catal., Vol. 243, pp. 389-394, 2006.

[28] D. Yang, S. Fu, S. Huang, W. Deng, Y. Wang, L. Guo, et al., "The Preparation of Hierarchical Pt/ZSM-5 Catalysts and their Performance for Toluene Catalytic Combustion", Microporous Mesoporous Mater, Vol. 296, p. 109802, 2020.

[29] C. Peng, Z. Liu, Y. Yonezawa, Y. Yanaba, N. Katada, I. Murayama, et al., "Ultrafast Post-Synthesis Treatment to Prepare ZSM-5@Silicalite-1 as a Core-Shell Structured Zeolite Catalyst", Microporous Mesoporous Mater, Vol. 277, pp. 197-202, 2019.

[30] S. Kim, G. Park, S.K. Kim, Y.T. Kim, K.W. Jun, G. Kwak, "Gd/HZSM-5 Catalyst for Conversion of Methanol to Hydrocarbons: Effects of Amounts of the Gd Loading and Catalyst Preparation Method", Appl. Catal. B. Environmental, Vol. 220, pp. 191-201, 2018.

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