Catalytic Cracking of Methyl Ester from Used Cooking Oil with Ni-Ion-Exchanged ZSM-5 Catalyst

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Catalytic Cracking of Methyl Ester from Used Cooking Oil with Ni-Ion-Exchanged ZSM-5 Catalyst

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Abstract

Fossil crude reserves continue to decline, eventually leading to a reduced availability of fuel oil in Indonesia. Thus, the use of alternative plant-derived renewable energy sources, such as biodiesel should be considered. However, biodiesel as a fuel alternative has many drawbacks. In this study, biodiesel was cracked using a Ni-ZSM-5 catalyst to improve its quality. This work aimed to synthesize and characterize the Ni-ZSM-5 catalyst obtained from ion-exchange and catalytically crack methyl esters from used cooking oil. Three Ni-metal concentrations (1%, 2%, and 3%) were used for the ion-exchange of ZSM-5. Ni catalysts were then utilized for catalytic cracking at three temperatures (450 °C, 500 °C, and 550 °C). X-ray diffraction and scanning electron microscopy (SEM) analysis showed that the catalyst was in an aggregate form. SEM-energy-dispersive X-ray spectroscopy analysis indicated that Ni was successfully adsorbed by the catalyst. The gravimetry of the catalytically cracked product revealed that the highest oil fraction was obtained using 1% Ni catalyst at 450 °C. The largest chain obtained with this catalyst was diesel oil (C13-C19) with total 92.96% of covered peak area in the chromatogram/component quantity from gas chromatography.

Keywords: catalyst, cracking, ion exchange, Ni-ZSM-5, renewable energy

Introduction

As global population increases, industrial and transportation requirements grow, leading to high energy demands. Around the world, environmental concerns and energy security issues have prompted legislation actions urging for alternative fuels. Biofuel has been considered as a perfect alternative energy source because it is renewable and has low toxicity emissions; thus, it can replace fossil fuels [1-7]. Biodiesel is usually obtained through the transesterification of vegetable and animal oils with alcohol. It can also be produced from used cooking oil; hence, it does not interfere with vegetable oil production for human consumption [2, 3, 8-10]. Using cooking oil waste minimizes environmental pollution and health risks associated with its repeated use [11-13].

Unfortunately, biodiesel obtained from transesterification has many disadvantages compared with conventional fuels for example, its high unsaturated content leads to corrosion, it has poor storage stability, it is inadequate for cold environmental conditions, it has a low energy content, it has a toxic methane content, and it is expensive. Accordingly, catalytic cracking has been proposed to improve the competitiveness of biodiesel [5, 14-20]. During catalytic cracking, long carbon chains are broken into short simple hydrocarbon chains or molecules with the help of a catalyst [21-23]. A catalyst reduces the activation energy of this reaction and controls the selectivity of products. Cracking has been accomplished with solid catalysts, such as H-ZSM-5, metal-impregnated MCM-41, and Y zeolite, which have good selectivity and appropriate pore size. Metal catalysts also support solid carriers, such as silica, alumina, carbon, zeolite, and zeotype structures [6, 14-16, 24-31].

Some methods used to prepare catalysts for cracking are impregnation, ion exchange, adsorption, and deposition precipitation. Impregnation is performed by immersing a catalyst carrier in a solution that contains a precursor salt with an active metal. using activated carbon as a catalyst carrier of active metals can increase catalyst selectivity [3, 32]. In this case, carriers provide a large surface so impregnation becomes more efficient. Impregnation is achieved when no anion or cation is
exchanged with the active phase [3]. Contrary to impregnation ion exchange involves the interchange of ions from a carrier with an active metal. This method is carried out by inserting cations into zeolites through the exchange of alkali or alkaline earth cations by using precursor salts [33-41].

This study aims to analyze the content of fuel oil obtained through the catalytic cracking of methyl esters from used cooking oil by utilizing a Ni-ZSM-5 catalyst and to examine the feasibility of the proposed methods or the catalyst for improving biodiesel quality.

Materials and Methods

Materials. The following materials were used in this study: used cooking oil acquired from household waste, CH3OH (96.0%, Bratachem), Si(Ott)4 (>99.0%, Merck), NaOH (>99.0%, Merck), TPAOH (38.0% 42.0%, Merck), Al(OPr)3 (>98.0%, Aldrich), Ni(NO3)2·9H2O (>99.0%, Merck), filter paper, litmus paper, and distilled water (H2O, Merck).

Instrumentation. The following analytical instruments were used in this study: distillation equipment, a stainless steel cracking reactor (developed from the model of Nazarudin [21]) for the catalytic cracking of methyl ester in the used cooking oil, a gas chromatograph, X-ray diffraction (XRD), SEM version EVO MA 10 (ZEISS) and other laboratory instruments, such as an oven, a hot plate, a magnetic stirrer, an analytical balance, a vacuum pump, a porcelain glass, and a measurement glass.

Preparation of samples. The used cooking oil from the used household frying oil was filtered via a method described by Nazarudin [7]. In this method, an adsorption device was constructed from a 2-inch pipe, and the adsorption medium was charcoal from kernel palm shells. It was mixed with methanol at a ratio of 1:3 and added with 0.25% sodium carbonate (NaOH) to make methyl ester. This process takes places for 1 h at 65 °C. Afterward, purification was conducted with the following steps: distillation at 70 °C, settling for 24 h, washing with distilled water at 50 °C, and reheating to 100 °C to separate water and methyl ester.

Catalyst synthesis. The catalyst synthesis process is shown in Fig. 1. Two steps were involved in catalyst synthesis: (1) ZSM-5 catalyst synthesis and (2) catalyst modification using Ni.

1. ZSM-5 catalyst synthesis
The ZSM-5 catalyst was synthesized in accordance with the method described by Nazarudin [21]. Si(Ott)4 was used as a zeolite source. Raw materials were prepared and weighed as follows: 4.178 g of H2O, 0.0043 g of NaOH, 6.348 g of Si(Ott)4, 3.098 g of TPAOH, and 0.138 g of Al(OPr)3 were mixed and stirred for 24 h. Then, the mixture was heated in the oven at 165 °C for 5 days. After 5 days, the ZSM-5 mixture was washed with distilled water while being filtered with a vacuum pump until neutral pH was reached. The ZSM-5 catalyst was placed in a porcelain cup and then in the oven at 105 °C for 24 h.

2. Modification of the ZSM-5 catalyst with Ni
The catalyst was modified in accordance with the procedure described by Nazarudin [42]. Ni(NO3)2 solutions were prepared with various concentrations (1%, 2%, and 3%). ZSM-5 and the nickel nitrate solution were mixed (1:10 ratio) and stirred for 24 h at room temperature. The solution was then washed to reach pH 7 and filtered. The residue was dried in the oven at 105 °C for 24 h.

Catalytic cracking. The catalytic cracking process is shown in Fig. 1. Methyl ester was placed inside the reactor, which was then filled with different concentrations of the catalyst (1%, 2%, and 3%). Catalytic cracking was performed under nitrogen gas flow. The output of the reactor was poured into an ice trap for cooling. Cracking was carried out at different temperatures (450 °C, 500 °C, and 550 °C), for 100 min. The cracking product was brown oil.

Results and Discussion

X-ray diffraction (XRD) analysis. XRD analysis is conducted to identify the crystalline phase in materials and to measure the size of particles. It can provide qualitative and semiquantitative data on solids or samples. Fig. 2 shows the diffraction pattern of the ZSM-5 catalyst with and without Ni. The peaks at 2θ = 7.9°, 8.1°, 8.8°, 23.1°, 23.3°, and 23.9° indicate that ZSM-5 is an MFI-type zeolite. This finding shows that all catalysts from catalytic synthesis have an MFI structure and that these catalysts meet the standards of tetrapropylammonium ZSM-5.

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX) analysis. SEM-EDX is used to determine and describe the morphological characteristics and contents of catalysts. The results of the SEM-EDX analysis of the modified catalyst are shown in Figs. 3 and 4. In Fig. 3, the ZSM-5 catalysts have an aggregate form with a nanoparticle size (20,000×). In Fig. 4, the ZSM-5 catalyst contains O, Al, and Si with a Si/Al ratio of 14.71 (Table 1). The active metal was added onto the catalyst surface to increase

Figure 1. Experimental Procedure
the active side on the catalyst surface so that the catalytic activity increased. Si was the most abundant element in the Ni-ion-exchanged ZSM-5 catalyst (Table 2). The Si/Al ratios were 23.34%, 25.96%, and 21.14% for 1%, 2%, and 3% Ni, respectively. In 2% Ni, no Na was observed because it depleted during ion exchange; however, the Na content increased in 3% Ni. Additionally, in 1% Ni, no Ni was found because it was lost during catalyst leaching. Therefore, a high catalyst concentration led to a high Ni content in ZSM-5 and an increase in number of active sites of catalysts. After the active site increases, the gasoline yield increases [1, 6, 26].

Figure 2. XRD Patterns of ZSM-5 (a) Without Ni and After the Ion Exchange Treatment with (b) 1%, (c) 2%, and (d) 3% Ni

Figure 3. SEM Image of ZSM-5
Figure 4. EDX Spectra of (a) ZSM-5, After the Ion Exchange Treatment with (b) 1%, (c) 2%, and (d) 3% Ni
Effect of temperature and catalyst content on cracking. Biodiesel was stable below 275 °C, and thermal decomposition occurred at 275 °C or above. Biodiesel decomposition mainly involves isomerization, polymerization (Diels–Alder reaction), and pyrolysis at temperature ranges of 275 °C–400 °C, 300 °C–425 °C, and >350 °C, respectively [5]. Cracking was carried out in a batch reactor by placing the catalyst into the bed in a vertical reactor and the raw material into the horizontal reactor. Gravimetric analysis was performed to evaluate the results of the processes at 400 °C, 450 °C, and 500 °C for 100 min with different catalyst concentrations (1%, 2%, and 3% from ion exchange). Fig. 5 and Table 3 show that the highest liquid yield (77.91%) was obtained during catalytic cracking with 1% Ni-ion-exchanged ZSM-5 at 450 °C. Increasing the temperature to more than 450 °C led to a decrease in the number of products. Using the HZSM-5 catalyst with or without impregnation decreases the activation energy of cracking [1]. Cracking becomes severe when reaction temperature and residence time increases. Under these conditions, chemical bonds are further cleaved, and the chain further shortens. Therefore, light molecules likely form when reaction temperature and residence time increase [17].

Gas chromatography-mass spectrometry (GC-MS). This technique is used to identify different compounds within a test sample. The GC-MS results showed that the used cooking oil contained carbon compounds with chains from C6 to C21 with boiling points ranging from 69 °C to 371 °C (Table 4). The GC-MS analysis of the methyl ester sample revealed that it contained carbon compounds from C6 to C24 with boiling points from 83 °C to 391 °C (Table 5). The catalytic cracking of
Table 3. Catalytic Cracking with Different Ni-ion-exchanged ZSM-5 Catalysts

| Ni concentration | Methyl ester sample (gr) | Temperature (ºC) | Liquid yield (%) | Residue (%) | Gas yield (%) |
|------------------|--------------------------|------------------|------------------|-------------|---------------|
| 1%               | 31.4                     | 400              | 63.50            | 0.67        | 35.83         |
|                  | 32.41                    | 450              | 77.91            | 1.05        | 21.04         |
|                  | 31.99                    | 500              | 41.45            | 16.82       | 41.73         |
|                  | 30.21                    | 400              | 58.29            | 1.09        | 40.62         |
| 2%               | 32.44                    | 450              | 70.72            | 3.18        | 26.11         |
|                  | 32.85                    | 500              | 39.30            | 7.91        | 52.79         |
|                  | 31.54                    | 400              | 47.50            | 0.60        | 51.90         |
| 3%               | 33.72                    | 450              | 64.74            | 1.01        | 34.25         |
|                  | 32.03                    | 500              | 36.25            | 1.65        | 62.10         |

Table 4. GC-MS of Used Cooking Oil

| No. | RT (minute) | Number of carbon | % Area | Boiling point (ºC) |
|-----|-------------|------------------|--------|--------------------|
| 1   | 2.161       | C₆                | 0.97   | 69                 |
| 2   | 19.227      | C₈                | 6.01   | 220.41             |
| 3   | 15.221      | C₈                | 8.34   | 220.41             |
| 4   | 13.638      | C₁₀               | 1.56   | 225                |
| 5   | 13.226      | C₁₂               | 1.77   | 82                 |
| 6   | 14.266      | C₁₉               | 5.81   | 351.45             |
| 7   | 14.489      | C₁₉               | 16.26  | 351.45             |
| 8   | 15.758      | C₂₁               | 35.29  | 371                |
| 9   | 17.461      | C₂₁               | 23.99  | 371                |

Table 5. GC-MS of the Methyl Ester Sample

| No. | RT (minute) | Number of carbon | % Area | Boiling point (ºC) |
|-----|-------------|------------------|--------|--------------------|
| 1   | 4.191       | C₆                | 0.02   | 83                 |
| 2   | 11.558      | C₆                | 0.02   | 83                 |
| 3   | 15.078      | C₇                | 0.05   | 115.6              |
| 4   | 6.505       | C₇                | 0.01   | 115.6              |
| 5   | 17.673      | C₈                | 0.02   | 218                |
| 6   | 7.363       | C₉                | 0.08   | 262.33             |
| 7   | 8.511       | C₉                | 0.01   | 262.33             |
| 8   | 8.46        | C₁₀               | 0.02   | 269                |
| 9   | 10.729      | C₁₀               | 0.03   | 269                |
| 10  | 8.706       | C₁₀               | 0.04   | 269                |
| 11  | 8.871       | C₁₀               | 0.08   | 269                |
| 12  | 9.643       | C₁₀               | 0.08   | 269                |
| 13  | 8.946       | C₁₀               | 0.01   | 269                |
| 14  | 9.083       | C₁₁               | 0.01   | 213.5              |
| 15  | 9.180       | C₁₁               | 0.02   | 213.5              |
| 16  | 7.214       | C₁₂               | 0.01   | 281.3              |
| 17  | 10.197      | C₁₃               | 0.2    | 252                |
| 18  | 11.74       | C₁₅               | 0.92   | 368.18             |
| 19  | 11.026      | C₁₆               | 0.07   | 351                |
| 20  | 12.826      | C₁₆               | 0.05   | 351                |
| 21  | 14.318      | C₁₇               | 32.44  | 181.55             |
| 22  | 14.712      | C₁₇               | 0.02   | 181.55             |
| 23  | 13.969      | C₁₇               | 0.65   | 181.55             |
| 24  | 16.278      | C₁₈               | 0.09   | 397.91             |
| 25  | 15.787      | C₁₈               | 0.04   | 397.91             |
| 26  | 18.399      | C₁₉               | 49.2   | 214.05             |
| 27  | 18.479      | C₁₉               | 2.4    | 214.05             |
| 28  | 19.079      | C₁₉               | 6.2    | 214.05             |
| 29  | 18.13       | C₁₉               | 7.12   | 214.05             |
| 30  | 12.678      | C₁₉               | 0.06   | 214.05             |
| 31  | 9.431       | C₂₄               | 0.02   | 391                |
| 32  | 10.369      | C₂₄               | 0.02   | 391                |
methyl ester with 1% Ni-ion-exchanged ZSM-5 yielded a liquid with carbon compounds from C6 to C19 with boiling points ranging from 80.1 °C to 445.58 °C (Table 6). Table 7 lists the compounds found in the used cooking oil, the methyl ester sample, and the liquid product of the cracking reaction. The total amount of the C17 methyl ester changed before and after cracking. Table 8 presents the results of analysis of the liquid produced from catalytic cracking under the optimized conditions. The GC-MS results indicated that the largest product obtained from catalytic cracking with 1% Ni was diesel oil with C17 = 35.66% area and C19 = 54.16% area. Temperature, time, and catalyst/feed ratio affect the total conversion and selectivity of catalytic cracking [17, 31]. The yields of hydrocarbon in catalytic cracking depend on the choice of shape-selective catalysts and the acidity of catalysts [3].

Mass and heat transfer in a reactor are necessary to achieve the required reactor performance, so they should be incorporated in the design of reactors. Process operation, reactors, and catalyst design should also be integrated to improve the effectiveness of different processes used for biofuel production in a typical biorefinery [3].

This work was a preliminary research to propose a method for improving biodiesel quality. This research was the first to use this method and the proposed catalyst for biodiesel cracking.

| No. | RT (minute) | Number of carbon | % Area | Boiling point (°C) |
|-----|-------------|------------------|--------|--------------------|
| 1   | 2.676       | C6               | 0.33   | 80.1               |
| 2   | 2.584       | C6               | 0.37   | 80.1               |
| 3   | 2.853       | C6               | 0.17   | 80.1               |
| 4   | 2.207       | C6               | 0.45   | 80.1               |
| 5   | 2.316       | C6               | 0.14   | 80.1               |
| 6   | 3.025       | C6               | 0.23   | 80.1               |
| 7   | 3.808       | C7               | 0.94   | 110.6              |
| 8   | 3.07        | C7               | 0.64   | 110.6              |
| 9   | 3.848       | C7               | 0.19   | 110.6              |
| 10  | 2.933       | C7               | 0.31   | 110.6              |
| 11  | 4.905       | C8               | 0.38   | 121                |
| 12  | 4.996       | C8               | 1.2    | 121                |
| 13  | 5.254       | C8               | 0.07   | 121                |
| 14  | 6.425       | C8               | 0.16   | 121                |
| 15  | 4.065       | C8               | 0.21   | 121                |
| 16  | 4.168       | C8               | 0.17   | 121                |
| 17  | 5.974       | C9               | 0.33   | 147                |
| 18  | 6.277       | C9               | 0.2    | 147                |
| 19  | 5.196       | C9               | 0.19   | 147                |
| 20  | 7.368       | C9               | 0.2    | 147                |
| 21  | 8.871       | C11              | 0.14   | 222                |
| 22  | 10.197      | C13              | 1.39   | 252                |
| 23  | 11.74       | C15              | 1.55   | 271                |
| 24  | 10.031      | C15              | 0.2    | 271                |
| 25  | 13.969      | C17              | 0.58   | 391.06             |
| 26  | 14.272      | C17              | 35.08  | 391.06             |
| 27  | 18.102      | C19              | 3.65   | 445.58             |
| 28  | 18.273      | C19              | 46.17  | 445.58             |
| 29  | 19.05       | C19              | 4.34   | 445.58             |
Table 7. Comparison of the Compounds Found in Used Cooking Oil, Methyl Ester Sample, and Liquid Product of Catalytic Cracking (1%)

| Component                              | Number of carbon | % Area | Chemical compound                      |
|----------------------------------------|------------------|--------|----------------------------------------|
| Used cooking oil                       | C19              | 22.07  | 10-Octadecenoic acid                   |
|                                        | C21              | 59.28  | 11-Eicosenoic acid                    |
| Methyl ester sample                    | C17              | 33.11  | Hexadecanoic acid, methyl ester        |
|                                        | C19              | 33.11  | 9-Octadecenoic acid, methyl ester      |
| Liquid yield of catalytic cracking     | C17              | 35.66  | Pentadecanoic acid, methyl ester       |
| with 1% Ni                              | C19              | 54.16  | 9-Octadecenoic acid, methyl ester      |

Table 8. GC-MS Analysis of Used Cooking Oil, Methyl Ester, and Liquid Product from Catalytic Cracking

| Component                              | Number of carbon | % Area | Boiling point (°C) | Type          |
|----------------------------------------|------------------|--------|-------------------|---------------|
| Used cooking oil                       | C19              | 22.07  | 351.45            | Diesel        |
|                                        | C21              | 59.28  | 371               | Diesel        |
|                                        | C6 – C16         | 1.75   | 83 – 351          | Gasoline + diesel |
|                                        | C17              | 33.11  | 181.55            | Diesel        |
|                                        | C18              | 0.13   | 397.91            | Diesel        |
|                                        | C19              | 64.98  | 214.05            | Diesel        |
|                                        | C24              | 0.04   | 391               | Diesel        |
| Methyl ester                           | C6 – C16         | 10.16  | 69 – 271          | Gasoline + diesel |
|                                        | C17              | 35.66  | 391.06            | Diesel        |
|                                        | C19              | 54.16  | 445.58            | Diesel        |
| Liquid yield of catalytic cracking     | C17              | 35.66  | 391.06            | Diesel        |
| with 1% Ni                              | C19              | 54.16  | 445.58            | Diesel        |

Conclusion

In this study, new methods are developed to improve biodiesel quality. In particular, catalytic cracking with Ni-ZSM-5 catalysts allows biodiesel to be developed as an alternative. This process is influenced by the temperature and concentration of Ni catalyst. The highest yield of the oil fraction is obtained by cracking with 1% Ni catalyst at 450 °C. With this catalyst, the product with the largest chain is diesel oil (C13–C19) with a 92.96% area from the total area in the chromatogram.

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Makara J. Sci. December 2019 | Vol. 23 | No. 4

Catalytic Cracking of Methyl Ester from Used Cooking Oil 177
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