

Biofuel Production from Catalytic Cracking of Palm Oil

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Abstract: Palm oil is a potential alternative energy source, since it has long hydrocarbon chains which is quite similar to the hydrocarbon chains in fossil oil. Thus, palm oil can be processed to produce biofuel which may replace the non-renewable fossil fuels, such as gasoline, kerosene and diesel oil. During utilization, biofuel produces fewer pollutants than fossil fuel. Therefore, biofuel is safer and environmentally friendly. The research was conducted through a catalyst synthesis and the catalytic cracking process. HZSM-5 was synthesized using an Absorption Atomic Spectroscopy (AAS) which produced a synthesized HZSM-5 Si/Al 198. Brunauer Emmet Teller (BET) analysis showed that surface area of synthesized catalysts was $21.3524 \text{ m}^2 \cdot \text{g}^{-1}$ and the average pore size of the catalysts was 13 \AA . This process confirmed that the synthesized catalysts meet the requirement as a catalyst used in the catalytic cracking process. The catalytic cracking was carried out in a fixed bed micro reactor at temperatures between $350 - 500 \text{ }^\circ\text{C}$ and N_2 flow rates between $100 - 160 \text{ ml} \cdot \text{min}^{-1}$ for 120 min. It was found that at 450°C and N_2 flow rate of $100 \text{ ml} \cdot \text{min}^{-1}$ resulted in the highest yield of gasoline fraction of 28.87%, 16.70% kerosene and 1.20% diesel oil. The synthesized HZSM-5 catalysts meet the standard of a catalyst used in the catalytic cracking of vegetable oil to produce biofuel.

Key words: Catalytic Cracking • Metal Impregnation • Palm Oil • Zeolite HZSM-5

INTRODUCTION

For some time now, Indonesia has been facing a fossil fuel crisis as indicated by fuel shortages in some areas. Fossil fuel is a non-renewable resource, thus it is a limited resource. The limited of fossil fuel and the rapid increase in the fossil fuel consumption due to the rise in the economic as well as the population growth are seen as the culprit of the oil crisis in Indonesia. The utilisation of fossil fuels are causing the global climate change due to the emission of CO_x , SO_x , NO_x and other organic compounds which are released during the combustion [1]. Therefore it is needed to find a new alternative energy source which is renewable and environmentally friendly. Crude Palm oil is a potential alternative energy source. Currently, Indonesia ranks second in the world as a palm

oil producer. In 2006 the total production of palm oil in Indonesia is 16 million tons; therefore Indonesia has a prospect to be the best palm oil producer in the world in the foreseeable future [2]. Crude palm oil can be processed to produce an alternative energy source to replace gasoline, kerosene and diesel fuel, since palm oil has a long carbon chain which is quite similar to the carbon chain in fossil oil [3].

Research on the production of biofuel from the catalytic cracking of palm oil has been well developed. This method is able to crack complex hydrocarbons to yield less complex structures. With the help of a catalyst, the reaction may be conducted at a lower temperature and pressure; moreover the quality and quantity of the products may be enhanced [4]. In the catalytic cracking of vegetable oil to produce biofuel, the type and products'

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compositions are influenced by several factors, such as time, temperature, flow rate of the raw materials and type of catalysts [5-7]. Many types of catalyst have been used in the catalytic cracking to produce biofuel, such as X, Y and faujasite. The previous catalysts are catalysts which usually used in the catalytic cracking of fossil fuel; the catalysts have been developed to be used in the catalytic cracking of vegetable oil to produce biofuel. Zeolite-based catalysts such as HZSM-5, Zeolite β dan ultrastabil Y (USY) has also been used [8]. HZSM-5 has shown to produce the highest conversion and yield. During catalytic cracking of palm oil at a temperature of 350°C and palm oil flow rate of 1L h⁻¹, under HZSM-5 catalyst the product conversion was 99% and the yield of gasoline was 28.3%, whereas under zeolit β catalyst the product conversion was 82% and the yield of gasoline was 7.3% [8].

Pre-treated Cu-ZSM-5 has been used in the catalytic cracking of palm oil in a fixed bed reactor at a flow rate of 2.5 L h⁻¹ for four hours producing 11.45% gasoline, 10.53% naphthene and 4.06% isoparaphine, respectively [9]. During catalytic cracking of methyl ester from palm oil to produce biogasoline using a natural zeolite catalyst in a continous stirred tank reactor, it was shown that the distillate compounds contain C₅ – C₁₁ structures [10]. C₉ – C₁₇ compounds were produced during a catalytic cracking of crude palm oil to produce biodiesel using natural zeolite as a catalyst [4]. A zeolite-based catalyst, ZSM-5, is reported to have unique characteristics; its pore size is 0.54 x 0.57 nm (less than the pore size of hydrocarbon C₁₁), it has 3-D structure and it is also organophile. The combination of those characteristics makes ZSM-5 a good select to produce hydrocarbons \leq C₁₁. The combination also has positive effects to the catalyst as it lasts longer and can be used under high temperature and acid conditions. Co-conversion of vacuum gas oil and vegetable oils under catalytic cracking conditions make it possible to increase the yield of gasoline fraction by 10 wt.%. A maximum promoting effect is attained by the addition of 5–10 wt% vegetable oil [11].

Jatropha oil can be cracked catalytically over solid acid catalysts to yield liquid fuels with superior characteristics. We presented here the hydrothermal syntheses of a microporous solid acid catalyst (HZSM-5 with Si/Al = 14), mesoporous materials (AIMCM-41) with varying Si/Al ratios (Si/Al = 18, 41, 72 and 95) and composite catalyst comprising HZSM-5 (as core) and varying coating percentages (5, 10 and 20%) of AIMCM-41 (as shell) [12]. Pyrolysis/cracking of non-edible plant seed oil Jatropha oil (JO) and the utilization of cracked liquid product as a transportation fuel have gained

importance due to the growing demand of renewable fuel oil source and depleting fossil fuel reserves. Thus, an attempt has been made to study the non-isothermal kinetics of JO cracking/pyrolysis using thermogravimetric analysis. The experiments were carried out at different heating rates of 5, 10, 15 and 20 K min⁻¹ under nitrogen atmosphere from ambient temperature to 1073 K [13].

The present study examines the performance of HZSM-5 catalysts during the catalytic cracking of palm oil to produce biofuel. Effects of nitrogen flow rate and reaction temperature during the catalytic cracking of palm oil to produce biofuel were also studied. From this current research it is expected that the value-added of vegetable oil can be enhanced by producing biofuel. Biofuel is renewable fuel, thus with its unlimited resource the fossil fuel shortage may be overcome by replacing the usage of fossil fuel with this renewable biofuel. During the utilisation, biofuel produces fewer pollutants than fossil fuel; therefore biofuel is safer and environmentally friendly fuel.

MATERIALS AND METHODS

Catalyst Synthesis: The zeolite catalyst is prepared by adopting a method developed by [14]. A solution of 360 g water glass (28.8% SiO₂, 8.9% Na₂O and 62.4% H₂O) and 450 g H₂O which was denoted as A was prepared. Meanwhile, another solution consisted of 12.3 g Al₂(SO₄)₃·18H₂O, 30 g H₂SO₄ 98% and 600 g H₂O denoted as B was also prepared. Solution B then was added slowly to solution A and stirred with a magnetic stirrer until a white gel was produced. To produce a smooth and homogenous gel, the white gel was stirred for another 1 h. Then to the homogenous gel, 124 g ethanol was added slowly. The mixture was stirred continuously for 1 h. The pH of the gel is between 10-11, if the pH is not in those ranges either H₂SO₄ or NaOH solution was added. The gel with SiO₂/Al₂O₃ ratio 94 was then heated at 176°C, stirred at 100 rpm for 24 h in an autoclave. The crystal produced then was filtered and washed with distilled water until the pH of the filtrate was 8. The crystal was then dried in an oven at 110°C for 24 h. The crystal produced was Na-Zeolite or so called ZSM-5.

H-Zeolite (HZSM-5) was prepared from ZSM-5 (Na-Zeolite) by ion-exchanged. ZSM-5 was dissolve in 2M ammonium chloride solution with the ratio of 1:10. The process was repeated three times. HZSM-5 produced then was filtered, washed and dried at 110 °C for 6 h, followed by calcination at 550°C for 5 h under N₂ atmosphere.

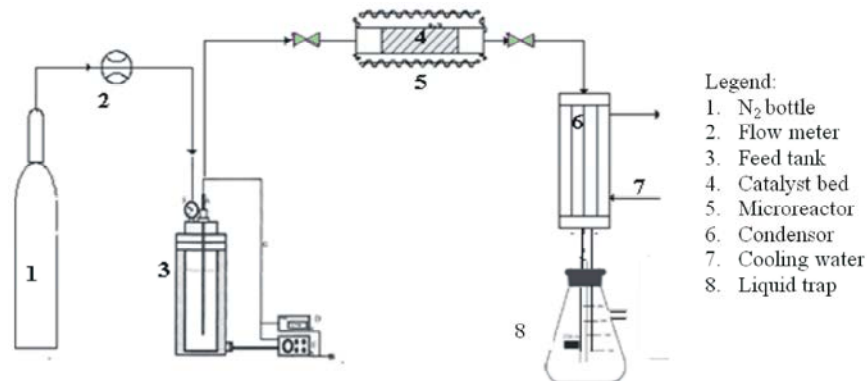


Fig. 1: Experimental set up of the catalytic cracking of palm oil to produce biofuel

Catalyst characterisations were carried out using Absorption Atomic Spectroscopy (AAS), X-ray diffraction (XRD) and Brunauer Emmet Teller (BET) analyses.

Catalytic Cracking Process: The catalytic cracking was carried out in a microreactor filled with approximately 1 g of a catalyst bed and the reactor was sealed with a heating element. Palm oil was fed to a feed tank which was heated at 350°C; nitrogen was also fed to the feed tank at flow rates between 100 – 160 ml.min⁻¹. Oil vapour and N₂ was then flown to the fixed bed reactor which was already heated to a desired temperature (350-500°C) *Absorption Atomic Spectroscopy (AAS) showed that synthesized HZSM-5 has Si/Al. Brunauer Emmet Teller (BET). The catalytic cracking reaction was conducted for 120 min. The products were analysed in a gas chromatography (GC) with Flame Ionization Detector (FID) column HP PORAPLOT QO4. Experimental set up was shown in Figure 1.*

used to analyzeze Si/Al ratio in the samples. Brunauer Emmet Teller (BET) was used to measure surface area and pore sizes of the catalysts, while X-ray diffraction (XRD) was used to study the type and structure of the catalysts. The catalyst characterization results were shown in Table 1 and Figure 2.

It can be seen from Table 1 that all catalysts have pore sizes > 13 Å. It is reported that the minimum pore size of a catalyst used in the cracking process is 8 Å [15]. The surface area of the catalysts >200 m²/g. also cited that the minimum surface area of a standard catalyst used in a catalytic cracking is 100 m²/g. Thus, the catalysts used in the current research meet the requirement of a standard catalyst used in the catalytic cracking process [15]. Meanwhile, Figure 2 shows the XRD diffractogram of standard HZSM-5, while Figure 3 shows XRD spectra of synthesized HZSM-5. HZSM-5 peaks were monitored at 2θ value between 7- 9° and 22 - 25°. It can be seen that HZSM-5 peaks of the standard (Figure 2) is somewhat similar to the synthesized samples (Figure 3). This confirms that the synthesized products were HZSM-5.

RESULTS AND DISCUSSION

Catalyst characteristics were studied using several techniques. *Absorption Atomic Spectroscopy (AAS)* was

Table 1: Catalyst characteristics

Catalyst	Si/Al (m/m)	Pore size(Å)	Surface area (m ² /g)
1. HZSM-5	198	13.255	213.3524

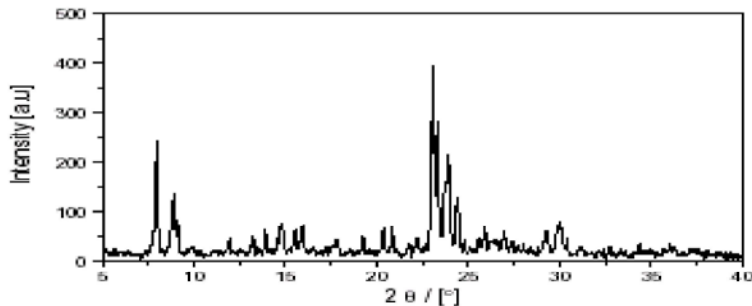


Fig. 2: XRD diffractogram of HZSM-5 standard

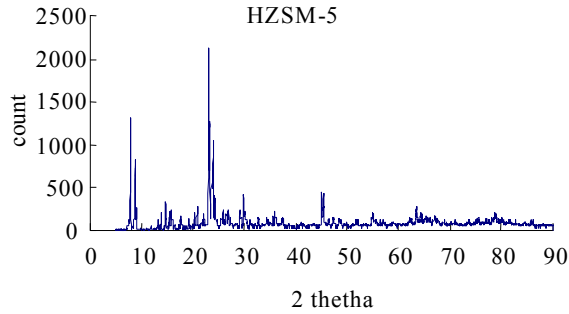


Fig. 3: XRD diffractogram of HZSM-5 synthesized

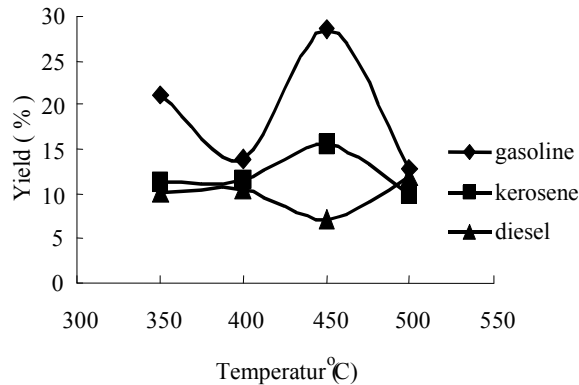


Fig. 4: Effect of temperature on the fuel yield at N_2 flowrate of $100 \text{ ml} \cdot \text{min}^{-1}$

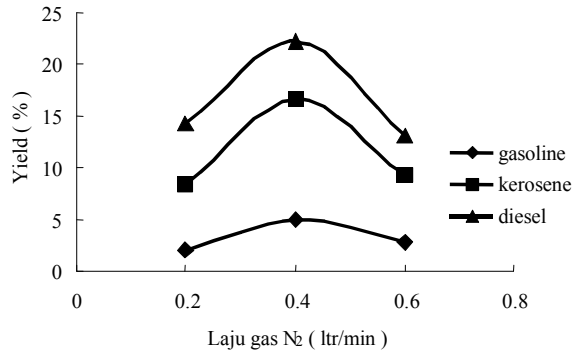


Fig. 5: Effect of N_2 flowrate on the fuel yield at a temperature of 450°C .

Figure 4 shows the effect of temperature on the yield of gasoline-like, kerosene-like and diesel oil-like during the catalytic cracking of palm oil using synthesized HZSM-5 at N_2 flowrate of $100 \text{ ml}/\text{min}$. It can be seen that the yield of gasoline-like, kerosene-like and diesel oil-like increases with increasing cracking temperatures. The increase in yield relates to the increase in a catalyst activity and reaction rate. According to the Arrhenius equation: $k = k_0 e^{-E/RT}$, with k is a reaction constant, k_0 is activity factor, E is activation energy, R is ideal gas constant and T is reaction temperature [16], k will increase by increasing the

reaction temperature. If k increases then the reaction rate is greater, so that the yield is also greater. However, at the highest temperature the yield decreases, this is due to the decrease in the catalyst activity with the increase in the temperature.

Figure 5 shows effect of N_2 flowrate on the yield of gasoline-like, kerosene-like and diesel oil-like during the catalytic cracking of palm oil using synthesized HZSM-5 at 450°C . It was found that at 450°C and N_2 flowrate of $100 \text{ m} \cdot \text{min}^{-1}$ produced the highest yield of gasoline fraction of 28.87%, 16.70% kerosene and 1.20% diesel oil. It can be seen that the yield of diesel oil-like increases with increasing N_2 flowrate. However, the yield of gasoline-like and kerosene-like decreases with increasing N_2 flowrate. Acrolein in gasoline-like and kerosene like tends to decompose to C_1-C_4 at high temperature. By increasing N_2 flowrate it seems that acrolein decomposition in gasoline-like and kerosene like favours, so that the yield of gasoline-like and kerosene like decreases.

CONCLUSION

The synthesized HZSM-5 catalysts meet the standard of a catalyst used in the catalytic cracking of vegetable oil to produce biofuel. The yield of biofuel increases with increasing reaction temperatures, however at the highest temperature the yield of biofuel decreases. The yield of diesel oil-like increases with increasing N_2 flowrates, however the yield of gasoline-like and kerosene-like decreases with increasing N_2 flowrates.

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