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GASOLINE PRODUCTION FROM PALM OIL VIA CATALYTIC CRACKING USING MCM-41: DETERMINATION OF OPTIMUM CONDITION

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ABSTRACT

The catalytic cracking of palm oil involves parallel cracking reactions which produce organic liquid product (OLP), non-condensable gas and coke. OLP consists of gasoline, kerosene and diesel; all can be used as alternative fuels. The objective of this study was to determine the effect of operating conditions: oil to catalyst (O/C) ratios and Weight Hourly Space Velocities (WHSVs)) to the feed conversion, OLP yield and gasoline yield. The optimum conditions of OLP production was also obtained in this study. The experiment was conducted in a fixed bed microreactor at a temperature of 450°C. The WHSVs were varied at a range of 15 to 25 h^{-1}. While the O/C ratios were varied at the range of 30 to 50. The results show that the highest yield of OLP was 60.73 wt% at O/C ratio of 32.50 and WHSV of 19.38 h^{-1}.

Keywords: palm oil, gasoline, production, cracking, organic liquid product, fuel, catalyst, WHSV, O/C ratio.

INTRODUCTION

Over the past decades, petroleum-based fuel had been used as the main energy source. Nowadays, along with rapid development of technology and economy, the demands of petroleum-based fuel also increase significantly. The main problem for this situation is that the petroleum, the raw material for the fuel, is a non-renewable resource. Because of that, the increasing demand on petroleum-based fuel would cause the depletion of petroleum reserve. This will lead to another problem, the escalating crude oil prices and even a global energy crisis. Another disadvantage of using petroleum-based fuel is the gas emission, such as carbon dioxide, nitrogen, and sulfur compounds. These gases are the main cause for air pollution and green house effect (Kloprogge et al., 2005). The scarce of new petroleum resources and the environmental problem caused by green house gases have increased interest in finding the alternative fuel, which is not only renewable but also environmentally friendly. One of the alternative fuels currently being studied is biofuel obtained from vegetable oil. Liquid biofuel offers alternative fuel option because the raw material, the vegetable oils, is renewable and also free of nitrogen and sulfur compounds (Ooi et al., 2004a, b). These biofuel can be used as fuel or fuel additive to reduce gas emission (twaiq et al., 2003).

Recently, there has been an interest in the catalytic conversion of triglycerides, which include vegetable oils, into liquid hydrocarbon fuels. Two conversion methods among the most prominent are low temperature liquid phase catalytic processes such as transesterification to methyl or ethyl esters, and high temperature pyrolytic processes involving solid catalyst. Transesterification can easily and convenient convert a variety of oil to almost quantitative yield of acceptable diesel-like fuel at room temperature (Vonghia et al., 1995). Although it produces diesel-like fuel, the product of reaction has lower ignition point compared with diesel itself. It has been a drawback of using transesterification product as a substitute fuel. Pyrolytic conversion

technologies may be further divided into hydrogenation and non-hydrogenation processes. Hydrogenation process will convert the triglyceride content in vegetable oil into diesel fuel which has lower cyclic hydrocarbon and aromatic contents compared with conventional diesel fuel. Non-hydrogenation processes have employed numerous catalyst to dehydrate and decarboxylate biomass oil into gaseous and liquid hydrocarbons, coke, and water (Vonghia et al., 1995).

Among all of the vegetable oils, palm oil is one of the vegetable oil that has the greatest possibility to be used in biofuel production. Palm oil is one of the most produced vegetable oil in the world, and Indonesia is one of the largest palm oil producers in the world, probably second to Malaysia. Several studies have been conducted in order to convert palm oil into biofuel such as gasoline and diesel fractions. These biofuels were obtained from catalytic cracking of palm oil using various kind of catalyst (Ooi et al., 2004a, b, c; twaiq et al., 2003a, b; Ooi et al., 2005a, b). However, in the previous experiments, the O/C (catalyst/oil) ratio used was very low, from 6 to 10. For industrial scale, the production of organic liquid product using low O/C ratio is not economically feasible. Therefore, it is necessary to explore the possibility of using higher O/C ratio, which gives higher yield of liquid product (gasoline fraction). Here we used MCM-41 as the catalyst, this mesopores material has narrow pore size distribution and ordered pore characteristic. The objective of this study was to obtain the optimum condition in the production of gasoline fraction from palm oil via catalytic cracking using mesopores catalyst.

MATERIALS AND METHODS

This research study consisted of two parts, the preparation of catalyst and its characterization and the catalytic cracking of palm oil over MCM-41.

Preparation of catalyst

The procedure of catalyst preparation is as follow:

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2.2778 g of CTAB was diluted with 50 ml of water in the three-neck round bottom flask. In separate volumetric flask, 0.04 g of sodium hydroxide was diluted with water to 50 ml. Then the sodium hydroxide solution was added into the flask to maintain the pH of reaction. The temperature of reaction was maintained at 80°C by submerging the flask into water bath. After the temperature of the mixture reach 80°C, 5.2159 g of TEOS was added into the mixture under stirring condition for 2 hours. After the reaction completed, the reaction product was centrifuged for 20 minutes to obtain the white precipitate. The precipitate then dried at 110°C for 4 hours and subsequently calcined using muffle furnace at 550°C for 4 hours.

Characterization of catalyst

The product catalyst was characterized using nitrogen sorption (Quadrasorb SI), X-ray diffraction (Rigaku Miniflex Goniometer) and scanning electron microscope (JEOL JSM-6300F field emission SEM).

The pore structure characteristic of the MCM-41 was determined by nitrogen adsorption at -194°C by a QuadraSorb SI... Prior to gas adsorption measurement, the MCM-41 was degassed at 200°C in a vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherm was measured over a relative pressure (P/P_o) range from approximately 0.005 to 0.985.

SEM image was recorded using JEOL JSM-6300F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during FESEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere using a current of 6mA for 3 min. The coated sample was then transferred to the SEM specimen chamber and observed at an accelerating voltage of 5kV, 8 spot size, 4 aperture and 15 mm working distance. While powder X-ray diffraction (XRD) pattern was recorded on a Rigaku Miniflex Goniometer at 30 kV and 15 mA (Cu Kα radiation) at a step size of 0.01^{o}.

Catalytic cracking

Catalytic cracking of palm oil was conducted in a fixed bed micro reactor equipped with temperature and feed controllers. The reaction temperature was set on 450°C and with WHSV (weight hourly space velocities) in the range of 15 to 25 h^{-1}, while the oil to catalyst (O/C) ratios were varied at the range of 30 to 50. A known amount of MCM-41 catalyst (1.0 g) was loaded over 0.2-0.4 g of rock wool supported with a stainless steel mesh in a microreactor. The nitrogen gas was introduced into the catalytic cracking apparatus one hour prior to the experiment at the flow rate of 1000 ml/min. The temperatures of the reactor and pre-heater were controlled by a thermocouples placed in the end of horizontal tube (pre-heating section) and catalyst bed. The palm oil was fed into the reactor at certain WHSV using a peristaltic pump. Once the maximum run time had been reached, the collected condensate in the condensate flask was filtered using filter paper Whatman 42. The total mass of liquid product was weighed and the liquid product's composition was analyzed using GC-2014.

RESULTS AND DISCUSSIONS

The XRD and nitrogen sorption analysis of catalyst MCM-41 are given in Figures 1 and 2. The XRD diffractogram obtained from the analysis is shown in Figure-1.
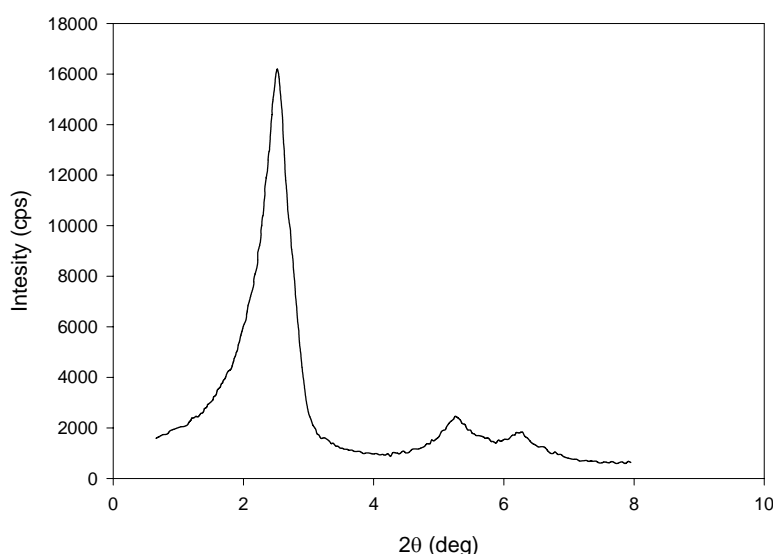
Figure-1. The XRD analysis of MCM-41.

The result shows matching crystalline properties with the MCM-41, with the identical peaks in the *hkl* indexes of 100, 110, 200, and 210. From the diffractogram, values of d_{100} and a_0 can be calculated using the following equations.
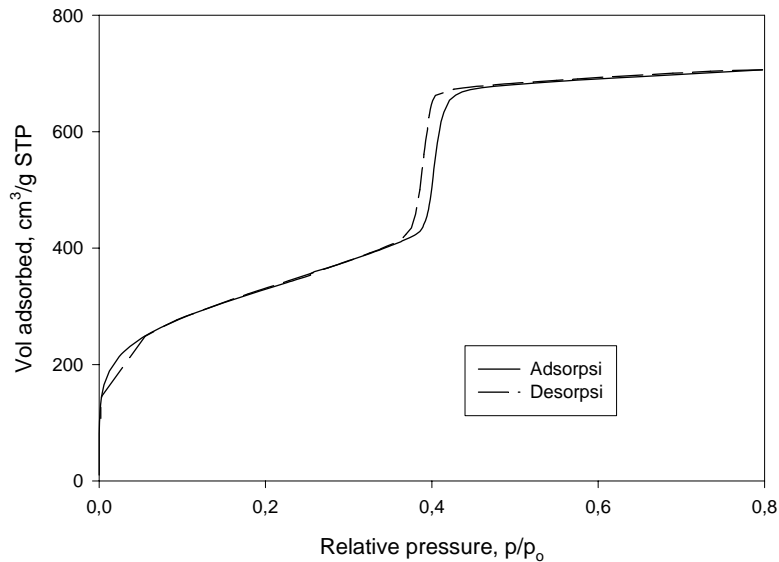
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$$d_{100} = \frac{n \cdot \lambda}{2 \cdot \sin \theta} \qquad \text{...........(1)}$$

$$a_0 = \frac{2 \cdot d_{100}}{\sqrt{3}} \qquad \text{..........(2)}$$

The values of each parameter are $d_{100} = 42.88$ Å and $a_0 = 49.52$ Å. The isotherm characteristics are
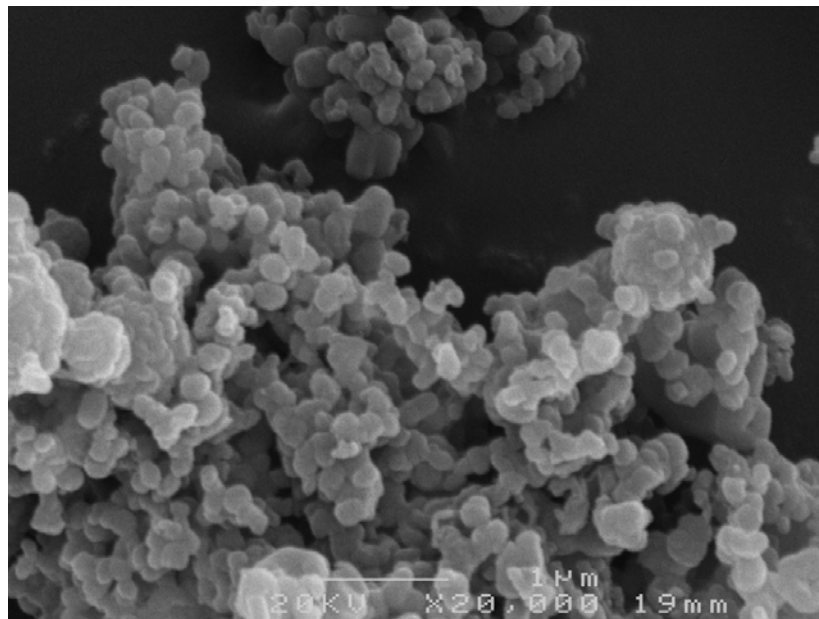
determined using nitrogen sorption analysis. The result is displayed as isotherm curve in Figure-2.

Figure-2. Nitrogen sorption analysis of MCM-41.

Hysteresis in the isotherm curve shows pores are tubular in shape and open at both ends. This particular specification shows MCM-41 with homogeneous pore distribution. SEM image of MCM-41 is given in Figure-3.


Figure-3. SEM image of MCM-41 particles.

The conversion of palm oil into organic liquid product (OLP) hydrocarbon involve very complex reaction, hundreds of new substances formed during the reaction, multiphase reaction are also occurs. The conversion of palm oil into various kinds of products not only affected by the catalyst itself, WHSV, and O/C ratio, but the

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thermal cracking also plays a significant role in the products formation. Using Sigmaplot 9.0 software, the experimental data were optimized and the result is given in Figure-4. The maximum OLP yield is 60.73%, obtained at the O/C ratio of 32.50 and WHSV of 19.38 h^{-1}, with R^2 of 0.8954. Furthermore, with the increase in WHSV, the OLP yield obtained would also increase and reach maximum before decreasing. This phenomenon occurs due to the diffusion process. Prior to catalytic cracking occurs, the palm oil will first diffuse through catalyst pores and after the oil enter the interior of catalyst, the cracking reaction then occurs within the catalyst pores, followed by product diffusion leaving the internal interior of catalyst in the form of gas phase.

At the same temperature, the diffusion coefficient of palm oil will stay constant. Increasing in WHSV will result in increasing OLP yield due to more palm oil will diffuse to catalyst internal interior. However, the internal interior of catalyst (pore) also has limitation. If palm oil flow rate (WHSV) further increased, some of the palm oil that enters the reactor will not convert to organic liquid product thus decreasing OLP yield.
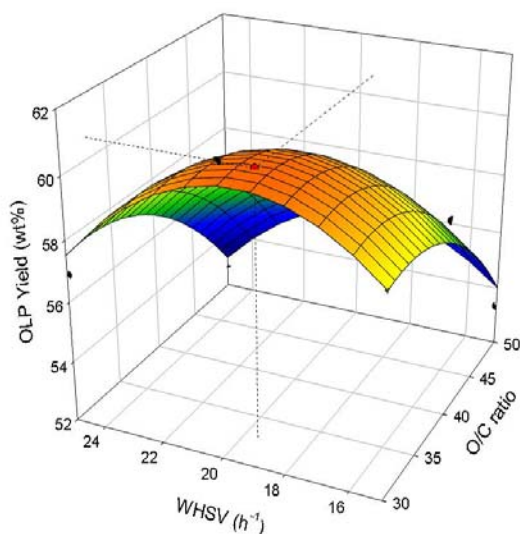

Figure-4. Graphic view of OLP yield (wt %) vs. WHSV (h^{-1}) and O/C ratio.

In general, it can be seen that increasing O/C ratio decreases OLP yield. The catalyst has certain number of active site in its internal interior of the pore and just can accommodate certain amount of reactant. Here, by increasing of O/C ratio, the number of molecules of palm oil that undergo of cracking reaction still remains constant. Since the catalytic cracking not only produce gas and liquid but also produce solid (coke), the presence of coke in the internal structure of MCM-41 also exhibit decomposition reaction of palm oil, therefore it will reduce the formation of organic liquid products.

In order to obtain the optimum condition for gasoline production from catalytic cracking of palm oil using MCM-41 as catalyst, the effect of process variable

on gasoline formation experimental data were optimized using Sigmaplot 9.0 software and the results are given in Figure-5.
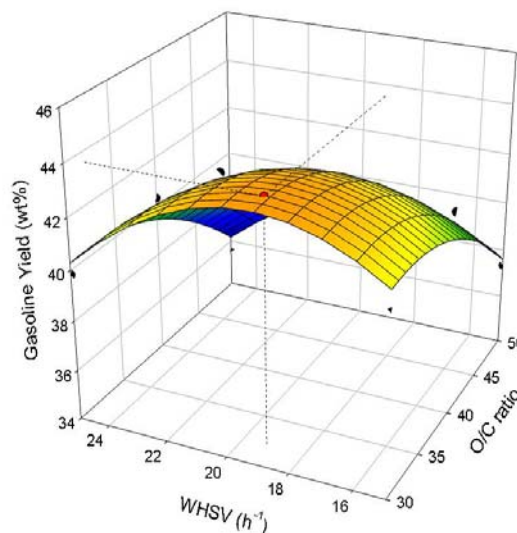
Figure-5. Gasoline yield (wt %) vs. WHSV (h^{-1}) and O/C ratio.

The maximum gasoline yield is 43.63% obtained at the WHSV of 19.00 h^{-1} and O/C ratio of 32.00 with R^2 of 0.9434. With the increase in WHSV, the gasoline yield obtained would also increase and reach maximum before decreasing. This phenomenon occurs due to the secondary cracking reaction. Palm oil will be cracked into several products (gas, coke, gasoline, kerosene, and diesel). The longer the space time (the inverse of WHSV), the cracking products having the medium-to-long chain would undergo the secondary cracking. At the WHSV higher than 19.00 h^{-1}, the kerosene and diesel fraction could be cracked into smaller fraction like gasoline.

CONCLUSIONS

The MCM-41 was prepared using CTAB as surfactant at 80°C. Subsequently this mesoporous material was used as catalyst for the production of gasoline from palm oil. It was found that MCM-41 is promising catalyst for biofuel production from palm oil. The maximum organic liquid product is 60.73 % was obtained at the O/C ratio of 32.50 and WHSV of 19.38/hour.

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