



Hydrocracking of Oil Residue from Palm Oil Mill Effluent to Biofuel

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Abstract

The total palm oil production has increased in the last few years, as a result, palm oil waste which is a by-product of the milling process will also increase. The palm oil production process in mills consists of several unit operations. The processing of fresh fruit bunches of oil palm results in the generation of different types of residue. Among the waste generated, palm oil mill effluent (POME) is considered as the most harmful waste for the environment if discharged untreated. POME is a thick brownish liquid that contains high solids, oil and grease. Several treatment technologies have been used for POME treatment, since the direct discharge of POME adversely affects the environment. Due to the presence of high oil residue in POME, attempts have been made to recover and convert it into valuable products such as useful chemicals and biofuel. Recovery of oil residue from POME is difficult and not economical; therefore, its alternative usage is explored. In a preliminary study, we observed that it was possible to produce various types of liquid hydrocarbons fuel (biofuel) from oil residue from POME. Oil residue from POME has been catalytically hydrocracked to biofuel with Ni/Mo-ZrO₂ pillared monmorillonite (NMZM) catalyst in fixed bed micro reactor. The data shows that the catalytic activity of ZrO₂ pillared montmorillonite (ZM) is more active than parent monmorillonite (M). While, catalyst Ni/Mo were loaded on ZM can increase the catalytic activity for hydrocracking of oil residue from POME into biofuel. The products were mainly gases, biofuel and solid coke. The biofuel products consist of gasoline, kerosen and diesel oil fraction.

Keywords: biofuel, palm oil, monmorillonite, hydrocracking, catalyst

1. Introduction

Palm oil industry has resulted sludge waste (POME) which contains amount of oil residu. Oil residues contained in the palm oil sludge could potentially processed as an energy resource. The success of treating palm oil waste sludge into fuel oil will be very significant in resolving the dependence of fuel oil from fossils and reducing environmental burdens. Processing of oil residu from POME into qualified fuel oil can be conduced through two processes at once, that are process of cracking and process of hydrogenation or called Hydrocracking.

Studies on catalytic cracking of vegetables oil into hydrocarbon fuels which is posfektif, have been done, such as Candelilla oil [1], rapeseed oil [2], palm oil [3, 4], soybean oil [5] and jatropha oil [6]. The result of these studies concluded that the main content of triglyserides in vegetables oil can be converted into hydrocarbon fuel, gasoline and diesel fraction. Design of catalyst for processing vegetable oil from waste sludge of POME into gasoline fraction is very important and must meet necessary requirements for its processing can take place. Ni and Mo metal both in the singular or combination form of both metal have been investigated the usage as a catalyst for for hydrogenation of benzene [7] and hydrocracking of coal crude oil [8]. The result of these studies concluded that Ni and Mo metal can be used as a catalyst reaction for hydrotreatment, hydrocracking and deoxygenation. In the early twentieth century, it was introduced cracking catalyst material using acidified natural clay. However, thermal resistance of clay is not so high that is not good to be catalyst. Montmorillonite clay is kind of clay mostly pillared and have good nature. Selection of pillared montmorillonite as supporting catalyst based on research conducted has sufficient ability to both as catalyst and supporting cracking catalyst [6, 8].

2. Methods

2.1 The oil residue from POME

The oil residue from POME-based fatty acid mixture residue was obtained from PT. Sriwijaya Palm Oil Indonesia-Palembang. It was received as dark brown liquid, having mild smell, lighter than water and free of water. The POME was extracted by soxlet extractor to find the fatty acid mixture.

2.2 Catalyst preparation and characterization

Natural clay of montmorillonite type (M) was precipitated and dried in oven. It was saturated by using Sodium Chloride solution and swirled for 24 hours. Furthermore, the clay was washed by demin water to clean the chloride ion of the clay. This product (Na-Montmorillonite) was pillared by zirconium oxychloride solution. This result is referred as ZrO_2 pillared montmorillonite (ZM). The ZM was soaked in solution of $NiNO_3$ and $(NH_4)_6Mo_7O_{24}$ for 24 hours and dried. The ZM containing Ni and Mo was dried at the temperature of $130^\circ C$ for 3 hours. Then, it was oxidized by flowing O_2 gas at the temperature of $350^\circ C$ and the flow rate of 1.0 cc/s for 3 hours. In order to get good catalyst, the result of oxidation was reduced by flowing H_2 gas at the temperature of $350^\circ C$ and the flow rate of 1.0 cc/s for 3 hours. The product is referred as Ni/Mo- ZrO_2 pillared montmorillonite catalyst (NMZM). The catalyst was characterized for its acidity by ammonia adsorption. The BET surface area and pore volume of the catalyst were measured by nitrogen adsorption using Autosorb I (Quantachrome Automated Gas Sorption System). The samples were degassed for 5 h under vacuum at $300^\circ C$ prior to the analysis. The physical and chemical characteristics of M, ZM and NMZM are presented in Table 1.

2.3 Equipment and experimental procedure

The experiments were conducted at atmospheric pressure in a continuous up flow fixed-bed microreactor. The reactor was a 400 mm long, 11.5 mm i.d. 316 stainless steel tube placed in the vertical tube furnace. The reaction temperature was in $475^\circ C$ and with a oil residue feed rate (weight hourly space velocity, WHSV) of 10 h^{-1} , while the catalyst to oil residue ratio was 0.20. The catalyst (12.0 g) with particle size ranged between 500 and 1000 μm was loaded over 1.0 g of quartz wool supported with a stainless steel mesh in the microreactor and the temperature was monitored by a thermocouple positioned in the center of the catalyst bed and connected to a temperature controller.

Hydrogen gas was passed through the reactor for 1 h before the oil recovery from POME was fed using a peristaltic pump. Once steady state had reached in the reactor, the liquid product (organic and aqueous fractions) was collected in a liquid sampler while the gaseous product was collected in a gas-sampling bulb. The unconverted fatty acid mixture was separated from the liquid product in a microdistillation unit operated at $200^\circ C$ for 30 min under vacuum. The residue remaining after the vacuum distillation was termed as the residual fatty acid mixture and the product was analyzed using gas chromatography.

3. Result and Discussion

3.1 Characterization Oil Residue from POME

The result of oil analyst of oil residu from POME shows that the residue was dominated by a mixture of free fatty acids in level between 40-80% of free fatty acids. While the main constituent of fatty acids from oil residue are shown in table 1.

Table 1 Composition of fatty acids in oil residue from POME

Fatty Acid	Percentage
Oleic acid	65.93
Stearic acid	7.64
Linoleic acid	9.28
Palmitic acid	6.12
Lauric acid	3.45
Arachidic acid	2.76
Lignoceric acid	2.42
Others	1.40

3.2 Result of Preparation and Characterization of Catalyst

The result of SEM analysis of catalyst M, ZM and MNZM at 10,000 times magnification are shown in figure 1. SEM figure shows no change on structure and surface texture of nature montmorillonite and ZrO₂ pillared montmorillonite form a layered surface.

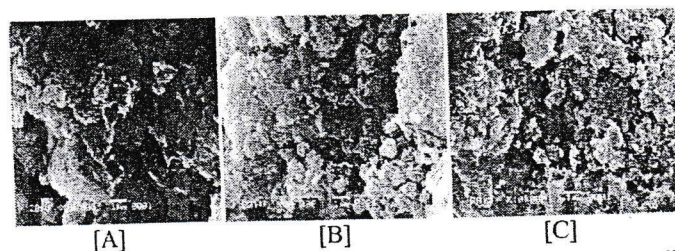


Figure 1. Result of SEM figure of catalyst M (A), ZM (B) and NMZM (C)



The comparison figure of SEM ZM and NMZM catalyst show that on NMZM catalyst has more small particles Ni and Mo metal, attaching on the surface of ZM. The entrance of Ni and Mo metal to the surface of ZM does not change the topology of surface of ZM layer.

2 Hydrocracking of Oil Residue

Result of hydrocracking oil residue by using catalysts M, ZM and NMZM is shown in table 2. The data shows that catalyst NMZM has the ability to catalyze hydrocracking process better than by using catalysts M and ZM. It can be seen from high percentage of conversion to 80% when using catalyst NMZM. The presence of iron, nickel and molybdenum metal in catalyst can increase the work of hydrocracking catalyst.

Table 2 Result of hydrocracking oil residue

Catalyst	Conversion (%)	Organic liquid product (%)	Gas product (%)	Coke (%)
M	33.87	12.37	14.82	2.77
ZM	54.43	32.45	16.98	1.34
NMZM	82.38	57.40	15.03	6.80

Liquid product is then analyzed by using gas chromatography to characterize the fraction into gasoline, kerosene and diesel, the result of research is shown in figure 2.

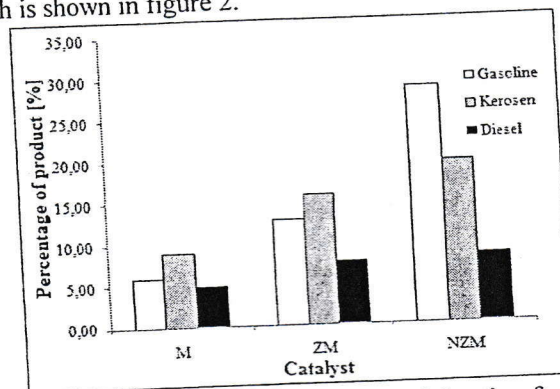


Figure 2. Analisis result of the gasoline, kerosene and diesel fraction from hydrocracking product

5. Conclusion

Based on the data, we can conclude that NMZM catalyst can be used as a catalyst for hydrocracking oil residue from POME by converting of more than 80% and 30% of gasoline fraction.

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