# THE EFFECT OF OIL-METHANOL MOLAR RATIO AND REACTION TIME ON THE SYNTHESIS OF BIODIESEL USING SODIUM ACETAT ACTIVATED CLAY HETEROGENEOUS CATALYST.

**Nurhayati*, Erman, Muhdarina, Sri Mulyani**

*Faculty* of Mathematics and Natural Science, University of Riau, Pekanbaru
* Email: n_yatisyam@yahoo.com

## ABSTRACTS

Biodiesel is mainly produced from vegetable oils or animal fats by the method of transesterification reaction using catalysts. Many heterogeneous solid acid and base catalysts have been studied for the transesterification of various vegetables oils. In this study the transesterification of vegetables oil to fatty acid methyl esters was studied using sodium acetat activated clay catalyst. The catalyst was prepared by adding 200ml $CH_3COONa$ 1M to 10gr clay, stirred, washed and calcined at 300$^oC$ for 3 hours. The transesterification reaction was performed with variation of the oil-methanol molar ratio and reaction time. Furthermore, the quality of biodiesel produced were characterized by ASTM (American Society for Testing Materials) method i.e. viscosity, flash point, carbon residue, cetane number and acid number, and the analysis result was compared with standardize (SNI). Free Fatty Acid (FFA) of waste cooking oil before synthesis was also calculated. It was found that the maximal production of biodiesel which is 78,033% when the oil-methanol molar ratio is 1:6 and 8 hours of transesterification. The characterizations of biodiesel produced have no significant different and all of those were in the range of Standar Nasional Indonesia (SNI).
*Key words: Biodiesel, Clay, Heterogeneous catalyst, Transesterification*.

## INTRODUCTION

Heterogeneous catalysis is widely applied in industry due to important advantages it offers to chemical processes such as improved selectivity and easy catalyst separation from reaction mixture, reducing process stages and wastes. This is the reason why nowadays heterogeneous catalysts are being developed to produce biodiesel. Biodiesel is fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), derived from the transesterification of triglycerides with methanol or ethanol. It can be used in existing engines and it is environmentally friendly because it can reduce the combustion emission of carbon monoxide, particulate matter, and sulfur compounds, as well as limit greenhouse emissions.

A sharp increase in the production of this kind of biofuel is expected in the near future. Several commercial processes to produce fatty acid methyl esters from vegetable oils have been developed and are available today. Most of the commercial biodiesel is produced from transesterification of vegetable oils (mainly jatropa, soybean, sunflower, palm oil) using very effective homogeneous base catalysts such as NaOH or KOH, or acid catalyst such as sulfuric acid or hydrochloric acid which are soluble in methanol or ethanol (Arzamendi et al., 2007).

The homogenous base catalysts have the advantage of gaining the fast reaction, but separation of the catalyst and the product is difficult and costly. Moreover, the washing operation is accompanied by formation of stable emulsion and saponification, resulting in not only the production loss but also in further contamination of the wastewater (Yang and Xie, 2007). Also, it is rather difficult to remove the homogeneous catalyst from glycerol which is the byproduct of the transesterification process. Although sulfuric acid or hydrochloric acid can also catalyze the transesterification, but the reaction time is very long and a high molar ratio of methanol to oil is needed (Li et al, 2007; Liu et al, 2007).

Different kinds of solid materials have been employed as heterogeneous catalysts or catalyst supports in biodiesel production (Nurhayati, 2011). Clay materials are ubiquitous in nature while heterogeneous in composition and particle size. The use of clay as heterogeneous catalysts for the sinthesis of biodiesel has been studied else where (Soetaredjo et al, 2011; Jaimasith and Phiyanalinmat, 2007).

In the present work, NaAcetat-doped Clay is prepared and characterized for biodiesel production from vegetable oil. We aimed to investigate if activated clay was an effective heterogeneous catalyst for biodiesel production. The catalysts were prepared by an impregnation method followed by calcination at temperature of 300$^{o}$C for 3 hours. The catalyst is then tested for the catalytic activities in the transesterification reaction of vegetable oil terms of the conversion to methyl esters. A screening of the reaction conditions has been carried out by examining the effect of oil-methanol molar ratio and reaction time.

## EXPERIMENTAL PROCEDURE

**Catalyst Preparation**.

Clay used in this study was obtained from Cengar, Riau, Indonesia. The catalyst was prepared by wet impregnation method. Prior to impregnation clay was washed and dried in oven overnight at 105°C to remove the moisture content. About 10g of clay was immersed in 200 ml $CH_3COONa$ 1M and stirred for 5 h. The slurry was left 24 hours, filtered and dried overnight in an oven at 105°C. Finally the catalyst was calcined in a furnace at a temperature of 300 °C for 3 h.

**Transesterification Reaction**.

The experiment was carried out in a 500 ml three-neck round bottom flask equipped with a reflux condenser, thermometer and a magnetic stirrer. The transesterification process was conducted with 100 g of the commercial grade palm olein (Sunco) purchased from local store. Before being used, the oil was heated to 105 $^{o}$C for 30 min to remove moisture and water content. The transesterification reaction was conducted at varied molar ratio oil/methanol and reaction time using 3 % wt catalyst and reaction temperature of 60$^{o}$C.

The transesterification process was started by stirring the mixture using magnetic stirrer. Stirring the mixture helped the heterogeneous catalyst to be distributed and suspended freely throughout the reaction mixture, thereby catalyzing the transesterification process. The reaction was allowed to occur for 6 hours. After 6 hours, transesterification process was stopped by immersing the batch reactor into water (at room temperature ~ 25$^{o}$C). The reaction stopped as the reaction mixture was cooled. Then, the heterogeneous catalyst was filtered out using filter paper and the reacted mixture was poured into the separating funnel. The top methyl esters (biodiesel) phase was then separated from the bottom glycerol phase and the excess alcohol was removed using warm water (at temperature ~60$^{o}$C).

## RESULT AND DISCUSSION

***Effect of the oil-methanol molar ratio.***

The experimental conditions for studying the effect of oil-methanol molar ration on the transesterification reaction were: the amount of catalyst at 3% (based on the weight of palm oil), reaction time of 6 h, the reaction temperature at 60 °C and oil to methanol molar ratio of 1:3, 1:6 and 1:9. The results clearly indicate that the ratio of oil methanol affected the conversion of vegetable oil into biodiesel as shown in Figure 1. In heterogeneous catalysis, mass transfer and reactant adsorption on the catalyst is very important; thus, a molar ratio higher than the stoichiometric molar ratio of methanol is needed to shift the equilibrium for the reaction. The maximum conversion was obtained when the oil/methanol molar ratio reached 1:6.

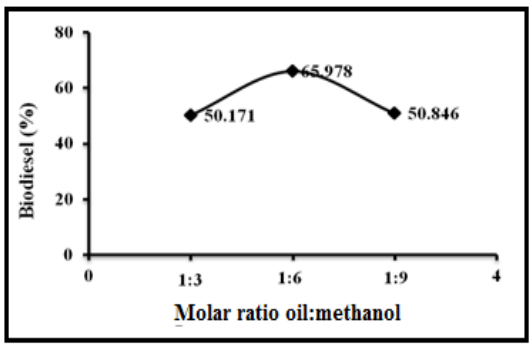


Figure 1. Biodiesel yield as a function of molar ratio oil:methanol.

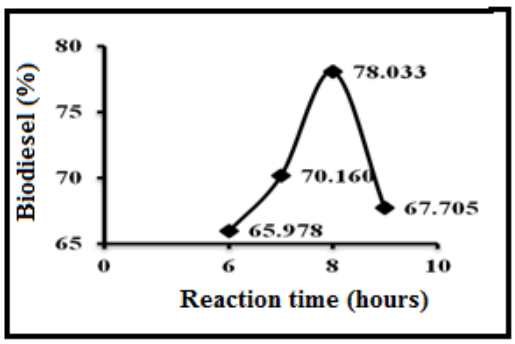


Figure 2. Biodiesel yield as a function of reaction time.

***Effect of reaction time***.

The operating conditions used to study the effect of reaction time on biodiesel yield were similar to those used before with the oil to methanol molar ratio 1:6 and reaction time of 6, 7, 8 and 9 h. The production of biodiesel increased with the reaction time (Figure 2) from six to eight hours which is the optimum reaction condition. After eight hours the yield of biodiesel was reduced as the equilibrium conversion had been reached. Maximum biodiesel produced here is 78,033 % with the optimum rection time is 8 h, which is longer time than result reported (Nurhayati et al, 2011; Soetaredjo et al, 2011). The longer time for the transesterification reaction may due to higher acidity of the clay catalyst used.

***Biodiesel characteristics***

Biodiesel produced from transesterification of vegetable oil using NaAcetat/clay as a heterogeneous catalyst were characterized including water content, acid number, density, viscosity, flash point, carbon residue, iodine number and cetane number. Most of the characteristics biodiesel produced from vegetable oil using Na-Acetat/clay as a catalyst fulfilled the standard for biodiesel (Table 1), except for viscosity. Higher viscosity here is may due to trigliceride of the palm olein used for the synthesis has a long chain carbon atom ($C_{18}$).

Table 1. Biodiesel characteristics compared to Standard Nasional, SNI-04-7182-2006

| No. | Parameter | Unit | Biodiesel produced | SNI |
|---|---|---|---|---|
| 1. | Water content | % V | 0,03 | Maks. 0,05 |
| 2. | Acid number | mg KOH/g | 0,41 | Maks. 0,8 |
| 3. | Density (40$^o$C) | kg/m$^3$ | 881 | 850-890 |
| 4. | Viskosity (40$^o$C) | cSt | 6,648 | 2,3-6,0 |
| 5. | Flash point | $^o$C | 148 | Min. 100 |
| 6. | Carbon residu | % m | 0,04 | Maks. 0,05 |
| 7. | Iodine number | g-$I_2$/100 g | 62,61 | Maks. 115 |
| 8. | Cetane number | - | 59,48 | Min. 51 |

## CONCLUSION

The results from this study confirmed that clay activated by sodium acetat was an effective heterogeneous catalyst for transesterification of palm olein with methanol to biodiesel with the maximal yield was 78,033% when the oil-methanol molar ratio is 1:6 and 8 hours of transesterification. The characteristic of biodiesel produced agree with SNI.

## REFERENCES

Arzamendi G., Campoa I., Argui˜narena E., S´anchez M., Montes M.,. Gand´ıa L.M. 2007, *Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH*, *Chemical Engineering Journal*, **134,** 123–130.

Jaimasith, M and Phiyanalinmat, S., 2007. *Biodiesel Syntehesis from Transesterification by Clay-based Catalyst*. *Chiang Mai J. Sci*. 34(2): 201-207.

Li X., Lu G., Guo Y,, Guo, Y., Wang Y., Zhang, Z., Liu X., Wang Y., 2007, *A novel solid super base of $Eu_2O_3/Al_2O_3$ and its catalytic performance for the transesterification of soybean oil to biodiesel*, *Catalysis Communication*, **8**, 1969-1972.

Liu, X., He H., Wang Y., Zhu S., 2007, *Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst*, *Catalysis Communications*, **8**, 1107-1111

Nurhayati et al, 2011. *The effect of reaction temperature and reaction time on the Transesterification of Palm olein using NaOH/ZnO heterogeneous catalyst*, Proceding Seminar HKI (Himpunan Kimia Indonesia) 2011, hal. 425-429.

Soetaredjo, FE., Ayucitra, A., Ismadji, S., Maukar,.AL., 2011, *KOH/bentonite catalysts for transesterification of palm oil to biodiesel*, *Applied Clay Science,* **53,** 341–346

Yang Z. and Xie W., 2007, *Soybean oil transesterification over zinc oxide modified with alkali earth metals*, *Fuel Processing Technology*, **88**, 631–638.