

Esterification of Waste Cooking Oil Using Heterogeneous Catalyst: An Experiment for the Catalytic Chemistry Laboratory

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Abstract. *The basic concept of the use of catalysts can be studied in the course of chemical catalysts. The use of heterogeneous catalysts offers many advantages, such as: the catalyst can be easily separated from the reaction mixture without the use of solvent. Chemical catalyst can be studied through experiments of esterification reaction of waste cooking oil with methanol using heterogeneous catalyst in the process of making biodiesel. Esterification results showed that the highest conversion (83%) was obtained by metakaolin catalyst at a reaction temperature of 160 °C for 2 hours at oil to methanol ratio of 1:30.*

Index Terms. *Chemical Catalyst, Esterification, and Metakaolin.*

INTRODUCTION

One of the problems that exist in Indonesia is the increasing fuel needs in line with the population growth. Alternative fuel that can be introduced to students is biodiesel. Educators can introduce the concept of biodiesel production and provide opportunities for students to make their own biodiesel using analytic approach. The ideas of learning covered in the preparation of biodiesel, include biology, physics, economics, and chemistry. Aspects of biodiesel production in terms of economics is the use of alternative fuels more efficient, while in terms of chemistry is acid-base titration, esterification and transesterification reactions, as well as catalytic reaction (Bladt et al., 2011).

The basic concept of the use of catalysts can be studied in the course of Chemical Catalysts. The use of heterogeneous catalysts offer many advantages, namely: the catalyst can be easily separated from the reaction mixture without the use of solvents, easily regenerated, not toxic, less expensive, and more environmentally friendly (Perego and Villa., 1997). Heterogeneous catalysts derived from natural materials that are readily available in the market is kaolin. Prior to use, the kaolin should be calcined at 800°C for 10 hours.

MATERIAL AND METHOD

I. Materials

The materials used in this study include: waste cooking oil, Kaolin, sulfuric acid (Merck, 98%), sodium hydroxide (Merck, 99%), demineralized water, methanol (Merck, 98%), phenolphthalein indicator, isopropanol (Merck, 99.5%), waste cooking oil.

II. Preparation of Catalyst

2 g of kaolin was calcined at 800 °C for 10 hours, with a heating rate of 10 °C per minute, to obtain metakaolin (Ortiz et. al., 2011). The kaolin and metakaolin were then characterized using a PANalytical X'PERT PRO MPD (PW 3040/60) diffractometer with CuK α (40kV and 30 mA) radiation at $5 < 2\theta < 50^\circ$ intervals.

III. Esterification of Waste Cooking Oils

The metakaolin was dried at 120 °C for 1 hour prior to use. 10 g of waste cooking oil was heated at a temperature of 60°C for 30 minutes, followed by addition of methanol and 3% of metakaolin catalyst (0.3 g). The ratios of oil to methanol were varied as follows: 1:20, 1:25, 1:30, and 1:35. The mixture was then refluxed at 160 °C for 2 hours. The reaction mixture was left to cool to room temperature, then poured in to a separator funnel and left to settle for about 10 minutes. The top layers, should be the biodiesel dissolved in methanol, was washed with n-hexane and heated at 60 °C to evaporate the solvent. The free fatty acid (FFA) content in the initial waste oil and in the reaction product were analyzed by titration method according to AOCS (*American Oil Chemistry Society*). The FFA content was calculated using the following formula:

$$\text{FFA (\%)} = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}} \times 25,6}{g_{\text{sample}}}$$

RESULTS AND DISCUSSION

I. XRD Analysis

The diffraction patterns of kaolin and metakaolin are shown in Figure 1. Peaks characteristics of kaolin were observed at 2θ of 12 and 25°, respectively. The kaolinite peaks disappear after calcination process, replaced by a wide band at 2θ of 21 and 27° and amorphous SiO₂

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(Nascimento et al., 2011). Al units are more susceptible to Al^{3+} and the observed increase in the amorphous phase.

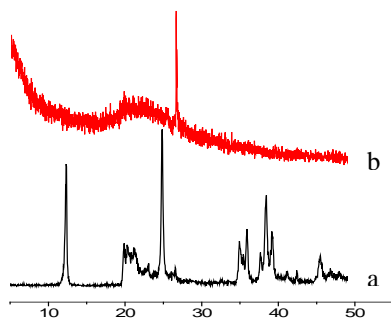


Figure 1. Diffractograms of kaolin (a), metakaolin (b).

II. Esterification Reaction

The oil to methanol molar ratio is one of the most important parameters affecting FFA conversion. Theoretically, the esterification reaction of oil requires 1 mol of oil per mole of methanol. Since this reaction is reversible, an excess of methanol shifts the equilibrium towards ester formation. Results of esterification reaction in the form of conversion of FFA at various ratios of oil to methanol are shown in Figure 2. As is shown in Figure 2, the conversion was increased with the increase in the ratio of oil to methanol up to 1:30. Esterification results showed that the highest conversion (83%) was obtained by metakaolin catalyst at a reaction temperature of 160 °C for 2 hours at oil to methanol ratio of 1:30. Further increase in the amount methanol, lead to the increasing of polarity of entire reaction system, finally affect the reaction rate and decrease the FFA conversion (Lianhua et.al., 2010). The increasing number of alcohol molecules around the catalyst could facilitate the removal of water molecules from the surface of the catalyst, increasing their catalytic activity. Furthermore, more excess of methanol cause the separation of the methyl ester phase was getting longer, thereby reducing the yield of biodiesel (Nascimento et al., 2011).

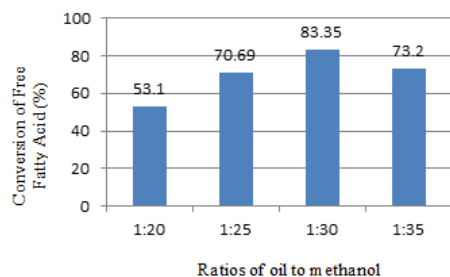


Figure 2. Conversion of Free Fatty Acid at Various Ratios of Oil to Methanol.

CONLUSSION

Esterification results showed that the highest conversion (83%) was obtained by metakaolin catalyst at a reaction temperature of 160 °C for 2 hours at oil to methanol ratio of 1:30.

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REFERENCES

- [1] Bladt, D., Murray, S., Gitch, B., Trout, H., Liberko, C. (2011), "Acid-Catalyzed Preparation of Biodiesel from Waste Vegetable Oil: An Experiment for the Undergraduate Organic Chemistry Laboratory", *Chemical Education*, vol. 88, no. 2, pp. 201-203.
- [2] Lianhua L., Pengmey L., Wen L., Zhongming W., Zhenhong Y. (2010) "Esterification of High FFA Tung Oil with Solid Acid Catalyst in Fixed Bed Reactor", *Biomass and Bioenergy*, vol. 34, pp. 496-499.
- [3] Nascimento do, S, Luis, Aldriano., Angelica, S.R., Costa da, E.F, Carlos., Zamain, J.R., Filho, Rocha da, N.G. (2011b) "Comparative Study Between Catalyst for Esterification Prepared from Kaolins", *Applied Clay Science*, vol. 51, pp. 267-273.
- [4] Ortiz, R.J., Valtierra, M.J., Rosales, M. (2011), "Used Frying Oil for Biodiesel Production Over Kaolinite as Catalyst", *World Academy of Science, Engineering and Technology*, vol. 5, pp. 764-767.
- [5] Perego, C. dan Villa, P. (1997), "Catalyst Preparation Methods", *Catalysis Today*, vol. 34, pp. 281-305.