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## Reaction Conditions of Two-step Batch Operation for Biodiesel Fuel Production from Used Vegetable Oils

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**Abstract:** During the reaction of triglycerides and methanol to produce the biodiesel-fuel by methanolysis the reaction mixture is composed of a methyl-ester phase and a glycerol phase. One of the reactants, triglyceride, is mainly contained in the ester phase. The other reactant, methanol, is easily dissolved in the glycerol phase. Therefore, the methanol in the system is not effectively used for the reaction due to interface mass transfer resistance. An excess amount of methanol is required to increase the conversion in single-step operation. Since the glycerol phase is removed and the fraction of the glycerol phase is reduced during the operation, a two-step batch operation can effectively increase the conversion of triglyceride and reduce the concentration of unreacted component such as triglycerides, diglycerides and monoglycerides. In the present study the optimal operating conditions to increase the conversion are studied for the methanolysis of used vegetable oil using a KOH catalyst. The unreacted components are successfully reduced less than 1 mass% by the two-step batch operation for the methanolysis of used vegetable oils. The condition can be estimated by considering the acid value and water content in used vegetable oils.

**Key words:** Biodiesel, used vegetable oil, homogeneous, potassium hydroxide, two-step reaction

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### INTRODUCTION

Recently, biodiesel fuel has been widely used as alternative fuels for diesel engines. One of the production methods of biodiesel fuels is the methanolysis of triglycerides, such as vegetable oils, with catalysts. This fuel has similar properties to that of diesel fuels produced from petroleum. In the last decade, investigations of biodiesel fuel have been intensively carried out and many review papers have also been published (Balat and Balat, 2008; Basha *et al.*, 2007; Helwani *et al.*, 2009; Kulkarni and Dalai, 2006; Marchetti *et al.*, 2007; Meher *et al.*, 2006; Singh and Singh, 2010; Zabeti *et al.*, 2009).

Some production methods have been proposed for the methanolysis of triglycerides: homogeneous catalyst method, heterogeneous catalyst method, enzyme catalyzed method and supercritical methanol method. However the alkali-catalyzed homogeneous process is still the main industrial production method for transesterification. In this method, sodium hydroxide, potassium hydroxide, and sodium methoxide are generally used as the catalysts. The produced biodiesel fuel should meet the standard as an appropriate fuel for diesel engines. Although the details of the specification of each

country are different, they are similar because of the substitution of diesel fuel. The maximum values required by standards for the unreacted components, such as triglycerides, diglycerides and monoglycerides are generally 0.2, 0.2 and 0.8 mass%, respectively.

In the single-step batch operation, more than two times the stoichiometric quantity of methanol, one of the reactants, is required to decrease the amount of the unreacted components. Although, methanol hardly dissolves in triglycerides, it is easily captured by the glycerol phase formed as a by-product of the transesterification. During the reaction the glycerol phase was dispersed in the oil phase mainly composed of methylesters and triglycerides. The methanol and catalysts distributed into the glycerol phase cannot be effectively used for the reaction due to the interface mass transfer resistance. Therefore, it is important to reduce the fraction of the by-produced glycerol in the mixture of the reactants and products during the reaction in order to effectively use methanol and catalysts. The two-step reaction process is known as an effective method to increase the yield of methyl esters. Many industrial processes use this method. The conversion is not so high after the first step operation. Since the glycerol is removed

from the system after the first operation the fraction of glycerol is reduced when the second step operation is started. Therefore, the methanol and catalysts are effectively used to enhance the conversion in the two-step reaction process.

There are many research studies of the two-step reaction in which an acid catalyst was used in the first step (Berchmans and Hirata, 2008; Van Gerpan, 2005; Ghadge and Raheman, 2005; Ramadhas *et al.*, 2005; Veljkovic *et al.*, 2006; Wang *et al.*, 2007; Zullaikah *et al.*, 2005). In the first step, fatty acids contained in oils are converted to methylesters in these studies. This method is effective for the raw materials containing large amount of fatty acids.

The reaction conditions have been extensively studied for the single-step batch operation of homogeneous alkali-catalyzed transesterification. However, there is little information for the two-step operation with an alkaline catalyst as Çaylı and Küsefođlu (2008) mentioned. In the two-step batch operation the by-produced glycerol is removed from the reaction system after the first batch reaction. The methanol and catalysts are then additionally used for the second step. This method yields not only a high conversion, but also reduces a requirement of methanol.

In industrial processes, an excess amount of methanol is used for the reaction. The unreacted methanol is separated by distillation and recycled as raw material. On the other hand, the distillation process of methanol is not suitable for small scale plants, such as a 100 L d<sup>-1</sup> plant, because of the initial and running costs. Therefore, it is better to increase the conversion without increasing the methanol requirement for the small scale plants.

We have already reported the minimum requirement of catalysts and methanol to satisfy a standard for fresh vegetable oils (Kai *et al.*, 2010). Since used vegetable oils contain more amounts of free fatty acid and water than fresh oils the obtained condition cannot be adapted to the used vegetable oils. In the present study the two-step batch operation was used for the production of biodiesel fuel from used vegetable oils. The purpose is to obtain the optimum operating conditions to keep the concentration of the unreacted components below 1 mass% without increasing the requirements of methanol used in the operation.

## MATERIALS AND METHODS

Fresh commercial rapeseed oil, used vegetable oils and simulated used vegetable oils were used as the raw materials. The Acid Value (AV) of the fresh oils was 0.1 mg KOH g<sup>-1</sup> oil. The used vegetable oils of different

acid value were used. One had AV = 2.4 mg-KOH g<sup>-1</sup>-oil and the other AV = 5.8 mg KOH g<sup>-1</sup> oil. The simulated used vegetable oil was prepared by adding oleic acid to the fresh vegetable oil. Therefore, the acid value of the simulated vegetable oil could be controlled by the amount of added oleic acid.

The transesterification was carried out in a 100 mL glass batch reactor. The mass ratio of methanol to vegetable oil was changed from 13 to 23 mass%. When the ratio was 13 mass% the amount of methanol was about 1.3 times the stoichiometric value. The concentration of the catalyst was also changed from 0.8 to 1.7 mass% based on the reaction conditions. In the present study, potassium hydroxide was used as a catalyst. Potassium hydroxide was dissolved in methanol before the reaction was started. The reactions were carried out when the mass ratio of potassium hydroxide to methanol,  $\alpha$ , was fixed, and the total amounts of added potassium hydroxide and methanol were varied. In the first step reaction, 80% of the methanol and potassium hydroxide that were totally used were supplied. This ratio was found to be optimum value to increase the conversion (Kai *et al.*, 2010). The reaction time was 1 h for each batch operation. The reaction temperature was maintained at 310 K using a constant temperature water bath. The reactant mixture was stirred by a magnetic stirrer during the reaction.

After the first batch reaction the products were separated by a separating funnel, and the upper ester phase was used for the second batch reaction as the raw material. The amounts of methanol and potassium hydroxide in the second step were 20% of those used in both the steps. After the second batch reaction the separated ester phase products were analyzed by a High Performance Liquid Chromatograph (HPLC) (Shimadzu Corp) equipped with a GPC column (GPC-801, Shimadzu Corp).

## RESULTS AND DISCUSSION

Figure 1 shows the criteria where the concentration of the glycerides satisfied a standard in the case of fresh vegetable oils (Kai *et al.*, 2010). When the concentrations of methanol and potassium hydroxide were higher than the values presented by the bold line the concentration of the unreacted components was lower than 1 mass%. A dotted line shows the stoichiometric amount of methanol. By increasing the concentration of potassium hydroxide the required methanol concentration was decreased. When single-step operation was carried out for  $\alpha = 0.038$ , three times the stoichiometric amount of methanol was required to reduce the unreacted components below

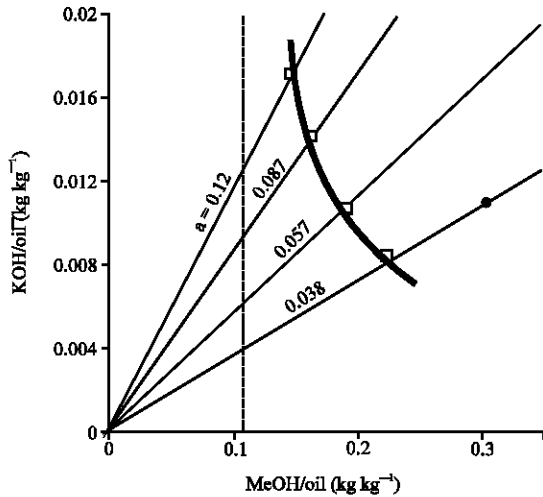


Fig. 1: Conditions to decrease the concentration of unreacted components less than 1 mass% for fresh vegetable oil

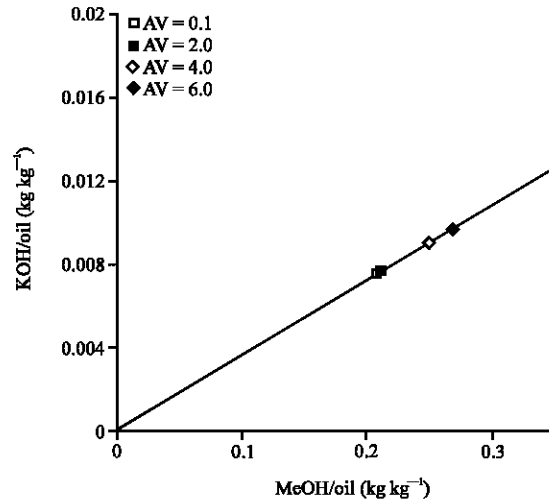


Fig. 3: Conditions to decrease the concentration of unreacted components less than 1 mass% for simulated used vegetable oil

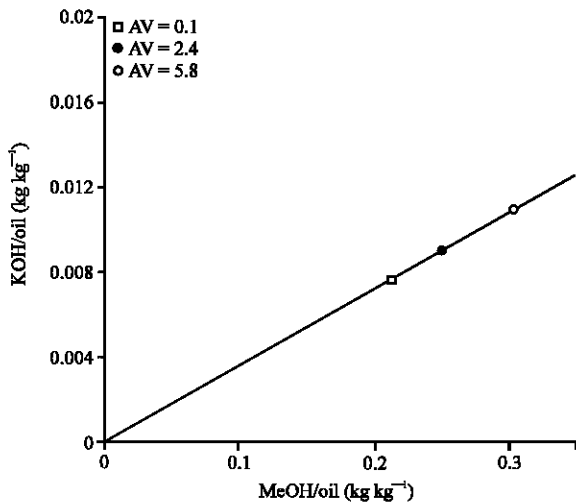


Fig. 2: Conditions to decrease the concentration of unreacted components less than 1 mass% for used vegetable oil

1 mass%. This result was also shown in Fig.1 as a closed circle. This Fig. 1 shows that the requirement of methanol to reduce the unreacted components in the methyl ester about phase was reduced by the two-step operation.

Influences of acid value of raw materials on the optimal reaction conditions were studied by using the simulated vegetable oils and used vegetable oils. The reaction was also carried out when  $\alpha = 0.038$ . Figure 2 shows the conditions to suppress the concentration of unreacted components less than 1 mass% when used

vegetable oils were used as raw materials. The unreacted unreacted components were decreased less than 1 mass% by increasing the concentrations of methanol and potassium hydroxide above the values indicated by a symbol at each condition. The required concentrations of methanol and potassium hydroxide were increased with increasing the acid value. This would be due to the fatty acid and water contained in the used vegetable oils. A portion of potassium hydroxide which was added as catalyst was consumed for neutralization with the fatty acid contained in the used vegetable oils. Figure 3 shows the required concentrations to suppress unreacted components to meet the specification of a standard value when simulated used vegetable oils were used as reactant. In this case the required amount of methanol and potassium hydroxide also increased with increasing the acid value.

The comparison between Fig. 2 and 3 show that the required methanol concentration was higher for used oil than simulated used oil even though the acid value of the oils was the same value. When the acid values was about 6 mg-KOH g<sup>-1</sup>-oil, 0.27 kg of methanol was required for 1 kg of oils in the case of the simulated used oil. On the other hand, 0.31 kg of methanol should be used in the case of used vegetable oils.

This is because the used vegetable oils contain more water than fresh vegetable oils. The saponification of triglycerides is generally enhanced by the presence of water. Therefore the reaction condition for the used vegetable oil was influenced not only the acid value but also water content in the oils. The line in Fig. 4 shows the

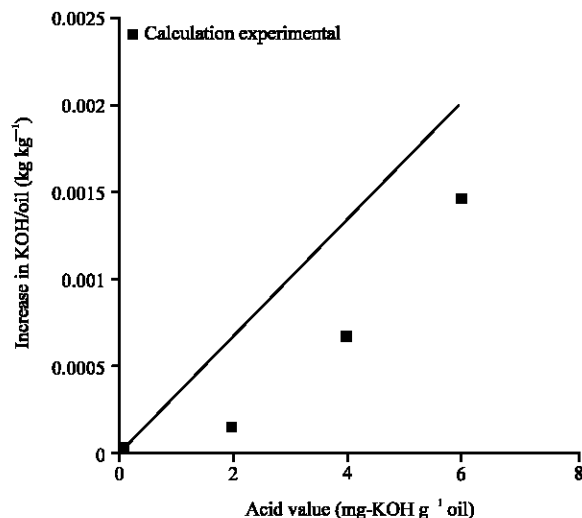


Fig. 4: Increment of KOH/oil from the condition of AV = 0

Additionally required potassium hydroxide to neutralize the fatty acid in the simulated used oils as a function of acid value. The values shown by square keys indicate the experimental results. Calculated line was the increase of required potassium hydroxide when it was used immediately for neutralization of fatty acid. Since the experimental values were lower than the calculation, potassium hydroxide was finally used for neutralization with fatty acid while performing as catalyst. Therefore, in the case of simulated used vegetable oil used as a reactant the required amount of potassium hydroxide and methanol increased with increasing the acid value. However, it was not necessary to add stoichiometric amount of potassium hydroxide to neutralize all the fatty acid contained in the raw material.

Figure 5 shows the effect of water content in simulated vegetable oils on the condition to decrease the concentration of unreacted components less than 1 mass%. The required methanol and potassium hydroxide increased with water content when the acid value was about 6 mg-KOH g<sup>-1</sup>-oil. This result indicates that the required amount of methanol and potassium hydroxide should be determined by considering the contents of fatty acids and water content in the used vegetable oils.

Table 1 gives the summary of the results. The ratio of methanol to oil shows the required methanol amount to suppress the unreacted components less than 1 mass%. Since the ratio of methanol to potassium hydroxide was constant the required amount of the catalyst was proportional to the value of methanol concentration given in this Table 1. For the fresh vegetable oil the required methanol concentration was 0.21 kg kg<sup>-1</sup>. However, it

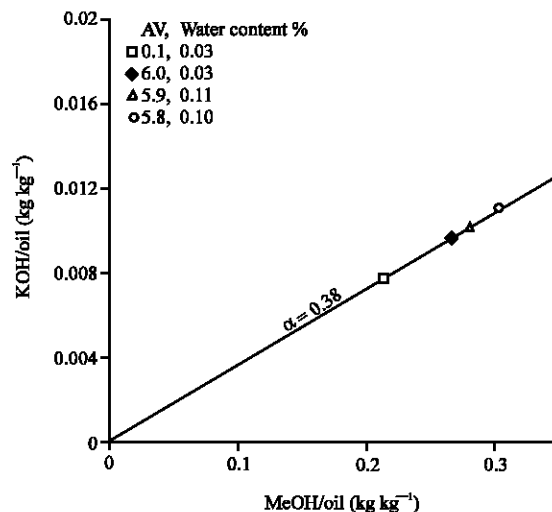


Fig. 5: Effect of water content on the conditions to decrease the concentration of unreacted components less than 1 mass% for simulated used vegetable oil

Table 1: The condition to reduce the unreacted components less than 1 mass%

Raw material	Acid value (mg-KOH g <sup>-1</sup> -oil)	Water content (%)	MeOH/oil (kg kg <sup>-1</sup> )
Fresh vegetable oil	0.1	0.03	0.21
SUVO*	6	0.03	0.26
SUVO*	5.9	0.11	0.28
Used cooking oil	5.8	0.1	0.3

\*Simulated used vegetable oil

to 0.26 kg kg<sup>-1</sup> when fatty acid was added to the oil and the acid value was 6.0 mg-KOH/g-oil. This is increased due to the consumption of potassium hydroxide by the neutralization with fatty acid. In addition, water was added to this raw material. The water content was increased from 0.03 to 0.11% and the required methanol concentration became 0.28 kg kg<sup>-1</sup>. The promotion of the saponification was promoted by the moisture and potassium hydroxide was consumed to produce soap. In the case of used cooking oil the required amounts of methanol and potassium hydroxide was larger than those estimated from the water content and acid value. This might be the influence of other components contained in used cooking oils.

## CONCLUSIONS

The unreacted components were successfully reduced less than 1 mass% by the two-step batch operation for the methanolysis of used vegetable oils. However, the required concentration of methanol and potassium hydroxide to satisfy this concentration was

higher for used vegetable oils than fresh oils. When the used vegetable oil with acid value of 6 mg-KOH g<sup>-1</sup>-oil was used the required amount of potassium hydroxide was 1.5 times the required quantity for the fresh vegetable oils. The condition could be estimated by considering the acid value and water content in used vegetable oils.

## REFERENCES

- Balat, M. and H. Balat, 2008. A critical review of bio-diesel as a vehicular fuel. *Energy Convers. Manage.*, 49: 2727-2741.
- Basha, S.M., K.R. Gopal and S. Jebaraj, 2007. A review on biodiesel production, combustion, emission and performance. *Renewable Sustainable Energy Rev.*, 13: 1628-1634.
- Berchmans, H.J. and S. Hirata, 2008. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresour. Technol.*, 99: 1716-1721.
- Cayli, G. and S. Küsefođlu, 2008. Increased yields in biodiesel production from used cooking oils by a two step process: Comparison with one step process by using TGA. *Fuel Process. Technol.*, 89: 118-122.
- Ghadge, S.V. and H. Raheman, 2005. Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass Bioenergy*, 28: 601-605.
- Helwani, Z., M.R. Othman, N. Aziz, W.J.N. Fernando and J. Kim, 2009. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Proc. Technol.*, 90: 1502-1514.
- Kai, T., Y. Mataka, T. Nakazato and H. Takanashi, 2010. Optimization of reaction conditions of two-step batch operation for biodiesel fuel production using KOH catalyst. *J. Chem. Eng. Japan*, 43: 90-94.
- Kulkarni, M.G. and A.K. Dalai, 2006. Waste cooking oil an economical source for biodiesel: A review. *Ind. Eng. Chem. Res.*, 45: 2901-2913.
- Marchetti, J.M., V.U. Miguel and A.F. Errazu, 2007. Possible methods for biodiesel production. *Renewable Sustainable Energy Rev.*, 11: 1300-1311.
- Meher, L.C., D.V. Sagar and S.N. Naik, 2006. Technical aspects of biodiesel production by transesterification-a review. *Renew. Sust. Energy Rev.*, 10: 248-268.
- Ramadhas, A.S., S. Jayaraj and C. Muraleedharan, 2005. Biodiesel production from high FFA rubber seed oil. *Fuel*, 84: 335-340.
- Singh, S.P. and D. Singh, 2010. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable Sustainable Energy Rev.*, 14: 200-216.
- Van Gerpan, J., 2005. Biodiesel processing and production. *Fuel Process Technol.*, 86: 1097-1107.
- Veljkovic, V.B., S.H. Lakicevic, O.S. Stannenkovic, Z.B. Todorovic and K.L. Lazic, 2006. Biodiesel production from Tobacco (*Nicotiana tabacum*) seed oil with a high content of free fatty acids. *Fuel*, 5: 2671-2675.
- Wang, Y., S. Ou, P. Liu and Z. Zhang, 2007. Preparation of biodiesel from waste cooking oil via two step catalyzed process. *Energy Conversion Manage.*, 48: 184-188.
- Zabeti, M., W.M.S.W. Daud and M.K. Aroua, 2009. Activity of solid catalysts for biodiesel production: A review. *Fuel Proc. Technol.*, 90: 770-777.
- Zullaikah, S., C.C. Lai, S.R. Vali and Y.H. Ju, 2005. A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. *Bioresour. Technol.*, 96: 1889-1896.