CONTINUOUS BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING HOMOGENEOUS CATALYST WITH MICROWAVE HEATING

[1]TINNABHOP SANTADKHA, [2]MALEE SANTIKUNAPORN

[1,2]Department of Chemical Engineering, Faculty of Engineering, Thammasat University
Pathumthani, Thailand 12120
E-mail: [1]santadkha.t@hotmail.com, [2]smalee@engr.tu.ac.th

Abstract- Biodiesel is a renewable transportation fuel consisting of fatty acid methyl esters (FAME), generally produced by trans-esterification of vegetable oils or animal fats. At present, a continuous flow system has been developed to increase manufacturing capacity of biodiesel from waste cooking oil that is generated from a number of sectors. Since waste cooking palm oil contained large amount of fatty acids, which inhibit the trans-esterification reaction and forms soap, it has to be treated in an esterification process first so that the free fatty acids content is lower than 1 wt. % of oil. This research aims to produce biodiesel from waste cooking palm oil in a continuous flow system assisted by microwave irradiation. Esterification of waste cooking palm oil at 60°C, alcohol-to-oil molar ratio of 12:1, catalyst concentration of 6 wt. % of fatty acid, volumetric flow rate of 520 ml/min, was able to reduce the amount of free fatty acids from 2.25 wt. % to 0.56 wt. % of oil. The optimum conditions for the production of biodiesel from treated waste cooking palm oil was at 60°C, alcohol-to-oil ratio of 12:1 volumetric flow rate of 520 ml/min and the catalyst concentration of 2.5 wt. % of oil, with 99.1% yield and 97.79 wt. % methyl ester.

Index term- Biodiesel, Palm Oil, Transesterification, Esterification, Microwave irradiation.

I. INTRODUCTION

Energy is an important factor that influence the growth of economies around the world. Currently, energy is derived from fossil fuels which is non-renewable, expensive and fluctuate unexpectedly due to the market at that time. According to the report from the Department of Mineral Fuels, oil will be use up in 47 years [1]. Thailand is one of the countries that depend on imported fossil fuels as the main source of energy, especially in the transportation sector. It was estimated that the demand for diesel oil will expand by 3-4 percent per year. In order to obtain more fuel and compile with the current awareness of global warming, researchers are motivated to study and develop sustainable alternative energy and cleaner energy to replace conventional petroleum-based fuel and responded for Thailand's policy which will increase biodiesel fuels porduction from 6.5 million liters per day in 2170 to 14 million liters per day in 2036 according to the Department of Energy's Alternative Energy Strategy [2]. Biodiesel is produced from trans-esterification reaction using alcohol and basic catalyst such as potassium hydroxide for homogeneous system and calcium oxide for heterogeneous system, under high intensity agitation and heat.

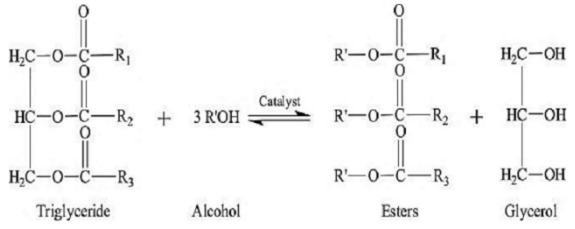


Figure 1 : Trans-esterification reaction

Biodiesel has lower viscosity compared to the vegetable oil feedstock but has the same great features as diesel fuel. Additional, biodiesel combustion emission profile demonstrated lower emission of carbon monoxide, particulate matter and unburned hydrocarbon compared to diesel fuel [3][4]. As the heating process used in the conventional heating method depend on thermal conductivity convection and radiation, which is considered as an inefficient heat transfer method, so the reaction time to relatively long. However, microwave irradiation deliver energy directly to the reagent. Therefore, by using microwave radiation it is often possible to reduce reaction time and energy consumption, as well as improve product yields [5],[6]. This is possible because the vegetable oil, methanol, and potassium hydroxide contain both polar and ionic component, rapid heating is observed upon microwave radiation, and b that is capable of induce the generation of energy on a molecular level [7].

So far not a lot of work have been done to evaluate the transformation of waste cooking palm oil to biodiesel in a continuous type flow and with microwave heating. Waste cooking palm oil is currently generated from local restaurants to food-process industries. This research aims to produce biodiesel from waste cooking palm oil in a continuous flow system assisted by microwave irradiation to produce large quantities of biodiesel in very short reaction time.[8] The waste cooking palm oil has a high amount of free fatty acid, so it has to be treated by esterification reaction first to reduce the amount of free fatty acids to less than 1 wt. % in order to prevent formation of soap. Parameters investigated in this experiment are the reaction

temperature, alcohol-to-methanol molar ratio, amount of catalyst, and volumetric flow rate of the feedstock.

II. MATERIALS AND METHODS

A. Materials and Instrument

The oil used in this experiment is waste cooking obtained from Thanachok Company Limited, Bangkok. The free fatty acid content is 2.5 wt.%. Potassium methoxide solution was freshly prepared by dissolving the fresh KOH pellets in the predetermined amount of methanol. Mixing was performed by continuous stirring for 5 – 10 min at 600 rpm. The catalyst purity is 85% and obtained from Carlo Erba.

Multi-mode microwave with 45 x 45 x 50 cm multi-mode cavity with double feed magnetrons (2x1000W, 2.45 GHz) was used. The designed oven offers clean, rapid and uniform heating for tran-sesterification and esterification. Equipped can be achieved resulting in fast and high yield reaction.

B. Acid-catalyzed esterification

The waste cooking oil had an initial free fatty acid (FFA) content of 2.25 wt.% of oil, which is above the 1% limit for a satisfactory transesterification reaction using an alkaline catalyst. Therefore FFAs were first converted to esters in a pretreatment process with methanol-to-oil ratio of 12:1 using H_2SO_4 as catalyst (6 wt.% of FFA) [4]. The reaction occurred in the reactor which has volume of 350 ml, flow rate of 520 ml/min and heated by microwave as shown in figure 1.

C. Base-catalyzed transesterification using microwave

Transesterification process was heated by the same microwave. This experiment had investigation many set of parameters values as shown in table 1 for finding the optimized conditions. The variables include the temperature range from 50 to 65°C, the concentration of catalyst from 1 to 2.5 wt. of % oil. The molar ratio of alcohol-to-oil is from 6:1 to 12:1 and flow rates ranging from 320 to 1,120 ml/min catalyzed by potassium hydroxide.

D. Analysis of biodiesel

The methyl esters were analyzed by using a Gas chromatograph (Hp 6890) equipped with a Flame Ionization Detector (FID) and a wax column (Stabilwax; 30 m × 0.25 µm × 0.25 µm). Analysis parameters was used as the carrier gas had a flow rate of 1 ml/min, linear velocity of 30 cm/s and a sample injection split ratio of 50:1. The temperature gradient maintained in the oven was 60°C (2 min), 10°C/min to 200°C, 5°C to 240°C and hold 240°C for 7 minutes were adopted throughout the runs [9]. The %FAME or purity of biodiesel (mg/mg of sample) was calculated using equation 1.

$$\%FAMEs = \frac{(\sum A - \sum A_{EI})}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \quad (1)$$

Where $\sum A$ is the total peak area from methyl esters in the range C_{14} to $C_{24:1}$, A_{EI} is the peak area of methyl heptadecanoate, C_{EI} is the concentration of the methyl heptadecanoate solution, (mg/ml), V_{EI} is the volume of the methyl heptadecanoate solution being used (ml) and m is the mass of the sample (mg). Similarly, biodiesel conversion (%) was calculated using equation 2.

$$\text{Biodiesel Yields (\%)} = \frac{\text{Weight of biodiesel product} \times 100}{\text{Weight of oil}} \quad (2)$$

Table. 1 Operation conditions

Parameters	Range
Temperature (°C)	55, 60, 65
Alcohol-to-oil molar ratio	7.5:1, 9:1, 12:1
Catalyst concentration (wt.%)	1.5, 2.0, 2.5
Volumetric flow rate (ml/min)	220, 520, 820,

Figure 2 : Microwave flow system.

III. RESULTS AND DISCUSSION

A. The effect of molar ratio of alcohol-to-oil

One of the main factors affecting the yield of biodiesel is the molar ratio alcohol-to-oil. Theoretically, the ratio for transesterification reaction require 3 mol of alcohol for 1 mol of triglyceride. An excess of alcohol is used in biodiesel production to ensure that the oils or fat will be completely converted to ester and a higher alcohol triglyceride ratio can result in a great ester conversion in a shorter time [10],[11].

In order to investigate the effect of molar ratio on biodiesel yield, experiment were conducted with various molar ratio ranging from 6:1 to 12:1 with a constant catalyst concentration of 1.5% wt. catalyst, volumetric flow rate of 520 ml / min and the temperature of 50°C. As shown, the maximum FAMEs was 90.5% and obtained by using 12:1 molar ratio of alcohol-to- oil. The amount of FAMEs has increased with alcohol quantity used because a methanol-to-oil molar ratio larger than the stoichiometric molar ratio can shift the equilibrium conversion of the reaction.

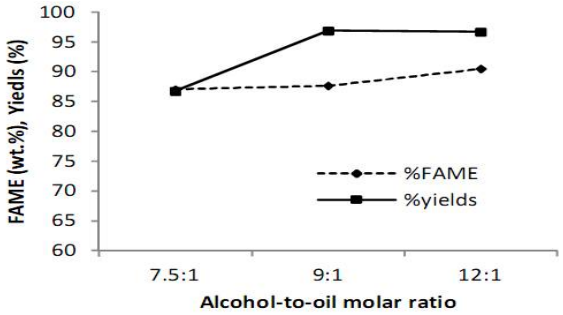


Figure 3: The effect of alcohol to oil molar ratio on FAMEs and yields (%).

B. The effect of concentration of catalyst

Catalyst concentration can affect the yield of the biodiesel product as well. In this part, the reaction temperature of 50°C, volumetric flow rate of 520 mL / min, and alcohol to oil molar ratio of 7.5:1 were maintained constant with four concentration of catalyst (1 %wt – 2.5 %wt). The result are given in Fig.3.

As shown, the maximum FAMEs was 89.9% wt.% and obtained by using 2.5 %wt of catalyst. However, biodiesel conversion efficiency was observed to decrease dramatically at high amount of catalyst, because excessive alkaline catalyst can cause more triglycerides to react with the alkali catalyst to form undesirable soap.[10],[12].

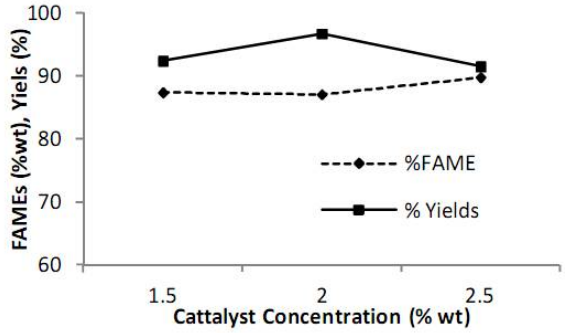


Figure 4 : The effect of catalyst concentration

C. Effect of react temperature

Figure 5 shows the results of experiments to find the optimum temperature. The synthetic of biodiesel fuel from the reactor by the substrate mole ratio of 7.5: 1 and the catalyst concentration of 1.5% wt. and flow rate of 520 ml/min. As shown in Fig.5, the maximum of FAMEs was 90.32 wt.% and obtained at a temperature of 60°C. FAMEs increased with increasing of reaction temperature, because transesterification reaction is an endothermic reaction. However, if the temperature increased beyond the appropriate temperature, the yield of biodiesel product decreases because at higher reaction temperature will promote saponification reaction of triglycerides [12],[14].

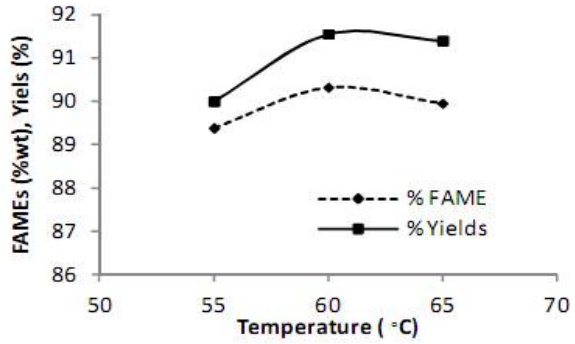


Figure 5 : The effect of catalyst concentration

D. The optimized operating conditions

The optimized conditions for trans-esterification can be operated at 60°C, alcohol-to-oil molar ratio of 12:1, the concentration of catalyst 2.5 wt.%., and flow rate of 820 ml/min. Biodiesel produced from these conditions was found to contain 96.98 wt.% FAMEs. Eevera et al. the retention time can affect to each concentration of catalyst. The research was conducted by adjusting the different four flow rate in the values found on the flow rate of 520 ml / min with retention time 40 seconds to give the amount of FAMEs as high as 97.79% wt, as shown in Figure 6. However when flow rate was reduced lower than 820 ml/min and biodiesel yield started to decrease with increasing flow rate because excess reaction time cause the transesterification reaction to be reversed [12],[13].

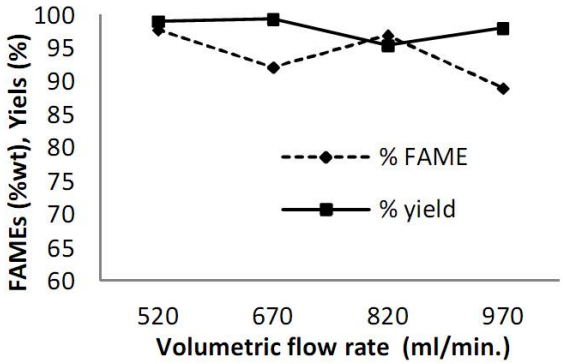


Fig.6. The effect of flow rate to 2.5 wt.% catalyst

CONCLUSION

The production of biodiesel from waste cooking palm oil with a continuous microwave reactor can be summarized as follows. The alcohol-to-oil molar ratio was found to have a significant effect on biodiesel yield and amount of FAMEs. The amount of catalyst was found to have a positive influence on biodiesel initially, but biodiesel yield will start to decrease if the amount of catalyst was increased to higher than 2.5 wt.%. Volumetric flow rate below 820 mL/min was found to cause trans-esterification reaction to be reversed. High reaction temperature was found to increase the activity of saponification, which caused biodiesel yield and FAMEs content to decrease. The experiment showed that the optimum conditions for the production process is at alcohol-to-oil ratio of 12: 1, catalyst concentration of 2.5% wt, a flow rate of 520 mL/ min and reacted to temperature of 60°C

ACKNOWLEDGEMENTS

Thanks to the Faculty of Engineering, Thammasat University to support scholarships and a research budget from Catalysis Energy Laboratory.

REFERENCES

[1] The Department of mineral fuel, “Petroleum reserves”, [Online]. Available: http://goo.gl/PxxbMw [Accessed 3 november 2016].

[2] Department of Alternative Energy Development and Efficiency, " Strategic Plan for Bio-diesel Use" , [online]. Available: http:// http://www4.dede.go.th, [Accessed 26 April 2017].

[3] S. Kent Hoekman, A. Broch, C. Robbins, E. Ceniceros, M. Natarajan, " Review of biodiesel composition, properties, and specifications", Renewable and Sustainable Energy Reviews, vol.16, pp.143-169, apr. 2011.

[4] Nirund Sumalee, "In order to get PSU biodiesel, Songkla", Book, Research and Development Office, 2014

[5] M. Bowman, J. Holcomb, C. Kormos, N Leadbeater, V William, "Approach for scale-up of microwave-promoted reaction", Org Process Res Dev, vol.12, pp.41-57, nov. 2007.

[6] N. Leadbeater, L stencil, "Fast, easy preparation of biodiesel using microwave heating, Energy Fuel, vol.20, pp. 2281-2283, 1 august 2006

[7] C. Koopmans, M. Iannelli, P Kerep, M. Klink, S. Schmitz, S. sinnwell, "Microwave -assisted polymer chemistry: heck-reaction, transesterification, Baeyer-villager oxidation, oxazoline polymerization, acrylamide and porous materials, Tetrahedron, vol.62, pp.4709-4714, January 2006

[8] J.M. Encinar, J.F. Gonzalez, G. Martinez, N. Sanchez, A. Pardal, " Soybean oil transesterification by the use of a microwave flow system", Fuel, vol.95, pp. 386-393, 17 November 2011 .

[9] DIN EN14103:2011, " Fat and oil derivatives – Fatty Acid Methyl Ester (FAME) – Determination of ester and linolenic acid methyl ester content" , European Committee for Standardization, Management Centre: Avenue Marnix 17: B-1000 Brussels.

[10] D.Y.C. Leung, Y. Guo "Transesterification of neat and used frying oil: optimization for biodiesel production", Fuel Process Technol, vol.87, pp. 883–890, 11 october 2006.

[11] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis" Bioresour Technol, vol.90, pp. 229–240, 3 december 2003.

[12] T. Eevera, K. Rajendran, S. Saradha "Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions", Renew Energy, vol.34 , pp. 762–765, 3 march 2009.

[13] F. Ma, L.D. Clements, M.A. Hanna, "The effects of catalyst, free fatty acids, and water on transesterification of beef tallow" Trans Am Soc Agric Eng, vol.41, pp. 1261–1264, 1998.d

[14] B. Freedman, E.H. Pryde, T.L. Mounts, "Variables affecting the yields of fatty esters from transesterified vegetable oils", J Am Oil Chem Soc, vol.61, pp. 1638–1643, 14 march 1984.

★★★