Continuous Transethylation of Vegetable Oils by Microwave Irradiation

V. Lertsathapornsuk[1], P. Ruangying[2], R. Pairintra[2] and K. Krisnangkura[2]

[1] School of Energy and Materials, King Mongkut's University of Technology Thonburi, Bangkok, Thailand. 10140.

Tel. 0-2470-9823 Fax 0-2452-3479 E-mail: veekmutt@yahoo.com.

[2] School of Bioresources and Technology, King Mongkut's University of Technology Thonburi (Bangkhuntien Campus),

Bangkok, Thailand. 10150. Tel: 0-2470-9787 Fax: 0-2452-3479

Abstract

The methods of continuous preparation of fatty acid ethyl esters (FAEE) from coconut, rice bran and used frying (palm) oils in a modified home made microwave oven (800 Watts) are described. Good yields FAEEs are obtained with 1.0 % sodium hydroxide (in excess) as a catalyst. With the alcohol to oils molar ratio of 9:1, 100% conversion is obtained within 30s for coconut oil, 94% conversion for rice bran oil and 83% conversion for used frying oil. Percent conversion is slightly increased for used frying oil but not for rice bran oil, when the reaction time is increased to 60s. The temperatures of the reaction mixtures are rapidly increased to the boiling point of alcohol within 30s and increased slightly above the boiling point of the alcohol, to 83.4°C at 60s.

When the used frying oil is thin with kerosene (1:1 v/v), percent conversion is 92% in 30s, which is slightly higher than the un-thinned oil. Percent conversions remain constant at longer reaction times. Reaction temperature is lower than the un-thinned oil (70.9 $^{\circ}$C at 30s and 80.2 at 60s).

Keywords: Biodiesel; Continuous transesterification;
Fatty acid ethyl ester; Microwave; Vegetable oils

1. Introduction

Biodiesel is one of the most famous alternative petroleum diesel fuel. It is derived from triglyceride (TG, oils, fats or used cooking oils) by transesterification with alcohol (methanol or ethanol) in the presence of a catalyst (alkali or acid) to chemically break the molecule of TG. Transesterification process can be carried out by batch process or continuous process, most of which use conventional heating for biodiesel production. The other technologies for production of biodiesel are super critical methanol process and microwave process.

For transesterification, the batch process [1-5] is a simple process but it requires higher capital cost for larger reactor volume. This process can convert oil to biodiesel up to 80 to 94 % in 30 minutes to 2 hours. The yield was dictated by molar ratio of oil to alcohol, reaction time, temperature, catalyst type, catalyst concentration, triglyceride properties, and mixing intensity. The continuous transesterification process [6-7] is being developed to reduce the reactor size and reaction time (1 minute to 1 hour). Krisnangkura et al. (1992) reported a 96% (palm oil methyl ester) complete within 60 seconds at methanol to palm oil ratio of 13:1 (palm oil was mixed with toluene at 1:1 of palm oil to toluene ratio). Noureddini et al. (1998) reported a 98% yield in 1 minute to 1 hour. The main factor that determined the rapid conversion was higher molar ratio of alcohol to oil. Biodiesel production in super critical methanol [8-11] was carried out with the oils and methanol in high pressure (>8.09 MPa) and temperature (>239.4°C). The transesterification can be performed without any catalyst. Good yields (90 to 97%) are obtained in short reaction time (120 to 240 seconds) but the process consumes very high energy for high pressure and temperature. Furthermore, higher methanol concentration is required. Transesterification of oils with the uses of microwave heating has been reported recently. Microwave energy is delivered directly to the reacting molecules, which undergo chemical reaction. Thus, heat transfer is more effective than conventional heat, which transfers from the environment. Some researchers [12-14] reported that microwave radiation could enhance the rate of transesterification in the batch process. Jeyashoke et al.(1998) reported that transmethylation of rice bran oil in toluene could be completed in 15 seconds at methanol-oil ratio of 17:1 of methanol to oil molar ratio. Lertsathapornsuk et al. (2003) reported the completed transethylation of used vegetable oil in 10 seconds at 9:1 molar ratio of ethanol to oil with 1% catalyst (NaOH).

In conventional heating of transesterification process (batch, continuous, and super critical methanol process), heat energy is transferred to the raw material through convection, conduction,

and radiation from surfaces of the raw material. Thus, the conventional heating consumes more energy and take long preheat and reaction time (usually from 30 minutes to 8 hours) to produce higher 90 percent conversion yield biodiesel product. While microwave-heating process used shorten time to heat the raw material without preheat. Therefore, the objective of this research was to develop a continuous transesterification process with enhancement of the transethylation of vegetable oils under the continuous microwave biodiesel reactor (CMBR) modified from domestic microwave oven.

2. Experimental

2.1 Materials

Coconut and rice bran oils (food grade) were purchased from grocery in Bangkok (Thailand). Used palm oil (UPO) was gifted of KFC International (Thailand) Company Limited. Ethanol (99.8%) was obtained from Liquor Distillery Organization, Excise Department (Thailand). Fatty acid ethyl esters (Caprylic, Capric, Lauric, Myristic, Palmitic, Stearic, Oleic, Linoleic and Arachidic) were obtained from Sigma Chemical Company (St. Louis, Mo).

2.2 Reactor

A house hold, 800 W 2450 Hz, microwave (Ecolux, Japan) was modified to CMBR as follows (Fig. 1):
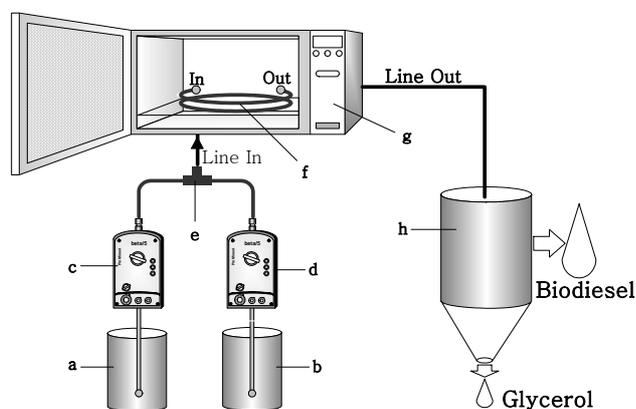

Fig. 1. The Schematic diagrams of continuous microwave biodiesel reactor. a, oils reservoir; b, alcohol reservoir; c, oils pump; d, alcohol pump; e, tee connector; f, reactor coil; g, microwave oven; h, product reservoir.

The glass plate on the carousel was removed and a stationary ceramic tile cut to the size of the oven was fit into the oven slightly above the carousel axis such that it can rotate freely. The surface on the top of the carousel axis was covered with aluminum foil to randomly reflect the microwave radiation. A poly-tetrafluoroethylene (Teflon) tubing (0.9 cm ID X 260 cm) was coiled into the oven and connected to the inlet pumps (via a stainless steel tee connector) and the outlet reservoir at the back of the oven (as shown in Fig. 1). A thermocouple (type K) was inserted at the outlet and connected to a digital thermometer (Fluke 52, Jonhn Fulke MFG, USA) for monitoring the reaction temperature. The microwave oven was operated at full power.

2.3 Preparation of FAEEs

Vegetable oils and ethanolic NaOH (1.0 %) solution were fed separately via 2 metering pumps (ProMinent model Beta5A, 22 W, Heidelberg, Germany) and mixed at the tee connector at the inlet. Reaction time and molar ratio of the oil to alcohol were controlled via a combination of percent stroke length and stroke frequency of the metering pumps. The outlet was slightly bended upward to keep the reactor filled at all flow rates and the reaction was acidified immediately with HCl (1.0 M) to stop the reaction. The esters fraction (upper layer) was separated and washed twice with half volume of de-ionized water and dried over anhydrous sodium sulfate.

2.4 Analysis

Fatty acid compositions of the oils were analyzed on an RTX-2330 fused silica capillary column (80% cyanopropyl polymethylsiloxane, 0.25 mm ID x 30 m, from Restex Co. Bellefont PA) connected to a Shimadzu Model 17-A gas chromatography (Shimadzu, Japan) with FID detector. Nitrogen was used as the carrier gas at a flow rate of 0.8 mL/min.

Percent conversions of the oil to FAEEs were analyzed by HPLC on Silica 60 column (4.6 mm ID x 250 mm, Tosho, Japan) connected to the Waters model 510 Pump (Waters Associate, Milford, MA01757 USA.) with a Rheodyne 7125 six-port injector (Cotati, CA, USA) and an evaporative light scattering detector (Sedex 55, Sedere Alfortville, France). The mobile phase was hexanes, diethyl ether, acetic acid 90:10:0.5 v/v at a flow of 2.0 mL/min.

3. Results and Discussion

It has generally been known that transesterification of vegetable oil, catalyzed by alkaline, is very sensitive to water. Water can react not only with triglycerides but it also hydrolyzes the monoalkyl esters. Fatty acid soap is the dead end product. Thus, the present of water would lead to a lower yield of the ester as well as the slower rate of transesterification due to diminishing catalytic strength. In order to eliminate water in the reaction system, sodium hydroxide was heated for half an hour at

280 $^{\circ}$C to expel free water. It is speculated part of the hydroxide is converted to the oxide.

Transesterifications of all the three different oils are very fast and can be completed within 30 s. This finding consistent with the reports in the literatures [6,13-14]. For coconut oil where there is no detectable amount of free fatty in the starting oil, free fatty acid formed in the product is also negligible (Table 1), suggesting that water in the reaction mixture is very low.

Table 1 Percent conversion of fatty acid ethyl ester from TGs.

Sample	Reaction Time (s)	Reaction Temp. ($^{\circ}$C)	Conversion (%)		
			FAEE	TG	FFA
*CCO			0	100	trace
CCOEE	30	79.5	100	0	0
	45	82.2	100	0	0
	60	83.4	100	0	0
*RBO			0	99.4	0.6
RBOEE	30	77.8	93.5	3.2	3.3
	45	80.4	93.2	3.3	3.5
	60	83.4	93.1	3.3	3.6
*UPO			0	95.5	4.5
UPOEE	30	77.5	82.5	10.7	6.8
	45	81.2	83.9	9.4	6.7
	60	84.1	90.6	2.7	6.7
*KUPO			0	96.8	4.5
KUPOEE	30	70.9	91.6	4	5.7
	45	76.5	91.5	3.9	5.9
	60	80.2	91.6	3.6	6.1

* starting material compositions

CCOEE is coconut oil ethyl ester.

RBOEE is rice bran oil ethyl ester.

UPOEE is used palm oil ethyl ester.

KUPO is mix kerosene to used palm oil ethyl ester.

Rice bran oil has relatively high free fatty acid (0.60 %). After transesterification, free fatty acid is increased by about 3 % (Table 1). This reflects the present of relatively high water content in the oil or in the reaction system. In case of used palm oils, free fatty acid is very high (4.50 %). If the same concentration of sodium hydroxide as those two oils is used, it is speculated that some or all the sodium hydroxide will react with the free acid and there will be very small amount or no sodium hydroxide available for catalytic action. Generally, the free fatty acid is removed by

pretreatment with sodium hydroxide and the sodium soap is repeatedly washed by water until neutral. We found that pretreatment of the oil is very time consuming and causes a great loss of oil in the washing process. Thus, the pretreatment step is then omitted. The neutralization and transethylation are carried out simultaneously. For used palm oil with free fatty acid of 4.50%, the sodium hydroxide concentration in ethanolic NaOH solution is increased to 2.0%. Results of transesterification in Table 1 show that the conversion of used palm oil to FAEEs are 83% and 91%, in 30 and 60 s, respectively. Free fatty acids are increased by 2.2 - 2.3%. Results in Table 1 show that the reaction rate of transethylation for used palm oil seem to be slower than coconut and rice bran oils. Only about 83% conversions are obtained on the used palm oil with 30s irradiation, whereas conversions are 94 and 100% (no triglyceride left in the reaction) for rice bran and coconut oils. However, percent conversions are increased to about 84 and 91% at 45s and 60s, respectively. The slower rate of transesterification for used palm oil may probably arise from higher viscosity of the oil or different concentration of the catalyst. When the oil is thinned with equal volume of kerosene, interesting result is obtained as shown in Table 1. About ninety two percent conversion is found in 30s and remains relatively constant thereafter.

Reaction temperature rises very rapidly from 30 $^{\circ}$C to 78.5 ± 1.0 $^{\circ}$C in the first 30s and slowly increases to 84 $^{\circ}$C at 60s. Jeyashoke et al. (1998) reported, in a batch process, that transmethylation could be completed in 40s with the 1100 watt microwave and the temperature was only 45 $^{\circ}$C. Fig.2 shows that the reaction temperatures in CMBR. At 60 seconds of reaction time, the temperatures of CCO, RBO, UPO and KUPO are 83.4, 83.4, 84.1 and 80.2 $^{\circ}$C, respectively. At 45, the temperatures of CCO, RBO, UPO and KUPO are 82.24, 80.4, 81.2, 76.5 $^{\circ}$C and at 30 seconds are 79.5, 77.8, 77.5 and 70.9 $^{\circ}$C, respectively. The reaction temperatures are close to the limit of ethanol boiling point after 30 seconds. When kerosene is added to the UPO, reaction temperature increases at much shallow rate. The kerosene seem to act as a coolant and consequently, decreasing the reaction temperature without affecting the percent conversion. An additional advantage of kerosene is the viscosity of UPO mixture is lower which facilitates pumping process.

The fatty acid composition of UPO is very similar to that of refined palm oil with the average molecular mass of 849.8 and iodine value is 55.19. The effect of reaction time on FAEE conversion was repeated three times. The reaction products are analyzed on a HPLC.

When the UPO is thinned with kerosene (1:1), the same percent conversion can be obtained in at the same reaction time. The merit of adding kerosene to UPO is not only on the lower viscosity of the mixture but glycerol is separated out faster than that without kerosene. FFA presented in the UPO does not interfere with transesterification so long as enough amount of NaOH is present for catalysis. FFA in the product is easily removed by repeated washing with water until neutral.

4. Conclusions

Under CMBR system, the experimental results were shown rapid in the reaction rate and higher conversion yield of transethylation base on alkali catalyst of three vegetable oils to biodiesel. The complete reaction had been occurred under the CMBR by excess volume ratio of EtOH to Oil. The reaction time was reduced to 30 to 60 seconds, which decreased to 30 to 60 times when comparing with conventional and super critical methods.

To this end, the rapid transethylation of vegetable oils by CMBR is an alternative production way to increase the reaction rate and decreasingly energy for producing the alternative petroleum diesel fuels of agricultural countries which protect the environment and its is energy security.

5. Acknowledgements

6. References

1. Antolín, G., Tinaut, F.V., Briceño, V., Castaño, V., Pérez,C. Ramírez, A.I., "Optimisation of Biodiesel Production by Sunflower Oil Transesterification," Bioresource Technology, Vol. 83, pp. 111-114, 2002.

2. Encinar, J.M, Gonzales, J.F., Rodriuez, J.J., Tejedor, A., "Biodiesel Fuels from Vegetable Oils: Transesterification of Cynara Cardunculus L. Oils with Ethanol." Energy and Fuels, Vol. 16, pp. 443-450, 2002.

3. Ma, F., Hanna, M.A., "Biodiesel Production: a Review," Bioresource Technology, Vol. 70, pp. 1-15, 1999.

4. Vicente, G., Martínez, M., Aracil, J., "Integrated Biodiesel Production: a Comparison of Different Homogeneous Catalysts Systems," Bioresource Technology, 92, 297-305, 2004.

5. Zhang, Y., Dube, M. A., McLean, D. D., Kates, M., "Biodiesel production from waste cooking oil: 1. Process design and technological assessment," Bioresource Technology, Vol. 39, pp. 1-16.4, 343-348, 2003.

6. Krisnangkura, K., Simamaharnnop, R., "Continuous Transesterification of Palm Oil in an Organic Solvent," JAOCS, Vol. 69, 166-169, 1992.

7. Noureddini, H., Harkey, D., Medikonduru, V., "A Continuous Process for the Conversion of Vegetable Oil into Methyl Ester of Fatty Acid" JAOCS, Vol. 75, No. 12, pp. 1775-1783, 1998.

8. Demirbaş, A., "Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey," Energy Conversion and Management, Vol. 44, pp. 2093–2109, 2003.

9. Fukuda, H., Kondo, A. and Noda, H., "Review Biodiesel Fuel Production by Transesterification of Oils," Journal of Bioscience and Bioengineering, Vol. 92, No. 5, pp. 405-416, 2001.

10. Saka, S., Kusdiana, D., "Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol," Fuel, Vol. 80, pp. 225-231, 2001.

11. Warabi, Y., Kusdiana, D., Saka, S., 2004. "Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols," Bioresource Technology, Vol. 91, pp. 283-287, 2001.

12. Dasgupta, A., Banerjee, P., Malik, S., Use of microwave irradiation for rapid transesterification of lipids and accelerated synthesis of fatty acyl pyrrolipidides for analysis by gas chromatography-mass spectrometry: study of fatty acid profiles of olive oil, evening primrose oil, fish oils and phospholipids from mango pulp. Chemistry and Physics, of Lipids. Vol. 62, pp. 281-291, 1992.

13. Jeyashoke, N., Krisnangkura, K., and Chen, S.T., "Microwave Induced Rapid Transmethylation of Fatty Acids for Analysis of Food Oil," Journal of Chromatography A, Vol. 818, pp. 133-137, 1998.

14. Lertsathapornsuk, V., Pairintra, R., Krisnangkura, K. Chindaruksa, S., "Direct Conversion of Used Vegetable Oil to Biodiesel and Its Use as an Alternative fuel for CI Engine," Proceeding of 1st International Conference on Sustainable Energy and Green Architecture, pp. SE091-096, 2003.