Ion Exchange Resin for Purification Process in Biodiesel Process with Waste Frying Oil

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Abstract

A biodiesel production plant using waste frying oil was studied in a step of transesterification. The free fatty acid value of the studied waste cooking oil was not more than 2%. The crude biodiesel was produced from the transesterification, catalyzed with KOH. The results indicate that the optimum conditions for more 90% biodiesel conversion, is a catalyst amount of 1.2% (w), an oil to methanol ratio of 1:6, 60°C reaction temperature, 30 minutes reaction time, and 600 rpm stirring rate. Furthermore, the optimum conditions can scale up for biodiesel production in a purification process with commercial ion exchange resin packed in a column of the plant, instead of a water washing process. Hence, the used resin prevented generating wastewater from the biodiesel production. The optimum conditions of biodiesel flow rate in a fixed bed was studied. The results of the optimum reaction and the washing process can be applied for environmental friendly biodiesel plants.

Keywords: Biodiesel, Waste cooking oil, Ion exchange resin, Purification, Catalyst

1. Introduction

Waste cooking oil is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment [1]. Besides, it reduces the need to use land for biodiesel-producing crops [2]. Waste cooking oils are currently collected from large-scale food processing and service facilities as a raw material for biodiesel production [3]. The Division of Vehicles, Building and Physical Plant, set up a biodiesel plant at Kasetsart University. The plant can produce biodiesel from 150 litters of waste cooking oil, which was collected from cafeterias of Kasetsart University and donated from officials and students. The production process consists of a two-step reaction. In the first step, sulphuric catalyzed esterification is used to reduce free fatty acids of the waste cooking oil [4]. The second step, potassium hydroxide catalyzed transesterification, is used to convert the waste cooking oil into biodiesel. After the two-step reaction, the chemical reagents in the crude biodiesel was remove by a water washing process [5, 6]. Next, water residue was remored from the biodiesel by adsorption with a sodium chloride column. However, the amount of free fatty acid contained in the waste cooking oil was less than 2%, therefore, this biodiesel-production plant can use only step on of the catalyzed process as the transesterification, in converting waste cooking oil into biodiesel [7, 8]. The objectives of this research were to optimize the potassium hydroxide-catalyzed transesterification process, using ion- exchange resin for biodiesel purification, replacing a water washing process for a sustainable production process, at the Kasetsart University biodiesel plant.

2. Methodology

Material and methods

Waste cooking oil was obtained from the cafeteria of Kasetsart University. This used vegetable oil was characterized by the free fatty acid content and fatty acid composition, following the European method EN129397, and EN14103 standard. The result of free fatty acid was 1.29%, and the fatty acid composition is represented in Table1.

Certified methanol of 99.8% purity was obtained from Sigma. The catalyst, potassium hydroxide, was pure grade from Merck. The gas-liquid chromatography reference standard of fatty acid methyl esters was purchased from Supelco. Ion exchange resin (Lewatit GF202) was donated from Bayer Thai Co., Ltd.

Equipment

Reactions were carried out in a 50 cm^3 glass three-necked batch reactor. This reactor was equipped with a reflux condenser, and a magnetic stirrer. The reactor was immersed in a constant-temperature bath, which was capable of maintaining the reaction temperature that is required for the reaction.

Experimental procedure

The reactor was initially filled with the desired amount of oil and placed in the constant-temperature bath with its associated equipment. The waste cooking oil was then agitated and heated to a predetermined temperature. The catalyst was dissolved in the methanol and the resulting solution was added to the waste oil in the reactor. The reaction was timed as soon as the catalyst/methanol solution was added to the reactor. After finishing the reaction, the mixture was transferred to a separatory funnel, allowing glycerol to separate by gravity for 2 hr. After removing the glycerol layer, the methyl ester layer was washed with water to remove methanol, the catalyst and glycerol residuals. The methyl ester yield was further determined by gas chromatography and expressed in term of the percentage (wt %).

Washing process of crude methyl esters

To determine the influence of washing step on the methyl ester properties and yields, two types of crude biodiesel from step two and step one of the production were purified by ion exchange resin column. The crude biodiesel products were introduced into a column with a bed of ion exchange resin (9 kg, 10 cm i.d. x 150 cm height).

Methyl esters characterization

The methyl ester concentration was obtained by gas chromatography equipped with DB-WAX column and flame ionization detector. Heptadecanoic acid methyl ester was used as internal standard.

Table 1 Fatty acid composition of waste cooking oil.

Fatty acid	Composition (%wt)
Lauric ($C_{12:0}$)	1.02
Myristic ($C_{14:0}$)	1.43
Palmitic ($C_{16:0}$)	31.37
Palmitoleic ($C_{16:1}$)	1.74
Stearic (C_{18})	4.89
Oleic ($C_{18:1}$)	40.14
Linoleic ($C_{18:1}$)	16.99
Linolenic ($C_{18:3}$)	0.95
Arachidic ($C_{20:0}$)	1.46

Table 2 Influence of KOH concentration on methanolysis of waste cooking oil.

KOH concentration (%)	0.8	1.0	1.2	1.4	1.6	1.8
% yield of ME	89	91	95	95	95	95

3. Results and discussion

Transesterification of waste cooking oil

The variables affecting transesterification such as catalyst concentration (0.8-1.8 wt% of oil), methanol/ oil molar ratio (3:1 to 9:1), temperature (45-70°C), reaction time (15-90 min) at constant stir rate were investigated to obtain optimum reaction conditions.

Influence of catalyst concentration

The effects of KOH concentrations on the transesterification of waste cooking oil was investigated with concentrations varying from 0.8% to 1.8%. The reaction conditions during the whole process were fixed at: reaction temperature of 60°C, reaction time of 30 min, molar ratio of methanol to oil at 7:1, and stir rate at 600 rpm. Table 2 shows the yield of methyl esters at different catalyst concentrations.

From Table 2, the methyl ester yield increased when the concentration of catalyst increased from 0.8 to 1.2%. At 1.2% KOH the methyl ester yield became constant, and the yield was 95%. The yield of methyl ester was not differen from 1.2% to 1.8%. Therefore, 1.2% KOH is optimal for the reactions of this study.

Influence of methanol/oil molar ratio

The alcohol to oil molar ratio is one of the important factors that affect the conversion efficiency of transesterification. Stoichiometrically, 3 moles of alcohol are required for each mole of triglyceride. In practice, a higher molar ratio is used for getting greater yields of fatty acid methyl esters. In this study, the transesterification of waste cooking oil was carried out at 4:1, 5:1, 6:1, 7:1, 8:1 and 9:1 molar ratios of methanol to oil. The reaction conditions were fixed at : reaction temperature of 60°C, reaction time of 30 min, catalyst concentration of 1.2%, and stir rate 600 rpm. The results of methyl esters yield are shown in Table 3.

As shown in Table 3, the yield was greatly influenced by the quantity of methanol. When the molar ratio was increased from 4:1 to 6:1, the yield of methyl eaters also increased from 90% to 95%. A further increase in the methanol to oil molar ratio to 9:1 resulted in a little bit increase in the yield. Therefore, the optimum quantity of methanol is a 6:1 molar ratio of methanol to oil.

Influence of reaction temperature

To study the effect of reaction temperature on waste cooking oil, experimental trials were carried out at temperatures 45°C, 50°C, 55°C, 60°C, 65°C, and 70°C. The reaction conditions were fixed at: reaction time of 30 min, catalyst concentration of 1.2%, stir rate 600 rpm, and molar ratio of methanol to oil at 6:1. The results of methyl esters yield are shown in Table 4.

As shown in Table 3, it was observed that the yield of methyl esters increased from 45°C to 60°C. After this temperature, the yield became constant. So, 60°C of temperature is the optimum reaction temperature, and the yield of methyl esters is 95%.

Influence of reaction time

The yield of methyl esters of transesterificaiton usually increases with the reaction time. In this study, the experiments were carried out at reaction times of 15 min, 30 min, 45 min, 60 min, 75 min, and 90 min under the reaction conditions of methanol/oil molar ratio 6:1, catalyst concentration at 1.2%, stir rate 600 rpm, and reaction temperature 60°C. The result of reaction time on the methyl esters yield are shown demonstrated in Table 5.

The result from Table 4 showed that the methyl esters yield arrived at the maximum value at the reaction time around 30 min to 60 min and then there was a slight increase in yield from 75 min to 90 min. It is observed that 30 min is the optimal reaction time of this reaction.

Table 3 Influence of molar ratio on methanolysis of waste cooking oil.

Methanol/Oil molar ratio	4:1	5:1	6:1	7:1	8:1	9:1
% yield of ME	90	92	95	95	97	97

Table 4 Influence of reaction temperature on methanolysis of waste cooking oil.

Temperature (°C)	45	50	55	60	65	70
% yield of ME	91	93	94	95	95	95

Table 5 Influence of reaction time on methanolysis of waste cooking oil.

Reaction time (min)	15	30	45	60	75	90
% yield of ME	94	95	95	95	96	96

Washing process with ion exchange resin

Waste cooking oil methyl esters from step one of reaction was prepared in a 1 liter reactor for many times to obtain about 10 liters of methyl esters by using the optimum conditions determined in this study (600 rpm, 6:1 molar ratio of methanol to oil, 1.2% KOH, 60°C, and reaction time for 30 min). The crude methyl esters product was used and the methanol residue was removed by Rota vacuum evaporation and further introduced into a column with a bed of Lewatit GF 202 resin (9 kg, 10 cm i.d. x 150 cm height). The flow rate of methyl ester was adjusted at 20 liters/hr. To compare the properties between step one and step two of biodiesel production, crude methyl esters from step two of reaction was also introduced into a resin column with the same flow rate as step one and the properties of both biodiesels after this washing process are shown in Table 6.

Table 6 Fuel properties of biodiesel from step one and step two of reaction, purified by ion exchange resin.

Properties	Test methods	Limits	Biodiesel from	
			Step one	Step two
Density (15°C) (g/cm3)	ASTMD 1298	0.860-0.900	0.877	0.875
Flash point (°C)	ASTMD 93-02a	> 120	205	215
Water content (%wt)	EN 12937	< 0.05	0.089	0.112
Acid value (mg KOH/g)	AOCS Ca 5a-40	< 0.50	0.23	0.17
Iodine value (g I2/100 g)	AOCS cd 1-25	< 120	76.10	75.26
Viscosity (140°C) (cst)	ASTM D 445	3.5-5.0	4.165	3.938
Free glyceride (%wt)	EN 14105	< 0.02	0.01	0.01
Monoglyceride (%wt)	EN 14105	< 0.8	0.4	0.27
Diglyceride (%wt)	EN 14105	< 0.2	0.01	0.01
Triglyceride (%wt)	EN 14105	< 0.2	0.01	0.01
Total glyceride (%wt)	EN 14105	< 0.25	0.1	0.07

Density at 15°C

It is known that biodiesel density mainly depends on its methyl esters content and the remained quantity of methanol; hence this property is influenced primary by waste cooking oil and to some extent by the applied purification steps. The results from Table 6 show that both biodiesels from one and step two meet the density value specified by ASTM D 1298 to be in the range 0.860-0.900 g/cm3 at 15°C. It show that both biodiesels obtained from the same purification process had almost the same density although the different reactions steps were applied. This property is important mainly in airless combustion system because it influences the efficiency of atomization of the fuel.

Kinematics viscosity at 40°C

Even more than density, kinematic viscosity at 40°C is an important property regarding fuel atomization and distribution. With regard to the kinematic viscosities of biodiesel that were in the range from 3.5 to 5.0 cst. The results form Table 6 show that both biodiesels from the same purification process meet this requirement values.

Acid value

The acid value measures the content of free fatty acid in the sample, which have influence on fuel aging. It is measure in terms of the quantity of KOH required to neutralize sample. Acid values of biodiesel were less than 0.5 mg KOH/g, specified as the maximum value according to AOCS Ca 5a-40. The results from Table 6 show that both biodiesels from the same purification process meet this requirement value.

Iodine value

The iodine value is a measure of unsaturation degree of fatty acid composition. This value has greatly influences fuel oxidation tendency. According to AOCS cd 1-25, biodiesel used as diesel fuel must has an iodine value less than 120 g I2 per 100 g sample. Both biodiesels obtained in this study had iodine value lower than 120 g I2/100 g, which meets the requirement of the biodiesel standard.

Water content

Biodiesel contaminated with water can cause engine corrosion or reaction with glycerides to produce soap and glycerol. Therefore the EN standard for alternative diesel fuel restricted the water content in biodiesel, setting the maximum allowable content of 0.05%. In this study both biodiesels had an water content higher than 0.05%; so on a plant scale, dewatering is needed to improve biodiesel properties after the purification process.

Glyceride content

The transesterification process is a step that produces monoglyceride and diglyceride as intermediates products. With regard to biodiesel standard that allow free glyceride content, monoglyceride content, diglyceride content, triglyceride content, and total glyceride content are less than 0.02, 0.80, 0.20, 0.20, 0.25, respectively. The results from Table 6 show that all glyceride contents (free glyceride, monoglyceride, diglyceride, triglyceride, and total glyceride) in both biodiesels had lower values than the requirements, These values indicated that ion exchange resin has high efficiently in removing glyceride content from biodiesel, the same way as the water washing process.

4. Conclusion

4.1 The optimum conditions of transesterification from waste cooking oil with less than 2 % free fatty acid to produce more than 90% biodiesel, was a catalyst amount of 1.2% (w), an oil to methanol ration of 1:6, 60°C reaction temperature, 30 minutes reaction time, and 600 rpm stirring rate.

4.2 The studied ion exchange resin in the purification process can replace a water washing.

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References

[1] Berrios, M., and R. L. Skelton. Comparison of purification methods for biodiesel. Chemical Engineering Journal, Vol. 144, No. 3, pp 459-465, 2008.

[2] Canakci, Mustafa. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology, Vol. 98, No. 1, pp.183-190, 2007.

[3] Gerpen, Jon Van. Biodiesel processing and production. Fuel Processing Technology, Vol. 86, No. 10 pp. 1097-1107, 2005.

[4] Koh, May Ying, and Tinia Idaty Mohd. Ghazi. A review of biodiesel production from Jatropha curcas L. oil. Renewable and Sustainable Energy Reviews, Vol. 15, No. 5, pp 2240-2251, 2011.

[5] Leung, Dennis Y. C., Xuan Wu, and M. K. H. Leung. A review on biodiesel production using catalyzed transesterification. Applied Energy, Vol. 87, No. 4, pp 1083-1095, 2010.

[6] Lu, Houfang, Yingying Liu, Hui Zhou, Ying Yang, Mingyan Chen, and Bin Liang. Production of biodiesel from Jatropha curcas L. oil. Computers & Chemical Engineering, Vol. 33, No. 5, pp 1091-1096, 2009.

[7] Monteiro, Marcos Roberto, Alessandra Regina Pepe Ambrozin, Luciano Morais Lião, and Antonio Gilberto Ferreira. 2008. Critical review on analytical methods for biodiesel characterization. Talanta, Vol. 77, No. 2, pp 593-605, 2009.

[8] Sharma, Y. C., B. Singh, and S. N. Upadhyay. Advancements in development and characterization of biodiesel: A review. Fuel, Vol. 87, No. 12, pp. 2355-2373, 2008.