Reduction of the Cloud Point of Biodiesel by Combination of Various Factors

Masatoshi Todaka, Toru Horinouchi, Koichi Yata, Wasana Kowhakul, Hiroshi Masamoto, and Mikiji Shigematsu

Abstract—**Optimization to reduce the cloud point of biodiesel fuel (BDF) was investigated by considering the combination of different kinds of alcohols for transesterification, catalyst type, and blending with castor BDF. Rapeseed oil (R), spent coffee oil (S), and jatropha oil (J) were used as raw materials. The cloud point of BDFs prepared with 1-butanol was found to be lower than that of those using methanol. H_2SO_4 was a more effective catalyst to reduce cloud point than NaOH. As for blending with castor BDF, the cloud point was decreased from −7 to −7.5 °C for a 25 wt% blend of castor BDF with R-BDF, from 10.2 to 8.0 ℃ with S-BDF, and from 8.2 to 2.8 ℃ with J-BDF with permissible increases of kinetic viscosities. From the above results, the optimized conditions of 1-butanol, H_2SO_4 and 25 wt% castor BDF were determined. Under these conditions, the cloud points were −7.5, 2.8 and −3.5 °C for R., S. and J. BDFs, respectively. This paper that the blend ratio of castor BDF was at 25 wt% or less, it was possible to suppress the increase in kinetic viscosity.**

Index Terms—**Biodiesel, cloud point reduction, kinetic viscosity, castor biodiesel.**

I. Introduction

In recent years, the development of fuels to replace those derived from fossil resources has attracted considerable interest, largely motivated by the increasing global warming resulting from combustion products of these fuels such as carbon dioxide, carbon monoxide, nitrogen oxides and sulfur-containing residues. This situation initiated and has sustained interest in identifying and channeling renewable raw materials, that is, biomass, to manufacture liquid fuel alternatives because development of such biomass-based power would ensure that technologies are available as renewable power alternatives for the future. Biodiesel fuel (BDF), which is vegetable oil- or fat-based diesel fuel consisting of long-chain alkyl esters, is expected to be an important alternative fuel [1], [2].

In our previous study, we investigated the properties of BDFs derived from inedible oils from spent coffee grounds and jatropha kernels combined with different alcohols [3]. We evaluated the thermal and oxidation stabilities of these fuels by analysis of their combustion and storage behaviors. The oxidation and thermal stabilities of these fuels were both satisfactory. The optimal combination of BDFs depends on region. For example, cloud point control and oxidation stability are important in cool and tropical regions, respectively.

Manuscript received February 15, 2014; revised April 20, 2014. This work was financially supported by Fukuoka University.

The authors are with the Department of Chemical Engineering, Faculty of Engineering, Fukuoka University, Fukuoka, Japan (email: shigem@fukuoka-u.ac.jp)

In this study, we reduced the cloud point of BDFs derived from inedible oils including rapeseed oil, spent coffee oil, and jatropha oil. The following methods were used to reduce the cloud point of BDFs.

1) BDFs produced from different alcohols: methanol (MeOH) or 1-butanol (BtOH) were the alcohols considered for transesterification.
2) BDFs produced from different catalysts: sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were investigated as catalysts. BDF produced by the combination of 1-butanol and an acid catalyst (H_2SO_4) has been reported previously [4], [5].
3) Blending of BDFs with castor BDF: BDFs were derived from inedible oils blended with castor BDF. Castor oil is composed mostly of triglycerides of ricinoleic acid, which has desirable low-temperature behavior and low cloud point [6], [7] because of its complex structure and hydroxyl group.

II. Materials and Methods

A. Materials

In this work, rapeseed oil, spent coffee grounds, and jatropha seeds were used as raw materials. Rapeseed oil (canola salad oil, Kato Oil, Mill Co., Ltd, Japan) and spent coffee grounds were obtained commercially and from a coffee shop in Fukuoka, respectively. Jatropha seed was purchased from Thailand.

Methanol (Wako Special Grade, 99.8%) and 1-butanol (Wako Special Grade, 99.0%) as alcohols, and NaOH (Wako Special Grade, 99.7%) and H_2SO_4 (Wako High Special Grade, 95.0%) as catalysts were purchased and used without further purification.

The spent coffee grounds were dried at 80 ℃ for 3 days. Jatropha seeds were descaled and then kernels were milled in a mortar. Next, inedible oils were extracted from the coffee grounds and milled jatropha seeds twice with 1 L of n-hexane for each 500 g of sample. n-Hexane was removed by evaporation at 360 hPa at 60 ℃, to give each oil.

B. Experimental

1) BDF production

BDFs were produced by transesterification using the alkali catalyst method or acid catalyst method [8], [9]. The conditions used to synthesize BDFs are presented in Table I. The molar ratio of oil and alcohol and stirring speed were fixed at 1:6 and 2,000 rpm, respectively. The temperature was determined by the boiling point of the alcohol used: 60 ℃ for MeOH and 110 ℃ for 1-BtOH. The amount of NaOH and H2SO4 catalyst was fixed at 1% (w/w) of the oil. Generally, in the transesterification reaction to form a BDF, the molar ratio of alcohol to oil is 3:1. However, an extremely large molar excess of alcohol ensures that the transesterification reaction will predominate.

TABLE I: CONDITIONS USED FOR BIODIESEL PRODUCTION

Alcohol	Catalyst	Oil : Alcohol (mol : mol)	Temperature (℃)	Reaction time (h)
Methanol	NaOH	1:6	60	1
	H_2SO_4	1:6	60	8
1-Butanol	NaOH	1:6	110	1
	H_2SO_4	1:6	110	4

TABLE II: PHYSICAL PROPERTIES OF RAW OIL

Raw oil	Cloud point (℃)	Kinetic viscosity (mm^2 s^{-1})	Density (g cm^{-3})
Rapeseed	−14	35.04	0.9063
Spent coffee	8	51.45	0.9109
Jatropha	14	28.95	0.9332
Castor	−19	253.1	0.9472

TABLE III: FATTY ACID COMPOSITION OF RAW OILS

Raw oil	Fatty acid composition (%)				
	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Rapeseed oil	4.16	62.03	30.15	0.10	3.56
Coffee oil	17.01	31.43	29.07	22.49	0.00
Jatropha oil	30.67	36.29	7.77	25.26	0.00

After reaction, each BDF was purified by removing catalyst, glycerol and unreacted alcohol. For the alkali catalyst method, catalyst and glycerol were removed by washing with water after neutralization of NaOH using a 1% aqueous solution of acetic acid. For BDFs formed using MeOH, unreacted alcohols were removed simultaneously with water washing. Unreacted butanol was removed by evaporation because butanol is immiscible with water.

In the case of the acid catalyst method, after reaction, each BDF was purified by removing catalyst, glycerol and unreacted alcohol. H_2SO_4 catalyst was removed by washing with water. The purification process of the acid catalyst method was simpler than that using an alkali catalyst.

2) BDFs blended with castor BDF

Blended BDFs were prepared by mixing rapeseed (R), spent coffee (S), and jatropha (J) oils with castor oil (C) in proportions of 25:75, 50:50 and 75:25 (w/w) to give blends named R75/C25, R50/C50, R25/C75, S75/C25, S50/C50, S25/C75, J75/C25, J50/C50 and J25/C75.

C. Analysis of BDFs

The cloud point and kinetic viscosity of blended BDFs were measured based on JIS K 2269 and JIS K 2249, respectively. The kinetic viscosity was standardized to 3.0–5.0 mm^2 s^{-1} at 40 ℃.

The fatty acid compositions of the BDFs were analyzed using gas chromatography with a Varian Column (select FAME 50 m × 0.25 mm) and flame ionization detector (FID) based on JIS K 3331. An oven temperature of 190 ℃ and detector temperature of 300 ℃ were used.

TABLE IV: PHYSICAL PROPERTIES OF BIODIESELS PRODUCED USING DIFFERENT ALCOHOLS AND CATALYSTS

Raw oil	Alcohol	Catalyst	Cloud point (℃)	Kinetic viscosity (mm^2 s^{-1})	Density (g cm^{-3})
Rapeseed	MeOH	NaOH	−1	4.33	0.8653
	MeOH	H_2SO_4	−12	29.06	0.9073
	BtOH	NaOH	−3	11.05	0.8884
	BtOH	H_2SO_4	−6.8	5.62	0.8622
Spent coffee	MeOH	NaOH	10.2	4.65	0.8672
	MeOH	H_2SO_4	9	24.82	0.8971
	BtOH	NaOH	12	14.79	0.8910
	BtOH	H_2SO_4	6	9.12	0.8237
Jatropha	MeOH	NaOH	8.2	4.01	0.8606
	MeOH	H_2SO_4	1.2	16.66	0.8832
	BtOH	NaOH	8.2	4.01	0.8606
	BtOH	H_2SO_4	−2	5.22	0.8912
Castor	MeOH	NaOH	−15.5	15.13	0.9098
	BtOH	H_2SO_4	−18	15.94	0.8912

III. RESULTS AND DISCUSSION

A. Characterization of Raw Oils and Their BDFs

Table II shows the physical properties of the raw oils. The cloud points of spent coffee and jatropha oils were very high compared with rapeseed oil as edible oil. Kinetic viscosity of castor oil was 253.1 mm^2 s^{-1}, which is very high.

Table III gives the fatty acid compositions of the raw oils. Saturated methyl ester (palmitic and stearic) of rapeseed, spent coffee, and jatropha BDF were occupied about 70, 50, and 70 wt%, respectively. It can be considered that high content of saturated methyl ester such as rapeseed and jatropha BDF suggests that BDF will be readily coagulate.

The physical properties of BDFs produced using methanol and alkali catalyst are presented in Table IV. Me-rapeseed (i.e., the BDF produced from rapeseed oil using MeOH) was regarded as the standard BDF, and showed a cloud point of 1 ℃ that is low inspite of high content of saturated methyl ester. The cloud points of Me-spent coffee and Me-jatropha BDFs were 10.2 and 8.2 ℃, respectively, which are very high. In this way, it is considered that the cloud point of BDF is regardress of the fatty acid composition, and is determined depending on the components derived from raw oils. Moreover, Me-castor possessed a very low cloud point, but it had very high kinetic viscosity.

B. Characterization of BDF

Table IV lists the physical properties of BDFs produced by the four different experimental conditions investigated using different combinations of alcohol and catalyst (MeOH-NaOH, MeOH-H_2SO_4, butanol-NaOH, butanol-H_2SO_4).

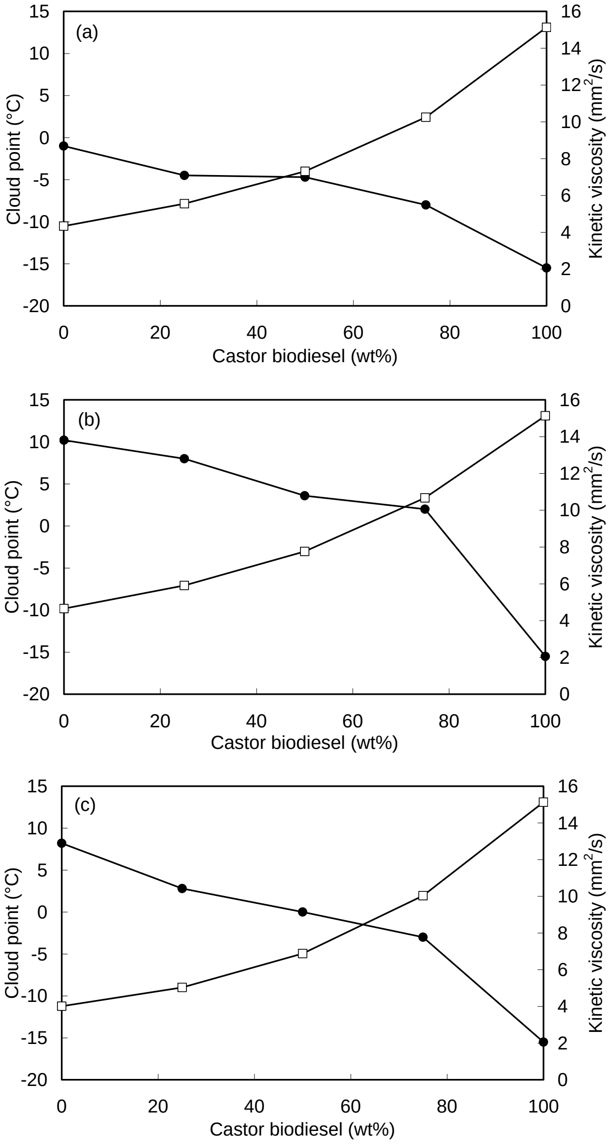

Fig. 1 Effect of blending with castor BDF. (a) rapeseed BDF,(b) spent coffee BDF, (c) jatropha BDF. Circles and squares indicate cloud point and kinetic viscosity, respectively.

1) Effect of different alcohols

To study affect of different alcohol on BDF, NaOH catalyst was using in this report.

For rapeseed BDF, the cloud point of Bt-BDF (Bt indicates 1-butanol) was lower compared with that of Me-BDF. However, its kinetic viscosity was increased. The cloud points of spent coffee and jatropha BDFs were not influenced by the type of alcohol. However, the kinetic viscosity of spent coffee BDF was higher using 1-butanol than MeOH. It can be considered that some coffee component remained in the coffee BDFs after some BDF purification method.

Bt-BDFs showed higher kinetic viscosity than Me-BDFs it can be consider that carbon chain length of the ester increased. The cloud points of Bt-BDFs were reduced compared with those of Me-BDFs because the degree of freedom of esters was increased.

2) Effect of catalysts

BDFs produced from same alcohol were focused to observe effect of different catalyst.

Kinetic viscosity of rapeseed, spent coffee, and jatropha BDF produced from MeOH and H_2SO_4 were 29.06, 24.82, and 16.66 $mm^2\ s^{-1}$, respectively, which are very high. It can be considered that the reaction rate became low in H_2SO_4 catalyst compared with NaOH catalyst.

On the other hand, in BtOH BDF, cloud point of all BDF produced from H_2SO_4 catalyst was reduced severely.

H_2SO_4 BDF was trended cloud point reduction although kinetic viscosity was increased.

3) Effect of castor BDF blend

The ability of blending the BDFs with castor BDF to reduce cloud point was investigated. Castor BDF was produced from MeOH and NaOH. Table IV shows the physical properties of castor BDF.

Fig. 1(a) shows the cloud point and kinetic viscosity of rapeseed–castor BDF mixtures. The cloud point was reduced for all blend ratios compared with that of rapeseed BDF alone. This effect is consistent with previous findings [10]. However, the kinetic viscosity of R50/C50 and R25/C75 were 7.31 and 10.25 $mm^2\ s^{-1}$, respectively, which are very high and do not achieve the required standard. The optimum blend ratio of rapeseed and castor BDF was R75/C25, which had a cloud point of −4.5 °C and kinetic viscosity of 5.5 $mm^2\ s^{-1}$.

Fig. 1(b) and Fig. 1(c) depict the cloud point and kinetic viscosity of spent coffee–castor and jatropha–castor BDFs, respectively. The cloud point and kinetic viscosity of these blended BDFs were similar to those of the rapeseed and castor BDF blends. The cloud points of S75/C25 and J75/C25 were reduced from 10.2 to 8 ℃ and 8.2 to 2.8 ℃, respectively. The kinetic viscosities of S75/C25 and J75/C25 were 5.91 and 5.03 $mm^2\ s^{-1}$. Other blend ratios showed lower cloud points; however, high kinetic viscosities were observed.

C. Optimal Combination to Reduce Cloud Point

The combination of that gave the lowest cloud point was examined further; i.e., the combination of 1-butanol and H_2SO_4, and castor BDF blend.

The cloud point and kinetic viscosity of blended BDFs produced from 1-butanol and acid catalyst were evaluated. The blending conditions were set to R90/C10, R75/C25, S90/C10, S75/C25, J90/C10 and J75/C25 and compared with the results obtained for BDFs formed using MeOH and alkali catalyst.

Fig. 2 shows the cloud point and kinetic viscosity of rapeseed, spent coffee and jatropha BDFs.

The cloud point of rapeseed BDF produced by acid catalyst was lower than that by alkali. However, cloud point reduction was not obtained when rapeseed BDF was blended with castor BDF. For these blend ratios, kinetic viscosity was increased a little.

In the case of spent coffee BDFs, cloud point showed the same tendency as rapeseed BDFs. However, the decrease of cloud point was minor. In contrast, kinetic viscosity increased considerably, which is because components from coffee remained in the BDFs following the synthesis condition (i.e., BDF produced from 1-butanol and H_2SO_4).

For the jatropha BDFs, the cloud point was much lower using 1-butanol than MeOH. The kinetic viscosity of Bt-BDF was similar to that of rapeseed BDF. Overall, butanol and the acid catalyst method were effective at lowering the cloud point of BDF prepared from jatropha oil.

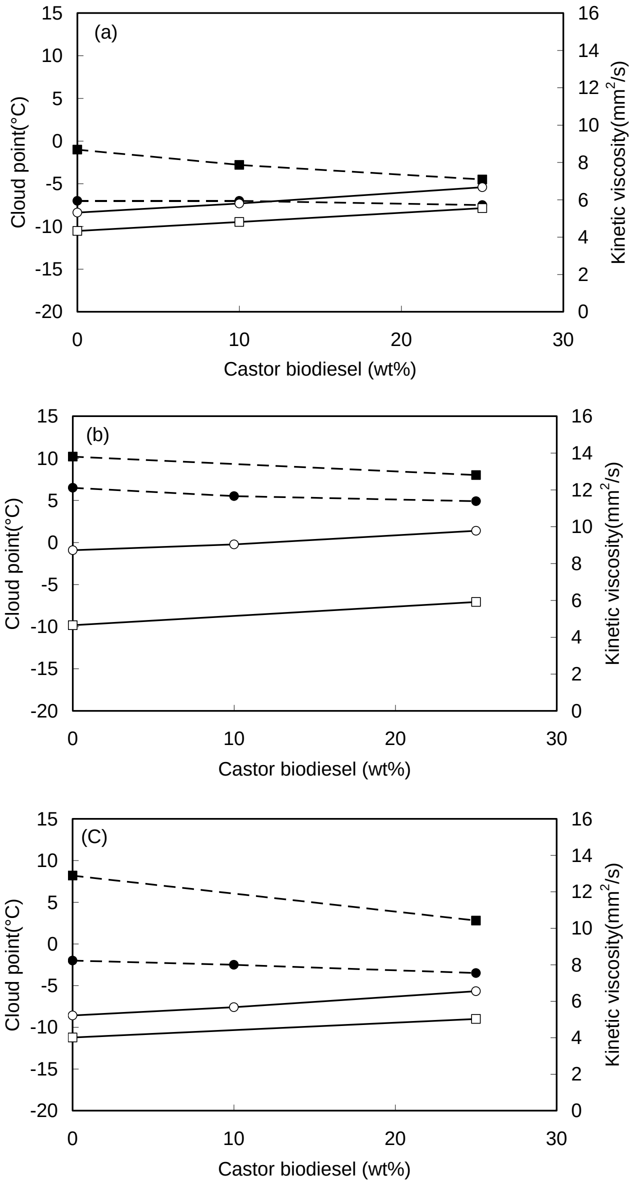

Fig. 2. Effect of the optimal combination of conditions on the properties of (a) rapeseed BDF,(b) spent coffee BDF, (c) jatropha BDF. Closed and open symbols were cloud point and kinetic viscosity, respectively. Circle and square were MeOH-NaOH BDF and BtOH-H_2SO_4 BDF

IV. Conclusions

We investigated that cloud point reduction method for BDF derived from inedible oils. BDF was produced from combination of alcohol and catalyst for transesterification as cloud point reduction method. Moreover, above BDFs were blended with castor BDF was also investigated.

BtOH BDFs were trended kinetic viscosity increasing compared with MeOH BDF. Also, the situation of cloud point reduction was existed by raw oil.

H_2SO_4 BDF was trended cloud point reduction although kinetic viscosity was increased compared with NaOH BDF.

The optimum blend ratio of castor BDF for lowering the cloud point was 25 wt% in all BDF. Kinetic viscosities of BDF blended castor BDF were increased. However, the blend ratio of castor BDF was at 25 wt% or less, it was possible to suppress the increase in kinetic viscosity.

References

[1] Y. Tanaka, “Synthesis of biodiesel fuel by transesterification,” *Biomass handbook*, 1st ed. Tokyo, Japan: Ohmsha, 2002, pp. 138-143. In Japanese

[2] S. Saka, *All about biodiesel*, Tokyo: Industrial Publishing & Consulting, Inc. 2006. pp. 87–92. In Japanese.

[3] M. Todaka, W. Kowhakul, H. Masamoto, M. Shigematsu, and S. Onwana-Agyman, “Thermal decomposition of biodiesel fuels produced from rapeseed, jatropha, and coffee oil with different alcohols,” *J. Therm Anal Calorim*, vol. 113, pp. 1355-1361, March 2013.

[4] P. C. Smith, Y. Ngothai, Q. D. Nguyen, and B. K. O’Neill, “The addition of alkoxy side-chains to biodiesel and the impact on flow properties,” *Fuel*, vol. 89, pp. 3517-3522, June 2010.

[5] J. C. Yori, M. A. D’Amato, J. M. Grau, C. L. Pieck, and C. R. Vera, “Depression of the Cloud point of biodiesel by reaction over solid acid,” *Energy and Fuels*, vol. 20, pp. 2721-2726, August 2006.

[6] J. A. C. D. Silva, A. C. Habert, and D. M. G. Freire, “A potential biodegradable lubricant from castor biodiesel ester,” *Lubrication Science*, vol. 25, pp. 53-61, September 2012.

[7] L. C. Meher, D. V. Sagar, and S. N. Naik, “Technical aspects of biodiesel production by transesterification—a review,” *Renewable and Sustainable Energy Reviews*, vol. 10, pp. 248-268, September 2004.

[8] F. Ma and M. A. Hanna, “Biodiesel production: a review,” *Bioresource Technology*, vol. 70, pp. 1-15, February 1999.

[9] E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, and J. G. Goodwin, “Synthesis of biodiesel via acid catalysis,” *Ind Eng Chem Res*, vol. 44, pp. 5353-5363, January 2005.

[10] E. C. Zuleta, L. A. Rios, and P. N. Benjumea, “Oxidation stability and cold flow behavior of palm, sacha-inchi, jatropha and castor oil biodiesel blends,” *Fuel Processing Technology*, vol. 102, pp. 96-101, May 2012.

Masatoshi Todaka was born in Miyazaki Prefecture, Japan, April 1989. He obtained a master's degree of chemical engineering from Fukuoka University, Japan, in 2014. He is currently a graduate student in the Department of Energy and Environment System, Graduate School of Engineering, Fukuoka University.