Appl Biochem Biotechnol (2008) 148:109–117
DOI 10.1007/s12010-007-8082-2

# Production and Characterization of Biodiesel from Tung Oil

**Ji-Yeon Park · Deog-Keun Kim · Zhong-Ming Wang · Pengmei Lu · Soon-Chul Park · Jin-Suk Lee**

Received: 18 April 2007 / Accepted: 11 October 2007 /
Published online: 6 November 2007


**Abstract** The feasibility of biodiesel production from tung oil was investigated. The esterification reaction of the free fatty acids of tung oil was performed using Amberlyst-15. Optimal molar ratio of methanol to oil was determined to be 7.5:1, and Amberlyst-15 was 20.8wt% of oil by response surface methodology. Under these reaction conditions, the acid value of tung oil was reduced to 0.72mg KOH/g. In the range of the molar equivalents of methanol to oil under 5, the esterification was strongly affected by the amount of methanol but not the catalyst. When the molar ratio of methanol to oil was 4.1:1 and Amberlyst-15 was 29.8wt% of the oil, the acid value decreased to 0.85mg KOH/g. After the transesterification reaction of pretreated tung oil, the purity of tung biodiesel was 90.2wt%. The high viscosity of crude tung oil decreased to 9.8mm$^2$/s at 40 °C. Because of the presence of eleostearic acid, which is a main component of tung oil, the oxidation stability as determined by the Rancimat method was very low, 0.5h, but the cold filter plugging point, −11 °C, was good. The distillation process did not improve the fatty acid methyl ester content and the viscosity.

**Keywords** Biodiesel · Eleostearic acid · Esterification by Amberlyst-15 · Fuel properties · Response surface methodology · Tung oil

## Introduction

An interest in biodiesel produced from triacylglycerols as an alternative fuel for diesel engines has increased because of the increase in the price of petroleum and the environmental concerns about air pollution from vehicles [1–3]. Countries produce

J.-Y. Park · D.-K. Kim · S.-C. Park · J.-S. Lee (✉)
Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea
e-mail: bmjslee@kier.re.kr

Z.-M. Wang · P. Lu
Guangzhou Institute of Energy Conversion, no.2 Nengyuan Rd, Wushan, Tianhe,
Guangzhou 510-640, China

biodiesel from various vegetable oils depending upon their agricultural policies, local crop availability, and/or feedstock price [4–6]. The focus of biodiesel production is typically on edible oils like soybean, rapeseed, and palm. Recently, waste oils and fats like used frying oil, greases, and tallow were proposed and used as biodiesel resources [3]. The basic constituent of vegetable oils is a triglyceride, which is an ester composed of three fatty acids and one glycerol. Because the fatty acids of vegetable oils vary in carbon chain length and the number of double bonds, biodiesel has different properties depending on the fatty acid composition of the feedstock [7]. Generally, saturated fatty acid methyl esters have good oxidation stability and poor low temperature properties. On the contrary, unsaturated fatty acid methyl esters have good low temperature properties and poor oxidation stability. Therefore, the standard specification concerning the minimum requirements such as EN 14214 was established to guarantee the quality of biodiesel [8–9].

The alkali process for biodiesel production can achieve high purity and yield of biodiesel in a short time. However, vegetable oils high in free fatty acids result in the production of soap and the loss of catalyst in the alkali process. To overcome this, the free fatty acids should be removed before the transesterification reaction. Because a homogeneous acid catalyst like sulfuric acid can not be recovered and is toxic, a heterogeneous acid catalyst can be used for the esterification of free fatty acids. Solid catalysts can be easily recovered after the reaction and reused [10–12].

As the supply of biodiesel increases, the interest in nonedible oils like jatropha, castor, jojoba, and tung oil has grown. Among these oils, tung oil is pressed from the nuts of the tung tree (*Vernicia fordii*), and the nut has an oil content of 30 to 40%. Tung oil has been used as a protective coating or drying agent [13–14].

As tung oil has a high acid value (AV), the esterification using solid acid catalyst, Amberlyst-15, was employed to produce biodiesel more efficiently. Optimal condition of methanol and catalyst for the esterification was established by response surface methodology. The fuel properties of tung biodiesel produced from pretreated tung oil by alkali catalyst were analyzed.

## Experimental Methods

### Materials

Tung oil was kindly supplied from Guangzhou Institute of Energy Conversion in China. For the pretreatment of tung oil, methanol (Duksan Pure Chemical, Ansan, Kyungki, Republic of Korea; >99.5%) and Amberlyst-15 (Aldrich Chemical, Milwaukee, WI) were used. Potassium hydroxide (Junsei Chemical, Chuo, Tokyo, Japan; >85%) and methanol was used for the transesterification reaction. For gas chromatography analyses, *n*-heptane (J.T. Baker, Phillipsburg, NJ; >99.0%), methyl heptadecanoate (Fluka, Buchs SG, Switzerland; >99.5%), 1,2,4-butanetriol (Supelco, Bellefoute, PA; >98.5%), 1,2,3-tricaproylglycerol (Supelco; >99.9%), and *N*-methyl-*N*-trimethylsilyl-trifluoroacetamide (Aldrich Chemical) were used.

### Pretreatment and Transesterification of Tung Oil

For the pretreatment of tung oil, the mixture of oil, methanol, and Amberlyst-15 was mixed by a magnetic stirrer at 80 °C for 2h. After the reaction, the AV of the samples was determined. Pretreated tung oil was used for the transesterification. Tung oil was mixed

with methanol and potassium hydroxide at 80 °C for 20min. After washing with distilled water and centrifuging at 15,000rpm for 15min, biodiesel properties were analyzed.

### Analyses

The AV of tung oil was measured by titration method, following American Oil Chemists' Society (AOCS) official method Cd 3d-63. The water content was measured by Karl Fischer Titrator (Mettler Toledo model DL31 Volumetric KF Titrator, Columbus, OH) in accordance with AOCS official method Ca 2e-84. The oxidation stability measurements were carried out with the model 743 Rancimat (Metrohm, Herisau, Switzerland). Samples were analyzed under constant air flow of 10L/h at 110 °C heating block temperature. The temperature correction factor $\Delta T$ was set to 1.5 °C. The cold filter plugging point (CFPP) measurements were carried out with the model FPP5Gs (ISL, Carpiquet, France). The sample was cooled following the EN 116 method. At intervals of 1 °C, a 200-mm $H_2O$ vacuum was applied to draw up the sample into a pipette through a filter. The temperature at which either the sample ceased to flow through the filter within 60s or failed to return into the test jar was recorded as the CFPP.

The fatty acid methyl ester (FAME) content was analyzed by gas chromatography equipped with an auto-injector (Agilent 6890A, Santa Clara, CA). The INNOWax (Agilent) column (30mm × 0.32mm × 0.5μm) was used for the analysis of FAME. The oven temperature was started at 50 °C for 1min, increased to 200 °C at a rate of 15 °C/min, held at the temperature for 9min, and again increased to 250 °C at a rate of 2 °C/min, and then held at the temperature for 2min. Methyl heptadecanoate was used as the internal standard. Total glycerin was determined by gas chromatography equipped with on-column injector (Agilent 6890N). The DB-5HT (Agilent) column (15m × 0.32mm × 0.1μm) was used for the analytical work. The oven temperature was held at 50 °C for 1min, increased to 180 °C at a rate of 15 °C/min, and increased to 230 °C at a rate of 7 °C/min, and again increased to 370 °C at a rate of 10 °C/min, and then held at the temperature for 10min. 1,2,4-Butanetriol and 1,2,3-tricaproylglycerol were used as the internal standards.

## Results and Discussion

### Properties of Tung Oil

The AV of crude tung oil was 9.55mg KOH/g, and its viscosity was 109.4$mm^2$/s at 40 °C. Because the free fatty acid of oil forms soap with the alkali catalyst and prevents the separation of biodiesel from glycerin, the pretreatment process to convert the free fatty acid to biodiesel is required [3]. Therefore, it is desired that the AV of tung oil decreases to less than 1mg KOH/g before the transesterification reaction using the alkali catalyst.

### Pretreatment of Tung Oil

The solid acid catalyst, Amberlyst-15, was used for the esterification reaction of the free fatty acids of the tung oil because Amberlyst-15 showed good efficiency for the esterification of oleic acid with methanol [10].

The central composite design was used to determine the optimal conditions for the esterification of tung oil using Amberlyst-15. The independent variables were the molar equivalents of methanol to oil and the weight percent of Amberlyst-15 to oil. Experiment 1

was performed to determine the condition for the lowest AV of tung oil (Table 1). Experiment 2 was performed to examine the effects of AV on methanol and catalyst when the molar equivalents of methanol to oil were less than 5 (Table 2). All experiments were performed at 80 °C for 2h, as determined from our previous works [10].

The regression analysis and the analysis of variance were performed using SAS package (SAS 9.1, SAS Institute, Cary, NC). The contour plots were developed using the fitted quadratic polynomial equation obtained from regression analysis [15–16].

From the statistical analysis of experiment 1, the relation of conversion ($F$) and the amount of methanol ($X$) and catalyst ($Y$) was obtained as follows:

$$F(\%) = 89.76 + 1.09X + 5.64Y - 1.39X^2 + 2.20XY - 5.50Y^2 \left(R^2 = 0.9767\right)$$

Maximum conversion was 92.5% at $X = 1.006$ and $Y = 0.777$ (Fig. 1). When the molar ratio of methanol to oil was 7.5:1 and Amberlyst-15 was 20.8wt% of oil, the final AV was 0.72mg KOH/g. At constant catalyst amount with varying methanol amount, the conversion slightly increased with the amount of methanol. At constant methanol amount with varying catalyst amount, the conversion rapidly increased with the catalyst amount but decreased again when the catalyst amount was more than 20% of oil. Therefore, the catalyst loading was an important factor to obtain the high conversion.

From the statistical analysis of experiment 2, the relation of conversion ($F$) and the amount of methanol ($X$) and catalyst ($Y$) was obtained as follows:

$$F(\%) = 86.39 + 9.10X + 1.55Y - 5.86X^2 + 0.51XY - 0.76Y^2 \left(R^2 = 0.9849\right)$$

Maximum conversion was 91.2% at $X = 0.833$ and $Y = 1.303$ (Fig. 2). When the molar ratio of methanol to oil was 4.1:1 and Amberlyst-15 was 29.8wt% of oil, the final AV was

**Table 1** Experimental matrix for the central composite design (experiment 1).

| Run | MeOH to oil (molar equivalents) | Amberlyst-15 to oil (wt%) | Final acid value (mg KOH/g) | $X$ | $Y$ | $F$ (%) |
|---|---|---|---|---|---|---|
| 1 | 3.41 | 7.5 | 2.03 | −1 | −1 | 78.7 |
| 2 | 3.41 | 15 | 1.14 | −1 | 0 | 88.0 |
| 3 | 3.41 | 22.5 | 1.43 | −1 | 1 | 85.1 |
| 4 | 5.45 | 7.5 | 1.38 | 0 | −1 | 85.6 |
| 5 | 5.45 | 22.5 | 1.00 | 0 | 1 | 89.5 |
| 6 | 7.49 | 7.5 | 2.27 | 1 | −1 | 76.3 |
| 7 | 7.49 | 15 | 0.93 | 1 | 0 | 90.2 |
| 8 | 7.49 | 22.5 | 0.82 | 1 | 1 | 91.4 |
| 9 | 2.56 | 15 | 1.40 | −1.414 | 0 | 85.4 |
| 10 | 8.34 | 15 | 1.07 | 1.414 | 0 | 88.8 |
| 11 | 5.45 | 4.395 | 3.32 | 0 | −1.414 | 65.3 |
| 12 | 5.45 | 25.605 | 1.05 | 0 | 1.414 | 89.0 |
| 13 | 5.45 | 15 | 0.92 | 0 | 0 | 90.4 |
| 14 | 5.45 | 15 | 1.05 | 0 | 0 | 89.0 |
| 15 | 5.45 | 15 | 0.99 | 0 | 0 | 89.6 |

MeOH to oil (molar equivalents)=2.04$X$+5.45, Amberlyst-15 to oil (wt%)=7.5$Y$+15

$F$ (%) The conversion of free fatty acid

**Table 2** Experimental matrix for the central composite design (experiment 2).

| Run | MeOH to oil (molar equivalents) | Amberlyst-15 to oil (wt%) | Final acid value (mg KOH/g) | *X* | *Y* | *F* (%) |
|---|---|---|---|---|---|---|
| 1 | 1.64 | 12.5 | 3.70 | −1 | −1 | 61.3 |
| 2 | 1.64 | 20 | 2.65 | −1 | 0 | 72.2 |
| 3 | 1.64 | 27.5 | 2.75 | −1 | 1 | 71.2 |
| 4 | 3 | 12.5 | 1.52 | 0 | −1 | 84.1 |
| 5 | 3 | 27.5 | 1.40 | 0 | 1 | 85.4 |
| 6 | 4.36 | 12.5 | 1.32 | 1 | −1 | 86.2 |
| 7 | 4.36 | 20 | 1.07 | 1 | 0 | 88.8 |
| 8 | 4.36 | 27.5 | 0.97 | 1 | 1 | 89.9 |
| 9 | 1.07 | 20 | 3.69 | −1.414 | 0 | 61.4 |
| 10 | 4.92 | 20 | 1.04 | 1.414 | 0 | 89.1 |
| 11 | 3 | 9.395 | 1.27 | 0 | −1.414 | 86.8 |
| 12 | 3 | 30.605 | 1.05 | 0 | 1.414 | 89.0 |
| 13 | 3 | 20 | 1.35 | 0 | 0 | 85.9 |
| 14 | 3 | 20 | 1.21 | 0 | 0 | 87.4 |
| 15 | 3 | 20 | 1.26 | 0 | 0 | 86.8 |

MeOH to oil (molar equivalents)=1.36*X*+3, Amberlyst-15 to oil (wt%)=7.5*Y*+20

*F* (%) The conversion of free fatty acid

0.85mg KOH/g. At constant catalyst amount with varying methanol amount, the conversion rapidly increased with the amount of methanol but decreased again when the ratio of methanol to oil was more than 4:1. At constant methanol amount with varying catalyst amount, the conversion nearly was not changed. Therefore, with the small loading of methanol, the effects of the catalyst loading was not significant and the methanol loading was an important factor to get the high conversion.

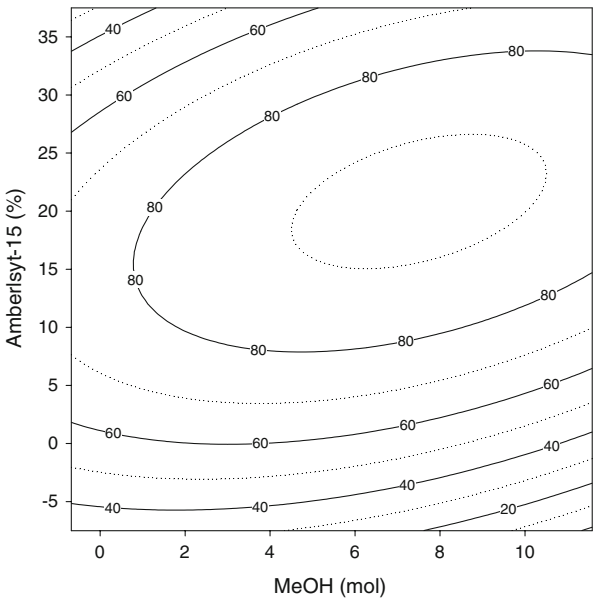


**Fig. 1** Contour plot of conversion of free fatty acid of tung oil during pretreatment (experiment 1)

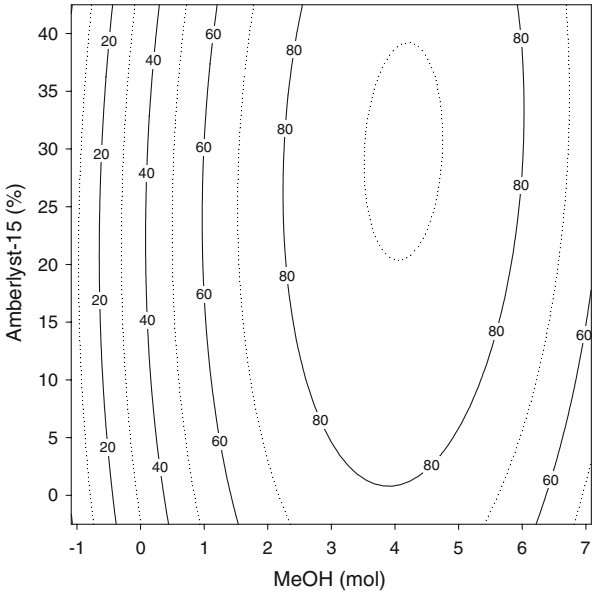


**Fig. 2** Contour plot of conversion of free fatty acid of tung oil during pretreatment (experiment 2)

## Transesterification of Tung Oil

Biodiesel was produced from pretreated tung oil. Reaction was performed using KOH as a catalyst at 80 °C for 20min. The final purity of tung biodiesel was 90.2wt% when the molar ratio of methanol to oil was 6:1 and KOH was 0.9% of oil and did not increase with increasing ratio of methanol to oil (Fig. 3).

Figure 4 shows the peaks of the components in the gas chromatogram. The highest peak was the peak of α-eleostearic acid. Although both eleostearic and linolenic acids have three double bonds, the structure and the properties of eleostearic acid are different from linolenic acid which was contained in soybean or rapeseed biodiesel (Fig. 5) [13, 17]. Table 3 shows the fatty acid composition of tung biodiesel. The saturated fatty acid content of tung biodiesel was 14.1% and the unsaturated fatty acid content was 84.6%. The content of

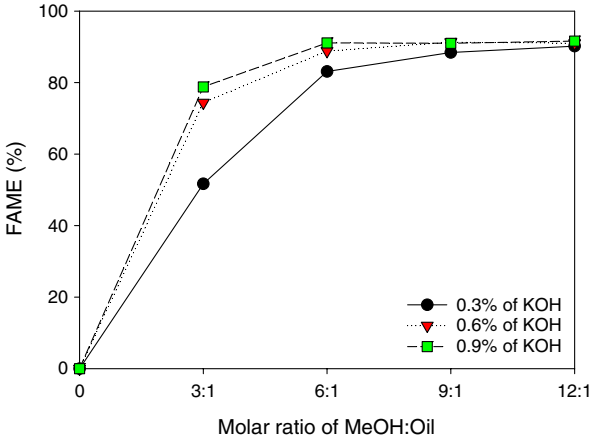


**Fig. 3** Profile of FAME with amount of methanol and KOH

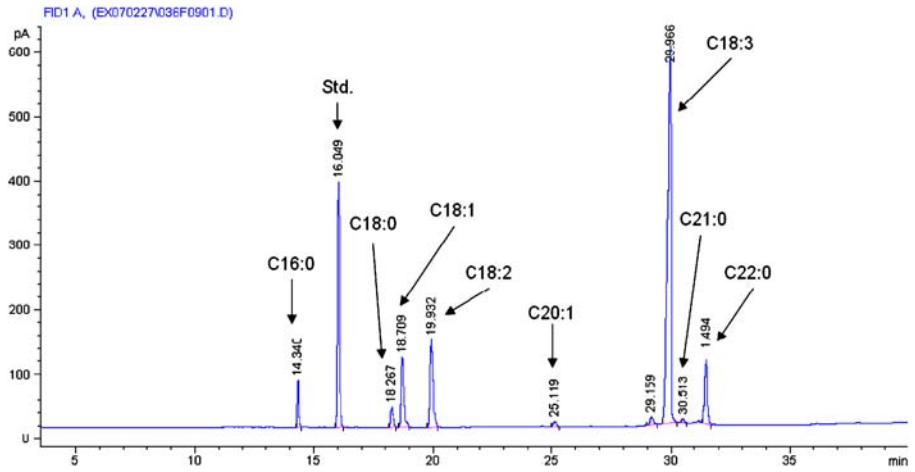


**Fig. 4** Gas chromatogram of tung biodiesel

major component, α-eleostearic acid, was 63.8%. After the distillation, the amount of α-eleostearic acid decreased about 12.2%, and the unsaturated fatty acid decreased by about 8.3%. It was thought that some of α-eleostearic acid was polymerized during the distillation more than 300 °C because the eleostearic acid is more susceptible to polymerization than linolenic or linoleic acids [17–18].

Table 4 shows the properties of tung biodiesel before and after the distillation. When biodiesel was produced from rice bran oil, the purity increased more than 99% after the distillation [19]. However, the purity of tung biodiesel after the distillation was not enhanced much. The distillation of tung biodiesel was started more than 300 °C, which was a very high temperature compared with 160–220 °C of rice bran biodiesel [19]. The total glycerin of tung biodiesel was very low. The oxidation stability of tung biodiesel was very low, 0.5 h, as determined by the Rancimat method, because of the high content of eleostearic acid [8–9]. The initial AV was 9.55 mg KOH/g, but the AV of tung biodiesel was 0.59 mg KOH/g. The high viscosity of crude tung oil decreased to 9.8 $mm^2/s$ at 40 °C after the transesterification. However, the viscosity of tung biodiesel was still much higher than the specification of biodiesel in most countries. The decrease in the viscosity by the distillation was trivial. The CFPP of tung biodiesel was −11 °C before the distillation. After

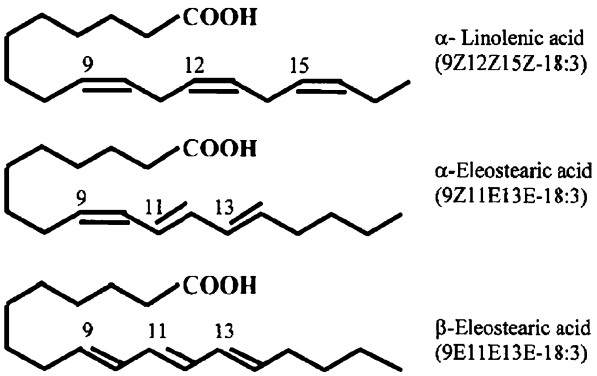


**Fig. 5** Chemical structures of linolenic and eleostearic acid

**Table 3** Fatty acid distribution of tung biodiesel.

| Fatty acid (%) | Before distillation | After distillation |
|---|---|---|
| Palmitic acid (C16:0) | 3.03 | 3.64 |
| Stearic acid (C18:0) | 2.20 | 2.55 |
| Oleic acid (C18:1) | 8.56 | 10.10 |
| Linoleic acid (C18:2) | 11.51 | 13.75 |
| Eleostearic acid (C18:3) | 63.80 | 51.64 |
| Eicosenoic acid (20:1) | 0.75 | 0.81 |
| Heneicosanoic acid (C21:0) | 0.46 | 1.02 |
| Behenic acid (C22:0) | 8.39 | 12.12 |
| Not identified | 1.30 | 4.37 |
| Saturated fatty acid | 14.08 | 19.33 |
| Unsaturated fatty acid | 84.62 | 76.30 |

the distillation, the CFPP increased a little because of the decrease in the unsaturated fatty acid content.

## Conclusions

Tung biodiesel was produced by the esterification/transesterification reactions using Amberlyst-15 and KOH from tung oil. Amberlyst-15 showed a good esterification efficiency for the pretreatment of tung oil. The AV of tung oil decreased from 9.55 to 0.72 mg KOH/g. For the esterification of oils having a high content of free fatty acids, Amberlyst-15 will be a promising solid catalyst.

After the transesterification, the content of FAME was 90.2 wt%. The viscosity of tung oil decreased from 109.4 to 9.8 $mm^2/s$ at 40 °C. Although the high viscosity of crude oil decreased much after transesterification, it was out of the biodiesel specification (EN 14214). Tung biodiesel contained 63.8% of α-eleostearic acid, which was an unsaturated fatty acid having three double bonds. Because of the high content of unsaturated fatty acid, tung biodiesel showed very low oxidation stability and very good cold temperature behavior. The distillation property of tung biodiesel was not good and needed a very high temperature more than 300 °C.

Tung biodiesel showed excellent cold temperature behavior, but its viscosity, FAME content, and oxidation stability did not satisfy EN 14214. If tung biodiesel is blended with palm biodiesel having a poor cold temperature performance, the blended biodiesel will have better cold temperature performance than neat palm biodiesel. The properties of tung

**Table 4** Properties of tung biodiesel.

| | Before distillation | After distillation |
|---|---|---|
| FAME (wt%) | 90.2 | 90.4 |
| Total glycerin (wt%) | 0.046 | 0.016 |
| Oxidation stability (h) at 110 °C | 0.50 | 0.17 |
| Water content (vol%) | 0.23 | 0.01 |
| Acid value (mg KOH/g) | 0.59 | 0.46 |
| Viscosity ($mm^2/s$) at 40 °C | 9.8 | 8.7 |
| CFPP (°C) | −11 | −9 |

biodiesel such as viscosity, FAME content, and oxidation stability can be improved by the blending with other biodiesels. Therefore, tung biodiesel produced from nonedible tung oil can be used as a blend component of an alternative engine fuel, although tung biodiesel is not enough as a fuel for diesel engines by itself.

**Acknowledgements** This study was supported by the Resource Recycling R&D Center, 21C Frontier R&D Program.

## References

1. Marchetti, J. M., Miguel, V. U., & Errazu, A. F. (2007). *Renewable & Sustainable Energy Reviews*, *11* (6), 1300–1311.
2. Hass, M. J., Bloomer, S., & Scott, K. (2000). *Journal of the American Oil Chemists' Society*, *77*(4), 373–379.
3. Ghadge, S. V., & Raheman, H. (2006). *Bioresource Technology*, *97*, 379–384.
4. Foidl, N., Foidl, G., Sanchez, M., Mittebach, M., & Hackel, S. (1996). *Bioresource Technology*, *58*, 77–82.
5. Canoira, L., Alcantara, R., Martinez, M. J. G., & Carrasco, J. (2006). *Biomass & Bioenergy*, *30*, 76–81.
6. Conceicao, M. M., Candeia, R. A., Silva, F. C., Bezerra, A. F., Fernandes, V. J., & Souza, A. G. (2007). *Renewable & Sustainable Energy Reviews*, *11*, 964–975.
7. Srivastava, A., & Prasad, R. (2000). *Renewable & Sustainable Energy Reviews*, *4*, 111–133.
8. Knothe, G. (2005). *Fuel Processing Technology*, *86*, 1059–1070.
9. Schober, S., & Mittelbach, M. (2004). *European Journal of Lipid Science and Technology*, *106*, 382–389.
10. Kim, Y. J., Kim, D. K., Rhee, Y. W., Park, S. C., & Lee, J. S. (2005). *Korean Chemical Engineering Research*, *43*(5), 621–626.
11. Marchetti, J. M., Miquel, V. U., & Errazu, A. F. (2007). *Fuel*, *86*, 906–910.
12. Wang, Y., Ou, S., Liu, P., Xue, F., & Tang, S. (2006). *Journal of Molecular Catalysis A, Chemical*, *252*, 107–112.
13. Sharma, V., & Kundu, P. P. (2006). *Progress Polymer Science*, *31*, 983–1008.
14. Gryglewicz, S., Grabas, K., & Gryglewicz, G. (2000). *Bioresource Technology*, *75*, 213–218.
15. Corino, C., Fiego, D. P. L., Macchioni, P., Pastorelli, G., Giancamillo, A. D., & Rossi, R. (2007). *Meat Science*, *76*, 19–28.
16. Abdullh, A. G. L., Sulaiman, N. M., Aroua, M. K., & Noor, M. J. M. (2007). *Journal of Food Engineering*, *81*, 65–71.
17. Tsuzuki, T., Tokuyama, Y., Igarashi, M., & Miyazawa, T. (2004). *Carcinogenesis*, *25*(8), 1417–1425.
18. Tsuzuki, T., Igarashi, M., Iwata, T., Yamamoto, T., Ogita, K., & Miyazawa, T. (2004). *Lipids*, *39*(5), 475–480.
19. Zullakah, S., Lai, C. C., Vali, S. R., & Ju, Y. H. (2005). *Bioresource Technology*, *96*, 1889–1896.