สภาวะการผลิตไบโอดีเซลจากน้ำมันมะพร้าว

วัฒนา ปิ่นเสม[1] และ นพวรรณ ชนัญพานิช[1]*

บทคัดย่อ

งานวิจัยนี้เน้นถึงการผลิตไบโอดีเซลเกรดชุมชนแบบประหยัดจากน้ำมันมะพร้าวซึ่งมีกรดไขมันอิสระ 11.5±0.5% โดยใช้เทคนิคการผลิตแบบสองขั้นตอนที่ใช้กรดตามด้วยเบสเป็นตัวเร่งปฏิกิริยา ปฏิกิริยาขั้นตอนแรกเป็นปฏิกิริยาเอสเทอริฟิเคชันของกรดไขมันอิสระในน้ำมัน เร่งด้วยตัวเร่งปฏิกิริยา $Fe_2(SO_4)_3$ จำนวน 2% อัตราส่วนโมลของเมทานอลต่อน้ำมัน 6:1 เป็นเวลา 4 ชั่วโมง ปฏิกิริยาขั้นตอนที่สองเป็นปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันจากขั้นตอนแรกโดยใช้อัตราส่วนโมลของเมทานอลต่อน้ำมันเท่าเดิม และใช้ตัวเร่งปฏิกิริยาเป็น NaOH ใช้เวลาทำปฏิกิริยา 1 ชั่วโมง ได้ผลผลิตไบโอดีเซล 86% (CB) ที่เตรียมได้มีความหนืดเท่ากับ 3.2 cSt และจุดไหลเทเท่ากับ -5°C ดังนั้นสามารถนำ CB ไปใช้ในพื้นที่ที่มีอากาศเย็นหรือผสมกับไบโอดีเซลจากน้ำมันชนิดอื่น จากผลการศึกษานี้อาจสรุปได้ว่า ในการเตรียมไบโอดีเซลจากน้ำมันมะพร้าวแบบใช้เบสเป็นตัวเร่งปฏิกิริยานั้น กรดไขมันอิสระในน้ำมันไม่ควรเกิน 4%

คำสำคัญ: ไบโอดีเซลจากน้ำมันมะพร้าว กรดไขมันอิสระ ทรานส์เอสเทอริฟิเคชัน เอสเทอริฟิเคชัน กรดลิวอิส จุดไหลเท

[1] รองศาสตราจารย์ Integrated Nanoscience Research Center สำนักวิจัยวิทยาศาสตร์และเทคโนโลยี และภาควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ประยุกต์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าพระนครเหนือ

* ผู้นิพนธ์ประสานงาน โทรศัพท์ 0-2555-2000 ต่อ 1538 อีเมล: ncn@kmutnb.ac.th

Optimization of Community Coconut Biodiesel Production

Watana Pinsem[1] and Noppavan Chanunpanich[1]*

Abstract

This research was aimed to find an economic condition producing community grade biodiesel from coconut oil, having free fatty acid (FFA) content of 11.5±0.5%. The coconut biodiesel, CB, production must be carried out via two-step acid-base catalyzed reaction. The first step was carried out under esterification of the FFA with $2\%Fe_2(SO_4)_3$ and a molar ratio of methanol to oil of 6:1 for 4 hours, following by the second step, transesterification, using NaOH as a catalyst with a molar ratio of methanol to oil of 6:1 for 1 hour, yielding 86% of CB. From our finding, it can be concluded that the coconut oil with less than 4% FFA was qualified to produce biodiesel via basic catalyzed reaction. CB exhibited viscosity of 3.2 cSt (mm^2s^{-1}) and pour point of -5°C, hence, it can be used or blend with other biodiesel in cold area.

Keywords: Coconut Biodiesel, Free Fatty Acid, Transesterification, Esterification, Lewis Acid, Pour Point

[1] Associate Professor, Integrated Nanoscience Research Center, Science and Technology Research Institute and Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok.

* Corresponding Author, Tel. 0-2555-2000 Ext.1538, E-mail: ncn@kmutnb.ac.th

1. Introduction

Biodiesel is an alternative fuel. It can be produced through transesterification of vegetable oils or fats with methanol or short chain alcohols using acid, base or enzyme [1], [2] as catalysts. The conventional alkali-catalyzed transesterification proceeds approximately 4,000 times faster than that of acid-catalyzed, and thereby is more competitive commercially [3]. However, alkali-catalyzed transes-terification is not suitable for high FFA content and high water content oil due to soap formation which makes difficulty on glycerin separation and washing. Naik et al. [4] proved that by using alkaline catalyzed transesterification reaction of Karanja oil, the yield of methyl esters decreased from 97% to 6% with increasing the FFA content from 0.3% to 5.3%.

Thailand has high potential to produce biodiesel, due to large variety of oil plants. Moreover, eating habits of fried food and snack end up in used oil abundant. As a result, the government issues two biodiesel standards, Fatty Acid Methyl Ester (FAME) and Community Biodiesel. The later standard is issued mostly for using in agricultural machines, hence glyceride content, such as methyl ester and glyceride derivatives are not considered. Moreover, some properties are also accepted in larger ranges, such as viscosity from 1.9-8.0 cSt (compared to 3.5-5.0 cSt) and acid value up to 0.8 mg KOH/g (compared to 0.5 mg KOH/g).

Coconut plants are grown in all areas of the country. Hence, it can be one of the raw materials for biodiesel production. Property of coconut biodiesel (CB) is quite unique. This is because it composes of low number of carbon in fatty acid, more than 50% of its fatty acid having C8-C14 [5]. Hence, it exhibits lower viscosity than that of palm biodiesel or other vegetable oil bio-diesels. Moreover, pour point is also low. As a result, it is expected that CB is a potential biodiesel for community and for biodiesel blend. Like Jatropha oil [6], [7], rice bran oil, Zanthoxylum bungeanum seed oil [8], salmon oil [9], waste lard [10], and waste cooking oil [11], coconut oil in local market in Thailand exhibits high FFA, suggesting the oil was coming from hot pressing process where heating process caused increasing in FFA. Hence, the CB production via conventional basic-catalyzed transesterification cannot be carried out. Acid-catalyzed esterification and transesterification commonly uses sulfuric acid [8], phosphoric acid [12], hydrochloric acid, and organic sulfonic acids as catalysts. Since this condition needs quite high ratio of methanol to oil, high separation cost, long reaction time, and corrosiveness [13], two-step acid-base catalyzed reaction is developed; [14]-[16] esterification of FFA using acid as a catalyst, following by transesterification of oil using base as a catalyst. Recently, Lewis acid, such as $Fe_2(SO_4)_3$, [17], [18] $AlCl_3$ or $ZnCl_2$ [19] was used in acid-catalyzed esterification reaction. Hence, two-step acid-base catalyzed reaction is comfortable. In this report, optimization for community biodiesel production was aimed to get the lowest chemicals and the shortest time.

2. Materials and Methods

2.1 Materials

Coconut oil was purchased from local market. $Fe_2(SO_4)_3$ and methanol were purchased from Fluka. NaOH and Na_2SO_4 anh. were provided from Acros. All chemicals and solvents were laboratory grade.

2.2 Pretreatment of Coconut Oil; Acid-catalyzed Esterification

The 500 g of coconut oil was poured and heated to 60°C in a round bottomed flask equipped with a

reflux condenser and a mechanical stirrer. Methanol to oil with molar ratio from 6:1 to 10:1 was added, followed by 1-5% of $Fe_2(SO_4)_3$. The mixture was stirred at this temperature for a certain time, then the mixture was allowed to settle overnight in a separatory funnel and water layer was removed. The oil layer was washed three times with warm water (60°C) and dried with anhydrous sodium sulfate (anh. Na_2SO_4).

2.3 Basic-catalyzed Transesterification of Pretreated Coconut Oil

The pretreated coconut oil was poured and heated to 60°C in the water bath. The methoxide solution was then added. (the amount of NaOH in methanol was calculated from acid-base titration technique and the molar ratio of methanol to oil of 6:1) The mixture was stirred at this temperature for one hour, and then allowed to settle and glycerin (lower layer) was removed. The oil layer was washed with warm water and dried with anh. Na_2SO_4.

2.4 Determination of Acid Value (Acid-base Titration)

Acid value of the oil and biodiesel was determined by acid-base titration: 10 cm^3 of isopropanol was added in 1.00 g of oil, following by two drops of phenolphthalein solution. The mixture was titrated with 0.025M NaOH. The acid value can be stoichiometric calculated and the percentage of FFA was approximately half of the acid value.

3. Results and Discussion
3.1 Pretreatment of Coconut Oil

Coconut oil in Thailand contains free fatty acid of 12%[5] while the value for oil in another country is only 4%[20], hence, biodiesel via a two-step acid-base catalyzed reaction was performed. Figure 1 showed the
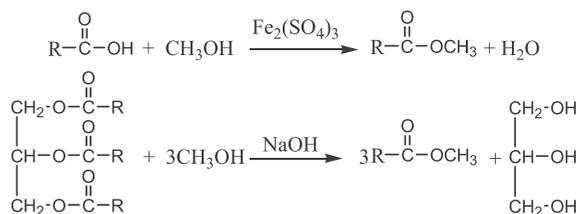
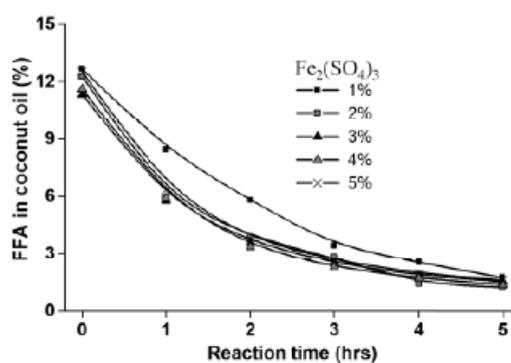**Figure 1** Two-step acid-base catalyzed reaction for producing coconut biodiesel.

Figure 2 The effect of $Fe_2(SO_4)_3$ on the FFA reduction in coconut oil: esterification was carried out at 60°C with a molar ratio of methanol to oil of 6:1

reaction of pretreatment step of FFA to methyl ester using Lewis acid, $Fe_2(SO_4)_3$ as a catalyst and second step, transesterification using NaOH as a catalyst.

Pretreatment step was carried out by varying the $Fe_2(SO_4)_3$. Figure 2 showed that the amount of $Fe_2(SO_4)_3$ more than 2% wt. did not affect the reduction of FFA in the oil at a given time. Hence, the optimum acid catalyst of 2% was used. In addition, the reaction time and the molar ratio of methanol to oil influenced the FFA reduction, as shown in Table 1.

It was observed that FFA dramatically decreased with time from 1-2 hours. Longer reaction time, the conversion was not much improved. Although the

increasing of methanol to oil molar ratio resulted lower the FFA in oil, longer time for separation was found. The reaction at the molar ratio of methanol to oil of 6:1 exhibited normal two layers with water and $Fe_2(SO_4)_3$ at lower and oil at the top. On the other hand, with higher methanol to oil molar ratio, the layers were reversed. This is because methanol exhibited low density and preferable dissolving in water phase, resulting water phase was on the top. After methanol evaporation process, phase separation reversed. Therefore, acid catalyzed esterification step of coconut oil was optimized using molar to oil ratio of 6:1 which was the same amount that used for transesterification of low FFA oil. [21], [22]

Table 1 Effect of reaction time and the molar ratio of methanol to oil on esterification of coconut oil using 2% wt. $Fe_2(SO_4)_3$ as a catalyst.

Reaction time (h)	FFA in oil (%) with various molar ratio of methanol:oil		
	6:1	8:1	10:1
0	11.5±0.5		
1	8.5±0.1	5.9±0.5	5.7±0.2
2	6.0±0.7	3.3±0.2	2.8±0.3
3	3.4±0.5	1.9±0.1	1.3±0.1
4	2.7±0.2	1.5±0.1	0.9±0.1

3.2 Transesterification

Conventional basic-catalyzed transesterification was confirmed for the optimum condition in that the molar ratio of methanol to oil of 6:1 and reaction time of 1 h. [14], [23] Hence, the biodiesel from pretreated coconut oil was carried out with this condition. However, FFA in the pretreated oil affected the biodiesel yield. Table 2 showed the biodiesel yield from various FFA in pretreated oil

Table 2 CB yield from pretreated oil with various value of FFA

Pretreated reaction time (h)	% FFA in coconut oil	% Yield
0	11.5±0.5	soap formation
1	8.5±0.1	soap formation
2	6.0±0.7	64.2±0.7
3	3.4±0.5	83.6±0.5
4	2.7±0.2	86.1±0.4

To prove the condition of producing conventional biodiesel, palm biodiesel with FFA of 0.26% has been tested, obtaining 92%. The biodiesel mixture was quite easy to separate and wash, due to less soap formation. Unfortunately, CB from coconut oil with FFA content more than 8% could not be carried out because no separation took place after settling. Moreover, when water was added, emulsion was clearly observed and transesterification of the pretreated coconut oil with FFA content of 6% yielded only 64% with a difficulty on separation and washing. This is because FFA in oil became emulsifier. However, biodiesel production of the pretreated oil with FFA content ≤4% (esterification more than 3 h.) obtained acceptable biodiesel yield of >83%. This result might be concluded that biodiesel production from oil with FFA content ≥4% was not recommended. Hence, community CB can be economically produced via two-step acid-base catalyzed reaction, The first step, esterification was carried out using 2% $Fe_2(SO_4)_3$ with a molar ratio of methanol to oil of 6:1 for 4 hours. The second step was conventional transesterification using NaOH as a catalyst and a molar ratio of methanol to oil of 6:1 for one hour. By this condition, the methanol can be saved and yield was acceptable.

3.3 Some Properties of Biodiesel from Coconut and Palm Biodiesel

Communities who produced biodiesel for their own usage were recommended to determine viscosity and acid value of their biodiesels. These properties were easy methods and clearly observed. The viscosity was tested to check how easy the oil be vaporized in injection system. The qualified biodiesel should exhibit viscosity of 1.8 to 8.0 cSt (viscosity of the oil was about 45 cSt). The acid value was tested to protect the corrosion in the engine. Both properties in Table 3 were within the standard, hence, it was safe to be used. It was also observed that the viscosity of the PB was higher than that of CB. This is because palm oil contained higher carbon content of C_{16}-C_{18} while carbon content of was only C_8-C_{12}. With this composition, it is not surprising why CB exhibited low cetane number-the time of vaporized fuel moved to combustion room and ignited. The higher centane number, the longer ignition time was.

Table 3 also displayed interesting properties in that pour point of CB was low, hence, it can be used neat or blend in cold area.

Table 3 Properties of biodiesel from palm and coconut oil

Properties	Community biodiesel standard	Palm biodiesel	Coconut biodiesel
Viscosity, cSt	1.9-8.0	4.8	3.2
Acid value, mgKOH/g oil	0.8	0.45	0.42
Density, kg/m³	860-900	869	883
Cetane number	Not less than 47	47	42.1
Flash point, °C	Not less than 120	178	178
Pour point, °C	-	14	-5
Carbon residue	0.05	0.049	0.045

4. Conclusion

Coconut oil under the study exhibited FFA content of 11.5±0.5, as a result, its biodiesel should be produced via acid-basic catalyzed reaction. The first step was via esterification of FFA in the oil using $Fe_2(SO_4)_3$ as a catalyst. The condition to lower FFA in the oil has been studied. It was found that the catalyst, $Fe_2(SO_4)_3$, of more than 2% wt. did not affect the reduction of FFA. Although, FFA reduction decreased with reaction time and the amount of methanol, the value did not much improved after reaction time more than 2 hours. The economics method to produce CB was esterification of the oil using 2% $Fe_2(SO_4)_3$ as a catalyst for 4 hours, followed by transesterification using NaOH as a catalyst for one hour. Both reactions were carried out in mild condition; a temperature of 60°C, methanol to oil molar ratio of 6:1, yielding 86.1±0.5% of product. The properties of CB was with in community biodiesel standard, except cetane number. Moreover, pour point of CB was low to -5°C, hence, it can be used in cold area.

5. Acknowledgement

References

[1] N. Dizge, C. Aydiner, D.Y. Imer, M. Bayramoglu, A. Tanriseven, and B. Keskinler, "Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer," *Bioresource Technol*, vol.100, pp.1983–1991, 2009.

[2] N. Dizge, B. Keskinler, and A. Tanriseven, "Biodiesel production from canola oil by using lipase immobilized onto hydrophobic microporous styrene–divinylbenzene copolymer," *Biochem Eng J*, vol.44, pp.220–225, 2009.

[3] H. Fukuda, A. Kondo, and H. Noda, "Biodiesel fuel production by transesterification of oils," *J Biosci. Bioeng*, vol.92, pp.405–416, 2001.

[4] M. Naik, L.C. Meher, S.N. Naik, and L.M. Das, "Production of biodiesel from high free fatty acid Karanja (Pongamia pinnata) oil," *Biomass and Bioenerg*, vol.32, pp.354– 357, 2008.

[5] P. Nakpong, and S. Wootthikanokkhan, "High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand," *Renew Energ*, vol.35, pp.1682–1687, 2010.

[6] H.J. Berchans, and S. Hirata, "Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids," *Bioresource Technol*, vol.99, pp.1716–1721, 2008.

[7] H. Lu, Y. Liu, H. Zhou, Y. Yang, M. Chen, and B. Liang, "Production of biodiesel from Jatropha curcas L. oil," *Computers and Chem Eng*, vol.33, pp,1091–1096, 2009.

[8] J. Zhang, and L. Jiang, "Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production," *Bioresource Technol*, vol.99, pp.8995–8998, 2008.

[9] M. Hamed, E. Mashad, R. Zhang, and R.J. Avena-Bustillos, "A two-step process for biodiesel production from salmon oil," *Biosystems Eng*, vol.99, pp.220–227, 2008.

[10] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, "Production of biodiesel from acid waste lard," *Bioresource Technol*, vol.100, pp.6355–6361, 2009.

[11] A.N. Phan, and T.M. Phan, "Biodiesel production from waste cooking oils," *Fuel*, vol.87, pp. 3490–3496, 2008.

[12] D.A.G. Aranda, R.T.P. Santos, N.C.O. Tapanes, A.L.D. Ramos, and O.A.C. Antunes, "Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids," *Catal Lett*, vol.122, pp.20–25, 2008.

[13] G. Guan, K. Kusakabe, and N.K. Sakurai, "Trans-esterification of vegetable oil to biodiesel fuel using acid catalysts Moriyama in the presence of dimethyl ether," *Fuel*, vol.88, pp. 81–86, 2009.

[14] Y. Wang, S. Ou, P. Liu, and Z. Zhang, "Preparation of biodiesel from waste cooking oil via two-step catalyzed process," *Energ Convers Manage*, vol.48, pp.184–188, 2007.

[15] V.B. Veljković, S.H. Lakićević, O.S. Stamenković, Z.B. Todorović, M.L. Lazic, "Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids," *Fuel*, vol.85, pp.2671–2675, 2006.

[16] A.S. Ramadhas, S. Jayaraj, and C. Muraleedharan, "Biodiesel production from high FFA rubber seed oil," *Fuel*, vol.84, pp.335–340, 2005.

[17] P. Patil, S. Deng, J.I. Rhodes, and P.J. Lammers, "Conversion of waste cooking oil to biodiesel using ferric sulfate and supercritical methanol processes," *Fuel*, vol.89, pp.360–364, 2010.

[18] G. Mengyu, P. Deng, M. Li, Y. En, and H. Jianbing, "The kinetics of the esterification of free fatty acids in waste cooking oil using $Fe_2(SO_4)_3/C$," *Chinese J Chem Eng*, vol.17, pp.83-87, 2009.

[19] U. Nestor, Jr. Soriano, R. Venditti, and DS. Argyropoulos, "Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification,"

Fuel, vol.88, pp.560–565, 2009.

[20] D. Kumar, K.G. Poonam, C.P. Singh, "Fast, Easy ethanolysis of coconut oil for biodiesel production assisted by ultrasonication," *Ultrason Sonochem*, vol.17, pp.555–559, 2010.

[21] N. Usta, "Use of tobacco seed oil methyl ester in a turbocharged indirect injection diesel engine," *Biomass Bioenerg*, vol.28, pp.77–86, 2005.

[22] L.C. Meher, S.S. Vidya, and S.N.N. Dharmagadda, "Optimization of alkali catalyzed transesterification of Pongamia pinnata oil production of biodiesel," *Bioresource Technol*, vol.97, pp.1392–7, 2006.

[23] U. Rashid, and F. Anwar, "Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil," *Fuel*, vol.87, pp. 265–273, 2008.