Roselle (*Hibiscus sabdariffa* L.) oil as an alternative feedstock for biodiesel production in Thailand

Piyanuch Nakpong *, Sasiwimol Wootthikanokkhan

Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology, Krungthep, Bangkok 10120, Thailand

ARTICLE INFO

ABSTRACT

The production of biodiesel fuel from crude roselle oil was evaluated in this study. The process of alkali-catalyzed transesterification with methanol was carried out to examine the effects of reaction variables on the formation of methyl ester: variables which included methanol-to-oil molar ratios of 4:1–10:1, catalyst concentrations of 0.25–2.0% w/w of oil, reaction temperatures of 32–60 °C, and reaction times of 5–80 min. The methyl ester content from each reaction condition was analyzed by gas chromatography (GC), the optimum condition having been achieved at a methanol-to-oil molar ratio of 8:1, a catalyst concentration of 1.5% w/w of oil, a reaction temperature of 60 °C, and a reaction time of 60 min. The resultant methyl ester content of 99.4% w/w, plus all of the other measured properties of the roselle biodiesel, met the Thai biodiesel (B100) specifications and international standards EN 14214:2008 (E) and ASTM D 6751-07b, with the exception of a higher carbon residue and lower oxidation stability.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

It goes without saying that petroleum is the most important commodity consumed in modern society, providing fuel for energy, heating, transportation, and industry. It is also a raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics. The demand for petrochemical feedstocks and petroleum products, particularly gasoline and diesel fuel, has been continually increasing throughout the world [1]; however, petroleum reserves are finite [2] and non-renewable [3].

The concern about dwindling worldwide petroleum reserves and the increase of environmental problems has stimulated researchers to develop alternative sources to petroleum-based fuels. Among these different possible resources, biodiesel has attracted much attention as an alternative fuel for diesel engines since it is renewable, non-toxic, environmentally acceptable [2,4,5], and can be domestically produced. In addition, a valuable by-product, glycerin (glycerol), may be used in the soap, pharmaceutical, and cosmetic industries [6].

Thailand does have abundant supplies of natural gas, in the Gulf of Thailand, but lacks sufficient crude oil (Petroleum resource) for domestic consumption; hence, most of it has to be imported from overseas. In addition, crude oil prices fluctuate in the international market, with a tendency over the years to steadily increase. Recognizing these facts, the Thai government is actively promoting the use of biodiesel as a partial, or even full, replacement for diesel

fuel, the wider use of which could decrease the nation's dependence on foreign crude oil and resulting benefit of conserving foreign currency reserves that would have been earmarked for crude oil imports. Moreover, the production of vegetable oils for industrial biodiesel production can open new markets for agriculturists while also providing more jobs.

Biodiesel, the monoalkyl esters of long chain fatty acids, is a chemically modified fuel derived from various kinds of vegetable oils and animal fats [2,5], which are composed primarily of high molecular weight triglycerides. The viscosity of vegetable oils and (especially) animal fats is higher than that of diesel fuel several times over (about 11–17 times) [2]; and since viscosity affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air–fuel mixing in a diesel engine's combustion chamber. The use of high viscous oils as a fuel leads to adverse effects on the combustion process [5]. Hence, these oils must be derivatized to be compatible with existing engines. One of the possible ways to achieve this purpose is conversion of large, branched triglycerides into smaller, straight-chain molecules of monoalkyl ester through a process called transesterification. This process has been widely used to reduce the high viscosity of triglycerides [2,7]. The transesterification of vegetable oil and fat can be represented by the general equation:

$$\text{Triglyceride} + 3\,\text{ROH} \overset{\text{catalyst}}{\to} 3\,\text{R}'\text{CO}_2\text{R} + \text{Glycerol} \qquad (1)$$
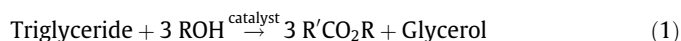
Transesterification reaction (also called alcoholysis), a very slow reaction, can be achieved, in principal, by acid catalysis or base catalysis [2]. However, alkaline conditions are preferable because

acid catalysis requires much longer reaction times than base catalysis [8,9]. Methanol is the preferable alcohol (because of its low cost and its chemical and physical advantages [10]), and the typical alkaline catalysts are sodium and potassium hydroxides [4].

Both edible and non-edible oils can be used for biodiesel production, but the majority currently used are edible [2,5]; however, production from edible oils is currently affected by the factor of cost-effectiveness due to its competition in food applications. Therefore, new, low-cost possible alternative feedstocks are undergoing continued evaluation by researchers [11–17]. In Thailand, biodiesel is produced mainly from palm oil; however, there are alternative oil-yielding crops which can be utilized as feedstocks, such as jatropha and coconut. A new contender is emerging as a potential feedstock: roselle oil, which has not yet been extensively studied, but is gaining a lot of attention.

Hibiscus sabdariffa L., a plant in the Malvaceae family, known worldwide by many different common names such as roselle, Jamaica sorrel, and, in Thai, as krachiap daeng. It is widely cultivated in tropical regions including the northern, south-eastern, and central parts of Thailand. (In fact, Thailand and China are the largest producers and control much of the world supply.) In Thailand, roselle is mostly used as a foodstuff, with its calyx and epicalyx used in the making of jams, jellies, and sorrel drink [18,19]. The seeds contain 18% oil [20], which can be used as a medicinal vehicle, with the seed residue for cattle feed [18]. However, in a commercial sense, this oil is not in current widespread use in Thailand, having relatively few competing medicinal and food uses, a fact having prompted our study of its potential for biodiesel production. The objectives of this study were: (a) to investigate the optimum reaction conditions for biodiesel production from crude roselle oil, and (b) to study the effects of the variables on its alkali-catalyzed transesterification with methanol.

2. Materials and methods

2.1. Materials

The crude roselle oil was obtained from Payakkaram Temple in Suphanburi. All chemicals used in the experiments, such as methanol, potassium hydroxide, and n-heptane, were of analytical reagent (AR) grade. The methyl esters such as methyl heptadecan-oate, methyl esters of palmitic, stearic, oleic, linoleic, and linolenic acids were standard for GC.

2.2. Alkali-catalyzed transesterification

In this study, transesterification of crude roselle oil with methanol via base (KOH) catalysis was carried out in a laboratory-scale setup. The equipment used for this study consisted of a 250 mL flat-bottom reaction flask and hot plate with magnetic stirrer. Reactions conducted in a three-neck round-bottom flask fitted with a condenser (to reduce the loss of methanol by evaporation) and a thermometer.

The mixture in the reaction flask was heated and well-stirred at a constant stirring speed of 600 rpm [3,21] for all test runs. The crude roselle oil, methanol, and potassium hydroxide were used in amounts established for each experiment, with the oil preheated to the desired temperature in the reaction flask. In order to maintain its catalytic activity, the solution of potassium hydroxide in methanol was freshly prepared for each run, since prolonged contact with air would diminish the effectiveness of the catalyst through interaction with moisture and carbon dioxide [2,3]. The potassium hydroxide-methanol solution was then added to the preheated oil in the reaction flask, at which point the time measurement began. Heating and stirring were continued at different reaction times at atmospheric pressure. After the reaction, the mixture was allowed to settle by gravity for 24 h in the separatory funnel. Two layers were formed: the upper layer consisted of methyl ester, methanol traces, residual catalyst, and other impurities, whereas the lower layer consisted of glycerin, excess methanol, catalyst, and other impurities. The glycerin layer was then drawn off and the methyl ester layer was purified by washing with hot distilled water at 60 °C until the washing water had a pH value similar to that of distilled water. The hot distilled water-to-crude methyl ester ratio was 1:1. The washing step was done gently to prevent the possibility of loss of methyl ester due to emulsion formation. Next, the methyl ester layer was dried under reduced pressure at 70 °C by rotary evaporator. Finally, the products from the reactions were analyzed by using the standard test method, EN 14103, to determine methyl ester content. (The averages of the results are shown in Figs. 1–3.) The optimum of each variable was determined by considering the methyl ester content while the
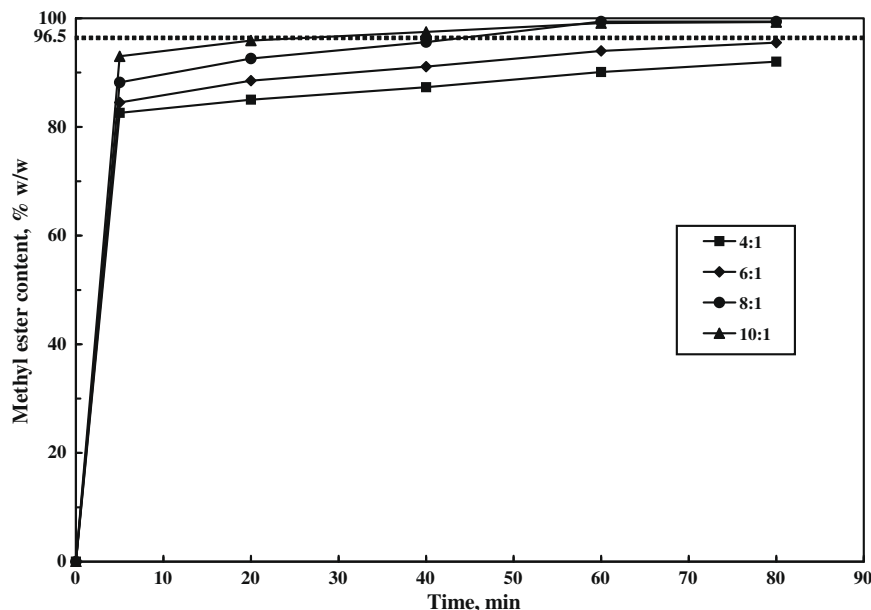

Fig. 1. Effects of methanol-to-oil molar ratio and reaction time on methyl ester formation (KOH concentration of 1.5% w/w of oil, reaction temperature of 60 °C).
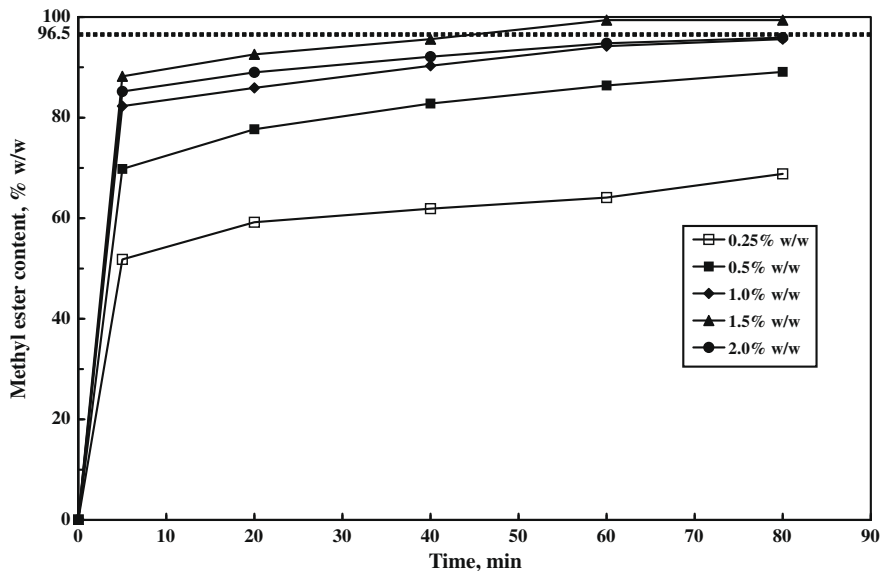
Fig. 2. Effects of catalyst concentration and reaction time on methyl ester formation (methanol-to-oil molar ratio of 8:1, reaction temperature of 60 °C).
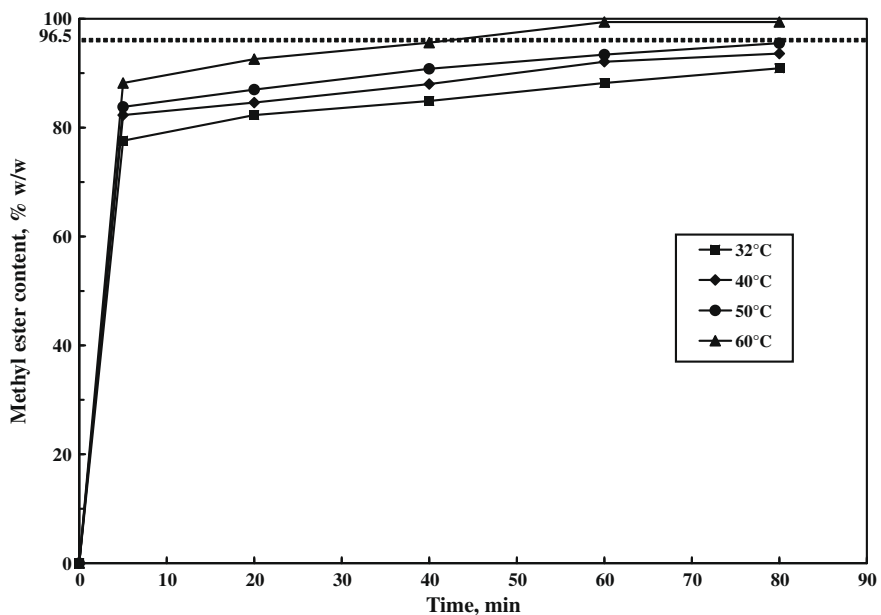

Fig. 3. Effects of reaction temperature and reaction time on methyl ester formation (methanol-to-oil molar ratio of 8:1, KOH concentration of 1.5% w/w of oil).

other variables remained constant. After an optimum was attained, this value was maintained constant, and then the optimum of the next variable was determined.

3. Results and discussion

3.1. Characterization of the crude roselle oil

The crude roselle oil used in this study was clear, viscous, and yellow in color, without having undergone any further refining for use as a biodiesel feedstock. Its properties were determined to ascertain suitability for biodiesel production and to determine a suitable production process for this feedstock. The predominant fatty acids in the oil and its various important properties are shown in Table 1.

The fatty acid composition of the oil plays a significant role when biodiesel is used as fuel in diesel engine [12]. Saturated fatty acid esters have higher cetane values and oxidation stability but poorer low temperature flow properties than those of unsaturated ones [15,22]. The crude roselle oil consisted of a high proportion of unsaturation, comprised primarily of oleic and linoleic acids and a lower proportion of saturation, comprised mainly of palmitic acid. In this study, the average molecular weight of the oil, from its composition, was calculated to be 854.1 g.

As in most other vegetable oils, the viscosity of the crude roselle oil was very high compared to diesel (about 11.8 times higher). To avoid any negative impacts on diesel engine performance, the viscosity had to be reduced to an acceptable level; therefore, alkali-catalyzed transesterification was performed. Several researchers have established that free fatty acid (FFA) and moisture contents in oils were significant factors affecting alkali-catalyzed transeste-

Table 1
Properties of crude roselle oil.

Property	Method	Crude roselle oil
Fatty acid composition (%)[a]	AOAC (2005),	
(i) Palmitic acid (C16:0)	963.22, 969.33	18.15
(ii) Stearic acid (C18:0)		4.09
(iii) Oleic acid (C18:1)		33.31
(iv) Linoleic acid (C18:2)		38.17
(v) Linolenic acid (C18:3)		2.09
Density at 15 °C, kg/m^3	ASTM D 4052-96	919.9
Free fatty acid content (as linoleic acid), % w/w	AOAC (2000), 940.28	0.67
Kinematic viscosity at 40 °C, mm^2/s	ASTM D 445-06	36.35
Water content, % w/w	AOAC (1990), 984.20	0.087

[a] Other fatty acids (myristic, arachidic, behenic, lignoceric, palmitoleic, and erucic acids) were presented in amounts of <1%.

rification [2,9,23]. The oil should have a low FFA content, and all materials used in the reaction should be substantially anhydrous [2]. Reports in the literature indicate that the FFA content in the oil should be less than 1% prior to alkali-catalyzed transesterification [13,14]. The oil used in this study had an FFA content below 1% and contained minute traces of water. Therefore, this oil had suitable characteristics to be used as a feedstock to produce biodiesel by a one-step process, alkali-catalyzed transesterification.

3.2. Alkali-catalyzed transesterification

3.2.1. Effects of methanol-to-oil molar ratio and reaction time

One important variable affecting the transesterification reaction was the methanol-to-oil molar ratio [2,3,14,23]. In determining the optimum, the alkali-catalyzed transesterification was carried out at various ratios (4:1, 6:1, 8:1, and 10:1) and reaction times (5, 20, 40, 60, and 80 min) to obtain a methyl ester content within the acceptable level of the Thai biodiesel (B100) specification (96.5% w/w). The operation conditions were fixed at a catalyst concentration of 1.5% w/w of oil and a reaction temperature of 60 °C. The data for methyl ester contents versus time at different methanol-to-oil molar ratios are shown in Fig. 1.

Theoretically, the stoichiometric ratio for transesterification reaction requires one mole of triglyceride and three moles of alcohol to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, since this reaction is in fact reversible [2], a higher molar ratio is required in order to drive the equilibrium to the right for achieving a greater alkyl ester product. Fig. 1 indicates that the alkali-catalyzed transesterification of the crude roselle oil proceeded quite fast (within 5 min) and the reaction rates accelerated with increased methanol-to-oil molar ratios, results similar to those noted by other researchers [3]. As noted, the reaction could occur at a methanol-to-oil molar ratio of 4:1, but the longer time was required to obtain higher methyl ester content. The production of roselle methyl esters reached the maximum value (99.4% w/w) at a methanol-to-oil molar ratio of 8:1 in 60 min, which is a value higher than the minimums of the Thai biodiesel (B100) and EN 14214:2008 (E) specifications. Although the methanol-to-oil molar ratio of 10:1 provided higher methyl ester content in shorter time, this molar ratio should be avoided for economic reasons; thus, a methanol-to-oil molar ratio of 8:1 was selected as being optimum.

In an industrial application, the excess methanol in glycerin and biodiesel phases can be recovered using distillation equipment, and recycled back into the process to minimize both operating costs and adverse environmental impacts.

3.2.2. Effects of catalyst concentration and reaction time

Because the presence of a catalyst accelerates the transesterification reaction [2], another important variable that affects the conversion of a triglyceride to its ester is the catalyst concentration. Several researchers have reported that it was not possible to convert *Cynara cardunculus* L. oil to its methyl ester by transesterification without the catalyst (0% NaOH) [11]. In this study, the alkali-catalyzed transesterification was carried out at different catalyst concentrations (0.25, 0.5, 1.0, 1.5, and 2.0% w/w of oil) and different reaction times (5, 20, 40, 60, and 80 min). The methanol-to-oil molar ratio and reaction temperature were fixed at 8:1 and 60 °C, respectively. The methyl ester contents versus time are plotted at different catalyst concentrations, as shown in Fig. 2.

As was expected, a further increase of catalyst concentration increased the methyl ester formation rate, which was in accordance with the results found by other researchers [3,11].

At the lowest catalyst concentration, 0.25% w/w of oil, the reaction was the slowest, being insufficient to catalyze the reaction to completion. The maximum methyl ester content (99.4% w/w) was obtained at a catalyst concentration of 1.5% w/w of oil in 60 min, and was higher than the minimums of the Thai biodiesel (B100) and EN 14214:2008 (E) specifications. It was noted that when the catalyst concentration was increased from 1.5 to 2% w/w of oil, the methyl ester content dropped from that of 1.5% w/w of oil, results which confirm those observed by other researchers [3,11]. This was due to the addition of a high amount of alkaline catalyst, causing the formation of soap which increased the viscosity of the reactants, thereby reducing the methyl ester content [3]. Therefore, a catalyst concentration of 1.5% w/w of oil provided the best results and was considered to be the optimum.

3.2.3. Effects of reaction temperature and reaction time

In this study, the effects of reaction temperature and reaction time on the alkali-catalyzed transesterification of crude roselle oil were investigated. Literature data shows that reaction temperature has an important role in alkali-catalyzed transesterification [3,11,23], and that this reaction could be carried out at a low temperature, such as 25 °C [11] and 32 °C [23]. In the actual study, the reactions were carried out at different temperatures (32, 40, 50, and 60 °C) and with various times (5, 20, 40, 60, and 80 min). In all these experiments, a methanol-to-oil molar ratio and a catalyst concentration of 8:1 and 1.5% w/w of oil, respectively, were used. Fig. 3 shows the methyl ester contents versus time plotted at different reaction temperatures. The results show that reaction temperature had a positive influence on alkali-catalyzed transesterification of the oil; that is to say, the rate of methyl ester formation increased with each increasing reaction temperature. (These results are in line with results obtained by other researchers [3,11,23].) The reaction could take place at room temperature (32 °C); however, the reaction was incomplete even after 80 min. Most likely, this was due to the high viscosity of the oil at lower temperature, causing problems in stirring [7], and which resulted in the poor mixing between the oil and potassium hydroxide-methanol phases. It was found that the reaction proceeded most satisfactorily at a reaction temperature of 60 °C, whereby after 60 min, the methyl ester content attained was 99.4% w/w, a value higher than the minimum specifications of Thai biodiesel (B100) and EN 14214:2008 (E). Thus, the reaction temperature of 60 °C was selected as the optimum.

Therefore, the optimum condition for alkali-catalyzed transesterification of the crude roselle oil was a methanol-to-oil molar ratio of 8:1, a catalyst concentration of 1.5% w/w of oil, a reaction temperature of 60 °C, and a reaction time of 60 min. Under these conditions was achieved a methyl ester content of 99.4% w/w. (The chromatogram of the resultant biodiesel is shown in Fig. 4.)
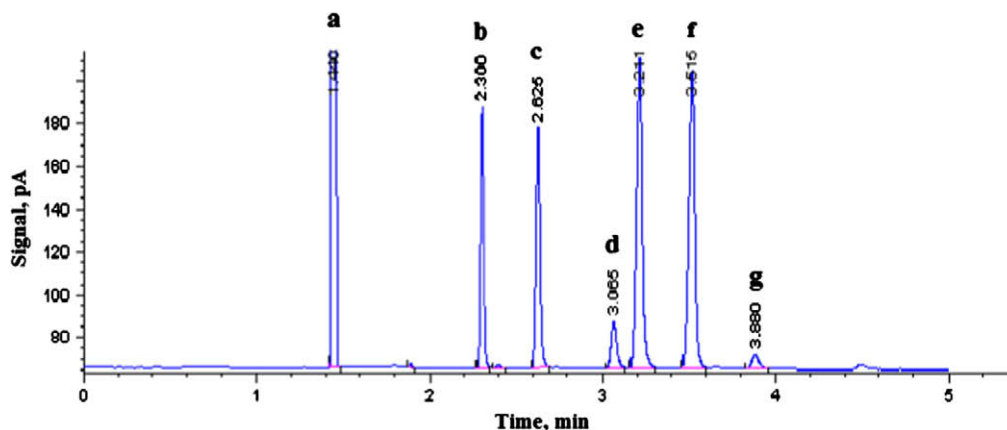
Fig. 4. Chromatogram of roselle biodiesel: (a) n-heptane; (b) methyl palmitate; (c) methyl heptadecanoate (used as internal standard); (d) methyl stearate; (e) methyl oleate; (f) methyl linoleate and (g) methyl linolenate.

3.3. Properties of the roselle biodiesel

Since the quality of any proposed new biodiesel fuel is essential for the performance and emission characteristics of diesel engines, it is necessary that it undergo testing with standard methods. Thus, the roselle biodiesel produced at the optimum condition was sent to the Quality Control Division of Petroleum Authority of Thailand Public Company Limited for quality testing. The results as compared with those of the Thai Biodiesel (B100) specifications and international standards EN 14214:2008 (E) and ASTM D 6751-07b are shown in Table 2.

The results show that alkali-catalyzed transesterification reduced the viscosity of the crude oil from a value of 36.35 to 4.588 mm^2/s (approximately one-eighth of initial value), and was closer to that of diesel (3.068 mm^2/s). The pour point of biodiesel is one of the important properties that reflect its cold weather performance [2,12], and the test results showed that the roselle biodiesel could indeed be used as a fuel in cold-weather conditions.

Also, the flash point of the biodiesel was higher than that of diesel (67.5 °C); and as the blending of even a small percentage of biodiesel with diesel can increase its flash point [5,15], roselle biodiesel or a roselle biodiesel–diesel mixture, compared to pure diesel, would be safer to store and transport. In transesterification, monoglycerides and diglycerides are the intermediates in this reaction; and their presence, along with triglycerides, in biodiesel cause engine performance problems such as fuel filter plugging, which adversely affect the fuel properties [2]. The test results showed that only trace amounts of monoglycerides and diglycerides were detected. These values, along with the high content of methyl ester and 0% triglycerides, indicate the completeness of alkali-catalyzed transesterification of the crude oil at the optimum condition, and did not cause engine problems. Considering the low free glycerol content, it was confirmed that the glycerol removal in the production process had been successfully accomplished. In addition, the other measured properties of the biodiesel also met the quality requirements according to the Thai biodiesel (B100) specifications

Table 2
Properties of roselle biodiesel in comparison with Thai biodiesel (B100) specifications, EN 14214:2008 (E), and ASTM D 6751-07b.

Property	Method	Roselle biodiesel	Biodiesel specification		
			Thai specification	ASTM D 6751-07b	EN 14214:2008 (E)
Viscosity at 40 °C, mm^2/s	ASTM D 445-06	4.588	3.50–5.00	1.9–6.0	–
Flash point, °C	ASTM D 93-02a	>130	Min. 120	Min. 130	–
Sulfur content, w/w	ASTM D 5453-06	0.00021	Max. 0.001	Max. 0.0015	–
Carbon residue, % w/w (on 10% distillation residue)	ASTM D 4530-00	0.84	Max. 0.30	Max. 0.050	–
Sulfated ash content, % w/w	ASTM D 874-00	<0.005	Max. 0.020	Max. 0.020	–
Water and sediment, % volume	ASTM D 2709-96	<0.005	Max. 0.20	Max. 0.050	–
Copper strip corrosion (3 h at 50 °C)	ASTM D 130-94	1a	Max. No. 1	Max. No. 3	–
Acid number, mg KOH/g	ASTM D 664-01	0.43	Max. 0.50	Max. 0.50	–
Phosphorous content, % w/w	ASTM D 4951-02	Nil	Max. 0.001	Max. 0.001	–
Oxidation stability, 110 °C, hours	EN 14112	2.58	Min. 6.0	Min. 3.0	Min. 6.0
FAME content, % w/w	EN 14103	99.4	Min. 96.5	–	Min. 96.5
Water content, mg/kg	EN ISO 12937	450	Max. 500	–	Max. 500
Total contamination, mg/kg	EN 12662	13	Max. 24	–	Max. 24
Iodine value, g iodine/100 g	EN 14111	62	Max. 120	–	Max. 120
Linolenic acid methyl ester, % w/w	EN 14103	2.1	Max. 12.0	–	Max. 12.0
MeOH content, % w/w	EN 14110	0.01	Max. 0.20	–	Max. 0.20
Monoglyceride content, % w/w	EN 14105	0.5733	Max. 0.80	–	Max. 0.80
Diglyceride content, % w/w	EN 14105	0.0163	Max. 0.20	–	Max. 0.20
Triglyceride content, % w/w	EN 14105	0	Max. 0.20	–	Max. 0.20
Free glycerol, % w/w	EN 14105	0	Max. 0.02	–	Max. 0.02
Total glycerol, % w/w	EN 14105	0.11	Max. 0.25	–	Max. 0.25
Group I metals (Na + K), ppm	ASTM D 5185-02	2.0	Max 5.0	–	–
Group II metals (Ca + Mg), ppm	ASTM D 5185-02	Nil	Max. 5.0	–	–
Density at 15 °C, kg/m^3	ASTM D 4052-96	880.1	860–900	–	–
Pour point, °C	ASTM D 5950-02	−1	Report	–	–
Gross heat of combustion, MJ/kg	ASTM D 240	39.5	Report	–	–

and the international standards EN 14214:2008 (E) and ASTM D 6751-07b, except for higher carbon residue and lower oxidation stability.

4. Conclusions

This study demonstrates that biodiesel can successfully be produced from crude roselle oil by alkali-catalyzed transesterification with methanol in the presence of a catalyst (KOH). The optimum conditions for production was a methanol-to-oil molar ratio of 8:1, a catalyst concentration of 1.5% w/w of oil, and a reaction temperature and time of 60 °C and 60 min, respectively. (However, at a catalyst concentration higher than 1.5% w/w of oil, the methyl ester content decreased due to soap formation, which was a hindrance for this reaction.) At this optimum, the methyl ester content of the biodiesel attained 99.4% w/w, and all its other measured properties were within the limits prescribed by the Thai biodiesel (B100) specifications and the international standards EN 14214:2008 (E) and ASTM D 6751-07b, except for a resulting higher carbon residue and lower oxidation stability. The results show that all of the reaction variables in this study clearly influenced the alkali-catalyzed transesterification in a positive manner. From all of these encouraging outcomes, and given further testing on diesel engine performance, crude roselle oil could be recommended as a supplementary oil feedstock for biodiesel production in Thailand.

Acknowledgements

References

[1] Speight JG. The chemistry and technology of petroleum. 4th ed. New York: CRC Press Taylor and Francis Group; 2007.

[2] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification – A review. Renewable Sustainable Energy Rev 2006;10(3): 248–68.

[3] Meher LC, Dharmagadda VSS, Naik SN. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. Bioresour Technol 2006;97:1392–7.

[4] Van Gerpen J. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.

[5] Ramadhas AS, Muraleedharan C, Jayaraj S. Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. Renewable Energy 2005;30:1789–800.

[6] Lewis RJ. Sr. Hawley's condensed chemical dictionary. 12th ed. New York: Van Nostrand Reinhold Company; 1993.

[7] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Chem Soc 2000;77(12):1263–7.

[8] Canakci M, Van Gerpen J. Biodiesel production via acid catalysis. Trans ASAE 1999;42(5):1203–10.

[9] Ma F, Hanna MA. Biodiesel production: A review. Bioresour Technol 1999;70: 1–15.

[10] Fukuda H, Kondo A, Noda H. Review biodiesel fuel production by transesterification of oils. J Biosci Bioeng 2001;92(5):405–16.

[11] Encinar JM, González JF, Sabio E, Ramiro MJ. Preparation properties of biodiesel from *Cynara cardunculus* L. Oil. Ind Eng Chem Res 1999;38:2927–31.

[12] Dorado MP, Ballesteros E, López FJ, Mittelbach M. Optimization of alkali-catalyzed transesterification of *Brassica Carinata* oil for biodiesel production. Energy Fuels 2004;18:77–83.

[13] Tiwari AK, Kumar A, Raheman H. Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process. Biomass Bioenergy 2007;31:569–75.

[14] Ghadge SV, Raheman H. Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. Biomass Bioenergy 2005;28:601–5.

[15] Ramadhas AS, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. Fuel 2005;84:335–40.

[16] Chongkhong S, Tongurai C, Chetpattananondh P, Bunyakan C. Biodiesel production by esterification of palm fatty acid distillate. Biomass Bioenergy 2007;31:563–8.

[17] Canoira L, Alcantara R, Garcia-Martinez MJ, Carrasco J. Biodiesel from Jojoba oil-wax: Transesterification with methanol and properties as a fuel. Biomass Bioenergy 2006;30:76–81.

[18] Phuphathanaphong L, Siriruksa P, Nuvongsri G. The genus *Hibiscus* in Thailand. Thai For Bull 1989;18:43–79.

[19] Bown D. The royal horticultural society new encyclopedia of herbs and their uses. London: Dorling Kindersley Limited; 2002.

[20] Ramanvongse S. Production of roselle seed oil and its physical and chemical properties. Bangkok: Applied Scientific Research Corporation of Thailand; 1976.

[21] Vicente G, Martinez M, Aracil J, Esteban A. Kinetics of sunflower oil methanolysis. Ind Eng Chem Res 2005;44:5447–54.

[22] Park JY, Kim DK, Lee JP, Park SC, Kim YJ, Lee JS. Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresour Technol 2008;99:1196–203.

[23] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Chem Soc 1984;61(10):1638–43.