As. J. Energy Env. **2009**, 10(04), 221-229

Asian Journal on Energy and Environment

ISSN 1513-4121

Available online at www.asian-energy-journal.info

Research Article

Biodiesel production from mixtures of vegetable oil and used cooking oil

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This paper was originally presented at the International Conference on the Role of Universities in Hands-On Education, Chiang Mai, Thailand, August 2009.

Abstract

In this study the production of biodiesel from three mixtures of vegetable oil and used cooking oil by alkali-catalyzed transesterification was investigated. Three kinds of vegetable oils, including jatropha, roselle and coconut oils were tested. The effect of used cooking oil content in oil feedstock (used cooking oil/vegetable oil ratios of 0.03-0.2 v/v) on methyl ester formation was investigated and optimized. The methyl ester content from each reaction condition was determined by gas chromatography (GC). The optimum used cooking oil/vegetable oil ratio was 0.03 v/v for all three kinds of oil feedstock. At this ratio, the methyl ester content of three kinds of biodiesel were higher than the minimum limit set for Thai biodiesel (B100) specification. The measured properties of three biodiesel products were within the limit prescribed by Thai standards, except for the lower viscosity of biodiesel produced from coconut-used cooking oil mixture. However, it was very close to that of Thai petroleum diesel.

Keywords: transport fuels, transesterification, methyl ester content, used cooking oil/vegetable oil ratio, Thailand

Introduction

Currently, biodiesel is becoming popular as a more environment friendly fuel. It has been used as a substitute for diesel fuel in the automotive industry, commonly known as No. 2 diesel. The advantage of this bio-fuel over the conventional diesel fuel includes high cetane numbers, low smoke and particulates, low carbon monoxide and hydrocarbon emissions, it is biodegradable and non-toxic [1].

According to the American Society for Testing and Materials (ASTM) definition, biodiesel is monoalkyl esters of long chain fatty acids derived from a renewable feedstock, such as vegetable oils, animal fats and used cooking oils [2]. Biodiesel can be produced by several processes, but the most common one is by transesterification, using an acid or alkaline catalyst. Alkaline catalyzation is preferred, because the reaction is rapid and thorough. This process occurs at a relatively low temperature and pressure when compared to those of other processes. Since transesterification is an equilibrium-controlled reaction, an excess of alcohol is used to shift the equilibrium forward as shown in Figure 1. Methanol is the most often preferred alcohol because of its low cost compared to other alcohols. As a result, the operating cost as well as the capital cost of this process is reduced.

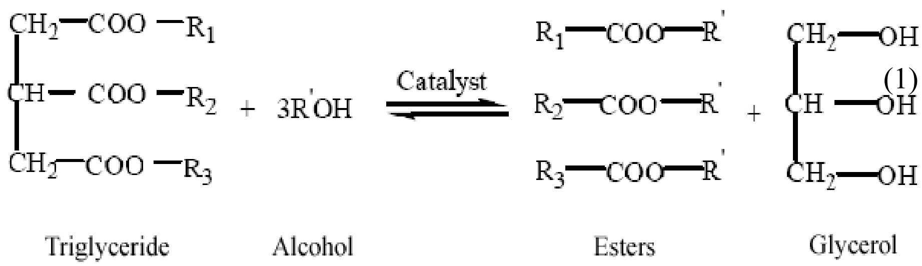

Figure 1. Transesterification of triglycerides.

During the past 20 years, many researchers explored different types of raw materials, including both new oils and used cooking oils, for the production of biodiesel. It was found that high purity methyl ester can be obtained by carrying out transesterification of fresh oils with methanol in the presence of an alkaline catalyst. However, the main disadvantage of this fuel is the considerably high cost of the feedstock, which leads to the high price of the biodiesel product [3]. In more recent years, attempts to utilize used cooking oil as a feedstock for biodiesel production have been made to overcome both the economic and environmental problems.

However, when used cooking oils are employed as a feedstock, more severe transesterification conditions are required as compared to those of the normal process utilizing new oils. This is attributed to the fact that properties of the used oils are different from those of refined and crude oils. As the result of the high temperature during cooking and the water from the food, triglycerides in the oils are hydrolyzed and this gives rise to an increase in free fatty acid (FFA) content [1]. The FFA content is one of the important factors for alkali-catalyzed transesterification. This is due to the FFAs reacting with the alkaline catalyst to produce soap, which inhibits the reaction and this results in the reduction of biodiesel yield [5, 6]. Nevertheless, some researchers [4, 7, 8] have pointed out that the alkali-catalyzed transesterification could be completed as long as the FFA content in the oil is not greater than 1% and all materials should be substantially anhydrous. While the mild conditions were applied to waste frying oil, the methyl ester content less than 95% w/w was obtained [4]. Recently, reports in the literature showed that satisfactory results were obtained when the mixture of canola oil and used cooking oil was used as feedstock for biodiesel production [3].

To date, the most common biodiesel feedstock in Thailand is palm oil. However, there are also several oil-producing plants which can be cultivated in this country and also potentially utilized as feedstock for biodiesel production. These include jatropha, roselle and coconut. In addition, quantities of used cooking oil are produced from restaurants and households.

These used cooking oils are often reused several times and disposed of in an inappropriate way. In this regard, the use of a combination of new vegetable oils, such as jatropha, roselle and coconut oils and used cooking oil as the feedstock for biodiesel production is of interest and has yet to be explored.

The purpose of this research is to investigate the effect of used cooking oil content in oil feedstocks on methyl ester formation and the optimum ratio of used cooking oil and the new vegetable oils which are used as feedstock for alkali-catalyzed transesterification under the same optimum conditions of the new vegetable oils. These blended feedstocks will be an alternative source of lower-cost biodiesel for future use.

Methodology

Materials

The roselle oil and coconut oil were obtained from Payakkaram Temple and Sangsook Industry Company Limited, respectively. The jatropha oil was mechanically extracted from seed using a screw press and then settled until impurities were precipitated. The used cooking oil was purchased from a local restaurant in Bangkok. All chemicals used in the experiments such as methanol, sodium and potassium hydroxides and n-heptane were of analytical reagent (AR) grade. The methyl esters such as methyl heptadecanoate, methyl esters of lauric, myristic, palmitic, stearic, oleic and linoleic acids were standard for GC.

Alkali-catalyzed transesterification

The alkali-catalyzed transesterification of three mixtures of vegetable oil and used cooking oil was carried out in a laboratory-scale setup. A 250 ml three-necked flat-bottom flask was used as a reactor. Two of the three necks were equipped with a condenser and thermometer, whereas the other was used as an inlet for the reactants. The mixture in the reactor was heated and well-stirred at the same speed for all experiments by hotplate with a magnetic stirrer.

The oil feedstock, methanol and alkaline catalysts were used in amounts established for each experiment. The vegetable oil and used cooking oil were charged into the reactor and heated to the desired temperature. The solution of alkaline catalyst in methanol was prepared freshly in order to avoid moisture absorbance and to maintain the catalytic activity [5, 6]. The methanolic solution was then gradually added to the preheated oil feedstock. The measurement of time was started at this point. Heating and stirring were continued at atmospheric pressure. After the reaction, the product was allowed to settle overnight under gravity in the separating funnel where it was separated into two layers. The upper layer consisted of methyl esters, residual methanol and catalyst, and impurities, whereas the lower layer contained a mixture of glycerol, excess of methanol, catalyst and impurities. The glycerin layer was drawn off and the methyl ester layer was then washed gently with hot distilled water at 60°C until washing water had a pH value that was similar to that of distilled water. The wet biodiesel was then dried at 70°C under reduced pressure by rotary evaporator. Finally, the methyl ester content in the biodiesel product was determined by GC. The reaction conditions for the three kinds of feedstock are shown in Table 1. The optimum blending ratio was considered from the methyl ester content based on the Thai biodiesel (B100) specification (minimum 96.5% w).

Table 1. Reaction conditions for biodiesel production from three mixtures of vegetable oil and used cooking oil.

Oil feedstock	Type of catalyst	Catalyst concentration	Reaction temperature	Reaction time
Jatropha-used cooking oil	NaOH	1% w/w of oil	60°C	40 min
Roselle-used cooking oil	KOH	1.5% w/w of oil	60°C	60 min
Coconut-used cooking oil	KOH	1.5% w/v 0f oil	60°C	60 min

Analytical methods
Methyl ester content

- Jatropha-used cooking oil and roselle-used cooking oil mixtures as feedstock.

The methyl ester content of biodiesel produced from the jatropha- used cooking oil and roselle-used cooking oil mixtures was determined by standard test method EN 14103.

- Coconut-used cooking oil mixture as feedstock.

The methyl ester content of biodiesel produced from the coconut-used cooking oil mixture was determined by GC technique. The GC of Agilent 6890N was equipped with a flame ionization detector and a capillary column of crosslinked polyethylene glycol (HP-INNOWax, 25 m x 0.20 mm x 0.2 µm). The GC oven was kept at 200°C for 5 min. The carrier gas was helium at a flow rate of 0.5 ml/min. The analysis was carried out by injecting 1 µl of sample solution into GC. The n-heptane was used as solvent for preparing the sample solution. The produced methyl esters were identified by comparing retention time to the retention time of standard methyl ester of FFAs and the methyl ester content was determined by using methyl heptadecanoate as the internal standard.

Properties of oil feedstock and biodiesel
The properties of oil feedstock and biodiesel products were determined by standard test methods as follows:

- Fatty acid composition AOAC (2000), 963.22, 969.33
- Free fatty acid content AOAC (2000), 940.28
- Density ASTM D 4052-96
- Kinematic viscosity ASTM D 445-06
- Water content AOAC (1990) 984.20 (for oil feedstock), EN 12937 (for biodiesel products) Flash point ASTM D 93-02a
- Total acid number ASTM D 664-01.

Results and Discussion

Characterization of oil feedstock
The used cooking oil was palm oil. The oil feedstocks, including jatropha, roselle, coconut and used cooking oils were clear and viscous. The three vegetable oils were yellow, whereas the used cooking oil was brown. The fatty acid composition and important properties of these oil feedstocks are shown in Table 2.

Table 2. Properties of oil feedstocks.

Property	Jatropha oil	Roselle oil	Coconut oil	Used cooking oil
Fatty acid composition (%) [a]				
(i) Caprylic acid (C8:0)			3.35	
(ii) Capric acid (C10:0)			3.21	
(iii) Lauric acid (C12:0)			32.72	
(iv) Myristic acid (C14:0)			18.38	1.0 [b]
(v) Palmitic acid (C16:0)	13.77	18.15	13.13	42.8 [b]
(vi) Stearic acid (C18:0)	6.77	4.09	3.60	4.5 [b]
(vii) Oleic acid (C18:1)	41.68	33.31	12.88	40.5 [b]
(viii) Linoleic acid (C18:2)	35.55	38.18	4.35	10.1 [b]
(ix) Linolenic acid (C18:3)		2.09		
Density at 15°C, kg/m^3	918.7	919.9	914.4	920.8
Kinematic viscosity at 40°C, mm^2/s	34.84	36.35	27.52	38.40
Free fatty acid content %w	0.52 (as oleic acid)	0.67 (as linoleic acid)	0.6 (as lauric acid)	1.897 (as palmitic acid)
Water content, %w	0.125	0.087	0.0146	0.5077

[a] Other fatty acids were present in amounts of < 1%.
[b] Ref. [9].

The fatty acid composition of oil has an important role in the performance of biodiesel in diesel engines. Saturation fatty acid methyl esters increase the cloud point, cetane number, and improve stability whereas more polyunsaturation reduces the cloud point, cetane number and stability [10, 11]. In addition, the fatty acid composition was important for the determination of methyl ester content in the biodiesel product. The result showed that the viscosity of oil feedstocks were higher than the average viscosity of Thai petroleum diesel (3.068 mm^2/s) for several times. The high viscosity of these oils leads to many problems after they are directly used in diesel engines [5, 12]. The reduction in viscosity leads to improved atomization, fuel vaporization and combustion [13]. In order to reduce the viscosity to an acceptable level, these oils had to be converted to biodiesel. It was observed that the used cooking oil had higher FFA and water content than that of the three vegetable oils. In addition, the FFA content was also higher than the limit required for alkali-catalyzed transesterification. Thus, this pure used cooking oil was not suitable to be the starting material in the alkali-catalyzed transesterification.

Alkali-catalyzed transesterification

In this present study, the effect of used cooking oil content in oil feedstock on the methyl ester formation was investigated and optimized. The alkali-catalyzed transesterification of three mixtures of vegetable oil and used cooking oil was carried out at different used cooking oil/vegetable oil ratios (0.03, 0.05, 1.00, 1.50 and 2.00 v/v). The averages of methyl ester content at different blending ratios are shown in Table 3.

Table 3. Variation of methyl ester content with used cooking oil/vegetable oil ratio.

Used cooking oil/ vegetable oil ratio (v/v)	Methyl ester content (% w)		
	Jatropha-used cooking oil biodiesel	Roselle-used cooking oil biodiesel	Coconut-used cooking oil biodiesel
0.03	96.8	97.2	97.5
0.05	95.9	95.5	95.3
0.10	95.1	92.6	92.5
0.15	92.6	91.5	89.7
0.20	88.7	89.0	87.1

The results showed that increasing the used cooking oil content in oil feedstock decreased the methyl ester content. This indicated that the used cooking oil content had a negative effect on methyl ester formation. This same trend was observed for all three kinds of oil feedstock. It was due to further increasing the used cooking oil content resulting in an increase of FFA and water content in the oil feedstock. During the reaction, the presence of heat and water accelerated the hydrolysis of triglycerides and resulted in the increase of FFA content in oil feedstock [14]. These FFAs led to the formation of soap which caused an increase in viscosity of the reactants and interfered with separation of glycerol from the methyl ester layer [5, 6]. This ultimately resulted in the decrease of methyl ester content in each biodiesel product.

It was found that a used cooking oil/vegetable oil ratio of 0.03 v/v was the only one which provided the methyl ester content higher than the limit of Thai standard for all three kinds of oil feedstock. Thus, used cooking oil/vegetable oil ratio of 0.03 v/v was selected to be the optimum blending ratio for biodiesel production from these three mixtures oil feedstock. The GC chromatograms of the three biodiesels produced from the mixtures of vegetable oil (jatropha or roselle or coconut oil) and used cooking oil are shown in Figs. 2-4.

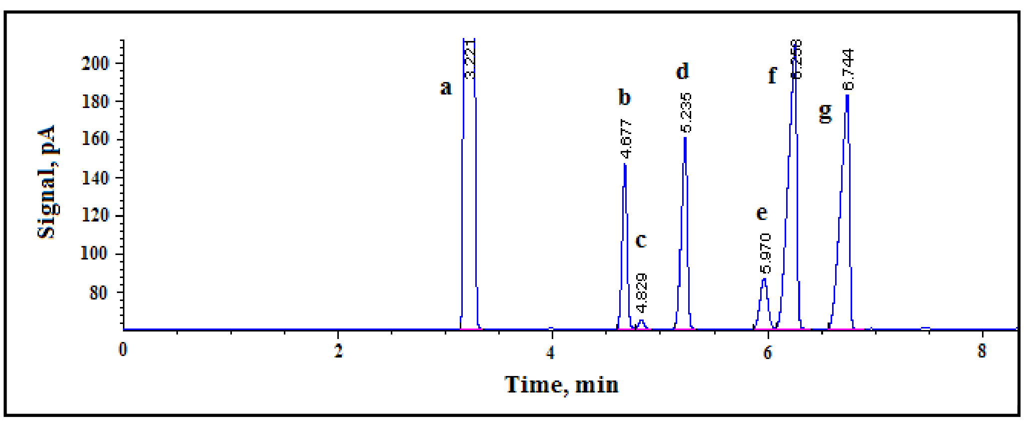

Figure 2. Chromatogram of jatropha-used cooking oil biodiesel.
(a) n-heptane, (b) methyl palmitate, (c) methyl palmitoleate, (d) methyl heptadecanoate; internal standard, (e) methyl stearate, (f) methyl oleate, (g) methyl linoleate.

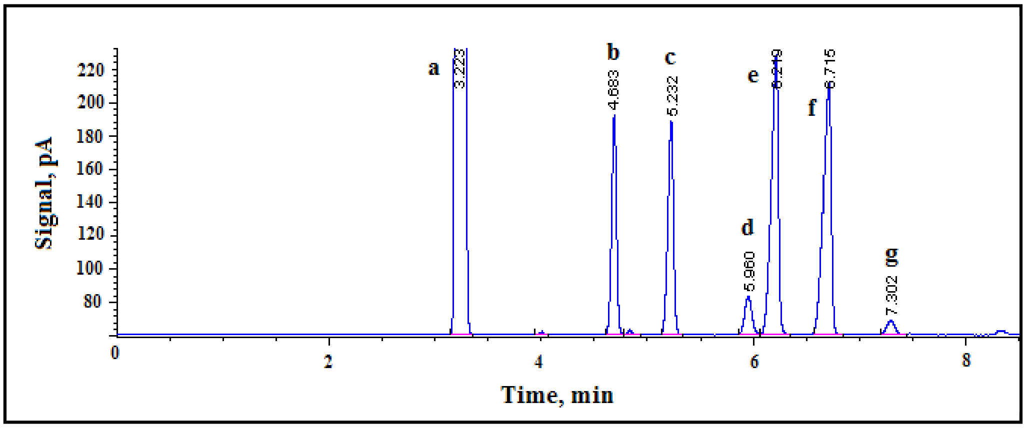

Figure 3. Chromatogram of roselle-used cooking oil biodiesel.
(a) n-heptane, (b) methyl palmitate, (c) methyl heptadecanoate (used as internal standard), (d) methyl stearate, (e) methyl oleate, (f) methyl linoleate, (g) methyl linolenate.

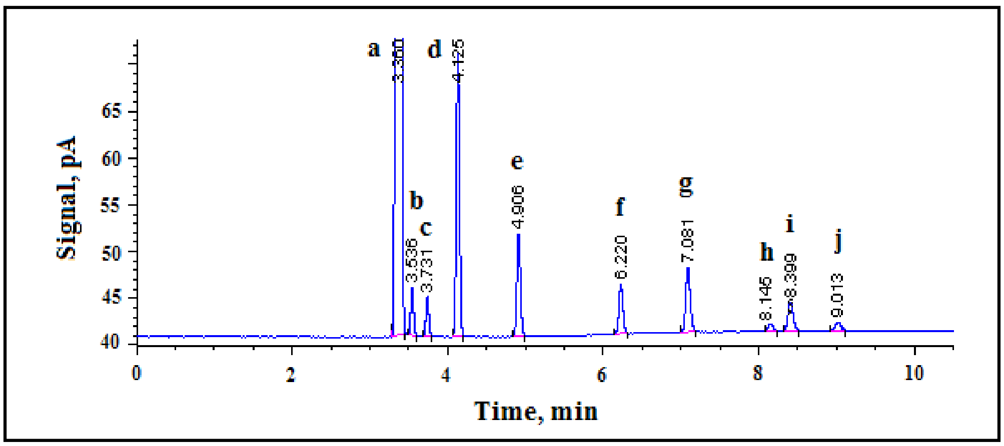

Figure 4. Chromatogram of coconut-used cooking oil biodiesel.
(a) n-heptane, (b) methyl caprylate, (c) methyl caprate, (d) methyl laurate, (e) methyl myristate, (f) methyl palmitate, (g) methyl heptadecanoate, (h) methyl stearate, (i) methyl oleate, (j) methyl linoleate.

Although in a laboratory-scale experiment this optimum blending ratio seems to consume only a small amount of used cooking oil, in actual industrial application this ratio would lead to the large scale consumption of used cooking oil for biodiesel production.

Properties of biodiesels

The biodiesels produced from the mixtures of vegetable oil (jatropha or roselle or coconut oil) and used cooking oil at the optimum blending ratio were sent to the Quality Control Division of PTT Public Company Limited to determine their properties by using standard test methods. The results in comparison with the Thai biodiesel (B100) specification are shown in Table 4. The results showed that the three biodiesels obtained had the measured properties within the limits prescribed by Thai standards, except the lower viscosity of biodiesel produced from coconut-used cooking oil mixture. However, it was closer to that of

Thai petroleum diesel than the other two biodiesels. This was due to coconut triglyceride consisting of 57.5% short chain fatty acids, comprised mainly of lauric acid containing 12 carbon atoms, whereas the jatropha and roselle triglycerides consisted mainly of long chain fatty acids containing 18 carbon atoms. Hence, biodiesel produced from coconut-used cooking oil mixture contained a high proportion of low molecular weight methyl esters, especially of methyl laurate, whereas the two other kinds of biodiesel contained chiefly high molecular weight methyl esters, especially methyl oleate and methyl linoleate. This resulted in the lower viscosity of biodiesel produced from coconut-used cooking oil mixture as compared with the two other kinds of biodiesel.

Table 4. Measured properties of biodiesel products in comparison with Thai biodiesel (B100) specification.

Property	Limit	Biodiesel		
		Jatropha-used cooking oil	Roselle-used cooking oil	Coconut-used cooking oil
Kinematic viscosity at 40°C, mm^2/s	3.5-5	4.307	4.549	3.057
Flash point, °C	min 120	> 120	> 120	> 120
Total acid number, mg KOH/g	Max 0.5	0.18	0.31	0.28

Conclusion

This study revealed that biodiesel could be produced successfully from the mixtures of vegetable oil (jatropha or roselle or coconut oil) and used cooking oil by alkali-catalyzed transesterification. The used cooking oil content in oil feedstock had a negative effect on methyl ester formation. The biodiesel products having methyl ester content higher than the minimum limit for Thai biodiesel (B100) specification were produced at the optimum used cooking oil/vegetable oil ratio of 0.03 v/v for three kinds of oil feedstock. Therefore, these mixtures of vegetable oil and used cooking oil can be recommended as the supplementary oil feedstock for biodiesel production if engine performance tests provide satisfactory results. This will result in the reduction of biodiesel production costs, as well as the negative environmental impacts.

Acknowledgements

The authors would like to thank Payakkaram Temple and Sangsook Industry Company Limited, for providing roselle and coconut oils for biodiesel production, respectively, the Agricultural Engineering Research Institute, Department of Agriculture, which performed the extraction of jatropha oil and the Quality Control Division of PTT Public Company Limited, which performed the standard test to determine the biodiesel properties. Finally, the authors express their gratitude to Rajamangala University of Technology Krungthep for the financial support.

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