Synthesis of biodiesel from Irvingiamalayana seed oil

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ABSTRACT

Because of the increasing of fossil oil prices, reducing petroleum reserves and the environmental concern of emission gases from fossil fueled engines, biodiesel has been used as a renewable energy source in recent years. In this research, the study of synthesis biodiesel from *Irvingiamalayana* seed oil (Krabok oil) by transesterification reaction with methanol and potassium hydroxide as catalyst were investigated. The parameters that effects on transesterification reaction consist of the ratio of methanol and krabok oil, the concentration of catalyst, reaction temperature and reaction time were studies. The preliminary results shown that the optimum conditions for the synthesis biodiesel from Krabok oil by transesterification reaction were the mole ratio of methanol and krabok oil 8:1, the concentration of catalyst 1%, reaction temperature of 60 °C and reaction time of 120 minutes. The content of methyl ester of Krabok biodiesel was determined by gas chromatography (GC) to be 98% under the optimum condition. The obtained biodiesel was then tested for its fuel properties. The result showed the feasibility of Krabok oil as a new suitable raw material for biodiesel preparation.

Keywords:Biodiesel,*Irvingiamalayana* seed oil, Transesterification reaction

Introduction

The attractive solution of biodiesel as a renewable transportation fuel in Thailand was increasing because it can be compensated fossil oil and produced from vegetable oils and fats that low cost. The advantages of biodiesel are its portability, ready availability, higher combustion efficiency, lower sulfur content, renewability and higher biodegradability[1].Biodiesel fuel can be produced by transesterification reaction of substantially any triglyceride feedstock. This consists of oil-bearing crops, animal fats, and algal lipids. Transesterification reaction can convert the triglycerides into smaller hydrocarbon. The alcohol catalyst mixtures with low molecular weight of alcohol such as methanol and ethanolwereadded into the reaction. For cost reasons, methanol is the alcohol most frequently used for triglyceride transesterification. Nevertheless, other alcohols arealso used.Various type of catalyst (acid, bases or enzyme) can be used in this reaction. However, transesterification reaction with homogeneous base catalysts requires a shorter reaction time and lower cost compared with enzyme catalysts[2].The reaction products are a mixture of desires esters, mono and diglycerides, glycerol, water and catalyst. Biodiesel is composed of mixture of fatty acid alkyl esters. The transesterification reaction using methyl alcohol is fatty acid methyl ester(FAME) which is called biodiesel [3].

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Various types of vegetable oil can be used for preparation of biodiesel such as soybean, rice bran, coconut, rapeseed, jatropha and sunflower [4,5]. The use of vegetable oil and triglyceride feedstock for biodiesel production depends on regional availability and economics.

*Irvingiamalayana*is a local tree that produced not only in north region but also in northeast region of Thailand. The Thai name of this tree is Krabok or Ka-bok.It is botanically classified in the family of *Irvingiamalayana*. Krabok tree produces a popular and inexpensive wood that can be used for made furniture. The nutritional value and physicochemical properties of Krabok fruit was evaluated by Sonwai[6]. The most important part of nut seems to be oil. The fatty acid composition of Krabok nut was found to contain primarily saturated fatty acids such as lauric acid and myristic acids. Therefore, the production of biodiesel fromThaiKrabokseed oilis very interesting research.

To our knowledge, no investigations have been conducted to optimize the parameters of transesterification reaction for biodiesel production from*Irvingiamalayana* seed oil. In this study, the synthesis biodiesel from Krabokseed oil by transesterification reaction was conducted. The parameters that effect on the content of fatty acid methyl ester including the ratio of methanol and Krabok oil, the concentration of catalyst, reaction temperature and reaction time are discuss

Materials and Methods

The *Irvingiamalayana* (Krabok) seed samples were taken from local market at Pitsanulok province in north region of Thailand. Reagents for biodiesel synthesis were methanol (99.8%, Ajax Chemical Co. Ltd.). FAME standard solution (Sulpelco FAME Mix 37 comp.) which contains 37 fatty acid methyl ester such as methyl myritate, methylpalmitate, methyl stearate, oleic methyl ester and methyl behenate was used for GC analysis. Methyl heptadecanoate was used as internal standard material for GC analysis. All reagents that used in reaction were analytical reagent grade.

The Krabokoilwas prepared by solvent extraction. Firstly, the seed were clean and sent to the de-hulling to remove the hulls from the kernel. The kernel of all samples were crushed and milled into fine particle. The small pieces of Krabok seed was extracted using hexane as a solvent. The compositions of fatty acid in Krabok oil were determined using gas chromatography. The extracted Krabok oil that used as raw material for biodiesel production was finally stored in the dark bottle until use.

In this work, we investigated the influence of each factor on transesterification to optimize the reaction condition. Methanol to oil molar ratio, potassium hydroxide concentration, reaction temperature and reaction time were each considered as single factor. Four levels of methanol to triglyceride molar ratio (4:1, 6:1, 8:1, 10:1), four levels of potassium hydroxide concentration base on the weight of Krabok oil (0.5, 1.0, 1.5, 2.0), three level of reaction temperature (40, 50, 60 ^{o}C) and four level of reaction time(60, 90, 120, 180 minute) were chosen as variables. The transesterification reaction was conducted in 250 ml glass batch reactor, placed in a thermostatic water bath, using magnetic stirring at 500 rpm. The mixture was stirred at the same rate in all run. The excess amount of methanol in the product was recovered by rotary funnel and left overnight for phase separation into two layers. The upper oil layer was crude biodiesel that was collected and washed with warm deionized water (55-60 ^{o}C). Excess water in products was recovered by heated at 120^{o}C for 4 hours. The Krabok biodiesel was filtered. The content of fatty acid methyl ester in product was analyzed by gas chromatography (GC) using EN14103 method.

GC analysis for fatty acid methyl ester of Krabok biodiesel was performed using Agilent 6890N gas chromatography with capillary column (HP-INNoWax) 30 m x 0.32 mm inner diameter(ID) x 0.25 um film thickness, equipped with a flam ionization detector(FID) and Agilent7683 Autosampler. The initial temperature program was 50 ^{o}C with 2 min hold, then raised to 200 ^{o}C at 20 V/min with 10 min hold. Final temperature was 280 ^{o}C at 5 ^{o}C/min with 2 min hold. The carrier gas was nitrogen, and fatty acid analysis was performed by injection of 1 μL of each sample. The run time for a single sample was 38.5 min. Additionally, the Krabok biodiesel that obtained from optimum condition was analyzed the percent methyl ester byquality analysis department (PTT public company limited) in order to certify the result of Krabok biodiesel.

Parameters	Level			
	1	2	3	4
Methanol to triglyceride molar ratio	4:1	6:1	8:1	10:1
Potassium hydroxide amount (wt %)	0.5	1.0	1.5	2.0
Reaction temperature (^{o}C)	40	50	60	
Reaction time (minute)	30	60	120	180

Results and Discussions

Krabok oil characteristic

The characterization of Krabok oil that used as starting raw material for biodiesel production is important because vegetable oil properties influence the biodiesel properties significantly. The physicochemical characteristic of Krabok oil was shown in Table 1.The major fatty acid compositions ofKrabok oil were capric, lauric, myristic, palmiticand oleic. There are a significant proportion of short chain fatty acids, such as C10, C12 and C14, compare to other oils typically used for biodiesel production such as rapeseed soybean and sunflower oil. These short-chain acids were converted in to ester and introduced complications during the biodiesel production process[7].

Table 1 Physicochemical properties of Krabok oil

Characteristic	
Free fatty acid (% as oleic acid)	0.9
Saponification value	243
Iodine value	8.3
Fatty acid composition (wt%)	
Capric acid (C10:0)	1.7
Lauric acid (C12:0)	41.7
Myristicacid(C14:0)	54.6
Palmitic acid (C16:0)	1.4
Oleic acid (C18:2)	0.6

Table 2 Parameters and levels of experimental design scheme for transesterification reaction

Optimum parameter for biodiesel synthesis from Krabok oil

For the transesterification reaction of Krabok oil, we investigated several operating conditions: molar ratio of methanol to Krabokoil, catalyst concentration, reaction temperature and reaction time

Molar ratio of methanol to Krabokoil

The most important factor of alkali-catalyzed transesterification was the molar ratio of alcohol and oil. An excess of methanol is required in order to drive the reaction towards completion because transesterification is a reversible reaction. The stoichiometry of this reaction require 3 mol of alcohol/ 1 mol of triglyceride to produce 3 mol of FAME and 1 mol of glycerol[8].The increase in molar ratio of methanol will result in high biodiesel yield. In this experiment, four different molar ratioswerestudies. The methanol to Krabok oil ratio was varied within the range of 4:1 to 10:1 with a reaction temperature of 60 ^{O}C and 1%KOH on the basis of oil weight as catalyst for 60 min. The maximum fatty acid methyl ester was found at the methanol to oil molar ratio of 8:1. As shown in Fig. 1, with increase in methanol to Krabok oil molar ratio, the content of methylester was increase and reached a maximum at the methanol to oil ratio of 8:1. However, the furtherincrease in molar ratio beyond 8:1 resulted in a small decrease inthe percent of methyl ester. The yield remains the same with further increase in the methanol to Krabok oil molar ratio.

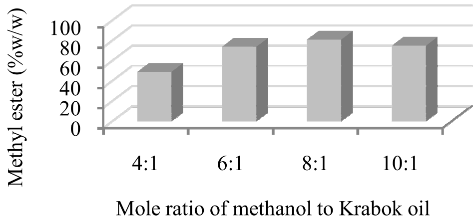

Figure 1 Effect of mole ratio of methanol to Krabok oil on fatty acid methyl ester. Experimental conditions: reaction temperature:60 ^{O}C; potassium hydroxide content: 1 wt%; reaction time: 60 min.; mixing speed: 500 rpm.

Catalyst concentration

Transesterification reaction of Krabok oil was performed using potassium hydroxide as catalyst. Potassium hydroxide has an advantage because it can serve as a fertilizer. Because potassium hydroxide can be convert into product which can serve as a fertilizer. Sine KOH is more economical than sodium hydroxide, it is the preferred choice for large-scale FAME production process[4,8]. The effect of potassium hydroxide content was studied in the range of 0.5 to 2% by weight. Figure 2 shows the influence of the amount of potassium hydroxide on biodiesel yield. The content of fatty acid methyl ester was quite low for small quantities of potassium hydroxide. The amount of potassium hydroxide depends on the amount of free fatty acid content. In this work, the optimum catalyst concentration of potassium hydroxide was 1 %. As shown in Figure 2, the content of fatty acid methyl ester was enhanced by increasing KOH concentration. Additionally, it was observed that the yield of biodiesel started to decline when the catalyst concentration was increased above 1.0%. There was a gradual increase in the content of methyl ester from 89 to 97 as the catalyst loading increased from 0.5 to 2 wt.%. However, the biodiesel from the reaction slightly increase with further increase in catalyst loading higher than 1wt.%. Therefore, the catalyst concentration of 1% was chosen for subsequent experiment.

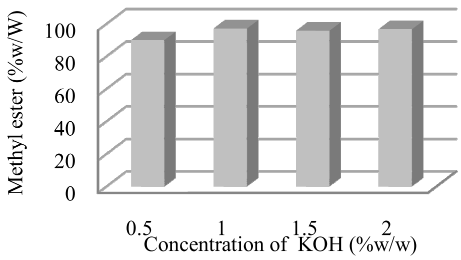

Figure 2 Effect of potassium hydroxide content on fatty acid methyl ester .Experimental conditions: reaction temperature:60 ^{O}C; reaction time: 2 h; methanol to Krabok oil mole ratio: 8:1; mixing speed: 500 rpm.

Reaction temperature

The effect of temperature on Krabok oil transesterification reaction was investigate at 40, 50 and 60 ^{O}C using potassium hydroxide concentration of 1 %(w/w) and molar ratio of methanol to oil of 8:1. As illustrated in Figure 3, the content of methyl ester was44, 70, and 95% at 40, 50 and 60 ^{O}Crespectively. The reaction temperature strongly affected the content of methyl ester. In general, transesterification reaction is performed near the boiling point of the alcohol at atmospheric pressure. Further increase in temperature is reported to have a negative effect on the content of methyl ester[9]. In this work, the optimum temperature was 60°C because the maximum content of methyl ester was observed.

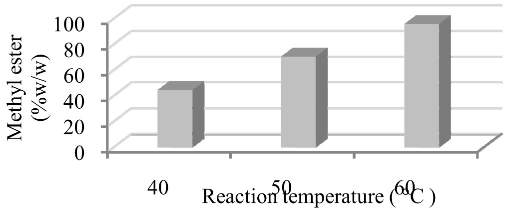

Figure 3 Effect of reaction temperature on fatty acid methyl ester .Experimental conditions: methanol to Krabok oil mole ratio: 8:1; potassium hydroxide content: 1%wt; mixing speed: 500 rpm; reaction time 120min.

Reaction time

Reaction time was significant operating parameters which are closely related to the energy costs of biodiesel production process. Different researchers have reported different reaction time for transesterification process[3].The effect of reaction time on the transesterification of Krabok oil at catalyst concentration of 2%, molar ratio of 8:1and 60°C were determined. In this work, the reaction times were determined at 30, 60, 120 and 180 minutes. The result shown that within 60 min, the reaction was rapid.The content of fatty acid methyl ester was enhanced by increasing the reaction time.However, it was observed that no significant increase in the content of methyl ester was observed with prolongation of the reaction beyond 120 minute. Therefore, the optimum reaction time in this study was 120minutes. Under optimum condition, the content of methyl ester in this study correlates well with the certificate of analysis byquality analysis department (PTT public company limited).

The physical and chemical properties of Krabok biodiesel were determined by standard method. The results were compared with those of Thai Biodiesel specification that shown in Table 3. It was found that Krabok biodiesel had some fuel properties correlated with Thai biodiesel specification.

Table 3 Properties of Krabok biodiesel in comparison with Thai biodiesel specification

Test item	Method	Limit	Result in this work
Density at 15 °C, kg/m^3	ASTM D 4052-96	860-900	871.7
Kinematic viscosity at 40°C, mm^2/s	ASTM D 445-06	3.5-5.0	3.753
Total acid number, mg KOH/g	ASTM D 664-01	Max.0.5	0.25
Water content, %wt	EN ISO12937	Report	0.03

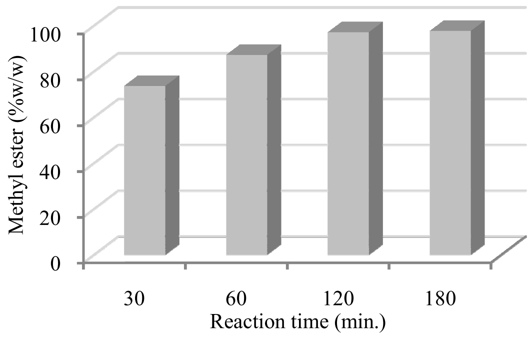

Figure 4 Effect reaction time on fatty acid methyl ester .Experimental conditions: reaction temperature:60 °C; methanol to Krabok oil mole ratio: 8:1; potassium hydroxide content: 1%wt; mixing speed: 500 rpm

Conclusion

This paper illustrated a new raw material and methods for sustainable biodiesel production from*Irvingiamalayana* seed oil. The synthesis of biodiesel fromKrabok oil by transesterification reaction with methanol and potassium hydroxide as catalyst was carried out. The experimental parameters that effect on the content of fatty acid methyl ester were investigated. Optimum parameters were 8:1 methanol to Krabok oil mole ratio, 1 wt. % of potassium hydroxide, 2 hours of reaction time, with mixing speed 500 rpm in this experiment range. Under optimum conditions, Krabok oil was converted into biodiesel with fatty acid methyl ester content reaching 98% which correlate the certificate of analysis from quality analysis department, PTT public company limited.Some fuel properties of Krabok biodiesel are agreement with Thai biodiesel specification. The result showed the feasibility of Krabok oil as a new suitable raw material for biodiesel production.

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