

## Biodiesel Production from Unrefined *Krating (Calophyllum Inophyllum)* Seed Oil Using Supercritical Methanol

Chuenkwan Tipachan<sup>1</sup>, Tanawan Pinnarat<sup>2</sup>  
and Somjai Kajorncheappunngam<sup>1\*</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Khon Kean University, Khon Kaen 40002, Thailand

<sup>2</sup>Department of Chemical Engineering, King Mongkut's Institute of Technology, Ladkrabang, Bangkok 10520, Thailand

\*Corresponding author. E-mail: [ksomja@kku.ac.th](mailto:ksomja@kku.ac.th)

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### ABSTRACT

*This study investigated the feasibility of biodiesel production from unrefined Krating (Calophyllum inophyllum) seed oil using supercritical methanol transesterification reaction. The experiments were conducted under various conditions of reaction temperature (200, 240, 260, 300, and 350°C), pressure (8, 12, 14, 16, and 18 MPa), and oil-to-methanol molar ratio (1:20, 1:40, and 1:60). All reactions were run at a constant reaction time of 10 minutes. Results showed that oil-to-methanol molar ratio, temperature, pressure, and their interactions significantly affected fatty acid methyl ester (FAME) yield. The highest FAME yield of 90.4% by weight was achieved at 260°C, 16 MPa, and an oil-to-methanol molar ratio of 1:40. This study also showed a significant decrease in acid value of Krating seed oil from 29 mg to 0.3 mg KOH per gram of oil compared to its biodiesel product. Moreover, most physical properties (kinematic viscosity, density, iodine number, flash point and water content) of our biodiesel product were comparable to the standard biodiesel EN14214.*

**Keywords:** Biodiesel, Transesterification, *Calophyllum inophyllum*, *Krating* seed oil, Supercritical methanol

### INTRODUCTION

Biodiesel is a renewable fuel that can serve as an alternative to petro-diesel. It is not only renewable and environmentally friendly, but also biodegradable (Demirbas, 2009). In the early period of biodiesel production, many edible plant oils, such as palm, soybean, sunflower, and rice bran oils, were used as raw materials, or feedstock (Georgogiannia et al., 2008; Kasim et al., 2009; Biktashev et al., 2011; Carrillo and Medina, 2011). However, as edible vegetable oils are expensive (Rizwanul Fattah et al., 2014), attention has turned to finding non-edible vegetable oils to replace them.

This study investigated using *Calophyllum inophyllum*, a non-edible vegetable oil native to East Africa and abundant in Thailand, where it is known as *Krating* seed oil. The seeds, when dried, yield substantial amounts of oil – roughly 18 kg per 100 kg of dried seeds (Venkana and Reddy, 2009). However, the high kinematic viscosity (74.5 mm<sup>2</sup>/s) and high acidity (29 mgKOH/g of oil) of *Krating* seed oil make it unsuitable as biodiesel raw material using conventional methods.

Conventional production of biodiesel using a transesterification reaction has generally utilized a homogeneous base, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), as a catalyst. However, this method is unsuitable with vegetable oils containing high amounts of free fatty acid (FFA) or high acid value and water. These impurities can react with the base catalyst, resulting in a saponification reaction that lowers the yield. The reaction byproduct, or soap, causes emulsification that makes it difficult to separate the biodiesel product, the result of which is low quality biodiesel (Marulanda et al., 2010). Acid catalysts, such as sulfuric acid, have been used with high FFA raw materials. However, if there is water in the feedstock, it will consume the catalysts, which leads to low biodiesel yield (Lotero et al., 2005). Using a supercritical fluid process solves this problem. It is a non-catalytic reaction, whereby the vegetable oil reacts with supercritical alcohol to produce biodiesel. Saka and Kusdiana (2001) found that biodiesel production from rapeseed oil using supercritical methanol produced 95% methyl ester within 4 min (rapid reaction) with no side reactions or unwanted products, despite the presence of high free fatty acid (high acid value) and water in the feedstock.

This study investigated the effects of temperature, pressure, and oil-to-methanol molar ratio on the production of biodiesel. The fatty acid methyl ester (FAME) content of the resultant biodiesel was analyzed using a gas chromatography-mass spectrometer (GC-MS). The properties of the biodiesel, including viscosity, density, heating value, and acid value, were determined and compared with standard biodiesel.

## MATERIALS AND METHODS

### Materials

*Krating* seeds were collected from Khon Kaen Province, Thailand. Crude *Krating* seed oil was obtained by using a hydraulic pressing. Methanol (99.9% purity) was purchased from Carlo Erba Reagent Co. (Italy).

### Methods

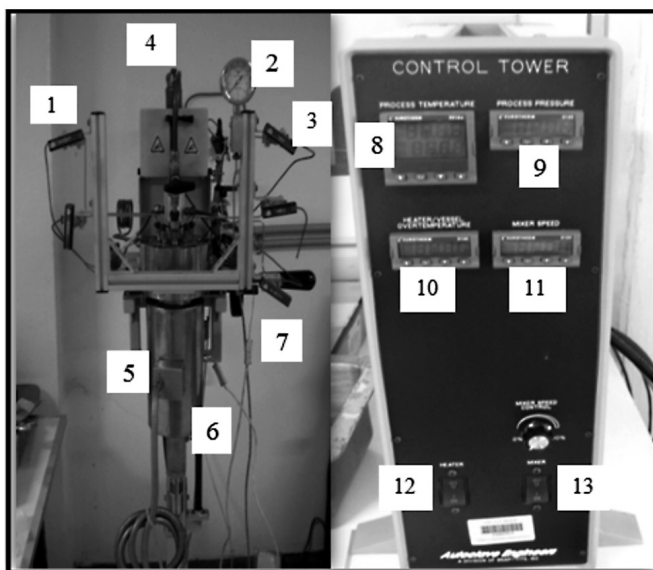
**Preparation of *Krating* seed oil.** The kernels of dried *Krating* seeds were squeezed in a hydraulic press to extract oil; every one kg of kernels produced approximately 0.5 liters of oil. The oil was filtered with a thin cloth to separate the solid particles and residues. This study used the unrefined filtered oil, which is dark green, as the reactant to produce biodiesel.

**Production of biodiesel.** The biodiesel was produced using the supercritical methanol method in an 800 cm<sup>3</sup> high pressure stainless steel reactor, with a maximum working volume of 500 cm<sup>3</sup> (Figure 1). The reaction conditions of temperature (from 200 to 350°C), pressure (8 to 18 MPa), and oil-to-methanol molar ratios (1:20 to 1:60) were varied in 27 different combinations at a constant reaction time of 10 min, as shown in Table 1.

**Table 1.** Experimental reaction conditions for producing biodiesel using supercritical methanol at a constant reaction time of 10 min.

Run	Oil: methanol (molar)	Temperature (°C)	Pressure (MPa)	Run	Oil: methanol (molar)	Temperature (°C)	Pressure (MPa)
1	1:20	200	16	16	1:20	260	8
2	1:20	240	16	17	1:20	260	12
3	1:20	260	16	18	1:20	260	14
4	1:20	300	16	19	1:20	260	18
5	1:20	350	16	20	1:40	260	8
6	1:40	200	16	21	1:40	260	12
7	1:40	240	16	22	1:40	260	14
8	1:40	260	16	23	1:40	260	18
9	1:40	300	16	24	1:60	260	8
10	1:40	350	16	25	1:60	260	12
11	1:60	200	16	26	1:60	260	14
12	1:60	240	16	27	1:60	260	18
13	1:60	260	16				
14	1:60	300	16				
15	1:60	350	16				

First, 100 g of unrefined *Krating* oil were mixed with liquid methanol according to the selected molar ratios. The oil-methanol mixture was then loaded into the reactor. After charging, the reactor was purged with nitrogen gas and closed. The desired reaction temperature and pressure were set on the controller. Both the reaction temperature and pressure inside the reactor can be monitored in real time on the control panel. Then the heater was switched on to start the reaction. The oil-methanol mixture was stirred at a constant rate of 250 rpm in all experiments. The reaction time was measured from when the reactor reached the targeted temperature and pressure. After 10 minutes of reaction, the reactor was depressurized and cooled to room temperature with cold water. The obtained product was then poured into a separating funnel (for 30 min) to separate the biodiesel layer from the glycerol layer. The resultant biodiesel product was loaded into a rotary evaporator at 40°C for 30 min to remove any excess un-reacted methanol. The biodiesel samples were subsequently analyzed for FAME content and other properties against standard biodiesel.



**Figure 1.** Experimental device for biodiesel production using supercritical methanol.

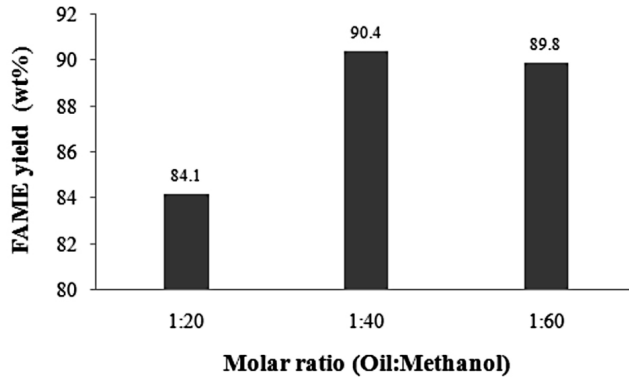
Descriptions: 1.) Gas inlet, 2.) Pressure gauge, 3.) Gas outlet, 4.) Mixing stirrer, 5.) High pressure reactor, 6.) Jacket, 7.) Thermocouple, 8.) Process temperature, 9.) Process pressure, 10.) Vessel temperature, 11.) Mixing speed, 12.) Heater ON-OFF switch, and 13.) Mixer ON-OFF switch.

**Analysis.** The *Krating* seed oil feedstock and the resulting biodiesel product were analyzed for their acid values by titration with potassium hydroxide solution based on ASTM D664, water content based on EN ISO 12937, iodine number based on EN14111, and saponification value based on AOCs official method Cd-3b-76. The heating value was analyzed according to ASTM D240, density according to ASTM D4052, kinematic viscosity according to ASTM D445, and flash point according to ASTM D93. Fatty acid methyl ester percentage (%FAME) of biodiesel product was analyzed with a gas chromatography-mass spectrometer (GCMS-QP2610, Shimadzu, Japan) based on EN 14103.

## RESULTS

### Effect of oil-to-methanol molar ratios

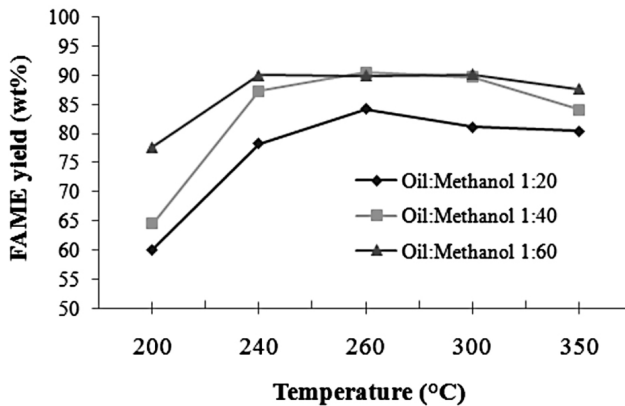
Figure 2 shows the plot of the FAME yield of the biodiesel versus the oil-to-methanol ratio. An increase in the oil-to-methanol molar ratio from 1:20 to 1:40 increased the FAME yield from 84.1 to 90.4 wt%. The FAME yield percentage dropped slightly with a further increase to 1:60.



**Figure 2.** Correlations between FAME yield percentage and oil-to-methanol molar ratios at 260°C, 16 MPa, and 10 min.

**Effect of temperature**

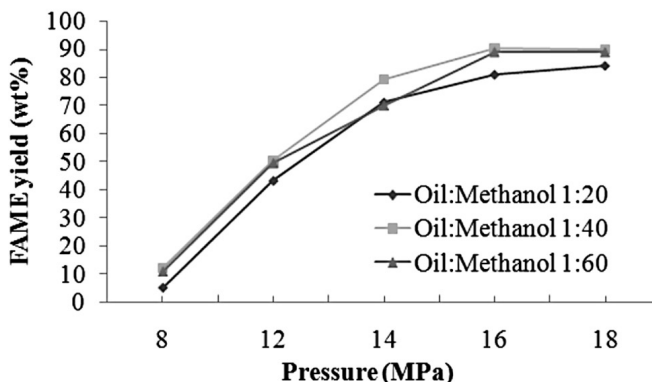
The FAME yield trend plotted against temperature was similar over all three oil-to-methanol molar ratios, increasing from 200 to 240°C, then stabilizing or falling off slightly as the temperature was further increased to 350°C (Figure 3).



**Figure 3.** Correlations between FAME yield percentage and temperature at various oil-to-methanol molar ratios, all at 16 MPa and a reaction time of 10 min.

**Effect of pressure**

Using a constant temperature of 260°C, the temperature that maximized biodiesel yield, we tested five pressure levels: 8, 12, 14, 16, and 18 MPa. As the reaction pressure increased from 8 to 16 MPa, FAME yield steadily increased; the yield leveled off with a further increase to 18 MPa (Figure 4). This behavior was observed in all three oil-to-methanol molar ratios.



**Figure 4.** Correlations between FAME yield percentage and pressure at various oil-to-methanol molar ratios, all at 260°C and a reaction time of 10 min.

### Analysis of *Krating* seed oil properties and its biodiesel product

The properties of crude *Krating* seed oil and its biodiesel product produced at the optimal condition (16 MPa, 260°C, oil-to-methanol ratio 1:40, and 10 min of reaction time) were compared to biodiesel standards (Table 2). Acid value, water content, and kinematic viscosity of *Krating* seed oil decreased after transesterification in supercritical methanol. The highest percentage of methyl ester is 90.4.

**Table 2.** Comparison of *Krating* seed oil, produced biodiesel, and biodiesel standard.

Properties	Krating seed oil	Produced biodiesel	Biodiesel standard (EN 14214)		Method
			Min	Max	
Acid value (mgKOH/g)	29	0.3	-	0.5	ASTM D664
Saponification value (mgKOH/g)	220.2	195.0	-	-	AOCS Cd-3b-76
Iodine Number (mgI <sub>2</sub> /100g of oil)	98.0	110	-	120	EN 14111
Kinematic Viscosity @ 40°C (mm <sup>2</sup> /s)	74.5	3.5	3.5	5.0	ASTM D445
Heating value (J/g)	37,857	38,453	36,550	-	ASTM D240
Density value @15°C (kg/m <sup>3</sup> )	887	921	860	900	ASTM D4052
Flash point (°C)	-	122	101	-	ASTM D93
Water content (wt%)	2.5	0.05	-	0.05	EN ISO12937
Methyl ester (wt%)	-	90.4	96.5	-	EN14103

## DISCUSSION

This study investigated the potential of using inedible *Krating* seed oil as a feasible alternative to produce biodiesel using a supercritical methanol process. We varied three main variables: oil-to-methanol molar ratio, temperature, and pressure, to determine the optimal production condition.

Increasing the oil-to-methanol molar ratio from 1:20 to 1:40 increased the FAME yield from 84.1 to 90.4 wt% (Figure 2). This phenomenon can be explained by the fact that at a higher molar ratio, more methanol molecules could surround and interact with the molecules of *Krating* seed oil, thereby resulting in a better reaction. This finding is consistent with Demirbas (2002), who conducted a study on cottonseed oil transesterification using supercritical methanol and found that increasing the oil-to-methanol molar ratio from 1:1 to 1:40 at 240°C increased the methyl ester content from 39 to 98%. Our lower yield (90.4%) might be due to the fact that *Krating* seed oil has more saturated fatty acids than cotton seed oil, thereby lowering the reaction rate. However, an additional increase in the ratio to 1:60 led to a slight drop in FAME yield, as the additional methanol likely diluted the reactant, resulting in less product. Another possibility is that excess methanol beyond the optimal amount is dissolved into both the biodiesel and glycerol layers during the separation process, obstructing the separation of biodiesel from glycerol; with incomplete separation, the methyl ester percentage decreases. The optimal molar ratio of oil-to-methanol of 1:40 was in good agreement with previous research on the synthesis of biodiesel using supercritical methanol from various kinds of feedstock, such as rapeseed oil, linseed oil, castor oil, and *Jatropha* oil (Rathore and Madras, 2007; Varma and Madras, 2007; Kusdiana and Saka, 2001).

The temperature effect from 200 to 260°C tended to increase the methyl ester percentage for all oil-to-methanol molar ratios. A sharp increase in biodiesel yield was observed when the temperature increased from the subcritical temperature of 200°C to 240°C, a supercritical condition; the critical temperature and pressure for methanol are 239.5°C and 8 MPa, respectively. At higher temperature, the molecules of the substances in this study possessed more kinetic energy, so collisions occurred more frequently, resulting in increased interaction. This is in line with Saka and Kusdiana (2001), who stated that while methanol is in the supercritical state, its capacity to dissolve is close to that of a fluid and its ability to diffuse is close to a gas, hence a better interaction. A similar trend was observed for biodiesel production using supercritical methanol from other vegetable oils, such as rapeseed oil, linseed oil, palm oil, and sunflower oil (Kusdiana and Saka, 2001; Madras et al., 2004; Rathore and Madras, 2007; Varma and Madras, 2007).

At even higher temperatures (300-350°C), the produced biodiesel turned viscous and black, suggesting that thermal decomposition of FAMEs occurred. The same results were observed during the supercritical methanolysis of linseed oil, safflower oil (Imahara et al., 2008), and soybean oil (Quesada-Medina and Olivares-Carrillo, 2011) at temperatures over 300°C.

Increasing the pressure increased in the FAME percentage in all three different oil-to-methanol molar ratios, as shown in Figure 4. This was probably due to the fact that under the supercritical condition, the viscosity of methanol is low and their diffusion coefficients are close to those of gas, enabling thorough diffusion. Methanol molecules could diffuse and penetrate well into the oil structure. With an increase in pressure, supercritical methanol became denser, with more mass for reaction to proceed, and hence higher FAME yield. The effect of reaction pressure on FAME yield followed the same trend as reaction temperature, but it was more pronounced (Figures 3 and 4).

Almost all of the properties of the biodiesel produced from crude *Krating* seed oil using supercritical methanol in this study were within the biodiesel standards, except methyl ester, which showed a slightly lower value (90.4 wt%) than that of standard biodiesel (96.5 wt%) (Table 2).

Based on experimental results, This study has validated the possibility of producing biodiesel from crude *Krating* seed oil that possesses the characteristics required by the EN 14214 standard. The optimal condition to produce biodiesel using a supercritical methanol process was at 260°C, 16 MPa, 1:40 oil-to-methanol ratio, and a reaction time of 10 min; this optimum yielded methyl ester yield of 90.4 wt%. Reaction pressure affected the methyl ester yield more than reaction temperature. Using supercritical methanol minimized the effect of *Krating* seed oil's high water and acid values, allowing for the production of biodiesel of acceptable quality without the need for pretreating the crude *Krating* seed oil.

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