



## Partial Hydrogenation of Calophyllum Inophyllum Methyl Esters to Increase the Oxidation Stability

Joelianingsih<sup>1\*</sup>, P. Putra<sup>1</sup>, A.W. Hidayat<sup>1</sup> & R. Fajar<sup>2</sup>

<sup>1</sup>Chemical Engineering Study Program, Institut Teknologi Indonesia  
Jalan Raya Puspiptek, Serpong, Tangerang Selatan 15320, Indonesia

<sup>2</sup>Center for Thermodynamics Motor and Propulsion System, BPP Teknologi,  
Gdg 230 Kawasan Puspiptek Serpong, Tangerang Selatan 15314 Indonesia  
E-mail: joelianingsih@iti.ac.id

**Abstract.** Calophyllum inophyllum methyl esters have a low oxidation stability value (5-6 h) caused by high amounts of polyunsaturated fatty acid methyl esters (FAME), especially methyl linoleate. Partial hydrogenation was done to reduce the number of polyunsaturated FAME to transform them into mono-unsaturated. This was performed at 6 bar and 900 rpm with Pd/Al<sub>2</sub>O<sub>3</sub> solid catalyst in a reactor with a capacity of 1 liter. The research purpose was to learn the effects of reaction temperature (80; 100; 120°C) and time (1; 1.5; 2 h) on the FAME composition. The optimum condition of the experiment was obtained at 120°C for 1 h, with 15.47 h as the oxidation stability value, 17.8°C as the cloud point value, and 51.17 as the cetane number. Under this condition, the methyl linoleate content decreased by 59.89% w/w (from 21.869% to 8.770% w/w) and methyl linoleate hydrogenated into methyl elaidate. Meanwhile, the methyl linolenate content decreased by 85.37% w/w (from 0.205% to 0.030% w/w) and methyl linolenate hydrogenated into methyl linolelaidate. These results show that the research met the following standards: a minimum oxidation stability value of 10 h in accordance with the World Wide Fuel Charter (WWFC) 2009, a maximum cloud point value of 18°C and a minimum cetane number 51 in accordance with SNI 7182-2012. The physical properties values of the Calophyllum inophyllum methyl esters were predicted using the empirical equations.

**Keywords:** *partial hydrogenation; Calophyllum inophyllum methyl esters; oxidation stability; WWFC*

### 1 Introduction

Biodiesel is an alternative fuel for diesel engines that can be produced from renewable feedstocks such as vegetable oil and animal fats. The chemical name of biodiesel is fatty acid methyl esters (FAME). Biodiesel has several distinct advantages compared to petrodiesel in addition to being fully competitive with petrodiesel in most technical aspects. It has low emission of CO<sub>2</sub>, CO, SO<sub>2</sub>, and hydrocarbon gas. Other advantages include a higher cetane number value, biodegradability, non-toxicity, higher flash point (leading to safer handling and

storage) and excellent lubricity. Unfortunately, a prohibitive price for feedstocks coupled with poor low temperature properties, such as pour point and cloud point, and inferior thermo-oxidative stability due to its chemical composition, are important issues that must be overcome in order to increase the viability of biodiesel.

The major practical issue facing biodiesel is its susceptibility to oxidation and autoxidation, mainly because of its unsaturated fatty acid chains and the double bonds in the chains of many fatty compounds. Therefore, oxidation stability is one of the most important characteristics in view of the practical use of FAME. FAME molecules typically have several double bonds and oxidize fairly easily. Initially, the oxidation process generates peroxides (hydrogen peroxide), which subsequently forms acids such as formic acid, acetic acid, propionic acid, and caproic acid. The acid itself also plays a role in the acceleration of oxidation. In the end, the acid reacts with sludge, deposits or other undissolved chemical compounds that accumulate as deposits [1].

There are many standard requirements that must be met by biodiesel, among which Indonesia's SNI 7182-2012, EN 14214 and ASTM D-6751, WWFC (World Wide Fuel Charter) 2009. These standards have different oxidation stability limits, i.e. 6 h, 6 h, 3 h, 10 h for SNI, EN, ASTM, and WWFC respectively. WWFC consists of four major world automotive industry organizations from Japan, the USA and the EU [2]. This means that by meeting the WWFC standard, all other standards will be met. Because of this, our research was focused on meeting the WWFC standard, especially in oxidation stability.

One drawback of biodiesel is that there is an inverse relationship between biodiesel's oxidative stability and its cold flow properties. Saturated compounds are less prone to oxidation than unsaturated compounds but they raise the cloud point of the fuel. Some of the properties of FAME, such as oxidation stability, cetane number and cold flow properties, depend on the natural characteristics of the feedstock. Raw materials (vegetable oils and animal fats) that contain highly saturated fatty acid components have better oxidation stability. On the other hand, the higher saturated fatty acid content in the feedstock, the poorer the cold flow properties. The major problem with a lack of oxidation stability is that it leads to clogging of the engine filter or engine pump, and the fuel eventually deteriorating. In addition to that, using biodiesel in cold weather conditions becomes a serious problem due to the cold flow properties. In order to enhance the utilization of biodiesel, upgrading technologies of biodiesel quality need to be investigated.

*Calophyllum inophyllum L.* is one of the plants that produce a non-edible oil seed that can be used as a source of biodiesel. It can be found in almost all parts of Indonesia, especially in coastal areas. *Calophyllum inophyllum L.* often has more than one name in every country. It is commonly called *bintangur*, *nyamplung* (in Indonesia), Alexandrian laurel, beach mahogany, beauty leaf, oil nut tree (English), *ponyal* (in Bangladesh); *polanga*, *pinnai* (in India); *ponnyet*, *p'hông* (in Myanmar); *bintangor laut*, *penaga laut* (in Malaysia); *tamanu*, *dilo*, *kamani*, *kamanu* (in Hawaii), portia tree, *rekich* (Pacific Islands); *palo maria*, *bitaog* (Filipines); *krathing*, *saraphee naea*, *naowakan* (Thailand); beach calophyllum, *poon* (Papua New Guinea) [3]. Calophyllum inophyllum methyl esters are produced from Calophyllum inophyllum oil seeds. The fatty acid composition of Calophyllum inophyllum oil is shown in Table 1.

**Table 1** Fatty Acid Composition of Calophyllum Inophyllum Oil [4].

No.	Fatty acid	Composition (% w/w)
1.	<b>Saturated fatty acids</b>	
	- Palmitic Acid (C16:0)	14.318
	- Stearic acid (C18:0)	15.097
	<b>Total</b>	<b>29.415</b>
2.	<b>Unsaturated fatty acids</b>	
	- Palmitoleic acid (C16:1)	0.406
	- Oleic acid (C18:1)	35.489
	- Linoleic Acid (C18:2)	33.873
	- Linolenic acid (C18:3)	0.557
	<b>Total</b>	<b>70.325</b>

Calophyllum inophyllum methyl esters as an alternative fuel are stunted by their low oxidation stability value caused by a high number of polyunsaturated FAME, as shown in Table 1. The FAME composition is very important for the properties of biodiesel, especially its polyunsaturated content such as methyl linoleate and methyl linolenate. A higher content means lower oxidation stability, which can reduce the degradation resistance of the biodiesel caused by oxidation. One of the methods to increase the oxidation stability is partial hydrogenation. Partial hydrogenation is a method that uses controlled operation conditions to change polyunsaturated FAME into mono-unsaturated [5], preventing them from becoming saturated. Partial hydrogenation is a kind of reaction of hydrogen (H<sub>2</sub>) molecules with another compound, which is intended to break the double bond contained inside.

Actually, there are two other ways that could be applied to improve the oxidation stability, i.e. antioxidant addition and blending. Antioxidant is a compound that can be used to slow or prevent the oxidation process [6]. In this

case, antioxidant acts as stabilizing agent. However, the addition of antioxidant may change the fuel physical properties [7]. Blending is the method most commonly used. It is a biodiesel treatment that is applied by blending two or more kinds of biodiesel, intended to combine their characteristics that may complement each other.

In addition, several factors, such as temperature, pressure, and stirring speed, also affect the success of partial hydrogenation. Partial hydrogenation has been investigated for *Jatropha* biodiesel [8]. The experiment was conducted at a temperature of 120°C, pressure 4 bars, and the speed of stirring at 1000 rpm with using Pd/C catalyst. The main contents of the FAME in the *Jatropha* biodiesel were methyl oleate (C18:1 *cis* and *trans*) and linoleate (C18:2) which were about 45.39% and 31.98% w/w, respectively. After the partial hydrogenation, the content of the polyunsaturated FAME (methyl linoleate and linolenate) decreased from 32.04% to about 23% w/w. The content of methyl oleate (C18:1 *cis* and *trans*) increased from 45.39% to 51.41% w/w. The fatty acid composition of *Calophyllum inophyllum* and *Jatropha* methyl esters are clearly different. Therefore, it is necessary to study new optimum conditions for *Calophyllum inophyllum* methyl esters with partial hydrogenation reactions.

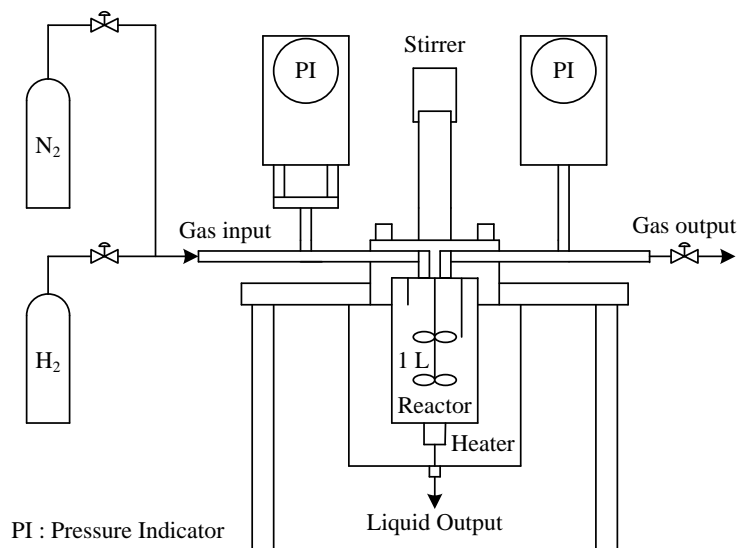
## 2 Experimental Methodology

The experiment was conducted at the Coal Liquefaction Laboratory, Center for Energy Resources Development Technology, Agency for the Assessment and Application of Technology, Puspiptek Serpong Indonesia. The main equipment to conduct the experiment was an autoclave (reactor) made by Kobelco in Japan ( $P_{\max} = 29.42$  MPa,  $T_{\max} = 500^{\circ}\text{C}$  and  $V = 1$  L) as shown in Figure 1.

*Calophyllum inophyllum* methyl esters were bought from domestic suppliers in Purworejo (Indonesia). Its partial hydrogenation was performed at 6 bar and 900 rpm with Pd/Al<sub>2</sub>O<sub>3</sub> solid catalyst in the reactor. The reactor was charged with 300 g of *Calophyllum inophyllum* FAME and 3 g of palladium-alumunim trioxide-supported (Pd/Al<sub>2</sub>O<sub>3</sub>) catalyst. After charging, the reactor was flushed with nitrogen (N<sub>2</sub>) for three times. After the nitrogen flushing, a leak test was performed to find out whether the reactor was in good condition or not. The reaction was carried out with three different temperatures (80; 100; 120°C) and three different reaction times (1; 1.5; 2 h).

The FAME composition of *Calophyllum inophyllum* methyl esters was determined before and after partial hydrogenation by gas chromatograph (GC) equipped with a flame ionization detector and a cyanopropyl methyl silicone column (60 m × 0.25 mm internal diameter and film thickness of 0.25 μm). The carrier gas was helium at 1 mL min<sup>-1</sup>. The oven temperature was initially held at

160°C for 5 minutes and then increased to 220°C at 5°C min<sup>-1</sup>. The GC analysis was conducted at the Integrated Laboratory of Bogor Agricultural University, Indonesia. The properties of *Calophyllum inophyllum* methyl esters were predicted using the empirical equations. The selected equation was simple and had the best accuracy.



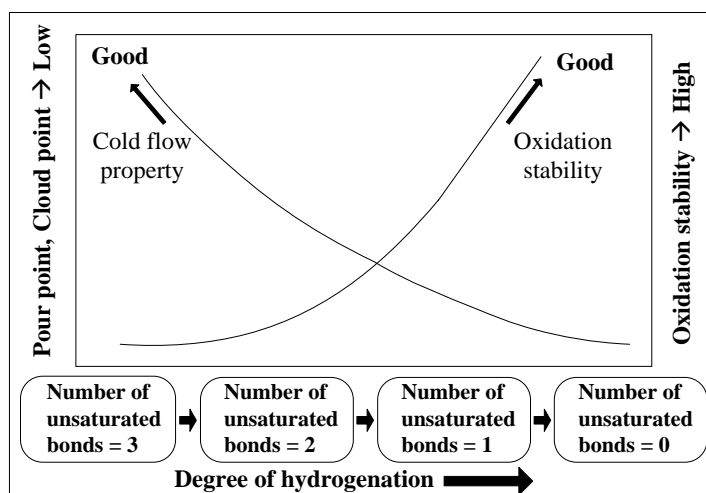
**Figure 1** Schematic of hydrogenation reactor.

This research studied the effects of reaction temperature (80; 100; 120°C) and time (1; 1.5; 2 h) against the *Calophyllum inophyllum* methyl esters quality, especially oxidation stability with a value of at least 10 h. This, to identify the properties as a result of partial hydrogenation in terms of cloud point (CP), pour point (PP), cold filter plugging point (CFPP), viscosity (VC), iodine number (IN) and cetane number (CN). In this research, partial hydrogenation was performed to change polyunsaturated FAME to mono-unsaturated, which have clearly different properties.

### 3 Results and Discussion

Unsaturated bonds (double bonds) contained in fatty acid methyl esters influence their oxidation and thermal stability. In fact, the influence of the number of double bonds on oxidation stability is dramatic. It has been reported that as the number of double bonds increases from 1 to 2 to 3, the oxidation rate increases about 10 times each step. Because of this, the oxidation stability of each type of FAME depends highly on its unsaturated fatty acid composition. Determining the oxidation stability using the Rancimat method showed that the

oxidation stability of the stearic acid methyl ester (C18:0) was higher than 24 h. The oxidation stability of the oleic acid methyl ester (C18:1), linoleic acid methyl ester (C18:2), and linolenic acid methyl ester (18:3) was 3.54, 0.98 and 0.08 h, respectively. Stearic acid methyl ester that did not contain unsaturated bonds showed extremely high oxidation stability. On the other hand, as the number of double bonds increased, the induction time decreased rapidly [1].



Source: EAS-ERIA Biodiesel Fuel Trade Handbook [1].

**Figure 2** Concept for partial hydrogenation of FAME.

As the number of double bonds contained in the fatty acid part of FAME decreases, oxidation stability improves. The cold flow property of FAME, however, deteriorates due to oxidation stability and cold flow property having a tradeoff relationship, as shown in Figure 2. Because of this, when improvement of the oxidation stability of FAME is given a higher priority and the low-temperature flowability is improved with a cold flow improver, the partial hydrogenation technology that converts polyunsaturated FAME produced with the current method to mono-unsaturated molecules, is considered to be a high-quality FAME technology [1].

The approach of high-quality biodiesel production via partial hydrogenation of currently available FAME has merits. It is not necessary to significantly redesign or revise FAME production equipment already in place. By installing a partial-hydrogenation apparatus as supplementary equipment, it is possible to utilize all the current process equipment. The discussion of hydrogenation of Calophyllum inophyllum methyl esters in this study is based on the concept of partial hydrogenation mentioned above.

### 3.1 Effects of Reaction Temperature and Time on the Composition of FAME

The FAME composition of *Calophyllum inophyllum* methyl esters before hydrogenation (CIME) and after hydrogenation (hydrogenated *Calophyllum inophyllum* methyl esters/HCIME) at various reaction times and temperatures, ignoring minor components, is shown in Tables 2, 3 and 4. It changed with the number of chains of carbon 18 (C18), as can be seen in Figure 3.

**Table 2** Fatty Acid Composition of CIME and HCIME at Reaction Temperature 80°C.

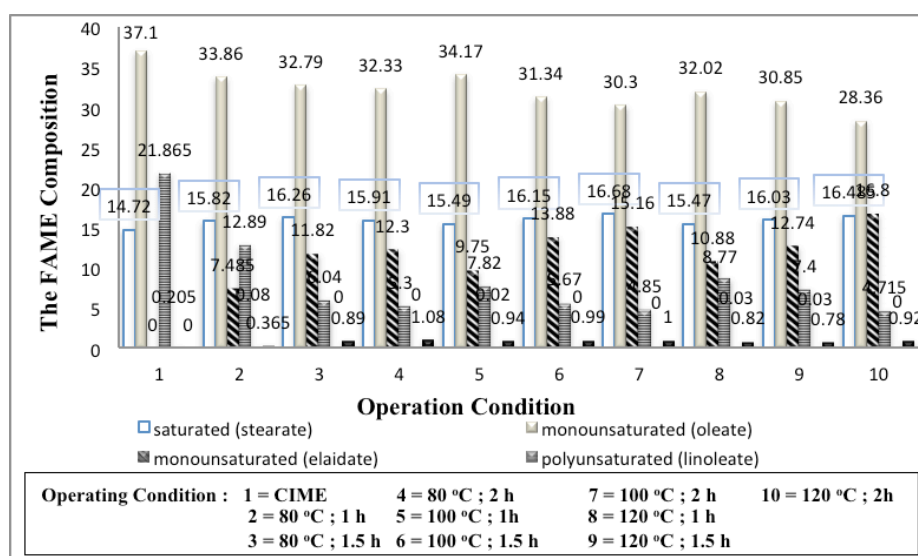
FAME	Composition (% w/w)			
	CIME	HCIME, with reaction time		
		1 h	1.5 h	2 h
Methyl Laurate, C12:0	5.495	5.360	5.360	5.650
Methyl Myristate C14:0	2.105	2.015	2.040	2.040
Methyl Palmitate C16:0	13.935	13.885	14.120	14.000
Methyl Palmitoleate, C16:1	0.270	0.195	0.180	0.160
Methyl Heptadecanoate, C17:0	0.115	0.115	0.120	0.120
Methyl Stearate, C18:0	14.720	15.82	16.260	15.910
Methyl Elaidate C18:1n9t	0	7.485	11.820	12.300
Methyl Oleate, C18:1n9c	37.100	33.860	32.790	32.330
Methyl Linolelaidate C18:2n9t	0	0.365	0.890	1.080
Methyl Linoleate, C18:2n6c	21.865	12.890	6.040	5.300
<b>Percentage of change</b>		<b>(-41.05)</b>	<b>(-72.38)</b>	<b>(-75.76)</b>
Methyl Arachidate, C20:0	0.745	0.730	0.730	0.740
Cis-11- Methyl Eicosenoate, C20:1	0.185	0.135	0.140	0.130
Methyl Linolenate, C18:3n3	0.205	0.080	0	0
<b>Percentage of change</b>		<b>(-60.98)</b>	<b>(-100)</b>	<b>(-100)</b>

**Table 3** Fatty Acid Composition of CIME and HCIME at Reaction Temperature 100°C.

FAME	Composition (% w/w)			
	CIME	HCIME, with reaction time		
		1 h	1.5 h	2 h
Methyl Laurate, C12:0	5.495	5.260	5.360	5.500
Methyl Myristate C14:0	2.105	2.010	2.020	2.050
Methyl Palmitate C16:0	13.935	14.010	14.100	14.180
Methyl Palmitoleate, C16:1	0.270	0.190	0.160	0.160
Methyl Heptadecanoate, C17:0	0.115	0.120	0.120	0.120
Methyl Stearate, C18:0	14.720	15.490	16.150	16.680
Methyl Elaidate C18:1n9t	0	9.750	13.880	15.160
Methyl Oleate, C18:1n9c	37.100	34.170	31.340	30.300
Methyl Linolelaidate C18:2n9t	0	0.940	0.990	1.000
Methyl Linoleate, C18:2n6c	21.865	7.820	5.670	4.850
<b>Percentage of change</b>		<b>(-64.24)</b>	<b>(-74.07)</b>	<b>(-77.82)</b>
Methyl Arachidate, C20:0	0.745	0.740	0.740	0.750
Cis-11- Methyl Eicosenoate, C20:1	0.185	0.130	0.120	0.140
Methyl Linolenate, C18:3n3	0.205	0.020	0	0
<b>Percentage of change</b>		<b>(-90.24)</b>	<b>(-100)</b>	<b>(-100)</b>

**Table 4** Fatty Acid Composition of CIME and HCIME at Reaction Temperature 120°C.

FAME	CIME	Composition (% w/w)		
		HCIME, with reaction time		
		1 h	1.5 h	2 h
Methyl Laurate, C12:0	5.495	5.450	5.660	5.650
Methyl Myristate C14:0	2.105	2.040	2.080	2.105
Methyl Palmitate C16:0	13.935	14.030	14.030	14.145
Methyl Palmitoleate, C16:1	0.270	0.190	0.160	0.140
Methyl Heptadecanoate, C17:0	0.115	0.110	0.110	0.115
Methyl Stearate, C18:0	14.720	15.470	16.030	16.485
Methyl Elaidate C18:1n9t	0	10.880	12.740	16.800
Methyl Oleate, C18:1n9c	37.100	32.020	30.850	28.36
Methyl Linolelaidate C18:2n9t	0	0.820	0.780	0.920
Methyl Linoleate, C18:2n6c	21.865	8.770	7.400	4.715
<b>Percentage of change</b>		<b>(-59.89)</b>	<b>(-66.16)</b>	<b>(-78.44)</b>
Methyl Arachidate, C20:0	0.745	0.720	0.720	0.710
Cis-11- Methyl Eicosenoate, C20:1	0.185	0.120	0.120	0.095
Methyl Linolenate, C18:3n3	0.205	0.030	0.030	0
<b>Percentage of change</b>		<b>(-85.37)</b>	<b>(-85.37)</b>	<b>(-100)</b>

**Figure 3** The FAME composition changing with the number of chains of carbon 18 (C18).

The results of the partial hydrogenation test show that the amount of saturated FAME (methyl palmitate and methyl stearate) relatively increased with the hydrogenation temperature, which was the result of the hydrogenation reaction of methyl palmitoleate and methyl oleate (C18:1 *cis*). The composition of



methyl linoleate (C18:2 *cis*) decreased over reaction time and temperature, which was hydrogenated to methyl elaidate, so the composition of methyl elaidate increased. The same phenomenon also occurred in the methyl linolenate, which was hydrogenated to methyl linolelaidate. Methyl elaidate (C18:1 *trans*) and methyl linolelaidate (C18:2- *trans*) are isomers with an opposite chain double bond (*trans* isomer), usually as the products of partial hydrogenation of naturally unsaturated fats [9].

### 3.2 FAME Composition Effect on Oxidation Stability and Other Properties of Biodiesel

The oxidation stability of *Calophyllum inophyllum* methyl esters was predicted by calculating the induction period (IP) using the equation listed in Table 5. This equation was obtained from linear regression of the logarithmic value of the induction period of *Calophyllum inophyllum* methyl esters and total content of methyl linoleate and methyl linolenate. The data used for the induction period of the regression were from measurement results by Chen, *et al.* [10]. The equations to calculate CP, PP, and CFPP were based on content of unsaturated FAME (wt%). Both CP and PP equations were obtained from Sarin, *et al.* [11], while, the CFPP equation was obtained from Su, *et al.* [12].

**Table 5** Empirical Equations to Predict FAME Properties.

Property	Calculation Method	Reference
Oxidation Stability	$\ln(\text{IP}) = -1,104 \ln(X) + 5,238$ IP = Induction periode; X = Total content of methyl linoleate and methyl linolenate (% w/w)	[10]
Cloud Point (CP)	$\text{CP} = A \times U_{\text{FAME}} + B$ A = -0.576; B = 48.255; $U_{\text{FAME}}$ = content of unsaturated FAME	[11]
Pour Point (PP)	$\text{PP} = A \times U_{\text{FAME}} + B$ A = -0.626; B = 45.594	[11]
Cold Filter Plugging Point (CFPP)	$\text{CFPP} = -0,561 \times \text{US} + 43,967$ US = unsaturated FAME content for biodiesel	[12]
Viscosity (VC)	$\ln(\eta_{\text{mix}}) = \sum X_i f(\eta)$ $X_i$ = Mass fraction of each FAME compositions; $\eta$ = Viscosity value of each FAME composition.	[13]
Iodine Number (IN)	$\text{IN} = 3,96 + 78,15 \text{ MO} + 201,06 \text{ ML}$ MO = Methyl oleate content (% w/w); ML = Methyl linoleate content (% w/w)	[10]
Cetane Number (CN)	$\text{CN} = 61,1 + 0,088 X_2 + 0,133 X_3 + 0,152 X_4 - 0,101 X_5 - 0,039 X_6 - 0,243 X_7 - 0,395 X_8$ $X_2$ = Methyl laurate (% w/w); $X_3$ = Methyl myristate (% w/w); $X_4$ = Methyl palmitate (%w/w); $X_5$ = Methyl stearate (% w/w); $X_6$ = Methyl palmitoleate (% w/w); $X_7$ = Methyl oleate (% w/w); $X_8$ = Methyl linoleate (% w/w)	[14]

The viscosity (VC) equation was obtained from Clements [13] and based on the viscosity value of all FAME. The iodine number equation was obtained from Chen *et al.* [10] and based on content of methyl oleate and methyl limoleate (% w/w). Meanwhile, the cetane number equation was obtained from Bamgboye and Hansen [14] and based on the content of methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl palmitoleate, methyl oleate and methyl linoleate (% w/w). Table 5 shows the empirical equations used to predict the physical properties of FAME.

The prediction values of IP, CP, PP, CFPP, VC, IN and CN of CIME and HCIME at various hydrogenation temperatures and reaction times are shown in Tables 6, 7 and 8.

**Table 6** Prediction of CIME and HCIME Properties at Reaction Temperature 80°C.

Properties of biodiesel	CIME	HCIME at reaction time		
		1 h	1.5 h	2 h
Oxidation Stability (h)	6.18	10.79	22.22	24.34
Cloud Point (CP) (°C)	13.88	16.54	18.35	18.68
Pour Point (PP) (°C)	8.23	11.13	13.10	13.45
Cold Filter Plugging Point (CFPP) (°C)	10.48	13.08	14.84	15.16
Viscosity (mm <sup>2</sup> /s)	4.16	4.09	4.04	4.01
Iodine Number (g I <sub>2</sub> /100g)	76.91	56.34	41.73	39.88
Cetane Number	44.83	49.02	51.99	52.43

**Table 7** Prediction of CIME and HCIME Properties at Reaction Temperature 100°C.

Property of biodiesel	CIME	HCIME at reaction time		
		1 h	1.5 h	2 h
Oxidation Stability (h)	6.18	17.11	23.21	26.78
Cloud Point (CP) (°C)	13.88	17.69	18.18	18.50
Pour Point (PP) (°C)	8.23	12.37	12.91	13.25
Cold Filter Plugging Point (CFPP) (°C)	10.48	14.19	14.78	14.99
Viscosity (mm <sup>2</sup> /s)	4.16	4.02	4.05	4.07
Iodine Number (g I <sub>2</sub> /100g)	76.91	46.39	39.85	37.39
Cetane Number	44.83	50.99	52.49	53.04

In this experiment, the partial hydrogenation of CIME was able to increase oxidation stability from 6.18 to 27.92 h. This was due to a substantial decrease in the content of polyunsaturated components, especially methyl linoleate. Referring to standards such as WWFC 2009, the oxidation stability should be at least 10 h. This requirement was met by the HCIME that was hydrogenated at a temperature of 80°C and reaction time of 1 h.

**Table 8** Prediction of CIME and HCIME Properties at Reaction Temperature 120°C.

Property of Biodiesel	CIME	HCIME at reaction time		
		1 h	1.5 h	2 h
Oxidation Stability (h)	6.18	15.47	18.42	27.92
Cloud Point (CP) (°C)	13.88	17.80	18.23	18.83
Pour Point (PP) (°C)	8.23	12.49	12.96	13.62
Cold Filter Plugging Point(CFPP) (°C)	10.48	14.30	14.72	15.31
Viscosity (mm <sup>2</sup> /s)	4.16	4.02	4.03	4.04
Iodine Number (g I <sub>2</sub> /100g)	76.91	46.62	42.95	35.60
Cetane Number	44.83	51.17	51.96	53.60

The values of CP, PP, CFPP relatively increased with the hydrogenation temperature and reaction time. The CP value increased from 13.88 to 18.83°C; the PP value increased from 8.23 to 13.62°C, while the CFPP value increased from 10.48 to 15.31°C. Based on WWFC 2009, there is no limit for CFPP; this can be interpreted as an indication that the CFPP limit is determined by the local climate where the biodiesel is being used. For the climate in Southeast Asia, particularly in Indonesia, this would certainly not be a problem. The cold flow property listed in the Indonesian standard of biodiesel (SNI 7182-2012) is a cloud point which requires a minimum temperature of 18°C. Based on SNI 7182-2012, the hydrogenated biodiesel that meets the requirements is HCIME-treated with a reaction time of 1 h and reaction temperatures of 80, 100 and 120°C.

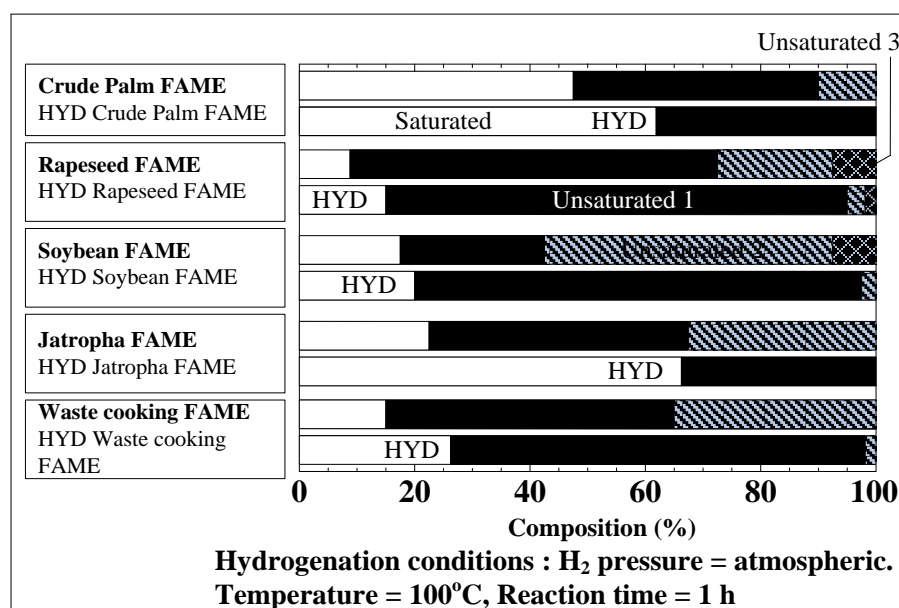
The partial hydrogenation only slightly affected the viscosity value, so that its value was relatively constant between 4.01 and 4.16 mm<sup>2</sup>/s. This value complies with the requirements of SNI 7182-2012 (2.3-6.0 mm<sup>2</sup>/s) and WWFC 2009 (2.0-5.0 mm<sup>2</sup>/s). Changes in the composition of the FAME after partial hydrogenation resulted in CIME iodine numbers decreasing from 76.91 to 35.6. This decrease was due to the decreased content of polyunsaturated FAME. The iodine number of the HCIME was lower than the maximum value of 115 as specified in SNI 7182-2012 and of 130 as specified in WWFC (2009).

Changes in the composition of the FAME after partial hydrogenation resulted in the CN of the Calophyllum inophyllum methyl esters increasing from 44.83 to 53.6. The CN values relatively increased with the hydrogenation temperature and reaction time. The cetane number of the HNME exceeded the minimum value of 51 as specified in SNI 7182-2012 and WWFC (2009). Based on SNI 7182-2012, the hydrogenated biodiesel that met the requirements was HCIME treated with a reaction time of 1 h and reaction temperature of 120°C (the cetane number value was 51.17). The increase in cetane number was due to the increased content of mono-unsaturated and saturated FAME (C18: 1 and C18: 0) as Bamgboye and Hansen [12] have reported that the cetane number of

saturated and mono-unsaturated FAME is higher than that of polyunsaturated FAME.

### 3.3 Comparison to the Results of Similar Research

Partial hydrogenation of various types of FAME has been reported by Goto, *et al.* [1]. After oxidation stability improvement via partial hydrogenation of FAME, the optimal hydrogenation level varies depending on the unsaturated chemical compounds present.



Source: EAS-ERIA Biodiesel Fuel Trade Handbook [1].

**Figure 4** Changes in composition of FAME derived from crude palm oil, rapeseed oil, soybean oil, Jatropha oil and waste cooking oil after partial hydrogenation.

Figure 4 describes the changes of fatty acid composition from five different types of oil (crude palm oil, rapeseed oil, soybean oil, Jatropha oil and waste cooking oil) after partial hydrogenation. The partial hydrogenation process was executed at 1 atm 100°C. This shows that conversion from mono-unsaturated to saturated FAME occurred (increased saturated FAME concentration). The conversion reaction also took place from unsaturated: 2 to unsaturated: 1, unsaturated: 3 to unsaturated: 1 and/or unsaturated: 2. High selectivity was maintained for the mono-unsaturated FAME except for the Jatropha FAME. Based on research results obtained in this study, as shown in Figure 2, it is evident that these results are similar to the results reported by Goto, *et al.*

Reaction selectivity to mono-unsaturated FAME is high, especially methyl elaidate. The similarity of the results of this research is not only valid for the same operating conditions (100°C and a 1 hour hydrogenation treatment time) but also for other operating conditions.

#### 4 Conclusion

Partial hydrogenation of *Calophyllum inophyllum* methyl esters successfully reduced the content of polyunsaturated FAME, especially methyl linoleate and methyl linolenate. The optimum condition was obtained at 120°C for 1 h, with 15.47 h as the oxidation stability value, 17.8°C as the cloud point value, and 51.17 as the cetane number. The results obtained in this research met the following standards: a minimum value of oxidation stability of 10 h in accordance with the WWFC 2009, a maximum cloud point value of 18°C, and a minimum cetane number of 51 in accordance with SNI 7182-2012.

#### Acknowledgements

This research was supported by *Kementerian Riset dan Teknologi* (Kemenristek) of the Republic of Indonesia, under the *Insentif Riset Sistem Inovasi Nasional* (SINas) scheme with contract nr. 27/SEK/INSINAS/PPK/I/2014.

#### References

- [1] Benchmarking of Biodiesel Fuel Standardization in East Asia Working Group 2010, *Biodiesel Fuel Quality*, in Goto, S., Oguma, M., and Chollacoop, N. *EAS-ERIA Biodiesel Fuel Trade Handbook: 2010*, Jakarta: ERIA, pp. 27-62, 2010.
- [2] World Wide Fuel Charter (WWFC) 2009, *Biodiesel Guidelines*, Fuels and Lubricants Committee Japan Automobile Manufacturers Association, Available from: <http://www.truckandenginemanufacturers.org/file.asp?A=Y&F=20090326+B100+Guideline+Final.pdf&N=20090326+B100+Guideline+Final.pdf&C=documents> (7 December 2011)
- [3] Bustomi, S., Rostiwati, T., Sudradjat, R., Leksono, B., Kosasih, A.S., Anggraeni, I., Syamsuwida, D., Lisnawati, Y., Mile, Y., Djaenudin, D., Mahfudz & Rachman, E., *Nyamplung (Calophyllum inophyllum L), Sumber Energi Biofuel yang Potensial*, Badan Litbang Kehutanan. Jakarta, 2008.
- [4] Hadi, W.A., *Pemanfaatan Minyak Biji Nyamplung (Calophyllum inophyllum L) sebagai Bahan Bakar Minyak Pengganti Solar*, *Jurnal Riset Daerah*, **8**(2), 2009.

- [5] Goto, S., Oguma, M. & Chollacoop, N., *EAS-ERIA Biodiesel Fuel Trade Handbook*, Economic Research Institute for Asean and East Asia, Jakarta, p.196, 2010.
- [6] Prakoso, T., Udomsap, P., Tanaka, A., Hirotsu, T. & Goto, S., *Characteristics of Oxidative Storage Stability of Canola Fatty Acid Methyl Ester Stabilised with Antioxidants*, ITB J. Eng. Sci., **44**(3), pp. 303-318, 2012.
- [7] Wadumesthrige, K., Salley, S.O. & Ng, K.Y.S., *Fuel Processing Technology*, **90**, pp. 1292-1299, 2009.
- [8] Fajar, R., Sugiarto, B. & Prawoto, *Predicting Fuel Properties of Partially Hydrogenated Jatropha Methyl Ester: Used for Biodiesel Formulation to Meet the Fuel Specification for Automobile and Engine Manufacturer*, Kasetsart J. (Nat. Sci.), **46**, pp. 629-637, 2012.
- [9] Tambun, R., *Buku Ajar Teknologi Oleokimia*, Hibah Kompetisi Konten Mata Kuliah E-Learning USU-Inherent, 2006.
- [10] Chen, Y.H., Chen, J.H. & Luo, Y.M., *Property Modification of Jatropha Oil Biodiesel by Blending with Other Biodiesels or Adding Antioxidants*. Energy, **36**, pp. 4415-4421, 2011.
- [11] Sarin, A., Arora, R., Singh, N.P., Sarin, R., Malhotra, R.K. & Kundu, K., *Effect of Blends of Palm-Jatropha-Pongamia Biodiesels on Cloud Point and Pour Point*, Energy, **34**, pp. 2016-2021, 2009.
- [12] Su, Y.C., Liu, Y.A., Diaz-Tovar, C.A. & Gani, R., *Selection of Prediction Methods for Thermo-physical Properties for Process Modeling and Product Design of Biodiesel Manufacturing*, Ind. Eng. Chem. Res., **50**, pp. 6809-6836, 2011.
- [13] Clements, L.D., *Blending Rule for Formulating Biodiesel Fuel*, [www.angelfire.com/ks3/go\\_diesel/files042803/gen-277.pdf](http://www.angelfire.com/ks3/go_diesel/files042803/gen-277.pdf) (8 July 2013)
- [14] Bamgboye, A.I. & Hansen, A.C., *Prediction of Cetane Number of Biodiesel Fuel From the Fatty Acid Methyl Ester (FAME) Composition*, Int. Agrophysics, **22**, pp. 21-29, 2008.