Production of Biodiesel from Rubber Seed Oil and Its Effects to Engine Performances

Kulachate Pianthong and Prachasanti Thaiyasuit*

Abstract**—** *This study aims to examine methods and the most suitable conditions for producing methyl ester from crude rubber seed oil. An acid esterification-alkaline transesterification process is proposed. In the experiment, the 20% FFA of crude oil could be reduced to 3% FFA by acid esterification. The product after esterified was then tranesterified by alkaline transesterification process. By this method, the maximum yield of methyl ester was 90% by mass. The yielded methyl ester was tested for its fuel properties and met requirement standards. The major fatty acid methyl ester compositions are methyl linoleate 41.57%, methyl oleate 24.87%, and methyl lonolenate 15.16%. Therefore, the cetane number of methyl ester can be estimated as 47.9, while the tested result of motor cetane number is 51.2. The engine performance tests were carried out with a small single cylinder engine at full load conditions. Testing in the engine, with neat methyl ester (B100), it was found that the torque and brake horse power of the engine using B100 were averagely 5% lower than those of the engine using diesel. The specific fuel consumption of B100 engine was averagely about 10% higher than that of diesel engine depending on engine speeds. At low engine speed, the brake thermal efficiency of the engine using B100 was higher than that using diesel by 5%. Also, it was found that the emission from B100 engine i.e. CO, and CO_2 are lower than those of the diesel engine.*

Keywords**— Methyl ester; crude rubber seed oil; esterification, transesterification, engine performance tests.**

1. INTRODUCTION

Nowadays, the shortage or crisis of fossil fuel lately becomes one of the most concerns in automotive industry and world energy sector. This influences researchers and industries to search for a renewable energy to compensate the fossil fuel. Methyl ester fuel is one of the possible choices, because it is renewable and free of sulfur. Methyl ester contains about 10 to 11% oxygen by weight. This characteristic reduces the emissions of CO, HC, and particulate matter in the exhaust gas compared with diesel fuel. As it is obtained mainly from plantation resources, it is able to reduce the lifecycle of carbon dioxide by almost 78% compared to conventional diesel fuel [1], while its fuel properties are very closed to diesel. Also, methyl ester can be used in diesel engines with few or no engine modifications [2].

Usually, methyl ester has been produced from the edible plant oils such as soybean oil and palm oil. However, it is always controversial on using edible oil or food resource as fuels. Therefore, in recent years, considerable research effort has been directed towards replacing food oils with various non-edible, wasted, or low-cost oils. The unrefined non-edible oils have been considered, however they have high impurities such as free fatty acid (FFA) and phosphatide. These impurities impede the transesterification process in the methyl ester production. For instance, Ramadhas et al. [3] have found that the FFA content in the crude rubber seed oil is about 17% and 19% of FFA in mahua oil was found by Ghadge and Raheman [4]. This FFA value is significantly high and obstructs the transesterification process in the methyl ester production. It has been confirmed that the ester yield decreases with increasing in FFA significantly. Usually, the alkaline-catalyzed transesterification takes place well only with refined oil having FFA value of less than 2% [3]-[5]. Canakci and Van Gerpen [6] have found that transesterification would not occur if the FFA content in the oil were above 3%. Usually, free carboxylic acids form soaps with alkaline-catalyzed transesterification, hence they impede the separation of the glycerin phase due to the emulsifying effects of soaps and lower their catalytic activity [7], [8]. In extreme cases, of more than 5% FFA oil, Canakci and Van [9] reported that the reacted mixture might completely gel after the addition of KOH or NaOH, so that the charge has to be discarded. Therefore, the single step alkaline-catalyzed tranesterification process is not suitable to produce methyl esters from high FFA crude oil. In order to reduce the FFA, the crude oil should be refined, but the overall production cost of the methyl ester will be increased. The single step acid transesterification is a typical method of producing methyl ester from high FFA oil, however, it requires more methanol, high temperature, and is also time consuming.

Recently, researchers searched for means to produce methyl ester from high FFA oil such as non-edible crude plant oils, animal oils, and fish oils. The reduction of FFA in crude oil before tranesterification process has been examined. This method is also efficient to produce methyl ester from high FFA oils. However, it consumes more methanol, as Ghadge and Raheman [4] studied the production of methyl ester from mahua oil having 19% FFA by pretreatment process and transesterification process. The pretreatment process comprised of double

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acid-esterification. The 19% high FFA level of mahua oil was reduced to less than 1% by this pretreatment process. This process consumed 0.7 v/v (16.8:1 molar ratio) methanol-to-oil ratio. Then, the product of pretreatment process was proceed to transesterification process and consumed methanol 0.25 v/v (6:1 molar ratio), thus the overall of methanol consumption was 22.8:1 in molar ratio. Ramadhas et al. [3] investigated on the production of methyl ester from 17% FFA rubber seed oil by two steps transesterification process. The first step was acid-esterification and consumed methanol 6:1 in molar ratio. The second step consumed methanol 9:1, thus the overall of methanol consumption was 15:1 in molar ratio. By this method, over usage of methanol, compare to theoretical requirement, is unavoidable. EL-Mashad et al. [10] found the two steps transesterification was effective method for producing methyl ester from the acidified salmon oil having 6% FFA. The 6% FFA salmon oil was reduce to 1.5% by esterification and consumed methanol about 9:1 in molar ratio. In the second step, the methanol was used at molar ratio about 5:1 for transesterification. The overall methanol consumption of this studied was 14:1. Even thought the two steps transesterification can be suitable for produce methyl ester from high FFA crude oils, however it consume too much methanol.

Therefore, the aim of this study is to examine the method to reduce the consumption of methanol in methyl ester production from non–edible high FFA crude oil. The non–edible high FFA crude oil in this study was crude rubber seed oil. It was extracted from the rubber seed kernels and then carried out to produce methyl ester by the acid esterification-alkaline transesterification process. The acid esterification process was for reducing FFA content of the crude rubber seed oil. Then the product of acid esterification is transesterified using alkaline catalyst in the alkaline transesterification process. Then fuel properties of methyl ester from rubber seed oil were examined and compared with diesel and methyl ester standards. The engine performances were tested in parallels among using 100% (or neat) methyl ester, standard diesel, and their blends. The engine emissions from those fuels are also measured.

2. MATERIALS AND METHODS APPARATUS

Fresh rubber seeds were collected from the local area called Ubon Ratchathani, Thailand. The rubber tree is RRIM 600 seeds which is widely growth in Thailand. The rubber seeds were cracked and the kernels (52.5% of seed weight) were dried in the oven at 100°C for 20 hours. The crude rubber seed oil was extracted from kernels by hydraulic press machine and was about 10% of seed weight. The extracted crude rubber seed oil usually contains sediment of kernel and moisture. The crude rubber seed oil should be cleared from adulterants before the acid esterification process in order to avoid the imperfection of the process. The dregs of the kernel can be removed by the filter fabric. The moisture in the crude rubber seed oil is in water form. It is found that existence the addition of 0.5% water to a mixture of oil, methanol, and sulfuric acid could reduce ester conversion from 95% to below 90%. Also at a water content of 5%, ester conversion decreased to only 5.6% [9]. Thereby, the filtered oil is heated at 120°C for 5 minutes to remove the moisture. Then, the free fatty acid (FFA) content of crude rubber seed oil was determined. It was found that the FFA content was increased associate with the times keeping the rubber seed before extracting crude oil as shown in Fig. 1. The crude rubber seed oil using in this study has FFA content of 20% (Oleic). The physical properties of crude rubber seed oil tested by the Research and Technology Institute of the Petroleum Authority of Thailand (PTT Public Company Limited) are shown in Table 1. The fatty acid compositions analysis carried out by the Thailand Institute of Scientific and Technological Research (TISTR) with gas chromatographic method are shown in Table 2. Knowing the fatty acid composition, the molecular mass of the crude rubber seed oil can be then estimated. In this research, the molecular mass of crude rubber seed oil was determined as 872.4 g/mole. This molecular mass is very useful for the calculation of the amount of the catalyst and methyl alcohol in the esterification and tranesterification reactions. This study is to determine the optimum condition for producing methyl ester from crude rubber seed oil by the acid esterification-alkaline transesterification process. Note that, the study is performed in the laboratory and in a small batch process (0.5 kg).

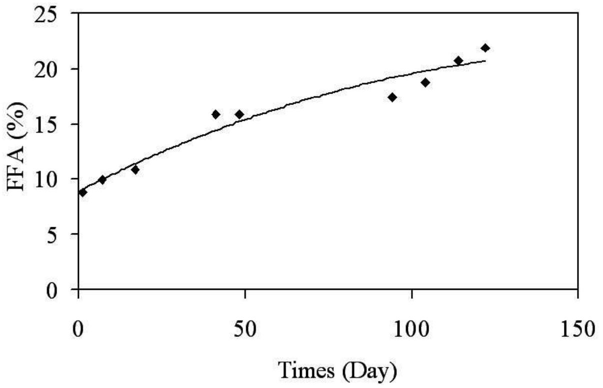
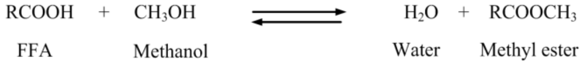


Fig. 1. Relation between FFA and collecting times of rubber seed.

2.1 Acid esterification process

Acid esterification process offers the advantage of partial esterifying FFA contained in the crude rubber seed oil as shown in Fig. 2. This is to reduce FFA value of the crude rubber seed oil to about 3% or less. In addition, this step is the removal of phosphatides, which is also known as acid degumming. Phosphatides promote the accumulation of water in the ester product. Moreover, they increased catalyst consumption during alkaline transesterification [13].



$$RCOOH + CH_3OH \underset{}{\overset{\text{Acid catalyst}}{\rightleftharpoons}} H_2O + RCOOCH_3$$

Fig. 2. Esterification of free fatty acids.

Table 1. Properties of crude rubber seed oil compared to others

Property	Test Method	Unit	Result [a]	B	C
Specific gravity	ASTM D4052	kg/m^3	918.2	922	910
Viscosity	ASTM D445	cSt	31.84	41.24[b]	66.2
Flash point	ASTM D93	° C	240	294	198
Water content	ASTM D6308	%wt	0.108	NA	NA
Heating value	ASTM D240	J/g	39.223	39.25	37.5

N.A., not available.

[a], Tested by the Petroleum Authority of Thailand (PTT Public Company Limited).

[b], Tested at 30°C.

B, from Ikwuagwu et al. [11]

C, from Ramadhas et al.[3]

Table 2. Fatty acids composition of crude rubber seed oil

Property	Test Method	Result (%wt)[a]	C	D
Myristic acid C14:0	GC	0.11	NA	0.1
Palmitic acid C16:0	GC	9.89	10.2	12.0
Plamitoleic acid C16:1 n-7	GC	0.24	NA	NA
Stearic acid C18:0	GC	7.96	8.7	10.7
Oleic acid C18:1 n-9	GC	24.43	24.6	20.0
Linoleic acid C18:2 n-6	GC	41.38	39.6	36.0
Linolenic acid C18:3 n-3	GC	15.55	16.3	23.5
Arachidic acid C20:0	GC	0.27	NA	NA
Cis-11-Eicosenoic acid C20:1 n-9	GC	0.17	NA	NA

N.A., not available.

a, Tested by the Thailand Institute of Scientific and Technological Research (TISTR).

C, from Ramadhas et al. [3].

D, from Okieimen et al. [12].

Although a variety of alcohols can be used to produce methyl ester such as methanol, ethanol or butanol. The methanol is normally used as the reactor, because it is a short chain alcohol (provide simpler and faster reaction) and low cost. Sulfuric acid is used in this stage because of its low price, and higher catalytic activity. Sulfuric acid is also hygroscopicity, which is important for the esterification of free fatty acids, removing released water from the reaction mixture [13]. This step is sometimes called "pre-treatment" step. The important parameters affecting the acid esterification step such as molar ratio between crude rubber seed oil and methanol, catalyst (sulfuric acid) amount and reaction duration are investigated. The reaction temperature at 60°C is chosen, even though an increase in the transesterification rate was found with increasing reaction temperature. However, the maximum temperature should not exceed the boiling point of the reactant; e.g. 64.4°C for methanol [14]. If the reaction temperature is above this point, some portion of methanol will be loss during reaction process.

The amount of the FFA in crude rubber seed oil affects the appropriate molar ratio of methanol:oil. Therefore, this experiment is to find the optimum molar ratio of methanol:oil. The molar ratio at 3:1, 4.5:1, 6:1, 7.5:1 and 9:1 are varied in this experiment. Sulfuric acid (H_2SO_4) is the catalyst to reduce the FFA value in the crude rubber seed oil. The appropriate amount of sulfuric acid will shorten the reacting time to reduce FFA to 3%. Also, the sulfuric acid may affect dark coloring in the methyl ester product [15] and its corrosiveness, if it is abundantly added. So this experimental is also to find the optimum amount of the sulfuric acid. The amount of sulfuric acid is varied in the range of 1.5 to 5.5% by mass of the crude rubber seed oil. The mixture of crude rubber seed oil, methanol, and sulfuric acid has reacted by high speed mixing machine at 14,000 rpm in a closed glass jar. The optimum reaction time (mixing) is also determined at 15, 30, 45, 60, 75, 90 minutes. This is to save the energy in the production process and to protect the reversion of the chemical reaction process. Then product is poured in to a separating funnel and at each 6 hours, the product was taken to measure the FFA content. But from previous experimented [3], product was continued to transesterification process without measuring the FFA content. However, acid-catalyzed esterification is usually far slower than alkali-catalyzed reaction [13].

1.2 *Alkaline transesterification process*

Alkaline transesterification process is the process that one mole of triglyceride reacts with three moles of alcohol to from one mole of glycerin and three moles of the respective fatty acid alkyl esters as shown in Fig.3.

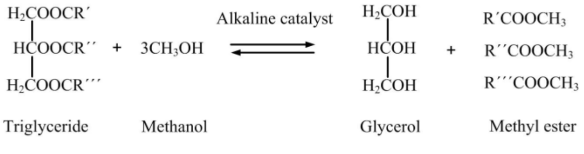


Fig. 3. Transesterification reaction between triglyceride and methanol.

However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right direction. The molar ratio of alcohol to triglyceride has no effect on acid, peroxide, saponification and iodine value of methyl esters [16]. However, the high molar ratio of alcohol to triglyceride interferes with the separation of glycerin [17], because there is an increase in solubility. The separation of glycerin is difficult and the apparent yield of esters decreased, because a part of the glycerin remains in the methyl ester phase. When glycerin remains in solution, it drives the equilibrium backward to the left, lowering the yield of the esters [18]. The alkaline catalyst used in this study is the Potassium hydroxide (KOH). Because it decreases the tendency for soap formation when using KOH as a catalyst compared to NaOH. Also it reduces the amount of methyl esters dissolved in the glycerin phase after reaction and thus reduces ester losses [19].In addition, the glycerin of the KOH catalyst is in liquid form, which is easier to separate from methyl ester compared to the muddy gel glycerin from NaOH catalyst.

The amount of KOH used in the alkaline transesterification process, g KOH/g methanol, can be calculated as follows:

$$KOH_{Transesterification} = (A\times B)/100 \quad (1)$$

$$KOH_{Neutralization} = (B\times AV)/1000 \quad (2)$$

$$KOHTotal = KOH_{Transesterification} + KOH_{Neutralization} \quad (3)$$

Where A is the KOH/crude rubber seed oil for catalysis (%w/w) and B is the molar ratio (oil/methanol). AV is the acid value of product from acid esterification process (mg KOH/g oil). The amount of A is varied in the range of 0.5 to 2.5% by mass of the crude rubber seed oil. In order to find the optimum ratio between methanol and crude rubber seed oil, the molar ratio at 3:1, 4.5:1, 6:1, 7.5:1 and 9:1 are varied in this experiment. The required amount of KOH was dissolved into the required methanol amount. The KOH-methanol mixture was added to the product obtained from the acid esterification step. Similar to the acid esterification step, the reaction was performed at 60°C. After the reaction, resting the mixture for more than 4 hrs, there will be two layers of the products. The upper layer is the alkyl ester and the lower layer is the glycerin. The glycerin is in the liquid form and can be drained from the reacting tank easily.

2.3 Engine performance test

In this study, engine performance test was carried out using a small CI engine without any modification. The investigations of engine performance are torque, horse power, brake specific fuel consumption, thermal efficiency, and specific emissions. The single cylinder, 411 cc displacement volume, and four-stroke direct injection CI engine is used in the performance test. The engine specification is detailed in Table. 3. The engine was coupled to an electro dynamometer (Eddy– Current brake type). This electro dynamometer model is EA-10 made by Tokyo Meter Co. The engine performance test set-up and measuring instruments are shown in Fig. 4. The engine was operated with neat methyl ester, standard diesel, and methyl ester-standard diesel blend as fuels. The engine performance test is performed at the full load condition and various speed from 1300 to 2100 rpm. The results presented in this paper are the average values from similar 5 tests. The test procedures are as follows;

1) Prepare sample fuels which are methyl ester from rubber seed oil blended with diesel by mass ratio of 10% methyl ester (B10), 25% methyl ester (B25), 100% methyl ester (neat or B100), and diesel.

2) Replace the lubrication oil, using the new one

3) Calibrate the load cell of the dynamometer

4) Prepare the engine and dynamometer, adjusting the cooling water flow rate to be 100 L/hr

5) Warm up the engine for around 20 minutes

6) Run the engine at the full load condition

7) Adjust the dynamometer to obtain the engine speed of 1300 to 2300 rpm. At each speed, keep the engine running for 3 minutes, and then record all parameters and measure CO_2, CO, and NO_x.

Table 3. Specification of the tested engine

Model	D-800 (Mitsubishi diesel engine)
Bore x Stroke	82 x 78 mm.
No. of cylinder	1
Piston displacement	411 cc
Link ratio	3.54
Maximum output	8.0 PS (hp in metric) / 2400 rpm
Maximum torque	2.6 kg-m / 1900 rpm
Compression ratio	18

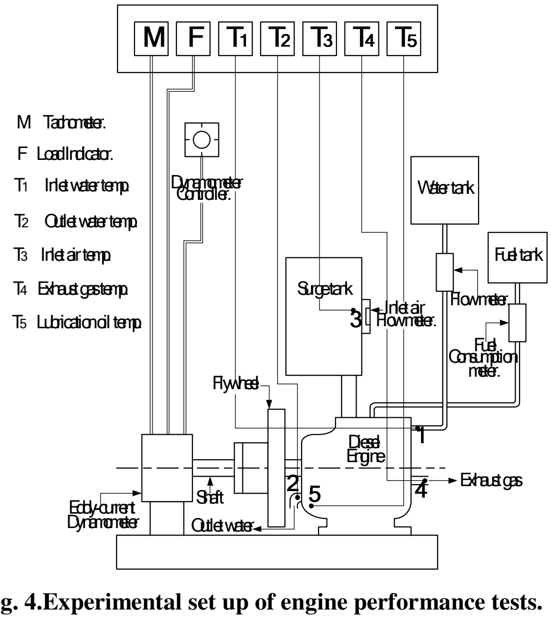


Fig. 4.Experimental set up of engine performance tests.

The indicators of emissions levels used this study are specific emissions. The specific emission is defined as the mass flow rate of pollutant per unit power output. The Infrared Industries HM5000 exhaust gas analyzer is used to measure gases emission. The Non-Dispersive infrared analyzer (NDIR) is for CO_2 and CO concentration measurements and the Electrochemical Cell is for NO_x concentration measurement.

3. RESULTS AND DISCUSSIONS

3.1 FFA reduction by acid esterification

From the experiment, on completion of the acid esterification reaction (high speed mixing), product is poured in to a separating funnel. Initially, the reaction was very fast and could notice the separation easily. The products of this process separated into two layers as show in Fig. 5. The upper layer was the products of this process. The lower layer was a solution which contains water (from esterification of FFA), hydrate gum, sulfuric acid and excess methanol. They were dissolved to a solution (lower layer) thus the density of this solution was higher than the upper layer. The lower layer was then drawn off. The upper layer was the emulsion between triglycerides and monoesters. It became the low FFA product which is suitable to use in the alkaline transesterification. The effectiveness of the acid esterification was evaluated by measuring the FFA of this intermediate product. From FFA measurement, at each 6 hour interval between 0-48 hours, the FFA content in product became lower, but it had not changed afterwards.

Fig. 5. Product from step 1 (acid esterification) during the separation process.

From Fig. 6, it is found that the proper molar ratio, which can reduce the FFA from 20% to 3%, is 6:1. With further increase in molar ratio the effectiveness was remained constant and some excess methanol moves over the product layer, which also found by Ramadhas et al. [3] and Ghadge and Raheman [4] studied. In their studied, the reason that excess methanol is required, because there are not sufficient of sulfuric acid and high water content in crude oil. These yield the lower esterification reaction efficiency. Fig.7 shows the relationship between the concentrations of sulfuric/crude oil used to the FFA reduction. It reveals that the amount of the sulfuric should be more than 2.5% by weight of the crude rubber seed oil. The appropriate reaction period (mixing) is around 30 minutes or more as show in Fig.8.

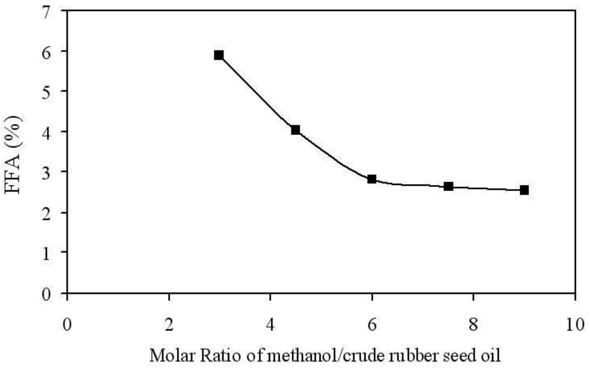


Fig. 6. Effect of molar ratio of methanol/crude rubber seed oil to FFA reduction.

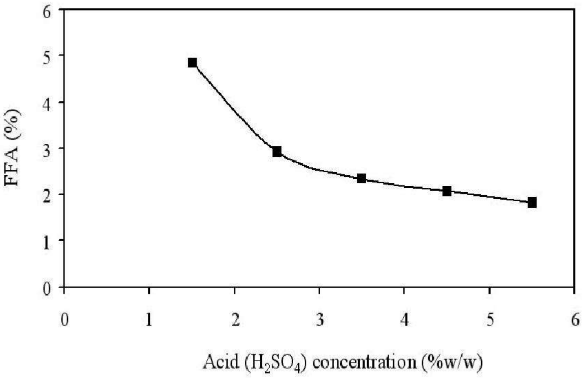


Fig. 7. Effect of sulfuric/crude rubber seed oil to FFA reduction.

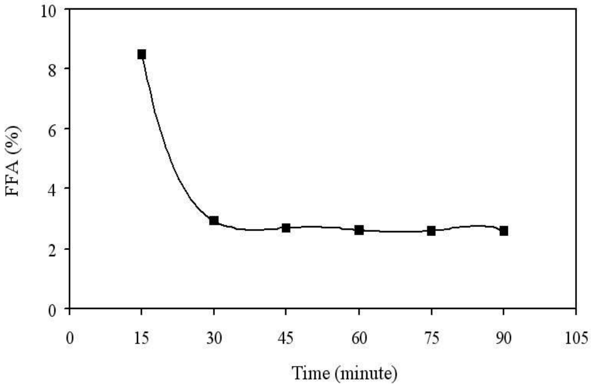


Fig. 8. Effect of reaction period (high speed mixing) to FFA reduction.

3.2 Methyl ester production by alkaline transesterification

The product after esterified from acid esterification was then transesterified by alkaline transesterification process. The product from the alkaline transesterification is separated into two layers as shown in Fig.9. The lower layer is glycerin and the upper layer is methyl esters. The glycerin in lower layer is drawn off to only remain the methyl ester. Methyl ester is then washed to remove the left over impurities and glycerin by warm water temperature of 50°C. The warm water used is about 50% of methyl ester by volume. The washing is carried out for three to four times or until the ph of the methyl ester is neutral (ph of around 7-8). After that, the methyl ester is heated at 120°C for 15 minutes to remove the moisture. The final product of methyl ester was used to calculate the yield of each condition. The yield is defined by the obtained methyl ester divided by the initial crude rubber seed oil (by mass). From the results of this step, the KOH (A) concentration of 1.5% and the methanol to oil molar ratio of 6:1 give the highest yield of methyl ester which is around 90%. These results are plotted in Fig. 10 and Fig. 11. Fig. 11 shows that the molar ratio, in this study, can be significantly lower than previous study [3]. Because the most FFA content in crude rubber seed oil (20%) were pretreated to methyl ester in the first step (acid esterification) and the gum was separated before transesterification.

Fig. 9. Methyl ester and glycerin during the separation process.

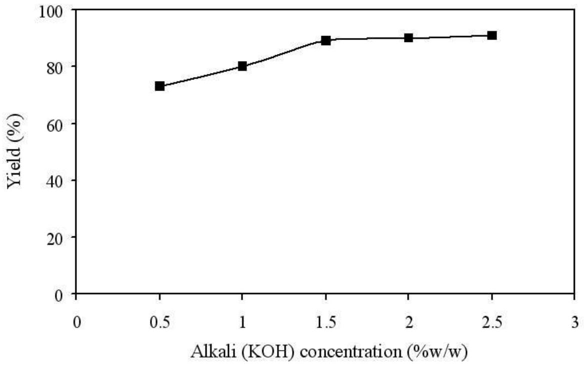


Fig. 10. Effect of alkali (KOH)/crude rubber seed oil to yield of methyl ester.

The optimum final product of methyl ester was tested for its composition by the Thailand Institute of Scientific and Technological Research (TISTR). The major fatty acid methyl ester compositions of methyl ester are methyl linoleate 41.57%, methyl oleate 24.87%, and methyl lonolenate 15.16%. They are unsaturated and long fatty acid chain. The unsaturated fatty acid methyl ester influence to cetane number, as detailed in Table. 4, which affects to ignition quality in CI engine. Therefore, the cetane number of this methyl ester can be estimated as 47.9. Knowing the fatty acid methyl ester composition, the chemical formula of methyl ester from rubber seed oil is calculated as $C_{18.8}H_{34.5}O_2$. This formula of methyl ester is useful for the calculation of the methyl ester combustion characteristics. The methyl ester properties were tested by the National Metal and Materials Technology Center of Thailand (MTEC). Then compared with the methyl ester from previous study [3] and methyl ester standard of Europe (EN 14214:2003), USA (ASTM D6751) as detailed in Table. 5. Most of methyl ester fuel properties met require standard except methyl ester content met nearby lower.

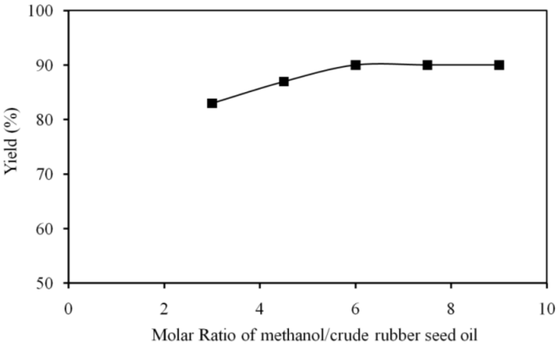


Fig. 11. Effect of molar ratio of methanol/crude rubber seed oil to yield of methyl ester.

The cost of methyl ester production is 37.30 Bath per liter. This cost can be divided into rubber seed of 22 Bath, electricity of 3.30 Bath, Chemical of 10.23 Bath and another cost of 1.77 Bath. The major cost is rubber seed because the efficiency of the oil extractor from kernels process is quite low (around 10% only). With the improvement of the oil preparation the cost of methyl ester will be decreased.

3.3 Engine performance tests

Engine performance tests were carried out on a naturally aspirated small single cylinder direct injection CI engine with neat diesel oil, neat methyl ester (B100) and blend of 10% methyl ester (B10), and 25% methyl ester (B25) with diesel. Tests were conducted at full load condition at various speeds from 1300-2100 rpm. The torque result is plotted in Fig. 12. It was found that the torque of the engine using B100 was averagely about 5% lower than that of diesel. Because the heating value of methyl ester (39.63 MJ/kg, shown in table 5) is lower than that of diesel (44.8 MJ/kg) [20] about 11.5%. In all fuel types, the torque has tendency to increase with increasing in engine speed and its maximum is at 1900 rpm. Due to the fact that, at high engine speed, air swirl increases providing more fuel-air mixing. The power of the engine is also averagely 5% lower than that of diesel when B100 is used as shown in Fig. 13. However, at low engine speed (1300-1700 rpm), the torque and the power of B100 engine are close to diesel engine. In the B10 and B25 tests, the torque and the power are quite close to those of diesel at low engine speed (1300-1700 rpm). This means the viscosity of the methyl ester does not affect much on the fuel injection and the mixture of air-fuel of B10 and B25 at low speed.

Table 4. Composition of methyl esters from crude rubber seed oil and their properties

Fatty acid Methyl ester	Formula	Molecular Weight (g/mole)	Result[a] (%wt)	Melting point[b] (°C)	Cetane[b] number
Methyl palmitate	$C_{17}H_{34}O_2$	270.45	9.90	30.5	74.5
Methyl palmitoleate	$C_{17}H_{32}O_2$	268.43	0.26	N.A	N.A
Methyl stearate	$C_{19}H_{38}O_2$	298.50	7.73	39	75.7
Methyl oleate	$C_{19}H_{36}O_2$	296.48	24.87	-20	55.0
Methyl linoleate	$C_{19}H_{34}O_2$	294.47	41.57	-35	42.2
Methyl linolenate	$C_{19}H_{32}O_2$	292.45	15.16	-52	22.7
Methyl arachidate	$C_{21}H_{42}O_2$	326.67	0.30	39.25	N.A
Methyl eicosenoate	$C_{21}H_{40}O_2$	324.54	0.21	N.A	N.A

N.A., not available.

[a], Tested by the Thailand Institute of Scientific and Technological Research (TISTR).

[b], from Mittebach and Remschmidt [13]

Table 5. Fuel properties of methyl ester from rubber seed oil compared to others

				Methyl ester standard		Diesel
Fuel properties	Testing method	This work	A	EN 14214:2003	ASTM D6751	EN 590:1999
Density (g/cm^3)	ASTM D4052	0.8874[a]	0.874	0.86-0.90	N.A.	0.82-0.845
Viscosity (mm^2/s) at 40°C	ASTM D445	4.456[a]	5.81	3.5-5.0	1.96-6.0	3.8
Cloud point (°C)	ASTM D2500	3.4[a]	4	N.A.	report	N.A.
Flash point (°C)	ASTM D93	187[a]	130	120 min	130 min	55 min
Gross heating value (MJ/kg)	ASTM D240	39.63[a]	36.50	N.A.	N.A.	N.A.
Methyl ester content (%wt.)	EN 14103	96.4	N.A.	96.5 min	N.A.	N.A.
Total glycerin (%wt.)	EN 14105	0.23[a]	N.A.	0.25 max	0.24 max	N.A.
Carbon residue (%wt.)	ASTM D4530	0.22[a]	N.A.	0.3 max	N.A.	2.0-4.5
Acid value (mg KOH/g)	ASTM D664	0.18[a]	0.118	0.5 max	0.8 max	N.A.
Iodine value (g I_2/100 g oil)	EN 14111	82.9[a]	N.A.	120 max	N.A.	N.A.
Oxidation stability (hour)	EN 14112	7.82[a]	N.A.	6 min	N.A.	N.A.
Cetane number	ASTM D613	51.2[b]	N.A.	51 min	47 min	51 min

N.A., not available.

[a], Tested by the National Metal and Materials Technology Center of Thailand (MTEC).

[b], Tested by the Petroleum Authority of Thailand (PTT Public Company Limited).

A, from Ramadhas et al. [3].

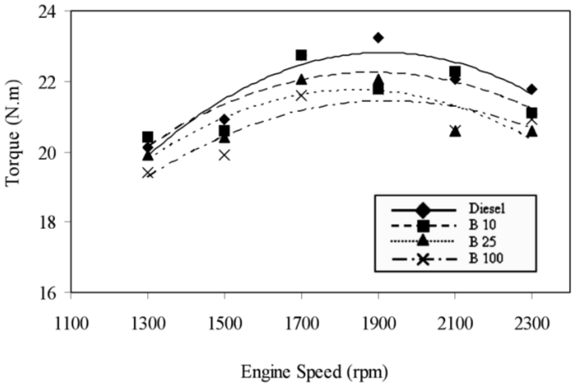


Fig. 12. Engine torque at various speeds.

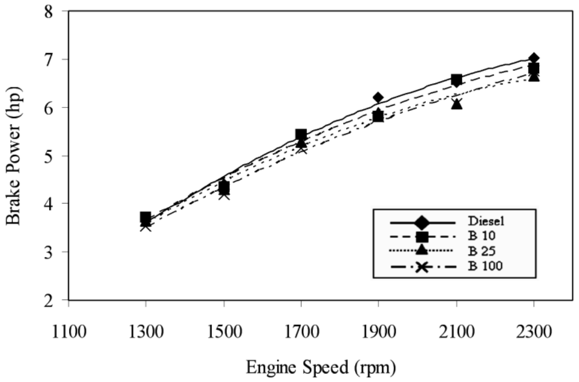


Fig. 13. Engine brake horse power at various speeds.

For the brake specific fuel consumption (bsfc), in all fuel types, the bsfc tends to decrease with increasing in engine speed as shown in Fig. 14. The B100 engine consumes more fuel than diesel engine averagely around 10% at various speeds. However, at low engine speed (1300-1700 rpm), the bsfc of B100 is found to be higher than that of diesel only about 5%, due to the benefit of the better combustion of B100. The B10 and B25 tests show closed amount of bsfc at the low engine speed.

In this paper, the brake thermal efficiency is defined as brake horsepower output divided by the rate of heat released from the fuel burning process. The trends of brake thermal efficiency of all fuels are found to increase when increasing in engine speed as plotted in Fig. 15. However, their efficiencies drop below the diesel after 1900 rpm. At low engine speed (1300-1700 rpm), the B100 engine provides the highest thermal efficiency and about 5% higher than that of diesel. As at low engine speed, the swirl in cylinder was not sufficient to achieve adequate fuel distribution and rate of mixing with the air. However, the benefit of having oxygen contents in the methyl ester molecule improves its combustion quality [21], [22] Thus, the thermal efficiency of an engine operating on methyl ester is generally better than that operating on diesel [23]. The B10 and B25 give very closed brake thermal efficiency to the diesel.

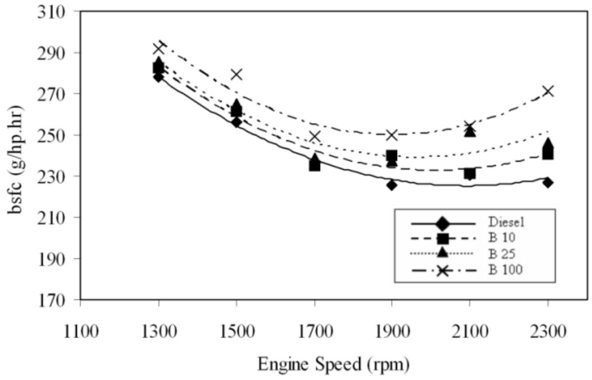


Fig. 14. Specific fuel consumption at various speeds.

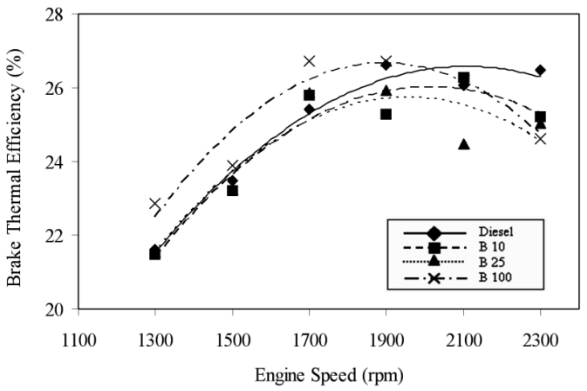


Fig. 15. Brake thermal efficiency at various speeds.

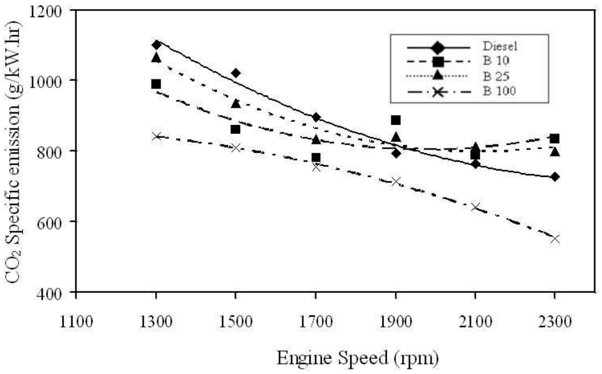


Fig. 16. Carbon dioxide specific emission at various speeds.

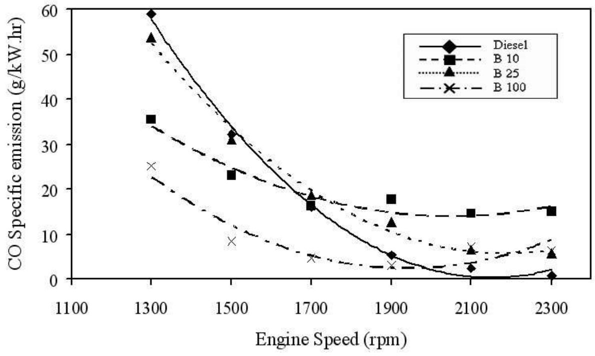


Fig. 17. Carbon monoxide specific emission at various speeds.

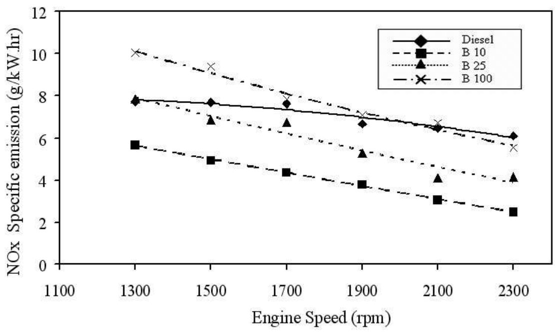


Fig. 18. Nitrogen oxide specific emission at various speeds.

In the specific emissions tested, the CO_2 specific emission of B100 engine is the lowest one as shown in Fig. 16, because the methyl ester structure contains the proportion of hydrogen to carbon or H/C more than that of diesel. The CO specific emission of the B100 engine, at low engine speed (1300-1700 rpm), is also the lowest one, while the diesel engine gives the highest value. As methyl ester is an oxygenated fuel and leads to more complete combustion, hence CO emissions reduce in the exhaust [23]. Kalligerous et al. [24] and Ramadhas et al. [22] also reported lower CO emissions for methyl ester using in the low speed diesel engine. Trends of CO specific emission, in all of fuel tests, are found to decrease when increasing in engine speed as shown in Fig. 17. When engine speed more than 2000 rpm, the CO specific emission of the B100 engine rises and gets higher than that of diesel engine, due to more methyl ester injected in to combustion chamber as shown in the bsfc resulted. This resulted can be clearly seen in fuelrich mixtures, then CO from insufficient oxygen is appeared. The B10 and B25 give the CO_2 and CO specific emission in between B100 and diesel. For the NO_x specific emission, all of fuel engine tests are found to decrease when engine speed is increased. The NO_x specific emission of methyl ester at 1300-1900 rpm is the highest as shown in Fig.18. The complete combustion of B100, as also found in highest brake thermal efficiency study, results high temperature of combustion and closed to adiabatic flame temperature. Therefore the NO_x forms by oxidation of atmospheric nitrogen at sufficiently high temperatures. Kinetics of NO_x formation is governed by Zeldovich mechanism, and its formation is highly dependent on temperature and availability of oxygen. Canaki et al [25] and Kalligerous et al [24] also reported results of slight increase in NO_x emissions for methyl ester.

4. CONCLUDING REMARKS

In this study, the production of methyl ester from crude rubber seed oil has been successfully performed. The acid esterification-alkaline transesterification reaction was adopted. The first step is the acid esterification purposed to reduce the FFA from the crude oil. At the same time, it also extracts the gum from the crude oil and converts some of FFA molecules to be mono methyl ester and water at this stage. The benefit of using the acid esterification is to reduce the chance to waste crude oil which may occur in the soap form, in stead of using the alkaline catalyst in the FFA reduction process. The optimum conditions in the acid esterification to reduce the FFA from 20% in crude oil to less than 3% were using 2.5% by mass of sulfuric acid, and molar ratio of methanol to oil is 6:1. The alkaline transesterification is the core reaction process which is KOH transesterification. The optimum conditions in the alkaline transesterification process for the production were 1.5% of KOH for catalysis (%by mass), while the amount of KOH for neutralization depends on the FFA value, and molar ratio of methanol to oil is 6:1. Therefore, the overall consumption of methanol was 12:1 and it is much less than previous study [3], [4], and [10]. The yielded methyl ester was tested for it fuel properties and met requirement standard except methyl ester content met nearby lower. The engine performance and emission test were performed. The neat methyl ester (B100) tends to give the better brake thermal efficiency and gasses emission than those of diesel at low engine speed (1300-1700 rpm). However, at low engine speed, the torque and the brake power of B100 engine were lower than that of diesel engine about 5% and consumed more fuel than diesel engine about 10% averagely due to the lower heating value. From this study, the methyl ester produced from crude rubber seed oil seems to suit with the low speed diesel engine such as farm machineries or big engines. However, if it is applied in the much higher injection pressure engine, such as common rail engine, the benefit of better mixing and atomization may overcome the pit falls of such methyl ester. Further investigation should be done in the near future.

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