Lao
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Biofuel Series

Jatropha oil and biodiesel testing procedures

Report

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Vientiane

120206_BFUEL_FR_029

February 2012

Lao Institute for Renewable Energy

LIRE

REPORT 120206_BFUEL_FR_029

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DOCUMENT REVISION HISTORY				
Rev	**Date**	**Description**	**Author(s)**	**Reviewer(s)**
#1	06/02/2012	Internal report	L. Sourya Doré	L. Branlant

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LIRE is a non-profit organisation dedicated to the sustainable development of a self sufficient renewable energy sector in the Lao PDR. The institute offers agronomical, technological and socio-economic research services, and works to provide a free public resource of information and advice on the use of renewable energy technologies in Laos. LIRE strives to support the development of the country by exploring commercially viable means to establish renewable energy technologies in rural parts of the country, in areas without connection to the national grid and with little access to technical expertise.

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Introduction

Bio-diesel processing by trans-esterification is sometimes confronted with problem in case of using oil having an amount of free fatty acid over 1 %. Free fatty acid can react with the trans-esterification catalyst for making soap. The presence of soap makes difficult the purification of bio-diesel because it makes stable emulsion with fatty methyl esters and glycerol.

In order to decrease acid value of the oil before trans-esterification, two procedures can be considered, the esterification of fatty acid or the trap of free fatty acid with compound containing silica like rice husk ash before trans-esterification. The trap of free fatty acid with rice husk ash seem to be a versatile solution for decreasing these compounds in the oil or in bio-diesel because rice husk is a cheap local raw material, the process can be implementing at room temperature and after processing the ash can be regenerate.

However it will be necessary to implement testing in order to find the best proportions of oil and rice husk to mix together for an efficient removal of free fatty acid. After testing calcium, magnesium and phosphorus will also be measuring in order to know if theirs quantities in the oil match the standards (ASTM or EU).

After removing free fatty acid from Jatropha oil, bio-diesel procedure will be testing from laboratory chemical in order to assess the yield and the quality of the bio-diesel. Two processes will be testing, one by heating the oil at 60 ^{o}C and one at room temperature. Some parameter like acid value, calcium, magnesium, sodium (or potassium), distillation and if it is possible total glycerol will be measure in order to know if the produced bio-diesel match the standards (ASTM or EU).

I Esterification of free fatty acid contained in vegetable oil before trans-esterification of fatty esters

The amount of free fatty acid in vegetable oils depends on the oil seed species, refining process and storage conditions. When exposed to air, heat, water, light or micro-organisms, oil quality is rapidly deteriorated resulting in the increasing of the amount of free fatty acid in the oil. High contain of free fatty acid in vegetable oil make difficult bio-diesel processing because they react with trans-esterification catalyst for producing soap.

In presence of soap, stable emulsion of bio-diesel and glycerol can be produce making difficult the separation of the two products. Glycerol phase contains some amount of bio-diesel and bio-diesel phase contains some amount of glycerol thus affecting the yield and the quality of bio-diesel. In case of processing biodiesel from oil containing an amount of free fatty acid over 1%, the process should be implemented in two steps. The first step consists in the esterification of free fatty acid in presence of acid catalyst for decreasing acid value of the oil and the second step consists to make trans-esterification of oil by conventional method.

1 Esterification of free fatty acid by methanol in presence of acid catalyst

Esterification is a reaction between an acid and an alcohol that produces ester and water according the scheme 1.

Scheme 1 : *Reaction of esterification*

If the quantities of acid and alcohol are implemented according the stockiometry of the chemical equation e.g. one mol of acid for mol of alcohol as show by scheme 1, after some time of reaction, the esterification reaches an equilibrium and no more ester is produced. In order to shift completely the reaction to the right side of the equation an excess of alcohol is use on the left side of the equation or one product on the right side should be remove during the reaction.

Esterification also needs catalyst for increasing the rate of the reaction. The catalysts that are used for esterification are acid catalyst like sulfuric acid, hydrochloric acid, para-sulfonic acid, trifluoroacetic acid, strongly acid cationic resin or Lewis acid catalyst. Esterification of free fatty acid contained in vegetable oil can be implementing with methanol and sulfuric acid. The quantities of methanol and sulfuric acid to implement for esterification depend on the weight fraction of free fatty acid in the oil. Weight fraction of free fatty acid in the oil can be measured by gas chromatography or it can be estimate from the acid value of the oil. The weight fraction

of free fatty acid in the oil is calculated by dividing acid value by two hundred. The calculations of the quantities of methanol and sulfuric acid to implement according the weight fraction of free fatty acid are listed in the table 1.

Table 1 : *Calculation of methanol and sulfuric acid quantities for implementing esterification according the weight fraction of free fatty acid in the oil.*

Mass of oil (g)	Acid value (mg KOH/g)	Weight fraction of free fatty acid	Methanol (99 %)	Sulfuric acid (98 %)
m	a	a/200	m×2.25 gram × a/200	m×0.05 gram × a/200

Example of calculations of the quantities of methanol and sulfuric acid to implement for the esterification of fatty acid contained in 250 gram of vegetable oil with an acid value of 5 mg KOH/g are listed in the table 2.

Table 2 : *Quantities of methanol and sulfuric acid to implement according initial mass of oil and the weight fraction of free fatty acid in the oil.*

Mass of oil (g)	Acid value (mg KOH/g)	Weight fraction of free fatty acid	Mass of methanol (g)	Mass of sulfuric acid (g)
250	5	0.025	14.06	0.31

Generally esterification is implemented at the boiling temperature of the solvent or the boiling temperature of the alcohol is there no solvent in the reaction. In the case of esterification of free fatty acid the temperature is set few degrees under the boiling temperature of the alcohol.

2 Procedure for the esterification of free fatty acid

Weight the quantity of methanol and the quantity of sulfuric acid and slowly introduce the sulfuric acid in methanol under mixing. Weight 250 grams of oil, put it in a flask of 500 ml equipped with condenser and thermometer and stir the oil with magnetic or mechanical stirrer. Add the mixture of methanol and sulfuric acid to the oil and heat to 60 ^{o}C. The monitoring of esterification can be accomplished by thin layer chromatography (TLC) or by the measurement of acid value during the reaction.

After the completion of reaction, cool to the room temperature and pour the content of the flask in a separating funnel of 500 ml. Add 100 ml of distillated water in the separating funnel and shake vigorously for 2 minutes in order to wash methanol and sulfuric acid from the oil. After shaking let in rest for decanting the two phases in order to separate the oil layer from the water

layer and drain off the water layer. Repeat the washing until the pH of the water is between 6.5 and 7. After washing with distillated water, dry the oil on anhydrous magnesium sulfate monohydrate for one night and filtrate the oil. After drying the oil can be use directly for trans-esterification.

2.1 Esterification monitoring by thin layer chromatography (TLC)

The monitoring of esterification reaction can be implementing by thin layer chromatography using silica gel plate as stationary phase and solvents like hexane, petroleum ether or chloroform with some small quantities of polar solvents like acetone, diethyl ether, ethanol or methanol as mobile phase. Revelation of the elution products can be implementing by spraying an alkaline solution of potassium permanganate with bromocresol green or bromophenol blue on the plate. After spraying the plate, residual fatty acid will make blue-green spot on the plate.

2.2 Esterification monitoring by the measurement of acid value

Before heating the flask and after introducing all the reagents take a sample of 2 ml and pour it in a separating funnel of 20 ml and add 10 ml of distillated water. Shake vigorously 2 minutes for washing methanol and sulfuric acid from oil and let in rest in order to separate water layer from oil layer and discharge the water layer. Wash again three times with the same quantity of distillated water and measure the acid value of the oil layer with conventional method. After one hour of reaction remove the heater, take a sample of 2 ml and repeat the procedure described above. The ratio of acid value after one hour of reaction to the acid value at the beginning of the reaction should be less than 0.1, if not heat again for 30 minutes and repeat the procedure until the ratio of acid value be less or equal to 0.1.

2.3 Remarks

Methanol is a flammable and toxic chemical. It should be handled in place with good ventilation. Sulfuric acid is a very corrosive chemical and its handling should be implementing with safety glasses and protective gloves. Vegetable oil and methanol should be anhydrous, if they contain some water, the reaction will reach equilibrium and the esterification will not achieve the completion.

II Adsorption of free fatty acid contained in vegetable oil by rice husk ash

Rice husk is an agricultural waste containing about 20 % in weight of pure silica. After charring rice husk, the ash contains about 90 % of pure silica. Silica is a mineral compound with good adsorption properties and it is very efficient for trap polar compounds like water, organic and mineral acid or salts. However from our knowledge no testing has been implemented for removing fatty acid of Jatropha oil by rice husk ash. In order to know if rice husk ash can be

efficient for removing fatty acid from Jatropha oil it will be necessary to implement some testing under specified experimental conditions.

1 Procedure for testing the efficiency of rice husk ash treatment

Rice husk will be previously grind and char at 500 ^{o}C for two hours for removing organic materials. The testing will consist to mix vegetable oil with rice husk ash according specified proportions and to let the mixture at room temperature for one night. After one night at room temperature the oil will be filtering and the acid value will be measuring on filtrated oil. The ratio of the acid value after treatment to initial acid value of the oil will allow estimating the efficiency of the treatment.

2 Proportions of oil and rice husk ash to mix together

The proportions of oil and rice husk ash to mix together should be optimized for having the highest free fatty acid percent removing with the lowest quantity of rice husk ash for a specified amount of oil. The optimization of the proportions to implement will be making by the method of Fibonacci. The Fibonacci series is a series of integer in which each integer is the sum of the two previous integers in the series. The Fibonacci series begins as follow 0, 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144.

The Fibonacci method can be apply to optimize phenomena that have only one optimum. In the case of adsorption of free fatty acid by rice husk ash one assumes that after reaching the optimal quantity of rice husk ash, additional quantities of rice husk ash will not increase the percentage of free fatty acid removing. In Fibonacci method the parameter to optimize should be proportional to the number of the series. For our purpose the parameter to optimize will be the mass of rice husk ash and it will be equal to the numbers of Fibonacci series. The domain of optimization will be between 0 and 21 gram of rice husk ash for 100 gram of oil. The proportions of oil and rice husk ash to mix together for starting optimization are listed in the table 3.

Table 3 : *Proportions of oil and rice husk ash to mix together for starting optimization*

Experiment no	Mass of oil (g)	Mass of rice husk ash (g)
1	100	13
2	100	8

According the results of experiment 1 and 2 the optimization of mass of rice husk ash will go on as follow:

- If the result of experiment 1 is better than the result of experiment 2, the interval between 0 and 8 of Fibonacci series will be eliminate from the domain of study and a new experiment will be make with a mass of rice husk ash equal to 16 gram;

- If the result of experiment 1 is lower than the result of experiment 2, the interval between 13 and 21 of Fibonacci series will be eliminate and a new experiment will be making with a mass of rice husk ash equal to 5 gram.

As the optimization go on the interval of study will be reduce until reaching the optimum and the optimization will stop when two consecutive experiments will have similar results.

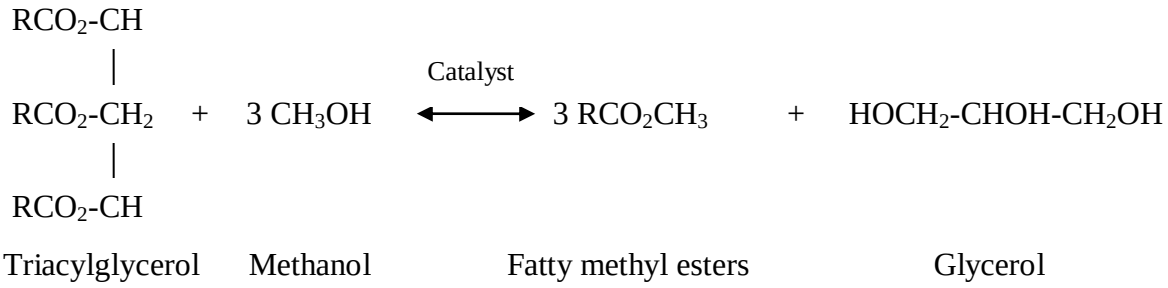
III Trans-esterification of fatty esters

Vegetable oils or animal fat cannot be use directly as substitute for fuelling common diesel engine due to their high viscosity and for this purpose they should be chemically transformed in order to decrease their intrinsic viscosity. The chemical reaction that is use for decreasing viscosity of vegetable oils and animal fats is call trans-esterification. Trans-esterification is a reaction of an ester with an alcohol that produces an ester of the implemented alcohol and glycerol in presence of a basic catalyst.

1 Trans-esterification of acyl-glycerol by methanol in presence of basic catalyst

Lipid in vegetable oils and animal fats contain mainly triacylglycerol compound (ester) that can be subject to trans-esterification with an alcohol for producing an ester of the implemented alcohol and glycerol in presence of basic catalyst according the scheme 2.

Scheme 2 : *Reaction of oil trans-esterification*



If the quantities of triacylglycerol and alcohol are implemented according the stockiometry of the chemical equation e.g. one mole of triacylglycerol for 3 moles of alcohol as show in scheme 2, after some time of reaction the trans-esterification reaches an equilibrium and no more ester is produced. In order to shift completely the reaction to the right side of the equation an excess of

methanol is use on the left side of the equation. Unlike esterification, product on the right side of the chemical equation are not remove in the case of the trans-esterification of vegetable oils or animal fats because they have high boiling temperature. Catalysts that are use for trans-esterification are mainly Brønsted bases such as sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide or metallic sodium. Some researchers have also used anionic exchange resin, cationic exchange resin, metallic oxide or enzyme but trans-esterification with these kind of catalyst have only been implemented at laboratory scale. Generally the main catalyst that is use for trans-esterification is sodium hydroxide because it is cheap and the weight ratio that is use for trans-esterification is 1.5 %. In case of use potassium hydroxide the weight ratio for trans-esterification is 2.1 %.

Generally trans-esterification is implemented at the boiling temperature of the solvent or the boiling temperature of the alcohol if no solvent is use for the trans-esterification. In the case of trans-esterification of vegetable oils or animal fats the temperature is set few degrees under the boiling temperature of the alcohol but it can also be implementing at room temperature with good yield.

The quantity of alcohol to use for trans-esterification is calculated on the basis of the number of moles of oil involved in the reaction or on the basis of the weight of oil. Generally one uses a molar ratio of 6 moles of alcohol for one mole of oil or a weight ratio of 24 % of methanol to oil. For the reaction of trans-esterification, the number of moles of alcohol should exceed the number of moles of oil for the completion of the reaction, but large excess of alcohol can complicate the separation of biodiesel phase from glycerol phase after trans-esterification. The table 4 compares the quantities of alcohol (methanol) that are use for trans-esterification according the basis of calculation.

Table 4 : *Quantities of methanol to implement according the basis of calculation*

Basis of calculation	Masse of oil (g)	Oil (mole)	Masse of methanol (g)	Methanol (mole)
Molar ratio: 6/1	200	0.234	44.93	1.404
Weight ratio: 24 %	200	0.234	48.00	1.5

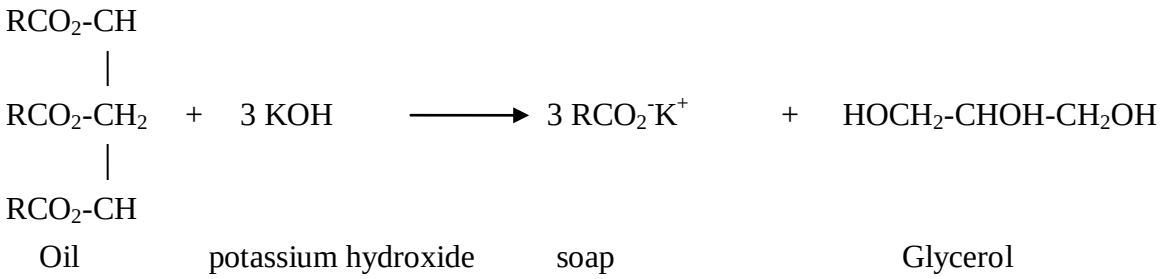
The quantity of methanol to use for trans-esterification should preferably be calculate from molar ratio basis instead weight ratio because the composition and the percentages of triacylglycerol present in vegetable oils or animal fats can change according harvest process, oil processing or storage conditions. The number of moles of triacylglycerol (oil) can be calculating from the ester value of the oil (table 5).

Table 5 : *Calculation of the oil number of moles from ester value*

Ester value (mg KOH/g)	Masse of oil (g)	KOH (mol)	Oil (mol)
a	m	$n\,KOH = \frac{a \times m}{56000}$	$\frac{n\,KOH}{3}$

Ester value is calculated by subtracting acid value from oil saponification value. The product of ester value by the mass of oil divided by 56000 (molecular mass of potassium hydroxide in mg/mol) gives the number of moles of potassium hydroxide that are need for the complete saponification of the oil. Saponification is the reaction that transforms completely oil in soap according the reaction of the scheme 3. The complete saponification of one mole of oil needs three moles of potassium hydroxide. The number of oil mole is equal to the number of moles of potassium hydroxide divided by 3.

Scheme 3 : *Reaction of oil saponification*



2 Procedure for the trans-esterification of oil

Weight the 60 grams of methanol, 5.25 grams of potassium hydroxide and slowly introduce the potassium hydroxide in methanol under mixing. Weight 250 grams of oil, put it in a flask of 500 ml equipped with condenser and thermometer and stir the oil with magnetic or mechanical stirrer. Add the mixture of methanol and potassium hydroxide to the oil and heat to 60 ^{o}C for one hour. The monitoring of trans-esterification can be accomplished by thin layer chromatography (TLC).

After one hour, cool to the room temperature and pour the content of the flask in a separating funnel of 500 ml and let at rest one night for decantation. After one night of decantation, the mixture should be separate in two layers, drain off the lower layer (glycerol phase). Add 100 ml of distillated water in the separating funnel and shake vigorously for 2 minutes in order to wash methanol and potassium hydroxide from the oil. After shaking let in rest for decanting the two phases in order to separate the oil layer from the water layer and drain off the water layer. Repeat

the washing until the pH of the water is between 6.5 and 7. After washing with distillated water, dry the oil on anhydrous magnesium sulfate monohydrate for one night and filtrate the oil.

The same procedure can be implementing at room temperature with the same proportions of reactants and during 3 hours in order to compare the yield in bio-diesel. The yield of fatty methyl esters can be measured by gas chromatography (GC) or high performance liquid chromatography (HPLC).

2.1 Trans-esterification monitoring by thin layer chromatography (TLC)

The monitoring of esterification reaction can be implementing by thin layer chromatography using silica gel plate as stationary phase and solvents like hexane, petroleum ether or chloroform with some small quantities of polar solvents like acetone, diethyl ether, ethanol or methanol as mobile phase. Revelation of the elution products can be implementing by spraying a solution of rhodamine B in ethanol on the plate. Fatty methyl ester will be coloring in red-violet spot on the plate

2.2 Remarks

Methanol is a flammable chemical and its vapors are toxic. It should be handled in place with good ventilation. Potassium hydroxide is a very hygroscopic and corrosive chemical and its handling should be implementing with safety glasses and protective gloves. Vegetable oil and methanol should be anhydrous, if they contain some water, the trans-esterification will not achieve the completion.

IV Testing to implement

The scope of the testing to implement will cover procedure for the preparation of potassium hydroxide standard solution of, rice husk ash testing and trans-esterification of Jatropha oil

1 Procedure for the preparation of potassium hydroxide standard solution

Considering the results of acid value that have been measured on Jatropha oil samples and according the procedure (plastic bottle and drinking water) that was use for preparing standard solution of potassium hydroxide, it will be necessary to make a new standard solution of potassium hydroxide by using calibrated volumetric flask in order to reduce the error on the concentration coming from an uncertain volume and distillated water instead drinking water. After preparing standard solution of potassium hydroxide, acid value will be measure on the freshly processed oil. In order to make a statistical treatment of the result, five analyses will be making on Jatropha oil sample.

2 Rice husk ash testing

Rice husk testing will be implementing in order to know if is it possible to decrease the acid value of Jatropha oil and what will be the proportions to implement. At present it is not possible to expect how many experiments will be necessary for the optimization of free fatty acid removing process. In case of good result the best procedure will be do again five times for statistical treatment of the result. After oil treatment some parameter like calcium, magnesium and phosphorus will also be measure in order to know if rice husk ash can also traps these compounds. For indication residual quantity of calcium and magnesium should be no more than 5 ppm and residual quantity of phosphorus should be no more than 0.001 %. After treatment of the oil, testing will also be implementing on the ash after oil treatment in order to know if the fatty acid that are trapped by the ash can be esterified with methanol.

3 Trans-esterification of Jatropha oil

After decreasing acid value of Jatropha oil to an acceptable value, trans-esterification of the oil will be implementing with methanol and potassium hydroxide. Two testing will be implementing one at 60 ^{o}C and one at the room temperature in order to compare the yield and the quality of bio-diesel from the two procedures. Some parameter like acid value, calcium, magnesium, sodium (or potassium), distillation and if it is possible total glycerol will be measure in order to know if the produced bio-diesel match the standards (ASTM or EU).

The best procedure will be implementing five times for making a statistical treatment of the results. In case of good yield the procedure will be scale up to 1 kg of oil and to 5 kg of oil with laboratory chemical in order to know if the scale up gives similar yield. The result of the scale up will allow implementing bio-diesel procedure with Jatropha oil and chemicals from local market (methanol and sodium hydroxide) for comparing the obtained results from the two kinds of chemical (laboratory grad and local market grad). The result of the batch with chemical from local market will allow knowing if some corrective actions should be implementing for reaching the yield and the quality of bio-diesel implemented with from laboratory chemical.