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Jatropha oil treatments before trans-esterification

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L. Sourya Doré

Vientiane

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LIRE

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About us

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.

Lao-Thai Friendship Road
Wattnak village, Vientiane, Lao PDR
P.O. Box 8010

Tel: +856 21 353 430. Fax: +856 21 353 897.
Email address: contact@lao-ire.org.
Web-site: www.lao-ire.org

1 Contents

1 Introduction

After Jatropha seed pressing, the oil contains impurities that have to be remove before trans-esterification in order to avoid processing problem (emulsion) and to produce safe fuel for engine. The main impurities that have to be removing from crude oil are free fatty acid, metals (calcium, magnesium, phosphorus, potassium and sodium), sediments, and water. Few amount of free fatty acid naturally occur in oil seed but theirs amount in the seed can increase with relative humidity of storage place, duration and temperature of storage (Ghasemnezhad & Honermeier, 2007). After harvesting the seed should be dry quickly to remove water because the presence of water in the seed can promotes the hydrolysis of acyl glycerol and releases free fatty acid. Free fatty acid can also occur in the oil after pressing if the oil still contains water.

Metal like calcium, magnesium and phosphorus are naturally present in oil seed in the form of phospholipids. Phospholipids are located in the cells of oil seed and are release during the oil processing. The temperature of pressing has also an influence on the amount of phospholipids that are release in the oil after pressing. Other impurities like glycerol, methanol, potassium and sodium can also be present in biodiesel because the trans-esterification of the oil is implemented with methanol and potassium or sodium catalyst. Glycerol is also a by-product of the trans-esterification. The presence of glycerol, methanol, potassium and sodium in the biodiesel is due to an un-efficient washing of biodiesel after processing (washing procedure and/or water quality).

The quantities of sediments and water that are present in the final product (biodiesel) are mainly related to the extraction and purification methods that are use for producing crude oil and biodiesel. Dirty or un-dried process equipments can also introduce impurities or water in the final product. Several procedures have been tested for decreasing the amount of impurities in crude Jatropha oil. Procedures for decreasing the amount of free fatty acid (14 testing) and procedures for decreasing the amount of phospholipid compounds (6 testing). Trans-esterification of Jatropha oil has also been implemented (one testing) after oil treatment.

2 Procedures for decreasing the amount of free fatty acid in crude Jatropha oil

Free fatty acid can cause processing problem, biodiesel instability and engine problem. They can react with the catalyst of trans-esterification and produce soap. Soap can make stable emulsion during the washing of biodiesel with water resulting in biodiesel yield loss or glycerol contamination.

Free fatty can also cause biodiesel instability. During the time free fatty acid can undergo oxidation and produce compounds like aldehydes, ketones, epoxydes and alcohols which can react with ethylenic bonding of oil for making resin that can plug fuel system. Fatty acid can also attack metal components of fuel system and contaminate engine oil resulting in the endangering of lubricating system (Banga & Varshney, 2010).

For the processing of biodiesel from Jatropha oil, free fatty acid should be removing to avoid the formation of stable emulsion during the trans-esterification. According to the literature dealing with biodiesel processing (Canacki & Van Gerpen, 2001), an acid value under or equal to 2 mg of KOH per gram of crude oil is satisfactory for the trans-esterification and the most used process for decreasing the amount of free fatty acid in the oil is the esterification with methanol and catalyst like sulfuric acid. However this process has two main drawbacks that are the need to recover methanol after the esterification and the need of specific equipment for implementing the esterification of fatty acid.

After esterification of free fatty acid, methanol should be recovered for decreasing processing costs because it is use in large excess to ensure the completion of the esterification. Methanol is recovered by distillation and the reactor for esterification should be equipped with condenser for condensing methanol vapor and recover methanol in liquid state.

Esterifications that use concentrated acid like sulfuric acid or hydrochloric acid should be implemented in corrosion though vessel (glass, glass lined or thermal tough plastic). If esterification is implemented with concentrated acid in stainless steel reactor leak of the equipment can occur quickly and heating system can be corroded resulting in electrical shock if an electrical heater is use inside the reactor.

Taking into account these two technical issues (methanol recovering and corrosion) alternative process have been considered for decreasing the amount of free fatty acid of crude Jatropha oil and the following procedures have been tested :

- Rice husk ash treatment;
- Lime treatment;
- Anionic exchange resin.

Esterification of free fatty acid has also been implemented with methanol and glycerol. Esterification with methanol has been implemented because it is the reference process for comparing the

efficiency of the alternative procedures. Esterification has also been implemented with glycerol as alternative to methanol process because glycerol is a waste coming from trans-esterification that can potentially react with free fatty acid.

During the procedures testing, two kinds of Jatropha crude oil have been tested; one with high acid value (26 mg of KOH per gram of crude oil) pressed by the Lao State Fuel Company and an two others pressed by LIRE at the Institute of Renewable Energies of KM14 with an acid value between 6 to 8 mg of KOH per gram of crude oil. After the testing the acid value before and after the treatment have been measured for calculating the percentage of free fatty acid removing and compare the efficiency of the implemented procedures.

2.1 Rice husk ash treatment

Rice husk is an agricultural waste commonly encountered in rural area of Lao PDR. It contains about twenty percents by weight of silica which has good adsorption properties especially for polar compounds like mineral and organic acid, metals, salt and water. After complete charring at 500 ^{o}C, rice husk leaves ash with about ninety percents by weight of silica.

Rice husk has been charred for two hours at 500 ^{o}C at the laboratory of Quality Control of Pharmaceutical Factory no 3 of Vientiane and a sample of ash has been extracted according a specified procedure (Kamath & Proctor, 1998) in order to assess the amount of carbon residue in the ash. The result of the amount of carbon residue contained in the ash is about thirty percent by weight.

After charring rice husk, two testing were implemented with the Jatropha oil pressed by LIRE and two different percentages of ash at room temperature and without agitation. The tests have been implemented at room temperature and without agitation because the quantity of ash was not sufficient and glassware and laboratory equipments of Lao State Fuel laboratory are not suitable for implementing small quantities (less than 20 grams).The results of the testing are gather together in the table 1.

Table 1 : *Results of rice husk ash treatment for decreasing acid value of Jatropha crude oil*

Reference of testing	Percentage of rice husk ash (%)	Duration	Percentage of	Residual acid value

			free fatty acid removing (%)	(mg KOH/g)
JORHA-1	16.0	One night	12.1	6.89
JORHA-2	23.0	One week	62.8	2.91

One can note from the results of table 1 that quantity of rice husk ash and duration have a strong influence on free fatty acid removing but the residual acid value is still higher than 2 mg of KOH per gram of crude oil (JORHA-2). According to the literature (Manique, Faccini, Onorevoli, Benvenuti, & Caramao, 2011) rice husk ash can be efficient for removing free fatty acid and other impurities of biodiesel like glycerol, methanol, water and some metals like potassium if biodiesel is treated with rice husk ash at 60^{o}C and with agitation.

Rice husk should also be charred for at least five hours in order to remove the entire carbon residue and reach a purity of about ninety percents. The sample that was produced at the laboratory of Quality Control of Pharmaceutical Factory no 3 of Vientiane was only charred for two hours because the laboratory needed the oven for analytical work. Two hours of charring is not sufficient because the amount of silica in the ash was only seventy percent by weight and not ninety percents according to the literature. Rice husk treatment can be more effective if rice husk is charred for at least five hours at 500 ^{o}C and if heat and agitation is provide during the treatment.

2.2 Lime treatment

Natural lime is made up of calcium carbonate, a weak base that can react with free fatty acid for producing fatty acid calcium salts which have low solubility in water. Tests have been implemented with the oil pressed by LIRE for two temperature conditions, different percentages of lime and water but with the same stirring rate (1500 rpm) for all the tests. The results of the testing are gathered together in the table 2.

One can note according the result of table 2 that lime and water percentages are important parameters for decreasing the amount of free fatty acid in Jatropha oil. The best result of lime treatment gives a residual acid value of 2.34 mg KOH per gram with 69 % of fatty acid removing (LT-3).

Table 2 : *Results of lime treatment for decreasing acid value of Jatropha crude oil*

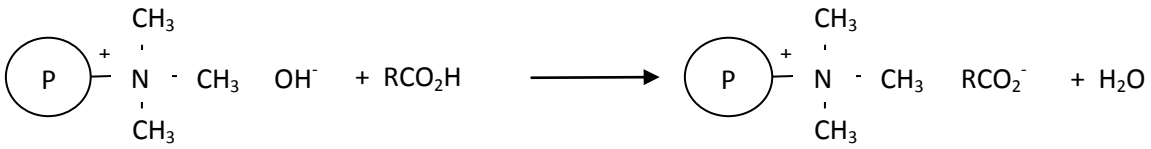
Reference of testing	Percentage of lime (%)	Percentage of water (%)	Temperature (°C)	Duration (minutes)	Percentage of free fatty acid removing (%)	Residual acid value (mg KOH/g)
LT-1	0.43	5.3	80	15	29.9	5.30
LT-3	0.67	12.7	Room temperature	30	69.0	2.34
LT-4	0.7	8.2	Room temperature	30	65.9	2.58

Lime treatment can be effective for decreasing oil acid value to an acceptable level and lime is an affordable raw material in Lao PDR. However the main drawback of this treatment is the occurrence of stable emulsion during the treatment that needs lengthy time of centrifugation and decantation for separate oil and water. This treatment should also be following by a second treatment for efficiently remove calcium in oil. The amount of calcium contained in the oil should be in accordance with biodiesel quality standards.

2.3 Anion exchange resin treatment

Anion exchange resins are made up from insoluble synthetic polymers containing functional groups that can react with mineral or organic acid. There are two kinds of anion exchange resins, strongly basic and weakly basic. Strongly basic resins are functionalized with trimethyl ammonium groups and weakly basic resins are functionalized with amino groups. Amberlite IRA 900 ® is a strongly basic resin that contains trimethyl ammonium hydroxide groups. Trimethyl ammonium hydroxide groups can react with free fatty acid contained in the oil for producing an ammonium salt of fatty acid and water as shown in scheme 1.

Scheme 1 : *Reaction of free fatty acid with strongly basic resin*



The salt of fatty acids produced by the reaction is fixed on the resin and the water that is release during the reaction can be evaporated by heating the oil. The resin with fixed salt of fatty acid can be separate from the oil by filtration or centrifugation. The resin can be regenerated by washing with a solution of mineral acid like hydrochloric acid or sulfuric acid followed by a washing with a solution of sodium hydroxide.

Two testing have been implemented with Amberlite IRA 900 ® for trying to decrease the amount of free fatty acid in the Jatropha oil. The result of the testing are gathered together in the table 3.

Table 3 : *Results of strongly basic resin treatment for decreasing acid value of Jatropha crude oil*

Reference of testing	Percentage of resin (%)	Temperature (°C)	Duration (hours)	Percentage of free fatty acid removing (%)	Residual acid value (mg KOH/g)
ANT-1	5	Room temperature	3	45.77	3.33
ANT-2[a]	15	60	2	69.65	2.37

a: the test ANT-2 has been ran two hours at 60 °C and let one night at room temperature with no agitation

The two testing have been implemented with a stirring rate of 1000 rpm. One can note according the results of the table 3 that temperature and the amount of resin are key parameters for decreasing the amount of free fatty acid in Jatropha oil. It is also expected that stirring rate and

viscosity of the oil should also affect the kinetic of the reaction. By increasing the amount of resin it is expected that the acid value will decrease under the recommended value (2 mg of KOH per gram of oil). However one still don't know if this procedure is suitable for oil with high acid value (e.g. more than 10 mg of KOH per gram of oil) because it is expected that the amount of resin to implement will increase with acid value of the oil. Strongly basic resin can also be use for decreasing the acid value of biodiesel after trans-esterification.

2.4 Esterification of fatty acid

Esterification of fatty acid has been implemented with methanol and glycerol for different operational conditions and the results of the experimentations are gathered together in the table 4.

Table 4 : *Results of esterification for decreasing acid value of Jatropha crude oil*

Reference of testing	Kind of alcohol	Percentage of alcohol (%)	Percentage of Sulfuric acid (%)	Temperature (°C)	Duration (hours)	Percentage of fatty acid removing (%)	Residual acid value (mg KOH/g)
EFAJO-1	Methanol	22.5	0.5	60	1	96.1	1
EFAJO-2	Glycerol	1.86	0.27	110	2	0	6.14

Esterification of free fatty acid by methanol has been implemented with oil pressed by Lao State Fuel Company with an initial acid value of about 26 mg of KOH per gram of crude oil (EFAJO-1) and with oil pressed by LIRE with an acid value of 6.14 mg of KOH per gram of crude oil (EFAJO-2). One can note according the result of the test (EFAJO-1, table 4) that the procedure is very efficient because it remove about 96 percents of free fatty acid resulting to a residual acid value of 1 mg of KOH per gram of crude oil which is lower than the recommended value of 2 mg of KOH per gram of crude oil. Esterification of free fatty acid has also been implemented with glycerol and (EFAJO-2, table 4) but the conditions at which the testing has been implemented did not allow decreasing the initial amount of free fatty acid in the oil.

Esterification of free fatty acid with methanol and sulfuric acid can be effective for decreasing the amount of free fatty acid under the recommended value (2 mg of KOH per gram of oil). However

the two main drawbacks of this process are the amount of methanol and sulfuric acid that are used for the esterification. The quantity of methanol to implement increase with the acid value of the oil and for an acid value of about 26 mg of KOH per gram, one needs twenty percents by weight of methanol. After esterification methanol should be recover for economic reason. The process should also be implemented with corrosion tough equipment like glass, glass lined or plastic vessel. Stainless steel equipments are not suitable for this process. The quantity of sulfuric acid to implement increase with the acid value and sulfuric acid can corrode stainless parts of process equipment like reactor wall and heater resulting in product leakage or electrical shock with possible fire or explosion because methanol is a flammable chemical.

2.5 Trans-esterification of Jatropha oil

The oil that has been treated with strongly basic resin (ANT-1) has been use for trans-esterification testing according operational conditions of table 5.

Table 5 : *Results of trans-esterification of Jatropha crude oil*

Reference of testing	Percentage of methanol (%)	Percentage of potassium hydroxide (%)	Temperature (°C)	Duration (hours)	Yield (%)	Residual acid value (mg KOH/g)	Methanol solubility (1 vol / 1vol)
TAG-1	19	1.6	60	2	61.1	0.24	soluble

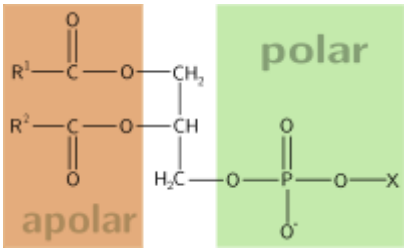
The result of the table 5 shows that trans-esterification has been accomplished with a yield of about 61 %. The low obtained yield is due to the formation of stable emulsion during the washing of the product that increases the loss of product. The residual acid value of the obtained bio-diesel is under the recommended value (0.5 mg of KOH per gram) and one volume of bio-diesel can be dissolved in all proportion in one volume of methanol showing that all the acylglycerol of the oil have been trans-esterified by methanol. However testing should be implementing again for increasing yield of biodiesel and analysis should be making for assessing the amount of fatty methyl esters, calcium, magnesium, potassium, phosphorus, glycerid (mono, di and total) and all the others parameters that are necessary for assessing the quality of biodiesel.

3 Procedure for decreasing the amount of phospholipid compounds in crude Jatropha oil

Vegetable oils and fat contain gums mainly constituted by two types of phosphorus derivatives, hydratable phospholipids (HPL) and non hydratable phospholipids (NHPL) and theirs quantities and the type of phospholipids (HPL or NHPL) can vary according vegetable oil species or animal fat. Phospholipids should be quickly remove from crude oil after oil pressing because they have emulsifying properties that making difficult the separation of glycerol from fatty methyl ester after the processing of biodiesel. They also accelerate the hydrolysis of acyl glycerol thus increasing the amount of fatty acid in the oil. Process for removing phospholipids in the oil is call degumming. Oil degumming consists to treat the oil with water and/or chemical or enzyme for separate phospholipids from the oil.

The molecular structures of phospholipids present in vegetable oils and fat are depicted by the scheme 2. The molecular structure of phospholipids is constituted by two parts, an apolar part which has affinity for lipid and a polar part which has an affinity for water according its chemical structure. The radical X in the molecular structure of phospholipids can be a derivative of choline (lecithin), ethanolamine, hydrogen (phosphatidic acid), inositol (sugar) or serine (protein). There are two kinds of phospholipids, hydratable and non hydratable phospholipids. Hydratable phospholipids can interact with water for producing gel that can be separated from the oil. Non hydratable phospholipids do not interact with water directly and need chemical additives in order to change their chemical conformation and make possible interaction with water for forming gel that can be separated from the oil.

Scheme2 : *Molecular structure of phospholipids*

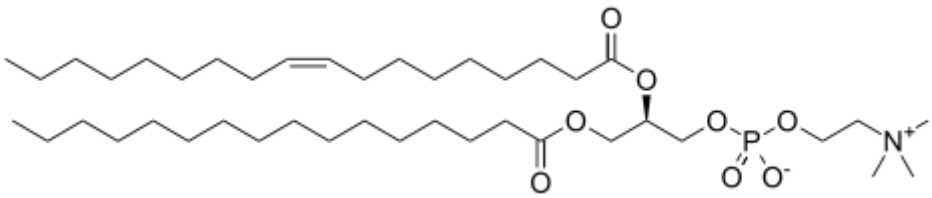


3.1 Hydratable phospholipids

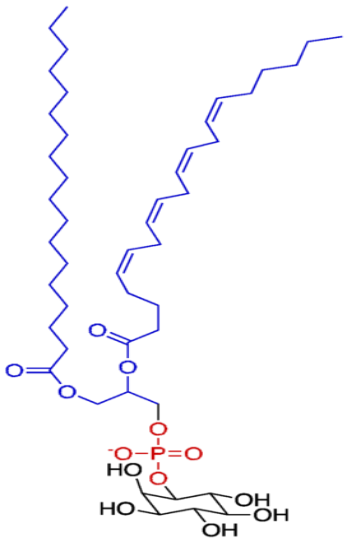
Phosphatidyl choline (PC) and phosphatidyl inositol (PI) are completely hydratable with water and can be removing by mixing the oil with some quantities of water. PC contains a quaternary ammonium salt (scheme 2) with a positive charge at all pH values and good affinity for water. At pH less than 3 phosphatidyl choline has only a positive charge. PC is hydratable at all pH value. At

pH less than 5 phosphatidyl inositol (scheme 3) has no charge and at pH over 5 PI has one negative charge. Hydroxyl group of inositol structure give to PI hydrophilic behavior and consequently PI is hydratable by water at all pH values.

Scheme3 : *Molecular structure of phosphatidyl choline (PC)*



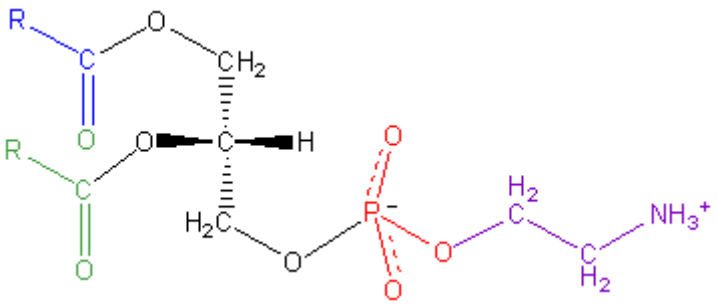
Scheme4 : *Molecular structure of phosphatidyl inositol (PI)*



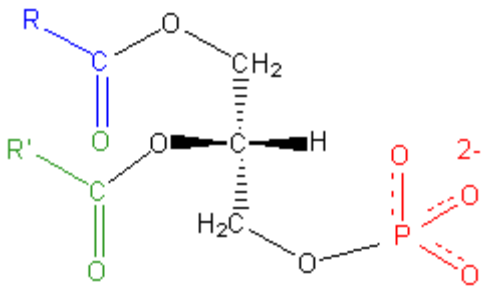
3.2 Non hydratable phospholipids

Non hydratable phospholipids are compounds that cannot make direct interaction with water because of their chemical structure and properties. The main non hydratable phospholipids that are found in vegetable oils and fat are phosphatidyl ethanolamine (PE), phosphatidic acid (PA) and the salts of phosphatidic acid. According the scheme 4 polar part of phosphatidyl ethanolamine can make a six membered ring with no net charge which is stable at neutral condition. PE has a net charge only if the pH is lower than 3 and higher than 9 and is only hydratable in this range of pH. Phosphatidic acid (PA) is not hydratable if the pH is under 3 because it has no net charge (scheme 5). To make PA hydratable it should be dissociated and be present as alkali salt. Salt of phosphatidic acid can be removing by phosphoric acid and citric acid and by increasing the pH.

Scheme5 : *Molecular structure of phosphatidyl ethanolamine (PE)*



Scheme6 : *Molecular structure of phosphatidic acid (PA)*



3.3 Implemented procedures for decreasing the amount of phospholipids in crude Jatropha oil

Two procedures have been implemented for decreasing the amount of phospholipids in Jatropha crude oil, one with distilled water and the other with citric acid. Procedure with distilled water consists heating the crude oil with distilled water (5 % in volume) at 80 °C and a stirring rate of 1000 rpm for 15 minutes then to cool the oil to room temperature. After one night at rest the by-products of the treatment settle at the bottom of the vessel and are separated from the oil. The water treatment only removes hydratable phospholipids, calcium and magnesium.

Citric acid treatment consists to heat the oil with an aqueous solution of citric acid (2 % in volume) at 80 °C and a stirring rate of 1000 rpm for 15 minutes then to cool the oil to room temperature. After one night at rest the by-products of the treatment settle at the bottom of the vessel and are separated from the oil. The citric acid treatment removes hydratable and non hydratable phospholipids, calcium and magnesium.

The two procedures have been tested at the laboratory of Lao State Fuel Company and samples of treated oils have been sent to the laboratory of Soils Survey for analyzing calcium, magnesium and phosphorus in order to assess the efficiency of the two treatments. At present the laboratory of Soils Survey still not send the results of the analysis.

4 Conclusion

Before trans-esterification of oil for producing bio-diesel the amount of free fatty acid contained in the oil should be decreased under a value of 2mg of KOH per gram of crude oil to avoid processing problem (stable emulsion) and yield loss. The procedures that have been tested for decreasing the amount of acid value of Jatropha crude oil are the following :

- Rice husk ash treatment;
- Lime treatment;
- Strongly basic resin treatment;
- Esterification of free fatty acid.

Rice husk ash is effective for decreasing the amount of free fatty acid in Jatropha crude oil if the amount of silica contained in the ash is at least ninety percent of ash weight. To reach this amount of silica rice husk should be char at least five hours at 500 °C. Lime is mainly constituted by calcium

carbonate and it can react with free fatty acid for making insoluble salt. However during the treatment of Jatropha crude oil emulsions occur making difficult the separation of oil and water and this treatment needs lengthy time of centrifugation.

Strongly basic resin treatment can decrease the acid value of Jatropha crude oil under 2 mg of KOH per gram of crude oil but it is not sure that the strongly basic resin treatment can be efficient for oil with high acid value (e.g. over 10 mg of KOH per gram of crude oil) because the amount of resin to implement increase with the acid value of the oil. This process should be developed in order to optimize the quantity of resin to implement, to know if the free fatty acids fixed on the resin can be esterifies for producing bio-diesel, to know what is the maximum weight of resin to implement according the acid value and given weight of crude oil and how many time the resin can be regenerated.

Esterification of free fatty acid with methanol and sulfuric acid can effectively decrease the acid value under the recommended value but this treatment has two main drawbacks that are the need to recover the methanol for economic reason and the need of corrosion thought process equipments. Methanol should be recovered after esterification process because the quantities to implement for the esterification of free fatty acid increase with the acid value. The quantity of sulfuric acid to implement also increase with acid value and this process should be implementing with corrosion thought equipment like glass vessel, glass lined or thermal though plastic reactor. Vessel assembled in stainless steel 304L like the pilot of Lao State Fuel Company is not suitable for the esterification of free fatty acid by methanol and sulfuric acid.

5 Recommendations

Considering the large variation in acid value of Jatropha crude oil (6 to 26 mg of KOH per gram of crude oil) on can make some recommendations for limiting the occurrence of free fatty acid in Jatropha seed after harvesting and for limiting the amount of phospholipids in the oil after pressing. Quality of water use in the procedure for decreasing the amount of impurities in the oil before trans-esterification can also affect the quality of the final product.

After harvesting the Jatropha oil seed they should be dry and process quickly to avoid lengthy storage duration that can increase the amount of free fatty acid in the seed. The drying of Jatropha oil seed can be implementing with solar dryer in Lao PDR. Solar dryer are cheap to build and efficient for removing water from agricultural crops.

After drying the oil seed should be process as soon as possible to avoid long time storage and limit the risk of free fatty acid occurrence. After pressing the oil should be centrifugated for removing gums and water. Oil with high acid value can also be mix with oil with low acid value. The pressing of Jatropha seed oil should also be implementing at room temperature without heating for limiting the occurrence of phospholipids in the oil.

The water that is use for degumming, decreasing acid value of Jatropha oil and for bio-diesel washing should be distilled water or deionized water with an electrical conductivity of not more than 10 µS/cm and total dissolved solids of less than 10 mg/liter.

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