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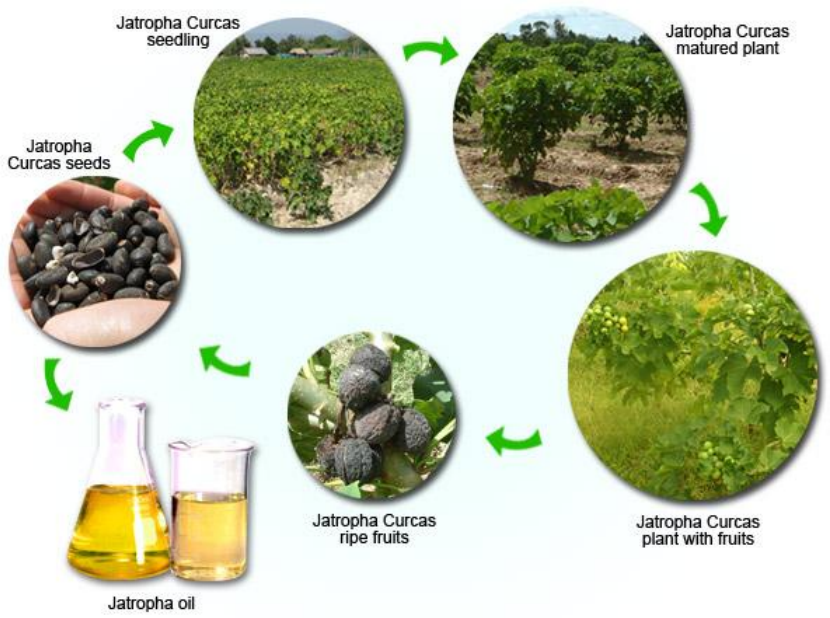


Biofuel Series

# Biodiesel process from Jatropha oil

Report

**L. Sourya Doré**
Vientiane

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Lao Institute for Renewable Energy

# LIRE

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**Sourya Doré**

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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.



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*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*

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# Introduction

This report gathers the results of experimental works that have been implemented at the laboratory of Lao State Fuel Company with the objective to implement oil treatment before biodiesel processing. Oil treatment before biodiesel processing is necessary because some compounds like free fatty acid and phospholipids should be removing from the oil before trans-esterification to avoid processing problem and to match quality standards.

Several procedures have been tested for this purpose but only one has given satisfactory results for decreasing free fatty acid contained in the oil. The studied treatment has shown efficiency for decreasing acid value of the oil, more than ninety percents of free fatty acid can be removed by the treatment. However this treatment has shown some sensitivity to oil contamination that can happen during oil pressing and need to be optimized for increasing oil yield after the treatment.

Oil treatment before trans-esterification is a key step of biodiesel process because the process behavior (easiness to remove impurities and chemical input during the washing) and the yield of the final product (biodiesel) closely depend on oil quality before trans-esterification.

After treatment the obtained oil has been trans-esterified for producing biodiesel. The biodiesel process also needs to be optimized because we use sodium hydroxide as catalyst for trans-esterification. We have chosen this chemical according to the local context because sodium hydroxide is affordable and it can be bought in many shops of Lao PDR. Sodium hydroxide is also the catalyst of trans-esterification that gives the lowest of yield in biodiesel.

# I Jatropha oil treatment before trans-esterification

After Jatropha seed pressing, the oil contains compounds that have to be remove before trans-esterification in order to avoid processing problem and to produce biodiesel according quality standards. The main impurities that have to be removing from crude oil are free fatty acid and phospholipids. Few amount of free fatty acid naturally occur in oil seed but theirs amount can increase with the water contain of the seed during the storage, relative humidity of storage place, duration and temperature of storage. The presence of water in seed can promotes the hydrolysis of acyl glycerol and produces free fatty acid. Free fatty acid can also occur in the oil after pressing if the oil is contaminated by water during the storage.

The presence of free fatty acid in the oil before trans-esterification can cause processing problem. During trans-esterification free fatty acid can react with the catalyst of trans-esterification and decrease the efficiency of the reaction. By reaction with catalyst free fatty acids produce soap that can make stable emulsion during the washing (purification step) of biodiesel. The occurrence of stable emulsion during the washing increases the solubility of biodiesel in water and consequently decreases its yield. Stable emulsion also increases the risk of biodiesel contamination. According to the literature dealing with biodiesel processing, an acid value less than 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 mineral catalyst like sulfuric acid or hydrochloric acid.

However this process has three main drawbacks that are the need to recover methanol after the esterification, the need of specific equipment for implementing the reaction and the impossibility to implement esterification if the amount of free fatty acid in the oil is less than five percents. When implementing esterification an excess of one of the reactant (acid or alcohol) should be used for the completion of the reaction. If esterification is implemented with an equal number of moles of acid and alcohol after some time the reaction reaches equilibrium and no more ester is produced resulting in low yield conversion. In the case of esterification of free fatty acid an

excess of methanol should be used for completely transform free fatty acid in fatty methyl esters. Consequently after esterification of free fatty acid methanol should be recovered for economic reasons because it is use in excess in order to reach the completion of the reaction. Methanol can be recovered by distillation and the reactor used for esterification should be equipped with condenser for condensing methanol vapor and recover methanol in liquid state. After the recovery of methanol it should also be dehydrated in order to remove water coming from the esterification. Esterification process that uses concentrated sulfuric acid or hydrochloric acid should also be implemented in corrosion though vessel (glass, glass lined or thermal tough plastic). Esterification should also be implementing from oil with an acid value higher than 10 mg of KOH per gram (5 % of free fatty acid). If the acid value is less than 10 mg of KOH per gram of oil the process can be un-economic because it will need a large excess of methanol for the completion of the reaction.

Beside free fatty acid other impurities like calcium, magnesium and phosphorus should also be removed from the oil before processing biodiesel. Calcium, magnesium and phosphorus are naturally present in oil seed in the form of phospholipids. Phospholipids are located in the cells of seed and are release during the pressing. The temperature and pressing process influence the amount of phospholipids that are release in the oil after pressing. Hot pressing and solvent extraction process release more phospholipids than cold pressing. They are two kinds of phosphorus derivatives in vegetables oil and animal fat, hydratable phospholipids (HPL) and non hydratable phospholipids (NHPL) and theirs quantities and theirs nature (HPL or NHPL) can vary according vegetable oil species or animal fat. Phospholipids should be removed from crude oil after oil pressing because they also promote the hydrolysis of acyl glycerol thus increasing the amount of free fatty acid in the oil. They can also react with the catalyst of trans-esterification and make emulsion during the washing of biodiesel.

As we state previously the two main compounds that have to be removing from the oil before trans-esterification are free fatty acid and phospholipids however theirs occurrence and theirs amount in the oil differ widely. Free fatty acid contain in the oil can range from less than one percent to more than thirty percents for the same oil specie whereas phospholipids only range

between one or two percents if there is no cross contamination during oil pressing. According to some researchers (Rao & Chakrabarti, 2009) the amount of phospholipids in crude Jatropha oil is about 1.45 % and they are mainly constituted by phosphatidyl choline (60.5 %), phosphatidyl inositol (24 %) and phosphatidyl ethanolamine (15.5 %). Others researchers (Sandford, White, Shah, Wee, Valverde, & Meier, 2009) have also made the analysis of Jatropha oil and theirs results have showed the presence calcium and magnesium beside phosphorus indicating the presence of phosphatidic acid salts. Several Jatropha oil treatment have been tested in the laboratory of Lao State Fuel Company mainly focusing on free fatty acid removing because the frequency of theirs occurrence and theirs amount in Jatropha oil can vary widely according the local context (no or bad post harvest procedure, storage conditions, climate).

# 1 Previous Jatropha oil treatment

Previous treatments have been implemented in the Laboratory of Lao State Fuel Company on oil with an acid value less than 10 mg of KOH per gram of crude oil (about five percents of free fatty acid). The treatments that have been implemented for removing free fatty acid are the following:

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

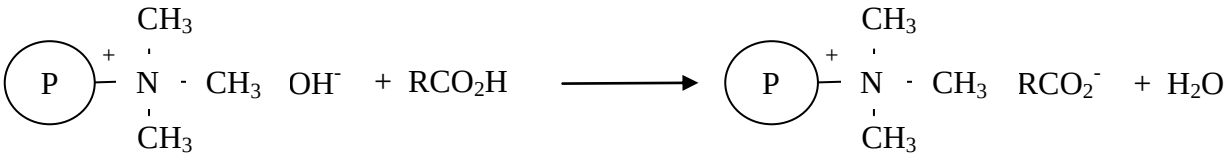
Treatments have also been implemented for removing phospholipids like water degumming and citric acid degumming however theirs efficiencies could not be assess because of the lack of equipments of the laboratory of Lao State Fuel Company for analysis calcium, magnesium and phosphorus compounds contained in phospholipids.

## 1.1 Anionic exchange resin

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.

### 1.2 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.

### 1.3 Rice husk ash

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.

### 1.4 Summary of the result of previous Jatropha oil treatment

The table 1 summarizes the results of the three previous treatments that have been implemented on Jatropha oil for decreasing the amount of free fatty acid in the oil. Among

the three treatment that have been tested for decreasing the amount of free fatty acid in Jatropha oil the anionic exchange resin treatment is the most efficient but percentage of free fatty acid removing is less than seventy percents with a residual acid value of 2.37 mg of KOH per gram of oil. This value is over the endorsed value (2 mg of KOH/g) for trans-esterification.

**Table 1 :** *Results of previous treatment for decreasing free fatty acid contained in Jatropha oil*

| Treatment | AVi (mg KOH/g) | AVf (mg KOH/g) | FFA removing (%) | Remark |
|---|---|---|---|---|
| Anionic exchange resin | 7.81 | 2.37 | 69.65 | Expensive resin |
| Lime | 7.56 | 2.58 | 65.90 | Calcium contamination problem |
| Rice husk ash | 7.84 | 2.91 | 62.88 | Lengthy time for decreasing acid value (one week) |

AVi: Initial acid value

AVf: Residual acid value

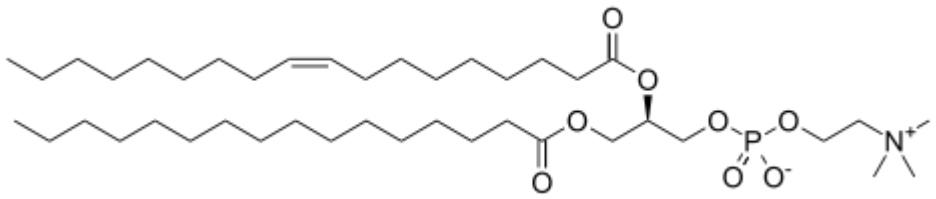
FFA: Free fatty acid

The un-efficiency of the previous treatments for decreasing the amount of free fatty acid contained in Jatropha oil brings us to looking for another alternative for decreasing the amount of free fatty acid in Jatropha oil.

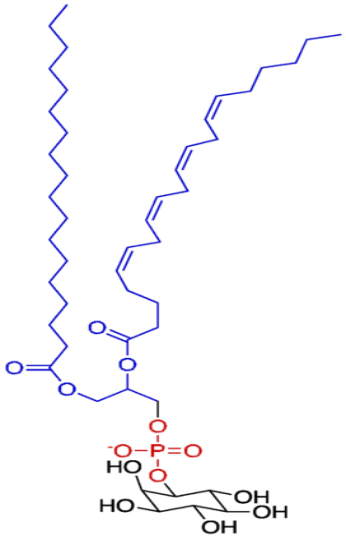
## 2 Chemical background

According to the literature Jatropha oil contains phosphatidyl choline and phosphatidyl inositol. Phosphatidyl choline (PC) and phosphatidyl inositol (PI) belonging to the group of hydratable phospholipids because they have good affinity for water due to the presence of hydrophilic group in their respective molecular structure (scheme 2 and 3). In contact with water they produce gums that are not soluble in oil and they can be separated by centrifugation or filtration.

**Scheme 2 :** *Molecular structure of phosphatidyl choline (PC)*

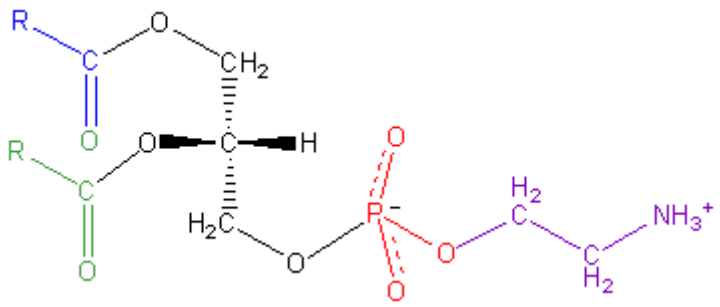


**Scheme 3 :** *Molecular structure of phosphatidyl inositol (PI)*



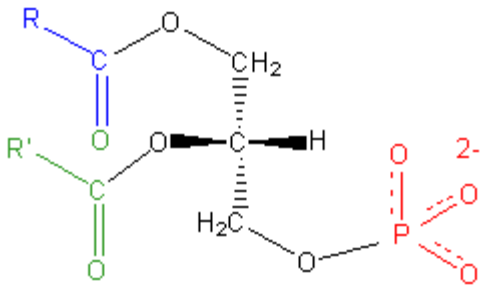
Jatropha oil also contains non hydratable phospholipids (NHPL) like phosphatidyl ethanolamine (PE) and phosphatidic acid salts (PAS). The molecular structure of PE (scheme 4) make it only hydratable if the pH is under 3 or over 9.

**Scheme 4 :** *Molecular structure of phosphatidyl ethanolamine (PE)*



PAS (scheme 5) in the oil form calcium and magnesium salt that should be dissociated and transformed in alkali salt (potassium or sodium salt) for been hydrated by water. The dissociation and the transformation of PAS in alkali salt can be done by introducing citric or phosphoric acid in the oil followed by the introduction of sodium or potassium hydroxide.

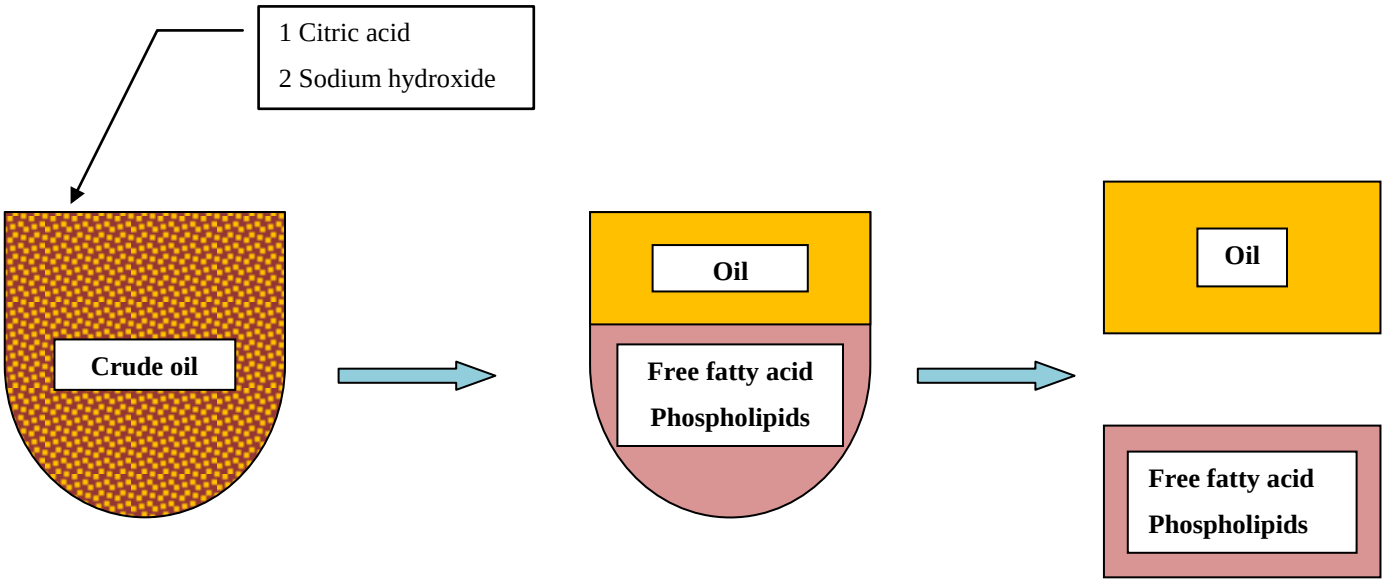
**Scheme 5 :** *Molecular structure of phosphatidic acid salt (PAS)*



## 3 Treatment of Jatropha oil by citric acid and alkali before trans-esterification

The idea of this treatment is to put in contact with oil an aqueous solution of citric acid followed by the addition of an amount of sodium or potassium hydroxide that is sufficient for hydrating phospholipids and neutralize free fatty acid. The gums and the soap produced during the treatment can be separated from the oil by centrifugation or filtration. The steps of the process are depicted by the scheme 6.

**Scheme 6 :** *Process for removing free fatty acid and phospholipids from Jatropha oil*




**Treatment** **Segregation** **Separation**

The oil treatment is implemented in three steps; the first step consists to mix oil with citric acid solution at 80 $^{o}$C in order to produce gum from hydratable phospholipids and to dissociate calcium and magnesium from phosphatidic acid. The second step consists to introduce in the mixture a solution of sodium or potassium hydroxide at room temperature for raise the pH of the media allowing by this way the formation of gums from non hydratable phospholipids and soap from free fatty acid. High shear rate is necessary to well disperse the aqueous phase in the oil and to improve the mass transfer between the two phases during the treatment. The third step consists to separate gums and soap from the oil by centrifugation or filtration after the segregation of the two phases.

### 3.1 Procedure of oil treatment

After centrifugation of crude Jatropha oil for removing solid impurities, acid value of the oil is measured and 200 milliliters of oil are measured with graduated cylinder. Four milliliters of citric acid solution (30 % on weight basis in distilled water) are added to the oil and the all is heated at 80 $^{o}$C and stirred at 1000 revolution per minute (rpm) for 35

minutes in order to well emulsify the mixture. After the mixture is allowed to cool at room temperature and a sodium or potassium hydroxide solution (50 % on weight basis in distilled water) is added and the mixture is stirred again (1000 to 1500 rpm according the viscosity) at room temperature for 15 minutes and let one night in contact at room temperature (the details of the calculation of the quantities of sodium hydroxide or potassium hydroxide to introduce are in annex 1).

After one night at rest the solid residue settling in the bottom of the vessel is separated from oil by centrifugation at 2000 rpm during 30 minutes. After centrifugation the amount of oil and solid residue are weighted for calculating the raw yield of oil and residue then the oil is put in a separatory funnel for washing. The oil is washed with distilled water until the pH decrease under 7.5[1] and dried to remove any trace of water. After complete drying the oil is weighed for calculating the total yield of the treatment and the acid value is measured for assessing the efficiency of the treatment for removing free fatty acid.

The efficiency of the treatment for removing calcium, magnesium and phosphorus from the oil is still not know because the laboratory of Lao State Fuel does not has equipment for analyzing these compounds. We are currently looking for a laboratory in Vientiane for implementing the analysis of these compounds.

### 3.2 Results of oil treatment

The oil treatment has been implemented with several batches of Jatropha oil with an acid value ranging from 1.5 to 29.6 milligrams of KOH per gram of oil. The results of the tests are gathered together in the table 2. This table is divided in three parts that are the input before treatment, the output after treatment and the output after washing.

**Table 2 :** *Results of the oils treatment*

| Input before treatment | Output after oil treatment | Output after oil washing |
|---|---|---|

[1] The washing of oil is stop when no bright yellow color appears in the water used for washing after the introduction of few drop of an alcoholic solution of 4-nitro phenol. The introduction 4-nitro phenol in water with pH equal or higher 7.5 gives a bright yellow color and under 7.5 the water is colorless.

| Batch number | Acid value (mg KOH/g) | Oil (%) | Precipitate (%) | Loss (%) | Oil (%) | Loss (%) | Acid value (mg KOH/g) | FFA removing (%) |
|---|---|---|---|---|---|---|---|---|
| CAD-8 | 1.53 | 80.08 | 14.50 | 3.55 | Problem during the washing | | | |
| CAD-6 | 5.97 | 83.06 | 13.54 | 3.25 | 80.04 | 3.02 | 0.30 | 94.97 |
| CAD-7 | 5.97 | Loss | 20.48 | 4.92 | Loss | | 0.84 | 85.93 |
| CAD-4 | 7.95 | 88.67 | 6.28 | 1.22 | 85.21 | 3.46 | 0.63 | 92.08 |
| CAD-5 | 12.21 | 77.26 | 16.45 | 3.95 | 72.60 | 4.66 | 0.32 | 97.38 |
| CAD-9 | 29.68 | 60.74 | 29.14 | 7.01 | 58.04 | 2.70 | 0.39 | 98.69 |

FFA : Free fatty acid

### *3.2.1 Input before treatment*

The input before treatment is made up by two columns one for the batch number of the trial and one for the acid value of the oil before the treatment.

### *3.2.2 Output after oil treatment*

Three columns constitute this part one for the yield of oil after centrifugation, one for yield of solid residue (precipitate) after the centrifugation and one for the percentage of oil loss after centrifugation. The yield of solid residue is calculated on a dry basis. After centrifugation the solid residue is mixed with isopropanol to dissolve oil kept by the solid and the all is filtrated and washed again with isopropanol until the washing is colorless. Then the residue is dried on a plate heater. After complete drying the residue is weighted and the yield of the solid residue is calculated. The washing containing oil and isopropanol is evaporated to dryness and the oily residue is weighted for calculating the quantity of oil retained in the precipitate after centrifugation and the percentage of oil loss after centrifugation.

### *3.2.3 Output after oil washing*

This part of table 2 contains four columns one for yield of oil after washing, one for the percentage of oil that is lost during the washing, one column for the acid value after the treatment and one for the percentage of free fatty acid removed by the treatment in order to assess the efficiency of the treatment.

### 3.3 Analysis of oil treatment result

We can observe from the results of table 2 that the treatment is efficient for decreasing the acid value of the oil under the endorsed value (2 mg of KOH/g), more than ninety percents of free fatty acid can be removed by this treatment. This treatment is also sound for removing free fatty acid from oil with high acid value like the oil that has been used in the batch CAD-9. For this batch after measuring acid value of the oil after treatment a Fourier transform-infrared (FTIR) spectroscopy has been implemented on the oil before and after the treatment in order to confirm the result of the acid value (annex 2). We can also observe from the part "Output after washing" that oil loss after washing are not so high and are between 2.7 to 4.7 percents.

However we can observe from the part "Output after oil treatment" of the table 2 that for all the batches the yield of oil after treatment is less than ninety percents that is quiet low. The results of table 2 also show inconsistencies of the results and in order to try to explain these inconsistencies the results of column "Output after oil treatment" have been extracted from the table 2 and compare with the column "Expected output" in the table 3. The "Expected output" contains one column indicating the theoretical yield of precipitate that can be obtained after the treatment. The details of the calculation of theoretical yield of precipitate after treatment are in annex 3.

**Table 3 :** *Results of the oils treatment-Comparison of the column "Output after oil treatment" with column "Expected output"*

| Input | | Output after oil treatment | | | Expected output |
|---|---|---|---|---|---|
| **Batch number** | **Acid value (mg KOH/g)** | **Oil (%)** | **Precipitate (%)** | **Acid value (mg KOH/g)** | **Precipitate (%)** |
| CAD-8 | 1.53 | 80.08 | 14.50 | 0.09[2] | 2.08 |
| CAD-6 | 5.97 | 83.06 | 13.54 | 0.30 | 4.36 |

[2] Estimation from the average percentage of free fatty acid removed from the table 2.

| | | | | | |
|---|---|---|---|---|---|
| CAD-7 | 5.97 | Loss | 20.48 | 0.84 | 4.07 |
| CAD-4 | 7.95 | 88.67 | 6.28 | 0.63 | 6.77 |
| CAD-5 | 12.21 | 77.26 | 16.45 | 0.32 | 9.36 |
| CAD-9 | 29.68 | 60.74 | 29.14 | 0.39 | 17.10 |

From the table 3 we can observe from the part "Output after treatment" that apart from the batch CAD-4 all the percentages of the precipitate are higher than the expected percentage calculated from the mass balance, initial and residual acid value of the oil (annex 3).

All the batches have been implemented with oil coming from the same specie (Jatropha seed) and with the same pressing process so we can assume that the percentage of phospholipids will be the same for all the batches. Assuming the same percentage of phospholipids for all the batches the increasing of precipitate percentage should only due to the initial acid value and the efficiency of free fatty acid removing.

If we look to the results of the batch CAD-8 we can observe very inconsistent result for the percentage of precipitate after treatment. For this batch the initial acid value was quiet low (1.53 mg of KOH/g) but the percentage of precipitate after treatment is higher than the obtained percentage of batch CAD-4 and CAD-6. The oils used in the batch CAD-4 and CAD-6 have higher acid value than the oil used for the batch CAD-8, 7.95 and 5.97 mg of KOH/g respectively.

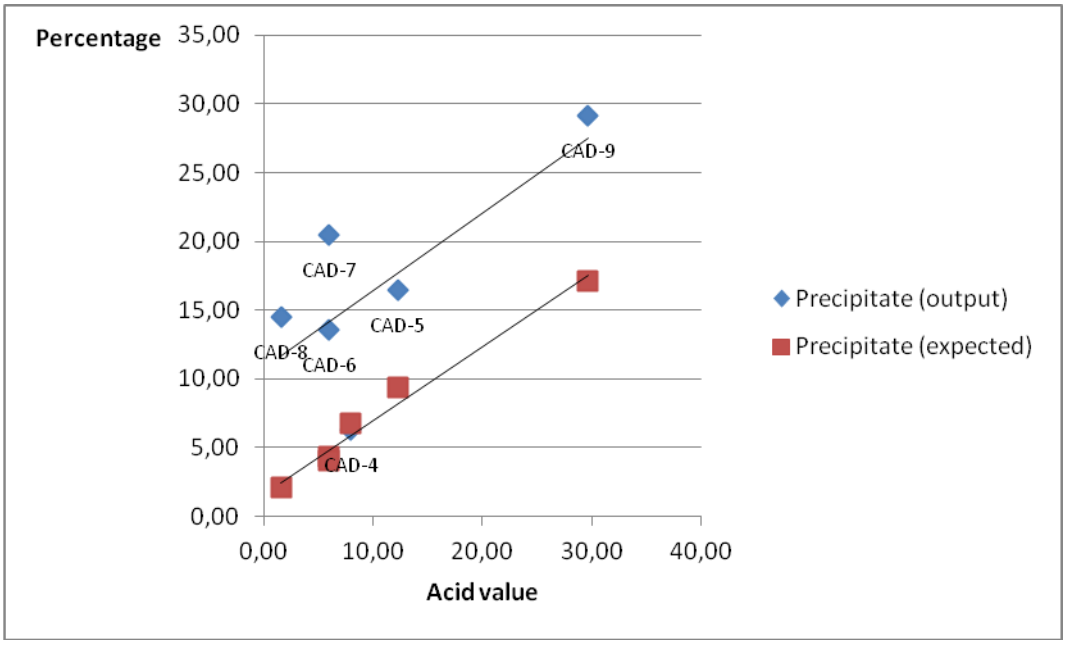
During the treatment of the batch CAD-8 we were confronted to lengthy washing time and emulsion problem and the treatment of this batch has been stopped without measuring the final acid value of the oil. According to the table 3 the percentage of solid residue of this batch is 14.5 % which is quiet high for the initial acid value. We also know that the oil used in the batch CAD-8 has been subject to cross contamination during the oil pressing. Pictures of Jatropha oils that have been used during the treatment are in annex 4.

Two other inconsistencies can be observed from the table 3. The batch CAD-6 and CAD-7 have been implemented with same oil (5.97 mg of KOH/g of acid value) but the percentages of precipitate after the treatment are quiet different, 13.54 % for the batch CAD-6 and 20.48 % for the batch CAD-7. For this later obtained percentage of precipitate is higher than the percentage of the batch CAD-5 that has been implemented from oil with higher acid value (12.21 mg of KOH/g).

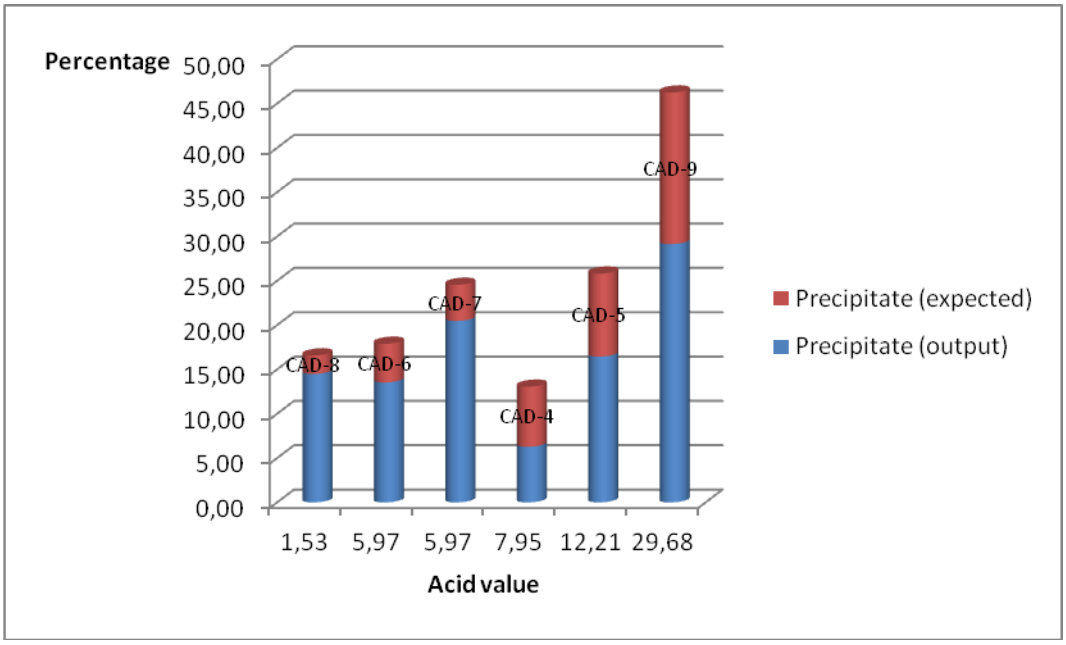
In order to compare the behavior of the treatment percentages from the part "Output after treatment" and part "Expected output" were plotted versus acid value of the oil (graphic 1). We can observe from the graphic 1 that percentages of batches CAD-5, CAD-6 and CAD-9 vary linearly with acid value but are higher than the expected percentage. For the others batches (CAD-7, CAD-8) the percentage are very scattered with no linear relationship. From the graphic 1 we can also observe that only the batch CAD-4 gives a percentage of precipitate similar to the theoretical percentage.

For comparison the percentage from the treatment and the expected percentage have been plotted in column of cumulated percentage versus acid value (graphic 2) in order to see if some trend of treatment behavior can be observed.

**Graphic1 :** *Percentage of precipitate versus acid value of oil-Scattered representation (table 3)*




**Graphic2 :** *Percentage of precipitate versus acid value of oil-Column representation (table 3)*



From the graphic 2 we can observe two areas one ranging from 1.53 to 5.97 mg of KOH/g and the other ranging from an acid value of 7.95 to 29.68 mg of KOH/g. In the first area we are sure that the batch CAD-8 has been contaminated during oil pressing (annex 4). At present we do not know about the nature of the contamination products we have only observed an increasing amount of precipitate despite the low acid value of the oil use in this batch. The others batches CAD-6 and CAD-7 show also high percentage of obtained precipitate despite low acid value and we can assume that the oil use for these batches has also been contaminated during oil pressing.

For the area ranging from an acid value of 7.95 to 29.68 mg of KOH/g (CAD-4, CAD-5, CAD-9) the obtained percentage of precipitate are higher than the expected percentages except for the batch CAD-4 which has an obtained percentage of precipitate similar to the expected percentage. The results of these batches also show more linear relationship with acid value. For this area we assume that saponification of oil has occurred beside neutralization of free fatty acid and this can explain why the percentage of obtained precipitate is higher than the expected percentage.

### 3.4 Conclusion on the results of oil treatment

The oil treatment that has been studied for removing free fatty acid and phospholipids seem to be sound for decreasing the amount of free fatty acid over a wide range of acid value. However according to experimental conditions we assume that saponification reaction occurs in a same time than free fatty acid neutralization and this can explain why the amount of precipitate is higher than the expected amount and why the oil yields are less than ninety percents. This treatment should be optimized for increasing oil yield because it may be an alternative to the esterification of free fatty acid by methanol and sulfuric acid. The optimization of the treatment should be making by set up experimental conditions that minimize the amount of solid residue, increase oil yield and decrease acid value under the endorsed value (2 mg of KOH /g). After centrifugation the precipitate can also be wash with solvent for recovering the oil that is kept by the solid residue. The amount of oil kept

by the solid residue is about twenty percent of solid weight (dry basis). Biodiesel can be use for this purpose because it has very good solvent properties.

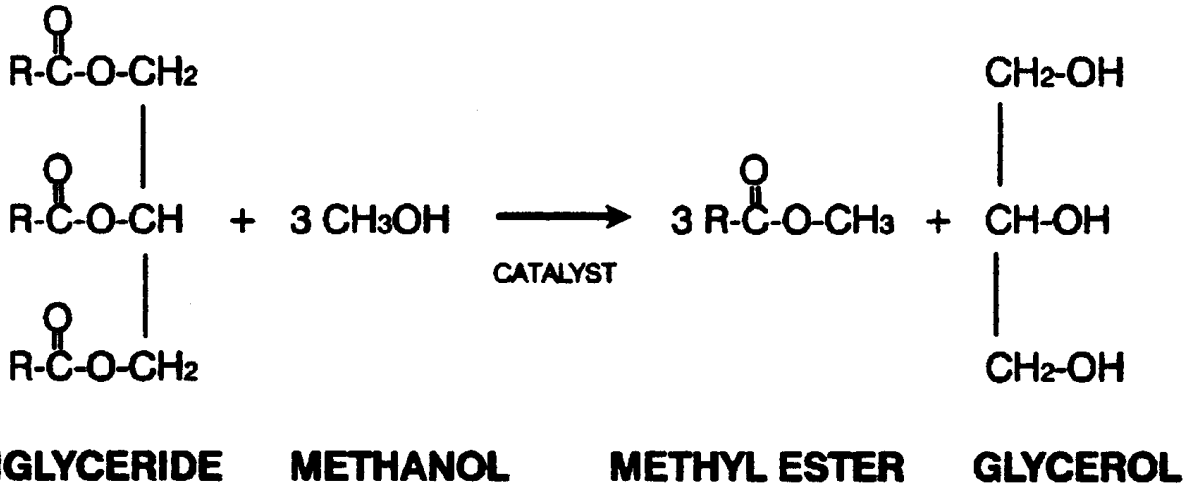
# II Biodiesel processing from Jatropha oil

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.

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

Lipid in vegetable oils and animal fats contain mainly triacylglycerol compound (triglyceride) 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 to the scheme 7.

**Scheme 7 :** *Trans-esterification of triacylglycerol by methanol*




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 7, after some time the reaction 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 should be use

on the left side of the equation. 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 chemical. Trans-esterification of acyl-glycerol is generally completed with a good yield with more than ninety percents of completion but several factors can affect the yield of biodiesel. The factors that can affect the yield of the trans-esterification are the following :

- The molar ratio of methanol;
- The amounts of water and free fatty acid;
- The reaction time;
- The reaction temperature;
- The catalyst concentration;
- The agitation speed.

### 1.1 The molar ratio of methanol

According to the reaction of scheme 7 the reaction of trans-esterification needs 3 moles of methanol for completion but in practice a molar ratio of 6 moles of alcohol for one mole of oil or a weight ratio of 24 % of methanol to oil is used. An increase of methanol amount increases the conversion of acyl-glycerol and decreases reaction time up to certain concentration. Large excess of alcohol can complicate the separation of biodiesel from glycerol phase after trans-esterification because both biodiesel and glycerol are soluble in methanol (Rostami, Mahmoudi, & Raeissi, 2011).

### 1.2 The amount of water and free fatty acid

Water and free fatty acid can react with trans-esterification catalyst resulting in catalyst effect decreasing. Water can promotes hydrolysis of triglycerides and producing free fatty acid which can react with the catalyst and producing soap. Soap can make emulsions that

increase the solubility of biodiesel with glycerol phase during the purification step resulting in yield decreasing.

### 1.3 The reaction time

Trans-esterification reaction is slow at the beginning because it needs some time to mix and disperse the alcohol in the oil phase but after complete dispersion the reaction is fast and is generally completed in 90 minutes. Longer time reaction result in yield decreasing because of the reversible reaction (trans-esterification is an equilibrium reaction) and soap formation.

### 1.4 The reaction temperature

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.

### 1.5 The catalyst concentration

The most common catalysts that are used for trans-esterification are sodium hydroxide and potassium hydroxide but sodium and potassium methoxide are more efficient and give higher yield because they do not introduce water in the oil unlike sodium and potassium hydroxide. When use sodium and potassium hydroxide as catalyst for trans-esterification they should be mixed with methanol for producing sodium or potassium methoxide before been introduced in the oil. The reaction of sodium or potassium hydroxide with methanol produces methoxide but also water that is known to decrease biodiesel yield and promote soap occurrence (Singh, He, Thompson, & Van Gerpen, 2006). According to the literature the weight ratio for sodium hydroxide is 1.4 % on oil weigh basis and the weight ratio for potassium hydroxide is 1.96 % (Berchmans & Hirata, 2008).

### 1.6 The agitation speed

Agitation plays a key role in the beginning of trans-esterification for dispersing methanol in the oil phase and it has been observed that an agitation of 400 rpm gives the best yield (Mathiyazhagan & Ganapathi, 2011).

## 2 Biodiesel process procedures

The procedures for producing biodiesel at the laboratory of Lao State Fuel have been implemented at 60 $^{o}$C and at room temperature. The catalysts used during the testing were sodium and potassium hydroxide and for all the tests the quantity of methanol was 24 % to the oil weight.

### 2.1 Biodiesel procedure

The alkali (sodium or potassium hydroxide) is mixed with methanol until complete dissolution and add to the oil previously heated at 60 $^{o}$C for two hours with stirring rate of 500 rpm. After two hours of contact the mixture is cool to the room temperature and let in rest for one night (for the procedure at room temperature after complete dissolution, the mixture of methanol and alkali is add to the oil and the all is stir at 1000 rpm for 15 minutes and let one night at room temperature).

After one night the mixture is poured in separatory funnel, the glycerol phase is separated from the oil phase and the washing of biodiesel is implemented with distilled water until the pH is neutral then the biodiesel is dried for removing any trace of water. After complete drying the biodiesel is weighted for calculating the yield, the acid value is measured and a FTIR spectrum is implemented to assess the quality of biodiesel (annex 5).

### 2.2 Results of biodiesel process procedures

The results of the tests are gathered together in the table 4. This table is made up of 7 columns indicating the batch number, the oil treatment, initial acid value, the percentage and the kind of catalyst, the yield, the residual acid value and some remark about the testing. The testing have been implemented with crude Jatropha oil, oil treated with anionic

exchange resin and oil treated with citric acid followed by alkali. The oils used during the testing have acid value ranging from 0.32 to 6.14 mg of KOH/g. The implemented quantities have been choosing according the literature except for the batch TAG-5.

**Table 4 :** *Biodiesel procedures testing*

| Batch No | Oil treatment | AVi | Catalyst (%) | Temperature ($^{o}$C) | Yield (%) | AVf | Remark |
|---|---|---|---|---|---|---|---|
| TAG-1 | ANT-2 | 2.37 | 1.96 (KOH) | 60 | 61.1 | 0.24 | Formation of emulsion during the washing |
| TAG-2 | CJO-3 | 6.14 | 1.96 (KOH) | 60 | | | Impossible to wash biodiesel from because of the formation of stable emulsion |
| TAG-3 | CAD-4 | 0.63 | 1.96 (KOH) | 60 | Loss | Loss | Five washing. Loss during the drying |
| TAG-4 | CAD-5+6 | 0.32 | 1.40 (NaOH) | RT | 73.1 | 0.5 | Eight washing |
| TAG-5 | CAD-7 | 0.84 | 1.10 (NaOH) | 60 | | | Impossible to wash biodiesel because of the formation of stable emulsion |

AVi: Initial acid value (mg KOH/g)
AVf: Residual acid value (mg KOH/g)
ANT: Anionic exchange resin treatment
CJO: Crude Jatropha oil
CAD: Citric acid and alkali treatment
RT: Room temperature

### 2.3 Analysis of biodiesel procedures results

We can observe from the results of the table 4 that initial acid value and quality of oil have a strong influence on the emulsion occurrence during the washing and biodiesel yield. Concerning the batches TAG-1 and TAG-2 the remark of the table 4 show that if the acid

value is higher 2 mg of KOH/g it is very difficult to wash and recover biodiesel. If we look to the batches TAG-3, TAG-4 and TAG-5, the oils used form these batches have been previously treated by citric acid followed by alkali (chapter I, paragraph 3.3). We can observe from table 4 that oil quality has also a strong influence on the number of washing and consequently on biodiesel yield. For the batch TAG-4 the residual acid value is higher than the initial acid value because during the washing of biodiesel a washing has been implemented with water at pH=1 because of emulsion occurrence. The oil used for this test is a mix of two oils (CAD-5 and CAD-6) and it is possible that one of the oil (CAD-6) has been contaminated during oil pressing. Concerning the biodiesel yield is quiet low and consequently the process should be optimized.

### 2.4 Conclusion on biodiesel process procedures

The results of biodiesel process procedures have shown that oil quality and initial acid value have a strong influence on biodiesel yield. Trans-esterification reaction can be implemented at a temperature slightly below the boiling point of the methanol or at room temperature. However the process should be optimized in order to reach a yield around 86 % the maximum yield that can be obtained by using sodium hydroxide as catalyst (Singh, He, Thompson, & Van Gerpen, 2006).

# III Conclusion

The treatment that have been studied for removing free fatty acid and phospholipids is efficient for decreasing acid value of Jatropha under the endorsed value (2 mg of KOH/g) but we still have no result on the efficiency of the process for removing phospholipids from Jatropha oil. According to the results the studied treatment seems to be very sensitive to oil contamination.

By comparison of experimental results and calculated results from an approximate modeling based on mass balance of free fatty acid neutralization we assume that beside the neutralization of free fatty acid a saponification reaction occurs resulting in the increasing weight of solid residue and oil loss after the treatment. Oil is also loss by retention in the solid residue but it will be possible to recover it after the treatment by washing the residue with some quantities of biodiesel that is a good solvent.

Concerning the application range and according the experimental result the treatment can be an alternative to the esterification up to an acid value of 12 mg of KOH/g if the treatment is optimized for limiting side reaction like saponification. It is also assumed that this treatment can be applied to other oil species after some process adaptation.

The results of biodiesel process procedure have shown that oil quality and acid value have a strong influence on biodiesel yield. The process can be run with sodium or potassium hydroxide and at room temperature or a temperature slightly below the boiling point of methanol. The highest yield of the testing is around 73 % optimization should be implementing for reach a yield around 86 % that is the maximum biodiesel yield when using sodium hydroxide as catalyst.

# IV Recommendations

Following the experimentations that have been mad at the laboratory of Lao State Fuel Company and according the obtained results we can make some recommendations concerning all the steps of the biodiesel process that are oil seed harvesting and storage, oil pressing, oil treatment and trans-esterification.

After harvesting oil seed should be dry quickly for removing water in order to limit the release of free fatty acid in the seed. After drying the oil seed should be store in dry place and cool place if possible. These post harvesting conditions are important for avoiding high amount of free fatty acid in the seed (less than 12 mg of KOH/g) and be able to apply the studied treatment.

Before oil pressing all the equipments that will be in contact with the seed and the oil (press, filter and container) should be clean to avoid cross contamination with seed cake coming from previous pressing because the studied treatment seems to be very sensitive to contamination.

After oil treatment the solid residue still contains some oil up to twenty percents on the dry basis. The oil that is kept by the residue should be recovered in order to increase the economic balance of the process. The recovering of the oil can be done by washing the solid residue with some quantities of biodiesel. After the recovering the oil and biodiesel can be washing together to remove any trace of alkali and dry before trans-esterification.

After oil treatment or trans-esterification the oil or biodiesel are washing with distilled water to remove any trace of alkali, catalyst and glycerol. The washings are stopped when the pH is neutral. In order to know when stop the washing it is preferable to use pH indicator instead pH-meter. When pH-meter is used for assessing the end of the washing oil or biodiesel makes thin film on the probe of the pH-meter making inaccurate the measure of the pH. Instead pH-meter one can use an alcoholic solution of 4-nitro phenol that changing color with pH. Colorless when the pH is under 7.5 and bright yellow above 7.5. One can also use an alcoholic solution of

turmeric (curcuma longa) that gives yellow color under 7 and red color above 7. Curcuma longa rhizome is finding easily in rural areas of Lao PDR.

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# Annex

# Annex 1

## Quantities of sodium or potassium hydroxide to implement during oil treatment according the amount of citric acid and the acid value of the oil

Sodium or potassium hydroxide is introduced during the oil treatment in order to raise the pH for hydrating phospholipids and producing soap from free fatty acid. The amount of sodium or potassium hydroxide to introduce can vary according the kind of alkali (sodium or potassium hydroxide), the amount of citric acid and the acid value of the oil. The theoretical quantity of sodium or potassium hydroxide necessary for the neutralization of the total number of acid equivalent is calculated by multiply the total number of acid equivalent of citric acid and free fatty acid by the molecular weight of the alkali (40 grams for sodium hydroxide or 56 grams for potassium hydroxide). Table A gives the details of the calculations of the total number of acid equivalent to neutralize during the treatment of 200 milliliters of Jatropha oil with a density of 0.906 gram per milliliter and an acid value of 7 mg of KOH per gram.

**Table A :** *Calculations of the total number of acid equivalents*

| Compounds | Volume (ml) | Weight (g) | Number of acid equivalent |
|---|---|---|---|
| Jatropha oil | 200 | $200 \times 0.906 = 181.2$ | |
| Citric acid (30 % w/w) | 4 | $4 \times 1.13 \times 0.3 = 1.356$ | $1.356 \times \frac{3}{192} = 0.0211$ |
| Free fatty acid | | | $181.2 \times \frac{7}{56000} = 0.0226$ [3] |
| **Total number of acid equivalent** | | | $0.0211 + 0.0226 = 0.0437$ |

[3] The number of acid equivalent of one mole of free fatty acid is 1 because fatty acid has only 1 carboxylic acid group in its molecular structure. The number of acid equivalent is calculated by multiply the weight of oil by acid value and by dividing the product by the molecular weight of potassium hydroxide expressed in milligram per mole (56000 mg/mol).

Then the quantity of alkali to introduce is calculated by multiplying the theoretical quantity of alkali by a coefficient (1.43) in order to have an excess of alkali for raise the pH. Table B gives the details of calculations of the quantity of sodium hydroxide or potassium hydroxide to introduce according the total number of acid equivalent.

**Table B :** *Calculations of the quantity of sodium of potassium hydroxide to introduce according the total number of acid equivalent*

| **Total number of acid equivalent** | **Coefficient** | **Quantity of sodium hydroxide to introduce(g)** | **Quantity of potassium hydroxide to introduce (g)** |
|---|---|---|---|
| 0.0437 | 1.43 | $0.0437 \times 40 \times 1.43 = 2.49$ | $0.0437 \times 56 \times 1.43 = 3.49$ |

# Annex 2

## Fourier transform infrared spectroscopy (FTIR) of Jatropha oil before and after the treatment for removing free fatty acid and phospholipids

FTIR spectroscopy analysis has been implemented with a Bruker-Alpha 6 spectrophotometer equipped with Opus 6.5 software. All the spectrums have been scan between 4000 and 500 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The samples of oil (CJO-1 and CAD-9) have been scanned without any solvent and the results of the two scan are depicted by the pictures A and B. The table C lists the band attribution of the two spectrums.

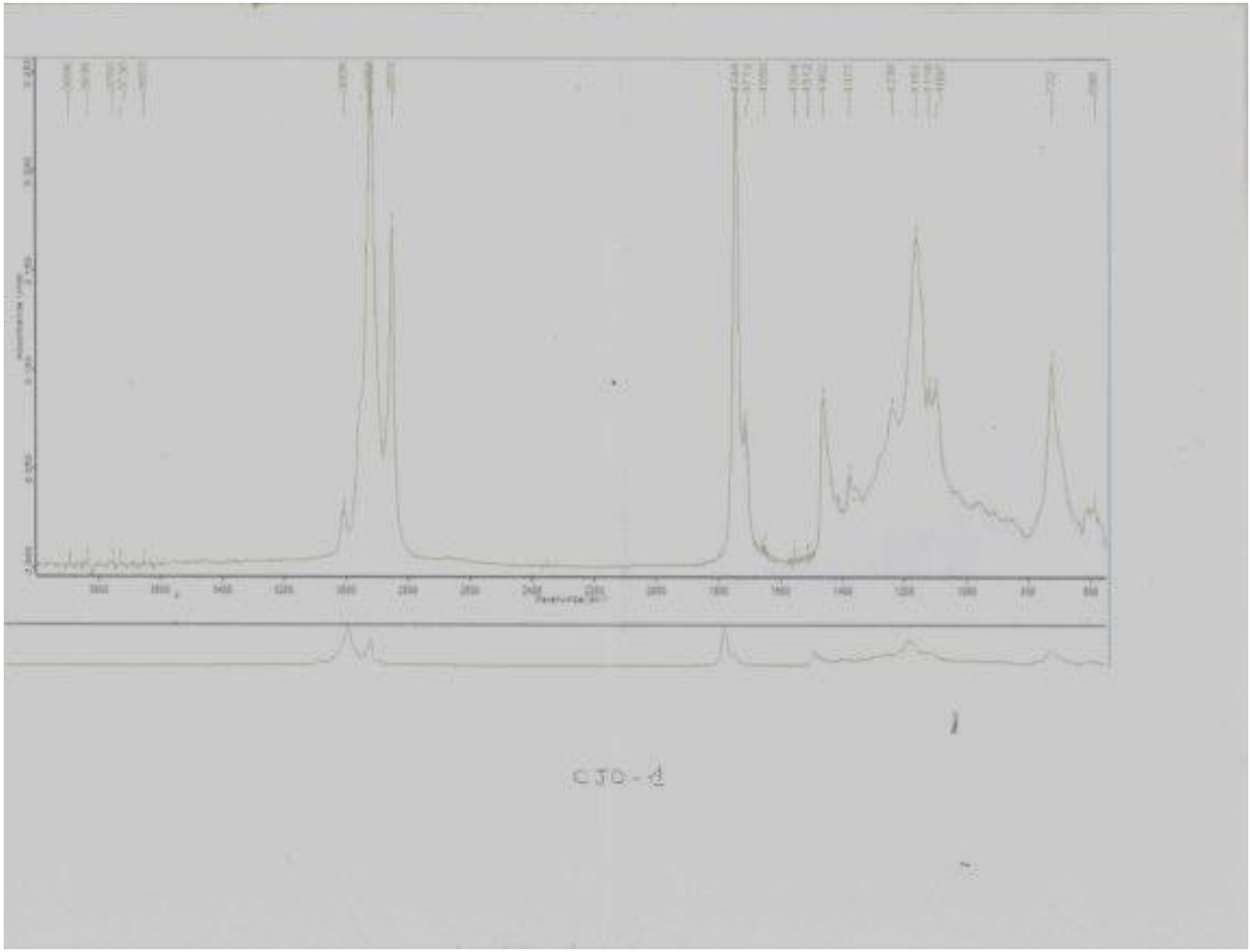
**Table C :** *Band attribution of FTIR spectrum of the oil before and after the treatment for removing free fatty acid and phospholipids*

| **Oil before treatment (picture A)** | | **Oil after treatment (picture B)** | |
|---|---|---|---|
| **Band (cm-1)** | **Interpretation** | **Band (cm-1)** | **Interpretation** |
| 3008 | C-H stretching vibration of the cis double bond (C=CH) | 3007 | C-H stretching vibration of the cis double bond (C=CH) |
| 2922, 2853 | Symmetric and asymmetric vibrations of aliphatic $CH_2$ group | 2922, 2853 | Symmetric and asymmetric vibrations of aliphatic $CH_2$ group |
| 1744 | Double bond stretching of ester carbonyl functional group of triglycerides | 1744 | Double bond stretching of ester carbonyl functional group of triglycerides |
| 1712 | Double bond stretching of ester carbonyl functional group of free fatty acid | | No band appears at 1712 $cm^{-1}$ after the treatment |
| 1462 | Bending vibrations of $CH_2$ and $CH_3$ aliphatic groups | 1463 | Bending vibrations of CH2 and CH3 aliphatic groups |
| 1377 | Bending vibrations of $CH_2$ aliphatic groups | 1377 | Bending vibrations of $CH_2$ aliphatic groups |
| 1238, 1161 | Stretching vibrations of C-O ester groups | 1237, 1160 | Stretching vibrations of C-O ester groups |

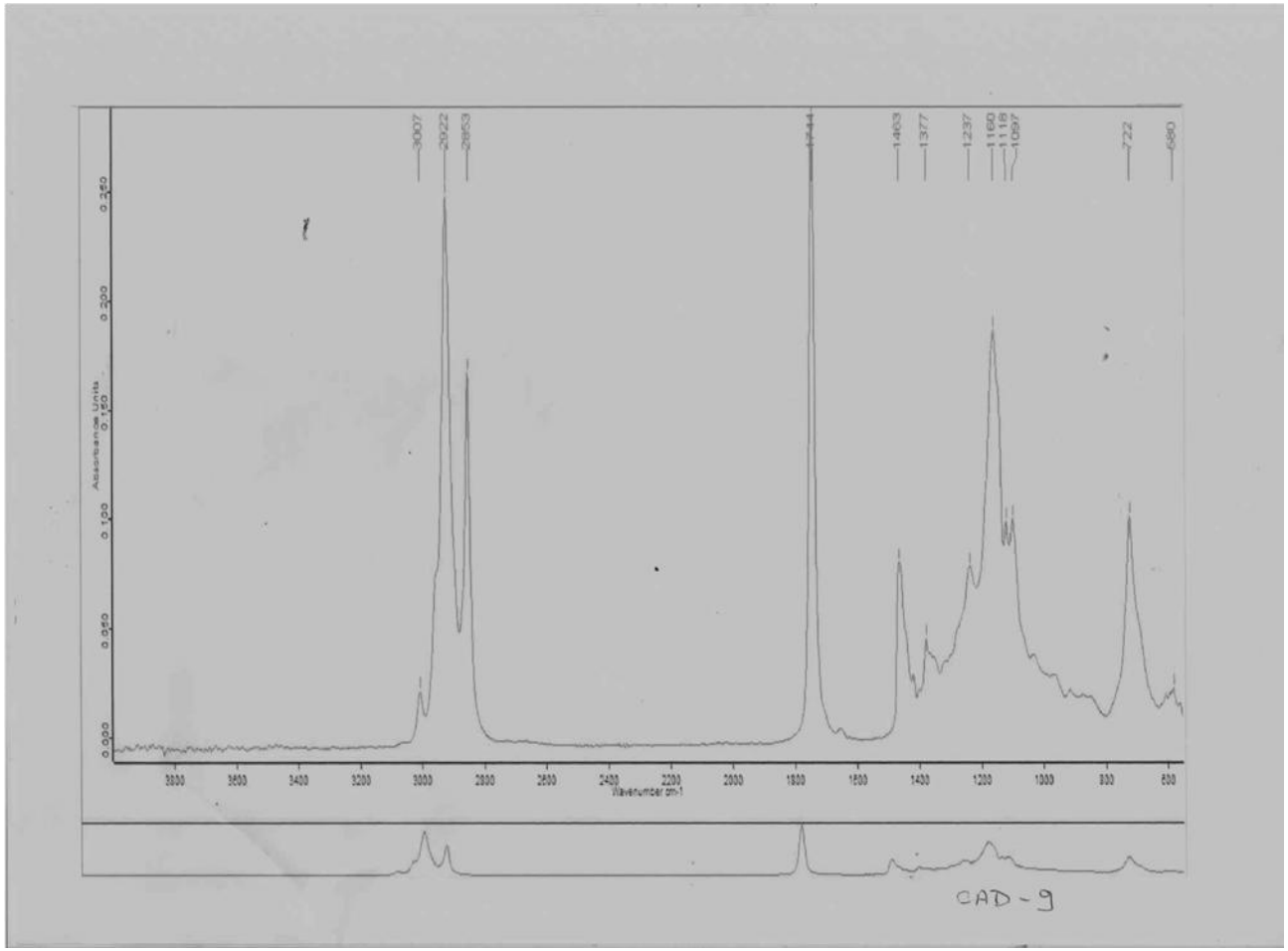
The two spectrum are very similar before and after treatment but the disappearance of the band at 1712 $cm^{-1}$ attributed to free fatty acid confirm the decreasing of acid value after the treatment.

Phospholipids have characteristic bands at 1200 and 970 $cm^{-1}$ but these bands cannot be identified because they are overlapping by the stretching vibrations band of C-O ester group located between 1160 and 1238 $cm^{-1}$.

**Picture A :** *FTIR spectrum of Jatropha oil before the treatment*



**Picture B :** *FTIR spectrum of Jatropha oil after the treatment*



# Annex 3

## Calculation of the expected yield of precipitate after treatment

The objective of oil treatment is to remove free fatty acid and phospholipids to avoid processing problem during biodiesel processing. The treatment should be efficient and profitable. The efficiency of the treatment is assessing by comparing the initial and residual amount of free fatty acid and phospholipids contained in the oil. The efficiency has been assessed qualitatively by FTIR and quantitatively by measuring acid value before and after treatment. These two methods only provide information on the efficiency of free fatty acid removing but give no information about the efficiency of phospholipids removing. This lack of information concerning phospholipids is due to the fact that there are no specialized laboratories in Lao PDR for analyzing phospholipids in vegetable oils.

The profitability of treatment is assessing by comparing the amount of oil and precipitate after treatment with theoretical yield of oil and precipitate after treatment. For calculating theoretical yield of oil and precipitate we were faced with one problem that is the lack of information about the percentage of phospholipids and free fatty acid contained in the oil. To overcome this problem we have made two assumptions. The first assumption concerns the amount of phospholipids that is removed from the oil. According to the literature (Rao & Chakrabarti, 2009) Jatropha oil contains 1.45 % of phospholipids and we assume 90 % of phospholipids removing. The second assumption concerns the amount of free fatty acid in the oil. According to the literature the percentage of free fatty acid contained in oil can approximately be estimated by dividing the acid value of the oil by 2.

Assuming that the treatment only involve two main reactions that are the producing of gums from phospholipids and the neutralization of free fatty acid for producing soap we can calculate the theoretical amount of gums and soap that will be produce by the treatment. The amount of expected phospholipids can be calculating by multiplying the initial amount of oil by the assumed percentage of phospholipids (1.45 %) and the assumed treatment efficiency (90 %). By adding this quantity to the expected amount of soap produced by the treatment we can calculate the theoretical amount of solid residue that will be produce by the treatment.

The calculation of the expected amount of soap that can be produce by the oil treatment is more complicated than the calculation of the expected amount of phospholipids and it is based on the mass balance established on the dry basis (without water) of the neutralization equation of the scheme A

**Scheme A :** *Neutralization of free fatty acid*

| $RCO_2H$ | + | NaOH (or KOH) | → | $RCO_2Na$ | + | $H_2O$ |
|---|---|---|---|---|---|---|
| Free fatty acid | | Alkali | | Soap | | Water |

The neutralization of 1 mole of free fatty acid by sodium or potassium hydroxide produce 1 mole of soap with a positive mass variation because soap has higher molecular weight than free fatty acid. The mass gap (Δm) for 1 mole between soap and free fatty acid is equal to the molecular weight of sodium minus the molecular weight of hydrogen because neutralization reaction subtracts one atom of hydrogen and adds one atom of sodium per mole of neutralized free fatty acid because only these two atoms are exchanged during the neutralization.

If potassium hydroxide is used instead sodium hydroxide the mass gap for one mole is equal to the molecular weight of potassium minus the molecular weight of hydrogen. Knowing mass of oil before the treatment, initial and final acid value and the weight fraction of free fatty acid in the oil, the theoretical quantity of soap that can be produce by the neutralization can be calculate approximately. The weight fraction of free fatty acid removed by the treatment is approximately equal to the difference in acid value before and after the treatment divided by 200.

The expected quantity of soap produced during the treatment is calculated by the following steps:

- Calculate the acid value difference (ΔAV);
- Calculate the number of moles of free fatty acid removed (nFFA) by the treatment by multiply the weight of oil by acid value difference and divide by 56000;
- Calculate the increase in weight by multiply the mass gap (Δm) by the number of moles of free fatty acid removed by the treatment;

- Calculate the weight of free fatty acid removed and add the increase in weight previously calculated to obtain the theoretical weight of soap (m Soap).

AVi: initial acid value (mg KOH/g)

AVf: residual acid value (mg KOH/g)

ΔAV: difference between initial and residual acid value (mg KOH/g)

$$\Delta AV = AVi - AVf$$

m Oil: weight of oil (g)

nFFA: number of moles of free fatty acid removed by the treatment (mol)

$$nFFA = \frac{m\ Oil \times \Delta AV}{56000}$$

mFFA: weight of free fatty acid removed by the treatment (g)

$$mFFA = \frac{m\ Oil \times \Delta AV}{200}$$

Δm: mass gap (g/mol)

Δm = (23-1) for sodium hydroxide or (39-1) for potassium hydroxide

m Soap: weight of soap (g)

$$m\ Soap = m\ Oil \times \Delta AV \times [\frac{1}{200} + \frac{\Delta m}{56000}]$$

An example of calculation for 100 grams of oil with an initial acid value of 29.68 mg of KOH/g and a residual acid value of 0.39 mg of KOH/g is detailed in the table D.

**Table D :** Example of *calculation of expected quantity of soap after treatment*

| m Oil (g) | Alkali | AVi (mg KOH/g) | AVf (mg KOH/g) | ΔAV (mg KOH/g) | nFFA (moles) | mFFA (g) | Δm (g/mol) | m Soap (g) | Yield of soap (%) |
|---|---|---|---|---|---|---|---|---|---|
| 100 | NaOH | 29.68 | 0.39 | 29.29 | 0.0523 | 14.645 | 22 | 15.80 | 15.80 |
| 100 | KOH | 29.68 | 0.39 | 29.29 | 0.0523 | 14.645 | 38 | 16.63 | 16.63 |

The calculations of theoretical yield of solid residue that can be obtained after treatment are gathered together in the table E and F. The calculations have been implemented according the kind of alkali used in the treatment, initial and residual acid value of oil.

**Table E :** *Calculation of the theoretical yield of precipitate after treatment with citric acid and sodium hydroxide*

| **Initial acid value (mg KOH/g)** | **Residual acid value (mg KOH/g)** | **Solid residue (%)** |
|---|---|---|
| 1.53 | 0.09 | 2.08 |
| 5.97 | 0.30 | 4.36 |
| 5.97 | 0.84 | 4.07 |
| 7.95 | 0.63 | 5.25 |
| 12.21 | 0.32 | 7.72 |
| 29.68 | 0.39 | 17.10 |

The results of table D allow plotting a graphic of the percentage of solid residue and versus the acid value of the oil for the treatment with citric acid and sodium hydroxide (graphic A).

**Graphic A :** *Theoretical percentage of solid residue versus initial acid value of oil after treatment with citric acid and sodium hydroxide*

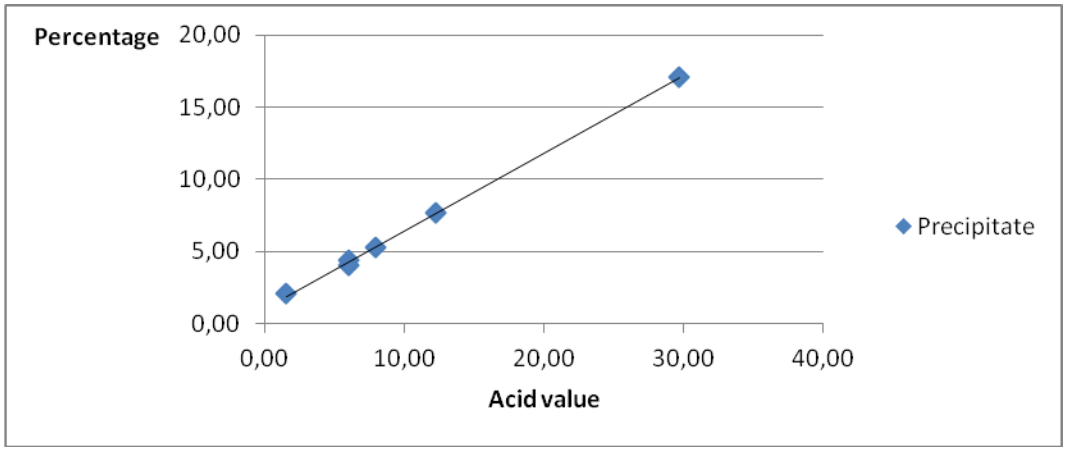
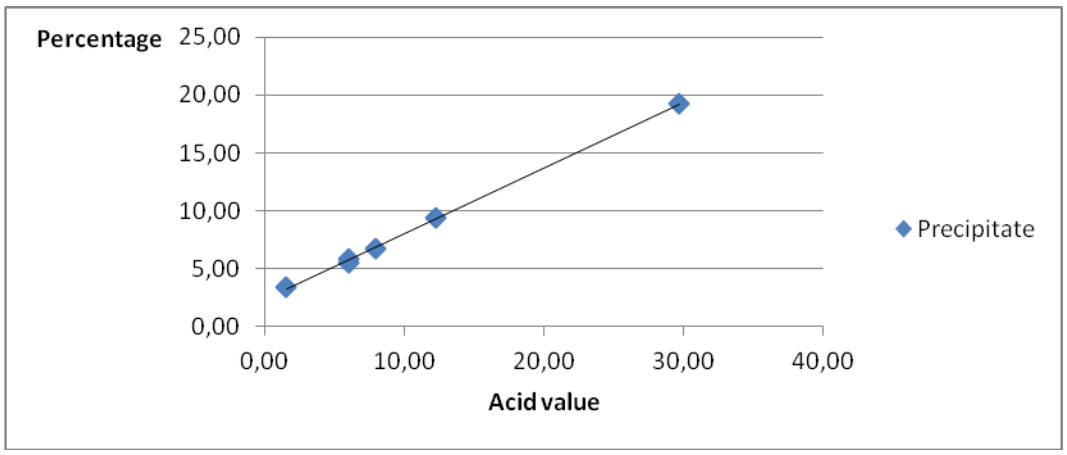



**Table F :** *Calculation of the expected quantities of solid residue after treatment with citric acid and potassium hydroxide*

| Initial acid value (mg KOH/g) | Residual acid value (mg KOH/g) | Solid residue (%) |
|---|---|---|
| 1.53 | 0.09 | 3.43 |
| 5.97 | 0.30 | 5.83 |
| 5.97 | 0.84 | 5.52 |
| 7.95 | 0.63 | 6.77 |
| 12.21 | 0.32 | 9.36 |
| 29.68 | 0.39 | 19.24 |

The results of table E allow plotting a graphic of the percentage of solid residue versus the acid value of the oil for the treatment with citric acid and potassium hydroxide (graphic B).

**Graphic B :** *Theoretical percentage of solid residue and versus initial acid value of oil after treatment with citric acid and potassium hydroxide*




The both graphic A and B show a linear relationship that is the theoretical yield of precipitate (solid residue) increase when the initial acid value of oil increases.

# Annex 4

## Jatropha oils used in the treatment for removing free fatty acid and phospholipids

Some pictures of the oils that have been used for the treatment are gathered in the table G

**Table G :** *Kind of Jatropha oils that have been used in the treatment for removing free fatty acid and phospholipids*

| Batch number | Picture | Acid value (mg KOH/g) | Remark |
|---|---|---|---|
| CJO-1 |  | 29.68 | This oil has been used in the batch CAD-9 and after the treatment about 98 % of free fatty acids have been removed from the oil. |
| CJO-2+3 |  | 12.21 | This oil has been used in the batch CAD-5 and after the treatment about 97 % of free fatty acids have removed from the oil. |
| CJO-5 |  | 1.53 | This oil has been used in the batch CAD-8 but it has been contaminated during the oil pressing by oil seed cake coming from a previous oil pressing. High percentage of precipitate has been obtained despite its low acid value. The treatment of this oil could not be run to the completion |

# Annex 5

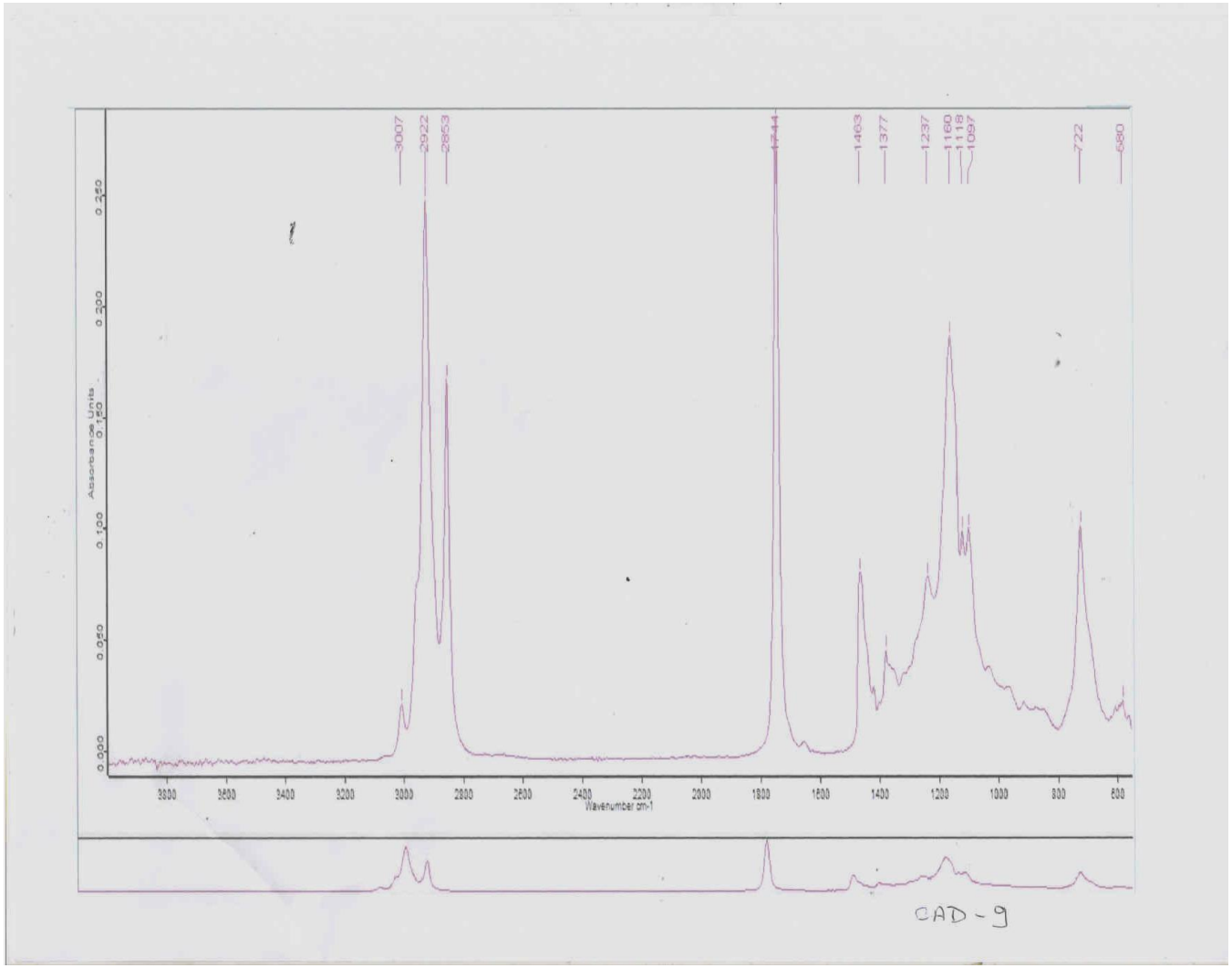
## Fourier transform infrared spectroscopy (FTIR) of oil before and after trans-esterification (biodiesel)

FTIR spectroscopy analysis has been implemented with a Bruker-Alpha 6 spectrophotometer equipped with Opus 6.5 software. All the spectrums have been scan between 4000 and 500 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The samples of oil (CAD-9) and biodiesel (TAG-4) have been scanned without any solvent and the results of the two scan are depicted by the pictures C and D. The table C lists the band attribution of the two spectrums.

**Table H :** *Band attribution of FTIR spectrum of the oil before and after the treatment for removing free fatty acid and phospholipids*

| **Oil before trans-esterification (picture C)** | | **Biodiesel (picture D)** | |
|---|---|---|---|
| **Band (cm-1)** | **Interpretation** | **Band (cm-1)** | **Interpretation** |
| 3007 | C-H stretching vibration of the cis double bond (C=CH) | 3008 | C-H stretching vibration of the cis double bond (C=CH) |
| 2922, 2853 | Symmetric and asymmetric vibrations of aliphatic $CH_2$ group | 2923, 2853 | Symmetric and asymmetric vibrations of aliphatic $CH_2$ group |
| 1744 | Double bond stretching of ester carbonyl functional group of triglycerides | 1742 | Double bond stretching of ester carbonyl functional group of methyl esters |
| 1463 | Bending vibrations of CH2 and CH3 aliphatic groups | 1461 | Bending vibrations of CH2 and CH3 aliphatic groups |
| 1237 | Stretching vibrations of C-O ester groups | 1244 | Stretching vibrations of C-O methyl ester groups |
| | | 1195 | ρ Methyl vibration |
| 1160 | Bending vibrations of $CH_2$ aliphatic groups | 1169 | Methyl group near carbonyl group |

**Picture C** **:** *FTIR spectrum of oil before trans-esterification*



**Picture D :** *FTIR spectrum of Biodiesel*