Lao
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Jatropha oil degumming and stability testing procedures

Report

L. 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.

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

The oil obtained from mechanical expelling or solvent extraction content a number of impurities. Some of these impurities like seed fragment or meal fines are not soluble in the oil and can be remove by filtration. Others including fatty acid, hydrocarbons, ketones, tocopherols, glycolipids, phytosterols, phospholipids, proteins, pigments, metal and resins, are soluble or form stable colloidal suspensions in the oil. Most of these have unfavorable effects on the flavor, odor, appearance, and shelf life of the oil, and therefore have to be removed from the vegetable oils by chemical or physical refining processes.

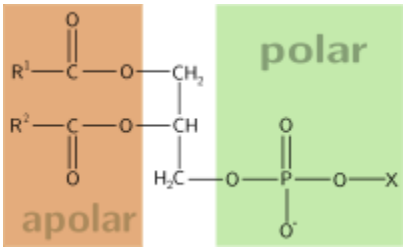
Among these impurities phospholipids are gums that pose many problems during the storage and processing of the crude oil due to their emulsifying action and theirs potentiality for splitting acyl glycerol in fatty acid. Phospholipids are also present in oil in the form of calcium and magnesium salts. According ASTM biodiesel should not contain more than 15 ppm of phosphorus and no more than 5 ppm of calcium and magnesium (combined).

Phospholipid should be removing from crude oil in order to avoid the degradation of the oil during the storage and for decreasing the quantities of some metal like calcium and magnesium in the oil to an acceptable level. Several processes for removing phospholipids can be considered according their nature and their occurrence in the crude oil.

I Brief introduction on phospholipids chemistry

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. Oil degumming can also be implementing by membrane technology.

The molecular structures of phospholipids present in vegetable oils and fat are depicted by the scheme 1. 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.

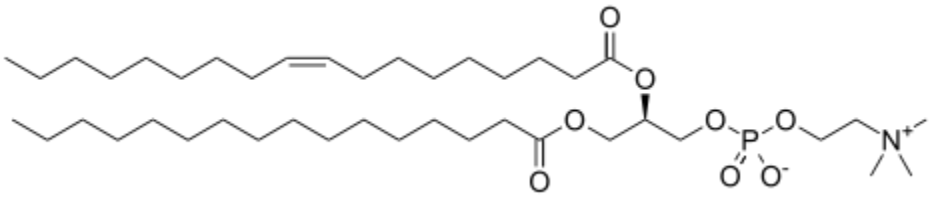


Scheme 1 : *Molecular structure of phospholipids*

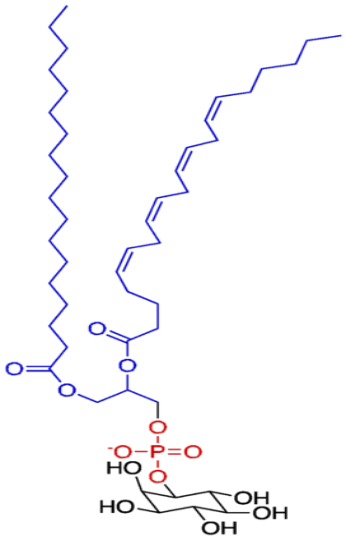
1 Hydratable phospholipids

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.



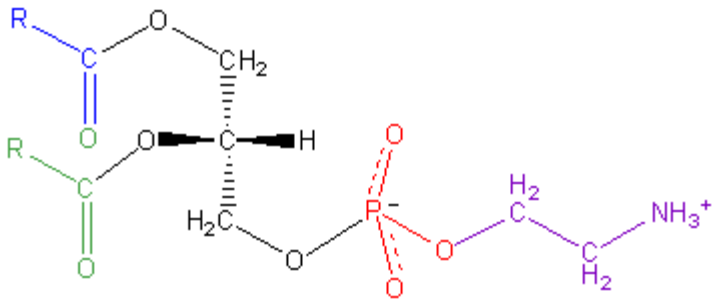
Scheme 2 : *Molecular structure of phosphatidyl choline (PC)*



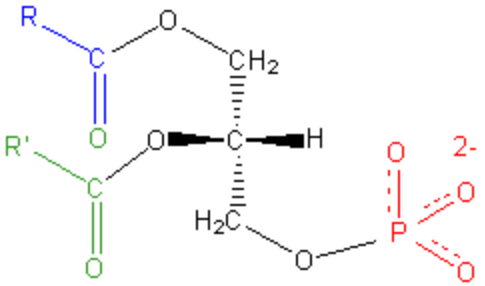
Scheme 3 : *Molecular structure of phosphatidyl inositol (PI)*

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.



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



Scheme 5 : *Molecular structure of phosphatidic acid (PA)*

II Procedures for removing phospholipids in vegetable oils and animal fats

Different processes should be considered for the removing of phospholipids from oil because of the difference in their chemical structure. Hydratable phospholipids are removed from oil by mixing oil with some quantities of water without taking in account the pH value. Non hydratable phospholipids can only make interaction with water in specific range of pH or need additives to improve their interaction with water. Three processes can be considered for the removing of phospholipids from oils that are water degumming, acid degumming and TOP degumming.

1 Water degumming

Crude oil is heated at 80 ^{o}C and water at the same temperature is added to the oil (5 % of oil volume) and the all is stirred for 15 minutes at 80 ^{o}C and cool to the room temperature. The mixture is then centrifugated for 20 minutes in order to separate the aqueous layer from oil layer.

This process can only remove hydratable phospholipids from oil.

2 Acid degumming

Crude oil is heated at 80 ^{o}C; a solution of citric acid in water (30 % w/w) is added to the oil (2 % of oil volume). The mixture is stirred for 35 minutes at 80 ^{o}C and cool to the room temperature. Water is added to the mixture (1 % of oil volume) and the all is transferred to a separating funnel. After settling for 60 minute the lower layer is drain off and the upper layer is centrifugated for 20 minutes for separating the gums from the oil.

This process can remove hydratable and non hydratable phospholipids from oil.

3 TOP degumming

After water degumming, water degummed oil is heated at 80 ^{o}C and a solution of phosphoric acid (14 % w/w) is added to the oil in amount of 0.1 % of weight oil. After intensive mixing for 5 minute at 80 ^{o}C, the acid is partially neutralized by a solution of sodium hydroxide (20 % w/w) is added to the mixture in amount of 0.3 % (w/w) of oil and the mixture is mixed again for 5 minutes. The mixture is then cool to the room temperature and centrifugated during 20 minutes for separating gums from oil.

This process can remove hydratable and non hydratable phospholipids from oil but also calcium and magnesium salts.

III Testing to implement on crude Jatropha oil

According to the literature phospholipids that are present in crude Jatropha oil are mainly phosphatidyl choline (PC), phosphatidyl inositol (PI) and in lower quantities phosphatidyl ethanolamine (PE). PC and PI can be removing by water degumming because they are hydratable phospholipids but PE should be remove by an another process like acid degumming or TOP degumming because it is a non hydratable phospholipid. In other to know what will be the suitable process for the crude Jatropha oil, the three processes will be implementing on the crude oil and calcium, magnesium, phosphorus and acid value will measure on the crude oil and after each treatment. The acid value of the oil after treatment will also be measuring in order to assess the stability of oil according to the time. Instability of oil is characterized by the formation of acid product due to oxidation or hydrolysis of acyl glycerol compounds that produce free fatty acids.

1 Water degumming

Two hundred grams of crude oil is poured in a graduated cylinder of 250 ml in order to measure the volume of the oil then the oil is heated at 80 ^{o}C and water at the same temperature is added to the oil (5 % of oil volume). The mixture is stirred for 15 minutes at 80 ^{o}C and cool to the room temperature. The mixture is then centrifugated for 20 minutes in order to separate the aqueous layer from oil layer.

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