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## Optimization of *Jatropha curcas* pure plant oil production

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# Chapter 6

## **Purification of Jatropha oil by means of a centrifugal contactor separator device**

Erna Subroto, Louis Daniel, M. Yusuf Abduh, Robert Manurung, Hero Jan Heeres, Antonius Augustinus Broekhuis

## **Abstract**

A conventional degumming and deacidification of jatropha oil were conducted in a small-scale batch system. Several important parameters such as refining agent type, acid concentration and operation temperature were investigated to optimize the oil quality in terms of phosphorus, calcium and magnesium content, and acid value. Simultaneous degumming and deacidification delivered the desired oil quality. The phosphorus, Ca+Mg content and free fatty acid were easily achieved with levels of 0.9 ppm, 0.5 ppm and 0.28 (mgKOH/gr oil), respectively. From this it was concluded that two chronological operations with oxalic or citric acid solutions, followed by base treatment with KOH, NaOH or ammonia solutions can be used to produce oils that satisfy commercial standards, DIN 51605: 2010-10. Execution of these steps in a CCS device with the intention to achieve simultaneous degumming and deacidification was found to be inadequate. Nevertheless, it is foreseen that a process based on one CCS device in a sequential mode or on two units in series can be applied for the required mixing and separation operations.

**Keywords:** *Jatropha curcas L.*, oil purification, oil quality, CCS, process parameters

## 6.1 Introduction

Crude vegetable oil obtained by extracting or pressing oilseeds contains contaminants such as phosphatides, free fatty acids, mono and diglycerides, pigments, oxidation products, carbohydrates, proteins and metal compounds that negatively affect taste, smell, appearance, and storage stability [1]. Common processes known to remove these compounds are degumming, deacidification/neutralization, bleaching, and deodorization. Degumming is designed to remove phospholipids and mucilaginous material while deacidification is performed to remove free fatty acids. Bleaching is aimed to remove color compounds and oxidation products. Finally, deodorization is performed to remove volatile compounds. Degumming and deacidification are the two main processes that determine the final quality of the oil as fuel. Major impurities in the oil are to be removed during these processes.

Phospholipids should be removed because of their strong emulsifying action and the tendency to complex with pro-oxidant metal. They cause problems in the next refining step and settling out in storage [2]. Gerpen and Dvorak (2002) [3] found that phosphorus levels above 50 ppm in the oil reduced the yield of methyl ester by 3–5%; this was due mostly to the increased difficulty of separating the glycerol from the esters. The presence of phospholipid in plant oil or biodiesel also causes problems in diesel engines such as plugging and gumming of filters, lines and injectors and it leads to the build-up of carbon residue [4].

Deacidification is conducted to reduce the FFA content in vegetable oils. FFA is responsible for the development of an undesirable rancid flavor (hydrolytic rancidity) [5]. Presence of FFA resulted in reduced yield in biodiesel production [6]. In addition, a high acid value in the fuel leads to corrosion, abrasion and deposits in the engine. Furthermore the free fatty acids may react with the alkaline components of the lubricating oil and affect its lubricity [7].

In a typical refining process, undesirable impurities in crude vegetable oil are combined with one or more refining agents to form hydrophilic components. The hydrophilic components are then removed from the oil by separation of oil and aqueous phase. If these steps can be integrated to one single step, process intensification is achieved. With this consideration, a promising powerful tool to be used is a Centrifugal Contact-Separator (CCS). A CCS device enables contact, reaction, and separation between two immiscible phases in a single unit. Thus, this device is attractive to be used for vegetable oil processing. However, to the best of our knowledge, this device has never been used in vegetable oil purification.

We therefore investigated the applicability of a CCS device to be used as an integrated degumming and refining unit for jatropha oil. In this report, preliminary experiments on JO purification were conducted in batch scale. Several important parameters such as refining agent type, acid concentration and operation temperature were investigated to optimize

the oil quality in terms of phosphorus, calcium and magnesium content, and acid value. The best conditions obtained from batch experiments were applied in the CCS device.

## **6.2 Materials and methods**

### **6.2.1 Materials**

Dried jatropha seeds were obtained from a jatropha plantation in Ciamis, West Java, Indonesia. The seeds were harvested manually during July 2010, sun-dried and stored in jute bags in a warehouse facility at temperatures between 20-30 °C and at a relative humidity of 60-70%. The seeds were deshelled manually and the kernels were conditioned to moisture contents of 4% w.b. The oils were pressed from dehulled seeds using a hydraulic press (self-manufactured laboratory scale) at 2012, respectively. The oil content of jatropha kernel was 61.4% d.b. with the original moisture content of kernel in the range of 7 - 7.2% w.b. The oil analyses were conducted directly after purification.

Potassium hydroxide (pellets, 85%, Vetec), sodium hydroxide (pellets, 98%, Sigma-Aldrich), ammonium hydroxide (70%), oxalic acid anhydrous ( $\geq 99\%$ , Sigma-Aldrich), citric acid monohydrates ( $\geq 99\%$ , Sigma-Aldrich), diethyl ether ( $\geq 99\%$ , Sigma-Aldrich) were bought from Sigma-Aldrich (Amsterdam, The Netherlands).

### **6.2.2 Batch purification**

The mixing vessel for the batch purification experiments was a round bottom flask heated inside an oil bath equipped with a magnetic stirrer, heating plate and temperature control system.

#### *Degumming*

The crude jatropha oil was degummed in a batch reactor using various reagents: water, citric acid or oxalic acid solution; various acid strengths: 2.5, 5 and 10% (w/v) acid solution in water and various degumming temperatures: 60, 70 and 80 °C. In a typical experiment, a total of 30 g of crude jatropha oil was heated to 80 °C. Then 2% w/w of water or aqueous acid solution was added. The mixture was stirred at 500 rpm for 15 min and then at 50 rpm for 30 min for hydration. The mixture was then centrifuged at 3000 rpm for 45 min to separate the oil and the white precipitate. The degummed oil was dried at 60 °C under reduced pressure of 50 mbar for 30 min by use of a rotary vacuum evaporator.

### *Ethanollic degumming*

The crude jatropha oil was mixed with acidified ethanol 70% (v/v) at ratio 1:1 (w). Various acid strengths: 0 and 1% (w/w) citric acid in Ethanol 70%. In a typical experiment, a total of 20 g of crude jatropha oil was heated to 80 °C. Then 20 g of acidified ethanol 70% (v/v) was mixed with oil. The mixture was stirred at 1000 rpm for 20 min. The mixture was then centrifuged at 3000 rpm for 45 min to separate the oil and the ethanol phase. The degummed oil was dried at 60 °C under reduced pressure of 50 mbar for 30 min by use of a rotary vacuum evaporator.

### *Deacidification*

The degummed jatropha oil was deacidified with various alkaline solutions (KOH, NaOH or NH<sub>4</sub>OH). In a typical experiment, the oil was pre-heated at 60 °C, the aqueous alkaline solution of 3 N was added at 1.1 stoichiometry with the free fatty acid (FFA) and stirred at 100 rpm for 30 min. The mixture was then centrifuged at 3000 rpm for 45 min to separate the oil and the formed soapstock. The oil was heated to 70 °C for further water washing. The water was added at 2% w/w and mixed at 100 rpm for 15 min. The oil was centrifuged (3000 rpm 45 min) to remove the remaining soaps. This water washing procedure was repeated twice. The separated oil was dried at 60 °C under reduced pressure of 50 mbar for 30 min by use of a rotary vacuum evaporator.

The appropriate amount of alkaline solution to neutralize the free fatty acids was calculated by the following equation:

$$V = \frac{1.1 \times W_{\text{FFA}} \times 10}{M_{\text{FFA}} \times N}$$

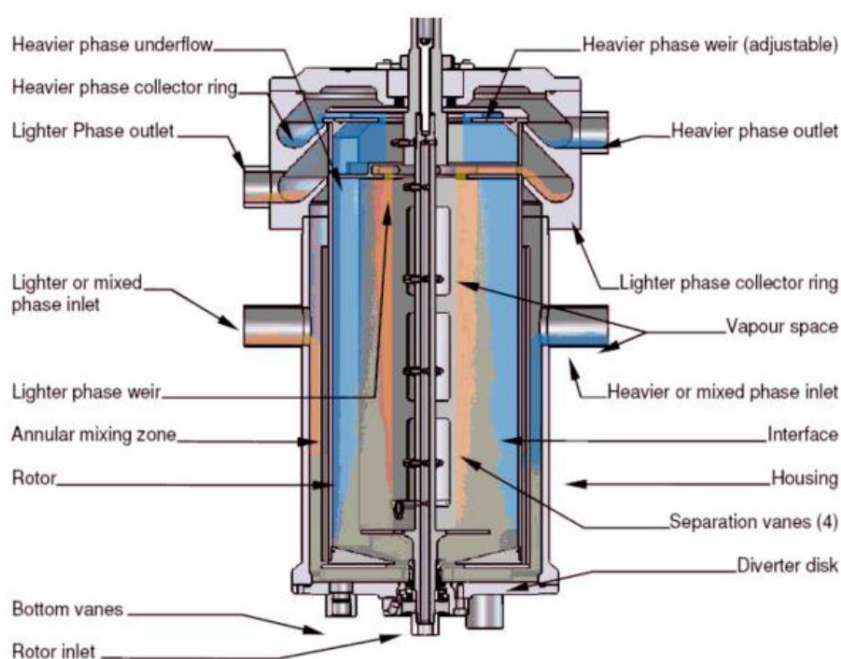
Where, V- volume of aqueous alkali solution (ml); W-weight of the oil (g); M-average molecular weight of the FFA (M=278 g/mol); N-concentration of the aqueous alkali solution (mol/L). The value of 1.1 means that stoichiometry ratio between alkali and FFA.

### *Simultaneous degumming and deacidification*

A total of 30 g of crude jatropha oil was heated to 60 °C. Then 2% w/w of aqueous oxalic acid solution was added. The mixture was stirred at 500 rpm for 15 min and then at 50 rpm for 30 min for hydration. Thereafter aqueous alkaline solution was added as a 3 N solution and the mixture was stirred again at 100 rpm for 30 min. The mixture was then centrifuged at 3000 rpm for 45 min to separate the oil and the white precipitate. The oil was dried at 60 °C under reduced pressure of 50 mbar for 30 min by use of a rotary vacuum evaporator.

### 6.2.3 Oil purification in CCS

The CCS device used in this study was a CCS type V02 obtained from CINC Solutions BV, Doetinchem, The Netherlands. The CCS was equipped with a heating/cooling jacket, a low-mixing sleeve, and weir size of 22.86. The CCS was operated at ambient pressure and a pre-determined temperature controlled by a water bath controller connected to the jacket. One Verderlab peristaltic tube pump equipped with a double pump head (3.2 x 1.6 8R with suitable hose) with a maximum capacity of 100 mL/min was used to feed the CCS. The representative cutway of CCS device was shown in Figure 1.



**Figure 1** Cutaway view of the CINC CCS (Source: CINC CCS Type V-02 Manual Handbook)

Crude jatropha oil and 2% v/v of 5% oxalic acid solution were pre-mixed at 60 °C under constant stirring at 500 rpm for 15 min before fed to the CCS. The CCS was preheated to 60 °C before used. The CCS was started at desired speed (50 Hz) and the CCS was fed with the pre-mixed oil and oxalic acid solution at one inlet. During feeding, the pre-mixed oil and water in the pre-mixing vessel was maintained under constant stirring of 50 rpm at 60 °C. After 60 min of circulation, no separation was observed and the outlet was recycled back to the oil feeder. The KOH solution was added to the oil, and the process continued. After 30 min of circulation, separation was observed. And the purified oil was collected after 60 min of separation operation.

#### **6.2.4 Oil quality analysis**

In this study, the quality of the purification was focused on three parameters, i.e. acid value, phosphorus content, and alkali metal content. Chemical analyses of the samples were carried out according to the standard test methods: DIN EN 14104, DIN EN 14107, DIN EN 14538 for acid value, phosphorus content and calcium and magnesium content, respectively. The standard quality of vegetable oil as target in this research is the German Standard number DIN 51605: 2010-10. The maximum content of these parameters are 2 mg KOH/g oil, 3, 1 and 1 ppm for acid value, phosphorus, calcium and magnesium content, respectively. Most of chemical property analysis of plant oil samples was conducted in our laboratory with the exception of phosphorus, calcium and magnesium content analyses which were conducted by ASG Analytik-Service GmbH, Germany. Duplicate measurements were performed on each sample and average values were taken.

### **6.3 Results and discussions**

The best conditions for the CCS experiment have been determined by separate batch degumming and subsequent deacidification experiments, followed by the same treatment in a simultaneous mode.

#### **6.3.1 Batch purification**

##### *Degumming*

The phosphorus content of crude jatropha oil was approximately 37.9 ppm. Crude jatropha oil treated with water gave insignificant reduction in phosphorus content (see Table 1) which indicated that the phospholipids present in this jatropha oil are mostly non-hydratable, i.e. that the phospholipids are not separated by hydration. This is in contrast to the data reported in the literature [8] which shows a composition with a high level of hydratable phospholipids (PC 60.5%, PI 24% and PE 15.5%, along with traces of lyso PE and lyso PC). This is due the fact that the jatropha oil was pressed from aged jatropha seed. The amounts of the non-hydratable phospholipids (PA, PE and lysophospholipids) usually increase with age, physical and microbial damage of the seeds [9].

From the various agents tested, degumming with oxalic acid gave the lowest phosphorus content of 9.8 ppm. Smiles (1988) [10] showed that degumming oil from canola, soybean and sunflower with 0.2% oxalic acid solution (10% w/v) and 0.25% citric acid solution (50% w/v) gave comparable phosphorus contents for the two acid treatments. In fact the citric



acid concentration in these experiments was the higher than oxalic acid suggesting that oxalic acid is more effective as degumming agent.

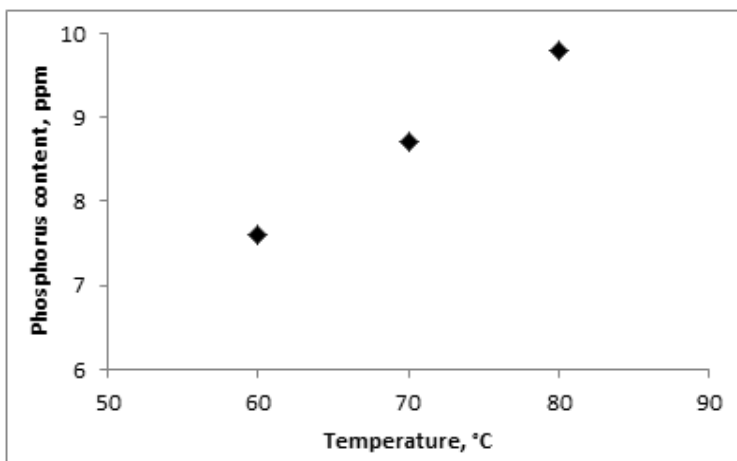
As it has been suggested in literature [11] that better purification results can be obtained by using alcoholic solvents, some experiments have been conducted using ethanol. Acidified ethanolic degumming indeed gave better quality oil in terms of metal and phosphorus content. However, this process needed a higher acid concentration compared to acid degumming and may have left some acid in the oil as the value for free acid increased.

**Table 1** Analytical data for degummed oils

Degumming condition		Oil quality			
Reagent	Condition	P (ppm)	Ca+Mg (ppm)	AV (g KOH/g oil)	OSI (h)
Crude oil	-	37.9	35	2.83	10.82
Water	2% w/w water	30.7	31.2	2.76	9.9
Citric acid	2% w/w of 5% w/v acid in water	15.7	6.0	2.82	9.41
Oxalic acid	2% w/w of 5% w/v acid in water	9.8	1.7	2.79	9.48
Ethanol 70%	Ethanol 70% : JO = 1:1	26.8	31.2	2.28	8.75
Acid E 70%	Ethanol 70% : JO = 1:1, + 1% w/w citric acid	10.8	1.2	3.12	9.38
DIN 51605:2010-10		<3	<2	<2	>6

Note: all experiments carried out at 80 °C

As only a small amount of the hydratable phospholipids are removed during the water degumming step (row 2 in Table 1), the rest of the phospholipids is expected to be present in the non-hydratable form. Thus, the acid concentration added became crucial for the elimination of the non-hydratable phospholipids. Various acid strengths were investigated from 2.5 to 10% (w/w) oxalic acid solution. The phosphorus content of degummed oil treated with 2.5, 5 and 10% (w/w) oxalic acid solution were 13.6, 9.8 and 13 ppm, respectively. The phosphorus content indeed decreased from the high level in the crude oil, but the purity of the acid treated oils can hardly be correlated with the concentration of the acid.



**Figure 3** Effect of temperature during acid degumming on phosphorus content of jatropa oil

Figure 3 shows the influence of the degumming temperature on phosphorus content. Phosphorus removal was slightly better at low temperature. At higher temperatures, the solubility of phospholipids in oil increases leading to incomplete degumming [12].

#### *Deacidification*

The degummed jatropa oil (oxalic acid 2% w/w of 5% w/v acid in water; 60 °C) was further deacidified with various alkaline solutions (KOH, NaOH or NH<sub>4</sub>OH). From Table 2, It was shows that various alkali can reduce the phosphorus, metal alkali and acid value to acceptable level described in DIN DIN 51605:2010-10. PA, PE and free fatty acid were neutralized using alkali. Dijkstra and van Opstal [13] found that hydration using alkaline sodium hydroxide makes the acidulated phospholipids more quickly hydratable and insoluble in oil. The soap mixture formed during this saponification also helps in the encapsulation of other phosphorus compound and impurities.

**Table 2** Analytical data for deacidified oils

Deacidification condition		Oil quality		
Reagent	Condition	P (ppm)	Ca+Mg (ppm)	Acid value (gKOH/g oil)
Degummed oil		7.6	1.2	2.5
NH <sub>4</sub> OH	1.1 stoichiometry, 3 N	0.8	<0.5	0.27
KOH	1.1 stoichiometry, 3 N	0.7	<0.5	0.26
NaOH	1.1 stoichiometry, 3 N	0.9	<0.5	0.35
DIN 51605:2010-10		<3	<2	<2

Mixed at 100 rpm for 30 min, using oil degummed at 60 °C with oxalic acid

### *Simultaneous degumming and deacidification*

The experiments carried out in batch mode, as described above, were combined in a simultaneous treatment using the optimum conditions obtained. The degumming was using oxalic acid and followed by deacidification using KOH. The most critical oil standards for phosphorus, Ca+Mg content and free fatty acid were easily achieved with levels of 0.9 ppm, <0.5 ppm and 0.28 mgKOH/g oil, respectively.

### **6.3.2 Purification by CCS**

As described in the experimental section, the CCS operation is carried out in two sequential steps. In the first step, degumming with oxalic acid solution did not show any phase separation. In the subsequent neutralization step with potassium hydroxide, the oil and the soap solution could easily be separated. Compared to the crude oil values for phosphorus of 37.9 ppm, the alkali metals (Ca and Mg) of 35 ppm, and AV of 2.83 (mg KOH/g oil), the CCS based oil gave numbers of 3.5 ppm, 3.5 ppm, and 1.07 mg KOH/g oil, respectively.

Compared to the required oil standard DIN 51605:2010-10 which specified 3 ppm, 2 ppm and 2 mg KOH/g oil for phosphorus, alkali metals (Ca+Mg) content and acid value, respectively; this experiment did not exactly deliver the desired results. This may be explained by insufficient decomposition of the metal phosphatidic salts [13]. Other possible explanations might be that the equilibrium distribution for phosphorus and metals has not been reached or that different ratios between both liquids have to be applied.

Although the desired result is not fully achieved and integrated mixing and separation cannot be executed in one operation, the data obtained after these sequential experiments

suggest that the CCS single unit can be applied to perform two unit operations in chronological order.

#### **6.4 Conclusions**

In this study a jatropha oil obtained from seeds with a long storage time has been subjected to different purification operations. Due to enzymatic action, the impurity level in the oil was high in comparison to fresh oils. This makes the oil less representative but nevertheless with its high phosphorus content an excellent test-case for the purification procedures envisaged.

Degumming as a single purification operation to remove phosphorus compounds, metal salts and free fatty acids appeared insufficient to prepare oil according industry standards. Subsequent deacidification using various base systems delivered the desired oil quality. From this it was concluded that two chronological operations with oxalic or citric acid solutions, followed by base treatment with KOH, NaOH or ammonia solutions can be used to produce oils that satisfy commercial standards.

Execution of these steps in a CCS device with the intention to achieve simultaneous degumming and deacidification was found to be inadequate. Nevertheless, it is foreseen that a process based on one CCS device in a sequential mode or on two units in series can be applied for the required mixing and separation operations.

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