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Biodiesel production from *Jatropha curcas*: Integrated process optimization

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ABSTRACT

Energy obtained from renewable sources has increased its participation in the energy matrix worldwide, and it is expected to maintain this tendency. Both in large and small scales, there have been numerous developments and research with the aim of generating fuels and energy using different raw materials such as alternative crops, algae and lignocellulosic residues. In this work, *Jatropha curcas* plantation from the North West of Argentina was studied, with the objective of developing integrated processes for low and medium sizes farms. In these cases, glycerine purification and meal detoxification processes represent a very high cost, and usually are not included in the project. Consequently, alternative uses for these products are proposed. This study includes the evaluation of the *Jatropha curcas* crop during two years, evaluating the yields and oil properties. The solids left after the oil extraction were evaluated as solid fuels, the glycerine and the meal were used to generate biogas, and the oil was used to produce biodiesel. The oil pretreatment was carried out with the glycerine obtained in the biodiesel production process, thus neutralizing the free fatty acid, and decreasing the phosphorous and water content.

1. Introduction

Jatropha curcas is a plant that belongs to the Euphorbeaceas family. Within this genus there are more than 170 species distributed around the world, especially in tropical regions. This plant comes from Central America (México), and it is possible to obtain an oil yield higher than 1500 kg per hectare. This oil is adequate to be used as a raw material in the biodiesel production [1].

In Argentina, several wild species have been found, mainly in the semiarid Chaco (a region in the north of Argentina) [2]. However, the technical knowledge regarding the handling of this crop is very limited.

Marginal and non-productive areas are explored in order to grow *Jatropha curcas*, to foster the industrialization and to add value to the primary production improving the socioeconomic condition in the region. In Argentina, the northeast and northwest regions are studied with this aim [3].

There are few industrial facilities that produced biodiesel from *Jatropha curcas* oil; however, at laboratory level there are several reports that indicate that this oil is adequate to obtain biodiesel that meets the international standards [4–7]. Nevertheless, these publications address specific parts of the process, being necessary to do a more comprehensive and global study. Achten et al. [4] presented a review related to the use of *Jatropha curcas* to obtain fuels. Both, agricultural aspects of this crop and the characteristics of the obtained products were discussed. Recently, the use of different catalytic systems has been reported, such as enzimatic [8,9], ionic liquids [10,11], and solid catalysts [12–15]. The use of alternative technologies has also been explored in order to obtain biodiesel from *Jatropha curcas* oil, for example ultrasound assisted transesterification [13,16], and supercritical methanol reactive extraction [17,18]. The properties of different samples of biodiesel obtained using different acid (H_2SO_4 and HCl) and alkaline catalysts (NaOH, KOH, CH_3ONa and CH_3OK) have been compared [19]. The kinetics of the transesterification of *Jatropha curcas* oil has also been studied [20].

Argentina is currently one of the major biodiesel producer worldwide, using soybean oil as raw material. The installed capacity is above 3 millions tons/year, and growing very fast. Most of these industries, approximately 80%, are located nearby Rosario city, in the centre of the country. Therefore, it is very important to assess the feasibility of growing new crops in different regions of Argentina.

In this work, integrated processes for biodiesel production from different samples of *Jatropha curcas* oil, are studied. The samples of *Jatropha curcas* seeds were obtained from Salta and Jujuy provinces, located in the Northwest region of Argentina. The by-products utilization to generate energy is also addressed.

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The main objective is to develop integrated processes for low and medium sizes farms. In these cases, glycerine purification and meal detoxification processes represent a very high cost, and usually are not included in the project. Consequently, alternative uses for these products are proposed in this work.

2. Experimental

2.1. Raw material characterization

The raw material used in this work was obtained in different places in the northwest region of Argentina. Seeds were obtained in Jujuy province (Yuto city), and in Salta province (Pichanal city).

A portion of the seeds was manually peeled off, weighting the kernel and the husks. The seeds were dried in an oven at 100 °C until a constant weight was obtained. The oil was extracted both by pressing, and using hexane. In the latter procedure, the seeds were ground to a size smaller than 1 mm. The extraction was carried out as described in AOCS Aa 4-38 2001.

Another set of experiments was carried out obtaining the oil by pressing the seeds before peeling.

The oil was characterized by measuring the content of phosphorus (AOCS Ca 12-55), acidity (AOCS Cd 3d-63), iodine index (AOCS Cd 3d-63), and water content (AOCS Ca 2e-84).

2.2. Biodiesel production

The biodiesel production process used in this work included the following steps: (i) esterification and/or neutralization; (ii) transesterification; (iii) biodiesel purification.

2.2.1. Esterification and neutralization

This part of the process has the objective of diminishing the oil acidity, in order to make it possible to feed the oil to the alkaline transesterification process. A combination of an acid catalyzed esterification reaction and neutralization with glycerine, obtained from the transesterification reactor, has been analyzed. The esterification was carried out using methanol and sulphuric acid or paratoluen-sulphonic acid (PTSA) as catalysts, at 65 °C, while stirring at atmospheric pressure in a glass reactor with a condenser to reflux the methanol. During this reaction, the acidity has been determined in small samples taken from the reactor.

Oil samples with acidity in the range 3–9 g oleic acid/100 g were neutralized using the glycerine phase obtained in the acylglycerides transesterification reaction. The composition of this phase was approximately the following: 15–20 wt.% methanol, 3–5 wt.% soaps, 60–70 wt.% glycerine, 0.45–0.65 mmol/g sodium methoxide catalyst, 5–10 wt.% non-glycerol organic material.

In those cases in which the sodium methoxide content in the glycerine was not enough to neutralize the fatty acids present in the oil, potassium hydroxide solution (50 wt.% in water) was added.

The free fatty acids content in the ester-rich phase was determined according to the EN 14104 standard, and the water content according to EN 12937 standard.

2.2.2. Transesterification

The transesterification reaction was carried out under similar conditions to those used by other researchers with *Jatropha curcas* oil [21–23]. In summary, the conditions were as follows:

- Alcohol:methanol; alcohol:oil molar ratio 6:1.
- Catalyst: sodium methoxide 30 wt.%, or potassium methoxide 32 wt.%, in both cases dissolved in methanol. The catalyst was loaded with a concentration in the range 2.3–4.5 g solution/100 g oil.
- Reaction temperature: 65 °C, at atmospheric pressure with reflux.
- Vigorous agitation (Reynolds number higher than 12.000).
- Reaction time: 90 min.

The catalysts dosification was calculated as the sum of the desired catalyst concentration and the amount needed to neutralize the free fatty acids present in the raw material.

The soap concentration in the glycerine phase was determined according the EN 14108 or AOCS Cc17-79.

The total glycerine content in the biodiesel was measured both by the EN 14105 standard, and by a volumetric procedure [24] to overcome the limitations mentioned in this standard.

2.2.3. Biodiesel purification

The conventional procedure to purify biodiesel includes as a first step an extraction with acidified water, followed by an extraction with water. In this work, we adjusted a methodology in which the first step was carried out using neutral water, to avoid the hydrolysis of the soaps present in the biodiesel. This first step is followed by an extraction with acidified water, and finally with water. This modification is very important, since it avoids the soap hydrolysis that leads to an increase in the acidity of the product. The soap content was also measured in the biodiesel phase, and in the water used in the extraction step. The final step was the biodiesel drying, carried out by stripping with nitrogen at 60 °C.

Quality parameters in the final products were measured, and mass balances were carried out.

2.3. By-products utilization

The main by-products obtained in the biodiesel production process from *Jatropha curcas* oil, are the fruits and seeds husks, the meal obtained in the oil extraction step, and the glycerine-rich phase.

The heating values of the fruits and seeds husks were determined according to ASTM D-2382 standard.

2.3.1. Biogas production

The meal and the glycerine phases were feed to an anaerobic reactor, to generate biogas. The gas was collected in a variable volume gasometer, with a maximum capacity of 2 l. The reactor was a 2 l flask, heated at 32 °C ± 3 °C. The content of this reactor was agitated using a mechanical stirrer at 30–35 rpm. The reactor was fed with 1–6 g of volatile solids (VS) per liter per day. This amount is equivalent to less than 12 g of residues per day. The residence time was 25 days.

The solid raw material was characterized by determining nitrogen by the Kejdhal method (AOAC Ba 4a-38), phosphorus (Methods of Analysis for nutrition labeling 970.39), potassium (Methods of Analysis for nutrition labeling 965.3), total solid content (APHA 2540 B) and volatile compounds (APHA 2540 E).

The glycerine phase was analyzed in order to determine the glycerine content (BS 5711-3), methanol (EN14110), ashes (ASTM D482), and water by Karl-Fischer titration (AOCS Ca 2e-84). The carbon content was determined by volatile compounds (APHA 2540 E) and correcting by Van Bemmelen factor[1].

The process was followed by measuring the biogas volume obtained in the gasometer, and the CO_2 content was determined by the Orsat method (APHA 2720 B). The liquid in the bioreactor was analyzed in order to determine the free fatty acid and the alkalinity as proposed by Jenkins et al. [25]. In this technique, the

[1] This factor considers the organic matter has in averaged 58% of carbon, its value is 1.74.

effluent from the biodigestor is titrated with H_2SO_4 0.1 N, determining the volume used to obtain pH 5.75 and pH 4.3. The first represent the amount of calcium carbonate present in the sample (ALK 1), and the second one indicate the content of volatile acids (mainly acetic and propionic) (ALK 2). The ratio of these values (ALK1/ALK2) is an indication of the buffer capacity of the reacting system. The best performance of the biodigestor is obtained when this value is between 0.6 and 0.8.

The total acidity of the system was also followed titrating a sample previously acidified to pH 4, using NaOH 0.1 N. The volume used to modify the pH from 4 to 7 is a measure of the total acidity. This number represents the content of acetic acid that can be transformed in biogas, and should be below 5000 mg/l.

3. Results and discussion

3.1. Biodiesel production

3.1.1. Jatropha curcas oil

The properties determined to *Jatropha curcas* oil varied in a wide range among samples obtained from seeds recollected along several months. The results are summarized in Table 1. The acidity is a very important parameter, since it determines the process required to transform the oil in biodiesel. As shown in Table 1, the acidity was between 8.7% and 20.5% for samples obtained by pressing, and between 0.6% and 12.2% in the case of solvent extraction. A recent study indicated that the pressing procedure to obtain the oil is more efficient regarding the total exergy consumption than the solvent extraction process [26].

Results shown in Table 1 indicate that a facility designed to use *Jatropha curcas* oil, must take into account this large variability and, therefore, include the esterification module, in order to transform the free fatty acids in alkyl-esters, by an acid catalyzed reaction. Therefore, the process to produce biodiesel using this raw material should include: (i) esterification, using acid catalyst, to process the oil with high acidity (above 7% approximately), (ii) neutralization of oils with acidity between 7% and 2%, (iii) transesterification of oils with low acidity (below 2), (iv) purification. The following sections present results obtained in each of these process stages.

3.1.2. Esterification

A single esterification step was carried out in the case of *Jatropha curcas* oil with high acidity (15% or higher). According to Tiwari et al. [6] and Pisarello et al. [27] and results obtained in our laboratory, it has been verified that using 40 vol.% of methanol (referred to the oil) and 0.35 equivalents of sulphuric acid for 890 g of oil, the acidity decreased to values lower than 2% in an hour, approximately.

Results of esterification experiments carried out using two acid catalysts are shown in Fig. 1. Two different samples of oil were used in these experiments. One of them has an initial acidity of 21% and a water content of 1570 ppm. The other oil had an acidity of 16%, and it was dried to a final water content of 100 ppm. The PTSA was slightly more active than the sulphuric acid, as indicated by the results obtained with the oil containing 1570 ppm of water. Nevertheless, the differences in activity are small, and after 30 min of reaction, in both cases the acidity decreased below 1%. The catalyst concentration of 0.35 equivalents/lt of oil corresponds to a weight concentration of PTSA 5.3 times higher than in the case of SO_4H_2. This should be taken into account to select the catalyst, due to the higher cost associated with the PTSA catalyst, although this is a much less corrosive acid. Sulphuric acid has been typically used for esterification of acid oils [27–30].

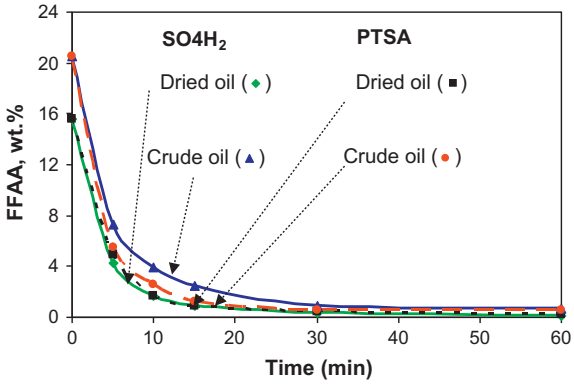

Fig. 1. Esterification of *Jatropha curcas* oil, using different catalysts and initial water content. Raw material: Crude oil with initial acidity 21% and 1570 ppm of water; dried oil with acidity 16%, and 100 ppm of water. Catalysts concentration: 0.35 Eq/Lt. Volume of methanol: 40% referred to the oil.

In order to optimize the process diminishing the consumption of methanol and catalysts, other experiments were carried out using *Jatropha curcas* oils with acidity between 9% and 12% (see Table 2). For example, the esterification was carried out with 20 vol.% of methanol (referred to the oil), and 0.087 equivalents of catalyst for 890 g of oil. This amount corresponds to 0.25 vol.% of catalyst (referred to the total reaction volume). Under these conditions, the final acidity was 1.5%, which is adequate in order to feed this stream in the neutralization step and in the transesterification reactor. It has to be emphasized that under these conditions, i.e. using lower methanol and catalyst concentrations, the reaction has a lower rate compared to the results shown in Fig. 1, reaching the final value at approximately 1 h, and that is the reason why in Table 2 the conversion reported corresponds to 1 h on oil.

3.1.3. Neutralization with glycerine

The glycerine-rich phase obtained during the transesterification reaction, contained high amount of alkaline catalyst, typically sodium methoxide or hydroxide. Therefore, this phase can be used to neutralize the free fatty acids present in the oil used as raw material. However, in those cases in which the oil acidity is in the order of 6% (or higher), additional alkali must be added to the glycerine phase, since the catalyst contained in it is not enough to neutralize all the free fatty acids. Fig. 2 shows results obtained in the neutralization of different *Jatropha curcas* oil samples using the glycerine-rich phase. The amount of sodium methoxide contained in the glycerine phase, plus the KOH added to the system, was equal to the amount of FFA contained in the oil. Results shown in Fig. 2 indicate that the pretreatment of the oil with the glycerine phase was very efficient to neutralize the free fatty acids and also to remove the water. The glycerine phase extracted the water from

Table 1
Properties of *Jatropha curcas* oil obtained by solvent extraction and by pressing.

Property	Solvent extraction	Pressing
Acidity (% FFAA)	0.6–12.2	8.7–20.5
Phosphorus (ppm)	99.7–341.0	86.4–174.5
Iodine index	89.1–110	100–102
Water (ppm)	140–500	1094–1567

Table 2
Esterification of free fatty acids, in *Jatropha curcas* oil with 8.9% acidity. Temperature 60 °C; reaction time 60 min.

Exp. no.	Methanol (v/v_{oil} %)	H_2SO_4 (v/v_{mix} %)	% FFAA final
1	30	0.25	0.4
2	20	0.25	1.5
3	20	1	0.6

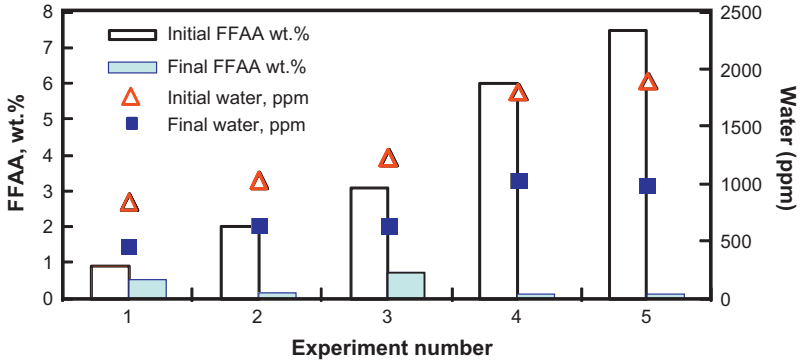

Fig. 2. Acidity and water content in the oil before and after neutralization with glycerine and KOH solution (50 wt.% in water). Experiment: 1: no KOH solution added; vol KOH solution/vol oil, Experiment 2: 0.004; 3: 0.009; 4: 0.022; 5: 0.029.

Table 3
Mass balance of oleates in the transesterification reaction.

Catalyst	Inlet	Outlet		
	Oleic acid in oil (mol)	Oleate in biodiesel (mol)	Oleate in glycerine (mol)	Oleate total amount (mol)
Sodium methoxide	0.019	0.018	0.0059	0.0144
Potassium methoxide	0.027	0.018	0.0083	0.0188

the oil, even though in several experiments KOH dissolved in water was added to this phase. It can be observed that in all cases, the FFA content decreased below 1%, and additionally, the water content was reduced approximately to half of the initial value.

Another important issue, is that the phase separation between the glycerine and the neutralized oil was fast, being possible to perform this operation without a centrifuge. Only in the case of the oil with acidity above 9%, what led to a glycerine phase with a soap concentration of 200 g/kg, there was a phase separation problem due to emulsion formation.

3.1.4. Transesterification and purification

Similar conversions were obtained both with sodium and potassium methoxide as catalysts. The total glycerine determined in the final product was 0.16% and 0.14% respectively. The sodium and potassium hydroxides had not been tested with the *Jatropha curcas* oil, since according to the literature they are less effective than the methoxides [15–17].

The effect of each catalyst in the process yield and in the soap formation was analyzed measuring the soaps concentrations in both phases after the transesterification reaction. The total amount of soaps should be at least the same (in a molar basis) than the amount of fatty acids entering the reactor with the raw material, since these acids are saponified due to the reaction with the catalyst, forming a sodium oleate molecule per each oleic acid molecule. The water that entered the reactor and the water formed by neutralization of the free fatty acids contributed to the increase in the amount of soaps formed during the transesterification. This is because the saponification reaction of esters (glycerides and methylesters) occurs in an alkaline media only in the presence of water (see Ref. [31] and references cited therein). The overall stoichiometry is that one molecule of ester (e.g. methyloleate) reacts with sodium hydroxide in presence of water, forming one molecule of soap (e.g. sodium oleate) and one of alcohol (e.g. methanol). Table 3 shows the results obtained with both catalysts, regarding the soaps formation.

Using sodium methoxide as catalyst, there is a negligible amount of soaps formed during the reaction. The amount of free fatty acids that entered the reactor was 0.018 mol, and the total amount of soaps detected in the biodiesel phase and in the glycerine phase was 0.019 mol. However, in the case of the potassium methoxide there was 50% increase in the oleate amount, compared to the initial amount of fatty acids. This is a twofold problem, on one hand this soap formation represents a yield loss, and on the other hand, it complicates the purification stage. If a biodiesel containing more than 0.25 wt.% soaps is fed to the neutralization step, the final biodiesel would have an acidity out of specification, due to the oleate hydrolysis that occurs during the washing with an acid such as hydrochloric, sulphuric and citric, according to the following reaction:

$$\text{Sodium Oleate} + \text{HCl} \rightarrow \text{Oleic acid} + \text{NaCl}$$

In this reaction one mol of oleic acid is formed per mol of soap present in the biodiesel that enters the neutralization step, being the oleic acid soluble in the biodiesel phase. Thus, if the soap content is 0.25 wt.%, the oleic acid concentration in the biodiesel would be 0.23 wt.%, and the acidity index 0.47 mg KOH/g, being the limit 0.50 mg KOH/g.

Therefore, it is necessary to use a purification procedure in which the first step extracts the soaps, without hydrolysis. If a water-based process is used, the first step cannot be a treatment with an acid solution in those cases in which the soaps concentration in the biodiesel phase is higher than the limit above mentioned.

The biodiesel purification after the transesterification was carried out using water-based extraction steps, and a final drying. The washing stage was modified, as suggested by Mendow et al. [32], including a first step using neutral water, in a proportion of less than 10 vol.% water referred to the biodiesel phase. The water phase extracts the soaps from the biodiesel phase, as shown in Table 4. In both cases, with sodium and potassium methoxides, there is a significant increase in the amount of oleates in the system. However, the purification of the biodiesel phase was adequate, indicating that this procedure is a good option to purify biodiesel after the transesterification reaction in those cases in which a high concentration of soap is present.

3.1.5. Process selection and product characterization

In all the experiments described in this section, neutralized crude oil has been used, being possible to obtain high quality biodiesel as shown below.

It was possible to obtain biodiesel with both catalysts, with little differences between them, both regarding the conversion and the purification stages. One advantage of the potassium methoxide

Table 4
Balance of oleates in the neutral washing procedure.

Catalyst	Inlet		Outlet		Final biodiesel acidity (FA%)
	Oleates in water (mol)	Oleates in biodiesel (mol)	Oleates in water (mol)	Oleates in biodiesel (mol)	
Sodium methoxide	0	0.0059	0.0087	0.0005	0.12
Potassium methoxide	0	0.0083	0.0142	0.0009	0.19

is that the salts left in the water and in the glycerine phase are adequate to be used in the agricultural step of the *Jatropha curcas* crop. On the other hand, the availability and price of the sodium methoxide makes the latter the preferred option.

Table 5 shows the yields and the final acidities obtained with various samples of *Jatropha curcas* oils, following different pretreatments (esterification or neutralization with glycerine), and after transesterification and purification steps.

The process yield was higher than 90% in all the experiments in which esterification was carried out as pretreatment. The disadvantage of this reaction is the high methanol consumption needed to convert the initial free fatty acid content that, in these experiments, was 9% approximately. Methanol recovery, although technically not very complex, requires equipment that is comparatively expensive in a low scale facility.

Processes combining esterification and transesterification using other raw materials have been previously reported [6,7,23]. In all cases the conversion was higher than 90% using methanol and sodium or potassium hydroxides.

The neutralization with glycerine removes the free fatty acids from the oil, in the form of soaps that are accumulated in the glycerine phase. The yields reported in Table 5 correspond to the neutralization and transesterification reaction, without including the free fatty acids that are recovered from the glycerine phase. As shown in Table 3, the soaps formed in the transesterification step are accumulated preferentially in the glycerine phase. If this glycerine phase is treated instead of using it for feeding the biodigestor (see below), the soaps are converted in free fatty acids during the acid treatment. Then, these FFA can be esterified obtaining biodiesel, thus increasing the yield of the process regarding the biodiesel, being possible to approach 100%.

This procedure, i.e. the use of glycerine to neutralize the acid oil, has not been previously reported, although it is known that it is used in some technologies in large-scale facilities.

Even though it is possible to carry out the process using a raw material with acidity of approximately 4%, the yield is low if no fatty acid recovery is included in the process. An acidity of 0.5 mg KOH/g in the biodiesel is a parameter difficult to meet in cases like this (using raw materials with acidity well above 1%), however the purification process used in this work makes it possible to fulfill this requisite. Table 5 shows the case of the oil with 3.6% acidity that was transesterified without pretreatment, obtaining a final acidity of 0.24%.

Chitra et al. [33] used oil with 3% acidity, and carried out a single transesterification reaction. The decantation time used to assure a good quality biodiesel was very high, and consequently, the production capacity was low. In the study of Kywe and Oo [34] oil with 22% acidity was used, obtaining a final yield of 70%.

The properties of samples of biodiesel obtained in this study are summarized in Table 6.

The phosphorus content is within the EN 14214 limits, even though the oil was not degummed. This result shows that it is possible to use the crude oil with high acidity to obtain high quality biodiesel, what is very important mainly in a small scale facility. The iodine number is lower than in the case of the soybean oil-based biodiesel [35].

The oxidation stability is lower than the minimum limit established in the standards, but it is because no antioxidant additives have been added to the product. Similar values of density, carbon residue, viscosity, and cloud point have been reported [6].

Anchen et al. [4] showed similar values of total glycerine as those shown in this work. Kywe and Oo [34] obtained a total glycerine value of 1% in the case of methyl ester production (methanol/oil ratio 6:1, 1 wt.% NaOH as catalyst, 65 °C, 1 h) and 1.1% in the case of ethyl esters (ethanol/oil ratio 8:1, 1 wt.% KOH as catalyst, 30 °C; 5 h), values that are out of specification.

3.2. By-products treatment

The main by-products obtained in the biodiesel production process from *Jatropha curcas* fruits, are the fruits and seeds husks, the meal obtained in the oil extraction step, and the glycerine.

3.3. Husks as solid fuels

The fruits and seeds husks can be used directly as a source of heat by direct burning. The higher heating value determined on these products was 4100 kcal/kg and 3420 kcal/kg for the seed and fruits husks respectively, and the ash content was 7.02 g/100 g and 15.32 g/100 g, respectively. These values were

Table 5
Results obtained following different oil pretreatments.

FFA %	Pretreatment	Reaction[a]		Final acidity and yield	
		CH_3OH (v/v %)	$NaCH_3O$ (wt.%)	FFAA %	η (%)[b]
8.90	Esterif. 30% CH_3OH + 0.25% H_2SO_4	24.50	0.73	0.13	91.8
8.90	Esterif. 30% CH_3OH + 0.46% H_2SO_4	25.00	0.8	0.21	95.0
12.35	Esterif. 40% CH_3OH + 1% H_2SO_4	24.45	1.05	0.19	90.0
9.00	Neut.: 19%p/p glyc. + 2.9% p/p KOH 50%	25.00	0.85	0.25	70.0
8.80	Neut.: 22.2% p/p glyc. + 3.15% p/p KOH 50%	24.70	0.65	0.18	73.1
5.54	Neut: 18.9% p/p glyc. + 0.5% p/p NaOH 10%	24.67	1.14	0.21	82.1
3.67	No pretreatment	24.40	1.35	0.27	85.3
3.63	No pretreatment	24.40	1.34	0.24	84.6
1.00	No pretreatment	24.60	0.85	0.10	95.5
1.00	No pretreatment	24.60	0.85	0.11	94.0

[a] Reaction time: 90 min, temperature 65 °C, decantation time 30 min. Purification: three washing steps, and drying at 90 °C with nitrogen stripping.
[b] Process yield.

Table 6
Quality parameters of the biodiesel samples obtained from *Jatropha curcas* oil.

Property	Values		Mean value	No. samples	IRAM 6515		EN 14214	
	Max	Min			Min	Max	Min	Max
Phosphorous (ppm)	3.93	1	1.98	6		10		10
Acidity (FFAA %)	0.27	0.10	0.19	6		0.25		0.25
Density 15 °C (g/cm^3)	0.887	0.878	0.88	5	0.875	0.9	0.86	0.9
Viscosity 40 °C (cp)	4.69	4.15	4.46	5	3.5	5	3.5	5
Oxidation stability (hs)	6	1.75	3.64	6	6		8	
Cloud point (°C)	5	2	3.38	4	5–0	5–0		
Pour point (°C)	3	0	1.38	4				
Iodine number	108.6	97.3	101.4	6		150		120
Ashes (%)	0.010	0.005	0.0075	3				
Carbon residue (%)	0.028	0.001	0.015	2		0.05		
Total ester content (%)	99.60	99.30	99.45	2	96.5		96.5	
Total glycerine (%)	0.13	0.07	0.11	3		0.25		0.25

determined without drying the solids. The humidity content was 9.6% and 10.9% for the fruits and seeds husks, respectively. Therefore, drying these solids would increase the heating power in 10% approximately.

3.4. Biogas production: utilization of meals and glycerine

A biodigestor was fed with the meal generated in the oil extraction step, and with the glycerine phase, after neutralization and separation of the free fatty acids. Table 7 shows the main physical properties of these products. The nitrogen and the phosphorus content in the meal were higher in the case of the peeled off seeds.

The (C/N) ratio that results from the combination of both products was in the range 20–30. This is adequate in order to have a good biogas production. Table 8 shows the composition of each stream fed to the bioreactor. The (meal/glycerine) weight ratio generated in the production process was approximately 2.9:1 in the case of using peeled off seeds (PSM) during the oil extraction, and 6.7:1 in the case of using the whole seeds (WSM). These are average values due to the variability in composition of the different products obtained in the process. In order to adjust the total solid concentration in the bioreactor, it was necessary to dilute both streams with water in a total weight ratio of 5.2:1 (water referred to meal plus glycerine). Table 8 shows that the volume of biogas obtained was 487 ml/g VS in the case of using peeled of seeds meal (PSM), and 239 ml/g VS in the case of the whole seeds meal (WSM). Therefore, it is convenient to peel off the seeds before the oil extraction in order to increase the biogas production. This is due to the higher phosphorus and nitrogen content in the case of the meal obtained from the peeled off seeds, favouring the anaerobic digestion. It is very important to highlight that the biogas production per unit mass of volatile solids is higher than in the cases of using bovine manure or urban solid wastes [36].

In preliminary results obtained in this study, it was found that the anaerobic digestion shows higher sensitivity to the glycerine than to the meals, with a higher biogas production as a function of the amount of glycerine in the feed stream. However, if this proportion was too high, the process stability was affected, and in some cases it was stopped.

In order to analyze this effect, experiments with different meal/glycerine ratio in the feed were carried out. The parameters that indicate how the bioreactor is working are the acidity and the

Table 7
Properties of the by-products fed to the bioreactor.

Property	Jatropha meal		Glycerine
	Whole seed (WSM)	Peeled off (PSM)	
Total solids, 100 °C (g/100 g)[a]	9.0–12.7	7.55–9.13	94.11–94.96
Volatile solids 550 °C (g/100 g)[b]	91.0–92.5	88.0–89.0	9.66–11.7
Carbon content (g/100 g)	45–46	44–44.5	14–15.6
Nitrogen (g/100 g)[b]	4.14–4.42	8.0–9.0	<0.1
Phosphorus (mg/100 g)[b]	725–1140	2128–2330	5.51–5.71
Potassium (mg/100 g)[b]	1030–1760	1650–1893	<1
Glycerine (g/100 g)	–	–	27.7–30.81
pH	–	–	6.8–7.4
Methanol (g/100 g)	N/D	N/D	8.4–9.6
Water (g/100 g)	9.0–12.7	7.55–9.13	45.8–48.4

WSM: meal obtained using the whole seed for oil extraction: PSM: meal obtained from peeled off seeds.
[a] Wet base.
[b] Dried base.

Table 8
Production of biogas for different meal loadings.

Exp.	Feed		Biogas production (ml)[a]				
	Meal (g)	Glycerine (g)	Daily	% CO_2	Per g of feed[b]	Per g VS	*n*
WSM	5.69	1.12	1106	16.3	164	239	6
PSM	3.47	1.11	1305	19.0	285	487	6

n: number of samples; VS: volatile solids.
[a] Vol. of biogas (ml), 293 K; 1 atm.
[b] ml of biogas/(g meal + g glycerine).

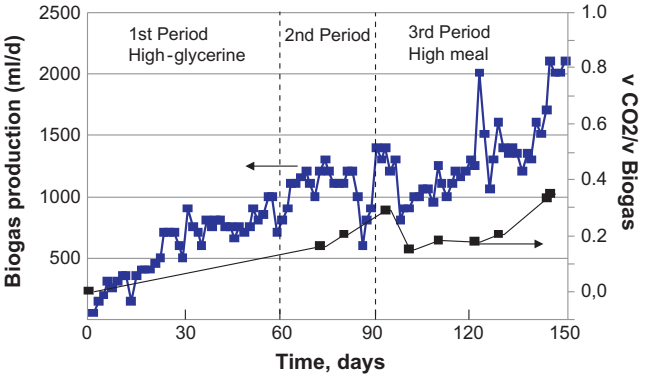

Fig. 3. Biogas production and CO_2 content in the biogas.

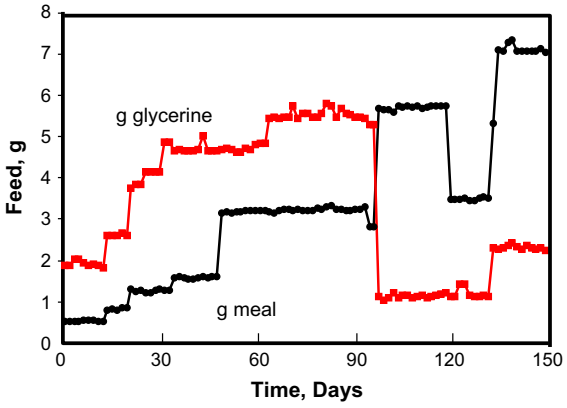

Fig. 4. Amount of meal and glycerine fed to the bioreactor.

alkalinity of the liquid contained in the reactor, as discussed by Jenkins et al. [25]. Results are shown in Figs. 3–5. During the first period (initial sixty days of biodigestor operation), a higher proportion of glycerine compared to meal was fed (Fig. 4). Fig. 5 shows that under this condition the acidity increased, and the ALK1/ALK2 ratio decreases This is due to the formation of a higher amount of fatty acids, that cannot be transformed into products (methane and CO_2), thus introducing instability in the reactor. During the stationary period (second period, days 60–90), the acidity was high and the ALK1/ALK2 was low, maintaining a constant value. This is an unwanted situation, since a minor modification in any process variable (e.g. the temperature) could lead to problems,

Table 9
Composition of the effluent of the bioreactor.

Parameter	Effluent	
	1	2
Wet base		
Volatiles and humidity 105 °C (g/100 g)	4.67	4.59
Volatiles 550 °C (g/100 g)[a]	53.29	55.78
Nitrogen (g/l)	7.5	7.5
Phosphorus (g/l)	0.81	0.86
Potassium (g/l)	0.83	0.67
Dried base		
Nitrogen (g/kg)	162.95	162.87
Phosphorus (g/kg)	17.42	18.64
Potassium (g/kg)	17.73	14.64
N:P:K	9.4:1:1	8.7:1.3:1

[a] Dried base.

such as inhibition of the biogas production and bacteria growth. The biogas production was maintained within the 600–1500 ml/day range, and the CO_2 concentration between 15 and 25 v/v %. As the acidity increased, higher values of CO_2 in the biogas were found, as can be inferred from Fig. 3 (CO_2 increases) and 5 (acidity increases).

In the third period (days 90–150) the biodigestor was fed with a proportion of meal and glycerine equivalent to the one obtained in the process. A decrease in the acidity and an increase in the ALK1/ALK2 ratio were observed. This means that the reactor was more stable, as discussed by Jenkins et al. [25]. This was due to the fact that the meals provided a higher amount of nitrogen that favoured the balance of the acidogenic and methanogenic bacteria and the C/N ratio in the reactor. The biogas production during this period was higher than in the other two periods. It was between 800 and 2000 ml/d. However, further increases in the reactor loading might lead to a higher CO_2 production, and the reactor may become unstable, as shown in Fig. 5, during the final days of the experiment. Consequently, the feed to be used in the anaerobic reactor should contain meal obtained from peeled off seeds and glycerine, using a mass ratio of 3–3.5/1. Under this condition, the biogas produced was 1–1.3 ml/ml of bioreactor, containing 19% CO_2.

The effluent from the bioreactor was analyzed, taken samples during a week, after 90 days of operation. The results are shown in Table 9. This effluent can be used as fertilized, providing nutrient to the soil. This effluent should be used together with a supplement of phosphorus and potassium, in order to meet the requirements of this crop. According to Achten et al. [4], in each crop the nutrients used from the soil are 14.3 to 34.3 kg of nitrogen, 0.7 to 7 kg of phosphorus, and 14.3 to 31.6 kg of potassium, per hectare. In this

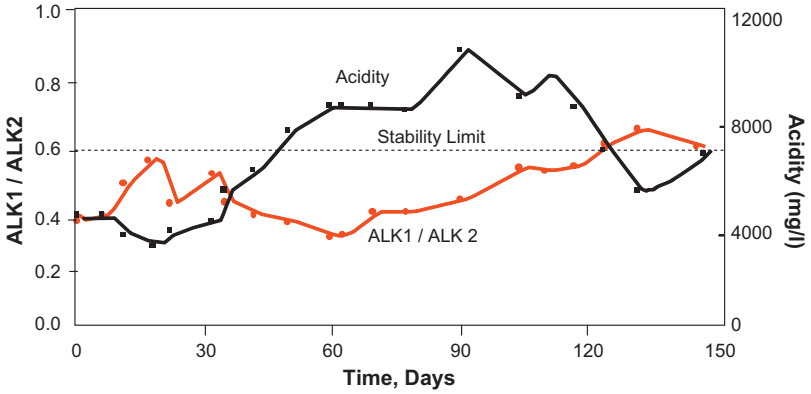

Fig. 5. Control parameters in the bioreactor.

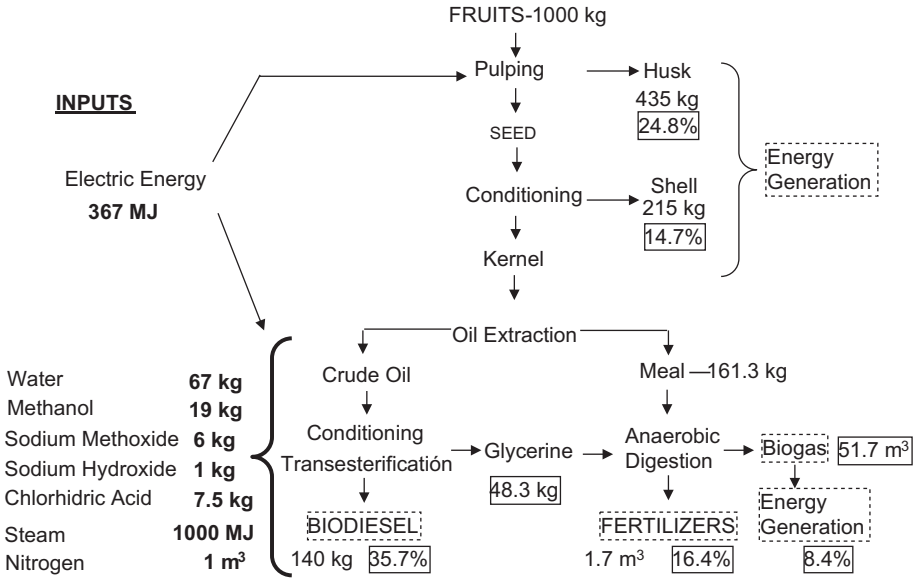

Fig. 6. Mass balance and energy streams in *Jatropha curcas* system.

case, applying 4–5 m^3 of effluent per hectare, would supply the nitrogen that was removed by the crop, being necessary to add potassium and phosphorus. Reinhardt et al. [37] estimated that *Jatropha curcas* require 81, 13.5, and 73.8 kg of nitrogen, phosphorus, and potassium respectively, per hectare per year. According to this estimation, it would be necessary to add 11 m^3 of effluent to recover the soil nitrogen content.

3.5. Mass balance

Fig. 6 shows the mass balance for the whole process, taking 1 ton of Jatropha fruits as reference. It can be observed that the fruits and seed husks represent the main energetic vectors in this process (24.8% and 14.7% respectively) and, therefore, its utilization has an important positive effect in the energy balance. The use of the fertilizer obtained from the anaerobic digestion is also very important, in order to partially substitute the use of inorganic fertilizers. The biodiesel represents 35.7% of the total energy output of the process.

4. Conclusions

In this work, an integrated process to obtain biofuels from *Jatropha curcas* crop is presented. Taking into account that the oil acidity is variable along the year and the plantation age, it is necessary to design the production process including an efficient neutralization stage using the glycerine obtained from the transesterification reaction. On the other hand, the purification must be carried out with a modified process, using as a first washing step, neutral water. In this way, the acidification of the biodiesel is avoided.

The biogas production using the meals and the glycerine is important, both to generate additional energy and an effluent that can be used as fertilizer, in order to reincorporate nitrogen, potassium, and phosphorus in the soil.

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