“Improving the sustainability of the Jatropha-biodiesel chain in the Yucatán Peninsula”

Project DBM02050

“Public Final Report”

Context and reasons to start the project.

Mexico has shown a recent interest in bioenergy and sustainability, but unfortunately lacks experience and local information in this field. Like other countries, Mexico is trying to reduce its oil dependence to produce energy and its encouraging the development of new renewable energies. Biofuels are one important target and the development of viable sustainable processes is needed.

For biodiesel production, several plantations of *Jatropha curcas* L have been established in the country, based on reported literature data from plantations all over the world. Although the plant is known to originate from this part of the world, specific location related data on extended plantation areas such as plagues, irrigation and fertilization requirements, yields, is not known. These data have to be generated in order to implement a sustainable exploitation of this plant.

In México, *Jatropha curcas* L. is known as "piñón". The centre of origin of this plant is Central América and México but now it has spread out to several tropical countries, mainly India and Philippines. The genus *Jatropha* belongs to the Euphorbiaceae family and comprises approximately 175 known species. The *Jatropha curcas* plant is considered a small perennial tree or large shrub which can attain 8-10 m under favorable conditions. The plant shows a straight trunk and thick branches of soft wood (Divakara et al., 2010). Its fruits are elliptic capsules containing 2-3 seeds from which the oil is extracted. The *Jatropha* plant grows well in poor soils with low fertility and can be used to restore them due to the organic matter produced during its life. Irrespective of the species, extracts from different parts of the plant (stem, roots, leaves, bark) have been used in traditional ethno-medicine for a long time (Duke, 1985) as Jatropha is a rich source of phytochemicals.

However, for commercial exploitation, *Jatropha* is considered a wild type plant. Some culture problems have been addressed when extensive areas are cultivated (mainly pests and diseases). In México, the INIFAP (Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias) has developed a research program to generate information and cultivation technology of *Jatropha* for oil production (Zamarripa et al., 2008). The estimate land surface with potential for *Jatropha* cultivation in México is 6 million hectares from which 2.6 million have a high potential due to climate and geographic conditions.

The Yucatan peninsula is known for its favourable plant growth conditions, however, the northern part of this land present a thin soil layer, nutrient poor, and rocky which complicates mechanization of cultures. Since *Jatropha* can grow on poor soils where food crops are difficult to, a good opportunity to establish *Jatropha* plantations for biodiesel production in this lands exist, but agronomical and economic studies are needed.

KUO (later KUOSOL) was an enterprise dedicated to the development of sustainable *Jatropha* plantations in Yucatan. In 2008, it has started with 300ha and three varieties of *Jatropha*. In 2012, the plantations have reached 850ha. Part of its interest was to improve oil yields applying sustainable technologies but no data was available on the jatropha-biodiesel chain for this part of the country, giving the opportunity to begin this project.

The CICY is a public research centre and has a Renewable Energy Unit (department) where studies on biomass for bioenergy are carried out so collaboration with KUOSOL was easy and naturally started.

Aim and objectives of the project.

Aim.

The aim of this project is to generate new knowledge based on local conditions to improve the sustainability of the jatropha-biodiesel chain giving emphasis to the utilization of waste and sub-products generated along the chain.

Objectives.

1. Contribute to federal policies for the development of environmental protection programmes and implementation of new sources of energy.
2. Determine the type and amount of waste and sub-products generated by biodiesel production form *Jatropha* oil.
3. Implement selected technologies at laboratory level that could be used to reduce the environmental impact of waste and sub-products generation.
4. Transfer of knowledge and technology generated by this project to KUOSOL in order to increase the economic viability of biodiesel production from *Jatropha* oil in Yucatan, Mexico.
5. Contribute to the knowledge of Jatropha as an energy crop and the establishment of sustainable processes.

Activities undertaken in the project.

The activities that were carried out in this project are described below:

Literature study. A deep research on technologies available for the use of waste and sub-products was carried out in different scientific and technological databases. The search was also conducted towards the biological, agricultural and chemical newest data specific to Jatropha that could complement what we already had. After the literature study, a selection of the most promising technologies available for use of waste and sub-products from the jatropha-biodiesel chain was done, taking into account the general (climate, type of soil, economy) conditions on the Yucatan peninsula.

Field work. Field measurements were undertaken at KUOSOL plantations in order to have real data of biomass production under local conditions. This will allow us to simulate more accurate future scenarios.

Laboratory experiments. After selecting the applicable technologies, experiments were carried out in our laboratories to obtain data based on local materials and compare them to other works in other countries. Technologies considered in this project that were tested in our laboratories are: production of bio-ethanol from jatropha branches, production and characterization of bio-oil from jatropha branches, production of bio-ethanol from fruit kernel, identification of secondary metabolites from fruit kernel, and use of waste water from biodiesel washing. These results allowed giving recommendations on what technologies were more suitable to use.

Simulations. With local field data of biomass production, it was possible to carry out an analysis of the emissions generated during the cultivation of *Jatropha curcas* taking into account a sustainability scheme, the transport of the seeds to an extraction plant and the oil extraction process. Emissions were determined using the Roundtable on Sustainable Biofuels (RSB) greenhouse gas (GHG) calculation tool for biofuel production processes. A review of the options for exploiting the different waste products, as well as their impact on emissions was presented.

Capacity building. Courses were given on the different aspects of biodiesel production and waste and sub-products use to employees of LODEMO (an enterprise dedicated to produce biodiesel). Students involved in this project attended conferences to show their work.

Project boundaries. This project was intended to help improve the sustainability of the biodiesel-jatropha chain. Although field data was collected at KUOSOL plantations, the technologies for waste and sub-products treatments were done at laboratory levels. Technologies with potential to be used have to be scaled-up before commercial implementation. Also, this project was intended to study the technological aspects of improving sustainability. Our group do not specialize in social issues. This has to be done by other people. However, the data generated is very useful for further project implementations.

Project partners. KUOSOL was the main and most important partner from the beginning of this project. Collaboration was always pleasant and we had access to all information necessary to go on with the project.

Results of the project

In this section we provide a summary of the results obtained on the different activities. *In extenso* reports (NL-CICY Reports for Activities 1 to 6) containing the methodology employed were provided to NL Agency.

Literature study. As a result of literature search, four sub-products and two waste products from the jatropha-biodiesel chain process were identified, as shown in Figure 1.

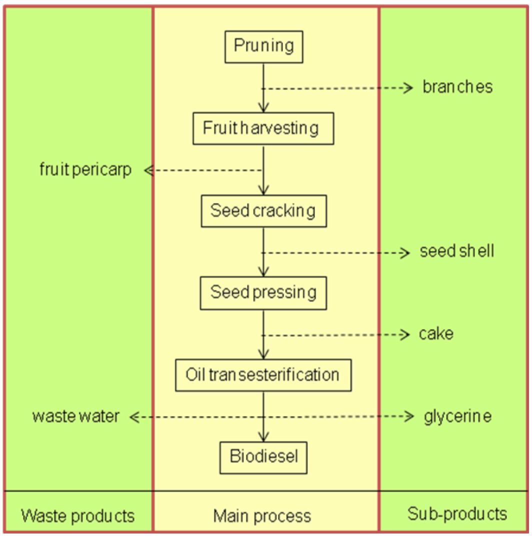


Figure 1. Sub- and waste products originated from the jatropha-biodiesel chain.

From Figure 1, it can be noticed that the branches, fruit kernel, hard shell and press cake are lignocellulosic biomass while the glycerin is an organic compound and the waste water is an inorganic one. After selection of available technologies, we decided the following: the branches were processed to obtain lignocellulosic ethanol and bio-oil. The fruit pericarp was employed to produce ethanol and secondary metabolites were identified from its extracts. The seed cake and the shell were not studied because there is a great quantity of work done with these residues. The waste water from biodiesel rising was tested for toxicity by germination of plant seeds.

Field work. The first activity was to measure biomass production. Branches from pruning yield approximately 1-2 kg/year·plant of dry biomass depending on the age of the plant. If two pruning are made, then 1.5 to 3 tons of branches can be obtained each year with the actual area of cultivation (850ha). For 2013, it is expected to obtain 17.5 to 35.1 tons/year (10,000ha). From the chemical point of view, the amount of biomass can be calculated to be:

Biomass Yield for two scenarios (t/year)

	Actual	Future[1]
Total extractives	0.49-99	5.75-11.54
Lignin	0.36-0.71	4.15-8.32
Holocellulose	0.65-1.3	7.6-15.24

[1] Estimated for 2013

Fruit pericarp must be separated from the seeds before oil extraction. According to KUOSOL information, this fruit component accounts for 29.7 ± 2.4% (w/w) of the total fruit fresh weight. For estimation purposes, an annual production of 97 ton/d of oil was adopted.

To produce 97 ton/d of jatropha oil
451.26 ton/d of fruits must be harvested
134 ton/d of pericarp will be produced

In the case of seeds, the following balance was calculated from field data:

To produce 97 ton/d of jatropha oil
451.26 ton/d of fruits must be harvested
317 ton/d of seeds will be obtained
123 ton/d of seed shell will be produced

Laboratory studies. The first technology applied to pruning residues (branches) was the pretreatment and saccharification of this material to produce lignocellulosic ethanol. After pretreatment and saccharification, 1.36 g of fermentable sugars were obtained from 20 g of dry, milled *Jatropha curcas* branches. 1.08 g of these sugars were consumed by the yeast through fermentation and after distillation, 0.34 mL of ethanol were obtained. $Y_{P/S}$ was 0.248 g ethanol/g sugar giving 48.6% of theoretical yield. With these results, an ethanol production of 17 L from 1 ton of dry biomass was calculated. From Report 1, 1.5 to 3 tons of dry biomass can be obtained as pruning residue per year. With the actual cellulosic ethanol yields obtained in our laboratory, a production of only 25.5 – 51 L of ethanol per year will be achieved.

This production level is very low. On one side, the pretreatment-saccharification methodology used in this work needs further optimization. If 43 % of the dry biomass is holocellulose and considering that in the case of soft wood stems one third corresponds to cellulose, 2.8 g of fermentable sugars should be obtained. It is also necessary to at least duplicate ethanol production yield to reach 80-85% of theoretical yield. But even with these achievements, cellulosic ethanol production from *Jatropha curcas* stems will still be debatable because of the low production levels of this source of biomass with the expected cultivation area.

Bio-oil from *Jatropha curcas* branches was obtained and characterized to determine if this process can be considered as a part of the jatropha-biodiesel chain production. The pyrolysis products obtained at the end of the experiments were a bio-oil (liquid phase), char (solid phase) and gas. The yields for each pyrolysis product were 45.62±0.69, 33.08±0.95 and 21.28±0.25 % w/w, respectively.

In the literature, most of pyrolysis studies with jatropha were made using seed shells as raw material. We did not find reports on pyrolysis of jatropha branches. Nevertheless, the bio-oil yield obtained in this study is similar to that obtained for corncob (41±0.9 %). Bio-oil yields are strongly affected by biomass composition and pyrolysis conditions. Chemically, bio-oil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. The composition will also vary according to biomass nature. Bio-oil was extracted with hexane, dichloromethane and ethyl acetate. The compounds identified in each partition are presented in Tables 1, 2 and 3 (respectively).

Table 1. Compound profile of the Jatropha branches bio-oil hexane partition.

Compound	Retention time (min)	Peak area (%)
2-methyl-2-cyclopenten-1-one	4.362	0.396
2-methoxyphenol	7.88	15.514
3-ethyl-2-hydroxy-2-cyclopenten-1-one	8.34	2.428
2-methoxy-5-methylphenol	9.596	2.742
2-hydroxy-3-propil-2-ciclopenten-1-one	9.78	1.129
4-ethyl-2-methoxyfenol	10.879	2.108
2-methoxy-4-vinilphenol	11.326	1.008
Dodecanoic acid methyl ester	14.225	2.116
Tetradecanoic acid methyl ester	16.520	1.368
1,2-benzendicarboxilic acid (2-ethylhexyl) isohexyl ester	23.765	17.607

Table 2. Compound profile of the Jatropha branches bio-oil CH_2Cl_2 partition.

Compound	Retention time (min)	Peak area (%)
1-hydroxy-2 propanone	3.473	4.137
1-hydroxy-2 butanone	5.28	4.286
Butyrolactone	9.19	3.064
2-(5H) furanone	9.336	2.062
2-Hydroxy-3-methyl-cyclopent-2-en-1-one	10.174	5.505
Phenol	10.618	1.338
2-methoxy phenol	10.861	1.235
3-ethyl-2-hydroxy-2-cyclopentan-1-one	11.492	1.524
Maltol	11.555	1.687
1,4:3,6-dianhydro-α-D-glucopyranose	13.979	0.94
1,2-benzendiol	14.888	6.8
Dodecanoic acid, methyl ester	15.636	2.862
Vanillin	16.211	3.118
1-(4-hydroxy-3-methoxyphenyl) etanone	17.185	1.515
Tetradecanoic acid, methyl ester	17.871	2.663
4-hydroxy-3,5-dimethoxybenzaldehyde	19.4	1.229
Hexadecanoic acid, methyl ester	19.893	1.83
1-(4-hydroxy-3,5-dimethoxyphenyl) etanone	20.115	0.716
9-octadecanoic acid, methyl ester	21.609	1.627
9,12-octadecadienoic acid, methyl ester	21.653	0.651
Octadecanoic acid, methyl ester	21.736	0.565
1,2-benzendicarboxilic acid (2-ethylhexyl) mono ester	25.951	26.652

Table 3. Compound profile of the Jatropha branches bio-oil EtOAc partition.

Compound	Retention time (min)	Peak area (%)
1,4:3,6-dianhydro-α-D-glucopyranose	13.963	4.523
1,2-benzendiol	14.872	14.288
Dodecanoic acid, methyl ester	15.636	2.964
Hydroquinone	16.233	7.236
1,4-benzendiol	16.724	1.186
Tetradecanoic acid, methyl ester	17.801	16.83
Hexadecanoic acid, methyl ester	19.885	2.547
9-octadecanoic acid, methyl ester	21.604	2.845
9,12-octadecadienoic acid, methyl ester	21.650	1.356
Octadecanoic acid, methyl ester	21.732	0.849
1,2-benzendicarboxilic acid (2-ethylhexyl) mono ester	25.916	18.747

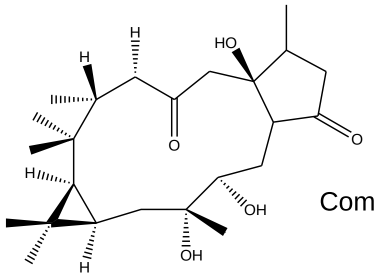
Char was obtained as the main component from pyrolysis of *Jatropha curcas* seed shells. This process was carried out following the same procedure for pruning residues pyrolysis. The yields for bio-oil (liquid phase), char (solid phase) and gas were 34.288±2.06, 43.25±3.99 and 22.46±1.93 % w/w, respectively. A thermogravimetric analysis indicated that the activated carbon and pellets from seed shells from KUOSOL plantations have similar properties to those reported in the literature.

As part of this project, studies on ethanol production from the pericarp of jatropha fruit have been conducted. Water content of this residue was 55 %. From 20g pericarp samples of *Jatropha curcas* L var. Veracruz fruits, 2.32 g of fermentable sugars were obtained after pretreatment and saccharification. During the fermentation process, 1.68 g of sugars were consumed and after distillation, ethanol production was 2.14 mL. $Y_{P/S}$ was 0.5 g ethanol/g sugar, giving 98.8% of theoretical yield. With these results, an ethanol production of 107 L from 1 ton of dry biomass was calculated. From biomass data, 134 ton/d of fresh pericarp can be obtained as residue. Dry pericarp production will be 60.3 ton/d; consequently cellulosic ethanol production from this residue will be 6452 L/d.

The difference on ethanol production between pruning residues and fruit pericarp is due mainly to the amount of the latter and because fermentation yields were better. It is better to produce ethanol from pericarp fruit than pruning residues (in the case of Jatropha).

An analysis of the main metabolites present in the pericarp fruit was carried out. The presence of secondary metabolites other than phorbol esters (widely reported in Jatropha) can be of interest in the search of new applications of the Jatropha residues. Eight compounds were identified:

1. β-amirine
2. α-amirine
3. Phytane
4. Compound A (isomer 1)
5. Compound A (isomer 2)
6. Compound A (isomer 3)
7. 2,4,6,9-tetraen-5,8,12-trimethyl tetradecanyl-1,2,5,8a-trimethyl-3,4,7,8-tetrahydronaphtalene
8. Jaherin
9. 8-methyl-7-hydroxy-nonan-4-one
10. 4-methyl-3-pentenyl butanoate
11. octadecanoic acid



Compound A

A study on the quality of biodiesel washing waste water and the possibility of a subsequent use, germination of sweet sorghum seeds, was carried out. KOH and NaOH were used as catalyzers. The final pH of the biodiesel washing water was 7.5 which indicate a slight basicity. The wash water was not transparent, it was cloudy. This indicates an incipient formation of an emulsion (soap) due to the presence of free fatty acids in the sample. Filtration, centrifugation, salt addition or detergent addition failed to clarify the wash water. We decided to carry out the germination experiments with this water. Water analysis showed that wash water with NaOH had a Na^+ concentration of 3.5 $mg \cdot L^{-1}$. Wash water with KOH had a K^+ concentration of 16.75 $mg \cdot L^{-1}$. After 7 days of incubation, contrary to expected, the higher germination yield (100%) was obtained with biodiesel wash water obtained from transesterification of jatropha oil using NaOH while 90% germination was obtained when KOH was used in biodiesel reaction. These results show that both NaOH and KOH concentrations did not inhibit seeds germination. Root and plant elongation did not show statistical difference between treatments indicating that the presence of NaOH or KOH in the irrigation water had no effect on these variables. However, it is necessary to carry out additional studies to use this residue. For example, it is necessary to determine if these salts are absorbed by the plants or they will accumulate in the soils and become toxic. Also, it is necessary to determine if the main purpose of the crop is unaffected by the irrigation with this residue.

Lessons learned

At the end of the project, experience on the different topics and lessons learned can help state the following recommendations about the use of all sub- and waste products from the jatropha-biodiesel chain.

1. The best way to use the branches from jatropha pruning is direct combustion for energy production. They can also be used for bio-oil production via pyrolysis, but more research in this area should be done taking into account the main product to obtain. Although they have a good cellulose content, production of bioethanol is not suitable for two reasons: pretreatments make this process more complex and expensive than the production of bioethanol from sugar or starch. At this moment, lignocellulosic bioethanol is still at pilot plant scale essays. The second reason is that the amount of biomass produced at the jatropha plantations is too small to produce significant volumes of bioethanol. This will not pay the investment required for a lignocellulosic bioethanol plant.

2. The fruit pericarp gave good lignocellulosic bioethanol yields but the amount of this type of biomass is still small to make this process economically viable. Other options are the direct use of this material to produce bio-oil via pyrolysis (together with branches) or to continue the search for secondary metabolites with any biological activity.

3. The jatropha seed shell can be used for pelletization and combustion. This is the more studied process found in the literature and that is the reason because it was not implemented in this project. Pelletization was an activity originally proposed in this project but due to the amount of work already done in the subject, it was decided to focus on other activities less investigated.

4. The cake is another by-product that has been extensively studied, that is why it was not considered in this project. The cake can be used as animal feed, fertilizer or in a combustion process. But particular studies have to be undertaken in order to maximize yield processes.
5. Actual biodiesel plants do not purify the biodiesel by rising with water, because of the great quantities of waste water produced. Instead, they now use ion exchange resins. The waste water is not a problem anymore.

6. The glycerin can be used in different applications. It is considered the main sub-product from the oil-biodiesel reaction. It is advisable to purify it according to the market needs. It can also be sold as crude glycerine.

7. From an economic point of view, regardless of the waste or sub-product produced, if a side process has to be implemented, it will add costs to the total chain. The key is to find how to save production costs, either by producing energy and recycling it to the process or by selling the sub-products at good prices.

8. Another advantage on the use of waste and sub-products is that they can generate energy back for the biodiesel production process resulting in important reductions of greenhouse gas emissions.

9. Another project of economical viability of biodiesel production in the Yucatán peninsula was carried out and the results showed that the higher costs within the whole chain are situated in the plantation site (similar results can be found in the literature). And they are due mainly to men labor (64% of the price of 1 L biodiesel). Fruit ripening on the jatropha plant is not homogeneous and this prevents the use of machinery for harvesting.

10. Agronomic enhancement (through genetic improvement) is necessary to attain a viable economic process. It was calculated that in this region, the jatropha plantations must have a productivity of 3700 kg seeds per hectare per year to achieve economic viability.

At the time when this project ended, KUOSOL, LODEMO and Global Clean Energy Holdings have abandoned their commercial jatropha plantations. Only LODEMO is keeping 200 hectares for research purposes.

The main problem encountered was the plantations management. The three companies based their plantations on cultivars acquired all over the world and hence grown at different conditions so they were not adapted to the peninsula soils and weather. No flowering, pests attack, and low yields were the main reasons jatropha cultivation proved not economical.

For Jatropha, it is necessary to develop a cultivation method particular to the conditions encountered in the Yucatan peninsula, before the establishment of large commercial plantations. Once the optimal production level for economic viability with healthy, free of pathogen plants is attained, the establishment of commercial plantations can be started, not the contrary.

In the Yucatan peninsula, the production of jatropha biodiesel will succeed when plantations be healthy, the varieties produce good yields and all sub- and waste products be well utilized.

For implementers of similar projects, it is important to take into account literature data, but there will always be the need to adapt this data to local conditions and sometimes differences will be significant.

Biofuels technology is rapidly changing, it is necessary to know the state of the art for each of the technologies that can help improve the sustainability of a given process. Also, in order to assure economic viability, the concept of biorefinery is becoming a new exploitation strategy.

Follow up of the project

Our main follow up activities are to remain in contact with other research groups and enterprises dedicated to biodiesel production from Jatropha and other sources of oil.

We keep on working on the study of potential local sources of oil, like *Thevetia peruviana*, a small tree that grows very well in this region, and its fruits are similar to those of Jatropha.

We will keep improving our knowledge on sustainability, and apply it to other processes of biofuels production (like bioethanol, biogas).

The project results can serve us as a guide for future biorefinery process implementations. We know how to determine the waste and subproducts in a process, the technologies that can be applied, and how to find out the main issues that have to be addressed to improve the viability of a project.

This project is important because the activities carried out and lessons learned, could be of great help to other organizations dealing with sustainability of biodiesel production processes.

Colophon

	May 23rd 2013
Date	
Status	Final report
Project number	DBM02050
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This study was carried out in the framework of the Global Sustainable Biomass Fund, with financial support from the Ministry of Foreign Affairs.

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