Article

J. Mex. Chem. Soc. **2010**, *54(2),* 88-91

ISSN 1870-249X

Extraction and Characterization of Oils from Three Mexican *Jatropha* Species

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Received January 12, 2010; accepted April 12, 2010

Abstract. The composition of seed oil of three endemic Mexican species of *Jatropha* is described. Oils were analyzed through the formation of their corresponding methyl esters and their yield and composition were found to be close to that of the oil of *Jatropha curcas* L. The results show that the three species studied are potential sources of biofuels and therefore are promising alternative crops for biodiesel production in the arid regions of Mexico.
Keywords: Fatty Acids, Plant oils, seeds, *Jatropha* species.

Resumen. Se describe la composición de los aceites de semillas de tres especies de *Jatropha* endémicas de México. Los aceites fueron analizados a través de la formación de los ésteres metílicos y se encontró que sus rendimientos y composición guardan similitud al aceite de *Jatropha curcas* L. Los resultados muestran que las tres especies analizadas son fuentes potenciales para la producción de biocombustibles y por lo tanto son cultivos alternativos promisorios para la producción de biodiesel en las regiones áridas de México.
Palabras clave: Ácidos grasos, aceites vegetales, semillas, especies de *Jatropha*.

Introduction

The production and consumption of petroleum oil increases constantly; nowadays consumption is about 75 million barrels of crude oil daily and in the coming years it will increase by 7% annually [1]. About 36% of world energy comes from petroleum oil and 22% from gas. This dependence on fossil fuels has many disadvantages, for example increasing pollution and increasing costs [2].

To reduce the use of petroleum oil as fuel, alternative energies need to be developed; biofuels, biogas and bioethanol are now the most promising alternatives in energy generation. Biodiesel is produced in some countries and used efficiently either alone or in blends with mineral diesel in cars and transport vehicles [3]. Considering that most plant oils have densities much higher than mineral diesel, their use is limited for indirect-injection engines. One more difficulty in the use of natural glycerides is that they possess low cloud points (around 20°C) so they are not useful as fuels in cold seasons [4]. However, the transesterification of the triglycerides present in plant oils to the methyl or ethyl esters, generates a mixture that has similarities to mineral diesel, mainly in the cetane number, density, viscosity and calorific value. The cetane number for the mixture of methyl esters from *Jatropha curcas* L. is higher (50) than that for the currently used mineral diesel (47), while for the mixture of glycerides or their free carboxylic acids it is about 45. Biodiesel has some advantages: it is non-flammable and, in contrast to petrodiesel, is non-explosive; it has a flash point of 150 °C while that of mineral diesel is lower (64 °C); it is biodegradable, and it has significantly lower toxicity and other emissions when burned.

The main species analyzed for production of biodiesel have been castor oil, palm, cabbage palm, cotton, copra, sunflower, *Jatropha curcas* and sugar cane and relatively fast growing forestry species for bioethanol [5,6]. Because of the strong political and social pressures to avoid the use of edible oils as a biodiesel source, *J. curcas* has been regarded as a valuable multipurpose crop. *J. curcas* is native to Mesoamerica but has been distributed worldwide since the XVI century by Spaniards and Portuguese to their tropical and subtropical colonies in Africa and Asia. In India and other countries of the Far East, villagers used *J. curcas* as a hedge crop, and the extracted seed oil to make soap or fuel for lamps. *J. curcas* is easily propagated, hardy, drought/disease resistant, and produces seeds with up to 50% or more oil [7,8]. In Europe, biodiesel production is based on the methyl ester of rapeseed oil, while in the United States, the methyl esters of soybean and rapeseed oils are more used. In tropical countries, *J. curcas* seed oil is being promoted for biodiesel production, and the technology has been optimized. Although it has been identified as a suitable plant species for the production of biodiesel in countries of the developing world, it has not been the subject of formal genetic improvement programs [9].

A biofuel plant was recently built in the state of Chiapas, Mexico; the plant uses technology developed by the Colombian Agricultural Research Institute to produce 20,000 liters of oil annually from *J. curcas.* The yield from this species is a function of the environment and genetics as has been mentioned by several authors [9,10]. In the state of Puebla, *J. curcas* grows successfully in areas with relatively high rainfall [11]. Several species of *Jatropha* grow naturally in arid conditions but the feasibility of producing acceptable quantities of oil has received little attention. The genus *Jatropha* consists of 175 species, of which 45 can be found in Mexico, with 77% of them endemic [11,12]. In Argentina *J. hyeronymi* and *J. macrocarpa* were investigated because they produced good oil yields [13]. Considering the above, we investigated the oil production of three species of *Jatropha* native of Puebla, not studied before

to the best our knowledge. The goals of this research are: 1) to determine the oil yield in each species; 2) to determine the components of the oil of each species; and 3) to contribute to the knowledge of biofuel potential of *Jatropha* species.

Results and Discussion

Oils are currently obtained mechanically, when samples are big enough (several kg), but in most cases their extraction efficiency is low (about 80%). Chemical extraction with n-hexane has been reported with an extraction efficiency of 95-99% when working with a Soxhlet apparatus during 24 h [10]. The extraction by hexanes, isopropyl alcohol, and trichloroethylene gave 36, 37 and 39% respectively, by means of a Soxhlet extractor and 10 g kernel samples. Extractions with trichloroethylene afforded optimum yield in 6 h, with an extraction efficiency of 97% (a second and a third extraction gave only minute oil quantities; so, an exhaustive oil extraction was considered to be obtained since no more oil was obtained in the fourth). In Table 1, oil yields from the three *Jatropha* species are presented and compared to the well studied *J. curcas*. For the latter, a very wide range of oil yield (25-60%) has been reported [14,15], but 40-60% yields have been described in most cases. Large variations in the content of crude protein (19-31%), crude fat (43-59%), neutral detergent fiber (3.5-6.1%), and ash (3.4-5.0%) in kernels, are also reported [16]. On the basis of the obtained yields, *J. elbae* and *J. rzedowskii* can be visualized as potential species for biofuel production (Table 1).

Table 1. Comparison of oil yield and seed characteristics in *Jatropha* species.

Species	Length ± SD (cm)	Width ± SD (cm)	Weight ± SD (g)	Oil Yield % ± SD (n=5)
J. elbae	1.4 ± 0.1	1.3 ± 0.1	1.29 ± 0.3	55.25 ± 0.80
J. andrieuxii	0.9 ± 0.1	0.6 ± 0.1	0.07 ± 0.0	39.77 ± 1.15
J. rzedowskii	0.9 ± 0.2	0.9 ± 0.2	0.41 ± 0.06	47.69 ± 2.20
J. curcas	1.7 ± 0.1	0.8 ± 0.1	0.54 ± 0.09	25-60[14,15]

*Length, Width and Weight were obtained by measuring 100 seeds, except for *J. rzedowskii* that were obtained from 50 seeds. The oil yield is the mean value of five replicates (n=5). Oil extractions were carried out using trichloroethylene; except for *J. curcas* (see references).

The oil composition was analyzed through the components of their fatty acid methyl esters, cited below. In the three cases, it was concluded that the crude oils are composed mainly of oleic, linoleic, palmitic, and stearic acids.

Besides oil yields, data of some important biodiesel indexes were determined. For example, it is necessary to determine the iodine number in order to evaluate the oil unsaturation degree. For *J. curcas* properties a wide range of data has been reported [10,17]; in this work acidity number, saponification value, iodine value and relative density, were determined using standard ASTM methods. Table 2 shows data from oils of *J. curcas* compared to the three studied *Jatropha* species; data concerning combustion properties will be reported separately. The seeds were analyzed immediately after collection.

At present, about 400 plant oils have been characterized; many of them could be considered as potential fuels for compression ignition engines after being derivatized [19]. To produce the methyl esters, the *Jatropha* oils were mixed with methanol, and heated in the presence of a catalyst. Although *t*-butylamine and triethylamine have been reported to yield excellent results in the esterification of carboxylic acids [20], we obtained non-complete reactions even using long term reactions. Better results were obtained using boron trifluoride etherate. With this Lewis acid, the reactions were completed in 2 h. After work-up, the organic layers were dried and evaporated, and the crude was characterized by GC-MS; the results for the main components are presented in Table 3. As shown, the main esters correspond to four fatty acids: palmitic, linoleic, oleic and stearic; only in one case was methyl palmitoleate detected; in the Table, the oil composition is compared to data of *J. curcas* oil [18,21]. To stop the reaction, the crude was dropped into cold water; in this way glycerin and the boron derivative were rapidly removed from the esters mixture.

We were unable to separate the esters mixture by column chromatography using silica gel as adsorbent, even when low

Table 2. Comparative properties of crude oils of *Jatropha* species extracted with trichloroethylene. Values are the mean of four replicates including standard deviation.

Characteristic	*J. curcas**	*J. andrieuxii*	*J. elbae*	*J. rzedowskii*
Acidity number (mg KOH/g sample)	0.92-6.16	0.3 ±0.054	0.3 ±0.047	0.3 ±0.09
Saponification number (mg KOH/g sample)	188-209	202.5 ±9.36	192.1 ±6.82	193.6 ±1.23
Iodine number (g I_2/100 g sample)	89-112	92.56 ±14.36	76.11 ±6.0	88.55 ±6.85
Unsaponifiables (% w/w)	0.79-3.8	0.8 ±0.10	0.3 ±0.05	0.8 ±0.19
Relative density, at 20°C (d sample/d H_2O)	0.860-0.933	0.922 ±0.005	0.93 ±0.004	0.929 ±0.006

*Values for *J. curcas* were obtained from the literature [11].

Table 3. Main components from the transesterification of *Jatropha* oils.

Methyl ester		*J. curcas* %	*J. andrieuxii* %	*J. elbae* %	*J. rzedowskii* %
Methyl palmitoleate	C16:1	0.9-1.5			2
Methyl palmitate	C16:0	10-15	7	10	12
Methyl linoleate	C18:2	35-44	38	34	48
Methyl oleate	C18:1	37-49	24	26	22
Methyl stearate	C18:0	2-9	5	7	7

polarities were used. The ^{1}H-NMR spectra of fractions always presented a components mixture.

Conclusions

Physical and chemical characteristics of the three studied *Jatropha* species oils are similar to those of *J.* curcas oil. Good yields (40-56%) of kernel oils from *J. elbae* and *J. rzedowskii* were obtained, and the derivatization to their methyl esters was afforded quantitatively using boron trifluoride etherate as catalyst. The composition of the mixture of the fatty acid methyl esters is similar to that of *J. curcas*, reported in several papers. The results show that the previously untested species *J. elbae* and *J. rzedowskii* are considered as potential biodiesel producers. They are able to grow in arid conditions, and could augment the production of biofuels in semiarid regions.

Experimental Part

Seeds of *Jatropha* species were collected in the region "Mixteca" in the south part of Puebla State. Herbarium samples were taken, taxonomically determined by Jaime Jiménez Ramírez and deposited in the Herbarium of the Benemérita Universidad Autónoma de Puebla under the numbers 27973, 18290, and 27980 for *J. elbae*, *J. rzedowski* and *J. andrieuxii,* respectively. After physical characterization (length, width and weight), seeds from *J. elbae* (from Jolalpan) and *J. rzedowskii* (from Coxcatlán) were peeled and finely cut. Seeds from *J. andrieuxii* from the Balsas basin were macerated, because of the difficulty in removing the thin shell.

The seed oils were obtained using Soxhlet apparatus and trichloroethylene as solvent. Extractions using trichloroethylene gave better results than using hexanes or isopropyl alcohol, as stated above. After 6 h, the extraction mixture was cooled, filtered, and dried over anh. Na_2SO_4. The filtrated was concentrated under vacuum in a rotary evaporator. Each procedure was repeated 5 times for each kind of seed, using 10 g samples.

The determination of the acidity number, saponification value, iodine value and relative density was effectuated following standard techniques: ASTM D664-09, ASTM 5558-95, ASTM D6584-08, and ASTM D4052-09, respectively.

The transesterification reactions were carried out by heating to reflux the crude oils (1 mL) with methanol (6 mL), in the presence of $BF_3{\cdot}OEt_2$ (0.5 mL). All reactions were followed by thin layer chromatography on silica gel, verifying that all starting material reacted before 2 h (eluting system: hexanes / ethyl acetate 95:5). Crudes of reaction were washed with water (15 mL) 3 times and extracted with CH_2Cl_2 (15 mL). The organic layer was dried over anh. Na_2SO_4, filtered and evaporated *in vacuo*.

The chemical composition of the mixture of methyl esters was analyzed using a Jeol GC-MATE GC-MS. The GC had a 30 m x 0.32 mm HP-5 capillary column containing a 0.25 mm film of 5% phenyl methylsiloxane. Helium was used as carrier gas with a 1mL/min flow rate. The samples were dissolved in chloroform. The temperature of the oven started at 40 °C (0 min), then ramp 25 °/min to reach 100 °C (1 min), ramp 10 °C/min to reach 310 °C (16 min). The oils from the three species (Table 3) exhibited the same main components, in similar proportions, and close to those of *J. curcas* from Africa, Asia and South-America [18]. All mass spectra of the fatty acid methyl esters were in agreement with those of the NIST 08 Mass Spectral Library.

Acknowledgements

The authors express their thanks to PROMEP for financial support (Grant BUAP-EXB-6200).

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