



## Preliminary experimental study on biofuel production by deoxygenation of Jatropha oil



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### ABSTRACT

Deoxygenation through decarboxylation of *Jatropha curcas* (non-edible) oil under a nitrogen atmosphere was performed using alumina (Puralox SBA200) and hydrotalcite (Pural MG70) as catalysts at 350 and 400 °C. In general, liquid product yields obtained exceeded 80%. FTIR spectroscopy showed that the oxygen contained in the liquid product decreases significantly when hydrotalcite is used as the catalyst with a reaction time of 6 h. At the end of the tests, a liquid biofuel was produced with a high proportion of hydrocarbons – around 83% – of mainly C8–C18. The product also showed good properties as a heating value of around 44 MJ/kg, higher than biodiesel (40 MJ/kg) and near to diesel (46 MJ/kg), and a lower viscosity (4 cSt) than biodiesel (4.5 cSt). Using GC analysis it was possible to identify the CO<sub>2</sub> and CO as the principal compounds present in the reaction gas, confirming that oxygen is removed mainly through decarboxylation and decarbonylation reactions.

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### 1. Introduction

Over the years, different strategies are being considered to mitigate the impact of greenhouse gases. Among them, the production of liquid biofuels without causing limitation to agro-food production represents an important approach. In fact, the European Union introduced directives 2003/30/EC, 2009/28/EC and 2014/94/EU with the aim of increasing biofuel utilization in the transport sector.

Vegetable oils are considered important raw material in the production of biofuels due to their capacity to store large amounts of energy, this capacity is directly related to their chemical structure (e.g. triglycerides have similar carbon chains to the carbon chains of the liquid fuels derived from fossil sources). However, vegetable oils also contain oxygen atoms incorporated in the form of carboxyl or carbonyl groups. Many properties of the vegetable oils such as high viscosity, high flash point and low heating value compared to fuels as diesel or gasoil are attributed to their chemical structures and oxygen content [1,2].

Pyrolysis of vegetable oils at medium temperatures allows the production of hydrocarbon biofuels [3]. Pyrolysis of different raw material under atmospheric pressure and temperatures ranging between 350 °C and 550 °C was reported: soybean, palm, and castor oils [4], palm oil over alumina catalyst [5], several animal (lamb, poultry and

swine) fatty wastes [6] and the effects of oil type on products obtained in the presence of zeolite catalysts [7]. Also, the non-isothermal kinetics of Jatropha oil pyrolysis using thermogravimetric analysis was studied [8]. As well as the use of very acidic catalytic materials such as protonic zeolites has been the object of several tests, although, the use of milder acidic materials as catalysts seems to be more convenient to produce liquid fuels in the diesel range [9–11]. Conventional pyrolysis is associated with the promotion of C–O cleavages and poor selectivity due to uncontrollable reactions such as cracking or polymerization of the hydrocarbons, resulting as product a type of biofuel with a high amount of oxygenated compounds as unreacted carboxylic acids, acrolein and ketones [1,6,12].

On the other hand in the transesterification process, C–O cleavages are achieved using catalysts and an alcohol as co-reactant to produce fatty acid methyl esters (biodiesel) [13,14], but this product results to be also a oxygenated biofuel (fuel quality directive 2009/30/EC has limited the use of biodiesel to maximum 7 vol.%). Additionally, the co-production of impure glycerol is a strong drawback of this technology.

Recently, processes as catalytic hydrotreating (carried out under similar conditions to those normally used for hydrotreating in oil refineries) were used to obtain free-oxygen biofuels from vegetable oils. If followed by mild hydrocracking to improve cold properties, the biofuel produced using this technology was demonstrated to have almost identical properties to normal petrochemical diesel [15]. Literature reports the reaction pathways of the catalytic hydrotreating of soybean oil using different catalysts (Ni, Pd, CoMoS<sub>x</sub>, and NiMoS<sub>x</sub>) for various temperatures, hydrogen pressures, and reaction times [16]. Also, different

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materials including waste cooking oils and model feed of waste fats (oleic acid and tripalmitin) were treated through this technology with optimum results [17,18]. And being the temperature and pressure the most important parameters on the process, their influence on the intermediate and final products was studied [19–22]. Despite the good results obtained through the process an important drawback was identified: typical catalysts used in the process are based on metal sulfides (e.g. Ni/Mo and Ni/W combinations supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), which need to be operated under high pressures of hydrogen [23,24]. The use of high amounts of hydrogen represents a significant production cost, consequently, needs to be reduced to ensure the large-scale industrialization of advance biofuels.

As result of the above considerations, the conversion of vegetable oils into hydrocarbon biofuels without the use of hydrogen appears an important subject of study. The conversion of vegetable oils into liquid biofuels without using hydrogen can be further optimized from a quantitative as well as qualitative point of view if the selective removal of oxygen is promoted by the reactions of decarboxylation (removal of the carboxylic group through C–C cleavages to release CO<sub>2</sub>) and decarbonylation (removal of the carbonyl group through C–C and C–O cleavages to release CO) [1,16]. Certain studies have been conducted on this topic by Murzin et al. analyzing the deoxygenation of stearic acids and their derivatives in a semi-batch reactor using different metal catalysts and supports combination [25–27]. Santillan-Jimenez and Crocker proposed cheaper catalysts, obtaining good results for deoxygenation in semi-batch and batch reactors of tristearin, triolein and soybean oil over Ni/C [28,29] and Ni supported by alumina [30]. Na et al. tested decarboxylation of oleic acid using hydrotalcites having three different MgO compositions (30, 63 and 70 wt.%) instead of precious metals in a batch process [31]. In a second step, the catalytic decarboxylation of pyrolysis oil from *Chlorella* sp. KR-1 cells over hydrotalcite MG63 was tested [32]. The use of basic materials as catalysts for biofuel production can also be considered, so as already suggested in a previous work [33]. Among basic catalytic materials [34,35] Mg–Al mixed oxides obtained by calcining hydrothalcite (layered double hydroxides) are cheap and industrially available.

The aim of this paper is the deoxygenation through decarboxylation and decarbonylation of *Jatropha curcas* oil, as a model of non-edible oil. *J. curcas*, a perennial plant, appears to be an ideal plant for producing second-generation biofuels, i.e. arising from non-food feedstock, it is easily cultivated and strongly resistance to drought [36]. Literature shows that *J. curcas* oil was treated through different processes, including pyrolysis [8], transesterification [37], and catalytic hydrotreating [38,39] under different conditions and catalysts. Further information about the composition, properties and advantages of the use of the *J. curcas* can be found in selected literature [14,37,40–44]. Our tests have been performed using a mechanical stirred batch reactor without

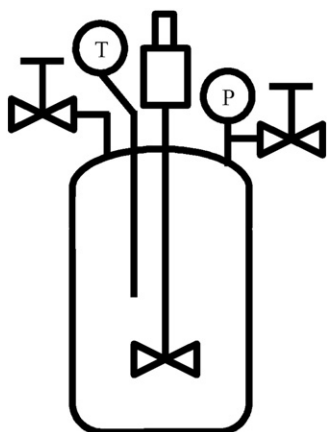


Fig. 1. Scheme of the batch reactor used for the experiments.

Table 1

Composition of *Jatropha* oil measured by GC analysis of the fatty acid methyl esters.

Fatty acid methyl ester	FAME g/100 g oil
Methyl palmitate	36.02
Methyl stearate	5.16
Methyl oleate	28.86
Methyl linoleate	29.87
Methyl linolenate	0.11

catalysts, with alumina as an acid catalyst and with calcined hydrotalcite as a basic catalyst, at 350 °C and 400 °C and a pressure that can achieve during the operation 40 bar and 110 bar respectively at the two used temperatures.

## 2. Materials and methods

### 2.1. Raw materials and catalyst

*J. curcas* oil was provided by Ancient Green-Fields Pltd. in India. The triglyceride composition, as measured by GC analysis (Dani 1000, DANI INSTRUMENTS, Milan, Italy) of the fatty acid methyl esters produced by transesterification, was obtained following the methodology described by Converti et al. [45]. PURAL MG70 (hydrotalcite with weight ratio of MgO:Al<sub>2</sub>O<sub>3</sub> = 70:30) and PURALOX SBa200 (pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) supplied by Sasol were used as catalyst. The PURAL MG70 catalyst was activated for 5 h at 500 °C under an air atmosphere. The specific surface area of both catalysts was obtained by Brunauer–Emmett–Teller (BET) isotherm-equation, as result it was identified a specific surface area of 159 m<sup>2</sup>/g and 193 m<sup>2</sup>/g for the treated hydrotalcite and alumina respectively.

### 2.2. Reaction experiments

Different tests for *Jatropha* oil deoxygenation were performed in a mechanically stirred 500 mL reactor (Model 4575A – PARR Instrument Company) operating in batch mode and configured to operate at high temperatures and pressures (Fig. 1) [46]. In a typical experiment, approximately 180 g of *Jatropha* oil and 3% of catalysts were added to the reactor. *Jatropha* oil deoxygenation was tested also without using a catalyst. Before each experiment, the reactor was purged with nitrogen for 3 min to remove the remaining oxygen and pressurized to approximately 3 bar. The temperature was increased up to 350 °C or 400 °C, maintaining isothermal conditions for either 3 or 6 h depending on the test carried out. At the end of the process, the pressure reaches around 40 and 110 bar at 350 °C and 400 °C, respectively, depending

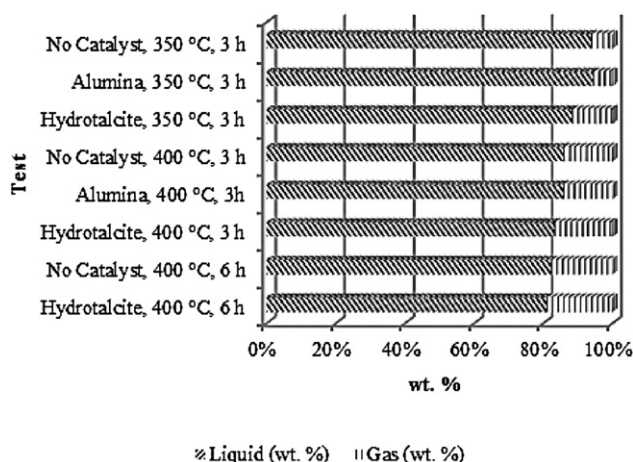


Fig. 2. Yields of liquid and gaseous products obtained after the treatment of *Jatropha* oil.

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