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Deoxygenation of Non-Edible Vegetable Oil to Produce Hydrocarbons Over Mg-Al Mixed Oxides

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The transition from the use of fossil fuels to alternative and innovative fuels is a complex process involving two main points: the research of a new generation of raw materials and the development of the related technology. Regarding to raw materials, vegetable oils have the capacity to storage large a+mounts of energy, a capacity directly related to their chemical structure, which have similar carbon chains to the common fuels such as gasoil or diesel. However, vegetable oils, which are mostly constituted by triglycerides, cannot be easily used as such. Additionally, they contain significant amounts of oxygen atoms incorporated in the form of carboxyl groups. Consequently, they need to be treated through a deoxygenation process to be converted into useful fuels.

Selective deoxygenation can be obtained by promoting the reactions of decarboxylation and decarbonylation in limited presence of hydrogen or even in absence of this gas. Selective decarboxylation of fatty acids results in the elimination of carboxylic groups producing CO_2 and a paraffin hydrocarbon (n-alkane with one less carbon atom than the starting fatty acid) while selective decarbonylation leads to the formation of CO, H_2O and an olefinic hydrocarbon (the corresponding alkene). When realized over triglycerides these reactions imply also the cracking of the glycerol moiety producing light hydrocarbons. Additionally, ketonization occurs producing high molecular weight ketones that can later be cracked to lighter methyl-ketones. Such pyrolytic processes may bring different benefits, such as the production of high-cetane-number linear hydrocarbons within the diesel range coming from biological sources, which are fully compatible with existing engines and infrastructure. Also, by-products as CO_2 could be recovered and used in an integrated biorefinery.

Previously, we studied the deoxygenation of oil a non-edible oil (Jatropha curcas *oil)* and waste cooking vegetable oil in a hydrogen free atmosphere using γ-Al_2O_3, CaO and Mg-Al mixed oxides (obtained from treated hydrotalcite) as catalysts. Mg-Al mixed oxides (calcined hydrothalcite) revealed interesting catalytic activity. This communication reports on the analysis of the chemical composition of the products obtained during the catalytic pyrolysis of *Jatropha curcas* oil, at different temperatures and reaction times, using the same catalyst. In the experiments, it was evidenced that the liquid biofuel recovered at 400 °C was composed mainly by hydrocarbons (66 mol % including n-paraffins and aliphatics), this amount increased for the product recovered at 425 °C (77 mol % including n-paraffins and aliphatics). Those compositions are not very different from that of commercial Diesel B7 (91 mol % of hydrocarbons including n-paraffins and aliphatics). It is suggested that *Jatropha curcas* oil deoxygenation proceeds mainly through the reactions of decarboxylation and ketonization (also involving a decarboxylation). While, ketonization reaction was favored at the lowest temperature tested, it was evident that decarboxylation reaction was predominantly by increasing the temperature.

1. Materials and Methods

1.1 Raw material and catalyst

The triglyceride composition of the *Jatropha curcas* oil, provided by Ancient Green-Fields Pltd. located in India, was measured by GC analysis (Dani 1000, DANI INSTRUMENTS,Milan, Italy) of the fatty acid methyl esters produced by transesterification. Considering the results of our previous work in Romero et al. (2014) and Romero et al. (2015), PURAL MG70 (magnesium- aluminum hydroxyl-carbonate compound with weight ratio of $MgO:Al_2O_3$ = 70:30) commonly known as hydrotalcite was used as catalyst (supplied by Sasol). In order to obtain Mg–Al oxides, PURAL MG70 was calcined during 5 h at 500 °C under air atmosphere before use. After calcination it showed a specific surface area of 159 m^2/g according to Brunauer–Emmett–Teller (BET) isotherm-equation.

1.2 Deoxygenation experiments

The experiments were performed in a mechanically stirred 500 mL reactor (Model 4575A — PARR Instrument Company) operating in the batch mode. Approximately 180 g of *Jatropha curcas* oil and 3 % of catalysts were added into the reactor, then it was purged with nitrogen for 3 min to remove the remaining air and pressurized to approximately 3 bars. The temperature of the reactor was increased up to 400 °C or 425 °C. Consequently, the pressure also increased depending essentially of the gas produced in the reaction system. Liquid samples were obtained from different experiments having different reaction times with intervals of ~ 35 min (e.s. 0 min indicate that a sample was obtained when the desired temperature was reached, while 180 min indicate that sample was obtained after this period of time maintaining isothermal conditions). Once the liquid samples were obtained, they were weighed to determine mass yields and stored in plastic containers for subsequent GC/MS analysis.

1.3 Product analysis

To identify the main compounds in our liquid samples (such as hydrocarbons, oxygenates, acids and others) produced during the course of the reaction, analysis was conducted using a GC/MS (Focus-ISQ Thermoscientific) equipped with TG-SQC column (30 m 0.25 mm 0.25 μm) and a split injector. TIC signal acquisition mode was used. The starting temperature was calibrated at 70 °C (hold time 5 min), with an initial increase of 5 °C/min up to 130 °C (hold time 1 min), then a second ramp of 5 °C /min up to 270 °C (hold time 1 min), and a final ramp of 25 °C/min up to 320 °C (hold time 5 min).

2. Results

As reported by Busca (2014) and Sannita et al. (2012), vegetable oils, mainly if they come from non-edible plants or waste materials, might have a key role in the transition from the use of fossil fuels to alternative biofuels. In Romero et al. (2016) we studied the deoxygenation of oil a non-edible oil (*Jatropha curcas* oil*)* and waste cooking vegetable oil in a hydrogen free atmosphere using CaO and Mg-Al mixed oxides (obtained from treated hydrotalcite) as catalysts. Considering the low cost of the materials derived from Ca, Asikin-Mijan et al. (2016) and Asikin-Mijan et al. (2017) have also studied the performance of CaO-based catalysts derived from waste clamshell in the deoxygenation of triolein to produce advanced biofuels. While, Gao et al. (2017) have reported the deoxygenation of natural algae over a series of Mg-Al layered double oxide/ZSM-5 composites (MgAl-LDO/ZSM-5) obtained from MgAl-LDH/ ZSM-5 precursors. This communication provides more information on the analysis of the chemical composition of the products obtained during the deoxygenation of *Jatropha curcas* oil, using Mg-Al mixed oxides as catalysts.

2.1 Chemical composition of the products obtained

According to the GC analysis, the oil used in our experiments was composed by unsaturated and saturated fatty acids in the following decreasing order: linoleic acid (40 wt.%), oleic acid (34 wt.%), palmitic acid (23 wt.%), steric acid (4 wt.%) and linolenic acid (<1%). Table 1 shows the composition, obtained by GC-MS analyses, of the liquid phase samples recovered at 0 min and the composition of the final products obtained after a reaction time of 180 min. To have a reference point, the results were compared with the composition of a commercial Diesel B7. The results were encouraging, because it was evidenced that the liquid biofuel recovered at 400 °C was composed mainly by n-paraffins and other aliphatic hydrocarbons, reaching a total amount for both compounds of 66 mol %, and increasing in the product recovered at 425 °C up to 77 mol %. Those compositions are not very different from that of commercial Diesel B7, which is composed mainly by aliphatic hydrocarbons of 91 mol %. From Table 1 is also evident the reduction of acid compounds in the liquid products, which agrees with the results obtained by Tani et al. (2011) and Trieu et al. (2017).

2.2 Routes in the formation of the products

Figure 1 shows how the reaction proceeds until the formation of the final products. It is possible to observe that at 400 °C the molar fraction of n-paraffins increased with time reaching levels of 56 mol% (after 180 min) and the molar fraction of acid compounds tends to decrease rapidly, reaching minimum values after 70 min. Although, the behaviour of other aliphatic hydrocarbons seems to be not very stable, the amount of these compounds tends to rise and fall reaching around 10 mol% at the end of the experiments. At 425 °C the molar fraction of n-paraffins increases rapidly reaching levels of 65 mol% (just after 70 min), and the quantity of other aliphatic hydrocarbons reaches levels of 14 mol% at the end of the experiment (180 min), further it is clear that at this temperature the acid compounds are practically not present.

Figure 2 and Figure 3 show the amount of n-paraffins (C8 - C17) and C17 iso-paraffins present in the products. If we put our attention on the results obtained at 425 °C, we can observe that the main type of n-paraffin is the n-pentadecane (C15), derived from the decarboxylation of the saturated C16 fatty acid (palmitic acid) contained in the Jatropha curcas oil. The other decarboxylation product detected was n-heptadecane (C17), resulting from the decarboxylation of saturated (stearic) C18 fatty acids, and potentially from the decarboxylation of unsaturated (linoleic and oleic) C18 fatty acids. The high content of aliphatic compounds has also been reported by Uttamaprakrom et al. (2017), however, because the experiments were carried out under a hydrogen atmosphere the production of olefins (50.62 wt%) was preferred to the production of paraffins (9.49 wt%). These results could indicate that under a hydrogen atmosphere, decarbonylation reaction is preferred to the decarboxylation reaction. Snåre et al. (2008) have reported that in a previous step to the decarboxylation, linoleic acid could hydrogenate to oleic acid and stearic acid even under an inert atmosphere. The explanation given is that the source of hydrogen may come from the same raw material, through a hydrogen redistribution reaction, for example dehydrogenation of the fatty acids to unsaturated by-products such as diunsaturated acids, triunsaturated acids or aromatics. This fact has also been reported in limited presence of hydrogen (1 vol % H_2 in argon) by Mäki Arvela et al. (2011). Furthermore, in both temperatures, another decarboxylation product identified was the C17 iso-paraffin “tetradecane, 2,6,10-trimethyl-” (considered in the voice of other aliphatic hydrocarbons). At 425 °C after 70 min, n-heptadecane and “tetradecane, 2,6,10-trimethyl” showed decline their molar compositions with reaction time.

Table 1: Comparison between the composition of liquid phase samples recovered at 0 min, 180 min and conventional Diesel B7. Results obtained by GC-MS analysis (mol%).

Sample	n-paraffins	Other aliphatic hydrocarbons	Aromatics	Ketones	Acids	Other oxygenates	Others
0 min - 400 °C	0.52	5.00	0.00	1.10	63.10	10.13	20.10
0 min - 425 °C	14.60	22.39	0.00	18.19	2.34	9.14	33.35
180 min - 400 °C	56.33	9.98	1.69	11.22	0.00	17.89	2.89
180 min - 425 °C	63.29	14.09	2.44	4.08	2.73	5.10	8.28
Diesel B7	46.48	44.00	1.34	0.00	0.00	5.33	2.85

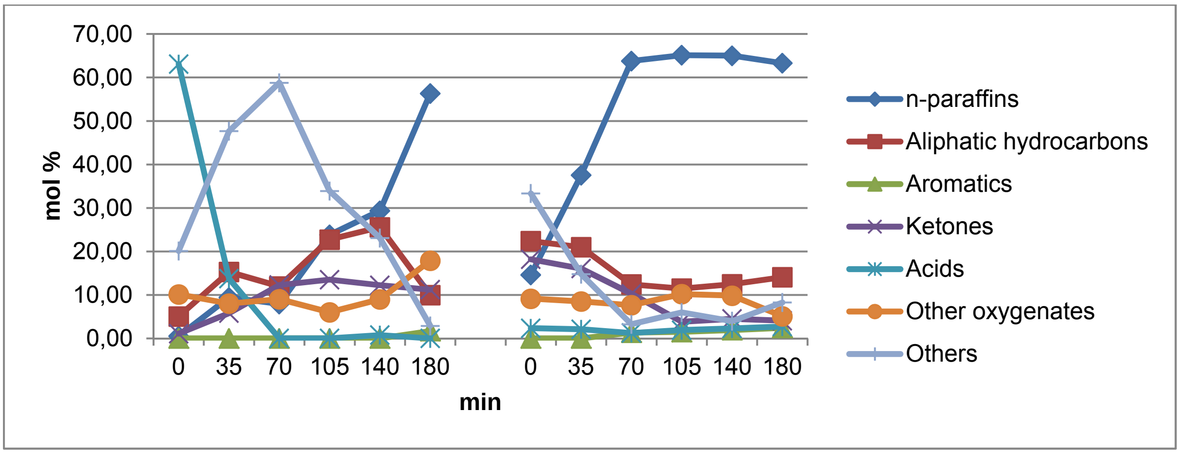

Figure 1: Products formation in the deoxygenation of the Jatropha curcas oil at 400 °C (left) and 425 °C (right), results based on GC-MS analysis.

2.3 Formation of ketones during the reaction

Another type of compound in which we put our attention were the ketones. These compounds are relevant because their presence is indicative of the ketonization reaction, additionally, they result in the retention of oxygen in the final fuel, as reported by Parida and Das (2000) and more recently by Khromova et al. (2013) and Phung et al. (2015). As discussed by Lopez-Ruiz et al. (2015) and Shylesh et al. (2017), in the ketonization two acid molecules couple to form one carbon-carbon bond, and the deoxygenation of the acid molecules through a decarboxylation reaction is also involved, since three oxygen atoms are eliminating as carbon dioxide and water. In our experiments (see Figure 4) we identified ketones of middle chains such as 2-heptadecanone and 2-nonadecanone (the products of ketonization and cracking of palmitic acid). The molar fraction of ketones obtained at 400 °C was higher than the molar fraction of ketones obtained at 425 °C. In the first case the molar fraction of ketones increases up to 13 mol% after 105 min to then drops to around 9 mol% after 180 min. While, at 425 °C the molar fraction of ketones decreased throughout the course of the reaction reaching its lowest level after 180 min (3 mol%). Concerning ketones over conversion, it is remarked that while the molar fraction of these products decreases, there is a small increase in the amounts of aromatic compounds, reaching in both cases around 2 mol % after 180 min. Accordingly, Adjaye et al. (1995), Gayubo et al. (2004) and Witsuthammakul and Sooknoi (2015) have previously reported that involving different reaction mechanisms ketones tend to become alcohols and different types of hydrocarbons such as olefins, paraffins and aromatics.

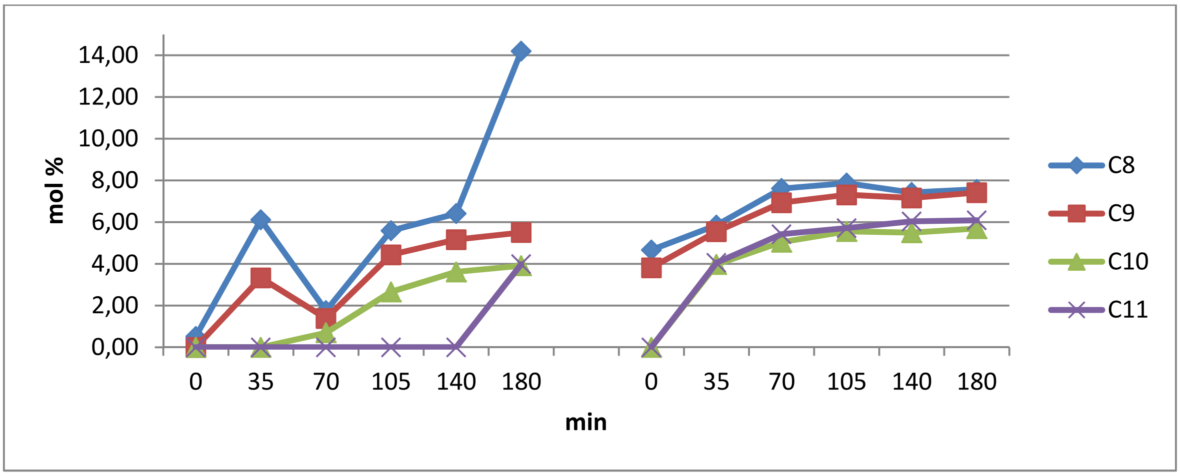

Figure 2: n-paraffins ranging between C8 – C11 as products of the deoxygenation of the jatropha curcas oil at 400 °C (left) and 425 °C (right), results based on GC-MS analysis.

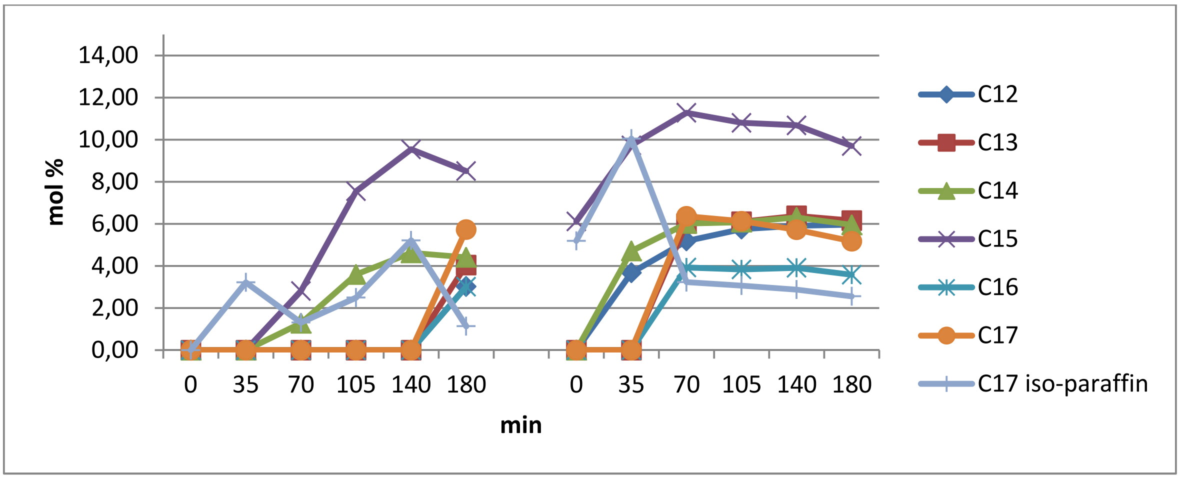

Figure 3: n-paraffins ranging between C12 – C17and C17 iso-paraffin as products of the deoxygenation of the Jatropha curcas oil at 400 °C (left) and 425 °C (right), results based on GC-MS analysis.

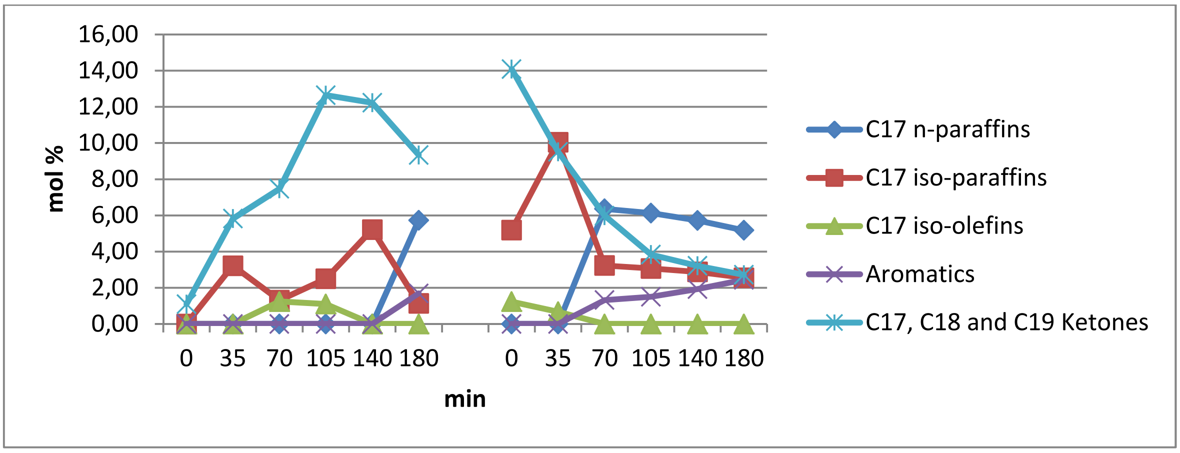

Figure 4: C17 paraffins, C17 iso-olefins, aromatics and C17-C19 ketones as products of the deoxygenation of the Jatropha curcas oil at 400 °C (left) and at 425 °C (right), results based on GC-MS analysis.

3. Conclusions

In this work *Jatropha curcas* oil was successfully deoxygenated by catalytic pyrolysis over Mg-Al mixed oxides in a hydrogen-free atmosphere and converted into a biofuel (composed mostly of hydrocarbons 77 mol % at 425 °C) potentially suitable for its use in transportation sector. The reaction conditions (temperature and pressure) and the catalyst played an important role in the experiments, in which was evidenced that the main routes of the *Jatropha curcas* oil deoxygenation were the decarboxylation and ketonization (also involving a decarboxylation) reactions. While, ketonization reaction was favoured at the lowest temperature tested, it was evident that decarboxylation reaction was favoured by increasing the temperature. The main types of n-paraffin identified were n-pentadecane, decarboxylation products of the saturated C16 fatty acid (palmitic acid) and n-heptadecane resulting from the decarboxylation of saturated (stearic) C18 fatty acids, and potentially from the hydrogenation/decarboxylation of unsaturated (linoleic and oleic) C18 fatty acids. Both reactions, decarboxylation and ketonization, could be considered valuable ways in the deoxygenation of vegetable oils, because are able to remove large amounts of oxygen in limited presence of hydrogen or even, as our case, in a complete absence of this gas.

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