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Deoxygenation of waste cooking oil and non-edible oil for the production of liquid hydrocarbon biofuels

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ABSTRACT

Deoxygenation of waste cooking vegetable oil and *Jatropha curcas* oil under nitrogen atmosphere was performed in batch and semi-batch experiments using CaO and treated hydrotalcite (MG70) as catalysts at 400 °C. In batch conditions a single liquid fraction (with yields greater than 80 wt.%) was produced containing a high proportion of hydrocarbons (83%). In semi-batch conditions two liquid fractions (separated by a distillation step) were obtained: a light fraction and an intermediate fraction containing amounts of hydrocarbons between 72–80% and 85–88% respectively. In order to assess the possible use of the liquid products as alternative fuels a complete chemical characterization and measurement of their properties were carried out.

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1. Introduction

The European Union has encouraged the utilization of biofuels in the transport sector through directives such as 2003/30/EC, 2009/28/EC and 2014/94/EU. In this context, the use of waste cooking vegetable oil (WCO) and non-edible oils (e.g. *Jatropha curcas* oil, JCO) play an important role as second generation raw materials not only providing economic and environmental benefits, but also improving the efficiency in the use of waste materials (Fernández et al., 2015; Gui et al., 2008). In addition, the waste cooking oil is a typical food waste fully classified in bio-waste category that is attracting the interest of the scientific community for its possible important role in the recycle and energy recovery processes.

In the matter of processes, conventional pyrolysis has been used for many years to obtain a type of bio-oil from biomass, including vegetable oils. However, the main drawback of the bio-oil is its high content of oxygenated compounds, in particular carboxylic acids (Sannita et al., 2012). For example, the pyrolysis of several animal fatty wastes (lamb, poultry and swine) was reported, resulting into bio-oils containing carboxylic acids (C7–C10), alkanes, alkenes and cyclic hydrocarbons (Ben Hassen-Trabelsi et al., 2014). As a consequence of the presence of the oxygenate compounds in the bio-oil, a further improvement should be applied before its use as engine fuel (Ben Hassen-Trabelsi et al., 2014; Bridgwater, 2012). Also, the treatment of WCO and other

materials through transesterification and catalytic hydrotreating was reported (Alptekin et al., 2014; Andrade et al., 2013; Bezergianni et al., 2012; Charpe and Rathod, 2011; Felizardo et al., 2006; Madsen et al., 2011; Martinez-Guerra and Gnaneswar, 2014; Mohammadshirazi et al., 2014; Sabudak and Yildiz, 2010). At present, the Directive 2009/30/EC limites at 7 vol.% maximum the blending of biodiesel in conventional diesel, because this fuel showed some drawbacks such as a low heating value, high-density, and tendency to form deposits in the fuel injection systems (Knothe, 2010). On the other hand the catalytic hydrotreating, that allows the production of a high quality biofuel mainly composed of hydrocarbons, has the drawback of a high cost related mainly to the high amount of hydrogen used in the process (Aatola et al., 2009).

In the light of the above analysis, the conversion of vegetable oils into hydrocarbon biofuels without the use of hydrogen appears an important research topic. The conversion of natural oils into hydrocarbons in a hydrogen-free atmosphere using quite inexpensive catalysts such as alkaline earth metal oxides was reported in previous works (Dos Anjos et al., 1983; Romero, 2012; Sannita et al., 2012). The aim is to obtain a selective deoxygenation of natural oils by promoting the reactions of decarboxylation and/or decarbonylation, being the oxygen atoms removed mainly in the form of carbon dioxide and/or carbon monoxide, respectively. As a result, a liquid biofuel mainly composed of hydrocarbons with high atomic ratio H/C and low atomic ratio O/C is expected to be produced. The high atomic ratio H/C and low atomic ratio O/C are a signal of a possible greater amount of energy contained in

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Table 1
Standard analysis performed on the liquid fuel products.

Analysis	Standard method of reference	Instrument	Method
Sulfur content	EN ISO 20846	Antek – MODEL 900 nitrogen/sulfur analyzer	Ultraviolet fluorescence method
Nitrogen content	ASTM D4629	Antek – MODEL 900 nitrogen/sulfur analyzer	Syringe/inlet oxidative combustion and chemiluminescence detection
Carbon residue	ASTM D4530	Micro carbon residue tester Alcor MCRT120	Micro Corradson method
Density	UNI EN ISO 12185	Mettler Toledo DM40 densitymeter	Oscillating U-tube method
Boiling range distribution	ASTM D5307	A.C. Analytical Controls combined gas chromatographic system	GC simulated distillation analysis

the fuel. In fact, in a previous work we have reported encouraging features for a liquid biofuel obtained in batch experiments such as heating value of 44 MJ/kg and a low viscosity of 4 cSt (Romero et al., 2014), although the literature on this topic is still limited (Morgan et al., 2010; Murzin and Mäki-Arvela, 2010; Na et al., 2012; Santillan-Jimenez and Crocker, 2012; Snåre et al., 2006).

In the current research a selective deoxygenation promoting the reactions of decarboxylation and/or decarbonylation of WCO and JCO in the absence of hydrogen was evaluated. For the study two approaches were carried out: batch setup and semi-batch setup (with purge gas flow). Two types of alkaline earth metal oxides as catalysts were tested: Mg–Al mixed oxides (obtained from treated hydrotalcite) and CaO. In order to assess the possible use of the liquid products as alternative fuels to the diesel derived from a fossil source a complete chemical characterization and measurement of their properties were carried out.

2. Materials and methods

2.1. Characterization of raw materials and products

The WCO used in this study was collected after typical domestic use, while the JCO was provided by Ancient Green-Fields Pltd. in India. In order to make a comparison with liquid products, starting raw materials and a conventional fossil fuel (Diesel B7 purchased in fuel station) were subjected to the same analysis.

The elemental composition of WCO, JCO, liquid products and Diesel B7 was determined using an Elemental Analyser (mod. CHN 2400, Perkin Elmer).

Infrared spectra for both raw materials and solid products were recorded using a Fourier Transform Infrared Spectrometer (FTIR Nicolet 380, Thermo), equipped with a DTGS detector and using transmission analysis with the help of potassium bromide (KBr) pastilles (100 scans and resolution 2 cm^{-1}). The different functional groups absorb specific frequencies depending on their structures, they were identified in output spectras (infrared light absorbance on the vertical axis vs. wavelength on the horizontal axis).

A detailed analysis of the chemical composition of liquid products and Diesel B7 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).

Also, the properties of the liquid products and Diesel B7 were measured using the similar standard procedures used for petroleum products (reported in Table 1).

On the other hand, the composition of gaseous products was analyzed using a gas chromatograph Chrompack MICRO-GC CP 2002 equipped with a microTCD detector and two parallel columns: the first a PoraPLOT Q column used for analyzing the CO_2 and light hydrocarbons (CH_4 excluded), the second a CP-Molsieve 5A column for analyzing the H_2, O_2, CH_4 and CO.

2.2. Catalyst

PURAL MG70 (aluminum–magnesium hydroxyl carbonate compound with weight ratio of $MgO:Al_2O_3$ = 70:30) commonly known as hydrotalcite was supplied by Sasol and CaO by Sigma Aldrich. In order to obtain Mg–Al oxides, PURAL MG70 was calcinated during 5 h at 500 °C under air atmosphere before use. In order to remove any accumulated moisture in the CaO, this catalyst received the same treatment. After treatment the specific surface area of both catalysts was obtained by the Brunauer–Emmett–Teller (BET) isotherm-equation, the results showed for the treated hydrotalcite and CaO a specific surface area of 159 m^2/g and 1 m^2/g respectively.

2.3. Deoxygenation experiments

The different experiments in the deoxygenation of WCO and JCO were performed in a mechanically stirred 500 mL reactor (mod. 4575A, PARR Instrument Company) operating in two diverse configurations: batch setup (Fig. 1A) and semi-batch setup (Fig. 1B). In a typical experiment, approximately 180 g of raw material and 3 wt.% of catalyst were added to the reactor. Before each experiment, under constant stirring of the mixture, the reactor was purged with nitrogen for 3 min to remove the remaining oxygen. In the batch experiments the reactor was initially pressurized to approximately 3 bar before the heating, depending essentially on the gaseous products produced during the reaction: at the end of the experiments a pressure of around 110 bar was achieved. The temperature was increased to reach in 1 h the desidered value (400 °C), and maintained at this value for 6 h. In
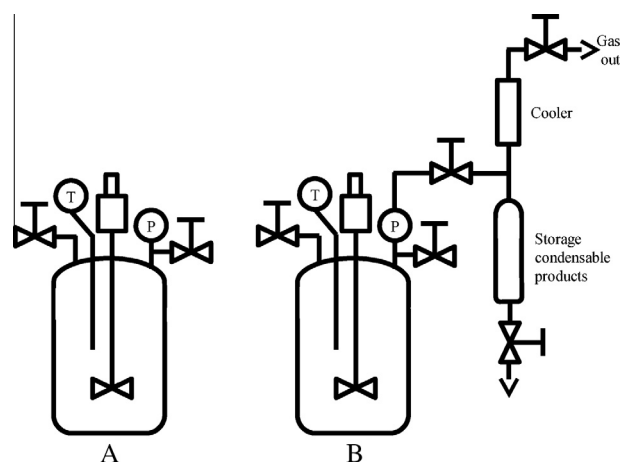

Fig. 1. (A) Batch reactor; (B) semi-batch reactor.

semi-batch experiments the pressure was maintained between 15 bar and 20 bar during all the test, by gaseous products releasing. In order to avoid losses of condensable products, these were condensed using a cooler. By this way a second liquid phase was obtained and stored in a vessel located downstream the semi-batch reactor. At the end of the test, the reactor was cooled down until room temperature by a cooling system based on external water circulation. In the batch tests the gaseous products were collected in special bags to allow gas chromatography analysis. Liquid products were weighted to determine mass yields then stored in small plastic containers for subsequent analysis.

3. Results and discussion

3.1. Products obtained after experiments

Batch experiments were characterized by high yields of liquid phase (designated as single fraction) respect to semi-batch test. The liquid yields in batch tests were greater than 80 wt.%, the highest yield was obtained in the treatment of the WCO using CaO as catalyst (84 wt.%). Typically, in batch experiments a solid product was not produced, only a small amount of solid fraction was identified after the treatment of the JCO using CaO as catalyst. The product distribution of the semi-batch experiments differs significantly from the batch one. Liquid products were obtained in two separate fractions (designated as light fraction and intermediate fraction) so as previously explained. In these tests, regardless of the raw material used, yields of liquid products were significantly higher when CaO was used as catalyst (68 wt.% in the treatment of WCO and 83 wt.% in the treatment of JCO). The use of treated hydrotalcite as catalyst resulted in lower yields of liquid products (53 wt.%), while the production of gaseous and solid products was promoted and a small amount of water was identified (2 wt.%). The presence of water and a high amount of linear olefinic hydrocarbons in the light fractions (reported in the next section) suggested that the decarbonylation reaction was preferred instead to the decarboxylation reaction (Snåre et al., 2007). Results of product yields are reported in Fig. 2.

3.2. Characteristics of the WCO and JCO

As it is evidenced by elemental analysis (reported in Table 2) the WCO and JCO have high carbon content (77 wt.%), this characteristic makes them as optimal alternative raw materials for the production of hydrocarbon biofuels. Nevertheless, it is also evident their high oxygen content (9 wt.% and 12 wt.% for the WCO and JCO respectively), likely the main chemical characteristic that differentiates an oil from a hydrocarbon fuel. In fact, many limitations (including its high viscosity) in the use of a vegetable oil as fuel, are related to the oxygen content. The amount of hydrogen present in the raw materials was 12 wt.% and the amount of nitrogen was not greater than 1 wt.%. FTIR spectroscopy also provided the evidence of the presence of oxygenated compounds in the raw materials. In our analysis spectra of WCO and JCO have not shown differences, but it should be noted that due to thermolytic, oxidative and hydrolytic reactions occurring during frying, WCO can differ from fresh vegetable oil in its chemical composition: WCO is rich in free fatty acids, diglycerides and monoglycerides (Gui et al., 2008; Lam et al., 2010). The O—H stretching vibration bands between 3200 and 3600 cm^{-1} indicate that carboxylic acids and alcohols are present in the sample. The presence of intense bands in the 3000–2800 cm^{-1} region are attributable to symmetric and asymmetric stretching of C—H bonds. Other bands with moderate intensity in the 1500–1200 cm^{-1} region also indicate that aliphatic groups are present in the raw materials, while the complex band in
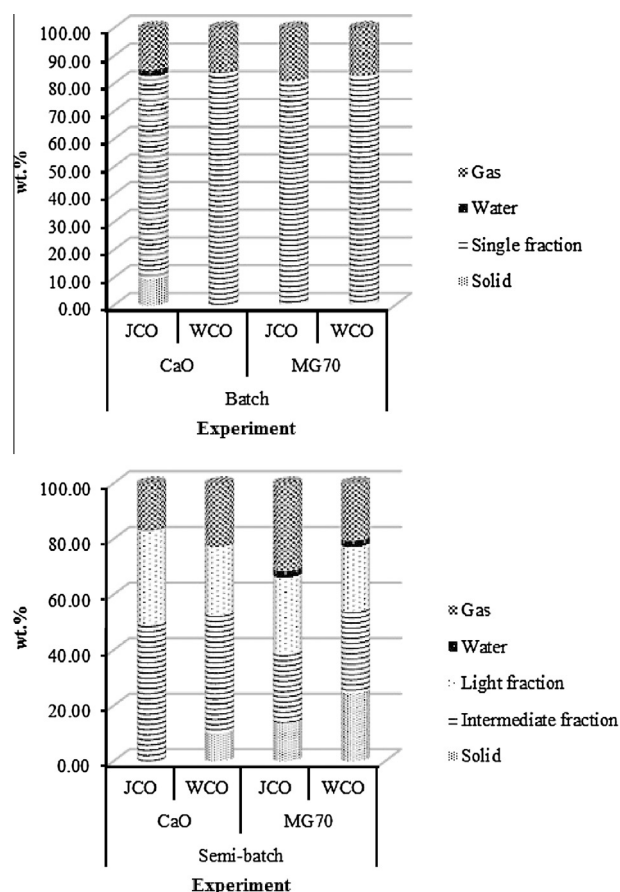

Fig. 2. Yields of the different products obtained in the deoxygenation of JCO and WVO.

the 1680–1750 cm^{-1} range is due to the stretching mode of C=O group contained in compounds such as esters, carboxylic acids and carbonyl compounds. A small peak identified at 1650 cm^{-1} is attributable to the presence of C=C group (e.g. alkene) and in addition a typical band indicating the presence of esters, C—O—C stretching mode band, was identified at 1230 cm^{-1}. FTIR spectroscopy of WCO is reported in Fig. 3. Additional information about the composition, properties and advantages in the use of the raw materials proposed can be found in selected literature (Atabani et al., 2013; Balat, 2011; Gui et al., 2008; Karmakar et al., 2010; No, 2011; Ong et al., 2011; Pandey et al., 2012).

3.3. Characteristics of the liquid products

As it was expected, elemental analysis has also shown that Diesel B7 is a virtually oxygen-free fuel (the amount of oxygen in the Diesel B7 was 1 wt.%), and that after the experiments, the oxygen initially contained in the raw materials was significantly reduced. After batch experiments the oxygen content in liquid products was reduced to an amount ranging between 3 wt.% and 5 wt.%, while the carbon content increased to an amount ranging between 82 wt.% and 84 wt.%. Thus, the atomic ratio H/C remained constant and the atomic ratio O/C decreased, suggesting that the selective removal of oxygen was favoured and carbon atoms were mainly conserved in the liquid products. Consequently, the liquid products have a greater amount of energy, and desired characteristics such as a high heating value are provided. Similar results were obtained for intermediate fractions of semi-batch experiments; however the deoxygenation in light fractions was less advantageous, in fact here the amounts of oxygen content resulted

Table 2
Comparison of the elemental analysis of raw materials, Diesel B7 and liquid products.

| Raw material and products			C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H/C	O/C
WCO			77.94	11.98	0.95	9.13	0.15	0.12
JCO			76.08	11.75	0.20	11.97	0.15	0.16
Diesel B7			84.28	13.37	0.87	1.48	0.16	0.02
Semi-Batch	Intermediate fraction	WCO – MG70	85.95	12.09	0.01	1.95	0.14	0.02
		JCO – MG70	86.39	12.01	0.30	1.30	0.14	0.02
		WCO – CaO	84.53	11.95	0.31	3.21	0.14	0.04
		JCO – CaO	85.43	12.20	0.03	2.34	0.14	0.03
	Light fraction	WCO – MG70	78.42	12.67	0.36	8.55	0.16	0.11
		JCO – MG70	78.27	12.64	1.14	7.96	0.16	0.10
		WCO – CaO	76.99	12.39	0.51	10.11	0.16	0.13
		JCO – CaO	77.37	12.51	0.73	9.39	0.16	0.12
Batch	Single fraction	WCO – MG70	83.94	12.25	0.72	3.09	0.15	0.04
		JCO–MG70	83.00	11.67	1.04	4.29	0.14	0.05
		WCO – CaO	82.00	11.97	0.58	5.45	0.15	0.07
		JCO – CaO	82.84	12.26	0.75	4.15	0.15	0.05
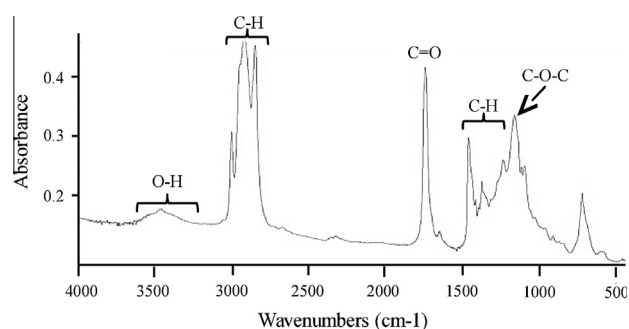
Fig. 3. IR spectra of the WCO.

similar to the raw materials. One of the reasons for the poor deoxygenation of light products can be attributed to the shorter residence time compared to the batch experiments one (light products were continuously condensed and separated in the storage vessel during the process).

The results of gas chromatography–mass spectrometry analyses (reported in Figs. 4 and 5) show in greater detail the chemical composition of Diesel B7 and liquid products. Diesel B7 was composed mainly of hydrocarbons (90%), although complex oxygenates (such as 2-decen-1-ol, (Z)-; 2-methyl-cis-7,8-epoxynonadecane and 2-methyl-1-undecanol) and pentadecanoic acid were identified in 8% and 1% respectively. Possibly, due to the content of biodiesel in the fuel. The hydrocarbons were mainly alkanes (91%), alkenes (7%) and aromatics (2%).

When batch experiments were carried out, CaO provided better results in the deoxygenation of the WCO: the liquid product was composed mainly of hydrocarbons (81%); oxygenated compounds were identified in 16% (including 5% of ketones: 2-heptadecanone and 2-nonadecanone) and acids compounds were only present in amount of 1%. An additional analysis concerning the type of the hydrocarbons in the liquid products showed that hydrocarbons were mainly alkanes (between 81% and 91%), although cycloalkanes (between 2% and 8%), alkenes (between 2% and 6%) and aromatics (between 3% and 6%) were also identified. On the contrary, the use of treated hydrotalcite provided better results than CaO in the deoxygenation of the JCO: the liquid product was composed mainly of hydrocarbons (83%), while the acids compounds were totally converted and an amount of 15% of oxygenated compounds (including a 6% of ketones: 2-heptadecanone, 4-octadecanone and 2-nonadecanone) was identified. CaO allowed the production of an amount of hydrocarbon compounds slightly lower (79%) with a small trace of acid compounds (1%).

After semi-batch experiments, light fractions were characterized having a greater similarity to a gasoline fraction, due to the high percentage of C8–C11 hydrocarbons (between 46% and 65%). They contained a slightly lower amount of hydrocarbons (between 72% and 80%) and a higher amount of oxygenates (between 17% and 22%), such as 2-methyl-1-undecanol and bicyclo[2.1.1]hexan-2-ol, 2-ethenyl and hexadecen-1-ol, trans-9-, compared with the other liquid products. When CaO was used as catalyst it was noticed that an amount of 5% of carboxylic acids (hexanoic, heptanoic and octanoic acids) was present in the light fractions. For these products it
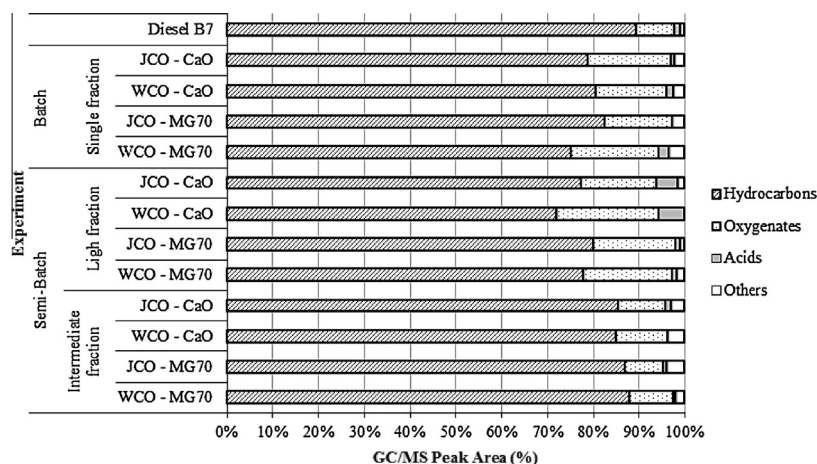
Fig. 4. Results concerning the composition of the liquid products obtained using GC/MS analysis.
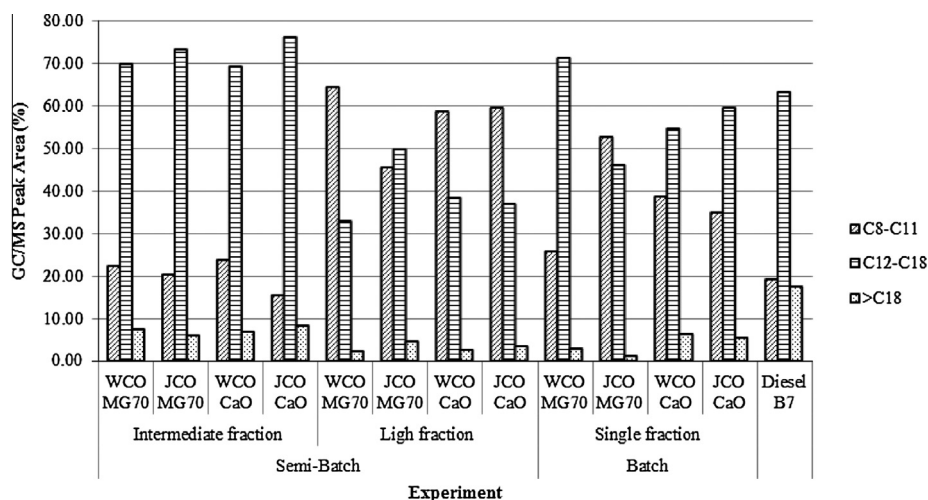
Fig. 5. Composition of hydrocarbon based on the number of carbon atoms per molecule, according to GC/MS analysis.

was also possible to verify that the main type of hydrocarbons was alkanes (between 67% and 76%), although, cycloalkanes (between 3% and 15%), alkenes (between 16% and 24%) and aromatics (between 1% and 3%) were also identified. On the other hand, intermediate fractions were more similar to a diesel due to the high concentration of C12–C18 hydrocarbons (between 69% and 76%). The proportion of hydrocarbons (between 85% and 88%) in the intermediate fractions was closer to the amount of hydrocarbons present in the Diesel B7, while the amount of oxygenated compounds (between 9% and 11%) was slightly lower than in the single fractions obtained in batch experiments, and only a small trace of acid compounds was identified (1%). So as for the other liquid products it was possible to put in evidence that the main type of hydrocarbons was alkanes (between 85% and 87%), even if cycloalkanes (between 1% and 4%), alkenes (between 6% and 8%) and aromatics (between 3% and 6%) were detected.

The most plausible approach for the conversion of the WCO and JCO into hydrocarbons, suggests that initially free fatty acids are released from the portion of the triglyceride corresponding to the glycerol by cleavage of the C—O bonds (Santillan-Jimenez and Crocker, 2012). Hydrolysis or hydrogenation can contribute to this step (Morgan et al., 2012; Tani et al., 2011). Then, involving C—C scissions, the carboxylic and carbonylic groups of the free fatty acids would be removed selectively, producing the hydrocarbon products and carbon dioxide (decarboxylation) or water and carbon monoxide (decarbonylation) as by-products (Lu et al., 2013; Olusola et al., 2010). By an action of acid-base neutralization, treated hydrotalcite and CaO would favour the development of these reaction under the given conditions (Ko et al., 2013).

On the other hand, the boiling range distributions of the liquid products are reported in Fig. 6. The Diesel B7 showed an initial boiling point of 140 °C and the 98% of its mass boils below 420 °C. A significant portion (75 wt.%) of the single fractions obtained in the batch experiments boils within the same temperature range of the Diesel B7 (below 420 °C). It can be noticed that although single fractions do not contain a C8–C11 hydrocarbons as in light fractions, they showed a lower initial boiling point (between 30 °C and 41 °C). As it was expected, light products have showed low boiling ranges compared with the other liquid products: in fact most of the mass of these products (95 wt.%) boils below 360 °C. Under this temperature only a portion, between 54 wt.% and 60 wt.%, of the intermediate fractions boils, reaching values of 64–70 wt.% under 420 °C.

The results of the analyses concerning sulfur, nitrogen, carbon residue and density of liquid fuel products are summarized and compared with the results obtained for the Diesel B7 and the EN 590-2009 diesel standard in Table 3. Encouraging results were obtained for sulfur content analyses of single and intermediate fractions: they showed to be free-sulfur liquid fuels (containing amounts below 10 ppmw) with respect to raw material. The only exception was the product from the treatment of WCO with CaO in batch experiments which has shown a sulfur content higher than the standard. On the other hand, the light products showed the higher amounts of sulfur (between 19 ppmw and 22 ppmw). The lower amounts of nitrogen in liquid products were obtained when WCO was used as raw material. Although the liquid products obtained from JCO showed a higher amount of nitrogen, the results were not largely different compared to the Diesel B7. The amount of carbon residue for the single fractions and intermediate fractions was higher than the amount detected in Diesel B7 and the standard limit, suggesting that an improvement of this feature can be required. Instead of this, light fractions showed better results, because carbon residue amounts were below than the limit required by the standard. Single fractions and intermediate fractions typically exhibited a higher density than the Diesel B7 and the limit of the standard, differently light fractions exhibited a lower density than Diesel B7 and standard reference.

3.4. Characteristics of the solid and gaseous products

The presence of the band corresponding to 3600–3200 region (O—H group) may be due to the presence of moisture in the sample, but clearly, the obtained solid product spectra showed an aliphatic nature, that is indicated by the presence of absorption bands in the 3000–2800 cm^{-1} region and near 1450 cm^{-1}, due to stretching and bending bonds of C—H groups. An absoption band observed at 2350 cm^{-1} arises from the presence of CO_2 while, the bands at 1710 cm^{-1} indicate the presence of ketone compounds (C=O group). The infrared absorption spectra recorded at 850 cm^{-1} is attributable to the presence of inorganic carbonate compounds in the solid products. This band was evident when CaO was used as catalyst. In fact, although $MgCO_3$ can convert into MgO and CO_2 at 400 °C, it can be required about 700 °C to decompose $CaCO_3$ (Tani et al., 2011). As an example IR spectroscopies of solid products obtained in semi-batch experiments of WCO are reported in Fig. 7.

The result of gaseous analysis for experiment of JCO without catalyst reports the following volumetric gas composition: 50% CO_2, 24% CO, 15% ethane, 6% methane, 2% *n*-butane and 3% as sum of propane, propylene, hydrogen and oxygen. The presence
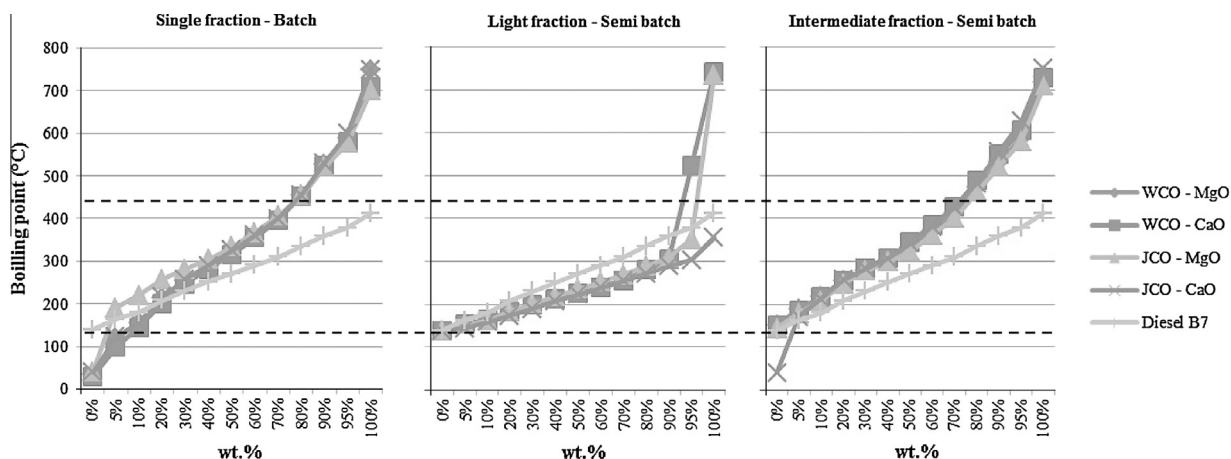
Fig. 6. Boiling point distribution of the liquid fuel products obtained through GC simulated distillation analysis.

Table 3
Fuel properties of the liquid products obtained after the treatment of WCO and JCO.

| Products			Sulfur (ppmw)	Nitrogen (ppmw)	Carbon residue (% m/m)	Density at 15 °C (Km/m³)
Diesel B7			8.40	60.70	<0.01	839.40
EN 590-2009			⩽10.00	n.a.	⩽0.30	820.00 … 845.00
Semi-Batch	Light fraction	WCO – MgO	21.50	10.60	n. a.	801.00
		WCO – CaO	30.30	9.40	0.07	812.40
		JCO – MgO	n.a.	47.90	0.03	807.50
		JCO – CaO	18.70	27.50	<0.01	806.70
	Intermediate fraction	WCO – MgO	5.50	11.50	4.09	895.60
		WCO – CaO	8.20	10.20	3.38	888.30
		JCO – MgO	n.a.	>70.00	4.67	884.60
		JCO – CaO	9.30	79.50	3.11	887.00
Batch	Single fraction	WCO – MgO	7.90	17.90	2.89	877.60
		WCO – CaO	14.00	8.50	2.22	869.00
		JCO – MgO	7.70	91.30	4.01	899.10
		JCO – CaO	n.a.	81.30	2.30	876.00
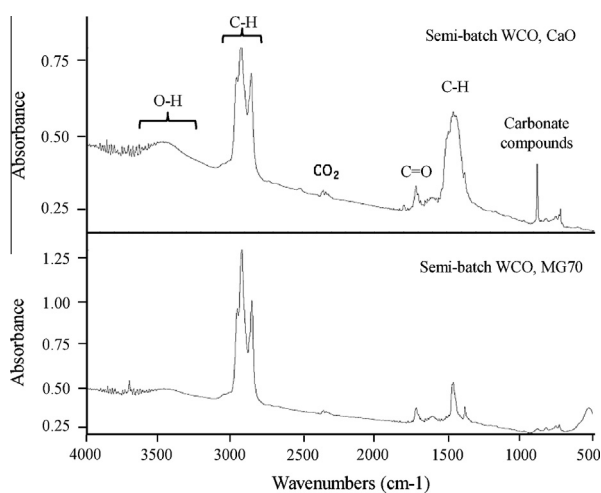
Fig. 7. IR spectroscopies of solid products obtained in semi-batch experiments of WCO.

of oxygen could be ascribable to air contained in the connection line between bag and the instrument before the analysis. Instead, when treated hydrotalcite or CaO were used as catalyst, the total volumetric percentage of CO_2 increases up to 60%, while the amount of CO is reduced to about 13%. The other gases were produced in an amount similar to one without catalyst. The presence of CO_2 and CO as main compounds confirmed that decarboxylation and decarbonylation reactions were promoted.

4. Conclusions

Waste cooking vegetable oil and *J. curcas* oil were successfully deoxygenated and converted into hydrocarbon biofuels in a hydrogen-free atmosphere. Features obtained of the liquid products such as high hydrocarbon composition, boiling range distributions within the Diesel B7 fraction (below 420 °C) and low sulfur content (below 10 ppmw) make of them suitable potential candidates for engines used for transportation. Batch experiments were characterized by providing high yields of liquid products (greater than 80 wt.%) and similar performance of both catalysts used (treated hydrotalcite and CaO). On the contrary, with the exception of the treatment of the Jatropha oil with CaO, it was typical obtain less yields of liquid products after semi-batch experiments. The deoxygenation of light fractions was less advantageous: one of the reasons could be attributed to the shorter residence time. These products were characterized by containing similar amount of oxygen to the raw materials and a greater amount of unsaturated hydrocarbons.

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