

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

4 M.J.A. Romero ^{a,*}, A. Pizzi^b, G. Toscano^b, G. Busca^a, B. Bosio^a, E. Arato^a

5 ^a DICCA, Department of Civil, Chemical and Environmental Engineering, University
6 of Genoa - Via Opera Pia, 15, 16145 Genoa, Italy

7 ^b D3A, Department of Agricultural, Food and Environmental Sciences, Polytechnic
8 University of Marche – Via Brecce Bianche, 10, 60131 Ancona, Italy

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

* Corresponding author:

max.romerorivas@unige.it,

University of Genoa – DICCA, via Opera Pia 15, 16145 Genova Italy

Ph: +39 010 3532560

18 Keywords

19 Bio-waste, deoxygenation, hydrotalcite, CaO, hydrocarbon biofuels

20 **1. INTRODUCTION**

21 The European Union has encouraged the utilization of biofuels in the transport sector through
22 directives such as 2003/30/EC, 2009/28/EC and 2014/94/EU. In this context, the use of waste
23 cooking vegetable oil (WCO) and non-edible oils (e.g. *Jatropha curcas* oil, JCO) play an important
24 role as second generation raw materials not only providing economic and environmental benefits,
25 but also improving the efficiency in the use of waste materials (Fernández et al., 2015; Gui et al.,
26 2008). In addition, the waste cooking oil is a typical food waste fully classified in bio-waste
27 category that is attracting the interest of the scientific community for its possible important role in
28 the recycle and energy recovery processes.

29 In regard to the processes, conventional pyrolysis has been used for many years to obtain a type
30 of bio-oil from biomass, including vegetable oils. However the main drawback of the bio-oil is its
31 high content of oxygenated compounds, in particular carboxylic acids (Sannita et al., 2012). In fact,
32 the pyrolysis of several animal fatty wastes (lamb, poultry and swine) was reported, resulting into
33 bio-oils containing carboxylic acids (C7-C10), alkanes, alkenes and cyclic hydrocarbons (Ben
34 Hassen-Trabelsi et al., 2014). So that, a further improvement should be applied before its use as
35 engine fuel (Ben Hassen-Trabelsi et al., 2014; Bridgwater, 2012). Also, the treatment of WCO and
36 other materials through transesterification and catalytic hydrotreating was reported (Bezergianni et
37 al., 2012; Charpe and Rathod, 2011; Madsen et al., 2011; Mohammadshirazi et al., 2014; Sabudak
38 and Yildiz, 2010). However, the Directive 2009/30/EC has limited the content of biodiesel in fuel
39 mixtures to 7 vol.% maximum, due to the some drawbacks of the fuel such as a low heating value,

40 high-density, and tendency to form deposits in the fuel injection systems (Knothe, 2010). And the
41 catalytic hydrotreating that allows the production of a high quality biofuel mainly composed of
42 hydrocarbons, has the drawback of a high economic cost related mainly to the high amount of
43 hydrogen used in the process (Aatola et al., 2008).

44 As a result of these considerations, alternative processes to convert vegetable oils into
45 hydrocarbon biofuels in a hydrogen-free atmosphere is an important research topic. The conversion
46 of natural oils into hydrocarbons in a hydrogen-free atmosphere using quite inexpensive catalysts
47 such as alkaline earth metal oxides was reported in previous works (Dos Anjos et al., 1983;
48 Romero, 2012; Sannita et al., 2012). The aim is to obtain a selective deoxygenation of natural oils
49 by promoting the reactions of decarboxylation and/or decarbonylation, the oxygen atoms being
50 removed mainly in the form of carbon dioxide and/or carbon monoxide. As a result, a liquid biofuel
51 composed of mainly hydrocarbons with high atomic ratio H/C and low atomic ratio O/C, is
52 expected to be formed. These features would provide a greater amount of energy to the product. In
53 fact, in a previous work we reported for a liquid biofuel obtained in batch experiments encouraging
54 features such as heating value of around 44 MJ/kg and a low viscosity of around 4 cSt (Romero et
55 al., 2014). Literature reported on this topic is still limited (Morgan et al., 2010; Murzin and Mäki-
56 Arvela, 2010; Na et al., 2012; Santillan-Jimenez and Crocker, 2012; Snåre et al., 2006).

57 In the current research a selective deoxygenation promoting the reactions of decarboxylation
58 and/or decarbonylation of WCO and JCO in the absence of hydrogen was evaluated. For the study
59 two approaches were carried out: batch setup (without mass transfer) and semi-batch setup (with
60 purge gas flow). Two types of alkaline earth metal oxides as catalysts were tested: Mg-Al mixed
61 oxides (obtained from treated hydrotalcite) and CaO. In order to assess the possible use of the liquid
62 products as alternative fuels to the diesel derived from a fossil source a complete chemical
63 characterization and measurement of their properties were carried out.

64 **2. MATERIALS AND METHODS**

65 **2.1 Characterization of raw materials and products**

66 The WCO used in this study was collected after typical domestic use, while the JCO was provided
67 by Ancient Green-Fields Pltd. in India. In order to make a comparison with liquid products, starting
68 raw materials and a conventional fossil fuel (Diesel B7 purchased in fuel station) typically were
69 subjected to the same analysis. The elemental composition of WCO, JCO, liquid products and
70 Diesel B7 was determined using an Elemental Analyser (mod. CHN 2400, Perkin Elmer). Infrared
71 spectra for both raw materials and solid products were recorded using a Fourier Transform Infrared
72 Spectrometer (FTIR Nicolet 380, Thermo), equipped with a DTGS detector and using transmission
73 analysis with the help of potassium bromide (KBr) pastilles (100 scans and resolution 2 cm^{-1}). A
74 detailed analysis of the chemical composition of liquid products and Diesel B7 was conducted using
75 a GC/MS (Focus-ISQ ThermoScientific) equipped with TG-SQC column (30 m x 0.25 mm x 0.25
76 μm) and a split injector. TIC signal acquisition mode was used. The starting temperature was
77 calibrated at $70\text{ }^{\circ}\text{C}$ (hold time 5 min), with an initial increase of $5\text{ }^{\circ}\text{C}/\text{min}$ up to $130\text{ }^{\circ}\text{C}$ (hold time 1
78 min), then a second ramp of $5\text{ }^{\circ}\text{C}/\text{min}$ up to $270\text{ }^{\circ}\text{C}$ (hold time 1 min), and a final ramp of 25
79 $^{\circ}\text{C}/\text{min}$ up to $320\text{ }^{\circ}\text{C}$ (hold time 5 min). Also, the properties of the liquid products and Diesel B7
80 (reported in the Table 1) were measured using the similar standard procedures used for petroleum
81 products. On the other hand, The composition of gaseous products was analyzed using a gas
82 chromatograph Chrompack MICRO-GC CP 2002 equipped with a microTCD detector and two
83 parallel columns: the first a PoraPLOT Q column used for analyzing the CO_2 and light
84 hydrocarbons (CH_4 excluded), the second a CP-Molsieve 5A column for analyzing the H_2 , O_2 , CH_4
85 and CO .

86 **2.2 Catalyst**

87 PURAL MG70 (aluminum-magnesium hydroxyl carbonate compound with weight ratio of

88 MgO:Al₂O₃ = 70:30) commonly known as hydrotalcite was supplied by Sasol and CaO was
89 supplied by Sigma Aldrich. In order to obtain Mg-Al oxides, PURAL MG70 was calcinated during
90 5 h at 500 °C under air atmosphere before use. In order to remove any accumulated moisture in the
91 CaO, this catalyst received the same treatment. After treatment the specific surface area of both
92 catalysts was obtained by the Brunauer–Emmett–Teller (BET) isotherm-equation, the results
93 showed a specific surface area of 159 m²/g and 1 m²/g for the treated hydrotalcite and CaO
94 respectively.

95 **2.3 Deoxygenation experiments**

96 The different experiments in the deoxygenation of WCO and JCO were performed in a
97 mechanically stirred 500 mL reactor (mod. 4575A, PARR Instrument Company) operating in two
98 diverse configurations: batch setup (Figure 1A) and semi-batch setup (Figure 1B). In a typical
99 experiment, approximately 180 g of raw material and 3wt.% of catalyst were added to the reactor.
100 Before each experiment, under constant stirring of the mixture, the reactor was purged with
101 nitrogen for 3 min to remove the remaining oxygen. In the batch experiments the reactor was
102 initially pressurized to approximately 3 bar before the heating, depending essentially on the gaseous
103 products produced during the reaction, at the end of the experiments a pressure of around 110 bar
104 was achieved. The temperature was increased up to 400 °C and maintained at this value for 6 h. In
105 semi-batch experiments the pressure was maintained between 15 bar and 20 bar for the whole test
106 releasing the gaseous products evolved during the reaction. In order to avoid losses of condensable
107 products a cooler and a storage vessel were used downstream the semi-batch reactor, this involved
108 the production of a second separated liquid phase by a distillation step of the vapour purge. At the
109 end of the test, the reactor was cooled down by cooling system based on external water circulation
110 until room temperature. In the batch tests the gaseous products were collected in special bags to
111 allow gas chromatography analysis. Liquid products were weighed to determine mass yields then

112 stored in small plastic containers for subsequent analysis.

113 **3. RESULTS AND DISCUSSION**

114 **3.1 Products obtained after experiments**

115 Batch experiments were characterized by high yields of liquid phase (designated as single fraction)
116 respect to semi-batch test. The liquid yields in batch tests were greater than 80 wt.%, the highest
117 yield was obtained in the treatment of the WCO using CaO as catalyst (around 84 wt.%). Typically,
118 in batch experiments a solid product was not produced, only a small amount of solid fraction was
119 identified after the treatment of the JCO using CaO as catalyst. The products distribution of the
120 semi-batch experiments differs significantly from the batch experiments one. Liquid products were
121 obtained in two separate fractions (designated as light fraction and intermediate fraction) so as
122 previously explained. In these tests, regardless of the raw material used, yields of liquid products
123 were significantly higher when CaO was used as catalyst (68 wt.% in the treatment of WCO and 83
124 wt.% in the treatment of JCO). The use of treated hydrotalcite as catalyst resulted in lower yields of
125 liquid products (around 53 wt.%), while the production of gaseous and solid products was promoted
126 and a small amount of water was identified (around 2 wt.%). The presence of water and a high
127 amount of linear olefinic hydrocarbons in the light fractions (reported in the next section) suggested
128 that the decarbonylation reaction was preferred instead to the decarboxylation reaction (Snåre et al.,
129 2007). Results of product yields are reported in the Figure 2.

130 **3.2 Deoxygenation of WCO and JCO**

131 As it is evidenced by elemental analysis (reported in the Table 2) the WCO and JCO have high
132 carbon content (around 77 wt.%), this characteristic makes them optimal alternative raw materials
133 for the production of hydrocarbon biofuels. Nevertheless, it is also evident their high oxygen
134 content (around 9 wt.% and 12 wt.% for the WCO and JCO respectively), likely the main chemical

135 characteristic that differentiates an oil of a hydrocarbon fuel. In fact, many of the limitations of a
136 vegetable oil to be used as fuels, including its high viscosity, are related to the oxygen content. The
137 amount of hydrogen present in the raw materials was around of 12 wt.% and the amount of nitrogen
138 was not greater than 1 wt.%. FTIR spectroscopy (reported in the Figure 3) also provided evidence
139 of the presence of oxygenated compounds in the raw materials. Although, spectra of WCO and
140 JCO have not shown differences, it should be noted that due to thermolytic, oxidative and
141 hydrolytic reactions occurring during frying, WCO can differs from fresh vegetable oil in its
142 chemical composition: WCO is rich in free fatty acids, diglycerides and monoglycerides (Gui et al.,
143 2008; Kee et al., 2010). The C-O-C stretching mode band at ca 1230 cm^{-1} in the spectra of the
144 WCO and JCO is a typical band indicating the presence of esters. While, the complex band in the
145 1680-1750 cm^{-1} range is due to the stretching mode of C=O group contained in compounds such as
146 esters, carboxylic acids and carbonyl compounds. Bands in the 3000-2800 cm^{-1} region and near
147 1450 cm^{-1} region are due to stretching and bending of CH bonds respectively.

148 On the other hand, as it was expected, elemental analysis also showed that Diesel B7 is a
149 virtually oxygen-free fuel (the amount of oxygen in the Diesel B7 was around 1 wt.%), and that
150 after the experiments, the oxygen initially contained in the raw materials was significantly reduced.
151 After batch experiments the oxygen content in liquid products was reduced to an amount ranging
152 between 3 wt.% and 5 wt.%, while the carbon content increased to an amount ranging between 82
153 wt.% and 84 wt.%. Thus, the atomic ratio H/C remained constant and the atomic ratio O/C
154 decreased, suggesting that the selective removal of oxygen was favoured and that carbon atoms are
155 mainly conserved in the liquid products. Consequently, a greater amount of energy is kept in the
156 liquid, and desired characteristics such as a high heating value are provided to the biofuel. Similar
157 results were obtained for intermediate fractions of semi-batch experiments; however the
158 deoxygenation in light fractions was less advantageous, in fact here the amounts of oxygen content
159 resulted similar to the raw materials. One of the reasons for the poor deoxygenation of light

160 products can be attributed to the shorter residence time compared to the batch experiments one
161 (light products were continuously condensed and separated in the storage vessel during the
162 process).

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

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

182 After semi-batch experiments, light fractions were characterized having a greater similarity to a
183 gasoline fraction, due to the high percentage of C8-C11 hydrocarbons (between 46% and 65%).
184 They contained a slightly lower amount of hydrocarbons (between 72% and 80%) and a higher

185 amount of oxygenates (between 17% and 22%), such as 2-methyl-1-undecanol,
186 bicyclo[2.1.1]hexan-2-ol, 2-ethenyl- and hexadecen-1-ol, trans-9-, compared to the other liquid
187 products. When CaO was used as catalyst it was noticed that an amount of around 5% of carboxylic
188 acids (hexanoic, heptanoic and octanoic acids) was present in the light fractions. Also for these
189 products it was also possible to verify that the main type of hydrocarbons was alkanes (between
190 67% and 76%). Although, cycloalkanes (between 3% and 15%), alkenes (between 16% and 24%)
191 and aromatics (between 1% and 3%) were also identified. On the other hand, intermediate fractions
192 were more similar to a diesel due to the high concentration of C12-C18 hydrocarbons (between
193 69% and 76%). The proportion of hydrocarbons (between 85% and 88%) in the intermediate
194 fractions was closer to the amount of hydrocarbons present in the Diesel B7, while the amount of
195 oxygenated compounds (between 9% and 11%) was slightly lower than in the single fractions
196 obtained in batch experiments, and only a small trace of acid compounds was identified (around
197 1%). So as for the other liquid products, it was possible to put in evidence that the main type of
198 hydrocarbons was alkanes (between 85% and 87%), even if cycloalkanes (between 1% and 4%),
199 alkenes (between 6% and 8%) and aromatics (between 3% and 6%) were detected.

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

209 On the other hand, the boiling range distributions of the liquid products are reported in Figure 6.

210 The Diesel B7 showed an initial boiling point of about 140 °C and the 98% of its mass boils below
211 420 °C. A significant portion, about 75 wt.%, of the single fractions obtained in the batch
212 experiments boils within the same temperature range of the Diesel B7 (below 420 °C). It can be
213 noticed that although single fractions do not contain a C8-C11 hydrocarbons as in light fractions,
214 they showed a lower initial boiling point (between 30 °C and 41 °C). As it was expected, light
215 products have showed low boiling ranges compared to the other liquid products: in fact almost the
216 mass of these products (around 95 wt.%) boils below 360 °C. Under this temperature only a
217 portion, between 54 wt.% and 60 wt.%, of the intermediate fractions boils, reaching values of 64 -
218 70 wt.% under 420 °C.

219 The results of the analyses concerning sulfur, nitrogen, carbon residue and density of liquid fuel
220 products are summarized and compared with the results obtained for the Diesel B7 and the EN 590-
221 2009 diesel standard in the Table 3. Encouraging results were obtained for sulphur content analyses
222 of single and intermediate fractions: they showed to be free-sulfur liquid fuels containing amounts
223 below 10 ppmw, regardless of the raw material. The only exception was the product from the
224 treatment of WCO with CaO in batch experiments which has shown a sulfur content higher than the
225 standard. On the other hand, the light products showed the higher amounts of sulfur (between 19
226 ppmw and 22 ppmw). The lower amounts of nitrogen in liquid products were obtained when WCO
227 was used as raw material. Although the liquid products obtained from JCO showed a higher amount
228 of nitrogen, the results were not largely different compared to the Diesel B7. The amount of carbon
229 residue for the single fractions and intermediate fractions was higher than the amount detected in
230 Diesel B7 and the standard limit, suggesting that an improvement of this feature can be required.
231 Instead of this, light fractions showed better results, because carbon residue amounts were below
232 than the limit required by the standard. Single fractions and intermediate fractions typically
233 exhibited a higher density than the Diesel B7 and the limit of the standard, differently light fractions
234 exhibited a lower density than Diesel B7 and standard reference.

235 3.3 Characterization of solid and gaseous products.

236 The obtained solid product spectra showed an aliphatic nature, indicated by the presence of
237 absorption bands in the 3000- 2800 cm^{-1} region and near 1450 cm^{-1} , due to stretching and bending
238 bonds of C-H groups. Bands near 1710 cm^{-1} region are due to the presence of ketone compounds.
239 The infrared absorption spectra of inorganic carbonate compounds were very clear, they were found
240 around 3600-3300 cm^{-1} , 1420 cm^{-1} and 850 cm^{-1} . These bands (mainly at 850 cm^{-1}) were more
241 evident when CaO was used as catalyst. In fact, although MgCO_3 can convert into MgO and CO_2 at
242 400 °C, it can be required about 700 °C to decompose CaCO_3 (Tani et al., 2011). IR spectroscopies
243 of solid products are reported in the Figure 7.

244 The result of gaseous analysis for experiment of JCO without catalyst reports the following
245 volumetric gas composition: 50% CO_2 , 24% CO, 15% ethane, 6% methane, 2% n-butane and 3% as
246 sum of propane, propylene, hydrogen and oxygen. The presence of oxygen could be ascribable to
247 air contained in the connection line between bag and the instrument before the analysis. Instead,
248 when treated hydrotalcite or CaO were used as catalyst, the total volumetric percentage of CO_2
249 increases up to 60%, while the amount of CO is reduced to about 13%. The other gases were
250 produced in a similar amount as when a catalyst was not used. The presence of CO_2 and CO as
251 main compounds confirmed that decarboxylation and decarbonylation reactions were promoted.

252 4. CONCLUSIONS

253 Waste cooking vegetable oil and *Jatropha curcas* oil were successfully deoxygenated and
254 converted into hydrocarbon biofuels in a hydrogen-free atmosphere. Features obtained of the liquid
255 products such as high hydrocarbon composition, boiling range distributions within the Diesel B7
256 fraction (below 420 °C) and low sulfur content (below 10 ppmw) make of them suitable potential
257 candidates for engines used for transportation. Batch experiments were characterized by providing

258 high yields of liquid products (greater than 80 wt.%) and both catalysts showed similar
259 performances. On the contrary, with the exception of the treatment of the Jatropha oil with CaO, it
260 was typical to obtain less yields of liquid products after semi-batch experiments. The deoxygenation
261 of light fractions was less advantageous, one of the reasons attributed to the shorter residence time.
262 These products were characterized by containing similar amounts of oxygen to the raw materials
263 and a greater amount of unsaturated hydrocarbons.

264 **ACKNOWLEDGMENTS**

265 The authors would like to thank Chemical Laboratory of the API Refinery (Ancona) for the
266 measurements of fuel properties reported in § 3.4.3 as well as Prof. M. Rovatti, Dr. Phung T. and
267 Dr. G.Garbarino of DICCA (University of Genoa) for making available their laboratory instruments
268 and for fruitful discussions.

269 **REFERENCES**

- 270 Aatola, H., Larmi, M., Sarjovaara, T., 2008. Hydrotreated Vegetable Oil (HVO) as a Renewable
271 Diesel Fuel: Trade-off between NO_x, Particulate Emission, and Fuel Consumption of a Heavy
272 Duty Engine. SAE International, Helsinki.
- 273 Ben Hassen-Trabelsi, A., Kraiem, T., Naoui, S., Belayouni, H., 2014. Pyrolysis of waste animal fats
274 in a fixed-bed reactor: Production and characterization of bio-oil and bio-char. Waste
275 Management 34, 210-218.
- 276 Bezergianni, S., Kalogianni, A., Dimitriadis, A., 2012. Catalyst evaluation for waste cooking oil
277 hydroprocessing. Fuel 93, 638-641.
- 278 Bridgwater, A., 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass and
279 Bioenergy 38, 68-94.

280 Charpe, T., Rathod, V., 2011. Biodiesel production using waste frying oil. *Waste Management* 31,
281 85-90.

282 Dos Anjos, J., De Araujo Gonzalez, W., Lam, Y., Fretty, R., 1983. Catalytic decomposition of
283 vegetable oil. *Applied Catalysis* 5, 299-308.

284 Fernández, C., Fiori, L., Ramos, M., Pérez, Á., Rodríguez, J., 2015. Supercritical extraction and
285 fractionation of *Jatropha curcas* L. oil for biodiesel production. *The Journal of Supercritical*
286 *Fluids* 97, 100-106.

287 Gui, M., Lee, K., Bhatia, S., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as
288 biodiesel feedstock. *Energy* 33, 1646-1653.

289 Kee, M., Teong, K., Rahman, A., 2010. Homogeneous, heterogeneous and enzymatic catalysis for
290 transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review.
291 *Biotechnology advances* 28, 500-518.

292 Knothe, G., 2010. Biodiesel and renewable diesel: A comparison. *Progress in Energy and*
293 *Combustion Science*, vol. 36, 364-373.

294 Ko, C., Na, J., Kim, J., Yi, K., Park, S., Park, J., et al. Method for making hydrocarbons by using a
295 lipid derived from a biological organism and hydrotalcite. United States Patent 8,513,475, 2013.

296 Lu, J., Behtash, S., Heyden, A., 2013. Theoretical investigation of the reaction mechanism of the
297 decarboxylation and decarbonylation of propanoic acid on Pd(111) model surface. *The Journal*
298 *of Physical Chemistry* 58, 374-381.

299 Madsen, A., Ahmed, E., Christensen, C., Fehrmann, R., Riisager, A., 2011. Hydrodeoxygenation of
300 waste fat for diesel production: study of model feed with Pt/alumina catalyst. *Fuel* 90, 3433-
301 3438.

302 Mohammadshirazi, A., Akram, A., Rafiee, S., Kalhor, E., 2014. Energy and cost analyses of
303 biodiesel production from waste cooking oil. *Renewable and Sustainable Energy Reviews* 33,

304 44-49.

305 Morgan, T., Grubb, D., Santillan-Jimenez, E., Crocker, M., 2010. Conversion of triglycerides to
306 hydrocarbons over supported metal catalysts. *Top Catal* 53, 820-829.

307 Morgan, T., Santillan-Jimenez, E., Harman-Ware, A., Ji, Y, Grubb, D., Crocker, M., 2012. Catalytic
308 deoxygenation of triglycerides to hydrocarbons over supported nickel catalysts. *Chemical*
309 *Engineering Journal* 189, 346-355.

310 Murzin, DY., Mäki-Arvela, P., 2010. Catalytic deoxygenation of fatty acids and their derivatives
311 for the production of renewable diesel. In *Thermochemical conversion of biomass to liquid fuels*
312 *and chemicals: Crocker, RSC Publishing, Cambridge, 496-510.*

313 Na, J., Kyu-Han, J., Oh, Y., Park, J., Jung, T., Han, S., Yoon, H., Chung, S., Kim, J., Ko, C., 2012.
314 Decarboxylation of microalgal oil without hydrogen into hydrocarbon for the production of
315 transportation fuel. *Catalysis Today* 185, 313-317.

316 Olusola, J., Ademiran, M., Oluseyi, A., Ajao, U., 2010. Processing of triglycerides to diesel range
317 hydrocarbon fuel: Easily practicable small scale approach. *Energy & Environment* 21, 1325-
318 1341.

319 Romero, M., 2012. Biofuel production through the technology of catalytic hydrotreating in
320 Lambayeque-Peru. *Proceeding Venice 2012, Fourth International Symposium on Energy from*
321 *Biomass and Waste. CISA publisher. ISBN 978-88-6265-006-9.*

322 Romero, M., Pizzi, A., Toscano, G., Bosio, B., Arato, E., 2014. Study of an innovative process for
323 the production of biofuels using non-edible vegetable oils. *Chemical Engineering Transactions*
324 37, 883-888.

325 Sabudak, T., Yildiz, M., 2010. Biodiesel production from waste frying oils and its quality control.
326 *Waste Management* 30, 799-803.

327 Sannita, E., Aliakbarian, B., Casazza, A., Perego, P., Busca, G., 2012. Medium-temperature

328 conversion of biomass and wastes into liquid products. *Renewable and Sustainable Energy*
329 *Reviews* 16, 6455-6475.

330 Santillan-Jimenez, E., Crocker, M., 2012. Catalytic deoxygenation of fatty acids and their
331 derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. *Journal of Chemical*
332 *Technology and Biotechnology* 87, 1041-1050.

333 Snåre, M., Kubičková, I., Mäki-Arvela, P., Eränen, K., Murzin, D.Y., 2006. Heterogeneous
334 catalytic deoxygenation of stearic acid for production of biodiesel. *Industrial & Engineering*
335 *Chemistry Research* 45. 5708-5715.

336 Snåre, M., Kubičková, I., Mäki-Arvela, P., Eränen, K., Murzin, D.Y., 2007. Continuous
337 deoxygenation of ethyl stearate: a model reaction for production of diesel fuel hydrocarbons, in:
338 Schmidt, S.R., Chandler, B.D., Chen, B., Chen, J.P., Davis, B., James, B., Johnson, T.A.,
339 Malhotra, S.V., McGuire, M.,A., Scott, S., Tanielyan, S., Van Gorp, K. (Eds.), *Catalysis of*
340 *organic reactions*. CRC Press, Florida, pp. 415-425.

341 Tani, H., Hasegawa, T., Shimouchi, M., Asami, K., Fujimoto, K., 2011. Selective catalytic
342 decarboxy-cracking of the triglyceride to middle-distillate hydrocarbon. *Catalysis Today* 164.
343 410-414.

344

345 Table 1. Property analysis performed to the liquid fuel products.

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

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

348 Figure 1. A) Batch reactor B) Semi-batch reactor.

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

350 Figure 3. Spectra of the waste cooking oil and *Jatropha curcas* oil.

351 Figure 4. Results concerning the composition of the liquid products obtained using GC/MS

352 analysis.

353 Figure 5. Composition of hydrocarbon based on the number of carbon atoms per molecule,

354 according to GC/MS analysis.

355 Figure 6. Boiling point distribution of the liquid fuel products obtained through GC simulated

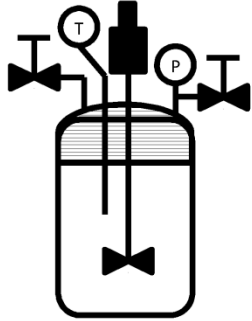
356 distillation analysis.

357 Figure 7. IR spectroscopies of solid products.

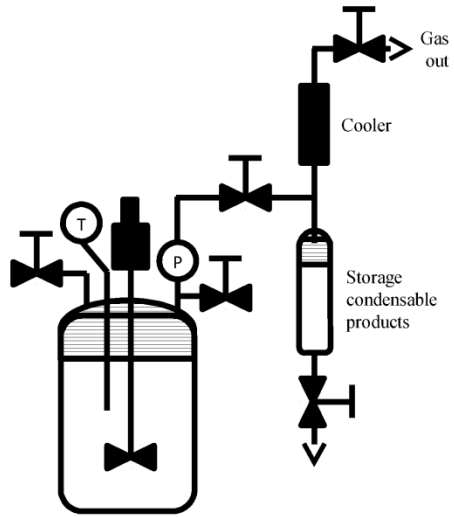
Analysis	Standard method of reference	Instrument	Method
Sulfur content	EN ISO 20846	Antek – MODEL 900 nitrogen/sulfur analyzer	ultraviolet fluorescence method
Nitrogen content	ASTM D 4629	Antek – MODEL 900 nitrogen/sulfur analyzer	syringe/inlet oxidative combustion and chemiluminescence detection
Carbon residue	ASTM D 4530	micro carbon residue tester Alcor MCRT120	micro Conradson method
Density	UNI EN ISO 12185	Mettler Toledo DM40 density meter	oscillating U-tube method
Boiling range distribution	ASTM D 5307	A.C. Analytical Controls combined gas chromatographic system	GC simulated distillation analysis

Product		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
	WCO - MG70	85.95	12.09	0.01	1.95	0.14	0.02
Intermediate fraction	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
Semi- Batch	JCO - CaO	85.43	12.20	0.03	2.34	0.14	0.03
	WCO - MG70	78.42	12.67	0.36	8.55	0.16	0.11
Light fraction	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
	WCO - MG70	83.94	12.25	0.72	3.09	0.15	0.04
Batch Single fraction	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

Product		Sulfur ppmw	Nitrogen ppmw	Carbon residue % m/m	Density at 15 °C Kg/m ³			
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	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	
			Single	WCO - MgO	7.90	17.90	2.89	877.60
				WCO - CaO	14.00	8.50	2.22	869.00
Batch	fraction	JCO - MgO	7.70	91.30	4.01	899.10		
		JCO - CaO	n.a.	81.30	2.30	876.00		
		Diesel B7	8.40	60.70	<0.01	839.40		
		EN 590-2009	≤10.00	n.a.	≤0.30	820.00 ... 845.00		



A



B

