

1 **UPGRADING OF MOIST AGRO-INDUSTRIAL WASTES BY**
2 **HYDROTHERMAL CARBONIZATION**

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10
11 **ABSTRACT**

12
13 This work focuses in the application of the hydrothermal carbonization (HTC)
14 technology as a possible moist agro-industrial waste management treatment. Through
15 this technique, olive mill, canned artichoke and orange wastes (OMW, CAW and OJW,
16 respectively) were carbonized in a lab-scale high pressure reactor at different
17 temperatures (200-250°C) and durations (2, 4, 8 and 24 hours) in order to obtain useful
18 bioenergy feedstocks. The effect of the residence time and temperature on the properties
19 of the bio-char obtained was studied through different characterization techniques.
20 Material and energy balances were also performed to determine the potential energy
21 saving of hydrothermal carbonization versus dry thermal treatments like torrefaction
22 (TF). It is found that the moisture content of HTC-hydro-chars decreases as the
23 temperature and duration increase, which implies that wet biomass can be upgraded and,
24 at the same time, dewatered through HTC. The best results are found for the OMW,
25 whose moisture content decreases from over 70% to less than 30% for the experiments
26 carried out under the more severe conditions. Consequently, it is be possible to reach
27 energy savings over 50% by using HTC instead of TF technologies. Regarding the
28 hydro-char properties, the hydrothermal carbonization of the three organic wastes
29 treated leaded to hydro-chars that present carbon contents and heating values closed to
30 those of brown coal and great energy densifications, depending on the type of waste.
31 Accordingly, it can be concluded that it is feasible to manage moist agro-industrial
32 wastes via HTC, which is ostensibly more efficient than TF in terms of energy
33 consumption.

35 **Key words:** hydrothermal carbonization, agro-industrial wastes, biomass, hydrochar,
36 process conditions, energy.

37

38 1. INTRODUCTION

39

40 The Mediterranean region concentrates an important fraction of wine, olive oil, canned
41 fruits and vegetables industries worldwide. Currently, part of the canning industrial
42 wastes are intended to animal feeding, but a significant fraction ends in the landfill and
43 increases the existing problem of lack of space. Meanwhile, fresh wine and olive mill
44 wastes, which are high polluting by-products, are usually managed through biological
45 treatments such as composting to produce fertilizers. However, this technology needs
46 large processing volumes to treat the large amounts of wastes that are generated every
47 year and, on the other hand, the digestate storage is also a problem because of the
48 associated costs and the vast occupied space. Thus, to decrease such amounts of wastes,
49 it would be interesting to use them as bio-energy feedstocks. Nevertheless, the
50 combustion characteristics of agro-industrial wastes pose some technical and economic
51 challenges and, as a consequence, the use of this kind of wastes as a bioenergy source
52 has not been extended. Agro-industrial wastes present moisture contents that in most
53 cases reach the 80%. As a result, this kind of wastes has low calorific values and
54 difficult and costly handling, transport and storage. Then, to make them suitable for
55 energy production and reach all their potential as alternative energy sources, the
56 aforementioned limitations must be overcome.

57

58 A range of pre-treatment and upgrading technologies have been developed in order to
59 improve the biomass characteristics as bioenergy feedstocks. Among these methods, dry
60 pyrolytic treatments such as torrefaction are being widely evaluated to produce
61 carbonaceous solids from different biomass materials. Torrefaction (TF) is a mild
62 pyrolysis process at temperatures between 200 and 300°C that converts biomass into an
63 upgraded solid that is more suitable for international long-distance shipping for use in
64 centralized heat and power generation [1]. Though, before conversion through dry
65 pyrolysis, wet biomass needs to be actively dried. Therefore, moisture is a limiting
66 factor in the thermal process efficiency due to the great deal of energy required in the
67 pre-drying step of moist wastes.

68

69 To avoid the costly pre-drying step, wet pyrolysis, often called hydrothermal
70 carbonization (HTC), is mentioned as an efficient technology to carbonize moist
71 biomass [2], [3], [4], [5], [6] and [7]. In the HTC process, biomass is heated in a high
72 pressure reactor at temperatures lower than 350°C. As a result, the feedstock is
73 decomposed by a series of simultaneous reactions that occur in liquid phase, including
74 hydrolysis, dehydration, decarboxylation, aromatization and recondensation [7], that
75 lowers both the oxygen and hydrogen content of the feed. The reaction products are
76 gases, mainly carbon dioxide, carbon monoxide, hydrogen, methane, ethane and
77 propene, and a mechanically easy to separate mixture of solid, referred to as hydro-char,
78 and liquid, which contains the solvent used in the HTC reaction and solubilized organic
79 products [5], [7], [8], [9], [10] and [11].

80

81 Through HTC technique, the water that is inherently in green biomass could be used as
82 solvent to pressurize the reaction medium and then, it is not necessary to remove it from
83 the material before to apply this method. During HTC, the phase change from water to
84 steam is largely avoided due to the high pressures involved in the process. Then, the
85 required energy to heat the water is smaller in comparison to that required to evaporate
86 the same mass of water before dry pyrolytic treatments. Additionally, carbonization
87 reactions and disruption of colloidal structures have been shown to improve the
88 dewaterability properties of the hydro-char [12]. As a consequence, the HTC process is
89 expected to have a great potential of energy saving versus dry thermal conversion
90 techniques regarding to the avoided pre-drying step and the improvement in the
91 dewatering properties of the hydro-char compared to those of the raw material.

92 Besides, the ash content of the biomass and its chemical composition determines its
93 application as a bio-fuel. Biomass from agricultural products is rich in alkali metals (Na
94 and K), which melt at combustion temperatures and lead to slagging and fouling
95 deposits on the surfaces of the equipment involved in the process (furnaces, boilers)
96 [13] and [14]. Through HTC, part of the inorganic matter of the raw biomass is found to
97 be transferred to the liquid phase [15]. Consequently, the hydro-char ash content is
98 expected to be lower than that of the bio-char obtained by other pyrolytic techniques,
99 which retains the 100% of the metals contained in the raw biomass [15]. Thus, in terms
100 of energy consumption and ash content, HTC appears as a more energy efficient
101 disposal treatment for moist organic residues and is expected to be beneficial to improve

102 the quality of the hydro-char as bio-energy feedstock compared to dry pyrolytic
103 treatments.

104

105 Several research works related to the conversion of organic wastes via HTC exist in the
106 literature, since the HTC process, first described by Bergius in 1913 [16], was
107 rediscovered by Bobleter in the nineteen-eighties [2] and applied to organic wastes at
108 the University of Applied Sciences Ostwestfalen-Lippe in co-operation with the Max-
109 Planck Institute of Colloids and Interfaces in Golm/Postdam (MPI) [5]. Within the last
110 project, different organic wastes from households and industries were successfully
111 carbonized. The produced hydro-chars were found to maintain approximately 75-80%
112 of the carbon input. In addition, their elemental compositions and calorific values were
113 very similar to brown coals, which make hydro-chars interesting for energy production.
114 In the most recent literature, Lu et al. [17] found that the HTC of solid municipal waste
115 leads to raise the departure energy density between 6.39 and 9.0 times. Xiao et al. [18]
116 studied the HTC of cornstalk and observed that the heating value of the hydro-char was
117 66.8% higher than that for fresh biomass. In a similar way, Román et al. [19] treated
118 walnut shells and sunflowers stems through HTC under different operating conditions to
119 optimize the heating value of the hydro-char and obtained that the heating value
120 increased from 1.5 to 1.75 fold when compared with the natural biomass. Regarding the
121 variables studied, these authors found that temperature and water/biomass ratio were
122 more influential on the hydrocarbonization process than residence time. Meanwhile,
123 Oliveira et al. [6] applied the HTC process to several mixtures of agricultural wastes in
124 order to analyze the hydro-char grade and the mass and energy losses during the
125 treatment. They conclude that the mass and energy recoveries are increased as the waste
126 mixtures are more lignocellulosic while the hydro-char grade improves as the waste
127 mixtures were richer in low molecular weight carbohydrates. Pala et al. [20] compared
128 the fuel, morphological and structural properties and the combustion characteristics of
129 chars produced from grape pomace by both hydrothermal carbonization and
130 torrefaction. These authors found that the char produced by torrefaction was more
131 aromatic in nature than that obtained by HTC. However, HTC led to chars with greater
132 energy density and combustion reactivity, which showed that HTC appears as a
133 promising process for a winery waste having high moisture content.

134

135 Studies indicate that the hydro-char properties and the performance of the products
136 depend on both the experimental conditions and the type of raw material used. Our aim
137 in this work was to upgrade moist agro-industrial wastes typical in the Mediterranean
138 region via hydrothermal carbonization to obtain profitable bio-energy feedstocks. Olive
139 mill, artichoke and orange wastes, which have not been assessed yet, were evaluated
140 because they suppose a concerning problem for the producing companies due to the
141 large volume of wastes involved. The Mediterranean area is the main producer of olive
142 oil and canned artichokes worldwide. In addition, 67% of processed artichokes resulted
143 in wastes. As a consequence, more than $10 \cdot 10^6$ and $7 \cdot 10^5$ tones are produced per year,
144 respectively. On the other hand, the production of orange juice is also important,
145 especially in Spain, and consequently more than $5 \cdot 10^5$ tons of orange waste are
146 produced per year. HTC experiments were carried out under different time and
147 temperature conditions to study their effect on the hydro-char properties and estimate
148 the energy saving of hydrothermal carbonization versus dry thermal treatments, such as
149 torrefaction.

150

151 **2. MATERIALS AND EXPERIMENTAL DESIGN**

152

153 **2.1. Materials**

154

155 Fresh olive mill waste (OMW) was supplied by Extremadura Agricultural and Food
156 Technological Centre during the 2012-2013 campaign. The OMW appearance was
157 typical of sludge. Specimens used for reactions and analyses were taken from below the
158 surface layer of the OMW to gain a homogeneous sample, as the surface of the sludge
159 becomes oxidized. In a similar way, fresh canned artichoke waste (CAW) and fresh
160 orange juice waste (OJW) were collected from different artichoke canning industries
161 and orange juice industries located in the south east of Spain. In this case, both CAW
162 and OJW were milled in a grinder to attain homogeneity and sieved to obtain a particle
163 size between 1 and 3 mm. Moisture and ash content of OMW, CAW and OJW prior
164 HTC experiments were obtained.

165

166 **2.2. HTC experimental procedure**

167

168 Two series of experiments were addressed to study the effect of residence time and
169 temperature on the reaction products. In the first series, OMW was thermally treated at
170 225°C during residence times of 2, 4, 8 and 24 hours. In the second series, OMW, CAW
171 and OJW were processed under 200, 225 and 250°C during 2 hours. The reaction
172 conditions were chosen because they are known to be effective for the hydrothermal
173 degradation of a wide range of lignocellulosic materials (190-240°C) [5, 7, 21]. The
174 reactor pressure was not controlled in the experiments and was kept autogenic with the
175 vapor pressure of water at the corresponding reaction temperature: 1.5 MPa at 200 °C,
176 25 MPa at 225 °C and 40 MPa at 250 °C, as indicated by the pressure gauge attached to
177 the reactor.

178

179 The HTC experiments were conducted in a high pressure lab-scale non-stirred reactor
180 with an internal volume of 1 L from Amar Equipments Pvt. Ltd. The walls of the
181 reactor were heated by an external electrical resistance heater that was controlled using
182 a Proportional-Integral-Derivative (PID) temperature controller. Temperatures inside
183 and at the walls of the reactor were monitored by two K thermocouples. Table 1 sum up
184 the conditions of the different experiments carried out.

185

186 Approximately, 200 g of moist waste was fed into the stainless steel canister of the
187 reactor, and subsequently, this was closed and bolted shut. Note that no solvent apart
188 from the moisture content of wastes was added for the HTC reaction. The band heater
189 was turn on. When the reactor reached the HTC operating temperature, measurement of
190 the residence time began. After the specified residence time period, the heater was turn
191 off and the reactor was cooled overnight until room temperature. Afterwards, the reactor
192 was depressurized by opening the pressure release valve and the gaseous products were
193 collected in Tedlar bags. The solid and liquid products were removed from the canister
194 and separated using filter paper (5-13 µm). After weighing each fraction, hydro-chars
195 were dried in an oven at 105°C, ground into <0.5 mm particles and stored in plastic
196 sealed buckets for the subsequent characterization.

197

198 **2.3. Analytical methods**

199

200 The moisture and ash contents of OMW, CAW and OJW were obtained prior HTC
201 experiments. The moisture content was obtained by calculating the total mass loss of
202 samples placed in an oven model UFP500 from Memmert GmbH at 105°C until no
203 further decrease in weight was observed (typically after 24 hours), accordingly to the
204 European Standard EN 14774-1:2009. The ash content of the specimens was
205 determined by treating the samples in a Muffle serie-74 model 12-R/300 from Heron at
206 550°C during 8 hours under atmospheric conditions, accordingly to the European
207 Standard EN 14775:2009. In addition, a Philips Analytical MagiX-PRO X-ray
208 Fluorescence Spectrometer (XRF) was used to determine the ash composition in terms
209 of weight fractions of the main oxide constituents.

210

211 After the experiments, the gaseous products and the hydro-char were analyzed. A low
212 resolution mass spectrometer Agilent 5975 C fitted with a quadrupole analyzer and
213 coupled to a gas chromatograph Agilent7890A for capillary columns with splitless
214 injection was used to identify the main gases generated in the HTC experiments.
215 Regarding to the hydro-char characterization, moisture and ash contents were measured
216 the same way than those values for the raw materials. Additionally, elemental analysis
217 CHNS and heating value measurements of the three types of wastes and the produced
218 hydro-chars were also carried out. The elemental analysis CHNS was conducted in an
219 Elemental CHNS Microanalyzer Thermo Finningan Flash 1112 Series. Oxygen content
220 was calculated by subtraction of the ash and the CHNS content from the total. Heating
221 values were measured, accordingly to the European Standard EN 14918:2009, using a
222 Leco AC-350 oxygen bomb calorimeter, which had an integral water-measuring and
223 combustion vessel-filling station. Before the samples measurement, the equipment was
224 calibrated using approximately 1g of benzoic acid. Each heating value measurement
225 was conducted at least twice. Approximately 0.7 g of sample was loaded into the
226 apparatus and combusted at 25°C under a pressure of 450 psi of pure oxygen. Results
227 are summarized in Table 1.

228

229 Additionally, a mass balance for each HTC experiment was performed with the data
230 obtained in the weighing of the reaction products. The equations used for the
231 determination of the product yields (%) were:

232

$$\text{Hydro - char Yield (\%)} = \frac{m_{\text{hydro-char}}}{m_{\text{bio}}} \cdot 100 \text{ [Eq. 1]}$$

233

$$\text{Moisture Yield (\%)} = \frac{m_{\text{evap}}}{m_{\text{bio}}} \cdot 100 \text{ [Eq. 2]}$$

234

$$\text{Liquid Yield (\%)} = \frac{m_{\text{liquid}}}{m_{\text{bio}}} \cdot 100 \text{ [Eq. 3]}$$

235

$$\begin{aligned} \text{Gas Yield (\%)} = & 100 - \text{Hydro - char Yield (\%)} - \text{Moisture Yield (\%)} \\ & - \text{Liquid Yield (\%)} \text{ [Eq. 4]} \end{aligned}$$

236

237 where m_{bio} is the mass of moist waste feedstock, $m_{\text{hydro-char}}$ is the mass of hydro-char
238 after filtering the mixture removed from the canister and oven drying, m_{liquid} is the mass
239 of the liquid phase collected after filtering the above mixture; m_{evap} is the mass of water
240 that still remains in the hydro-char after filtering.

241

242 Spill or droplet losses when emptying the reactor and during separation of the output
243 materials were assumed negligible. Furthermore, as the liquid phase consisted of water
244 and solubilized organic products, the hydro-char may also have retained small amounts
245 of volatile products that could have been released during its oven drying. However, for
246 calculation purposes, all mass lost registered during the oven drying of the hydro-char
247 was assumed to be water.

248

249 Finally, HTC was energetically compared with TF in terms of the thermal treatments
250 applied over the water involved in both processes. Fig. 1 shows the schemes evaluated
251 for comparison. The scheme related to the TF process also illustrates the pre-drying
252 treatment. The scheme associated to HTC process also includes the hydro-char drying
253 step.

254

255 The energies considered for comparison were: the energy required to evaporate the
256 moisture content of the wastes (Energy 1); the energy required to heat the water until
257 each experimental temperature (Energy 2), assuming that the steady state during the
258 reaction was closed to the vapor-liquid equilibrium; and the energy required to

259 evaporate the residual moisture of the hydro-chars after being separated from the liquid
260 phase by filtering (Energy 3). As mechanical processes expend much less energy than
261 heating processes, the mechanical energy invest to separate the hydro-char from the
262 liquid phase by filtering was assumed negligible compared to the heating energy and
263 consequently was not considered in the energy balance. In addition, neither the energy
264 required to heat the solid during the drying steps nor the energy invested in the solid
265 during HTC experiments were considered since the first was assumed negligible
266 compared to that required for the evaporation of water and the second was supposed to
267 be similar to that required during TF experiments.

268

269 Energies 1 and 3 were calculated accordingly with equation 5:

270

$$\text{Energy } i = m_i \left[\int_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} C_p(T) dT + \Delta H_{\text{vap}} \right] \quad [\text{eq. 5}]$$

271

272 where m_i is the mass of water in the samples (m_1 : mass of water in wastes, equal to its
273 moisture content; m_3 : mass of water in hydro-chars, equal to the product of the moisture
274 content of the hydro-char and the moisture content of the corresponding waste), $C_p(T)$
275 is the specific heat capacity of water as a function of temperature and ΔH_{vap} is the
276 enthalpy of vaporization of water at 100°C and 101325 Pa, which is 2257 kJ/kg. For this
277 case of study, the calculated integral value was 318 kJ/kg.

278

279 Energy 2 was defined as indicated in Eq. 6:

280

$$\text{Energy } 2 = m_2(H_2 - H_1) \quad [\text{Eq. 6}]$$

281

282 where m_2 is the mass of water in the initial wastes, equal to its moisture content, H_1 is
283 the enthalpy of water at 20°C and 101325 Pa, which is 84 kJ/kg, and H_2 is the enthalpy
284 of water at the operating reaction conditions.

285

286 For comparison, the energy considered in the TF process was Energy 1, which was
287 defined as E_{TF} (Eq.7), while the energy considered in the HTC process was defined
288 accordingly to Eq. 8:

289

$$E_{TF} = \text{Energy 1} \quad [\text{Eq. 7}]$$

290

$$E_{HTC} = \text{Energy 2} + \text{Energy 3} \quad [\text{Eq. 8}]$$

291

292 Additionally, the energy saving that is possible to achieve by using HTC instead of TF
293 is defined as indicated in Eq. 9:

294

$$\text{Energy saving (\%)} = \frac{E_{TF} - E_{HTC}}{E_{TF}} \cdot 100 \quad [\text{Eq. 9}]$$

295

296 3. RESULTS AND DICUSSION

297

298 3.1. Mass balance

299

300 The variation between the reaction products obtained was visibly notable. In the
301 experiments carried out under the softer conditions (low residence time and
302 temperature), the product removed from the canister was a homogenous wet slush
303 constituted by the mixture of hydro-char and liquid phase. As the reactor residence time
304 or temperature increased, there was a well-defined separation between the hydro-char
305 and the liquid phase produced. After being filtered and oven dried, the hydro-chars
306 appearance varied from a brown lignocellulosic to a black coal like material with
307 increasing residence time or temperature.

308

309 Fig. 2 shows the reaction product yields for each experiment carried out. In the first
310 series of experiments, it is observed that the solid yield decreases while the liquid and
311 gas yield increase as the residence time does. In the second series, when the temperature
312 is increased, the tendency is found to be similar to that observed with increasing
313 residence time, and this behavior is independent of the type of waste, as all of them
314 present the same trend. The initial lower mass yields reported are attributed to the
315 combination of the initial feedstock solubilization and the partitioning of the feedstock
316 to the gaseous and liquid products as a result of the reactions involved [22]. As the
317 conditions become more severe, the rate of the initial solids disappearance increases due
318 to the intensification of the reactions involved, and, accordingly to the results obtained
319 by other authors [23] and [24], also probably to the dilution of aqueous extractives

320 present in the solids. During HTC process, the high pressure conditions produced by the
321 steam generated degrade hemicellulose and cellulose into water soluble monomers,
322 which are assumed to primarily consist of sugars that could be absorbed on the
323 remaining porous solid product [24], [25], [26] [27] and [28], thus contributing to the
324 moist hydro-char yield. However, at higher temperatures or residence times those sugars
325 are further degraded [25], thus, resulting in less deposition and in lower recovered mass
326 of the solid product.

327

328 Through GC/MS, it was possible to bear out that the main gaseous products were
329 carbon dioxide and carbon monoxide followed by methane, ethylene and hydrogen for
330 all the experiments carried out, which represent between 35 and 40 % of the total
331 gaseous products generated in the HTC process, depending on the conditions.

332

333 Table 1 shows the moisture content of the raw wastes and the hydro-chars obtained after
334 mechanical dewatering. It can be noted that for the OMW, the moisture content
335 decreases from over 70% to less than 30% for the experiments carried out under the
336 more severe conditions (longer residence time or higher temperature). With increasing
337 residence time or temperature, it was easier to remove the hydro-char from the liquid
338 phase. This observation may be explained as follows. For lignocellulosic biomass,
339 moisture can be absorbed into the cell walls and hydrogen-bonded to the hydroxyl
340 groups of the cell wall components. With the thermal treatment, the breakdown of these
341 hydroxyl groups jointly with the hydrolysis of the hemicellulose and cellulose to
342 monosaccharides occur and these reactions become increasingly significant with an
343 increase in temperature and/or residence time. As a consequence, the solid becomes
344 more hydrophobic under the more severe conditions. Thereby, the reduction in
345 hydrophilic nature of the solid allows physical dewatering to occur easier and, as a
346 result, the moisture of the hydro-chars decreases.

347

348 The reduced moisture content and the improved hydrophobic properties are
349 advantageous in the storage of the hydro-chars. These solids could be stored stably over
350 time, with low risk of biological deterioration, to accommodate seasonal availability.
351 Also, its transportation would be less expensive, because there would be less moisture
352 to transport along with the biomass.

353

354 For CAW and OJW derived hydro-chars, the moisture content drop is less pronounced,
355 what suggests that their hydrophobicity is not as improved as that of the OMW derived
356 hydro-chars. For the CAW, the moisture content decreases from 86% to 84% for the
357 hydro-chars obtained at 200 and 225°C and to 79% for the sample obtained at 250°C.
358 For the OJW, the moisture content only decreases from almost 79% to about 76% for
359 the hydro-chars obtained at 200 and 225°C and 71% for the sample obtained at 250°C.
360 These results agree with those observed by Oliveira et al. [6], who found that,
361 depending on the input material, the decrease in the moisture content after mechanical
362 dewatering could be completely different. Then, hydrothermal carbonization improves
363 the dewatering properties of materials with high moisture content but, in addition of
364 residence time and temperature, the hydro-chars moist degree also depends on the type
365 of waste carbonized.

366
367 3.2. Characterization of the hydro-chars (CHNOS analysis, heating value and ash
368 content and composition)

369
370 Table 1 shows the elemental composition of the raw materials and the hydro-chars
371 obtained after mechanical dewatering and oven drying. By comparing the elemental
372 composition of input and output materials, it is possible to realize about the intensity of
373 the carbonizations process. The more severe were the reaction conditions, the higher the
374 carbon content that remained in the solid phase. For the three wastes studied, it can be
375 observed that the H content keeps almost constant, while the oxygen content is
376 decreased as the residence time or temperature rise and, consequently, the carbon
377 content increases from 56% to 73% for the OMW derived hydro-chars, from 43% to
378 66% for the CAW derived hydro-chars and from 45% to 68% for the OJW derived
379 hydro-chars. From these data, the carbon percentage retained in the solid products was
380 calculated and these values are indicated in Table 1. It is shown that the hydro-chars
381 obtained from OMW and CAW retained between 70% and 50% of the C content in the
382 initial wastes, which decreases as the severity of the reactions increases. Regarding to
383 those obtained from OJW, it is found that these hydro-chars present higher percentages
384 of carbon retained in the solid product, which range from 93% for the softest conditions
385 to 77% for the most aggressive environment. By comparing the effect of residence time
386 and temperature, it is seen that the elemental composition of the hydro-char obtained
387 from OMW at the longest residence time is similar to that of the hydro-char obtained

388 from OMW at the highest temperature. Then, high temperatures compensate the long
389 residence time needed at lower temperatures, since the elemental composition of the
390 hydro-char prepared at 250°C during 2 h matches the hydro-char prepared at 200°C
391 during 24 h. The sulfur content is significantly low for all the samples analyzed, as it is
392 under the detection limit of the elemental microanalyzer used in all cases. The N content
393 increases with longer residence times and higher temperatures, although this tendency is
394 not clear for the hydro-chars obtained from CAW and OJW.

395

396 From the elemental analysis data, H/C and O/C molar ratios were calculated. The results
397 are plotted in the Van Krevelen diagram to illustrate the hydrothermal carbonization
398 process (Fig. 3). It is observed that as the severity of the HTC process increases, both
399 H/C and O/C ratios linearly move from upper right to lower left, which indicates that
400 dehydration and decarboxylation reactions occur during the carbonization, resulting in
401 hydro-chars with more aromatic structures and, consequently, more hydrophobic than
402 the input materials [8]. Nevertheless, the evolution essentially follows the path of a
403 dehydration process, what suggests that significant decarboxylation only appears after
404 plenty of water has been generated [9]. On the other hand, these reactions are more
405 intense as the severity conditions are intensified, accordingly to the greater length of the
406 vector, which starts at the input analysis and ends at the output analysis [4] and [5].

407

408 It is worth mentioning that the carbonization of the OMW is slightly different from the
409 other wastes possibly due to the high organic matter content [29] and [30] and the olive
410 oil that still remains in the olive mill residue, which is mainly constituted by oleic acid.
411 This content in organic matter contributes to increase the molar ratio H/C and as a
412 consequence, the carbonization pathway is over those that CAW and OJW describe,
413 although the pathway direction is the same in all cases. At 200°C, it seems that the
414 organic matter present in the input material remains in the hydro-char obtained.
415 However, at 225°C, there is a significant drop in the H/C molar ratio, which suggests
416 that from this temperature the organic matter is partly removed from the hydro-char,
417 either because they are thermally degraded or transferred to the liquid phase.

418

419 The quality of the carbonaceous solids produced by hydrothermal carbonization could
420 be compared to that of bituminous reach brown coal, lignite or even sub-bituminous
421 coal, depending on the reaction severity and the type of organic waste used. Fig. 3

422 shows that the organic wastes go towards those forms of brown coal via interim steps
423 peat and lignite. Only the hydro-chars produced from OJW nearly reach the region of
424 lignite coal, which is high quality lignite. In the case of CAW, the hydro-chars obtained
425 at 200 and 225°C are typically lignite brown coal, while the one obtained at 250°C
426 reaches the region of bitumen rich brown coal due to the higher H/C molar ratio.
427 Likewise, the hydro-chars obtained from OMW are also typical bitumen-rich brown
428 coal due to the major content of H associated to the olive oil that still remains in the
429 hydro-char after the thermal treatment. Therefore, the coalification degree is relevant to
430 both the HTC conditions and the material used, which agree the results found by other
431 authors [5], [6], [31] and [32].

432

433 The energy density of the raw organic wastes is improved due to the decrease in the
434 number of low energy H/C and O/C bonds and the increase of high energy C–C bonds
435 [31]. Fig. 4 shows the evolution of the low heating value for the two series of
436 experiments carried out. It is observed that the heating value of the hydro-chars
437 produced from OMW is enhanced with the increasing residence time. Similar trends are
438 observed when the type of waste and the effect of time are discussed since the low
439 heating value is improved as the reaction temperature increases, independently of the
440 type of waste. However, as expected from the H/C and O/C molar ratios, this
441 improvement is higher for CAW and OJW. In these cases, the best values almost
442 duplicate the calorific value of the raw wastes. Table 1 indicates the energy
443 densification ratio. In all tests, a significant increase in energy density can be confirmed.
444 It is seen that the residence time and temperature have the same effect over this
445 parameter. In addition, the maximum energy densification ratios are found for the
446 hydro-chars produced from CAW, followed by those produced from OJW and OMW.
447 Thus, for the CAW derived hydro-char prepared under the more severe reaction
448 conditions, the energy densification ratio is 1.87, while for the OJW and OMW derived
449 hydro-chars these values drop until 1.73 and 1.26 (highest temperature) or 1.23 (longest
450 residence time), respectively.

451

452 Fig. 5 illustrates the hydro-chars low heating value and carbon content. It is shown that
453 there is a significant correlation between the carbon content and the heating value of the
454 materials tested, as expected from the literature [5]. The resulting vector connecting
455 input to output material is directed from lower left to upper right and displays the

456 increasing carbon content and heating value as the environmental conditions of the
457 reaction become more severe. The carbon content and the low heating values obtained
458 are typical of brown coal [5]. Therefore, the hydrochars derived from OMW, CAW and
459 OJW might be of interest for energy production and they could partly replace the
460 mineral brown in power energy generation plants.

461

462 Another important property of a fuel material is the ash content and its composition,
463 since alkaline metals, such as K, are involved in reactions that lead to slagging and
464 fouling deposits on the combustor heat transfer surfaces [33] and [34], S and Cl are
465 known to promote corrosion problems on the combustion facilities [35], and Cl can also
466 serve as a source for chlorinated dioxin formation in a furnace, increasing the risk to
467 emit toxic dioxins and furans [35] and [36]. Biomass ashes are rich in such elements.
468 Then, in order to decrease its slagging, fouling, corrosion and Cl-dioxin formation
469 potential, it is imperative to decrease the content of these elements in the final bioenergy
470 product.

471

472 Table 1 indicates the ash content of the hydro-chars produced in each HTC experiment.
473 For the experiments carried out with OMW at 225°C during different residence times it
474 is noted that all the samples have similar ash contents, but these are much lower than the
475 initial ash content of the OMW, due to the transfer of metals to the liquid phase during
476 the HTC reaction. With increasing temperature, the trends observed are different
477 depending on the type of waste. The ash content of the hydro-chars produces from
478 OMW decreases as the temperature rises. However, the values obtained for the hydro-
479 chars produced from CAW and OJW are kept almost constant or even slightly
480 increased, what suggests that the metals that remain in the solid phase could have led to
481 insoluble compounds during the HTC reaction, resulting in higher ash contents.

482

483 Table 2 shows the ash composition obtained through X-ray fluorescence (XRF) analysis
484 and the high heating value of the respective hydro-char. Accordingly to these values,
485 the alkali index of each sample was calculated accordingly to Eq. 10, where Q is the
486 high heating value of the fuel, Y_f^a is the mass fraction of ash in the fuel and $Y_{K_2O}^a$ and
487 $Y_{Na_2O}^a$ are the mass fractions of K_2O and Na_2O in the ash [34].

488

$$\text{Alkali Index} = \frac{Y_f^a (Y_{K_2O}^a + Y_{Na_2O}^a)}{Q} \quad [\text{Eq. 10}]$$

489

490 The alkali index is one of the most significant threshold indicator for fouling and
 491 slagging and expresses the quantity of alkali oxide in the fuel per unit of fuel energy (kg
 492 alkali·GJ⁻¹). Above 0.17 kg alkali GJ⁻¹ fouling is probable and above 0.34 kg GJ⁻¹
 493 fouling is theoretically certain to occur [34].

494

495 The alkali index is found to be 0.66, 1.09 and 0.52 kg alkali·GJ⁻¹, for OMW, CAW and
 496 OJW, respectively. These values are typical from herbaceous and fruit biomass and
 497 imply that fouling per alkali metals during combustion of these agro-industrial wastes
 498 would theoretically occur. Nevertheless, the alkali index decreases when the wastes are
 499 treated by hydro-thermal carbonization as a consequence of the lower K₂O content,
 500 what suggests that the slagging and fouling potential of the hydro-chars is lower than
 501 that of the unreacted wastes. The best results are found for the OMW derived hydro-
 502 chars, whose values are under 0.17 kg alkali GJ⁻¹ and closed to the alkali index of coal
 503 (approximately 0.03 kg alkali GJ⁻¹) [34] when the more severe conditions are applied
 504 during the HTC process. In this sense, the possible slagging and fouling problems
 505 associated to the OMW combustion are improved via HTC. On the other hand, the
 506 alkali index drop obtained for the CAW and OJW derived hydro-chars is less pronounce
 507 and only the hydro-chars obtained from OJW present values under 0.34 kg GJ⁻¹, what
 508 suggests that for these kind of wastes slagging and fouling are more likely to occur.

509

510 Furthermore, oxides and Cl mass balances were carried out. Fig. 6 shows the percentage
 511 of the main oxides detected in the dry hydro-chars prepared. The amount of Si, Mg, P,
 512 Fe and S oxides recovered in the hydro-chars increases with increasing residence time
 513 (Fig. 6a), what suggests that, although part of this compounds are transferred to the
 514 liquid phase, those remaining in the carbonaceous solid lead to insoluble compounds
 515 and contribute to higher oxide yields. Otherwise, most of the Cl is removed from the
 516 solid and shift to the liquid phase as the residence time increases. Similar trends are
 517 observed for the OMW derived hydro-char with increasing temperature (Fig. 6b), with
 518 the exception of Fe₂O₃ and SO₃, which in this case decrease. Regarding to Fig. 6c and
 519 Fig. 6d, it is observed that the trends also depend on the type of waste. The percentage
 520 of K₂O, MgO, SO₃ and Cl recovered in the hydro-chars produced from CAW decreases

521 with increasing temperature, while the MgO and SO₃ yields in the hydro-chars produced
522 from OJW increase. The MgO recovery is 100%. On the other hand, K₂O and Cl do not
523 show a clear trend with increasing temperature.

524

525 3.3. Energy considerations

526

527 Table 3 shows the results obtained in the energy balance. The drying step needed before
528 torrefaction requires 1821 MJ/kg OMW, 2213 MJ/kg OMW and 2045 MJ/kg OMW to
529 entirely evaporate the water in each type of waste. However, if we treat these wastes via
530 HTC, the energy consumption decrease until the values indicated in Table 3 depending
531 on the operating conditions and the type of waste. The lower the moisture content of the
532 hydro-char mechanically dewatered, the lower the total energy invested in the HTC
533 process. Then, the moisture of the hydro-char obtained after mechanical dewatering is a
534 key factor in the energy efficiency of the HTC process.

535

536 It is possible to achieve excellent energy savings by using HTC instead of TF, which are
537 over 50% and 40% when the highest experimental temperature is applied to OMW and
538 CAW, respectively. However, as the hydro-char moisture content drop is less
539 pronounced E_{HTC} increases and, consequently, the energy savings are lower. Thus, in
540 the case of OJW, the energy saving for the highest temperature is lower than 30%,
541 which is not as good as for the other wastes. These results could have been improved if
542 a filter press had been used for the mechanical dewatering of the hydro-chars. Even
543 though, HTC process appears as a more energetically efficient process than TF process
544 for the agro-industrial wastes studied.

545

546 Table 3 also shows the same analysis for OMW with increasing residence time at
547 225°C. It is seen that the energy saving is increased as the residence time is longer due
548 to the reduction in the hydro-char moisture content. However, the effect of time in the
549 hydro-char moisture content is less important than that of temperature, and this is
550 traduced into a minor effect on the energy savings calculated. The energy saving found
551 for the 24 h experiment is closed to that of the experiment carried out at 250°C during 2
552 h. In addition, the energy to maintain the HTC reaction during longer residence times
553 would be also higher. Then, no significant holding time over 2 h is needed to achieve
554 better results.

555

556 **4. CONCLUSIONS**

557

558 Accordingly to the results obtained, it is concluded that the organic wastes produced in
559 olive mill, canned artichoke and orange juice industries could be transform into
560 profitable bioenergy feedstocks similar to brown coal by employing the hydrothermal
561 carbonization technology. The HTC process allows upgrading and dewatering these
562 substrates, which initially had moisture contents over 70%. The carbon content, heating
563 value, ash content and composition and the dewatering properties are improved by
564 increasing the residence time and the reaction temperature. Additionally, these
565 properties are also found to be affected by the type of organic waste carbonized. The
566 dewatering properties are more improved for the OMW derived hydro-chars, and
567 consequently, it was possible to achieve better energy savings when comparing the HTC
568 process of OMW with the torrefaction.

569

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577

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Tables

Table 1. Ultimate analysis (wt.% dry basis), moisture content (wt.%), ash content (wt.% dry basis), C-content retained in the solid phase (%) and energy densification ratio.

Sample Id.	Ultimate Analysis (wt.% d.b.)					Moisture content (wt.%)	Ash content (wt.% d.b.)	C-solid (%)	Energy densification ratio
	C	H	S	N	O				
OMW	56.11	7.39	< 0.1	0.75	30.24	70.71	5.51	100	-
CAW	43.17	5.96	< 0.1	2.95	41.46	85.95	6.46	100	-
OJW	45.37	6.20	< 0.1	1.34	43.75	79.41	3.34	100	-
OMW (225°C, 2h)	66.05	7.96	< 0.1	1.43	22.30	55.10	2.26	70	1.12
OMW (225°C, 4h)	68.24	8.18	< 0.1	1.47	19.92	52.16	2.19	69	1.18
OMW (225°C, 8h)	70.10	7.97	< 0.1	1.60	18.26	45.10	2.07	67	1.20
OMW (225°C, 24h)	73.01	8.33	< 0.1	1.72	14.76	29.63	2.17	61	1.26
OMW (200°C, 2h)	63.25	8.20	< 0.1	1.12	24.08	59.51	3.35	70	1.03
OMW (250°C, 2h)	71.85	8.27	< 0.1	1.66	16.27	27.13	1.95	58	1.23
CAW (200°C, 2h)	55.52	5.77	< 0.1	3.52	28.14	83.67	7.06	71	1.54
CAW (225°C, 2h)	55.96	5.70	< 0.1	3.31	27.79	83.76	6.96	65	1.61
CAW (250°C, 2h)	66.24	5.75	< 0.1	4.52	16.15	78.77	7.35	50	1.87
OJW (200°C, 2h)	62.93	5.49	< 0.1	1.26	26.32	76.68	4.01	93	1.48
OJW (225°C, 2h)	64.92	5.40	< 0.1	1.25	23.98	76.44	4.45	89	1.58
OJW (250°C, 2h)	68.19	5.36	< 0.1	1.35	21.05	70.60	4.05	77	1.73

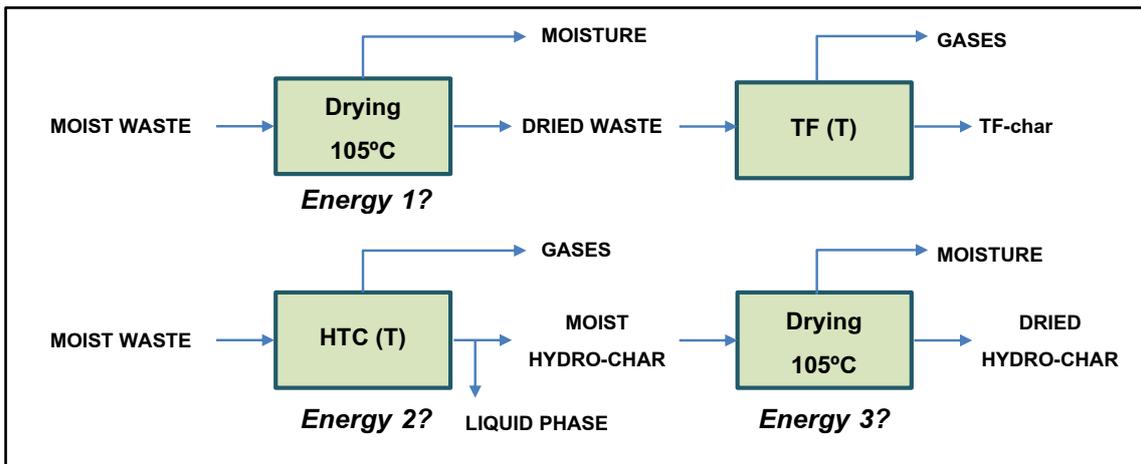
Table 2. Ash composition (w.t.%) and alkali index of the hydro-chars produced.

Sample	%									HHV (MJ/kg)	Alkali index (kg alkali/GJ)
	K ₂ O	SiO ₂	MgO	P ₂ O ₅	CaO	Fe ₂ O ₃	SO ₃	Na ₂ O	Cl		
OMW	31.90	27.75	18.43	6.83	5.52	1.64	1.10	n.d.	1.40	26.43	0.66
OMW (225°C, 2h)	28.11	2.83	2.47	4.76	n.d.	0.90	3.03	n.d.	0.72	29.63	0.21
OMW (225°C, 4h)	22.17	2.74	2.05	3.30	n.d.	0.39	3.05	n.d.	0.38	31.04	0.16
OMW (225°C, 8h)	17.48	5.97	3.22	13.15	0.24	0.97	n.d.	n.d.	0.08	31.57	0.11
OMW (225°C, 24h)	11.81	3.66	3.52	15.88	7.83	1.54	4.70	n.d.	n.d.	33.21	0.08
OMW (200°C, 2h)	32.82	4.52	0.99	n.d.	n.d.	0.67	1.98	n.d.	1.43	27.45	0.40
OMW (250°C, 2h)	12.59	3.01	3.47	10.56	n.d.	1.25	2.39	n.d.	0.14	32.50	0.07
CAW	25.64	n.d.	3.52	n.d.	n.d.	n.d.	1.35	2.62	4.08	16.80	1.09
CAW (200°C, 2h)	23.95	n.d.	3.20	n.d.	n.d.	n.d.	1.42	4.44	5.21	25.09	0.80
CAW (225°C, 2h)	25.70	n.d.	2.42	n.d.	n.d.	n.d.	1.56	1.99	4.02	26.17	0.74
CAW (250°C, 2h)	20.73	n.d.	3.54	n.d.	n.d.	n.d.	2.01	n.d.	6.46	30.26	0.50
OJW	28.99	n.d.	2.46	n.d.	n.d.	0.13	2.70	n.d.	1.16	18.21	0.53
OJW (200°C, 2h)	8.08	n.d.	0.87	n.d.	n.d.	n.d.	1.13	n.d.	0.10	26.78	0.12
OJW (225°C, 2h)	16.21	n.d.	3.06	n.d.	n.d.	n.d.	2.67	n.d.	0.44	27.73	0.26
OJW (250°C, 2h)	12.08	n.d.	4.10	0.41	n.d.	n.d.	4.19	n.d.	0.26	30.35	0.16

Table 3. Energy estimation to evaluate the TF and HTC processes in terms of the thermal treatments applied to the water contained in the wastes.

Type of waste	E _{TF} (kJ/kg waste)	Time (h)	T _{HTC} (°C)	H ₂ (kJ/kg water)	Energy 2 (kJ/kg waste)	Energy 3 (kJ/kg waste)	E _{HTC} (kJ/kg waste)	Energy Saving (%)
OMW	1821	2	225	971	627	554	1181	35.1
		4	225	971	627	465	1093	40.0
		8	225	971	627	330	958	47.4
		24	225	971	627	150	777	57.3
		2	200	855	545	698	1243	31.7
		2	250	1092	713	126	839	53.9
		CAW	2213	2	200	855	663	1029
2	225			971	763	935	1698	23.3
2	250			1092	867	438	1305	41.0
OJW	2045	2	200	855	612	1131	1744	13.04
		2	225	971	705	994	1698	13.05
		2	250	1092	801	655	1456	28.8

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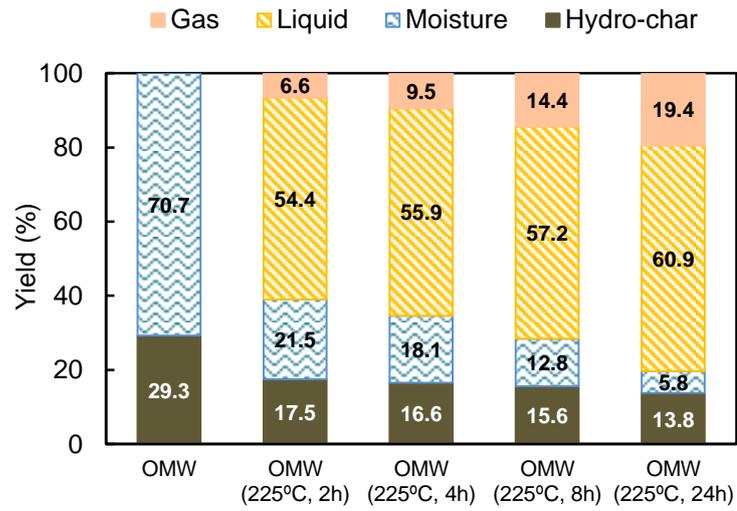


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Fig. 1. TF and HTC schemes to compare the energy requirements in terms of the thermal treatment of the water contained in wastes.

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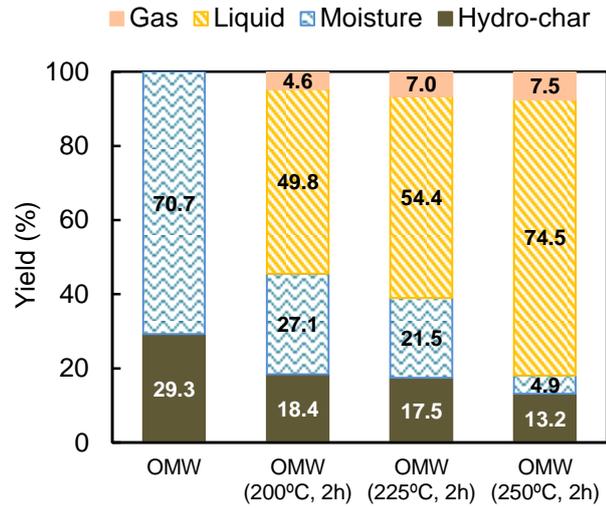
(a)



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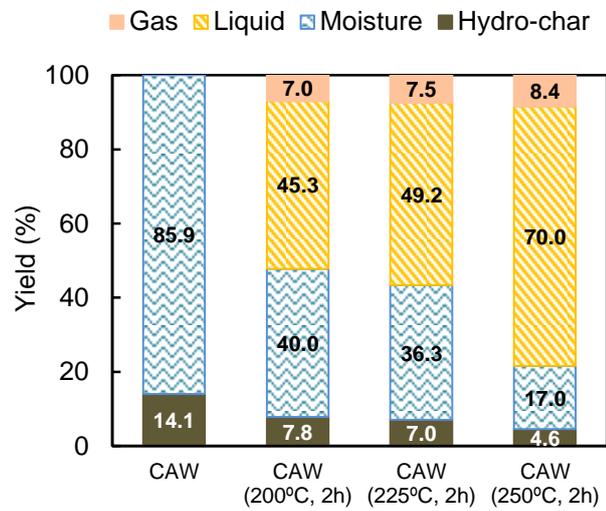
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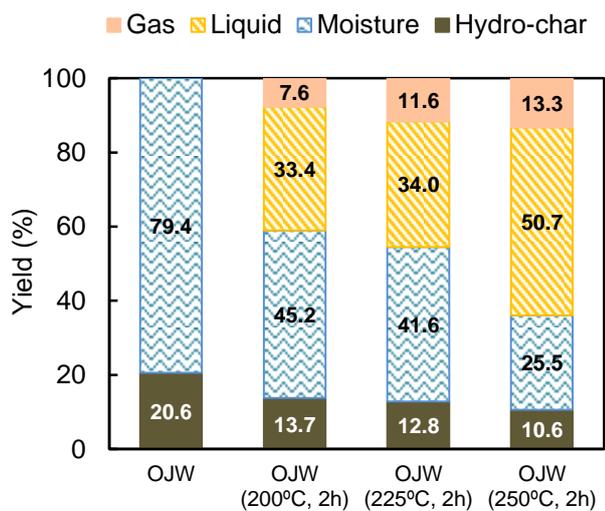
(c)



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d)



8

9

10 Fig. 2. Reaction product yields (w.t.%) of wastes and hydro-chars from (a) OMW at
11 225°C and different residence times. (b) OMW at different temperatures during 2 h. (c)
12 CAW at different temperatures during 2 h. (d) OJW at different temperatures during 2 h.

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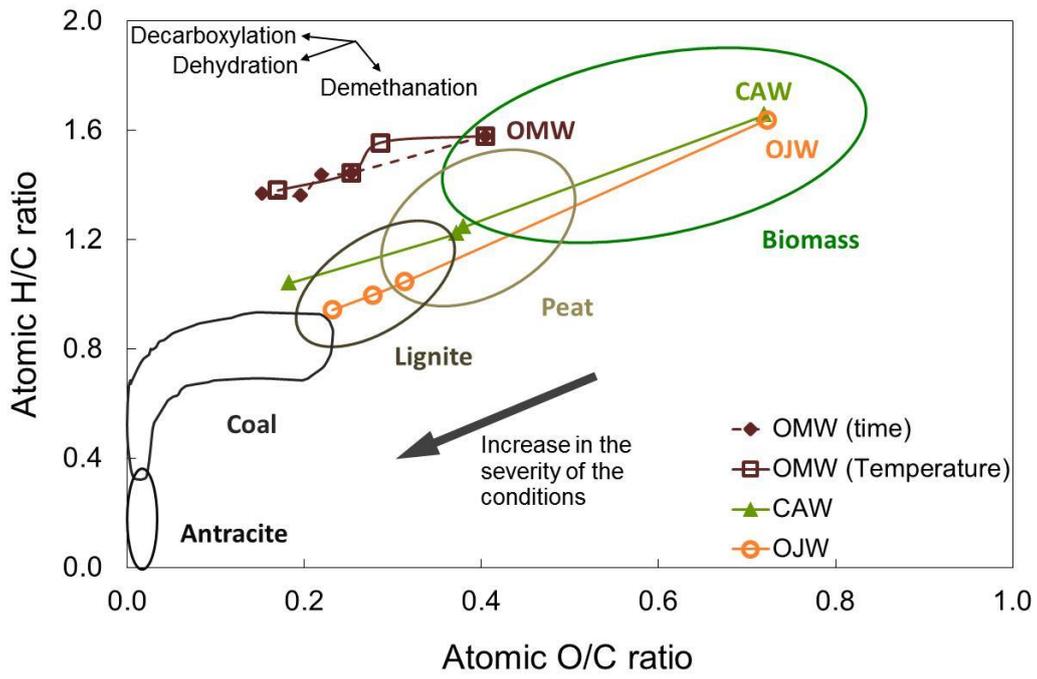
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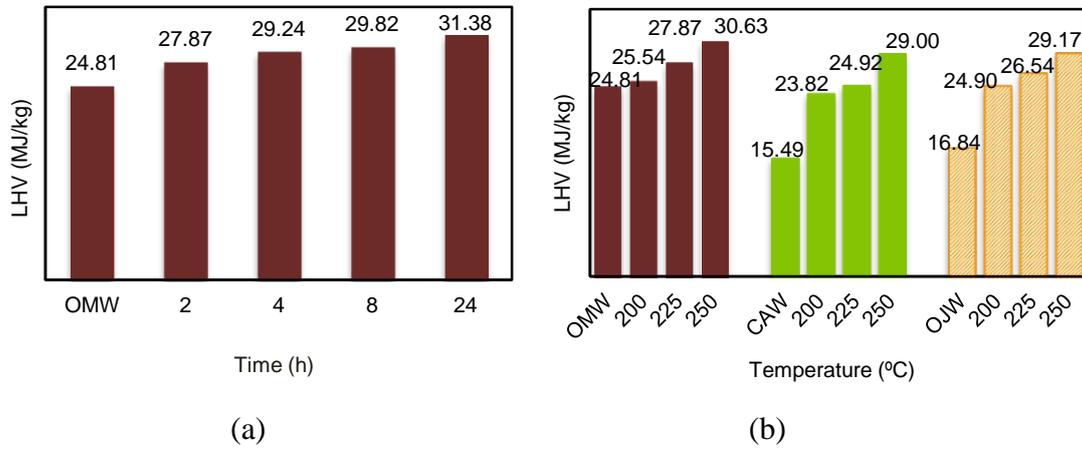
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Fig. 3. Van Krevelen diagram for the solid fuel production from OMW, CAW and OJW through hydrothermal carbonization.

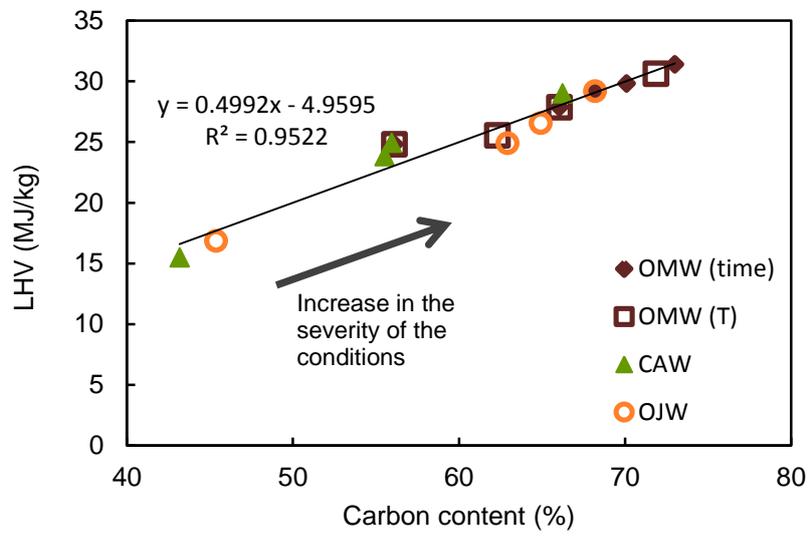
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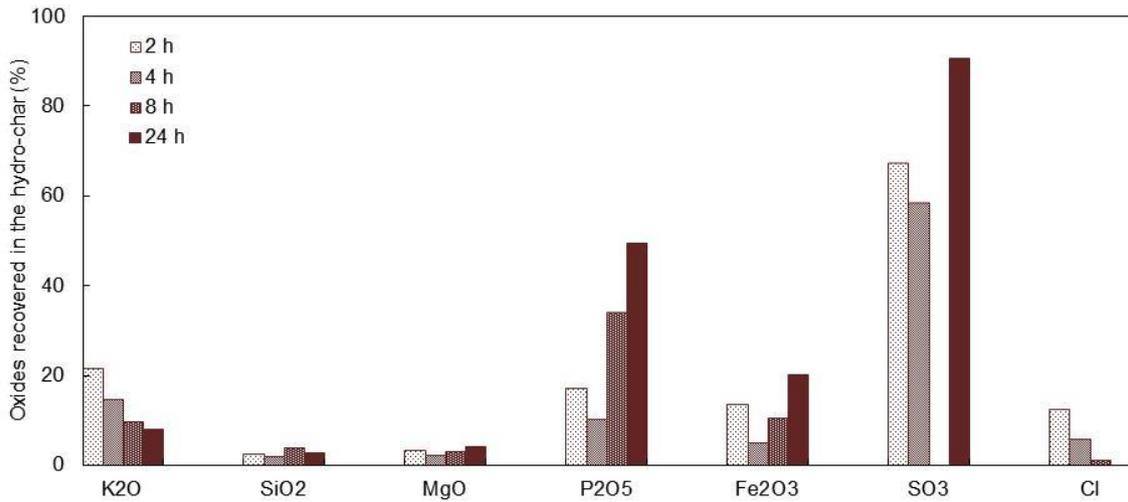
Fig. 4. Low heating value (MJ/kg) of the hydro-chars obtained (a) from OMW at 225°C and different residence times. (b) OMW, CAW and OJW at different temperatures during 2 h.

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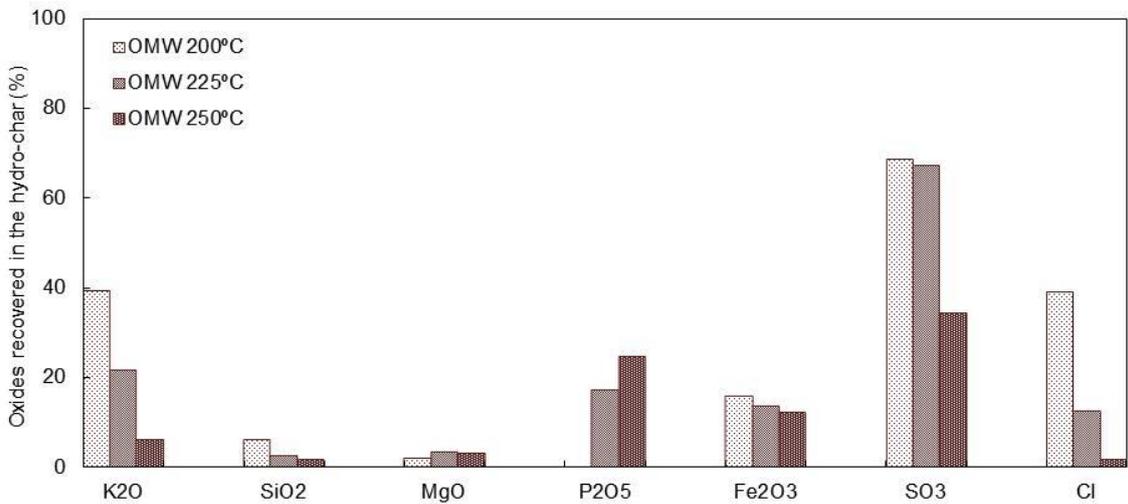


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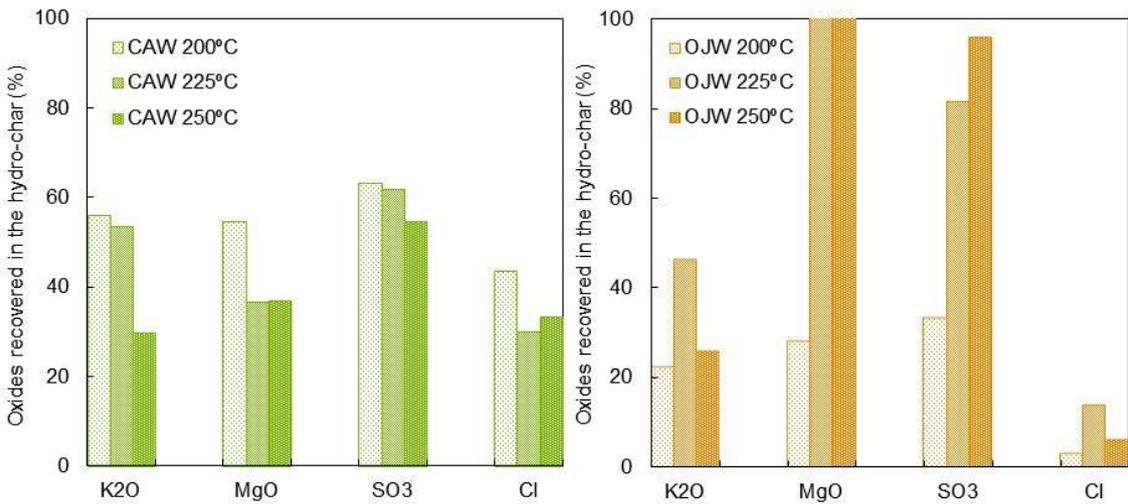
Fig. 5. Low heating value and carbon content diagram representing the hydro-chars obtained from OMW, CAW and OJW under different experimental conditions (OMW(time): 225°C during 2, 4, 8 and 24 hours; OMW (T), CAW and OJW: 200, 225 and 250°C during 2 hours).



(a)



(b)



(c)

(d)

Fig. 6. Percentage of oxides retained by the hydro-chars obtained from (a) OMW at 225°C and different residence times. (b) OMW, (c) CAW and (d) OJW at different temperatures during 2 h.