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Modelling the production of solid and liquid products from the hydrothermal carbonisation of two biomasses

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2 **Modelling the production of solid and liquid**
3 **products from the hydrothermal**
4 **carbonisation of two biomasses**

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15 **Abstract**

16 This work focuses on the hydrothermal carbonisation (HTC) of two bioresources,
17 olive stones (OS) and beechwood (BW), within the ranges of temperature and time of
18 160-240°C and 1-24 hours, respectively. The final pH of the liquid phase, the yields of
19 solid and liquid, and the nature and amounts of a broad range of molecules (two furanic
20 and nine phenolic compounds) were produced and studied. The experimental results
21 obtained were discussed in relation to predictive equations developed in a previous
22 study (Borrero-López et al., 2018) regarding the cellulose, hemicellulose and lignin
23 contents of the two bioresources. Adequate fits were obtained for the pH of the liquid
24 phase (9-11% overestimation for OS and BW, respectively), the yields of solid (7-8%
25 error for OS and BW, respectively) and liquid (6-16% error for OS and BW,
26 respectively) and the production of 5-hydroxymethylfurfural and several phenolic
27 compounds, while some discrepancies for the production of furfural and a few phenolic
28 compounds were observed but were properly analysed and discussed.

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35 **Keywords:** olive stones; beechwood; modelling; hydrothermal carbonization; furfural,
36 phenolics.

37

38 **1. Introduction**

39 Hydrothermal carbonisation (HTC) is attracting increasing interest because of the
40 mild pressure and temperature conditions involved in this process (Liu et al., 2012), the
41 production of valuable products in the aqueous phase (Guardia et al., 2019), and the
42 possibility of using the hydrochars obtained as precursors of new carbonaceous (Yahia
43 et al., 2019) or oxide materials (Kavil et al., 2019). Hydrothermal carbonisation of
44 biomass is indeed a simple process in which bioresources are treated in hot pressurised
45 water in an autoclave at moderate temperatures, within the typical range of 140-240°C.
46 Then, hydrothermal reactions occur at the medium pressures generated by water
47 evaporation in the hermetically sealed autoclave (Borrero-López et al., 2018). The
48 hydrochars produced when biomass was subjected to HTC have been used for soil
49 conditioning (Bento et al., 2019), development of lubricants (Huang et al., 2019),
50 stabilisation of Pickering emulsions (Xie et al., 2018), conversion to solid fuels (Lucian
51 et al., 2018; Ma et al., 2018; Zhao et al., 2018), adsorbents (Lei et al., 2018), and metal
52 detection (Liu et al., 2012).

53 In addition to hydrochar, the release of many valuable products from the main
54 components of biomass, i.e., from hemicellulose, cellulose and lignin, is achieved
55 through bond cleavage and self-catalysed reactions due to the presence of water
56 (Borrero-López et al., 2017). Materials scientists often neglect the liquid phase although
57 various phenolic compounds (Borrero-López et al., 2018), as well as furfural (FU) and
58 5-hydroxymethyl furfural (5-HMF) (Grote et al., 2018; Wataniyakul et al., 2018), can
59 be obtained, making this phase a high-added value, cheap and safe source of chemicals
60 (Borrero-López et al., 2018; Nakason et al., 2018; Zhao et al., 2018). However, products
61 separation is still difficult and therefore, restricting production to a limited number of
62 product by catalysis (Sun et al., 2018) seems a very interesting strategy. Moreover, the

63 importance and applications of FU and 5-HMF have been ubiquitously highlighted
64 (Borrero-López et al., 2017). Among the phenolic compounds, some interesting
65 chemicals such as vanillin and syringaldehyde have also been found (Rodrigues Pinto et
66 al., 2012, Borrero-López et al., 2017). Others, such as acetosyringone, guaiacylacetone,
67 guaiacol or syringol, have also been produced, all of them having noteworthy
68 antioxidant and antimicrobial activity (Conde et al., 2011; Gullón et al., 2017). Finally,
69 the production of gases at higher temperatures, usually catalysed by acids and/or metal,
70 has also been extensively studied (Salimi et al., 2018). In conclusion, HTC undoubtedly
71 is an outstanding biorefinery tool for converting lignocellulosic resources into valuable,
72 useful solid, liquid and gaseous products.

73 On the other hand, efforts have focused on understanding the kinetics of the involved
74 transformation mechanisms. Thus, Keiller et al. (2019) stated that hydrothermal
75 carbonisation may occur through direct reactions, often of first order, whereas others
76 have discussed the possibility of intermediates and side products (Borrero-López et al.,
77 2017; Gallifuoco et al., 2018; Gallifuoco and Di Giacomo, 2018; Zhao et al., 2018). The
78 modelling of HTC products was carried out by applied statistical methods (Gallifuoco
79 and Di Giacomo, 2018), response surface methodology (Heidari et al. (2019) and Zhao
80 et al., 2018) and process simulators (Gómez et al. (2019)). Overall, these studies require
81 powerful calculation tools in addition to the development of sophisticated models, due
82 to the complexity of kinetics (Marcotullio, 2011), as well as accurate experimental and
83 analytical studies. In a former work, the solid and liquid products obtained when
84 cellulose, hemicellulose and lignin were subjected to HTC have been meticulously
85 studied. Various models were presented that were able to predict solid and liquid yields,
86 the final pH of the liquid phase and the concentrations of FU, 5-HMF and several
87 phenolic products (Borrero-López et al., 2018).

88 The objective of the present study is to test the validity of these models when the
89 entire lignocellulosic biomass, instead of its independent components, is submitted to
90 HTC. To this end, olive stones (OS) (*Olea europaea*) and beechwood (BW) (*Fagus*
91 *sylvatica*) have been subjected to HTC at temperatures ranging from 140 to 240°C and
92 durations ranging from 1 to 24 hours. The severity factor, which is a useful tool for
93 understanding HTC, was used to simultaneously account for the effects of time and
94 temperature. The experimental data were finally compared to the predictions of the
95 models.

96 **2. Materials and Methods**

97 **2.1. Raw materials**

98 The cellulose, hemicellulose and lignin contents of OS and BW were determined
99 according to the Tappi standards (T 264, T 203 and T 222, respectively). Each analysis
100 was repeated three times and the average error was lower than 3%. More details can be
101 found elsewhere (Borrero-López et al., 2017).

102 Olive stones (OS) were purchased at a local factory in Gabès (Tunisia) and ground at
103 a size of less than 2 mm. The cellulose, hemicellulose and lignin contents were 40.5,
104 21.7 and 29.9 wt.%, respectively (Borrero-López et al., 2017). Beechwood (BW) was
105 cut and milled and the resultant chips of an average size of less than 1 mm were
106 recovered by using a powder collector. The corresponding cellulose, hemicellulose and
107 lignin contents were 43.6, 33.5 and 22.1 wt.%, respectively.

108 All compounds used for identification and quantification of phenolic and furan
109 compounds using HPLC equipment were analytical grade and purchased from Sigma-
110 Aldrich (Steinheim, Germany).

111

112 2.2. Hydrothermal carbonisation

113 Hydrothermal carbonisation tests were performed according to the conditions
114 established elsewhere (Borrero-López et al., 2018). In brief, 2 g of the selected biomass
115 were introduced into a glass vial with 16 g of distilled water. The vial was then placed
116 in a 100 mL Teflon-lined autoclave, sealed and placed in a preheated oven at the desired
117 temperature (140-240°C) for times ranging from 1 to 24h.

118 The combined effect of time and temperature on the process was taken into account
119 through the severity factor, $\log R_0$, (Overend and Chornet, 1987), as follows:

$$120 \quad \log R_0 = \log \left[t \cdot \exp \left(\frac{T-100}{\omega} \right) \right] \quad (1)$$

121 where the higher importance of temperature, T (°C), with respect to time, t (min), can be
122 observed in the exponential dependence of R_0 on T and its linear dependence on t .
123 Regarding the empirical parameter ω , a value of 14.75 has been traditionally used with
124 lignocellulosic materials. However, it has been modified as needed to accommodate a
125 variety of bioresources and temperatures (Kim et al., 2014; Ko et al., 2015). Table 1
126 shows the experimental conditions and consequent severity factors used for OS and
127 BW.

128

129 **Table 1.** Performed tests and corresponding values of severity ($\log R_0$).

| Olive Stones | | Beechwood | |
|-----------------|------------|-----------------|------------|
| Test conditions | $\log R_0$ | Test conditions | $\log R_0$ |
| 160°C, 6h | 4.32 | 160°C, 1h | 3.54 |
| 170°C, 2h | 4.14 | 160°C, 2h | 3.85 |
| 170°C, 4h | 4.44 | 160°C, 3h | 4.02 |
| 170°C, 6h | 4.62 | 160°C, 6h | 4.32 |
| 180°C, 2h | 4.43 | 160°C, 12h | 4.62 |
| 180°C, 4h | 4.74 | 160°C, 24h | 4.92 |
| 180°C, 6h | 4.91 | 180°C, 1h | 4.13 |
| 190°C, 4h | 5.03 | 180°C, 2h | 4.43 |
| 190°C, 6h | 5.21 | 180°C, 3h | 4.61 |
| 190°C, 8h | 5.33 | 180°C, 6h | 4.91 |
| 200°C, 2h | 5.02 | 180°C, 12h | 5.21 |
| 200°C, 4h | 5.32 | 180°C, 24h | 5.51 |
| 200°C, 6h | 5.50 | 200°C, 1h | 4.72 |
| 220°C, 2h | 5.61 | 200°C, 2h | 5.02 |
| 240°C, 1h | 5.90 | 200°C, 3h | 5.20 |
| 240°C, 2h | 6.20 | 200°C, 6h | 5.50 |
| | | 200°C, 12h | 5.80 |
| | | 200°C, 24h | 6.10 |

130

131 **2.3. Liquid/Solid separation**

132 Upon completion of the HTC, the brownish solid, or hydrochar, was separated from
 133 the liquid by vacuum filtration and completely dried in a vacuum oven, where it was
 134 held for 6h at 60°C before being weighed and stored. After separation, the liquid was
 135 also weighed and refrigerated to avoid further reactions until analysis.

136 **2.4. Chromatographic analysis**

137 The quantitative analysis of the main compounds in the liquid phase was carried out
 138 using an Ultimate 3000 high-performance liquid chromatograph (Thermo Fisher
 139 Scientific, Germany), coupled to an automatic sampler and with both diode array and
 140 fluorescence detectors. Two different columns were used for the appropriate separation
 141 and quantification of furan and phenolic compounds: Hypersyl Green PAH (Thermo

142 Fisher Scientific, Germany) and Pinnacle DB BiPh 5 μm (Restek, USA), respectively.
143 The quantification of furans was performed at UV absorption wavelengths of 220, 276,
144 284 and 291 nm by selecting water and acetonitrile as mobile phases. For the
145 determination of phenolic compounds, the same mobile phases were used, but 195, 201,
146 231 and 300 nm were the selected UV absorption wavelengths. More information on the
147 analysis protocol can be found elsewhere (Borrero-López et al., 2018). The limits of
148 detection for HPLC measurements were around 0.0004 g/L.

149 **2.5. Yield analysis**

150 The hydrochar and liquid-phase yields, i.e., Y_{HC} and Y_{LC} , respectively, were
151 calculated according to the following equations (2) and (3):

$$152 \quad Y_{HC} (\%) = \frac{W_{HC}}{W_{BC}} \times 100 \quad (2)$$

$$153 \quad Y_{LC} (\%) = \frac{L}{L_0} \times 100 \quad (3)$$

154 where W_{HC} expresses the dry weight of the resultant hydrochar, W_{BC} is the initial weight
155 of the biomass compound (BC) fed into the autoclave, L is the resultant liquid content
156 after HTC, and L_0 is the initial amount of distilled water added.

157 **2.6. Procedure to estimate HTC products**

158 The present procedure is based on recent models (Borrero-López et al., 2018)
159 initially developed to describe the behaviour of the three main biomass components:
160 cellulose, hemicellulose and lignin, submitted to HTC separately, in terms of final pH,
161 hydrochar and liquid yields, and concentrations in FU, 5-HMF and phenolic molecules.
162 Based on these former models, we tried to assess whether it was possible to predict the
163 final composition and yields of HTC products or the possible synergistic effects when
164 the real biomass is submitted to HTC. For that purpose, we used two rather different

165 biomasses, OS and BW, the former being much richer in lignin than the latter. The final
 166 pH of the liquid phase reads as follows:

$$167 \quad \text{Final pH} = p1 + p2 (\log R_0) + p3 (\log R_0)^2 \quad (4)$$

168 where $p1$, $p2$ and $p3$ are experimental parameters. A polynomial expression was then
 169 determined for each biopolymer: cellulose, hemicellulose and lignin.

170 The hydrochar yield from each biomass compound is as follows:

$$171 \quad Y_{HC,BC} = \frac{Y_0 + Y_\infty (k \log R_0)^m}{1 + (k \log R_0)^m} \quad (5)$$

172 where the hydrochar yield of each lignocellulosic polymer ($Y_{HC,BC}$) depends on the
 173 constant initial and final hydrochar yields (Y_0 and Y_∞ , respectively), and on two
 174 parameters, k and m , which account for the slope of the yield drop and the severity value
 175 at which the drop starts, respectively.

176 The concentrations of FU and 5-HMF produced when submitting biomass to HTC
 177 read, respectively:

$$178 \quad \text{Model A; } C = C_{BC} \cdot \left(\frac{k_{1F}}{k_{3F} - k_{1F}} \right) \cdot [e^{-(k_{1F}) \cdot t} - e^{-(k_{3F}) \cdot t}] \quad (6)$$

$$179 \quad \text{Model B; } C = C_{BC} \cdot \left(\frac{k_{1F}}{k_{3F} - k_{1F} - k_{2F}} \right) \cdot [e^{-(k_{1F} + k_{2F}) \cdot t} - e^{-k_{3F} \cdot t}] \quad (7)$$

180 Both models were applied because the latter takes into account an intermediate in the
 181 production of FU from xylose. C_{BC} was the initial concentration of the BC (cellulose,
 182 hemicellulose or lignin) while k_1 , k_2 and k_3 were the constants corresponding to the
 183 various reactions taking place.

184 The concentrations of the following phenolic molecules produced from lignin read as
 185 follows:

186 Vanillin, syringaldehyde and acetosyringone:

$$187 \quad C_{phenolic\ compound} = a + b(\log R_0) + c(\log R_0)^2 \quad (8)$$

188 Guaiacylacetone:

$$189 \quad C_{phenolic\ compound} = \alpha + \beta(\log R_0) \quad (9)$$

190 Syringol, guaiacol and phenol production:

$$191 \quad C_{phenolic\ compound} = \delta + B \cdot e^{(\kappa(\log R_0))} \quad (10)$$

192 where a determined set of parameters has been developed for each compound.

193 Using the corresponding model and taking into account the lignocellulosic
194 composition of both OS and BW, the aforementioned yields and concentrations of the
195 main HTC products were estimated.

196 **2.7. Relative error analysis**

197 To determine to what extent the various models match the real data, the following
198 expression was used to calculate the relative error:

$$199 \quad error\ \% = \frac{|V_{th} - V_{exp}|}{V_{exp}} \cdot 100 \quad (11)$$

200 where V_{exp} and V_{th} are respectively the experimental and predicted data, whether for pH
201 value, hydrochar or liquid yields, or concentration of a given product obtained during
202 the HTC of OS or BW.

203

204 **3. Results**

205 **3.1. Final pH of the liquid phase**

206 The final pH after HTC gives information on the severity of the process and on the
207 reactions that have taken place. Fig. 1a shows the pH of the liquid fraction after HTC of
208 OS and BW along with the predicted data obtained.

209 *Figure 1*

210 As can be seen, the pH of the liquid fraction after HTC was generally higher for BW
211 than for OS within the studied range of severity, which is in good agreement with their
212 lignocellulosic composition. At low severity, the higher the cellulose and hemicellulose
213 contents, the higher the pH final values (Borrero-López et al., 2018). In the former
214 paper it was shown that, as severity increases, lignin produces a slight increase in the
215 final pH, cellulose decreases it considerably, and hemicellulose gives a minimum of
216 about pH 5. Therefore, the experimental results observed represent a clear combination
217 of the degradations of the three biopolymers. Although a slight overestimation of pH
218 was observed (about +9% and +11% for OS and BW, respectively), the predicted
219 evolution of pH with severity followed the same trend as the experimental one.

220 **3.2. Hydrochar yield**

221 Fig. 1b shows the values of $Y_{HC,BC}$ for OS and BW. At low severity, $Y_{HC,BW}$ was
222 higher than $Y_{HC,OS}$ due to the higher cellulose content of BW, a biopolymer that was
223 found to lead to the highest yields under these conditions (Borrero-López et al., 2018).
224 Nevertheless, at the highest severities, lignin began to play a more significant role in the
225 hydrochar yield, leading to values of $Y_{HC,OS}$ closer to those of $Y_{HC,BW}$.

226 The differences between the predicted and experimental $Y_{HC,BC}$ were as low as about
227 7% and 8% for OS and BW, which shows the relevance of the proposed equation for
228 predicting the yield of hydrochar of two very different biomasses submitted to HTC.

229 **3.3. Liquid yield**

230 Fig. 2a shows the liquid yield for both biomasses, that of OS being higher than that
231 of BW due to its higher lignin and lower cellulose contents, respectively. Nevertheless,
232 due to the high hemicellulose content of BW, the two datasets were very similar. In our
233 former work (Borrero-López et al., 2018), no model could be obtained for the liquid
234 yields from the HTC of hemicellulose, cellulose and lignin, due to the scattering of the
235 results. However, the experimental liquid yields of lignin, cellulose and hemicellulose
236 and the corresponding compositions were used here to predict the results. Thus, for each
237 severity value and for each bioresource, the liquid yields previously obtained from raw
238 cellulose, hemicellulose and lignin were weighed with the lignocellulose concentration,
239 generating the predicted values. In spite of that impossibility to previously obtain a
240 proper model (Borrero-López et al., 2018), the predicted data were found to be in very
241 good agreement with the OS liquid yield, with an average error of about 6%; however,
242 the BW liquid yield was slightly overestimated, with an average error of 16%.

243 Fig. 2b shows the differences between experimental and predicted values from the
244 model. The general overestimation of the liquid yield, especially for BW, can be
245 explained by some synergistic effect that may occur when the three biopolymers are
246 linked together. As a result, some reactions can be hindered and the extraction of water
247 from the raw biomass can be limited. In addition, it can be concluded that both cellulose
248 and hemicellulose must be responsible for this higher resistance to HTC, because OS,

249 with a higher lignin content, does not present such an overestimation of liquid yield
250 (Xiao et al., 2012).

251 *Figure 2*

252 **3.4. Concentrations of FU and 5-HMF and estimates**

253 Fig. 3 shows the concentrations of FU and 5-HMF experimentally produced from OS
254 and BW. Unexpectedly, the FU concentration from OS was significantly higher than
255 that from BW. Such a finding was surprising because BW contains a much higher
256 fraction of hemicellulose, which is directly responsible for the production of FU.
257 Moreover, the latter from both materials was much higher than expected, based on their
258 hemicellulose content and our previous study (Borrero-López et al., 2018), as clearly
259 seen in Fig. 3a and 3b, which also show the predictions of models A and B. This can be
260 explained because higher concentrations of pentoses are known to be responsible for
261 side reactions, so the lower hemicellulose concentration of both biomasses may actually
262 increase the yields (Marcotullio, 2011). In addition, since FU is generally produced
263 under acid-catalysed conditions (Dashtban et al., 2012; Matsagar et al., 2017), cellulose
264 degradation, which produces a substantial decrease in pH, can potentially enhance the
265 production of FU from OS and BW compared to hemicellulose itself. Moreover, the
266 lower pH reported for OS can also explain the difference between the two biomasses.
267 The FU yields obtained are in the range of other studies, as already shown in a previous
268 work (Borrero-López et al., 2017).

269 *Figure 3*

270 Regarding 5-HMF production, overall, the predictions were closer to the
271 experimental data than for FU. Nonetheless, it is worth mentioning the extremely high
272 overestimation shown by model A when considering a constant calculated from the

273 equations (data not shown). The production of 5-HMF was higher for BW for almost all
274 the considered severity factors, which was consistent with its higher cellulose content
275 when compared to OS. Nevertheless, the highest 5-HMF production was obtained from
276 OS at the highest tested severity factor. In summary, the most reliable predictions
277 obtained were those considering equations developed from the application of model B.

278 **3.5. Concentrations of phenolic compounds and estimates**

279 It is well known that lignin can produce a wide range of phenolic compounds from
280 the decomposition of its structure into its constituent units (Borrero-López et al., 2018;
281 Cesari et al., 2019; Yang et al., 2019). In the present work, nine different types of
282 phenolic compounds have been identified and quantified for OS and BW, the
283 concentrations of which have also been estimated by application of the previous models
284 developed from HTC tests on lignin (Borrero-López et al., 2018). These phenolic
285 compounds are vanillin, guaiacylacetone, syringol, syringaldehyde, guaiacol,
286 acetosyringone, phenol, acetovanillone and creosol. Only the first seven compounds
287 were plotted in Fig. 4 for OS and BW, because the concentrations of acetovanillone and
288 creosol were below the limits of detection (0.0005 and 0.0004 mg/L, respectively)
289 throughout the whole range of conditions studied. The absence of creosol was somehow
290 expected, since previous studies on the HTC of lignin only produced it at severities
291 greater than 6 (Borrero-López et al., 2018). However, the concentration of
292 acetovanillone had comparable values to syringaldehyde (Borrero-López et al., 2018),
293 thus the production of acetovanillone should be somewhat limited by the synergistic
294 action of both cellulose and hemicellulose and the corresponding reduction of pH.

295 *Figure 4*

296 Since the concentration of lignin in OS is the highest, one would think that the
297 concentrations of phenolic compounds from this bioresource would be the highest.
298 However, similar to what occurred with FU production, this was true only for vanillin,
299 guaiacylacetone and final phenol concentration, while the remaining phenolic
300 compounds concentrations from OS were similar to or less than from BW. This fact
301 highlights the extreme importance of the lignin content, which may vary significantly
302 from one bioresource to another. Since the concentration of monolignols and other units
303 may be very different, different concentrations of the resulting products can be obtained
304 (Anderson et al., 2019; Santos et al., 2015a; Santos et al., 2015b). Both OS and BW
305 derive from hardwoods, thus close syringyl(S) / guaiacyl(G) (p-hydroxyphenylpropane)
306 ratios are expected. Some authors (Simon et al., 2014) have reported that BW has a S/G
307 ratio close to 1, while others suggest lower ratios that depend on the extraction process
308 (Choi et al., 2001). In contrast, the OS S/G ratio was postulated at 1.08 (Harman-Ware
309 et al., 2015). On the contrary, the lignin used for modelling was PROTOBIND 1075,
310 which comes from softwood, so that the S/G ratio drops dramatically to very low values
311 depending on the initial biomass (Anderson et al., 2019), which makes the structure of
312 lignin completely different. Therefore, this fact may compromise the accuracy of the
313 model (Borrero-López et al., 2018; Li et al., 2013; Sameni, 2015).

314 Nevertheless, the predicted data showed adequate fits for the vast majority of them,
315 highlighting the validity and adaptability of the model. However, here again, the
316 influence of the simultaneous HTC of the remaining lignocellulosic biopolymers affects
317 the prediction of the results by modifying the interactions and modifying the
318 composition of the liquid phase. Thus, in our previous work, it has been shown how the
319 final pH from lignin HTC increased with severity (Borrero-López et al., 2018),
320 although, for the bioresources studied in this work, the final pH has decreased as a result

321 of the presence of both cellulose and hemicellulose. Thus, the compounds that depend
322 on acidic or basic catalysis can have a completely different behaviour, as shown for
323 vanillin, acetosyringone, acetovanillone and syringaldehyde, whose concentration was
324 generally overestimated as a result of low pH.

325 In addition, the general underestimation observed for syringyl-derived units may also
326 result from the higher S/G ratio of hardwoods, with respect to softwoods, which is
327 known to facilitate the effectiveness of delignification (Anderson et al., 2019; Schmetz
328 et al., 2019).

329 **4. Conclusions**

330 The hydrothermal carbonisation of OS and BW was successfully performed in a
331 wide range of severity factor values. pH, hydrochar and liquid yields as well as some
332 furan and phenolic compounds were determined, and the experimental results were
333 compared to estimates. These estimates were obtained taking into account the
334 hemicellulose, cellulose and lignin contents of the biomasses as well as the results of the
335 fits obtained for the same parameters when these components of biomass were
336 separately submitted to HTC. The following general trends could be derived.

- 337 - The final pH of liquids derived from BW was generally higher than that
338 measured in OS-derived liquids, which is in good agreement with their
339 lignocellulosic composition. An average overestimate of 10% of the pH value
340 was obtained because of the synergistic effect between the three lignocellulosic
341 compounds, but the trends were well predicted.
- 342 - A similar trend was observed in the hydrochar yield although the agreement
343 between predicted and experimental values was much better (around 7%).

- 344 - The liquid yield was higher for the OS because of its higher lignin and lower
345 cellulose contents. A good fit was obtained, reaching about 6 and 16% average
346 error for OS and BW, respectively.
- 347 - Extremely high concentrations were obtained for FU, which is attributable to
348 lower rates of side reactions and the influence of the final pH. The
349 concentrations of 5-HMF were lower, and a better approximation was obtained
350 with model B. The concentrations of phenolic compounds were of the same
351 order as those predicted, but highly dependent on the selected biomass and pH.

352 Although further analysis is needed to explain the unexpected concentrations of FU,
353 the models predicted trends similar to those determined experimentally. A systematic
354 study in which mixtures of biomass components would be submitted to HTC would be
355 necessary to understand the undergoing reaction mechanisms and synergistic effects.

356 **Declaration of interest**

357 The authors declare no competing financial interest.

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525

526 **Figure Captions**

527 **Fig. 1.** a) Final pH of the liquid phase; and b) hydrochar yield after HTC of OS and
528 BW. The dashed lines represent the predicted values from the models.

529 **Fig. 2.** a) Experimental liquid yields for OS and BW; b) Differences between
530 experimental and predicted values from the models.

531 **Fig. 3.** Concentrations of FU and 5-HMF produced from OS (a & c) and BW (b & d).
532 The dashed lines represent the predicted values from the models.

533 **Fig. 4.** Phenolic compounds concentration from OS (left) and BW (right). The dashed
534 red lines are predicted data from modelling and lignin content of the bioresource.

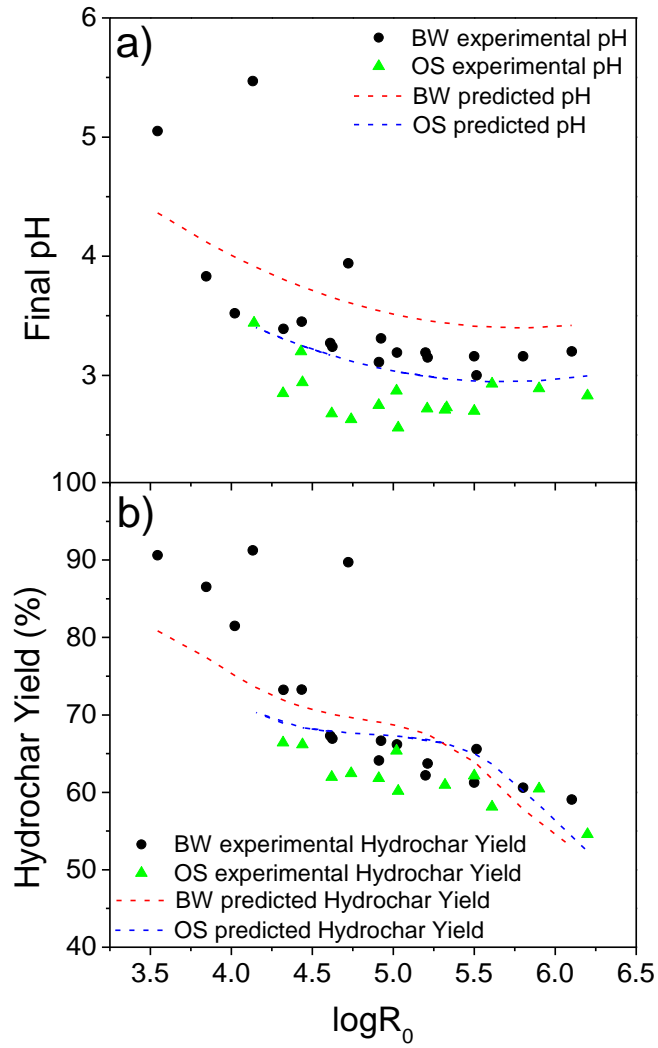
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Figure 1

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540 a) Final pH of the liquid phase; and b) hydrochar yield after HTC of OS and BW. The

541 dashed lines represent the predicted values from the models.

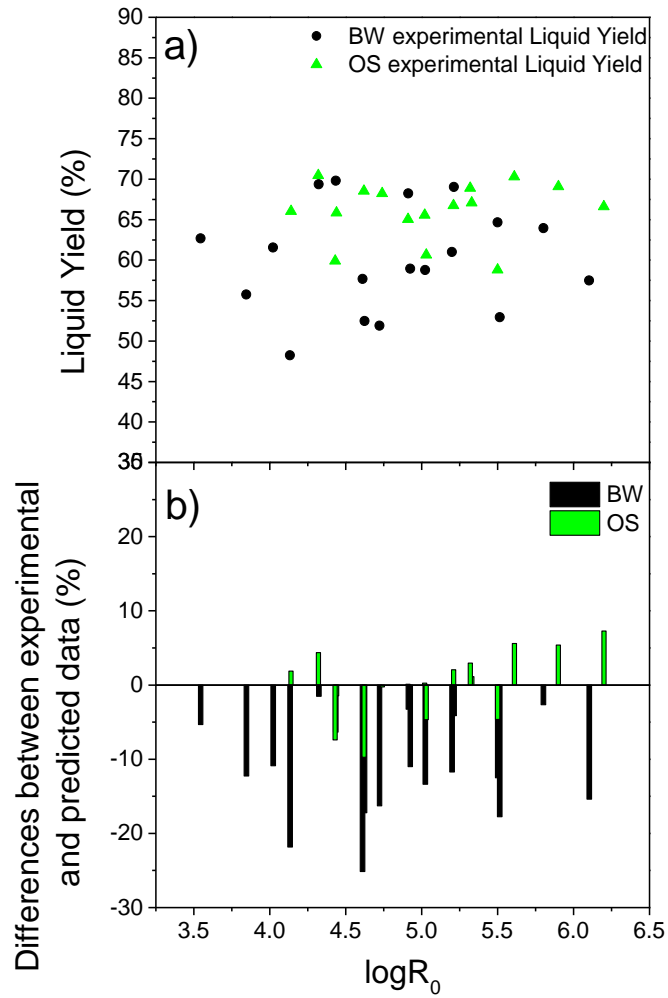
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Figure 2

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547 a) Experimental liquid yields for OS and BW; b) Differences between experimental and

548 predicted values from the models.

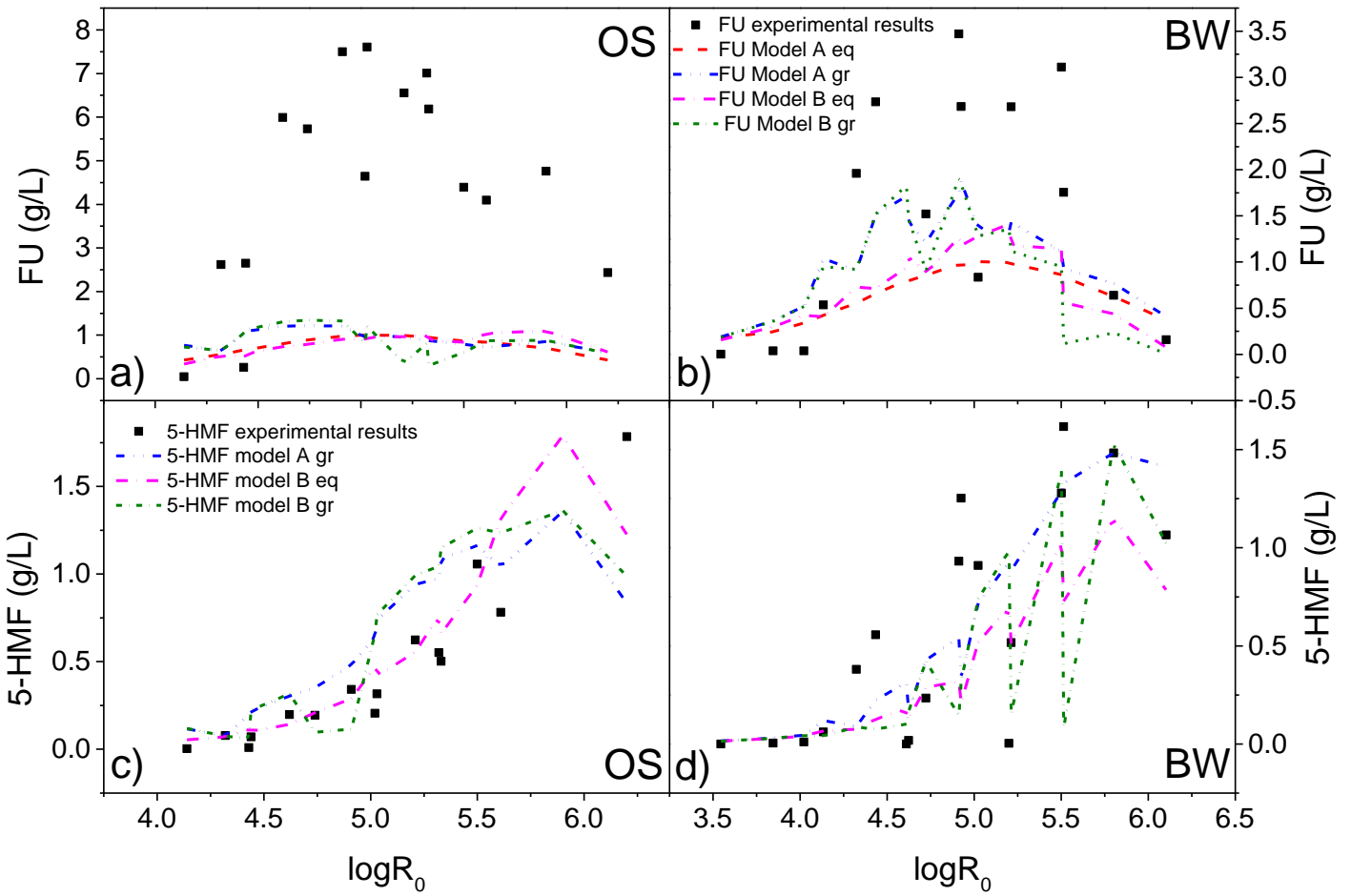
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Figure 3

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555 Concentrations of FU and 5-HMF produced from OS (a & c) and BW (b & d). The

556 dashed lines represent the predicted values from the models.

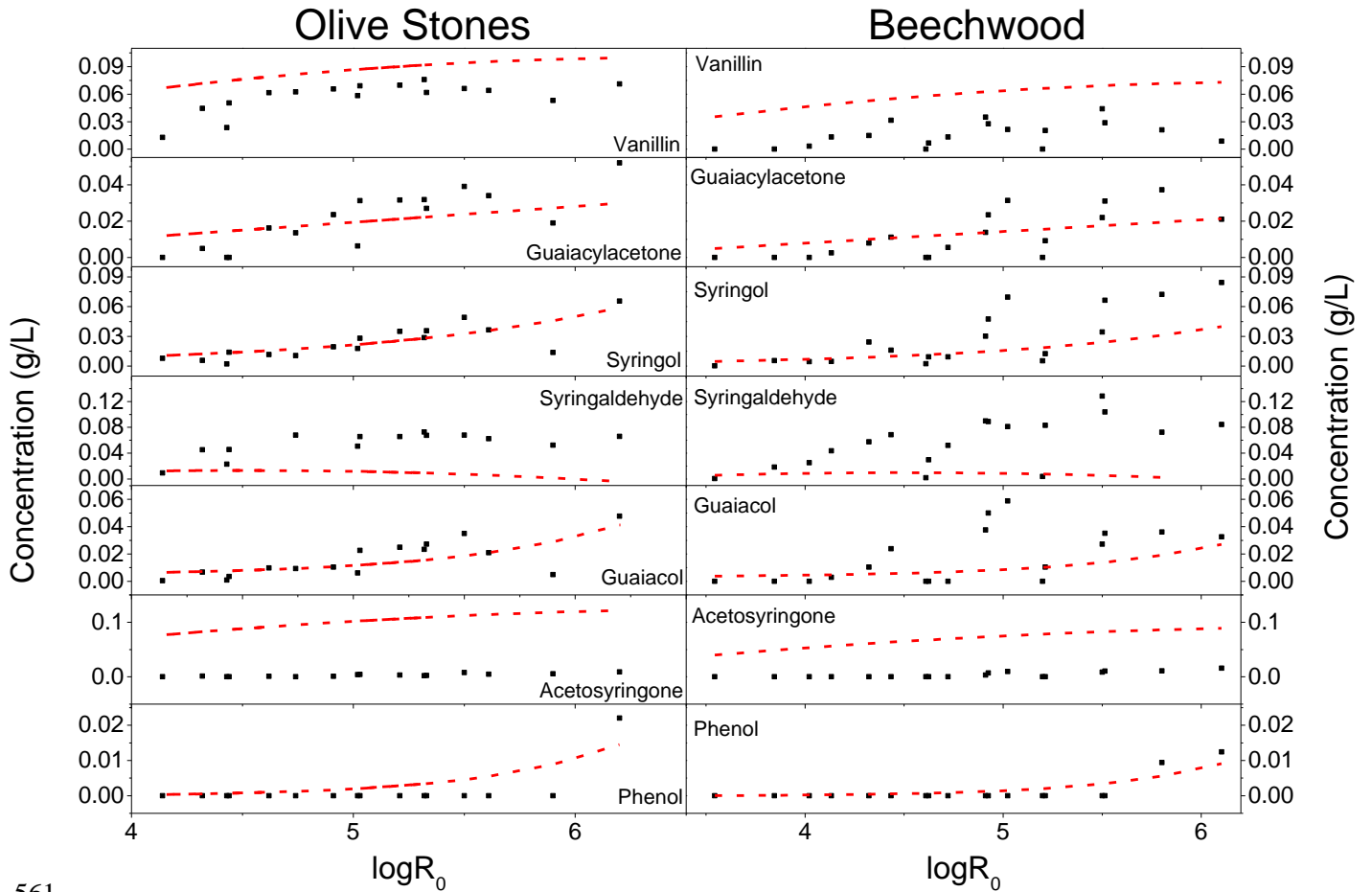
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Figure 4

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563 Phenolic compounds concentration from OS (left) and BW (right). The dashed red lines

564 are predicted data from modelling and lignin content of the bioresource.

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