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A.M. M Borrero-López, E. Masson, A. Celzard, V. Fierro. Modelling the reactions of cellulose, hemicellulose and lignin submitted to hydrothermal treatment. *Industrial Crops and Products*, 2018, 124, pp.919-930. 10.1016/j.indcrop.2018.08.045 . hal-03207572

HAL Id: hal-03207572

<https://hal.univ-lorraine.fr/hal-03207572v1>

Submitted on 30 Apr 2021

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Modelling the reactions of cellulose, hemicellulose and lignin submitted to hydrothermal treatment

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Abstract

The main compounds of plant biomass, i.e., cellulose, lignin and hemicellulose, were submitted to hydrothermal carbonisation (HTC) in ranges of temperature and time of 140-240°C and 0.5-24 h, respectively. Those parameters were combined into a single one, the severity factor, and its effect on hydrochar yield on the one hand, and on pH, yield and composition of the liquid fraction on the other hand, was investigated in depth. The production of furanic and phenolic compounds was correlated with both severity and pH. The kinetics of furfural (FU) and 5-hydroxymethylfurfural (5-HMF) production and consumption were also investigated and modelled, and the results were compared to those reported in the literature. The production of nine phenolic compounds from lignin HTC was also considered.

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21 **1. Introduction**

22 Hydrothermal carbonisation (HTC), whose history dates from the early 1900's
23 (Bergius, 1915), is a very simple process by which a bioresource is submitted to mild
24 temperatures (130-250°C) in a pressurised liquid medium (generally pure water) using a
25 closed reactor, i.e., an autoclave. In the latter, the pressure is self-generated and allows
26 obtaining both solid and liquid products (Borrero-López et al. 2017).

27 HTC is cost-effective as it does not require chemicals and avoids costs related to
28 materials drying, and it perfectly allows biomass conversion into high added-value
29 organic compounds through hydrolysis and subsequent dehydration and fragmentation
30 (Braghiroli et al., 2015). Cellulose, hemicellulose and lignin are the main
31 macromolecular compounds of wood and plant biomass in general, and the former two
32 macromolecules are well-known precursors of furfural (FU) and 5-hydroxymethylfurfural
33 (5-HMF), respectively, when submitted to HTC. HTC of lignin can also provide some
34 valuable compounds like vanillin, used for cosmetics and flavouring, or syringaldehyde,
35 used as ingredient for food and flavour (Onwudili, 2015, Zhou, 2014), amongst others.

36 However, a solid carbonaceous residue, called hydrochar, is also obtained in the
37 same process, having many interesting features such as porosity and functional groups
38 like hydroxyls, carbonyls, etc (Chen et al., 2017). Hydrochars are interesting by-products
39 as they present higher heating values (Basso et al., 2015) than their corresponding
40 biomass precursors, and have been proposed for soil amendment (Steinbeiss et al.,
41 2009), for CO₂ capture (Jatzwauck and Schumpe, 2015) or as precursors of carbon
42 materials (Borrero-López et al., 2017, Braghiroli et al., 2012, 2015b).

43 Extensive work has been carried out on HTC of many kinds of bioresources, like
44 wheat straw (Reza et al., 2015), plant biomass wastes (Fang et al., 2015), loblolly pine
45 (Lynam et al., 2011), soft rush (Jatzwauck and Schumpe, 2015) as well as on each

46 individual major compound of such biomass (Lu et al., 2013, Gao et al., 2012,
47 Pińkowska et al., 2011, Wang et al., 2015). However, only a few works combined the
48 studies of cellulose, hemicellulose and lignin. For instance, Kang et al. (2012)
49 previously focused on HTC of the latter compounds, amongst others, but only a rather
50 narrow temperature range was investigated and no detailed studies of the liquid
51 products was performed. As far as we know, no research related to the liquid and solid
52 fractions obtained from cellulose, hemicellulose and lignin submitted together to HTC
53 has been published.

54 In the recent past, the kinetics of FU production / decomposition competitive
55 reactions (Marcotullio et al., 2009) were thoroughly studied for several biomasses or
56 biomass-derived molecules such as wheat straw (Yemiş and Mazza, 2012) and xylose
57 (Liu et al., 2014) submitted to HTC. Most works generally focused either on production
58 or on decomposition reactions separately (Liu et al., 2014, Danon et al., 2014, Kim et
59 al., 2011). Simple consecutive reaction models as well as models taking into account
60 side reactions have been developed (Jing and Lü, 2007, Liu et al., 2014) and are in
61 agreement with published studies on degradation compounds from sugars (Rasmussen
62 et al., 2014, Yang et al., 2012, Chen et al., 2012). An intermediate between xylose and
63 furfural has also been proposed for explaining the kinetics of FU production
64 (Marcotullio, 2011 and Chen et al., 2015).

65 Regarding the kinetics of reaction of 5-HMF, Chen et al. (2010) studied its
66 production whereas Girisuta et al. (2006) studied its decomposition to levulinic acid, but
67 again there was not too much work related with these two competitive processes in the
68 same study (Jing and Lü, 2008, Shen and Wyman, 2012). The case of 5-HMF is more
69 complex than that of FU, because some degradation products are known to decompose
70 afterwards, such as levulinic acid.

71 The main purpose of the present work was to assess the effect of HTC conditions on
72 lignin, cellulose and hemicellulose in a broad range of temperatures (140-240°C) and
73 time (0.5-24 hours), by studying the production of FU, 5-HMF and up to nine aromatic
74 compounds as a function of HTC severity, and to apply simple models for describing
75 the observed kinetics. Relationships between the latter and pH, and yields of resultant
76 liquid and solids, were also looked for.

77

78 **2. Material and Methods**

79 **2.1. Raw material**

80 Cellulose was Type 102 VIVAPUR (high-purity) microcrystalline cellulose
81 provided by JRS Pharma (Rosenberg, Germany). Hemicellulose was high-purity xylan
82 extracted from beech wood and supplied from Roth (Karlsruhe, Germany). Lignin used
83 was lignin powder Lignine PROTOBIND 1075 (Asian Lignin Manufacturing India
84 Private Limited), which is soda lignin. All compounds used for identification and
85 quantification of phenolic and furanic compounds by HPLC were analytical grade and
86 purchased from Sigma-Aldrich (Steinheim, Germany).

87 **2.2. Hydrothermal carbonisation (HTC)**

88 HTC experiments were performed in 100 mL Teflon®-lined autoclaves. The liquid
89 to solid (L/S) weight ratio was 8 (16 g / 2 g) where L stands for liquid (i.e., pure water)
90 and S for the considered biomass compound (BC) on dry basis. BC and distilled water
91 were thus weighed and introduced in a glass insert so as to protect the PTFE liner of the
92 autoclave from any contamination. Autoclaves were next hermetically closed and
93 placed in a ventilated oven preheated at the desired temperature (160, 170, 180, 200,
94 220 or 240°C) for the required reaction time (from 0.5 to 24 hours). Afterwards, the

95 autoclaves were removed from the oven and let to cool down to room temperature for
96 several hours before opening.

97 Since both time (t) and temperature (T) produce changes in the results of the HTC
98 process, their effect was investigated through the severity factor ($\log R_0$) which was
99 introduced to combine these two parameters into a single one (Overend and Chornet,
100 1987). Indeed, $\log R_0$ takes into account the different significances of these two
101 parameters through an exponential factor for the temperature, and through a
102 proportional factor for time. It reads:

$$103 \quad \log R_0 = \log \left[t \cdot \exp \left(\frac{T-100}{\omega} \right) \right] \quad (1)$$

104 where t is the residence time (min), T the working temperature ($^{\circ}\text{C}$) and ω is an HTC
105 parameter. The initial value for lignocellulosic materials that was suggested for ω was
106 14.75, since it corresponds to the activation energy of a first-order hydrolytic process
107 (Xu et al., 2011). As it remains an empirical parameter, ω was sometimes changed when
108 using other bioresources and different temperature ranges, as did Ko et al. (2015) for
109 glucose by using the value 4.6.

110

111 **2.3. Liquid/solid separation and analysis**

112 After HTC, liquid and solid products obtained together in the autoclave were
113 separated by vacuum filtration. The amount of liquid was weighed immediately after
114 filtration, whereas solids were placed in a vacuum oven for 6 hours at 60°C for complete
115 drying and subsequent weighing.

116 Qualitative identification of the main volatile compounds in the liquid phase was
117 carried out by gas chromatography coupled with mass spectrometry (Clarus 500
118 GC/MS). Regarding quantitative analyses, furanic and phenolic compounds were

119 determined using an Ultimate 3000 high-performance liquid chromatograph equipped
120 with auto-sampler, diode array and fluorescence detectors, and columns described
121 below.

122 A Hypersyl Green PAH column was used for FU, 5-HMF and 5-MF quantification.
123 Four UV absorption wavelengths were used, i.e., 220, 276, 284 and 291 nm. Doing so,
124 fluorescence and emission occurring at wavelengths of 360 nm and 443 nm,
125 respectively, could be avoided. Water and acetonitrile were used as mobile phases and
126 the acetonitrile/water ratio was changed from 5/95 to 100/0 during the 35 min of the
127 total analysis time as follows: in the first 1.5 min, the 5/95 ratio was maintained; from
128 1.5 to 15min, acetonitrile increased linearly up to a 50/50 ratio; from 15 to 20 min, the
129 acetonitrile again increased up to 100/0 and this ratio was maintained for 5 min more.
130 From 25 to 30 min, acetonitrile decreased until the initial ratio, i.e., 5/95, and it was
131 maintained 5 min until the end of the analysis.

132 Phenolic compounds were quantified with a Pinnacle DB BiPh 5 μ m column, and UV
133 absorption wavelengths of 195, 201, 231 and 300 nm were used. Mobile phases were
134 water and acetonitrile too. The program started with an acetonitrile/water ratio of 10/90
135 during the first 3 min. Later, the acetonitrile content increased up to 15/85 at min 5, and
136 remained constant until min 13. From 13 to 15 min, acetonitrile increased up to the ratio
137 20/80 and was kept constant 13 min more. From 28 to 33 min, the acetonitrile
138 concentration increased up to the ratio 100/0, which was kept for 5 min more. From 38
139 to 43 min, acetonitrile concentration decreased to 90/10 ratio, and remained constant for
140 7 min more, until the end of the experiment at 50 min. Again, all the aforementioned
141 changes of the acetonitrile/water ratio were linear.

142 The yield of each considered organic molecule X, Y_X , was calculated according to the
143 following equation:

144
$$Y_X (\%) = \frac{[X]V}{W_{BC}} \times 100 \quad (2)$$

145 where $[X]$ is the concentration (g mL^{-1}) of each soluble organic compound within the
146 volume V of liquid (mL) obtained after HTC, and W_{BC} is the mass (g) of the biomass
147 component studied on dry basis.

148 The hydrochar yield, Y_{HC} , was determined from Eq. (3):

149
$$Y_{HC} (\%) = \frac{W_{HC}}{W_{BC}} \times 100 \quad (3)$$

150 where W_{HC} is the mass of dry hydrochar after HTC.

151 The liquid yield from HTC, LY_{HC} , was calculated as follows:

152
$$LY_{HC} (\%) = \frac{LW_{HC}}{LW_0} \times 100 \quad (4)$$

153 where LW_{HC} is the amount of liquid weighed after filtration, and LW_0 is the initial
154 amount of liquid added in the autoclave.

155

156 **2.4. Kinetics**

157 The fits to experimental kinetic data was carried out with OriginPro 8.5.1 software
158 by minimising χ^2 through the Levenberg-Marquart algorithm. Simple models
159 considering successive decomposition reactions either without or with side reactions,
160 herein called A and B models, respectively (Perez and Fraga 2014, Marcotullio, 2011)
161 were applied to the data, and allowed deriving kinetic parameters for each temperature
162 and for each raw material. The as-obtained kinetic parameters were investigated as a
163 function of temperature using Arrhenius equation, Eq. (5). Both activation energy (E_a)
164 and pre-exponential factor (k_0) were obtained from the slope and intercept of the
165 corresponding fitting, respectively.

166
$$k = k_0 e^{-\frac{E_a}{RT}} \quad (5)$$

167 3. Results

168 3.1. Changes of pH

169 HTC of cellulose, lignin and hemicellulose produced some changes in the pH of the
170 water in which the process was carried out. Different behaviours were observed,
171 depending on the raw material and on the conditions of the experiments.

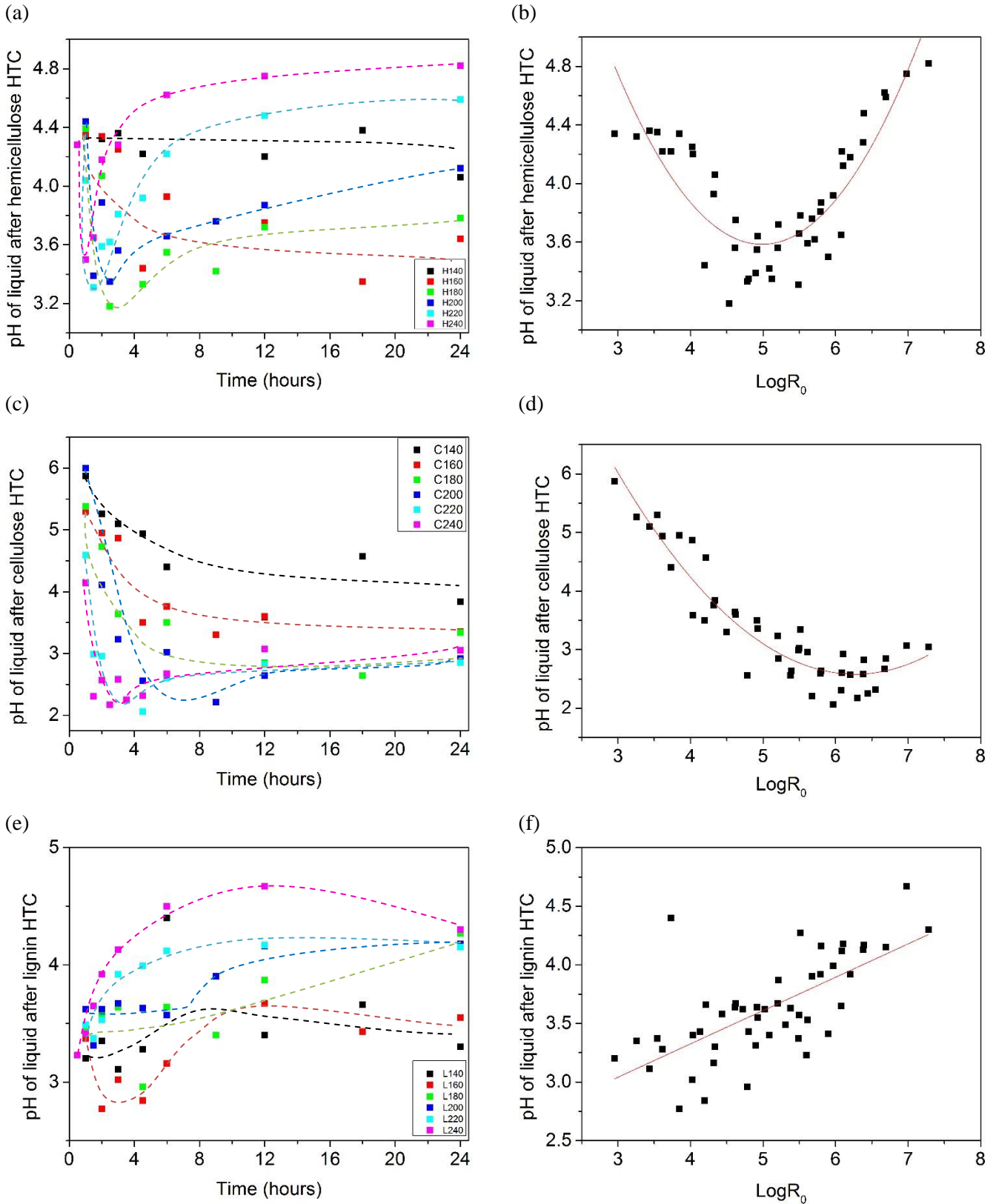
172 Thus, for hemicellulose, the pH first decreased with time (Fig. 1a) likely due to the
173 production of significant amounts of small acidic molecules. Then, the pH either
174 remained low or increased afterwards at higher reaction time, depending on the
175 temperature. Such behaviour is more clearly seen when the pH is plotted versus severity
176 (Fig. 1b), i.e., once time and temperature have been combined into one single
177 parameter. The pH thus increased above a severity of 5, probably because more severe
178 conditions produced secondary reactions which led to the decomposition of low
179 molecular-weight acids as already observed elsewhere (Shen et al., 2012). It might be *a*
180 *priori* thought that FU and 5-HMF account for the decrease of pH of the solutions
181 recovered after HTC of hemicellulose and cellulose, respectively, since they are
182 generally found at the highest concentrations when the pH decreased the most.
183 However, as furfural is not acidic and 5-HMF possess a pK_a of 12.82, the conditions of
184 their formation at highest concentration may be responsible of the production of other
185 species such as acetic acid, furoic acid, formic acid, lactic acid, propionic acid, butyric
186 acid and others (Zeitsch, 2000, Reza et al., 2014), which really account for the low pH
187 observed.

188 Roughly similar trends were found when cellulose was submitted to HTC (Fig. 1c),
189 i.e., the pH was the highest at the beginning of the process then decreased and stabilised
190 or slightly increased after 6 – 12h, depending on the temperature. The pH dropped more
191 at higher temperature, but also increased more after the minimum. This trend can be

192 again explained in terms of increased degradation of soluble products when the severity
193 increased (Fig. 1d), and the apparently constant pH at lower HTC temperature is likely
194 due to reaction times that were too low for causing any significant change of pH.

195 As for lignin submitted to HTC, the pH of the liquid phase increased with severity
196 (Fig. 1f). This is due to the fact that lignin degradation mainly produces phenolic (i.e.,
197 basic) compounds, and not acids. The red solid lines in Fig. 1b, 1d and 1f are fits of a
198 second-order polynomial, Eq. (6), to the experimental data, where p_1 , p_2 and p_3 are
199 adjustable parameters. The values of the latter are given in Table 1.

200
$$\text{Final pH} = p_1 + p_2 (\log R_0) + p_3 (\log R_0)^2 \quad (6)$$



202 Figure 1. Final pH of liquid fractions as a function of time and temperature (left row),
 203 and as a function of severity (right row), measured after HTC of: (a) and (b)
 204 hemicellulose; (c) and (d) cellulose; (e) and (f) lignin.

205 Table 1. Values of the parameters of Eq. (6) after fitting the data of Fig. 1b, 1d and 1f.

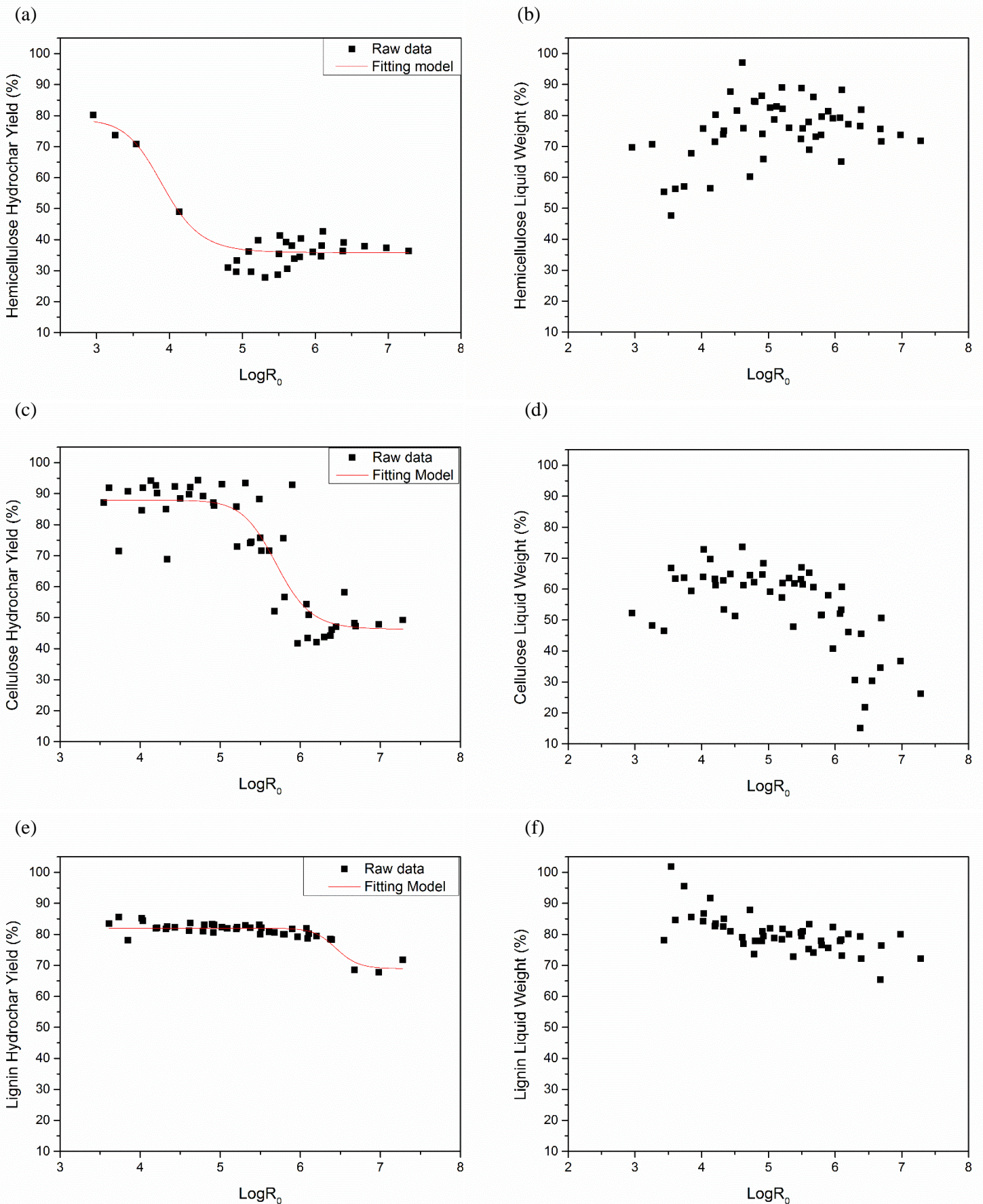
| Biomass component (BC) | P_1 | P_2 | P_3 |
|------------------------|-------|-------|-------|
| Cellulose | 15.20 | -4.04 | 0.32 |
| Lignin | 2.19 | 0.28 | - |
| Hemicellulose | 10.90 | -2.94 | 0.29 |

206

207 3.2. Yield to hydrochar

208 The hydrochar yield from hemicellulose ($Y_{HC,H}$) at high severity was lower than that
 209 of cellulose and lignin (compare Fig. 2a, 2c and 2e), and the corresponding weight loss
 210 also occurred at much lower severity. The yield was indeed around 35% above a
 211 severity of 4.5 – 5, and roughly stabilised for higher severity values (Fig. 2a). It is also
 212 possible that the curve goes through a minimum at a severity close to 5, as suggested by
 213 Fig. 2b showing a slight maximum of liquid fraction, but the natural scattering of the
 214 data doesn't allow any firm conclusion about this. Moreover, solid and liquid yields are
 215 not necessarily directly related with each other since hydrochars may have retained
 216 water bound to their structure, and gases may also have formed (see next subsection).

217



218 Figure 2. Yields of hydrochar (left row) and of liquid fraction (right row) as a function of
 219 severity, measured after HTC of: (a) and (b) hemicellulose; (c) and (d) cellulose; (e) and
 220 (f) lignin. The red lines are fits of Eq. (7) to the experimental data.

221 At low severity, cellulose produced the highest amount of HC since the yield was as
222 high as 88%, on average. The weight loss stabilised around 46% at a severity around
223 6.5, i.e., higher than for hemicellulose. Moreover, the weight loss really started at a
224 severity above 5.5, whereas hemicellulose lost weight from the mildest conditions. This
225 finding is explained by the higher stability of cellulose that remained almost intact until
226 220°C, above which degradation began (Fig. 2c).

227 Lignin was also quite stable since the HC yield was around 81% at low severity, on
228 average, and remained constant up to temperature and time as high as 220°C and 12h,
229 respectively, corresponding to a severity close to 6.5 (Fig. 2e). Such a yield is a bit
230 lower than that of cellulose in the same conditions because part of the lignin is soluble
231 in water (Overend and Chornet, 1987). Anyway, a lower weight loss than for the
232 previous BCs was observed beyond a severity of 6.5 and quickly seemed to stabilise to
233 around 69%, which was the highest value of the 3 BCs in the most severe conditions.

234 A kinetic model able to account for the aforementioned trends was applied to the
235 data of Fig. 2a, 2c, and 2e. This model, known as Cross model (Cross, 1965) and
236 described by Eq. (7), has been extensively applied to rheological studies but, to the best
237 of our knowledge, it is the first time that it is applied to hydrothermal carbonisation. It
238 reads:

$$239 \quad Y_{HC,BC} = \frac{Y_0 + Y_\infty (k S)^m}{1 + (k S)^m} \quad (7)$$

240 where $Y_{HC,BC}$ is the hydrochar yield at a given severity, Y_0 and Y_∞ are the initial and final
241 hydrochar yields, and m and k are parameters accounting for both the slope of the yield
242 drop and the severity value at which the drop starts, respectively. The red lines in Fig.
243 2a, 2c and 2e show the fits of Eq. (7) to the experimental data. The corresponding
244 adjustable parameters are given in Table 2 for hemicellulose, cellulose and lignin. This

245 table also includes the coefficient of determination for the three raw materials,
246 demonstrating the good fitting despite the data scattering.

247
248 Table 2. Values of the parameters of Eq. (7) after fitting the data of Fig. 2a, 2c and 2e.

| Raw material | Y_0 (%) | Y_∞ (%) | k | m | R^2 |
|---------------|-----------|----------------|------|-------|-------|
| Hemicellulose | 77 | 35 | 0.25 | 21.33 | 0.89 |
| Cellulose | 88 | 46 | 0.17 | 26.42 | 0.77 |
| Lignin | 81 | 69 | 0.16 | 46.46 | 0.79 |

249

250 3.3. Yield to liquid phase

251 As observed in Fig. 2, the yields of solid and liquid phases are not strictly correlated
252 with each other. On the one hand, the amount of liquid produced should increase
253 because of the loss of water from biomass but, on the other hand, volatile compounds
254 are likely to be released in the gas phase.

255 Concerning hemicellulose, the decrease of HC yield was related to the increase of
256 liquid yield until a severity around 5, and the latter remained constant or decreased very
257 slightly at higher severity (Fig. 2b), suggesting that no or negligible amount of gas was
258 produced. When cellulose was submitted to HTC, the liquid fraction was initially
259 roughly constant until a severity of 5.5, above which it decreased very significantly
260 (Fig. 2d). Since the hydrochar yield also decreased, it can be deduced that more and
261 more gas was produced when the conditions turned more severe. As for lignin, the
262 liquid fraction decreased rather linearly with severity over the whole investigated range
263 (Fig. 2f), suggesting that lignin degradation produced volatile compounds from the very
264 beginning, and all the more so at higher severity, as expected.

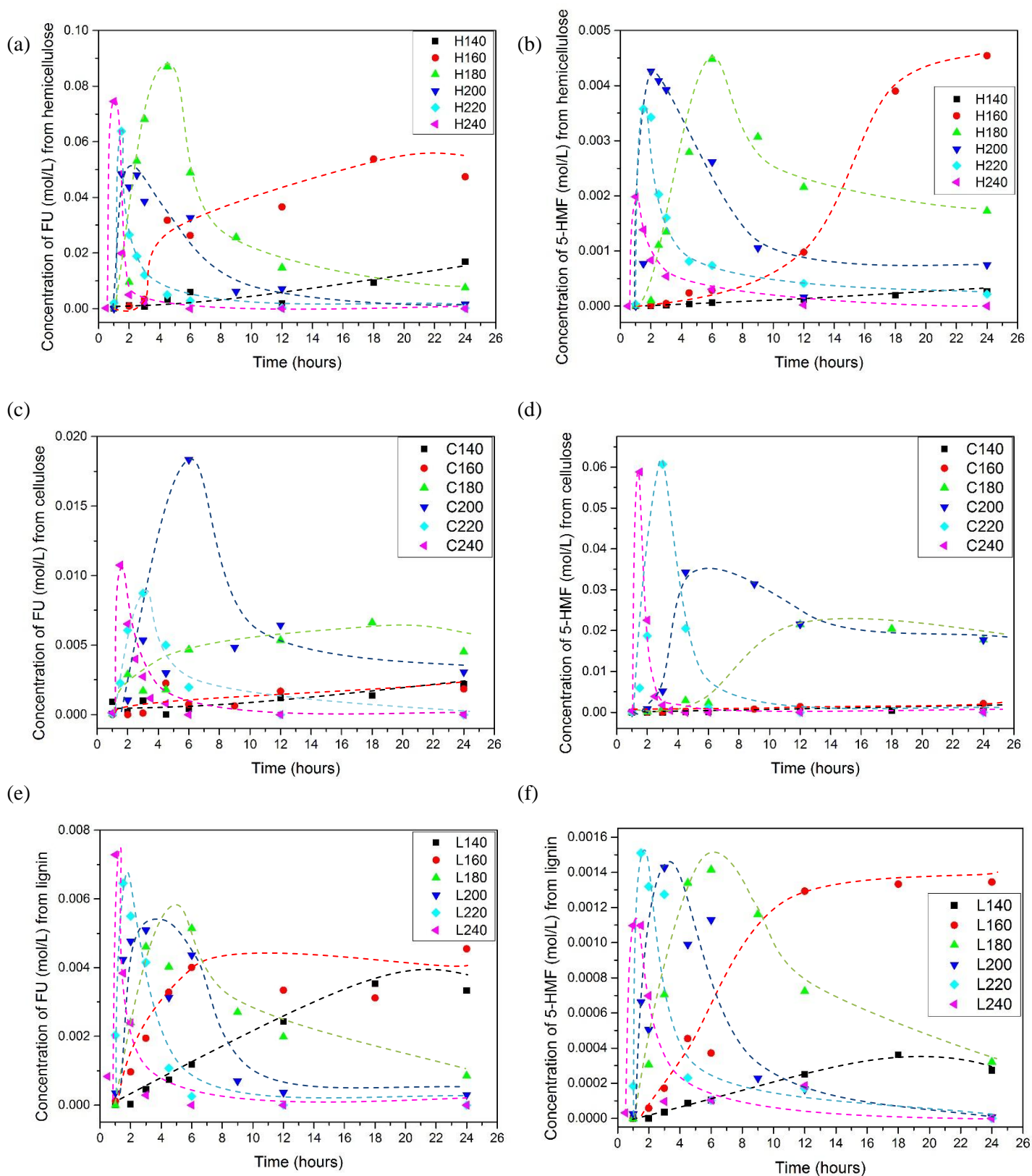
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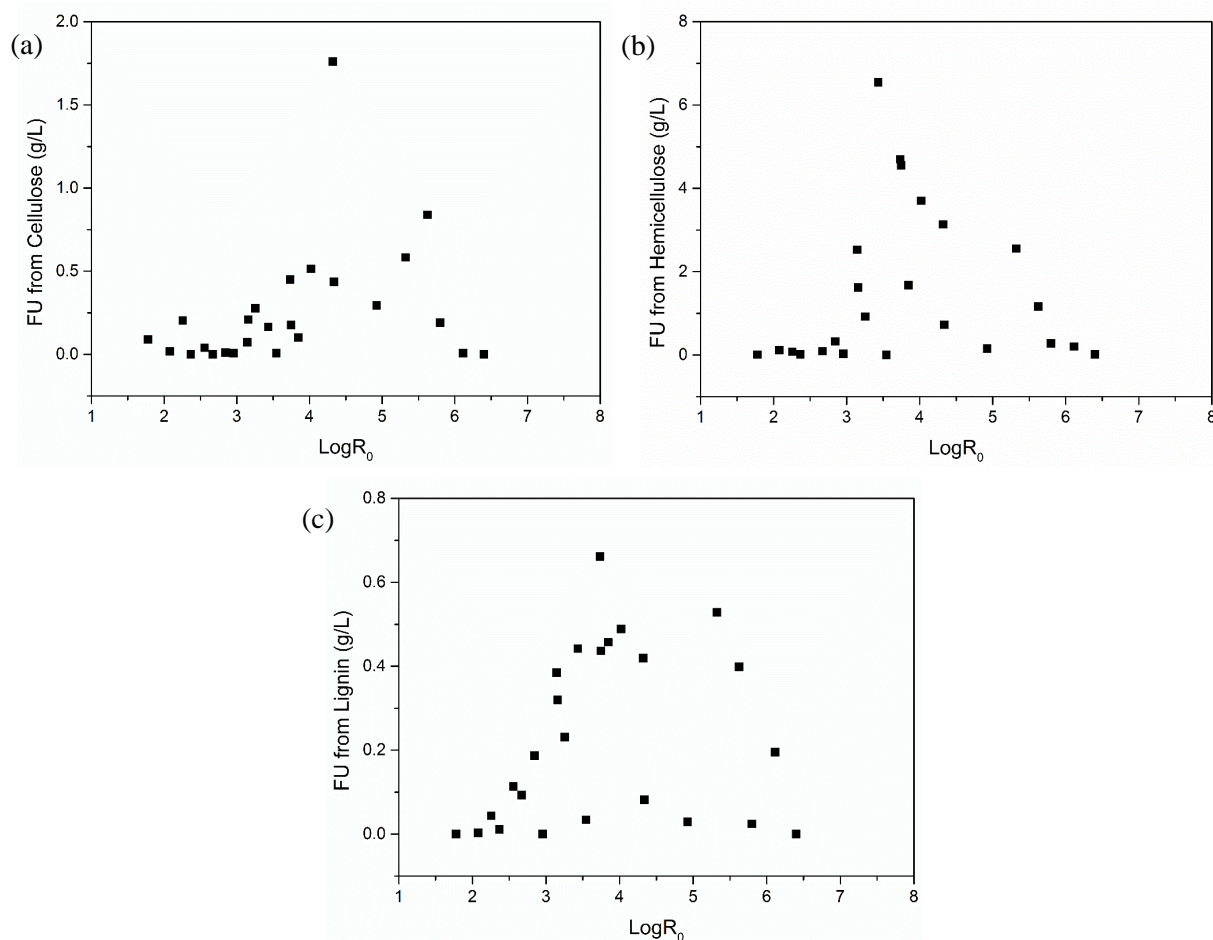
267 **3.4. FU and 5-HMF production**

268 The production of FU and 5-HMF as a function of HTC time followed the same
269 behaviour, whatever the biomass compound investigated. Thus, at the lowest
270 temperature, FU and 5-HMF production increased monotonously with time. When the
271 HTC temperature increased, a peak of production clearly appeared and was shifted to
272 lower reaction times. Therefore, at the highest investigated temperature, the highest
273 concentration of FU and 5-HMF was obtained in less than 1 h. All these features are
274 shown in [Fig. 3](#). Those trends were more complex than the ones observed above for the
275 changes of pH and yields of hydrochar and liquid fraction, hence the production of FU
276 and 5-HMF as a function of severity were much more scattered than in [Fig. 1](#) and [2](#).
277 However, a peak of production was still visible in the range of severity 3.5 – 4.5. [Fig. 4](#)
278 shows the example of FU production from cellulose, hemicellulose and lignin.

279 According to [Fig. 3 and 4](#), the highest concentration peak of FU was obtained from
280 hemicellulose, followed by cellulose and, far behind, lignin. On the contrary, the peak
281 of 5-HMF concentration was the highest for cellulose, followed by hemicellulose and
282 finally lignin (see again [Fig. 3](#)). These results are logical since the precursors of FU and
283 5-HMF are xylans and glucoses, respectively, as they are the main structural units of
284 hemicellulose and cellulose, respectively. FU and 5-HMF production from lignin was
285 thus not expected, and might be due to remaining polysaccharides present as impurities.



286
 287 Figure 3. Molar concentration of FU (left row) and 5-HMF (right row) as a function of
 288 reaction time, measured after HTC of: (a) and (b) hemicellulose; (c) and (d) cellulose;
 289 (e) and (f) lignin.



290

291

292 Figure 4. Production of FU by HTC of: (a) cellulose, (b) hemicellulose; and (c) lignin,

293 as function of severity.

294

295 3.5. Reaction kinetics

296 During HTC, FU and 5-HMF were produced but disappeared due to various

297 decomposition reactions. Two different models taking into account consecutive

298 reactions were considered in order to fit the kinetics of both production and

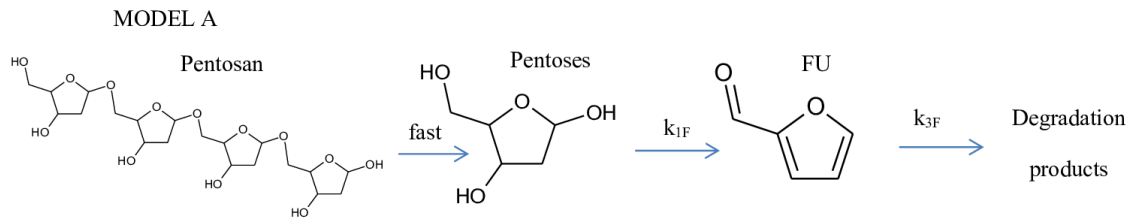
299 decomposition reactions.

300 The first one, referred to as model A in the following, considers FU and 5-HMF as

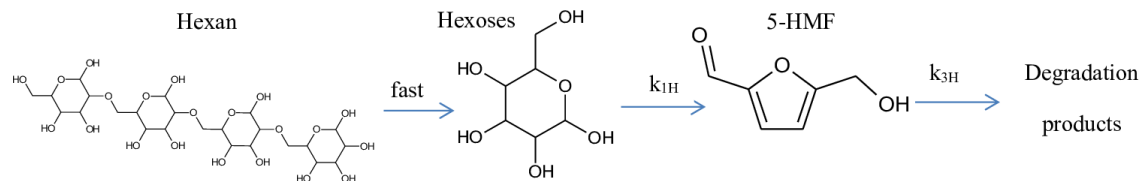
301 intermediates between simple sugars derived from BCs and final products, whether

302 those BCs are hemicellulose, cellulose or lignin. All reactions were assumed to be first-

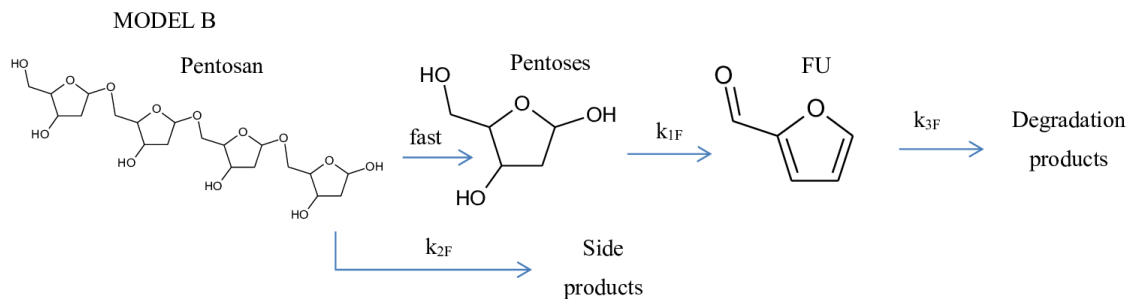
303 order and are presented in Fig. 5 for FU and 5-HMF, respectively.



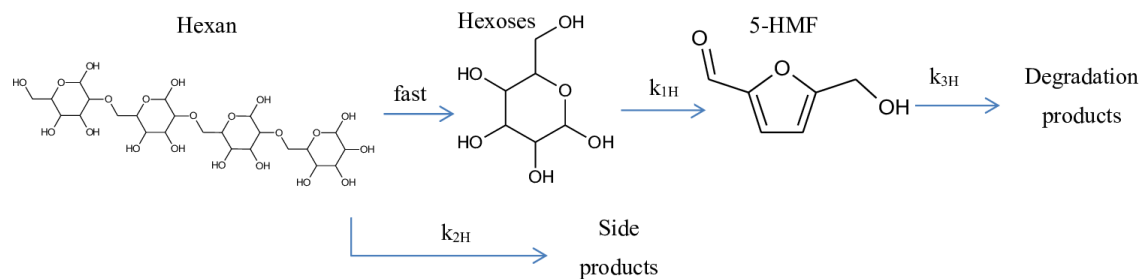
$$C_{FU} = C_{BC} \cdot \left(\frac{k_{1F}}{k_{3F} - k_{1F}} \right) \cdot [e^{-(k_{1F}) \cdot t} - e^{-(k_{3F}) \cdot t}] \quad (8)$$



$$C_{5-HMF} = C_{BC} \cdot \left(\frac{k_{1H}}{k_{3H} - k_{1H}} \right) [e^{-(k_{1H}) \cdot t} - e^{-(k_{3H}) \cdot t}] \quad (9)$$



$$C_{FU} = C_{BC} \cdot \left(\frac{k_{1F}}{k_{3F} - k_{1F} - k_{2F}} \right) \cdot [e^{-(k_{1F} + k_{2F}) \cdot t} - e^{-k_{3F} \cdot t}] \quad (10)$$



$$C_{5-HMF} = C_{BC} \cdot \left(\frac{k_{1H}}{k_{3H} - k_{1H} - k_{2H}} \right) \cdot [e^{-(k_{1H} + k_{2H}) \cdot t} - e^{-k_{3H} \cdot t}] \quad (11)$$

304

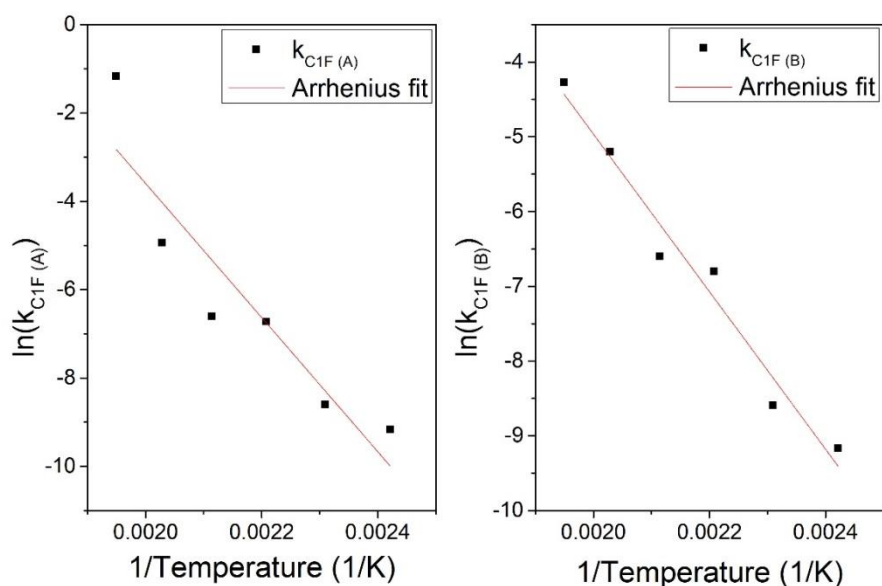
305 Figure 5. Models A and B Governing pentosan and hexan reactions. Model B takes into
306 account competitive reactions to give side products, other than FU and 5-HMF.

307 The second model, called model B, considers, in addition to the same
308 aforementioned successive reactions, the existence of side reactions leading to the
309 production of other species. In this case, all reactions were assumed first-order too. Side
310 reactions were suggested by Liu et al. (2014), who showed that better fits to the kinetics

311 data were obtained compared to the case of the simple model of consecutive reactions
312 (model A). In other studies, an intermediate compound for each process has been
313 postulated, but could never be isolated or identified (Marcotullio, 2011). Model B,
314 taking into account side reactions, is also sketched in [Fig. 5](#).

315 Herein, it is considered that pentosan directly gives furfural and that hexan gives 5-
316 HMF with kinetic constants k_{1F} and k_{1H} , respectively. FU and 5-HMF decompose to
317 final products with kinetic constants k_{3F} and k_{3H} , respectively. Pentosan and hexan also
318 react by side reactions with constants k_{2F} and k_{2H} , respectively. After resolution of the
319 corresponding differential kinetics equations, FU and 5-HMF concentrations can be
320 expressed by Eq. (8) and (9) for model A, respectively, and by Eq. (10) and (11) for
321 model B, respectively. In those equations, C_{FU} , C_{5-HMF} and C_{BC} are the initial
322 concentrations of FU, 5-HMF and BC (cellulose, hemicellulose or lignin). Having in
323 mind that xylans and glucoses are the main structural units of hemicellulose and
324 cellulose, respectively. We assumed that BCs decomposed following exclusively model
325 A or model B. This assumption could be less logic for lignin but it is necessary to take
326 into account that here, the fraction of lignin considered is that giving FU and 5-HMF
327 and corresponding to polysaccharides present in lignin as impurities. As it was seen in
328 [Fig. 2e](#), lignin produced more hydrochar, in the whole range of severities tested, than C
329 and H because L is an aromatic molecule prone to condensate as it happens with other
330 polyphenolic compounds as tannins (Braghiroli et al., 2014, 2017, Selmi et al., 2018).

331 By application of these two models, the different constants were obtained, and
332 activation energy (E_a) and pre-exponential factor (k_0) were also determined by
333 application of Arrhenius' Eq. (5) to each kinetic constant. Examples of those Arrhenius
334 fits can be seen in [Fig. 6](#).



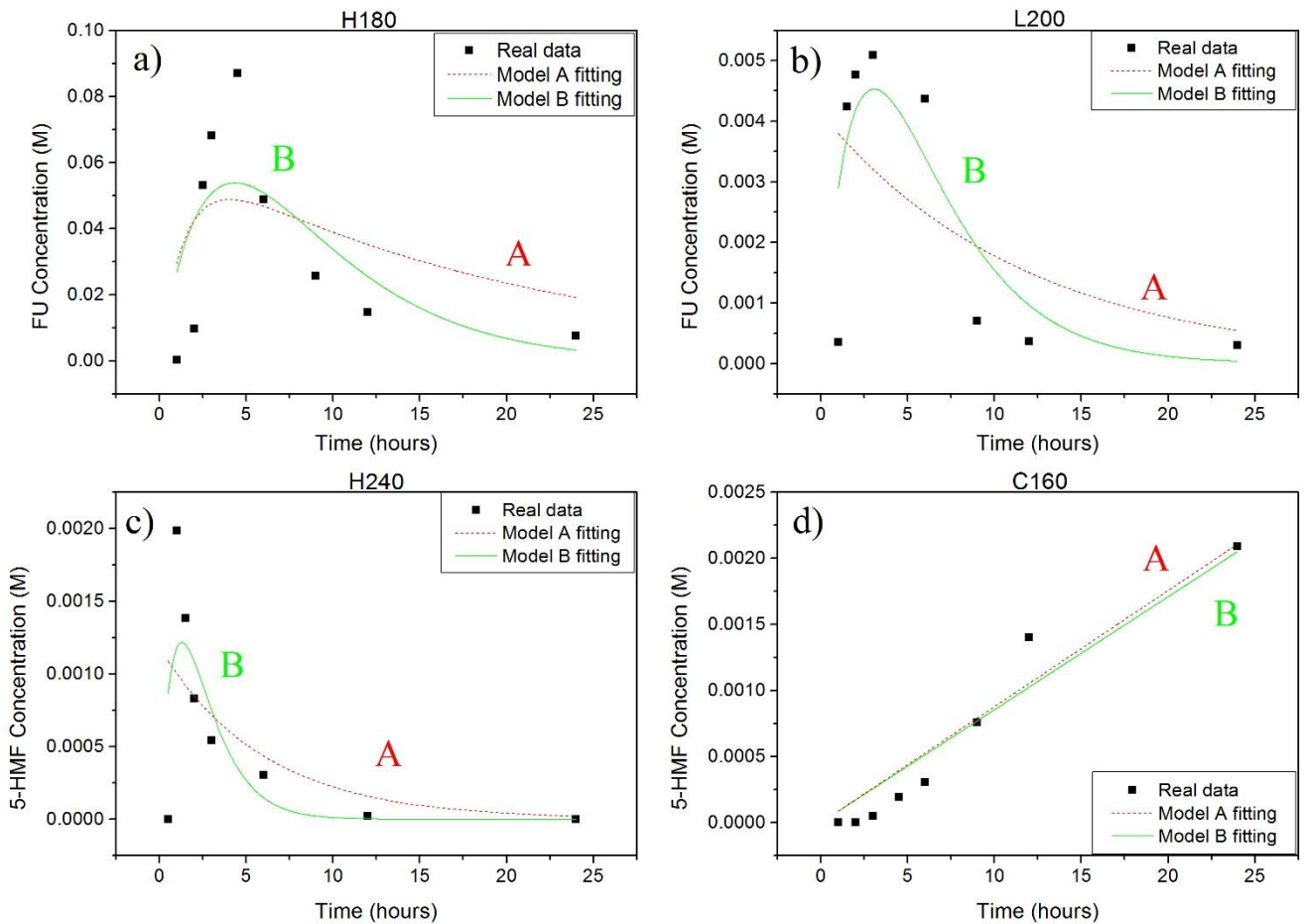
335
336 Figure 6. Examples of Arrhenius fitting applied to kinetic constants for cellulose.

337
338 Table 3. Activation energy (E_a , $\text{kJ}\cdot\text{mol}^{-1}$) and pre-exponential factor (k_0 , s^{-1}) for each FU
339 and 5-HMF reaction constant in models A and B.

| | Hemicellulose | | Cellulose | | Lignin | |
|--------------|---------------|----------|-----------|----------|----------|----------|
| | Model A | Model B | Model A | Model B | Model A | Model B |
| FU | | | | | | |
| $k_{0,1F}$ | 2.68E+7 | 2.93E+4 | 1.18E+8 | 2.69E+03 | 1.87E+10 | 5.94E+01 |
| $E_{a,1F}$ | 109.52 | 85.48 | 126.25 | 87.54 | 138.34 | 69.41 |
| $k_{0,2F}$ | | 3.88E+4 | | 1.28E+04 | | 6.90E+03 |
| $E_{a,2F}$ | | 78.67 | | 77.29 | | 71.60 |
| $k_{0,3F}$ | 3.75E+8 | 2.62E+4 | 2.50E+11 | 1.37E+04 | 5.53E+12 | 6.94E+03 |
| $E_{a,3F}$ | 108.22 | 76.56 | 136.52 | 77.49 | 138.71 | 71.56 |
| 5-HMF | | | | | | |
| $k_{0,1H}$ | 2.22E+13 | 2.16E+04 | 4.83E+15 | 1.09E+11 | 2.09E+11 | 1.47E+01 |
| $E_{a,1H}$ | 171.96 | 97.52 | 176.89 | 152.49 | 155.53 | 71.57 |
| $k_{1,2H}$ | | 1.31E+03 | | 2.20E+09 | | 8.78E+01 |
| $E_{a,2H}$ | | 66.01 | | 126.70 | | 55.79 |
| $k_{0,3H}$ | 5.08E+19 | 1.26E+03 | 9.33E+13 | 2.31E+09 | 9.38E+13 | 3.44E+02 |
| $E_{a,3H}$ | 207.03 | 65.82 | 179.30 | 126.56 | 152.77 | 61.50 |

340

341 In Fig. 7, representative examples of FU and 5-HMF concentrations measured when
 342 H, C or L were submitted to hydrothermal treatment at various experimental conditions.
 343 In general, model B fitted the experimental data better than model A, thus supporting
 344 the existence of side reactions. The corresponding values of E_a and k_0 for each model
 345 and each BC are presented in Table 3.



3. Figure 7. Variation of FU (a) and (b) and 5-HMF (c) and (d) concentration with time for
 347 a) H submitted at 180 °C, (b) L submitted at 200°C, (c) H submitted at 240 °C, and (d)
 348 C submitted at 160°C. Fitting with models A and B to the experimental data are
 349 included as dashed and continuous lines, respectively.

351

352 Table 4 shows the kinetic parameters reported in the open literature for xylose
 353 conversion. These results are compared to those obtained in the present study for
 354 hemicellulose, to which model B was applied. Most published works reported higher E_a
 355 values than those obtained here (Danon et al., 2014, Liu et al., 2014, Jing and Lü, 2007),
 356 which suggests that the effect of temperature observed herein is not as high as that
 357 reported in other studies. However, results regarding the same temperature range as in
 358 the present work led to lower E_a , thus in agreement with our findings (Kim et al., 2011).
 359 Concerning the pre-exponential factors, there is no obvious agreement between the
 360 various available results. The reason might be related to the too different ranges of time,
 361 temperature or initial concentrations used in this study with respect to those reported in
 362 other published works.

363

364 Table 4. Activation energies (E_a , kJ mol⁻¹) and pre-exponential factors (k_0 , s⁻¹) for
 365 xylose conversion into FU (k_1), side products (k_2) and degradation products (k_3) reported
 366 herein and in the literature.

| Ref | Catalyst | T (°C) | k_{1F} (s ⁻¹) | | k_{2F} (s ⁻¹) | | k_{3F} (s ⁻¹) | |
|-------------------------------|----------------|---------|----------------------------------|---------------------------------------|----------------------------------|---------------------------------------|----------------------------------|---------------------------------------|
| | | | $k_{0,1F}$ (s ⁻¹) | $E_{a,1F}$ (kJ·mol ⁻¹) | $k_{0,2F}$ (s ⁻¹) | $E_{a,2F}$ (kJ·mol ⁻¹) | $k_{0,3F}$ (s ⁻¹) | $E_{a,3F}$ (kJ·mol ⁻¹) |
| This study | None | 140-240 | 2.94E+04 | 85.5 | 3.89E+04 | 78.7 | 1.37E+04 | 76.56 |
| Danon et al., 2014 | HCl & NaCl | 160-200 | 1.05E-03 | 133.3 | 2.30E-04 | 125.8 | - | - |
| Liu et al., 2014 | Acetic acid | 150-190 | 9.81E+12 | 156.6 | 2.94E+12 | 149 | 3.69E+09 | 115.1 |
| Jing and Lü, 2007 | None | 180-220 | 6.28E+06 | 111.47 | 1.40E+10 | 143.14 | 3.31E+01 | 58.84 |
| Kim et al., 2011 | None | 140-240 | 2.05E+01 | 76.6 | 3.31E-1 / 2.66E+12* | 58.8 / 154* | 4.92E-16 | 24.2 |

367 *Two values are presented since the reaction is a combination between first and second order
 368 reaction (first and second values, respectively).

369

370 Table 5 shows the kinetic parameters obtained here for cellulose decomposition
 371 using model B, compared to those available in the open literature for 5-HMF
 372 conversion. E_a values were similar to those previously reported, but k_0 values were
 373 lower than those of previous works, probably due, again, to the wider range of
 374 temperatures studied in this present work.

375

376 Table 5. Activation energies (E_a , kJ mol⁻¹) and pre-exponential factors (k_0 , s⁻¹) for
 377 hexose conversion into 5-HMF (k_1), side products (k_2) and degradation products (k_3)
 378 reported herein and in the literature.

| Ref | Raw material | Catalyst | T (°C) | k_{1H} (s ⁻¹) | | k_{2H} (s ⁻¹) | | k_{3H} (s ⁻¹) | |
|----------------------------|----------------------------|-------------------|---------|----------------------------------|---------------------------------------|----------------------------------|---------------------------------------|----------------------------------|---------------------------------------|
| | | | | $k_{0,1H}$ (s ⁻¹) | $E_{a,1H}$ (kJ·mol ⁻¹) | $k_{0,2H}$ (s ⁻¹) | $E_{a,2H}$ (kJ·mol ⁻¹) | $k_{0,3H}$ (s ⁻¹) | $E_{a,3H}$ (kJ·mol ⁻¹) |
| This study | Microcrystalline cellulose | Non catalysed | 140-240 | 1.09E+11 | 152.49 | 2.20E+09 | 126.70 | 2.31E+09 | 126.55 |
| Jing and Lü, 2008 | Glucose | Non catalysed | 180-220 | 8.44E+07 | 108.03 | 7.22E+10 | 135.71 | 2.02E+06 | 95.4 |
| Shen and Wyman 2012 | Microcrystalline cellulose | Hydrochloric acid | 180-200 | 4.67E+13* | 137 | - | - | 2.20E+15* | 144.83 |

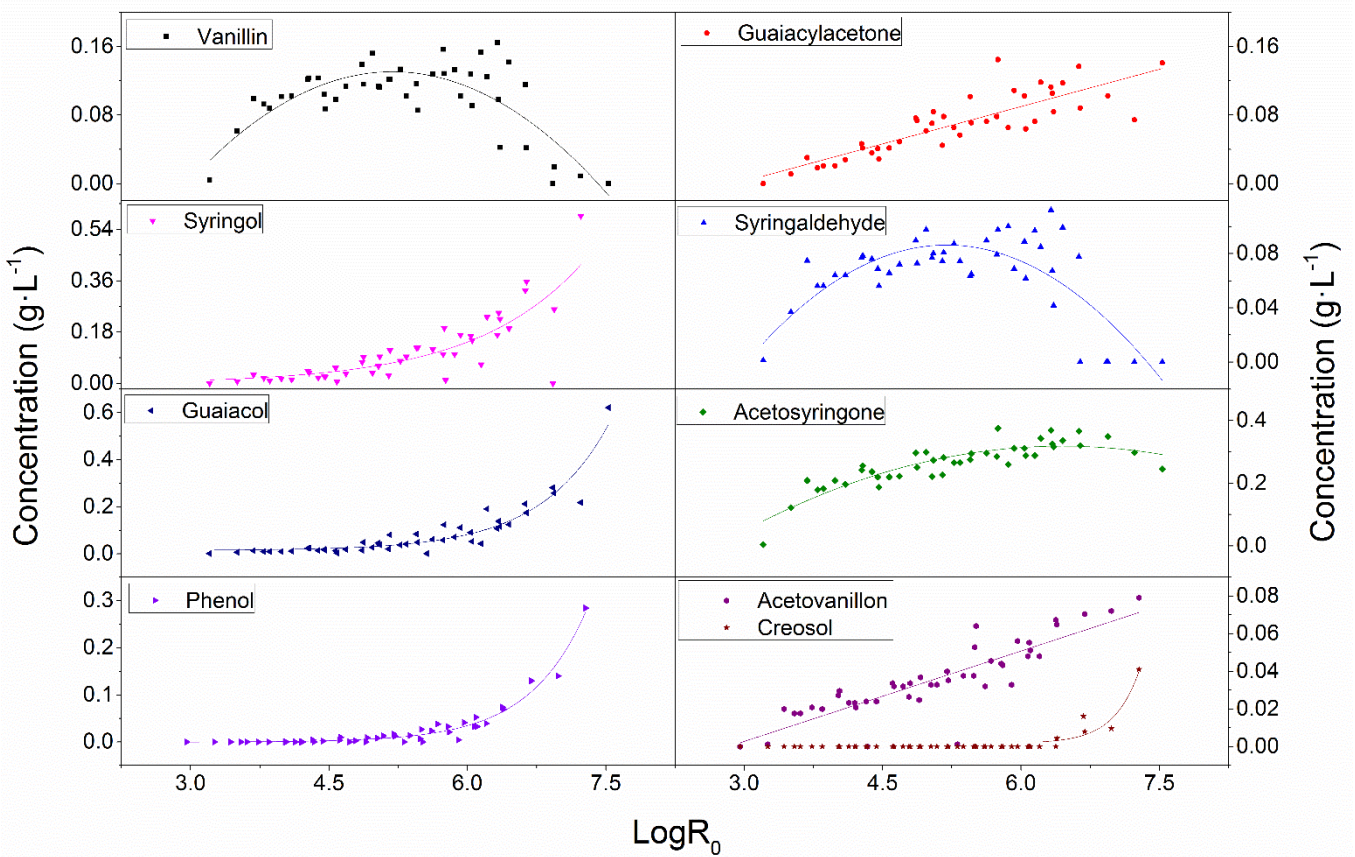
379 *Unit of L·(mol·s)⁻¹ instead of s⁻¹ because proton concentration was not taken into account.
 380

381 3.6 Phenolic compounds production

382 Fig. 8 shows the production of nine phenolic compounds obtained by HTC of lignin
 383 as a function of severity: 4-hydroxy-3-methoxy benzaldehyde (vanillin), 4-hydroxy-3-
 384 methoxy phenylacetone (guaiacyl acetone), 4-hydroxy-3,5-dimethoxy benzaldehyde
 385 (syringaldehyde), 2,6-dimethoxyphenol (syringol), 4'-hydroxy-3',5'-dimethoxy
 386 acetophenone (acetosyringone), 2-methoxyphenol (guaiacol), phenol, 4-hydroxy-3-
 387 methoxyacetophenone (acetovanillone), and 2-methoxy-4-methylphenol (creosol).

388 Different behaviours can be observed in the investigated range of experimental
 389 conditions: vanillin, syringaldehyde and acetosyringone showed a maximum of

390 concentration, followed by a decrease. Despite the natural scattering of the data, it can
 391 be seen that the maximum of vanillin and syringaldehyde production both appeared at a
 392 similar severity around 5, whereas the maximum of acetosyringone was reached at a
 393 severity close to 6.2. Above such optimal severity values, vanillin and syringaldehyde
 394 concentrations dropped significantly whereas that of acetosyringone only decreased
 395 moderately. Meanwhile, guaiacyl acetone and acetovanillone presented a linear increase
 396 of concentration. Guaiacol, syringol and phenol concentrations also increased, but in a
 397 somewhat exponential way. Finally, creosol was only produced at the highest severity,
 398 at which its concentration also increased quite fast.



400 Figure 8. Concentration of the nine phenolic compounds studied in this work as a
 401 function of severity.

402

403 Regarding the exhibited behaviours, various fitting trends were found whose
 404 polynomial, linear or exponential character is accounted for by Eq. (12), (13) and (14),
 405 respectively. The values of the corresponding parameters for each compound are given
 406 in Table 6, and may be use for predicting the production of phenolic compounds from
 407 lignin submitted to hydrothermal treatment at a given severity $\log R_0$.

$$408 \quad C_{phenolic\ compound} = a + b(\log R_0) + c(\log R_0)^2 \quad (12)$$

$$409 \quad C_{phenolic\ compound} = \alpha + \beta(\log R_0) \quad (13)$$

$$410 \quad C_{phenolic\ compound} = \delta + B \cdot e^{(\kappa(\log R_0))} \quad (14)$$

411

412 Table 6. Parameters from the fits of Eq. (12), (13) or (14) to the data of Fig. 8.

| Phenolic Compound | Parameters of the fits | | |
|-------------------|------------------------|----------|----------|
| | Polynomial | | |
| | <i>a</i> | <i>b</i> | <i>c</i> |
| Vanillin | -0.51 | 0.26 | -0.02 |
| Syringaldehyde | -0.36 | 0.18 | -0.02 |
| Acetosyringone | -0.56 | 0.28 | -0.02 |
| | Linear | | |
| | α | β | |
| Guaiacylacetone | -0.08 | 0.029 | |
| Acetovanillon | -0.05 | 0.016 | |
| | Exponential | | |
| | δ | <i>B</i> | κ |
| Syringol | 1.4E-3 | 0.001 | 0.851 |
| Guaiacol | 0.014 | 2.87E-5 | 1.35 |
| Phenol | -6.17E-4 | 2.27E-6 | 1.61 |
| Creosol | 1.65E-3 | 1.63E-13 | 3.58 |

413

414 4. Conclusion

415 The reactions of cellulose, lignin and hemicellulose submitted to HTC were
 416 investigated in a broad range of times and temperatures. The main kinetic parameters
 417 were determined, and final pH and hydrochar yield were plotted versus the severity of
 418 the process. Hemicellulose and cellulose submitted to HTC produced more acidic

419 solutions containing higher amounts of FU and 5-HMF, respectively, but the latter
420 compounds did not account for the low pH, which was instead due to low molecular-
421 weight acids obtained at the same time.

422 The hydrochar yields increased in the order hemicellulose < cellulose < lignin. The
423 hydrochar yields of cellulose and hemicellulose decreased, around 40%, when the
424 severity increased, and lignin was the most stable compound in the most severe
425 conditions. The amount of liquid fraction recovered after HTC of hemicellulose did not
426 change much with severity, whereas that of cellulose was first stable and then
427 dramatically dropped down to 20%. That of lignin slightly decreased when the severity
428 increased.

429 The kinetics of FU and 5-HMF production were described, using two different
430 models involving consecutive reactions with or without additional side reactions. The
431 pre-exponential factors and activation energies were determined and were comprised
432 within the range of those reported in the open literature. Observed differences were
433 attributed to the broader range of severities used in the present study. Finally, nine
434 phenolic compounds produced by HTC of lignin were also studied, and different
435 behaviours were observed in the range of severities used herein: either a maximum
436 concentration at some optimal severity (vanillin, syringaldehyde and acetosyringone), a
437 continuous linear increase of concentration (guaiacyl acetone and acetovanillone), or a
438 somewhat exponential increase (guaiacol, phenol, syringol and creosol).

439 The present results are expected to be useful for further modelling the behaviour of
440 complex biomass submitted to HTC at various severities. These studies are presently in
441 progress.

442

443

444 **Acknowledgements**

445 The authors gratefully acknowledge the financial support of the CPER 2007–2013
446 “Structuration du Pôle de Compétitivité Fibres Grand’Est” (Competitiveness Fibre
447 Cluster, France), through local (Conseil Général des Vosges), regional (Région
448 Lorraine), national (DRRT and FNADT) and European (FEDER, France) funds. This
449 work was also supported by a grant overseen by the French National Research Agency
450 (ANR) as part of the “Investissements d’Avenir” program (ANR-11-LABX-0002-01,
451 Lab of Excellence ARBRE).
452

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