

# 1 Understanding biomass fractionation in subcritical & supercritical 2 water

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## 9 Abstract

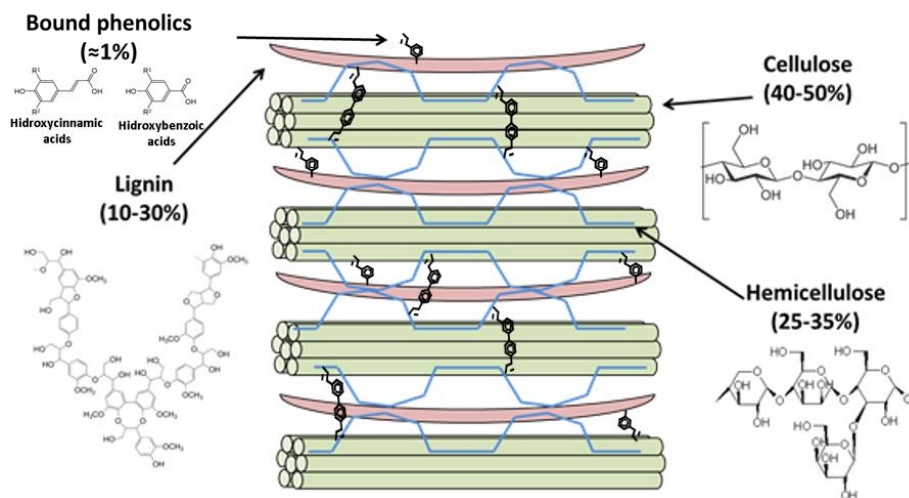
10 Biomass fractionation into its individual building blocks poses a major challenge  
11 to the biorefinery concept. The recalcitrance of the lignocellulose matrix and the  
12 high crystallinity of cellulose make typical feed stocks difficult to separate into  
13 their components. Hydrothermal processing fractionates biomass by its  
14 hydrolysis. However, a deep knowledge of hydrolysis principles is required since  
15 an inappropriate selection of the operating parameters such as an excessive  
16 temperature and a long residence times causes dramatic selectivity losses. This  
17 review is divided in four main sections which present the fundamentals of  
18 lignocellulosic biomass fractionation in hemicelluloses, cellulose and lignin. As  
19 the biomass structure plays an important role, a section to study the extraction of  
20 the linked phenols that joint lignin and hemicelluloses is included.

## 21 1. Introduction

22 Shifting the chemical industry away from petrochemical feedstocks towards  
23 renewable, bio-based chemicals and materials is a long-term strategy of the  
24 European Union. This “biorefinery” concept, despite being proposed as early as  
25 the late 1980s, has still not come to fruition because the cost and complexity of  
26 processing biomass to generate practical, usable, saleable feedstocks makes it  
27 unfeasible.

28 Lignocellulose is the most abundant, cheapest and easiest grown form of  
29 biomass, and it is composed of three main fractions: cellulose (40-50%),

30 hemicellulose (25-35%) and lignin (10-30%), in addition to minor compounds.  
 31 These fractions represent potential feedstocks for bio-sourced commodity  
 32 chemicals, but due do their differing chemical functionalities (lignin made up of  
 33 linked aromatic units, hemicellulose of C5 sugars and cellulose of C6 sugars)  
 34 separation steps are necessary to isolate the appropriate fraction and break it  
 35 into its individual building blocks (e.g. sugars for cellulose/hemicellulose and  
 36 aromatic units for lignin).  
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*Figure 1: Lignocellulosic biomass structure*

41 This fractionation of biomass into its individual building blocks poses a major  
 42 challenge to the biorefinery concept, because the recalcitrance of the  
 43 lignocellulose matrix and high crystallinity of cellulose makes typical feedstocks  
 44 difficult to separate into their components. For this reason, it typically requires  
 45 long reaction times (from 30 minutes for the hydrothermal hydrolysis to 24-70  
 46 hours for enzymatic hydrolysis) and the presence of strong reagents (sodium  
 47 hydroxide and sodium sulfide during Kraft pulping, for example). This leads to  
 48 degradation of the non-cellulosic fractions as well as large volumes of effluent  
 49 which requires expensive treatment to reduce environmental load.

50 To truly harness the potential of the biorefinery concept, this fractionation step  
 51 needs to be revolutionized. It needs to be considerably more process intensive  
 52 (ideally seconds per unit volume of biomass -as opposed to minutes or hours) to  
 53 enable modular units to deal with large volumes of biomass at decentralized

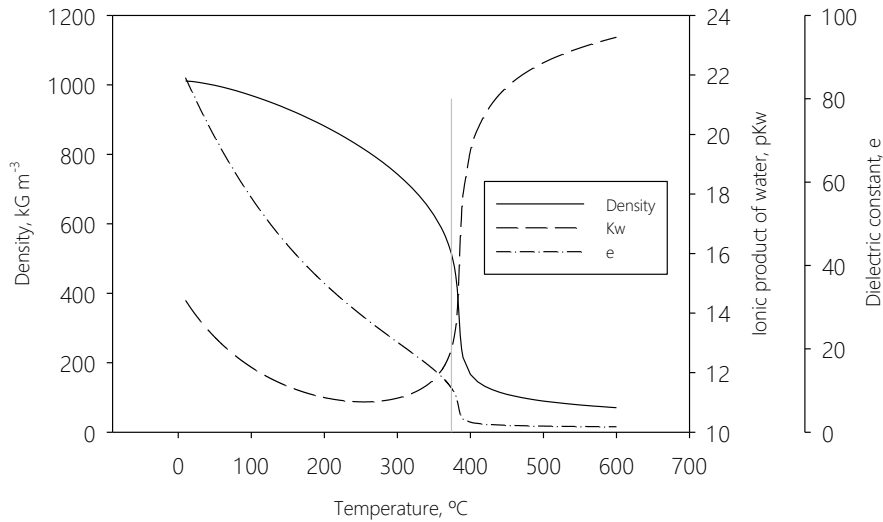
54 locations. It must not involve the use of harsh reagents in order to minimize  
55 environmental impact and cost, whilst maintaining quality of the fractions.

56 Water above its critical point ( $T_c$  374°C, 22 MPa), is an alternative solvent for  
57 dissolution/hydrolysis of biomass. Its low viscosity and high diffusivity facilitate  
58 the penetration of water into the complex structure of the lignocellulosic matrix,  
59 whilst its low dielectric constant, similar to non-polar organic solvents, enhances  
60 solubility of organic compounds. Physical properties of water (such as density,  
61 ionic product, dielectric constant) can be finely tuned by varying temperature and  
62 pressure. At these conditions, the hydrolysis of biomass fractions is rapid and  
63 presents a mean to achieve significantly more process intensive fractionation of  
64 biomass.

65 Reaction speed – whilst being an advantage to process intensification – is also a  
66 significant disadvantage to selectivity at longer reaction times, leading to  
67 degradation of hydrolysis products and resulting in complex reaction mixtures.  
68 This degradation and mixture complexity leads to inefficient recovery of biomass  
69 derived products and intermediates. There is therefore a need for understanding  
70 the hydrothermal fractionation processes to improve processes selectivity, which  
71 can harness the potential of subcritical and supercritical water fractionation.

72 Even under water's critical point, certain fractions of biomass face reactions that  
73 proceed too rapidly to be controlled by conventional methods. For instance, lignin  
74 undergoes rapid hydrolysis and subsequent hydrolysis product conversion in less  
75 than 1 second at 350 °C. Whilst poor selectivity is common to both sub- and  
76 supercritical water (SCW), there are some significant differences between the  
77 reaction media – most notably the difference in ionic product of water (for  
78 example the  $H^+/OH^-$  concentration at 300°C and 22 MPa is around  $3 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$   
79 vs  $3 \cdot 10^{-10}$  at 400 and 22 MPa) which means that subcritical water has a higher  
80 concentration of ions ( $[H^+]$  and  $[OH^-]$ ) thus favoring ionic reactions vs the radical  
81 reactions that are prevalent under SCW conditions.

82



83

84 *Figure 2. Subcritical and supercritical water properties around the critical*  
 85 *(22 MPa).*

86 This manuscript studies the lignocellulosic biomass fundamentals fractionation in  
 87 subcritical and supercritical water, in order to improve the selectivity of the  
 88 hydrothermal biomass fractionation. The manuscript presents four main sections  
 89 to presents the fractionation of biomass in hemicellulose, sugars and lignin. As  
 90 the biomass structure plays an important role, a section to study the linked  
 91 phenols that joint lignin and hemicelluloses is included.

## 92 2. Hemicellulose(s) fractionation fundamentals

93 Hemicellulose is a biopolymer present in lignocellulosic materials that acts as a  
 94 connection between the fibbers (cellulose) and the 3-dimensional structure  
 95 (lignin), constituting between 25% and 35% of the whole biomass [1]. It is  
 96 characterized by their amorphous structure and by the fact that it is acetylated  
 97 [2]. Regarding its composition, it is a biopolymer mainly composed of pentoses  
 98 with few hexoses in between, with a maximum length around 200 or 300  
 99 monomeric sugars, which makes it a renewable source of chemicals based on 5-  
 100 carbon molecules. The maximum molecular weight is lower than 70 kDa in most  
 101 cases [3]. However, there are discrepancies between species. For instance,  
 102 xylose is the most common monomer in hemicelluloses of hardwood trees, while  
 103 softwood trees are principally composed of mannans, like mannose [2]. In  
 104 addition, there are two different types of hemicellulose from the extraction

105 viewpoint: one hemicellulose easy to extract and another one that is associated  
106 with the fibers of cellulose that can be recovered only when cellulose is also  
107 removed (temperatures above 240 °C) [4–6]. Since hemicelluloses have some  
108 potentially acidic groups (acetyl groups among others), it can be recovered by  
109 Kraft pulping. However, the use of this technique leads to a degradation of  
110 hemicellulose, so a different technique is required to obtain it with a high quality.  
111 Thus, hydrothermal extraction would be one of the most promising options since  
112 it only requires water and mild temperatures (160-210 °C) to extract it [7,8]. If the  
113 operational temperature is around 180 °C, 60% of the initial hemicellulose can be  
114 recovered as oligomers and sugars [4,9]. Higher yields can be obtained if  
115 temperature increases but undesired degradation products appear [10,11].  
116 However, hemicellulose can be recovered also at low temperatures (90 °C) if the  
117 operating time is high enough (days) [12]. Hemicellulose extraction has been  
118 performed in both systems, batch and packed bed reactors. Therefore, it should  
119 be also marked that two different operating times can be defined, the solid and  
120 liquid time. The former is the time used to treat the solid. The liquid time has the  
121 same value as the solid time in batch systems. However, it is fixed by the  
122 volumetric flow when semi-batch or continuous system are used, being the  
123 residence time (see appendix 1 for more details about the different residence  
124 times). Moreover, hemicellulose hydrothermal fractionation is a complex process  
125 that involves several physical phenomena [6,8,13,14], which are present as in  
126 batch as in continuous systems, and a good knowledge of them is mandatory for  
127 designing a profitable and sustainable hemicellulose extraction plant. These  
128 phenomena are:

- 129 • Hemicellulose cleaving into decreasing molecular weight oligomers
- 130 • Hemicellulose deacetylation (autohydrolysis)
- 131 • Hemicelluloses dissolution and mass transfer between the solid and the  
132 liquid
- 133 • Production of sugars & sugars degradation into furfural or other  
134 substances
- 135 • Porosity changes: extraction, swelling and biomass compaction

136 Additionally, and once the phenomenology is explained, a short summary about  
137 the effect of the main operational variables on hemicellulose selectivity is  
138 included.

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## 140 2.1. Hemicellulose cleaving into decreasing molecular weight 141 oligomers

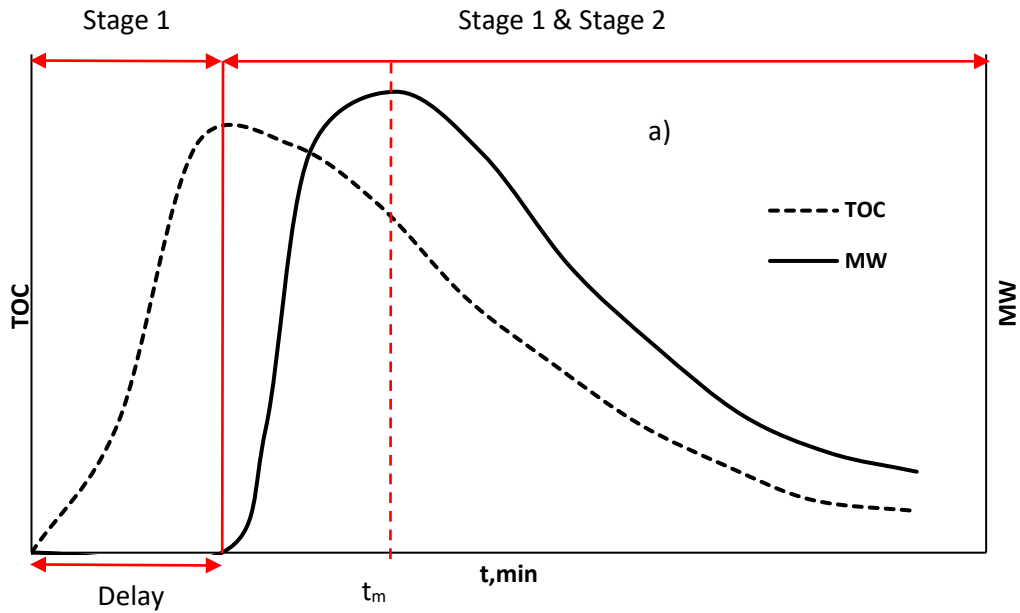
142 The following discussion is focused on the behavior observed in a semi-  
143 continuous system since only globalized values can be obtained from a batch  
144 reactor. Hemicellulose cleaving is one of the first phenomena that takes place  
145 inside a chip or a particle of biomass. Due to the mild operating temperature (e.g.  
146 120 to 185 °C), the bonds between the monomeric sugars start breaking  
147 randomly, producing progressively shorter oligomers. This process continues  
148 until the moment in which the oligomer has a length low enough to be extracted  
149 from the solid by solubilization or dragging [6,14,15]. In this moment, both  
150 phenomena are present, oligomer dissolution and oligomer cleaving, and two  
151 distinct stages can be differentiated: (1) solid oligomer cleaving, which is present  
152 from the beginning, and (2) solid & liquid oligomer cleaving with hemicellulose  
153 dissolution. The fact that these two phases are present at the same time explain  
154 why there is a delay in the extraction profiles (Figure 3.a). Before this first soluble  
155 oligomer releasing, only raw material free sugars and a little number of cleaving  
156 products (small oligomers and monomers) could be removed. Nevertheless,  
157 there are cases where no delay is present due to the biomass diversity [16]. This  
158 is possible when the initial hemicellulose length is so low that it is initially soluble  
159 or it is so acetylated that only stage 2 is present. Therefore, if both stages are  
160 present, the molecular weight evolution during the extraction should have a  
161 maximum (the first soluble oligomer) near the time ( $t_m$ ) when the concentration in  
162 the liquid reaches the highest value (Figure 3.b). After this molecular weight peak,  
163 it would continuously decrease due to the cleaving. This Behavior was already  
164 observed in literature [15,16]. However, when only stage 2 is present the  
165 molecular weight would decrease with time.

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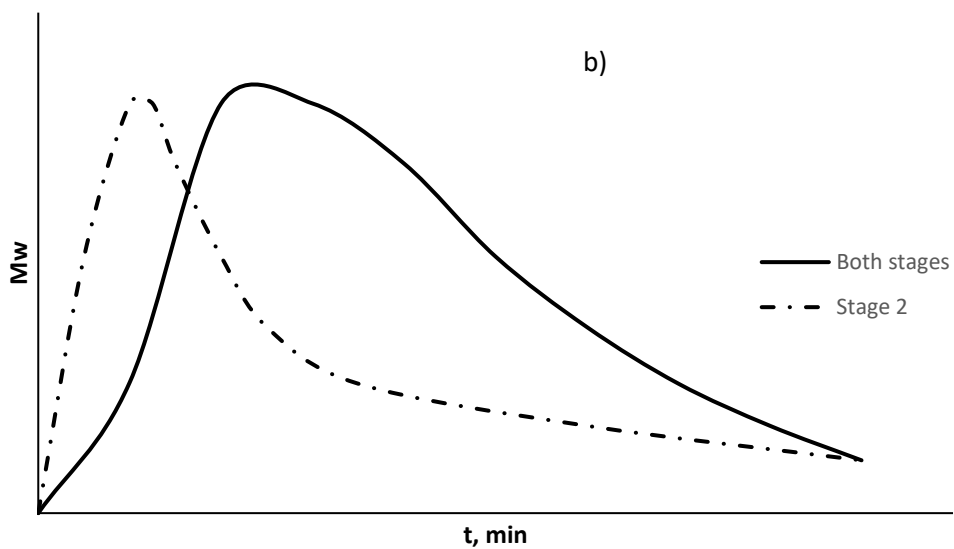
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Figure 3: Liquid profiles at the output of a packed bed reactor during a hydrothermal extraction process: (a) TOC evolution, (b) molecular weight evolution (Mw) when both stages are presents and molecular weight evolution when only stage 2 is present.

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178 To sum up, temperature, the molecular weight and de acetyl contents plays an  
179 essential role in hemicellulose extraction since they directly affect hemicellulose  
180 solubility.

## 181 2.2. Sugar production from the cleaving processes

182 As it was explained in the previous section, the cleaving can also produce  
183 monomeric sugars and, if temperature is high enough, all the hemicellulose could  
184 be converted into monomeric sugars. However, the operational conditions  
185 required to achieve a complete conversion are so high that they also imply sugar  
186 degradations. *Gallina et al.* [4] studied the optimal conditions for the hydrothermal  
187 fractionation of *eucalyptus* in a semi-continuous reactor. They found that the  
188 optimum monomeric sugar yield was at 185 °C (67.41%), starting to decrease at  
189 higher temperatures. *Yedro et al.* [9] assessed the hemicellulose extraction from  
190 *holm oak* in a batch system, obtaining that the highest monomeric yield was at  
191 170 °C (60%) and that degradation started at temperatures as low as 150 °C.  
192 *Rissanen et al.* [10] analyzed the hydrothermal degradation of spruce in the same  
193 reactor as *Yedro et al.* [9], reaching a similar optimum. *Sukhbaatar et al.* [11]  
194 worked with sugarcane bagase also in a batch system, being their monomeric  
195 yield optimum at 180 °C and observing a huge degradation above 190 °C. The  
196 same biomass was considered by *Vallejos et al.* [17] who reached the best  
197 monomeric yield at 180 °C too (70%). Similar result were reported by *Thomsen*  
198 *et al.*[18], *dos Santos Rocha et al.*[19] and *Makishima et al.* [20] for wheat straw,  
199 sugarcane straw and corncob, respectively.

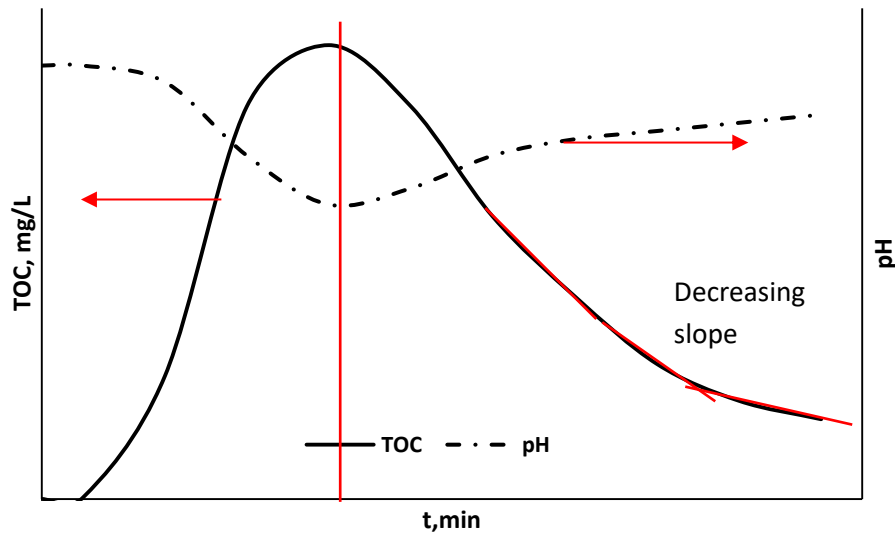
200 Focusing on direct sugar production is of interest since they can be used to  
201 produce fuels (bioethanol) or chemicals (like xylitol via hydrogenation). These so-  
202 called “degradation products” can also be the target [8]. For instance, furfural and  
203 its derivatives can be used as fungicides or lubricants [21] while lactic acid is a  
204 precursor for biodegradable polymers production [22]. Therefore, to  
205 avoid/promote sugar degradation the operating temperature and the volumetric  
206 flow (the less time in the reactor, the lower degradation [4,7,18,20] are the main



207 involved variables. It is worth highlighting that when the reactor is a batch system,  
208 the liquid/solid ratio has the same role as residence time.

### 209 2.3. Hemicellulose deacetylation

210 Hemicellulose deacetylation and cleaving take place in parallel, which is reflected  
211 in a releasing of acetic acid during the hemicellulose extraction, decreasing the  
212 pH of the water. It should be remarked that this acetic acid production only  
213 happens in the solid phase [6,14,23–25]. However, acetic acid can be obtained  
214 from sugar degradation in liquid phase too [8]. Similarly, uronic acid can be also  
215 released during the hydrothermal treatment [26,27]. Nevertheless, it is not  
216 completely clear if the pH change accelerates extraction or if this change is only  
217 a consequence of the extraction [10,12]. This phenomenon is deeply related with  
218 the hemicellulose extraction process selectivity since these acids are a source of  
219 protons that catalyze the cleaving and degradation reactions in liquid phase if the  
220 residence time is high enough [6,14]. A statement that was verified by *Song et al.*  
221 [28], showing that degradation is much lower if the pH is maintained above 4-5.  
222 Moreover, the releasing of acetyl groups also means that the solubility of the  
223 remained part of the hemicellulose would be lower since the capacity of linking  
224 by hydrogen bonds with water would be lower. Additionally, the steric hindrance  
225 also would be higher. Following this idea, it can be seen in Figure 4. that the  
226 minimum of the pH corresponds to the maximum in the TOC profile. Thus, the  
227 oligomers involved in the stage (2) defined in Figure 3 will be more soluble since  
228 they are smaller but, at the same time, their solubility also decreases due to the  
229 lack of acetyl groups, explaining why the extraction is more difficult after the  
230 maximum (decreasing slope). Moreover, extraction would also be slower  
231 because the available amount of hemicellulose is much lower. Thereby, the  
232 acetylation degree (and uronic content) is another variable to consider.



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Figure 4: Relation between the pH and the extracted biomass.

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#### 2.4. Hemicellulose dissolution and mass transfer

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Hemicellulose solubility has been already discussed in section 2.1. External and internal mass transfer resistances can be present in this process. External mass transfer can be enhanced by a proper mixing for batch extraction in a stirred vessel or by high volumetric flows for semi-continuous and continuous extraction in tubular beds. Furthermore, internal diffusion problems can be minimized if the particle diameter is low enough. *Rissanen et al.* [10] indicated that the size of the extracted hemicelluloses is highly dependent on the initial particle diameter. When using particle size below 2-3 mm hemicelluloses are relatively easily extracted from the matrix and higher molecular weights are obtained. By contrast, when a bigger particle size is used, e.g. 1 cm chips, water comes inside the chip and the hydrolysis starts to take place. If deacetylation occurs, which is probable, then the acetic acid lowers the pH inside the chip accelerating the cleavage. Depending on the internal and external mass transfer of the protons, the time with low pH inside particle will be different and the final molecular weight will be also affected. In general, the smaller the particle sizes, the higher the molecular weights. However, it has been widely demonstrated that temperature and solid operating time have a bigger impact on the yield, promoting extraction when they are increased [4,7,9–13,15–20,29].

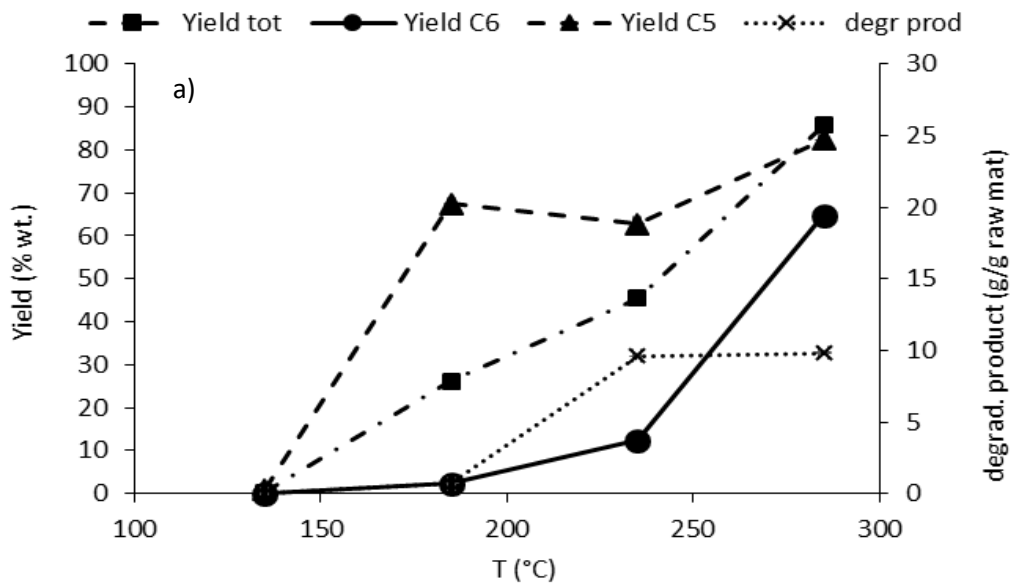
254        2.5.        Porosity changes: extraction, swelling and bed  
255                    compaction

256        During extraction, it is expected that the porosity of the bed increases since a  
257        certain amount of mass is being removed. However, if this extraction was  
258        important enough, the bed could collapse, reducing the porosity and making it  
259        impossible to continue the extraction (tremendous pressures drops). Additionally,  
260        biomass also can swell [6,13,14]. Therefore, a preliminary study about the  
261        behavior of the packed during the extraction should be required to avoid  
262        operational problems.

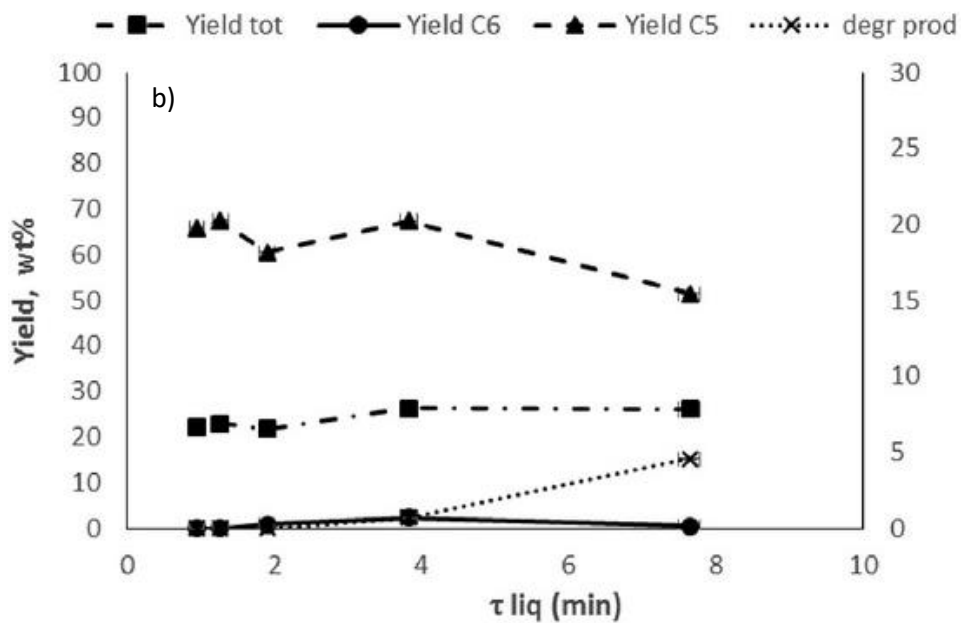
263        2.6.        Main variables on extraction selectivity: oligomers and  
264                    monomers as target compounds

265        It can be concluded from the discussion done from sub-section 2.1 to 2.5 that the  
266        main variables to promote hemicellulose extraction yield are the solid operational  
267        time and the operating temperature. Therefore, the higher the temperature/time  
268        is, the bigger yield is obtained. However, if these two variables are too high,  
269        hemicellulose sugars and oligomers start to degrade, reducing the selectivity  
270        [4,30]. For instance, this temperature effect can be easily seen in **Figure 5.a**,  
271        where it can be checked that at temperatures higher than 180 °C the yield of  
272        pentoses (C5) decreases although the global yield increases (Yield tot).  
273        Additionally, it is also worth mentioning that if temperature goes above 240 °C,  
274        cellulose extraction would take place making it possible to recover the  
275        hemicellulose **fraction associated with cellulose** and explaining the increase in  
276        the yield. Nevertheless, this higher temperature would also mean the releasing  
277        of hexoses and cellulose oligomers and the extraction of some lignin fractions  
278        [6,31,32], which would reduce the hemicellulose selectivity. On the other hand,  
279        not only does the solid time and the temperature control selectivity, but also the  
280        liquid residence time and the operational pH affect it. If residence time is low  
281        enough, sugar degradation can be avoided (**Figure 5.b**). Regarding pH, it has  
282        been demonstrated that degradation can be reduced up to around 90% if pH is  
283        maintaining upper than 4-5 [33]. To sum up and provided that a high

284 hemicellulose selectivity is desired, temperatures around 180 °C, pH above 4 and  
 285 high volumetric flows (residence time lower than 4 min) are required.



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287

288 *Figure 5: Hydrothermal extraction of eucalyptus in a semi-continuous reactor*  
 289 *(solid time of 90 min): evolution of the hemicellulose extraction yield (Yield tot),*  
 290 *the yield of hexoses (C6), pentoses (C5) and degradation products for*  
 291 *eucalyptus with temperature (a) and residence time at 185 °C (b) [4]*

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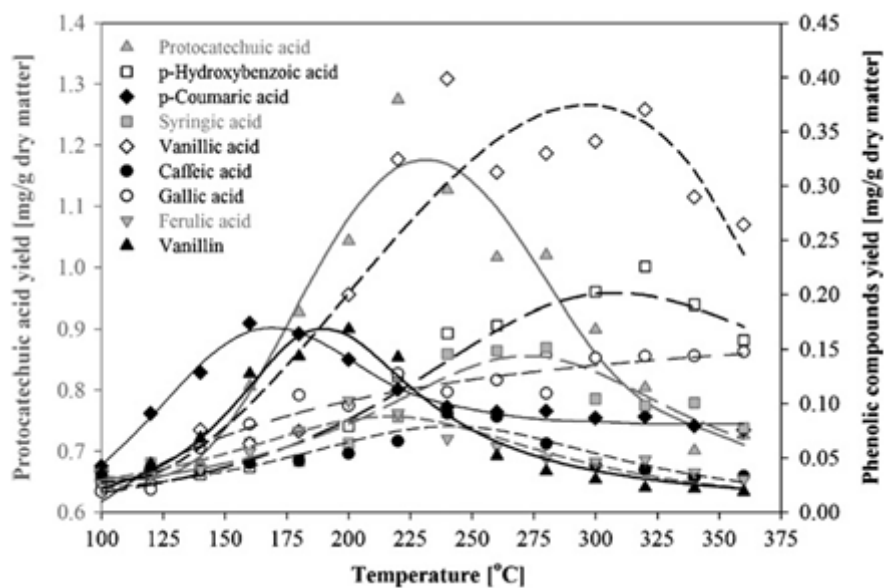
### 294 3. Bound phenolics

295 Phenolic compounds are of great interest due to their antioxidant properties and  
296 potential health benefits that make them useful in numerous commercial  
297 applications in the food, cosmetic and pharmaceutical industries [34]. They can  
298 be present in the matrix in three forms: free, soluble-bound (esterified to low  
299 molecular mass compounds) or in an insoluble-bound form (esterified and/or  
300 etherified to cell wall structural components) [35]. **In cereal brans and in some  
301 whole cereals, they are found approximately in the proportion 0.1:1:100, so at the  
302 beginning the free and soluble-bound moieties are negligible, but after applying the  
303 treatment that release the bound moiety from the solid, both soluble forms are of  
304 great importance. Moreover, the free and soluble-bound moieties present initially  
305 in the solid** are removed with the extractives and in this section the release of the  
306 bound moiety is analyzed.

307 Phenolic acids are a subgroup of phenolic compounds of great importance in  
308 cereal grains, which are mostly found in the insoluble form. Among them, ferulic  
309 and coumaric acid (two hydroxycinnamic acids) are the most studied ones due to  
310 its abundance in the plant kingdom. They provide rigidity to the cell wall [36] as  
311 they crosslink the sugar moieties and also the lignin. Despite being minor  
312 compounds (around **0.5-1%** in cereal brans) their high value can enhance the  
313 profitability of the biorefinery and in order to recover them, it is necessary to  
314 hydrolyze the ester and/or ether bonds that maintain them attached.

315 Alkaline hydrolysis is the most common procedure used for their releasing [37]  
316 but it is a non-selective method that also alter the whole matrix. On the other  
317 hand, enzymatic hydrolysis can be selective if the proper enzymes are chosen,  
318 but it must be taken into account the matrix as well as the main phenolics present  
319 [38]. Feruloyl esterases (EC 3.1.1.73) are a family of enzymes able to cleavage  
320 the ester bond between the hydroxycinnamic acids and the sugar moieties, but in  
321 some cases where the yield is low, the use a mixture of enzymes including  
322 xylanases lead to increase it significantly [39]. In this context, the use of  
323 pressurized water emerge as an interesting technique, which shorten  
324 considerably the extraction time and avoid the use of solvents and/or expensive  
325 enzymes. The optimum temperature, pressure and extraction time vary

326 depending on the raw material used and the main phenolic present. As the major  
 327 part of them are etherified to hemicelluloses and the ether bonds are labile at  
 328 170°C [35], temperatures higher than that are commonly used and as  
 329 consequence, the co-extraction of the hemicellulose also takes place. After a  
 330 certain temperature, or long extraction times, the phenolic compounds start to  
 331 decompose due to their thermal degradation. The effects named above can be  
 332 seen in Figure 6 where *Pourali et al.* [40] studied the effect of temperature on the  
 333 extraction yield of different phenolic acids from defatted rice bran, and obtained  
 334 different optimum temperatures for each phenolic acid. In the first stage, the ether  
 335 links are being released and the co-extraction of the hemicellulose enhance the  
 336 extraction, favoring the solvent penetration and the mass transfer; in the second  
 337 stage, the degradation of the phenolic compounds turn out to be higher than the  
 338 release, and so on, the extraction yield decrease.



339

340

341 *Figure 6. Effect of subcritical water temperature on the extraction of different*  
 342 *phenolic compounds from defatted rice bran (residence time = 10 min).*

343

*Obtained from Pourali et al [40]*

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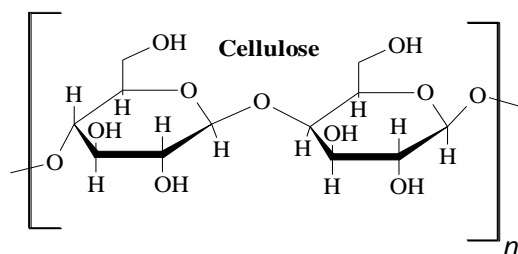
345 Therefore, after selecting the optimum conditions to maximize the extraction of  
 346 the target compound(s), a purification step is necessary to separate the phenolic  
 347 fraction from the hemicellulose fraction. However, this optimum condition should

348 be chosen avoiding or reducing the alteration of the cellulose and lignin fractions,  
349 as in the biorefinery process they will be separated in a next step.

350

#### 351 4. Cellulose

352 Cellulose is a renewable, cheap and worldwide-distributed polymer with very  
353 promising applications for the future industries. Cellulose is a linear-chain  
354 polysaccharide consisting on units of glucose linked by  $\beta$ -1,4 glucosidic bonds,  
355 which structure is shown in Figure 7. Its formula is  $(C_6H_{10}O_5)_n$ , where  $n$  is the  
356 degree of polymerization and goes from several hundred to many thousands of  
357 glucose units, depending on the raw material. The hydrogen bond network  
358 between OH groups in its structure promotes the aggregation of cellulose chains  
359 forming fibrils [41]. These fibrils are tough, water insoluble and forms the  
360 foundations of the plant cell walls [42–44]. For mass production, cellulose is  
361 obtained from plants, bacteria, algae and fungi via biosynthesis or in-vitro  
362 synthesis [45]. Although synthesized cellulose has numerous applications and  
363 uses, it is not the only way to make profit out of residual biomass.



364

365

*Figure 7. Cellulose formula*

366 Lignocellulosic biomass is a complicated matrix formed by an intricate network  
367 where cellulose, hemicellulose and lignin are linked and interacting together.  
368 Conversion of these biomass fractions into valuable products is the key step for  
369 the success of the bio-based future industries, where agricultural or industrial  
370 wastes usually regarded as worthless would be converted into chemicals, fuels  
371 and/or energy. In order to get these valuable products from lignocellulosic  
372 biomass, depolymerization and hydrolysis of cellulose to monomer glucose is  
373 regarded as a necessary first step [46]. Hydrolysis reaction implies the cleavage  
374 of a chemical bond by the addition of water [47]. However, as mentioned above,

375 cellulose is a water insoluble polymer so that it is not possible to simply dissolve  
376 and hydrolyze cellulose in water at ambient conditions. As a result, the hydrolysis  
377 of cellulose in lignocellulosic biomass usually involves the use of strong acids as  
378 catalysts [46], which cause a negative impact in the environment and yields a  
379 high concentration of degradation products. However, when using supercritical  
380 water cellulose is more effectively converted to oligomers and monomer sugars  
381 instead of yielding mainly degradation products.

382 Therefore, the objective of this section is to clarify the mechanisms involved in  
383 both the dissolution and the hydrolysis of cellulose in water as well as to discuss  
384 the influence of the key parameters which affect both processes.

#### 385 4.1. Cellulose dissolution

386 The dissolution of cellulose in water have been explained [48–50] from a  
387 thermodynamic point of view. The Gibbs free energy is a thermodynamic  
388 magnitude commonly considered to analyze whether a chemical process is  
389 spontaneous or not. Its variation is expressed as a combination of the variation  
390 of the enthalpy and the variation of the entropy of the system:

$$391 \Delta G = \Delta H - T\Delta S \quad (1)$$

392 “G” is the Gibbs free energy, “H” the enthalpy, “T” the temperature and “S” the  
393 entropy. When the variation of the Gibbs free energy is negative, the process is  
394 spontaneous. In the reaction of two different compounds, the variation of enthalpy  
395 represents the heat of reaction or the heat of mixing. In the combination of  
396 cellulose and water this parameter is almost negligible since no additional heat is  
397 generated or consumed. Therefore, the previous expression is reduced to:

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$$399 \Delta G = -T\Delta S \quad (2)$$

400

401 Consequently, the dissolution and hydrolysis of cellulose in water is carried out  
402 (spontaneous process) when the entropy variation is positive. From a structural  
403 point of view, the entropy of cellulose increases when its molecular conformation  
404 changes from a rigid structure to a more flexible one which benefits dissolution.  
405 Since cellulose structure is characterize by its complexity and rigidity, at lower



406 temperatures no conformational changes will be produced, the entropy will not  
407 increase nor the Gibbs free energy will decrease and therefore no dissolution will  
408 be produced. Only in the cases in which the temperature is considerably  
409 increased and therefore the internal energy of the structure, conformational  
410 changes could be produced.

411 In literature, three main characteristics of the cellulose structure are considered  
412 of fundamental interest in its dissolution in water:

413

414 1) The presence of intra and intermolecular hydrogen bonds [48,49,51].  
415 Cellulose is constituted by glucose molecules joined together forming long  
416 fibers which are connected by hydrogen bonds. This fact results in a rigid  
417 and cohesive structure which avoids the penetration of water molecules and  
418 consequently the dissolution of the structure.

419 2) Cellulose is considered an amphiphilic molecule [48,49,52]. Its structure has  
420 both hydrophobic and hydrophilic zones as a consequence of the orientation  
421 of its functional groups. While the hydroxyl groups located in equatorial  
422 position create the hydrophilic regions, the axial glycosidic bonds produce  
423 hydrophobicity. This is considered the reason why the water molecules are  
424 not able to easily create hydrogen bonds with the cellulose which will  
425 produce its dissolution.

426 3) Crystallinity: crystallinity has always been considered a key parameter when  
427 analyzing the dissolution of cellulose in water [48,53]. The high crystallinity  
428 of the cellulose molecule is responsible of its rigid structure avoiding  
429 conformational changes which could facilitate its dissolution.

430 Considering the lack of a robust model which explains the dissolution of cellulose  
431 in water, several authors have performed experiments with the objective of  
432 analyzing the influence of the process parameters.

433 From a structural point of view, [54,55] studied the influence of the raw cellulose  
434 used in the dissolution. They demonstrated that the cellulose allomorph directly  
435 affects the dissolution process. For example, although cellulose I is the most  
436 abundant type in nature, cellulose II is more stable [49]. Moreover, not only the  
437 cellulose type influences the dissolution, also the amount of water has to be  
438 considered [48,56]. Regarding to the crystallinity of the structure, [57] analyzed

439 the dissolution of cellulose after milling. Milling produces an amorphous structure  
440 which facilitates the action of water. They stated that the critical factor is not the  
441 reduction of the particle diameter but the cleavage of the hydrogen bonds and  
442 the consequent generation of amorphous zones. Amorphous and semi-crystalline  
443 zones are easier to be hydrolyzed since water molecules can avoid the  
444 hydrophobic zones which are present in the structure as a consequence of the  
445 amphiphilic nature of the cellulose [58].

446 From an operating point of view, the majority of experiments analyzed the  
447 process focusing in the variation of the pressure, the temperature and the  
448 reaction time. As it has been explained in this section, due to the physical  
449 structure and the nature of cellulose, its dissolution is greatly limited by  
450 temperature. Common working temperatures usually range from 200°C to more  
451 than 400°C. Therefore, in order to maintain water in liquid or supercritical state  
452 when the working conditions surpasses its critical point, ( $T_c=374^\circ\text{C}$ ,  $P_c=22.1$   
453  $\text{MPa}$ ) the pressure shall be increased. The analysis of the influence of pressure  
454 has been studied by [53]. They proved that when the pressure is increased above  
455  $50\text{MPa}$  (reaching pressures up to  $700\text{MPa}$ ), even at relative low temperatures  
456 the water molecules are able to enter inside the cellulose structure and swell the  
457 polymeric matrix which finally collapses. When the pressure is only considered in  
458 order to maintain the water in liquid or supercritical state, its influence is negligible  
459 and the fundamental parameters to be considered are the temperature and the  
460 reaction time. An increase of temperature clearly benefits the dissolution of  
461 cellulose since it modifies its structure favoring the combination of cellulose and  
462 water molecules. However, it also accelerates its hydrolysis consuming the  
463 cellulose which is being dissolved. Consequently, the only possibility of dissolving  
464 cellulose and reduce its hydrolysis rate is selecting an optimum combination of  
465 temperature and reaction time. In literature, the analysis of cellulose dissolution  
466 at high temperatures is generally combined with hydrolysis studies. Hydrolysis is  
467 considered one of the fundamental processes in green chemistry since it allows  
468 obtaining high value products from renewable resources such as biomass. As  
469 biomass is a complex raw material and due to the lack of enough know-how in  
470 this field, the majority of authors have started working with cellulose instead of  
471 with biomass. When cellulose is mixed with water at high temperatures, it is first

472 dissolved and subsequently it reacts with the water molecules present in the liquid  
473 medium producing the cleavage (hydrolysis) of the glycosidic bonds. As the  
474 cleavage of these bonds is not completely simultaneous nor instantaneous, first,  
475 oligosaccharides are generated which are then hydrolyzed to monosaccharides.  
476 Finally, if the hydrolysis reaction is not stopped, the monosaccharides are  
477 degraded to organic compounds such as acids [59,60]. As it has been stated, it  
478 is fundamental both in dissolution and in hydrolysis to find the optimum pair of  
479 temperature and reaction time values in order to reduce the generation of  
480 undesired products.

481 The experiments presented in literature are clearly divided in three zones:  
482 subcritical region, vicinities of the critical point and supercritical region.

483 In this paper, the subcritical region is considered the one in which the temperature  
484 remains below 320°C. In this zone the dissolution and subsequent hydrolysis is  
485 produced as a result of the consumption of superficial cellulose which is able to  
486 interact with water molecules [61]. Furthermore, the cellulose which can be easily  
487 dissolved is the one which was present in an amorphous state. Below 280°C, it  
488 is observed that the cellulose dissolution rate decreases with time since water is  
489 not able to dissolve crystalline cellulose once the amorphous cellulose has been  
490 already dissolved [55]. At temperatures between 280°C and 320°C increasing  
491 either the reaction time or the temperature only increases the degradation of the  
492 cellulose, mostly amorphous, which has been already dissolved [55,62].  
493 Therefore, working with low reaction times produces high DP (degree of  
494 polymerization) molecules [63]. At temperatures below 250°C [64] proved that  
495 cellulose is dissolved but not hydrolyzed and therefore that it is possible to obtain  
496 high DP molecules. However, the process is limited by the amount of amorphous  
497 cellulose available. In these cases reaction times in the order of hours are  
498 required which implies the operation in batch and semi-continuous reactors.  
499 Finally, milling the raw cellulose creates amorphous zones which can be easily  
500 dissolved, even at temperatures below 230°C, generating high DP molecules  
501 [57]. At this temperatures, no modifications are observed in the solid residue  
502 when the cellulose structure is crystalline instead of amorphous [65].

503 In the region near the critical point, when the reaction time is increased, the  
504 dissolved cellulose is hydrolyzed to glucose and lately to degradation products.

505 It has been experimentally demonstrated [51] that at temperatures between  
506 320°C and 330°C (25MPa) a transition from a crystalline to an amorphous  
507 structure is produced. This transition explains the rapid dissolution of cellulose in  
508 water and the absence of any swelling phenomena [51]. The fact that when  
509 cellulose and water react at these or higher temperatures during a short reaction  
510 time the final product obtained is cellulose II when the initial cellulose allomorph  
511 is cellulose I is justified as a consequence of the higher stability of cellulose II.  
512 When the temperature is increased above 330°C cellulose I is converted into  
513 amorphous cellulose. Then, when the temperature decreases, the amorphous  
514 cellulose is converted into the more stable cellulose II allomorph [59,61]. This is  
515 also confirmed working at temperatures below 320°C since only cellulose I is  
516 obtained [66].

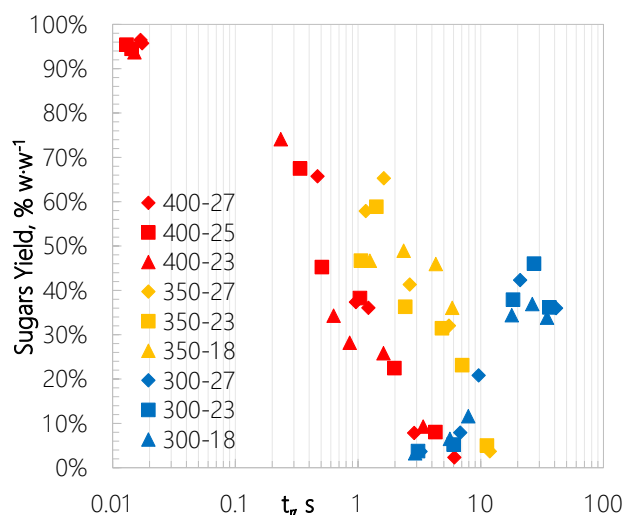
517 Finally, in the supercritical region the dissolution and hydrolysis of cellulose when  
518 working at low concentrations is produced simultaneously, in homogeneous  
519 phase and without mass transfer limitations [53,67]. The transition between  
520 crystalline cellulose to amorphous cellulose at 330°C, the high temperatures of  
521 reaction which produce the cleavage of the hydrogen bonds [53,68] and the  
522 properties of supercritical water such as high diffusivity, high density compared  
523 with water in vapor state and its ability to dissolve organic compounds, observing  
524 the total dissolution of cellulose [69,70], explain the homogeneity of the process.  
525 Recently it has been proved that when the concentration of cellulose is increased  
526 the dissolution and hydrolysis processes are not completely simultaneous nor  
527 homogeneous [71].

## 528 4.2. Cellulose hydrolysis

529 It is noted that in this reaction zone the hydrolysis of biomass has gained a lot of  
530 attention [67,68]. In fact, special attention has been paid to the hydrolysis of  
531 cellulose, since it is the major component of lignocellulosic biomass and therefore  
532 is the key to better understand the reaction mechanisms, kinetics and  
533 performance of supercritical water hydrolysis of real biomass [71,72].

### 534 4.2.1. Production of sugars from cellulose hydrolysis in supercritical 535 water

536 The conversion of cellulose to sugars in supercritical water has been extensively  
537 studied using different kinds of reactors. The hydrolysis in batch-type reactors is  
538 usually carried out with long reaction times, favoring the decomposition of glucose  
539 to degradation products [73,74]. However, the flow-type system makes it possible  
540 to reduce the reaction time and therefore increasing the yields of sugars instead  
541 of degradation products [61,70]. Recently our research group developed an  
542 experimental set up to perform the hydrolysis of cellulose suspensions in  
543 supercritical water by using a continuous micro-reactor, giving as a result a total  
544 conversion of cellulose in milliseconds and yielding a sugars production of 96 %  
545 w/w [67]. This continuous micro-reactor is shown in Figure S2, where it can be  
546 seen that the reaction section consisted of a tee junction (M) where the cellulose  
547 (or biomass) was instantaneously heated up by mixing it with a supercritical water  
548 stream. In order to effectively stop the hydrolysis reaction, a sudden  
549 depressurization through a needle valve was carried out, so that the effluent was  
550 immediately cooled down from 400°C to around 100°C and therefore reaction  
551 was over. Then, depending on the dimensions of the pipe between the junction  
552 and the depressurization valve, the reaction time was calculated as a function of  
553 reactor volume and flow to the reactor, so that just by changing the dimensions  
554 of the reactor of the pumped flow, different reaction times would be provided. In  
555 terms of sugars yield from cellulose hydrolysis in hydrothermal medium, several  
556 conditions were tested by changing temperature, pressure and reaction time in  
557 the micro-reactor mentioned above. As a result, it was found that the optimal  
558 conditions to obtain soluble sugars (up to six units of glucose) were achieved at  
559 400 °C with extremely short reaction times (around 0.01 s). If the reaction time  
560 was increased, the sugars were hydrolyzed and the yield decreased, as it can be  
561 seen in Figure 8. The combination of supercritical water medium and the effective  
562 method for the reaction time control allowed such a high sugars yield from  
563 cellulose hydrolysis. This fact can be explained taking into account than under  
564 those conditions, the cellulose hydrolysis kinetics are improved and the glucose  
565 hydrolysis kinetics are slow enough so that using the sudden expansion micro-  
566 reactor is possible to stop the reactions after complete cellulose hydrolysis but  
567 before glucose degradation [67]. It was also proven that cellulose hydrolysis  
568 reactions were highly influenced by temperature, meanwhile pressure did not  
569 affected cellulose hydrolysis rate in the studied range [75,76].



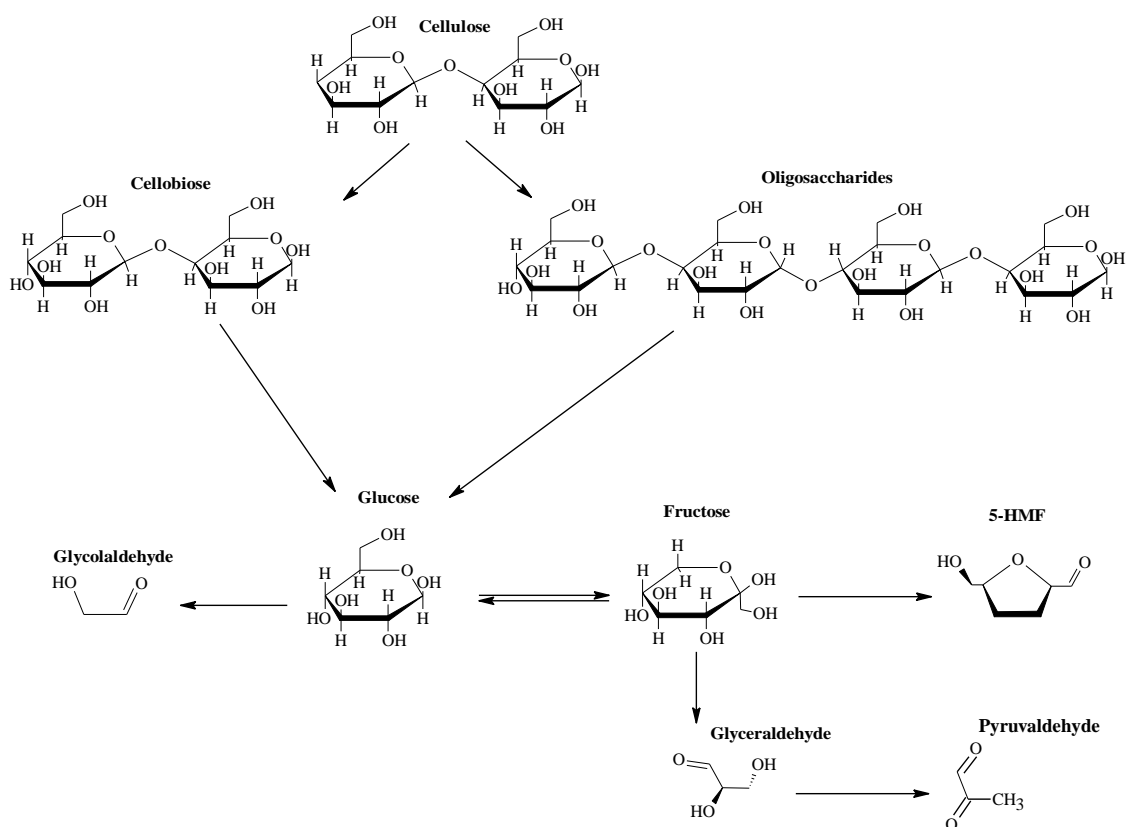
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571 *Figure 8. Sugars yield from cellulose hydrolysis in hydrothermal medium along*  
 572 *reaction time. Experiment temperature: red = 400°C; yellow = 350 °C; blue =*  
 573 *300°C. Experiment pressure (♦) 27 MPa; (■) 25 / 23 MPa and (▲) 23 / 18 MPa*  
 574 *[76].*

575

#### 576 4.2.2. Cellulose hydrolysis kinetics in supercritical water

577 Cellulose was hydrolyzed following the main hydrolysis reaction pathway in  
 578 supercritical water which is shown in Figure 9 [71], where it can be seen that  
 579 cellulose is firstly hydrolyzed into oligosaccharides and then into glucose. Once  
 580 the glucose has been produced, it can be isomerized to fructose and then  
 581 converted into dehydrated (5-HMF) or retro-aldol condensation products  
 582 (glycolaldehyde, pyruvaldehyde and/or glyceraldehyde). As mentioned above,  
 583 working at 400 °C and very short reaction times, the reaction would be stopped  
 584 at glucose. However, if the reaction time is increased, retro-aldol condensation  
 585 products would be produced, yielding aldehydes as glycolaldehyde,  
 586 pyruvaldehyde and/or glyceraldehyde. Therefore, the control of reaction time was  
 587 the key factor to selectively hydrolyze cellulose in supercritical water.



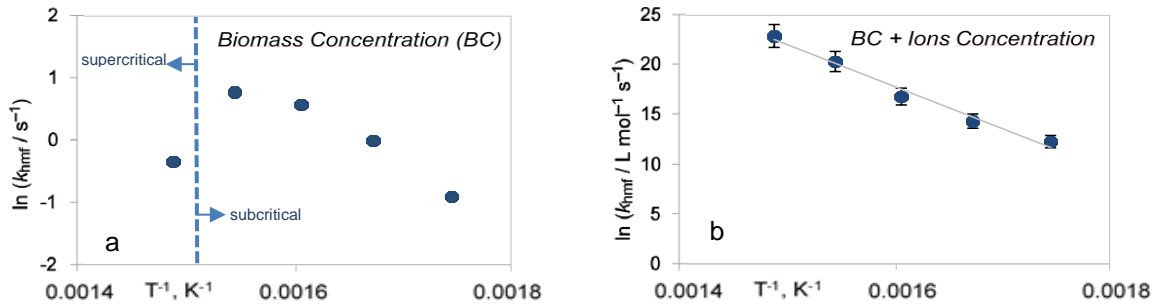
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589 *Figure 9. Reaction pathway for cellulose hydrolysis in supercritical water based*  
 590 *on [71].*

591 The properties of water may vary considerably when changing the conditions  
 592 from subcritical to supercritical, affecting to the products yielded from cellulose  
 593 hydrolysis [72]. Just by changing pressure and temperature, different reaction  
 594 mechanisms are favored. Water at 25MPa and temperatures below 300 °C has  
 595 a density around 800 kg/m<sup>3</sup> and an ionic product (as *pK*) between 11 and 14.  
 596 Under those conditions, water is highly dissociated and H<sup>+</sup>/OH<sup>-</sup> ions are highly  
 597 available in the reaction medium and therefore ionic reactions are favored [77,78].  
 598 However, when temperature is increased up to 400 °C at constant pressure, the  
 599 density considerably decreases (being around 150 kg/m<sup>3</sup>) and the ionic product  
 600 increases up to 21 [79]. This change in the ionic product affects the kinetics of  
 601 glucose and fructose degradation, avoiding the ionic degradation reactions  
 602 (which are the governing chemistry when using acid catalysts) and favoring the  
 603 radical reactions [72]. In fact, it was found that the concentration of H<sup>+</sup>/OH<sup>-</sup> due  
 604 to water dissociation was a determining factor in the selectivity of cellulose  
 605 hydrolysis in supercritical water [76]. So far, kinetic models for cellulose  
 606 hydrolysis only considered the concentration of cellulose and its derived products

607 into the equations, so that first order kinetics were selected to predict cellulose  
608 hydrolysis in supercritical water. Following those traditional kinetic models  
609 Cantero *et al.* [76] found an incongruity for the kinetic constants of fructose  
610 dehydration to 5-HMF when carrying out the hydrolysis of cellulose in supercritical  
611 water at temperatures between 300 – 400 °C and 25 MPa. In Figure 10 it can be  
612 seen the fitted kinetic constants of 5-HMF formation ( $k_{\text{hmf}}$ ) versus the reciprocal  
613 temperature, according to Arrhenius law. A break point can be clearly observed  
614 in Figure 10a, corresponding to the surroundings of the critical point of water,  
615 which represents a deviation from Arrhenius law. So that, the traditional models  
616 where only cellulose concentration was taken into account in a first order kinetics  
617 equation were only capable to predict the kinetic constants of fructose  
618 dehydration to 5-HMF at subcritical conditions. That suggested that another  
619 factor was not taken into account into the kinetic equation. To solve the problem,  
620 the concentration of protons and hydroxide ions were added to the kinetic model,  
621 turning it into a second order kinetic equation. As a consequence of that  
622 transformation, the kinetic constants followed the Arrhenius law for the full  
623 temperature spectra, meaning that the dehydration to 5-HMF under both  
624 subcritical and supercritical conditions was lineally fitted as it can be observed in  
625 Figure 10b. That would suggest that the selectivity of the process was strongly  
626 affected by the protons and hydroxide ions concentration in the reaction medium,  
627 so that improving the understanding of the reaction mechanisms of the hydrolysis  
628 of cellulose in supercritical water. In that way, retroaldol condensation reactions  
629 from glucose and fructose (to produce aldehydes) are not very demanding of ions  
630 and therefore they are favored when water is highly associated (as it occurs at  
631 supercritical state). On the other hand, isomerization glucose-fructose and  
632 dehydration reactions are not favored since these reactions take place forming  
633 transition states with  $\text{OH}^-$  and  $\text{H}^+$  and thus they are diminished when water is  
634 highly dissociated [76].





635

636

637 *Figure 10. Kinetic constants Arrhenius fitting for fructose dehydration to 5-HMF*  
 638 *at 25 MPa and temperatures between 300 and 400°C [76]. a) Kinetic evaluation*  
 639 *just considering cellulose and derived products concentration. b) Kinetic*  
 640 *evaluation also considering protons and hydroxide ions concentrations as*  
 641 *reagents.*

642

#### 4.2.3. Cellulose concentrations as a mass transfer limitation

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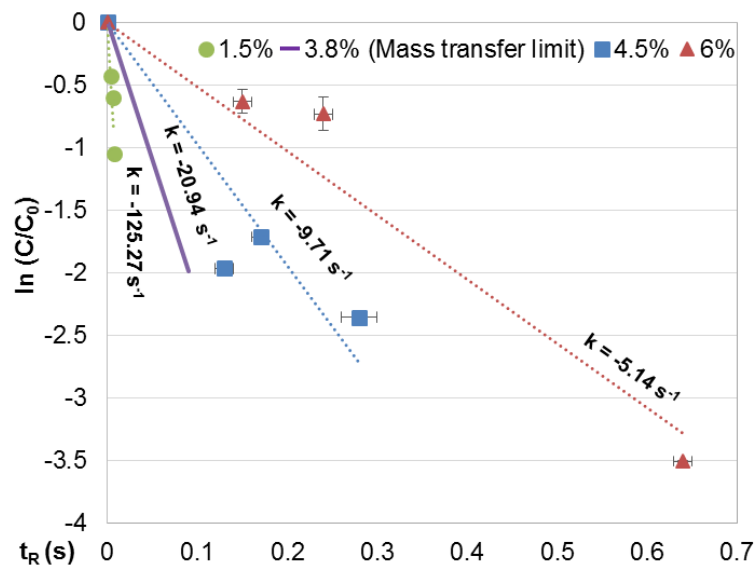
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Another factor recently revised concerning cellulose hydrolysis and dissolution in supercritical water was the effect of cellulose concentration itself [71]. So far, existing models describing the conversion rate of cellulose assumed that the hydrolysis of cellulose particles takes place at their surface and therefore the particle size was considered the key parameter for the conversion rate. That shrinking-core model implied the use of a nonconventional kinetic equation [66,72]. On the other hand, to take into account the reagent concentration, a first order kinetic was assumed to describe the conversion rate of cellulose in supercritical water. As it can be seen in Figure 11, experimental results of cellulose hydrolysis in supercritical water at 400 °C and 25 MPa and different concentrations were fitted to the first order kinetic equation by plotting the logarithm against the reaction time. In all cases, a linear dependence was found, where the slope represented the kinetic constant,  $k$ . In Figure 11 it can be observed that when increasing the cellulose inlet concentration the reaction rate is slower, suggesting that mass transfer resistances must have an important effect over cellulose hydrolysis kinetics. Also, combining those data with the ones from a previous work [67] it was possible to calculate the so called *mass transfer limit* for cellulose hydrolysis in hydrothermal media. Those calculations are

661 detailed in another work from our research group [71]. It was mathematically  
 662 possible to distinguish between homogeneous and heterogeneous reaction  
 663 medium, just by calculating a new kinetic constant ( $-20.94 \text{ s}^{-1}$ ), which  
 664 corresponded to an inlet concentration of 3.83 % w/w (identified as *mass transfer*  
 665 *limit*). When the concentration was lower than the *mass transfer limit*, cellulose  
 666 was completely solubilized in supercritical water and it can be considered that the  
 667 hydrolysis occurred in a homogeneous phase and thus the conversion rate was  
 668 higher. On the contrary, if the concentration was higher than 3.83 %, the cellulose  
 669 behaved as if it was hydrolyzed at subcritical conditions. For this subcritical  
 670 hydrolysis-like, the cellulose was not totally dissolved and hydrolysis reaction  
 671 occurred in a heterogeneous phase.



672  
 673 *Figure 11. Kinetic analysis for cellulose concentrations of 5, 15 and 20 % w/w*  
 674 *(corresponding to 1.5, 4.5 and 6 % w/w at the reactor inlet). The regression*  
 675 *coefficients were: 0.90, 0.81 and 0.96, respectively [71].*

676 4.2.4. From cellulose hydrolysis to real biomass hydrolysis in  
 677 supercritical water

678 Then, once all the parameters affecting cellulose hydrolysis/dissolution were  
 679 revised, it is worth mentioning that the key parameters to selectively hydrolyze  
 680 cellulose and therefore biomass in supercritical water are the effective control of  
 681 reaction time and the medium properties. As the hydrolysis rate of cellulose is  
 682 higher than the glucose under supercritical conditions [68], effectively stopping  
 683 the reaction after cellulose hydrolysis but before glucose degradation is essential

684 to obtain high sugar yields. Increasing the reaction time would only produce the  
685 degradation of the glucose generated. In order to avoid glucose degradation  
686 when working above the critical point of water, reaction times below 1 seconds  
687 should be selected [67]. It was also found that both cellulose [71] and H<sup>+</sup>/OH<sup>-</sup> ions  
688 [76] concentrations should be taken into account in kinetic equations in order to  
689 better explain the performance of cellulose hydrolysis in supercritical water. The  
690 studies of hydrolysis of cellulose in supercritical water demonstrated that this  
691 technology is very promising to obtain mono and oligo-saccharides from  
692 cellulose. Working with very short reaction times (lower than 1 second) it was  
693 possible to obtain high yields of sugars and low degradation products content. In  
694 fact, this technology already proved to be an effective method not only for pure  
695 cellulose hydrolysis but also for complex biomass hydrolysis, such as wheat bran  
696 [80] and sugar beet pulp [81]. Working with the continuous sudden expansion  
697 micro-reactor mentioned above, it was possible to obtain both sugars and building  
698 blocks (as glycolaldehyde [43,44]) just by changing the reaction time. When  
699 working with wheat bran, the highest recovery of cellulose and hemicellulose as  
700 soluble sugars was 73 % w/w operating at 400 °C, 25 MPa and 0.19 s of reaction  
701 time. On the other hand, starting with sugar beet pulp as raw material, working at  
702 similar conditions (400 °C, 25 MPa and 0.2 s), a significant amount of  
703 glycolaldehyde (more than 10% w/w) was produced apart from sugars. That  
704 effluent after supercritical water hydrolysis containing sugars and glycolaldehyde  
705 was then hydrogenated over Ru/MCM-48 catalyst obtaining hexitols and ethylene  
706 glycol as products. It is clear that working with a real biomass implies not only  
707 dealing with cellulose, but also with hemicellulose, pectins, lignin, proteins, etc.  
708 The intricate matrix formed by all those polymers in plant cell wall makes cellulose  
709 and hemicellulose less accessible for hydrolysis and therefore, higher reaction  
710 time are needed in order to hydrolyze them into sugars. That would explain the  
711 need to move optimal conditions from 0.015 s for pure cellulose hydrolysis to 0.2  
712 s for biomass hydrolysis in supercritical water. That increase on reaction time  
713 promotes the appearance of other compounds such as glycolaldehyde.  
714 Therefore, through supercritical water hydrolysis of cellulose and biomass it was  
715 possible to obtain high yields of sugars and building blocks for further production  
716 of added value compounds, just by changing the reaction time.

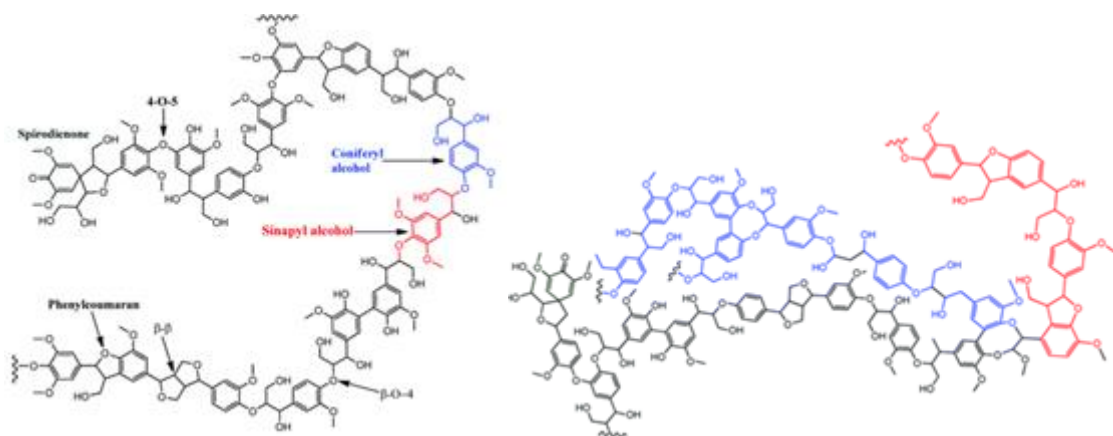
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## 719 5. Lignin

720 Lignin, after cellulose, is the second most abundant raw material of organics [82].  
721 However, lignin is still under use compared to other biomass products due to its  
722 difficult decomposition and the high amounts of solid residue obtained during its  
723 depolymerization [83].

724 Traditionally, lignin has been considered as a low value by-product of the pulping  
725 industry. Only 2% of lignin isolated from spent pulping liquor is used for  
726 specialties [84]. In spite of its amorphous and highly branched structure, it is  
727 widely accepted that lignin structure comes from the polymerization of three  
728 phenylpropane monomer units, namely coniferyl, synapyl, and p-coumaryl  
729 alcohol [85]. These monolignols produce guaiacyl, syringyl and p-hydroxyphenyl  
730 propanoic units into the lignin polymer. These substituted phenols yield a huge  
731 number of functional groups and linkages, which vary from species to species,  
732 tree to tree, and even in woods from different parts of the same tree [83]. Lignin  
733 structure is also influenced by environmental and developmental cues [86]. For  
734 instance, hardwood lignins are primarily composed by guaiacyl and syringyl units  
735 with traces of p-hydroxyphenyl propanoid units, whereas softwood lignins are  
736 composed mainly of guaiacyl units with low levels of p-hydroxyphenyl propanoid  
737 units. The theoretical structure of hardwood and softwood lignins, is shown in  
738 Figure 12.



739

740 *Figure 12. Typical structure of lignin derived from hardwood (left) and softwood*  
741 *(right) [87]*

742 Despite its non-well known structure, it suggests that lignin can be a valuable  
743 source of chemicals if would be broken into smaller molecular units.  
744 Depolymerization of lignin is an alluring route to an important functionality class.  
745 Unfortunately, nowadays this route is deceptive. Despite a large volume of  
746 research, there are very few reports of efficient ways of recovering such as high  
747 value-added products. Thus, if it would be possible to carry out the lignin  
748 depolymerization with high yields, lignin would increase its potential as valuable  
749 chemicals source, making more competent the lignocellulosic biorefinery with the  
750 efficient use of the main three components of biomass, and not only cellulose and  
751 hemicellulose as until now. Recently, the hydrolysis of lignin and its model  
752 compounds (vanillic acid, guaiacol, syringol, coniferyl and synapyl alcohol) in sub  
753 and supercritical water is being considered as a probable pathway in lignin  
754 depolymerization. As is well known, the hydrolysis process has some advantages  
755 compared to other methods, it is performed at lower temperatures, the employed  
756 reactants are cheap and favors higher yields of liquid including monomeric  
757 phenols [88].

## 758 5.1. Model compounds

759 The hydrothermolysis of vanillic acid (VA) was studied using a tubular flow  
760 reactor, with residence times from 5 to 70 seconds, between 300 and 375 °C. It  
761 was found that below the critical temperature of water, VA was converted  
762 exclusively to 2-methoxy-phenol (guaiacol) through decarboxylation. At 350°C  
763 the conversion was achieved faster (after only 15 s) than at 300°C (60 s). At  
764 temperatures of 375 °C the conversion was even more rapid, but the selectivity  
765 towards guaiacol was lower, with catechol being formed as the main secondary  
766 product. Phenol was also formed, through the free radical decomposition of  
767 guaiacol. As the temperature was increased further, more of the secondary  
768 products were formed [89].

769 Guaiacol decomposition in supercritical water was investigated in sealed reactors  
770 using both water and in water-salt solutions (NaCl, CaCl<sub>2</sub> and FeCl<sub>3</sub>). The  
771 reaction temperature was 383 °C with reaction times between 0 and 30 minutes.  
772 It was concluded that at low water density, the reactions led to the formation of  
773 phenol, catechol, cresol and char, but at higher water densities and with addition

774 of salts the rate of hydrolysis and the selectivity towards hydrolysis products,  
775 catechol and methanol, was increased [90]. On the other hand, it was also  
776 investigated batch reactions of guaiacol using a 5 ml reactor with residence times  
777 between 5 and 180 minutes (including 3 minutes of heating up), at 380, 390 and  
778 400 °C. The main products were catechol, phenol and o-cresol. Catechol was  
779 formed quickly over the first 10 minutes of the reaction. Phenol and o-cresol were  
780 both formed gradually over the entire reaction time [91] .

781 Formation of formic and acetic acid from syringol decomposition was studied  
782 under oxidizing conditions in a batch reactor, with and without NaOH catalyst.  
783 Reaction times of 30 to 150 seconds and temperatures between 250 and 300 °C  
784 were investigated. NaOH had been shown to inhibit the decomposition of organic  
785 compounds at these temperatures. The phenolic compounds formed were  
786 catechol, 1, 2, 4-benzenetriol, 1, 4 benzenediol and 9 short chain carboxylic  
787 acids, ranging from 1-6 carbons. The optimal temperature for formic and acetic  
788 acid production was 280 °C though this led to a lower formation of other products  
789 [92].

790 The formation of organic acids from the decomposition of coniferyl and synapyl  
791 alcohols using a batch reactor at 380 °C, 1000 bar and 4 minutes was  
792 investigated. Coniferyl and synapyl alcohols formed formic, acetic, glycolic and  
793 lactic acid. It was suggested that these were formed from decomposition of the  
794 aliphatic side chains, being the aromatic rings resistant to ring opening reactions  
795 under these reaction conditions [93].

## 796 5.2. Lignin Depolymerization

797

### 798 5.2.1. Reactions in water and co-solvent

799 Existence of the additional hydrolysis reaction in water at elevated temperatures  
800 and pressures catalyzed by  $H^+$  and  $OH^-$  should cause significantly different  
801 decomposition from pyrolysis, and the associated phase behavior. As a weak-  
802 polar solvent with a high value of ion product supercritical water could be a

803 possible solvent that can dissolve and hydrolyze lignin for potentially production  
804 of phenolic chemicals or for upgrading lignin for fuels [94].

805 *Saisu et al.* reported the decomposition of organosolv lignin in a batch reactor in  
806 supercritical water with and without phenol at 400 °C. As properties of lignin  
807 depend on the lignin origin, not just on the isolation way, it is important to  
808 emphasize that in this work authors did not give additional information about the  
809 lignin origin. Both the lignin to phenol ratios and the volume of water in the reactor  
810 were varied in order to investigate the effect of phenol and water density.  
811 Residence times were 10-64 minutes. The reaction products were separated into  
812 THF soluble (TS) and THF insoluble (TIS) fractions. In the absence of phenol it  
813 was found that the molecular weight distribution of TS products shifted to lower  
814 molecular weight as the water density increased. The TS products (syringols,  
815 guaiacols and catechol) were derived from lignin structure. Authors explained that  
816 the conversion of lignin in supercritical water probably proceeded through  
817 hydrolysis and dealkylation, which leads to the formation of lighter fraction, such  
818 as alcohols, aldehydes and their functional groups within the macromolecules.  
819 The functional groups could form not only as decomposed fragments but also as  
820 lignin itself. In the presence of phenol, there was a lower yield of TIS products,  
821 which were also of a lower mass. The yield of TS increased and their average  
822 mass also decreased. This can be rationalized by enhanced hydrolysis of lignin  
823 at high water density, which produces reactive fragments such as formaldehyde.  
824 In the absence of phenol, these reactive fragments act as cross linkers between  
825 depolymerization products such as guaiacol, catechol, and larger fragments of  
826 lignin, repolymerising the lignin molecule. It is believed that phenol acts as a  
827 capping agent by reacting with these species to prevent the repolymerization and  
828 the formation of the TIS molecules [95].

829 *Okuda et al.* studied the depolymerization of organosolv lignin in phenol-water  
830 mixtures at 400 °C for 6-60 minutes. As in previous work, the information about  
831 lignin origin is not given. In this study they were focused on the production of  
832 phenolic chemicals from lignin and examined the depolymerization of lignin in a  
833 water-phenol mixture with higher phenol ratio in order to assess the possibility of  
834 complete conversion of lignin to phenolic chemicals without the formation of char.  
835 It was found that the yield of TS compounds decreased with time, and after 1

836 hour the lowest yield was given when just water was used as solvent. The best  
837 performing solvent was a water-phenol mixture, which achieved nearly total  
838 suppression of char formation with 99% TS molecules [96].

839 *Fang at al.* followed decomposition of organosolv lignin in water/phenol solution  
840 in micro-reactor coupled with optical microscopies at temperatures up to 600°C  
841 and water densities up to 1165 kg/m<sup>3</sup>. **The microreactor, diamond anvil cell (DAC)**  
842 **allows for in-situ observations of samples in the fully-visible chamber via optical**  
843 **microscopy. The DAC consisted of a hole and sealed by compression of two**  
844 **opposing anvils made of diamond. The chamber was rapidly heated by two**  
845 **electric microheaters by cutting power, which is convenient for the study of phase**  
846 **behavior and chemical reactions.** Experiments have been done at different water  
847 densities, heating rate, maximum temperatures and lignin concentration. Three  
848 different types of products were obtained: a non-dissolved black residue, a  
849 precipitated residue and reddish oil. A homogenous phase was formed for the  
850 phenol + lignin system where phenolic char precipitated as the main product.  
851 Adding water to this system de-polymerization of lignin was promoted by  
852 hydrolysis in a homogeneous phase and its re-polymerization was inhibited by  
853 phenol. The homogenous phase was not found in the case of lignin + water  
854 system. After initial dissolution at above 377 °C lignin underwent hydrolysis and  
855 pyrolysis to phenolic, which are further changed to oil in the aqueous phase. At  
856 higher temperatures, solid particles precipitated from the aqueous via  
857 homogeneous re-polymerization of the phenolics and water soluble compounds  
858 to form a phenolic char. At these same conditions, non-dissolved lignin underwent  
859 heterogeneous pyrolysis and formed polyaromatic char. Higher water density  
860 decrease lignin dissolution. Therefore, polyaromatic char, with a lighter molecular  
861 weight was the main product along with a smaller fraction of phenolic char. It can  
862 be conclude that for water and phenol mixtures, lignin can be completely  
863 solubilized and undergoes homogeneous hydrolysis and pyrolysis that prevents  
864 further re-polymerization [94].

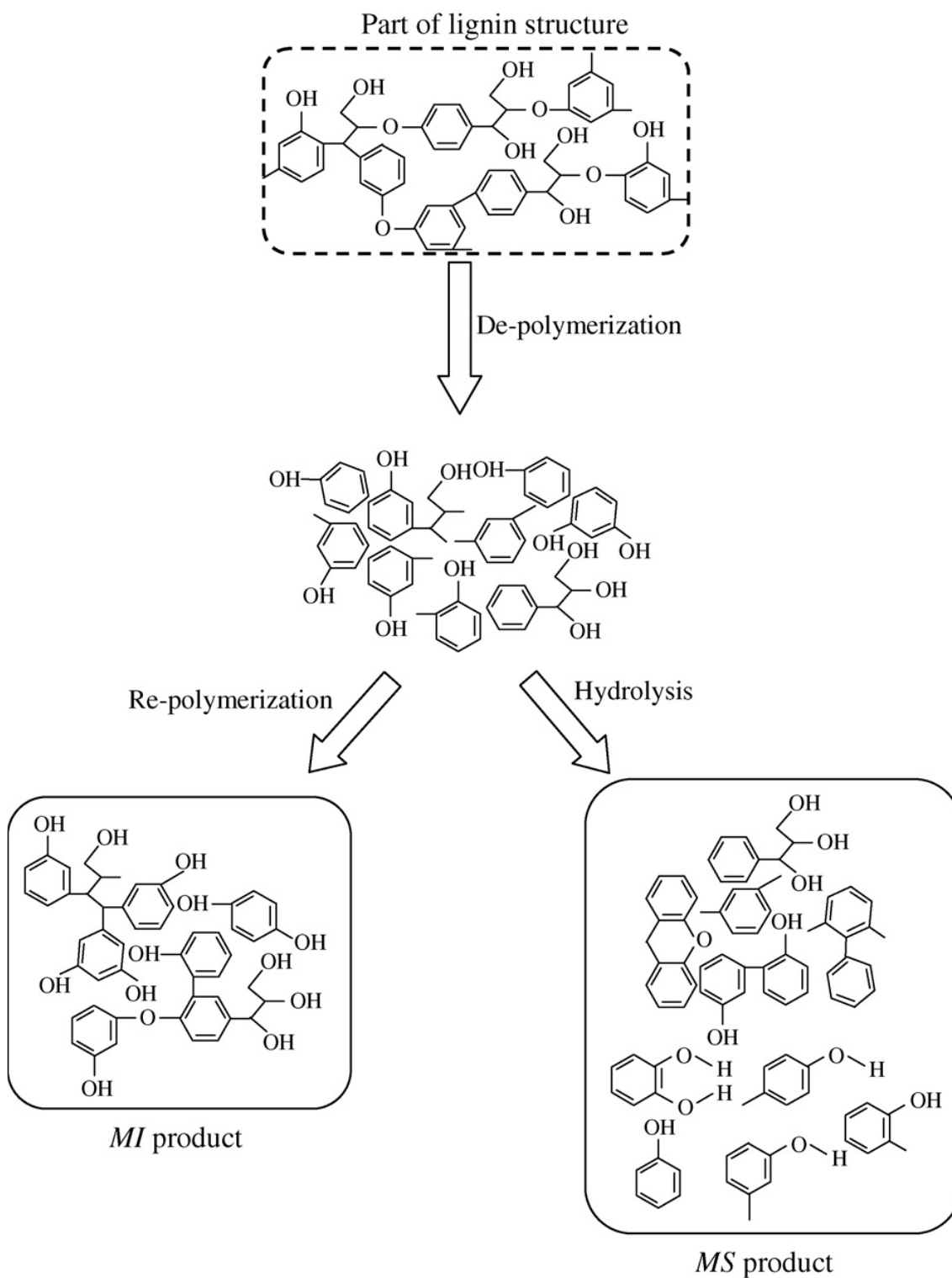
### 865 5.2.2. Water without co-solvent

866 *Sasaki and Goto* presented a work in which the chemical conversion of alkali  
867 lignin in near and supercritical water at 350 °C and 400 °C and a pressure of 25-



868 40 MPa using a batch reactor without catalyst, having 5-240 minutes residence  
869 time was studied. The products were separated into two fractions, methanol  
870 soluble (MS) and methanol insoluble (MI). The main products observed in the MS  
871 fraction were catechol, phenol, and o, m, p- cresols, while MI product was defined  
872 as a residual solid. It was proposed that catechol is formed via hydrolysis of  
873 guaiacol which is the main compound in structure of lignin. In further hydrolysis,  
874 phenol, m, p and o-cresol were obtained. Dependence of reaction time showed  
875 that the yield of catechol rapidly increased with reaction time (till 30 min) and then  
876 decreased, especially at 400 °C, while the yields of phenol, m, p and o-cresol  
877 increased with reaction time. After 90 min the yields of m, p and o-cresols were  
878 almost constant while the yield of phenol slightly increased. At 400 °C after  
879 catechol was consumed, the majority of the reaction most likely terminated. The  
880 decreasing of catechol was not followed by the increasing of phenol, m, p and o-  
881 cresol significantly. Water density influence yields of products where the yield of  
882 catechol was gradually decreased with increasing the water density at 350 °C  
883 and dramatically decreased at 400 °C. The yields of phenol, m, p and o-cresol  
884 increased gradually with increasing the water density at 350 °C and 400 °C. It  
885 was suggested that an increase in water density enhanced the hydrolysis rate of  
886 ether and carbon-carbon bonds of alkylphenol in lignin. According to this results  
887 it was proposed reaction mechanism showed in scheme below (Figure 13) where  
888 lignin was degraded into its derivate compounds by dealkylation and hydrolysis  
889 reaction. Under SCW conditions hydrolysis takes place at ether and ester bonds  
890 in lignin. Hydrolysis is accelerated by a high ion product of water. Dealkylation of  
891 lignin gives catechol, which is then hydrolyzed into phenol. This reaction pathway  
892 suggests that some useful chemical intermediates (MS fraction) might be  
893 recovered in a rapid and selective manner by changing the temperature, reaction  
894 time under near and supercritical water condition. At the same time, re-  
895 polymerization of low molecular weight compounds occurs as seen by the  
896 formation of char through condensation reaction [97].

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900

*Figure 13. Proposed scheme for degradation of lignin under near and supercritical condition*

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Lignin conversion was also investigated in the continuous system for short residence time 0.5-10 s, pressure of 25 MPa and different temperatures under supercritical conditions at 390 °C and 450 °C and subcritical condition at 300 °C

904 and 370 °C [98] [99]. Temperature plays an important factor in deciding the  
905 dominant pathway because of the existence of the parallel ionic and radical based  
906 pathways. Lignin products were divided in char, gas, TOC, phenolic and aromatic  
907 hydrocarbons. Under hydrothermal condition lignin was rapidly converted into  
908 lower molecular weight products for all temperatures which was followed with  
909 high yields of TOC, phenolic compounds and aromatic hydrocarbons, while  
910 decomposition was accelerated under supercritical condition [99]. Increasing  
911 decomposition rate with temperature follows Arrhenius behavior of lignin  
912 degradation what was already obtained by *Zhang and Ramaswamy* [100]. The  
913 rapid depolymerization is cause by cleavage of ether bonds from abundant  $\beta$ -aryl  
914 ether ( $\beta$ -O-4) linkages in softwood lignin [101] [102]. The low dissociation  
915 enthalpies of the ether bond in the  $\beta$ -O-4 linkage initiated the reaction to form a  
916 phenoxy radical and a secondary alkyl aromatic radical [103]. The Arrhenius  
917 behavior shown by lignin decomposition under hydrothermal conditions even in  
918 subcritical region further supported the conclusion that the initial decomposition  
919 was a radical reaction. TOC yield decreased with temperature and the yield was  
920 much higher under subcritical condition. The TOC yield in subcritical water  
921 increased within short residence time and remained stable or decrease slowly  
922 despite longer residence time. The increasing in the polymerization during the  
923 increase of temperature should be reflected in the TOC yield. Low TOC yield  
924 under supercritical condition suggested the occurrence of secondary reaction.  
925 This could be due to the cross-linking between reactive degradation fragments  
926 obtained from the lignin depolymerization to produce fragments with higher  
927 molecular weights. Increase in the lower molecular weight compounds during the  
928 time resulted with the simultaneous formation of the higher molecular weight  
929 compounds because of the repolymerization. The minimal decrease in TOC yield  
930 for subcritical temperatures implied that the crosslinking reactions between these  
931 lower-molecular weight compounds did not take place actively under these  
932 conditions. This suggested the significance of radical's involvement in enhancing  
933 the reaction [98][99].

934 Char has significantly higher yields in the supercritical region and formation was  
935 enhanced at elevated temperatures. Formation of char from lignin follows  
936 Arrhenius behavior and it is not affected with change in water properties under

937 subcritical condition what point radical reaction. In order to examine the  
938 suggested hypothesis of formation of low molecular-weight fragments and  
939 formation of higher molecular weight fragments by cross linking of the smaller  
940 fragment it was determine the yields of the phenolic compounds and aromatic  
941 hydrocarbons. The main phenolic compound from lignin decomposition is  
942 guaiacol, which is followed by minor composition of other phenolic compounds  
943 such as o, m, p-cresol, catechol and phenol. Formation of guaiacol was higher in  
944 supercritical temperature, but rapidly decreased at longer residence time [98]  
945 [99]. Guaiacol is an intermediate degradation product and highly reactive, since  
946 the methyl C–O bond is the weakest in the guaiacol unit and is susceptible to  
947 undergo cleaving. The aliphatic C–O bond of the methoxyl group is more likely to  
948 react because the bond energy of the aliphatic C–O bond (245 kJ/mol) is smaller  
949 than that of the aromatic C–O bond (256 kJ/mol). This was concluded in the study  
950 of *Wahyudiono et al.* where also was found that guaiacol showed a fast  
951 decomposition rate and the formation of high-molecular-weight substances  
952 reformed to char was important for the guaiacol decomposition to reach  
953 equilibrium [104]. However, high yield of guaiacol was also obtained under  
954 subcritical conditions. The high yield of guaiacol under two separate regions of  
955 temperature (subcritical and supercritical) with different water properties  
956 indicated guaiacol formation via two different pathways. The formation of guaiacol  
957 from lignin probably proceeded through hydrolysis under subcritical conditions  
958 because of the high ionic product and dielectric constant of water. On the  
959 contrary, under supercritical condition and high temperature free radical reaction  
960 should be enhanced that lead to the formation of guaiacol from lignin [98]. In both  
961 studies it was showed that the decomposition of lignin occurred rapidly with  
962 residence time below one second, which indicate that kinetic study should be  
963 done for residence time below 1s.

### 964 5.2.3. Water and base catalyst

965 In order to enhance the obtaining of monomeric phenols, basic compounds such  
966 as hydroxides are used as catalyst [105][106] [107]. Studies on lignin model  
967 compound dihydro-diisoeugenol, showed that the basic agent caused ether and  
968 C–C bond cleavage which yielded volatile phenols [108]. Furthermore, the

969 analysis of products from model compound reactions revealed that phenyl ether  
970 linkages were effectively broken in the base catalyzed hydrolysis reaction while  
971 C-C linkages were less affected [109]. In another study, it was concluded that in  
972 alkaline depolymerisation of lignin, ether bonds are hydrolyzed at random, most  
973 likely from the outside of the oligomer and not in the sequence of their bond  
974 strengths, forming first large units and then smaller subunits [106]. In addition, it  
975 was stated that the formation of monomers is directly proportional to the  
976 concentration of sodium hydroxide in the aqueous medium. Furthermore, a  
977 mechanism for the NaOH catalyzed breakdown of the ether bonds of lignin is  
978 proposed explaining the preferential formation of syringol derivatives, based on  
979 the stabilizing effect that the methoxyl groups provides to the transition states of  
980 the carbenium ions. It was also concluded that the production of monomers is  
981 limited by the oligomerization and polymerization reactions of the products  
982 formed.

983 *Miller et al.* showed that in the alkali depolymerization of lignin using water as  
984 solvent the most important factor in lignin depolymerization was base  
985 concentration. Moreover, it was observed that concentration excess of a strong  
986 base gave better results on lignin depolymerization. In addition, a little amount of  
987 a strong base (NaOH) together with a larger amount of less expensive base  
988 ( $\text{Ca}(\text{OH})_2$ ) produced positive results [105].

989 *Silva et al.* studied the catalytic depolymerization of organosolv lignin with both  
990 NaOH catalyst and with boric acid as a capping agent, aiming to produce oils of  
991 monomeric and dimeric products. In the case of reactions with NaOH and no  
992 capping agent, the highest oil yield was obtained at 300 °C with a residence time  
993 of 4 minutes. This gave a yield of 23% oil and no char formation. Lignin  
994 conversion increased steadily with increasing temperature but char was formed  
995 as well as oil. In order to increase oil yields, boric acid was used as a capping  
996 agent. Without base, the boric acid increased the yield of oils to a maximum of  
997 36% after 40 minutes at 300 °C, but at longer residence times or higher  
998 temperatures the yield decreased again. The results showed that the molecular  
999 weights of the oils from the boric acid catalyzed reactions were around 500 Da,  
1000 compared to 300 Da for the base catalyzed depolymerization [88].

1001 In contrast to a basic environment, leading to deprotonation of phenolic hydroxyl  
1002 groups and decreased hydrogen bonding, the acidic environment enhances the  
1003 degree of internal hydrogen bonding. As result, the probability of acid-catalyzed  
1004 cleavage of ether bonds is reduced compared to base-catalyzed cleavage. Thus,  
1005 in acid-catalyzed hydrolysis the primary products produced are larger (dimers to  
1006 tetramers) than in the base-catalyzed route. For both cases, the primary products  
1007 undergo easy addition and condensation reactions leading to higher molecular  
1008 weight products [110].

1009 Under supercritical and subcritical condition lignin is hydrolyzed and different  
1010 phenolic and other aromatic compounds could be obtained. These hydrolysis  
1011 reactions occur in the shortest time than the residence time that has already been  
1012 used in literature (more than one second). It is very important to have better  
1013 understanding of reaction pathways, intermediate reaction products and reaction  
1014 products for first milliseconds of reaction time, thus the specific weaknesses and  
1015 strengths of the polymer and its intermediates – i.e. the substructures which are  
1016 the most susceptible to chemical attack. Kinetic models that have been obtained  
1017 until today are justified with the final reaction products, without information about  
1018 intermediate produced.

1019 Considerable effort is still required to address the separation challenges  
1020 associated with lignin depolymerization. The supercritical water ultrafast  
1021 hydrolysis could open a new way to improve the understanding of lignin  
1022 depolymerization, as has been done in the cellulose hydrolysis.

1023

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## 1441 Figures captions

1442 *Figure 1: Lignocellulosic biomass structure*

1443 *Figure 2. Subcritical and supercritical water properties around the critical point.*

1444 *Figure 3: Liquid profiles at the output of a packed bed reactor during a*  
1445 *hydrothermal extraction process: (a) TOC evolution, (b) molecular weight*  
1446 *evolution (Mw) when both stages are presents and molecular weight evolution*  
1447 *when only stage 2 is present.*

1448 *Figure 4: Relation between the pH and the extracted biomass.*

1449 *Figure 5: Hydrothermal extraction of eucalyptus in a semi-continuous reactor*  
1450 *(solid time of 90 min): evolution of the hemicellulose extraction yield (Yield tot),*  
1451 *the yield of hexoses (C6), pentoses (C5) and degradation products for eucalyptus*  
1452 *with temperature (a) and residence time at 185 °C (b) [4]*

1453 *Figure 6. Effect of subcritical water temperature on the extraction of different*  
1454 *phenolic compounds from defatted rice bran (residence time = 10 min). Obtained*  
1455 *from Pourali et al [40]*

1456 *Figure 7. Cellulose formula*

1457 *Figure 8. Sugars yield from cellulose hydrolysis in hydrothermal medium along*  
1458 *reaction time. Experiment temperature: red = 400°C; yellow = 350 °C; blue =*  
1459 *300°C. Experiment pressure (♦) 27 MPa; (■) 25 / 23 MPa and (▲) 23 / 18 MPa*  
1460 *[76].*

1461 *Figure 9. Reaction pathway for cellulose hydrolysis in supercritical water based*  
1462 *on [71].*

1463 *Figure 10. Kinetic constants Arrhenius fitting for fructose dehydration to 5-HMF*  
1464 *at 25 MPa and temperatures between 300 and 400°C [76]. a) Kinetic evaluation*  
1465 *just considering cellulose and derived products concentration. b) Kinetic*  
1466 *evaluation also considering protons and hydroxide ions concentrations as*  
1467 *reagents.*

1468 *Figure 11. Kinetic analysis for cellulose concentrations of 5, 15 and 20 % w/w*  
1469 *(corresponding to 1.5, 4.5 and 6 % w/w at the reactor inlet). The regression*  
1470 *coefficients were: 0.90, 0.81 and 0.96, respectively [71].*

1471 *Figure 12. Typical structure of lignin derived from hardwood (left) and softwood*  
1472 *(right) [87]*

1473 *Figure 13. Proposed scheme for degradation of lignin under near and*  
1474 *supercritical condition*

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1476 Appendix 1. Solid and liquid residence time

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1478 During an extraction or reaction process where a packed bed reactor is involved (Figure S1) two  
1479 different residence times can be defined, one for the solid and another one for the liquid. The  
1480 solid residence time corresponds to the amount of time spent during the operation since it is  
1481 fixed inside the reactor. For instance, the solid residence time in the work of *Cabeza et al.* [1]  
1482 was 94 min because they treated 5 g of *holm oak* with hot pressurized water during 94 min. In  
1483 contrast, the liquid is continuously flowing through the reactor. Therefore, the liquid residence  
1484 depends on the reactor volume ( $V$ ), the reactor porosity ( $\epsilon$ ) and the volumetric flow ( $Q$ ) fed,  
1485 being this time defined as  $V \cdot \epsilon / Q$ . For this reason, it was between 2 and 15 min in the work of  
1486 *Cabeza et al.* [1] since each experiment was done with a different volumetric flow.

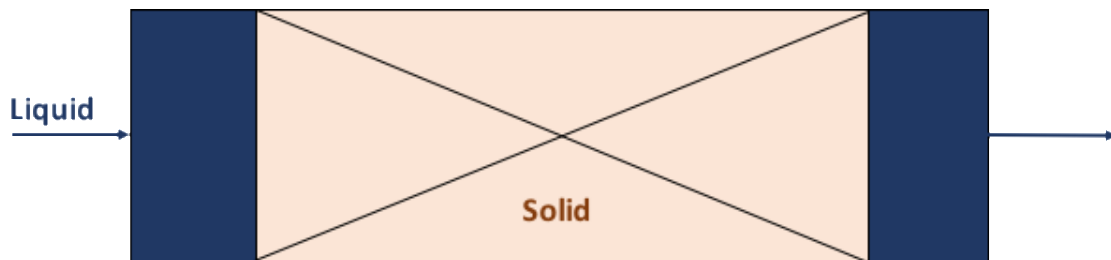
1487

1488 To sum up, the solid residence time refers to the time that the solid is being treated with the  
1489 liquid. And the liquid residence time is the time that the liquid is inside the reactor.

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Figure S1: packed bed reactor scheme

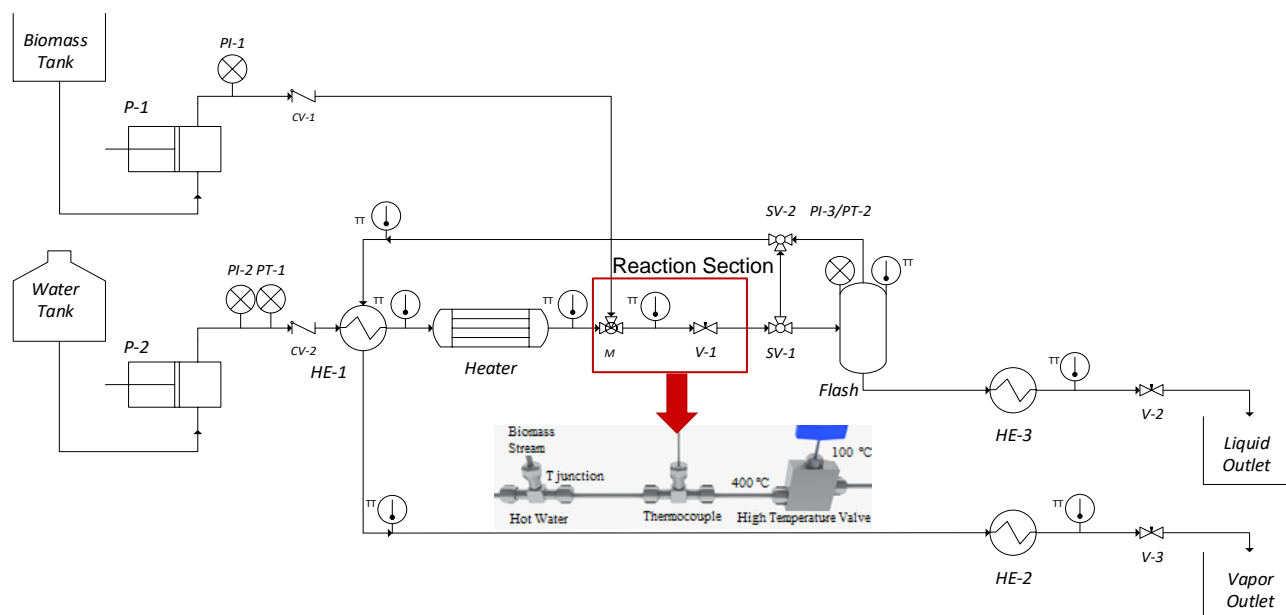
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1506 Figure S2. Experimental set-up where a micro-reactor was used to hydrolyze cellulose and biomass at  
 1507 supercritical water conditions [1].

1508

1509 The results of cellulose and biomass hydrolysis in supercritical water discussed in the main  
 1510 manuscript [1–7] were performed in the continuous plant of the FASTSUGARS process, able to  
 1511 hydrolyze biomass in SCW at temperatures up to 400 °C and pressures up to 30 MPa. A scheme  
 1512 of the experimental set-up designed by the High Pressure Processes Group is shown in Figure  
 1513 S2.

1514 Briefly, water and a biomass suspension were continuously pumped to the reactor at the operating  
 1515 pressure (25 MPa). At the inlet of the reactor (as a tee junction-M-) the biomass was  
 1516 instantaneously heated up by mixing it with a SCW stream, reaching in that way the operating  
 1517 temperature (400 °C). After the desired reaction time was achieved, the reactor effluent was  
 1518 suddenly depressurized through a high temperature valve (V-1) obtaining an instantaneous  
 1519 cooling and therefore, stopping the reactions. The cooling method was an important part of the  
 1520 FASTSUGARS process, because it was the mechanism used to effectively stop the reactions,  
 1521 avoiding uncontrolled reactions and the dilution of the products, which would occur if they were  
 1522 cooled down by quenching.

1523 An electric heater was used to control the temperature of the water stream with an adjustable  
 1524 power up to 10 kW. Also, a heat exchanger (HE-1) was used to both preheat the water stream  
 1525 and cool down the product, introducing in that way a heat integration system. SCW was supplied  
 1526 up to a maximum flow rate of 5 kg/h by pump P-2 and biomass suspension was fed to a maximum  
 1527 flow rate of 3 kg/h by pump P-1.

1528 Finally, a flash chamber separator was installed after the reactor, allowing the separation of the  
 1529 products into two phases: a vapor phase mainly composed of water and a liquid phase with the  
 1530 concentrated product. After this stage, two heat exchangers were used to cool down the sample  
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