Online Integrated Fractionation-Hydrolysis of Lignocellulosic Biomass using Sub- and Supercritical Water

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Abstract

A novel process coupling the fractionation and hydrolysis reactors is presented. Holm oak was used as real lignocellulosic biomass to be treated. In the fractionation reactor, hemicellulose and cellulose were solubilized and partially hydrolyzed in different stages with the aim of feeding the hydrolysis reactor with high C5 concentrations or C6 concentrations. The fractionation was performed in two stages: at 180ºC optimizing the hemicellulose extraction and at 260ºC extracting cellulose and hard hemicellulose remaining in the biomass structure. Three water flows were tested: 11, 17 and 26 cm^3/min. Sugar yields from 71 to 75% were reached, mainly composed of xylose and glucose oligomers and lower amounts of other chemicals, like retro-aldol products, acetic acid or 5-HMF. The outlet stream from the fractionation reactor was directly mixed with sub or supercritical water at the inlet mixer of a SHR where the reaction time was precisely controlled. The temperature, pressure and reaction time were modified to get an insight of their effect on the yield of retro-aldol condensation products. Yields of 24% for glycolaldehyde, and pyruvaldehyde were found at 8.3 s, 350ºC and 162 bar (hydrolysis reactor conditions). In other hand, 25% of lactic acid was found at 0.23 s, 396ºC and 245 bar. A discussion based on a known reaction pathway is proposed. Moreover, a kinetic model for the hydrolysis reactor was proposed, being able to reproduce the experimental data with deviations lower than 10 % for sugars and other products extracted. This combined process performs a selective valorization of real lignocellulosic biomass, avoiding the costly process of extreme grinding needed for the fluidization in a continuous hydrothermal process.

Introduction

Even if it is reasonably assumed that biomass from plants will be the main carbon source in the future, the choice of which reaction medium should be used to depolymerize and valorize biomass has not been taken yet. Pressurized fluids, especially sub and supercritical water (Tc=374ºC and Pc= 221 bar), can be pointed as a promising alternative to depolymerize and valorize biomass [1-5]. Physical and chemical properties of water can be modified by adjusting pressure and temperature around the critical point, making water a reaction medium able to favor different kind of reactions [1]. Because of this reason, hot pressurized water has been used as reaction medium for fractionation [6-9] , hydrolysis [10-12] and valorization of biomass [13-16].

The composition of lignocellulosic biomass is highly dependent on the plant species and growth conditions. However, it can be considered that the average composition of lignocellulosic biomass is approximately: cellulose (40% wt.), hemicellulose (25% wt.), lignin (25% wt.), extractives and ashes (10% wt.) [17]. Although biomass is composed by diverse and complex molecules, it can be fractionated principally into C6 sugars (mainly glucose), C5 sugars (mainly xylose) and lignin [3]. These three fractions can be further modified to produce a wide range of products like: ethanol, hydrogen, glycolaldehyde, pyruvaldehyde, lactic acid and 5-HMF among others [3, 18-25].

The fractionation of biomass can be defined as the selective separation of C5 sugars, C6 sugars and lignin from the original biomass matrix. This process was studied under hydrothermal conditions in different ways of operation: batch, semi batch and continuous [3, 26]. Semi batch and continuous processes allow obtaining higher yields of sugars and chemical compounds than batch reactors, because it is possible to control the temperature (T) and the residence time (t_r) more accurately than in batch processes [27]. Continuous processes are the most appropriate to control the reaction conditions (T and t_r), however, in most cases it is necessary to apply expensive pretreatments to the raw material before the fractionation+hydrolysis process, for example: exhaustive size reduction [28]. On the other hand, the continuous process can be

performed at different operating conditions in order to separate the C5 sugars from the C6 sugars.

The extraction of hemicellulose from woody biomass can be carried out at temperatures between 130ºC and 260ºC, solid reaction times between 20 and 60 min and liquid residence times inside the reactor between 0.1 min and 1 min. At those conditions, hemicellulose can be both extracted and hydrolyzed [29, 30]. After the extraction at 180ºC, two products are usually obtained: a liquid composed mainly of C5 sugars and a solid composed of C6 sugars and lignin. These two products can be separated by filtration. Then, the cellulose in the solid can be hydrolyzed at supercritical conditions to obtain a water solution of C6 sugars and a solid enriched in lignin. These processes can be carried out in two reactors with a filtration operation between them. Another option which allows the intensification of the process is using one fixed bed reactor. In such a case, the biomass is loaded in the reactor and the hydrolysis temperature is changed in order to hydrolyze C5 or C6 sugars [31]. The semi batch process allows high performances on the yields of C5 sugars hydrolysis. However, when the reaction temperature is increased to hydrolyze the recalcitrant cellulose and hemicellulose, the yield of recovered sugars decreases because of the increment of the sugars further reactions [10, 11, 32].

The continuous reactors have been employed in many applications for the valorization of sugar streams allowing a precise control over the reactions [19-21]. These reactions can be managed using pressurized water and choosing the adequate reaction conditions. For example, at temperatures between 200ºC and 300ºC (250 bar) the water molecules are highly dissociated favoring the ionic reactions, like the production of 5-HMF from fructose and glucose [1]. On the other hand, at 400ºC (250 bar) the water molecules are highly associated favoring the non-ionic reactions, like the retro aldol condensation reactions [1].

In this article, a novel integrated fractionation-valorization process was designed and built using wooden biomass as raw material and water (subcritical and supercritical) as reaction medium. The wooden biomass was fractionated in a fixed bed reactor at different temperatures. The solubilized products were directly injected to a continuous near critical water reactor to

efficiently convert C5 and C6 sugars into valuable products, like glycolaldehyde, pyruvaldehyde and lactic acid avoiding a further hydrolysis to organic acids. In addition, a kinetic analysis of the biomass hydrolysis was done in order to study the differences in the process when subcritical and supercritical conditions were used.

The objective of this research paper was to design a novel process capable of converting lignocellulosic biomass into valuable products eluding the excessive milling of biomass and decreasing the number of reactors.

1. Experimental

2.1 Materials

Deionized water produced by Elix® Advantage purification system was used as reaction medium to run the experiments. The standards used in a High Performance Liquid Chromatography (HPLC) analysis were: cellobiose (≥98%), glucose (≥99%), xylose (≥99%), galactose (≥99%), mannose (≥99%), arabinose (≥99%), glyceraldehyde (≥95%), glycolaldehyde dimer (≥99%), lactic acid (≥85%), formic acid (≥98%), acetic acid (≥99%), acrylic acid (≥99%), furfural (99%) and 5-hydroxymethylfurfural (≥99%) purchased from Sigma. 0.01 N solution of sulfuric acid (HPLC grade) in Milli-Q® grade water was used as the mobile phase in the HPLC analysis. Sulfuric acid (≥96%) and calcium carbonate (≥99%) supplied by Panreac, Spain, were used as reagents for the quantification procedure of structural carbohydrates and lignin [33]. Also, Milli-Q® water was used in this determination. Holm oak wood employed as raw material was collected in Spanish forests. The wood was milled obtaining chips with average width of 2 mm and average length of 5 mm, as it is shown in Figure S1 of Supplementary Material.

2.2 Analytical methods

The composition of the holm oak wood raw material, exhausted solid and extracted liquor was determined through two Laboratory Analytical Procedures (LAP) from NREL [33, 34]. The procedure for solid samples consists in quantifying the structural carbohydrates and lignin in the biomass as follows. A) The biomass was weighted before and after being dried in an air driven oven at 105 °C for 24 hours in order to calculate the moisture content. B) Dried biomass was

122 treated in a Soxhlet equipment with n-hexane, leaving a solid free of oils and other extractives.
123 C) 300 mg of dried and free-extractives solid from step (b) were hydrolyzed in 3 ml of 72% wt
124 sulfuric acid solution at 30 °C for 30 min, in order to break the bonds between biopolymers and
125 the main solid structure. D) The mixture of oligomers obtained in step (c) is diluted using 84 ml
126 of deionized water and heated at 120 °C for 60 min with the aim of hydrolyzing hemicellulose
127 and cellulose to obtain their correspondent monomers [35]. E) The solid is separated from the
128 solution by vacuum filtration. F) The total mass of solubilized sugars was quantified as the
129 difference in weight between the original solid and the exhausted solid after oven drying at 105
130 °C in oven for 24 hours. G) The exhausted solid is placed in a muffle at 550 °C for 24 h and the
131 remaining residue was weighted before and after this step to calculate the insoluble lignin and
132 the ash content of the sample. H) A liquid aliquot was analyzed with UV-Vis spectrophotometer
133 at 320 nm with extinction coefficient of 34 $Lg^{-1}cm^{-1}$ [36] to calculate the amount of soluble
134 lignin. I) Another liquid aliquot was neutralized to pH range 6 to 7, then it was filtered using a
135 0.2 µm membrane and analyzed by HPLC determining the carbohydrates composition. This
136 procedure is performed using a column SUGAR SH-1011 (Shodex) with a 0.01 N of sulfuric
137 acid solution as a mobile phase. To identify the soluble products, two detectors were used:
138 Waters IR detector 2414 (210 nm) and Waters dual λ absorbance detector 2487 (254 nm). In
139 order to calculate the amount of carbohydrates, each chromatogram was integrated numerically
140 by decomposing it into a sum of 9 to 13 Gaussian peaks, minimizing chi squared function of a
141 Levenberg-Marquardt-Flecher algorithm [37]. Glycolaldehyde and Pyruvaldehyde resulted to be
142 overlapped, since the retention time of their standards is extremely close (11.99 vs 12.24
143 minutes, respectively). So we refer to them as glycolaldehyde-pyruvaldehyde.
144 The raw material contained 1.6 % wt. extractives, 1.8% wt. moisture, 0.2% wt. ashes, 24.2% wt.
145 Klason lignin (from which 4.0% corresponds to soluble lignin), 45.7% wt. of hexoses, 23.9%
146 wt. pentoses. The sum of all the components represents the 97.4% of total weight, the
147 discrepancy is due to experimental errors like the loss of solid material after the recovery at the
148 end of the experiments, or the inhomogeneity of the material which can have slightly different

compositions depending on the analyzed aliquot; in any case, it is inside the acceptable experimental error.

The amount of C6 was calculated as the sum of glucose, cellobiose and fructose concentrations. Xylose was the only C5 detected. Acetic acid was considered to come from the deacetylation of xylan during the extraction process or, as explained in the next sections, from the hydrolysis of pyruvaldehyde. The hydrolysis products from hexoses and pentoses were mainly glyceraldehyde, glycolaldehyde, pyruvaldehyde, lactic acid, 5-hydroxymethylfurfural and in some cases acrylic acid were detected in very low concentration.

The procedure followed to analyze liquid samples consists in the steps (C), (D) and (I) described above. In this case, the carbon content liquid solutions was determined by total organic carbon (TOC) analysis using a Shimadzu TOC-VCSH equipment. Every sample was previously filtered using a 0.2 μm syringe filter and diluted 1:10 times with Millipore water.

The pH of the outlet stream was measured online using an electronic pH-meter (Nahita model 903).

2.3 *Experimental setup and operation procedure*

The setup used in this work is shown in Figure 1. The system consisted in two reactors online integrated: 1) the fractionation reactor (R.1), where the C5 and C6 are solubilized and partially hydrolyzed; 2) the supercritical hydrolysis reactor (SHR), which converts the soluble compounds into added value products. The fractionation line is composed of a water deposit (D.1), downstream an American Lewa EK6 2KN high pressure pump (P.1, maximum flow rate 1.5 kg/h) propels water through a pre-heater (H.1, 200 cm of 1/8" SS 316 pipe, electrically heated by means of two resistors of 300 W) which ensures an uniform temperature at the reactor inlet. The reactor (R.1), a tube of SS 316, 40 cm length, 1.27 cm O.D., is heated by three flat resistors of 300 W each, placed axially along a machined aluminum bar with 5.08 cm O.D. Both, preheater and the reactor are located inside a former chromatographic oven HP5680. The out-flow stream from the extraction line is mixed with the supercritical water stream, entering in a second reactor (SHR) (R.2). The supercritical water line is composed of a heater (H.2), a tube of 18 m, 1/8 in O.D. SS316 wrapped around a brass cylinder and heated by two cartridges and

two flat resistors, which provided adjustable power of up to 10 kW, in order to control the temperature of this stream. The water flow was generated by a Milton Roy XT membrane pump (P.2, maximum flow rate 6 kg/h). The SHR allows a fast heating of the biomass stream, which is mixed almost instantaneously with the supercritical water stream, and a rapid cooling of the products, which takes place through a sudden expansion which efficiently stops the hydrolysis. In this way, the reaction time could be precisely calculated, as the reactor works isothermally. Pressure was controlled Micro Metering valve 30VRMM4812 from Autoclave Engineering (V.4). The setups of the two reactors were presented in detail in previous works [32, 38].

An average amount of 6.12±0.03 gr of holm oak biomass was placed inside the reactor R.1 for each experiment. Two metallic filters were used (pore diameter ≈200 μm), located on the top and bottom of the reactor, avoiding the release of the solid during the experiments. A pressure test with cold pressurized water was carried out before every experiment, with the aim to check the presence of leaks in the system. Then, the supercritical line was heated ensuring the functioning of the system at required operating conditions. Once these conditions were stable, the pumps were switched off and both, the preheater and the reactor R.1, were heated up until the temperatures reached the respective set values. Afterwards, both pumps were switch on again and the flow and pressure were set to the desired conditions, zero time is considered when pressure reached the desired value.

A total of 11 experiments were performed (3 fractionations and 8 coupled reactions), obtaining a total of 130 liquid and 11 solid samples, characterized with the methods described above. Six experiments were performed varying the temperature in the SHR from subcritical (350ºC) up to supercritical (400ºC) conditions, maintaining the pressure at 250±10 bar. The reaction time in this reactor was modified by varying the water flow-rate and changing the reactor volume (2.2 or 12.4 cm^3); reaction times between 0.25 s and to 12 s were tested. Three different water flows (11, 17, 26 cm^3/min) were tested in the fractionation line, maintaining constant the ratio with the flow of supercritical water stream, to get the desired conditions during the further hydrolysis. The feed composition to the SHR was analyzed by carrying out three fractionations without the

second hydrolysis stage, at the same conditions of temperatures, flow-rates and pressure tested with the coupled reaction.

The fractionation in the fixed bed reactor was performed in two stages marked by two distinct temperatures: 180ºC to extract the hemicellulose and 260ºC to remove most of the cellulose fraction from the biomass. The heating time between both setpoints was in the range of 5-10 min, while the flow was temporarily stopped for the experiment running at 26 cm^3/min. In order to follow the reaction evolution, the pH of the outlet stream was measured online sampling every 1 minute. Liquid samples (30-40 cm^3) were taken according the pH variations every 5 to 20 min for the experiment at 11 cm^3/min, and every 2 to 8 min for the other experiments. The overall experiment time varied from 110, 60 and 45 min for the runs at 11, 17, 26 cm^3/min, respectively (called here as (1), (2) and (3)). After the last sample was grabbed, the heating was turned off and the reactor R.1 was let to cool down to room temperature with air flux. Both pumps were set to zero flow and the system was depressurized. The solid was removed from the reactor, filtered and dried 24 h at 105ºC for further analysis. After cleaning, the fixed bed reactor was placed back, tightened and the system was washed out with deionized water.

3. Results and Discussion

3.1. *Biomass fractionation*

From the analysis of the raw holm oak, the amount of soluble material was 4.65 ± 0.03g, corresponding to 72.1% of the biomass weight. 3.02 ± 0.02g of this soluble mass were composed of hexoses (C6) and 1.58 ± 0.01g of pentoses (C5). The spatial time of the liquid (τ_l), is determined using the liquid flow rate, the reactor volume and the average porosity of the bed (ε_{i0}=0.457±0.01, ε_f=0.948±0.019). The latter was calculated by means of Eq. (1), taking into account the initial and the final fraction of void volume in the bed, due to the shrinking size of the biomass particles, and also considering a constant density for water [38] (since its variation with temperature is less than 2%) and a constant density of the holm oak wood (800 kg/m^3, dry

based for holm oak species). In this sense, residence time for the liquid inside the fixed-bed reactor was in the range of 1.0 min $<\tau_l<$2.1 min.

$$\varepsilon_f = \varepsilon_0 + (1-\varepsilon_0)\frac{(m_0-m_f)}{m_0} \quad (1)$$

Figure 2 shows the cumulated mass of total soluble materials, oligomers and monomers of C5 and C6, as well as products deriving from the further reaction of sugars. These values were determined using TOC and HPLC analysis of the products. The different conditions were obtained by changing water flow-rates in the fractionation line for the experiments 1, 2 and 3. The ~~break points shown in the curves and~~ dashed lines signals ~~present~~ the time when transition between the two temperature stages takes place. The mass of soluble compounds detected by TOC was calculated by dividing the value of total organic carbon concentration recognized by the equipment by a factor 0.42 (Eq. (2)).

$$r = \sum_1^c r(i) = \sum_1^c \left(\frac{m(i)}{\sum_1^c m(i)}\right)\left(\frac{n(i)MwC}{Mw(i)}\right) = 0.42; \qquad i = 1..c \quad (2)$$

The factor *r* is the sum of the ratio between the molecular weight of carbon atoms in the soluble compounds extracted from raw material to the molecular weight of the compounds itself. This value is an approximation that allows comparing the mass obtained by TOC analysis (total amount of C) with the mass quantified by HPLC (total amount of soluble compounds).

This approximation is based only on the sugar contents and it is used as a general value for all the experiments. It does not consider the effect in the carbon ratio of the condensation and dehydration reactions happening during the extraction and hydrolysis. In addition, it does not take into account the amount of soluble lignin since it is relatively low (only a 4% in the raw material, see section 2.2). However, in all the experiments, the mass balance matched with a maximum error around 20%.

The overall material balance was calculated by summing the mass of the solid recovered from the reactor R.1 at the end of the experiment to the mass of the soluble material estimated using the quantified amount by TOC and the assumed factor showed in equation 2; and the mass of

insoluble lignin flushed by the water stream. For experiments 1, 2 and 3, this mass balance was equal to 103.8, 93.7 and 84.9% related to the amount of biomass fed to the reactor.

The mass of soluble material obtained by TOC with the same values obtained by HPLC for each sample are compared in the first row of graphs in Figure 2 (a). The values plotted in Figure 2 are the yields of soluble compounds obtained from each technique related to the same amount in the raw biomass (calculated as observed soluble compounds [g]/4.65 g). The discrepancy between both values is reduced when the water flow-rate through the extraction reactor is increased from 11 to 26 cm^3/min (23.6, -4.1 and -3.2% for the three flows, respectively). This fact could be explained by the increasing production of compounds derived from the sugars hydrolysis (mainly organic acids) not identified by HPLC or whose value is so low that it cannot be detected. From HPLC chromatographs of experiment 1, some peaks do not fit with the retention time of the 17 standard compounds identified in this column (e.g. Figure S2 in Supplementary Material). Besides, some other peaks were not completely resolved. The amount of sugars and soluble oligomers of C5 and C6 obtained from fractionation are displayed in the second line of graphics in Figure 2 (a). Most of the hemicellulose is hydrolyzed to oligomers, in fact hemicellulose is highly soluble in water because of the abundance of acetyl groups in its amorphous structure [39], and after the first breaking leads to the production of soluble oligomers.

The yield of C5 at the end of second stage of temperature was 87.3, 89.8 and 93.1%, for experiments 1, 2 and 3, respectively. On the contrary, the crystalline nature confers to cellulose a water insoluble character, so, the oligomers with only very low molecular weight would be water soluble [40]. In this sense, when the flow rate increases in R.1 (decreasing τ_l), cellulose is hydrolyzed mainly to hexoses in oligomer form, giving rise to lower amounts of monomers. This result is observed by comparing the amounts of C6 oligomers (Oligo C6) to monomers (C6) in experiment 1 respect to experiments 2 and 3. This selectivity to oligomers occurs mostly during the first stage of temperature in R.1 (see second row of graphs in Figure 2 a). The oligomers quantification was obtained from the difference between glucose, celobiose, fructose and xylose of the liquid containing all the soluble sugars and the same compounds obtained

from the total acid hydrolysis of this liquid [38]. So, high liquid spatial times enhanced the hydrolysis and solubilization of hexoses. This distribution could be related to the difference in the activation energy of the cleavage of the hydrogen bonds between celluloses and the α1-4 glycosidic bond hydrolysis, which is known that is favored at subcritical conditions [10, 32]. The last row of graphs in Figure 2 (a) displays different amounts of products from the hydrolysis of xylose, glucose and fructose. These amounts are depreciable at the first stage and are increased after temperature is raised. However, these compounds are one order of magnitude lower than the soluble sugars during the extraction. An example is 5-HMF, which is produced mainly in the second stage of fractionation temperature where the conditions make the water a highly ionic medium in the reactor R.1. The main components in the output stream were pyruvaldehyde, glycolaldehyde and lactic acid. The decrease of the reaction time of liquid inside the reactor diminished the further transformation of sugars.

3.2 *Biomass valorization with sub and supercritical water hydrolysis*

The outlet stream from the fixed bed reactor was fed to the SHR together with a water stream at temperatures and pressures above to its critical point. The aim was to obtain a fast and selective hydrolysis of the oligomers and sugars extracted from the biomass. The reaction time in the supercritical reactor (*t*) was varied in order to modify the selectivity to different chemicals.

The optimum temperatures and flow-rates in R.1 have been identified in extraction step, as they lead to the maximum yield of soluble material. For this reason, a flow rate of 11 cm^3/s and temperatures of 180º and 260ºC (for the two stages, respectively) were chosen for most of the experiments. Only the experiments 10 and 11 were performed with the same liquid flow-rates used in the fractionation experiments 2 and 3 (17 and 26 cm^3/s, respectively).

This approach also allows knowing the composition of the stream entering in the second reactor. Eight experiments were performed, as shown in Table 1. Three temperatures and 6 reaction times were tested, keeping constant the temperatures of water through the first reactor.

Three reactions (5, 7 and 8) were performed in a longer reactor (100 cm), aiming to increase the residence time in SRH (*t)*. A lower pressure was used in reaction 6 (162 bar) to observe the influence of water density in the products distribution.

Overall mass balance for each experiment, calculated as described in section 3.1, is presented Table 1. Mass balances indicate that no significant gasification takes place in the supercritical reactor. First row of graphs in Figure 2 (b), (c) and (d) presents the mass of the soluble materials quantified in the outlet stream of SHR by TOC and HPLC. The percentage yield of each experiment respect to the soluble mass in the raw holm oak is presented as the number in the each graph. Some differences between these two procedures are observable, mainly increasing t_e in the second stage of fractionation or at higher sugars conversion. These findings could be related to the production of small organic acids, ketones and aldehydes (levulinic and acrylic acids, dihydroxyacetone, formaldehyde) and other compounds not identified by HPLC, see Figure S2 in Supplementary Material. This hypothesis agree with the decrease of the mass difference observed by both techniques when a high water flow is involved (as commented in section 3.1), indicating an over breaking and oxidation of the products of interest at higher *t*.

3.2.1 Oligomers and sugars conversion

Oligomer conversion to C5 and C6 monomers was calculated by difference between the stream entering to the SHR (composition obtained in experiment 1 corresponding to reactions 4 to 9 and composition of experiment 2 and 3 for experiments 10 and 11, respectively), and the stream leaving the reactor after the hydrolysis.

The conversion of oligomers to C5 and C6 monomers are reported in the seventh column of Table 1. In all the runs, oligomers conversion was higher than 85%. The exception was experiment 11, in which the small *t* and high dilution (four times lower than in the experiments 4 to 8) could be the cause of the low conversion. C5 Sugars (xylose) and C6 (cellobiose, glucose and fructose) are intermediate compounds in the reaction pathway. Conversion of sugars is faster than cleavage of oligomers to monomers at subcritical temperatures and even at a temperature a little higher than the critical point of water (e.g. 380ºC). This is showed by comparing the amount of Oligo C6 and Oligo C5 with C6 and C5 in experiments 4 and 6 (see Figure 2 (b) and (c)). A different behavior is detected near to 400ºC, like in experiment 9, where oligomers conversion seems to be faster than sugars hydrolysis, in agreement with the

observations reported in the literature for oligomers originating from microcrystalline cellulose [5],[11]. Surprisingly the time needed for a complete conversion of sugars is quite larger than the pure cellulose hydrolysis at the same temperature (eg. 350ºC: 2 s in ref. [29] vs 12 s in this work). This could be related to the hydrolysis of C5 and C6 contained inside the porous structure of fluidized microparticles of biomass coming from the reactor R.1 with the stream of fluidized biomass. Also the presence of other ions or compounds could be linked to this attenuation.

3.2.2 Added value products (AVP) from the sugars hydrolysis

The third row of graphs in Figure 2 (b), (c) and (d) displays the amount of added value chemicals (AVP) (glyceraldehyde, glycolaldehyde, pyruvaldehyde, lactic acid, formic acid, acetic acid and 5-HMF) produced from hydrolysis of cellobiose, glucose, fructose and xylose. The reaction pathway of cellulose hydrolysis involving oligomers and cellobiose as intermediaries was reported in the literature [32]. Xylose hydrolysis in near critical and supercritical water was analyzed by several authors [41, 42]. The combined pathway is presented in Figure 3. Not all the products involved in this scheme were identified by the liquid chromatography. ~~The cellulose pathway shown in Fig. 3 involves two consecutive hydrolysis, the first one in which the oligosaccharides are hydrolyzed to glucose and xylose and the second one in which glucose and xylose are involved in two possible pathways: isomerization and dehydration or retro-aldol condensation [18, 42].~~ The cellulose and hemicellulose pathways are similar. They involve two consecutive hydrolysis steps, the first one in which the oligosaccharides are hydrolyzed to glucose and xylose, respectively, and the second one in which glucose and xylose are implicated in two possible routes: isomerization and dehydration or retro-aldol condensation [18, 42]. Glucose can follow a reversible isomerization to produce fructose, however, the reverse reaction is almost inhibited at the same conditions [19, 20]. Glucose can also be transformed into 1,6 anhydroglucose and fructose can be transformed into 5-hydroxymethylfurfural through a dehydration reaction [43]. The other alternative of glucose conversion is the retro-aldol condensation producing glycolaldehyde and erythrose [32, 44]. Erythrose is further transformed into glycolaldehyde by the same reaction mechanism [18]. The

368 retro-aldol condensation reaction of fructose produces glyceraldehyde and dihydroxyacetone.
369 These molecules are further isomerized into pyruvaldehyde [19], which is transformed to lactic
370 acid by an extra oxidation. Hemicellulose hydrolysis is quite similar; the first step is the
371 depolymerization to produce xylose and xylose oligomers. After that, xylose can be isomerized
372 to D-xylulose, assuming that D-xylulose as an intermediate for furfural and retro-aldol products
373 (glyceraldehyde, pyruvaldehyde, glycolaldehyde, lactic acid, dihydroxyacetone, formaldehyde)
374 [41, 42]. This reaction pathway consists of a retro-aldol reaction (Lobry de Bruyn-Alberta van
375 Ekenstein (LBET)) from D-xylose and D-xylulose, similar to that involving D-glucose and
376 fructose.
377 In the experiments, a considerable amount of glycolaldehyde-pyruvaldehyde and lactic acid was
378 observed. The distribution of these chemicals was similar for experiments 4 and 6 (Figure 2 (b)
379 and (c)) in spite of the difference of water properties at both temperatures. At 352ºC and 241.3
380 bars, the water density and pKw are 614.7 kg/m^3 and 11.7, respectively. On the other hand, at
381 383ºC and 245.7 bar, those properties take a value of 319.7 kg/m^3 and 15.3, both calculated as
382 developed in literature [1]. A little difference in the amount of glycolaldehyde-pyruvaldehyde as
383 well as in the 5-HMF is perceived, principally at times corresponding to the first stage of
384 temperature of the reactor R.1. This means that this variations of density and Kw, do not
385 modified largely the selectivity between isomerization-dehydration and retro-aldol pathways
386 like it does in the pure cellulose hydrolysis. In this last, isomerization of glucose to fructose is
387 highly inhibited by decreasing density [32]. This behavior could be explained by the presence of
388 of H^+ ions coming from the acetylation taking place during the fractionation, in addition to the
389 H^+ produced by the water ionization. Also, considering the nature of raw biomass, other ions in
390 solution could be present. Under 352 ºC and pressure, isomerization of glucose to fructose and
391 further dehydration is favored for pure cellulose hydrolysis [43]. But, in the present cases, the
392 high yields of glycolaldehyde-pyruvaldehyde and lactic acid are evidences that the retro-aldol
393 pathways take place as well. Experiments 4 and 5 were performed at similar temperature and
394 pressure but involving different residence times (t=1.06 vs 11.15 s, respectively). For
395 experiment 5, the acetic acid amount was highly increased, mostly in the time period

corresponding to the first stage of temperature in R.1. This acetic acid exceeded the amount produced in the hemicellulose deacetylation. ~~The retro-aldol pathway coming from xylose by means of glyceraldehyde route, could explain the difference of acetic acid obtained directly from lactic acid decarbonylation. This extra amount of acetic acid could not be considered only from the hemicellulose source, since there is also a large concentration of C6 in the first fraction of the feed stream (see Figure 2 (a)). This C6 portion could also contribute to the glyceraldehyde route.~~ Besides, acetic acid could be obtained directly from lactic acid decarbonylation [15]. Both, glucose and xylose, are able to produce lactic acid by means of the retro-aldol pathway with glyceraldehyde and pyruvaldehyde as intermediaries (see Figure 3). In this sense, these retro-aldol pathways could explain the extra amount of acetic acid obtained at longer residence times in the SHR. Figure 4, displays the pH of the output stream after the fractionation stage (experiment 1) and the coupled process fractionation+hydrolysis (experiments 4, 5, 6 and 8). The pH in the outlet stream, after SHR, was always lower to the pH of the output stream from the fractionation step itself. ~~comparing the H^+ concentration of the experiments during the time period of the first stage during the extraction.~~ This observation agrees with the fact that extra amount of acetic acid was produced when a deeper hydrolysis was performed (see experiments 5 and 8). After this ~~time period~~, no difference in the pH can be detected. Similar behavior was observed from experiments 6 and 8, ~~however, in this case, larger amount of formic acid was observed compared to the experiments above mentioned~~ in spite of the difference of formic acid produced in both (see Figure 2 (c)).

The pressure change in the range studied, had no effect on the chemicals distribution (see Figure 2 (c), experiments 6 and 7). Under the conditions of experiment 7, pKw is 11.9, calculated by means of an empiric equation [45]. This value is quite similar than pKw of the experiment 6. In this way, in spite of density change, the same AVP distribution is observed. Longer residence time of experiment 7 explains the difference in oligomers with experiment 6. The distribution of the AVP of experiment 6, is independent of the change in pKw, as was discussed above for experiments 4 and 6. The highest yield of glycolaldehyde-pyruvaldehyde (calculated as mass of

product/mass of soluble material in raw biomass) was obtained for experiment 7 (24.4%), probably due to the combination of higher H+ concentration and longer *t*.

A different AVP distribution is observed in the experiment 9, where lactic acid is the most abundant product and acetic acid is depleted compared to the experiment 4 and 6 (see Figure 2 (d)). This finding could be explained by the short *t* of the mixture at high temperature, conditions in which the reactions are stopped ~~before~~ after lactic acid production in the retro-aldol route, inhibiting the acetic acid formation. This selectivity seems to take place in the SHR mainly during the first stage of temperature in the reactor R.1. After that, the formation of lactic acid in the SHR is reduced. ~~This selectivity seems to take place mainly during the time period of the first stage of the fractionation, because after that, the formation of lactic acid as well as of glycolaldehyde pyruvaldehyde is lower~~. The highest yield of lactic acid was found at Experiment 9 (25.5%). The water flow increase in the first reactor has no clear effect on the production of retro-aldol compounds (see reactions 10 and 11 in Figure 2 (d)). Under these conditions, the oligomers breakup seems to become slower, since their amount is enlarged related to the monomeric sugars. In both cases, the retro aldol pathways are followed producing glycolaldehyde-pyruvaldehyde and lactic acid with similar yields.

The combination of many variables influencing the distribution of a large number of products, involved in a complex reaction path as the described in Fig. 3, is hard to be easily explained. Furthermore, as was mentioned above, we are dealing with the hydrolysis of a real biomass, in which other components could be influencing the observed behavior.

3.3 Hydrolysis kinetic model

Aiming to analyze further the results obtained by the coupled system, a kinetic model for the second reactor is proposed in this section. This model takes into account the solubilized biomass composition fed to the second reactor. It was specially focused on the time period corresponding to the first stage of the solubilization (at the conditions of experiment 1) since this step produces an outlet stream with higher amount of the chemicals of interest (see last two columns of Table 1). The bigger added valued compounds production from stage 1 is due to the fact that the operational temperature was around 180 ºC, which means a lower degradation. The reaction

pathway proposed in this case, showed in Figure 45. It is a simplified version of the real hydrolysis described in Figure 3. The modelling was done by the transient regime mass balances for each compound in the fluid: oligomers, sugars and products (Eq. (3)). Moreover, the following assumptions have been considered: (1) the reaction order for all the kinetics is 1 for the biomass compound and proton concentration in water, (2) there are no diffusional effects in fluid phase, (3) kinetic constants follows Arrhenius' law and (4) the reactor works at the same temperature at any point. Regarding kinetics, a conventional expression was used including the effect of the concentration of water proton since it is a hydrolysis process (Eq. (4)).

$$\frac{\delta C_{L\,j}}{\delta t} = r_j - \frac{u}{L} \cdot \frac{\delta C_{L\,j}}{\delta z} \qquad (3)$$

$$r_j = \mathrm{C}_{H^+} \cdot \sum_{i=1}^{i=N} \propto_{i,j} \cdot K_{L_i} \cdot C_{L_i} \qquad (4) \qquad (4)$$

3.3.1 Numerical resolution

Eq. (3) is a set of 6 partial differential equations (PDE) which has to be discretized to obtain a set of ordinary differential equation (ODE). The resolution of this set of ODEs was performed by the Runge-Kutta's method with a 8th convergence order and the discretization by coupling orthogonal colocation method on finite elements [46]. The fitting of the experimental data constitutes an optimization problem. Due to its complexity, it was previously seeded by manual iteration, and then, optimized by the Nelder-Mead-Simplex method. Moreover, as the inlet concentration of the hydrolysis reactor was variable and the oligomer properties changed with extraction time [47], the problem was optimized at every experimental point. Finally, the solution was reviewed in order to ensure the physical meaning of the parameters. The objective function was the minimization of the Absolute Average Deviation (A.A.D., Eq. (5)) for oligomer, sugar and products concentration at the SHR output.

$$A.A.D. = \sum_{i=1}^{n} \frac{1}{n} \cdot \left| \frac{X_{exp} - X_{sim}}{X_{exp}} \right| \cdot 100 \qquad (5)$$

475 *3.3.2 Experimental data fittings*

476 In order to validate the model, only experiments 4, 6 and 9 were used because they were
477 carried out at similar residence times and three different temperatures (see Table 1). For
478 experiment 4, the data at extraction time of 9 and 14 min were not considered because they do
479 not follow the tendency fixed by the set of the three experiments used (4, 6 and 9). Moreover, as
480 each experiment was carried out independently, the inlet for the reactor was assumed to have the
481 same composition that experiment ~~3~~ 1 but with TOC profile of the fitted experiment (4, 6 and
482 9). It is also remarkable that the volumetric flow was the addition of the provided flow by the
483 two pumps for all the experiments (see Figure 1). The deviation between the model and the
484 experimental data is arrayed in Table 2 and for experiment 6 it also can be seen in Figure 6. The
485 model was able to reproduce successfully the hydrolysis of solubilized biomass, being the
486 average A.A.D. 21.14 %, 37.37 %, 18.41 % and 7.24 % for instant hemicellulose and cellulose
487 oligomers, sugars C6, sugars C5 and their degradation products (the added value products
488 respectively or AVP). These discrepancies changed to 27.46 %, 7.61 %, 9.31 % and 3.99%
489 respectively when cumulated values were used. Taking into account these last values, it can be
490 checked that the highest error is in the estimation of the oligomers mass, which can be caused
491 by the fact that the experimental data were obtained by the difference between the TOC and the
492 sum of the other compounds (sugars and AVP). Moreover, the deviation between the
493 experimental and simulated TOC was also calculated in order to check that the mass
494 conservation law is followed. For all the cases, this mass balance deviation result in zero percent
495 with three significant figures (0.00%). The kinetic constants and the stoichiometric coefficients
496 (K_{L_i} and $\propto_{i,j}$ in Eq. (4), respectively) had to be obtained from fitting. Regarding to $\propto_{i,j}$, it was
497 always 1 less for the final products coming from hemicellulose oligomers since they are
498 composed by pentoses and hexoses [48, 49]. These fitted parameters, which are shown in Table
499 4, require a deeper analysis and they are discussed in the next section.

500 *3.3.3 Analysis of kinetic parameters*

501 The dependence of the kinetics parameters with temperature was proved. The regression
502 coefficient (R^2) according the Arrhenius' theory was higher than 0.84 for all the cases (see

Table 3). No change in the kinetic behavior was observed through the critical point (see Table 3) like does in the hydrolysis of microcrystalline cellulose [44, 50] according to the commented in section 3.2.2, since there is not simultaneous solubilization in the SHR. However, a dependence of the kinetic behavior was observed with the extraction time, since the rates of production of valuable chemicals is decreased after the maximum of solubilized mass is reached (see Figure 7 (a) and (b)). This observation could be related with the influence of some of the chemicals produced by the further hydrolysis of sugars on the hydrothermal hydrolysis. In addition, it is also interesting that after this change, the kinetics of the sugar transformation tend to their initial value while the kinetic of the oligomer breakdown grows exponentially. This difference would be originated by the changes in the molecular weight of the extracted oligomers and the fact that they would be transformed more quickly if the molecular weight is lower. Moreover, it can be seen that temperature can compensate this negative effect, being negligible for oligomers at 400ºC (Figure 7 (c)).

Other interesting result is the evolution of the ratio between the four kinetic constants. In section 3.2.1 it was indicated that sugar transformation is faster than oligomer cleavage in subcritical conditions and lower in supercritical water. This behavior agrees with the obtained from the fittings, but only before the time of maximum of extraction (Figure 7 (a) and (c)). So, from this point, the changes in molecular weight and the raw material transformation makes the oligomer cleavage always greater. As the oligomer composition changes with extraction time, the kinetic cannot be reproduced by a typical Arrhenius' kinetic. So, two equations function of this time (t_e) are proposed, one for the ~~pre-exponential factor~~ oligomer cleaving (Eq. ~~4~~6) and other for the ~~activation energy~~ sugar further reactions (Eq. ~~5~~7).

$$P = C \cdot \left| t_{e_{max}} - A \cdot t_e \right|^B \qquad (~~4~~6)$$

$$P = D + \frac{E}{1+e^{(F\cdot(t_e-G))}} \qquad (~~5~~7)$$

Where P refers to both, the activation energy (Ea/R) and the natural logarithm of the pre-exponential factor (ln(k)). In Eq. 46, the parameter *C* is the natural logarithm of the pre exponential factor or activation energy at the maximum extraction time ($t_{e_{max}}$) and parameters *A* and *B* introduce the effect of the changes in the structure and reaction medium. A would be related with the strong of the compound against its degradation by hydrolysis. B would be a measure of how structure or reaction medium can accelerate or restrain the degradation. In Eq. 57, *D* is the pre exponential factor or the activation energy at the time where the biggest solubilization takes place, *E* and *F*, are the parameters that consider the role of the structure and reaction medium and *G* is the time when the maximum extraction is reached. In this case, E would represent how the medium or the structure can enhance the hydrolysis or hinder it. F would be the compound resistance against degradation.

Finally, the evolution of the hexoses content in hemicellulose oligomers is represented in Figure 7 (b). It can be observed that the ratio between these values grows with time. This result was expected because hexoses would make the dissolution more difficult and would explain the fact that in experiment 5 the extraction was faster than 4 and 9 experiments (see Figure 7 (c)). Moreover this result agree with the data reported by other authors [51].

3.3.4 Simulated experiments

As it was mentioned in section 3.3.2, only experiments 4, 6 and 9 were used to validate the model. Experiments 5 and 8 were not considered because their reaction time were much higher, which implies almost a total conversion at the reactor outlet. However, it checked if the model was able to reproduce their behavior. The result of the simulations are presented in Figure 8, being the absolute deviation around 4% for both experiments. Therefore, the model can predict successfully the hydrolysis at both low (0.2 – 1.0 s) and high (11.1-12.5 s) residence times.

3.3.5 Model limitations

From the results showed in the three previous sections, the model was able to successfully reproduce the experimental behavior of the set-up. In fact, this model can be used for any other lignocellulosic biomass because of the fact that it has been developed for a general biomass hydrolysis pathway. However, it is limited to processes where soluble lignin is low and when

the aim is to reproduce the overall behavior of a solubilized biomass stream hydrolysis instead of an analysis of each individual compound. Furthermore, this model can be also adapted to processes where the inlet stream is variable in time.

Conclusions

A new process coupling fractionation and hydrolysis steps was developed. By means of this process, up to 64.2% of feed Holm oak wood was solubilized mainly as oligomers of hexoses and pentoses and sugars with a small fraction of retro-aldol compounds. The low ratio of the amount of oligomers to monomeric sugars in the outlet stream could be explained by a similar behavior than in the case of pure cellulose hydrolysis: the rate of monomers hydrolysis is higher to the oligomers break up in subcritical conditions, but this tendency is reverted at supercritical temperatures.

The main products of the further hydrolysis in the second reactor were glycolaldehyde, pyruvaldehyde and lactic acid. Yield (related to the amount of soluble sugars in the raw biomass) of 24 wt% of Glycolaldehyde-Pyruvaldehyde was found at long reaction times (350ºC, 160bar and 8,6 s) and 25 wt% of lactic acid was found at short reaction time but high temperature (400ºC, 250 bar and 0.23s). An increasing amount of acetic acid was observed at the highest residence times (e.g. 12 s).

The distribution of products is related with a combined reaction hydrolysis pathway of cellulose and hemicellulose involving oligomer cleavage to monomers, isomerization steps and two competing paths: Retro-aldol condensation and dehydration. The influence of the water density and the amount of ions H^+ coming from the dissociation process is not clear as it is in the case of the hydrolysis of pure cellulose, in which the glucose dehydration is highly inhibited and retro aldol pathways clearly favored at temperatures and pressures above the water critical point. In the present work, products coming from retro-aldol paths as well as products of dehydration are observed in both conditions: sub and supercritical. Finally, a general kinetic modelling for the hydrolysisreactor was proposed. This model could reproduce the experimental data for sugar and added value products with deviations lower than 10%. Besides, the calculated kinetic parameters reproduced the changes in oligomer and sugar conversion when the

hydrolysis is performed in supercritical conditions instead of in subcritical water. This model can be applied to any other lignocellulosic biomass with a low content of soluble lignin.

The main advantage of this combined process consist in providing a liquefied biomass stream to a selective hydrolysis reactor giving the valorization of the raw material avoiding the costly grinding of particles from several millimeters to less than two hundred microns needed to pump it in a water stream belonging to a high pressure process.

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Abbreviations and symbols

Acronyms

A.A.D.: Average absolute Deviation.

Olig: Hemicellulose and cellulose oligomers.

C6/OligC5: ratio hexoses to hemicellulose oligomers.

Greek letters and symbols

A-*G*: Parameters for kinetics constant estimation.

$\propto_{i,j}$: Stoichiometric coefficient of the compound "j" for the reaction "i", dimensionless.

C_{H^+} : Concentration of the protons, mg/L.

C_{L_j} : Concentration of the compound "j", mg/L.E_a/R: Activation energy, K.

ε: Porosity of the bed, dimensionless.

ε_f : Porosity of the bed, calculated at the end of the experiment, dimensionless.

ε_{av}: Average porosity of the bed, between the beginning and the end of the experiment, dimensionless.

ε_o: Porosity of the bed, calculated at the end of the experiment, dimensionless.

K_{L_i} : Kinetic constant, min^{-1}.

k: Pre-exponential factor of the kinetic constant, $mg^{-1} \cdot min^{-1}$.

L: Length of the reactor, m.m_0: initial mass of the solid in the reactor, g.

m_f: final mass of the solid in the reactor, g.

m(i) (RM): total amount of component (i) in the raw material, extracted by acid hydrolysis and detected by HPLC analysis, g.

Mw(i): molecular weight of component i, g/mol.

MwC *:* molecular weight of the a carbon atom, g/mol.

m_{sol}*tot(RM):* total amount of soluble compounds in the raw material, extracted by acid hydrolysis and detected by HPLC analysis, g.

N: Number of compounds, dimensionless.

n: Total number of experiments, dimensionless.

n(i): Number of carbon atoms in the soluble component *i*, dimensionless.

P: Calculated kinetic parameter, activation energy or the natural logarithm of the pre-exponential factor

R^2: Coefficient R^2, dimensionless.

r: ratio between the molecular weight of the soluble compounds extracted and the molecular weight of the atoms of carbon, dimensionless.

r(i): ratio between the molecular weight of the soluble compounds extracted and the molecular weight of the atoms of carbon for compound *i*, dimensionless.

r_j : Reaction rate of the compound "j", mg/min·L.

u: Liquid velocity in the reactor, m/min.

t: Residence time in the SHR, s.

t_e: Extraction time, min.

$t_{e_{max}}$: Maximum extraction time, min.

$x_{i_{EXP}}$: Experimental value of the fitted variable.

$x_{i_{SIM}}$: Simulated value of the fitted variable.

z: Coordinate along the length of the reactor, dimensionless.

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Figure 2. Product distribution and mass balance in the biomass valorization.

(a) Results from the fractionation without further hydrolysis for 11, 17 and 26 cm^3/min in the extraction line. The first line of graphs represents to the percentage of soluble compounds identified by total organic carbon (TOC) and HPLC. The yields, calculated by the obtained soluble fractions [g] / (4.65 g), are showed above each curve. Second row of graphs in Figure 2 shows the amount of carbohydrates in the form of sugars and oligomers. The last row displays the time evolution of the products derived from the hydrolysis of sugars in the fixed bed reactor.

(b) Products distribution at 380ºC

(c) Product distribution at 350ºC

(d) Product distribution at 400ºC and short residence times.

In experiment 11, the absence of water flux in Reactor 1 makes heating process it faster (5 min). We choose this option in order to avoid a large transition state.

Figure 3. Combined reaction pathway of oligomers C5 and C6 including the glucose and xylose further reactions in hot pressurized water.

Figure 4. pH of the liquid product vs time. Comparison of the reactions at low (experiments 4 and 6) and high conversions (experiments 5 and 8) at sub and supercritical conditions of water.

Figure 5. Simplified reaction pathway for solved biomass hydrolysis.

Figure 6. Experimental and simulated amounts of soluble material by TOC, C5+C6 Oligomers, sugars C6, sugars C5 and added value products obtained in experiment 6.

Symbols represents the experimental values and continuous lines represents the results of the kinetic model using the optimized kinetic parameters.

Figure 7. Evolution of the logarithm of the kinetic constants for experiment 6(a), 4(b) and 9 (c). Ratio C6/OligoC5 (d). Solubilized mass with the extraction time for the experiments 6, 4 and 9 (e).

k_1: Cellulose oligomer breakup kinetic constant, k_2: Hemicellulose oligomer breakup kinetic constant, k_3: Sugars C6 hydrolysis kinetic constant, k_4: Sugars C5 hydrolysis kinetic constant.

Figure 8. Comparison between the experimental and simulated data for AVP in experiment 5 and 8.

Symbols are the experimental data and full lines shows the prediction of the model with optimized kinetic parameters for each data.

Figure 1.

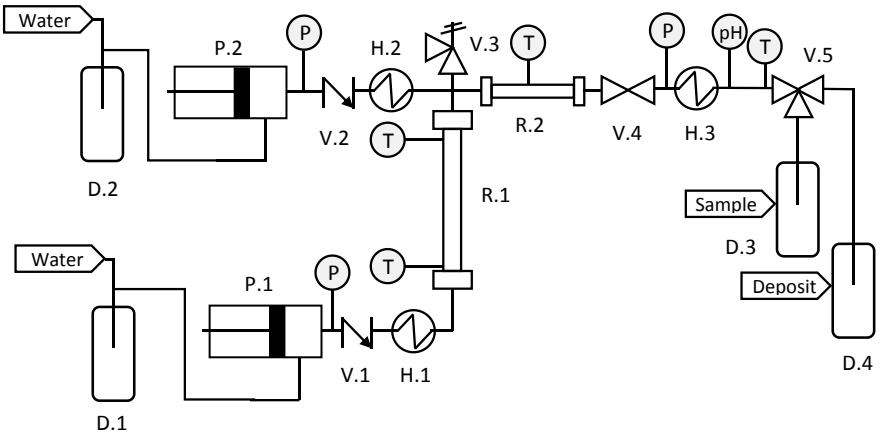
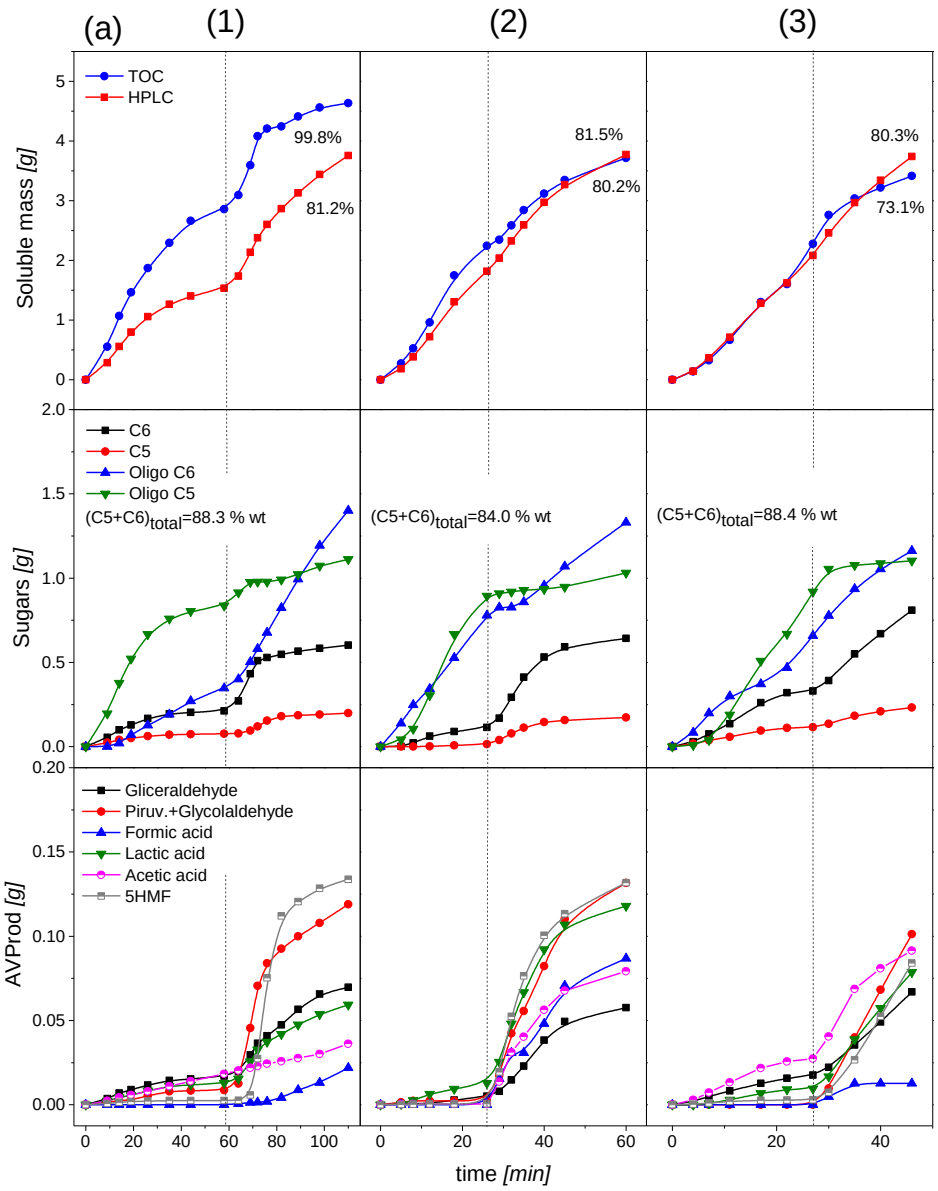
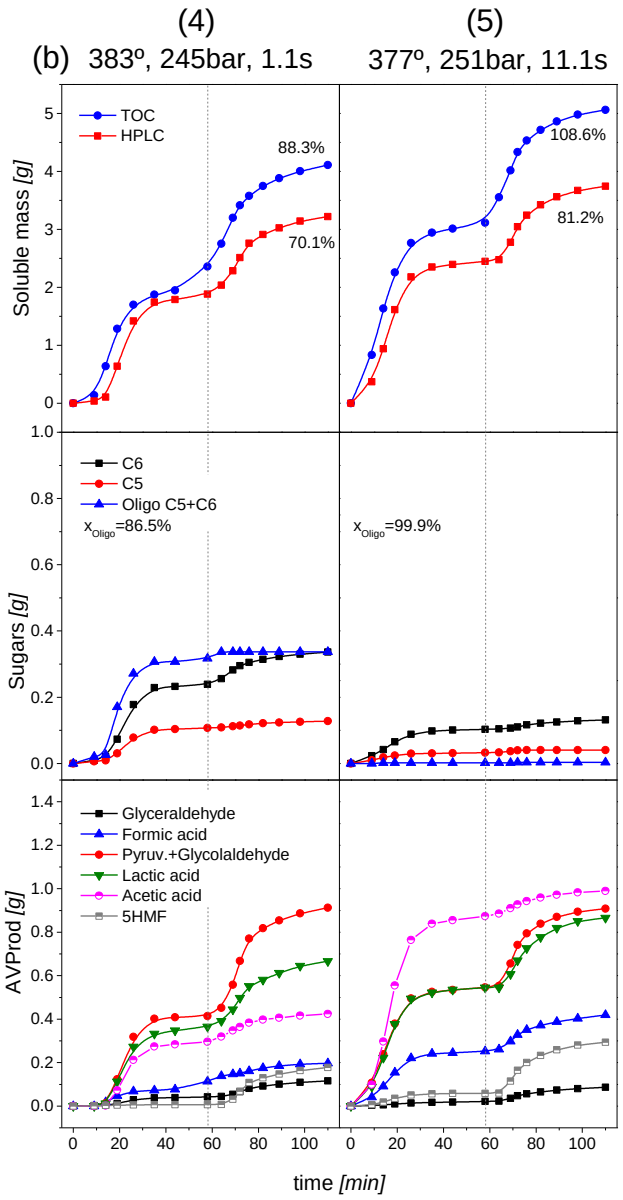
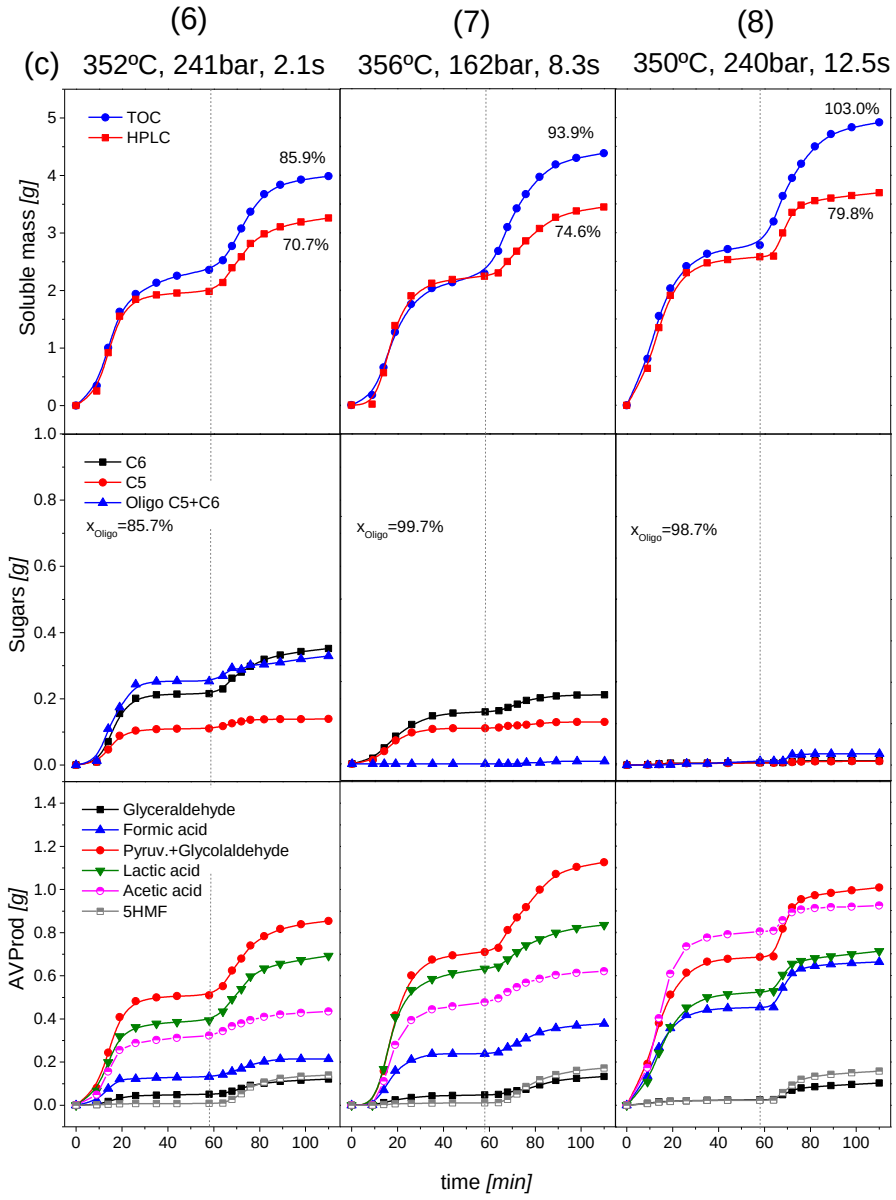


Figure 2.


(a)
(1)
(2)
(3)
TOC
HPLC
99.8%
81.2%
81.5%
80.2%
80.3%
73.1%
Soluble mass [g]
C6
C5
Oligo C6
Oligo C5
(C5+C6)total=88.3 % wt
(C5+C6)total=84.0 % wt
(C5+C6)total=88.4 % wt
Sugars [g]
Gliceraldehyde
Piruv.+Glycolaldehyde
Formic acid
Lactic acid
Acetic acid
5HMF
AVProd [g]
time [min]


(4)
(5)
(b) 383º, 245bar, 1.1s
377º, 251bar, 11.1s
Soluble mass [g]
TOC
HPLC
88.3%
70.1%
108.6%
81.2%
Sugars [g]
C6
C5
Oligo C5+C6
x_Oligo=86.5%
x_Oligo=99.9%
AVProd [g]
Glyceraldehyde
Formic acid
Pyruv.+Glycolaldehyde
Lactic acid
Acetic acid
5HMF
time [min]


(6)
(7)
(8)
(c) 352ºC, 241bar, 2.1s
356ºC, 162bar, 8.3s
350ºC, 240bar, 12.5s
TOC
HPLC
85.9%
70.7%
93.9%
74.6%
103.0%
79.8%
Soluble mass [g]
C6
C5
Oligo C5+C6
x_Oligo=85.7%
x_Oligo=99.7%
x_Oligo=98.7%
Sugars [g]
Glyceraldehyde
Formic acid
Pyruv.+Glycolaldehyde
Lactic acid
Acetic acid
5HMF
AVProd [g]
time [min]

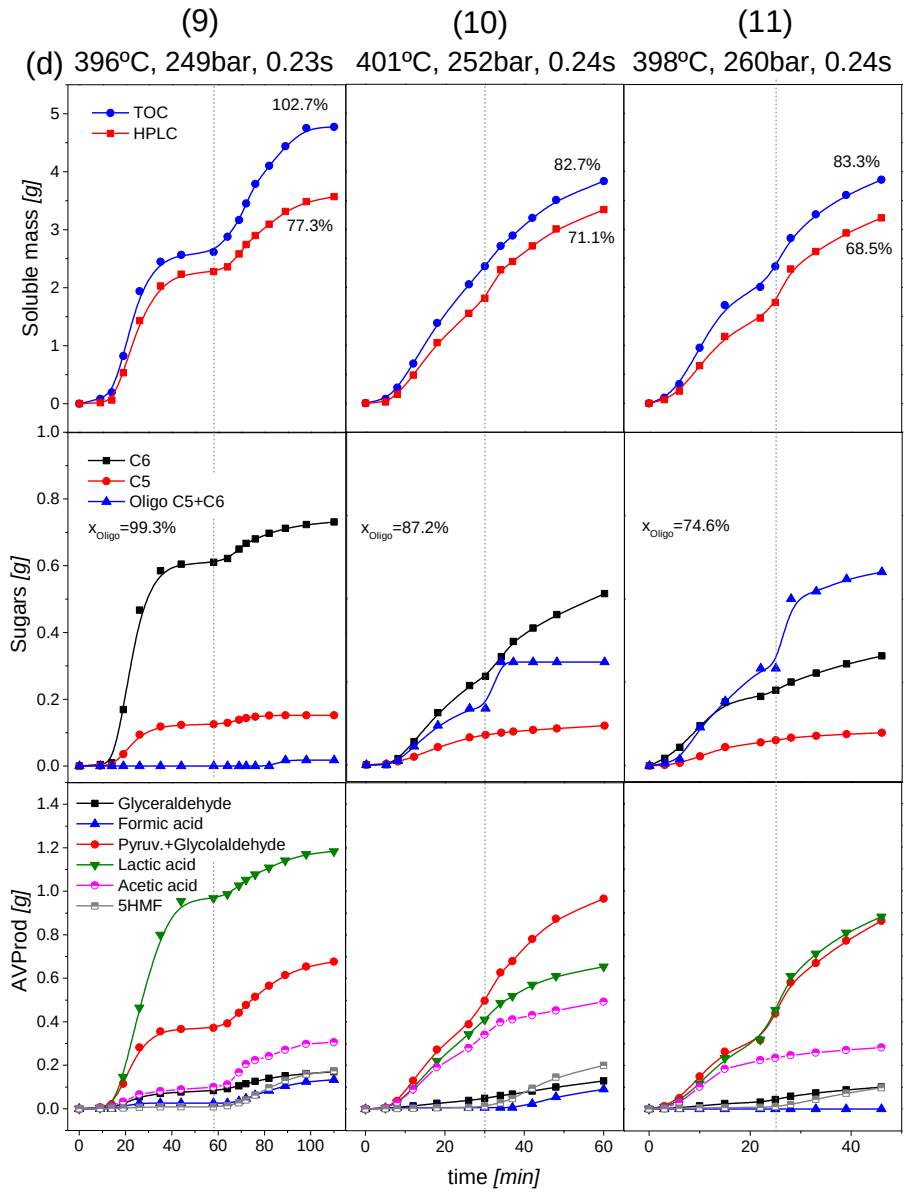


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Figure 3.

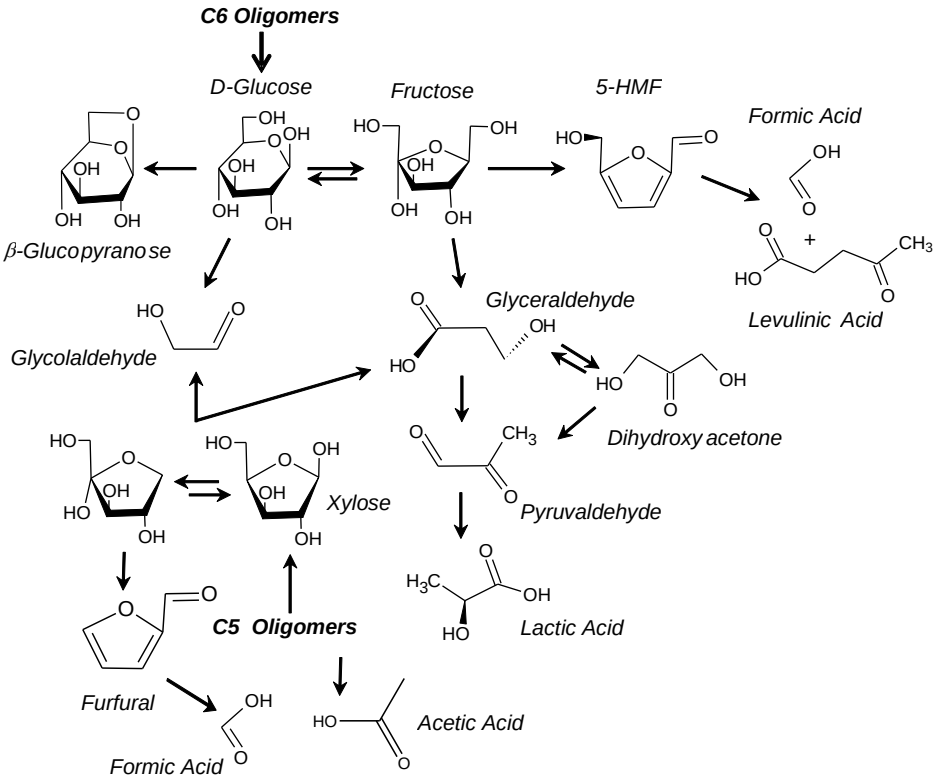

Figure 4.

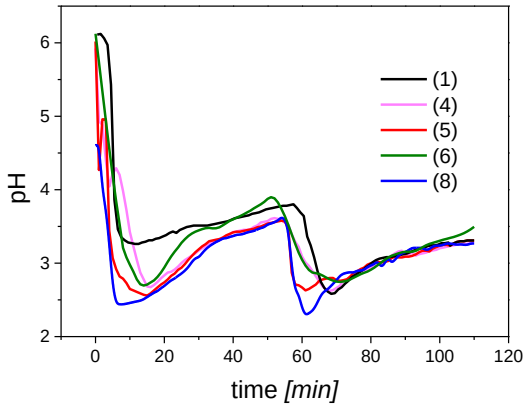

Figure 5.

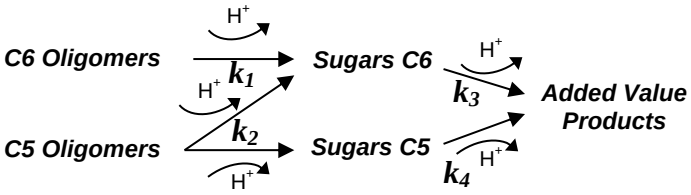

Figure 6.

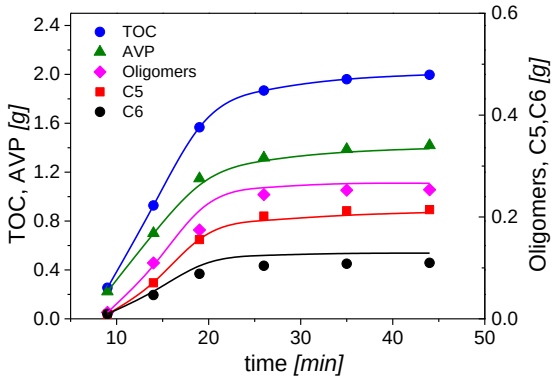

Figure 7.

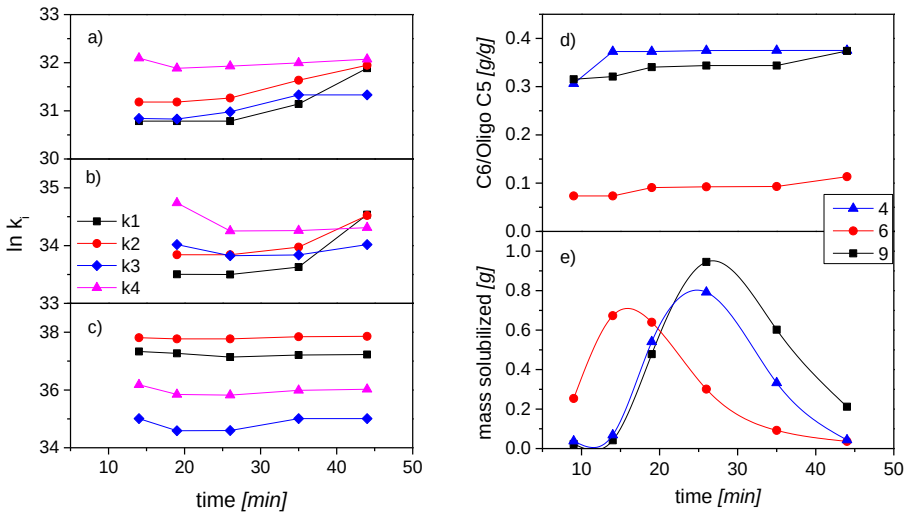

Figure 8.

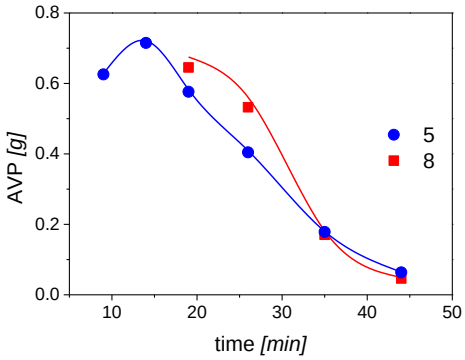

Table 1.

Exp	T [ºC]	P [bar]	t^1 [s]	$Q_{SHR}{}^2$ [cm^3/min]	$MB_{TOC}{}^3$ [%]	$x_{Oligomers}{}^4$ [%]	$Y1_{AVP}{}^5$ -	$Y2_{AVP}{}^6$ -
4	383.7 ± 5.1	245.7 ± 4.6	1.06	36.0	92.2	86.5	0.008	0.079
5	377.2 ± 3.5	251.9 ± 5.9	11.15	38.5	105.9	99.9	0.247	0.281
6	352.5 ± 4.4	241.3 ± 3.7	2.10	35.2	89.3	85.7	0.004	0.109
8	349.9 ± 2.4	239.6 ± 4.2	12.50	35.8	103.1	98.7	0.233	0.132
9	396.1 ± 3.6	249.1 ± 5.1	0.23	36.8	103.6	99.3	0.440	0.254
10	401.2 ± 2.8	252.2 ± 3.9	0.24	90.1	93.0	87.2	0.481	0.278
11	398.3 ± 3.0	259.9 ± 3.4	0.24	106.2	91.2	74.6	0.530	0.228

[1] t: reaction time in hydrolysis reactor, [2] Flow rate in the SHR, [3] Global mass balance of the coupled process, [4]Conversion of oligomers from hemicellulose and cellulose, [5,6] Yields of added value products in the time period of the first and second stage of temperature during fractionation Y_i=mass$_i$ / mass soluble material in raw biomass

Table 2.

	ADD %							
	Instantaneous				Cumulated			
Experiment	Oligomers[1]	C6[2]	C5[3]	AVP[4]	Olig[1]	C6[2]	C5[3]	AVP[4]
4	21.70	21.88	21.92	7.38	26.85	10.78	4.98	7.52
6	20.58	29.11	22.16	6.27	6.99	2.15	14.82	1.78
9	*	61.04	11.15	8.07	48.53	9.90	8.15	2.66
Average	21.14	37.34	18.41	7.24	27.46	7.61	9.31	3.99
5	*	*	*	5.77	*	*	*	4.94
8	*	*	*	0.93	*	*	*	1.02
Average	*	*	*	4.65	*	*	*	3.32

*[1] Oligomers from hemicellulose and cellulose, [2] Sugars C6, [3] Sugars C5,[4] degradation products. * Compound not detected. ADD% of total organic content was 0.0.*

Table 3.

$t_e{}^1$[min]	$k_1{}^a$	$k_2{}^b$	$k_3{}^c$	$k_4{}^d$
		R^2		
19	0.88	0.87	0.99	0.999
26	0.88	0.86	0.99	0.98
35	0.87	0.85	0.99	0.97
44	0.93	0.89	0.9999	0.96
Average	0.89	0.87	0.99	0.97

[a] Cellulose oligomer cleavage constant, [b] Hemicellulose oligomer cleavage constant, [c] Sugars C6 hydrolysis kinetic constant, [d] Sugars C5 hydrolysis kinetic constant. [1] Fractionation time.

Table 4.

k_1 [a]	ln(k) [e] -	Ea/R [f] [K]	k_2 [b]	ln(k) [e] -	Ea/R [f] [K]
A	1.04	1.03	A	1.08	1.08
B	0.04	0.06	B	0.03	0.05
C	106	46,543	C	109	48,553
k_3 [c]	ln(k) [e] -	Ea/R [f] [K]	k_4 [d]	ln(k) [e] -	Ea/R [f] [K]
A	3.26	2069	A	2.85	1834
B	22.05	24.22	B	21.25	20.15
C	1.35	4.01	C	1.70	3.58
D	87.32	35,238	D	89.63	36,081

[a] Cellulose oligomer breakup constant, [b] Hemicellulose oligomer breakup constant, [c] Sugars C6 hydrolysis constant, [d] Sugars C5 hydrolysis constant, [e] Natural logarithm of the Arrhenius' pre-exponential factor, [f] Activation energy.