Integrated Fractionation-Hydrolysis Process using Sub- and Supercritical Water for Lignocellulosic Biomass Valorization

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Abstract

~~L~~Lignocellulosic biomass coming from holm oak ~~(holm oak)~~ was fractionated, solubilizing ~~two of their major constituents:~~ hemicellulose~~,~~ and cellulose. This procedure was performed in two stages of temperature, lower one (180 ºC) optimizing the hemicellulose extraction and higher one (260 ºC) aiming to extract the major proportion of cellulose and the hard hemicellulose remaining in the insoluble lignin structure. Three different flows of water ~~was~~ were employed, reaching sugar yields from 71 to 75% mainly in oligomer form and low amount of subproducts (eg. 5.9% retro aldol product, 0.8% acetic acid and 2.5% 5-HMF). This stream was feed together with a near and supercritical water stream in a sudden expansion microreactor ~~in which the time of residence~~where the residence time could be precisely controlled. Temperature, pressure and residence time~~time of residence~~ ~~was~~ were modified in order to maximize the yield of ~~the products from~~ retro aldol condensation products~~ pathways~~. The main products of this further hydrolysis were pyruvaldehide and lactic acid, reaching yields of 26% (at 350ºC, 160 bar and 8.3 s) and 27% (at 400ºC, 245 bar and 0.23 s) respectively. A discussion based on the known reaction pathway is proposed. This combined process, performs the valorization of real lignocellulosic biomasses avoiding the costly process of extreme grinding needed for their fluidization in a continuous process.

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Introduction

Even if it is reasonably assumed that ~~plant~~ biomass from plants will be the main carbon source in the future, the choice about 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= 22.1 MPa), can be pointed as a promising alternative to depolymerize and valorize biomass (Akiya & Savage, 2002; Cantero et al., 2014; Peterson et al., 2008; Ragauskas et al., 2006; Savage et al., 1995). Physical and chemical properties of water can be modify by adjusting pressure and temperature around the critical point, ~~Around the critical point of water it is possible to modify the physical and chemical properties of water by adjusting pressure and temperature~~ making water a reaction medium ~~which is~~ able to favor different kind of reactions (Akiya & Savage, 2002).

For this reason, pressurized water has been used as reaction medium for fractionation (Cantero et al., 2015; Gullón et al., 2012; Kim & Lee, 2006; Sasaki et al., 2003) , hydrolysis (Cantero et al., 2013b; Fang & Fang, 2008; Sasaki et al., 2004) and valorization of biomass (Chen et al., 2015; Holgate et al., 1995; Wang et al., 2013; Yan et al., 2010).

The average composition of lignocellulosic biomass is: cellulose (≈40% wt.), hemicellulose (≈25% wt.), lignin (≈25% wt.), extractives and ashes (10% wt.) (Bobleter, 1994). Although biomass is composed ~~of~~ by diverse and complex molecules, it can be fractionated principally~~mainly~~ into C-6 sugars (mainly glucose), C-5 sugars (mainly xylose) and lignin (Cantero et al., 2014). 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 (Bicker et al., 2005a; Bicker et al., 2005b; Cantero et al., 2014; Kabyemela et al., 1997a; Kabyemela et al., 1999; Kabyemela et al., 1997b; Lü & Saka, 2012; Román-Leshkov et al., 2010; Sasaki et al., 2002).

The fractionation of biomass can be defined as the ~~obtaining~~ selective separation of C-5 sugars, C-6 sugars and lignin from the original biomass ~~in separate streams from biomass~~. This process was studied under hydrothermal conditions in different ways of operation: batch, semi batch and

continuous (Cantero et al., 2014; Elliott et al., 2015). ~~The s~~Semi batch and continuous processes allow to obtain higher yields of sugars and chemical compounds respect to ~~than~~ batch reactors, because it is possible to control the temperature (T) and the residence time ~~of residence~~ (tr) more accurately ~~e~~ than ~~it is achieved~~ in ~~the~~ batch processes. ~~The c~~Continuous processes are the most appropriate to control the reaction conditions (T and tr), however, in most cases it is necessary to apply some expensive pretreatments to the raw material ~~prior~~ before the fractionation – hydrolysis process, for example: exhaustive size reduction (Yu & Wu, 2011). In addition, the continuous process ~~should~~ can be ~~set~~ performed at different operating conditions ~~if it is desired to~~ in order to separate the C-5 sugars from the C-6 sugars.

In a first step, carried out at temperatures between 180ºC and 260ºC, and reaction times between 0.1 min and 1 min, hemicellulose is extracted and hydrolyzed.

~~One way to achieve a continuous fractionation of biomass is to hydrolyze hemicellulose first at temperatures between 180ºC and 260ºC with reaction times between 0.1 min and 1 min.~~

After this ~~first hydrolysis~~ process two products are obtained: ~~a liquid and a solid. The~~ a liquid ~~will be~~ composed mainly ~~of~~ by C-5 sugars ~~while the~~and a solid ~~will be~~ composed ~~of~~ by C-6 sugars and lignin. These two products can be further ~~separated~~ splitted by operations of liquid-solid separation, like filtration. Then, the solid can be hydrolyzed at supercritical conditions to obtain ~~the~~ a water solution of C-6 sugars ~~in the liquid product~~ and a solid enriched in ~~and~~ lignin ~~as solid~~. This process ~~is~~ can be carried out in two reactors with a filtration operation in between~~.~~, but can be intensified by using only ~~A similar fractionation can be done in one reactor if it is used a~~ one fixed bed reactor. In such a case the ~~plant~~ biomass is ~~fed to~~loaded in the reactor and the hydrolysis temperature is changed in order to hydrolyze ~~the~~ C-5 or C-6 sugars (Kilambi & Kadam, 2013). The semi batch process allows high performances on the yields of C-5 sugars hydrolysis. However, when the reaction temperature ~~for the hydrolysis should be~~is increased to hydrolyze recalcitrant cellulose and hemicellulose, the yield of sugars ~~recovery~~ recovered decreases because of the increment of the sugars degradation reactions (Cantero et al., 2013b; Sasaki et al., 2004).

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The continuous reactors have been employed in many applications for the valorization of sugar~~s~~ streams allowing a precise control over the reactions (Kabyemela et al., 1997a; Kabyemela et al., 1999; Kabyemela et al., 1997b). These reactions can be managed using pressurized water by choosing the adequate reaction conditions. For example, at temperatures between 200ºC and 300ºC (25 MPa) the water molecules ~~will be~~are highly dissociated favoring the ionic reactions, like the production of 5-HMF from fructose and glucose (Akiya & Savage, 2002). On the other hand, at 400ºC (25 MPa) the water molecules ~~will be~~are highly associated favoring the non-ionic reactions, like the retro aldol condensation reactions (Akiya & Savage, 2002).

In this article, a novel integrated fractionation-valorization process~~it~~ was designed and built ~~a novel integrated fractionation-valorization process consuming~~ using ~~plant~~ wooden biomass as raw material and water ~~using~~ (subcritical and supercritical) ~~water~~ as reaction medium. The ~~plant~~ 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 C-5 and C-6 sugars into valuable products, like glycolaldehyde, pyruvaldehyde and lactic acid avoiding a further hydrolysis to organic acids. The objective of this research paper was to design a novel process capable of converting ~~plant~~ lignocellulosic biomass into valuable products eluding the excessive milling of biomass and decreasing the number of reactors. Optimum conditions for the fractionation of holm oak in a fixed bed reactor were found, followed by a valorization process of C-5 and C-6 sugars in the continuous reactor.

~~It was optimized: (1) the fractionation process for Holm Oak as a model biomass in the fixed bed reactor and; (2) the valorization process of C-5 and C-6 sugars in the continuous reactor.~~

1. Experimental

2.1 Materials

Type 2 water ~~from~~ distilled with Elix® Advantage purification system~~,~~ was used as the reaction medium to run the experiments. The standards used in a High Performance Liquid Chromatography (HPLC) analysis were: cellobiose (≥98%), glucose (≥99%), xylose (≥99%),

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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 sulphuric acid (HPLC grade) in Type 1 Milli-Q® ~~water and were~~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 (Sluiter, 2011). Also, Milli-Q® water was used in this determination. Holm oak wood used as raw material came from ~~Turku and surrounding area, Finland~~Spain. The wood was milled to obtain fibers ~~shape~~ with average wide of ~~of~~ 2 mm and average length of 5 mm, ~~wide and length average sizes, respectively~~, 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 ~~the liquefied biomass~~extracted liquor were determined ~~by means of trough~~through two Laboratory Analytical Procedures (LAP) from NREL (Sluiter, 2011; Sluiter, 2006). The procedure for solid sample consists in quantifying the structural carbohydrates and lignin in the biomass~~. A brief description is as follow~~ as follow: a) biomass was weighted before and after being~~is~~ dried in an air driven oven at 105 °C for 24 hours in order to ~~obtain~~ calculate the moisture content, b) ~~exhaustive extraction is performed~~dried biomass was treated in a Soxhlet equipment with ~~using~~ n-hexane, leaving a solid free of oils and other ~~substances~~extractives, c) ~~a first acid hydrolysis is performed to~~ 300 mg of free- extractives solid from step (b) were hydrolyzed in ~~a~~ with 3 ml of 72% wt sulphuric acid solution at 30 °C for 30 min, in order to break the bonds between biopolymers ~~with~~ and the main solid structure, d) the mixture of oligomers obtained in ~~of~~ step (c) is diluted using 84 ml of deionized water ~~for a second acid hydrolysis~~and warm at 120 °C for 60 min with the aim to break internal bonds in hemicellulose and cellulose oligomers to obtain their correspondent monomers ~~in solution~~, e) the solid is separated from the solution by vacuum filtration, f) the total

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mass of solubilized sugars ~~content are~~was quantified ~~by weight~~as the difference in weight ~~with~~ between the original solid and the exhausted solid after oven drying at 105 °C in oven for 24 hours, g) exhausted solid is placed in a muffle at 550 °C for 24 h and the remaining residue was weighted to calculate the insoluble lignin and the ash content of the sample, ~~insoluble lignin and the ash content is determined when the sample is placed in a muffle at 550 °C for 24 h and the remaining residue is weighted obtaining both values by weight difference,~~ h) a liquid aliquot was analyzed with UV-Vis spectrophotometer at 320 nm with extinction coefficient of 34 $Lg^{-1}cm^{-1}$ (S.-N. Sun, 2014) to calculate the amount of soluble lignin~~ is obtained by UV-Vis spectrophotometer at 320 nm with extinction coefficient of 34 $Lg^{-1}cm^{-1}$ (S.-N. Sun, 2014) from a liquid aliquot~~; i) another liquid aliquot is neutralized to pH range 6 to 7, then it is filtered using a 0.2 µm membrane and analyzed by HPLC determining the carbohydrates composition. This procedure is performed using a column SUGAR SH-1011 (Shodex) with a 0.01 N of sulfuric acid solution as a mobile phase. To identify the ~~hemicelluloses, celluloses and reduced sugars~~soluble products, two detectors were used: Waters IR detector 2414 (210 nm) and Waters dual λ absorbance detector 2487 (254 nm). In order to calculate the amount of carbohydrates, each chromatogram was decomposed into a sum of 9 to 13 Gaussian peaks by means of a commercial software, minimizing chi squared function of a Levenberg-Marquardt-Flecher algorithm (Fletcher, 1971). Pyruvaldehyde and Glycolaldehyde ~~could not be resolved by this configurations~~resulted to be overlapped, since the retention time of their standards are extremely close (11.99 vs 12.24 minutes, respectively). ~~From the analysis (Sluiter, 2011), t~~The raw material contained 1.6 % wt. extractives, 1.8% wt. moisture, 0.2% wt. ashes, 24.2% wt. Klason lignin (from which 4.0% corresponds to soluble lignin), 45.7% wt. of hexoses, 23.9% wt. pentoses, the sum~~mation~~ of all the components represents the 97.4% of total weight, the discrepancy of 2.6% is due to experimental errors like the loss of solid material after the recovery at the end of the experiments, or the inhomogeneity of the material which can have slightly different compositions depending on the analyzed aliquot.

The amount of C6 was calculated as the sum of glucose, cellobiose and fructose concentrations; the only C5 detected was xylose, acetic acid was considered to come from the ~~acetyl groups~~

~~bonded to~~deacetylation of xylanes forming hemicellulose, during ~~in~~ the fractionation process~~,~~ ~~however~~ or, as ~~is~~ explained in the next sections, ~~it could be produced~~ from ~~an exhaustive~~ the ~~hydrolisis~~hydrolysis of piruvaldehyde. Hydrolysis products from hexoses and pentoses were mainly glyceraldehyde, glycolaldehyde, piruvaldehyde, lactic acid 5-hydroxymethylfurfural and in some cases ~~acrilic~~acrylic acid were detected in very low concentration.

The procedure followed ~~for~~ to analyze liquid samples consist in the steps (c), (d) and (i) ~~above~~ described above. Furthermore, the carbon content ~~of this fraction~~liquid solutions is determined by total organic carbon (TOC) analysis using a Shimadzu TOC-VCSH equipment. Each sample ~~is~~ was previously filtered using a 0.2 µm syringe filter and ~~is~~ diluted 1:10 times with Type 2 Millipore water.

2.3 *Experimental setup and procedure*

The setup used in this work is shown in Figure 1. The ~~coupled~~ system consisted in two reactors integrated: a) the fractionation process, from which the ~~liquefied~~ biomass liquid ~~stream~~ solution is produced, b) the supercritical reactor hydrolysis, which converts all the ~~biomass stream~~soluble compounds into added value products. The fractionation line is composed by a water deposit (D.1), downstreams 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 ~~500~~ 300 W each, placed axially along a machined aluminum bar with 5.08 cm O.D. Both, preheater and the reactor are located inside ~~an oven of~~ a former chromatographic oven HP5680 for security reasons. The ~~out~~ out-flow stream ~~of~~ from the fractionation line is mixed with the supercritical water stream, entering in a sudden expansion ~~directly at the inlet of the sudden expansion~~ micro-reactor (SEMR) (R.2). The supercritical water line~~,~~ is composed by a heater (H.2), a tube of 20 m, 1/8 in O.D. SS316 wrapped around a brass cylinder and heated by two

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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 is generated by a Milton Roy XT membrane pump (P.2, maximum flow rate 6 kg/h). ~~The main advantages of the~~ SEMR ~~are:~~allows a fast ~~the~~ heating of the biomass stream, which is mixed almost instantaneously with the supercritical water stream, and ~~the~~ a ~~cooling~~rapid cooling ~~process~~ of the products, which takes place ~~by~~through ~~means~~ a sudden expansion which efficiently stops the hydrolysis. In this way, the reaction time could be precisely calculated, ~~because~~ as the reactor works isothermally. Pressure is generated by closing a Micro Metering valve 30VRMM4812 from Autoclave Engineering (V.4). ~~A detailed description of both s~~Setups of the two reactors ~~were~~ presented in detail in previous works ~~19,24,32,~~(Cantero DA 2013; Gallina et al., 2016).

6.12±0.03 gr of holm oak biomass ~~are~~ were fed into the fractionation reactor. Two metallic filters ~~are~~ were used, located ~~in~~ on the top and bottom of the reactor, avoiding the removal of the solid during the experiments~~to keep the raw material in place~~. A pressure test with cold pressurized water was carried out ~~Cold water is pressurized into the system~~ before each experiment, with the aim to check the presence of leaks in ~~fractionation line~~the system.

Then, the supercritical line ~~is~~ was heated ~~in order to~~ ensure the functioning of the system at required operating conditions. ~~ensure the temperature, pressure and water flow with cold water flowing through fractionation line~~. Once this conditions ~~are~~ were stable, the ~~flow~~ pumps were momently switched off ~~is stopped~~ and both, the preheater and the fractionation reactor, ~~are~~ were heated up until the ~~. When the control~~ temperatures ~~reached~~ ~~the~~ the respective set values, then both pumps ~~are~~ were switch on again ~~started,~~and the flow and pressure ~~are~~ were adjusted ~~with V.4~~ to the desired conditions~~,~~. Zero time was defined at that moment~~then, zero time is considered~~. Six experiments were performed varying the temperature in the ~~supercritical~~ micro-reactor from subcritical (350ºC) up to supercritical (400ºC) conditions, maintaining the pressure at 25.0±1.0 MPa. ~~Also, t~~The reaction~~sidence~~ time ~~of liquefied biomass~~ in this reactor ~~was varied from 0.25 s up to 12 s, which~~ was ~~obtained~~ modified by ~~modifying~~ 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. ~~In this sense, two reactors with 2.2 and 12.4 cm^3 were utilized.~~ Three different water flows (11, 17,

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26 cm^3/min) ~~in the fractionation line~~ were tested in the fractionation line, maintaining constant the ratio with the flow of supercritical water stream, ~~in order~~ to get the desired conditions during the further hydrolysis.

The feed composition to the SEMR was analyzed by carrying out ~~Also,~~ three fractionations without the second hydrolysis stage, at the same conditions of temperatures, flow-rates and pressure tested with the coupled reaction ~~were performed in the same conditions., with the aim to know the feed composition to the SEMR.~~

Fractionation ~~I~~in ~~fractionation~~ the fixed bed reactor, was performed in two stages marked by two distinct temperatures~~were run at different temperature,~~: 180ºC to extract the hemicellulose and 260ºC to remove most of the cellulose fraction from the ~~raw~~ biomass. Heating time between both temperatures was between 5-10 min, ~~where~~ when the flow was temporarily stopped ~~during this period~~ for the experiment at 26 cm^3/min. In order to follow the reaction evolution, the pH of the ~~product~~ outlet stream was measured online ~~between periods~~with intervals of 1 min, using an electronic pH-meter (Nahita model 903). Liquid samples (30-40 cm^3) were taken following the pH variations, between 5-20 min for the experiment at 11 cm^3/min, and every 2-8 min for the other experiments. The final time varies from 110, 60 and 45 min for the experiments at 11, 16, 26 cm^3/min, respectively (named here as (1), (2) and (3)). After the last sample was withdrawn, the heating was shut off and the fractionation reactor was let to ~~gradually~~ cool~~ed~~ down to room temperature ~~with air flux~~. Both pumps were set to zero flow and the system was depressurized. The solid was removed from~~inside of~~ the ~~reactor~~ reactor~~was collected~~, filtered and dried 24 h~~s~~ at 105ºC ~~for further analysis~~. After cleaning, the ~~fractionation~~ fixed bed reactor reactor was ~~reconnected~~ replaced and the system was washed out with Type 2 water ~~flow~~. 10 experiments were performed (3 fractionations and 7 coupled reactions), ~~characterizing~~ obtaining a total of 130 liquid and 10 solid samples, characterized with ~~by~~ the methods ~~above~~ described above.

3. Results and Discussion

3.1. *Biomass fractionation*

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The total amount of soluble ~~materials~~ compounds ~~of unmodified holm oak biomass~~in the raw material, ~~quantified as sugars and other products obtained from their further hydrolysis,~~ was equal to 4.65±0. 03g, corresponding to the 72.1% of the raw biomass weight. ~~From this soluble material,~~In details, 3.02±0.02g are hexoses (C6), 1.58±0.01g are pentoses (C5). ~~-~~The residence time of the liquid (τ_l), ~~depends~~ is determined mainly ~~on~~ by the liquid flow rate and ~~on~~ by the average~~d bed~~ porosity of the bed (ε_{avb}=0.71±0.05). ~~This last is calculated based on~~The last was calculated as in equation 1, by considering the initial and the final fraction of void volume of the bed due to the shrinking size of the biomass particles, ~~-~~ and considering constant the density of the water (Gallina et al., 2016) (since its variation with temperature is less than 2%) and the density of the holm oak wood (800 kg/m^3, dry based ~~-average~~ for holm oak species) ~~(Gallina et al., 2016)~~ . Residence time for the liquid inside the fixed-bed reactor was in the range of 1.0 min ~~2.6 min>~~<τ_l~~></~~2.6 min~~1.0 min~~.

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

Figure 2 shows the cumulated mass quantified by TOC and HPLC techniques of: total soluble materials ~~quantified by TOC and HPLC techniques~~, ~~the amounts of~~ oligomers and monomers of C5 and C6 ~~as, well as the mass of the~~ products deriving ~~obtained~~ from the dehydration ~~the hydrolysis~~ of ~~these~~ sugars, ~~- all of them in cummulative values for different~~obtained by changing ~~flows of~~ water flow-rates in the fractionation line.

Break points in the curves, ~~signals~~ indicate the transition between the two temperature stages. The total mass of soluble compounds detected ~~products from~~ by TOC ~~were~~ was calculated by dividing the value of total organic carbon concentration recognized ~~detected~~ by the equipment by a factor 0.42 (equation 2).

This factor is the sum of the mass fractions of every compound in the raw material multiplied by the ratio between the molar weight of carbon and the molar weight of the compound.

$$r = \Sigma r(i) = \sum \frac{m(i)\,(RM)}{m_{sol\,tot}\,(RM)} \frac{Mw(i)}{Mw\,\Sigma C(i)} = 0.42 \quad (2)$$

The factor r indicates the ratio between the molecular weight of the soluble compounds extracted from holm oak and the molecular weight of the atoms of carbon of the same compounds. It allows

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to compare values directly obtained by TOC analysis (total amount of C) with values obtained by HPLC (total amount of soluble compounds).

~~This number results from the sum of the mass fractions of every compound in the raw material multiplied by the ratio between the molar weight of carbon and the molar weight of the compound, in each of the components detected by HPLC.~~ The mass balance calculated by summing ~~of~~ the ~~s~~mass of the solid recovered from the reactor at the end of the experiment ~~added~~ to the mass of the soluble material quantified ~~from~~ by TOC analysis and to the mass of insoluble ~~ligning~~lignin flushed ~~in~~ by the water stream was equal to 103.8, 93.7 and 84.9 % of the total biomass fed to the reactor, respectively.

In the first row of graphs in Figure 2 are compared the mass of soluble material obtained by TOC with the same values obtained by HPLC for each sample. The number in the figure is the ~~percentage of the soluble material in the water stream at the end of the experiment respect to the same value in the raw material~~yield. From the graphs is clear that the ~~difference~~ discrepancy between the values obtained with~~between~~ ~~both~~ the two techniques is reduced when the water flow-rate through the fractionation reactor is ~~augmented~~ increased (23.6, -4.1 and -3.2% for the three flows, respectively). This could indicate that there are sub-products from the sugars hydrolysis (mainly organic acids) not identified by HPLC. In fact, some peaks identified were not completely resolved, then, the calculation of the area was not a trivial task. The ~~S~~second line of graphics in Figure 2, shows the sugars and soluble oligomers of C5 and C6 obtained from fractionation in the two temperature stages. ~~The mayor fraction~~Most of the hemicellulose is hydrolyzed ~~from lignin matrix and comes out from the reactor in the form of~~to oligomers~~.~~, in fact ~~H~~hemicellulose is highly soluble in water because ~~of it has a lot~~ of the abundance of acetyl groups in ~~their~~ its ~~structure as well as it is~~ amorphous structure (Miller-Chou, 2003), and after the first breaking leads to the production of~~.~~ ~~So, it would be expected that produce~~ soluble oligomers ~~(~~(which size would be around 200 monomers~~)~~) ~~after the first breaking~~.

The yield of C5 at the end of second stage of temperature was 87.3, 89.8 and 93.1%, respectively. ~~At~~ On the contrary, cellulose is insoluble in water due to its cr~~y~~istallinity ~~and its low acetylation degree~~, so only oligomers with a very low molecular weight would be water soluble (e.g. 10

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glucose units). In this sense, the amount of hexoses in form of oligomers is similar to the monomers at lower flow (experiment 1) and this difference is enlarged with the flow increase (2 and 3) . This distribution could be related to the difference in the activation energy of the cleavege of the ~~hidrogen~~ hydrogen bonds between celluloses and the α1-4 glycosidic bond, which is known that is favored at subcritical conditions (Cantero DA 2013; Sasaki et al., 2004). The last row of graphs in Figure 2 displays different amounts of products from hydrolysis of xylose, glucose and fructose. These amounts are ~~despreciable~~depreciable in the first stage and ~~are enlarged~~increased ~~to in the second stage of~~after increasing temperature, however, they are one order of magnitude lower than ~~to~~ the soluble sugars. An example is 5 HMF, which takes places mainly in the second temperature stage where conditions makes water highly ionic medium in the fractionation reactor. The main components in this graphs are pyruvaldehyde-glycolaldehyde and lactic acid. The decrease of the residence time ~~of sugars~~of liquid inside the reactor diminish their further hydrolysis or transformation. ~~An example is 5 HMF, which takes places mainly in the second temperature stage where conditions makes water highly ionic medium in the fractionation reactor.~~

3.2 *Biomass valorization with sub and supercritical fast hydrolysis*

The ~~ouput~~ outlet stream ~~of~~ from the ~~fractionator~~ fixed bed reactor was feed to the SEMR together with ~~the~~ a distillate water stream at temperature ~~and pressure around their critical point~~at near critical conditions of temperature and pressure, with the aim to obtain a fast and selective hydrolysis of the oligomers extracted from the biomass. ~~Time of residence~~The reaction time (*tr*) was ~~modified~~ varied in order to ~~find a major yield to some~~modify the selectivity to obtain different valuable chemicals.

Optimum temperatures and flow-rate for the extraction, have been identified in experiment 1, as they lead to the maximum yield; for this reason, a flowrate of… and temperatures of…were chosen for most of the experiments; only experiments 10 and 11 were performed with the same liquid flow-rates used in the fractionation experiments 2 and 3 (…and …respectively). This approach, moreover, allows to know the composition of the stream entering in the SEMR.

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~~In this sense, e~~Eight experiments were performed, as shown in ~~and their working conditions are summed up in~~ Table 1. Three temperatures (….) and 6 reaction times (…..) were tested in the SEMR, keeping constant the temperatures of sub-critical water through the fixed bed reactor, and of super-critical water to hydrolyze the oligomers. ~~at the same flow in the fractionation reactor than experiment (1), 350 ºC (5 and 8), 380ºC (4 and 7) and 400 ºC (9), and other two experiments (10 and 11) were performed at same temperature bur at the same flows than experiments 2 and 3.~~ Two ~~-~~reactions (7 and 9) were carried out in a longer reactor~~at longer tr~~, with the aim to increase the reaction time~~observe the effect of deeper conversions~~. A lower pressure was used in ~~Only one condition at lower pressure were tested (r~~reaction 6 ~~, see Table 1) with the aim~~ to observe the influence of the variation of ~~the~~ density ~~variation~~ in the product distribution.

Global mass balance, calculated as ~~was commented~~ described in section 3.1, ~~-~~is presented ~~in the fourth column of~~ Table 1. The values (avg=96.9%, sd=6.5 %) indicates that no significant gasification takes place in the supercritical reactor.

First row of graphs in ~~the~~ Figure 2 (b), (c) and (d) ~~are~~ presents the mass balance between the soluble materials in the raw biomass and the mass quantified in the output stream of SEMR by ~~means of~~ TOC and HPLC techniques. Some difference between these two analytic procedures is observable, mainly at the second stage of ~~temperarute~~temperature of the fractionation or at high sugars conversions. This findings could be due to the productions of small organic acids, ketones and aldehydes (levulinic and acrylic acids, dihydroxyacetone, formaldehyde) and other compounds not identified in the HPLC analysis, see Figure S2 in Suplementary Material. This hypothesis agree with the decrease of the mass difference indentified by both techniques when a high water flow is involved (see first row of graphs in Figure 2 (d)).

3.2.1 Oligomers and sugars conversion

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Comentado [u14]: temperaturas

Comentado [u15]: tiempos

Comentado [u16]: Especificar flujo

Con formato: Fuente: Sin Cursiva

Comentado [u17]: Indicar Presión

Comentado [u18]: Especificar: less residence time→less degradation.

Oligomer conversion to C5 and C6 monomers was calculated by difference between the stream entering to the SEMR (composition obtained in experiment 1), and the stream leaving the reactor after the hydrolysis.

T~~- By mass balance between the inlet (all the products from the fractionation) and outlet stream,~~ ~~t~~he conversions of oligomers ~~of~~ to C5 and C6 monomers ~~were calculated and their values~~are reported in the upper left corner of each graph in second row of Figure 2 (b), (c) and (d). In all the runs, oligomers conversion was higher than 85%, the exception seems to be experiment (11), in which the small *tr* and high dilution of the inlet stream could be the cause of the low conversion. Sugars ~~in~~ C5 (xylose) and C6 (cellobiose, glucose and fructose) are intermediary compounds in the reaction pathway. From Figure 2, comparing the amount of sugars C6 and C5 in experiments 4 and 5, it is shown that the conversion of sugars to other products is faster than the oligomers hydrolysis to monomers ~~in~~ at subcritical temperatures, even at temperatures higher than the water critical point (380 ºC), however near to 400 ºC , like in experiment 9, oligomers conversion is faster than sugars hydrolysis, in agreement with the observations reported in the literature for oligomers originating from microcrystalline cellulose (Peterson et al., 2008) (Cantero et al., 2013b). ~~Suprinsingly~~Surprisingly the time needed for complete conversion of sugars is quite ~~greater~~ larger than the pure cellulose hydrolysis at the same temperature (eg. 350ºC: 2 s vs 12 s), which could be related with the hydrolysis of fluidized biomass microparticles whiting the fractionation stream, which contain an insoluble lignin structure where C5 and C6 were contained inside of it. Also concentration of the biopolimers and the presence of other ions or substances could be linked to this atenuation.

3.2.2 Added value products (AVP) produced from the sugars hydrolisis

Thirth row of Figure 2 (b), (c) and (d) displays the added value chemicals produced from further hydrolisis ~~from~~ of cellobiose, glucose, fructose and xylose. Reaction pathway of cellulose hydrolisis involving oligomers and cellobiose as intermediaries was reported in the literature (Cantero et al., 2013a; Kabyemela et al., 1997a; Kabyemela et al., 1999; Kabyemela et al., 1997b; Lü & Saka, 2012; Sasaki et al., 2004; Sasaki et al., 2002). Xylose hydrolisis in

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near critical and supercritical water was analized by several authors (Aida T.M. et al., 2010; Sasaki M. et al., 2003). The combined reaction pathway is presented in Figure 3. Not all the products involved in this scheme was identified in the liquid chromatography. The cellulose pathway shown in Fig. 3 involves two main steps: 1st step in which the oligosaccharides are hydrolyzed to glucose and xylose; 2nd step in which glucose and xylose are involved in two possible pathways: isomerization and dehydration or retro-aldol condensation (Aida T.M. et al., 2010; Sasaki et al., 2002). Glucose can follow a reversible isomerization to produce fructose, however, the reverse reaction, is almost inhibited at the same conditions (Kabyemela et al., 1999; Kabyemela et al., 1997b). Glucose can also be transformed into 1,6 anhydroglucose and fructose can be transformed into 5-hydroxymethylfurfural through a dehydration reaction (Kimura et al., 2011). The other alternative of glucose conversion is the retro-aldol condensation reaction that produces glycolaldehyde and erythrose (Cantero et al., 2013a). Erythrose is further transformed into glycolaldehyde by the same reaction mechanism (Sasaki et al., 2002). The other important reaction of fructose is the retro-aldol condensation to produce glyceraldehyde and dihydroxyacetone. These molecules are further isomerized into pyruvaldehyde (Kabyemela et al., 1997a) that is considered as a lactic acid precursor. From the hemicellulose hydrolysis, depolymerization takes place up to xylose, and after that, xylose can be isomerized to D-xylulose, assuming that D-xylulose as an intermediate for furfural and retro-aldol products (glyceraldehyde, pyruvaldehyde, lactic acid, glycolaldehyde, dihydroxyacetone, formaldehyde) (Aida T.M. et al., 2010; Sasaki M. et al., 2003). This reaction pathway consists, a Lobry de Bruyn-Alberta van Ekenstein (LBET) a retro-aldol reaction from D-xylose and D-xylulose similar to that involving D-glucose and fructose.

In all the ~~cases the products distribution is complex~~experiments~~,~~ ~~though major~~a considerable amount of pyruvaldehyde/glycolaldehyde and lactic acid is observed. From Figure 2 (a) and (b) reactions 4 and 5 the product distribution is similar, but a little difference in the amount of pyruvaldehyde is perceived principally in the first stage of temperature of the fractionation step. Different density and Kw of water prevails at both temperatures (352 vs 383ºC, 614.7 vs 319.7 kg/m^3 and 5 10^{-6} vs 1 10^{-8}, respectively) (Akiya N. & Savage P.E., 2002), which means

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Comentado [u22]: Que entiendes?

different concentration of H^+ and OH^- (1.2 vs 22.810^{-3} M) coming from water dissociation are involved. However, under such ~~disimilar~~dissimilar conditions, the product distribution after the hydrolysis of the fractionation stream seems to be not so different. This behavior could be explained by the presence of large amounts of H^+ coming from the fractionation in addition to that produced in the water ionization, since the autohydrolysis produces acetic acid and other ions. Under such conditions, isomerization of pure cellulose to fructose is favored and dehydration reactions could be favored too (Kimura et al., 2011). In spite of this, retro aldol pathways seems to take place as well, which is evidenced by the high yields of pyruvaldehyde/glycolaldehyde and lactic acid. The reactions (4) and (7) were performed at similar temperature and pressure but involving deeper conversion in the last case (tr = 1.06 vs 11.15 s, respectively). For this one, the acetic acid amount is highly increased, mostly in the first stage of temperature of the fractionation reactor. This amount of acetic acid, exceeds the amount produced in the hemicellulose hydrolysis process. This finding could indicate that the retro aldol pathway coming from Xylose by means of Glyceraldehyde route, must contribute mainly to the acetic acid production obtained directly from lactic acid decarbonylation (Jin et al., 2005). The contribution to the acetic acid could not only be considered from the hemicellulose source, since there is also a large concentration of C6 in monomer and oligomer form in the first fraction of the inlet stream (see Figure 2 (a)), which could also contribute to the glyceraldehyde route. Figure 4 displays the pH of the output stream after the Fractionation (1) and the –Fractionation+Hydrolysis coupled process (4),(5),(7) and (8). The pH after a further hydrolysis is lower than the outcoming from the fractionation during the first stage, and after this, the pH values becomes similar, in accord to the fact that extra amounts of acetic acids are produced when a deeper hydrolysis is performed (7 and 8). Similar result is observed from reactions 5 and 8, however in this case large amount of formic acid is observed than the above mentioned (see Figure 2 (c)).

The pressure change has no great effect on the products distribution (see reactions 5 and 6). This observation means that the density as well as Kw variation, do not modified largely the selectivity between isomerization-dehydration and retro aldol pathways like it does in the pure

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cellulose hydrolysis, where isomerization of glucose to fructose is highly inhibited by decreasing density (Cantero DA 2013). The ~~major~~ highest yield of pyruvaldehyde/glycolaldehyde was obtained at this conditions~~.~~ (24.4%). A ~~Different~~ different product distribution is observed in the reaction (9), where lactic acid is the most abundant product and the acetic acid amount is depleted compared to the reactions above mentioned (see Figure 2 (d)). This finding could be explained by short time of residence of the mixture at high temperature condition in which the reactions are stopped at lactic acid stage in the glyceraldehyde route, inhibiting the acetic acid formation. This selectivity seems to take place principally during the first stage of temperature in the fractionation reactor, because after that, the production of lactic acid and pyruvaldehyde is lower. The major yield of lactic acid was found at this conditions ~~.~~(25.5%). The ~~augment~~ increase of water flow-rate in the fractionation reactor has no clear effect on the product distribution (see reactions 10 and 11 in Figure 2 (d)). In both cases the retro aldol pathways are followed equitatively in both stages of temperature producing pyruvaldehyde and lactic acid~~, however more acetic acid is formed in reaction 10 for which we have no explanation.~~.

Conclusions

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Acknowledgements

The authors acknowledge the Spanish Economy and Competitiveness Ministry, Project FracBioFuel: ENE2012-33613, Spanish Government through the Research Project CTQ2015-64892-R (MINECO/FEDER) and~~and~~ the regional government (Junta de Castilla y León), Project Reference: VA330U13 for funding. MEng. Gianluca Gallina wish to acknowledge the Spanish Economy and Competitiveness Ministry for the scholarship/predoctoral contract BES-2013-063556.

Abbreviations and symbols

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_0: Porosity of the bed, calculated at the end of the experiment, dimensionless.

m_0 initial mass of the solid in the reactor.

m_t final mass of the solid in the reactor.

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.

MwΣC(i) molecular weight of the sum of the atoms of carbon in component i, 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)

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.

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Comentado [u23]: •Falta lista tablas.
•Se podría poner otra tabla con los rendimientos de todos los compuestos después del fracciónamento, después de la primera temperatura, y después de la segunda.
•Otra tabla con los rendimientos de los compuestos después de la hydrolisis.

List of Figures

Figure 1. Experimental setup coupling Fractionation-Hydrolysis reactors.
D.1, D.2: Type II Millipore water deposits, P.1: American Lewa EK6 2KN High pressure piston pump. P.2: Milton Roy XT membrane pump, V.1, V.2: Parker check valve. H.1: Electric low temperature heater, 100 cm of 1/8 in SS316 piping and 2 kW resistor. H.2: 1800 cm of 1/8 in SS316 piping and, high temperature heater and 5 kW resistor. R.1: Fractionation reactor, 40 cm length, ½ in O.D. SS316 piping. V.2: Parker relieve valve. R.2: Sudden Expansion Micro-Reactor (SEMR) built with ¼ in O.D. SS316 tubing. Two reactore sizes were used 11 cm and 100 cm of length. V.3: Parker relief valve. V.4: high temperature valve Autoclave Engineers 30VRMM4812, IE: 200 cm of concentric tube heat exchanger ½ in- ¼ in. V5: Three way Parker valve, D.3: Falcon® flasks. D.4: 25 L polyethylene products deposit.

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

(a) Results from the fractionation without ~~supercritical~~ further hydrolysis for different water flow-rates in the fractionation line. The ~~F~~first line of graphs ~~corresponds~~ represent to the percentage of soluble sugars ~~liquefied~~ identified by total organic carbon (TOC) and HPLC techniques. Second row of graphs in Figure 2 shows the amount of carbohydrates

Comentado [u24]: Especificar los caudales de supercrítico y las temperaturas del fraccionamento.

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 fractionation reactor.

(b) Products distribution ~~around~~ at 380ºC

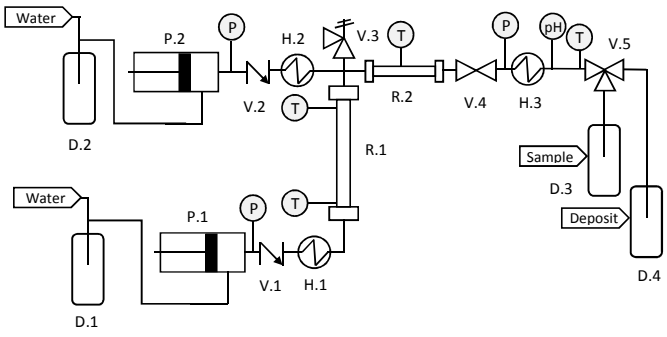
(c) Product distribution ~~around~~ at 350ºC

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

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

Figure 4. pH vs time comparison of the reactions at low (4 and 5) and high conversions (7 and 8) at sub and supercritical conditions of water.

Figure 1.



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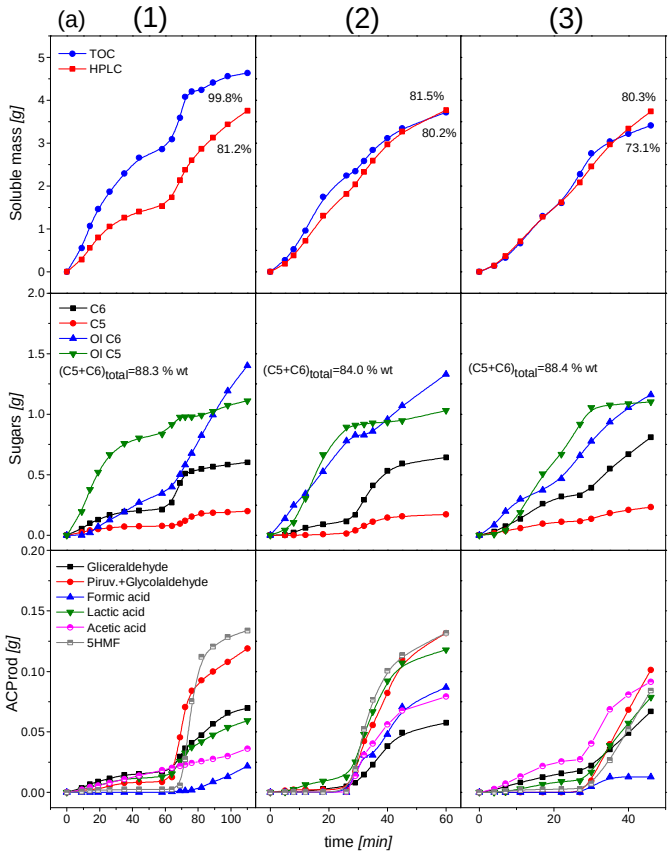
•Yo pondría las figuras en orden de temperatura (a 350, b 380, c 400 ºC).
•Especificar los caudales de fraccionamento
•Una línea vertical cuando hay el cambio de temperatura.

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
OI C6
OI 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
ACProd [g]
time [min]

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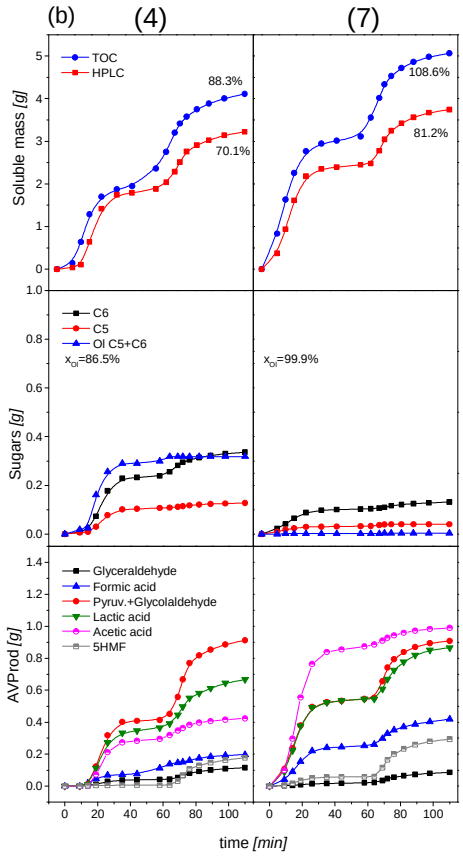

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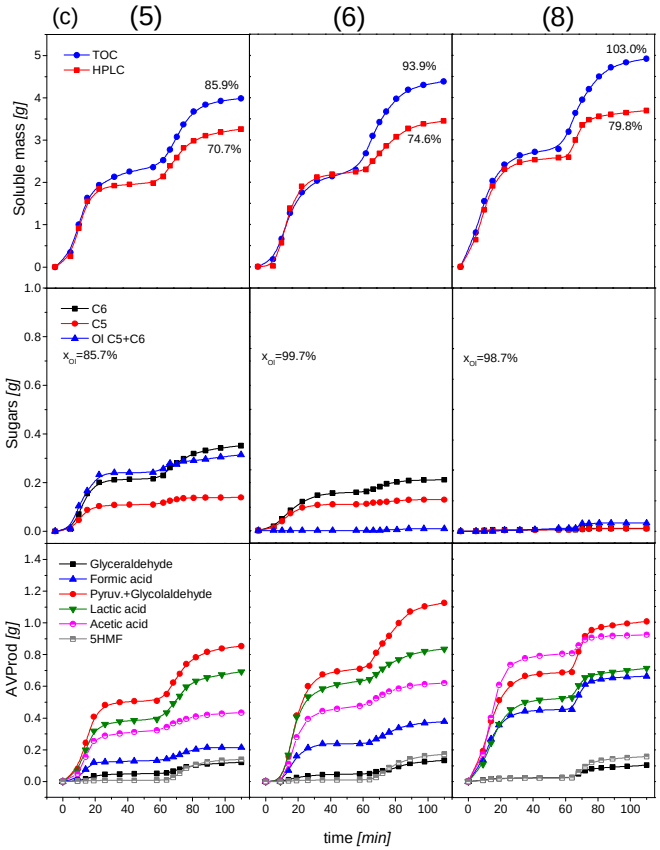

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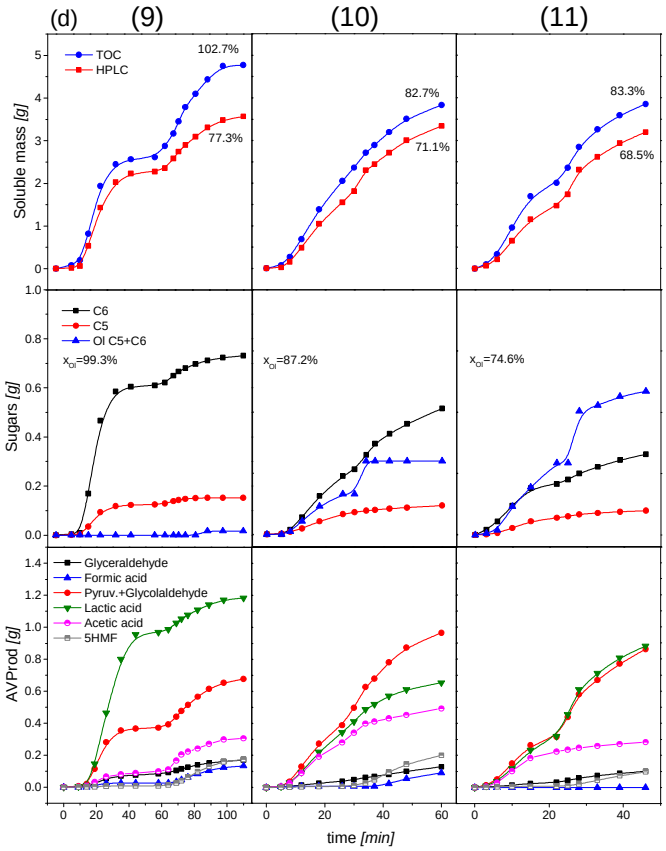

(d)
(9)
(10)
(11)
TOC
HPLC
102.7%
77.3%
82.7%
71.1%
83.3%
68.5%
Soluble mass [g]
C6
C5
OI C5+C6
x_{OI}=99.3%
x_{OI}=87.2%
x_{OI}=74.6%
Sugars [g]
Glyceraldehyde
Formic acid
Pyruv.+Glycolaldehyde
Lactic acid
Acetic acid
5HMF
AVProd [g]
time [min]

Figure 3.

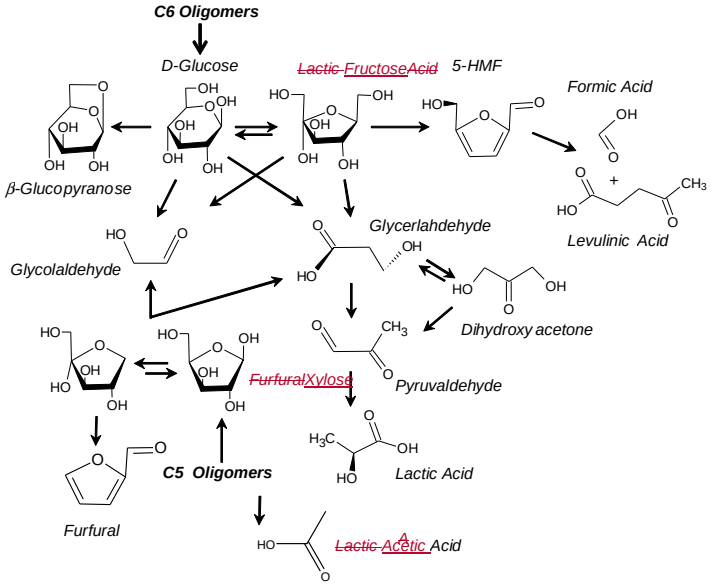
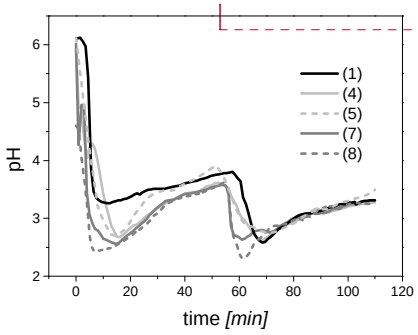


Figure 4.



Comentado [u26]: Poner misma formatacion en todas las graficas

Table 1.

Experiment	T [ºC]	P [MPa]	t_r [s]	MB_{TOC}[%]
4	383.7 ± 5.1	245.7 ± 4.6	1.06	92.2
5	352.5 ± 4.4	241.3 ± 3.7	2.10	89.3
6	355.9 ± 5.7	161.8 ± 1.1	8.31	97.3
7	377.2 ± 3.5	251.9 ± 5.9	11.15	105.9
8	349.9 ± 2.4	239.6 ± 4.2	12.50	103.1
9	396.1 ± 3.6	249.1 ± 5.1	0.23	103.6
10	401.2 ± 2.8	252.2 ± 3.9	0.24	93.0
11	398.3 ± 3.0	259.9 ± 3.4	0.24	91.2

Comentado [u27]: Juntar longitud reactor y caudales (sub y supercr)