Hydrolysis of Cellulose in Supercritical Water: Reagent Concentration as Selective Factor

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Comentado [Lola1]: Tienes un Segundo apellido muy fuerte y muy sonoro. Por que no pones los dos con un guión Martínez-Fajardo. Si no te gusta la idea, nada

Abstract

In this study, the influence of reagent concentration over the hydrolysis reactions of cellulose in a hydrothermal media was analyzed. The hydrolysis process was carried out in a continuous facility at 400 ºC and 25 MPa with reaction times between 0.07 and 4 s. An increment in the reaction time was needed for obtaining total cellulose conversion when the starting biomass~~es~~ were highly concentrated. High reaction times also favored the production of derived products instead of sugars. On the other hand, the experimentation with low concentrations and low reaction times allowed high yields of sugars. The best result for sugars production (79 % w/w) was obtained working with a cellulose concentration of 5 % w/w and 0.07 s of reaction time. The best result for glycolaldehyde production (80 % w/w) was obtained for a biomass concentration of 20 % w/w and 1 s of reaction time.

Keywords: Biorefinery · Biofuels · Mass transfer · Solubility

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1. Introduction

Biomass is an abundant and renewable resource of carbon which has the potential to produce energy, chemicals and fuels for the future sustainable industries (Aida et al., 2007a). Also, cellulosic materials including agricultural residues and herbaceous and woody crops are sufficiently abundant to provide a major resource for making commodity products (Wyman et al., 2005). Biobased industries, based on the use of renewable materials and energy, are still in development to success in supporting a decentralized production that can be an alternative to the centralized petrochemical production plants. To achieve this challenge it is necessary (a) to reduce the number of process steps by searching opportunities among new raw materials and by using clean solvents as water and carbon dioxide; (b) to reduce equipment cost by developing compact apparatus with short operation times: changing the reaction time from minutes to milliseconds allows reactor volume reduction from m^3 to cm^3 (Arai et al., 2009; Cantero et al., 2013b).

Biomass is mainly composed by three polymers: cellulose, hemicellulose and lignin (Zhang et al., 2010) being cellulose the major component of plant biomass, representing in general the 50 % in mass (Bobleter, 1994). Cellulose is the most abundant natural polymer on earth and it consists of β 1-4 glucose-glucose linkages in linear chains (Kim et al., 2006). Theoretically it is possible to obtain all the chemical materials produced by petroleum from biomass. Biomass can be converted to useful products (chemical products, fuels or energy) by two main processes: thermo-chemical processes and bio-chemical processes (Goyal et al., 2008). Generally thermo-chemical conversion processes have

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Las reacciuones en ASC proporcionan un medio selectivo para procesar la biomasa (quizá 10-15 líneas)
Pero los experimentos hechos hasta ahora se hn obtenido efluentes diluidos/se ha prestado poca atención a la influencia de la concentración (menciona artículos de este tipo donde se usen alimentaciones más concentradas o se estudie el efecto de la concentración. Puedes hablar incluso del tipo de bombas necesarias para vehicularlas, u mencioar reactores tipo extrusores (TE MANDO REFERENCIA)
Así que en este estudio se pretente….
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Cita el review de Danilo

higher efficiencies than bio-chemical processes in terms of the lower reaction time required (few seconds or minutes for thermo-chemical processes instead of days for bio-chemical processes) and the higher ability to decompose most of the organic compounds. Different thermo-chemical conversion processes include combustion, gasification, hydrothermal treatment/liquefaction and pyrolysis. Bio-chemical conversion can be carried out using processes as fermentation or anaerobic digestion (McKendry, 2002).

The main components of biomass (cellulose, hemicellulose and lignin) could be separated and then used as starting materials to produce interesting compounds via hydrolysis (Sasaki et al., 2003a). Glucose would be the main product from cellulose hydrolysis, hemicellulose would release its component sugars (xylose, arabinose, galactose and mannose) and lignin would produce ~~poly~~phenolic compounds (Zhang et al., 2010). Once obtained these derived compounds, conversion reactions can be carried out to obtain bio-fuels and chemical products. Choice of conversion process depends on the type and quantity of biomass feedstock, the desired product, environmental standards, economic conditions, etc. (Goyal et al., 2008). Taking into account the wide range of possibilities for biomass refineries, lignocellulosic biomass is considered a promising source to replace fossil fuels as feedstock for the sustainable production of various chemicals, materials and fuels.

The hydrolysis of cellulose to obtain reducing sugars such as glucose is essential for using biomass in chemical processes, since the reducing sugars can be converted then into a wide range of important chemicals (Guo et al., 2012). Therefore, selective hydrolysis of cellulose into glucose is a key process for the effective use of biomass (Onda et al., 2009; Tollefson, 2008).

In the recent years supercritical water has attracted much attention because of its suitability as a non-toxic, environmentally benign and inexpensive media for chemical reactions (Kumar et al., 2010) since water at around the critical point (T_c = 374.2 ºC, P_c = 22.1 MPa and ρ_c = 0.323 g/cm^3) shows properties that are very different from those of ambient liquid water (Sasaki et al., 2003b). The main variations in water properties are: (1) around the critical point the dielectric constant is decreased by increasing temperature, enhancing the solubility of small organic compounds (2) the ionic product (Kw) above the critical point decreases drastically (from 10^{-14} to 10^{-25}) promoting in that way the free-radical reaction mechanisms instead of ionic reaction mechanisms (3) moreover, increasing density favors the hydrolysis pathway working as a control factor for the reaction selectivity (Akiya & Savage, 2002). These changes in the water properties (density, dielectric constant and Kw) are plotted along temperature at a pressure of 25 MPa in Figure S.1 in the Supporting Information (SI).

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Supercritical water technology ~~provides a novel method to quickly convert~~allows fast conversion of cellulose into sugars~~ and to conduct tunable reaction~~being a tunable reaction media for the synthesis ~~of specialty~~of selected chemicals from biomass (Matsumura et al., 2006). In addition~~Also~~, from the point of view of decentralized chemical processes, supercritical water allows fast reaction rates, high selectivities and high yield conversions of many biomass feedstocks and allows chemical transformations to occur with compact devices (Arai et al., 2009).

The conversion of cellulose and lignocellulosic biomass to valuable chemical intermediates using supercritical water have been previously reported, using different kind of reactors. The hydrolysis in batch-typereactors are usually carried out at temperatures between 150 ºC and 300 ºC with long reaction times (in the order of minutes). Therefore, the produced glucose by hydrolysis can be easily decomposed, providing low yields of glucose between 23–33% w/w (Ehara & Saka, 2002; Zhao et al., 2009b) with a selectivity around 60 % w/w to sugars working with concentrations lower than 5 % w/w of cellulose (Zhao et al., 2009a). The flow-type system makes it possible to shorten the heating, treating and cooling times and therefore reduces the degradation of sugar products. In this way, higher glucose yields around 30-40% w/w could be obtained in supercritical water or combining supercritical and subcritical water treatment with initial concentrations between 4 and 10% w/w of cellulose (Ehara & Saka, 2005; Sasaki et al., 2003b). Then, the challenging step in the conversion of cellulose is the production of glucose with high selectivity and yield. Recently, our research group could improve the hydrolysis of cellulose suspensions (7.5 % w/w) in supercritical water by using a continuous micro-reactor, giving as a result a total conversion of cellulose in 0.02 s of reaction time and yielding a sugar production of 98% w/w (Cantero et al., 2013b). A comparison between the yields obtained working with the aforementioned technologies is shown in Table S.1, in the SI.

Although the thermo-chemical hydrolysis technologies have been intensively improved in the last years, some issues have to be developed. The concentration of sugars in the product stream is an important factor to take into account. A concentrated product will facilitate its~~the~~ handling and shipping~~ of it~~. Two methods for reducing the water content in the product stream are proposed: (a) increasing the biomass concentration before the reaction or (b) taking out water after the reaction.

Then, in this work two ways to increase the concentration of the products obtained after cellulose hydrolysis in supercritical water were studied. Feeding cellulose concentrations of 5, 10, 15 and 20 % w/w in the biomass stream were tested with different reaction times in the continuous micro-reactor aforementioned. Also a modification on the experimental set-up was included to maximize the concentration of the products by using a flash separator.

2. Materials and Methods

2.1. Materials

Micro-crystalline cellulose (99%) used in the experiments was purchased from VWR chemical company. Distilled water was used to carry out the experiments.

The standards used in High Performance Liquid Chromatography (HPLC) analysis were: cellobiose (≥ 98%), glucose (≥ 99%), fructose (≥ 99%), erythrose (≥ 75%), glyceraldehyde (≥ 95%), glycolaldehyde dimer (≥ 99%) and 5-hydroxymethylfurfural (≥ 99%) purchased from Sigma.

Sulfuric acid (≥ 96%) and calcium carbonate (≥ 99%) supplied by Sigma were used as reagents in the determination of structural carbohydrates. Milli-Q water was also used in this procedure.

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2.2. Analysis

The carbon content in the liquid product was determined by total organic carbon (TOC) analysis with Shimadzu TOC-VCSH equipment. The composition of the liquid product was determined by using HPLC analysis. The column used for the separation of the compounds was Shodex SH-1011 at 50 ºC, using sulfuric acid (0.01 N) as mobile phase with a flow rate of 0.8 mL/min. A Waters IR detector 2414 was used to identify the sugars and their derivatives and Waters UV-Vis detector was used to determine the 5-hydroxymethylfurfural (5-HMF) concentration at a wavelength of 254 nm.

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The solid fraction (cellulose when X < 1) in the final product was separated by centrifugation. Then, it was dried at 60 ºC for 24 h and finally it was weighted. That solid fraction represented the concentration of cellulose at the outlet of the reactor. Then, the cellulose conversion was determined by Equation 1, where *'X'* is the cellulose conversion, *'W_0'* is the concentration of cellulose at the inlet of the reactor (g cellulose/g total) and *'W'* is the outlet concentration of cellulose also as g cellulose/g total.

$$X = \frac{W_0 - W}{W_0} \qquad (1)$$

Código de campo cambiado

The soluble oligosaccharides concentration in the liquid samples was determined by acid hydrolysis to glucose and HPLC determination following a Laboratory Analytical Procedure (LAP) from NREL (Sluiter et al., 2010) as follows. To 10 mL of filtered liquid aliquots 4 mL of 96 % H_2SO_4 were added. The sample was maintained in an oven at 30 ºC during 60 min. Then 86 mL of Milli-Q water were added and the sample was incubated at

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121 ºC for 60 min. Calcium carbonate was added to 20 mL of this sample to neutralize the pH and finally the supernatant was filtered and analyzed with HPLC.

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The yield of the main compounds (C-6 sugars, glycolaldehyde, 5-HMF, erythrose and glyceraldehyde) was determined by Equation 2, where *‘Y_s’* is the yield of compound *‘s’*, *‘C_s’* is the concentration of *‘s’* in the liquid product determined by HPLC in carbon basis and *‘M_t’* is the total mass of carbon in the product (liquid and solid), calculated as shown in Equation 3.

$$Y_s = \frac{C_s}{M_t} \qquad (2)$$

Código de campo cambiado

$$M_t = \frac{M_{TOC}}{X} \qquad (3)$$

Código de campo cambiado

In Equation 3, *‘M_t’* is the total mass of carbon in ppm, *‘M_{TOC}’* is the mass of carbon in the liquid, measured with TOC in ppm and *‘X’* is the conversion of cellulose, calculated with Equation 1.

2.3. Experimental set-up

The experiments were performed in ~~a~~ the continuous~~continuous~~ pilot plant of the FASTSUGARS process designed to operate at temperatures up to 400 ºC and pressures up to 30 MPa~~. Figure S.2 in the SI represents the pilot plant designed and built in a~~presented in previous work of our research group (Cantero et al., 2013a), and modified for this work as shown in figure 1. The process can be divided ~~divided in the different~~in four stages stages ~~of the process~~:~~.~~

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i. ~~The first step is the pressurization of the feed streams~~1) Pressurization. To do so, positive displacement pumps were used to continuously pump water and the cellulose suspension (5, 10, 15 or 20 % w/w) up to the operating pressure (25 MPa) at room temperature. It is important to ~~notice~~ note that cellulose is not soluble in water and because of this, particular attention should be paid to biomass or pure cellulose pumping, avoiding clogging problems. Supercritical water was supplied up to a maximum flow rate of 5 kg/h and the cellulose suspension was fed to a maximum flow rate of 3 kg/h.

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~~i. In this set of experiments, cellulose concentration at the inlet of the reactor varied from 1 to 7 % w/w due to the dilution in the mixing point.~~

~~The third and the most important stage is the reaction~~3) Reaction. Once desired temperature was reached, the reaction time of biomass at reaction conditions became the critical factors to control the reaction, so, the selectivity of the FASTSUGARS process~~.~~ ~~Supercritical water hydrolysis of cellulose is fast, so high reaction times would promote a product with high rate of degradation products~~ (Cantero et al., 2013a). ~~In this experimental set up the reaction time was changed~~is achieved by modifying the flows and the reactor volume, by the instantaneous heating and by ~~. As mentioned above, the reaction started when the suspension and supercritical water met in the mixing point. The other key point of the reactor is~~ instantaneously ~~the~~ stopping ~~of~~ the reactions~~.~~ ~~This was achieved instantaneously~~ by sudden decompression ~~in~~ using a high temperature valve high temperature valve Autoclave Engineers 30VRMM4812 . ~~A scheme of the reaction section and its temperature profile is shown in Figure S.3 in the SI.~~

~~. A high temperature valve Autoclave Engineers 30VRMM4812 was used to carry out the sudden decompression. With this method it was possible to suddenly decrease the temperature of the product from 400 ºC to 150 ºC, as it can be seen in the temperature~~

~~profile shown in Figure S.3 in the SI. After the valve stage, two heat exchangers were used~~ in the reactor. The volume of the reactor, 'V', was calculated using the dimensions of the reactor ('D', 'L') and the flow, 'F_v', was calculated using the density of the reaction medium at reactor and at room conditions, considering the fluid as pure water. Since the reactor was thermally isolated and the heating and cooling methods are instantaneous it can be considered that the temperature along it was constant. Therefore, the density can be considered constant in the reactor and t_R (reaction time) can be calculated by Equation 4.

$$t_R = \frac{V}{F_v} = \frac{\pi D^2}{4} L \frac{\rho_h}{F_{v,0}\rho_0} \tag{4}$$

In Equation 4, 'ρ_h' and 'ρ_0' represents the density at the reaction conditions and ambient conditions, respectively. '$F_{v,0}$' is the flow measured at ambient conditions. Using the ratio ρ_h / ρ_0, $F_{v,0}$ is transformed into F_v.

4) Concentration. ~~As the aim in this work was to evaluate the effect of the concentration over the final products, another way to get high concentration of the products was to concentrate the product after the reaction. The cooling method used in this facility is the sudden decompression. This step represents a flash operation after which two phases are produced, vapor and liquid phases. So, a flash chamber separator was installed a~~After the reactor and the depressurization valve, the previous experimental facility was modified to include a flash chamber separator that allows ~~in the experimental set-up, allowing~~ the separation of the products into two phases: a vapor phase mainly composed of water; and a liquid phase with the concentrated product. The liquid product would be a mixture of hydrolysis products with lower content of water compared to the product obtained without using the flash separator. ~~This facility is shown in Figure 1.~~

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Código de campo cambiado

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~~3.~~

~~4.1.~~3.1. ~~Operation without Flash Chamber~~Influence fo feed concentration

The influence of cellulose concentration over the product yield and composition was analyzed at the best experimental conditions obtained in a previous work (400 ºC and 25 MPa) (Cantero et al., 2013b). To do so, a set of experiments ~~was carried out~~ at different feed concentrations and reactions times was carried out. The concentration at the inlet of the reactor was varied by changing the concentration of cellulose in the starting biomass suspension. The biomass concentration was varied between 5 % and 20 % w/w obtaining in this way cellulose concentration at the reactor inlet between 1 and 7 % w/w at the entrance fo the reactor after mixing the suspension with the supercritical water stream. ~~In this case, the facility with a bypass to the flash chamber was used.~~ The experimental conditions and cellulose conversion after hydrolysis for these experiments are presented in Table 1. In these experiments, the flash chamber was bypassed.

~~The concentration at the inlet of the reactor was varied by changing the concentration of cellulose in the starting biomass suspension. The biomass concentration was varied between 5 % and 20 % w/w obtaining in this way cellulose concentration at the reactor inlet between 1 and 7 % w/w.~~ The main hydrolysis reaction pathway for cellulose in supercritical water is shown in Figure 2 (Cantero et al., 2013a). Cellulose is firstly hydrolyzed into oligosaccharides and then into glucose. Once glucose is produced, it can be converted into dehydrated (5-HMF) or retro-aldol condensation products (glycolaldehyde and glyceraldehyde).

Comentado [Lola19]: Best experimental conditions para qué en concreto

Comentado [Lola20]: Poner también en la tabla la concentración real a la entrada del reactor que es la que realmente cuenta

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~~The tendency of the experiments shown in Table 1 is easier to follow by plotting~~ initical concentrations is shown in Figure 3. It can be seen that when the cellulose concentration is higher, the residence time needed for a complete conversion increases from XX at % to XX s at %. ~~the increment in the~~Higher cellulose concentrations for a constant resulted in lower conversion rates. Also, while increasing the reaction time, the conversion was increased in all cases. These two trends can be explained by assuming that for higher concentrations it was necessary higher reaction time to obtain the same conversion than those with lower concentration. This fact can be also evaluated in terms of kinetics. A first order kinetic was assumed, represented by Equation 5 where 'C_0' is the inlet concentration, 'C' is the final concentration calculated by Equation 6 where 'X' is the conversion of cellulose. 'k' is the kinetic constant and 't_R' is the reaction time. Then, plotting the logarithm against the reaction time, a linear dependence was found. Only data from experiments with 15 % and 20 % w/w of cellulose were used in this plot. Data for 5 % w/w of cellulose were taken from a previous work (Cantero et al., 2013b). As it can be seen in Figure 4, the slope decreased when increasing the concentration. This confirms that for highly concentrated suspensions, the conversion rate was lower and therefore the kinetic constant (slope) was lower. This can be explained considering that the mass transfer resistance increased when the cellulose concentration was higher. So, as previous studies reported, it can be assumed that the mass transfer rate coefficient was strongly dependent on reagent concentration (Rearden et al., 1998) and mass transfer limited overall conversion yields in systems with high-solids loadings (Griggs et al., 2010).

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Comentado [Lola24]: Yo creo que puedes empezar diciendo que en trabajaos nuestros previos y de otros autores se ha considerado que la celulosa reacciona en la superficie obteniéndose una expresión cinética independiente de la concentración, y que estos resultados contradicen esa hipótesis y mostrar las ecuaciones

Comentado [Lola25]: En que expresas la concentración?

Comentado [Lola26]: Pon la concentración a la entrada del reactor que es la que le importa a la cinética

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$$\ln\left(\frac{C}{C_0}\right) = k\cdot t_R \tag{5}$$

Comentado [Lola28]: No sé si entiendo lo que has hecho con las cinéticas. Estás partiendo de la que usaba Danilo o estás proponiendo una cinética dependiente de la concentración

Código de campo cambiado

$$C = C_{in}\cdot(1-X) \tag{6}$$

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Código de campo cambiado

Using Equation 3, the TOC values (*'M_{TOC}'*) were transformed into total mass (*'M_t'*) and HPLC results for each compound were converted into carbon basis concentrations (*'C_s'*), multiplying each value by a carbon factor (C-6 sugars: 0.41; Glycolaldehyde: 0.40; 5-HMF: 0.57; Erythrose and glyceraldehyde: 0.40). Once these transformations were done, the yield of each compound was obtained using Equation 2. The yields of each component are presented in Table S.2 in the SI.

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The C-6 sugars and glycolaldehyde yields are shown in Figures 5 and 6, respectively. The yield of derived products such as 5-HMF, erythrose and glyceraldehyde were plotted in Figures S.4, S.5 and S.6, respectively, in the SI. Bars without borderline represent the experiments performed with a bypass to the flash chamber.

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For C-6 sugars (glucose and soluble oligosaccharides up to six units of glucose) it can be seen in Figure 5 that the maximum yield (66 % w/w) was obtained at the lowest concentration (5 % w/w) and lowest reaction time (0.12 s). This dependence with the reaction time was something expected, because as reported in a previous study (Cantero et al., 2013b), just 0.02 s were necessary to obtain high yield in sugars recovery (98 % w/w) when hydrolyzing cellulose in supercritical water. Then, the increment in the reaction time favored the degradation reactions by consuming the produced sugars. So C-6 sugars yield decreased while increasing reaction time. This trend was the same for all the concentrations evaluated, except in the case of 20 % w/w. In that case it can be seen that by increasing the reaction time (from 0.12 to 0.64 s), the sugars production was increased. This can be explained if it is considered that for a high concentration of cellulose such as 20%, reaction times lower than 0.7 s were not enough to achieve complete conversion of cellulose (see Figure 3). When the hydrolysis was incomplete (X < 1) it can be assumed that an increase in the reaction time, allows higher hydrolysis rates and therefore more sugars are produced.

In the case of glycolaldehyde yield it can be noticed that two trends were observed (see Figure 6). Working with a constant reaction time, when increasing the concentration of cellulose, the yield of glycolaldehyde decreased (that trend was especially important in reaction times between 0.12 and 0.32). As mentioned above, for these low reaction times cellulose conversion for high concentrations ~~was~~ were incomplete and therefore the production of glucose was relatively low. Then, taking into account that glycolaldehyde is the main product of glucose retro-aldol condensation (Aida et al., 2007a), low production of glucose implied low glycolaldehyde yields. On the other hand, by increasing the reaction time, for the full range of concentrations, the yield increased due to the sugars were derived into other products mainly glycolaldehyde, increasing in that way glycolaldehyde production. The maximum yield for glycolaldehyde in this section (34 % w/w) was achieved at the higher reaction time and 10 % w/w of cellulose. The yield of glycolaldehyde was not so high. It should be taken into account that the maximum yield was obtained in a sample with more than 50 % w/w of sugars. This means that glycolaldehyde yield will be enhanced increasing the reaction time.

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5-Hydroxymethylfurfural is a dehydration product of fructose and it is an undesired compound in the sugars production if a microorganism post-processing of the product is requiered (Rogalinski et al., 2008). The production of 5-HMF was lower than 1 % w/w in all the experiments, being the maximum amount (1 % w/w) achieved at the highest concentration and highest reaction time. The behavior observed for 5-HMF yield was almost the same than for glycolaldehyde, since at a constant range of reaction times, while increasing the concentration, the yield decreased (see Figure S.4 in the SI). On the other hand, by increasing the reaction time, the yield of 5-HMF increased. The degradation reactions were favored consuming the produced sugars, increasing in this way the yield of degradation product such as 5-HMF.

The behavior of other compounds as erythrose and glyceraldehyde (see Figures S.5 and S.6, respectively in the SI) showed a strong dependence on reaction time. For low reaction times (lower than 0.2 s) only erythrose was yielded whereas glyceraldehyde was produced for the rest of experiments. This can be explained by following the reaction pathway shown in Figure 2. It can be seen that glucose could be converted into fructose or erythrose plus glycolaldehyde by isomerization or retro-aldol condensation, respectively (Sasaki et al., 2002). The fructose would also produce glyceraldehyde via retro-aldol condensation (Aida et al., 2007a). As it was demonstrated before, the production of fructose was favored by increasing the reaction time (Aida et al., 2007b). So when working with low reaction times the production of fructose was low and as a consequence, the yield of glyceraldehyde was negligible. Furthermore, when increasing the reaction time, the erythrose produced was decomposed into glycolaldehyde via retro-aldol condensation

(Sasaki et al., 2002), so the yield of erythrose for high reaction times was also negligible. So, while increasing the reaction time for all the range of concentrations, the yield of erythrose decreased and the production of glyceraldehyde increased. On the other hand, working with a constant reaction time, the yield of erythrose decreased when increasing the concentration of cellulose. In the case of glyceraldehyde, no clear tendency was shown for the different concentrations. Maximum yield of erythrose (5 % w/w) was achieved for the lowest concentration and lowest reaction time. For glyceraldehyde the maximum (6 % w/w) was produced at the highest concentration and highest reaction time.

Another experiment was performed for the concentration of 20 % w/w of cellulose, with a reaction time of 1 s in order to obtain total conversion. These results were also plotted in Figures 3, 5 and 6, represented by a dashed bar. Following the reaction pathway shown in Figure 2, it can be seen that the first step in cellulose hydrolysis was the production of oligosaccharides, cellobiose and glucose (C-6 sugars). Then as a second step, the glucose turned into glycolaldehyde and other products. ~~So~~Thus, when the hydrolysis of cellulose was incomplete (X < 1), the first sign was the low yield of glucose and as a consequence, the low yield of glycolaldehyde (experiments 4 and 8). Conversion came closer to 1 when the reaction time was increased (experiment 12) and as a result the conversion of cellulose into glucose was enhanced because the hydrolysis rate was higher. When total conversion was achieved (X = 1) all the glucose produced was rapidly degraded into other products, providing at the same time low yields for glucose and high yields for degradation products (experiment 13). The results of this last experiment were presented in Table 1 and S.2 in the SI. It can be seen that it was achieved the minimum yield of C-6

Comentado [Lola33]: Yo pondría siempre las concentraciones en el reactor, y no en la bomba sugars (1 % w/w) and also the maximum yields for the rest of the products evaluated (80 % w/w glycolaldehyde, 4.5 % w/w 5-HMF and 10 % w/w of glyceraldehyde).

Comentado [Lola34]: Se podría esto reproducer con el modelo de alguna manera? Quedaría mucho mejor

~~4.2.~~3.2. Operation with Flash Chamber

Once it was evaluated the influence of the inlet cellulose concentration and the reaction time over the product yield, it was found that the maximum yield for C-6 sugars was obtained at the lowest concentration and lowest reaction time (5 % w/w cellulose, 0.13 s). To optimize this result another experiment was carried out, using a micro-reactor to maximize the amount of sugars that can be obtained with a lower reaction time (0.07 s) and using the lowest concentration of cellulose at the inlet (5 % w/w). The same conditions of pressure and temperature were used (25 MPa, 400 ºC) and total conversion was achieved (X = 1).

Comentado [Lola35]: Y si sustituyes este párrafo por lo que te pongo a continuación para que sea más corto? Yo creo que a veces es importante no enrollarse con las explicaciones e ir al grano

To study the performance of the process when using a flash chamber for concentrating the products in the final effluent conditions of XXXX has been selected to maximize sugar production

This experiment (numbered as 14 in table XX) was performed using the facility shown in Figure 1, following two steps: (A) first, ~~hydrolysis with~~using the bypass to the flash chamber~~ was carried out with the selection valves closed. This part helped to identify the effect of the lowest reaction time over the yield~~; (B) ~~then, opening the selection valves the product stream from part A went through the~~making the the product stream passed through the flash chamber ~~and~~ where it was separated into two streams, allowing to take samples of the liquid and vapor phases. In that way the efficiency of using a flash chamber as a way to concentrate the product was evaluated. Results obtained in this experiment were presented in Tables 2 and S.2 in the SI.

Comentado [Lola36]: Poner la P, t de operación del flash? Podría ser interesante hacer experimentos a diferentes T y P del flash

Comentado [Lola37]: Que hay en esta tabla?

The yields obtained for each component were plotted together with the previous results in Figures 3, 5 and 6 and also in Figures S.4, S.5 and S.6 in the SI. In Figure 5 it can be seen that the yield of C-6 sugars obtained by using the lowest reaction time was the biggest one. In Section 3.1 it was discussed that lower reaction times, produced lower glucose degradation and thus higher yield of sugars. In this case, experiment 14 was performed with a reaction time of 0.07 s, lower than those used in the previous experiments. So as it was expected when decreasing the reaction time, the yield of sugars increased. Therefore, the reaction time worked as a key factor for the reaction selectivity as it was reported in previous studies (Cantero et al., 2013b). In experiment 14 the highest yield of sugars was achieved, giving as a result a yield of 79 % w/w.

With this first part of the experiment (part A) it was possible to maximize the yield of sugars just by changing the reaction time. Once the cellulose was hydrolyzed, the product went through the flash (part B) and it was separated into two phases (liquid, B-L and vapor, B-V), being the~~. All the results obtained are presented in Table 2, where it can be also seen than the~~ separation ratio (L:V) ~~was~~ approximately 2:1. ~~Indeed, the separation was taking place in the flash chamber in terms of flow distribution.~~ In Figure S.7 in the SI, the results were plotted in ppm in order to compare the effect of the separation over the final concentration of product. ~~As it can be seen in Table 2, t~~The flash allowed to increase the concentration of sugars from 10000 ppm to 15000 ppm in the liquid phase only by setting a flash separation after the reaction. In the case of derived products it can be observed that the concentrations of glycolaldehyde and erythrose remained almost the same. The vapor phase was mainly composed by water and that was the reason why the

Comentado [Lola38]: Yo esto lo pondría en el otro apartado son distinguir unos experimentos de otros, y en este partado me centraría en el aumento de la concentración de salida con el flash

Comentado [Lola39]: Yo quitaría esta frase

Comentado [Lola40]: Pero debía de ser bastante más altas y tampoco se ve que hayan pasado a la fase vapor. La explicación que pones después no e dice nada. Lo que quieres decir es que como están muy diluidos los productos el análisis es poco preciso? Igual deberías poner la incertidumbre de los datos
Igual también deberías facilitar datos de voilatilidad de los componentes para explicar por ejemplo si es esperable que el glicoaldehido se encuentre en la fase vapor por evaporación o sólo por arrastre, porque su concentración es relativamente alta en comparación con los otros productos

concentration of hydrolysis products was so low, because just a ~~few~~ little amount of organic compounds went diluted in the vapor phase. So, the flash chamber proved to be an effective way to increase the concentration of sugars in the final product. The use of the flash chamber in this case gave as a result a liquid stream rich in valuable products such as sugars or glycolaldehyde with lower concentration of 5-HMF. On the other hand, the vapor stream was mainly composed by water and 10 times less carbon content regarding the initial sample (5165 ppm of carbon in part A versus 593 ppm in the vapor phase).

Comentado [Lola41]: Poner si es por arrastre o por possible evaporación

~~5.~~4. Conclusions

Cellulose hydrolysis in supercritical water was studied experimentally for evaluating the effect of biomass concentration ~~over~~ on the reactions. It was necessary to increase the reaction time to get total cellulose conversion when highly concentrated suspensions were used. This also favors the conversion of glucose into its derived products. So, cellulose (and biomass) can be selectively (80%) hydrolyzed in supercritical water to sugars with low reaction times and using low concentrations of biomass. If the desired products are glucose derivatives, the biomass concentration did not affect the product yield.

To increase the concentration of the products it was proposed the addition of a flash separation, which allows a concentration of 50%.

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Con formato: No revisar la ortografía ni la gramática

Con formato: No revisar la ortografía ni la gramática

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Tables and Figures Caption

Table 1. Experimental conditions (at 400 ºC, 25 MPa) and cellulose conversion for experiments without using the flash.

Table 2. TOC and HPLC results for liquid products operating with (B) or without (A) flash chamber (Fig. 1).

Figure 1. Experimental set up with flash chamber and heat integration.

Figure 2. Reaction pathway for cellulose hydrolysis.

Figure 3. Conversion depending on reaction time and cellulose concentration.

Figure 4. Kinetic study for 5, 15 and 20 % w/w of cellulose using a first order kinetic.

Figure 5. C-6 sugars yield depending on reaction time and cellulose concentration. Blue arrow represents concentration trend and orange arrow represents reaction time trend.

Figure 6. Glycolaldehyde yield depending on reaction time and cellulose concentration.

Tables and Figures

Table 1.

Exp	Concentration (% w/w)	Reaction time, t_R (s)	Conversion, X (Eq. 1)
1	4.8	0.13	1.00
2	10.0	0.12	1.00
3	15.0	0.13	0.86
4	20.0	0.15	0.47
5	5.0	0.19	1.00
6	10.0	0.31	1.00
7	15.0	0.17	0.82
8	20.0	0.24	0.52
9	5.0	0.64	1.00
10	10.0	0.64	1.00
11	15.0	0.40	1.00
12	20.0	0.64	0.97
13	20.0	1.00	1.00
14A	5.0	0.07	1.00

Table 2.

				HPLC (ppm)				
Exp	**t_R (s)**	**Flow rate (mL/s)**	**M_{TOC} (ppm)**	C-6 sugars	Glycolaldehyde	5-HMF	Erythrose	Glyceraldehyde
14A	0.07	0.60	5165	10005	2084	26	588	0
14B-L	0.08	0.39 (66 % A)	9303	14499	2402	29	666	0
14B-V	0.08	0.18 (30 % A)	593	135	637	1	0	0

Figure 1.

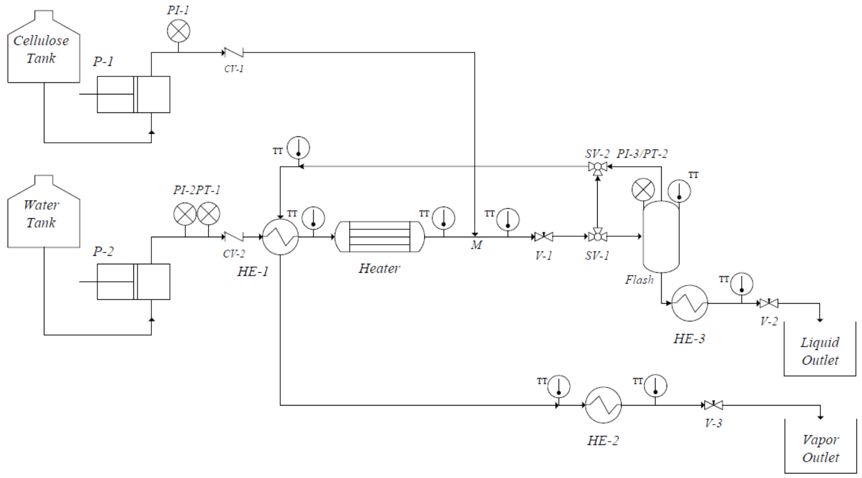

PI-1
Cellulose Tank
P-1
CV-1
TT
SV-2
PI-3/PT-2
TT
Water Tank
PI-2PT-1
TT
TT
TT
P-2
CV-2
HE-1
Heater
M
V-1
SV-1
Flash
TT
HE-3
V-2
Liquid Outlet
TT
TT
HE-2
V-3
Vapor Outlet

Figure 2.

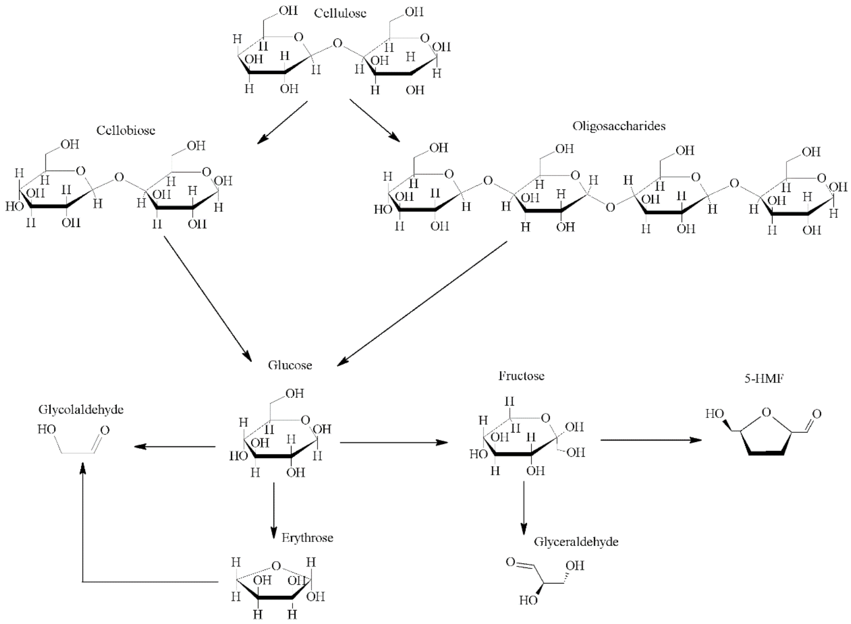
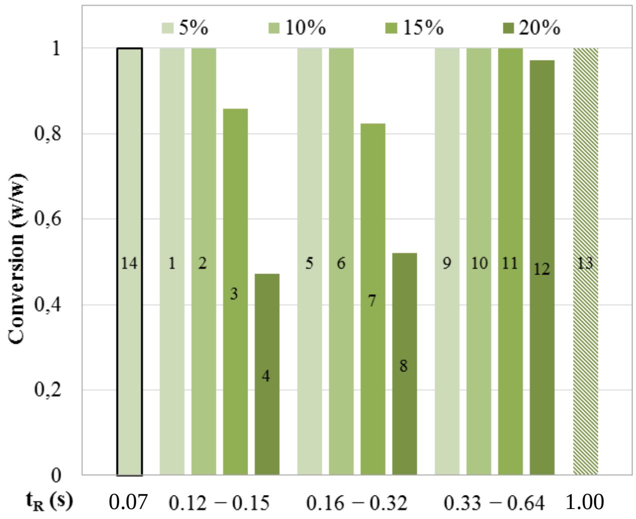

Cellulose
Cellobiose
Oligosaccharides
Glucose
Fructose
5-HMF
Glycolaldehyde
Erythrose
Glyceraldehyde

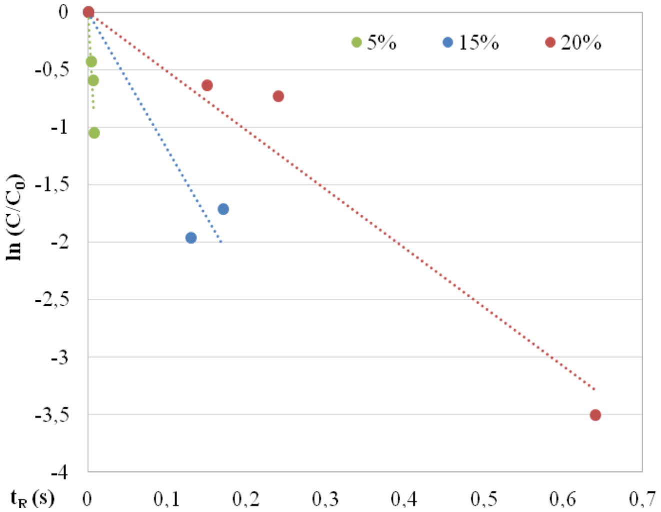
Figure 3.



Comentado [Lola42]: Yo pondría la concentración de celulosa a la entrada del reactor, y pondría que esos % son de concentración de celulosa para que la figura pueda ser leída individualmente

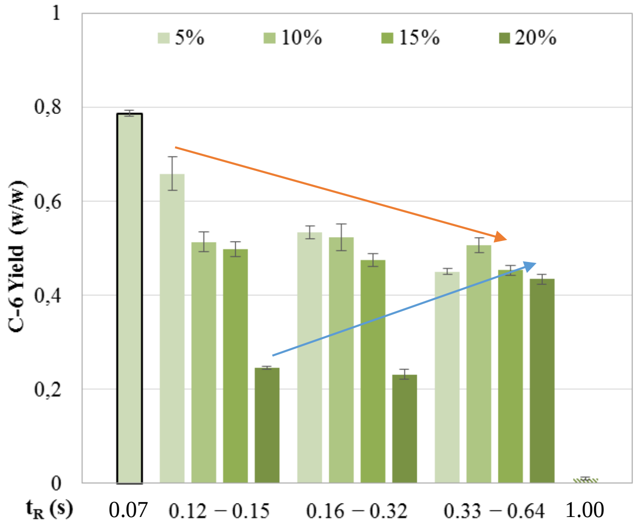
Una sugerencia, en este caso en vez de poner los bloque no sería más claro 4 líneas de tendencia con los puntos experimentales(una por concentración) que indiquen como evoluciona la conversión con el tiempo? Yo creo que sería muchísimo más claro

Figure 4.



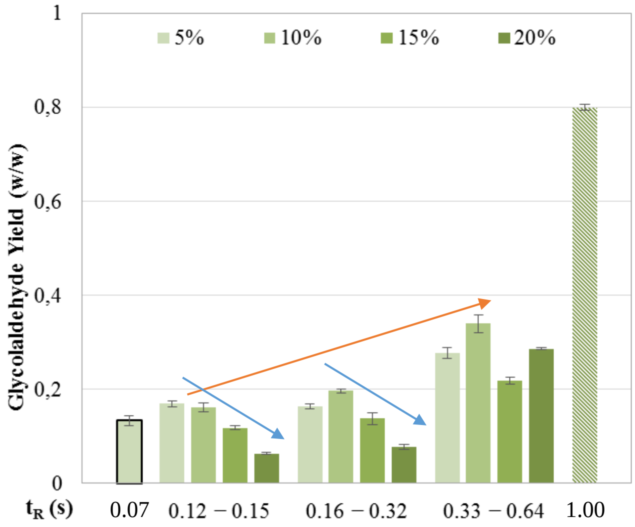
Código de campo cambiado

Figure 5.



Comentado [Lola43]: Sugiero concentraciones a la entrada del reactor y mencionan en la figura cuales que son estos %
Él que está a 1 s por qué tiene otro color?
A mi lo de las flechas no me resulta una forma de expresarlo muy clara, yo le daría una vuelta
Lo mismo para la figura 6

Figure 6.


1
0,8
0,6
0,4
0,2
0
Glycolaldehyde Yield (w/w)
5%
10%
15%
20%
t_R (s)
0.07
0.12 − 0.15
0.16 − 0.32
0.33 − 0.64
1.00