

Reducing Sugars Production from Cellulosic Wastes by Subcritical Water Hydrolysis in a Continuous Lab Scale Unit

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Second generation biofuels are those produced from lignocellulosic biomass or crops that do not compete with food production. Cellulose and hemicellulose in plants can be transformed to building blocks, pentoses and hexoses, by hydrolysis. However, most processes require a physic-chemical pretreatment to remove lignin, which acts as a barrier for chemicals during hydrolysis. In fact, pretreatment for removal of lignin or lignin byproducts formed during hydrolysis can be considered as limiting steps for subsequent sugar transformation processes. Alternatively, industrial cellulosic residues, in which lignin and most of hemicellulose have been previously removed through chemical treatment, could be used as raw material for the production of reducing sugars without the drawbacks related to pretreatment and purification steps. Such is the case for diaper industry, which generates a polyacrylate-cellulose dust (POCEL), which cannot be recycled to the process. POCEL is comprised by around of 60 wt. % cellulose and 40 wt. % super absorbent polymer sodium polyacrylate. Due to the high content of cellulose in comparison to lignocellulosic biomass, in which the cellulose content usually oscillate between in the range 20 to 40 wt.%, POCEL could be used as a low cost raw material for glucose production, that can be subsequently fermented to produce bioethanol.

In this work, experimental results of POCEL suspensions hydrolysis under subcritical water conditions in a continuous laboratory scale unit are presented. POCEL suspensions in water at 1.2 wt. % were prepared by adding a few drops of hydrochloric acid up to pH 2 to prevent sodium polyacrylate jellification with water. The hydrolysis unit in subcritical water at continuous laboratory scale consisted of a high pressure pump, preheater, a tubular reactor immersed in an electrical oven, heat exchanger and needle valve to regulate system pressure. Experiments were carried out in the temperature range 350 to 420 °C, pressures of 100 to 136 atm and suspension flowrates of up to 6.4 mL/min. Reactor effluent samples were characterized by means of dinitrosalicylic acid (DNS) colorimetric method. The highest concentration of reducing sugars was obtained at 390 °C and a water flowrate of 1.9 mL/min, which corresponds to a residence time of 126.7 s in the reactor. The estimated productivity of sugar production based on a cellulose content of 60 wt.% in POCEL was 85.4%, which indicates this kind of cellulosic waste could be used to obtain high reducing sugars concentration in hydrolysates through a continuous subcritical water process.

1. Introduction

Second generation biofuels are those produced from lignocellulosic biomass or crops that do not compete with food production (Naik et al., 2010). Cellulose and hemicellulose in plants can be transformed to building blocks, pentoses and hexoses, by hydrolysis (Aditya et al., 2016). Alternatively, industrial cellulosic residues, in which lignin and most of hemicellulose have been previously removed through chemical treatment, could be used as raw material for the production of reducing sugars without the drawbacks related to the pretreatment and purification steps. Such is the case for diaper industry, which generates a polyacrylate-cellulose dust (POCEL), which cannot be recycled to the process. POCEL is a by-product obtained during pneumatic transport and cellulose shredding and is comprised by very fine particles collected through vacuum systems. Due to its size characteristics, POCEL cannot be recycled back into the process and must be disposed of by incineration or in sanitary landfills, where its high hygroscopicity can cause terrain instability. POCEL utilization has been scarcely studied in literature. The composition of super adsorbent polyacrylate in POCEL varies in

the range 38 to 60 wt. % and some research studies have focused in its water sequestration capacity for several industrial applications to replace pure polycrylate consumption. Alternately, high cellulose content in POCEL could be hydrolysed to fermentable hexoses, with the added advantage of the absence of hemicellulose and lignin present in biomass materials which form pentoses and phenolic decomposition products during hydrolysis (Limayem & Ricke, 2012).

The hydrolysis of cellulose can be accomplished by conventional acid, basic and enzymatic methods (Nguyen et al., 2018). These processes usually required steps of physical, chemical or biological pretreatment of biomass to separate lignin (Haghighi et al., 2013), which acts as a barrier to cellulose and hemicellulose chemical attack (Prado et al., 2014). These pretreatment steps not only increase processing costs but also could produce decomposition products that inhibit subsequent fermentation. Alternatively, a hydrolysis process that uses only water at high temperature and pressure, conditions, known as subcritical water hydrolysis, has gained increased attention (Kruse & Dahmen, 2015). This process takes advantage of the well-known tunable properties of water in the vicinity or above the supercritical point, 374 °C and 22.1 MPa, to favor or disfavor acid/basis catalysis (Cantero et al., 2015), avoiding the use of corrosive acids such as sulphuric and hydrochloric acids commonly employed in the conventional acid catalysed hydrolysis. Due to the properties of subcritical/supercritical fluids, water can easily penetrate biomass structures to hydrolyze cellulose and hemicellulose (Cocero et al., 2018). Hydrolysis in subcritical and Supercritical water has been conducted through reactor configurations for the batch, semi-continuous and continuous, as reviewed by Prado & coworkers (2015). Semibatch and continuous mode operation data can be transferred to industrial-scale reactors (Schacht et al., 2008). Accordingly, in this work we report on the production of total reducing sugars (TRS) by subcritical water hydrolysis of POCEL in a continuous mode operation in order to assess its usability as a raw material for biofuels or chemicals production.

2. Materials and methods

2.1 Polyacrylate-cellulose (POCEL) dust

POCEL dust was provided by a diaper industry located near Bogotá and the reported cellulose and polyacrylate composition as used in diaper processing was 60% and 40% respectively. In this particular industry, POCEL is a waste problem and its proper handling and disposition is carried out by incineration with additional costs. POCEL physical aspect is shown in Figure 1a. It is a compacted dust which can be easily disintegrated. POCEL was prepared as a water suspension 1.2 wt. % by adding a few drops of hydrochloric acid in order to avoid water jellification caused by polyacrylate super adsorbent as shown in Figure 1b. Higher POCEL concentrations could not be prepared because of the resulting high viscosity which makes its handling difficult.

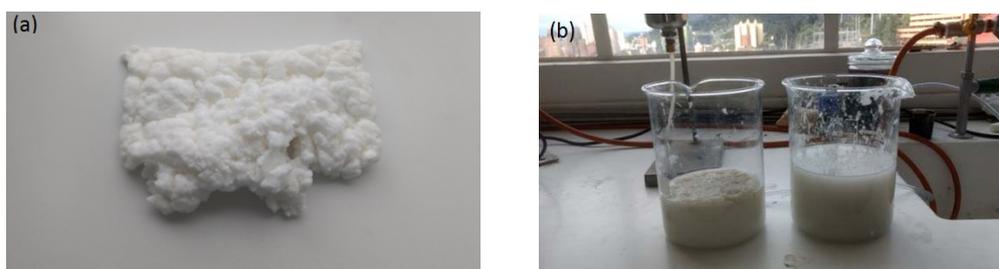


Figure 1: Polyacrylate-cellulose dust (POCEL) a) Physical aspect. b) water suspension 1.2 wt. %

2.2 Experimental set-up

The scheme of the continuous lab scale subcritical hydrolysis unit is shown in Figure 2. It consisted of deionized water supply tanks and POCEL suspension, a Williams Milton Roy (PA, USA) pneumatic high pressure pump model CP250V225, two POCEL suspension reservoirs made of 1/2 in O.D. stainless steel tubing 3 m long placed in parallel, a preheater made of 316SS Swagelok tubing 1/8 in O.D. (3.175 mm), length of 3 m coiled tubing and electrical resistances, an insulated tubular reactor made of 316SS Swagelok tubing 0.5 in O.D. (1.27cm), 0.065 in (0.17 cm) wall thickness, length of 100 cm and volume of 67.9 cm³, a concentric tube heat exchanger with water as cooling media, a needle depressurization valve model SS-1RS4 (Swagelok, Barranquilla Colombia) valve and sample collection recipient, pressure gauges (Ashcroft CT, USA) and thermocouples, as shown in Figure 2. In a typical run, both reservoirs are filled up with POCEL suspensions but only one is feeding the reactor by means of water that flows from the high pressure pump

and pushes the suspension through the system. After a specific time, depending on the water flow rate, high pressure water is diverted to the second reservoir while the other is emptied of the water and filled up again with suspension. This approach avoids passing POCEL suspension through the pump, which can cause clogging in check valves. Samples were collected under steady state conditions, which were obtained after at least four residence times in the reactor had passed, and was verified for an steady temperature and pressure and the physical aspect of the effluent.

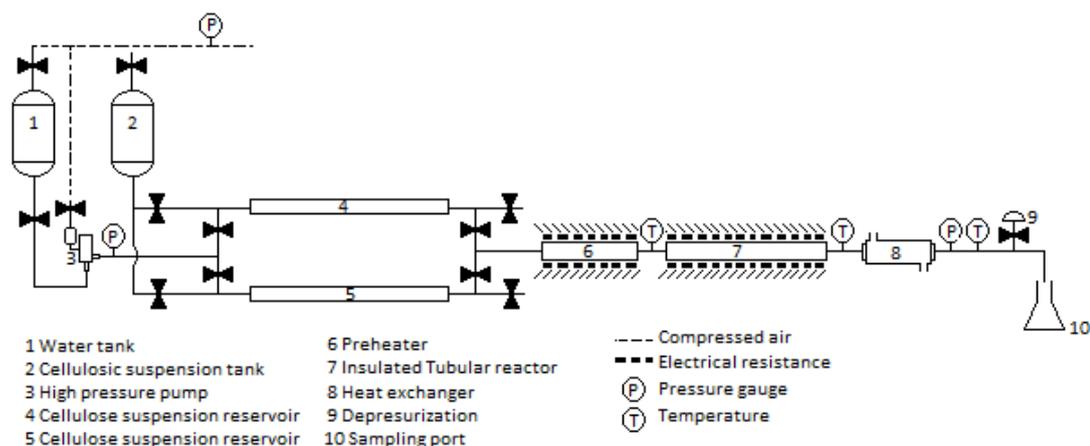


Figure 2: Scheme of the continuous lab scale subcritical hydrolysis unit

2.3 Analytical methods

The determination of total reducing sugars (TRS) consisted of the measurement of reactor effluent samples by the dinitrosalicylic (DNS) colorimetric method using d-glucose as standard (Panreac, Barcelona Spain) (Miller, 1959). Briefly, for each ml of hydrolysate sample, 1 ml DNS reagent previously prepared was added, boiled for 15 min, and 1 ml deionized water added afterwards to keep for 10 min in cold water before reading the absorbance in a Macherey-Nagel Nanocolor 500 D photometer at 540 nm. The concentration of reducing sugars was calculated based on a standard curve obtained with glucose concentrations of up to 1 mg/ml. TRS yield was calculated with the concentration and volume collected to find the mass of total reducing sugars (TRS) in hydrolysate samples and it was assumed a 60 wt. cellulose composition in POCEL to approach total cellulose mass fed to the system.

3. Results and discussion

Figure 3 shows the physical appearance of POCEL hydrolysate samples obtained at different reaction conditions, which were selected based on preliminary experimental studies that showed hydrolysis experiments carried out at temperatures lower than 350 °C did not proceed considerably. System pressure was kept constant at 2000 psi. A brownish color and pleasant sweet scent indicate a high total reducing sugar (TRS) concentration in hydrolysate samples. The darker the brown color the higher the measured absorbance or TRS concentration in the obtained hydrolysate at that specific reaction time, as in sample 3 (a).



Figure 3: Physical appearance of POCEL hydrolysate samples. (a) Highest TRS yield. (b-d) Decreasing TRS yield due to biomass exhaustion. (e) End of hydrolysis

A lighter brown color, as shown in samples (b), (c), and (d), indicates a lower TRS concentration as a result of subsequent biomass exhaustion in the reactor, until effluent becomes transparent again as in sample (e), which is practically water and indicates the end of hydrolysis. Table 1 summarizes continuous hydrolysis experimental conditions and obtained TRS concentration and yield. Average TRS was taken as the average of at least four consecutive samples taken under steady state operation conditions. STDV is the standard deviation. Since POCEL is comprised by mostly cellulose, it can be assumed that TRS concentration is equivalent to glucose concentration or fermentable sugars concentration, since pentoses obtained from hemicellulose, which are not fermentable by *Saccharomyces cerevisiae*, could not be produced from cellulose. Total reducing sugars (TRS) yield was approximated by having into account a 60 wt.% cellulose composition in POCE dust, according to the weight percent characterization provided by the diapers producer, which is equivalent to a 0.72 wt.% in POCEL suspension fed to the system. Residence time in the reactor τ (min) was calculated with the reactor volume V (m^3) and the volumetric flowrate at reaction conditions ϑ_{SC} (m^3/min) which was estimated by means of a mass balance between the pump outlet at room temperature conditions (RT) and reactor inlet at subcritical reaction conditions (SC), as shown in Equation (1). Mixture density at reaction conditions ρ_{SC} (Kg/m^3) was approximated as that of water in steam tabs, since water comprises more than 98% of reactive mixture. Residence time calculation is shown in Equation (2).

$$\vartheta_{RT} \cdot \rho_{RT} = \vartheta_{SC} \cdot \rho_{SC} \quad (1)$$

$$\tau = \frac{V \cdot \rho_{SC}}{\vartheta_{RT} \cdot \rho_{RT}} \quad (2)$$

Table 1: Continuous hydrolysis experimental conditions and obtained TRS concentration and yield

Experimental Run	Temperature (°C)	Flowrate (mL/min)	[TRS] (mg/mL)	Average [TRS] (mg/mL) (STDV)	TRS yield (%)	Residence time (s)
1	350	6.4	0.158 1.158 0.707 2.715 0.218 1.160	1.02 (0.94)	14.1	46.8
2	350	3.2	0.160 1.637 0.244 1.277 1.557 1.437 2.275	1.23 (0.77)	17.1	93.6
3	370	3.2	4.411 5.689 7.305 4.611 5.269	5.50 (1.15)	76.4	82.4
4	390	3.2	6.447 5.030 6.607 6.188 7.046 4.371	5.95 (1.02)	82.6	75.3
5	390	1.9	6.707 5.589 6.214 6.112	6.15 (0.46)	85.4	126.7
6	390	5.1	5.609 4.651 5.289 6.128 5.888 5.349 6.487 3.972	5.42 (0.81)	75.3	47.2
7	420	5.1	6.747 7.565 6.070 5.828 4.371	6.11 (1.18)	84.9	42.5
8	420	3.2	5.269 5.649 6.128 6.048	5.77 (0.40)	80.1	67.7

Results in Table 1 indicate a large amount of variation in experimental results for TRS measurements at temperatures up to 370 °C, whereas runs 4-8 displayed a lot less variation as evidenced by the standard deviation of data when compared to runs 1-3. This could be attributed to a faster hydrolysis reaction rates at higher temperatures and the establishment of homogeneous phase conditions in contrast to the existence of solid POCEL and liquid phases at lower temperatures, which at the same time difficult depressurization control and sample collection. TRS concentration and yield varied in the range 1.02 to 6.15 mg/mL and 14.1 to 85.4 %, respectively, and highest TRS concentration and yield was obtained in run 5, which was carried out at 390

°C and a water flowrate of 1.9 mL/min, which corresponds to a residence time of 126.7 s. However, similar results were obtained when working at a higher temperature in a considerable shorter residence time as indicated in run 7, which was carried out at 420 °C, 5.1 mL/min flowrate and a residence time of 42.5 s. A shorter residence time when working at 390 °C produced a decrease in concentration and yield, as indicated in run 6, which can be attributed to insufficient time for hydrolysis to proceed. Runs 1 and 2 indicate hydrolysis does not occur significantly at temperatures lower than 350 °C, even at longer residence times. Hydrolysis proceeds only at temperatures higher than 370 °C and it is observed the effect of temperature is more significant than the effect of flowrate, since TRS yield increases only 3% at 390°C as a result of increasing residence time by decreasing flowrate by half. These results suggest high TRS yields can be obtained at temperatures around 400 °C and that high temperatures make possible to attain high TRS yields in considerably shorter residence times.

The vast majority of subcritical water hydrolysis studies with different types of biomass are carried out by means of semibatch, also known as semicontinuous, reactor set-ups. In this type of reactor, a fixed amount of biomass is charged to the reactor and water flows continuously, removing reaction products to avoid degradation (Marulanda & Marulanda, 2017). This approach is useful for lignocellulosic materials due to the technical difficulties that might arise from pumping solids at high pressure, or the requirements with respect to size reduction to facilitate this operation. Only a few studies have been carried out with continuous reactors and have studied the supercritical hydrolysis of pure cellulose in order to elucidate kinetic mechanisms, products and degradation products at different reaction conditions. For example, Cantero and coworkers (2013) pointed out cellulose hydrolysis is completed at subcritical temperatures with a high concentration of glucose and oligosaccharides but the reaction has a low selectivity and needs bigger reactors and longer residence times. In order to improve selectivity, a novel reactor capable of operating under supercritical conditions with an effective control of residence time was developed, deemed as a sudden expansion micro reactor, in which heating and cooling slopes were avoided. Experiments were carried out with a micro-crystalline cellulose concentration 1.6 wt. % and temperature in the range 300 to 400 °C at a constant 25 MPa pressure and residence times were varied from 0.004 s to 5 s. Experimental results showed that above 375 °C cellulose hydrolysis accelerated more than was predicted by the Arrhenius parameters of the reaction for subcritical temperature, which could be attributed to the reaction taking place under homogeneous phase conditions without mass transfer limitation that could be present when working at subcritical conditions, and the highest selectivity of 98% was achieved at 400 °C and residence time of 0.023 s. Experimental results shown in Table 1 agree well with these results in which a high yield of sugars was obtained only at temperatures higher than 370 °C with a maximum at 390 °C even if pressure was lower than supercritical pressure, which suggest effect of temperature is more significant than pressure. Longer residence times needed in this study when compared to experimental data obtained by Cantero and coworkers (2013) could be attributed to the heating procedure, which was gradual instead of instantaneous, and the use of an industrial polyacrylate-cellulose fiber waste instead of micro-crystalline cellulose.

Use of higher temperatures with short residence times in the continuous subcritical or supercritical hydrolysis of biomass materials could improve obtained sugar yields as experimental results in Table 1 suggest.

Table 2: Experimental data of semibatch studies for different biomass materials and TRS yield

Raw material	Reaction conditions	TRS yield	Reference
Cellulose/hemicellulose	T(°C), P(psi), Flowrate, Time	%	
Kikuyo grass (26.9% 26.2%)	300 °C, 3190 psi, 9 ml/min, 11 min	22%	(Marulanda & Marulanda 2017)
Sugar cane bagasse (35%, >30%)	290°C, 2900 psi, 33 ml/min, 16 min	23%	(Prado et al., 2014)
Rice husks (18.5%, 28%)	220 °C, 2900 psi, 5 min	18%	(Abaide et al., 2019)
POCEL suspension (0.72% cellulose)	390 °C, 2000 psi, 1.9 mL/min, 126.7 s 420 °C, 2000 psi, 5.1 mL/min, 42.7 s	85.4% 84.9%	This work

In this regard, a direct comparison of residence times with semibatch studies is not practical since water is passed through the packed bed reactor until cellulose and hemicellulose are practically depleted. Although a rapid removal of reaction products is accomplished in semibatch reactors, decomposition reactions due to an extended reaction time could decrease yield. Table 2 shows experimental data of semibatch studies for different biomass materials and reported data in this work.

As shown in Table 2, continuous flow of water through the packed biomass bed in semibatch studies can take several minutes and decomposition due to an extended reaction time in the fixed bed could result in loss of

productivity and the formation of several decomposition products such as furfural, hydroxymethyl furfural, acetic acid, acrylic acid and formic acid, which could prevent the fermentation process (Mussatto & Roberto, 2004). In order to avoid or minimize decomposition products formation, shorter residence times should be preferred. In this regard, continuous subcritical or supercritical hydrolysis of cellulosic materials such as POCEL, cotton and paper waste and other cellulosic industrial residues is a promising process due to the fact that these raw materials have high cellulose compositions, practically no lignin and hemicellulose and could be pumped at high pressure and temperature with special equipment or flow arrangements that make possible to work in a continuous mode operation.

4. Conclusions

Continuous subcritical hydrolysis of polyacrylate-cellulose dust (POCEL) waste, which is currently discarded without any valorization, was carried out. Highest TRS concentration and yield was obtained at 390 °C and a water flowrate of 1.9 mL/min, which corresponds to a residence time of 126.7 s. However, similar results were obtained when working at 420 °C, 5.1 mL/min flowrate and a residence time of 42.5 s. Hydrolysis did not occur significantly at temperatures lower than 350 °C, even at longer residence times. Hydrolysis proceeds only at temperatures higher than 370 °C and it is observed the effect of temperature is more significant than the effect of flowrate, since TRS yield increases only 3% at 390°C as a result of increasing residence time by decreasing flowrate by half. These results suggest high TRS yields can be obtained at temperatures around 400 °C and that high temperatures make possible to attain high TRS yields in considerably shorter residence times. Continuous subcritical or supercritical hydrolysis of cellulosic wastes is a promising process to obtain TRS increased yields in considerable shorter residence times than in semibatch mode operation.

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