

Subcritical Water Hydrolysis of Sugarcane Bagasse and Coconut Husk Assisted by Carbon Dioxide

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The objective of this work was to evaluate the effect of operation conditions on sub/supercritical water hydrolysis (SWH) of sugarcane bagasse and coconut husk, adding carbon dioxide (CO₂) as acid catalyst. The assays were carried out in a semi-bath unit equipped with a 50 mL reaction vessel. The process was conducted at 250°C for 30 min, with water and carbon dioxide 20 MPa. The results of SWH of sugarcane with the addition of carbon dioxide indicate that there was no change in the content of reducing sugars in the hydrolysate (13.5%). However, for coconut husk the total reducing sugars recovered increased 15% in the hydrolysate more effectively and showed greater percentages of sugars compared to sugarcane. The pH varied indicating that other compounds were degraded by the addition of carbon dioxide to water at both raw materials. The phenolic compound analysis indicated that the fermentation inhibitors increased with carbon dioxide addition for sugarcane bagasse, and decreased for coconut husk. Therefore, the addition of carbon dioxide as an acid catalyst in the SWH of sugarcane bagasse did not improve the process, but it did improve the sub/supercritical water hydrolysis of coconut husk. Therefore, sub/supercritical water hydrolysis should be optimized individually for each raw material

1. Introduction

The renewable fuels economically attractive, like ethanol, at lower prices than gasoline is a difficult task as one of the current greatest challenges is the increasing demand of energy associated with the dependence on fossil fuels. Although some innovative technologies are technically feasible, they remain more expensive than non-renewable sources. The combustible ethanol provides more power than gasoline due to the higher-octane content, although it contains 33 % less energy per gallon (Zaldivar et al., 2001). Moreover, the ethanol use can take advantage of the installed infrastructure for distribution of liquid fuels, in countries, like Brazil, that use the of road transport and beyond relatively simple modifications of the engines are needed so they can run with ethanol. Therefore, it is a natural candidate as a short-term solution in our energy supply by renewable sources (Serrano-Ruiz & Dumesic, 2011). The first generation ethanol production from sugarcane and corn has seen wide development in the last decades, and tends to continue improving its economic feasibility (Berni et al., 2013). Brazil is trying to achieve sustainable growth quickly through domestic consumption and marketing of biofuels, specifically ethanol from sugarcane, to substitute fossil fuels. Moreover, the knowledge generated about processes to produce other products from the bagasse is sufficient to indicate that this raw material can be better exploited (Mudhoo et al., 2011). Biofuels are fuels produced from biomass, such as wood, sugarcane, corn, palm oil, among others, with carbon dioxide emissions arising from their burning being mitigated by their own uptake by the cultures (Leite et al., 2009). In a comparison with greenhouse gases emissions from gasoline, the advantage of ethanol from sugarcane is even more evident since during the life cycle of its production only 0.9 kg of carbon dioxide is released per liter of gasoline-equivalent, which means 70% less emissions than gasoline (Leite et al., 2009). Additionally, residues generated from biomass worldwide

represent a great potential resource for energy achievement (Olivarez et al., 2012). The Brazil is the world's largest producer of sugarcane, with approximately 570 million tons in the 2011/2012 season. Forster-Carneiro et al. (2013) studied agricultural species cultivated in Brazil, and showed that the culture with the highest biomass production was sugarcane with 714.0 10⁶tons in 2009/2010 and estimated production of 893.0 10⁶tons for the year 2019/2020. Therefore, in Brazil it represents the culture with greater production of biomass residues, 157.0 10⁶tons of agriculture residues of sugarcane (2009/2010) and growth of 25.2% by 2019/2010 with a production of 196.5 10⁶tons of total waste, only sugarcane. The lignocellulosic biomass is a particularly attractive feedstock because it is the cheapest, most abundant, and fastest growing form of terrestrial biomass. In Brazil, among the raw materials, agricultural residues are attractive supply sources, since the current technology is already capable of processing them into fermentable sugars (Prado et al., 2013). Therefore, the hydrolysis process should be optimized so that the yield of fermentable sugars is maximized, while formation of degradation products is minimized. Unfortunately, this is a difficult task since sugars degradation rate can be higher than the hydrolysis rate of the lignocellulosic material to fermentable sugars (Sasaki et al., 2003). Therefore, the main challenge is to achieve high fermentable sugars yields and low concentrations of the compounds that are inhibitory to the fermentation microorganisms in order to allow an efficient fermentation process for second-generation bioethanol production (Schacht et al, 2008).

The sub/supercritical water hydrolysis (SHW) is a clean and fast hydrolysis method applicable to lignocellulosic biomass with the advantages of no need of pre-treatment, short reaction time, low corrosivity, low residue generation and no use of toxic solvents (Resende et al., 2007). The technology of supercritical water is environmentally friendly processes because it only uses water under high pressure and temperature. The simple sugars that can be obtained from the cellulosic and hemicellulosic fractions lignocellulosic materials can be used as substrate to produce second-generation bioethanol or other precursors of bio-products (Petchpradab et al., 2009). There are relatively few examples of applications of SWH for the hydrolysis of agricultural and food industry residues. Most relevant examples include corn stalks and stover, sugarcane bagasse and rice bran. The sugarcane bagasse is an agricultural residue produced in large amounts in Brazil with a great potential to be used for the recovery of value added sub-products (Prado et al., 2014). Besides these important residues there are other potential raw materials that can be used to produce simple sugars using SWH, including and coconut husk. Coconut husk is a lignocellulosic material produced from processing of coconuts for beverages and coconut powder, categorized as hard wood and characterized by high toughness due to its high lignin content (Prado et al., 2014). Processing residues represents an opportunity to make better use of cheap and abundant wastes to produce high value sub-products. However, considering the complexity of polymers interaction and the diversity of their composition, each raw material represents a technological challenge that should be studied separately. Additionally, the process is far from being optimized. The objective of this work was to optimize process conditions for subcritical water hydrolysis of sugarcane bagasse and coconut husk by SWH, using carbon dioxide as an acid catalyst.

2. Material and Methods

2.1 Raw materials origin

The sugarcane bagasse was provided by the Brazilian Bioethanol Science and Technology Laboratory (CTBE, Campinas, Brazil). The coconut husk resulting from coconut processing to produce coconut water and milk was donated by Ducoco Alimentos (Linhares, Brazil). The raw materials were stored at -18 °C and then they were comminute in a knife mill (Marconi, model MA 340, Piracicaba, Brazil) equipped with a 1 mm sieve before they were used as samples in the experiments. Distilled water was used in all experiments.

2.2 Hydrolysis equipment

The semi-batch unit shown in Figure 1 was built to hydrolyze lignocellulosic biomasses using sub/supercritical water technology. The equipment can operate up to 400 °C. The system is composed by a liquid high pressure pump that works up to 400 bar (LabAlliance, model Series III, State College, PA) for water pumping, an air driven liquid pump (Maximator GmbH, model M18, Thüringen, Germany) for carbon dioxide pumping, a thermostatic bath (Marconi, model MA-184, Piracicaba, Brazil) operated at -10 °C to assure that CO₂ is liquid before entering the pump, two static mixers (Autic, Campinas, Brazil), one stainless steel heating coil (Autic, 6 m × 1/8" i.d., Campinas, Brazil) for the reaction medium heating, one stainless steel 50 mL reactor (Autic, 2.34 cm i.d. × 11.7 cm, Campinas, Brazil) with metal-to-metal fit to allow using temperatures up to 400 °C, one micrometric needle valve (Autoclave Engineers, Erie, PA) for

pressure control, one stainless steel refrigeration coil coupled to a thermostatic bath (Marconi, model MA-184, Piracicaba, SP, Brazil) operating at 40 °C to assure that the reaction is quickly quenched after the hydrolysate exits the reactor, and one glass gas-liquid separator to separate the liquid hydrolysate from the gas (dioxide carbon). The equipment also contains block valves, thermocouples and manometers.

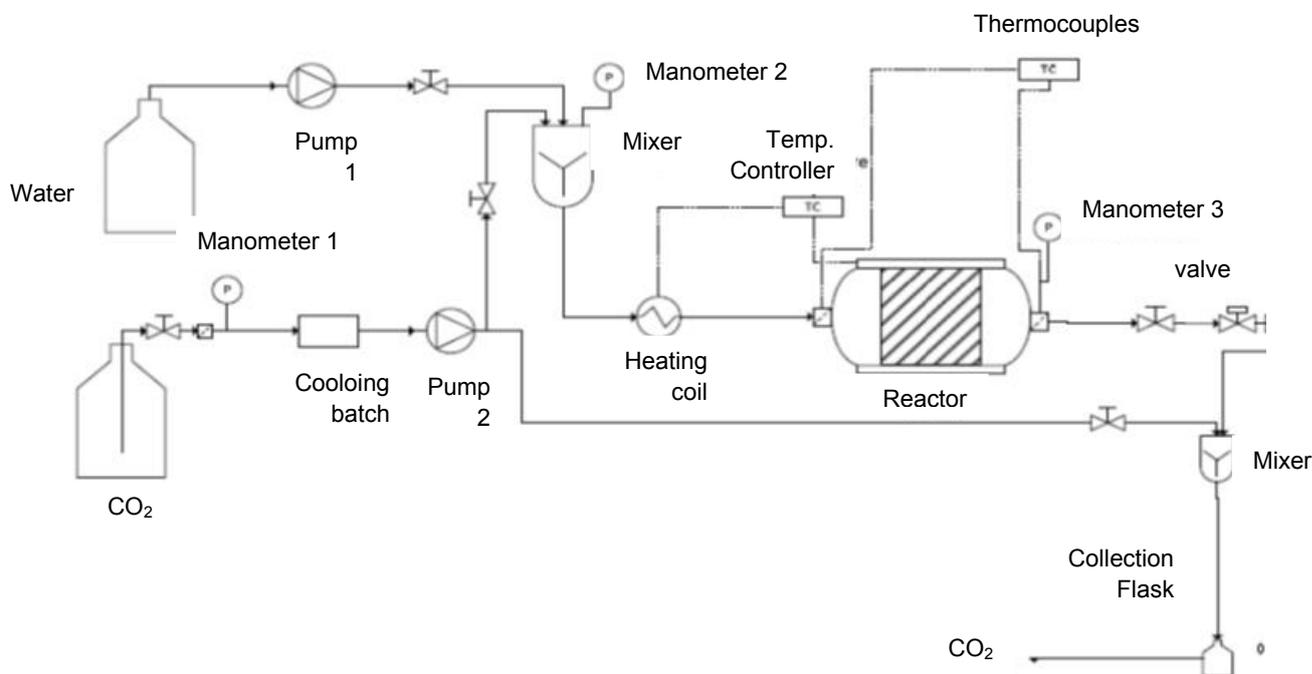


Figure 1: Sub/supercritical water hydrolysis unit equipment with addition of CO₂

2.3 Hydrolysis of raw materials

Experiments were carried out using 10 g of raw material, approximately. The sample was inserted in the reactor, which was connected to the equipment. Distilled water was pumped to the system until reaching the specified pressure (20 MPa). After the pressurization the pump the process was stopped, the micrometric valve was closed and the heating of the coil and of the reactor was started. The temperature of process was 250 °C, while the reactor was pre-heated to 120 °C to assure that there was no hydrolysis of cellulose during the pre-heating time. After temperature stabilized, the dynamic period of the process was started, the pumping water was set at 33 mL/min (ambient conditions) and the pumping of CO₂ was set at 7 g/min through the system for 30 min. At the same time, the reactor temperature was set to 250 °C, causing a temperature profile until its stabilization. The samples of hydrolysates were collected each 2 min. The experiments were performed in duplicate.

2.4 Analysis of the hydrolysate

The total reducing sugars, that is, sugars with open-chain form with an aldehyde group or a free hemiacetal group, were determined by the colorimetric Somogyi-Nelson method (Nelson, 1944). The hydrolysate was subjected to acid hydrolysis to assure that all the oligomers would be broken to monomers, and in this way could be detected as reducing sugars (Miller, 1954). After the coloring reaction (Nelson, 1954) the absorbance was recorded at 730 nm by a spectrophotometer (Femto, model 800 XI, São Paulo, Brazil). The concentration of total reducing sugars was calculated using an external calibration curve of glucose (10-600 mg/L), and expressed as glucose equivalents. The pH of the hydrolysates was determined using a digital pHmeter (Digimed, model DM-22, Santo Amaro, Brazil).

Degradation products of sugars and of the lignin that are inhibitors to fermentation microorganisms were determined by HPLC. The analyses were carried out using a Waters system (Waters Corp., Milford, Massachusetts), consisting of separation module (2695A) with integrated column heater and auto-sampler, and a photodiode array detector (2998). Some of the samples of the hydrolysates were diluted in deionized water and filtered through a 0.45 µm nylon membrane. Separation of compounds present in the samples was carried out using a fused-core type column (XSelect HSS, C18, 2.5 µm, 100 Å, 100 × 4.6 mm, Waters Corp.) (Rostagno et al., 2011; Farias-Campomanes et al., 2013). The temperature of the

column was maintained at 40 °C and the mobile phase consisted of water containing 0.1 % of acetic acid (solvent A) and acetonitrile containing 0.1 % of acetic acid (solvent B). Separation was achieved using the following gradient: 0 min: 10% B; 2.0 min: 10% B; 5.0 min: 20% B; 6.0 min: 20% B; 10 min: 90% B; 12 min: 90% B; 13 min: 10% B. Equilibration time between runs was 7 min; total time was 20 min per sample. The mobile phase flow rate was 0.8 mL/min and the injection volume was 10 µL. UV absorbance was monitored from 200 to 400 nm with a sampling rate of 10 points per second. The software for control of equipment and data acquisition was Empower 3. The identification of each compound was achieved by comparison of retention times and UV spectra of each compound. The standard curve (8 points) of each compound was prepared by plotting concentration (0.1-100 mg/L) against area. Regression equations and correlation coefficient (r^2) were calculated using Microsoft Excel 2010 software and were higher than 0.99 for all compounds. The standard calibration curve was built with pure standards of furfural, 4-hydroxybenzoic acid (4-HBA), 5-HMF, and vanillin (Sigma-Aldrich, Milwaukee, WI).

3. Results and Discussion

The results of the hydrolysis experiments with the addition of carbon dioxide as an acid catalyst were compared to data from experiments conducted with pure water as an acid catalyst. In the first experiment using the sugarcane bagasse the results showed that was not change in the content of reducing sugars in the hydrolysate (13.5%) (Table 1), or is both in processes using water or carbon dioxide no representative difference between them. The pH of the hydrolysates remained approximately constant during the process between 3 and 4. These results, values of pH (3.0-4.0) are considered to be higher than values of pH presented by Kumar and Gupta (2008) with values of the pH 2.3-3.0, in subcritical water hydrolysis at 200-405 °C of temperature with cellulose in a continuous system. The low pH indicates a high concentration of organic acids, derivative from monomers degradation. Total fermentation inhibitors in the hydrolysate increased, from 60.5 mg/g to 115.7 mg/g. Furfural + 5-HMF, which are also products of sugars degradation, increased 99% with CO₂ addition, while the phenolic compounds, which are products of lignin degradation, decreased 75% with CO₂ addition. Therefore, the addition of dioxide of carbon in the subcritical water hydrolysis process was not effective for sugarcane bagasse; on the one hand the this technology improved the depolymerisation of the lignocellulosic complex, leading to a constant yield of sugars

Table 1: Experimental results obtained for subcritical water hydrolysis of sugar cane bagasse with and without CO₂

	Without CO ₂	With CO ₂
Total reducing sugars	13.5 %	13.5 %
pH	5.43 – 4.41	5.34 – 4.60
Furfural + HMF	57.7 mg/g	115.0 mg/g
Phenolic compounds	2.8 mg/g	0.7 mg/g

In the experiments of coconut husk samples the results were completely different (Table 2). The subcritical water hydrolysis with CO₂ addition increased the yield of total reducing sugars by 15%. The values of the pH were lower when dioxide of carbon was added, implying more formation of organic acids that come from sugars degradation. On the other hand, furfural + 5-HMF yield did not change with CO₂ addition, while phenolic compounds yield has increased 36%, indicating improved cellulose depolymerization. As total sugars recovered increased, for coconut husk the addition of CO₂ improved the process.

Table 2: Experimental results obtained for SWH of coconut husk with and without CO₂

	Without CO ₂	With CO ₂
Total reducing sugars	11.7 %	13.5 %
pH	5.6 – 3.63	5.34 – 4.29
Furfural + HMF	252.1 mg/g	250.6 mg/g
Phenolic compounds	8.6 mg/g	11.7 mg/g

The coconut meal, a residue from coconut milk production, was study also of the Khuwijitjaru and colaborates (2012) in the subcritical water hidrolise process (100-250 °C) using a batch system. The results of pH were similar to those studied in this work, the pH profile showed a rapid decrease with

increased of temperature and in a short period of time. The results of the concentration of the sugar in the samples are similar in both works because, at 100-150 °C of temperature, the glucose was the main sugar of the hydrolysate and another condition at 175-200 °C of the temperature the mannose became the major sugar component. Finally the authors concluded that the residues from coconut processing industries are interesting raw materials for the production of fermentable sugars. Also, Cardenas and collaborators (2014) studied the subcritical water hydrolysis with defatted pressed palm fiber and the results indicated that also this raw materials is indicated for the production of fermentable sugars, the biomass conversion (40 - 97%) increased with temperature indicating the formation of by-products and there is the highest selectivity for saccharide formation was at 423 K (20 - 59 mol glucose/mol furfural equivalent).

In this work, the results indicated large differences between the raw materials. The different behaviour is probably associated with the different composition of the materials. The coconut husk presented higher lignin content than of the sugarcane bagasse. Lignin protects the lignocellulosic complex from degradation; therefore, less aggressive conditions (using water alone) are sufficient to depolymerize it when the lignin content is low. On the other hand, as lignin content increases, it is necessary to use more aggressive conditions (higher temperature or a catalyst) to achieve the same depolymerisation degree. Therefore, the addition of dioxide carbon can improve the SWH process, depending on the raw material used.

4. Conclusion

In sugarcane bagasse experiments with the subcritical water hydrolysis with dioxide carbon or without dioxide carbon, the results showed no change in the content of reducing sugars in the hydrolysate (11.5%). In conclude, for sugarcane bagasse the use of dioxide carbon as acid catalizate is not necessary. However, the total fermentation inhibitors increased, indicating improved depolymerisation of the lignocellulosic complex associated with more sugars degradation. In the experiment of the coconut husk the content of total reducing sugars increased 15%, this results were higher than compared with SWH of sugarcane bagasse. The pH values decreased, and the fermentation inhibitors increased, indicating a more pronounced effect of dioxide carbon addition on the lignocellulosic complex depolymerization than on the sugars degradation. The results indicated large differences between raw materials. The addition of carbon dioxide as an acid catalyst in the SWH of sugarcane bagasse is not economically viable, but for the sub/supercritical water hydrolysis of coconut husk is an attractive process. Therefore, sub/supercritical water hydrolysis should be optimized individually for each raw material

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