OPTIMIZATION OF PROCESS CONDITIONS FOR SUBCRITICAL WATER HYDROLYSIS OF SUGARCANE BAGASSE

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ABSTRACT
Optimization of operation conditions (temperature, time, solvent: solid proportion) of subcritical water hydrolysis (SWH) is needed so that it can be considered an effective process for second generation bioethanol manufacturing. The objective of this study was to optimize operation conditions using a semi-batch SWH system equipped with a 50 mL reaction vessel. Initially, the process was carried out at constant temperature (200 °C), pressure (20 MPa) and amount of raw material (2 g), using different flow rates (11, 22, 33, 44 and 55 mL/min) during 30 min. Reducing sugars recovery rate increased with flow rate increase. In the second part of the work, the flow rate was kept constant at 33 mL/min, the amount of raw material was increased by a factor of 5.5 (i.e. 11 g) and the SWH was performed at different temperatures (213, 251 and 290 °C) while maintaining pressure constant (20 MPa). Reducing sugars recovery rate increased up to a maximum and then decreased for the three temperatures. The hydrolysis process finished earlier for higher temperatures; however, the reducing sugars recovery decreased with temperature increase, possibly due to degradation of glucose. Therefore, the less aggressive condition, of 210 °C, was selected for sugarcane bagasse hydrolysis.

Keywords: Optimization; Subcritical water hydrolysis; Sugarcane bagasse

INTRODUCTION
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 [1]. One of them is carbohydrates. As most agricultural residues, sugarcane bagasse is composed by cellulose, hemicellulose and lignin. Simple sugars can be used as fermentation substrate to produce bioethanol, or as precursor for producing other bio-products, such as liquid alkanes, dimethyl-furan, etc. from through either fermentation or catalysis [2]. However, to obtain carbohydrates from sugarcane bagasse it is first necessary to hydrolyze cellulose and hemicellulose. The hydrolysis of agricultural residues can be achieved by the addition of acid, basic or enzymatic catalysts. The cellulose resistance to biological and chemical hydrolysis treatments implies that more aggressive conditions/techniques are necessary to achieve its hydrolysis [3].

There are several hydrolysis methods and techniques that have been developed over the last decades. The most extended techniques are acid, basic and enzymatic hydrolysis. As the knowledge of the processes taking place during the hydrolysis of lignocellulosic raw materials is increasing, new techniques are being exploited to overcome the drawbacks of these techniques. Among the available technologies, the clean and rapid method of sub/supercritical water hydrolysis (SWH) is proving to be an attractive alternative to conventional chemical and biological processes. However, further optimization of operation conditions (temperature, time, solvent: solid proportion) is still needed so that the process can be scaled-up to industrial level.
SWH has been proven technically feasible in face of acid and enzymatic hydrolysis, with the advantages of no need of pre-treatment, shorter reaction time, less corrosion, lower residue generation, no use of toxic solvents and lower formation of degradation products. A few studies on SWH have been conducted with sugarcane bagasse [4]; however, the process is far from being optimized. Therefore, the objective of this work was to optimize process conditions for subcritical water hydrolysis of sugarcane bagasse.

**MATERIAL AND METHODS**

**Raw material** - Dry sugarcane bagasse was supplied by the Laboratório Nacional de Ciência e Tecnologia do Bioetanol (CTBE) in Campinas (Brazil). Samples were stored at -18 °C and were milled before being used as sample in the experiments.

**Hydrolysis equipment** - A semi-batch unit that can operate up to 400 °C and 400 bar, was assembled to hydrolyze lignocellulosic biomasses using sub/supercritical water. The system is composed by a liquid high pressure pump (Thar, model P-50, Pittsburgh, USA) for water pumping, a stainless steel heating coil (Aotic, 6 m x 1/8” i.d., Campinas, Brazil) for the reaction medium heating, a 50 mL stainless steel reactor (Aotic, Campinas, Brazil) with metal-to-metal fit to allow using temperatures up to 400 °C, a micrometric needle valve (Autoclave Engineers, Erie, USA) and a stainless steel refrigeration coil coupled to a thermostatic bath (Marconi, model MA-184, Piracicaba, SP) operating at 40 °C to assure that the reaction is interrupted quickly after the hydrolysate exits the reactor. The equipment also contains block valves, thermocouples and manometers.

**Hydrolysis of sugarcane bagasse** - Initial experiments were carried out using 2.0 g of raw material. 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 was stopped, the micrometric valve was closed and the heating of the coil and of the reactor was started. The heating coil temperature was set at process temperature (200 °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 by pumping water at the experimental flow rate (11, 22, 33, 44 and 55 mL/min) through the system for 30 min. At the same time, the reactor temperature was set to process temperature, causing a temperature profile until its stabilization. Pressure was kept constant in 20 MPa. Hydrolysate samples were collected each 2 min. In the second set of experiments, the amount of raw material was increased by a factor of 5.5 (11.0 g) and SWH was performed with different temperatures (213, 251 and 290 °C) while maintaining flow rate (33 mL/min) and pressure (20 MPa) constant. The process was also performed for 30 min and samples were collected each 2 min. All experiments were performed in duplicate.

**Total reducing sugars determination** - Total reducing sugars were determined by the colorimetric Somogyi-Nelson method [4,5].

**RESULTS AND DISCUSSION**

In the first set of experiments, the inlet and outlet temperature in the reactor were the same, and adjusted to 200 °C in the equipment. However, the outlet temperature increased a little with flow rate, probably due to more efficient heat transfer, so that for the flow rates of 11 mL/min, 22 mL/min, 33 mL/min, 44 mL/min and 55 mL/min the reactor outlet temperatures were 194 °C, 205 °C, 208 °C, 212 °C and 214 °C, respectively. Also, the higher the flow rate, the longer the time to stabilize the temperature.
The liquefaction degree of the samples was the same for all flow rates studied (68-72 %); however, in Figure 1 it can be noticed that total reducing sugars increased with flow rate, probably due to the lower residence time in the reactors, which decreases time for degradation of glucose.

In the second set of experiments, the influence of water temperature was evaluated. The flow rate was kept constant at 33 mL/min. The inlet and outlet temperatures in the reactor were the same in each experiment (213, 251 and 290 °C). Increasing the raw material load in the reactor from 2 g to 11 g, keeping the other operation conditions constant, did not affect the sugars yield; however, the maximum concentration of sugars in the hydrolysate increased from 600 mg/L to 3500 mg/L.

The solid residue in the end of the process was 31 %, 5 % and 8 % for 213 °, 251 ° and 290 °C, respectively. However, total reducing sugars recovered did not increase with temperature (Figure 2). On the other hand, the higher the temperature the lower was the time to reach maximum sugars recovery.

CONCLUSION

Maximum total reducing sugars recovered for sugarcane bagasse using SWH was 23.1 % from total raw material. Considering the cellulose + hemicellulose content of sugarcane bagasse is around 60-70 %, sugars yield was 33-38 %, which is close to literature data on optimized SWH of pure cellulose. Therefore, SWH seems a promising technology for the recovery of fermentable sugars from sugarcane bagasse, to be considered among other chemical and biological methods of hydrolysis.

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REFERENCES


FIGURES

Figure 1. Total reducing sugars in glucose equivalents recovered in the SWH of sugarcane bagasse at different water flow rates.

Figure 2. Total reducing sugars in glucose equivalents recovered in the SWH of sugarcane bagasse at different temperatures.