ACID PRETREATMENT ON CORN COB AND SOYBEAN HULLS TO PRODUCE HEMICELLULOSIC AND CELLULOSIC HYDROLYSATE

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ABSTRACT

Soybean and corn production are among the largest in the world, generating residues such as soy husks and corn cobs. An alternative is using these residues in a biorefinery concept. For that, it is necessary to perform a pretreatment to recover the sugar from the cellulose and hemicellulose fraction. The acid pretreatment presents advantages allows to generate separate fractions of sugars (xylose and glucose). In this sense, the main goal of this study was to apply the acid pretreatment to corn cob and soybean hulls to generate fermentable sugars. By using 2% sulfuric acid and a biomass liquid-solid ratio of 10 ($Kg_{water}/Kg_{biomass}$) for 121ºC and 60 min was possible to obtain a hemicellulosic hydrolysate of 34.99 ± 0.25 and 16.69 ± 0.22 $g \cdot L^{-1}$ of xylose for corn cob and soybean hulls, respectively. Meanwhile, after 4 days of saccharification, using 15 $FPU/g_{biomass}$ and liquid-solid ratio of 10 ($Kg_{water}/Kg_{biomass}$) , it was possible to obtain 18.1 ± 1 and 25.6 ± 1.1 $g \cdot L^{-1}$ of glucose for corn cob and soybean hulls, respectively. However, due to factors such as temperature and time, the concentration of glucose was lower than expected. Lastly,these results showed that the pretreatment has a high capacity for valuing agricultural residues.

Keywords: Biomass. Fermentable sugars. Acid pretreatment. Hydrolysate.

1 INTRODUCTION

The implementation of a new technology in biofuel production can allow the reduction in the use of fossil materials. In this way, it is necessary to seek more balanced ways that promote sustainability in the economic, social, and environmental spheres [1]. A strategy for global geoeconomic development is the use of biomass, which has resources available worldwide, in biorefineries [2]. Brazil is one of the largest grain producers in the world, for the 2023/24 harvest a production of 146.9 million tons of soybean and 87.35 million tons of corn was estimated [3]. The production of these biomasses generates waste such as straw, cob, and hull, which are generally destined for combustion or left in the field, so one way of valorize these wastes is the production of biofuels [4].

Pretreatment is essential for removing recalcitrant constituents from biomass (hemicellulose and lignin), seeking richness in cellulose and improving the yield and efficiency of the lignocellulosic biomass bioconversion process [5]. Chemical pretreatment (such as acid pretreatment) breaks the structure of the biomass, solubilizing its cell wall, and facilitating access for the cellulolytic enzyme. This type of pretreatment is influenced by treatment time and temperature and is higly effective for biomasses with higher lignin content [6]. This study aims the production of hydrolysate, resulting from the decomposition of biomass by the acid pre-treatment, investigating the structure of the in natura biomass and of its constituents after the pre-treatment.

2 MATERIAL & METHODS

The lignocellulosic composition of the solid samples was determined according to National Renewable Energy Laboratory (NREL). Soybean hull was used without milling and corn cob was used with a particle size ≥ 1 mm. Sequential extraction with ethanol and water in raw material was used to determine extractive content according to the procedure NREL/TP-510 − 42,619. Cellulose, hemicellulose, lignin, and ashes were quantified according to the protocols [7]. After acidic biomass treatment (300 mg material in 72% H_2SO_4 for 1 h at 30ºC followed by 4% dilution (84 mL water) and autoclaved at 121 ◦C for 1 h), the solid was separated from the liquid. The liquid was filtered using a gravity filtration apparatus - ratus and the acid-soluble lignin was measured at 240 nm in a quartz cuvette. The solid was washed and placed in an oven at 100ºC overnight to obtain the insoluble lignin value. The dry solid was subsequently taken to a muffle furnace at 575ºC for up to 24 h to determine the ash content.

The acid pretreatment was carried out as described by Li et al, (2016). Briefly, diluted sulfuric acid (H_2SO_4) at 2% was added to the biomass at a liquid-solid ratio (LSR) of 10 ($Kg_{water}/Kg_{biomass}$). After, the serum bottle was placed in the autoclave at 120°C for 60 min. Subsequently, the solid residues were filtered and washed until reaching a neutral pH. The solid fractions were separated and taken to an oven at 100°C for 24 h and weighed. The liquid fraction was characterize by High-Performance Liquid Chromatography (HPLC), according to describe bellow.

The saccharification was performed using the LSR of 10 at pH 4.8 using citrate buffer (50 mM). The enzyme (Celic® Cetec 2) was added at 15 $FPU/g_{biomass}$. The flasks were placed on a shaker at 50°C and continuously shaken for 6 days at 200 rpm. Samples were taken for 6 days and centrifuged to separate insoluble solids. The supernatant was analyzed by HPLC to determine the concentration of fermentable sugars, as described below.

The quantification of xylose, glucose, arabinose, HMF, furfural, and cellobiose was carried out by HPLC (Shimadzu, Japan) equipped with RI detector and an Aminex HPX 87H column (300 mm × 7.8 mm). The 15 µL injection was eluted with a mobile phase of 5 mM H_2SO_4 at a flow rate of 0.6 mL/min at 45ºC. Sugar concentrations were determined from standard lines.

3 RESULTS & DISCUSSION

The composition of both types biomass is shown in Figure 1. The hemicellulose contents of 24.2% and 13.2% are found for the corn cob and soybean hulls, respectively. While, the cellulose content was 30.4% and 36.8% for corn cobs and soybean hulls. The composition of the biomass varies with the species and the measured values are within the range reported in the literature, about 20-40% hemicellulose and 30-50% cellulose [8].

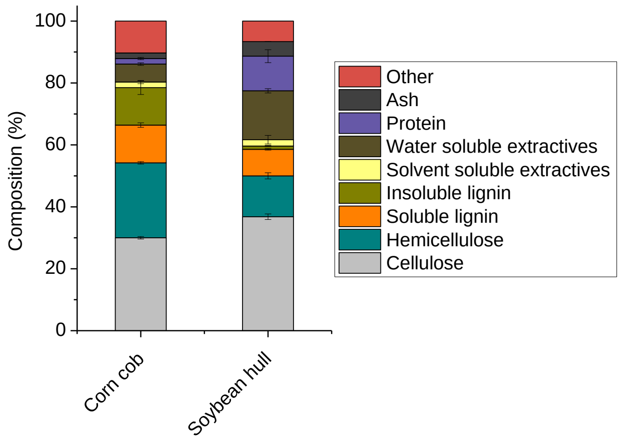

Figure 1: Composition of corn cobs and soybean hulls

Table 1 presents the determination of sugars for both corn cob and soybean hulls after acid pretreatment. The high xylose concentration values indicate that degradation of hemicellulose occurred, according to the composition of the biomass, as shown in Figure 1. This occurs because corn cobs contain more hemicellulose than soybean hulls, generating a greater quantity of xylose, while soybean hulls have higher cellulose content than corn cobs. The low production of HMF and furfural in both biomasses is highly positive. The formation of these compounds might inhibit further fermentation process [9].

Table 1: Composition of the hemicellulosic hydrolyzate obtained by acid pre-treatment of soybean hulls and corn cobs.

Component	Corn cob hemicellulosic hydrolyzate	Soybean hull hemicellulosic hydrolyzate
Cellubiose (g L^{-1})	1.9 ± 0.01	1.99 ± 0.08
Glucose (g L^{-1})	2.9 ± 0.01	4.11 ± 0.01
Xylose (g L^{-1})	34.9 ± 0.25	16.69 ± 0.22
Arabinose (g L^{-1})	3.4 ± 0.11	5.70 ± 0.1
Acetic acid (g L^{-1})	7.6 ± 0.19	2.82 ± 0.05
HMF (g L^{-1})	-	0.31 ± 0.01
Furfural (g L^{-1})	0.4 ± 0.03	-

After 4 days of saccharification, the glucose concentration reached a maximum of 18.1 ± 1.0 g·L^{-1} for corn cobs (Figure 2A). While, after the saccharification of soybean hulls (Figure 2B) the glucose concentration was 25.6 ± 1.1 g·L^{-1}.

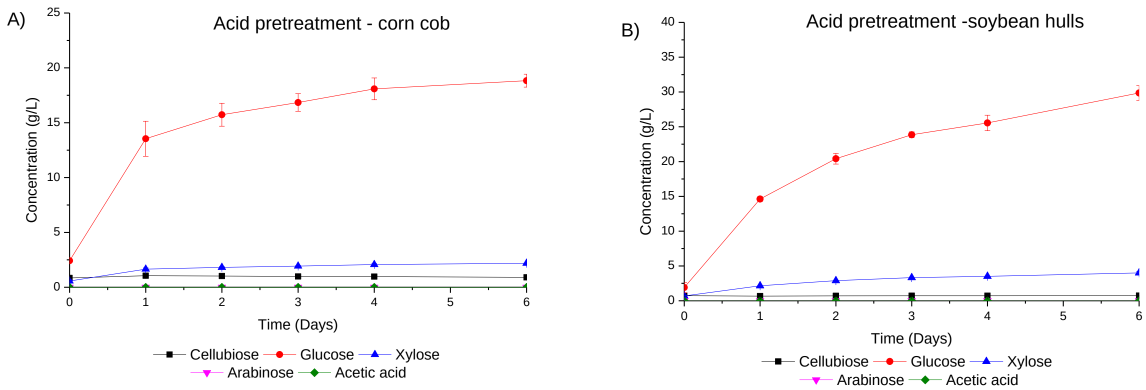

Figure 2: Concentration of the components after the saccharification. A) corn cob and B) soybean hulls.

The low concentration of xylose, after the saccharification of both biomasses, corroborate with the results shown in Table 1, which present high values for this component. Meanwhile, the glucose concentration is lower than expected. This can be attributed to the time and temperature used in pre-treatment.

4 CONCLUSION

Acid pretreatment shows high performance in breaking down the structure of soybean hulls and corn cobs, obtaining a significant amount of xylose, one of the main components for the production of value-added products. However, some changes in the methodology will be necessary to improve the saccharification result.

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