EVALUATING THE EFFICIENCY OF PLASMA PRETREATMENT: A CASE STUDY WITH CORN COB

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This study aims to evaluate the performance of the delignification of corn cob as well as well as the release of cellulose and hemicellulose using non-thermal plasma for future application in biorefineries. The corn cobs were first characterized following the protocol of the National Renewable Energy Laboratory (NREL). The plasma pretreatment was carried out in a quartz reactor with Teflon cap and flat-tip electrodes attached 17 kV power source, at a voltage of 220 V, and alternating current of 30 mA. The ground corn cob particle size range chosen for pretreatment was up to 0.6 mm, with a liquid-to-solid ratio (LSR) of 20:1 and an exposure time varying between 5 to 60 min. The characterization of the chemical composition before pretreatment of the corn cobs revealed 31.92 % cellulose, 22.80 % hemicellulose, and 25.10 % total lignin. Plasma pretreatment of ground corn cobs also caused an increase in the crystallinity index, proving to be a promising alternative for pretreatment.

Keywords: Corn cob. Plasma pretreatment. Lignocellulosic biomass. Biorefinery.

1 INTRODUCTION

The usage of fossil fuels brings up various environmental impacts. Therefore, the search for alternative resources becomes imperative (AKRAM et al., 2023). In this sense, lignocellulosic biomass becomes a great candidate for this change since it is abundant, renewable, and can be converted into various products with high added value, including biofuels (KARUPPASAMY et al., 2023).

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, lignin, and other minor components (proteins, extracts, and ashes) (AKRAM et al., 2023; MARTINS-VIEIRA et al., 2023). Lignocellulosic biomass such as corn cobs, soybean hulls, sugar cane bagasse, and coconut shells, among others can be utilized as raw materials to produce a range of products (KRISHNA KOUNDINYA et al., 2023; LEE et al., 2022), such as biofuels, chemicals, biopolymers, and other bioproducts (MUJTABA et al., 2023)

Corn is the second most produced crop in Brazil, with approximately 107.72 million tons of grain produced in 2021 (MARTINS-VIEIRA et al., 2023), with corn cob representing about 14% of its total mass (KUNTAPA; SUDAPRASERT; TACHAAPAIKOON, 2021). However, most of the corn residues (corn cob, corn husks, leaves, and stalks) are often abandoned in the field or burnt (CHOI et al., 2022), resulting in environmental pollution and not to mention the waste of resources. In terms of composition, corn cob presents cellulose (30 ± 0.5%), hemicellulose (34.0 ± 1.0%), and lignin (18.4 ± 0.3%) (XU et al., 2017). Nevertheless, to access the sugars it is imperative to perform a pretreatment process to dismantle its structure due to the rigidity imposed by the presence of lignin (DESHPANDE et al., 2022; SUNKAR; BHUKYA, 2022).

A variety of methods have been utilized for biomass pretreatment (QIAO et al., 2022). Lately, there has been increasing curiosity in investigating innovative emerging technologies that are environmentally friendly and maintain the innate properties of biomass, such as plasma treatment (PEREIRA et al., 2022). Plasma is an innovative technology that operates by generating a discharge current between two conductive electrodes (LAROQUE et al., 2022). This discharge, in contact with water or air, generates free radicals, reactive species, and ions, and promotes high-energy levels that significantly enhance reaction rates in the reactor (PEREIRA et al., 2021a). Plasma is highly effective in breaking down recalcitrant materials, such as lignocellulosic materials, due to its ability to produce a range of highly reactive species (LIM; ZULKIFLI, 2018). Furthermore, plasma technology is environmentally sustainable, conserving the inherent characteristics of biomass and causing minimal adverse environmental effects. Pereira et al. (2021) demonstrated that plasma pretreatment of brewery industry residues results in significant lignin removal. In this context, the objective of this study was to evaluate the effectiveness of non-thermal plasma for the pretreatment of corn cob and to investigate the effect of exposure time on this process.

2 MATERIAL & METHODS

2.1 Raw Material

The corn cobs used in the experiments were purchased in a local store in the city of Mafra (SC), ground, and sieved to select particles with a particle size X ≤ 0.6 mm and stored in polyethylene bags at room temperature for subsequent uses.

2.2 Compositional Analyses of raw material

The compositional analysis of corn cob was carried out using standard protocols for biomass analysis from National Renewable Energy Laboratory (NREL), USA as reported by (SLUITER et al., 2008; NREL, 2014).

The extractives were determined by sequential Soxhlet extraction with water and ethanol using a cellulose cartridge. The ash content was measured by keeping the dried samples in a muffle at 575 °C for 4 h and finally decreased to 105 ºC.

The contents of cellulose, hemicellulose, and lignin were determined after acid hydrolysis (NREL, 2014). First, 300 mg of dried corn cob was weighed and hydrolyzed by adding 3 mL of 72 % (v/v) sulfuric acid (H_2SO_4) for 1 h at 30 °C. Then, 84 mL of distilled water was added to the reaction mixture. Next, the samples were autoclaved at 120 °C for 1 h and passed through crucibles. The weight of acid-insoluble lignin was determined using the retentate, and soluble lignin was quantified in the permeate by UV-Vis spectrophotometry at 280 nm. Structural sugars, after the acidic hydrolysis, were quantified using an Aminex HPX-87H column in HPLC, using a RI detector at 45 °C and a mobile phase 0.005 M H_2SO_4 at a flow rate of 0.6 mL/min. Monomeric sugars were used as standards for structural carbohydrate HPLC analysis.

2.3 Plasma pretreatment of biomass

The plasma pretreatment was performed using a quartz reactor of 200 mL, with Teflon cap, having flat-tip electrodes in it, operating under atmospheric pressure. To generate plasma, the reactor was coupled to a 17 kV power source, at a voltage of 220 V, and alternating current of 30 mA. Around 8 g of corn cob with particle size of x ≤ 0.6, and liquid-to-solid ratio (LSR) of 20:1 was used in 150 ml of distilled water and kept under stirring at 500 rpm in the reactor. In total, fifteen samples were prepared, kept for 30 min to ensure hydration, and finally, five different exposure times were used: 5, 15, 30, 45 and 60 min of plasma pretreatment, which were performed in triplicate.

After the pretreatment, the samples were filtered under vacuum. Firstly, the liquid was collected and the retained solid, was washed with distilled water until a neutral pH was reached, dried in an oven at 105°C and the collected liquid sample stored at -20 °C. The characterizations were made the same way as described in item 2.2.

3 RESULTS & DISCUSSION

3.1 Characterization of the raw corn cob

The chemical composition of corn cob regarding the structural (cellulose, hemicellulose and lignin content) and the non-structural components (ash and extractives) is shown in Table 1.

Table 1*: Main components of corn cob.*

Composition	This work	(Xu et al. 2017)	(Baptista et al. 2018)	Pointner et al. 2014
Cellulose (%)	31.92 ± 1.08	30.0 ± 0.5	27.32 ± 0.24	32-42
Hemicellulose (%)	22.80 ± 0.87	34.0 ± 1.0	Xylan: 30.89 ± 0.45 Arabinan: 3.52 ± 0.22	42-48
Lignin (%)	25.10 ± 0.22	18.4 ± 0.3	22.92 ± 0.84	10-18
Extractives (%)	7.61 ± 0.42	16.0 ± 0.8	6.05 ± 0.22	-
Protein (%)	1.75 ± 0.35	-	-	4.26 ± 0.96
Ash (%)	1.82 ± 0.04	1.6 ± 0.2	-	2.88 ± 0.11

The percentages of cellulose and lignin respectively were within the ranges reported in previous studies (Baptista et al. 2018; Pointner et al. 2014). The difference in hemicellulose content comparing to literature, may be attributed to seasonal or genetic variations within the corn plants. In addition, it is notable that this value is close to the hemicellulose content typically found in sugarcane bagasse (24%), a biomass extensively utilized in the production of diverse bioproducts (SAHA et al., 2019).

3.2 Corn cob pretreatment

The effect of plasma pretreatment exposure time, was evaluated in this study. Table 2 shows the weight loss, cellulose, hemicellulose lignin and crystallinity after plasma pretreatment.

Table 2*: Effect of exposure time during corn cob pretreatment with plasma*

Composition	**Raw Corn Cob**	**5 min**	**15 min**	**30 min**	**60 min**
Weight loss (%)	-	15.84 ± 0.35	16.16 ± 0.174	16.16 ± 0.174	17.14 ± 1.05
Cellulose (%)	31.92 ± 1.08	34.48 ± 0.87	32.04 ± 1.15	24.97 ± 2.20	32.81 ± 0.59
Hemicellulose (%)	22.80 ± 0.87	25.82 ± 0.37	22.89 ± 0.88	21.45 ± 1.94	28.58 ± 0.71
Total Lignin (%)	25.10 ± 0.22	24.20 ± 3.64	22.12 ± 0.91	22.13 ± 0.74	25.26 ± 0.68
Crystallinity index (%)	33.45 ± 0.91	38.84 ± 3.40	38.41 ± 2.47	38.64 ± 0.65	37.21 ± 1.19

Under tested conditions, plasma was not effective in altering the composition of solid fraction of ground corn cobs in the 5 min to 60 minute of exposure time. On the other hand, there has been an increase in crystallinity, indicating a change in the structure of the material. In this way, to draw a more conclusive assessment, it is necessary to characterize further properties, such as the composition of the liquid fraction after the pretreatment, as well as to evaluate the properties of the sugars after enzymatic saccharification.

4 CONCLUSION

The conclusions of this work are preliminary, as this is an ongoing study. While the use of plasma pretreatment resulted in weight loss and increase in crystallinity, further analysis is necessary to evaluate the efficiency of plasma pretreatment. Specifically, the composition of the corn cob after an evaluation of the liquid fraction as well as the release of sugars after enzymatic saccharification will be performed in the next steps of the study.

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