

THE CONVERSION OF CORNCOB BIOMASS CAN BE ACCELERATED BY AUTOHYDROLYSIS WITH CITRIC ACID

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ABSTRACT

Hydrothermal pretreatment (HTP) of biomass, specifically corncob, shows promise for biorefining, and citric acid (CA) enhances the depolymerization of lignocellulosic biomass, particularly hemicellulose. This study investigated the effects of CA on the chemical and physical changes of residual biomass and the extraction of bioproducts such as xylooligosaccharides (XOS) and phenolic compounds (PC). Corncobs were processed in a pressurized reactor at 180 °C for various periods (0, 20, 40, 60 min), with and without AC. The residual biomass was characterized for cellulose, hemicellulose, lignin; the liquid fractions were analyzed for sugars, furfural, hydroxymethylfurfural and phenolic compounds. AC effectively removed hemicellulose within 20 min, increased cellulose (~62%) and lignin (~38%) content, and induced significant physical changes detectable by X-ray diffraction and thermogravimetric analysis. CA drastically reduced the XOS content in the liquid fraction compared to samples without CA and altered the profile of phenolic compounds obtained. These results highlight the potential for biorefinery applications, although optimization is required to improve efficiency.

Keywords: Corncob. Citric acid. XOS. Hydrothermal pretreatment. Phenolic compounds.

1 INTRODUCTION

Corncob, a significant byproduct of corn farming, represents an important agroindustrial waste stream. Meanwhile, hydrothermal pretreatment is a promising technology for biorefining corncob into valuable products. CA is a non-toxic and biodegradable organic acid that has been shown to effectively remove hemicellulose from lignocellulosic biomass. HTP of corncobs with citric acid shows promise for enhancing the production of biofuels and bioproducts. Lignocellulosic materials such as corncobs can pose problems during enzymatic hydrolysis, as lignin acts as a barrier and prevents enzyme access to cellulose and hemicellulose components¹. To overcome this challenge, several pretreatment methods have been explored to remove or modify the lignin content in corncobs². One such method is pretreatment with dilute acid to break down lignin and facilitate separation of cellulose and hemicellulose from the lignocellulosic matrix¹. On the other hand, it is important to analyze the structural changes of the biomass, in order to evaluate its potential to obtain bioproducts. The present study explored the potential of HTP with citric acid in the medium to evaluate changes in residual biomass and liquid extraction of bioproducts such as xylooligosaccharides and phenolic compounds.

2 MATERIAL & METHODS

Corncob (5-8 mesh) were subjected to a HTP in a pressurized reactor with a 2 L stirred tank to process 50 g of corn cob with a solid-liquid ratio of 5%. Two series of experiments were conducted: one with CA (1% liquid) and one without acid. The process was constantly maintained at 180 °C for varying periods (0, 20, 40, 60 min from the time the target temperature was reached). The main components of the corncob and residual biomass, the oligosaccharides such as cellulose, hemicellulose and lignin were determined according to the National Renewable Energy Laboratory (NREL). Physical changes were analyzed by X-ray diffraction including crystallinity³ and thermogravimetric analysis (TGA). The supernatant was analyzed by high-performance liquid chromatography to determine the content of sugars and PC, including furfural (FF) and hydroxymethylfurfural (HMF), and the XOS content was estimated by subsequent hydrolysis.

3 RESULTS & DISCUSSION

To evaluate the effect of HTP, the solid and liquid fractions obtained were evaluated. According to these analyses, citric acid (CA) effectively removed hemicellulose from the cob in only 20 minutes of processing, which resulted in an increase in cellulose (~62%) and lignin (~38%) content. The absence of citric acid in HTP did not result in complete removal of hemicellulose, leaving a residual content of approximately 6% after 40 and 60 minutes of processing. These results were quite efficient when compared to what was previously reported⁴, where despite optimizing with twice the CA, hemicellulose was still detected in the residual cocoa husk biomass⁵. It also compares with another work, where the residual hemicellulose content was reduced to 15%⁶.

The HTP process with citric acid was also able to increase the corncob crystallinity index from 35% in the untreated sample to 54% at 0 minutes, 60% at 20 and 40 minutes of processing, and up to 65% at 60 minutes of processing. In contrast, the HTP process without CA also gradually increased the crystallinity from 45% at 0 minutes, 52% at 20 and 40 minutes, to 59% at 60 minutes processing. The crystallinity calculations were performed according to Segal's method³. The crystallinity estimated by Segal's method may overestimate the degree of crystallinity of the biomass, but at the same time it provides a parameter for

comparison⁷. When analyzing the X-ray diffraction patterns of the biomass (Figure 1A and 1B) a trend towards increasing peaks ($\sim 16.5^\circ$, $\sim 22^\circ$ and $\sim 34.5^\circ$) was observed, of which we have reference that at least in the case that the first two are associated with increasing crystallinity⁸. X-ray diffraction patterns of biomass are useful for determining the composition and crystalline structure of cellulose and lignin present in corncob or other lignocellulosic materials. Both during the X-ray pattern changes and in the case of TGA analysis, a higher rate of change associated with the presence of CA was noted. TGA showed that the main degradation step occurred in the temperature range of 200 to 500 °C, showing a mass loss of $\sim 90\%$ in most of the biomasses. In the first derivative of the sample weight shown in Figure 1C and 1D, two overlapping peaks are noted producing a single peak, which could represent the decomposition of hemicellulose, and a higher temperature peak, representing the decomposition of cellulose⁹.

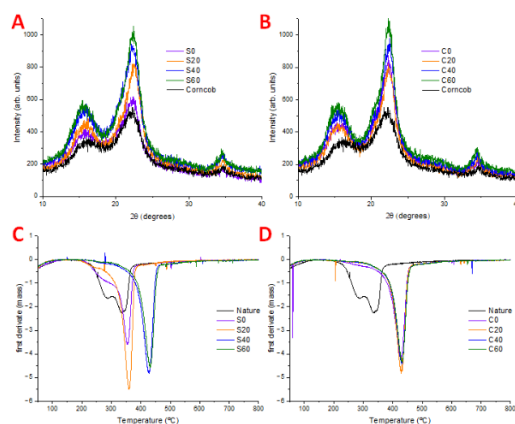


Figure 1. X-ray diffraction patterns of the biomass (A, B). First derivative curves of the mass from the biomass (C, D). Where, corncob is the unprocessed biomass; S0 is biomass processed for 0 minutes without AC; S20 is biomass processed for 20 minutes without AC; S40 is biomass processed for 40 minutes without AC; S60 is biomass processed for 0 minutes without AC; C0 is biomass processed for 0 minutes with AC; C20 is biomass processed for 20 minutes with AC; C40 is biomass processed for 40 minutes with AC; C60 is biomass processed for 60 minutes with AC.

Notably, starting the process with citric acid at 20 min yielded a higher concentration of xylose sugars in the liquid phase ($\sim 14\text{g/L}$). This could lead to the generation of by-products such as FF ($\sim 6\text{ g/kg d.m.}$) and HMF ($\sim 13\text{ g/kg d.m.}$) with longer process times (Figure 2A and 2C). In the case of FF, it is well known that it is a product of xylose dehydration¹⁰, whereas HMF can be produced from any six-carbon sugar¹¹. This corresponds to a hemicellulose degradation, that under more severe process conditions oligosaccharides and glucose are released from crystalline cellulose¹², which can be related to the increase in FF and HMF. Regarding the XOS content, while the acid-free process produced up to 175 g/kg d.m. after 20 and 40 minutes of processing, the presence of citric acid seems to drastically decrease the XOS content in the liquid fraction. Other literature reports do not make this type of comparison⁴⁻⁶; therefore, it is a challenge to continue with this type of comparison. Another important aspect is the increase in the release of phenolic compounds (Figure 2A), with a significant increase when citric acid was used in the medium. Phenolic compounds are usually formed as a result of hydrothermal degradation of lignin¹³. The comparisons by principal component analysis (Figure 2B) manage to group more than 70% of the total variability, and the differences between treatments are notable in the first principal component, where at least three groups can be observed: processing biomass without addition of CA (associated with the release of gallic acid, vanillic acid, vanillin and 4-hydroxybenzoic acid); processing with a heating time of zero minutes, with and without CA; and processing biomass with CA in medium (associated with release of ferulic acid and coumaric acid).

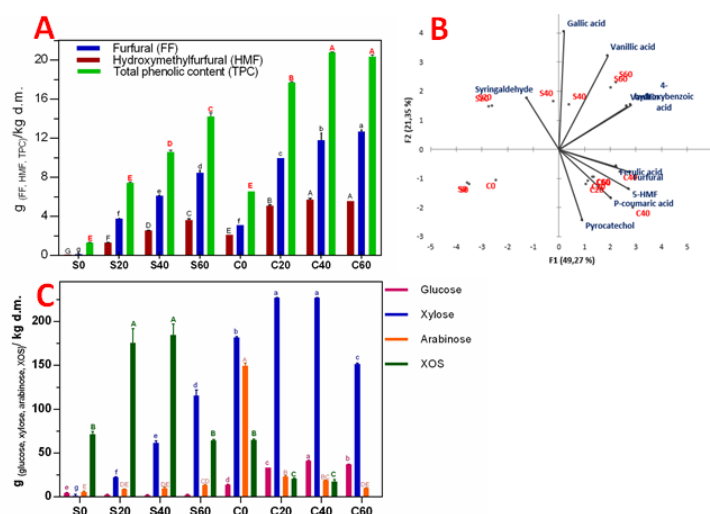


Figure 2. Phenolic compounds (PC), furfural (FF), and hydroxymethylfurfural (HMF) content in liquid fraction (A). Principal Component Analysis for PC (B). Sugars and XOS content in the liquid fraction (C). Where, corncob is the unprocessed biomass; S0 is biomass processed for 0 minutes without AC; S20 is biomass processed for 20 minutes without AC; S40 is biomass processed for 40 minutes without AC; S60 is biomass processed for 0 minutes without AC; C0 is biomass processed for 0 minutes with AC; C20 is biomass processed for 20 minutes with AC; C40 is biomass processed for 40 minutes with AC; C60 is biomass processed for 60 minutes with AC.

These results are related to those reported previously, where some monomers of phenolic and benzene derivatives such as vanillin, 2-methoxyphenol, 2-ethylphenol, p-xylene and 1,3-dimethylbenzene were also identified¹⁴. These findings are of utmost importance, since recently, bioactive compounds, and especially phenolic compounds (PC), have aroused enormous interest in the scientific community due to their positive effects on human health related to antioxidant activity¹⁵.

4 CONCLUSION

HTP with CA in the medium successfully removed all hemicellulose from the cob. Treatments without CA also depolymerized hemicellulose, though not completely. HTP processing increased cellulose and lignin concentrations in the residual biomass and induced physical changes, as evidenced by X-ray crystallinity patterns and TGA analysis. The liquid fraction from treatments without CA was rich in XOS, indicating further depolymerization, while citric acid in the medium resulted in a different PC content profile. These findings highlight HTP's potential for biorefinery applications and offer opportunities to enhance process sustainability.

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