

Pre-treatment of biomass with HCl gas for selective removal of hemicellulose

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ABSTRACT

In this study, anhydrous hydrogen chloride gas was employed to selectively hydrolyze hemicellulose from aspen wood flour samples by utilizing a gas-solid system. Selectivity towards hemicellulose was achieved by adjusting the acid concentration inside wood flour samples to 36%, so only hemicellulose and disordered cellulose would be degraded during hydrolysis. The study demonstrates that pre-hydrolysis with HCl gas is an effective and selective method for removing hemicellulose from biomass.

KEYWORDS

Biomass, Concentrated acid hydrolysis, Gas-solid system, Hydrogen chloride gas, Pre-hydrolysis

INTRODUCTION

Anhydrous HCl gas has been used for concentrated acid hydrolysis in various studies and pilot scale operations since the late 19th century to convert biomass into oligo- and monosaccharides. However, most of this earlier research has concentrated on breaking down crystalline cellulose into glucose. [1,2,3,4] Concentrated acid hydrolysis can also be used for pre-hydrolysis, when the acid concentration is kept below the threshold required for the dissolution of crystalline cellulose. For example, hydrochloric acid has the acid concentration threshold of 40%. Under this threshold only hemicellulose and disordered regions of cellulose are hydrolyzed. [2] However, there have been no studies conducted with anhydrous HCl gas, where the acid concentration inside the biomass would have been deliberately adjusted to below 40% concentration for pre-hydrolysis. In this work the HCl concentration inside biomass is adjusted to 36% during gas hydrolysis under the pressure of 0.1 MPa for selective removal of C5-sugars from aspen wood flour samples.

EXPERIMENTAL

Materials

Oven-dried aspen (*Populus Tremula*) wood chips were provided by Avantium NV (the Netherlands). Wood chips were manufactured from debarked aspen logs sourced from Europe. Analytical grade furfural, 5-hydroxymethylfurfural, formic acid, acetic acid, levulinic acid and 25% analytical grade sulfuric acid were purchased from Merck. Millipore grade water (resistivity 18.2 MΩ, conductivity 0.8 μS/cm) was used for chromatography analyses. Deionized water was obtained from BIO2 departments de-ionized water system with water softener, reverse osmosis,

ion exchanger and UV-light manufactured by Eurowater (conductivity <1 uS/cm).

Methods

Carbohydrate composition of oven dried aspen wood flour samples was determined according to the analytical method NREL/TP-510-42618 [5]. Sugars were quantitated with high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) under the Dionex ICS-3000 system (Sunnyvale, CA, USA). MilliQ water was used as the mobile phase at a flow rate of 0.38 mL/min with a CarboPac PA20 column. Extractives were determined according to the analytical method SCAN-CM 49:03 and ash content was determined according to the analytical method NREL/TP-510-42622 [6]. Sugar composition in hydrolysis filtrates was determined according to the analytical method NREL/TP-510-42623 [7]. Dry matter content of the samples was determined according to the analytical method NREL/TP-510-42621 [8]. Furfural, hydroxymethylfurfural (HMF), formic acid acetic acid and levulinic acid were determined via high-performance liquid chromatography (HPLC) by using Dionex UltiMate 3000 HPLC (Dionex, Sunnyvale, CA, USA) equipment outfitted with ultraviolet (UV) detector and Rezex ROA-Organic Acid column (Phenomenex). Sulfuric acid solution (0.0025 mol/L) was used as the eluent at a flow rate of 0.5 mL/min. The column temperature was 55°C. Furfural and HMF concentrations in the liquid samples were determined by the UV detector at wavelengths of 210 and 280 nm.

Pre-hydrolysis of aspen wood flour samples with gaseous HCl

Aspen wood chips were grinded down with Wiley grinder through 1.9 mm screen and placed to 105°C oven for 24 h on open tray. After this the moisture content in the oven dry wood flour samples was adjusted to 20%, 40% and 60% by weight. Moisture content adjustment was conducted by spraying water to wood flour while mixing. Wood flour samples were then placed into sealed Minigrip packs and stored for 7 days in 5°C cold room to allow the wood flour to reach moisture equilibrium. After 7 days the dry matter content of wood flour samples was tested prior to hydrolysis. Pre-hydrolysis with anhydrous HCl gas was conducted with the HCl gas reactor at Aalto [9]. Hydrolysis was conducted with reaction times of 30 minutes, 2 h, 4 h, 6 h and 24 h under pressure. For each sample point 5 g of wood flour by dry weight was loaded to the 1 L reactor bottle. The reactor bottle was then placed into -1°C ice bath for half an hour to cool down the wood flour prior to hydrolysis. Cooling was necessary to avoid C5-sugar degradation from heat formation during HCl gas absorption. After the cooling, precalculated amount of HCl gas by weight was added to the reactor bottle to get HCl concentration to 36% inside the water phase. After the desired amount of HCl gas was

added to the bottle, the reactor bottle was pressurized with anhydrous nitrogen gas to reach 0.1 MPa pressure. The reactor bottle was kept in ice bath for the first 15 minutes of the reaction time and then placed to 21°C fume hood. Samples with total reaction time of 30 minutes were instead placed in 1 L of 21°C water to speed up warming to room temperature. For the last 10 minutes of the reaction time, the reactor bottle was placed in 3.7 liters of 55°C water to speed up the hydrolysis. After the heating pressure was released through the neutralization system and 1000 g of 95°C water was added to the bottle to stop hydrolysis reaction. Diluted sample was then left to cool down overnight. On the next day the hydrolysis filtrate was separated from hydrolysis residue by filtering it through 10 µm wire fabric. The dry matter content of residue was measured and hydrolysis filtrate was analyzed with HPAEC-PAD for carbohydrates and with HPLC for degradation products. To calculate the water-soluble carbohydrate yield from aspen wood flour, the total amount of sugar in the hydrolysis filtrates was measured, and then divided by the total available sugar in the wood flour.

RESULTS AND DISCUSSION

The total yields of water-soluble carbohydrates from pre-hydrolysis with anhydrous HCl gas are presented in Figure 1. From the Figure 1 can be seen

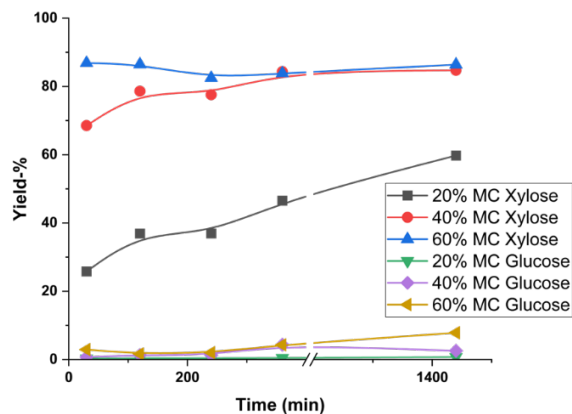


Figure 1. Yields of water-soluble carbohydrates from pre-hydrolysis with hydrogen chloride gas. With all moisture contents mainly hemicellulose is degraded.

that the degradation of cellulose to glucose and celooligosaccharides was minimal with all moisture contents. This indicates that mainly disordered regions of cellulose are degraded during hydrolysis. The yield of water-soluble xylose and xylooligosaccharides was moderate in the 20% moisture content but is significantly increased in 40% and 60% moisture contents. With these moisture contents it is possible to reach over 80% yields even with shorter reaction times. The highest yield of xylose and xylooligosaccharides (87%) was achieved with 60% moisture content and 30-minute reaction time. According to HPLC measurements from the

hydrolysis filtrates, the formation of furans and acids was minimal, with furfural being the most common degradation product. The highest amount of furfural was formed in the sample point with 60% moisture content and 24 h reaction time. In this sample point the furfural formation corresponded to only 1.6 % of the total available xylan in the sample. It is noteworthy, that unlike with higher HCl concentrations in gas hydrolysis [10], the wood flour does not turn into sticky paste when the acid concentration is adjusted to 36%. This would make the process more suitable for upscaling and could offer an alternative to the pre-hydrolysis step with 35% liquid hydrochloric acid in the Bergius-Rheinau process [11].

CONCLUSIONS

In this study aspen wood chips were successfully hydrolyzed with HCl gas for selective and efficient removal of C5-sugars. The optimal conditions were found to be at 60% moisture content and 30 minutes reaction time. Under these parameters it was possible to retrieve 87% of the available xylan from aspen wood flour with only 1% glucan degradation. This pretreatment process could have potential as a replacement for the pre-hydrolysis step with 35% hydrochloric acid in Bergius-Rheinau process.

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