

Production of water-soluble carbohydrates from aspen wood flour with hydrogen chloride gas

Antti Kilpinen and Eero Kontturi

Aalto University, Finland

Corresponding author: Antti Kilpinen >antti.kilpinen@aalto.fi <

ABSTRACT

The overall aim of this study was to optimize the reaction conditions for concentrated acid hydrolysis of aspen wood flour by employing anhydrous hydrogen chloride gas to produce fermentable sugars. Gas hydrolysis with HCl was conducted both with and without temperature control during the hydrolysis under relatively low pressure of 1 bar. Process parameters for HCl gas hydrolysis included the moisture content of aspen wood flour (0.7-50 %) and reaction time under pressure (30 minutes to 24 hours). Temperature control during gas hydrolysis was used to prevent excess degradation of C5-sugars during the gas application phase via cooling in ice bath and to speed up the hydrolysis reaction during the last 10 minutes via heating to 50°C. This enabled the hydrolysis to proceed in comparably mild temperature conditions, resulting in higher yields of water-soluble carbohydrates. In addition, liquid-phase hydrolysis with concentrated hydrochloric acid was conducted in concentrations of 32%-42% and 15 minutes to 24 hours reaction times for comparison with gas-phase process. Highest yield for water-soluble carbohydrates from aspen wood flour (92 % of available glucan and 91 % of available xylan) was achieved with temperature-controlled gas hydrolysis using 50% moisture content and 2 h total reaction time, which is in line with previous research and comparable to hydrolysis with concentrated (42%) hydrochloric acid.

Keywords: Concentrated acid hydrolysis, HCl, Biomass, Hydrogen chloride gas, Gas-solid system

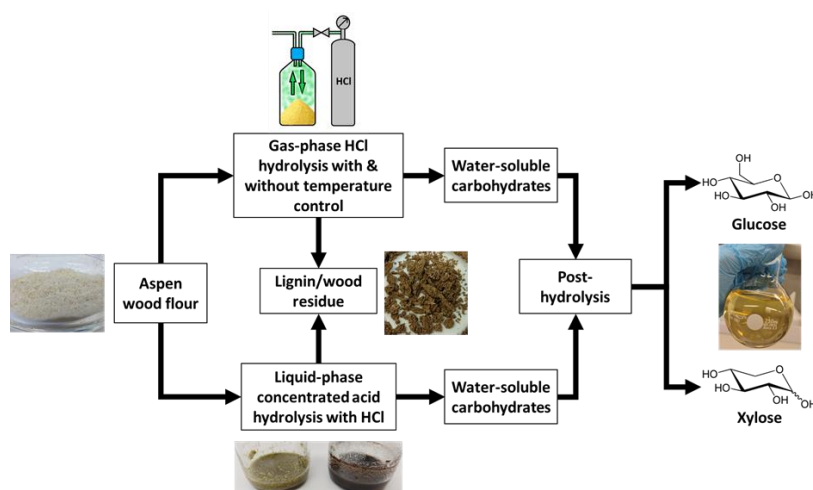


Figure 1. Visual abstract.

Introduction

Anhydrous HCl gas has been utilized for concentrated acid hydrolysis to break down lignocellulosic biomass into fermentable sugars with high yields (>80%) in various laboratory and pilot scale trials. (Blanch *et al.* 2011; Wenzl 1970; Higgins & Ho 1982; Kauko 1921) However, in previous studies the used HCl gas pressure has either been relatively high (5–42 bars) (Sharkov *et al.* 1971; Antonoplis *et al.* 1983; Wenzl 1970) or the wet biomass has been merely exposed to HCl gas without pressurizing in fluidized bed reactor (Hawley *et al.* 1983; Wenzl 1970; Higgins & Ho 1982) or blown through the hydrolysis feedstock in a blow through reactor (Higgins & Ho 1982).

In this study, wood flour from aspen (*Populus Tremula*) was hydrolyzed both with concentrated hydrochloric acid and gas-phase HCl by employing the gas hydrolysis reactor used by Pääkkönen *et al.* in 2018. The aim is to find optimal parameters to produce fermentable sugars using the relatively low HCl gas pressure of 1 bar.

Materials and methods

Hydrochloric acid stock solutions in concentrations of 32% and 36.1% were purchased from VWR. Aspen (*Populus Tremula*) wood chips were provided by Avantium and milled with Wiley mill M02 through a 1.9 mm screen. Reactor used by Pääkkönen *et al.* in 2018 was utilized for gas hydrolysis and for the concentration of hydrochloric acid to 39% and 42%

Anhydrous HCl gas hydrolysis was conducted both with and without temperature control during the hydrolysis under the relatively low pressure of 1 bar. Process parameters for HCl gas hydrolysis included the moisture content of aspen wood flour (0.7-50 %) and reaction time under pressure (30 minutes, 2 h, 6 h, & 24 h). Temperature control during gas hydrolysis was used to prevent excess degradation of C5-sugars during the gas application phase via cooling in ice bath and to speed up the hydrolysis reaction during the last 10 minutes via heating to 50°C. Liquid-phase hydrolysis with concentrated hydrochloric acid was conducted in concentrations of 32%, 36%, 39% and 42% and reaction times of 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 16 h and 24 h for comparison with gas-phase process.

Hydrolyzed carbohydrates in hydrolysis filtrates and carbohydrate composition of aspen were quantified according to analytical methods NREL/TP-510-42618 and NREL/TP-510-42623 by employing 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. Furfural and hydroxymethylfurfural (HMF) were determined from hydrolysis filtrates 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.

Results and discussion

Hydrolysis with concentrated hydrochloric acid

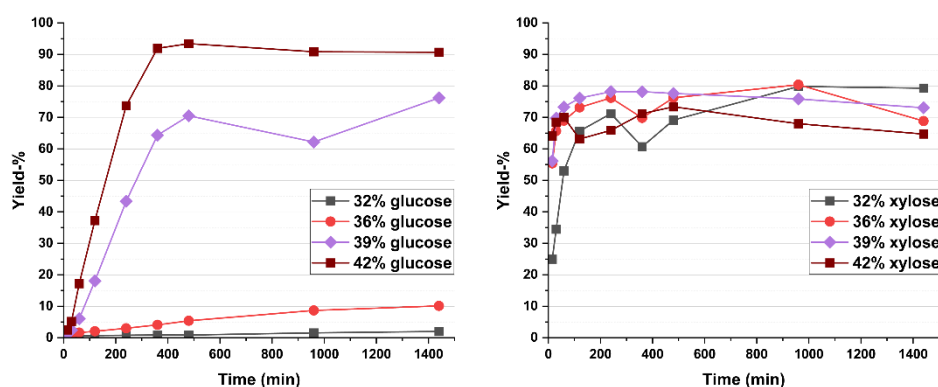


Figure 2. Yields of glucose and xylose (water-soluble carbohydrates) from aspen wood flour in hydrolysis with liquid hydrochloric acid at different acid concentrations over time in 21°C.

From the Figure 2 it can be observed that with HCl concentrations of 32% and 36% mainly the hemicellulose fraction is hydrolyzed along with some degradation of disordered regions of cellulose. When the HCl concentration is increased to 39%, around 70% of the cellulose is hydrolyzed to water-soluble oligosaccharides after 6 hours. After the HCl concentration is further increased to 42%, the yield of glucose rises to over 90 % after 6 h. This indicates that almost all crystalline cellulose has dissolved and broken down to water-soluble mono- and oligosaccharides during the hydrolysis.

From the yield of xylose, we can see that with all employed acid concentrations the maximum yield of xylose eventually plateaus to 60-80% after 2 hours of hydrolysis. This might indicate that in such high acid concentrations xylose degrades to furfural and other degradation products as the hydrolysis progresses. However, according to HPLC results, the amount of furfurals formed during the concentrated acid hydrolysis was quite negligible unless they turn immediately to humins.

Hydrolysis with anhydrous HCl gas

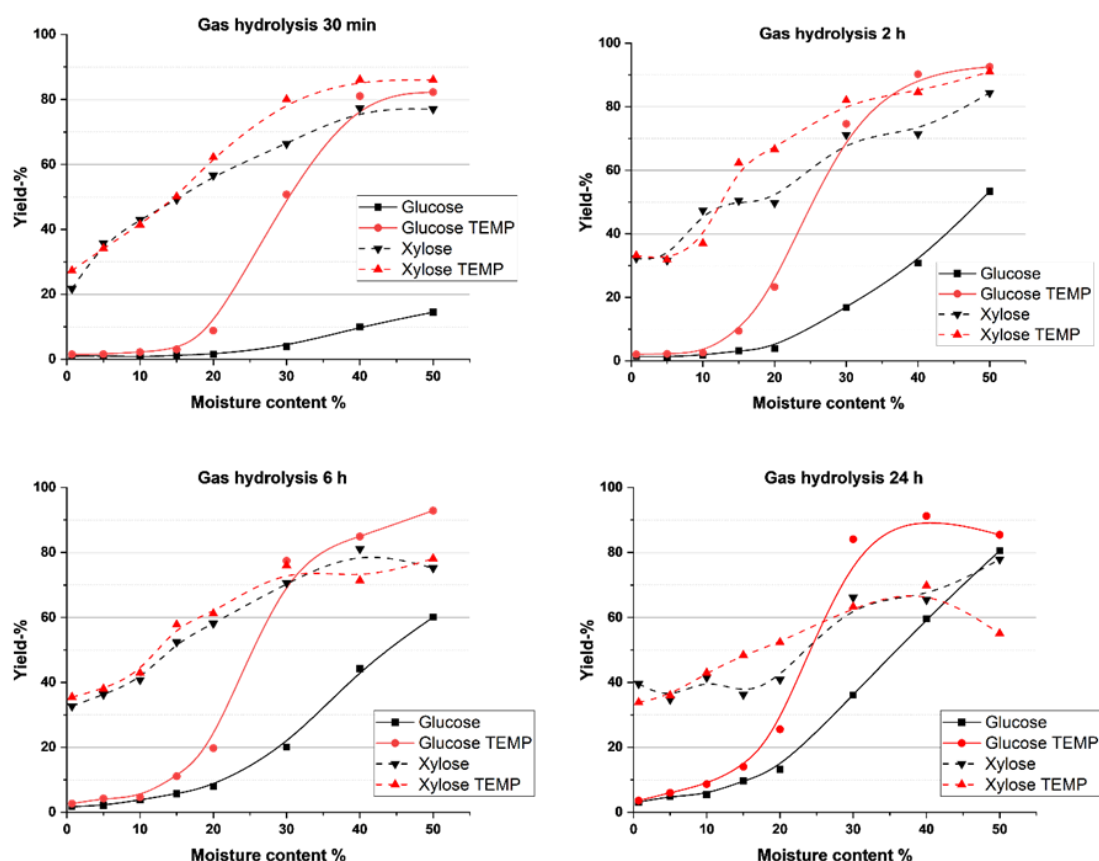


Figure 3. Yields of glucose and xylose from aspen wood flour in gas hydrolysis. TEMP refers to gas hydrolysis with temperature control.

In gas hydrolysis without temperature control, the yield of glucose and xylose increases with reaction time and moisture content. However, without temperature control the glucose yield starts to rise over 80% only with longer reaction time of 24 h and moisture content of 50%. With temperature control the hydrolysis efficiency is significantly improved and over 80% yields for both glucose and xylose are achieved already after 30 minutes of hydrolysis in moisture contents of 40% and 50%. Longer reaction times than 30 minutes increase the glucose yields to over 90%. However, the xylose yield starts to go down with increased reaction time due to sugar degradation.

Conclusions

It was possible to gain high yields of water-soluble carbohydrates from aspen wood flour both with liquid and gaseous HCl hydrolyses. Temperature-controlled gas hydrolysis produced high yields for both xylose and glucose without pre-hydrolysis step, even with relatively low pressure of 1 bar. The highest water-soluble carbohydrate yield from available xylan and glucan were 91% and 92% respectively. These yields were achieved with temperature-controlled gas hydrolysis at 50% moisture content using 2 h reaction time. Results are in line with previous research employing anhydrous HCl gas for hydrolysis.

Acknowledgements

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