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Pretreatment to Retrieve Xylose and Xylooligosaccharides by HCl Gas Directly from Biomass

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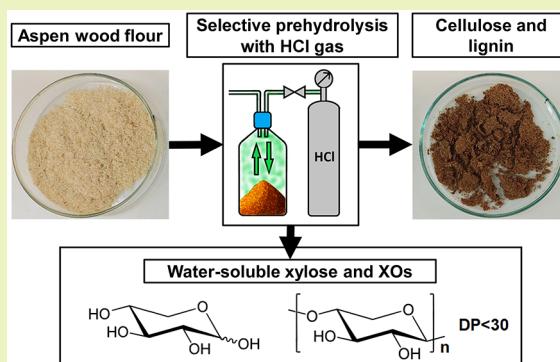
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ABSTRACT: In this study, anhydrous hydrogen chloride gas was employed to selectively hydrolyze hemicellulose from aspen wood flour utilizing a gas–solid system. Selectivity toward hemicellulose was achieved by adjusting the acid concentration inside wood flour to 36% during gas hydrolysis, so only hemicellulose and disordered cellulose would be degraded during hydrolysis. Process parameters included the moisture content of the aspen wood flour (20%, 40%, and 60%) and reaction times from 30 min to 24 h. The optimal reaction conditions for the production of xylose and xylooligosaccharides was achieved with 40% moisture content and 6 h reaction time. Under these parameters, it was possible to retrieve 84% of the available xylan from aspen wood flour with only 1% glucan degradation.

KEYWORDS: acid hydrolysis, biomass conversion, chain scission model, gas–solid reactions, selective hemicellulose saccharification



INTRODUCTION

Out of all macromolecular components in biomass—cellulose, hemicellulose, and lignin¹—the selective isolation and utilization of hemicellulose is probably the least scrutinized.² Particularly the degradation products of hemicellulose, i.e., mono- and oligosaccharides, would serve as versatile precursors for a diverse range of compounds through chemical or biotechnological processes.³ Xylan is among the most common hemicellulose species, and the monosaccharide of its backbone, xylose, can be utilized in the production of xylitol, ethanol, hydrogen, and single-cell proteins.⁴ Xylooligosaccharides (XO), in turn, have been promoted as prebiotics in food and dietary supplements, as functional additives in animal feed to promote gut health, and as potential ingredients in pharmaceutical and cosmetic formulations due to their bioactive properties.^{4–6} Pretreatment methods that degrade xylan into xylose and XOs directly from biomass do exist with hydrothermal pretreatment and dilute acid hydrolysis being the most extensively studied methods.⁷ However, high process temperatures in such processes may lead to the formation of unwanted degradation products.⁸ Concentrated acid hydrolysis can solve the problem as the hydrolysis of the polymer chain proceeds faster than the degradation product formation at low temperatures.⁹ Conventionally, concentrated acid hydrolysis is conducted via a liquid–solid system, but it is also possible to use a gas–solid system with anhydrous HCl gas. In this gas–solid system, HCl is sorbed into trace amounts of water, ambiently present within the solid biomass, leading to the formation of hydrochloric acid, which catalyzes the hydrolysis reaction. The benefits of this gas–solid approach include the

potential to utilize nearly dry biomass and the ease of acid separation through simple evaporation.¹⁰ 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 oligosaccharides and monosaccharides. However, most of earlier research has concentrated on breaking down crystalline cellulose into glucose^{11–17} or on isolating cellulose nanocrystals from fibers.^{10,18,19} The purpose of this study is to demonstrate the utilization of HCl gas as a pretreatment step for nearly exclusive hydrolysis of xylan directly from an aspen wood flour sample. The idea is to adjust the HCl concentration inside biomass to 36% under the pressure of 0.1 MPa, which enables the selective removal of C5 sugars as the HCl concentration is maintained under the 40% threshold where crystalline cellulose would be degraded.

RESULTS AND DISCUSSION

Aspen wood flour was hydrolyzed with anhydrous HCl gas in moisture contents of 20%, 40%, and 60% and with reaction times of 30 min and 2, 4, 6, and 24 h under pressure. While hydrolysis tends to be more effective at higher moisture levels, this comes with the drawback of increased HCl absorption into

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the wood, resulting in a higher HCl consumption and a greater demand on the recovery process. Therefore, different moisture contents were explored to determine the lowest efficient moisture content for hydrolysis.

During gas-phase hydrolysis, xylan molecules are broken down into xylose and XOs of different lengths. The total yields of these water-soluble carbohydrates from prehydrolysis with anhydrous HCl gas are presented in Figure 1. Figure 1 shows

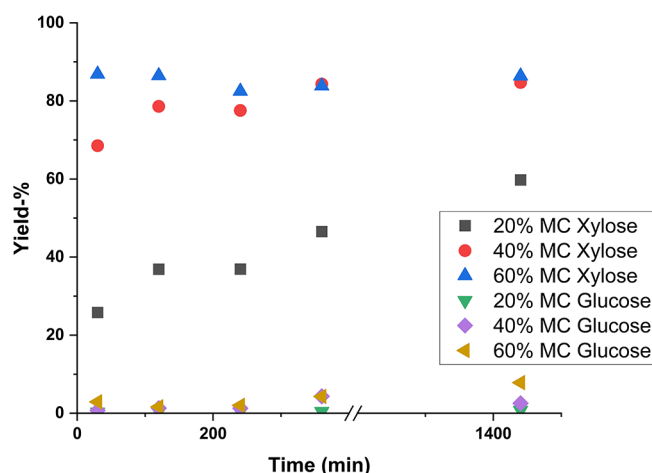


Figure 1. Total yields of water-soluble carbohydrates from prehydrolysis with hydrogen chloride gas on samples with varying moisture contents (MC).

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

Figure 2 shows the ratios between water-soluble monomeric xylose and XOs directly from HCl gas hydrolysis. In general, at

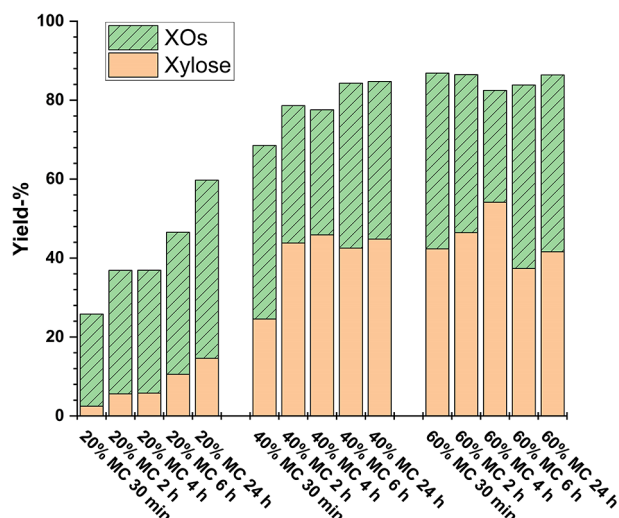


Figure 2. Ratios between water-soluble monomeric xylose and XOs directly from HCl gas hydrolysis.

moisture contents of 40%–60%, around half of the hydrolyzed xylan is in monosaccharide form with the rest being XOs with degree of polymerization of <30.²⁰ However, at 20% moisture content, most of the hydrolyzed water-soluble xylans are in oligosaccharide form.

Under acidic conditions, C6 (hexose) and C5 (pentose) sugars in biomass can undergo dehydration reactions, leading to the formation of key intermediates, such as 5-hydroxymethylfurfural (HMF) and furfural. These intermediates can further react into formic acid, levulinic acid, and humins through complex chemical pathways, ultimately affecting the overall yield of valuable products in biomass conversion processes.²¹ According to HPLC measurements from the hydrolysis filtrates (Figure S1), the formation of furans and acids was minimal, with furfural being the most common product of further reactions. The highest amount of furfural was formed at the sample point with 60% moisture content and 24 h reaction time. In this sample point, the furfural formation corresponded to only 1.55% of the total available xylan in the sample. There might still be some further condensation of furfurals to humins, especially with higher moisture contents and longer reaction times. The humin formation is visible as discoloration of the samples during hydrolysis (Figure S2), but humins are such strong chromophores that even trace amounts result in darkening.^{15,22} According to HPLC measurements, the degradation of HMF to formic and levulinic acid was negligible. In addition, the samples do contain acetic acid (0.7%–7% of the dry weight of wood) originating from the acetyl groups of hemicellulose.

One of the main challenges with upscaling HCl gas hydrolysis process has been the formation of a sticky intermediate product, which is a syrup-like mixture of water, lignin residue, and oligosaccharides. This is problematic because without a water phase—that would transport the hydrolyzed material forward in the process—this mixture can get stuck to the reactor surfaces. In earlier accounts, this problem has been addressed by employing fluidized bed reactors and antisticking agents.¹³ However, operating a fluidized bed reactor on an industrial scale would be problematic because it involves maneuvering a large amount of solid particles in a pressurized system.²³

Hence, it is noteworthy that unlike with higher HCl concentrations in gas hydrolysis,²³ the wood flour does not turn into a sticky intermediate product when the acid concentration is adjusted to 36% (Figure S2). This renders the process more suitable for upscaling and offers an alternative to the prehydrolysis step with 35% liquid hydrochloric acid in the Bergius–Rheinau process.²⁴ Removal of C5 sugars via prehydrolysis is an essential step in the Bergius–Rheinau process to prevent the degradation of C5 sugars during the following hydrolysis step with 42% hydrochloric acid.²⁵ The industrialization of the HCl gas pretreatment process could be realized by employing a modified screw extruder or a comparable continuously operating mixing reactor.

Modeling of the concentrated acid hydrolysis of aspen wood flour with HCl gas was conducted based on sugar yields in filtrates without posthydrolysis, employing a chain scission model with a constant scission probability (Table S2). The calculations and limitations to accuracy of parameter estimations are elaborated more in detail in the Supporting Information. In general, the chain scission model for xylan (Figure S3) indicates a significant increase in scission rate at

moisture contents of 40%–60%, but there is some observable xylose degradation over a 24 h reaction period. In the case of glucan (Figure S4), the reactive portion undergoing scission is higher with moisture contents of 40%–60%, but the reaction rate remains almost constant (Table S3b). Overall, under the applied reaction conditions, both glucan chain scission and glucose degradation are minimal, while only a small portion of the glucan is susceptible to scission during the hydrolysis process.

Process mass intensity (PMI) is a metric that quantifies the environmental impact of a process by measuring the amount of chemical input required per unit mass of the product output. A lower PMI value is preferred, as it indicates that less mass is used or generated per unit of product during a manufacturing process. It is a valuable metric for assessing material efficiency due to its simplicity and broad applicability. However, it is important to note that its exclusive focus on input and output mass may oversimplify complex processes and miss certain environmental or technical considerations.²⁶ PMI was used for comparing prehydrolysis between 32% HCl(aq), HCl gas hydrolysis (this study), two dilute acid hydrolysis pretreatments with sulfuric acid, and one employing dilute HCl(aq)—all pretreatment methods that aim primarily at selective removal of hemicellulose as mono- and oligomers from a biomass sample. The comparison was based on yields of xylose and XOs directly from concentrated acid hydrolysis and on xylose yield after posthydrolysis. To represent HCl gas hydrolysis, the sample point with the lowest PMI value was chosen for comparison (40% moisture content 6 h of reaction time). The reaction flowcharts for three different processes and borders for PMI calculations are presented in Figure 3. Nominator and denominator values employed for the calculation of PMI values are presented in Table S4. The results of the PMI calculations are presented in Table 1.

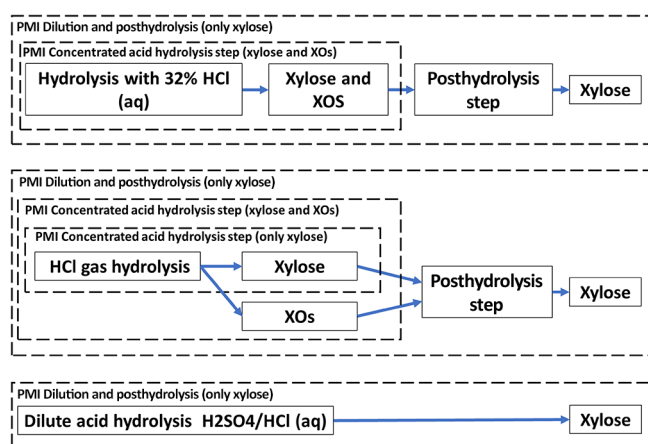


Figure 3. Reaction flowcharts for three different hydrolysis processes and borders for PMI calculations.

As can be seen from the Table 1, the concentrated acid hydrolysis step with HCl gas has a 56% lower PMI value than the liquid counterpart for the total yield of xylose and XOs. However, due to a higher amount of water used for the dilution in this gas hydrolysis tests, the PMI of gas hydrolysis with dilutions is significantly higher. Yet if the sample was diluted with the same water/acid ratio as in the hydrolysis with 32% HCl(aq), it would be possible to gain >70% lower PMI value when compared to prehydrolysis with liquid acid. If the

Table 1. Calculated PMI Values

	32% HCl(aq)	HCl gas hydrolysis	Dilute H ₂ SO ₄ /HCl(aq) hydrolysis
PMI Concentrated acid hydrolysis step (xylose and XOs)	52 ²⁴	23	—
PMI Concentrated acid hydrolysis step (only xylose)	—	46	—
PMI Dilution and posthydrolysis (only xylose)	393 ²⁴	1419 (112) ^a	45 ²⁹ /56 ²⁷ 82 ²⁸ /101 ²⁸

^aAdjusted dilution.

gas hydrolysis is compared to the lowest calculated PMI value for dilute H₂SO₄(liquid) acid hydrolysis, the PMI of the gas hydrolysis is still twice as large, even with the adjusted dilution. However, if the dilute (liquid) acid hydrolysis is compared directly to the HCl gas hydrolysis without dilution from the perspective of xylose yield, it is observable that the PMI value of the gas hydrolysis is comparable to lowest dilute acid hydrolysis PMI result. This is because 42% of the available xylan is already converted to monosaccharide form during gas hydrolysis. When factoring in the simultaneous generation of XOs alongside xylose during gas hydrolysis, easier acid separation, and low degradation product formation, it becomes apparent that HCl gas hydrolysis could offer an efficient method for xylan retrieval from biomass.

In summary, 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 6040% moisture content and 6 h reaction time based on PMI calculations. Under these parameters, it was possible to retrieve 84% of the available xylan from aspen wood flour with only 1% glucan degradation. PMI calculations revealed that with adjusted dilution, gas hydrolysis could potentially have >70% lower PMI than prehydrolysis with 32% HCl(aq). Hydrolysis modeling revealed that the xylan scission rate is significantly increased in the moisture contents of 40%–60% during gas hydrolysis. Overall, this pretreatment process could have potential as a replacement for the prehydrolysis step with 32% hydrochloric acid in Bergius–Rheinau process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07532>.

Experimental details, raw material aspen composition, HPLC results for furans, pictures of sample darkening and humin formation during hydrolysis, equations used for modeling, and modeling data (PDF)

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Notes

The authors declare no competing financial interest.

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