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Hydrolysis of semi-industrial aqueous extracted xylan from birch (*Betula pendula*) employing commercial catalysts: kinetics and modelling

Xiaojia Lu,^{a,b} Paula Junghans,^c Johan Wärnå,^a Gerd Hilpmann,^c Rüdiger Lange,^c Heather Trajano,^d Kari Eränen,^a Lionel Estel,^b Sebastien Leveneur^{a,b} and Henrik Grénman^{a*} 

Abstract

BACKGROUND: Acidic hydrolysis of a birch (*Betula pendula*) xylan produced by a novel semi-industrial-scale aqueous-based and highly sustainable method was studied in a batch reactor. Five commercial acidic heterogeneous catalysts were screened and significant differences in their performance were observed. Dowex 50WX2-100 was selected for further studies and the influence of the reaction parameters, including stirring speed, pH (0.5–1.5), temperature (115–145 °C) and catalyst particle size (50–400 mesh) were studied. The goal was to maximize xylose yield by balancing between the kinetics of hydrolysis and the undesired degradation of monosaccharides.

RESULTS: The results show that the maximum achieved yield of xylose was 76%, but higher yields were hindered by the consecutive dehydration of sugars. It was also observed that the hydrolysis and dehydration reactions do not follow the same dependence on the experimental parameters, which leaves room for optimization of the yield. A kinetic model was developed based on the data, which takes into account the consecutive reaction pathway and the influence of the experimental conditions, and a very good fit of the model to the experimental data was achieved. An activation energy of 119 and 88 kJ mol⁻¹ was obtained for the hydrolysis and dehydration steps, respectively.

CONCLUSION: Hydrolysis results of this novel, well-characterized hemicellulose extract have not been published previously, and they contribute significantly to the understanding of the hydrolysis and dehydration of real feedstock, instead of highly purified and typically very deacetylated model compounds with different characteristics and behaviour in hydrolysis.

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Keywords: hemicelluloses; xylan; industrial feedstock; hydrolysis; heterogeneous catalyst; modelling

INTRODUCTION

Lignocellulosic biomass¹ is the most abundant renewable resource on earth and it can be divided into non-woody biomass (agricultural waste, non-wood plant fibres, etc.)² and woody biomass (hardwoods and softwoods).³ The estimated annual production of plant biomass is 170–200 × 10⁹ tons.⁴ The primary components in lignocellulosic biomass are cellulose, hemicellulose and lignin, but the composition varies significantly depending on species, origin, humidity, etc.

Platform chemicals, such as sugar alcohols, sugar acids, furfural and hydroxymethylfurfural, can be obtained from sugars derived from biomass. Hemicellulose is one of the main components in lignocellulosic biomass, which constitutes 20–30% of the total mass.⁵ Large quantities of hemicellulose are produced in industries such as pulp mills every year; however, it remains relatively

underutilized.^{6,7} It consists of heteropolysaccharides that contain a mixture of C6 and C5 sugar units and sugar acids linked together

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through glycosidic bonds.^{5,7} The most important hardwood hemicellulose is xylan, especially *O*-acetyl-4-*O*-methylglucuronoxylan, amounting to about 80–90% of the hardwood hemicelluloses.⁸ Xylan is a heterogeneous linear heteropolysaccharide that mainly consists of xylose, in addition to other sugar units. Figure 1 shows an example of *O*-acetyl-(4-*O*-methylglucurono)xylan extracted from hardwood, where xylose units are connected by β -(1-4)-D-xylopyranose bonds. The side groups are glucuronic acids and some other sugars such as galactose, rhamnose and mannose. Xylose is the main monosaccharide obtainable from xylan via hydrolysis and it can be valorized to (for example) xylitol via hydrogenation,^{9,10} to furfural via dehydration or to xylonic acid through oxidation. These compounds can be utilized in a wide variety of biochemicals for use in such industries as the paper, alimentary, cosmetic and pharmaceutical.^{11–15}

In a hydrolysis process, the glycosidic bond is cleaved by protonation and water addition.¹⁶ The polymer is stepwise cleaved into smaller molecules, resulting in a mixture of oligomers with varying degree of polymerization. The oligomers can be further transformed into monomers via either thermal, physiothermal, microbiological or chemical cleavage. The general reaction mechanism for the acidic hydrolysis of xylan is shown in Fig. 2. According to the scheme, the reaction follows the specific proton-catalysed mechanism. In addition, a further dehydration to furfural is possible under harsher conditions.^{10,17–19} The formation of the covalent bond between the oxygen atom of the water and the carbon of the polysaccharide is the rate-determining step

in the reaction, which can be accelerated with a suitable catalyst. The hydrolysis can be carried out using homogeneous^{20–23} or heterogeneous²⁴ catalysts. High yields of sugar monomers can be achieved with homogeneous catalysts such as mineral acids; however, it usually brings a safety risk to both environment and workers, and it is challenging and expensive to separate the products.²⁵ Heterogeneous catalysts can be utilized to overcome such challenges as they are easy to recycle, which greatly reduces costs and makes them more attractive for industrial processes. However, heterogeneous catalysts do not typically provide equally fast kinetics as mass transfer limitations, for example, may be present, which affect the obtained overall reaction rates and result in a less efficient hydrolysis. Therefore, the selection of catalyst is essential as their characteristics such as acidity, surface area, particle size, porosity and degree of crosslinking vary greatly, which influence their performance.

Hemicellulose extracted from Finnish silver birch (*Betula pendula*) was selected as the raw material, as birch is one of the major tree species in Finland and other boreal areas; it contains high amounts of xylan and does not compete with food production. The current work focuses on utilizing a novel, modified aqueous extraction-based xylan from silver birch, which is currently being produced on a pilot scale (500 kg d⁻¹).^{26,27} The novel semi-industrial process fractionates efficiently in an almost closed-loop system the hemicellulose and the lignin fraction from cellulose fibres, making it possible to utilize the whole biomass for further valorization. This is consistent with the requirements of modern sustainable biorefineries and complies with the principles of

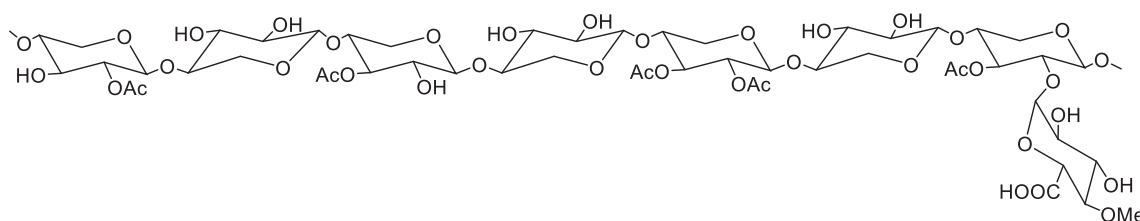


Figure 1. Partial chemical structure of *O*-acetyl-(4-*O*-methylglucurono)xylan.

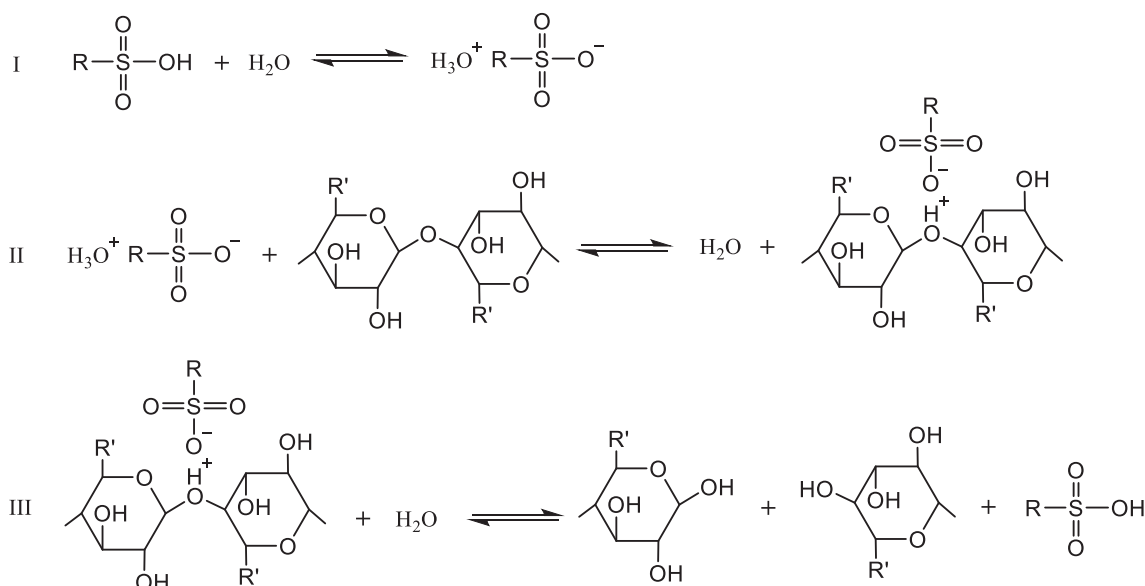


Figure 2. Reaction mechanism of acidic hydrolysis of xylan ($R' = \text{CH}_2\text{OH}$).

green chemistry and engineering. The extracted xylan has advantages such as being sulfur free, having a low lignin content and relatively high molar mass and low content of degradation products. These characteristics all contribute to the processing of xylan to platform chemicals and high-value products. The xylan was used as obtained from the semi-industrial process, without further purification or separation. It is crucial also to study real feedstock instead of highly purified, typically very deacetylated hemicelluloses model compounds.

Several commercial heterogeneous catalysts were screened and different reaction conditions (stirring speed, pH, temperature and particle size of the catalyst) were tested to obtain sufficient data for catalyst selection. The goal was to achieve high xylose yield and as few dehydration products as possible. One of the aims was also to perform mathematical modelling on the kinetics of the consecutive reactions in order to quantify the influence of reaction parameters on the reaction rates.

EXPERIMENTAL

Materials and chemicals

Semi-industrial xylan, originating from Finnish silver birch, was used in the current work. The xylan was extracted by a spin-off company with a process developed at Åbo Akademi University.^{26,27} First, the polysaccharides were isolated from the fibrous wood structure with a heated aqueous phase at 150 °C and a pressure below 8 bars. Then, nearly all of the oxygen present in the reactor was removed to minimize oxidation and degradation of hemicelluloses. The extraction was performed under continuous recirculation to increase the concentration of hemicelluloses in the liquid phase.

The same batch of xylan with a dry content of 38.8% and an average molar mass of 4.649 kg mol⁻¹ was used in all experiments. The degree of depolymerization was estimated to be around 31, assuming an average monomer molar mass of 150.13 g mol⁻¹ and 100% xylose in the substrate. The sugar composition was analysed by gas chromatography and the results are shown in Table 1. It is obvious that xylose is the main component of the substrate (79.3%).

Five commercial heterogeneous acidic catalysts were selected based on their properties, such as particle size, acidity, thermal stability and safety. As supplied, the particle sizes of three selected catalysts (Amberlite IR120, Amberlyst 15 and Dowex 50WX8-50) were in the same size range. Smopex 101 is a non-porous fibre catalyst supplied in one diameter. Dowex 50WX2-100 was selected to provide an alternative with lower degree of crosslinking, i.e. larger pore size. The source of acidity in all of the employed catalysts was sulfonic acid, which is a strong Brønsted acid. The basic properties of the catalysts are shown in Table 2.

Batch reactor experiments

A 300 mL reactor made of titanium was employed for batch experiments. It was equipped with a four-blade mechanical impeller stirrer to supply efficient mixing and diminish the influence of external mass transfer on the reaction kinetics. A sinter was installed to the end of the sample outlet tube to avoid catalyst loss during sampling.

The catalysts were used as received without drying before the experiments. The moisture in the catalyst was taken into consideration while calculating the pH of the reaction mixture and the amount of substrate when preparing the xylan solution. The amount of catalyst determined by the desired pH was calculated

Table 1. Composition analysis of industrial xylan

Compound	wt%
Xylose	79.3
4-O-Me-GlcA	9.3
Galactose	3.7
Rhamnose	2.4
Mannose	2.0
Glucose	1.8
Arabinose	1.8
Galacturonic acid	1.8
Glucuronic acid	0.5

based on the total ion exchange capacity (TEC_{dry cat}) listed in Table 2.

In a typical experiment, 150 mL xylan solution and a predetermined amount of catalyst were placed in the reactor. The heating was commenced once the reactor was closed and pressurized to 2 bar with argon. The first sample was taken after reaching the desired temperature and stirring was commenced. Samples were taken every 30 min and the outlet was flushed before sampling. Argon was used for obtaining an inert atmosphere and regulating the overall pressure. The pressure was kept constant at 8 bar during the experiment until the reaction was quenched after 4 h.

Analysis

High-performance liquid chromatography (HPLC)

The main compounds xylan and xylose were analysed using a VWR (PA, USA) Hitachi Chromaster high-performance liquid chromatograph equipped with a 5450 RI detector. A Bio-Rad (CA, USA) Aminex HPX-87C column with a diameter of 300 mm and a length of 7.8 mm was used. The eluent (1.2 mmol L⁻¹ CaSO₄ solution) was pumped into the column at a flow rate of 0.5 mL min⁻¹ and a constant temperature of 80 °C. Samples were filtered with 0.45 µm PVDF filters before injection and the injection volume was 25 µL. The calibration curves were determined by preparing five calibration samples in a concentration range of 0.31–5 g L⁻¹ with pure xylan and xylose, respectively, prior to the analysis of experimental samples.

Another high-performance liquid chromatograph equipped with a Bio-Rad Aminex HPX-87H column and an RI detector was also employed to determine the concentration of the degradation products. The eluent was 5 mmol L⁻¹ H₂SO₄ and the flow rate was 0.6 mL min⁻¹; the temperature was kept constant at 45 °C during the analysis.

Gas chromatography with flame ionization detection

An Agilent J&W gas chromatograph, model PerkinElmer Clarus 500, equipped with a 7.2 m × 0.530 mm column, was employed to analyse the hydrolysis samples. The carrier gas was hydrogen with a flow rate of 7 mL min⁻¹. The injection volume was 0.5 µL and the injector had an initial temperature of 80 °C. After 0.1 min of injection the temperature was increased by 50 °C min⁻¹ up to 110 °C and subsequently by 15 °C min⁻¹ to 330 °C. This temperature was kept stable for 7 min. The oven was heated at 100 °C for 0.5 min and the temperature was then increased at 12 °C min⁻¹ up to 340 °C for 5 min. A flame ionization detector was used with 45 mL min⁻¹ hydrogen and 450 mL min⁻¹ air at 340 °C. The samples were freeze dried overnight and diluted to 1 g L⁻¹ with

Table 2. Information about the chosen catalysts

Catalyst	Matrix	Moisture (wt%)	Particle diameter (μm)	Temp. max. ($^{\circ}\text{C}$)	TEC (mEq g^{-1})
Amberlite IR120	Styrene–divinylbenzene (gel)	45	620–830	120	4.4
Amberlyst 15	Styrene–divinylbenzene (macroreticular)	5	600–850	120	4.7
Dowex 50WX2-100	Styrene–divinylbenzene (gel)	78	150–300	150	4.8
Dowex 50WX8-50	Styrene–divinylbenzene (gel)	55	300–1180	150	4.8
Smopex 101	Styrene–sulfonic acid-grafted polyolefin fibre	6	35–45	120	2.6

distilled water. Cholesterol was added as the internal standard. The solutions were then mixed with the silylation reagent (pyridine–*N,O*-bis(trimethylsilyl)trifluoroacetamide–trimethylsilyl chloride, 1:4:1) prior to injection. Two parallel samples were always prepared for analysis.

RESULTS AND DISCUSSION

Catalyst screening

Five acidic heterogeneous catalysts were selected for catalyst screening.^{24,28} Based on literature and preliminary results obtained at ambient pressure, relatively high temperature and low pH are required in the hydrolysis of xylan compared to inulin, for example.^{28–30} We selected 115 $^{\circ}\text{C}$ as the operating temperature in the screening as some of the catalysts have a maximum operating temperature of 120 $^{\circ}\text{C}$. A pH of 0.75 was used to maintain a reasonable solid–liquid ratio. The experiments were carried out with a total volume of 200 mL for 8 h under isothermal conditions. The results are shown in Fig. 3.

The xylose yield increased rather linearly with the catalysts Amberlite IR120, Dowex 50WX8-50 and Amberlyst 15. Amberlite IR120 and Dowex 50WX8-50 resulted in a xylose yield of 40% after 8 h, whereas with Amberlyst 15 60% was obtained. The reaction rate was significantly faster with Dowex 50WX2-100 and Smopex 101, and a xylose yield of over 60% was obtained in less than 4 h, after which the yield was rather stable. It was evident that Smopex 101 and Dowex 50WX2-100 performed best, whereas Amberlite IR120 and Dowex 50WX8-50 led to the least efficient conversion. It can

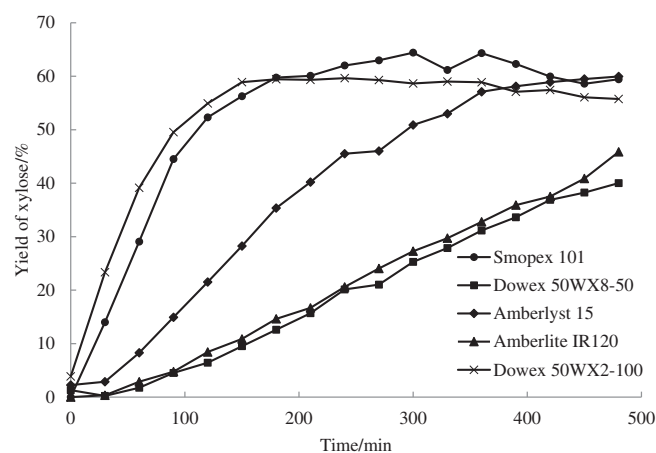


Figure 3. Influence of catalyst on the yield of xylose in experiments performed at 115 $^{\circ}\text{C}$ and pH 0.75.

be concluded that the pore size, which is closely related to the degree of crosslinking, significantly influenced the catalytic results, as the two Dowex catalysts performed very differently and the only difference between them was the degree of crosslinking. More crosslinking results in smaller pores and the bulky xylan molecules are more sterically hindered from diffusing inside the catalyst particles. The two best-performing catalysts were the non-porous Smopex 101 and the Dowex 50WX2-100, with lower degree of crosslinking compared to the other tested Dowex catalyst. The reproducibility of the experimental results was tested by repeating an experiment three times by recycling the catalyst, and the results showed that the difference in yield was very small, within a few per cent. Due to the stronger ion exchange capacity and higher maximum operating temperature (150 $^{\circ}\text{C}$) of Dowex 50WX2-100, it was chosen for further studies.

Influence of stirring speed

Different stirring speeds were tested to see if the agitation was intense enough to eliminate the influence of external mass transfer limitations. The conditions were otherwise kept identical in all the experiments, and 137 $^{\circ}\text{C}$ and pH 0.75 were selected to ensure the necessary reaction rate to make the influence of external mass transfer visible.

A large difference was observed in the reaction rate when the impeller rate was increased from 320 to 660 rpm (Fig. 4) The observed kinetics at the lower agitation rate was much slower for both hydrolysis and consecutive reaction, i.e. the dehydration of xylose to furfural. The difference between the observed kinetics at 660 and 850 rpm was practically negligible and it could be concluded that 660 rpm provided sufficient turbulence.

The influence of pH

The influence of pH was also investigated by keeping the other experimental parameters constant. A xylan solution containing about 1.25 g L^{-1} was used as the substrate, which corresponded to an initial xylose concentration of about 1 g L^{-1} . The experiments were conducted at a temperature of 145 $^{\circ}\text{C}$ to study the influence of pH under conditions where severe degradation would be present. Four different pH values were chosen in the range 0.5–1.5, giving a tenfold variation in the concentration of protons. The results are shown in Fig. 5.

It is evident from the results that the kinetics of the hydrolysis are heavily influenced by pH. However, the dehydration rate was also observed to increase with lower pH, resulting in a rapid decline in xylose concentration as soon as the highest yield was

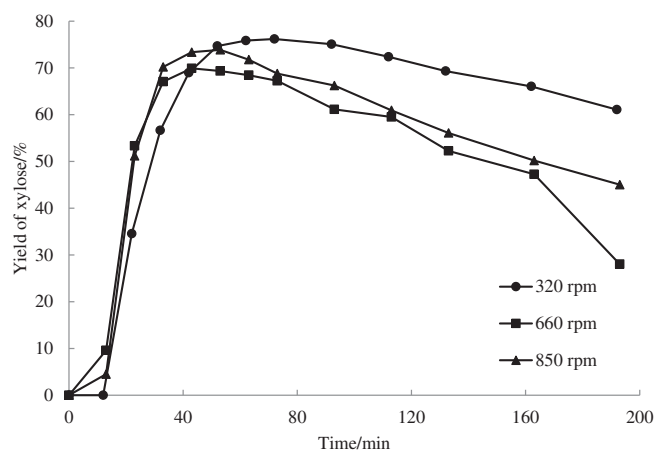


Figure 4. Influence of stirring speed on the yield of xylose in experiments performed at 137 °C and pH 0.75 with Dowex 50WX2-100.

reached and naturally influencing kinetics already from the start of the experiments. In the end, only a very small amount of xylose was remaining after 3 h of experiment. Nevertheless, pH 0.5 gave the highest xylose yield (71%) and the experiment at pH 1 did not yield as much xylose as at lower pH, but the hydrolysis was clearly faster than at pH 1.5 and the xylose concentration was relatively stable for 30 min. In the experiment at pH 1.5, it took about 70 min to reach the highest xylose yield of 69%.

Influence of temperature

Since a pH of 0.5 was already very harsh and resulted in rapid dehydration, pH 0.75 was chosen for evaluating the influence of temperature on the kinetics. The experiments performed in the catalyst screening indicated that at 115 °C and pH 0.75 a high xylose yield was obtained; however, the kinetics were too slow for practical applications. Therefore, three higher temperatures (130, 137 and 145 °C) were selected to study their influence on both the hydrolysis and dehydration kinetics.

As depicted in Fig. 6, the kinetics at higher temperature were considerably faster. The highest xylose yield was achieved in only 20 min at 145 °C, whereas at 115 °C it took 3 h to reach the same yield. However, the highest yield obtained at 145 °C (66%) was lower than that obtained at the lower temperatures. Significant

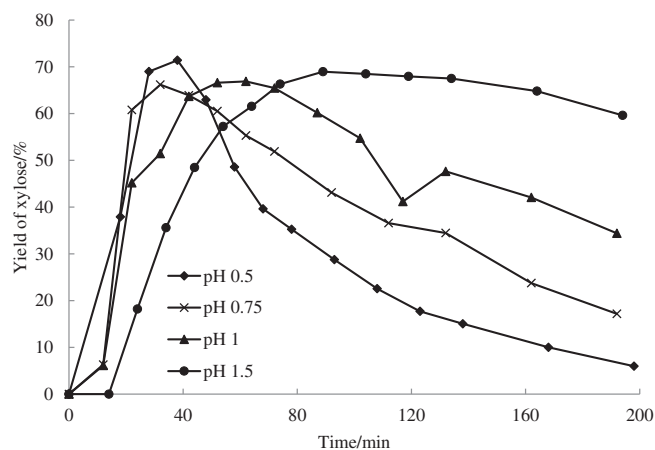


Figure 5. Influence of pH on the yield of xylose of experiments performed at 145 °C with Dowex 50WX2-100.

dehydration was observed immediately after the maximum was reached, and a xylose yield of only 17% was obtained by the end of the experiment. The hydrolysis kinetics at 137 °C were slightly slower than at 145 °C, but a higher xylose yield (70%) was obtained and there was no degradation observed for the first 40 min, even though some degradation most probably occurred. There was about 28% xylose left after 3 h experiment. The kinetics at 130 °C were even slower than at 137 °C and the highest xylose yield of 72% was reached after 40 min. However, the degradation was observed to be slow and the dehydration started to be visible after about 50 min, resulting in a relatively high xylose yield (60%) after 3 h experiment. It can be concluded that the kinetics are very temperature sensitive and careful optimization is required when performing the reaction in a larger batch reactor or a continuous reactor, for example.

Influence of particle size

The Dowex 50WX2-100 catalyst employed in the previous experiments was between 50 and 100 mesh, which corresponds to a particle size between 300 and 150 μm. The catalyst with a smaller particle size of 200–400 mesh (37–75 μm) was also tested at 137 °C and pH 0.75 in order to observe the influence of internal mass transfer resistance on the kinetics.

The results presented in Fig. 7 show that the catalyst with smaller particle size was slightly more efficient. The highest xylose yield of 74% was obtained in 30 min after reaching the desired temperature. Dehydration then converted two-fifths of the produced xylose in the reaction mixture, leading to a final xylose yield of 47% during the 3 h experiment. The kinetics in the experiment with larger catalyst were slower; the highest yield was reached in 1 h and less dehydration occurred. After the corresponding 3 h, the xylose yield decreased to 61%. Therefore, it was observed that both the hydrolysis and dehydration were faster when smaller catalyst particles were employed. This was most probably due to both the larger external surface area of the smaller particles as well as the decrease in internal mass transfer limitations. However, the difference observed in the kinetics was not very great when thinking about performing hydrolysis in a continuous reactor system, for example.

Catalyst stability

A preliminary catalyst deactivation study was carried out under harsh conditions, i.e. a temperature of 137 °C and a pH of 0.2, with

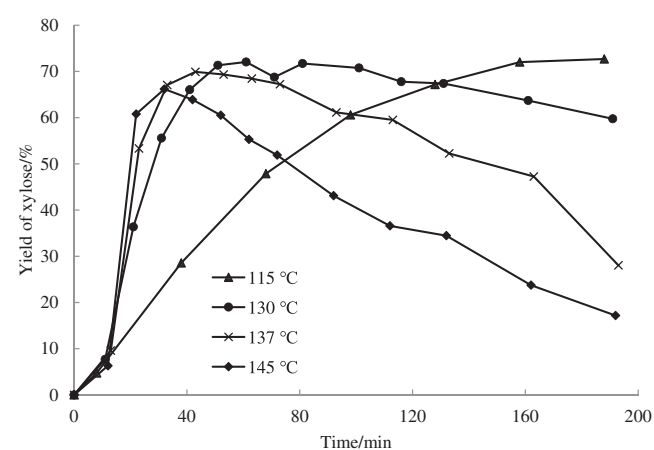


Figure 6. Influence of temperature on the yield of xylose in experiments performed at pH 0.75 with Dowex 50WX2-100.

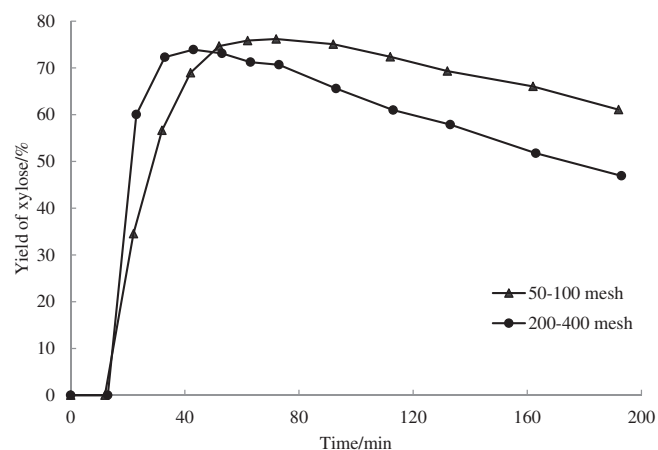


Figure 7. Influence of catalyst particle size on the yield of xylose of experiments performed at 137 °C and pH 0.75.

a high xylan concentration of 20 g L⁻¹. Catalyst stability started to decrease significantly after about 34 h due to the pore blockage, which is most probably caused by the repolymerization of degradation products.¹⁹ This indicates that process optimization avoiding degradation of monosaccharides is extremely important also for catalyst stability. This ties the sugar degradation study closely

to studying the deactivation of the catalyst employed for hydrolysis.

Modelling

Mathematical modelling was performed on the batch reactor data in order to quantify the influence of the experimental conditions on the kinetics. Preliminary experimental and literature data²¹ suggested that the hydrolysis of xylan proceeded through a type of 'end-biting' mechanism, in which monomers and short oligomers are cleaved from the end of the macromolecules. The hydrolysis took place when a glycosidic bond encountered the protons of the sulfonic groups on the external surface of the polymeric catalyst matrix. During the experiment, the degree of polymerization decreased as the long xylan polymeric chain was cleaved into smaller molecules, producing more bonds that were easily accessible for the protons in the catalyst. As a result, the probability of an encounter of the proton and the glycosidic bonds could increase, which could result in a greater reaction rate, i.e. observed autocatalysis. The small xylooligomers detected with HPLC confirmed this hypothesis.

A recently developed two-parameter model that takes the autocatalytic effect into account^{28,31} was utilized:

$$k = k_0(1 + \beta X^\alpha) \quad (1)$$

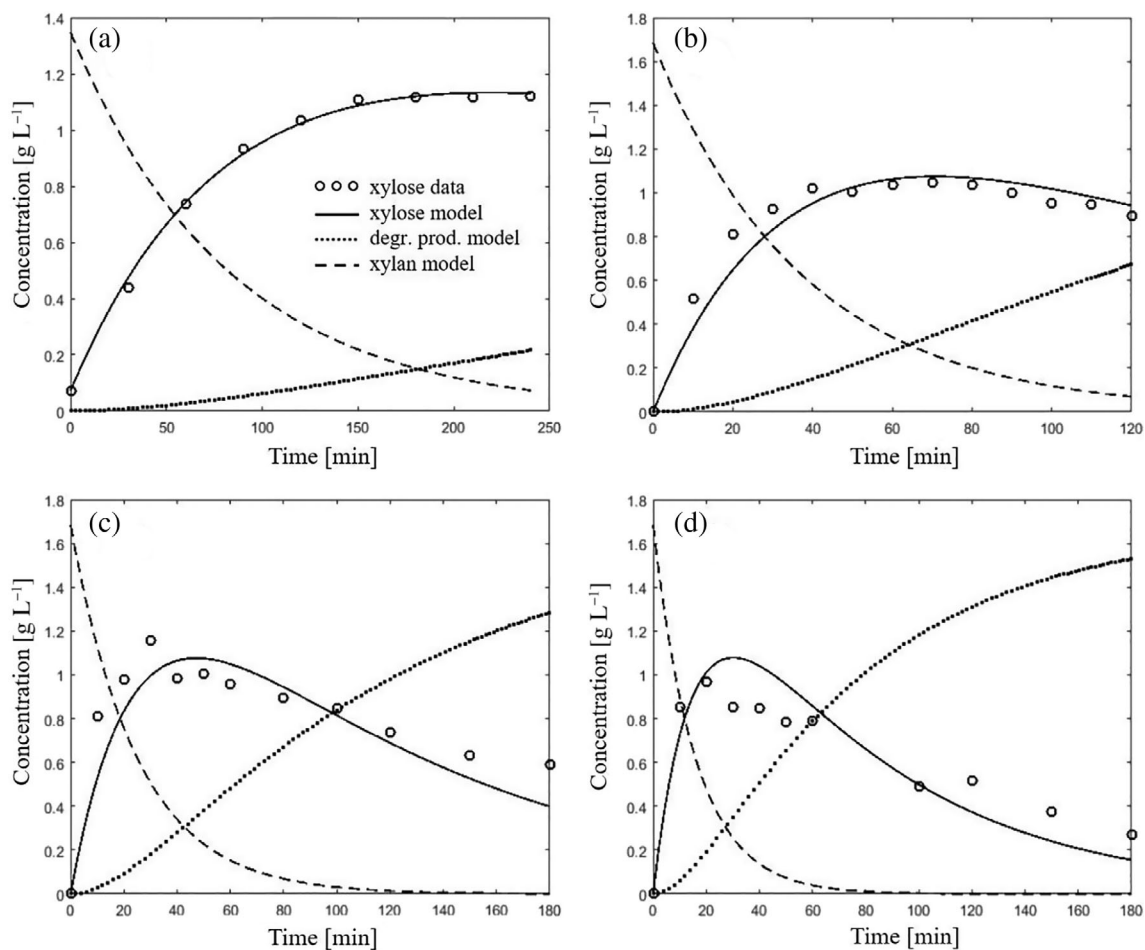


Figure 8. Concentration of xylan, xylose and degradation products as a function of time in experiments performed at pH 0.75 and different temperatures: (a) 115 °C; (b) 130 °C; (c) 137 °C; (d) 145 °C. The lines represent the model prediction and the lines represent the experimental xylose concentration.

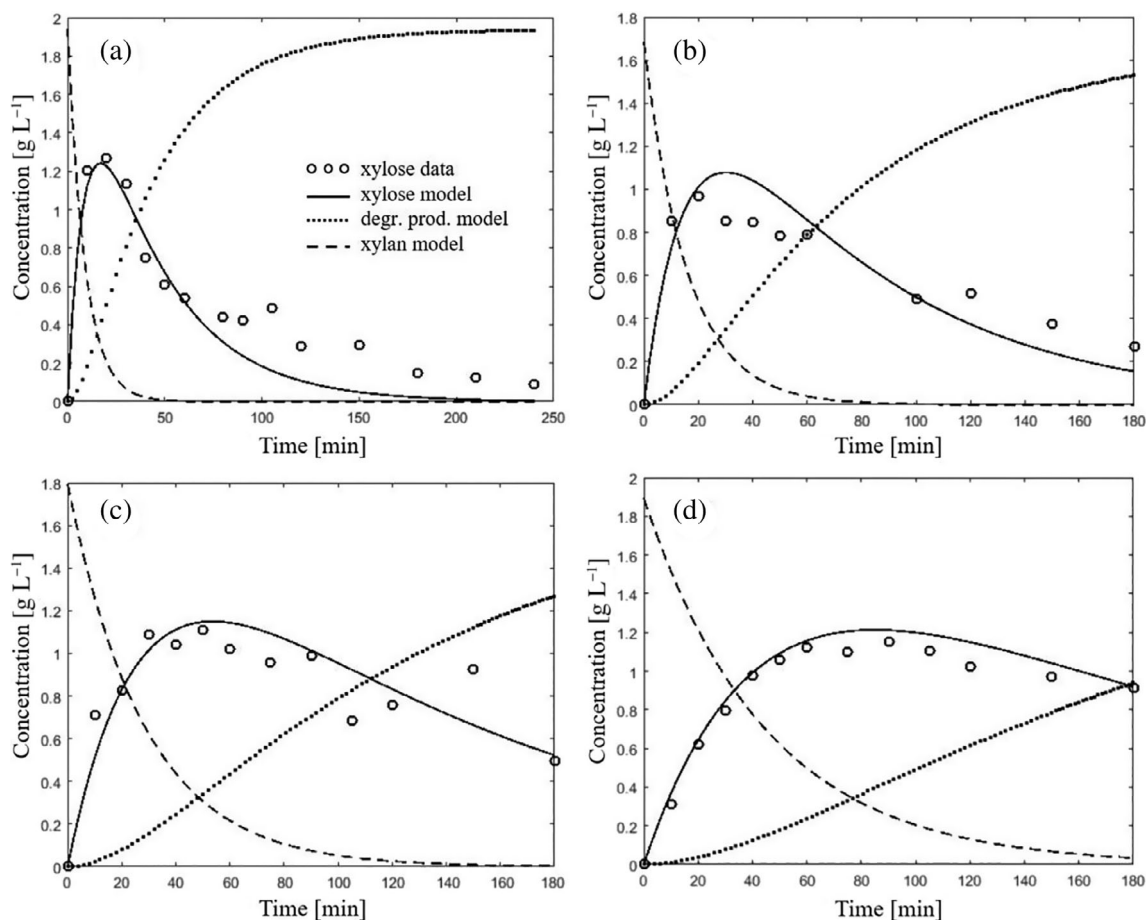


Figure 9. Concentration of xylan, xylose and degradation products as a function of time in experiments performed at 145 °C and different pH values: (a) pH 0.5; (b) pH 0.75; (c) pH 1; (d) pH 1.2. The lines represent the model prediction and the lines represent the experimental xylose concentration.

where k is the conversion-dependent observed rate constant, k_0 describes the reaction rate constant and X is the conversion of xylan.

The parameters α and β influence the way in which the conversion influences the rate constant; α describes the linearity of the dependence and β is expressed as follows:

$$\beta = \frac{(k_{\infty} - k_0)}{k_0} \quad (2)$$

If the final constant rate is the same as that at the beginning, β obtains a value of 0. Hence the model simplifies to $k = k_0$, meaning no autocatalysis occurs. However, if there is autocatalysis the parameter β turns into a positive number. The higher the value of β , the stronger the influence. If α obtains a value of 1, the relation with β is linear and values differing from unity give a non-linear dependence. Assuming a linear molecule, α should obtain a value of 1 in a pure monomer 'end-biting' mechanism.²⁸

The overall reaction can be described by a two-step consecutive reaction pathway $A \xrightarrow{r_1} B \xrightarrow{r_2} C$, where A is the xylan polymer, B is the xylose monomer and C are degradation products. The reactions were considered irreversible and first order with respect to the reactants and the proton concentration according to the reaction mechanism, and the concentration of water was assumed to be abundant and constant, so it was excluded from the model. Hence the reaction rates could be described as follows:

Table 3. Parameters after the final modelling approach			
Parameter	Value	Units	Est. relative standard error (%)
k_1	0.149	L/(mol min)	5.0
k_2	0.0357	L/(mol min)	6.2
E_{a1}	80 300	kJ/mol	6.6
E_{a2}	78 900	kJ/mol	8.3

$$r_1 = k_1 C_H + C_{xylan} \quad (3)$$

$$r_2 = k_2 C_H + C_{xylose} \quad (4)$$

The mass balance for each compound in the reaction liquid was then described as follows:

$$\frac{dc_{xylan}}{dt} = -r_1 = -k_1 C_H + C_{xylan} \quad (5)$$

$$\frac{dc_{xylose}}{dt} = r_1 - r_2 = k_1 C_H + C_{xylan} - k_2 C_H + C_{xylose} \quad (6)$$

$$\frac{dc_{degr.}}{dt} = r_2 = k_2 C_H + C_{xylose} \quad (7)$$

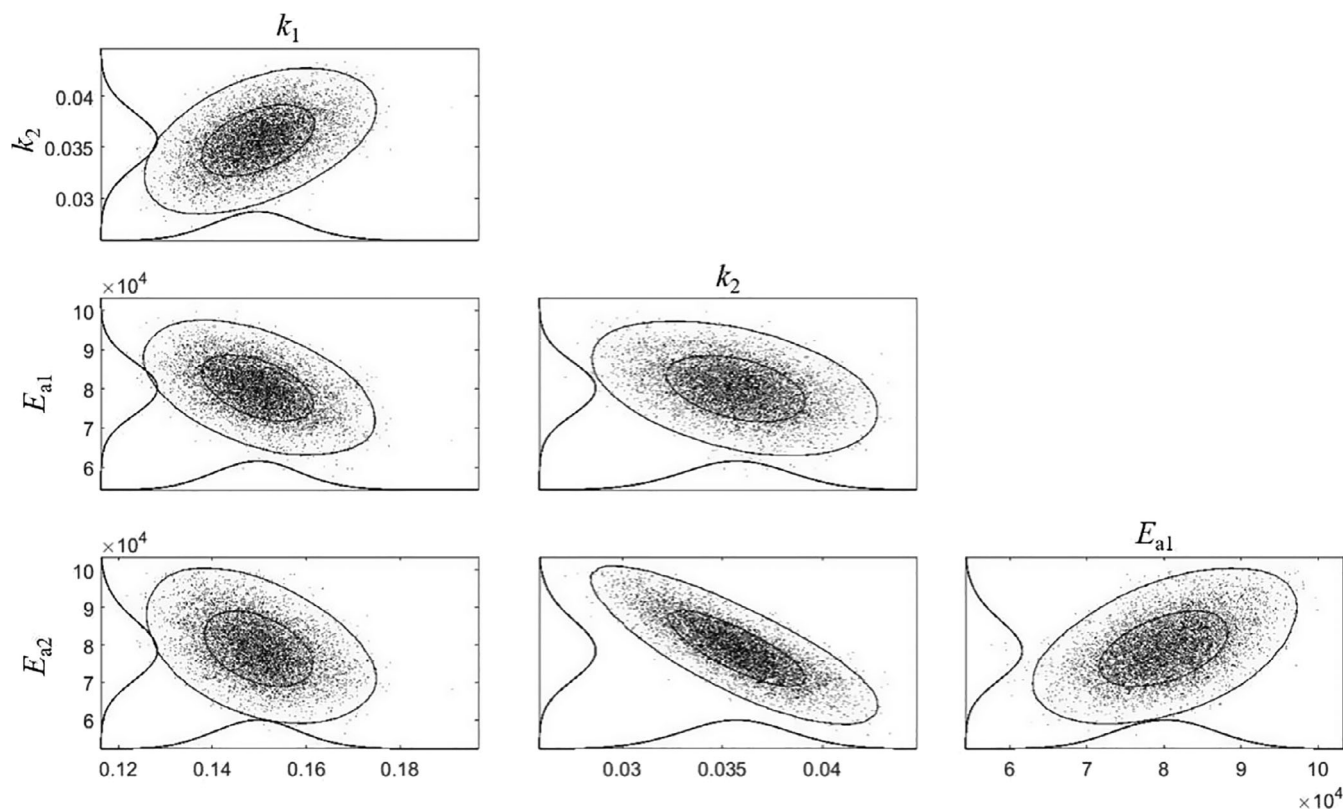


Figure 10. Sensitivity analysis of the obtained parameters.

where c_{H^+} is the concentration of protons, which can be calculated based on the number of sulfonic acid sites in the catalyst.

A modified form of the Arrhenius equation was used to decouple the correlation of the pre-exponential factor and the activation energy:

$$k_0 = k_{01} \exp\left(-\frac{E_a}{R\theta}\right) \quad (8)$$

where the parameter k_{01} is the pre-exponential factor, E_a is the activation energy and R is the universal gas constant. The temperature was transformed as follows:

$$\frac{1}{\theta} = \frac{1}{T} - \frac{1}{T_{ref}} \quad (9)$$

where the reference temperature T_{ref} was 137 °C.

The overall mass balance was then expressed as follows:

$$\frac{dc_{xylan}}{dt} = -k_{01} \exp\left(-\frac{E_{a1}}{R\theta}\right) \left[1 + \beta \left(\frac{C_{xylose}}{C_{xylose}^0}\right)^\alpha\right] c_{H^+} c_{xylan} \quad (10)$$

$$\frac{dc_{xylose}}{dt} = \left(k_{01} \exp\left(-\frac{E_{a1}}{R\theta}\right) \left[1 + \beta \left(\frac{C_{xylose}}{C_{xylose}^0}\right)^\alpha\right] c_{H^+} c_{xylan}\right) - k_2 \exp\left(-\frac{E_{a2}}{R\theta}\right) c_{H^+} c_{xylose} \quad (11)$$

$$\frac{dc_{degr.}}{dt} = k_2 \exp\left(-\frac{E_{a2}}{R\theta}\right) c_{H^+} c_{xylose}. \quad (12)$$

For the kinetic parameter estimation, a nonlinear regression analysis that included parts of the experimental data was utilized.

The data of xylose concentration was emphasized in the modelling as the xylan concentration measurement was slightly influenced by minor amounts (2.7% of total) of sulfonic groups leached from the catalyst, as they had very similar retention times in the high-performance liquid chromatograms. Furthermore, the xylan concentration was observed in some experiments at the highest temperatures to increase at the end of the experiments, showing that some repolymerization^{32,33} of the degradation products with the sugars occurred, which was detected as increasing xylan concentration. These factors were taken into account in data interpretation. The model consisting of a system of ordinary differential equations (ODEs) was solved with the backward difference method implemented in MODEST software.

The sum of residual squares Q was calculated according to the following equation:

$$Q = \|\|c_{exp} - c_{est}\|\|^2 \quad (13)$$

The objective function Q was then minimized by the Simplex–Levenberg–Marquard method, where c_{exp} represents the concentration obtained in the experiment and c_{est} the concentration calculated based on the model.

The value for α was very close to unity (1.08), which implied that the correlation of the rate constant and the xylan conversion was linear. In addition, the value for β was practically 0 (0.109×10^{-9}), which suggests that no autocatalytic effect was present. However, it can also be that the autocatalytic effect was masked by the degradation of the sugars, especially under the harsher experimental conditions. Based on the aforementioned, the model could be simplified to the following equations:

$$\frac{dc_{\text{xylan}}}{dt} = -k_{01} \exp\left(-\frac{E_{a1}}{R\theta}\right) c_{\text{H}^+} c_{\text{xylan}} \quad (14)$$

$$\frac{dc_{\text{xylose}}}{dt} = k_{01} \exp\left(-\frac{E_{a1}}{R\theta}\right) c_{\text{H}^+} c_{\text{xylan}} - k_{02} \exp\left(-\frac{E_{a2}}{R\theta}\right) c_{\text{H}^+} c_{\text{xylose}} \quad (15)$$

$$\frac{dc_{\text{degr.}}}{dt} = k_{02} \exp\left(-\frac{E_{a2}}{R\theta}\right) c_{\text{H}^+} c_{\text{xylose}} \quad (16)$$

With this approach, it was possible to minimize the relative standard errors slightly further. The fit of the model to the data is displayed in Figs 8 and 9.

The fit of the model to experimental data can be concluded to be good ($R^2 = 97.59$). The parameter values obtained in the modelling are presented in Table 3.

A sensitivity analysis was carried out to evaluate the correlations of the parameters k_1 , k_2 , E_{a1} and E_{a2} . Figure 10 displays the Monte Carlo plots of the objective function. Almost circular geometries with a clearly defined minimum value in the middle of the circular plot were obtained for most of the pairs of parameters, which shows a low or even negligible correlation between the parameters. Some correlation was observed between E_{a2} and k_2 ; however, the minimum was still centred to a small area in the middle of the plot and, as with the other parameters, the clear minimum confirms that the parameters were well defined.

CONCLUSIONS

It was shown that a semi-industrial xylan produced in a novel sustainable process could be efficiently hydrolysed by the commercial acidic catalyst Dowex 50WX2-100. It was observed that dehydration of the sugars influences the obtainable yield of monosaccharides significantly; however, the yield can be optimized by careful selection of the process parameters. It can be concluded that the optimum temperature most probably lies somewhere between 137 and 145 °C, depending on the chosen pH. The highest yield of 76% was achieved at a temperature of 137 °C and a pH of 0.75. A kinetic model was developed that took into account the dehydration step, and an excellent fit of the model to experimental data was obtained. The results show that the hydrolysis of this special semi-industrial xylan is possible in high yields with commercial catalysts and that the timeframe of the reaction kinetics allows operation in (for example) a continuous reactor setup.

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NOTATION

k	conversion-dependent pre-exponential factor (min^{-1})
k_0	pre-exponential factor (min^{-1})
β	ratio between rate constants in Eqn (1)
X	conversion
α	exponential factor in Eqn (1)

k_{∞}	pre-exponential factor at the end of the reaction (min^{-1})
C_{xylan}	concentration of xylan glucose (g L^{-1})
C_{xylose}	concentration of xylose (g L^{-1})
$C_{\text{degr.}}$	concentration of xylose degradation products (g L^{-1})
C_{0i}	initial concentration of component i (g L^{-1})
C_{H^+}	concentration of H^+ and water (mol L^{-1})
$k_{01/02}$	pre-exponential factors ($\text{L mol}^{-1} \text{min}^{-1}$)
E_a	apparent activation energy (kJ mol^{-1})
R	gas constant ($\text{J K}^{-1} \text{mol}$)
θ	modified temperature
T	temperature (K)
T_{mean}	mean temperature (K)
Q	sum of residual squares
C_{exp}	concentration measured experimentally (g L^{-1})
C_{est}	concentration estimated by modelling (g L^{-1})
R^2	degree of explanation

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