



# Selective hemicellulose hydrolysis of Scots pine sawdust

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## Abstract

The depletion of fossil resources is driving forward the search for new and alternative renewable feedstocks in the production of renewable chemicals, which could replace the petroleum-based ones. One such feedstock is pine (*Pinus sylvestris*) sawdust, which is generated enormous amounts in Finnish sawmills yearly. However, prior to the utilization in high-value applications, it needs to be fractionated into its constituents. In this work, the objective was to produce monomeric hemicellulose sugars from pine sawdust without degrading cellulose or lignin simultaneously. The influence of the reaction temperature and time, as well as acid type and concentration, was studied. Based on the results, the temperature was the main distinguishing feature between cellulose and hemicellulose hydrolysis. Promising results were achieved with acid mixtures consisting of 0.5% sulfuric acid and 5.5 or 10% formic acid. At 120 °C with the reaction time of 2 h, the mixtures produced hemicellulose sugars with the yields of 62%. These yields were comparable to the yields achieved in similar conditions with 1.5% sulfuric acid or 40% formic acid. Therefore, by using an acid mixture, the concentration of a single acid could be reduced significantly. The solid fractions remaining after the hydrolysis consisted mainly of cellulose and lignin, which verified the selectivity of the hemicellulose hydrolysis. Also, the fractionation of the remaining solids confirmed that the utilization of all the sawdust components is feasible.

**Keywords** Pine sawdust · Hydrolysis · Fractionation · Hemicellulose · Sulfuric acid · Formic acid

## 1 Introduction

Scots pine is the main raw material used by sawmills in northern countries, like Finland and Sweden. The utilization of wood produces enormous amounts of side streams like sawdust. Approximately, ten million m<sup>3</sup> of sawdust and woodchips is generated at sawmills in Finland yearly [1]. Typically, sawdust is utilized as pellets for energy production, but burning does not allow the full utilization of the potential in sawdust structure. Thus, sawdust and other side streams of lignocellulosic biomasses (LCBs) should be utilized otherwise in higher-value applications. LCBs are, e.g. an excellent source of platform sugars, which can be further refined to fuels

or chemicals and thus be used as a replacement for fossil- or food-based feedstocks [2].

A major challenge in the utilization of LCBs is the interweaving nature of biomass constituents: cellulose, hemicellulose, and lignin [3]. Lignin is a cross-linked phenolic polymer that fills the spaces on the cell wall between linear cellulose polymers and branched hemicellulose polymers [4]. In order to efficiently utilize the whole biomass, its large polymer constituents have to be separated. Separation is difficult due to the numerous intra- and intermolecular hydrogen bonds between the constituent polymers and it is constantly studied. However, the difference in the polymer size and chemical structure of cellulose, hemicellulose, and lignin gives them different reactivities. Lignin and hemicellulose can be separated from cellulose by an alkaline treatment, while hemicellulose can be separated from the other two constituents by a dilute (< 4 wt%) sulfuric acid hydrolysis. The use of concentrated acid on the other hand removes both hemicellulose and cellulose [2].

Hydrolysis of biomass, where the lignocellulosic polysaccharides are hydrolyzed into sugars, is utilized during the fractionation and pretreatment of LCB. Hydrolysis is usually performed in acidic conditions, in which the efficiency of the acid determines the extent of the hydrolysis. Commonly, diluted

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sulfuric acid (0.05–5%) is used as a reaction media at reaction temperatures of 100–150 °C [5–7]. On the other hand, organic acids, such as oxalic acid, maleic acid, and formic acid, are used, especially in the hydrolysis of hemicellulose [8–12]. The benefit of using organic acids is that they are less corrosive than sulfuric acid. However, their efficiency in hydrolysis is lower than the efficiency of sulfuric acid. Therefore, in pretreatment purposes, the high concentration of formic acid (40–60%) has been used at temperatures of 107–121 °C, but at higher temperatures (150–200 °C), also lower formic acid concentration has been used (e.g., 8%) [13–16]. To enhance the efficiency of hemicellulose hydrolysis, additional catalysts have been used, e.g., Sindhu et al. [13] used 0.6% sulfuric acid and Vanderghem et al. [14], 40% acetic acid as additional catalyst. In addition, very high formic acid concentration (up to 90%) has been used at moderate temperatures (100–130 °C) when the aim has been to remove hemicellulose and lignin from lignocellulosic feedstock prior to cellulose refining [11, 12, 17].

In this work, Scots pine sawdust was used as the raw material. The aim of the study was to separate hemicellulose from the sawdust as monomeric sugars via acid hydrolysis (Fig. 1). Similar approach has been used in recent studies for poplar wood, Scots pine chips, and maritime pine sawdust [18–20]. However, to the best of our knowledge, the selected approach has not been applied to Scots pine sawdust before. Since the

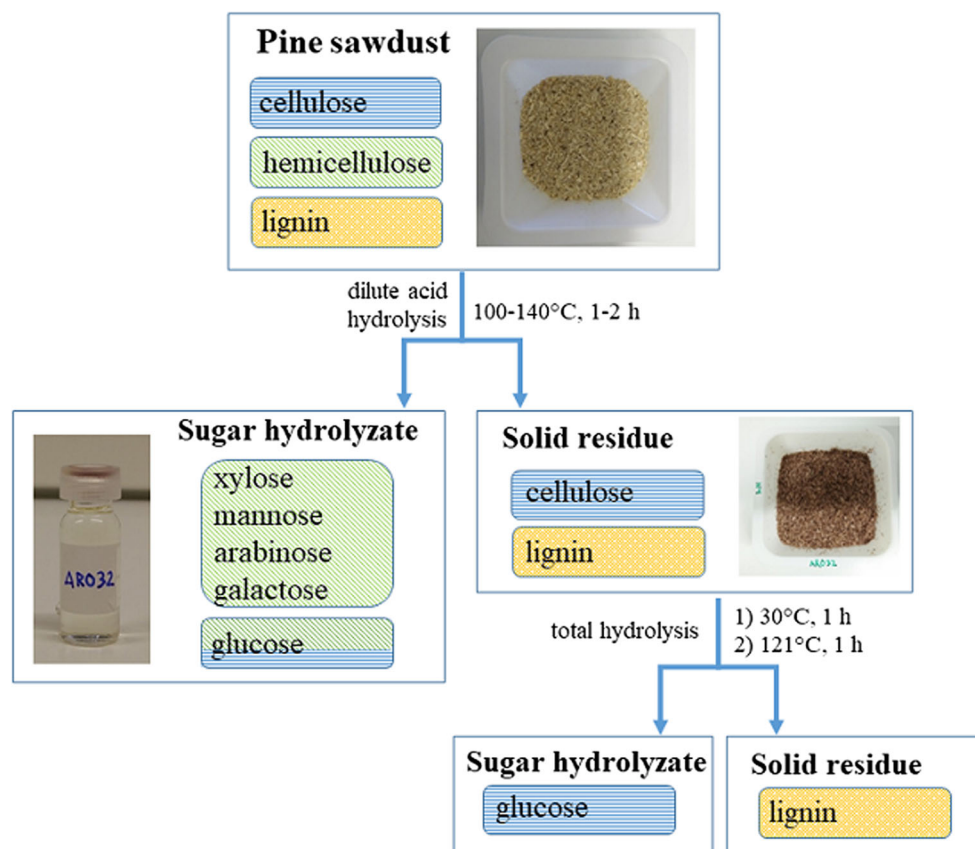
variety of lignocellulosic feedstocks is enormous, each biomass must be studied separately to find the optimal reaction conditions to produce desired products. In this study, the reaction conditions, e.g., reaction time and temperature, were optimized to maximize the sugar yield from hemicellulose and to minimize the further degradation of hemicellulose sugars as well as cellulose hydrolysis. Special attention was paid to the used acid concentration and type, i.e., sulfuric acid, formic acid, or their mixture. The aim was to find an acid mixture, which would be as efficient in hemicellulose hydrolysis as sulfuric or formic acids alone but in which the concentration of a single acid would be significantly lower than in single acid reactions. The results were confirmed by analyzing selected solid residues remaining after the hydrolysis experiments [21].

## 2 Experimental

### 2.1 Materials

The pine sawdust was received from a sawmill in northern Sweden and was used as such in hydrolysis reactions. Sulfuric acid (95–98 wt%) and formic acid (98 wt%) were purchased from J. T. Baker, and distilled water was used.

**Fig. 1** Schematic presentation of pine sawdust fractionation into its constituents



## 2.2 Methods

### 2.2.1 Chemical characterization of pine sawdust and unhydrolyzed solid residue

Pine sawdust and unhydrolyzed solid residues (USR) were dried in an oven at 105 °C until constant weight. The ash, lignin, extractive,  $\alpha$ -cellulose, and hemicellulose content of the pine sawdust were determined using multiple methods. All analyses were carried out in duplicates, and the results are presented in Fig. 2 as mean values of the duplicates.

The ash content was determined using the procedure described by Sluiter et al. [22]. To determine organic extractives, a biomass sample (3 g) was extracted with 150 mL of acetone for 4 h using Soxhlet extraction equipment, according to TAPPI standard [23]. The produced extractive-free samples were utilized further to determine lignin and holocellulose content. Klason lignin was determined after two-step acid hydrolysis of the wood sample according to Sluiter et al. [24]. Acid-soluble lignin was determined by UV spectroscopy from the hydrolysate obtained from the hydrolysis, as described by Ehrman [25]. The amount of lignin is presented as the sum of the acid-insoluble and acid-soluble lignin.

Holocellulose was prepared from the extractive-free sample by applying the procedure described by Rowell et al. [26]. Generally, 1.15 g of extractive-free sample, 38 mL of distilled water, 0.25 mL of acetic acid, and 0.6 g of sodium chlorite were allowed to react in a 250 mL Erlenmeyer flask at 70–75 °C in a water bath. After 60 min, an additional 0.25 mL of acetic acid and 0.6 g of NaClO<sub>2</sub> were added. After each successive hour, a fresh portion of 0.25 mL of acetic acid and 0.6 g of NaClO<sub>2</sub> was added. After 5 h, the flask was allowed to cool, and the solid holocellulose was filtered. The solid residue was washed with distilled water until the yellowish color was removed. Finally, the holocellulose was washed with acetone, dried in an oven overnight at 105 °C, and weighed. The residual lignin content in holocellulose was determined using a method similar to the method mentioned earlier.

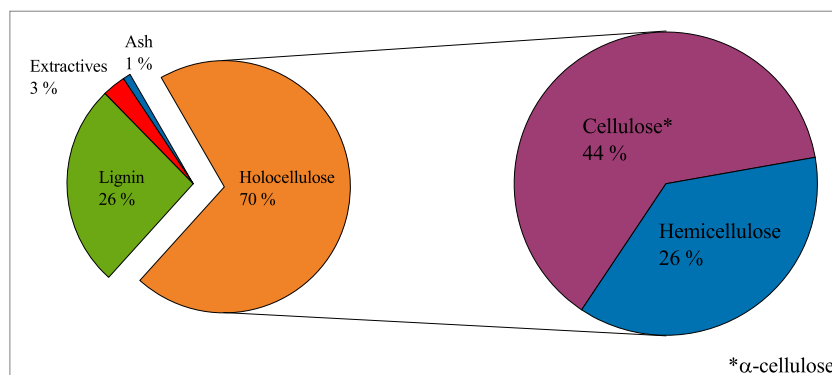
The  $\alpha$ -cellulose content of the holocellulose was determined by applying methods by Styarini et al., TAPPI standard, and Yokoyama et al. [27–29]. In this procedure, 0.5 g of holocellulose and 25 mL of 17.5% NaOH were placed in a 250 mL Erlenmeyer flask and stirred until the holocellulose was completely dispersed. The stirrer was then removed and washed with 5 mL of 17.5% NaOH to make the total reagent content in the flask 30 mL. The flask was stirred thoroughly with a glass rod and left in a water bath at 25 °C. Then, 30 min after the addition of the NaOH reagent, 30 mL of distilled water was added to the suspension and stirred thoroughly with a glass rod. The flask was left in the bath for another 30 min. Then, the suspension was stirred and filtered. The solid  $\alpha$ -cellulose was first washed with distilled water, then with 15 mL of 10% acetic acid, and finally with 400 mL distilled water. The hemicellulose content was obtained by subtracting the  $\alpha$ -cellulose content from the holocellulose content.

Ash, lignin, and extractive content of unhydrolyzed solid residue were measured similarly as described above [22–25]. In addition, carbohydrate content of USR was determined according to Sluiter et al. [24].

### 2.2.2 Hemicellulose hydrolysis procedure

Reactions were carried out with a Parr pressure reactor. A 300 mL Teflon cup was used as a reaction vessel inside the stainless steel reactor. Pine sawdust (7.5 g) was weighed into the reaction vessel, and 150 mL of studied acid solution was added (the liquid-to-wood ratio was a constant 20 mL/g). Sulfuric acid, formic acid, or a mixture of these acids was used at the different concentration levels, as described in Table 1. After feedstock and acid addition, the reactor was closed and heated to the desired temperature (100, 120, or 140 °C). After a reaction time of 1, 1.5, or 2 h, the samples were cooled with an ice bath and filtered with a 0.45- $\mu$ m PTFE syringe filter. The solid residue was washed with 100 mL of water, dried, and weighed. Some (1/5) of the reactions were randomly duplicated, and results from those reactions are shown as mean values of duplicates.

**Fig. 2** Chemical composition of pine sawdust according to dry wood mass percentage



**Table 1** Three different acid types were studied in hemicellulose hydrolysis: sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), formic acid (HCOOH), and an acid mixture (sulfuric acid + formic acid). Each of the acid types had three

different concentration levels: low, medium, and high. The concentrations are reported as mass percentages, and the measured pH values are marked in brackets

Acid type	Concentration levels and pH of the acid solutions		
	Low	Medium	High
H <sub>2</sub> SO <sub>4</sub>	0.5% (1.30)	1.5% (0.90)	2.5% (0.73)
HCOOH	15% (1.38)	30% (0.95)	40% (0.61)
H <sub>2</sub> SO <sub>4</sub> } HCOOH }	0.5% } 5.5% } (1.16)	0.5% } 10% } (1.09)	0.5% } 15% } (1.01)

### 2.2.3 HPLC analysis

The monosaccharide (mannose, xylose, galactose, glucose, and arabinose) and degradation product (HMF and furfural) concentrations of the hydrolysates were analyzed with high-performance liquid chromatography (HPLC). An Agilent 1200 series chromatograph equipped with an ICsep ICE-Coregel 87H3 (Transgenomic) column was used. The mobile phase was 5 mM sulfuric acid with a flow rate of 0.8 mL/min, and the column was operated at a temperature of 60 °C. Compounds were detected using a refractive index detector. The quantitation of the compounds was based on multiple-point external calibration. The validity and reproducibility of the calibration were confirmed by measuring control samples with each sample sequence. All samples were measured as duplicates, and the results have been reported as averages.

### 2.3 Equations

The theoretical amounts of hemicellulose and cellulose in the starting material were calculated from the biomass characterization results (see Section 2.2). The maximum amount of hemicellulose and cellulose was 26 and 44 wt% of the dry wood mass, respectively. Cellulose is known to be composed of glucose units, so its molar mass was calculated by subtracting water molecule from the glucose unit and was approximated to be 162.14 g/mol. Pine hemicellulose is known to compose of pentose and hexose units, whose amounts according to literature are mannose 11.43 wt%, xylose 6.30 wt%, galactose 2.56 wt%, and arabinose 1.60 wt% [30]. The amount of glucose in hemicellulose was approximated to be 4.1 wt%, by subtracting the amounts of other hemicellulose sugars from the total amount of hemicellulose. The abovementioned amounts of hexoses and pentoses in hemicellulose were used to approximate that their ratio is 7:3. The ratio was then used to calculate the molar mass of pine hemicellulose. Molar masses of 162.14 g/mol and 132.11 g/mol were used for hexoses and pentoses, respectively. When calculating the

molar yield percentages, the total glucose yield was calculated from the total amount of glucose in cellulose and hemicellulose (48.1 wt%). The hemicellulose sugar yield was calculated using an assumption that maximum glucose amount from hemicellulose is 4.1 wt%. If detected that mass of glucose was higher than that, the excess was not noticed as hemicellulose sugar.

The molar yield percentages (Y<sub>i</sub>) were calculated as follows:

$$Y_{\text{total glucose}} (\text{mol}\%) = \frac{m_{\text{glucose}}}{0.481 \times m_{\text{sawdust}}} \times \frac{162.14}{180.16} \times 100\% \quad (1)$$

$$Y_{\text{hemicellulose sugars}} (\text{mol}\%) = \frac{m_{\text{man+xy+gal+ara+glu}}}{0.26 \times m_{\text{sawdust}}} \times \frac{0.7 \times 162.14 + 0.3 \times 132.11}{0.7 \times 180.16 + 0.3 \times 150.13} \times 100\% \quad (2)$$

where  $m_{\text{sawdust}}$  is the mass (g) of the sawdust used in the reaction and  $m_{\text{glucose}}$  as well as  $m_{\text{man+xy+gal+ara}}$  are the masses (g) of corresponding monosaccharides obtained from the hydrolysate;  $m_{\text{glu}}$  is the mass (g) of glucose obtained from the hydrolysate if the value is below the maximum value of glucose originating from hemicellulose; otherwise, the maximum value of glucose originating from hemicellulose was used.

In USR composition analysis, results were calculated as wt% of USR dry mass. In addition, the amount of lignin in USR was calculated as wt% based on dry mass of original sawdust as follows:

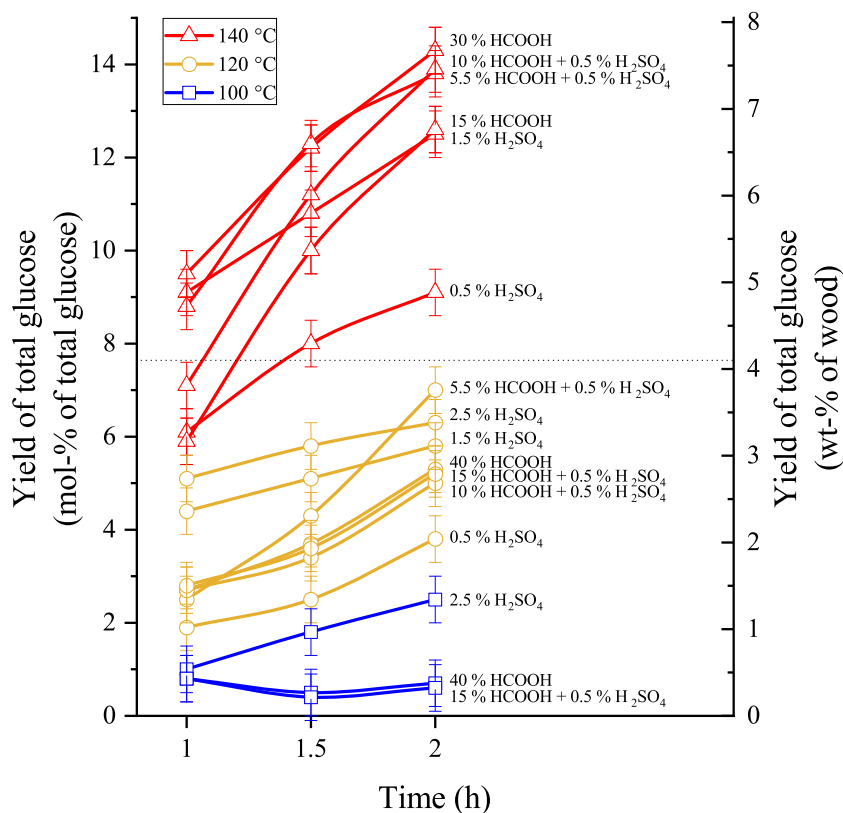
$$\text{Lignin in USR}_{\text{sawdust}} = \text{Lignin in USR} \times \text{Yield of USR} \quad (3)$$

where Lignin in USR is wt% of lignin in USR based on the dry mass of USR, and yield of USR is the ratio of the dry mass of USR and the dry mass of original sawdust.

### 3 Results and discussion

Three different reaction temperatures, reaction times, and acid concentrations were studied for each acid type to find the best reaction conditions to hydrolyze only the pine hemicellulose and not the cellulose. The lowest temperature was studied only with the most concentrated acid solutions, and the highest temperature was studied only with the least concentrated acid solutions to utilize reasonable reaction conditions. To observe hemicellulose hydrolysis, the total amount of hemicellulose sugars (mannose, xylose, galactose, arabinose, and glucose) were determined from a liquid hydrolysate. The presence of those sugars was used as a response of the conversion reaction. Presented total amounts of glucose include glucose from both hemicellulose and cellulose. If the amount of total glucose was higher than the maximum amount of glucose in hemicellulose (7.7 mol%), it indicated that the cellulose had hydrolyzed. Furthermore, the presence of furfural and HMF, which are degradation products of hemicellulose and cellulose sugars, respectively, indicated that the hydrolysis reaction had proceeded too far. Therefore, the objective was to keep the HMF, furfural, and excess glucose amounts as low as possible and to maximize the total amount of hemicellulose sugars.

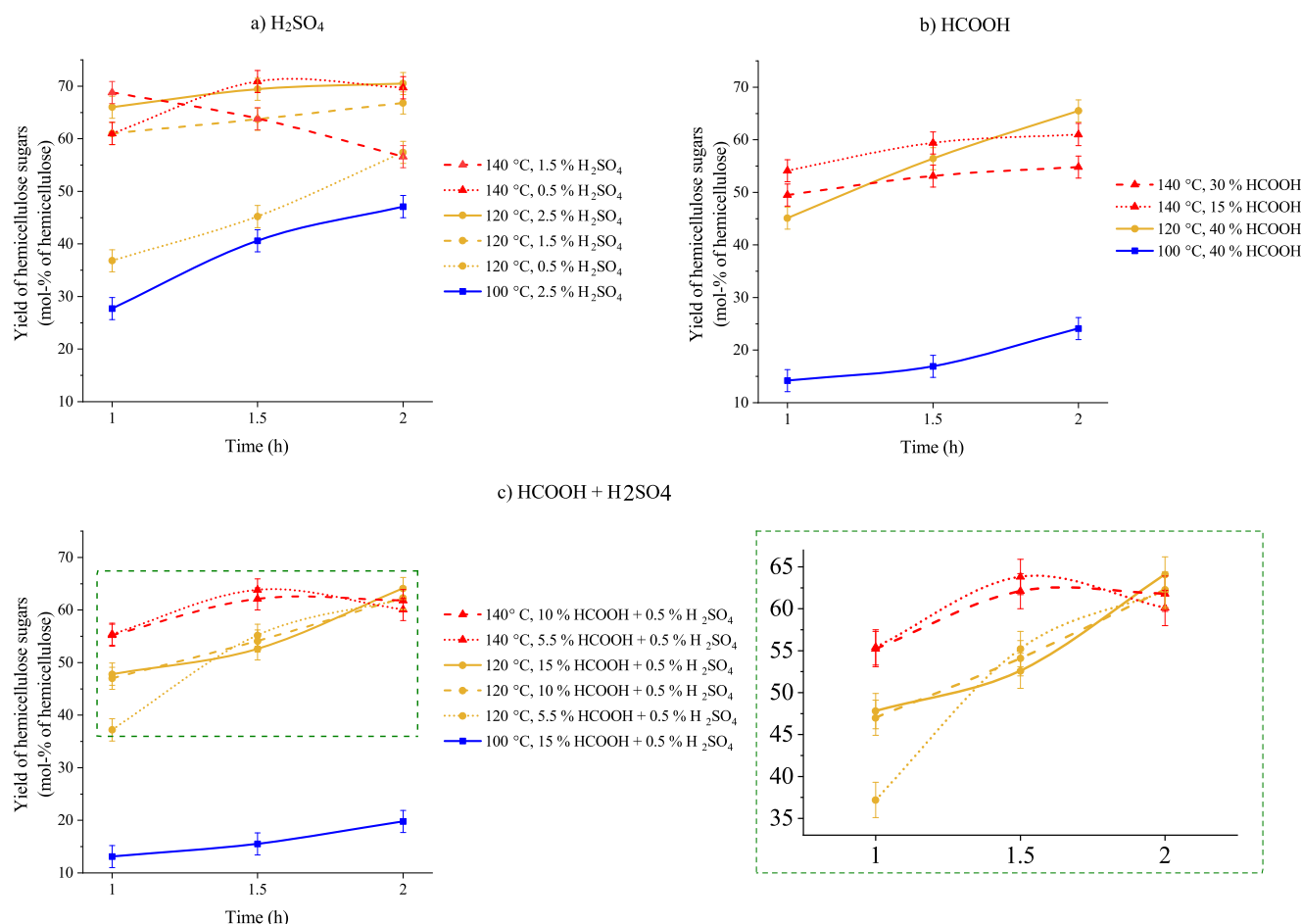
**Fig. 3** Influence of reaction temperature (red/orange/blue lines), acid type, and acid concentration on glucose yield as a function of time. The left y-axis shows the yield of glucose as mol% from total glucose and the right y-axis as wt% from the original pine sawdust. The dotted line illustrates the maximum amount of glucose (4.1 wt% of sawdust = 7.7 mol% of total glucose) that can be produced from hemicellulose



#### 3.1 Effect of temperature

Temperature was one of the studied variables, and the yields of hemicellulose sugars and total glucose were followed as a function of time during the reactions. The studied reaction temperatures were selected based on the literature [5]. The obtained results were divided into groups according to the temperature (100, 120, and 140 °C) regardless of the type or concentration of the acid used (Figs. 3 and 4). In Fig. 3, the yield of total glucose is shown as a function of time. The left y-axis shows the yield of total glucose as mol% of total glucose in sawdust (cellulose and hemicellulose) and the right y-axis as wt% of the original pine sawdust. A dotted line has been drawn in Fig. 3 to illustrate the maximum amount of glucose (4.1 wt% of sawdust = 7.7 mol% of total glucose) that could be produced from hemicellulose. Hence, the yields above the dotted line indicate that cellulose was hydrolyzing at the studied reaction conditions. The corresponding yield of hemicellulose sugars is presented in Fig. 4.

The temperature significantly affected the yields. As was assumed, the lowest temperature, 100 °C, produced the lowest yields for both hemicellulose sugars and glucose. After 1 h at 100 °C, the yields were 10–28% and 1% for hemicellulose sugars and total glucose, respectively (see the blue lines in Figs. 3 and 4). A longer reaction time (2 h) increased the yield of hemicellulose sugars to 15–41%, but total glucose yield



**Fig. 4** Influence of reaction temperature, classified by acid type and acid concentration, on the yield of hemicellulose sugars as a function of time

remained low ( $\leq 2\%$ ). Temperatures of 120 and 140 °C were both suitable temperatures to produce hemicellulose sugars with a yield of 35–71% (see the orange and red lines in Fig. 4). No clear distinction was observed between these temperatures when the hemicellulose sugar yields were compared. However, when the total glucose yields were studied, the disparity of the yields at 120 and 140 °C was clear. After 1 h, the total glucose yields were 2–5 and 6–10% at 120 and 140 °C, respectively, indicating that higher temperatures increased the hydrolysis of cellulose. At 140 °C, in reactions longer than 1 h, the yield of total glucose was above 7.7 mol%, which illustrated that cellulose was also hydrolyzing at these temperatures. In addition, at higher temperatures, the longer reaction time generally increased the yields, but the type and concentration of the acid strongly influenced the outcome of the hydrolysis.

Based on the results, 120 °C was the optimal temperature for selective hydrolysis of pine sawdust hemicellulose. At 140 °C, the cellulose was hydrolyzed along with the hemicellulose due to the higher temperature. The result is in

accordance with Arslan et al. who reported that cellulose of hazelnut shells hydrolyzed along with hemicellulose at temperatures above 120 °C [31].

### 3.2 Effect of acid and reaction time

Sulfuric acid and formic acid were chosen for the study based on the suggestions from the literature [6, 32]. Both acids were first studied as single acid solutions (Table 1), and the results were compared to literature in order to verify the selected methodology. Then the mixtures of sulfuric and formic acid were studied as the reaction medium (Table 1), and the results were compared to the results from single acid solutions as well as to literature. As previously stated, a temperature of 100 °C was too low to hydrolyze properly neither the cellulose nor the hemicellulose, so only higher temperatures are discussed in this section.

#### 3.2.1 Sulfuric acid

Sulfuric acid was studied as the reaction medium with concentrations of 0.5, 1.5, and 2.5%. The reactions were first

carried out at 140 °C with 0.5 and 1.5% sulfuric acid solutions. Based on the results, the yield of hemicellulose sugars depends on the reaction time (see the red lines in Fig. 4a). For 1.5% sulfuric acid, the highest yield (69%) was obtained in 1 h, and it decreased to 57% when reaction time increased to 2 h. This indicated that monomeric sugars were already degrading in those conditions after 1 h. With a 0.5% acid solution, the yield increased for 1.5 h (71% yield) and then started to decrease slightly. Total glucose yields increased also with the reaction time; the 1.5% sulfuric acid solutions produced more glucose (9–13%) than the 0.5% solutions (6–9%), corresponding with 1–2 h reaction times (Fig. 3). The results achieved with sulfuric acid are in accordance with literature. E.g., Ji et al. [21] produced xylose 0.185 g/g of wheat straw with 0.5% sulfuric acid, at 140 °C with 1.5-h reaction time. In our case, the yield of hemicellulose sugars was 0.207 g/g.

At 120 °C, reactions were carried out with 0.5, 1.5, and 2.5% sulfuric acid solutions (see the orange lines in Fig. 4a). With 0.5% sulfuric acid, the yield of hemicellulose sugars increased from 37 to 57% when the reaction time increased from 1 to 2 h. Total glucose yields increased as well, but they were low — only 2–4% (Fig. 3). The 1.5 and 2.5% acid solutions produced quite similar hemicellulose sugar yields, 61–67% and 66–71%, respectively, in 1–2 h. Since the yields did not increase notably, also a shorter reaction time, 1 or 1.5 h, would be feasible, when more concentrated sulfuric acid solutions (1.5 and 2.5%) are used. In addition, the total glucose yields were slightly higher (4–6%) than with 0.5% acid, as assumed, and these yields increased with reaction time (Fig. 3). Hemicellulose sugar yields in 1 h with 2.5 and 1.5% sulfuric acid correspond with masses of 0.193 and 0.178 g/g of sawdust, respectively. Therefore, results are comparable to diluted sulfuric acid hydrolysis of wheat straw, in which obtained xylose yield was 0.18 g/g, when 2% sulfuric acid was used at 120 °C with a reaction time of 1 h [21].

### 3.2.2 Formic acid

The effect of formic acid as a reaction medium was studied and compared with the sulfuric acid. The studied concentrations of formic acid were higher (15, 30, and 40%) than those of the sulfuric acid to produce equal pH to simplify the comparison of the acids (Table 1). However, the used concentrations were considerably lower than those reported in literature for experiments performed at temperatures below 150 °C [11, 13, 33]. At 140 °C with the 15 and 30% formic acid solutions, the hemicellulose sugar yields were lower, and the glucose yields higher than with the sulfuric acid (see the red lines in Figs. 4a, b, and 3, respectively). The reaction time did not seem to have much effect on the yields. With the 30% formic acid solution, the hemicellulose sugar yields increased only slightly, from 50 to 55%, and the total glucose yields from 10 to 14%, when the reaction time increased from 1 to 2 h. With

the 15% acid solution, similar increase in yields was observed; however, the hemicellulose sugar yield was somewhat higher (61%), and the total glucose yield slightly lower (13%) after 2 h than with 30% acid. The hemicellulose sugar yields achieved in this study with formic acid were clearly better than the xylose yield reported in the literature (41%), in which 14.52 wt% formic acid was used as an extraction medium for silver birch sawdust at 140 °C with a 2-h reaction time [34].

At a temperature of 120 °C, only the most concentrated formic acid solution (40%) was studied with the reaction times of 1–2 h. Based on the results, a longer reaction time clearly increased the yield, and the best hemicellulose sugar yield (66%) was achieved with a reaction time of 2 h (see the orange line in Fig. 4b). Some preliminary experiments were also done with 30% formic acid, but since the yields were only 57–58% in 2 h, no additional experiments with it or with 15% formic acid were performed. The result with the 40% formic acid was comparable with the results of the 1.5% sulfuric acid at the same temperature and differed from highest hemicellulose sugar yield (71%, with 2.5% sulfuric acid) by 5 percentage units. The total glucose yields with the 40% formic acid were 3–5%, increasing with reaction time. In addition, the glucose yields were lower than with the sulfuric acid solutions (Fig. 3). Forty percent formic acid was the most concentrated formic acid used in this study, but also notably higher concentrations have been reported in literature [11, 19].

### 3.2.3 Mixture of formic acid and sulfuric acid

Finally, the use of acid mixtures was studied. The idea was to explore whether the amount of formic acid could be reduced by adding a small constant amount of sulfuric acid to the reaction mixture. The studied acid mixtures contained 0.5% sulfuric acid and 5.5, 10, or 15% formic acid. Again, the reactions carried out at 100 °C were not very efficient. At other reaction conditions, the hemicellulose was hydrolyzed, producing hemicellulose sugar yields between 37 and 64%, depending on the acid strength, temperature (120 or 140 °C), and reaction time (1–2 h). At 140 °C, both the 5.5% formic acid + 0.5% sulfuric acid and the 10% formic acid + 0.5% sulfuric acid mixtures produced good hemicellulose sugar yields within 1.5 h: 64 and 62%, respectively (see the red lines in Fig. 4c). However, total glucose yields were high at that point (12 and 11%, respectively) with both acid mixtures (Fig. 3).

At 120 °C with a 2-h reaction time, all acid mixtures (0.5% sulfuric acid + 5.5/10/15% formic acid) produced very similar hemicellulose sugar yields (62, 62, and 64% respectively; see the orange lines in Fig. 4c) when compared to each other and to the yields achieved at 140 °C. The results were also comparable to those obtained with 1.5% sulfuric acid or 40% formic acid alone (67 and 65%, respectively). In addition,

the total glucose yields remained low when reaction temperature was decreased to 120 °C; the highest (7%) glucose yield was achieved after 2 h of heating when the acid mixture was the most diluted. However, the yield did not increase above the hemicellulose maximum value (Fig. 3). Based on the results, all acid mixtures were able to produce good hemicellulose sugar yields at 120 °C with reaction time of 2 h, while cellulose was not hydrolyzing. Especially, the mixture of 0.5% sulfuric acid and 5.5% formic acid seemed feasible alternative to single acids, since amounts of sulfuric acid and formic acid in the mixture were only 1/3 and 1/8 of the amounts of the single acids, respectively. Also, all mixtures contained considerably less sulfuric and formic acid than what is used in literature at similar temperatures, and therefore acid mixtures were seen as good alternatives to single acid solutions [13, 14, 35–38].

### 3.3 Amount of degradation products

C5 and C6 sugars can be converted into valuable products, such as furfural and HMF, respectively. In this study, the presence of these two compounds was not preferred since it indicated that the formed sugars had reacted further. Hence, the amount of HMF and furfural was analyzed by HPLC to confirm high sugar yield. In all experiments, the concentrations of HMF and furfural were < 0.5 g/L and < 1 g/L, respectively. The corresponding HMF yield was < 2% (mol% of total glucose), and the furfural yield was < 8% (mol% of pentose sugars). These amounts were considerably lower than the hemicellulose sugar yields. In addition to HMF and furfural, some acetic acid and formic acid were observed in the HPLC analysis. Acetic acid and formic acid are the side products of hemicellulose degradation.

### 3.4 Composition of unhydrolyzed solid residue

In addition to sugar hydrolysates, also the solid residues were characterized from two hydrolysis reactions: 1.5% sulfuric acid, 120 °C, 2 h (USR1) and 10% formic acid + 0.5% sulfuric acid mixture, 120 °C, 2 h (USR2). According to the characterizations, the ash and extractive contents of both unhydrolyzed solid residues (USRs) were zero. The lignin content for USR1 was 45 and for USR2, 40 wt% (corresponding to 29 and 27 wt% of lignin based on dry mass of sawdust, respectively). The amount of holocellulose was calculated to be 55 and 60 wt%, respectively. Finally, the determination of monomeric carbohydrates from USR1 and USR2 gave 49 and 51 wt% for glucose and only 5 and 7 wt% for nonglucosic hemicellulose sugars, respectively. Since the original lignin, cellulose, and hemicellulose content of the sawdust was 26, 44, and 26 wt%, respectively, the USR analysis revealed that the lignin and cellulose percentages increased and the hemicellulose percentage decreased significantly during to the

hemicellulose hydrolysis. The hemicellulose hydrolysis was thus effective and selective. Comparison between USRs showed that sulfuric acid hydrolysis was slightly more efficient to degrade hemicellulose than acid mixture, but the difference was very small. Overall, both residues would be feasible feedstocks to further delignification or cellulose hydrolysis.

## 4 Conclusions

In this work, hemicellulose from pine sawdust was selectively hydrolyzed into monomeric sugars using moderate reaction temperature and time as well as low acid concentrations. Temperature revealed to be the main distinguishing feature between cellulose and hemicellulose hydrolysis. Temperatures of 120 and 140 °C were both suitable to produce good yields of hemicellulose sugars, but at 140 °C, also cellulose hydrolyzed along with hemicellulose. At 120 °C acid mixtures (0.5% sulfuric acid + 5.5/10/15% formic acid), produced hemicellulose sugar yields 62, 62, and 64%, respectively in 2 h. Results were comparable to the yields from 1.5% sulfuric acid or 40% formic acid hydrolysis, which produced 67 and 66% of hemicellulose sugars in 2 h, respectively. Therefore, with acid mixtures, the amounts of single acids in the reaction solution could be reduced significantly. The remaining solid residue from acid mixture hydrolysis consisted of 40% lignin, 51% glucose, and only 7% hemicellulose sugars verifying selective hemicellulose degradation. Obtained solid fraction was further separated into its lignin and cellulose constituents, hence enabling the complete utilization of pine sawdust.

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