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Acid-catalyzed mechanocatalytic pretreatment to improve sugar release from birch sawdust: Structural and chemical aspects

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ABSTRACT

This study examined acid-catalyzed mechanocatalytic pretreatment of birch sawdust without a separate impregnation step. Catalyst amount and pretreatment time were the key variables. Pretreated material was mixed with water for hydrolysis (100 °C, 60 min). The efficient release of total reducing sugars from birch sawdust is significant to the path towards biofuels and biochemicals. Based on the results, the structure and surface of birch sawdust changed as a function of mechanocatalytic pretreatment. Milling time caused significant transformations in birch structure and also increased the yields of reducing sugars. The highest yield of total reducing sugar from pretreated sawdust was 23.0% after 30 min of hydrolysis with 1.0 mmol/g acid catalyst, whereas the highest glucose yield was 23.8 g/kg (1.5 mmol/g catalyst, 60 min) and the highest xylose yield was 37.5 g/kg (1.0 mmol/catalyst, 30 min). Overall, acid-catalyzed mechanocatalytic treatment seems to improve sugar yields from birch.

1. Introduction

Woody biomass is an abundant renewable source for manufacturing fuels, chemicals, heat, and power, and it cannot be used for food production [1–4]. The forest industry produces several side streams, like sawdust, which are consumed in heating and power plants. For example, in Finland, 2.5 million cubic meters of sawdust were used for energy generation in 2019 [5]. The utilization of woody biomass in biorefineries to produce value-added chemicals and fuels transforms biopolymers, such as cellulose, hemicellulose, and lignin, into platform chemicals, like sugars [1,2,4]. This kind of bioeconomic point of view is required to face social and environmental challenges like climate change and the growth of world population. More effort is put into research to support circular economy by biorefining strategies. New ways have to be created and settled to optimize the utilization of biomass resources, including biomass waste streams, and maximize the generation of bio-based products [6]. However, the recalcitrant nature of lignocellulosic biomass creates challenges for the design of biorefineries. Choosing the right pretreatment method for the chosen feedstock is thought to be a way to overcome the challenges and the limited effectiveness of enzymatic processes [2,4,7,8].

The pretreatment of lignocellulosic biomass can be performed by different methods. Several pretreatment methods have been introduced for birch, and the results show that the process of the depolymerization of birch will benefit from the pretreatment process. Chemical pretreatments with alkali materials, such as NaOH [9,10] and ammonia [11], or ionic liquids, such as 1-H-3-methylmorpholinium chloride [12], 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium chloride [13,14], and N-methylmorpholine-N-oxide [15] increase the glucose yields and affect the yield of enzymatic hydrolysis, fermentation to ethanol, or digestion to biogas. Using switchable ionic liquid with looping reactor has been shown to work for fractionation of lignin and hemicellulose from bich sawdust [16]. In addition, acidic 1-ethyl-3-methylimidazolium hydrogen sulfate ionic liquid has shown promising results for hydrolyzing the hemicellulose of wheat straw into pentoses [17]. Physical and physicochemical pretreatments, such as steam explosion [9,18] and electron beam irradiation [19], can also be used to increase sugar release from birch. In addition to these methods, different pretreatment methods can be combined. For example, combined electron beam-steam explosion provides additional benefits compared to

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pure steam explosion pretreatment [20].

Ball milling is an efficient method of making polymers in plant fiber more digestible for enzymatic hydrolysis [21]. Ball milling is a high-energy mechanical pretreatment method that reduces the particle size and disturbs the crystalline structure of lignocellulosic biomass, but it is also a complex mechanical-chemical process [22–24]. In mechanocatalytic pretreatment processes, a mechanical process, such as ball milling, is combined with a catalytic process. Mechanocatalytic processes increase sugar yield and shorten the milling time of corn stover [25], fiber sludge [26], and willow [27] and reduce the energy demand of the milling process. In the mechanocatalytic pretreatment process, the catalyst can be applied directly to the biomass or applied via a separate impregnation step. However, it has been shown that mechanocatalytic pretreatment without a separate impregnation step is beneficial for sugar yields compared to pretreatment with an impregnation step [26]. This will also intensify the pretreatment process by decreasing the number of process stages and the amount of chemicals needed in the pretreatment process. In addition to dry ball milling, wet ball milling can be utilized. They both have advantages and disadvantages; for example, dry ball milling is more effective in reducing particle size and crystallinity index [28,29].

In this study, mechanocatalytic pretreatment was applied to a forest industry side stream, birch sawdust. The mechanocatalytic pretreatment method applied in this study combines traditional ball milling pretreatment with a catalytic process involving sulfuric acid. In our study, the catalyst was introduced to the birch without an impregnation step. The method has previously been used on willow [27], which differs from birch with regard to chemical and structural features [12,13]. Thus, the results of experiments on willow cannot be generalized to birch. The objective of this study was to understand if the mechanocatalytic pretreatment can be used to modify birch sawdust and how it affects its structure and chemical composition, as well as its effect on sugar release. In addition to visual observation with field emission scanning electron microscopy (FESEM), determination of the crystalline structure via X-ray diffraction (XRD), and analysis of the released sugars, a Fourier-transform infrared spectroscopy (FTIR) analysis was conducted to determine chemical changes after mechanocatalytic pretreatment. The sugar release after the mechanocatalytic pretreatment of birch was also compared with the results of our earlier experiment on willow.

2. Experimental

2.1. Materials

Two birch species (*Betula pendula* and *Betula pubescens*) were collected from a stand in the coastland of Västerbotten, Sweden. The average age of the trees was 30 years. Delimbed birch logs were chipped in a stationary chipper with a chipping length of 12 mm and air-dried to about 15% water content at 30 °C. Samples were ground to a particle size of 0.5 mm using a Retsch SM100 Comfort mill and finally stored in air-tight containers at room temperature before the use. The moisture content of sawdust was 6.2%. The ground material is called birch sawdust in this paper.

Sulfuric acid (Suprapur® 96%, Merck KGaA) was used as the acid catalyst of the mechanocatalytic pretreatment. Chemicals used for analysis: Nitric acid (puriss. p.a., ACS reagent, ≥69% Honeywell Fluka), hydrogen peroxide solution (ACS Reagent, 30 wt% in H_2O, Honeywell), sulphuric acid (Titrisol® 0.5 mol/L solution, Merck KGaA) and acetic acid (100%, Merck KGaA), glucose (Sigma-Aldrich), hydroxymethyl furfural (Sigma-Aldrich) and furfural (Sigma-Aldrich) and xylose (Acros organics). All chemicals were analytical grade and used as received without further purification.

2.2. Methods

2.2.1. Characterization of birch sawdust

The metal content of the birch sawdust was measured by inductively coupled optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima 5300 DV instrument. First, 0.1–0.2 g of the sample was digested in a microwave oven (MARS, CEM Corporation) with 9 mL of HNO_3 at 200 °C for 10 min followed by the addition of 3 mL of H_2O_2, and the mixture was digested at 200 °C for 10 min. Next, the solution was diluted to 50 mL with water, and the elements were analyzed by ICP-OES. Prior to the mineral acid treatment, elemental analysis of the birch sawdust (i.e., carbon, hydrogen, nitrogen) was conducted via a Perkin Elmer 2400 Series II CHNS/O device. These measurements were conducted in triplicate. All analyses were conducted using the dry sample (moisture 0.94%). Cellulose, hemicellulose, holocellulose, lignin, ash, and extractives of birch sawdust were determined according to the procedure presented in our earlier article [27]. Hemicelluloses were determined according to method of Sundberg et al. [30] Experiments were performed in duplicates.

2.2.2. Mechanocatalytic pretreatment of birch sawdust and hydrolysis

Birch sawdust (2.0 g) and sulfuric acid were briefly mixed in the milling bowl. The catalyst-to-sample ratio was ranging from 0.25 to 1.5 mmol/g(sawdust), expressed in this article as mmol/g. The volume of the milling bowl was 45 mL, and the inside surface of the bowl was zirconium oxide. The milling balls, with a diameter of 10 mm and a mass of 2.98 g, were made of chemically robust zirconium oxide. In total, 16 milling balls were used. The rotation speed of the mill was 800 rpm. Milling was done using a planetary mill (Fritsch Pulverisette 7 Premium line, ldar-Oberstein, Germany). Experiments were performed in duplicates and values are given as mean value.

Milling was done with a 5 min milling time followed by 10 min cooling cycles to release the formed heat, if not otherwise mentioned. The total milling time used in this paper includes only active milling time and no pauses during the cooling cycles. The maximum number of cycles was 16.

After milling, the pretreated sample was divided into two batches in order to determine the sugars released from the mechanocatalytically pretreated sawdust, both at room temperature and at 100 °C. A sample (0.5 g) was mixed with 15 mL of distilled water. The solution was stirred at a speed of 400 rpm at room temperature for 20 min or heated up to 100 °C with an oil bath for 60 min at 400 rpm stirring speed and then quickly cooled to room temperature under running water. A reflux setup was used while heating the sample in the oil bath to prevent excess water evaporation and significant concentration of sugar solution due to boiling of water. The sugar solution was filtered through a filter (Whatman 1) before the sugar analysis.

As a reference sample, birch sawdust was mixed with sulfuric acid without ball milling. The sample was treated as described above to produce a sugar solution. A reference sample that was milled with water instead of sulfuric acid was also created.

2.2.3. Field emission scanning electron microscope and X-ray diffraction

The sawdust samples were analyzed via FESEM and XRD before and after mechanocatalytic pretreatment. The microstructures shown in the FESEM images were obtained with a Zeiss Sigma FESEM operated at 5 kV at the Centre for Material Analysis at the University of Oulu. X-ray diffractograms were recorded with PANalytical X'Pert Pro XRD equipment using monochromatic CuKα1 radiation (λ = 1.5406 Å) at 45 kV and 40 mA. Diffractograms were collected in the 2θ range of 5–60° at 0.017° intervals, with a scan step time of 110 s. The crystalline phases and structures were analyzed with the X'Pert HighScore Plus software.

The cellulose crystallinity index (CrI) of the birch sample was calculated according to Segal's method:

$$CrI = (I_{200} - I_{AM}) \times I_{200}^{-1}, \quad (1)$$

where I_{200} is $2\theta = 18°$ and I_{AM} is $2\theta = 21.9°$ [31].

2.2.4. Specific surface area

The birch sawdust and birch sawdust milled with water were dried at 104 °C. The specific surface area of birch sawdust and sawdust milled with water were determined at − 196 °C with a Micromeritics 3 Flex physisorption instrument (Micromeritics Instruments, Norcross, GA, USA). Portions of each sample (100–200 mg) were degassed with a Micromeritics Smart VacPrep gas adsorption sample preparation device at a pressure of 5 mmHg and at a temperature of 140 °C for 3 h to remove the adsorbed gas. Adsorption isotherms were obtained by immersing the sample-containing tubes in liquid nitrogen (−196 °C) to achieve constant temperature conditions and by adding a small dose of gaseous nitrogen into the samples. The specific surface area values were calculated from the adsorption isotherms according to the Brunauer–Emmett–Teller (BET) method [32].

2.2.5. Fourier transform infrared spectroscopy

The spectra were collected with a PerkinElmer Spectrum One FTIR spectrometer combined with a PerkinElmer Universal Attenuated Total Reflectance (ATR) Sampling Accessory. Samples were analyzed as either untreated sawdust or as mechanocatalytically pretreated sawdust, and they were analyzed without any further sample preparation directly from the solid material.

Lateral order index (LOI) [33] was calculated as follow:

$$\mathrm{LOI} = A_{1427} / A_{898} \quad (2)$$

2.2.6. Determination of total reduced sugars by UV/VIS spectrometry

The amount of total reduced sugars (TRS) in the sugar solution was determined according to the 3,5-dinitrosalicylic acid (DNS) method [27,34]. Sugar solutions with high sugar concentrations were diluted before adding the DNS reagent. The DNS reagent and the sample were mixed in equal proportions in a tube. The mixture was heated for five minutes in order to achieve color development and then cooled. Distilled water was added in order to achieve a total volume of 3 mL. A UV–VIS spectrophotometer (Ordior Shimadzu UV-1800, Shimadzu Corporation, Kyoto, Japan) at a wavelength of 540 nm was used. An external calibration method was used, and validity was confirmed by the control samples in each analysis set. The TRS yield was determined using the following equation:

$$\mathrm{TRS} = 100\% \times (c_{TRS} \times V) / m_{wood}, \quad (3)$$

where c_{TRS} is the concentration of sugars in the solution, V is the volume of the solution, and m_{wood} is the mass of processed wood.

2.2.7. Determination of glucose and xylose in sugar solutions

Sugar solutions were filtered through a Cronus syringe filter (nylon 0.45 μm) before analysis. Concentrations of compounds were analyzed with high-performance liquid chromatography (HPLC, Agilent 1200 series chromatograph equipped with Rezex ROA Organic Acid H^+ (Phenomenex) column). 5 mM sulfuric acid was used as the mobile phase with a flow rate of 0.8 mL/min, and the column was operated at a temperature of 60 °C. Sugars and acetic acid were detected with a refractive index detector and hydroxymethyl furfural and furfural with a diode array detector operated at a wavelength of 280 nm. The quantitation of the compounds was based on multiple-point external calibration. The validity and stability of the calibration was confirmed by measuring control samples with each sample sequence, which contained, on average, ten samples.

Table 1
Chemical characterization of birch sawdust and the composition of willow sawdust according to literature [27]. The amounts of all components are expressed as a percentage of dry matter.

	Birch	Willow
Lignin (%)	23	26
Holocellulose (%)	69	72
α-Cellulose (%)	37	42
Hemicellulose (%)	32	30
Ash (%)	0.6	
Extractives (%)	3.7	

Table 2
Elemental analysis of birch sawdust for carbon, hydrogen, nitrogen, and sulfur determined on the Perkin Elmer 2400 Series II CHNS/O device.

C (w%)	H (w%)	N (w%)	S (w%)
51	6.7	0.3	< 0.1

Table 3
Main trace inorganic elements (ICP-OES) for birch sawdust (total ash content in the birch sample was 0.64% and total organic matter was 99.36%).

Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Zn (mg/kg)	Mn (mg/kg)
1240	611	234	16	48	95

3. Results and discussion

3.1. Characterization of birch sawdust

The composition of the birch sawdust was determined, and the percentage of ash, extractives, lignin, and holocellulose (on dry matter basis) are presented in Table 1. The shares of lignin and α-cellulose are slightly higher in willow than birch, and birch has a bit more hemicellulose than willow. The hemicellulose of the dry birch sawdust consists of 67% xylose, 10% glucose, 4% mannose, 4% galactose, 3% arabinose and 2% rhamnose.

Carbon, hydrogen, nitrogen, sulfur, and main trace inorganic elements of birch sawdust were also determined (Tables 2–3). Calcium, potassium, and magnesium were the main trace inorganic elements, and approximately half of the sawdust was composed of carbon.

3.2. The effect of the duration of mechanocatalytic pretreatment on birch sawdust

The effect of mechanocatalytic pretreatment on the structure and morphology of birch was observed by FESEM images of the sawdust before and after the pretreatment process. It can be seen from Fig. 1A and B that the untreated birch sawdust was oblong and the cracks followed the shape of the particles.

The pretreatment of birch sawdust was done by milling with distilled water or in the presence of the acid catalyst. In our earlier study with willow sawdust, it was found that moisture was needed in order to intensify the milling process of the sawdust [27]. The shape of the birch sawdust particles turned out to be rounder, and their size reduced during the pretreatment. Due to the viscoelastic nature of wood, the heat produced in the process, and mechanical forces, the shape and surface of particles are altered in the pretreatment process [35]. In this study, particles turned out lumpy if the pretreatment process was done with water. 30 min milling increased the specific surface area from 0.6 to 1.5 m^2/g. Extending the milling time from 30 min to 80 min (Fig. 1 C–E) did not change any aspects of the wood significantly. The surface was lumpy and remained like the ones milled with water if the birch was milled with the acid catalyst in a catalyst-to-solid ratio of 1.0 mmol/g for

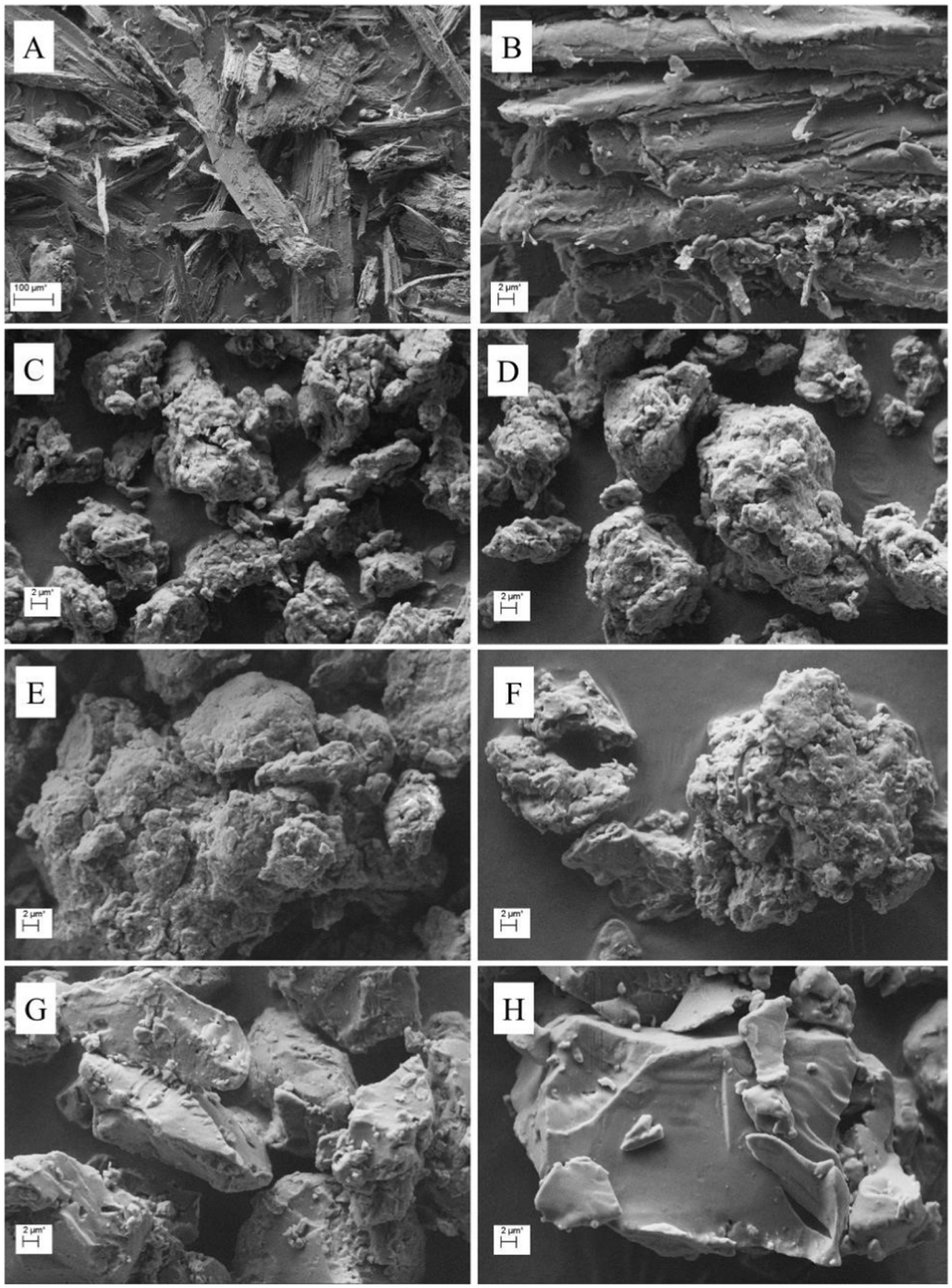

Fig. 1. FESEM images of untreated birch sawdust with magnifications of 250x (A) and 5000x (B). FESEM images of birch milled with distilled water for 30 min (C), 60 min (D), and 80 min (E) and with acid for 30 min (F), 60 min (G), and 80 min (H). Magnification 5000x.

30 min (Fig. 1F). However, the surface of the particles looked smoother if the milling process was carried out over 30 min (Fig. 1G–H). After 80 min of milling with sulfuric acid, the surface of the birch was flat and the edges were sharper.

The effect of the mechanocatalytic pretreatment on the phase of the birch was also analyzed with XRD (Fig. 2). The XRD pattern of untreated birch sawdust matched with monoclinic cellulose-Iβ (International Centre for Diffraction Data, ICDD, PDF 00–060–1502) and had peaks at 16.7°, 21.9°, and 34.6°, which are related to the crystalline structure of cellulose. The peak at 34.6° corresponds to the crystalline length and the peaks at 16.7° and 21.9° to crystallites' diameter [36,37]. After ball milling, the XRD patterns were all very similar to that of amorphous cellulose (ICDD, PDF 00–060–1501). Ball milling the birch sawdust with water for 30 min turned the first two peaks into one peak pattern, at 20.1°. If milling was extended to 60 or 80 min, the peak shifted to 20.7° or 20.8°, respectively. Also, the other peaks, observed with untreated birch at 34–46°, were broadened so that no specific peak was observed. Changing the water load into the acid load decreased the intensity of the major peak and shifted it to the right. For 30 min of milling with acid, the peak was at 20.8°, for 60 min at 20.7°, and for 80 min at 21.3°. The traces of the peak at 16.9° disappeared if the acid catalyst was used, whereas the pattern of the birch milled with water showed some traces of this first peak. Peaks in the area 28.1–31.4° as well as 50.2° indicate presence of impurity of wood, which react with sulfuric acid.

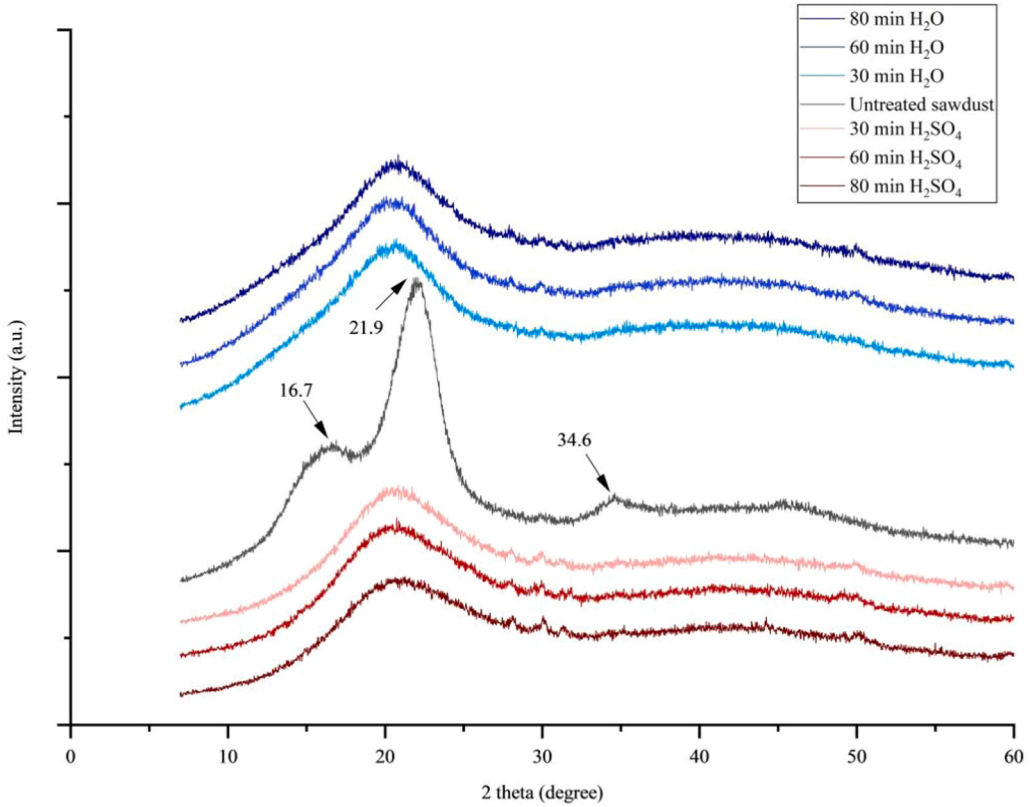

Fig. 2. XRD patterns of untreated birch sawdust and sawdust milled for 30 min, 60 min, and 80 min with water or acid catalyst (1.0 mmol/g).

Ball milling significantly decreases the degree of polymerization as well as the crystallinity of cellulose in biomass, like flax fiber or corn stover, leading to higher water sorption and lower thermal stability [22, 38]. Mechanochemical grinding destroys the network of inter- and intra-molecular linkages of cell wall polymers. Depolymerization of the cell wall occurs as a result of the dissociation of complexes between lignin and cell wall carbohydrates, degradation of arabinoxylans in hemicellulose polymers, and depolymerization of β-1,4 glycosidic bonds in cellulose macromolecules [21]. The FTIR spectra of untreated birch sawdust and birch ball milled with water or sulfuric acid are shown in Fig. 3.

A broad peak at the region of 3050–3600 cm^{-1} became stronger and shifted from 3336 to 3372 cm^{-1} as a result of pretreatment. This region corresponds to the O—H stretching vibration and is assigned for intermolecular and intramolecular bond stretching. The change in the intensities of the peaks may be due to the breakage of the inter- and intramolecular hydrogen bonds of cellulose and the formation of O—H bonds from the degradation of β-1,4 glycosidic bonds between glucose units [39,40]. A band at 2900 cm^{-1} was intensified when the birch was pretreated in a ball mill with water or the acid catalyst. The peak was highest when the birch was ball milled for 60 min with the acid load. The peak in this area is due to C—H stretching and indicates amorphous regions of cellulose [39,41]. The stronger peak at this location suggests that the crystallinity of cellulose decreases simultaneously with an increase in amorphous regions.

The peak near 1728 cm^{-1} was intensified according to the stage of intensity of the treatment conditions, and it was shifted from 1737 to 1721 cm^{-1}. The band at 1735 cm^{-1} has been shown to correlate with xylan concentration, together with peaks at 1600 and 1245 cm^{-1} [42]. The aromatic skeletal vibration in lignin correlates with bands at 1505 and 1597 cm^{-1} [43]. The peaks shifted from 1506 to 1514 cm^{-1} and from 1594 to 1606 cm^{-1} due to the mechanocatalytic treatment.

Milling affects the particle size and reveals the polymeric components of birch. A fingerprint region up to 1500 cm^{-1} showed more intensive peaks if the birch was treated with water or acid in a ball mill compared with the peaks of the birch sawdust that was not mechanocatalytically pretreated. The area is complex due to the contribution of various vibration modes of carbohydrates and lignin, but some changes could be observed. This area had common features for all samples, but intensities increased together with the intensity of the treatment process.

The peak at 1034 cm^{-1} is related to lignin and cellulose. The peak shifted from 1032 to 1025 cm^{-1} during the mechanocatalytic treatment. 832 cm^{-1} is related to lignin and was shifted to 811 cm^{-1} after 60 min of milling with the acid load. The peak at 760 cm^{-1} was observed when acid was used in the milling process. The band at 750 cm^{-1} is proposed to correlate with the change in the Iα and Iβ phases of cellulose [44].

The band around 1427 cm^{-1} is associated with crystalline structure of cellulose and the band around 898 cm^{-1} with amorphous region. Nelson and O'Connor [33] have proposed that the ratio of absorbances of these two bands describes lateral order index (LOI). Whereas CrI values decreased from 53% to range of 12–21% after pretreatment (Fig. 2), indicated LOI values significantly smaller change in ordered regions of cellulose structure and crystallinity (Table 4). Ball milling is an effective way to reduce CrI value of biomass. E.g., CrI value of eucalyptus reduced from 60% to 8% with 20 min milling [45]. In this study milling with acid decreased CrI value in 30 min from 53% to 21% and after 60 min milling to 17%, with water 30 min milling decreased CrI value to 13% and 60 min milling to 12%. LOI value remained 0.98 even if birch was milled with water. 30 min milling with acid decreased LOI value slightly, but the value increased back to 0.98 after 60 min milling.

3.3. The effect of the acid load of mechanocatalytic pretreatment on birch sawdust

The birch sawdust was mechanocatalytically treated in the ball mill for 60 min. Pretreatments were done with acid catalyst loads of 0.25, 0.5, 1.0, or 1.5 mmol/g, and milling with distilled water was used as a

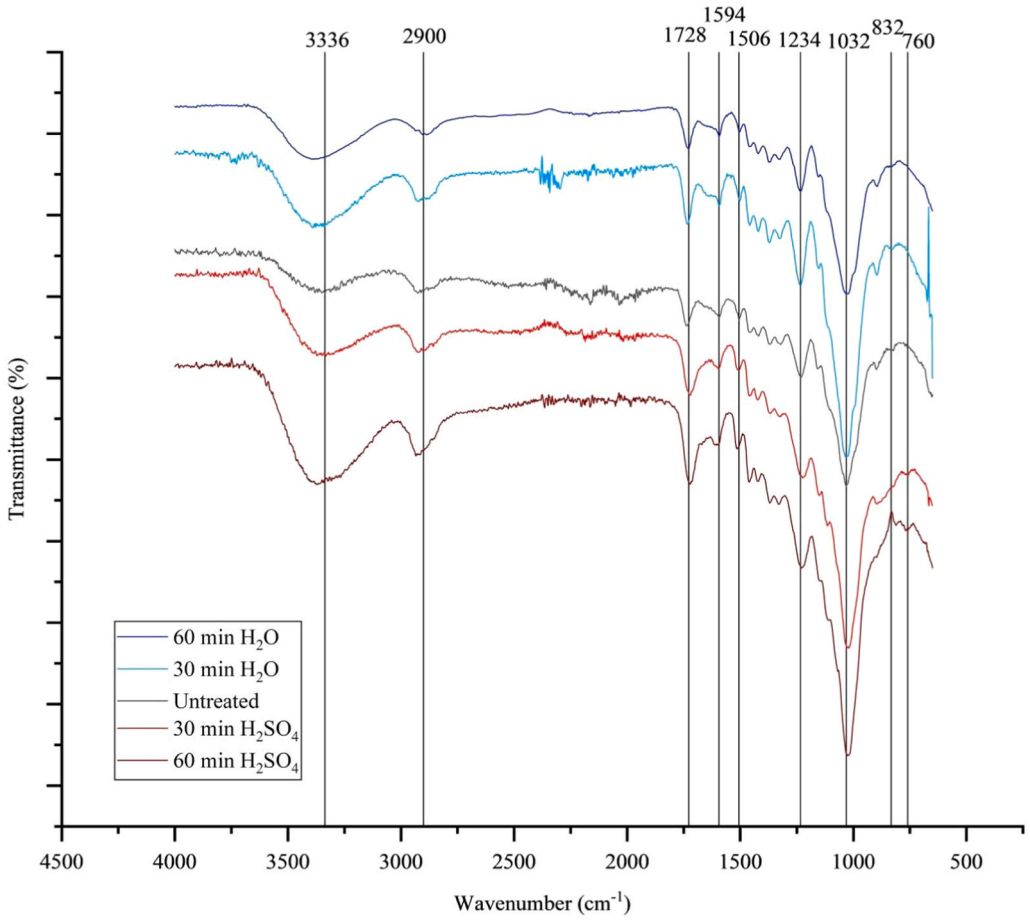

Fig. 3. FTIR spectra of untreated birch sawdust and sawdust milled for 30 min and 60 min with water or acid catalyst (1.0 mmol/g).

Table 4
Lateral order index of birch after pretreatment.

Pretreatment	LOI
60 min H_2O	0.98
30 min H_2O	0.98
Untreated	0.98
30 min H_2SO_4	0.95
60 min H_2SO_4	0.98

reference. According to experiments, mechanocatalytic pretreatment with a catalyst load of 2.0 mmol/g is not possible because the sample agglomerates on the surface of the milling bowl and milling balls. The amount of moisture in the ball milling process has an effect on the process, the changes in biomass, and the yield of the hydrolysis reaction. The changes in the shape and surface of particles depend on the solution used in the milling process or the absence of a solution [46]. According to earlier research, in high-energy milling, low moisture content intensifies the milling process of willow sawdust [27], so water was used in the milling of the reference sample. Similar effects on the surface morphology of the birch particles were noticed in this study when water was used in the milling process. The surface of the reference birch was lumpy after ball milling with water (Fig. 4A). The increase in acid dosage in the process changed the surface of the particle depending on the catalyst-to-solid ratio. The lumpy structure on the particles was already decreased with the 0.25 mmol/g acid load (Fig. 4B). If the acid load was increased to 0.5 mmol/g, sharp edges were observed on the particles, and cracks and pores were visible (Fig. 4C). Fig. 4D and 4E show melted-looking structures and particles that are attached to each other after 1.0 and 1.5 mmol/g acid loads. The excess acid caused the sample to adhere to the walls of the milling bowl. Applying more catalyst would require wet ball milling, in which the milling is done in solution. However, it has been shown that dry milling is more effective than wet milling [47]. High catalyst loads can also be avoided, for example, by adding some catalyst in a separate hydrolysis step after the pretreatment phase or by applying the catalyst in a separate impregnation step followed by distillation of the solvent. Particle size distribution was determined from FESEM images (Fig. 5). Milling with 0.25 mmol/g acid load and water load produced smaller particles, but when acid load was increased, the particle size of birch started to increase. It can be hypothesized that this increase is due to heat and chemical reactions during the milling, which lead to agglomeration of particles to each other and finally to milling equipment.

The XRD patterns revealed a decrease in the intensities if the water load was replaced with an acid load, as well as if the acid load was increased (Fig. 6). The main peak shifted to the right from 20.1° (water) to 20.3° when 0.25 mmol/g of acid was used in the milling process. Applying more acid in the process caused the peak to shift even further right to 20.6°, 20.7°, and 20.6° when acid loads of 0.5, 1.0, and 1.5 mmol/g, respectively, were used. It was observed that even the broad peak at 34–46° shifted slightly to the right. These areas are often connected with crystallite structures of cellulose [36,37] and suggest changes in the crystallinity of the birch due to mechanocatalytic pretreatment.

The FTIR spectra of the birch sawdust milled with water and different acid loads are presented in Fig. 7. The changes in FTIR patterns are largely similar to the changes in Fig. 3. The broad peak at 3388 cm^{-1} shifted gradually to 3323 cm^{-1} when pure water was replaced with an acid catalyst and the acid load was increased. The intensity of the peak was stronger if an acid catalyst was used instead of water. A broad peak

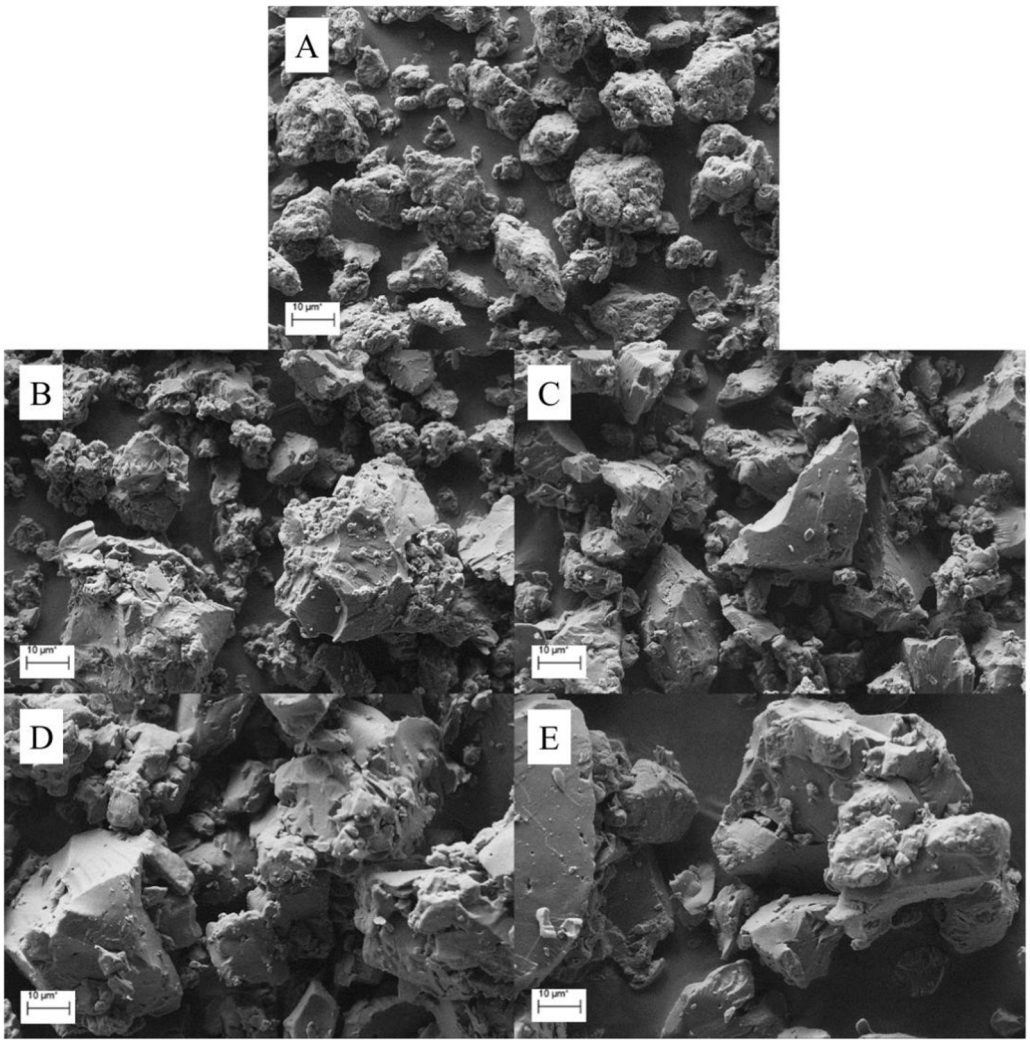

Fig. 4. FESEM images of birch milled with distilled water for 60 min (A, reference) and milling for 60 min with loads of 0.25 mmol/g (B), 0.5 mmol/g (C), 1.0 mmol/g (D), and 1.5 mmol/g (E). Magnification 2500x.

at 2889 cm^{-1} turned sharper and the peak's center shifted gradually to the left so that, with an acid load of 1.5 mmol/g, the peak's center reached 2919 cm^{-1}.

As mentioned earlier, in the fingerprint area, several peaks correlate with major cell wall components. There were several peaks in this region, and the intensities of this area were increased if acid was used in the milling process instead of water. The peaks at 1032 and 1232 cm^{-1} moved gradually to 1018 and 1213 cm^{-1}, respectively, when milling conditions were harshened. The peak at 894 cm^{-1}, which is assigned for polysaccharides' β-glycosidic linkages and C—H deformation in cellulose, was shifted, and the shape of the peak became wider so that with a 1.5 mmol/g acid load, the peak center was shifted to 863 cm^{-1}.

The peaks at 1502, 1594, and 1729 cm^{-1} correlate with lignin, and all of them shifted gradually to 1516, 1611, and 1716 cm^{-1}, respectively. However, the two peaks shifted back to 1501 and 1723 cm^{-1} if 1.5 mmol/g of acid was applied to the process. These changes suggest that the lignin of the birch was altered by the pretreatment process. The acid load in the mechanocatalytic process caused changes in the chemical bonds of the birch depending on the amount of catalyst.

CrI decreased from 12% to 10% when water was replaced with acid loads of 0.25 and 0.5 mmol/g. Similar effect was noticed with LOI values (Table 5). CrI increased to 17% when 1.0 mmol/g acid load was used and decreased to 15% when acid load was increased further to 1.5 mmol/g. From FESEM images (Fig. 4) can be seen how the surface of particles changed with these acid loads. The increase in CrI with the specific acid load was also seen in a previous study with willow. CrI of willow sawdust decreased from 59% to 22% after milling with water. Applying 1.0 mmol/g acid load to milling process decreased the CrI to 14%, but increasing acid load to 1.5 mmol/g increased the crystallinity index to 23%. It was also noticed that the surface of particles looked like molten and XRD pattern indicated amorphous phase [27].

3.4. *The effect of mechanocatalytic pretreatment on sugar yields*

The milling process reduced the size of the sawdust particles and thus increased the total surface area of the particles. According to XRD and FTIR analyses, the milling also altered the crystalline structure of the cellulose component of the sawdust. An increase in surface area as well as a decrease in the crystallinity of cellulose enhance enzymatic hydrolysis [48], but the particle size of lignocellulosic biomass does not always predict the digestibility [49,50]. It has been shown that the crystallinity and size of cellulose decrease with longer ball milling duration, leading to increased sugar yields [24]. However, with lignocellulosic biomass, the effect of particle size and crystallinity of cellulose on biomass utilization is not as straightforward [23,49]. In this study, the focus was on the pretreatment phase of biomass, so chemical hydrolysis was done without further catalyst addition, and enzymatic hydrolysis was excluded from the study.

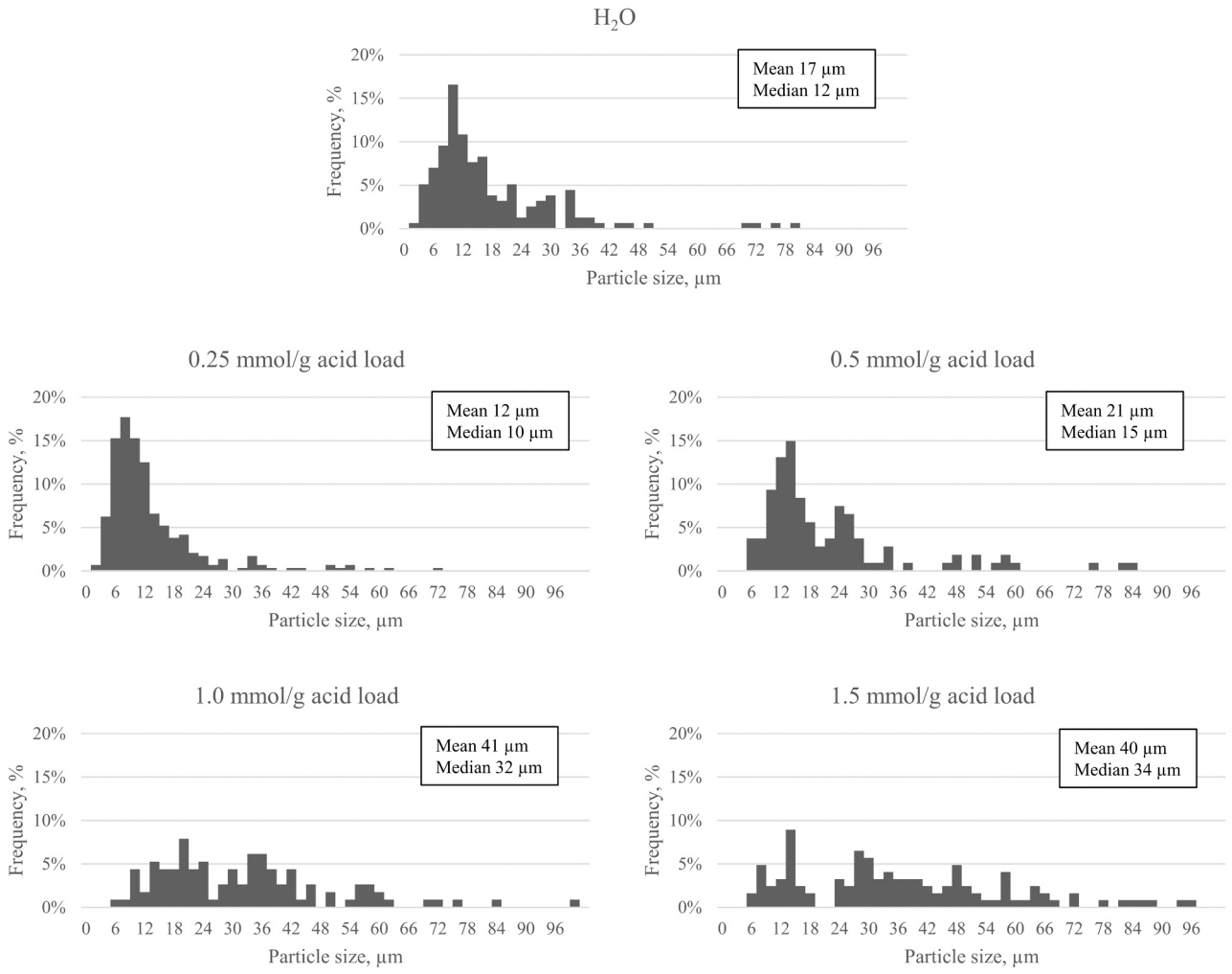

Fig. 5. Particle size distribution of birch milled with distilled water for 60 min and milling for 60 min with loads of 0.25 mmol/g, 0.5 mmol/g, 1.0 mmol/g, and 1.5 mmol/g.

Birch sawdust was milled with an acid catalyst for 30 min, and after milling, the pretreated birch was mixed with water for 20 min to release the sugars. Acid loads ranging from 0.25 mmol/g to 1.5 mmol/g were used. The total reducing sugar (TRS) in the solution was analyzed with the DNS method. The amounts of xylose and glucose in the sugar solutions were determined by HPLC.

The TRS yield increased from 13.9% to 17.5% when the acid load was increased from 0.25 to 1.0 mmol/g but decreased significantly to 9.3% if the acid load was increased to 1.5 mmol/g (Fig. 7). This decrease in TRS yield may occur due to the loss of the catalyst and sample because of adherence to the equipment during the milling process or even burning of the sample due to excess moisture in the process [26,27] and the further reactions of sugars in acidic conditions [51,52]. The TRS yield of birch sawdust milled with water was negligible despite the milling time and couldn't be measured reliably by this method.

As illustrated in Fig. 8, extending the milling time from 30 min to 60 min altered the slope of the TRS yield. Whereas the highest TRS yield achieved by 30 min of milling (17.5%) was reached with a 1.0 mmol/g acid load, the highest TRS yield achieved by 60 min of milling (17.3%) was achieved with a 0.25 mmol/g catalyst load. After reaching the highest TRS yield, the further addition of catalyst decreased the TRS yields, which can be explained by loss of catalyst due to the sample adhering to the walls because of the combination of heat, moisture, and the power of the milling balls, as well as the further reactions of sugars [51,52].

The addition of the acid catalyst in the mechanocatalytic pretreatment had a more significant effect on reducing sugar yield than in the earlier study on a different kind of woody biomass: willow sawdust [27]. The TRS yield of the birch was already relatively high in the case of the 0.25 mmol/g acid load after 30 min of milling, while the willow required a 0.5 mmol/g acid load before the yield was close to its maximum. The birch was relatively sensitive to the acid catalyst, even with higher doses. The TRS yield of willow remained at about the same level even though acid was added, but the TRS of birch changed after each catalyst addition. In the end, the TRS yield of birch decreased strongly if a 1.5 mmol/g acid load was applied. For willow, a similar effect was noticed if 2.0 mmol/g were added in the pretreatment process. An acid load of 2.0 mmol/g could not be used for birch because it caused agglomeration of the sample on the equipment. Agglomeration of particles can explain the decrease of TRS yield with high acid loads. From FESEM images in Fig. 4, it can be noticed that particles start to attach to each other and thus the surface area decreases. From the particle distribution figures can be seen, that particle size increases when more acid is added in milling process. It was also noticed that with high acid loads sample is tightly attached on the walls of equipment, which can cause loss of catalyst. The compositions of woods, such as xylan, lignin, and cellulose, can explain the sensitivity difference between tree species. Lignin can slow down the reactions [52]. On the other hand, xylose reaches the maximum yield faster but also degrades faster [53]. There is less cellulose and lignin and more hemicellulose in

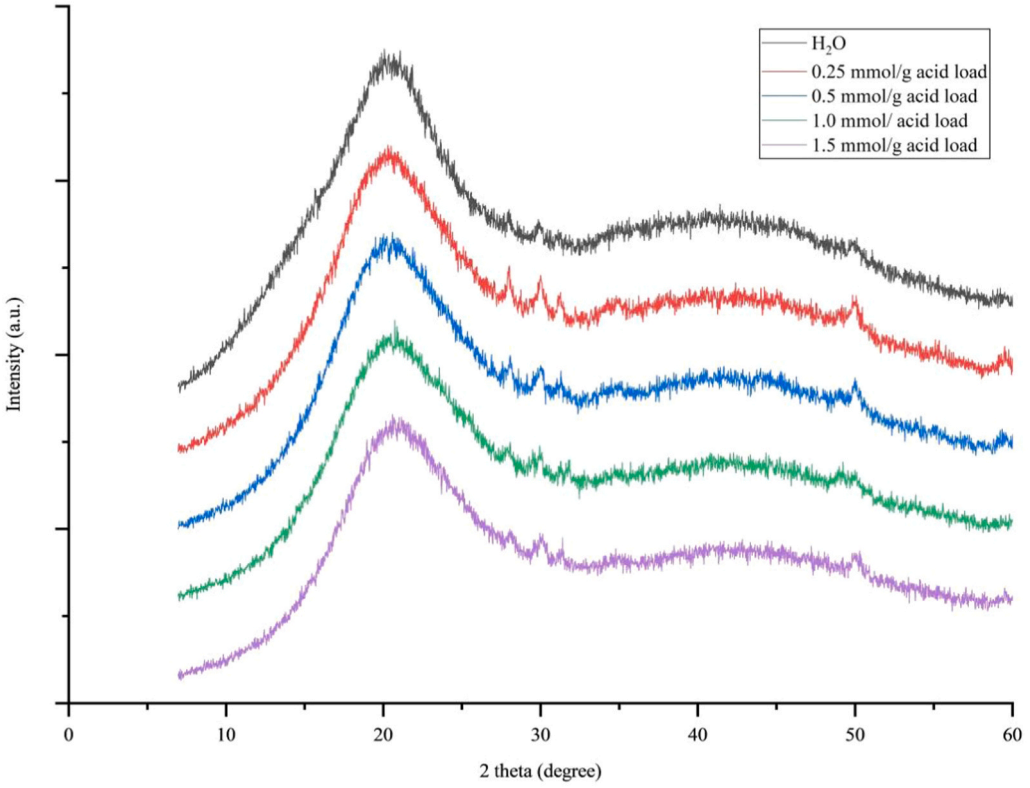

Fig. 6. XRD pattern of birch sawdust milled for 60 min with water and milling for 60 min with loads of 0.25 mmol/g, 0.5 mmol/g, 1.0 mmol/g, and 1.5 mmol/g.

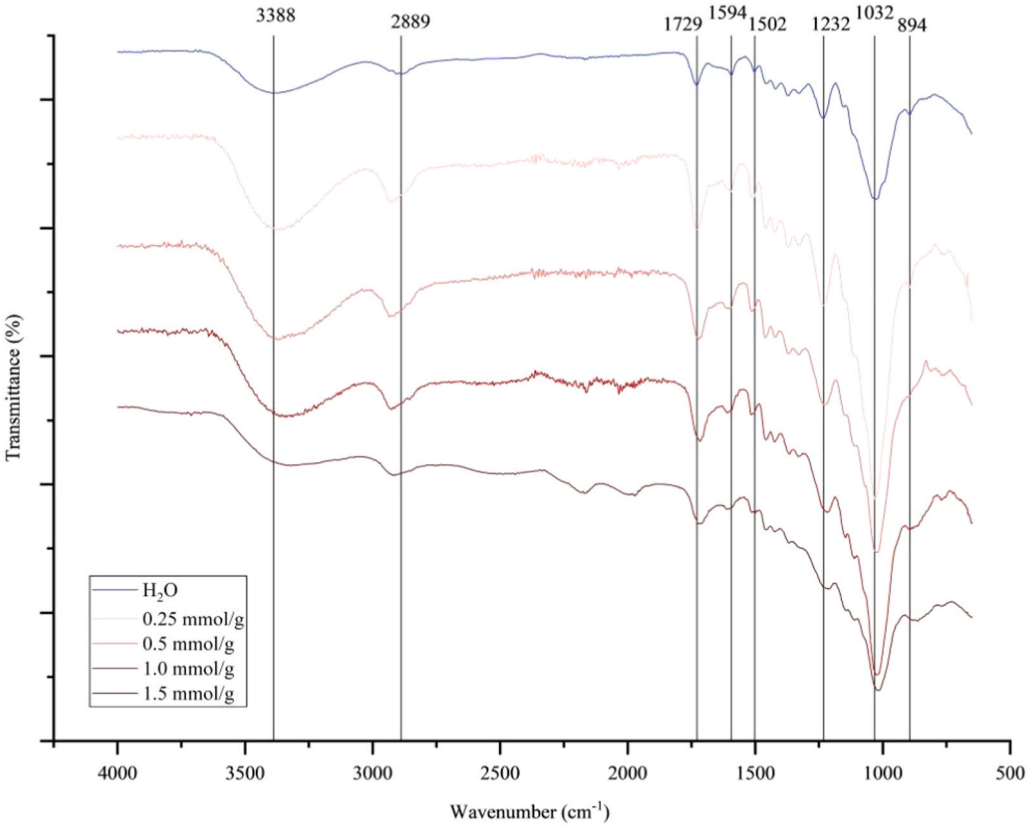

Fig. 7. FTIR spectra of birch sawdust milled for 60 min with water and milled for 60 min with loads of 0.25 mmol/g, 0.5 mmol/g, 1.0 mmol/g, and 1.5 mmol/g.

Table 5
Lateral order index of birch sawdust milled with water and acid loads.

Acid load/water added in the process	LOI
H_2O	0.98
0.25 mmol/g	0.96
0.5 mmol/g	0.96
1.0 mmol/g	0.95
1.5 mmol/g	0.96

birch than in willow (Table 1). Birch also contains more xylan (23.6% of dry matter) [25] than willow (15.0–18.6% of dry matter) [54,55]. These differences can lead to slightly better TRS yields for birch.

Fig. 9A shows the TRS, glucose, xylose, and acetic acid yields of birch samples milled for 60 min, which were hydrolyzed at 100 °C for 60 min. The best TRS yield (20.3%) was achieved with a 0.5 mmol/g acid load, and the yield decreased if the acid load was increased further. Glucose yield increased in parallel with acid load from 18.7 (0.5 mmol/g) to 23.7 g/kg (1.5 mmol/g), but the highest xylose yield (35.0 g/kg) was achieved with a 1.0 mmol/g acid load. This may be due to the decomposition of xylose and other monosaccharides in acidic conditions [56]. HPLC analysis showed some traces of HMF (0.5 g/kg) when the sawdust was milled with a 0.5 mmol/g acid load and furfural (maximum 1.4 g/kg) when acid was used in the milling process.

Fig. 9B illustrates how the milling time affects the TRS, glucose, xylose, and acetic acid yields. The acid catalyst load of 1.0 mmol/g was used in the milling process, and the birch was milled for 30 and 60 min before hydrolysis. As a reference, the catalyst was mixed directly into untreated sawdust, which was hydrolyzed without treatment with the ball mill. The TRS and glucose yields were low (1.1% and 2.7 g/kg, respectively) without milling, but the yields increased after 30 min of acid-assisted milling to 21.5% and 17.7 g/kg, respectively. The glucose yield further increased to 22.7 g/kg when the milling was extended to 60 min, but the TRS yield decreased to 16.1%. The milling increased released glucose from 0.6% to 5.3%. The xylose yield from the hydrolysis of non-milled sawdust was 24.9 g/kg, and the yield increased to 37.5 g/kg after 30 min of milling with 1.0 mmol/g of acid catalyst. The released xylose increased from 13.4% to 20.0%. After 60 min of milling, the xylose yield decreased slightly to 35.0 g/kg. The decrease in the xylose and TRS yields could be due to further reactions of sugars in

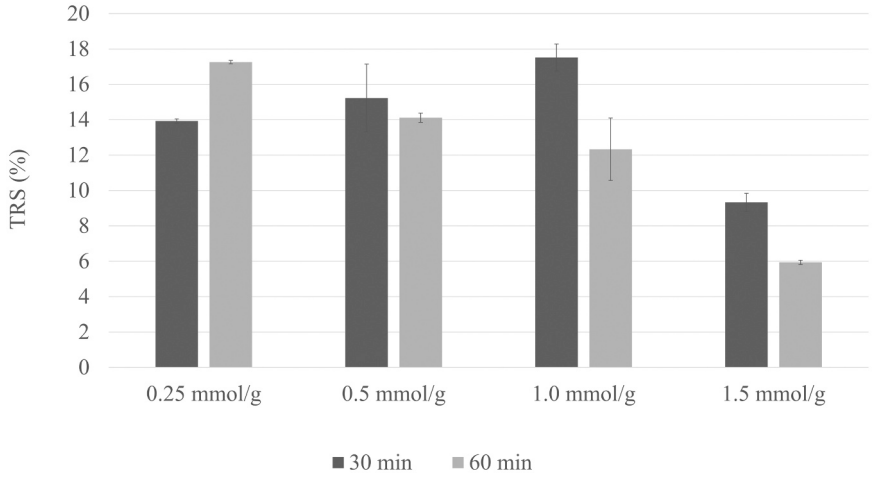

Fig. 8. TRS yields of 30 and 60 min milled birch with different catalyst loads. A sugar solution was produced from the pretreated sample by mixing it with water for 20 min at room temperature.

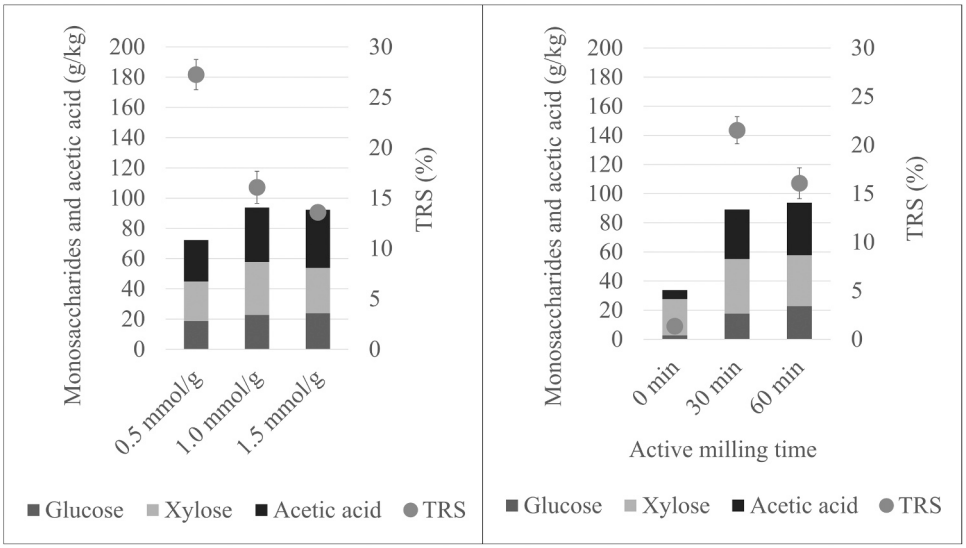

Fig. 9. Glucose and xylose yields of the hydrolysis of untreated birch sawdust and milled sawdust. No acid was added after the milling process. The milling time is expressed as active milling time, and the pauses are excluded. A: 60 min of milling with different acid loads was conducted. B: The acid catalyst load was 1.0 mmol/g. The reference: 0 min milling did not apply any milling, but the catalyst was mixed directly into untreated birch sawdust.

acidic conditions. A small amount of furfural (1.0 g/kg) was detected in the sawdust that was mechanocatalytically pretreated before hydrolysis. Milling significantly increased the yield of the acetic acid produced from the acetyl groups of xylan [57]. The acetic acid yield increased from 6.1 g/kg to 36.0 g/kg if the birch sawdust was milled for 60 min

The need to adjust the milling time or catalyst load can be balanced by controlling the other factors. The amount of catalyst applied in the mechanocatalytic pretreatment process can be decreased by finding the optimal milling time and chemical feeds for the process. Reducing the catalyst amount can reduce the corrosion of the equipment and make it more economically feasible. On the other hand, in order to decrease the energy demand of the milling process, the milling time can be decreased if the catalyst amount is increased.

4. Conclusions

Mechanocatalytic pretreatment was applied by a planetary ball mill, with sulfuric acid as the acid catalyst, in order to produce monosaccharides from birch sawdust. The catalyst was applied directly to the birch sawdust in the ball mill without a further impregnation step. The effect of catalyst load and milling time on the birch was followed by structural, chemical, and visual changes in the birch particles and changes in the yields of reducing sugars, glucose, and xylose. The size, shape, structure, and surface of the birch particles were altered by the mechanocatalytic pretreatment process. Milling for 30 min caused significant transformations in the birch and increased the surface area and the monosaccharide yields, but extending the milling time to 60 min did not have a remarkable impact. The amount of acid catalyst compared to the amount of birch had an impact on the structure of the birch and on the sugar yields. The highest total reducing sugar yield (23.0%) after 30 min hydrolysis at 100 °C without further acid addition was achieved with a 1.0 mmol/g acid catalyst load and 60 min of milling, whereas the highest glucose yield (23.8 g/kg) was achieved with an acid catalyst load of 1.5 mmol/g and 60 min of milling. Greater catalyst loads were not possible in this study; the glucose yield may increase if the catalyst load increases. The highest xylose yield was achieved with a 1.0 mmol/g acid load after 30 min of milling. Acid catalyst was needed to produce sugars, and as has been shown, some moisture from the catalyst intensifies the process, but high dosages of acid disturb the milling process of birch. Birch is more sensitive to mechanocatalytic pretreatment than willow due to its composition, and TRS yield is slightly better if pretreatment is done in similar conditions. Acid loads of 0.25 mmol/g released sugars from birch sawdust, whereas willow sawdust requires 1.0 mmol/g. On the other hand, the mechanocatalytic pretreatment process of birch was disturbed by an acid load of 1.5 mmol/g acid, whereas the pretreatment process of willow was disturbed by an acid load of 2.0 mmol/g.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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