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Effective saccharification of lignocellulosic barley straw by mechanocatalytical pretreatment using potassium pyrosulfate as a catalyst

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Abstract

The catalytic conversion of lignocellulosic biomass is attractive due to the feasible generation of valuable products such as reducing sugars which constitute the basic substrates for chemical and transportation fuel production, as well as the production of renewable hydrogen. This study shows the efficient conversion of lignocellulose, especially hemicellulose, into reducing sugars such as xylose and galactose, by mechanocatalysis using potassium pyrosulfate, $K_2S_2O_7$, as an effective salt catalyst. Ball milling was performed, introducing a mechanical force which, combined with chemical pretreatment, leads to reducing sugar yields (40 %) almost as high as when commonly used sulfuric acid was employed. Kinetic experiments as well as the optimization of the saccharification process are presented.

Keywords: Barley straw (Hordeum vulgare), Lignocellulose, Potassium pyrosulfate, Mechanocatalytical conversion, Ball milling

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1. Introduction

Lignocellulosic biomass-derived feedstocks typically comprise of three major fractions: cellulose, hemicellulose and lignin. These constituents form a complex structure which requires efficient pretreatment solutions to overcome the recalcitrance of the material towards chemical and microbial applications. Several catalytic strategies have been successfully implemented using e.g. physical pretreatment by milling (Meine, Rinaldi and Schüth, 2012), hydrothermal pretreatment (Onda, Ochi and Yanagisawa, 2009), biological or chemical pretreatment (Saha and Cotta, 2010). The aim of all methods is the disruption of the lignocellulosic matrix. Combinations of pretreatments are often used to improve lignocellulose depolymerization and saccharification.

For instance, Shen and Wymar recovered a higher total xylose yield when hydrothermal pretreatment was carried out with a catalytic amount of sulfuric acid which allowed a faster reaction of xylan directly into monomeric xylose, while autocatalytic hydrothermal pretreatment included the formation of oligomers as an intermediate step (Shen and Wyman, 2011). Recently, ionic liquids were uncovered as effective solvents for lignocellulose pretreatment. Addition of a solid acid catalyst to the dissolved cellulose showed high conversion rate into reducing sugars (Xiong et al., 2014). Overall, the addition of certain catalysts in pretreatment processes was often reported to enhance saccharification (Dhepe and Sahu, 2010; Ertas, Han and Jameel, 2014; Yabushita et al., 2014).

Most commonly used catalysts include inorganic acids such as sulfuric acid and hydrochloric acid (Meine, Rinaldi and Schüth, 2012), but also organic acids such as oxalic acid (Schneider et al., 2016) and maleic acid (Lim and Lee, 2013) were successfully employed in biomass conversion. Moreover, alkaline catalysts such as alkaline peroxide and lime were reported to efficiently convert lignocellulose into valuable products (Saha and Cotta, 2010). Apart from these homogeneous catalysts, heterogeneous catalysts are also effective, for instance zeolites, clays and metal oxides in the conversion of hemicellulose (Dhepe and Sahu, 2010),

mesoporous-carbon-supported ruthenium catalysts for the hydrolysis of cellulose to glucose (Kobayashi et al., 2010), alkali-activated carbon as well as sulfonated catalysts (Yabushita et al., 2014).

This study focuses on mechanocatalysis which combines physical and chemical processing driven by ball milling with the addition of a solid catalyst. The mechanical force reduces the particle size and decreases the crystallinity of lignocelluloses (Silva et al., 2012) while the catalyst contributes to the depolymerization of lignocellulose yielding water-soluble oligosaccharides (Meine, Rinaldi and Schüth, 2012; Ertas, Han and Jameel, 2014; Pedersen and Meyer, 2009; Motte et al., 2015). The formation of reducing sugars is catalyzed by water auto-ionization and acetic acid released from the acetyl groups of hemicellulose, in a subsequent hydrolysis reaction. The sugar rich liquid fraction contains mainly monomeric sugars such as glucose and xylose from cellulose and hemicellulose breakdown, respectively (Meine, Rinaldi and Schüth, 2012). These reducing sugars are the building blocks for the synthesis of fuels and valuable platform chemicals such as furfural, 5-(hydroxymethyl)furfural or levulinic acid (Girisuta, Janssen and Heeres, 2006; Zhou and Zhang, 2016; Liu and Zhang, 2016). They also constitute reforming feedstocks for the production of renewable hydrogen (Cortright, Davda and Dumesic, 2002).

This study presents the effective saccharification of lignocellulosic barley straw applying mechanical ball milling and chemical conversion simultaneously. The mechanocatalytical process showed great selectivity for hemicellulose turnover yielding high release of xylo-oligosaccharides and xylose. Potassium pyrosulfate, $K_2S_2O_7$, is introduced as a new catalyst in mechanocatalysis which, to date, has not been described in biomass conversion.

2. Materials and methods

2.1. Raw materials and chemicals

Barley straw (*Hordeum vulgare*) was provided from a local Finnish farmer in Central Ostrobothnia, Finland (63°25'46.7"N 22°39'38.2"E). Straw was harvested, collected from a round straw bale and processed the next day by grinding to a particle size of 0.5 mm using a Retsch SM100 Comfort cutting mill. Henceforth, it was stored in an air-tight container and dried at 70°C for 24 h prior to use. The compositional and elemental analysis of the used barley straw was investigated in our earlier publication (Schneider et al., 2016; Schneider et al., 2017). Barley straw contained a mass fraction of 13.7 % lignin, 78.4 % holocellulose (consisting of cellulose and water-insoluble hemicellulose) and 4.7 % water-soluble hemicellulose. Elemental analysis revealed mass fractions of total carbon 45.4 %, nitrogen 2.5 % and hydrogen 5.7 %, calculated from dry material.

Chemicals used were: Ammonium chloride (99.5 %, J.T.Baker), ammonium sulfate (99.5 %, Merck), potassium bisulfate (99.0 %, Merck) and potassium pyrosulfate (97.5 %, Merck).

2.2. Mechanocatalytical pretreatment

Barley straw and the salt catalyst (1.0 mol kg^{-1}) were shortly mixed with a spatula, applied to a stainless steel container (45 cm^3, 16 milling balls each 2.93 g and 1 cm in diameter) and grinded in a planetary ball mill (Fritsch premium line Pulverisette 7) at 100 RCF. The kinetic study was conducted with 15 cycles of 2 min grinding turns and 1 min pause turns. The grinding times for the optimization experiment were set with varying cycle numbers. The grinding time for testing different salt catalysts was set at 30 min including 5 milling turns of 6 min, each followed by a pause turn of 3 min. The temperature was controlled manually after every run (TM-903 LT Lutron).

2.3. Hydrolysis

Hydrolysis was carried out without any further catalyst addition. Grinded straw samples were hydrolyzed in a weight ratio of 5 % in distilled water for 1 h by shaking at room

temperature (RT) and by heating in an oil bath at 100℃, 130℃ and 160℃. The hydrolysis causes the formation of a precipitate which was separated from the sugar solution by filtration. Additionally, direct hydrolysis of the straw-catalyst mixture excluding mechanical pretreatment was performed.

2.4. Total reducing sugar analysis

The determination of total reducing sugars (TRS) by UV/ VIS spectrometry (Shimadzu UV-1800 spectrometer) was performed as described earlier (Schneider et al., 2016; Miller, 1959) . A (diluted) portion of the hydrolyzed biomass filtrate and a 3.5-dinitrosalicylic acid reagent (1 %) were mixed in a volume ratio of 1:1 and subsequently heated in a boiling water bath for 5 min. TRS was determined at a wavelength of 540 nm based on a glucose calibration. The analysis was carried out in duplicates.

2.5. Capillary electrophoresis

Capillary electrophoresis (CE) analysis was performed as described in our earlier publication (Schneider et al., 2016). The hydrolysate solutions were filtered with a 0.45 µm GHP Acrodisc syringe filter and diluted with distilled water (1:2). All analyses were carried out with a P/ACE MDQ CE instrument (Beckman-Coulter, Fullerton, CA, USA) equipped with a diode array detector (DAD) using uncoated fused-silica capillaries of I.D. 25 µm and length 30/ 40 cm (effective length/ total length). The samples were injected at a pressure of 3447.4 Pa for 10 s with a separation voltage of +16000 V. Calibration curves for the external quantification (50-500 µg cm^{-3}) of 5-(hydroxymethyl)furfural (HMF), lactose, cellobiose, galactose, glucose, mannose, arabinose and xylose were created. All samples were measured as duplicates. In addition, each sample run was performed with spiked standards to confirm the identity of the analytes.

3. Results and Discussion

3.1. Influence of different catalyst concentrations

Kinetic experiments with $K_2S_2O_7$ concentrations of 0.25 to 1.5 mol kg^{-1} were performed. The maximum amount of released reducing sugar was obtained when a catalyst concentration of 1.0 to 1.25 mol kg^{-1} was applied (Fig. 1). Concentrations as high as 1.5 mol kg^{-1} led to decreased saccharification yields, most probably as a result of degradation of the formed reducing sugars into byproducts (Ertas, Han and Jameel, 2014). Generally, a temperature rise to 130℃ released 7-10 % more amount of TRS when compared to hydrolysis at room temperature and 100℃ in regard to all studied $K_2S_2O_7$ concentrations. Saccharification levels remained almost constant when the catalyst concentration was raised from 1.0 mol kg^{-1} to 1.25 mol kg^{-1}, merely hydrolysis at 130℃ released slightly more amount of TRS (27.4 % compared to 25.2 %). Among the examined catalyst concentrations, a catalyst concentration of 1.0 mol kg^{-1} was proposed as the optimal concentration because applying the higher concentration of 1.25 mol kg^{-1} showed no significant enhanced saccharification. This catalyst amount accounts for a mass fraction of 20 % in the sample mixture.

Figure 1 here

Changes in texture, integrated in Fig. 1, show that the milled samples became finer and darker in color when the catalyst concentration increases. This observation indicates the bigger impact of the catalyst upon the mechanocatalytical reaction because the catalyst concentration was the only varied parameter while mechanical conditions were set constant (15 cycles of 2 min grinding and 1 min pause).

3.2. Influence of different milling parameters

To further improve the saccharification, the mechanocatalytical treatment conditions were optimized by varying the mechanical conditions (grinding and pause times and cycle numbers). Barley straw was briefly mixed with potassium pyrosulfate, 1.0 mol kg^{-1}, and subsequently processed with a ball mill under various milling conditions (A-H) which are listed in Table 1. The milling process is divided into several grinding turns, which each are followed by a pause turn in order to prevent overheating and as a result burning of the sample. Grinding times were fixed as 5 min and 2 min turns while pausing times were varied whose maxima were set twice as high as the grinding time (condition A and E). Additionally, grinding for 1 min including pause turns of 1 min was tested (condition H).

Table 1 here

Our previous research indicated that prolonged grinding turns of up to 10 min result in a fast and vast temperature increase inside the milling reaction vessel, reaching up to 85 °C after only 20 min of milling and applying sulfuric acid, 1.0 mol kg^{-1}, as a catalyst (Schneider et al., 2017). The temperature rise is considered to be a result of ball-to-ball, ball-to-substrate, ball-to-wall collisions and friction (Kwon, Gerasimov and Yoon, 2002). To avoid these rather harsh processing conditions, the focus was laid on shorter grinding durations in the present study. Nevertheless, it could not be avoided that samples were partly burned and even fully burned when milled according to condition C after mechanical treatment for 60 min. Most probably, point contacts of the grinding balls with the vessel and substrate resulted in an inhomogeneous temperature distribution inside the milling vessel (Kwon, Gerasimov and Yoon, 2002). At the same time, the temperature rises with progressing milling duration leading to the partly burning of samples. The final temperature inside the milling container is referred to as internal vessel temperature in this section. Hydrolysis was additionally carried out at

160℃ while hydrolysis at room temperature was no longer considered due to overall low TRS yields (Fig. 1).

The amount of TRS determined from the liquid hydrolysate fractions of the samples processed under conditions A-H, was plotted against the milling time (sum of grinding turns excluding pausing turns, Fig. 2).

Figure 2 here

The results show that milling significantly increased total reducing sugar levels compared to merely catalyzed hydrolysis reaction of the straw sample (milling time t = 0 min). This data is consistent with existing literature which reported increased turnover due to a mechanical force and a reduction in particle size (Ertas, Han and Jameel, 2014; Pedersen and Meyer, 2009). For instance, Ertas et al. increased the total sugar levels by 17 % when mechanical treatment was applied.

Generally, the reducing sugar yield increased with progressing milling time. Under most milling conditions a maximum TRS yield was reached after mechanical treatment for 50 to 60 min. Continuous milling exceeding 60 min resulted in fully or partly burned samples. When the pausing time was set twice as high as the grinding time (conditions A and E, Table 1 and Fig. 2), TRS levels were lower after 50 to 60 min and so, prolonged milling will be needed to reach similar TRS levels.

Due to long pausing turns, the reaction mixture and the milling container cooled slightly down, leading to a moderate internal vessel temperature (final temperatures ~60-70℃). The highest internal vessel temperature (82℃) was measured when 5 min grinding and 5 min pausing times were applied for a total grinding time of 60 min (condition B, Table 1) which, at the same time, yielded one of the highest cellulose and hemicellulose conversion, 47.2 %, and TRS levels, 39.2 %, when hydrolyzed at 130℃. Merely slightly higher TRS release, 39.7 % (cellulose and hemicellulose conversion 47.8 %), was achieved under milling condition D when a cyclic mode of 5 min of

grinding was performed for a total of 50 min followed by 2 min pause turns. However, this difference in TRS release and processing time is insignificant, when considering the standard deviation (Table 2) and that also under condition B TRS 39.2 % was released after 50 min of grinding. The TRS yields were comparable with our previous study in which we investigated the efficiency of sulfuric acid in mechanocatalysis (Schneider et al., 2017). Here, under a similar milling condition B which included 10 min pause time instead of 5 min, TRS 41-43 % was obtained after 50 min of grinding and harsher conditions yielded even TRS levels of up to 53 %. The partly higher efficiency of sulfuric acid might be attributed to its eroding effect creating micro- and mesopores in the lignocellulosic structure (Jiang et al., 2013). To the best of our knowledge, to date, there are no catalytic studies carried out based on potassium pyrosulfate used as a catalyst. However, numerous sulfonated catalysts have been explored. Recently, a sulfonated bamboo-based carbon catalyst was introduced yielding 54.7 % of xylo-oligosaccharides after microwave-assisted treatment at 150℃ for 45 min (Bai, Xiao and Sun, 2015). Amarasekara and Wiredu studied the acid-hydrolysis of cellulose in a temperature range of 140-190℃ using several alkyl/ aryl sulfonic acids yielding maximum TRS of approximately 33 % as well as high glucose yields (Amarasekara and Wiredu, 2012).

All milling conditions which include 5 min of grinding and any studied pausing turns (A-D) yielded higher TRS levels than 2 min grinding turns (E-G). This observation can be ascribed to the increased internal vessel temperature which evolves during longer processing times and enhances the chemical reaction between catalyst and substrate (Schneider et al., 2017). The additional experiment carried out with grinding and pausing turns, both of 1 min (condition H), yielded even lower TRS levels. Comparing the three conditions where grinding and pausing time were set equally (B, F, H), it can be noticed that a significant difference in TRS levels of samples hydrolyzed at 130℃, first occurred after a total milling duration of 40 min. At shorter processing times (<40 min) TRS yields were similar as with other studied conditions applied for the

samples. The TRS level differences were most distinct after a total grinding time of 60 min: 39.3 %, 29.1 %, and 24.7 % for conditions B, F and H, respectively. These results further strengthened the fact that increased reaction temperatures which evolve in the milling container at longer milling times, promoted catalyst-substrate interactions and thus, structural alterations of the straw feedstock. Not least, also because actual measured internal vessel temperatures of the reaction vessel increased with longer total grinding durations, for example for 1 min grinding turns (condition H) from 64 °C (after 20 min) to 69 °C (after 60 min) for 2 min grinding turns from 65-72 °C (condition F) and for 5 min grinding turns from 68-82 °C (condition B).
Moreover, comminution of the straw sample proceeds with prolonged milling, reducing the particle size which leads to increased sugar release (Pedersen and Meyer, 2009; Motte et al., 2015). Pederson and Meyer demonstrated by scanning electron microscopy that surface structure alterations of wheat straw particles occur also without the addition of a catalyst resulting in edged, non-spherical and porous particles. Mechanical force usually introduces a strong mechanical impact which results in diffusion and strong interweaving of catalyst and biomass substrate resulting in high conversion efficiency (Motte et al., 2015). Thus, the combination of increased internal vessel temperature, catalyst interaction and the enlargement of the particle surface due to comminution results in increased saccharification.

In regard to the hydrolysis temperature, it can be noted that the additional increase to 160 °C did not induce more saccharification, apart from minor exceptions (e.g. condition F). Predominantly, TRS levels were similar for both temperatures, hydrolysis at 130 °C and 160 °C. However, significantly higher saccharification levels were obtained compared to hydrolysis at 100 °C. In all cases, the hydrolysis reaction, most probably, is promoted by hydronium ions which are produced from water auto-ionization and from the ionization of acetic acid which is released from hemicellulose. It is known from literature that mechanical force in the form of ball

milling, promotes the hydrolysis reaction due to the decrease in crystallinity of cellulose (Onda, Ochi and Yanagisawa, 2008). However, our results revealed that milling did not improve the hydrolysis reaction at the elevated temperature (160 °C) indicating a limiting effect of ball milling. Similar results were observed by Ertas et al. who found a limiting effect of beating milling on enzyme hydrolysis at increased enzyme dosages (Ertas, Han and Jameel, 2014). They also pointed out that sugar levels decreased at higher temperatures (190 °C) due to degradation catalyzed by acids. This finding was further supported by Vyver et al. who reported that the catalytic hydrolysis of ball milled cellulose at 150 °C for 24 h using sulfonated hyperbranched poly(arylene oxindole)s as an acid catalyst, yielded a good glucose selectivity with low formation rate of levulinic acid and 5-(hydroxymethyl)furfural (Van de Vyver et al., 2011). However, increased catalyst concentration (2 %) combined with an elevated hydrolysis temperature (170 °C) significantly released a larger amount of byproducts. In our study, $K_2S_2O_7$ in a concentration of 1.0 mol kg^{-1} yielded sufficient TRS release after hydrolysis at 130 °C indicating that the applied lower temperature most probably suppressed the decomposition of the reducing sugars. The study of Amarasekara and Wiredu showed maximum TRS as well as glucose yields at temperatures of 170-180 °C which is even higher than in our study (Amarasekara and Wiredu, 2012).

3.3. Sugars in the hydrolysate filtrate of mechanocatalytical-treated samples

The concentration of monomeric sugars was analyzed for the samples which yielded the overall highest TRS levels (50 min of milling, hydrolysis at 130 °C). The main released monosaccharides were xylose, galactose, arabinose and glucose (see Table 2).

Table 2 here

Highest concentration of xylose (5.6 %) was released under milling condition D whereas condition B yielded the most galactose (3.0 %), arabinose (1.7 %) and glucose (1.6 %). The latter condition described less harsh pretreatment conditions, but showed no severe effect on sugar release when compared with milling condition D, except for xylose concentration which was reduced.

In general, xylose levels were approximately thrice as high and galactose levels twice as high as glucose yields. Since the determined sugars are major constituents of hemicellulose, it can be assumed that mainly hemicellulose was subject to conversion reactions under the conditions applied. Surprisingly, higher galactose than arabinose yields were obtained which is contradictory to the natural composition of barley straw which typically shows higher arabinan and arabinose levels than galactan and galactose levels (Pronyk and Mazza, 2012). A similar sugar ratio trend was observed in our previous work studying the catalytic activity of oxalic acid in mechanocatalysis (Schneider et al., 2016). The selectivity for hemicellulose conversion appears to be a result of the natural recalcitrance of the lignocellulosic structure of barley straw. Among the barley straw constituents, hemicellulose is most susceptible to its removal from lignocellulose and degradation into xylo-oligosaccharides and monosaccharides (Pronyk and Mazza, 2012). Unless enzymatic hydrolysis is applied using cellulases, only negligible amounts of cellulose are converted into gluco-oligomers and glucose (Saha and Cotta, 2010). Low levels of glucose originate mostly from hemicellulose breakdown or slight degradation of cellulose. In our study, less than 1 % of the glucose degradation product HMF was found which indicates that glucose was not subject to further degradation under the employed conditions which might have been the reason for the low glucose levels. Furthermore, it was shown that glucose is stable under hydrothermal reaction conditions lasting for 30 min with applied temperatures of up to 177℃ (Onda, Ochi and Yanagisawa, 2009).

The degree of hemicellulose removal and conversion depends on the choice of catalyst and pretreatment method. Hydrothermal pretreatment of wheat straw with water at

190-200 °C efficiently removed hemicellulose while the fibrillary structure of cellulose was not affected (Kristensen et al., 2008). Studies involving various sulfur oxoacid catalysts in dilute acid pretreatment efficiently converted biomass. For instance, Ertas et al. performed a sulfonic acid-catalyzed autohydrolysis of wheat straw at much higher temperatures (190 °C) than in our study, but obtained only 11 g of total reducing sugars (Ertas, Han and Jameel, 2014). Dilute acid pretreatment of switchgrass using sulfuric acid and sulfur dioxide released both approximately 20 % xylose including either 40 min pretreatment at 140 °C using sulfuric acid or 10 min reaction at 180 °C with 3 % sulfur dioxide loadings (Shi, Ebrik and Wyman, 2011). Amarasekara and Wiredu used several sulfonic acids in their hydrolysis reaction and yielded slightly lower TRS (~33 %) compared to our results, however with glucose yields of up to 20 % (Amarasekara and Wiredu, 2012). Recently, Wang et al. demonstrated the saccharification (89.3 %) of wheat straw via SO_3 micro-thermal explosion collaborative dilute alkali pretreatment and showed that lignin was significantly affected (Wang et al., 2016).

Assuming that no monomeric sugars were adsorbed onto the catalyst (Onda, Ochi and Yanagisawa, 2009) which would lower individual sugar yields, the ratio of monomeric sugars compared to TRS levels indicated a high amount of xylo-oligosaccharides in the liquid fractions after hydrolysis. These oligomers can consist of dimers, trimers, tetramers and pentameres which can be subject to continuous hydrolysis reactions yielding xylose and other minor monosaccharides (Dhepe and Sahu, 2010; Bai, Xiao and Sun, 2015).

High formation of byproducts was unlikely in the present study since sulfonated catalysts show much less generation of undesirable degradation products such as C_1 and C_2 carboxylic acids compared to sulfuric acid (Onda, Ochi and Yanagisawa, 2009). We expect our mechanocatalytical process to show high selectivity for hemicellulose removal and conversion, not only due to low glucose levels compared to xylose levels and low HMF formation (<1 %), but also because of the recalcitrance of crystalline

cellulose and its reported limited accessibility to surface acid sites (Luo, Wang and Liu, 2007). Similar conclusions were made by Dhepe and Sahu (Dhepe and Sahu, 2010).

The mechanocatalytic reaction of hemicellulose to its main degradation products using potassium pyrosulfate, $K_2S_2O_7$, was shown to be efficient in terms of xylo-oligosaccharide and xylose recovery. To date, this salt catalyst has not been applied in the conversion reaction of lignocellulose. The reasons for its catalytic activity are unknown. We believe that sulfuric acid might be produced during the mechanocatalytical process following the hypothetical Equation 1. Energy analysis by the Gibbs free energy (ΔG) is unknown as well as whether or not it is an equilibrium reaction.

$$K_2S_2O_7 + H_2O \rightleftharpoons K_2SO_4 + H_2SO_4$$

Equation 1. Possible release of sulfuric acid upon contacting potassium pyrosulfate with water.

Following Equation 1, hydronium ions originating from the formed sulfuric acid, would catalyze our hydrolysis conversion reaction of oligomers into reducing sugars. However, further extensive experiments will be needed to unreveal the exact reasons for its ability to function as a catalyst. A thorough investigation should be subject to future research and is not considered and discussed here.

4. Conclusions

The efficient recovery of xylo-oligosaccharides and xylose from lignocellulosic barley straw by mechanocatalysis was shown. Potassium pyrosulfate as a novel catalyst applied in the pretreatment process shows great potential and conversion efficiency. Future research is needed to provide a clear picture of the catalytic reaction

mechanism. Mechanocatalysis was revealed as an effective method for the generation of reducing sugars from inedible biomass feedstock. Much effort should be done in order to develop and establish a productive and selective industrial process. Finally, in terms of cost efficiency, waste disposal and energy consumption should be kept at an acceptable level.

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Captions

Fig. 1 TRS yields of hydrolysates from barley straw samples ball milled for 30 min with different $K_2S_2O_7$ concentrations and hydrolyzed at room temperature (RT), 100℃ and 130℃. The pictures above illustrate the grinded samples.

Fig. 2 TRS yields of the hydrolysate fractions from barley straw samples milled with $K_2S_2O_7$ under various ball mill conditions A-H (see Table 1). Hydrolysis was carried out at 100℃ (green bars), 130℃ (blue bars) and 160℃ (yellow bars).

Table 1 Ball mill conditions A-H applied in this study.

Table 2 Yields [g/ 100 g of initial dry barley straw] of main monomeric sugars analyzed in the liquid hydrolysate solutions of samples milled for 50 min and hydrolyzed at 130℃. A-H indicate the ball mill conditions.

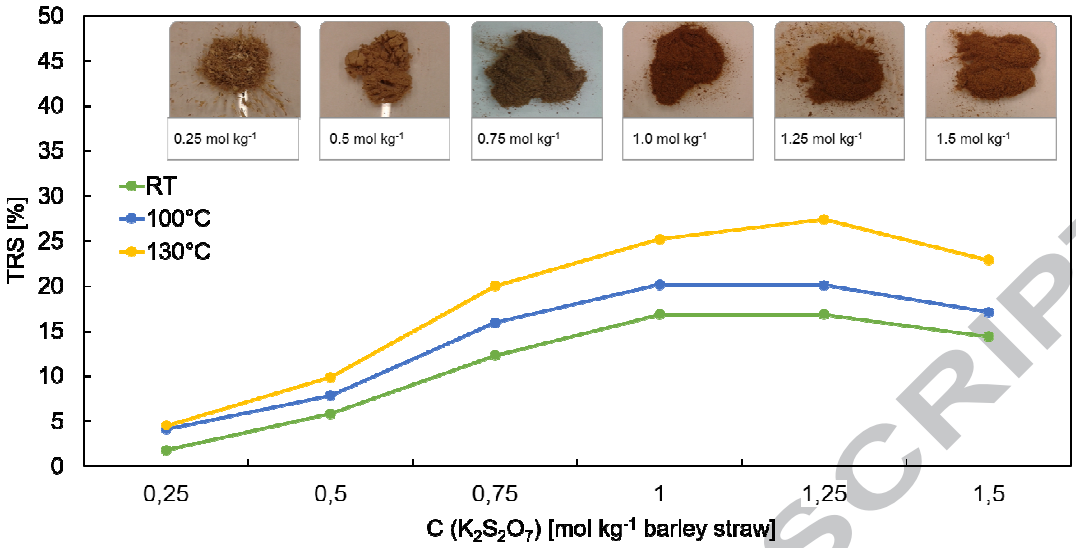

Figure 1

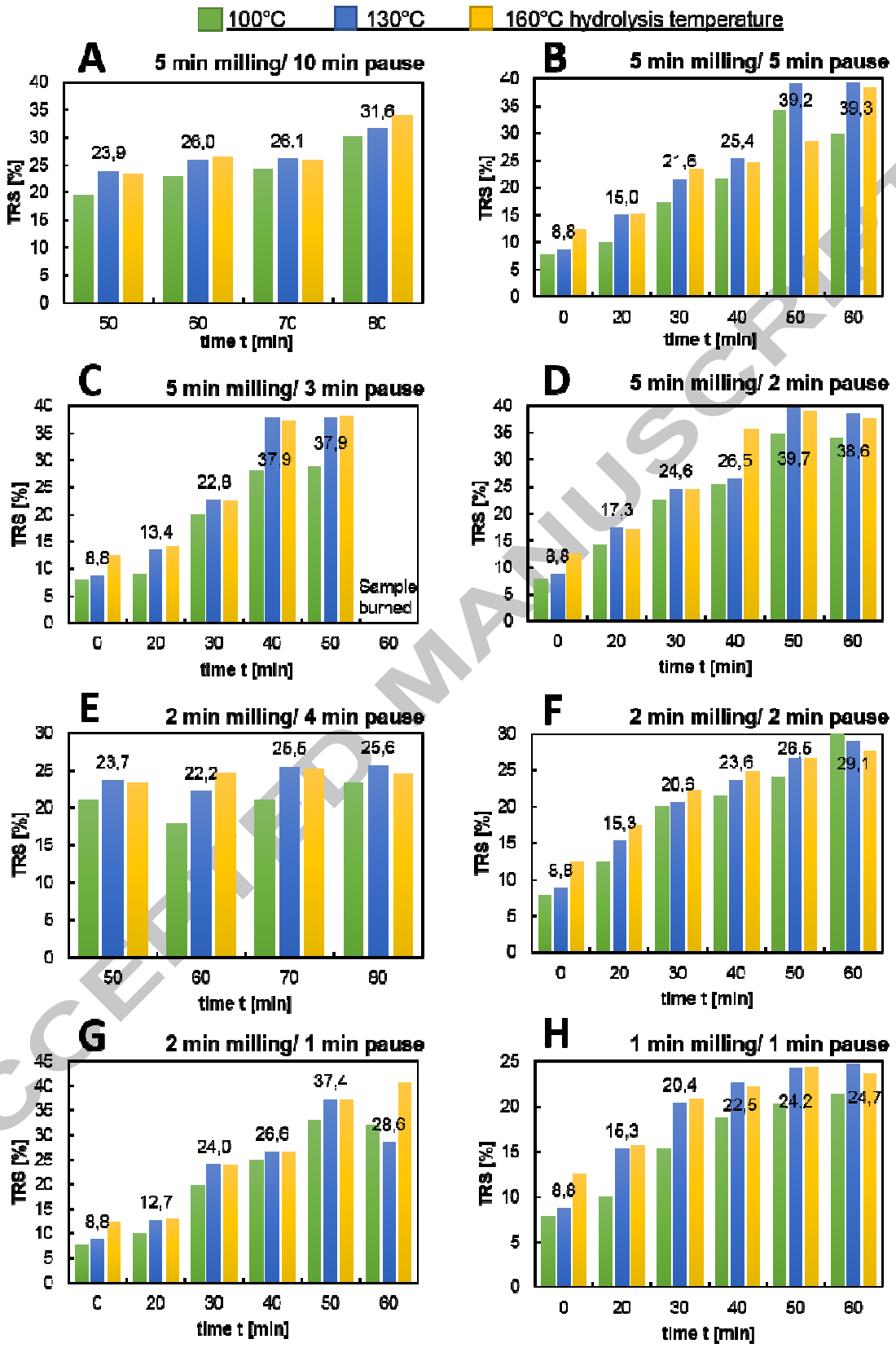

Figure 2

Table 1

milling condition	grinding time [min]	pausing time [min]
A	5	10
B	5	5
C	5	3
D	5	2
E	2	4
F	2	2
G	2	1
H	1	1

Table 2

milling condition	TRS	xylose	galactose	arabinose	glucose	cellulose and hemicellulose conversion[a]
A (5-10)[b]	23.9 ± 0.5	1.36 ± 0.36	1.99 ± 0.40	1.59 ± 0.33	0.81 ± 0.12	28.7
B (5-5)	39.2 ± 0.1	4.36 ± 1.32	3.04 ± 0.85	1.71 ± 0.16	1.60 ± 0.17	47.2
C (5-3)	37.9 ± 0.2	5.32 ± 1.66	2.57 ± 0.77	1.57 ± 0.21	1.39 ± 0.14	45.6
D (5-2)	39.7 ± 1.1	5.61 ± 1.52	2.84 ± 0.75	1.45 ± 0.20	1.61 ± 0.41	47.8
E (2-4)	23.7 ± 0.3	1.27 ± 0.30	1.60 ± 0.51	1.33 ± 0.36	0.76 ± 0.07	28.6
F (2-2)	26.5 ± 0.1	2.68 ± 0.71	2.34 ± 0.67	1.35 ± 0.41	1.05 ± 0.34	31.9
G (2-1)	37.4 ± 0.3	5.39 ± 0.52	2.95 ± 0.02	1.42 ± 0.20	1.56 ± 0.34	45.0
H (1-1)	24.2 ± 0.2	2.58 ± 0.47	1.97 ± 0.04	1.24 ± 0.12	0.88 ± 0.16	29.1

[a]calculated from water-soluble hemicellulose (4.65 %) and holocellulose (78.4 %).

[b]grinding time - pausing time

Highlights

- Lignocellulosic barley straw was fractionated using mechanocatalysis.
- The saccharification method showed selectivity for hemicellulose conversion.
- Potassium pyrosulfate was effective as a catalyst in mechanocatalysis.
- Total reducing sugar yields were comparable with dilute sulfuric acid pretreatment.
- Significant yields of reducing sugars were obtained.