Pretreatment and fractionation of lignocellulosic barley straw by mechanocatalysis

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Abstract

This study focuses on the mechanocatalytical process combining dilute acid pretreatment and mechanical processing driven by ball milling. Milled and hydrolyzed barley straw samples are subject to reducing sugar analysis by DNS assay and capillary electrophoresis. Optimization of the saccharification conditions was carried out with two different sulfuric acid concentrations, 0.5 mol kg⁻¹ and 1.0 mol kg⁻¹, and compared. A significant yield of total reducing sugar (53.4 %) was obtained from barley straw impregnated with sulfuric acid (1.0 mol kg⁻¹) after milling for only 20 min. Glucose and xylose concentrations accounted for 3.5 % and 11.3 %, respectively. Strikingly, the present study indicates a significant impact of the internal milling vessel temperature in the mechanocatalytical conversion process of barley straw in addition to the mechanical parameters and the catalyst concentration.

Keywords: Barley straw (Hordeum vulgare), Lignocellulose, Mechanocatalysis, Acid Hydrolysis, Saccharification

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1. Introduction

Lignocellulosic biomass is a domestic bioenergy source, abundantly available in high quantity throughout Europe, and is considered to be the most promising natural source for conversion to ethanol for biofuel and biochemical production, energy conversion and energy storage. Carbon materials obtained from renewable resources [1], utilized in supercapacitors, and functionalized cellulose polymer systems incorporated in lithium-ion batteries [2, 3] or fuel and biocells [4], enable the efficient electrochemical energy storage. Recently, the use of renewable resources as electrolytes in solar cells for energy conversion was investigated on [5, 6]. Not last, biomass offers an enormous opportunity to overcome environmental issues and meet the world's rising energy and oil needs by generating bioenergy, biofuels and platform chemicals. While thermal pathways such as pyrolysis and gasification convert biomass into pyrolysis oil [7] or synthesis gas [8], biomass pretreatment methods depolymerize biomass into their major constituents, which contain the building blocks for the production of a variety of chemicals. Most frequently used technologies are acid hydrolysis [9, 10], steam explosion [11] and hot water pretreatment [12]. All pretreatment methods aim at the destruction of the lignocellulosic biomass matrix, which possesses a natural recalcitrance, ascribed to its structural composition. Basically, the main constituent, cellulose, is surrounded and partially linked with hemicellulose. Empty spaces between the two straw constituents are filled with lignin [13].

In here, we present mechanocatalysis as an effective pretreatment method for biomass depolymerization and conversion into reducing sugars. Mechanocatalysis combines mechanical treatment driven by milling and chemical catalysis. The biomass sample is impregnated with an acid catalyst and mechanically treated using a ball mill yielding the conversion of cellulose and hemicellulose and the release of water-soluble oligosaccharides. In a subsequent hydrolysis step, which does not require further

catalyst addition, reducing sugars are formed, which are the starting material for valuable products such as ethanol [14], furfural and xylitol [15]. Barley straw, which is an agricultural crop residue is used as a feedstock and capable of producing ethanol $0.25 \text{ m}^3 \text{ kg}^{-1}$ [16].

The described mechanocatalytical process is of rising interest and has been pointed out as a key pretreatment in order to achieve optimal physical contact, which results in high conversion efficiency and enhanced hydrolysis rate without the formation of by-products [17, 18]. Beneficially, the process is solvent-free and requires no external heat [19]. Mechanical treatment in the form of ball milling decreases cellulose crystallinity, which results in smaller particle size reducing the crystalline regions while amorphous regions increase [20]. As a result, cellulose solubility increases and chemical hydrolysis is simplified [21-23].

Mechanocatalysis is yet a quite novel technique. Previous studies on the mechanocatalytical depolymerization of beechwood, pinewood and sugarcane bagasse yielded sugar yields of up to 98 % [24]. Yuan et al. [23] performed one-step wet ball milling, which uses fungi to degrade cellulose and hemicellulose, and obtained 22 % of sugars from wheat straw. Sulfuric acid and gaseous hydrochloric acid were pointed out to be very effective catalysts in mechanocatalysis [25]. Our previous studies, conducted with acetic acid and formic acid as well as sulfuric acid used as the reference acid, showed high total reducing sugar yields for sulfuric acid-catalyzed reactions compared to organic acid-treated samples [26]. In here, we now show the optimization of the saccharification conditions using sulfuric acid as a catalyst in mechanocatalysis. The objectives are to present a sustainable bioeconomic solution for the efficient saccharification of lignocellulosic barley straw using mechanocatalysis, which is a key intermediate process for the generation of e.g. ethanol. The catalytic performance of the acid catalyst combined with optimal milling conditions, is of major importance for high turnover with low co-formation of undesired by-products. Therefore,

the effect of different milling modes on sugar release will be discussed utilizing two different catalyst concentrations.

2. Material and methods

2.1. Chemicals

Sulfuric acid (95 %) was purchased from VWR. Other chemicals included: ethanol (99.5 %, ETAX Aa), sodium hydroxide pellets (99 %, Merck) and hydrochloric acid (37 %, Merck).

2.2. Barley straw

Barley straw (*Hordeum vulgare*) examined in the present study, 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 used barley straw contained a mass fraction of 13.72 % of lignin, 78.42 % of holocellulose (consisting of cellulose and water-insoluble hemicellulose) and 4.65 % of water-soluble hemicellulose. Furthermore, previous elemental analysis revealed mass fractions of total carbon 45.4 %, nitrogen 2.5 % and hydrogen 5.7 %, calculated from dry material [26].

2.3. Mechanocatalytical pretreatment

The acid catalyst (~0.98 g and ~0.49 g of sulfuric acid per 10 g of barley straw for a final concentration of 0.5 or 1.0 mol kg⁻¹ of barley straw, respectively) was dissolved in 150 cm³ of diethyl ether. Barley straw, 0.01 kg, was added to the acid solution and the mixture shaken for 30 min at room temperature (Stuart orbital incubator S1500,

2.84 Hz). The solvent was removed using a vacuum rotary evaporator (Heidolph Laborota 4010 digital, 40 C). Dry acid-impregnated straw (2.4×10^{-3} kg) was applied to a stainless steel container (45 cm³, 16 milling balls each 2.93 g and 1 cm in diameter made of zirconium dioxide) and ground in a ball mill (Fritsch premium line Pulverisette 7) at 100 RCF. The grinding time, pausing time and cycle numbers were set as listed in Table 1. One milling cycle refers to one grinding turn, e.g. 10 min of grinding, followed by a pause turn of e.g. 10 min. The internal temperature of the container was controlled manually after every run (TM-903 LT Lutron).

Table 1 here

2.4. Acid-catalyzed hydrolysis

Acid hydrolysis of the pretreated barley straw was carried out without any further addition of acid catalyst. Pretreated straw samples were hydrolyzed in distilled water in a weight ratio of 5 % for one hour either by shaking at room temperature (RT) or by heating in an oil bath at 100°C. Hydrolysis caused the formation of a precipitate, which was separated from the sugar solution by filtration.

2.5. Analytical methods

2.5.1. Determination of Total Reducing Sugar by UV/ VIS spectrometry

The amount of total reducing sugar (TRS) was determined by the DNS (dinitrosalicylic acid) method using a Shimadzu UV-1800 spectrometer [26]. A (diluted) portion of the hydrolyzed biomass filtrate and the 3,5-dinitrosalicylic acid reagent (1 %) were mixed in a volume ratio of 1:1. The final quantification was based on a glucose calibration. The analysis was carried out in triplicates.

2.5.2. Capillary electrophoresis

The hydrolysates were filtered with a 0.45 μm GHP Acrodisc syringe filter and diluted with water. CE analyses were performed with a P/ACE MDQ CE instrument (Beckman-Coulter, Fullerton, CA, USA) equipped with a diode array detector (DAD), as described in our earlier publication [26]. Uncoated fused-silica capillaries of I.D. 25 μm and length 30/ 40 cm (effective length/ total length) were used. 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 of 5-hydroxymethylfurfural, sucrose, 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

Barley straw was impregnated with sulfuric acid, mechanically treated applying various ball mill conditions, and hydrolyzed at room temperature or 100°C. The obtained results of the saccharification process using two different acid concentrations will be discussed separately before being compared in section 3.3 to get a clear picture on the influence of mechanocatalysis depending on the level of acid impregnation.

3.1. Effect of mechanocatalysis on acid-impregnated, 0.5 mol kg⁻¹, barley straw

Barley straw was impregnated with sulfuric acid, 0.5 mol kg⁻¹, and subsequently processed with a ball mill under various milling conditions, which are listed in Table 1. Several milling cycles were chosen in order to determine the effect on the total reducing sugar (TRS) release. The corresponding results are shown in Figure 1, which illustrates the obtained TRS yields depending on the milling time (sum of grinding time

excluding pausing time) under each ball mill condition A-D. The conditions described under F were only performed for the sulfuric acid concentration of 1.0 mol kg^{-1} . Applying these parameters (F) using the catalyst concentration of 0.5 mol kg^{-1} , would result in a protracted milling process until a satisfactory amount of TRS is released. Lengthy processing times are energy and time consuming and therefore not economic. As a result, they are not included within the focus of the present study.

Figure 1 here

The results revealed that the TRS yield generally increased with time, showing a maximum yield after grinding for 60, 70 or 90 min. Significant saccharification could be observed in terms of the ball mill conditions A and B. TRS yielded 45.0 % when the grinding and pausing time were both set at 10 min and milling was carried out for 70 min. When the pausing time was halved, slightly higher TRS levels could be observed. Interestingly, the hydrolysis temperature did not affect the saccharification extent significantly with respect to the conditions A and B at the described milling time. Acid hydrolysis carried out by shaking at room temperature was as effective as hydrolysis at 100°C . Regarding other milling times and the remaining ball mill conditions, the effect of the hydrolysis temperature on the TRS yield was more distinct with hydrolysis at RT yielding mostly lower TRS release. Since the TRS yield obtained under conditions A and B, was almost identical when hydrolysis was carried out at either RT or 100°C , it can be pointed out that the saccharification by mechanocatalysis was so efficient that subsequent hydrolysis did not require any additional energy input in terms of temperature increase to break down the generated oligosaccharide molecules.

When the grinding time was halved to 5 min and the pausing time set at 10 min (condition C), TRS yields reduced and a maximum yield of 28.8 % was achieved.

Extension of the pausing time to 15 min (condition D) decreased the yield of reducing sugars even more. The maximum TRS yield was 18.6 %, which accounts for only about 40 % of the initial maximum TRS release achieved under the ball mill conditions A and B.

Strikingly, the temperature, which evolved during the milling process due to the collision of the milling balls with the sample, the milling container and each other, appeared to be an important factor in terms of the extend TRS release. A kinetic study of sulfuric acid hydrolysis showed that the reaction rate is highly dependent on the temperature and the acid concentration [27]. Likewise, conversion rate in mechanocatalysis shows a temperature dependency. The temperature inside the milling vessel was manually monitored immediately after each run. Table 2 shows all measured vessel temperatures for all milling conditions and both examined sulfuric acid concentrations.

Table 2 here

Temperatures reached up to 85°C under the rather harsh milling conditions A and B, whereas conditions C to E reached maximum 70°C. Accordingly, conditions including longer pausing times, exhibited lower temperatures inside the milling container because the milling breaks interrupted the temperature increase and potentially allowed the reaction vessel to cool down slightly. The high internal temperature combined with the enlargement of the particle surface due to comminution, enhance the chemical reaction between catalyst and substrate, which, in turn, results in enhanced saccharification. The vessel temperatures were around 70°C and 65°C concerning the milling conditions C and D, respectively. The lower temperature reached for the latter, might explain the decrease in TRS yields.

A further mill condition E was tested, which displayed a reduction of grinding and pausing time, both to 2 min, to induce a higher number of milling cycles. These conditions allowed shorter grinding turns which prevented fast overheating and burning of the sample (also due to more pausing turns), even though they are shorter compared to the other milling conditions. The results revealed slightly higher TRS yield in contrast with grinding for 5 min and pausing for 10 min (condition C). However, the reducing sugar amount accounted for 27 % less compared to the maximum TRS achieved under condition A. Furthermore, the measured temperatures of around 70-73°C, which were slightly higher than the ones measured under condition C, assumed an increased TRS release.

3.2. Effect of mechanocatalysis on acid-impregnated, 1.0 mol kg⁻¹, barley straw

In a second saccharification approach, the catalyst concentration was doubled in order to obtain higher reducing sugar release during shorter processing times and thus, decreasing energy consumption and costs. The results are shown in Figure 2.

Figure 2 here

Strikingly, a high level of reducing sugars (53.4 %) could be released under condition A after only 20 min of milling and subsequent hydrolysis at 100°C. Surprisingly, TRS yield declined with continuous processing. These findings might be the result of forming by-products at longer processing times. Harsh pretreatment conditions were reported to induce degradation of the formed sugars into furan and phenol aldehydes, phenol ketones, phenol acids [28] and carboxylic acids such as formic acid and acetic acid [13]. The high internal temperatures of the reaction vessel (see Table 2) indicate the harsh milling conditions and promote the depolymerization process.

Almost the same level of saccharification was achieved regarding conditions D and F, however, these conditions required longer milling of 60 and 50 min, respectively. The internal vessel temperature reached up to 88°C under the harsh conditions A whereas the milling conditions D and F reached temperatures of maximum 70°C. The latter milling conditions describe mild milling methods, which would be suitable for processing e.g. sensitive samples. The milling conditions C, D and F included grinding turns of 5 min with pausing turns of 10, 15 and 20 min. In comparison, it can be concluded that higher TRS yields were achieved when a longer pausing time was chosen. Certainly, the high TRS release was associated with a prolonged exposure time. Internal temperatures of the reaction vessel were on average around 65°C. Thus, the longer the overall residence time of the sample inside the milling vessel, the longer the contacting time between sample and catalyst at high temperature, which allowed a more efficient conversion rate.

Grinding in 10 min turns including breaks of 5 min (condition B) turned out to be the most severe treatment method. Ball milling could be carried out to a maximum of 30 min while longer treatments resulted in burning of the sample due to a fast temperature raise. TRS release reached 44.3 % under the described conditions while the milling conditions E revealed no significant enhancement of the saccharification. After 30-40 min, the reducing sugar concentration reached approximately 30 %, which accounted for only 56 % of the maximum TRS yield achieved in terms of conditions A.

3.3. Comparison of the two saccharification approaches

Two saccharification approaches, using different sulfuric acid concentrations, 0.5 mol kg⁻¹ and 1.0 mol kg⁻¹, were reviewed for their efficiency in catalytic conversion of lignocellulosic barley straw. The maximum reducing sugar yields achieved under

each mechanocatalytical condition are listed with the respective milling time (sum of grinding time excluding pausing time) in Table 3.

Table 3 here

The highest possible reducing sugar yield that could be obtained under the examined conditions, was 53.4 %, almost as high as the reducing sugar yield (60.8 %) that was released from wheat straw by a continuous dilute sulfuric acid hydrolysis method [29]. Barley straw was previously converted into reducing sugars in a rate of 29.7 % by dilute sulfuric acid pretreatment [30]. Mechanocatalysis was demonstrated to be very effective in the depolymerization of beechwood, pinewood and sugarcane bagasse generating glucose yields of more than 88% relative to the glucan fraction [18]. Generally, it can be noted that saccharification was significantly enhanced and the overall processing time decreased when 1.0 mol kg^{-1} was used. Doubling of the acid concentration increased the yield of reducing sugars by more than 10 % in terms of milling condition A. Furthermore, efficient conversion could be achieved within substantial shorter processing times, reducing the milling time from 70 min to only 20 min. Prolonged pausing times (conditions C, D, F) reduced the TRS yields for sulfuric acid, 0.5 mol kg^{-1} , due to a decrease of the internal vessel temperature, whereas TRS release using 1.0 mol kg^{-1} increased when longer pausing times were applied. The latter observation seems likely to be a result of prolonged milling duration and hence, the extended contact time between the sample and a much more potent amount of acid catalyst. Predominantly, reducing sugars were released to a higher extent when hydrolysis was carried out at 100°C . However, catalysis with sulfuric acid, 0.5 mol kg^{-1} , revealed a maximum TRS yield by hydrolysis at room temperature in regard to the milling conditions B and E.

Milling condition E can be described as a rather mild milling method, in which the grinding and pausing time were both set at 2 min instead of 10 min. Both tested acid catalyst concentrations showed no significant effect on the conversion rate. However, the smaller acid concentration (0.5 mol kg^{-1}) revealed a higher TRS yield, even though a longer processing time was required.

Noticeably, the color of the filtrate solutions, which are depicted in Figure 1 and Figure 2 above each graph, changed from pale yellow to dark reddish brown with increasing processing time. This finding is consistent with the results of Kåldström et al. who proposed that the color is a result of formed depolymerized lignin [18]. The longer the processing duration, the darker the color. However, the present study does not show a dependency of the color on the TRS yield. For instance, a filtrate revealing TRS 43.4 % (condition C) showed a yellowish color, whereas another filtrate with a TRS release of 29.6 % (condition E) was already dark reddish brown in color. Both samples were achieved after milling for 30 min (1.0 mol kg^{-1}).

3.4. Monosaccharides in the hydrolysate solutions

Individual sugars of the hydrolysates for the milling conditions A (0.5 mol kg^{-1}) were determined using capillary electrophoresis (CE). Figure 3 shows the sugar concentrations of the hydrolysates obtained under milling condition A compared to the sugar yields obtained when barley straw was impregnated with sulfuric acid, 1.0 mol kg^{-1} , and processed under the same conditions for only 20 min.

Figure 3 here

The major sugars detected were xylose, glucose, galactose and arabinose. Strikingly, high dosages of xylose were released, which yielded a maximum of 4.1 % after milling for 70 min including hydrolysis at room temperature. Maximum 4.6 % were obtained

after milling for 80 min and hydrolysis at 100°C. Glucose concentrations increased depending on time and maximized at concentrations of 1.9 % and 2.3 % including hydrolysis at room temperature and at 100°C, respectively, both achieved after milling for 80 min. The amount of released arabinose and galactose was low and yielded on average each 1.0 %. Overall, hydrolysis at 100°C was more effective and resulted in greater sugar release. Xylose, galactose and arabinose are structural carbohydrates originated from hemicelluloses [13]. Their predominant presence is evidence that hemicellulose of barley straw is easily accessible and more likely prone to thermal degradation compared to cellulose and lignin [31]. This can be ascribed to its branched nature creating an amorphous structure [32], which shows susceptibility to mechanocatalysis.

Doubling of the catalyst concentration (1.0 mol kg^{-1}) revealed a significant increase of xylose concentration compared to the catalytic amount of 0.5 mol kg^{-1} . After milling for only 20 min, the xylose concentration reached 5.1 % including hydrolysis at room temperature and moreover, remarkable 11.3 % including hydrolysis at 100°C. The glucose concentration reached 3.5 % when the H_2SO_4 -impregnate (1.0 mol kg^{-1}) was milled for 20 min (hydrolysis at 100°C), the arabinose and galactose concentrations were 2.7 % and 1.7 %, respectively. The higher xylose concentration is very likely a result of the rather severe operating conditions, which induced a fast internal vessel temperature raise within a short processing time. Long pretreatment duration at high temperature may lead to the degradation of xylose into furfural [17, 31, 33, 34].

Likewise, the described severe milling conditions may induce xylose degradation. However, only small amount of the degradation product 5-hydroxymethylfurfural were detected, in concentrations below the limit of quantitation ($< 0.7 \%$). Our previous research indicated that also formic acid and acetic acid are generated in low amount during the mechanocatalytical barley straw depolymerization [26].

When TRS yields and the concentrations of individual sugars are compared, it is noticeable that individual sugar levels were relatively low. This observation might be a result of the presence of xylo-oligosaccharides and gluco-oligosaccharides, which are determined along with the monosaccharides following the DNS assay. These oligosaccharides have not been hydrolyzed completely due to processing limitations (sample burning), but represent a useful feedstock for the production of platform chemicals such as HMF and furfural [35], and also more monosaccharides by further hydrolysis [36].

It can be pointed out that mechanical treatment, driven by milling, is an effective method to break down the complex lignocellulosic matrix. Milling is a yet quite novel technique for the conversion of lignocellulosic biomass compared to commonly used methods such as dilute acid pretreatment and steam pretreatment including enzymatic hydrolysis. In comparison, Saha et al. generated 33.2 % of glucose and 18.7 % of xylose from wheat straw by dilute acid pretreatment, while Linde et al. produced 39.6 % of glucose and 21.6 % of xylose using steam pretreatment [14, 33]. However, their processes included enzymatic saccharification, which is time-consuming and requires exact balancing of the conversion reaction parameters. Kåldström et al. studied the mechanocatalytical depolymerization of beechwood and obtained 84 % of glucose and 4.89 % of xylose relative to the corresponding glucan and xylan fractions, when milling was carried out for 2 h. Likewise, they detected oligosaccharides in the mechanocatalytically treated samples [18].

4. Conclusions

Mechanocatalytical pretreatment of barley straw impregnated with sulfuric acid showed high saccharification efficiency. The mechanocatalytical process generates valuable reducing sugars, which are subsequently available for ethanol generation.

Optimization of the mechanical treatment in order to gain high conversion efficiency was performed. We found that not only the mechanical parameters, but also the internal temperature of the reaction vessel as well as the catalyst concentration, have an immense impact on the conversion rate and are crucial factors that play a key role in the catalytic conversion of barley straw. By adjusting grinding and pausing times of the milling process, harsh and mild conditions can be created. Under harsh conditions the internal vessel temperature rises and contributes to the release of reducing sugars. Doubling of the catalyst concentration increased the TRS yields by more than 10 % and significantly reduced the milling time.

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6. References

1. Z. Chen, X. Peng, X. Zhang, S. Jing, L. Zhong, R. Sun, Facile synthesis of cellulose-based carbon with tunable N content for potential supercapacitor application, *Carbohydr. Polym.* 170 (2017) 107-116.
2. L. Zolin, J.R. Nair, D. Beneventi, F. Bella, M. Destro, P. Jagdale, I. Cannavaro, A. Tagliaferro, D. Chaussy, F. Geobaldo, C. Gerbaldi, A simple route toward next-gen green energy storage concept by nanofibres-based self-supporting electrodes and a solid polymeric design, *Carbon* 107 (2016) 811-822.
3. J.R. Nair, F. Bella, N. Angulakshmi, A.M. Stephan, C. Gerbaldi, Nanocellulose-laden composite polymer electrolytes for high performing lithium–sulphur batteries, *Energy Storage Materials* 3 (2016) 69-76.

4. L. Yue, Y. Xie, Y. Zheng, W. He, S. Guo, Y. Sun, T. Zhang, S. Liu, Sulfonated bacterial cellulose/polyaniline composite membrane for use as gel polymer electrolyte, *Composites Sci. Technol.* 145 (2017) 122-131.
5. F. Bella, D. Pugliese, L. Zolin, C. Gerbaldi, Paper-based quasi-solid dye-sensitized solar cells, *Electrochim. Acta* 237 (2017) 87-93.
6. F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel, C. Gerbaldi, Approaching truly sustainable solar cells by the use of water and cellulose derivatives, *Green Chem.* 19 (2017) 1043-1051.
7. P.S. Marathe, S.R.G. Oudenhoven, P.W. Heerspink, S.R.A. Kersten, R.J.M. Westerhof, Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactions, *Chem. Eng. J.*
8. H. Ge, W. Guo, L. Shen, T. Song, J. Xiao, Experimental investigation on biomass gasification using chemical looping in a batch reactor and a continuous dual reactor, *Chemical Engineering Journal* 286 (2016) 689-700.
9. P. Lenihan, A. Orozco, E. O'Neill, M.N.M. Ahmad, D.W. Rooney, G.M. Walker, Dilute acid hydrolysis of lignocellulosic biomass, *Chem. Eng. J.* 156 (2010) 395-403.
10. D. Zhang, Y.L. Ong, Z. Li, J.C. Wu, Optimization of dilute acid-catalyzed hydrolysis of oil palm empty fruit bunch for high yield production of xylose, *Chem. Eng. J.* 181–182 (2012) 636-642.
11. M.D. Ferro, M.C. Fernandes, A.F.C. Paulino, S.O. Prozil, J. Gravitis, D.V. Evtuguin, A.M.R.B. Xavier, Bioethanol production from steam explosion pretreated and alkali extracted *Cistus ladanifer* (rockrose), *Biochemical Engineering Journal* 104 (2015) 98-105.
12. S. Imman, J. Arnthong, V. Burapatana, V. Champreda, N. Laosiripojana, Influence of alkaline catalyst addition on compressed liquid hot water pretreatment of rice straw, *Chemical Engineering Journal* 278 (2015) 85-91.
13. Y.L. Loow, T.Y. Wu, K.A. Tan, Y.S. Lim, L.F. Siow, J.M. Jahim, A.W. Mohammad, W.H. Teoh, Recent Advances in the Application of Inorganic Salt Pretreatment for Transforming Lignocellulosic Biomass into Reducing Sugars, *J. Agric. Food Chem.* 63 (2015) 8349-8363.
14. B.C. Saha, M.A. Cotta, Comparison of pretreatment strategies for enzymatic saccharification and fermentation of barley straw to ethanol, *New Biotechnology* 27 (2010) 10-16.
15. P. Zhou, Z. Zhang, One-pot catalytic conversion of carbohydrates into furfural and 5-hydroxymethylfurfural, *Catal. Sci. Technol.* 6 (2016) 3694-3712.

16. M. Balat, H. Balat, C. Öz, Progress in bioethanol processing, *Progress in Energy and Combustion Science* 34 (2008) 551-573.
17. A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, *Bioresour. Technol.* 100 (2009) 10-18.
18. M. Käldestrom, N. Meine, C. Farès, F. Schüth, R. Rinaldi, Deciphering 'water-soluble lignocellulose' obtained by mechanocatalysis: new insights into the chemical processes leading to deep depolymerization, *Green Chemistry* 16 (2014) 3528-3538.
19. S.M. Hick, C. Griebel, D.T. Restrepo, J.H. Truitt, E.J. Buker, C. Byldea, R.G. Blair, Mechanocatalysis for biomass-derived chemicals and fuels, *Green Chem.* 12 (2010) 468-474.
20. P. Phanthong, G. Guan, Y. Ma, X. Hao, A. Abudula, Effect of ball milling on the production of nanocellulose using mild acid hydrolysis method, *Journal of the Taiwan Institute of Chemical Engineers* 60 (2016) 617-622.
21. N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapfel, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 96 (2005) 673-686.
22. G.G.D. Silva, M. Couturier, J. Berrin, A. Buléon, X. Rouau, Effects of grinding processes on enzymatic degradation of wheat straw, *Bioresour. Technol.* 103 (2012) 192-200.
23. L. Yuan, Z. Chen, Y. Zhu, X. Liu, H. Liao, D. Chen, One Step Conversion of Wheat Straw to Sugars by Simultaneous Ball Milling, Mild Acid, and Fungus *Penicillium simplicissimum* Treatment, *Appl Biochem Biotechnol* 167 (2012) 39-51.
24. M. Käldestrom, N. Meine, C. Farès, R. Rinaldi, F. Schüth, Fractionation of 'water-soluble lignocellulose' into C5/C6 sugars and sulfur-free lignins, *Green Chem.* 16 (2014) 2454-2462.
25. N. Meine, R. Rinaldi, F. Schüth, Solvent-Free Catalytic Depolymerization of Cellulose to Water-Soluble Oligosaccharides, *ChemSusChem* 5 (2012) 1449-1454.
26. L. Schneider, Y. Dong, J. Haverinen, M. Jaakkola, U. Lassi, Efficiency of acetic acid and formic acid as a catalyst in catalytic and mechanocatalytic pretreatment of barley straw, *Biomass Bioenergy* 91 (2016) 134-142.
27. Y. Arslan, S. Takaç, N. Eken-Saraçoğlu, Kinetic study of hemicellulosic sugar production from hazelnut shells, *Chem. Eng. J.* 185-186 (2012) 23-28.

28. H.B. Klinker, B.K. Ahring, A.S. Schmidt, A.B. Thomsen, Characterization of degradation products from alkaline wet oxidation of wheat straw, *Bioresour. Technol.* 82 (2002) 15-26.
29. W. Ji, Z. Shen, Y. Wen, Hydrolysis of wheat straw by dilute sulfuric acid in a continuous mode, *Chem. Eng. J.* 260 (2015) 20-27.
30. I.A. Panagiotopoulos, R.R. Bakker, T. de Vrije, P.A.M. Claassen, E.G. Koukios, Dilute-acid pretreatment of barley straw for biological hydrogen production using *Caldicellulosiruptor saccharolyticus*, *Int J Hydrogen Energy* 37 (2012) 11727-11734.
31. C. Pronyk, G. Mazza, Fractionation of triticale, wheat, barley, oats, canola, and mustard straws for the production of carbohydrates and lignins, *Bioresour. Technol.* 106 (2012) 117-124.
32. I. Pavlovič, Z. Knez, M. Škerget, Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research, *J. Agric. Food Chem.* 61 (2013) 8003-8025.
33. M. Linde, E. Jakobsson, M. Galbe, G. Zacchi, Steam pretreatment of dilute H₂SO₄-impregnated wheat straw and SSF with low yeast and enzyme loadings for bioethanol production, *Biomass Bioenergy* 32 (2008) 326-332.
34. S.J. Horn, Q.D. Nguyen, B. Westereng, P.J. Nilsen, V.G.H. Eijsink, Screening of steam explosion conditions for glucose production from non-impregnated wheat straw, *Biomass Bioenergy* 35 (2011) 4879-4886.
35. R. Carrasquillo-Flores, M. Kåldström, F. Schüth, J.A. Dumesic, R. Rinaldi, Mechanocatalytic Depolymerization of Dry (Ligno)cellulose As an Entry Process for High-Yield Production of Furfurals, *ACS Catal.* 3 (2013) 993-997.
36. M. Ertas, Q. Han, H. Jameel, H. Chang, Enzymatic hydrolysis of autohydrolyzed wheat straw followed by refining to produce fermentable sugars, *Bioresour. Technol.* 152 (2014) 259-266.

Captions

Figure 1. TRS yields of hydrolysates from H₂SO₄-impregnated (0.5 mol kg⁻¹) barley straw processed under different ball mill conditions A-E (see Table 1). The time t refers to the sum of grinding turns. Hydrolysis was carried out at room temperature (blue bars) and 100°C (red bars). Pictures above each graph show the obtained hydrolysate solutions.

Figure 2. TRS yields of hydrolysates from H₂SO₄-impregnated (1.0 mol kg⁻¹) barley straw processed under different ball mill conditions A-F (see Table 1). The time t refers to the sum of grinding turns. Hydrolysis was carried out at room temperature (blue bars) and 100°C (red bars). Pictures above each graph show the obtained hydrolysate solutions. Some samples show less filtrate solution volume because the total volume of the suspension with a weight ratio of 5 %, was reduced for hydrolysis.

Figure 3. Concentration of the major sugars of the hydrolysates from H₂SO₄-impregnated (0.5 mol kg⁻¹) barley straw processed under ball mill condition A. The time t refers to the sum of grinding turns. Samples were hydrolyzed at room temperature (I) and 100°C (II). Sugar concentrations beside the dashed line illustrate the sample (1.0 mol kg⁻¹, 20 min, condition A) which yielded most amount of TRS. Concentrations are less than 0.7 % for bars which are not shown.

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

Table 2. Temperature measurements inside the reaction vessel carried out immediately after each milling process.

Table 3. Maximum TRS yields achieved with sulfuric acid, 0.5 and 1.0 mol kg⁻¹, performed under the indicated milling conditions A-F. The asterisk (*) indicates the TRS yield obtained by hydrolysis at room temperature.