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Mechanical Pretreatment in a Screw Press Affecting Chemical Pulping of Lignocellulosic Biomass

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ABSTRACT: To convert lignocellulose into transportation fuels and chemical products, pretreatment of the biomass, leading to the separation of the main components (cellulose, hemicellulose, and lignin), is a crucial and still challenging first step. Within this study, the screw press pretreatment of lignocellulosic biomass and its effect on the subsequent chemical pretreatment steps were evaluated. Macroscopic disruption and defibration of reed straw after screw press pretreatment were confirmed by scanning electronic microscopy and dye adsorption studies, showing an enhancement of the accessible surface area. Alkaline and dilute acid hydrolysis was tested to study the release of phenols or sugars from screw-press-treated and non-treated straw materials. To showcase a realistic subsequent chemical pretreatment step, kinetics of enzymatic hydrolysis after a biogenic and biphasic fractionation (OrganoCat) process was tested to evaluate the release of glucose from cut and pressed reed straw. Pretreatment by a screw press enhanced alkaline hydrolysis. A kinetic study showed that screw press pretreatment can reduce processing time and the amount of alkaline chemicals needed. A 75% and a 116% increase in the release of reducing sugars from screw-press-treated wheat and reed straw was detected, respectively. Whereas the OrganoCat fractionation of the screw-press-pretreated reed straw showed no significant improvement, a synergetic effect could be observed in the subsequent enzymatic hydrolysis of the cellulose pulp after combination of both pretreatments in comparison to applying only the cutting mill before chemical fractionation.

1. INTRODUCTION

Because of diminishing fossil fuel resources, increasing raw material prices, and environmental concerns, conversion of abundant lignocellulosic biomass into facility materials, chemicals, and fuels has become a global challenge today. However, one of the main challenges in the chemical conversion of lignocellulose is the feedstock pretreatment because of the complex structure of this composite material.

Lignocellulosic biomass consists of three main components: cellulose, hemicellulose and lignin, which are associated with each other. Besides other processes, e.g., thermochemical or hydrothermal, the biochemical valorization of the three main components, can lead to a broad variety of different bulk and fine chemicals, maintaining their functionality. According to Kumar et al.,[1] a crucial part of the pretreatment of lignocellulose to enable the full valorization of its main components is to remove lignin and hemicellulose, to reduce the crystallinity of cellulose, and to increase the porosity or surface area of the lignocellulosic materials. Various pretreatment techniques to enhance the digestibility of lignocellulosic biomass have been investigated.[2] However, for large-scale biofuel production, developing such a technology, fitting the above-mentioned needs, is still a challenge. Herein, crucial demands for such a process are applicability to a broad range of lignocellulosic biomass, being environmentally friendly, technologically uncomplicated, and economically profitable.

In general, size reduction is a fundamental preliminary step of any available pretreatment technology, which can alter the inherent structure of lignocellulose and decrease the particle size and degree of cellulose crystallinity.[3] However, traditional physical pretreatment, such as comminution, has a high-energy demand and is challenging to apply in large-scale applications, such as biofuel production.[4]

Recently, it was discovered that screw extrusion has a good prospect in biomass pretreatment. Extruders have the ability to provide high shear and normal force, effective and rapid mixing, and adaptability to many different processes, all in a continuous process.[5] More advantages of extrusion pretreatment are the short residence time, scalable temperature, and adjustable screw speed control as well as flexibility in screw configuration, according to the nature of the biomass and the process demands.[6] However, the mechanical effects of the extruder on the biomass have not yet been studied in depth. Additionally, the mechanism of extrusion pretreatment for biomass has not yet been fully understood. The screw press, which is originally

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designed for oil pressing, works similar to a single screw extruder, with the main difference that the water can be pressed out through the strainer barrel (Figure 1). Because of its

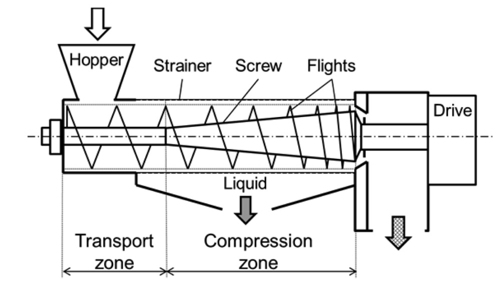

Figure 1. Principle of a screw press.

continuous shear and pressure forces, the walls of the oil-containing cells are broken and the oil is released. High compression and shear forces cause defibration and shortening of the fibers in the biomass.[7] In a previous study, the feasibility of the comminution as well as dewatering of lignocellulosic biomass in the screw press with lower energy demand compared to the conventional thermomechanical process was indicated.[8]

The aim of this work is to study the impact of the screw press pretreatment of lignocellulose on the following chemical conversion steps (Figure 2). An investigation of the kinetics

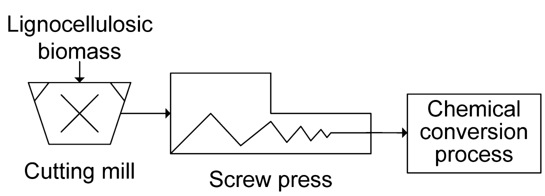

Figure 2. Simplified flow diagram for mechanical pretreatment.

of the chemical hydrolysis of lignocellulosic biomass, yielding phenols, will be presented. Moreover, the feasibility and possible synergies of the successive operation of the screw press and a recently published fractionation process (OrganoCat process)[9] will be evaluated as well as the impact on the subsequent enzymatic hydrolysis of the cellulose.

2. EXPERIMENTAL SECTION

2.1. Materials. Reed (*Phragmites australis*) and straw from wheat (*Triticum aestivum* L.) were obtained from local suppliers. Reed (length of about 2 m) was obtained from a location near Dümmer See, Germany. Wheat straw (length of about 0.5 m) was harvested and packed in a bale in Geilenkirchen, Germany. Because of the hard structure and length of the reed, which cannot be treated directly in the screw press, it was pre-comminuted by means of a cutting mill (Fritsch, Pulverisette 19) equipped with a sieve having 10 mm openings. For wheat straw, there is no pre-grinding step prior to screw press pretreatment. To have the same initial value, the moisture content of all feedstocks was adjusted via water spraying to about 100% (dry basis). The moisture content was determined according to TAPPI T 12 os-75.[10]

On the basis of the laboratory analytical procedure of the National Renewable Energy Laboratory (NREL), Klason lignin[11] (acid-insoluble lignin) and ash[12] in reed and wheat straw were determined (Table 1). With a preliminary study of the fractionation process, OrganoCat with suitable conditions, which claimed that hemicellulose could be separated quantitatively from the biomass, nearly 20%

Table 1. Ash and Klason Lignin Contents of the Raw Materials (Dry Weight)

biomass	treatment	ash (%)	Klason lignin (%)
reed straw	CM	4.4	23.3
	CM + SP	3.2	
wheat straw	CM	6.6	21.1
	SP	4.8	

hemicellulose were found in the reed straw. That gave approximately equivalent results as the literature value shown in Table 2.

Table 2. Chemical Composition of the Raw Materials (Dry Weight)

biomass	cellulose (%)	hemicellulose (%)	lignin (%)	reference
reed straw	42.51−45.04	23.88−27.27	22.09−23.88	13
wheat straw	36.3	21.1	25.5	14

2.2. Screw Press Pretreatment. In this study, a screw press (Reinartz, AP08) was used with an outer diameter of 80 mm and a screw length of 450 mm in the compression zone, equipped with a 4 kW motor. The screw press process can be divided into three consecutive steps. The first step is characterized by a compression with the air escaping from the cavities but without dewatering. By rotation of the screw shaft and friction on the barrel wall engaging the biomass with each other, a first comminution takes place for the long and tough material. In the second step, with increased pressure forces, the moisture in the biomass is released from the material and leaves the press through the strainer barrel. In the third step, after completion of the partial fluid release, the pressed material is in a state of equilibrium with the imposed compression forces. The combination of compression and screw rotation produces frictional forces between the biomass, the inner surface of the strainer barrel, and the screw surface, which generates heat. For this reason, a temperature rise along the barrel wall of the screw press for the processing of biomass is measured because of dissipation of mechanical energy.

Feeding of the biomass into the screw press was performed manually with the objective of achieving the maximal mass throughput in all experiments. The feed rate was about 5 kg h^{-1} (dry biomass). The screw speed was adjusted to 17 min^{-1}. The warming period to achieve thermal equilibrium takes about 30 min. The temperature range for the thermal equilibrium is from 48 °C (at the beginning) to 92 °C (at the end of the compression zone). After screw press pretreatment, the moisture content of both straw types decreased to 15−30% (dry basis). The partially dry cake was then collected and stored for further use. There was weight loss apart from water during the screw press pretreatment. About 1−2% water-insoluble biomass (small particles) was pressed through the strainer barrel. Moreover, according to the results obtained from the ash content before and after screw press pretreatment (Table 1), approximately 1.5% of the water-soluble portion was removed from the biomass.

2.3. Scanning Electron Microscopy (SEM) Observations and Dye Adsorption Study. The aim of mechanical pretreatment is to alter the lignocellulosic structure and increase the specific surface area of the biomass. A scanning electron microscope (HITACHI S300N) was used to take images of the materials. The samples were dried and coated with a thin layer of gold.

A dye adsorption method allows for the indication of the effective surface area of the straw sample before and after pretreatment in the screw press. The dye used in this study was Congo red (Sigma-Aldrich). Fu and Viraraghavan[15] have reported the removal of Congo red from an aqueous solution by biosorption. The pH of the sodium phosphate buffer solution was adjusted to 6.5.[16] The adsorption of Congo red was carried out by mixing 0.2 g of biomass in 20 mL of 50, 100, 150, 200, and 250 mg L^{-1} dye solution in a rotary shaker at 200 rpm. After 24 h, the dye solution was separated from the biomass by centrifugation at 10 000 rpm for 10 min. The final dye concentration

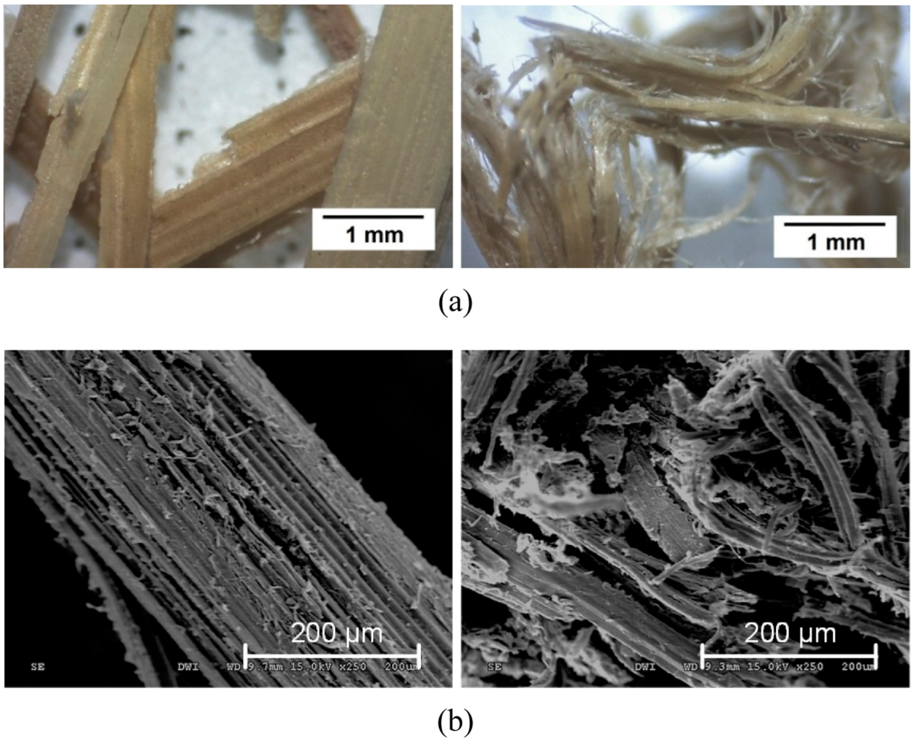

Figure 3. (a) Photograph and (b) SEM micrographs of the reed straw treated with (left) cutting mill and (right) screw press.

in the solution was measured using an ultraviolet−visible (UV−vis) spectrophotometer (Varian Cary 50) at a wavelength of 498 nm. The dye adsorption capacity of the samples was calculated by material balance. Using the Langmuir isotherm model described below, which can be used for adsorption of direct dyes on cellulose at low dye concentrations,[17] the theoretical maximum amount of adsorbed Congo red on biomass Q_m (mg g^{-1}) was estimated from a plot of c_e/q versus c_e

$$\frac{c_e}{q} = \frac{1}{Q_m}c_e + \frac{1}{K_L Q_m} \tag{1}$$

where q is the amount of dye adsorbed (mg g^{-1}), K_L is the Langmuir constant, and c_e is the concentration of dye not adsorbed (g L^{-1}). The specific surface area (SSA) was calculated from the following equation:[18]

$$\mathrm{SSA} = \frac{Q_m N_A \mathrm{SA}_{CR}}{M_{CR} \times 10^{21}} \tag{2}$$

where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), SA_{CR} is the surface area of one molecule of Congo red (1.73 nm^2), and M_{CR} is the molecular weight of Congo red (696.66 g mol^{-1}).

2.4. (Bio)chemical Pretreatment. *2.4.1. Alkaline and Dilute Acid Hydrolysis.* Alkaline hydrolysis of lignocellulosic materials with sodium hydroxide can remove its lignin. Dilute acid (e.g., sulfuric acid at concentrations below 4 wt %) can convert most hemicellulose to xylose and other sugars.[1]

Experiments with chemical hydrolysis were carried out in glass containers. A total of 0.5 g of dry weight of straw materials was added to containers and soaked in 15 mL of alkaline or acidic solutions. For alkaline hydrolysis, NaOH concentrations of 0.5 and 5% were used at room temperature. The hydrolysis time varied from 0.5 to 96 h. Samples from alkaline solution were taken at indicated time intervals, in the amount of 0.1 mL, to measure concentrations of phenolic units released from straw materials. For dilute acid hydrolysis, glass containers with 3% H_2SO_4 solution were put into a cooking pot for 70 min at 80 °C. Upon completion of hydrolysis, containers were cooled and samples were taken to evaluate the concentration of reducing sugars released from straws.

The reducing sugar concentration from dilute acid hydrolysis was measured with the dinitrosalicylic acid method (DNS)[19] and calculated from the standard curve plotted for xylose. The phenolic unit concentration from alkaline hydrolysis was evaluated with the total phenol analysis method[20] and calculated from the standard curve plotted for vanillin.

2.4.2. OrganoCat Process. A total of 100 g L^{-1} (relative to the aqueous phase) of screw pressed or cut reed straw was suspended in 20 mL of 0.1 M oxalic acid solution. A total of 20 mL of 2-methyltetrahydrofuran (2-MTHF) was added, and the reaction mixture was stirred for 3 h at 140 °C. After cooling to room temperature, the suspension was filtered and the two liquid phases were separated by centrifugation and decantation. Solid pulp was washed with distilled water until neutral pH and then dried. 2-MTHF was removed by distillation from the organic effluent, and yielded lignin was quantified gravimetrically. The xylose concentration was determined by Jasco high-performance liquid chromatography (HPLC) equipped with a refractive index (RI) detector and a SUGARSH1011 column with a 0.01 wt % aqueous acid solution as the eluent.

For the hydrolysis rate of Accellerase 1500 with the different cellulose pulps, 20 g L^{-1} of the dried cellulose pulp was suspended in 20 mL of 0.1 M citric buffer solution (pH 4.5) and stirred for 24 h, taking samples at indicated times. The samples were heated to 100 °C for 5 min and then stored at 4 °C until colorimetric analysis was conducted. The glucose concentration was determined with a commercially available enzymatic glucose kit (GAHK20). A calibration curve was recorded taking glucose as the standard substrate, as reported elsewhere.[9] All samples were diluted until absorbance values were within the linear region of the calibration.

3. RESULTS AND DISCUSSION

3.1. Optical Observation. The reed particles produced by the cutting mill using the sieve size of 10 mm do not have a uniform size and were not agglomerated. The lengths of the milled reed particles were inhomogeneous from 2 to 50 mm. Contrary to that, particles leaving the screw press are partially fluffy agglomerates, which easily deagglomerate within water under slight stirring. Changes of the cell structure and defibration without particle size reduction are possible. This statement is supported by Litzen et al.,[21] who claimed that pretreating sawdust with a twin screw extruder instead of a mill greatly increases the glucose recovery, although the resulting particles are significantly larger.

Figure 3a shows reed straw after treatment in a cutting mill and a screw press. The particles treated in the screw press are better disintegrated, despite the fact that the particle size is similar to that of the particles treated in the cutting mill. The defibration effect of the pressed material might indicate a higher disintegration of the particles. The morphological characteristics of the structure for treated reed straw were analyzed by SEM. As seen in Figure 3b, the surface structure of the cut reed straw is tight and orderly, whereas the fiber bundles in the pressed products are compressed, twisted, and partly separated from the initial connected structure.

3.2. Dye Adsorption Study. Table 3 shows the dye adsorption capacity and specific surface area (SSA) of non-treated, cutting-mill-treated, and screw-press-treated straw. The SSA of treated reed straw (cutting mill + screw press) is approximately 3.6 and 16 times higher than the cutting-mill-treated and non-treated materials, respectively. The screw-pressed reed straw enhanced the surface area to more than thrice the size of milled reed straw, because during the screw press process, a larger surface area was created, caused by the shear and pressure forces. The SSA of the screw-pressed wheat straw is 3.3 times higher in comparison to non-treated wheat straw. The increase of the available surface area might improve the efficiency of subsequent process steps.

Table 3. Amount of Dye Adsorbed at Saturation and SSA of Non-treated and Treated Straws[a]

biomass	treatment	amount of dye adsorbed, Q_m (mg g^{-1})	SSA (m^2 g^{-1})
reed straw	non-treated	0.9	1.4
	CM	4.2	6.3
	CM + SP	15.0	22.4
wheat straw	non-treated	5.4	8.1
	SP	18.0	26.8

[a]CM, cutting mill; SP, screw press.

3.3. Dilute Acid Hydrolysis. The effects of the screw press process on dilute acid treatment were investigated. It is hypothesized that, during the screw rotation, the combined effect of the temperature and high mechanical shear forces could create a larger surface area and also deconstruct some of the hemicellulose chains.[22] As expected, after screw press pretreatment, a substantial improvement in the amount of released sugars from the straw was observed. An increase of 116% (in the case of reed straw) and 75% (in the case of wheat straw) in the release of reducing sugars from screw-press-pretreated material was detected (Figure 4).

This indicates that the screw press pretreatment leads to a higher disruption of the lignocellulosic structure, which increases the accessible surface area and, consequently, increases effectively the extraction process of hemicellulose from the biomass.

3.4. Alkaline Hydrolysis. Using 5% NaOH, a substantial difference in phenol release was observed within the first 4 h for treated and non-treated reed as well as wheat straw. After 24 h, the difference diminished. When using alkaline hydrolysis with 0.5% NaOH, the phenolic unit release of the screw-press-treated straw was 40% (in the case of reed straw) and 21% (in the case of wheat straw) higher than for non-treated straw after a long hydrolysis time (96 h) (Figure 5).

It is also noteworthy that the standard deviation of treated reed straw was significantly smaller than that of the non-treated material. This indicates that the simultaneous mixing and disintegration when the biomass passes through the clearance

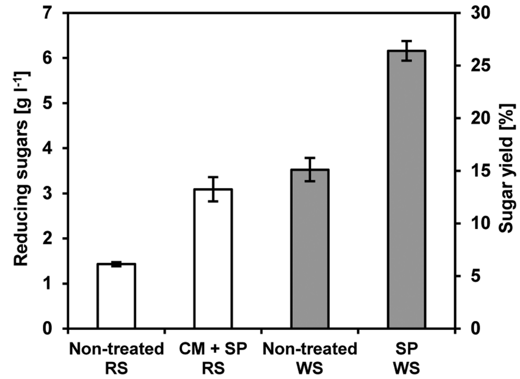

Figure 4. Dilute acid hydrolysis of screw-press-treated and non-treated straw (0.5 g of straw and 15 mL of 3% H_2SO_4 for 70 min at 80 °C). RS, reed straw; WS, wheat straw; CM, cutting mill; SP, screw press.

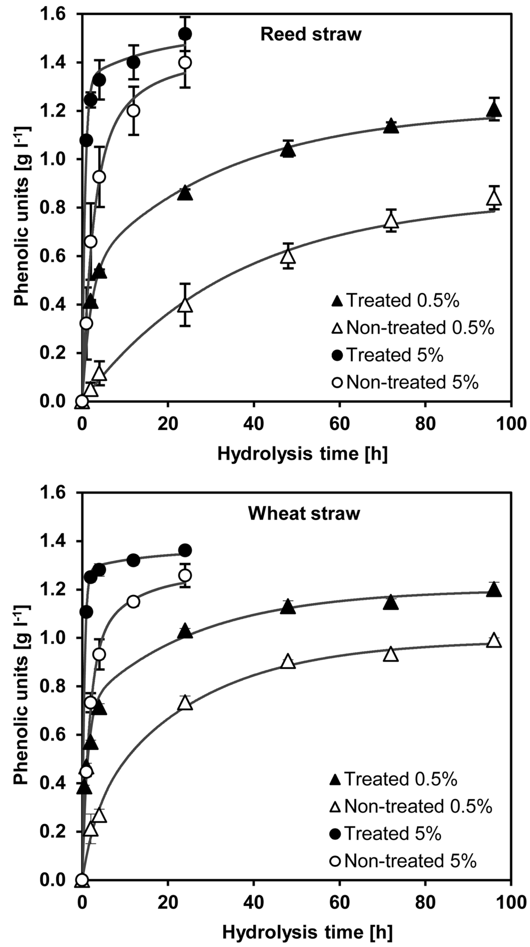

Figure 5. Alkaline hydrolysis of screw-press-treated and non-treated reed and wheat straw (0.5 g of straw and 15 mL of 0.5 or 5% NaOH at room temperature).

Table 4. Comparison of the Reaction Rate Constants k_1 and k_2 and Constants a_1 and a_2 of Treated and Non-treated Reed and Wheat Straw at Different NaOH Concentrations

material	NaOH concentration (wt %)	treatment	a_1	a_2	k_1 (h^{-1})	k_2 (h^{-1})	a_1 ratio	k_1 ratio	k_2 ratio
reed straw	0.5	non-treated	0.14	0.86	0.03	0.03	3.2	16.7	1.0
		treated	0.45	0.55	0.5	0.03			
	5	non-treated	0.66	0.34	0.43	0.10	1.4	3.5	0.6
		treated	0.94	0.06	1.5	0.06			
wheat straw	0.5	non-treated	0.27	0.73	0.30	0.04	2.2	2.8	1.0
		treated	0.59	0.41	0.85	0.04			
	5	non-treated	0.74	0.26	0.60	0.10	1.3	3.3	0.7
		treated	0.94	0.06	1.95	0.07			

between the screw and barrel additionally improves homogeneity within the sample.

Biomass delignification in alkaline pulping can be described using a first-order kinetic model.[23] On the basis of this model, the phenol release process of both straws in this study is expressed using a two-term first-order model as follows:

$$W = a_1(1 - \exp(-k_1 t)) + a_2(1 - \exp(-k_2 t)) \quad (3)$$

with

$$a_1 + a_2 = 1 \quad (4)$$

W is the fraction of the phenolic release

$$W = \frac{c}{c_\infty} \quad (5)$$

where c and c_∞ are the concentrations of phenolic units (g L^{-1}) at every considered time t and at equilibrium, respectively, a_1 is the maximum fraction of phenolic release in the first stage, a_2 is the maximum fraction of phenolic release in the second stage, and k_i (h^{-1}) (i = 1 and 2) is the reaction rate constant for the hydrolysis.

The fitted curves of the predicted concentration of the phenolic release c (g L^{-1}) compared to the experimental data are shown in Figure 5. Because the fitting was fairly good, this kinetic model was used to analyze the data obtained. The parameters, such as a_i and k_i (i = 1 and 2), were estimated and compared between non-treated and screw-press-treated samples for the alkaline pulping in Table 4.

In the first stage, 5% NaOH extracted 94% phenolic units of the treated materials, whereas only 66 and 74% of the phenolic units were removed from the non-treated reed and wheat straw, respectively (see a_1 in Table 4). In the case of using 0.5% NaOH, these values were smaller, reaching 45 and 59% for treated materials and only 14 and 27% for non-treated materials. As a comparison of reaction rate constants of fitted exponential functions for reed straw, when using 0.5% NaOH, the k_1 (h^{-1}) value improved greatly (17 times) with screw-press-treated material in comparison to non-treated material. The kinetic constant of screw-press-treated reed straw increased 3.5 times during the hydrolysis with 5% NaOH.

Because the hydrolysis time strictly affects the estimated k (h^{-1}) values, kinetic constants between experiments with different hydrolysis times (for 0.5 and 5% NaOH) cannot be compared directly. However, 0.5 and 5% NaOH hydrolyses can still be compared using the k_1 ratios ($k_{1,\text{treated}}/k_{1,\text{non-treated}}$), which are expressed as relative values. The use of the screw press for wheat straw results in a 3 times higher rate constant k_1, with k_1 ratio values approximately being the same for the hydrolysis with 0.5 and 5% NaOH. It indicates that the improvement of phenol release from wheat straw by means of screw press pretreatment is independent of the NaOH concentration. In contrast, a k_1 ratio value for reed straw hydrolyzed with 0.5% NaOH is much higher than that for 5% NaOH. It shows that improvement of chemical hydrolysis by screw press pretreatment also depends upon the type of lignocellulosic material used.

In the second stage, the k_2 values are almost the same for treated and non-treated materials in the case of using 0.5% NaOH. Because the major part of the phenolic units of treated material was removed in the first stage, with 5% NaOH, the reaction rate is a little smaller than for the non-treated material.

Clearly, with application of the screw press pretreatment, an efficient removal of phenolics from straw can be achieved, needing a shorter reaction time or lower NaOH concentration in the first hydrolysis stage. On the one hand, the screw press pretreatment can significantly reduce the processing time, while on the other hand, it can reduce the amount of necessary chemicals. Hence, the screw press pretreatment might avoid using strong chemicals in pretreatment and possibly lower environmental risks, needed investments, sugar loss, and huge amounts of water purging prior to enzymatic hydrolysis.[24]

3.5. OrganoCat Process and Enzymatic Hydrolysis of Cellulose Pulp. After those promising results mentioned above, showing the synergistic effects of the screw-pressing pretreatment with dilute acid and alkaline hydrolysis, the combination with a subsequent chemical-pulping process was studied. Therefore, reed straw samples, mechanically processed with a cutting mill or additionally with a screw press, were dried and then pulped with the OrganoCat process, a lignocellulose fractionation process recently reported.[9]

A direct impact of the screw press pretreatment on the chemical biomass fractionation process could not be confirmed (Figure 6). Small differences of xylose and lignin yields between the cut and screwed reed samples might be explained by the higher homogeneity of the screw-pressed reed, but no significant difference could be observed.

After the chemical fractionation process, the obtained cellulose pulp was hydrolyzed with a commercially available "cellulase cocktail" (Accellerase 1500). Interestingly, the reaction rate with the screw-pressed reed was higher than that with the cutting mill reed (Figure 7).

A possible explanation might be a synergetic effect of the two pretreatments, disrupting the cellulose structure and, thus, enhancing the available surface area for the cellulases by screw pressing and reducing the lignin content and crystallinity of the cellulose pulp by chemical fractionation. A similar effect was also reported for ball milling,[25] which might be considered as analogous.

However, without the chemical pulping, neither cutting-milled nor screw-pressed reed show significant activity with

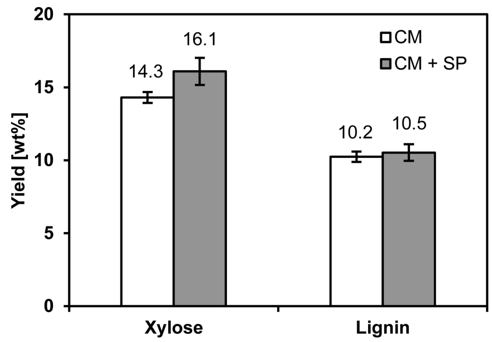

Figure 6. Impact of mechanical pretreatment on the OrganoCat process. Production of xylose (weight percent compared to the total biomass weight) in the aqueous effluent and lignin (weight percent compared to the total biomass weight) in the organic phase, detected after reaction for 1 h at 140 °C. Conditions: glass-made high-pressure reactor; biphasic system water/2-MTHF, 1:1 (40 mL total volume); oxalic acid, 0.05 M in the aqueous phase; and reed (10 mm), 100 g L^{-1} in the aqueous phase. Xylose production was analyzed by HPLC. Lignin production was determined gravimetrically after removing 2-MTHF via distillation. CM, cutting mill; SP, screw press.

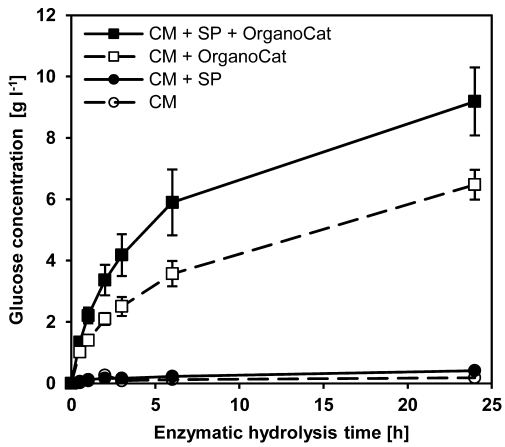

Figure 7. Kinetics of hydrolysis with Accellerase 1500 of screw-pressed reed and cut reed after the OrganoCat process. Conditions: cellulose pulp, 20 g L^{-1}; 0.1 M citrate buffer (pH 4.5); 1 vol % Accellerase 1500; and 50 °C. Glucose concentrations were determined with the glucose (HK) assay kit after reaction (see the Experimental Section). CM, cutting mill; SP, screw press.

Accellerase 1500, indicating that, in addition to the changes in cellulose structure enhancing the accessible surface, the removal of lignin is a key step for the subsequent hydrolysis of the cellulose. In consequence, the combination of mechanical screw press pretreatment and chemical fractionation of reed straw shows a promising synergy, efficiently enhancing enzymatic hydrolysis of the cellulose and potentially reducing investment and energy costs. A possible combination of both systems in one step might enhance efficiency further and should be considered for future research.

4. CONCLUSION

In the current study, the effect of the screw press pretreatment on lignocellulosic biomass as well as subsequent chemical hydrolysis was investigated. Rewardingly, a disruption of the surface was observed via SEM as well as significant enhancement of the surface accessible via dye adsorption. In addition, screw press pretreatment was shown to improve the chemical hydrolysis of reed and wheat straw, resulting in a higher release of phenols and reducing sugars. It was found within a kinetic study of alkaline hydrolysis that the screw-press-treated material required $^1/_3$ of the processing time to achieve the same release of phenols at a constant NaOH concentration compared to non-treated material. The screw press pretreatment led to a more effective removal of lignin with a shorter reaction time or lower NaOH concentration. This leads to a reduction of energy costs and environmental risks because of the reduction in the process time and amount of chemicals needed for the chemical process. For the combination of screw press and chemical fractionation via the OrganoCat process, an improvement could not be observed. However, the reaction rate of subsequent hydrolysis of the resulting cellulose pulp was raised. Considering that cellulose is the dominant fraction of lignocellulose, the improvement in the glucose yield from the cellulose pulp is highly beneficial for the lignocellulose valorization.

Overall, it could be shown that, by the screw press pretreatment, a significant improvement could be achieved, making it a promising processing step in the valorization of lignocellulose. However, for a final evaluation of the benefit of the screw press pretreatment contributing to lignocellulose valorization, much more research is needed, including an energy cost examination of the overall process.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kumar, P.; Barrett, D. M.; Delwiche, M. J.; Stroeve, P. *Ind. Eng. Chem. Res.* **2009**, *48* (8), 3713−3729.

(2) Hendriks, A. T. W. M.; Zeeman, G. *Bioresour. Technol.* **2009**, *100* (1), 10−18.

(3) Kratky, L.; Jirout, T. *Chem. Eng. Technol.* **2011**, *34* (3), 391−399.

(4) Brodeur, G.; Yau, E.; Badal, K.; Collier, J.; Ramachandran, K. B.; Ramakrishnan, S. *Enzyme Res.* **2011**, *2011*, No. 787532.

(5) Karunanithy, C.; Muthukumarappan, K. *Appl. Biochem. Biotechnol.* **2010**, *162* (6), 1785−1803.

(6) Karunanithy, C.; Muthukumarappan, K. Thermo-mechanical pretreatment of feedstocks. In *Green Biomass Pretreatment for Biofuels Production*; Gu, T., Ed.; Springer: New York, 2013; pp 31−65.

(7) de Vrije, T.; de Haas, G. G.; Tan, G. B.; Keijsers, E. R. P.; Claassen, P. A. M. *Int. J. Hydrogen Energy* **2002**, *27* (11−12), 1381−1390.

(8) Yan, Q.; Modigell, M. *Chem. Eng. Trans.* **2012**, *29*, 601−606.

(9) vom Stein, T.; Grande, P. M.; Kayser, H.; Sibilla, F.; Leitner, W.; Dominguez de Maria, P. *Green Chem.* **2011**, *13* (7), 1772−1777.

(10) Technical Association of the Pulp and Paper Industry (TAPPI). *T12 os-75. Preparation of Wood for Chemical Analysis*; TAPPI: Peachtree Corners, GA, 1975.

(11) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; National Renewable Energy Laboratory (NREL): Golden, CO, 2011; NREL/TP-510-42618.

(12) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. *Determination of Ash in Biomass*; National Renewable Energy Laboratory (NREL): Golden, CO, 2005; NREL/TP-510-42622.
(13) Holzmann, G.; Wangelin, M.; Bruns, R. Faserpflanzen im Bauwesen. *Natürliche und pflanzliche Baustoffe*; Vieweg+Teubner Verlag: Leipzig, Germany, 2012; pp 73−276.
(14) Kootstra, A. M. J.; Beeftink, H. H.; Scott, E. L.; Sanders, J. P. M. *Biochem. Eng. J.* **2009**, *46* (2), 126−131.
(15) Fu, Y.; Viraraghavan, T. *Adv. Environ. Res.* **2002**, *7* (1), 239−247.
(16) Lee, S. H.; Teramoto, Y.; Endo, T. *Bioresour. Technol.* **2009**, *100* (1), 275−279.
(17) Yoshida, H.; Kataoka, T.; Maekawa, M.; Nango, M. *Chem. Eng. J.* **1989**, *41* (1), B1−B9.
(18) Ougiya, H.; Hioki, N.; Watanabe, K.; Morinaga, Y.; Yoshinaga, F.; Samejima, M. *Biosci., Biotechnol., Biochem.* **1998**, *62* (10), 1880−1884.
(19) Miller, G. L. *Anal. Chem.* **1959**, *31* (3), 426−428.
(20) Slinkard, K.; Singleton, V. L. *Am. J. Enol. Vitic.* **1977**, *28* (1), 49−55.
(21) Litzen, D.; Dixon, D.; Gilcrease, P.; Winter, R. Pretreatment of biomass for ethanol production. U.S. Patent 20060141584 A1, June 29, 2006.
(22) Lamsal, B.; Yoo, J.; Brijwani, K.; Alavi, S. *Biomass Bioenergy* **2010**, *34* (12), 1703−1710.
(23) Kim, S.; Holtzapple, M. T. *Bioresour. Technol.* **2006**, *97* (5), 778−785.
(24) Zhang, S.; Xu, Y.; Hanna, M. A. *Appl. Biochem. Biotechnol.* **2012**, *166* (2), 458−469.
(25) Fan, L. T.; Lee, Y.; Beardmore, D. H. *Biotechnol. Bioeng.* **1980**, *22* (1), 177−199.