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Is Steam Explosion a Promising Pretreatment for Acid Hydrolysis of Lignocellulosic Biomass?

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Abstract: For the production of sugars and biobased platform chemicals from lignocellulosic biomass, the hydrolysis of cellulose and hemicelluloses to water-soluble sugars is a crucial step. As the complex structure of lignocellulosic biomass hinders an efficient hydrolysis via acid hydrolysis, a suitable pretreatment strategy is of special importance. The pretreatment steam explosion was intended to increase the accessibility of the cellulose fibers so that the subsequent acid hydrolysis of the cellulose to glucose would take place in a shorter time. Steam explosion pretreatment was performed with beech wood chips at varying severities with different reaction times (25–34 min) and maximum temperatures (186–223 °C). However, the subsequent acid hydrolysis step of steam-exploded residue was performed at constant settings at 180 °C with diluted sulfuric acid. The concentration profiles of the main water-soluble hydrolysis products were recorded. We showed in this study that the defibration of the macrofibrils in the lignocellulose structure during steam explosion does not lead to an increased rate of cellulose hydrolysis. So, steam explosion is not a suitable pretreatment for acid hydrolysis of hardwood lignocellulosic biomass.

Keywords: glucose; xylose; 2nd generation sugars; lignocellulose; hydrolyzate; biorefinery; furfural; hydroxymethylfurfural; bioeconomy

1. Introduction

In view of a bioeconomy, promising products from lignocellulosic biomass can be value-added platform chemicals produced in a biorefinery [1,2]. As lignocellulosic biomass consists mainly of the polymeric constituents cellulose, hemicelluloses and lignin, the fractionation of feedstock is the first step for maximizing the value of these materials. Cellulose is composed of glucose building blocks linked together by glycosidic bonds forming a linear polymer. Between adjacent cellulose chains, intermolecular hydrogen bonds are formed, which result in a water-insoluble and highly ordered configuration that makes cellulose partly crystalline [3]. Hemicelluloses hydrolyze faster than cellulose, because they are group of amorphous heteropolymers which are considerably shorter than cellulose. Hemicelluloses provide a linkage between cellulose and lignin in the lignocellulosic fiber structure. Lignin is constructed of phenylpropane units which form a complex three-dimensional macromolecule.

One method for the fractionation of lignocellulosic biomass is acid hydrolysis whereby cellulose and hemicelluloses are hydrolyzed to water-soluble sugars which are partly dehydrated to furfurals. In particular, furfural and hydroxymethylfurfural can be produced in a lignocellulose biorefinery. These furfurals were named as one of the top 10 value-added biobased chemicals [4].

However, the complex structure of lignocellulosic biomass generally causes a low hydrolysis rate, especially of cellulose during acid hydrolysis [5]. Hemicelluloses and lignin surrounding the cellulose form a physical barrier against the permeation for the hydrolysis catalyst [6]. Additionally, different hydrolysis rates for crystalline and amorphous cellulose regions exist. This, combined with the shielding matrix of lignin and hemicelluloses, results in a gradual sugar release [5].

A pretreatment is necessary to increase the accessibility of cellulose for the subsequent hydrolysis step [5]. As a general estimation, the pretreatment step accounts for about 40% of the processing cost in a lignocellulose biorefinery [7]. Therefore, it is important to choose pretreatment methods and conditions carefully. A relatively inexpensive pretreatment is steam explosion because no addition of an external catalyst is needed [8]. However, the energy consumption for steam explosion was estimated as 1.8 MJ/kg_{wood} and is therefore considerable [9]. Steam explosion converts biomass in a steam atmosphere at elevated temperatures ranging from 140–240 °C. The steam pressure is rapidly reduced to atmospheric pressure, whereby a mechanical disruption of the biomass occurs.

Acetic acid is formed during steam explosion via the cleavage of thermally labile acetyl groups in hemicelluloses [5]. The liberated acetic acid catalyzes the hydrolysis reactions of hemicelluloses. The solid residue after steam explosion pretreatment consists of cellulose, a chemically modified lignin and residual hemicelluloses. The sum of hemicelluloses in the residue and dissolved hemicellulose-derived sugars decreases with the pretreatment severity due to (1) condensation reactions leading to solid pseudolignin and (2) furfural formation by the dehydration of pentoses [10].

Steam explosion is a well-known effective pretreatment to increase the rate of enzymatic hydrolysis of lignocellulosic biomass [11–14]. For example, the enzymatic hydrolysis rate showed a 10-fold increase for steam-exploded hardwoods [15]. In addition, the glucose yields after enzymatic hydrolysis are higher, when a steam explosion pretreatment was applied. This increase in glucose yield is due to the removal of biomass components like hemicelluloses and lignin during the steam explosion pretreatment [16].

However, much less attention has been paid to the effect of steam explosion pretreatment on a hydrolysis step with diluted acids. Carrasco et al. [17] performed steam explosion pretreatments of different lignocellulosic biomasses followed by acid hydrolysis at 180 °C using diluted sulfuric acid. The steam explosion pretreatment lead to a decrease in the subsequent hydrolysis rate [17]. Schultz et al. [15,18,19] investigated the influence of steam explosion on concentrated acid hydrolysis. Among the lignocelluloses used, only steam-exploded rice husks showed a higher glucose yield after hydrolysis with concentrated sulfuric acid [15]. However, the concentration profiles of glucose were, in contrast to the present work, not recorded by Schultz et al. [15,18,19] and Carrasco et al. [17].

In this work, we evaluate the influence of a previous steam explosion on the acid hydrolysis of lignocellulosic biomass. Therefore, the steam explosion of beech wood as a representative of hardwood is performed in a batch system at different severities. The steam-exploded residues are characterized and, thereafter, subjected to acid hydrolysis. The acid hydrolysis step is done in a semi-continuous reactor at constant settings with diluted sulfuric acid. The concentration profiles of the main water-soluble hydrolysis products are recorded which also comprise glucose.

2. Materials and Methods

2.1. Pretreatment via Steam Explosion

As feedstock for pretreatment, pre-dried and bark-free beech wood is used. Beech trees are categorized as hardwoods and are one of the major forest trees in Europe. The dominant sugar in beech wood hemicelluloses is xylose [20]. The beech wood is used in chip size, has a moisture content of 8.0 wt.% and is obtained from Joh. Sinnerbrink GmbH & Co. (Verl, Germany). The chip dimensions are about 15 mm in width, 30 mm in length and 1–2 mm thick.

The steam explosion is performed in a self-constructed test rig, described in our previous work [21]. The stainless-steel reactor of the steam explosion has a volume of 1 L and is constantly agitated with a

cross-arm stirrer at 8 min^{-1}. The reactor is filled completely with beech wood chips, referring to 82–94 g dry mass, before each experiment. Then the reactor is electrically preheated by a surrounding electrical heating jacket. Steam is introduced into the reactor with a flow of up to 5 g/min. The explosion step is performed by pneumatically opening a ball valve. Solid products and steam are discharged by the explosion step into a flash tank. The pretreated solid is manually collected from the flash tank and dried at 105 °C for 16 h.

The reaction temperature is measured by two thermocouples in the top and the bottom of the reactor. The severity parameter S_0 is calculated, combining temperature T and time t of the steam pretreatment in a single factor [10]. Equation (1) shows the time integral of S_0, which considers the non-isothermal character of the heating process [22].

$$S_0 = log \int_0^t exp\left(\frac{T\,(°C) - 100\,°C}{14.75}\right) dt \quad (1)$$

Pretreatment conditions with different reaction time (25–34 min), steam input mass (60–150 g) and maximum temperature (186–223 °C) are investigated. Figure 1 shows the temperature profile during heat up and Table 1 provides an overview of the experimental conditions.

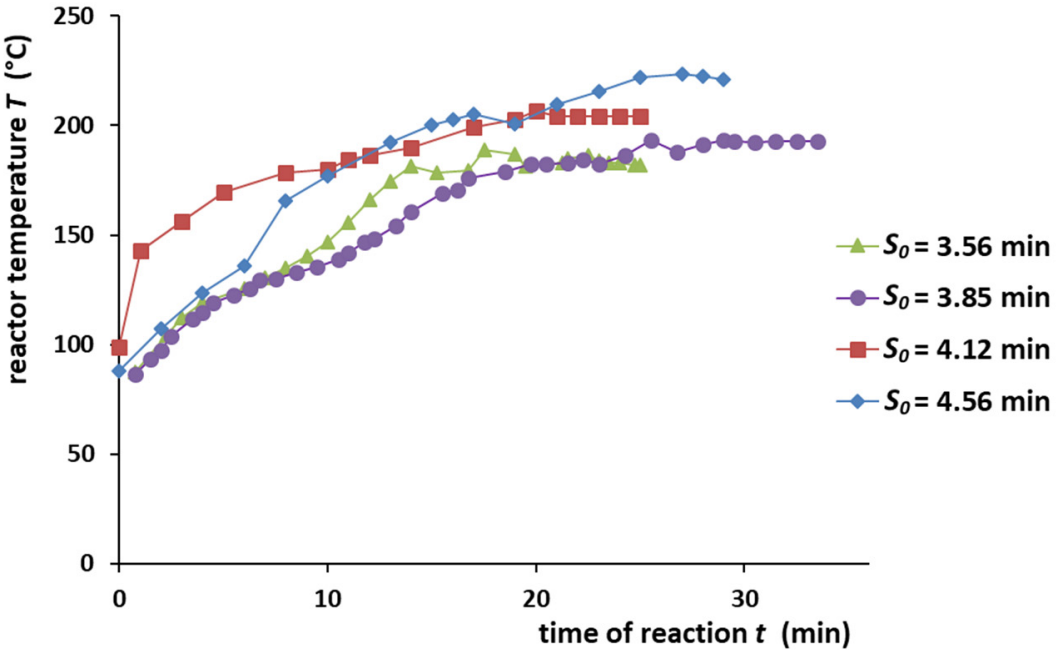

Figure 1. Temperature profile inside the steam explosion reactor, t = 0 min marks the beginning of steam input.

Table 1. Experimental setup for steam explosion of beech wood chips.

severity parameter S_0 (min)	3.56	3.85	4.12	4.56
beech wood mass (g_{dry})	91.6	81.8	83.4	93.8
steam input time (min)	25	33.5	25	29
steam input mass (g)	50	80	100	110
maximum reactor temperature (°C) [1]	186	193	206	223
maximum excess pressure (bar) [1]	11	13	19	26

[1] before explosion step.

2.2. Acid Hydrolysis of Steam-Exploded Residues

An acid-catalyzed hydrolysis of lignocellulose is performed to obtain a monosaccharide-containing product liquid, also called hydrolyzate. The solid residues after steam explosion as well as untreated beech wood chips are used as educts. Diluted sulfuric acid is used as a catalyst to hydrolyze hemicelluloses and cellulose polymers in the lignocellulose structure to water-soluble sugar monomers.

A semi-continuous test rig, described in our previous work [23], is used for acid hydrolysis, where the liquid phase is continuously exchanged. This has the advantage that liberated water-soluble molecules like sugar monomers are removed from the hot reactor and thus protected to a large extent from secondary reactions. The stainless-steel reactor has an internal volume of 100 mL and is loaded with 15.0 g of either untreated beech wood chips or steam-exploded residue as a fixed bed before the experiment. Demineralized water or dilute acid solution is continuously fed into the reactor at a volume flow of 15 mL/min. Demineralized water is pumped through the reactor during the heating phase. When the target temperature of 180 °C inside the reactor is reached, the feed stream is switched to a sulfuric acid solution of 0.05 mol/L. The hydrolyzate leaves the reactor continuously and is collected in interval samples of 5–8 min before storage at 4 °C.

2.3. Analytical Methods

After steam explosion, a wet solid residue is obtained, which is dried at 105 °C for 16 h to avoid microbiological degradation. After drying, the mass of the solid residue is measured. Then a sample of the solid residue is subjected to a two-hour Soxhlet extraction with water. In this way, a water-soluble and a water-insoluble fractions are obtained, which are examined for their composition. The mass of the water-insoluble fraction is determined gravimetrically, whereas the mass of the water-soluble fraction is calculated by difference.

The surfaces of dried beech wood and dried steam-exploded residues are examined via scanning electron microscopy (SEM) using a LEO 982 Gemini (Carl Zeiss, Jena, Germany) which is equipped with a Schottky-type thermal field emission cathode, a backscattered electron detector and two secondary electron detectors (inlens, Everhart-Thornley).

The Klason lignin content of steam-exploded residue and untreated beech wood is determined in triplicate according to the ASTM method D1106-96 (2013) [24]. In brief, two extractions of the biomass are performed with alcohol-benzene solution and with hot water. Then the residue is treated with 72 wt.% sulfuric acid which is afterwards diluted to 3 wt.% whereby the polysaccharides are completely hydrolyzed. The remaining solid gives, after correction with ash content, the Klason lignin content. The (polymeric) sugar content in water-insoluble steam-exploded residue and untreated beech wood is determined via a complete hydrolysis of polysaccharides to water-soluble monosaccharides according to Saeman [25].

Water-soluble sugar monomers are quantified via a gas chromatography method. As sugars cannot be evaporated, they are converted into stable, evaporable alditol acetate derivatives using a procedure described by Sawardeker et al. [26]. After extraction of the alditol acetates into chloroform, the sample is isothermally separated in a gas chromatograph type GC 5890A (Hewlett Packard, Palo Alto, CA, USA) at 240 °C and detection is performed via FID. The separation column RTX2330 (Restek, Bad Homburg, Germany) is used with a 30 m length and 25 µm diameter. The sugars, arabinose, xylose, rhamnose, mannose, galactose and glucose are calibrated. The accuracy of time-consuming derivatization and GC analysis is ensured by (1) performing a derivatization of a sugar standard solution in parallel for every analytical sequence and (2) the internal standard inositol, which is added in a known amount to any sample during derivatization.

The characterization of other water-soluble constituents in the hydrolyzate is conducted with two HPLC methods. To remove high-molecular-weight products, filtration is performed with syringe filters of type 0.45 µm GHP (Pall, New York, NY, USA). Furfural and hydroxymethylfurfural (HMF) are separated in a Lichrospher 100 RP-18 column (Merck, Darmstadt, Germany) at 20 °C and quantified by a UV detector at 290 nm. Therefore, an eluent of water-acetonitrile (9:1 *v*/*v*) is used at a flow rate of

1.4 mL/min. Formic acid, acetic acid, lactic acid and levulinic acid are separated with an Aminex HPX 87H column (Biorad, Hercules, CA, USA) at 25 °C. An eluent of 0.004 mol/L sulfuric acid is used at a flow rate of 0.65 mL/min and detection is performed by RI and DAD.

The cumulative yields of glucose and xylose after the hydrolysis step are calculated according to Equation (2). Thereby, the solid residue yield of the steam explosion step is considered. The volume flow of acid hydrolysis of 15 mL/min is multiplied with the measured concentration of glucose or xylose and integrated over reaction time.

$$cumulative\ yield\ = \frac{yield_{solid\ residue}}{m_{input\ hydrolysis}} \int^{t} \dot{V} \cdot c(t)\ dt \tag{2}$$

3. Results

3.1. Steam Explosion

Beech wood chips are pretreated via steam explosion. An increased severity parameter leads to a lower yield of solid residue (see Table 2). A Soxhlet extraction with water is performed whereby a water-soluble and a water-insoluble fraction are obtained. The yield of the water-insoluble fraction decreases with higher severity and fewer polymers of glucose are present (see Table 2). At the highest severity parameter of S_0 = 4.56 min, no polymeric bonded xylose can be detected in the solid residue. In contrast, the Klason lignin yield rises with severity. After all steam explosion runs, the Klason lignin yield is higher compared to untreated beech wood (0.229 $g/g_{beech\ wood}$).

Table 2. Solid residues after steam explosion of beech wood at different severities, fractionation of solid residues is performed via Soxhlet extraction with water, n.d.: not determined.

severity parameter S_0 (min)	3.56	3.85	4.12	4.56
solid residue mass (g)	85.5	74.8	61.8	64.0
solid residue yield ($g/g_{beech\ wood}$)	0.933	0.915	0.741	0.682
water-insoluble fraction ($g/g_{beech\ wood}$)	0.789	0.724	0.612	0.533
• polymeric bonded glucose ($g/g_{beech\ wood}$)	0.260	n.d.	0.210	0.192
• polymeric bonded xylose ($g/g_{beech\ wood}$)	0.103	n.d.	0.021	0.000
• Klason lignin ($g/g_{beech\ wood}$)	0.297	n.d.	0.353	0.346
water-soluble fraction ($g/g_{beech\ wood}$)	0.144	0.191	0.128	0.149
• glucose ($g/g_{beech\ wood}$)	0.002	0.001	0.002	0.000
• xylose ($g/g_{beech\ wood}$)	0.002	0.010	0.016	0.000

Figure 2 shows the topographical changes in the biomass macrostructure after steam explosion. Even in the photographs, a size reduction and defibration can be observed compared to the untreated wood chips. As the severity increases, the fibers become finer and the solid residue becomes darker. However, at the highest examined severity of S_0 = 4.56 min, no exposed fibers are visible and the biomass looks slightly carbonized. Additionally, the SEM images illustrate the defibration. Loosely present macrofibrils can be seen after intermediate severities (e.g., SEM at 100x at S_0 = 3.85 min). At the highest examined severity of S_0 = 4.56 min, the fiber structure can no longer be clearly recognized (see SEM image at 100× in Figure 2).

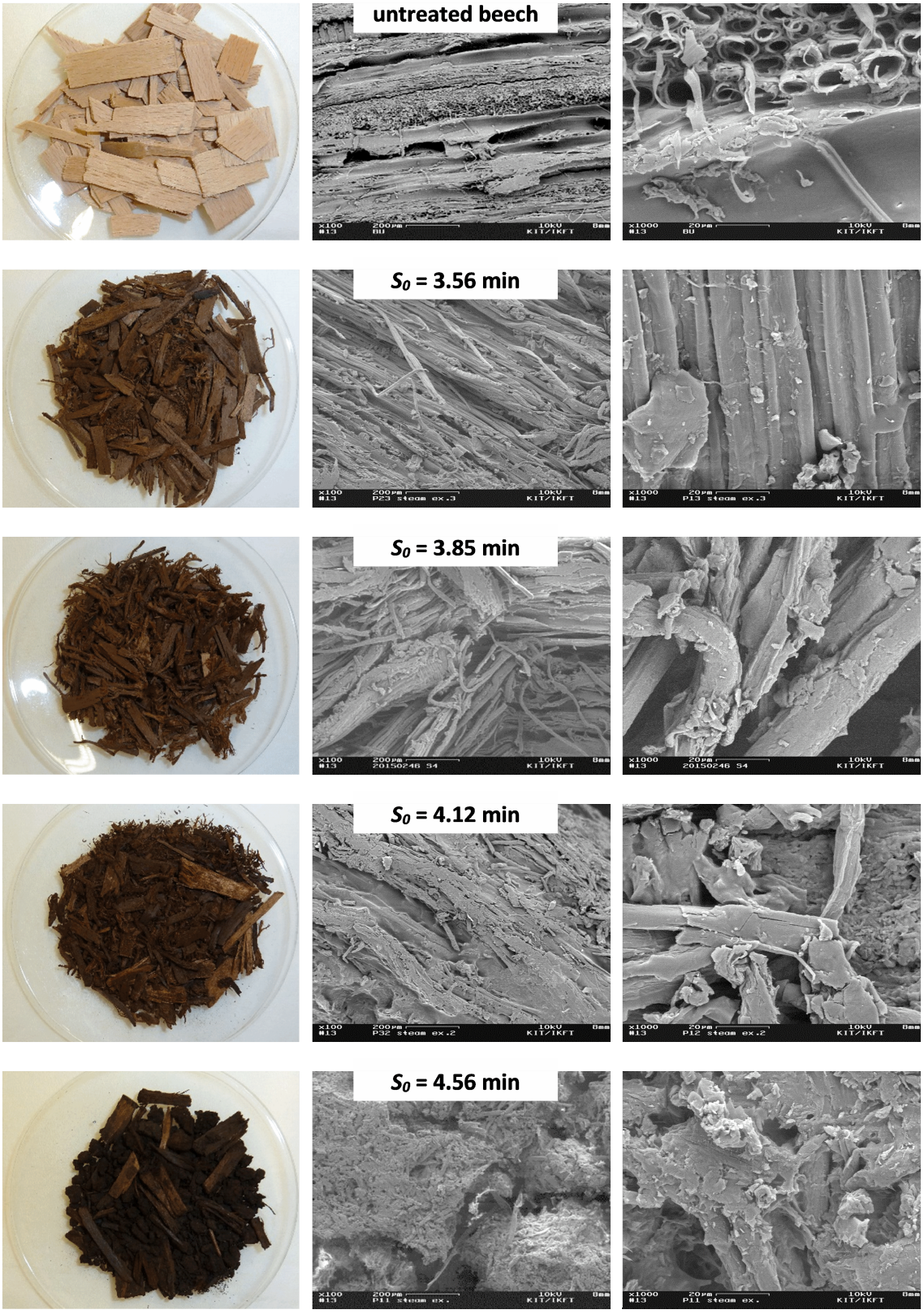

Figure 2. Beech wood and solid residues after steam explosion at different severity parameters S_0, photographs (**left**), SEM images at 100× (**center**) and 1000× (**right**).

3.2. Acid Hydrolyisis

To investigate the influence of the steam explosion pretreatment on acid hydrolysis, all influencing parameters during acid hydrolysis are kept constant and only the solid biomass input in the fixed bed reactor is varied. Acid hydrolysis is carried out with 0.05 mol/L sulfuric acid at a 180 °C reaction temperature. The volume flow of the diluted acid through the semi-continuous hydrolysis reactor is also constant. The biomass input originates from steam explosion runs with different severities. The solid residue after the highest examined severity of S_0 = 4.56 min is not subjected to acid hydrolysis, because the material appears to be already partly carbonized.

Figures 3 and 4 show the concentration profiles of the main water-soluble hydrolysis products during acid hydrolysis for different severities of steam explosion. The main hydrolysis products in our study using beech wood are the monosaccharides glucose, xylose and mannose, as well as furfural hydroxymethylfurfural and acetic acid. The principal trends in the concentration profiles of all main products are very similar regardless of the severity of pretreatment. However, there are big differences in the maximum concentration values. The maximum xylose concentration drops largely with increasing severity (from 4.5 g/L at S_0 = 3.56 min to 1.2 g/L at S_0 = 4.12 min). The maxima of acetic acid and furfural also decrease sharply with increasing severity parameters (see Figure 4). However, the influence of pretreatment severity on the glucose concentration is much less (see Figure 3). Figure 3 shows the concentration profiles of glucose and xylose during acid hydrolysis, where steam-exploded residue is compared with untreated beech wood.

Figure 5 shows the cumulative yields of glucose and xylose during acid hydrolysis for different steam explosion severities and a comparison to the untreated beech wood material is made. For the calculation of the cumulative yields according to Equation (2), the solid residue yield of stream explosion pretreatment from Table 2 is considered. For reaction times over 25 min, the yield of glucose is higher for untreated beech wood compared to all pretreated materials. Additionally, the yield of xylose is higher for untreated beech wood compared to stream-exploded residues.

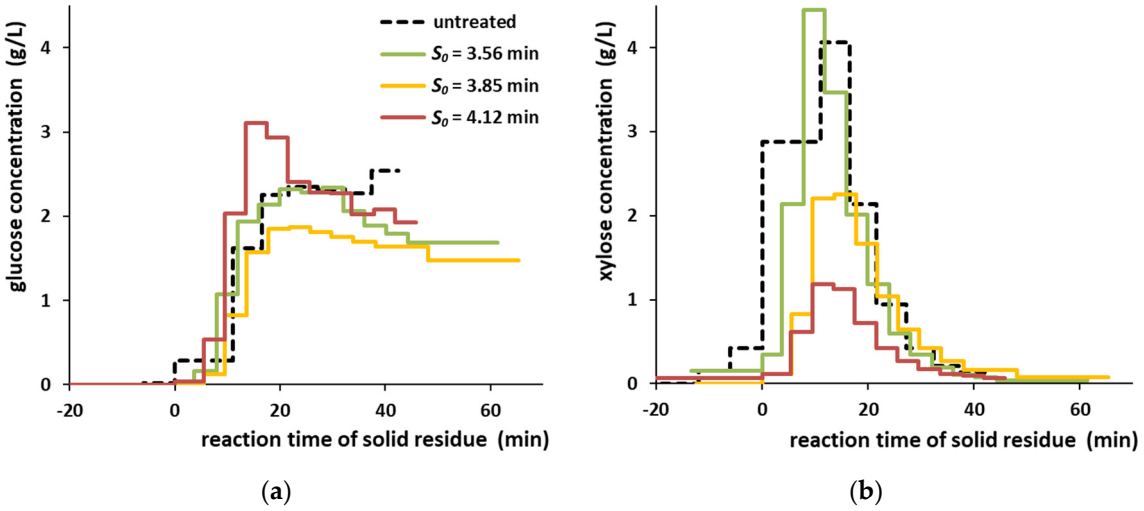

Figure 3. Formation of glucose (**a**) and xylose (**b**) during the hydrolysis of 15.0 g untreated beech wood or steam-exploded residue at different severity parameters S_0, hydrolysis with 0.05 mol/L sulfuric acid at 15 mL/min flow at 180 °C, t = 0 min marks the beginning of acid hydrolysis.

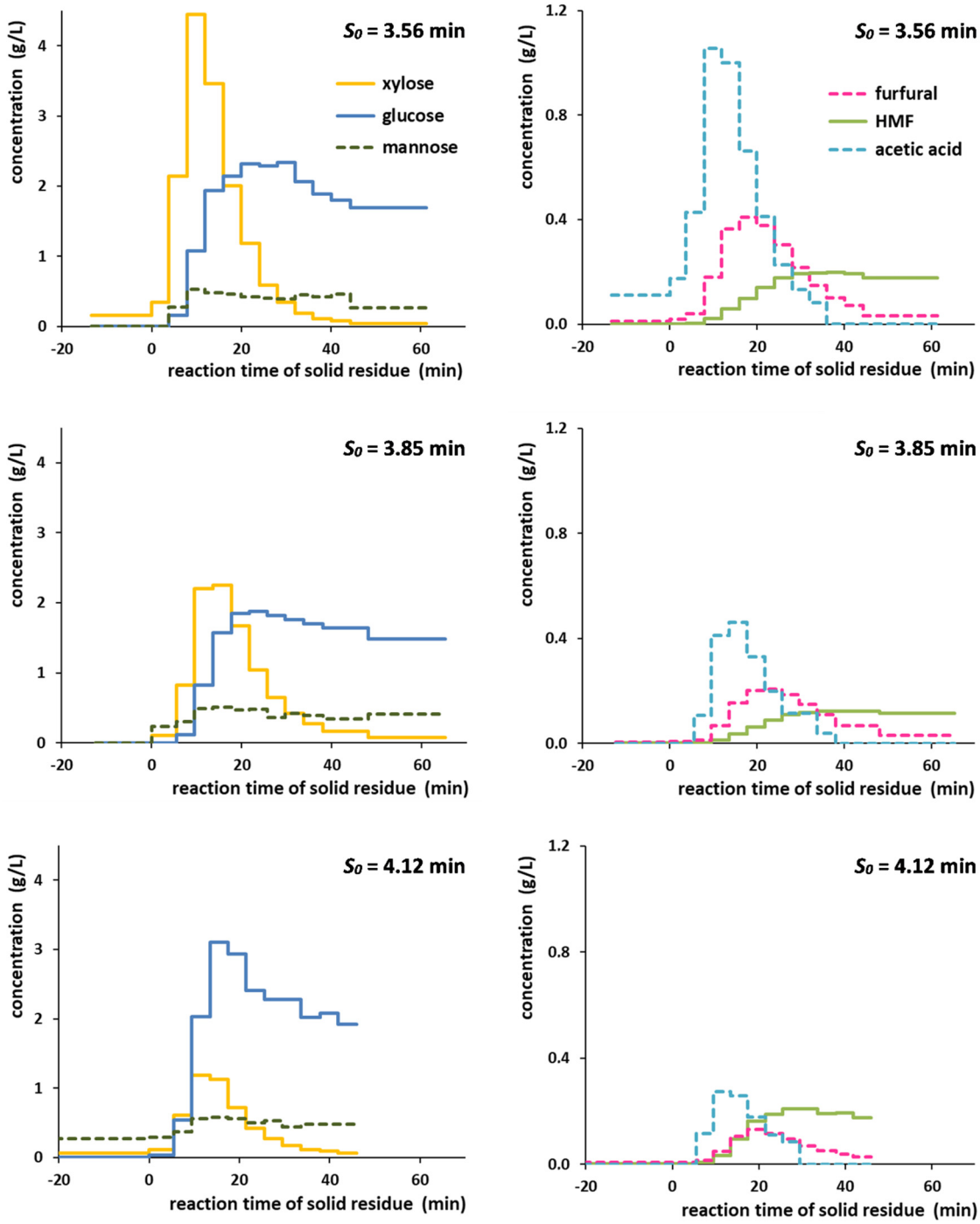

Figure 4. Formation of monosaccharides (**left**) as well as furfural, hydroxymethylfurfural and acetic acid (**right**) during the hydrolysis of 15.0 g steam-exploded residue at different severity parameters S_0, hydrolysis with 0.05 mol/L sulfuric acid at 15 mL/min flow at 180 °C, t = 0 min marks the beginning of acid hydrolysis.

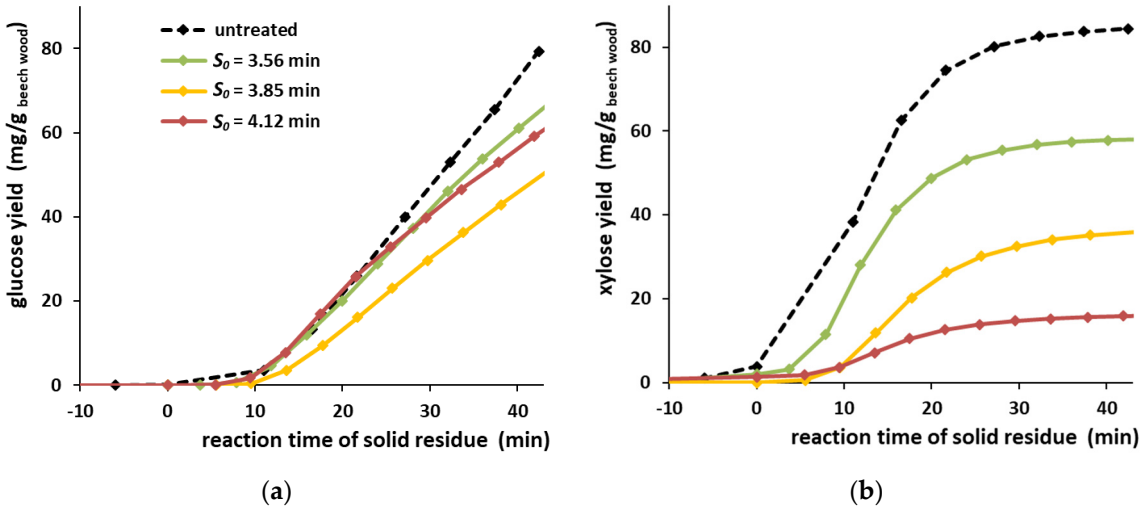

Figure 5. Cumulative yields of glucose (**a**) and xylose (**b**) during the hydrolysis of untreated beech wood or steam-exploded residue at different severity parameters S_0, hydrolysis with 0.05 mol/L sulfuric acid at 15 mL/min flow at 180 °C, t = 0 min marks the beginning of acid hydrolysis.

4. Discussion

The steam explosion increases the lignin mass according to the Klason method, which agrees with the results of other studies [18,27,28]. A lignin yield of 0.297–0.353 $g/g_{beech\ wood}$ is obtained after the steam explosion (see Table 2), while the Klason lignin content in beech wood is only 0.229 $g/g_{beech\ wood}$. Condensation reactions between hemicellulose constituents and lignin lead to the formation of an inert solid [29]. This solid is also measured in the gravimetric determination of Klason lignin and is therefore no longer distinguishable from lignin which was originally contained in beech wood. This is the reason why this newly formed solid is named pseudolignin. In principle, a reaction pathway via the repolymerization of water-soluble hemicellulose degradation products would also possibly form pseudolignin. This pathway could result in the formation of spherical structures on the solid product after steam explosion. This is known from the process of hydrothermal carbonization, where microspheres are formed by the polymerization of sugar degradation products [30,31]. However, in this study, such spherical structures were not found in the steam-exploded residues even at up to 50,000× magnification of the SEM.

The pretreatment via steam explosion was intended to increase the accessibility of the cellulose fibers so that the subsequent acid hydrolysis of the cellulose to glucose takes place in a shorter time. Consequently, a high glucose concentration should be achieved after a short time of acid hydrolysis, which then drops sharply after the cellulose has been completely converted. The intended effect of pretreatment on glucose formation did not occur. During acid hydrolysis, the steam-exploded residues begin to release glucose after roughly the same reaction time compared to untreated beech wood (see Figure 3). When steam-exploded residues are used, the maximum concentration of glucose is similar or even smaller (except for two measuring points at S_0 = 4.12 min). Additionally, no obvious drop in glucose concentration with longer reaction times can be observed. The comparison of glucose and xylose yields shows that a previous steam explosion pretreatment reduces the sugar yields, especially for xylose (see Figure 5).

Consequently, the defibration of the macrofibrils in the lignocellulose structure during steam explosion does not lead to an increased rate of cellulose hydrolysis. It can therefore be assumed that the rate-determining step in the hydrolysis is not the penetration of the acid to the individual macrofibrils. Rather, the penetration of the hydronium ions into the crystalline structure of cellulose can be assumed to determine the rate or hydrolysis might only occur at the exposed chain ends of the cellulose. This is in accordance with other studies [32]; the crystallinity of cellulose stabilized by hydrogen bonds is very strong and can only be broken by supercritical water, for example at 380 °C and 250 bar [33]. In the

case of enzymatic hydrolysis reactions, the situation is different. An enzyme is a much larger molecule than a hydronium ion with solvation shell, therefore the increase in surface area by steam explosion has an impact.

Xylose, which is the main structural unit of the hemicelluloses in beech wood, is largely converted by steam explosion at a higher severity into other compounds (see Table 2). Thereby, xylose could be either decomposed to low-molecular-weight compounds or converted to pseudolignin. It is generally known that the total mass of hemicelluloses in the steam-exploded residues decreases with an increasing severity parameter [10]. Therefore, it is reasonable that in the product liquid of acid hydrolysis, less xylose can be detected with increasing severity of the pretreatment (see Figure 3), as less hemicelluloses are in the feedstock for hydrolysis, which could form xylose.

The concentrations of furfural and acetic acid during acid hydrolysis also decrease with the severity of the pretreatment (see Figure 4). The reduction of furfural concentration is a consequence of the lower xylose concentration, since furfural arises from the dehydration of pentoses [5]. The decline in acetic acid concentration with the increasing severity of the steam explosion can be explained as follows. The acetyl groups of the hemicelluloses are hydrolyzed to a greater extent during the steam explosion at high severity and are therefore removed from the biomass before the acid hydrolysis step begins.

5. Conclusions

In this study, beech wood lignocellulosic biomass was subjected to steam explosion pretreatment before an acid hydrolysis step. The pretreatment via steam explosion was intended to increase the accessibility of the cellulose fibers so that the subsequent acid hydrolysis of the cellulose to glucose would take place in a shorter time. We showed that the defibration of the macrofibrils in the lignocellulose structure during steam explosion does not lead to an increased rate of cellulose hydrolysis. Additionally, steam explosion causes a mass loss of solid material and large losses of the hemicellulose-derived sugar xylose, especially at a higher pretreatment severity. That is why steam-exploded material resulted in lower sugar yields based on lignocellulose input. So, steam explosion is not a suitable pretreatment for the acid hydrolysis of hardwood lignocellulosic biomass.

Author Contributions: D.S. and J.S. (Jonas Storz) designed and performed the experiments as well as analyzed the data. D.S., A.K. and J.S. (Jörg Sauer) wrote the article. All authors have read and agreed to the published version of the manuscript.

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