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The importance of pretreatment and feedstock purity in the reductive splitting of (ligno)cellulose by metal supported USY zeolite

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Reductive hydrolysis of cellulose to hexitols is a promising technology to valorize cellulose streams. Several catalytic systems have been reported to successfully process commercially available purified cellulose powders according to this technology. Ruthenium-loaded USY zeolites in presence of minute amounts of HCl, among others, showed already very high hexitol yields. This contribution first investigates into more detail the impact of several cellulose accessibility-related properties like cellulose crystallinity, particle size and degree of polymerization on the conversion rate and hexitol selectivity. Therefore, a series of commercial cellulose samples and several mechano- and chemotreated ones were processed with the Ru/H-USY – HCl catalytic system in standard hot liquid water conditions. The results reveals that the polymerization degree has a large impact on both conversion rate and selectivity, but its impact fades for DPs lower than 200. From then on, the dominant parameters are the particle size and crystallinity. A second part addresses the influence of cellulose purity. Therefore, organosolv pulps of three lignocellulosic substrates (wheat straw, spruce and birch wood), optionally followed by a bleaching procedure, were processed in the same catalytic circumstances. Here factors like residual lignin fractions and acid buffer capacity appeared very crucial, pointing to the neccessity of a dedicated delignification and purification procedure step in order to form the most reactive cellulose feedstock for hexitol production. Complete removal of non-glucosic components is not required since processing of a ethanol organosolv birch cellulose and bleached ethanol organosolv wheat straw cellulose, both containing about 6 wt% of lignin and minor contents of ashes and proteins, showed a similar hexitol yield, viz. 34 – 39%, to that derived from pure microcrystalline cellulose.

1. Introduction

Pretreatment of cellulosic biomass is an essential process step to enable enzymatic hydrolysis of cellulose to glucose.[1-7] Commonly applied pretreatments include milling, hot water, steam explosion, dilute acid, alkaline, organosolv and ionic liquid pretreatment. Main purpose of these pretreatments is to improve the accessibility and reactivity of cellulose through a physical or chemical disruption of the cellulose structure. This disruption involves an extensive change in physicochemical features including particle size (d_p), porosity, crystallinity (CrI) and/or degree of polymerization (DP) which ultimately affect the chemical reactivity.[1, 2, 8-20] For example, the CrI and DP of cellulose govern the accessibility of enzyme-binding sites and the reactivity of the glycoside bonds, enclosed within its structure.[9] In crystalline cellulose regions, cellulose chains are tightly packed together through various intermolecular hydrogen bonds and hydrophobic or van de Waals forces.[21-24] A disruption of the internal cohesion greatly enhances the reactivity of cellulose. Reducing the DP of cellulose through pretreatment enhances the subsequent cellulose-to-glucose hydrolysis rate in two ways: on the one hand glycoside bonds are already broken in advance,[25] on the other hand more exoglucanase interaction sites are created through the generation of reducing ends.[9, 26] Also an increase in porosity and pore size/volume (internal surface area) or a reduction in d_p, viz. an increase of external surface area, improve the accessibility of cellulose, although it has been suggested that these features are less decisive in the biological conversions.[9, 27]

Direct conversion of cellulose enclosed within lignocellulosic biomass, like grasses or woods, is more challenging for catalysts than the direct conversion of pure cellulose feedstocks. In lignocellulosic biomass, cellulose is covered by hemicellulose and lignin fractions, which form a lignin-carbohydrate complex (LCC) through various covalent

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bonds.[28, 29] This particular supramolecular organization creates a more resistant cellulose, less prone to biological and chemical attack. Removal of the hemicellulose and lignin is expected to greatly increase the accessibility and therefore the reactivity of cellulose for further chemical or biological processing.

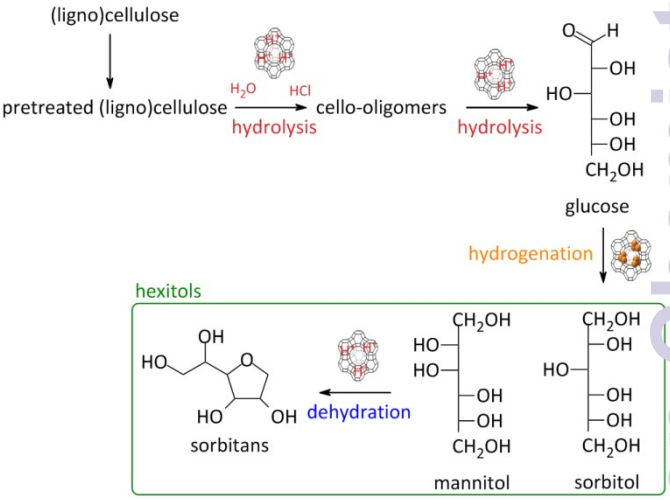
However, new challenges may arise when using real feedstocks. During chemical reactions in presence of an acid and/or metal catalyst, released lignin residues sometimes contaminate the catalyst by fouling, leading to reduced product yields.[30, 31] Furthermore, other constituents of lignocellulosic biomass may lead to catalyst neutralization, contamination or poisoning. Depending on the nature of the feedstock, small amounts of acid catalysts may be neutralized by the alkalinity of the inorganic part, like minerals, present in the biomass.[7, 32] This propensity to neutralize acids is quantitatively expressed as the acid neutralizing capacity (ANC, mol H^+/kg dry matter). Metal catalyst poisoning or contamination by biomass components like proteins, tannins, pectins, waxes, fatty acids, phosphorus and sulphur have also been described.[31, 33, 34] Inorganic salts like $CaCO_3$ or $NaHCO_3$ are known to initiate base-catalyzed side reactions, like retro-aldol, ultimately leading to the formation of ethylene glycol and propylene glycol instead of hexitols during the hydrolytic hydrogenation of real biomass feedstock.[34] Thus, a disruption of the lignocellulose structure and removal of inhibitory compounds should enable a more effective and selective cellulose-to-hexitol process.

Although the main focus of (ligno)cellulosic biomass pretreatment is to improve the accessibility of the (ligno)cellulose to enzymes, current research highlighted the importance of biomass pretreatment in the aqueous chemocatalytic conversion of cellulose. Recently, several authors have reported the beneficial effect of state of the art pretreatments on the hydrolytic hydrogenation of various lignocellulosic feedstocks, like wheat straw, corn stalk, silver grass, Japanese cedar and Miscanthus.[30, 31, 34-37] Pretreatments which dramatically reduce the CrI, like ball milling,[38-41] or diminish the lignin content appear to enable a substantial increase in product yield. Removal of several biomass constituents like proteins, tannins, pectins, waxes, fatty acids, salts, phosphorus and sulphur seems essential to prevent the formation of by-products or to poison and contaminate the catalysts.[31, 33, 34, 42]

The reported studies addressed the influence of pretreatment on the chemocatalytic activity of homogeneous (soluble) systems or, to a lesser extent, carbon-based (heterogeneous) catalysts. Due to environmental issues and corrosiveness, academia and industry are becoming more interested in the use of stable and efficient heterogeneous catalysts for biomass processing. The carbon-based catalysts, unfortunately, suffer sometimes from leaching of the catalytic active functional groups and low catalytic activity.[43, 44] Zeolites are robust and easily recyclable catalyst, which show an increased interest for the valorization of biomass. They have been associated with an outstanding performance in a wide range of biomass refining processes.[45-47] These studies mostly focussed on processing of pure cellulose feed streams or model compounds, whereas real lignocellulose feeds or industrially pretreated pulps have been somewhat overlooked, thereby ignoring the influence of the different lignocellulose components on the catalytic action. Moreover, the interaction of the porous crystalline zeolite catalysts with solid substrates like (ligno)cellulose, is different when compared to that of homogeneous catalysts and enzymes.

Recent research already showed a remarkable catalytic performance and stability of the Ru/H-USY – HCl catalytic system in the hydrolytic hydrogenation of ultrapure cellulose substrates to such hexitols.[48, 49] A similar system was also applied for hemicellulose conversion to the corresponding hexitol and pentitols.[50, 51] The produced polyols are important platform chemicals used in, for example, the food, cosmetic and pharmaceutical industry.[52, 53] Besides, it is also used as a synthetic precursor for ascorbic acid (vitamin C) and applied as an alcoholic component in the preparation of rigid polyurethane foams.[52] Finally, there is a massive amount of work studying its selective conversion to light naphtha compounds such as hexane.[54-60]

This work investigates the role of pretreatment on the zeolite-catalyzed conversion of lignocellulosic biomass to hexitols in presence of the earlier reported ruthenium-loaded USY/HCl catalytic system.[48, 49] Therefore, selected pretreatments were applied first to pure cellulose powders, which underwent ball milling, ammonia and NaOH pretreatment, or real lignocellulosic biomass, which were treated according to the ethanol organosolv process, with and without subsequent bleaching, in order to determine the influence of d_p, CrI, DP and purity on the cellulose reactivity in the reductive splitting process to hexitols, like sorbitol, mannitol and sorbitans in presence of the Ru/H-USY zeolite and trace amounts of HCl (Scheme 1).



Scheme 1 Overview of the reductive splitting process of cellulose, producing hexitols like sorbitol, mannitol and sorbitans through subsequent pretreatment, hydrolysis, hydrogenation and dehydration steps.

2. Results and discussion

2.1 Hydrolytic hydrogenation of pure cellulose powders

Scheme 1 presents the reaction pathway for the hydrolytic hydrogenation of cellulose to hexitols using minute amounts of HCl and Ru/H-USY.[48, 49] Hydrolysis of cellulose to water-soluble cellulose oligomers occurs by assistance of the Brønsted acidity, available in the hot liquid water and foreseen by the trace amounts of HCl and the acid sites in the pore mouths and on the external surface of the zeolite. Subsequent hydrolysis to glucose and hydrogenation to sorbitol are accomplished by reaction on the strong Brønsted acid sites in the zeolite pores and the metal sites of Ru/H-USY, respectively. Isomerization of glucose or sorbitol is expected to lead to the observed formation of small amounts of mannitol. Further dehydration of sorbitol and mannitol to their anhydrides (sorbitans) occurs to some extent in the acidic aqueous conditions. From here on in the manuscript, the term 'hexitols' will include both hexitols and sorbitans.

Characteristics of the commercial and pretreated pure cellulose powders

The CrI, d_p (particle diameter) and DP (DP_V, viscosity average DP) of variously processed cellulose powders are summarized in Table 1. The commercial microcrystalline cellulose powders, viz. Avicel PH-101 and Sigmacell Cellulose Type (SCT) 20, 50 and 101, were used as received. Except for SCT 101, DP (165 units) and CrI (76 - 80% based on XRD) are very comparable, but they show a significant difference in d_p, as illustrated in the Table below. The order of d_p is as follows: SCT 101 < SCT 20 < SCT 50 < Avicel PH-101. SCT 101 contains smaller, less crystalline particles but with mucher higher DP (440 units).

In addition, pretreated samples were prepared with varying physical and structural properties. Therefore, Avicel PH-101 cellulose was ball milled and pretreated with ammonia and NaOH. Ball milling of Avicel PH-101 cellulose clearly affects all three physicochemical features (Table 1), in agreement with earlier studies.[38-41, 61] It induces, for example, a continuing downward trend of the CrI and DP_V with the milling time. On the other hand, the d_p of ball milled cellulose decreases already after short contact times to 56 μm, but remain unaltered after longer milling times. A similar observation was reported by others.[62] The constant d_p after longer milling times may be due to the formation of certain agglomerates during the milling conditions. Another possibility is that the milling forces and/or reactor configuration are insufficient to mill the powder into finer fractions.

In contrast to ball milling, ammonia pretreatment selectively reduces the CrI, while keeping the d_p and DP_V unchanged. Comparison of the FTIR spectra of untreated Avicel PH-101 and ammonia treated Avicel PH-101 (see Figure S4) reveals conservation of the chemical structure after the pretreatment, excluding oxidation or degradation of the glucose units. So, this sample is an ideal model to investigate the specific influence of the CrI, independently from other cellulose properties.

Table 1 Properties of selected pure cellulose powders.

Feedstock	Pretreatment		CrI (%)		d_p	DP_V
			XRD	NMR	(μm)	(-)
Avicel PH-101	None		79	46	68	161
	Ball milling:	0.5 h	53	19	56	149
		2 h	n.d.r.	7	56	137
		6 h	n.d.r.	5	57	116
	Ammonia		n.d.r.	5	68	162
	NaOH:	0.25 h	81	42	61	148
		2 h	79	43	62	133
SCT 20	None		76	44	29	168
SCT 50	None		80	46	97	165
SCT 101	None		48	11	16	442

SCT: Sigmacell Cellulose Type, n.d.r.: could not be determined reliably.

Treatment with NaOH causes a substantial reduction of the DP_V, while the d_p is only slightly reduced and the CrI change is negligible. As in the case of the ammonia treated Avicel PH-101, also NaOH treated Avicel samples conserve the chemical cellulose functionality (see Figure S4 for the FTIR data), and therefore NaOH treated cellulose is an ideal feedstock to investigate the impact of DP.

Cellulose conversion rate during the reductive hydrolytic processing of the selected and pretreated pure cellulose powders

The 10 cellulose powders were processed at 463 K in the presence of HCl and Ru/H-USY in hot liquid water. Figure 1 and 2 present the cellulose conversion and hexitol yield in function of reaction time, respectively. The conversion after 7 h reaction time is taken as a measure for the cellulose conversion rate (c.c.r.). The fastest conversions were obtained after 2 h (c.c.r. = 67%) and 6 h (c.c.r. = 87%) ball milling pretreatment of Avicel PH-101 cellulose, corresponding to a 3 to 4 times increase of cellulose reactivity. This observation is not surprising since the three limiting physicochemical features of cellulose, namely DP, CrI and d_p, were substantially reduced during the mechanical treatment. Ammonia pretreated Avicel PH-101 cellulose, showing a 62% c.c.r., is also very reactive corroborating the importance of low CrI on cellulose convertibility.

The impact of d_p on cellulose conversion is illustrated by comparing the conversion rate of Avicel PH-101, SCT 20 and SCT 50. The three samples have very comparable DP and CrI values, but very different crystal sizes. It is apparent that the smallest sizes are converted most rapidly. SCT 20 shows a 55% c.c.r. for 29 μm average d_p, while the conversion of Avicel cellulose (with d_p = 68 μm) is slower. The slowest conversion, corresponding to c.c.r. of 20%, is observed for SCT 50 (d_p = 97 μm). The impact of DP is reflected in the conversion of NaOH treated Avicel PH-101 cellulose. Such treatment reduces DP from 161 units for the untreated to 133 units for the NaOH pretreated cellulose. Despite the lower DP, the reactivity of cellulose only slightly increases, from 33 to 38% c.c.r.

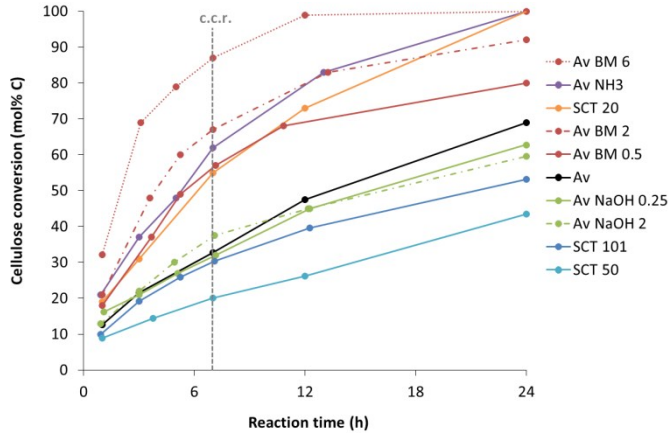


Figure 1 Conversion of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2h) and SCT 20, 50 and 101 in function of time. c.c.r.: cellulose conversion rate. Conversion of cellulose is defined as the fraction of insoluble cellulose that is converted towards soluble cello-oligomers as measured by the total amount of dissolved organic carbon (DOC).

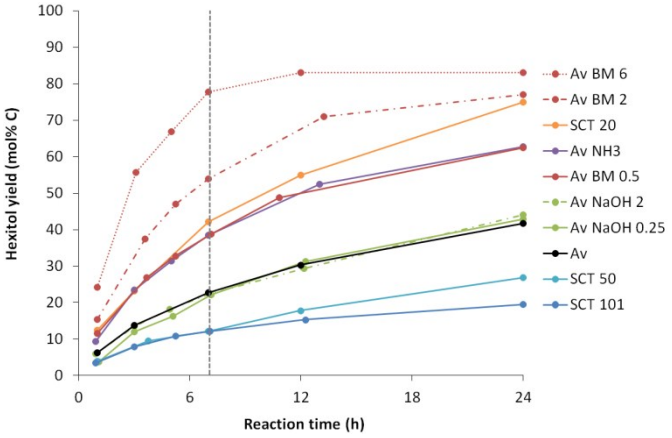


Figure 2 Hexitol yield of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2h) and SCT 20, 50 and 101 in function of time.

Since the smaller d_p of NaOH treated Avicel PH-101 (62 vs 68 µm) might have contributed in this small improvement, one might conclude that the DP is not rate-limiting during cellulose conversion. Remarkably, the conversion of SCT 101 was very slow, despite its small d_p (16 µm) and amorphous character (CrI of 11%). However, SCT 101 has a much higher DP_V (442) than the other studied substrates, which has to be at the origin of the low cellulose reactivity. The lower cellulose reactivity for substrates with high DP is a logical consequence of the solubility characteristics of cello-oligomers. There is more hydrolysis effort required to convert cellulose polymers into soluble cello-oligomers, having typical DP units between 2 to 13,[63] which are more readily converted by the heterogeneous catalyst. Previous work suggests that the soluble cello-oligomers are preferentially adsorbed in mesopores, in which they are rapidly converted to glucose.[64-68]

Hexitol yield and selectivity during the reductive hydrolytic processing of the selected and pretreated pure cellulose powders

Figure 3 presents the hexitol yield in function of cellulose conversion for the 10 selected commercial and pretreated cellulose powders. The slope of these yield-conversion curves represents a measure of the hexitol selectivity. A higher slope accounts for higher hexitol selectivity and vice versa. The linear behaviour of the slopes over the entire conversion range indicates that hexitols are steadily formed and stable under the given reaction conditions. However, at higher conversions, like in the case of 6 h ball-milled Avicel PH-101 cellulose, the slope of the curve decreases slightly. This deflection points to the occurrence of metal-catalyzed reactions of the hexitol products towards shorter polyols at high conversions.

In general, there is little difference between the hexitol selectivities of the reactions with the different cellulose substrates. A comparison of the ball-milled samples shows that the selectivity slightly increases with a decreasing d_p, leading to the highest hexitol yields with the most intensively milled cellulose. The higher selectivity with SCT 20 (75%) when compared to ammonia pretreated Avicel PH-101 cellulose (63%) emphasizes the predominant effect of d_p on selectivity, when compared to the CrI. SCT 50 shows a lower hexitol selectivity, in line with its larger d_p. Samples with equal d_p and DP, like in the case of ammonia pretreated Avicel PH-101 and Avicel PH-101, show comparable hexitol selectivities pointing to the minor influence of CrI on hexitol selectivity.

SCT 101 shows by far the lowest hexitol selectivity of the tested substrates despite its small d_p. A too high DP therefore does not only hinder fast cellulose conversion, but it also impede high hexitol selectivity. This can be rationalized by the importance of the optimal balance between the two catalytic sites, Brønsted acid sites vs. redox activity, on the zeolite catalyst to produce hexitols. When the acidity is too high, selectivity loss through thermal and acid degradation of glucose will occur,[69-73] while a too pronounced redox activity leads to selectivity loss through metal catalyzed hydrogenolysis.[69, 70, 74, 75] Though the amount and strength of the two catalytic functions impacts the optimal balance, also the nature of the substrate may influence this balance. When the hydrolysis of cello-oligomers is hindered by physicochemical parameters, in this case a high DP, glucose formation is too slow, forcing the metal catalyst to perform hydrogenolysis of the hexitol products, rather than hydrogenating glucose, leading to substantial loss in hexitol selectivity. Presence of short polyols in the product fraction of SCT 101, as ascertained by HPLC analysis, supports this hypothesis. Higher acid concentration likely will improve the hexitol selectivity.

The above results show that the cellulose characteristics largely determine the cellulose reactivity in the reductive hydrolysis process. DP is the most dominant parameter. However, its effect is only visible to a certain level.

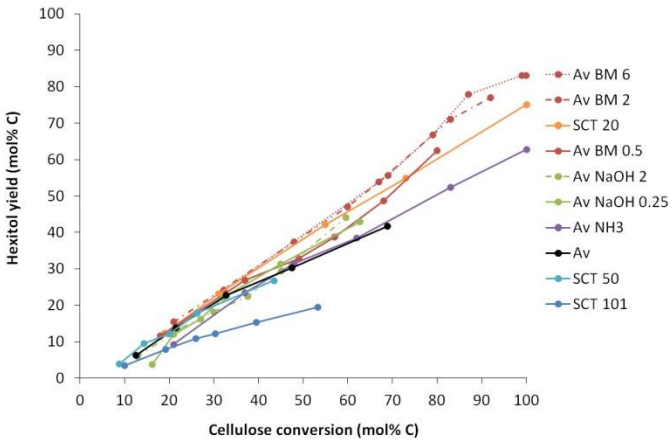


Figure 3 Hexitol yield of Avicel PH-101 cellulose (Av: unpretreated; Av BM: ball milled for 0.5 h, 2 h or 6 h; Av NH_3: ammonia pretreated; Av NaOH: NaOH pretreated for 0.25 h or 2h) and SCT 20, 50 and 101 in function of conversion.

Once the DP of a cellulose substrate is smaller than 200 units, like in the case of most of the commercial cellulose samples, the influence of the DP on the catalysis is negligible. At that moment the hydrolytic hydrogenation of cellulose is largely governed by its d_p followed by its CrI. Next to the cellulose properties, industrial relevant cellulose feeds are less pure, and therefore the impact of the cellulose purity is a challenging parameter, which is investigated in the next part.

2.2 Impact of cellulose purity on the reductive hydrolytic processing of (ligno)cellulose feedstocks

This part addresses the reductive hydrolysis of the carbohydrate fraction of three typical lignocellulosic biomass feedstocks (wheat straw, spruce and birch wood) to hexitols and pentitols (mainly xylitol and arabinitol) before and after specific ethanol-based organosolv pretreatments. The details of the different pretreatments are described in Table 2 (more details can also be found in Table S1 in the supporting information). The organosolv treatment contacts the biomass with an heated aqueous ethanol solution to disrupt the LCC, to hydrolyze hemicellulose and to extract lignin.[4, 5, 17, 76] The pretreatment ultimately fractionates the lignocellulosic biomass into two main parts: a solid, cellulose-enriched pulp fraction with improved cellulose accessibility and reactivity, and a liquid fraction containing dissolved hemicellulosic C5/C6 sugars, sugar derivatives like furfural and HMF, lignin fragments, organic acids, minerals and extractives. Lignin can then be recovered as a separate solid fraction after precipitation upon dilution with water or evaporation of the organic solvent. The extent of lignin and hemicellulose solubilization during organosolv pretreatment might be improved with the addition of a catalyst, like mineral acids, and depends, for example, on feedstock type, reaction temperature and time, catalyst type and concentration and ethanol-water ratio.[5, 7] Residual lignin in the organosolv pulps is further removed through oxidative bleaching as commonly applied in the pulp and paper industry.[77] Ethanol-based organosolv pretreatment is interesting because of the renewability and easy recyclability due to the volatility of ethanol in combination with the production of high quality cellulose pulp and lignin fractions.[4, 78-80]

As mentioned in the experimental section, after the organosolv treatment, the pulp samples were, for practical reasons, dried before catalytic conversion. Although mild temperatures were used (50 °C), it cannot be excluded that such mild drying steps influences the reactivity of the pulps as already described in literature for the enzymatic digestibility of pretreated lignocellulose.[81, 82] For this study, cellulose pulps were produced using different pretreatment conditions to introduce variation in the extent of delignification and cellulose purification. In this way, the importance of the pretreatment for an efficient conversion of cellulose to hexitols can be assessed.

Characteristics of the (pretreated) lignocellulose fractions

Table 2 shows the composition of the three lignocellulosic biomass substrates (wheat, spruce and birch) before and after organosolv pretreatment. The organosolv procedures were optimized for each biomass type to get the highest solid cellulose mass possible. Except for birch wood, the pretreated samples underwent an additional bleaching step to further remove residual lignin. The eight samples were thoroughly characterized for their C5 and C6 saccharides, lignin, extractables, ash, acetyl, uronyl and protein content and the ANC values.

In agreement with literature, wheat straw contains less lignin than the wood feedstocks, but it has much more extractables, ashes and proteins. Besides, both the C5 sugar content as well as the ANC are the highest for wheat straw. Spruce, a source of softwood, contains more lignin than birch (hardwood). In both wood types, the amount of extractables, ashes and proteins, but also the ANC levels, are generally low. The presence of acetyl and uronyl groups is the highest for birch wood.

Organosolv treatment removes lignin and hemicellulose, as apparent from the compositions, and delivers impure cellulose samples. Organosolv wheat straw still contains high levels of residual lignin (16 wt%) and ashes (3 - 4 wt%), while the C5 sugar fraction (from the hemicellulose) is seriously reduced. Organosolv wheat straw kept a relative high ANC of about 0.2 $mol.kg^{-1}$. The protein and extractives content of the wheat straw pulp was not determined, but it is known from literature that these components readily dissolve during the organosolv treatment.[6, 79, 80, 83] An additional bleaching step is required to deliver samples with lignin contents below 7 wt% (dry mass). Organosolv cellulose from spruce contains up to 20 wt% lignin with seriously reduced levels of hemicellulose and ashes. Additional bleaching led to a cellulose feedstock containing less than 2 wt% of lignin. ANC levels are low after both treatments. Organosolv cellulose from birch wood contains about 6 wt% lignin, some hemicellulose, and low contents of ashes and ANC values. The high delignification of birch during

the pretreatment (Table S1) is remarkable, which excludes the need for further bleaching. The pulp yields after all treatments for the 3 lignocellulose samples varies between 41 and 48% on dry weight (see Table S1).

Reductive hydrolytic processing of the original lignocellulosic feedstocks

The eight impure organosolv cellulose samples were processed in the standard reductive hydrolysis conditions (for 24 hours), and the catalytic results in terms of hexitol and pentitol yields are summarized in Table 2.

Notably, reaction with the original wheat straw yields a dramatically low amount of hexitols and pentitols. The most obvious explanation is found in the high ANC of wheat straw, which is up to 6 times higher than for the other feedstocks. Such neutralizing capacity, likely rooting from the high ash and protein content, demands for much higher concentrations of acids than provided in the catalytic system applied here, in order to be able to hydrolyze cellulose. It is therefore important to realize that whenever acid catalysis is involved in a cellulose processing technology, biomass feedstock with low ash and protein content, like woody feedstock, are preferred in order to keep loss of acidic catalysis capacity as low as possible.

Both wood substrates have a substantially lower ANC than wheat straw, as well as lower protein, ash and extractives content, and are therefore more suitable for the reductive hydrolysis process. Indeed, while wheat straw shows < 1% hexitol yield, higher yields were obtained with spruce (14%) and birch (21%) in the standard process conditions. Though spruce contains a large fraction of C6 sugars in the amorphous, easy hydrolysable hemicellulose fraction, evidenced by the large amount of mannan, spruce does not generate the highest hexitol yield among the crude lignocellulosic biomass feedstocks tested. Likely, the lower yield is due to the different accessibility of the carbohydrate fraction in both wood types, but also the presence of the acetyl and uronyl esters especially in birch wood, cannot be ignored. Spruce has a low ester content as a logic consequence of the type of hemicellulose, viz. glucomannan in softwoods (spruce) vs acetylated arabinoxylan in hardwoods (birch). These groups will be hydrolyzed and released in the process, forming acetic, glucuronic and galacturonic acids, which may accelerate cellulose hydrolysis. Although the fact that their stability under the given reaction conditions is unclear, the high hexitol yield from birch wood in combination with its high acetyl/uronyl content suggests indeed a positive impact of these constituents on the catalytic activity during hydrolytic hydrogenation.

The positive influence of the acidic hemicellulose constituents on the chemocatalytic conversion might look contradictory with our previously findings on the conversion of lignocellulosic feedstock into isosorbide, using highly concentrated heteropoly acids in combination with Ru on carbon.[37] That study demonstrated the importance of removing the hemicellulose fraction to afford high isosorbide yields. There, however, a very large concentration of acid was used when compared to the standard conditions in this contribution. Therefore the effect of additional formation of acids upon hydrolysis of the sugar esters would be negligible in that work.

The pentitol yields were high for both wood types, which is likely the consequence of a better accessibility of the hemicellulose in the lignocellulosic structure. Spruce processing led to 73 mol% of pentitol formation, while birch wood yielded 55 mol% pentitol fraction. Despite the somewhat lower pentitol yield with birch wood, considerably more C5 polyols are produced from birch thanks to its high C5 sugar content, which is 4 to 5 times higher than that in spruce.

Reductive hydrolytic processing of the organosolv derived celluloses

Processing of the untreated woods already showed encouraging pentitol and hexitol yields. Nevertheless, the hexitol value is considerably lower than that of highly purified cellulose powders, like Avicel PH-101 cellulose, showing values up to 42% hexitol yield. This comparison suggests a strong influence of the cellulose purity, accessibility and the intrinsic physical and structural properties of the lignocellulosic feedstock. To further investigate the aspects of purity and composition, organsolv treated samples, generally containing less hemicellulose, lignin, protein and ashes, were subjected to the same reductive hydrolysis process under the standard conditions. The results are also presented in Table 2.

The pentitol and hexitol yields from wheat straw increases from 6% and < 1%, respectively, into 53% and 16% after an organosolv pretreatment of the original wheat straw for 90 min in 50% ethanol at 483 K. Besides breaking up of the lignocellulose structure resulting in better cellulose accessibility, the higher hexitol and pentitol yields are also caused by a significant reduction of the ANC level (from 0.6 to to 0.2 mol H^+/kg DM). The lower protein and extractives content due to the organosolv procedure[6, 79, 80, 83] is likely also in favor of the metal catalyst stability, but further research is required to elucidate more details about the deactivation process of such contaminants.

Even higher hexitol yields (39%) were obtained after a more extensive wheat straw delignification, achieved through acetic acid-chlorite bleaching of a similar wheat straw pulp obtained by an acid-catalyzed ethanosolv pretreatment process. These improvement suggests a positive effect of extensive delignification of lignocellulose up to about 6 wt% residual lignin fraction. Note that the hexitol yield with this substrate is comparable to that of pure Avicel PH-101 (42%). Pentitol formation was not monitored due to the low content of C5 sugars in the bleached organsolv wheat straw.

A comparable organosolv treatment of spruce (60 min at 463 K in 60 wt% EtOH with 5 mM H_2SO_4) surprisingly did not lead to higher hexitol yields, showing a value of 14%. Likely, there is more cellulose converted due to the extra solvent treatment.

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Table 2 Composition and pretreatment conditions of the lignocellulose feedstocks (DM: dry matter, Glc: glucan, Man: mannan, Gal: galactan, Rha: rhamnan, Xyl: xylan, Ara: arabinan, Lign.: sum of acid soluble and acid insoluble lignin, Acet.: acetyl, n.d.(r.): not (be) determined (reliably), Other: undetermined dry matter. [a]sum of uronic acids, not corrected for hydrolysis factor; [b]Protein: N content * 6.25; [c]Extractives: sum of H_2O and EtOH extractives, corrected for extracted soluble inorganics; [d]determined at pH 2; [e]L/S: 11 L/kg DM in 20 L autoclave; [f]bleaching conditions: 343 K with chlorite/acetic acid; [g]defined as time at reactor temperature (excluding heating and cooling times); [h]L/S: 10 L/kg DM in 0.5 L autoclave and [i]10 L/kg DM in 20 L autoclave; [j]sugars dehydrated to furfural (C5) and 5-HMF (C6) during analytical acid hydrolysis.

	Pretreatment		Composition (wt% DM)															ANC (mol H^+/kg DM)[d]	Yield (mol% C)	
			Polysaccharides						Lign.	Ash	Acet.	Uronic acids[a]	Prot.[b]	Extr.[c]	Dehydrat. sugars[j]		Other			
			C6				C5												Pentitol	Hexitol
	Sort	Conditions	Glc	Man	Gal	Rha	Xyl	Ara							C5	C6				
Wheat straw	None		35.4	< 0.5	1.2	0.1	19.8	2.6	17.6	3.5	1.5	1.9	4.3	10.1	0.2	2.1	0.0	0.6	**6**	**< 1**
	Ethanol organosolv[e]	90 min, 483 K[g] 50 wt% EtOH	68.9	< 1.0	< 0.3	< 0.3	7.9	< 0.3	16.1	3.4	0.1	0.3	n.d.	n.d.	0.4	0.7	2.1	0.2	**53**	**16**
	Ethanol organosolv[e] + bleaching[f]	60 min, 463 K[g] 30 mM H_2SO_4 60 wt% EtOH	73.2	< 1.0	0.3	< 0.3	3.1	< 0.3	6.2	2.8	0.3	0.4	n.d.	n.d.	0.5	0.4	12.7	n.d.r.	n.d.r.	**39**
Spruce	None		45.2	10.9	1.3	< 0.3	4.4	0.7	27.7	0.3	1.3	1.0	1.2	1.3	0.3	0.5	3.8	< 0.1	**73**	**14**
	Ethanol organosolv[h]	60 min, 463 K[g] 5 mM H_2SO_4 60 wt% EtOH	72.8	1.0	< 0.3	< 0.3	1.2	< 0.3	19.8	0.2	0.1	0.6	n.d.	n.d.	0.5	0.2	3.6	n.d.r.	n.d.r.	**14**
	Ethanol organosolv[h] + bleaching[f]	See above	88.7	0.8	<0.3	< 0.3	1.2	< 0.3	1.6	0.1	< 0.1	0.4	n.d.	n.d.	0.6	0.2	6.6	n.d.r.	n.d.r.	**25**
Birch wood	None		37.3	1.4	0.6	0.3	20.0	0.2	22.3	0.2	4.5	3.0	1.0	3.6	0.3	2.0	3.3	0.1	**53**	**21**
	Ethanol organosolv[i]	30 min 473 K[g] 5 mM H_2SO_4 50 wt% EtOH	84.0	< 1.0	< 0.2	< 0.2	2.9	< 0.2	6.5	0.2	0.5	0.6	n.d.	n.d.	0.5	0.4	4.4	n.d.r.	n.d.r.	**34**

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However, the overall hexitol yield value stagnates because of the removal of the more easily convertible C6 sugar-rich hemicellulose (mannan content), also a substantial source of hexitols, during the ethanol pretreatment. The pentitol yield was not recorded because of the very low C5 sugar content in the treated spruce.

Interestingly, almost a doubling of the hexitol yield, up to 25 wt%, was observed with the bleached spruce. As with the wheat straw, low lignin contents seems very important to reach high hexitol yields from lignocellulosic feedstocks. Yet, since this value remains substantially lower than that of bleached organosolv wheat straw, other factors like structural aspects should also play a key role.

Organosolv pretreatment of birch wood increases the hexitol yield from 21 to 34%. Though the content of acid assisting acetates and other acids is considerably reduced through the pretreatment, likely the strong delignification is the main reason for the considerable hexitol yield increase. The hexitol yield is close to that obtained by processing microcrystalline cellulose Avicell PH-101 under the same standard conditions. This promising result reaffirms that a complete pure cellulose feed is not a necessity to valorize cellulose in the reductive hydrolysis protocol, but rather a breakage of the LCC structure and removal of a large part of the lignin and other inhibiting components (like proteins and ashes), especially the ones that allows acid neutralization, are important criteria. This information is especially valuable for existing lignin-first fractionation processes,[76, 84-87] but also the recently reported lignin-first process.[88-95] The latter is carried out in a polar organic solvent at elevated temperature in the presence of a redox catalyst, and is capable of delignifying birch wood up to 90% and more, while producing a lignin oil, containing mainly monomeric phenols and short phenolic di- and oligomers, and solid carbohydrate pulp, consisting of hemicellulose and cellulose. The latter lignin-poor carbohydrate pulp is therefore ideally suited for valorization towards C5 and C6 polyols through the reductive hydrolysis process.[88]

3. Conclusions

Processing of cellulose through a reductive hydrolysis approach is a potential valorization route towards the production of a family of hexitols such as sorbitol and sorbitans. To convert cellulose efficiently to hexitols in hot liquid water in presence of the Ru/H-USY-HCl catalytic system, a low degree of polymerization (< 200 units) in the cellulose is preferred. Once the degree of polymerization is lower than 200 units, its impact fades. Then, other physical parameters like the particle size and the crystallinity dominate the cellulose reactivity. Lower crystallinity and smaller particle size greatly influence the conversion rate of cellulose, but also higher hexitol selectivity can be realized with such cellulose powders.

Next, processing of lignocellulosic feedstocks, instead of pure cellulose, generally leads to lower hexitol production yields, and therefore pretreatments such as ethanol organosolv[4, 5, 17, 76] or other reactive extraction protocols like in the lignin-first approach[88-95] to deliver a more purified carbohydrate fraction, are required. Delignification degrees of 90% seem sufficient to form a reactive carbohydrate fraction. In this respect, use of hardwood is recommended since its delignification requires less harsh and costly treatments, though pretreated wheat straw and spruce with low lignin residue contents are readily converted as well.

Next to the lignin content reduction, the acid neutralization capacity of the feedstock is also an important factor to reduce as much as possible, since it neutralizes the acidity of the reaction mixture. The use of more acid in the reductive hydrolysis process might be helpful, provided that the products remain stable under the applied reaction conditions. Accordingly, the reductive hydrolysis process preferably uses lignocellulosic feedstock which are poor in minerals and (basic) protein impurities.

4. Experimental

Zeolite USY (CBV500) was purchased from Zeolyst International. Avicel PH-101 cellulose and Sigmacell Cellulose Type 20, 50 and 101 were purchased from Sigma-Aldrich and used as received. Two batches of wheat straw from France (Champagnes-Ardennes region) were kindly supplied by CIMV. As softwood source, fresh microships obtained from spruce stem wood obtained from a pelletizing company in Germany by Nova Institut, were used. Finally, birch wood (hardwood) chips were obtained from a mill in Finland by VTT. These raw lignocellulose samples were dried in a furnace at 60 °C and if necessary, milled and sieved to a fraction of about 250-500 µm in size to obtain a uniform sample. Ethanol organosolv pulps were prepared by contacting the non-dried lignocellulose samples with an aqueous ethanol solution according to the experimental conditions listed in Table 2 of the manuscript following published procedures.[5] The pulps were dried at 50 °C *in vacuo*. The composition of the raw and organosolv pretreated lignocellulosic samples was determined using published procedures.[5, 6, 96, 97]

Avicel PH-101 cellulose was ball milled in a Retsch PM 100 planetary ball mill for 30 min, 2 h and 6 h at 500 rpm (including

10 min cool down intervals after every hour of milling). Ammonia treated Avicel PH-101 cellulose was prepared as follows: liquid ammonia was first transferred into a flask, cooled with dry ice and acetone. Avicel PH-101 cellulose was then added to the liquid ammonia and stirred for 5 minutes. Afterwards, the suspension was brought to room temperature. The ammonia was removed under a flow of nitrogen. NaOH-pretreated samples were prepared as follows: 2.5 g Avicel PH-101 cellulose was contacted with 2% NaOH at 393 K for either 15 min or 2 h. The pretreated samples were subsequently filtered and washed with an excess of distilled water.

Solid-state ^{13}C CP MAS NMR experiments (see Figure S2 for the raw data) were performed with a Bruker Avance DSX400 spectrometer (B_0 = 9.4 T). 4400 scans were accumulated with a recycle delay of 10 s, the contact time was 4 ms. Samples were packed in 4 mm zirconia rotors. The spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. The C4 peak separation method[98] was used to calculate the CrI according to NMR (see ESI for more details about the calculation method). Powder X-Ray diffraction patterns (see Figure S1 for the raw data) were recorded at room temperature on a STOE STADI P Combi diffractometer. The diffracted intensity of the CuKα radiation (λ = 0.154 nm) was measured in a 2θ range between 0° and 62.5°. CrI based on XRD was determined according to the peak height method (see ESI for more information).[99] The DP was measured by viscosimetry according to the NF G 06-037 norm. Typically, 0.125 g cellulose was dissolved in 50 ml of a 0.5 M cupriethylenediamine solution. The solution was stirred for 2 hours at room temperature. Viscosity data were determined in a UBBELOHDE thermostated capillary tube viscosimeter at 298 K. The DP was calculated according to the NF G 06-037 norm. d_p was determined by laser diffraction using a Microtrac S 3500. In a typical measurement 0.2 g of cellulose powder was loaded in a turbotrac autofeeder. The machine was first flushed with air to remove all particles from earlier measurements, after which a series of blank measurements was performed. When blank measurements were found adequate, cellulose powders were systematically sucked for 10 s towards the cell where particles were measured with a TRI-LASER multi-detection system. The raw data are shown in Figure S3. Data handling was done with Microtrac flex 11.0.0.3 software.

Ru(0.2)/H-USY catalysts were prepared according to published procedures.[48, 49] USY zeolite was ion exchanged with the required amount of aqueous 0.1 mM hexamine ruthenium(III)chloride to obtain catalysts loaded with 0.2 wt% Ru. Ru-ion exchanged materials were activated at 673 K under a flow of H_2. Ru(0.2)/H-USY catalysts were pretreated in a 0.96 mM HCl solution (0.5 g Ru(0.2)/H-USY in 50 ml solution) for 24 h under 50 bar H_2 at a stirring rate of 750 rpm prior to reaction to increase their activity and stability.[48, 49]

In a typical catalytic experiment, a 100 ml stainless steel autoclave (Parr Instruments Co.) was loaded with 1 g substrate, 0.5 g pretreated Ru(0.2)/H-USY and 50 ml of a 0.96 mM HCl solution. The reactor was flushed with N_2 to remove air, afterwards the mixture was stirred at 750 rpm and heated to 463 K. The reactor was then pressurized to 5 MPa with hydrogen. This moment was used as the start of the reaction. Samples taken during the reaction were quickly cooled in an ice bath.

After derivatization to the corresponding trimethylsilylethers,[69] reaction product samples were analyzed on a Hewlett Pacard 5890 GC equipped with a 60 m HP-1 column and a FID detector. All hexitol yields are expressed as C mol% based on the total amount of C6 sugars and are calculated as: yield (%) = [moles C in hexitols and sorbitans / total moles C in C6 sugars loaded into the reactor] x 100. All pentitol yields are expressed as C mol% based on the total amount of C5 sugars and are calculated as: yield (%) = [moles C in xylitol and arabinitol / total moles C in C5 sugars loaded into the reactor] x 100. Conversion of cellulose was determined by dissolved organic carbon (DOC) analysis of the centrifuged product mixture, using an Analytik Jena Multi N/C 2100 TOC Analyzer equipped with an IR detector.

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