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Influence of bio-based solvents on the catalytic reductive fractionation of birch wood

W. Schutyser,[a,1] S. Van den Bosch,[a,1] T. Renders,[a] T. De Boe,[a] S.-F. Koelewijn,[a] A. Dewaele,[a] T. Ennaert,[a] O. Verkinderen,[b] B. Goderis,[b] C.M. Courtin[c] and B.F. Sels*,[a]

Reductive catalytic fractionation constitutes a promising approach to separate lignocellulose into a solid carbohydrate pulp and a stable liquid lignin oil. The process is able to extract and convert most of the lignin into soluble mono-, di- and oligomers, while retaining most of the carbohydrates in the pulp. This contribution studies the impact of the solvent choice on both pulp retention and delignification efficiency. Several bio-derivable solvents with varying properties were therefore tested in the Pd/C-catalyzed reductive liquid processing of birch wood. Though a high solvent polarity favors delignification, a too polar solvent like water causes significant solubilization of carbohydrates. A new empirical descriptor, denoted as lignin-first delignification efficiency' (LFDE), is introduced as a measure of efficient wood processing into soluble lignin derivatives and solid sugar pulp. Of all tested solvents, methanol and ethylene glycol showed the highest LFDE values, and these values could be increased by increasing both reaction time and temperature. Moreover, substantial differences regarding the process characteristics and analyzed product fractions between the two different solvents were discussed extensively. Most striking is the impact of the solvent on the pulp macrostructure, with methanol yielding a pulp composed of aggregated fiber cells, whereas the ethylene glycol pulp comprises nicely separated fiber cells.

Introduction

Pretreatment or fractionation of lignocellulose is regarded as an essential first step in the biorefinery to enable an efficient use of the different lignocellulose constituents, *viz.* cellulose, hemicellulose and lignin.[1-5] Though a number of well-known fractionation processes from the paper and pulping industry are highly relevant and inspiring,[6-8] new approaches are constantly being developed within the innovative context of the future biorefinery.[1, 2, 9-13] Whereas the main focus usually lies on providing a suitable (hemi)cellulose substrate for further chemo- and biocatalytic conversion to biofuels and chemicals,[1, 12, 14-25] valorization of lignin to for instance fuels, chemicals and materials was not a primary concern until lately. However, recent techno-economic studies clearly recognize the added-value of lignin for the lignocellulosic biorefinery.[26-29]

One promising approach that allows full exploitation of lignin's potential may be the reductive fractionation of lignocellulose.[26, 30-37] This process extracts and disassembles lignin from the lignocellulose matrix *via* hydrogenolysis,

forming a close-to-theoretical maximum amount of phenolic monomers and small oligomers, through the combined action of a suitable solvent and a redox catalyst under a mild hydrogen atmosphere or under hydrogen transfer conditions. In addition, a processable solid carbohydrate pulp is retained, which can be used for the production of biofuels, chemicals or, more conventionally, paper.[26, 31, 32] In this way, the lignin and carbohydrate fraction are processed separately, which simplifies downstream separation steps. There are similarities with conventional organosolv pulping,[1, 13, 38] but due to the presence of an appropriate catalyst, condensation of reactive lignin fragments to form an unreactive lignin derivative is avoided by fast hydrogenolysis and reductive stabilization of reactive unsaturates. The advantage of the process is the efficient removal of lignin from the lignocellulose matrix and a high yield production of phenolic mono-, di- and oligomers, while retaining most of the cellulose and hemicellulose as a solid pulp. The phenolics potentially find use as polymer additives and building blocks or they can act as platform chemicals for aromatics and other chemicals.[39-51]

As recently demonstrated, the chemical structure of phenolic products is significantly affected by the choice of redox catalyst, with Ru/C and Pd/C yielding respectively propyl- and propanol-substituted lignin products.[30] Whereas the catalyst type is under research, no systematic study is carried out that investigates the impact of the solvent type in the reductive fractionation process. As it plays a crucial role in solubilizing and disassembling the lignin fraction,[52] while ideally keeping the carbohydrate fraction untouched, the

a. *Center for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium. E-mail: bert.sels@biw.kuleuven.be.*
b. *Polymer Chemistry and Materials, KU Leuven, Celestijnenlaan 200f, 3001 Heverlee, Belgium*
c. *Center for Food and Microbial Technology, KU Leuven, Kasteelpark Arenberg 22, 3001 Heverlee, Belgium.*
1 *Authors contributed equally to this work.*

choice of solvent, next to the reaction conditions and the catalyst type, is expected to substantially influence the obtained product yields, *i.e.* the amount of lignin removed (delignification), yield of phenolic mono-, and dimers, and the amount of carbohydrates retained. This contribution therefore selected several bio-derivable solvents and investigated their effect on the process outcome of the catalytic reductive fractionation of birch wood. The examined process characteristics are the degree of delignification, a qualitative and quantitative analysis of the different phenolic mono-, di- and oligomers and the hexose/pentose carbohydrate retention.

Various solvents like water,[34, 53] dioxane,[33-36] methanol,[26, 30, 32, 33, 53] ethylene glycol,[33, 53] ethanol,[33, 37] 2-propanol,[31, 33] as well as mixtures of these organic solvents with water, have been used in the reductive delignification of lignocellulose. Interestingly, the different solvent performances were ascribed to a difference in lignin solubility, hydrogen solubility or hydrogen donating capacity, if the solvent was used as hydrogen source. However, these studies focused merely on the phenolic monomer yield, while other relevant aspects like the degree of delignification, the carbohydrate retention in the pulp and the occurrence of the solid carbohydrate fraction were not reported. A recent work pointed to the important role of water to foresee efficient delignification of poplar, proceeding through catalytic hydrogen transfer with isopropanol.[31] Though water was suggested to guarantee appropriate transport of the solvent to efficiently extract lignin out of the lignocellulose matrix, it happens at the cost of carbohydrate solubilization. Therefore, it remains a challenge to process wood with both high carbohydrate retention and delignification efficiency. A proper choice of solvent is likely the determining factor.

Results and discussion

Screening of solvents

A range of solvents were tested in the reductive delignification of birch sawdust in presence of Pd/C under a hydrogen atmosphere, in an effort to combine efficient lignin disassembling with high carbohydrate retention. Next to distinct solvent properties[52, 54-57] like polarity, hydrogen bonding capacity, Lewis acidity or basicity, the choice of solvent will likely also depend on its availability in the bio-refinery. After all, an ideal future bio-refinery should be able to foresee the production of all, if not, most of its necessary chemicals as to minimize the foot print of the refinery. Therefore, water, methanol, ethanol, 2-propanol, 1-butanol, ethylene glycol, tetrahydrofuran, 1,4-dioxane and hexane were selected as solvents.

Though methanol is a derivative of natural gas, it can also be derived from synthesis gas obtained in a biomass gasification unit.[58] A second origin of renewable methanol may be through demethoxylation of the abundant lignin-derived methoxyphenols.[34, 48, 59] Hydrolysis and microbial fermentation of lignocellulose biomass may serve the delivery of ethanol,[5]

but also higher alcohols like 2-propanol or 1-butanol can be obtained this way.[60] Ethylene glycol can be produced through a multistep process starting from bio-ethanol,[61, 62] but perhaps the most sustainable route applies the direct catalytic conversion of cellulosic biomass or cellulosic sugars.[63-65] Acid-catalyzed dehydration of the bio-derived ethylene glycol further yields 1,4-dioxane.[66] Production of tetrahydrofuran may be anticipated via subsequent decarbonylation and hydrogenation of furfural,[12] but also through 1,4-cyclodehydration of fermentatively-produced 1,4-butanediol.[3] Finally, straight-chain alkanes like *n*-hexane have been recently obtained in high yields from complete hydrodeoxygenation of cellulose.[18, 19]
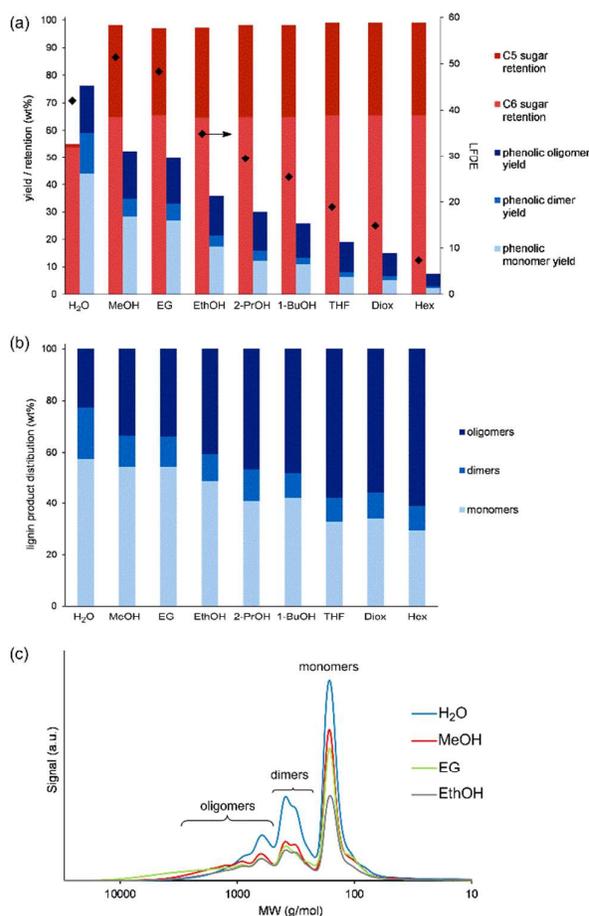
Figure 1 a) Lignin product yield (phenolic mono-, di- and oligomers), carbohydrate retention (C5 and C6 sugars), 'lignin-first delignification efficiency' (LFDE), and b) lignin product distribution after reductive fractionation of birch sawdust in various solvents. Abbreviations: water (H₂O), methanol (MeOH), ethylene glycol (EG), ethanol (EthOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), tetrahydrofuran (THF), 1,4-dioxane (Diox) and hexane (Hex). c) Molecular weight distribution of the lignin oils obtained after birch processing in water, methanol, ethylene glycol and ethanol measured by gel permeation chromatography (calibration with polystyrene standards). Reaction conditions: 2 g extracted birch sawdust (composition: 19.5 wt% Klason lignin, 41/21 wt% C6/C5 sugars), 0.2 g 5% Pd/C, 40 mL solvent, 200 °C, 3 h and 30 bar H₂ at RT.

Figure 1a shows the obtained lignin product yields and the carbohydrate retention after birch wood processing for 3 h at 200 °C in the aforementioned solvents. The total lignin product yield, being the sum of phenolic mono-, di- and oligomers,

corresponds to the weight of the lignin oil relative to the Klason lignin content and therefore represents the degree of delignification. The lignin oil, which is obtained after DCM extraction of the dried filtered liquid phase (see ESI†), can however also contain non-lignin derived compounds like extractives. To avoid overestimation of the degree of delignification due to the presence of extractives in the lignin oil, reactions were performed with extracted birch wood. Raw birch wood can however also be processed as was demonstrated in a previous study.[26] The delignification is highest in water and decreases for a range of alcohols with the number of C-atoms in the alkyl chain. Ethylene glycol reaches an equally high delignification as that in methanol. Compared to the alcohols, lignin disassembling is lower in the cyclic ethers, tetrahydrofuran and 1,4-dioxane, and is lowest in the apolar solvent *n*-hexane. The phenolic mono-, di- and oligomer yields roughly follow a similar trend.

In order to determine the solvent property that controls the delignification process, certain parameters of solvent properties[52, 53, 55-57] like polarity (E_T^N), Lewis acidity (AN) and Lewis basicity (DN) were plotted against the degree of delignification (Figures S1-S6 in the ESI†). The delignification was found to correlate well with the Reichardt parameter (E_T^N),[52, 54, 57] which is a measure for the solvent polarity (see Figure 2), but also with the acceptor number (AN),[52, 54, 56] which indicates the Lewis acidity of the solvent, and with the Kamlet-Taft α parameter,[52, 54, 55] a measure for the hydrogen-bond donating capacity of the solvent (Figures S2 and S5 in the ESI†).
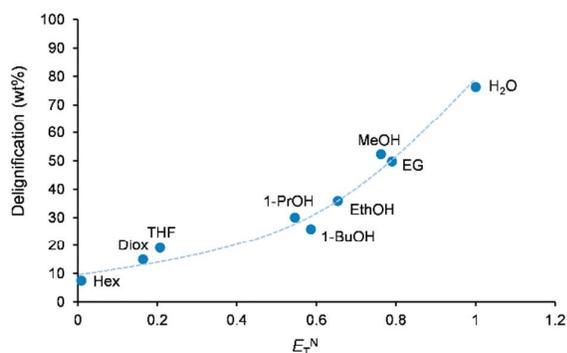
Figure 2 Birch delignification *versus* solvent polarity as described by the Reichardt parameter (E_T^N). Reaction conditions: see Figure 1.

Marcus compared the solvent parameters of more than 170 organic solvents and showed that for these solvents E_T^N, AN and α are interrelated, indicating that most polar solvents also exhibit Lewis acidity and the ability to donate hydrogen bonds.[54] From these results, we suggest that the more polar (or Lewis acidic) the solvent, the more easily it penetrates the lignocellulosic matrix and extracts/fragments the lignin. A possible explanation is that the polarity of the solvent enhances the swelling of the lignocellulose matrix and the lignin, making it more accessible. Although the exact mechanism is not clear and requires further study, a difference can already be noted between the solvent effect in the

reductive delignification process and organosolv pulping. Balogh *et al.* performed organosolv pulping of pine wood with various solvents and noted that the isolated lignin yield (which is a measure for the degree of delignification) depends on the solubility of the lignin fragments in the solvent, next to the solvent accessibility to the lignin and the efficiency of the solvent to cleave the linkages in lignin.[67] In their study, methanol and ethanol gave much lower lignin yields than 1-butanol and 1,4-dioxane, due to the lower lignin solubility. Our study indicates that the degree of delignification in the reductive fractionation process does not depend on the solvent ability to solubilize lignin, since a high delignification is obtained with solvents that exhibit a low lignin solubility (like water and methanol).[68]

Next to the degree of delignification and the product yield, the distribution of phenolic products within the lignin oil also varies for the different solvents. The relative content of phenolic mono- and dimers in the lignin oil, shown in Figure 1b, decreases in the same order as the degree of delignification, whereas the content of oligomers increases. A higher solvent polarity thus not only enhances the delignification, but also the fragmentation of the lignin oligomers to mono- and dimers.
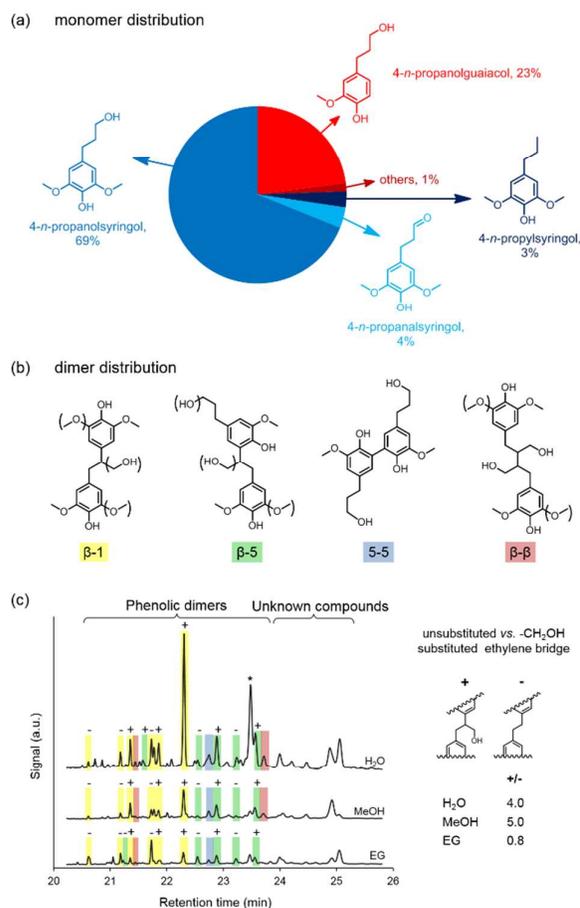
Figure 3 a) Average phenolic monomer distribution and b) structures of the phenolic dimers obtained from birch processing in the various solvents. The

abundance of the dimers decreases from left to right. c) Gas chromatograms of the trimethylsilylated dimer fraction obtained from processing in water, methanol and ethylene glycol. * indicates an unknown dimer compound with a molecular ion m/z value of 708. The mass spectra and structures of all identified dimers are provided in the ESI†. The unknown compounds eluting at retention times over 24 min likely constitute trimers. Abbreviations and reaction conditions: see Figure 1.

A comparison of product distributions in water, methanol, ethanol and ethylene glycol shows that water clearly promotes fragmentation of large phenolic oligomers favoring formation of dimers. The high dimer formation in water can also be deduced from the molecular weight distributions of the lignin oils, as presented in the GPC chromatograms in Figure 1c. Furthermore, processing in ethylene glycol yields oligomers with a higher molecular weight than processing in water, methanol, ethanol (Figure 1c) or any of the other solvents (see Figure S7 in the ESI†), although the yield of mono- and dimers in ethylene glycol is higher than in most other solvents. Lignocellulose processing in polar solvents thus shows appropriate fragmentation capacity, water, methanol and ethylene glycol giving the best results, whereas the use of less polar solvents leads to moderate fragmentation, resulting in soluble oligomers rather than phenolic mono- and dimers as the major product class.

The phenolic monomer composition is very similar in all solvents (see Table S1 and S2 in the ESI†) and the average composition is indicated in Figure 3a. In agreement with a previous study,[30] the Pd/C-catalyzed reductive processing of birch sawdust yields mainly 4-*n*-propanolsyringol and 4-*n*-propanolguaiacol, their combination constituting 92% of the monomer fraction. 4-*n*-Propanalsyringol, 4-*n*-propylsyringol, 4-ethylsyringol and 4-*n*-propylguaiacol make up the remaining part. As 4-*n*-propylsyringol and 4-*n*-propylguaiacol are the major compounds when the reaction is carried out in presence of Ru/C, the catalyst type clearly has a larger impact on the phenolic monomer selectivity than the solvent.

In contrast to the phenolic monomers, substantial differences exist in the composition of the dimer fraction obtained in the various solvents. In Figure 3b, the structures of the identified phenolic dimers in the different lignin oils are shown. The phenol units in the dimers are mainly linked by β-1 bonds, followed by β-5, and to a lesser extent by 5-5 and β-β bonds. In β-1- and β-5-linked dimers, the phenol units are connected through unsubstituted or –CH₂OH substituted ethylene bridges. Figure 3c shows the gas chromatograms of the trimethylsilylated (TMS) dimer fractions obtained in water, methanol and ethylene glycol. The assignment of each peak is provided in Figure S8 in the ESI†. Both in water and methanol, a β-1-linked dimer of syringol units with a –CH₂OH substituent is the main dimer (at a retention time of 22.3 min), while an unknown dimer with a molecular ion m/z value of 708 for the TMS derivative (at a retention time of 23.5 min, indicated with *) is much more abundant in water than in methanol and ethylene glycol. Although this compound is not identified, it is again clear from the chromatograms that water is more capable of fragmenting the lignin oligomers to low-molecular weight compounds. The dimer distribution obtained in the other alcohols (ethanol, 2-propanol and 1-butanol) is very similar to the dimer distribution obtained in methanol. A

comparison of the dimer distribution obtained in water, methanol and ethylene glycol shows that water and methanol mainly yield β-1- and β-5-linked dimers with a –CH₂OH substituted ethylene bridge, while ethylene glycol shows a higher selectivity towards the formation of the unsubstituted analogues. For instance, the ratio of –CH₂OH substituted to unsubstituted β-1- and β-5-linked dimers is around 4 to 5 in methanol and water, while this ratio is less than 1 in ethylene glycol (Figure 3 c). Reaction in ethylene glycol thus enables the partial removal of the –CH₂OH substituents, forming a dimer fraction lean in alcoholic substituents.

As already mentioned, the reductive delignification should also best be performed without loss of carbohydrates from the pulp into the solvent as to minimize downstream separation issues. Therefore, the retention of pentoses (C5 sugars) and hexoses (C6 sugars) in the pulp, which compose the hemicellulose and cellulose fractions, is monitored (see Figure 1 a). Except for water, all solvents exhibit a near complete carbohydrate retention under the applied conditions. Use of water leads to a dramatic removal of almost all pentoses and up to 20% of the hexose fraction. Both sugar types are converted to the corresponding polyols like pentitols (xylitol, etc.) and hexitols (sorbitol, mannitol, etc.), next to smaller quantities of C4 and C3 polyols. Water is thus not a suitable solvent for the reductive delignification process, if a high carbohydrate retention is required.
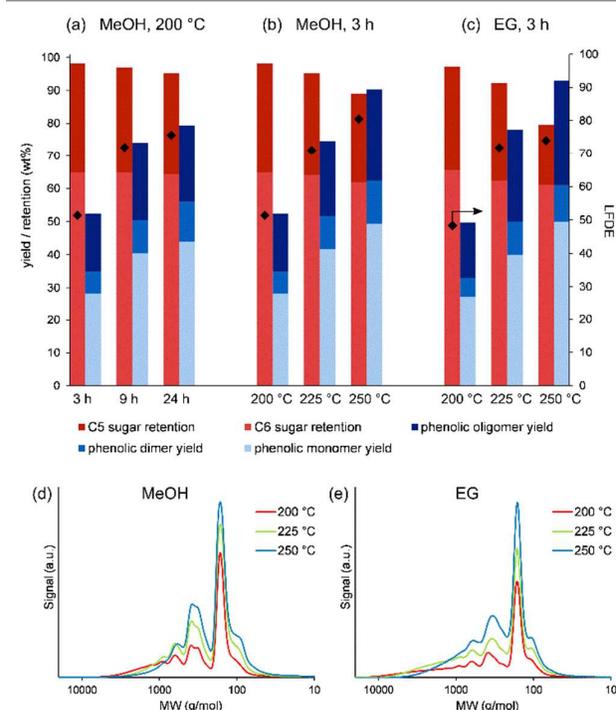
Figure 4 Lignin product yield (phenolic mono-, di- and oligomers), carbohydrate retention (C5 and C6 sugars) and LFDE for reductive fractionation of birch sawdust with Pd/C in a) methanol (MeOH) at 200 °C at various contact times, b) methanol for 3 h at various temperatures and c) ethylene glycol (EG) for 3 h at various reaction temperatures. The molecular weight distribution of the lignin products from b) and c) are indicated in respectively d) and e). Reaction conditions: see Figure 1.

Since both a high delignification and a high carbohydrate retention are pursued, a novel empirical descriptor is

introduced here, combining the two criteria to express the 'lignin-first delignification efficiency' (LFDE) of the process, *viz.* DL x CR, with DL and CR being delignification and carbohydrate retention, respectively (see Figure 1a). This LFDE value is highest for methanol and ethylene glycol, indicating that these solvents are most suited for an efficient delignification process with concomitant retention of the carbohydrates in a solid pulp. Under the applied reaction conditions, *i.e.* a contact time of 3 h and a temperature of 200 °C, methanol and ethylene glycol obtain a LFDE value of about 50%, while reactions in water are characterized by a value of 40% and even lower values were calculated for the other solvents. Therefore birch wood processing in methanol and ethylene glycol was further investigated in the following parts.

Comparison of birch processing in methanol and ethylene glycol

Although methanol and ethylene glycol reach the highest LFDE values of all tested solvents, their values are still relatively low under the applied reaction conditions. In an attempt to further improve the LFDE value, the effect of the reaction time and temperature was explored. As indicated in Figure 4a and b for reactions in methanol, the LFDE value increases with longer reaction times and higher reaction temperatures. The increase of the value is the result of a more efficient disassembling of the lignin part, without significantly compromising carbohydrate losses as soluble fractions under the applied conditions. For instance, after 24 h reaction time at 200 °C, a delignification and sugar retention of respectively 80 and 95% are obtained (*vs.* 52% and 98% after 3 h at 200°C), corresponding to a LFDE value of 76% instead of the previously described 50%. Also, 3 h reaction time at 250 °C yields a delignification and sugar retention of respectively 90% and 89%, resulting into 80% LFDE. Both process conditions thus result in an efficient removal of lignin, while keeping the carbohydrates largely solidified. Additionally, the phenolic mono- and dimer yields increase significantly with increasing contact time and temperature, reaching monomer yields of 44-49% and dimer yields of 11-13%. The lignin product distribution remains mostly the same for all reaction conditions, constituting 55% monomers, 14% dimers and 30% oligomers. The composition of the dimer fraction also remains largely unchanged for increasing contact times and temperatures, while in the monomer fraction, the content of propanalsyringol decreases and the content of propanol- and ethylsyringol slightly increases. Propanalsyringol is thus likely converted *via* hydrogenation and decarbonylation to propanol- and ethylsyringol, respectively. The monomer yield and distribution for the various contact times and temperatures is provided in Table S3 and S4 in the ESI†. Gel permeation chromatograms of the lignin products further show that the molecular weight of the oligomer fraction decreases with increasing temperature (Figure 4d) and contact time (Figure S9 in the ESI†).

Though both a higher temperature or contact time lead to similar results, the high temperature experiment enables shorter reaction times, yet faces a high operating pressure

(120 bar at 250 °C *vs.* 70 bar at 200 °C) due to the high vapor pressure of methanol. This puts serious demands to the reactor equipment. The pressure can however be lowered by performing the reaction at a lower temperature at a longer contact time or by lowering the initial hydrogen pressure. An initial H_2 pressure of 10 bar instead of 30 bar, corresponding to 95 bar at 250 °C, gives very similar results.[26]

Performing the reaction in ethylene glycol at a higher temperature also increases the LFDE value, namely from 50% at 200 °C to 74% at 250 °C (Figure 4c). Very high delignification (93%) was reached at 250°C, with a somewhat higher loss of carbohydrates compared to the same reaction in methanol. Over 40% of the C5 sugars were solubilized during this reaction, whereas the C6 sugar loss was less than 8%. High monomer and dimer yields, respectively 50 and 11%, were also obtained with ethylene glycol at 250 °C. The elevated temperature affects the monomer and oligomer composition in a similar way as during reaction in methanol, *i.e.* a decrease in propanalsyringol content, an increase in propanol- and ethylsyringol content (see Table S4 in the ESI†), and a reduced molecular weight of the oligomers (Figure 4e). The dimer fraction remains largely unchanged at increasing temperatures, with unsubstituted β-1- and β-5-linked dimers being the main compounds. Interestingly, in contrast to methanol, the operating pressure is moderate and not higher than 50 bars at 250 °C.

Table 1 Comparison between Pd/C-catalyzed reductive fractionation in methanol and ethylene glycol.

	Methanol	Ethylene glycol
Lignin-first delignification efficiency (LFDE)	high	high[a]
Operating pressure	high	low
Phenolic mono- and dimer yield	high (~ 50% monomers, 11-13% dimers)	
Structure of the lignin product	- free propanol side-chains	- free propanol side-chains
	- CH_2OH substituted inter-unit ethylene bridges	- partial loss of CH_2OH substituents on inter-unit ethylene bridges
	- low MW oligomers	- higher MW oligomers
Acetate groups	methyl acetate	ethylene glycol monoacetate
Solubilized C5 and C6 sugars	methylated sugars	2-hydroxyethylated sugars
Solvent recuperation	easy	difficult
Isolation of the lignin oil	easy	difficult
Isolation of the solubilized sugars	easy	very difficult
Pulp	aggregates of fiber cells	separated fiber cells
Solvent stability	high	high

[a] The carbohydrate retention is somewhat lower for ethylene glycol processing at high temperature, mainly due to loss of hemicellulose.

Regarding the lignin product structure, two remarkable differences can be noticed between processing in methanol or ethylene glycol. Both at 200 and 250 °C, reaction in ethylene glycol removes over half of the $-CH_2OH$ substituents on the ethylene bridges in β-1- and β-5-linked units, while these are mostly retained in methanol. Removal of the $-CH_2OH$ substituents can also be understood as a $C_β$-$C_γ$ cleavage of the linked propanol side-chains. The free propanol side-chains on the other hand are abundant in the lignin product of both solvents, as evidenced by ^{1}H and ^{13}C NMR (Figures S10 and S11 in the ESI†). Furthermore, methanol yields oligomers with a lower molecular weight than ethylene glycol (see Figure 1 c and Figure S12 in the ESI†).

Next to the operating pressure and molecular structure of the lignin products, a number of other differences exist between a process in ethylene glycol or methanol, as indicated in Table 1. For instance, in methanol, and in the other alcohols (ethanol, 2-propanol and butanol), the hemicellulose acetate groups are fully recovered as their respective alkyl acetates, which can be separated from the alcohol and valorized in other applications. In ethylene glycol, ethylene glycol

monoacetate was mainly analyzed, which can be hydrolyzed to ethylene glycol and acetic acid, or, if possible, isolated and used as such.

As described in previous works,[26, 30] the C5 and C6 sugars that are solubilized during reaction in methanol are mainly recovered as their methyl analogues, *e.g.* methyl xylopyranoside and methyl glucopyranoside. After reaction in ethylene glycol, an analogous sugar compound is detected, containing a xylopyranose entity that is coupled with EG via an ether bond at the C1 position (identification in Figures S13-14 in the ESI†). This compound, 2-hydroxyethyl xylopyranoside, constitutes the largest fraction of the solubilized sugars. The remaining solubilized C5 and C6 sugars are likely present as either methylated or 2-hydroxyethylated sugar di- and oligomers, for methanol and ethylene glycol respectively.

After reaction in methanol, the products in the liquid phase can be easily parted: methanol and methyl acetate are jointly removed by evaporation and the lignin oil can be separated from the solubilized sugars by solvent extraction using water as polar phase for the sugar fraction and a water insoluble phase like ethyl-, (iso)propyl- or t-butyl acetate[69] to extract the lignin products. After reaction in ethylene glycol, the separation of the liquid products is however more challenging: ethylene glycol and its acetate derivative have high boiling points (180-200 °C) and are thus difficult to remove by evaporation. A number of techniques can however be proposed to enable the evaporation, like spray drying, thin or wiped-film evaporation or vacuum distillation. Another possible route to separate the lignin products from the liquid phase is to perform the solvent extraction directly on the ethylene glycol phase, *e.g.* by also adding water or acidified water to increase the polarity of the polar phase. Other options might be membrane separation or liquid phase adsorption, in which the lignin products are selectively retained or adsorbed. Isolation of the soluble sugars from the ethylene glycol phase is even more challenging due to the similar chemical nature of the compounds. Therefore, evaporation is likely the most viable route.

A remarkable difference between the reaction in both solvents is the morphology of the remaining pulp. Figure 5a shows photographs of the pulps obtained at 250 °C. The dark color is due to the presence of the Pd/C catalyst. The pulp from methanol processing has a similar structure as the initial birch sawdust, while the pulp from ethylene glycol processing exhibits a more wool-like structure. Scanning electron microscopy (SEM) images (Figure 2b) clearly show that the methanol pulp is composed of particles of aggregated fiber cells, with diameters around 100-200 µm and lengths of about 1 mm, while the ethylene glycol pulp is composed of separated fiber cells with diameters of about 10-20 µm and lengths also up to 1 mm. SEM images at higher and lower magnification are provided in Figure S15 in the ESI†.
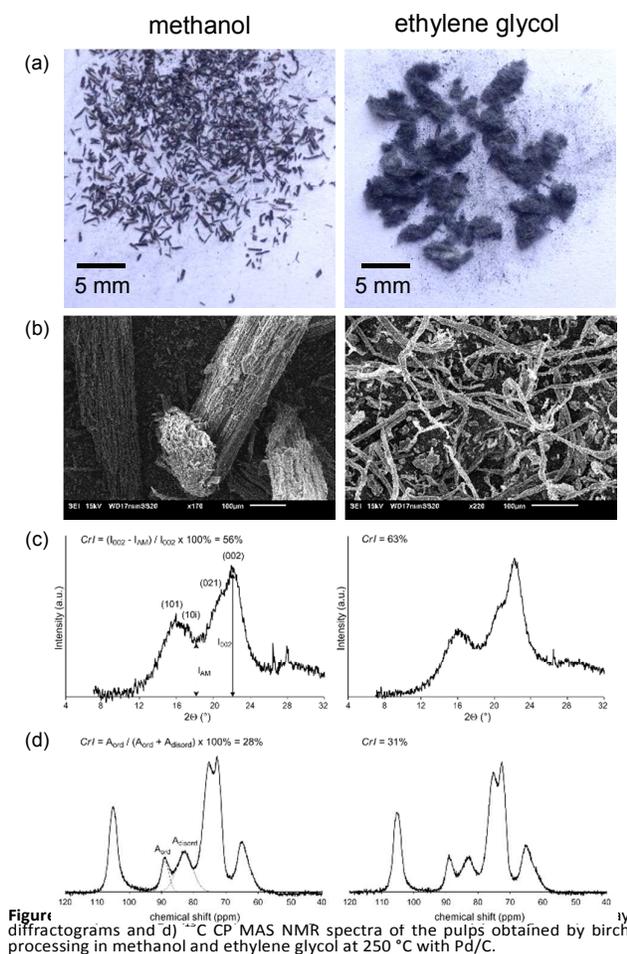
Figure diffractograms and d) ^{13}C CP MAS NMR spectra of the pulps obtained by birch processing in methanol and ethylene glycol at 250 °C with Pd/C.

Wood processing in ethylene glycol thus fragments the fiber cell aggregates into individual fiber cells, but seems not to cleave the fibers into shorter fragments. The fiber length, which determines the tensile strength of the pulp, is thus maintained. The fragmentation into individual fiber cells might explain the higher hemicellulose loss obtained by ethylene glycol processing, as lignin and hemicellulose are more easily removed from the cell wall of the separated fiber cells. Since the fragmentation increases the accessible outer surface of the fiber cells, it is expected that the ethylene glycol pulp is more prone to chemo- or biocatalytic conversion than the methanol pulp. In order to further examine the influence of methanol or ethylene glycol treatment on the cellulose fraction, the crystallinity of cellulose in the pulp was determined *via* X-ray diffraction (XRD) and solid state ^{13}C CP MAS NMR measurements (see Figure 5c and d). Both pulps were found to exhibit a very similar cellulose crystallinity, indicating that although ethylene glycol treatment liberates the individual fiber cells, it doesn't cause amorphization of the cellulose crystalline domains.

Next, the degree of polymerization (DP) of the cellulose in the pulps was determined. Therefore, the hemicellulose was largely removed from the pulp by hot water extraction in order to obtain a more pure cellulose substrate. A hot water extraction for 45 min at 200 °C resulted in a decrease of the C5 sugar content in the pulp from 20-28 wt% to 7 wt% (the composition of the pulps before and after hot water extraction is indicated in Table S5 in the ESI†). The DP was measured by viscosimetry, yielding very similar DP_v values for both pulps in the range of 350-400 (see Table S5 in the ESI†). This was more than double the value obtained for Avicel cellulose (DP_v of 160) which was measured as a reference. The DP of cellulose in the original pulp is however expected to be higher since hot water extraction is known to reduce the DP of cellulose.[70, 71] Future research efforts will also be directed to measuring the DP of cellulose in the pulp after reductive fractionation.

Another aspect to consider is the price of the solvent. The production price of bio-methanol is estimated to be 1.5 to 4 times higher than the price of methanol obtained from natural gas (200-300 Euro/ton),[58] while the price of bio-ethylene glycol, though being higher than that of methanol, could better match current petroleum derived ethylene glycol prices. Also, the production of ethylene glycol, directly from the obtained carbohydrate pulp, can be envisioned by converting it with a Pd/C-H_2WO_4–catalyst system in water under hydrogen atmosphere. In this way, the Pd/C catalyst, already present in the pulp, has a multiple function and does not have to be separated. As a proof of concept, the reaction was performed at 245 °C and yielded 26 wt% ethylene glycol based on the carbohydrate content of the pulp. The main byproducts were propylene glycol and sorbitol (respectively 4 and 3 wt%). Other products like sorbitans, glycerol and 1,2-butanediol were also obtained, yet in much lower yields (less than 1 wt%). In comparison, the same reaction with ball-milled cellulose, which exhibits low crystallinity and high reactivity towards catalytic conversion, yielded 35 wt% ethylene glycol. The ethylene glycol pulp, although containing considerable crystalline cellulose domains, is thus suited for further catalytic conversion. The complete product distribution for both reactions is indicated in Table S6 in the ESI†.

The chemical stability of the solvent should always be regarded as an important issue. Therefore, gas formation was monitored after birch wood processing. In both solvents, only minute quantities of carbonaceous gases like CH_4, C_2H_4/C_2H_6 or CO were analyzed (see Table S7 in the ESI†). In methanol, CH_4 is the only hydrocarbon in the gas phase, likely formed *via* catalytic methanation of methanol,[72] while for ethylene glycol, C_2H_4/C_2H_6 and CH_4 are present in almost equal amounts. CH_4 can originate from ethylene glycol reforming,[73, 74] producing CO, followed by its reduction to methanol and subsequent methanation, or by direct hydrogenolysis of ethylene glycol to methanol,[75] followed by methanation. The C2 hydrocarbons likely originate from hydrogenolysis/dehydration/ hydrogenation reactions of ethylene glycol, with ethanol as an intermediate. The conversion routes of ethylene glycol to C1 and C2 gases are confirmed by the presence of low amounts of methanol and ethanol in the reaction medium (see Table S6 in the ESI†). Both solvents thus show a high stability under high temperature conditions.

In the current study, dry birch sawdust (size 0.25-0.5 mm) was used as a feedstock. From an industrial point of view however, wet birch chips are a more interesting substrate since extensive milling and drying is not required. The conversion of larger birch particles was already demonstrated for the Ru/C-catalyzed reductive fractionation in methanol.[26] In order to give an indication about the processability of wet birch chips in the Pd/C-catalyzed reductive fractionation in ethylene glycol, reaction was performed with a larger fraction of dried birch sawdust (retained by a 1.5 mm sieve) and an equal amount of water to mimic a 50 wt% wet state. After 3 h reaction at 200 °C, a phenolic mono- and dimer yield of 37 and 9% respectively, a delignification of 70% and a carbohydrate retention of 94% were obtained, thus resulting in an LFDE value of 66%. This LFDE value is considerably higher than that of the same reaction with dry birch sawdust (0.25-0.5 mm) in pure ethylene glycol (50%). The higher LFDE value is suggested to be due to the presence of water (corresponding to 6 wt% of the reaction medium), which is known to be an efficient delignification agent. This indicates that wet biomass can be more easily processed than dried biomass, and additionally that aqueous organic solvent mixtures might constitute promising reaction media for the reductive fractionation process. Further research is needed to investigate the potential of these solvent mixtures.

A remaining obstacle in the reductive fractionation process is the presence of the catalyst in the pulp. As previously illustrated, the catalyst can be partially recovered by liquid-liquid extraction (about 30% recovery). The use of a magnetic catalyst[31, 33] or a microporous catalyst cage[32] to separate the substrate and catalyst are however more promising methods and are currently being investigated.

Conclusions

Reductive catalytic fractionation of lignocellulose feedstock enables the high yield production of lignin-derived phenolic mono-, di- and oligomers directly from wood. A solid carbohydrate pulp is retained that can be converted into chemicals and fuels or used as feedstock for material applications. The wood processing first encompasses lignin extraction from the lignocellulose matrix followed by catalytic disassembling of the lignin polymer and stabilization of the phenolic compounds. While recent work demonstrated the substantial impact of the catalyst type on the product selectivity,[30] here it is shown that also the choice of the solvent, amongst nine different bio-derivable solvents, highly determines the effectivity of lignin removal and pulp retention. High solvent polarity is a prerequisite to high delignification capability, but a too high polarity induces considerable loss of carbohydrate pulp due to solubilization. Since both a high delignification and pulp retention are desired, a novel empirical descriptor denoted as 'lignin-first delignification efficiency' (LFDE) was introduced to rank the solvents for their process efficiency. This LFDE factor represents the product of the degree of delignification and the carbohydrate retention and was found to be highest for methanol and ethylene glycol,

being 80 and 74% respectively, when reactions were carried out for 3 hours at 250 °C. Lignin is converted into phenolic mono- and dimers with yields of around 50 and 12% respectively, in both solvents. Interestingly, the dimeric lignin fraction in ethylene glycol contains less alcoholic hydroxyls, when compared to that produced in methanol. Other notable differences between the two solvents are the operating pressure, favoring the ethylene glycol process, and the ease of solvent recuperation in favor of the methanol process. Finally, the most striking difference was observed in the macrostructure of the resulting pulp. The methanol pulp is composed of particles of aggregated fiber cells, whereas the ethylene glycol pulp constitutes nicely separated fiber cells. Though their crystallinity is similar, ethylene glycol processed carbohydrate fibers have a higher surface accessibility, which is expected to enhance their chemical reactivity in chemo- or biocatalytic conversions, but likely also make them more suitable for material applications like paper manufacturing or functionalization to cellulose acetates.

Experimental section

Chemicals and materials

For a list of all used chemicals and materials as well as a more complete description of the experimental procedures, the reader is kindly referred to the ESI†.

Catalytic reaction

In a typical reaction, 2 g extracted birch sawdust (size 0.25-0.5 mm; *Betula pendula* from Ecobois, Ghent), 0.2 g Pd/C and 40 mL solvent were loaded into a 100 mL stainless steel batch reactor. The reactor was sealed, flushed with N_2 and pressurized with 30 bar H_2 at room temperature (RT). The mixture was stirred at 700 rpm and the temperature was increased to 200 °C (~ 10 °C.min^{-1}) and the reaction was started. After reaction, the autoclave was cooled in water and depressurized at RT.

Lignin product analysis

For the 'volatile' solvents (bp. < 125 °C; H2O, methanol, ethanol, 2-propanol, 1-butanol, tetrahydrofuran, 1,4-dioxane, hexane), the degree of delignification was determined by evaporating the raw filtered product mixture. In this way a brown oil was obtained, which was subjected to threefold liquid-liquid extractions using dichloromethane (DCM) and water to separate the soluble lignin- and sugar-derived products. The DCM-extracted phase was then dried to obtain a 'lignin oil' and its weight is used to determine the degree of delignification (based on Klason lignin weight). In the case of ethylene glycol (bp. = 197 °C), the solvent could not be evaporated with a rotary evaporator. Therefore, after filtration, 150 mL of water was added to the ethylene glycol product phase. This homogeneous H_2O:EG mixture was subjected to threefold liquid-liquid extractions with DCM. Analogous to above, the degree of delignification can be obtained from the weight of the dried lignin oil.

To analyse the lignin monomers after hydrogenolysis, a weighed amount of external standard (2-isopropylphenol) was added to the lignin oil after which the content was completely resolubilized in 10 mL methanol. A sample was used for GC analysis. To analyse the dimers, a derivatization step was performed, via trimethylsilylation with N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), to increase their volatility before GC analysis.[76-78] GC/MS was used to identify the phenolic mono- and dimers, while gel permeation chromatography (GPC), ^{1}H NMR and ^{13}C NMR were applied for qualitative analyses of the lignin oil.

Carbohydrate product analysis

The sugar retention was based on the amount of sugars in the lignocellulose substrates and in the carbohydrate pulp after reaction, using a standard total sugar procedure, adapted with hydrolysis conditions for cellulose-rich materials.[79-81] Scanning electron microscopy (SEM) was applied to illustrate the structural difference in the pulps. In addition X-ray diffraction spectroscopy (XRD) and ^{13}C CP-MAS NMR were used to indicate the degree of cellulose crystallinity in both pulps. The cellulose degree of polymerization (DP) was measured by viscosimetry according to the NF G 06-037 norm.

Acknowledgements

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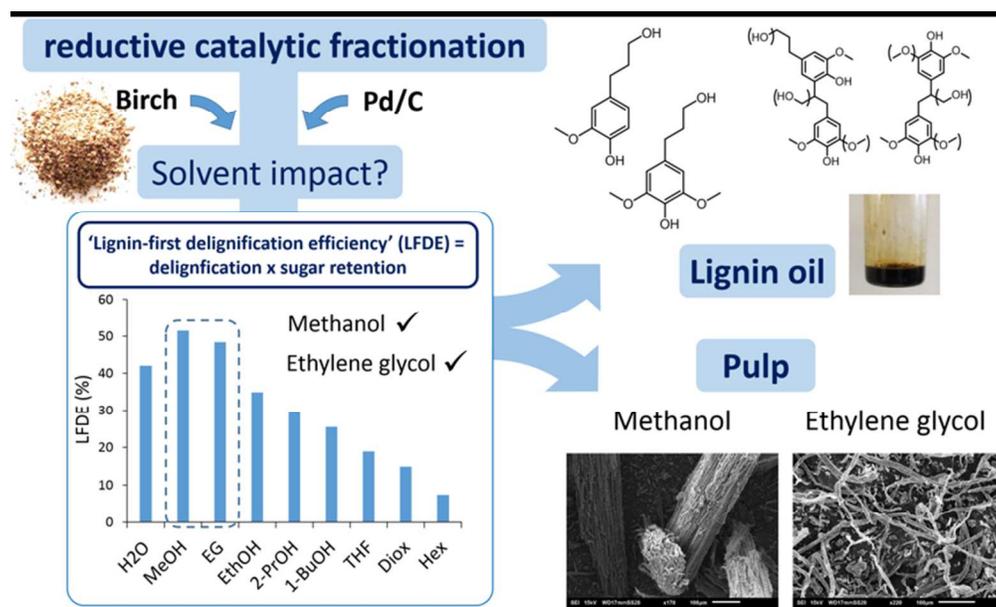
In the reductive catalytic fractionation of lignocellulose, the choice of solvent significantly impacts the delignification efficiency, carbohydrate retention in the pulp and the macrostructure of the pulp.
145x88mm (150 x 150 DPI)