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Published in:
Chemsuschem

DOI:
[10.1002/cssc.201903526](https://doi.org/10.1002/cssc.201903526)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

De Santi, A., Galkin, M. V., Lahive, C. W., Deuss, P. J., & Barta, K. (2020). Lignin-First Fractionation of Softwood Lignocellulose Using a Mild Dimethyl Carbonate and Ethylene Glycol Organosolv Process. *Chemsuschem*, 13(17), 4468-4477. <https://doi.org/10.1002/cssc.201903526>

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Lignin-First Fractionation of Softwood Lignocellulose Using a Mild Dimethyl Carbonate and Ethylene Glycol Organosolv Process

Alessandra De Santi,^[a] Maxim V. Galkin,^[a] Ciaran W. Lahive,^[b] Peter J. Deuss,^[b] and Katalin Barta^{*[a, c]}

A mild lignin-first acidolysis process (140 °C, 40 min) was developed using the benign solvent dimethyl carbonate (DMC) and ethylene glycol (EG) as a stabilization agent/solvent to produce a high yield of aromatic monophenols directly from softwood lignocellulose (pine, spruce, cedar, and Douglas fir) with a depolymerization efficiency of 77–98%. Under the optimized conditions (140 °C, 40 min, 400 wt% EG and 2 wt% H₂SO₄ to pine-wood), up to 9 wt% of the aromatic monophenol was pro-

duced, reaching a degree of delignification in pinewood of 77%. Cellulose was also preserved, as evidenced by a 85% glucose yield after enzymatic digestion. An in-depth analysis of the depolymerization oil was conducted by using GC-MS, HPLC, 2D-NMR, and size-exclusion chromatography, which provided structural insights into lignin-derived dimers and oligomers and the composition of the sugars and derived molecules. Mass balance evaluation was performed.

Introduction

The development of profitable and sustainable biorefineries relies on the optimal valorization of the three major lignocellulose constituents: cellulose, hemicellulose, and lignin.^[1] Among these, lignin valorization has proven to be a major bottleneck owing to its complex nature and recalcitrant structure, especially under classical processing conditions.^[2,3] Several elegant strategies have been reported for the depolymerization of organosolv lignins;^[2,4,5] however, the obtained monomer yields were not only dependent on the method used but also on the original lignocellulose fractionation conditions.^[4,6–8] To overcome this, recent attention has shifted to lignin-first strategies, which accomplish the depolymerization of lignin in its native form during the lignocellulose fractionation process.^[9] These novel strategies focus on the use of a heterogeneous metal catalyst and hydrogen gas.^[10–19]

Previously, we have found that stabilization of reactive intermediates during acid-catalyzed depolymerization of lignin leads to suppression of the recondensation processes and im-

proved aromatic monomer yield (Figure 1 and Figure S2 in the Supporting Information).^[20] Specifically, acidolysis was studied using various lignin model compounds and organosolv lignins with triflic acid (TfOH) or iron(III) trifluoromethanesulfonate (Fe(OTf)₃) as the catalyst, in dioxane or toluene.^[6,8,20–22] Trapping the as-formed reactive 2-(4-hydroxy-3-methoxyphenyl)-acetaldehyde and 2-(4-hydroxy-3,5-dimethoxyphenyl)acetaldehyde (G- and S-C2-aldehydes, respectively) with various diols, prominently ethylene glycol (EG), resulted in the formation of the corresponding cyclic acetals comprising either a guaiacyl (G-C2 acetal) or a syringyl (S-C2-acetal) moiety, respectively (Figure 1).

These compounds could be produced in up to 35.5% yield from various organosolv lignin sources.^[8] The yield of the obtained products was correlated, among others, with the β-O-4' moiety content of the lignins, which strongly depended on the method of isolation.^[8] Moreover, not all the employed lignin extraction methods were efficient enough, depending on the source. Starting from softwood, first organosolv lignin was extracted with limited efficiency (33% from cedar). The G-C2-acetal yield obtained in the next step was 17 wt%, meaning a total 2 wt% product yield compared with the lignin content of the raw biomass (Figure 2). Also, NMR studies showed partial condensation in the final lignins as a result of the isolation procedure.^[6–8]

Therefore, we set out to investigate the application of our previously developed method for the direct treatment of softwood lignocellulose, skipping the tedious lignin isolation step (Figure 2). Such a strategy would not differ much from a classical lignocellulose fractionation process except the reaction conditions, catalyst, and added stabilization agent (EG) should be specifically tailored to deliver the desired monophenolic G-C2-acetal instead of organosolv lignin. One related example

[a] A. De Santi, Dr. M. V. Galkin, Prof. Dr. K. Barta
Stratingh Institute for Chemistry, University of Groningen
Nijenborgh 4, Groningen (The Netherlands)
E-mail: k.barta@rug.nl

[b] Dr. C. W. Lahive, Dr. P. J. Deuss
Department of Chemical Engineering (ENTEG)
University of Groningen, Nijenborgh 4, Groningen (The Netherlands)

[c] Prof. Dr. K. Barta
Department of Chemistry, Organic and Bioorganic Chemistry
University of Graz, Heinrichstrasse 28/II, 8010 Graz (Austria)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/cssc.201903526>.

This publication is part of a Special Issue focusing on "Lignin Valorization: From Theory to Practice". Please visit the issue at <http://doi.org/10.1002/cssc.v13.17>

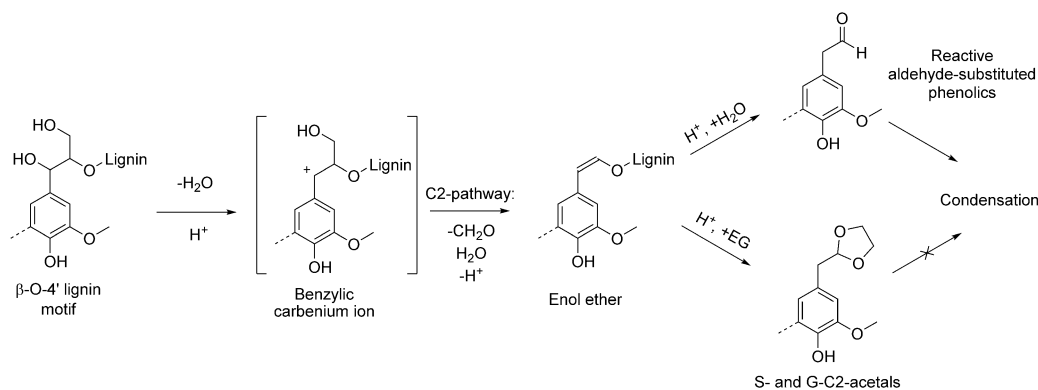


Figure 1. One of the dominant reaction pathways (C2) during acid-catalyzed depolymerization of lignin with and without ethylene glycol (EG) trapping.

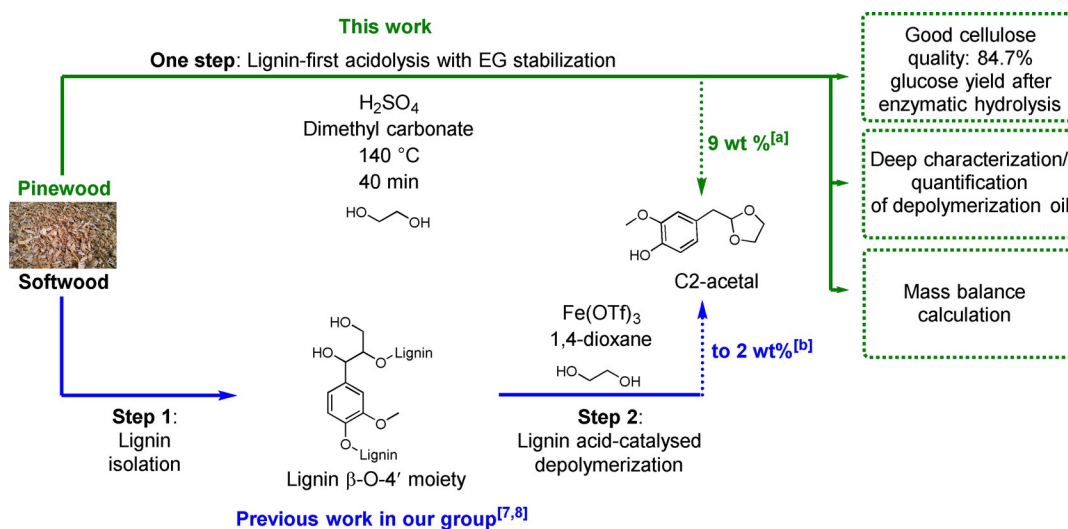


Figure 2. Lignin acidolysis in conjunction with stabilization of reactive intermediates with EG to obtain G-C2-acetal. Starting directly from lignocellulose (one-step) versus starting from the organosolv lignin (two-step) procedure. [a] Yield based on the initial lignin content; [b] yield based on the lignin extraction efficiency.

has been reported in the literature by Watanabe et al.^[23] using a mixture of toluene and methanol as solvent, whereby methanol also acted as a trapping agent and H_2SO_4 as a catalyst to produce a noncyclic C2-acetal^[24] from Japanese cedar wood with a monomer yield of approximately 5 wt% to lignin. Because of the different focus of this study in polymer chemistry, the effectiveness of the depolymerization method was not evaluated and no information regarding the quality of the cellulosic residue was provided.

Through systematic investigation of multiple reaction parameters, we found a novel system that successfully integrates lignocellulose processing and lignin depolymerization to deliver high yield of monophenolic G-C2-acetal directly from softwood lignocellulose while maintaining cellulose susceptibility to enzyme hydrolysis as evidenced from hydrolysis studies. Although the use of softwood generally leads to lower monomer yield compared with hardwood, mainly owing to lower β -O-4' linkage content, the presence of only G-units leads to exclusively one monomer (G-C2-acetal; Figure 2). We were able to

replace the previously used 1,4-dioxane and toluene to the green solvent dimethyl carbonate (DMC) and the corrosive and expensive triflic acid/triflates to sulfuric acid. The superior performance of the green solvent DMC was rationalized by the correlations between the solvent parameters and G-C2-acetal yield. An in-depth analysis of the depolymerization oil was performed to identify lignin dimers and oligomers, as well as carbohydrates or derived compounds and a good mass balance was achieved. The general applicability of the method was demonstrated with four different softwood species.

Results and Discussion

The two key factors necessary to obtain a high yield of monophenolic products from raw lignocellulose are: a) efficient delignification and b) rapid β -O-4' bond cleavage. Because both of these steps depend on multiple factors, an extensive optimization of the reaction parameters (catalyst type and amount, EG amount, solvent, reaction time, and temperature) was per-

formed to maximize the G-C2-acetal yield and at the same time maintain high cellulose quality.

C2-acetal production from pinewood: Evaluation of catalysts and solvents

First, benchmark conditions previously developed for organosolv lignin depolymerization (catalyst: Fe(OTf)₃, solvent: 1,4-dioxane) were evaluated by processing pine lignocellulose with a catalyst concentration range of 0.075–0.3 mmol (Table 1, entries 1–5), whereby 0.15 mmol was found to be the minimum requirement to obtain G-C2-acetal yield of 4.8 wt% (Table 1, entry 3). Then H₂SO₄, Bi(OTf)₃, and *p*-toluenesulfonic acid (*p*-TsOH) were screened as alternatives for Fe(OTf)₃^[25] (Table 1, entries 6–8). The use of Bi(OTf)₃ provided a similar yield of G-C2-acetal (5.0 wt% vs. 4.8 wt% for Fe(OTf)₃), whereas no G-C2-acetal was obtained with *p*-TsOH. Interestingly, sulfuric acid, as a much cheaper alternative, performed better than Fe(OTf)₃ with 5.7 wt% G-C2-acetal yield; therefore, it was chosen for further optimization.

Our next goal was to find greener alternatives for 1,4-dioxane, which is a solvent that is classified to have major known drawbacks,^[26] and at the same time maintaining a high product yield. Dimethoxyethane (monoglyme) and toluene performed similar to 1,4-dioxane (G-C2-acetal yield 6.1 wt% and 5.3 wt% respectively; Table 1, entries 9 and 10) whereas acetone gave a slightly lower yield (4.3 wt%). Very poor G-C2-acetal yield was obtained in alcohols (Table 1, entries 12, 13 and 19), as previously demonstrated for model compounds.^[20]

Previously, etherification of the β-O-4' motifs at the α-OH position was reported when alcohols were used as reaction media under similar conditions.^[6] It is likely that the resulting ethers are less reactive under these conditions.^[7] Treatment of lignin with EG under acidic conditions was previously reported by Jasiukaityte-Grojzdek et al.,^[27] who showed EG incorporation into the lignin structure in α and γ positions of the β'-O-4 linkage, even leading to cross-linking of lignin moieties. Additionally, Ono et al.^[28] studied the incorporation of EG moieties into lignin during softwood acid solvolysis to produce modified lignin, potentially applicable as an amphiphilic polymer and/or functional gels.

Carbonates have been identified as benign solvents for organic synthesis,^[29–31] and can be synthesized directly from CO₂ through sustainable pathways.^[31] Previously, these solvents have proven successful in extracting lignin from sugarcane bagasse while preserving a good cellulose quality (up to 90% glucose yield after enzymatic digestion).^[32,33] In our system, DMC and diethyl carbonate (DEC) appeared to be outstanding solvents, reaching 8.0 wt% G-C2-acetal yield (Table 1, entries 14 and 15). Ethylene carbonate (EC) was also considered as a viable option (Table 1, entry 18). However, the system was challenging because EC solidified upon cooling down, clogging the reactor. Therefore, lower-boiling-point carbonates were considered easier to work with.

Additional analysis was performed to rationalize the role of the solvent. It has been previously demonstrated that solvent properties play a key role in solubilization of biopolymers as well as the liquid-phase reaction rates of biomass-derived compounds. Therefore, we investigated the formation/yield of the G-C2-acetal and Hildebrand solubility parameter to observe the effect of the solvent solubilization properties.

Earlier studies of the solvent effects on biomass pretreatment and on solubility of lignins^[34–38] have employed the Hildebrand solubility parameter (δ -value).^[39] According to the Hildebrand solubility theory, materials with similar δ -values will be able to interact with each other, resulting in solvation, miscibility, or swelling. Solvents employed in this study and their corresponding δ -values are listed in Table S3. The δ -values for lignin can vary from 20 to 28 MPa^{0.5} depending on the origin and processing history.^[40–42] As a benchmark δ -value for the lignin in our study, we used 25.8 MPa^{0.5}, which was previously calculated for softwood organosolv lignin by Le et al.^[43] Furthermore, δ -values for mixtures of solvents with EG (Table S3) were calculated by averaging the Hildebrand values of the individual solvents by volume.^[44] Interestingly, the δ -values for all screened mixtures were lower than that of lignin and displayed no correlation with the G-C2-acetal yield, suggesting that G-C2-acetal formation was independent of the lignin release from the lignocellulose matrix, whereas several factors can effect G-C2-acetal yields.

In the study of Brønsted-acid-catalyzed reactions, the role of solvents in accelerating the reaction rates has been implicated in a number of ways. It has been shown that the appropriate choice of solvent can result in a reduced activation energy for dehydration reactions through improved stabilization of the transition state resulting from improved proton availability.^[35,45]

Table 1. Catalyst and solvent screening for G-C2-acetal production in lignin-first acidolysis with EG stabilization using pinewood.

Entry	Catalyst	Catalyst conc. [mmol]	Yield of G-C2-acetal [wt%]	Solvent
1	Fe(OTf) ₃	0.075	1.5	1,4-dioxane
2 ^[a]	Fe(OTf) ₃	0.075	1.3	1,4-dioxane
3	Fe(OTf) ₃	0.150	4.8	1,4-dioxane
4	Fe(OTf) ₃	0.210	4.3	1,4-dioxane
5	Fe(OTf) ₃	0.300	4.4	1,4-dioxane
6	Bi(OTf) ₃	0.150	5.0	1,4-dioxane
7	<i>p</i> -TsOH	0.150	0.0	1,4-dioxane
8	H ₂ SO ₄	0.150	5.7	1,4-dioxane
9	H ₂ SO ₄	0.150	6.1	dimethoxyethane
10	H ₂ SO ₄	0.150	5.3	toluene
11	H ₂ SO ₄	0.150	4.3	acetone
12	H ₂ SO ₄	0.150	1.1	<i>t</i> -amyl alcohol
13	H ₂ SO ₄	0.150	0.0	<i>n</i> -butanol
14	H ₂ SO ₄	0.150	8.0	dimethyl carbonate (DMC)
15	H ₂ SO ₄	0.150	8.0	diethyl carbonate (DEC)
16	H ₂ SO ₄	0.150	2.0	heptane
17	H ₂ SO ₄	0.150	2.8	GVL
18	H ₂ SO ₄	0.150	n.d. ^[b]	EC
19	H ₂ SO ₄	0.150	1	EG

Reaction conditions: Pine lignocellulose (1.5 g), EG (0.9 mL, 66 wt% to pine), solvent (29.1 mL), 140 °C, 30 min (excluding 10 min to reach 140 °C from room temperature); G-C2-acetal yield based on GC-FID calibration curve with octadecane as internal standard and based on lignin content of pine lignocellulose; [a] 90 min; [b] not determined.

In our case, dehydration of the α -position of the β -O-4' moiety is the first step towards the formation of the G-C2-acetal product, in which the acid-catalyzed reaction in nonaqueous solvents proportionally depends on the relative permittivity of the solvent.^[46]

The highest G-C2-acetal yields can be obtained by using solvents with a low relative permittivity ($\epsilon_r < 5$) and moderate dipole moments (μ). A volcano-shaped plot (Figure 3) of the solvent properties (relative permittivity and dipole moment) versus (vs.) G-C2-acetal yields demonstrated that both too polar and nonpolar solvents have a degenerative effect on the G-C2-acetal yield. It is likely that solvents that are too polar raise the acid strength, leading to both condensation of native lignin and/or product decomposition, whereas nonpolar solvents are ineffective at stabilizing the transition state.

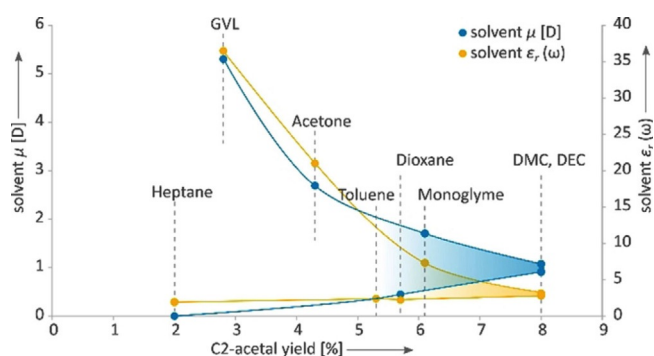


Figure 3. Dependence of the C2-acetal yield on solvent properties (dipole moment μ and relative permittivity ϵ_r). Aprotic solvents considered.

Future studies in this direction could be accelerated by quantifying the solvation effects in terms of initial and transition state contributions using experimental and computational methodologies, thereby elucidating the fundamental basis for predicting solvent effects and rational solvent design.

Optimization of reaction conditions for pine lignocellulose

Further optimization of the reaction parameters was conducted, including the EG/ H_2SO_4 ratio, time, and temperature. DMC was chosen for further optimization owing to its lower boiling point (91 °C vs. 126 °C for DEC), which potentially facilitates its recovery.

First, the EG content was varied in the range of 66 to 400 wt% with respect to pine lignocellulose using 0.15 mmol and 0.3 mmol H_2SO_4 (1 wt% and 2 wt% relative to pinewood, respectively; Figure S8). When 1 wt% H_2SO_4 was used together with 66 to 400 wt% EG, the G-C2-acetal yield drastically decreased from 8 wt% to 2.7 wt%. This can be owing to the presence of higher EG concentration and its incorporation into the α -position of β -O-4' motifs, which leads to a less effective β -O-4' cleavage.^[6] To verify this, an arylglycerol β -aryl ether lignin model compound (MC) was subjected to the same conditions (DMC, 140 °C) with 4, 8, 16, and 32 equivalents of EG (Figure S3), which led to a markedly slower cleavage reaction.

With increasing EG content from 4 to 32 equivalents, the G-C2-acetal yield decreased from 40% to 10%, whereas the EG-adduct formation was favored (Figure S4–S7). This was in line with previously observed EG incorporation at the α -position of the β -O-4' motifs of lignin.^[6,7,27,28] To promote the β -O-4' cleavage reaction in lignin, we increased the amount of catalyst to 2 wt%. At this catalyst concentration, a constant G-C2-acetal yield (9 wt%) was observed when EG was increased from 66 wt% to 400 wt% relative to pinewood. Because α -etherification is a reversible process,^[6,7] the EG-incorporated adduct becomes less stable in the presence of 2 wt% H_2SO_4 , rendering the subsequent bond scission easier. Then, the effect of EG was systematically studied in terms of G-C2-acetal yield and degree of delignification, from 66 wt% to 590 wt% EG in the presence of 2 wt% H_2SO_4 (Table S4 and Figure 4). As shown, the G-C2-acetal yield was constant (9 wt%) within the studied EG concentration range. However, when the EG concentration was increased further to 500–590 wt%, a decrease in monomer yield to 7 wt% was observed, likely owing to an inefficient cleavage reaction, as previously explained. Poor G-C2-acetal yield was found when pure EG was used as solvent (1.1%)

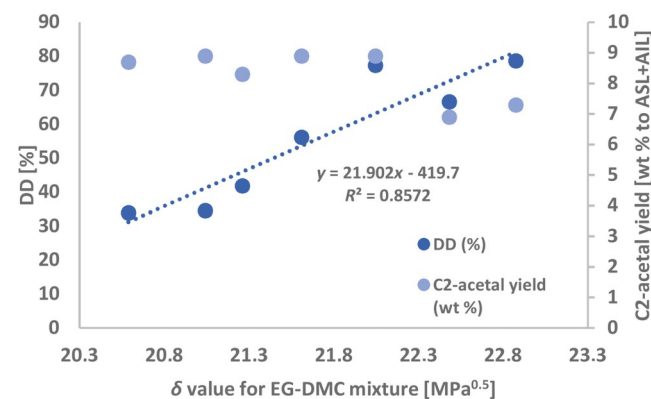


Figure 4. Degree of delignification (DD) and G-C2-acetal yield versus δ -value of solvent mixture with varying EG content of EG/DMC mixtures (Table S4). Pine lignocellulose (1.5 g), EG (0.9–8 mL, 66–590 wt% relative to pine), DMC (22–29.1 mL), H_2SO_4 (30 mg, 2 wt% relative to pinewood), 140 °C, 30 min (excluding 10 min to reach 140 °C from room temperature).

The degree of delignification (DD) increased from 34% to 77% following the increase in EG concentration from 66 to 400 wt%, and from there remained constant up to 590 wt% (Table S4 and Figure 4). The addition of EG has been previously shown to be effective for lignin removal from lignocellulose.^[47] Taking into consideration the Hildebrand solubility parameter, the δ -value of the used EG/DMC mixtures increased from 20.6 to 22.9 $\text{MPa}^{0.5}$ as the EG fraction of the reaction mixture increased from 3 to 27 vol.% (66 to 590 wt% with respect to pinewood) approaching the lignin δ -value of 25.8 $\text{MPa}^{0.5}$. Accordingly, the DD increased in line with the increase in δ -value of the mixtures (Figure 4). However, when EG was maintained in the range of 66–400 wt%, the G-C2-acetal yield was independent of the degree of delignification (Figure 4). This supports the idea that G-C2-acetal formation is independent of

lignin release from the lignocellulose matrix. β -O-4' linkages are the most labile and they are likely the first to be cleaved, releasing the desired G-C2-acetal monomer. Considering our previous findings on the effect of EG concentration, we postulate that increasing the EG content to 500 wt% and above promotes delignification but lignin is likely extracted in a more stable form (α -etherified with EG), which does not cleave in the timescale of the reaction. Therefore, 400 wt% EG concentration was considered optimal to reach a maximum *DD* and a G-C2-acetal yield close to the theoretical maximum (98%) based on derivatization followed by reductive cleavage (DFRC) theoretical monomer yield calculations (see Section S1.4 and S3). Interestingly, the G-C2-acetal yield (7.6 mol% to Klason lignin) was also comparable, but slightly lower than the total monophenol yield of 10.4–8.7 mol% (to Klason lignin content), previously obtained by the reductive catalytic fractionation (RCF) method for the same pinewood.^[17] This slightly lower yield is expected, as this particular product is the result of the cleavage of a β -O-4' moiety by the C2-pathway, whereas the minor C3 pathway would release Hibbert ketones as additional products (Figure 7).

Nonetheless, this method delivered G-C2-acetals that are generally not accessible by RCF, giving access to potentially important alternative lignin platform chemicals. Overall, the presented results were comparable with RCF methods applied to softwood (Table S6). *DD* values of 54–84% were previously reported, with aromatic monomer yields of 9–23 wt%. Because softwood contains only G-units, selectivity to a single aromatic monomer of 86–93% was reported.^[48–50]

Subsequently, the reaction time (Figure S9) and temperature (Figure S10) were investigated. Reaction times of longer than 30 min did not improve the G-C2-acetal yield. Interestingly, *DD* did not improve with time. With respect to temperature, 140 °C appeared to be the optimal temperature; 120 °C was too low to give satisfactory delignification and monomer yield (52.7% and 4.7 wt%, respectively), whereas 160 °C resulted in a lower monomer yield likely owing to decomposition of the product (6.5 wt%).

Overall, the system could be controlled by tuning the EG and H₂SO₄ content (Figure 5). The favorable properties of the DMC solvent facilitated the first dehydration step in acidolysis by stabilization of the formed carbocation intermediate, as previously discussed. Then, in the absence of EG or at a higher acid concentration, undesired condensation reactions occur, leading to a low target monomer yield. However, in the presence of EG, the G-C2 aldehyde formed upon acidolysis is stabilized in the form of its cyclic G-C2-acetal and at the optimum concentration of 400 wt% EG, the maximum *DD* was reached. Nevertheless, α -etherification occurred if the EG amount was increased or the H₂SO₄ concentration was too low, delivering a more stable lignin and lower yield of monophenols.

The optimum conditions (400 wt% EG to pinewood, 140 °C, 2 wt% H₂SO₄, 40 min) were applied to three softwood species (cedar, spruce, and Douglas fir) to expand the scope of the

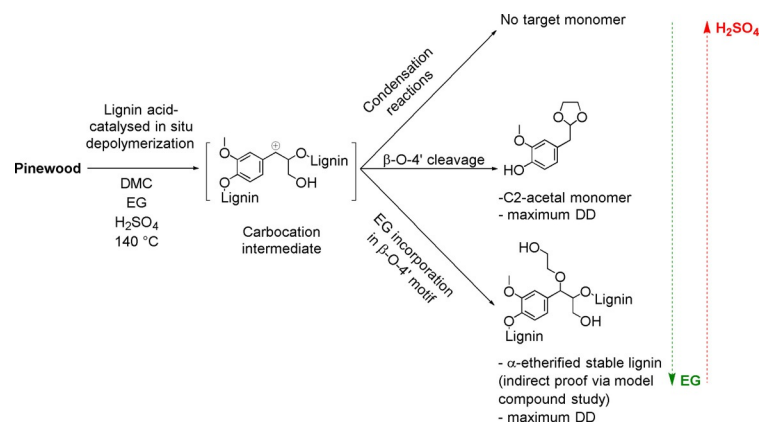


Figure 5. Tuning the system: A schematic representation of the main parameters that influence the G-C2-acetal yield and degree of delignification (EG, H₂SO₄).

method (see Section S3 for characterization data). Depolymerization efficiency (DE; see the Supporting Information, sections S1.4 and S3) was determined based on the theoretical maximum monomer yield by using the DFRC method as a benchmark^[51] (Table 2; see the Supporting Information for calculations). Spruce and Douglas fir were found to need half of the acid content to perform efficient depolymerization to G-C2-acetal (Table 2, entries 4 and 6). Importantly, the method resulted in high depolymerization efficiency (77–98%) for all tested wood species. Importantly, the obtained results were found comparable to reductive fractionation methods applied to softwood, in which a DE of 75–93% has been reported (Table S6).^[48–50]

Table 2. Testing the generality of the method by using cedar, spruce, and Douglas Fir as substrates.

Entry	Lignocellulose	G-C2-acetal yield [wt% to lignin]	DE ^[a] [%]
1	pine	8.8	98
2	cedar	7.1	92
3	spruce	4.0	42
4	spruce ^[b]	6.7	77
5	Douglas fir	3.7	44
6	Douglas fir ^[b]	6.7	80

Reaction conditions: lignocellulose (1.5 g), EG (5.4 mL, 400 wt% to pine), DMC (24.6 mL), H₂SO₄ (15–30 mg, 1–2 wt% relative to pinewood), 140 °C, time: 30 min (excluding 10 min to reach 140 °C from room temperature); G-C2-acetal yield based on GC-FID calibration curve with octadecane as an internal standard and based on lignin content of pine lignocellulose. [a] DE (depolymerization efficiency) based on DFRC analysis (see Section 1.4 and 3); [b] 1 wt% H₂SO₄ to lignocellulose.

Structural insights and identification of byproducts.

We developed a fractionation procedure to analyze the obtained depolymerization oil, as schematically represented in Figure 6. After filtration of the solid residues, the organic phase was extracted with water to separate the water-soluble carbohydrate products (aqueous phase, Fraction 2) from lignin depolymerization products (organic phase, Fraction 1). Fraction 1 was extensively characterized as follows. After evaporation of

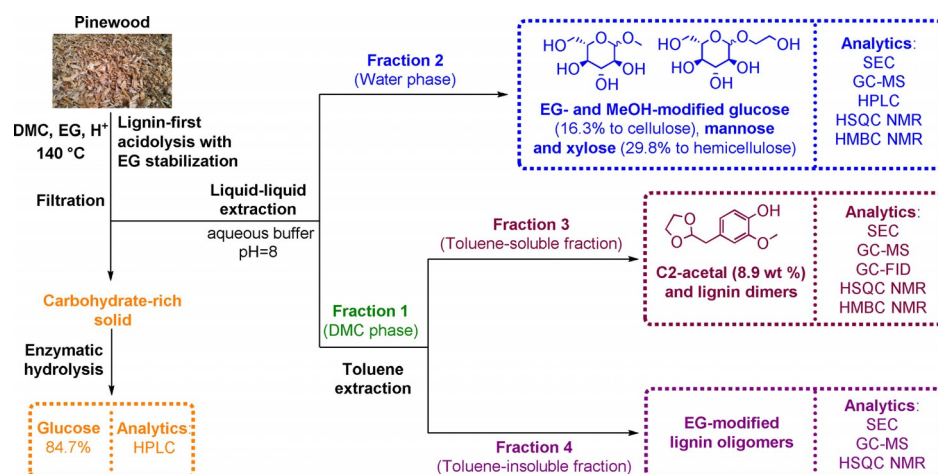


Figure 6. Fractionation of the depolymerization oil to provide structural insights. Reaction conditions: Pine lignocellulose (1.5 g), EG (5.4 mL, 400 wt % to pine), DMC (24.6 mL), H_2SO_4 (30 mg, 2 wt % to pinewood), 140 °C, 30 min (excluding 10 min to reach 140 °C from room temperature).

the solvent, Fraction 1 was subjected to GC-MS analysis (before and after derivatization by silylation), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR experiments as well as size-exclusion chromatography (SEC) analysis.

In the absence of silylation, a signal corresponding to the G-C2-acetal was the dominant signal in the GC-MS trace (Figure S11, black), together with traces of 2-methoxy-4-(3-methyl-5,6-dihydro-1,4-dioxin-2-yl)phenol^[52] (dioxene HB2; Figure 7) derived via the C3-pathway of lignin acidolysis (Figure S2 and 7). Furthermore, the formation of acetals originating from the reactions of carbohydrates with EG was observed.

Derivatization of the sample by silylation allowed the detection of additional signals in the higher temperature range of the GC-MS trace, which was attributed to higher molecular weight compounds, mainly dimers (Figure S11, pink). Here also, (C2-acetal-TMS was the main component together with 2-((trimethylsilyl)oxy)ethyl acetate (ethylene glycol monoacetate). These findings were also confirmed by 2DNMR analysis of the crude reaction mixture (Figure S12 and S13). Further fractionation of Fraction 1 was necessary to separate the possible lignin-derived oligomeric products from the monomer and dimer compounds. Therefore Fraction 1 was additionally extracted with toluene to give toluene solubles (Fraction 3) and

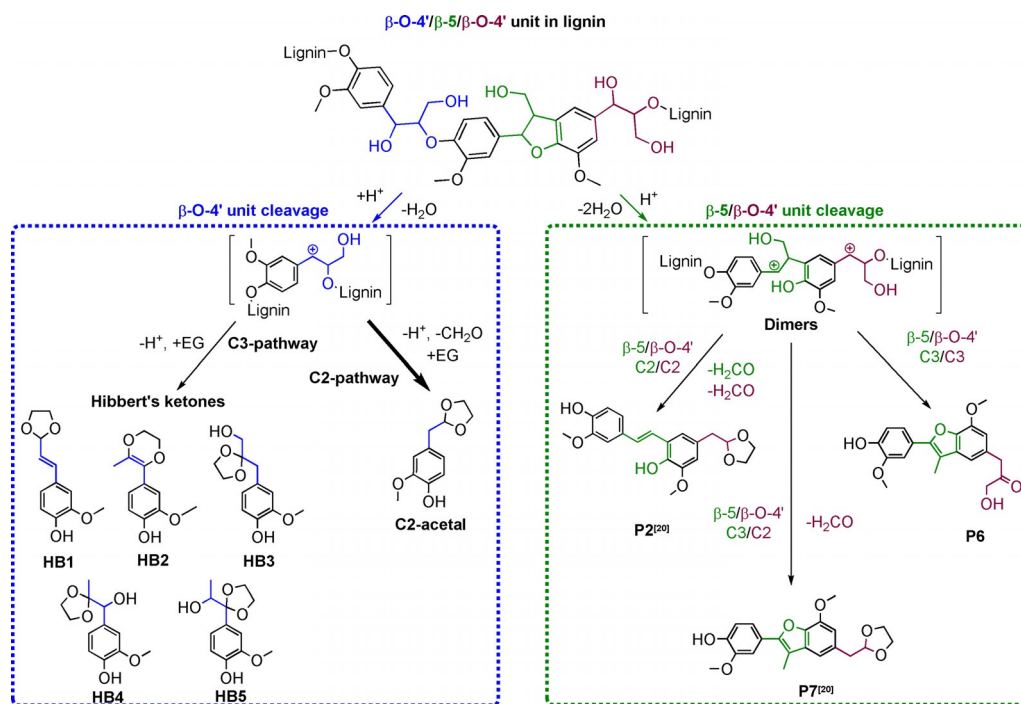


Figure 7. Proposed structures of the lignin-derived monomers and dimers based on GC-MS and 2D-NMR analysis (blue: β -O-4' moiety, C2 and C3 pathway; green/red: β -5'/ β -O-4' unit, combination of C2 and C3 pathways) in accordance with literature data.^[22]

toluene insolubles (Fraction 4) and both fractions were subjected to SEC analysis followed by HSQC and HMBC NMR studies and GC-MS analysis after silylation.

According to SEC analysis (Figure S15), Fraction 4 (Figure S15, dotted black line) mainly consisted of oligomers ($M_n = 1000 \text{ g mol}^{-1}$; $M_w = 1800 \text{ g mol}^{-1}$, $D = 1.8$). This was also confirmed by the absence of monomers in the GC-MS analysis after silylation of Fraction 4 (Figure S16). Fraction 4 accounted for 31 wt% of the initial lignin as gravimetrically determined. Interestingly, signals in the region of 4.9/105 ppm and 2.7/40 ppm, attributed to the α and β positions of the G-C2-acetal, were observed by 2D NMR (Figure S17 and S14). It is plausible that these signals were owing to lignin oligomers bearing the stabilized acetal residue on one end after cleavage of the β -O-4' linkage, whereas the other end would represent a phenolic moiety not cleavable under these conditions. In this case, the molecular weight would include the acetal functionality. This acetal group could be further functionalized during possible valorization of the oligomeric fraction. Also, signals owing to etherification of the α -position in the β -O-4' motifs were observed, indicating possible incorporation of EG.^[53]

According to the SEC analysis, Fraction 3 (Figure S15, dashed green line) primarily consisted of low molecular weight species and did not contain species with a molecular weight higher than 1000 g mol^{-1} . Indeed, when this fraction was subjected to silylation (Figure S18), the G-C2-acetal was the major product. Analysis of oligomeric fragments was performed based on GC-MS fragmentation patterns and previously reported data.^[8,22] Based on combined data from NMR and GC-MS analysis (Section S7.3), we proposed the presence of structures related to Hibbert's ketones (C3-pathway of β -O-4' cleavage; Figure 7 and Figures S19 and S20) and dimeric species (various pathways from β -O-4'/ β -5 units; Figure 7 and Figure S21), consistent with previous literature.^[8,22] Because of the presence of C_α/H_α and C_β/H_β signals, which were analogous to those of the C2-acetal (Figures S22 and S23, and Figure S14 for G-C2-acetal reference; $C_\alpha/H_\alpha = C1$, $C_\beta/H_\beta = C2$), it is reasonable to propose structures such as P2 or P7, as also reported previously by Lahive et al.^[22]

The aqueous phase (Fraction 2) was subjected to HSQC NMR, SEC, and GC-MS analysis, following derivatization through an acetylation procedure. According to SEC analysis, Fraction 2 mainly consisted of low molecular weight sugars and EG (Figure S24) and HSQC NMR indicated the presence of carbohydrates (Figure S25). Therefore, we focused on the anomeric carbon region considered as the fingerprint region for carbohydrate derivatives. Previous work has shown that during lignocellulose fractionation in butanol, the anomeric carbons in glucose and xylose display a characteristic shift comparable with native glucose and xylose.^[6,53] To understand whether modification at the anomeric carbon occurred in our system, the native hemicellulose monomers xylose and mannose (usually in a 1:3 ratio xylose to mannose in pinewood^[54]) and the cellulose monomer glucose were tested under the previously established reaction conditions (Figure 8). Indeed, a modification of the native monomers at the anomeric carbon by both EG and methanol (deriving from partial DMC decom-

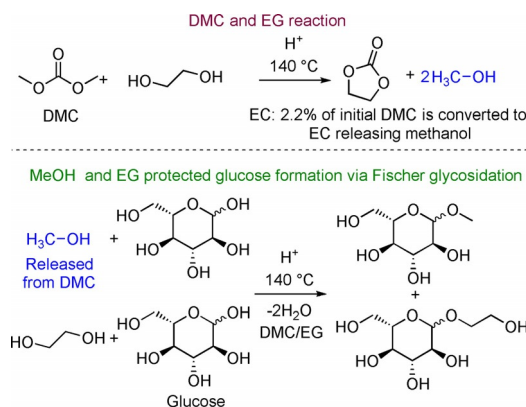


Figure 8. Compositional study of the reaction liquor: Partial transformation of DMC with EG to yield EC and methanol. Subsequent methanol and EG incorporation into glucose through the Fisher glycosidation.

position; Figure 8) was seen by combined HSQC and HMBC NMR experiments (Figure S27, S32, and S35). Furthermore, signals in the NMR spectra of Fraction 2 match with those of the model reactions of glucose, xylose, and mannose (Figure S28, S33, and S36). The presence of these modified sugars in Fraction 2 was also suggested by GC-MS analysis (Figure S37). In summary, part of the carbohydrates were hydrolyzed during the biomass treatment, resulting in xylose, mannose, and glucose modified by methanol or EG. The modification of xylose with EG during the treatment of sugarcane bagasse in a system consisting of EC/EG/ H_2SO_4 has been reported by Doherty et al.^[32]

Next, we investigated the possible reactivity of the solvent, DMC, in our system. EC was detected in the crude depolymerization mixture by 2D NMR, as previously mentioned, which indicated a partial reaction between DMC and EG, releasing methanol^[55] (Figure 8). In our system, 2.2% of the original DMC was converted to ethylene carbonate, as quantified by GC-FID measurements. EG oligomerization products were also detected, additionally contributing to solvent loss, even though their precise quantification was not possible. To further understand the role of DMC in the transformation of carbohydrates under our established conditions, a test reaction with glucose was performed (DMC, H_2SO_4 , $140 \text{ }^\circ\text{C}$, 20 min) in the absence of EG. Only native glucose was detected by NMR analysis (Figure S30). However, considering that DMC partially reacts with EG to release methanol, in our system, sugars can undergo Fisher glycosidation both with EG and methanol at the anomeric carbon (Figure 8). Quantification of the sugars in the aqueous phase (Fraction 2) by HPLC analysis indicated a combined mannose and xylose yield of 29.8% compared with the initial hemicellulose and a glucose yield of 16.3% compared with initial cellulose. Because approximately 70% of purified cellulose in softwood is crystalline,^[56] it is plausible that the sugar monomers mainly originate from the amorphous fraction of carbohydrates, which were partially dissolved and hydrolyzed during our fractionation process. As mentioned, EG was a reactive component in the system. The amount of unreacted EG present in the system (Fraction 2) was calculated by HPLC was

52.4% of the initial EG. An overview of the EG distribution in the different fractions is shown in Table S7.

Pulp analysis and enzymatic digestion

The carbohydrate-rich solid residues (Figure 6) obtained from experiments using different amount of EG at a constant G-C2-acetal yield (0, 66, 300, 400 wt% relative to pinewood) were characterized in terms of lignin, cellulose, and hemicellulose content (Table S5) and tested for enzymatic digestibility. Interestingly, EG was also found in the reaction mixture after hydrolysis with sulfuric acid, indicating its incorporation into carbohydrates.

The EG concentration was broadly constant (0.130–0.154 wt% relative to the solid residue) and independent of the amount of the EG used in the parent fractionation experiment (66 to 400 wt%); therefore, it is very likely that the saturation of the reactive groups of the carbohydrates with EG occurs. Based on the composition of Fraction 2 determined earlier, EG should also be able to react with the anomeric carbon of polysaccharides according to the Fischer glycosylation mechanism. The incorporation of EG in the solid residues contributes to EG solvent loss (Table S5 and S7).

The characterized dry residual pulps (0, 66, 300 and 400 wt% EG relative to pinewood) were used to screen the enzymatic digestibility (Figure S38), in which the residue treated with the highest EG amount (400 wt%) provided the highest glucose yield (28.8%). This result was reasonable given that it had the lowest lignin content (13.4%) because lignin is known to deactivate enzymes.^[57] However, subjecting dry pulp to enzymatic digestion faces the problem that the surface is less accessible for the enzyme. Therefore, enzymatic hydrolysis of the freshly treated feedstock using 400 wt% EG was also performed to obtain the maximum glucose yield of 84.7%, comparable with previous results reported on residual pulp from lignin extraction under similar conditions.^[6,58] owing to the incorporation of EG in the solid residue, the fresh pulp was tested for enzymatic digestion after the removal of EG by hydrolysis with aqueous sulfuric acid to obtain the “free” cellulose available (Section S1.6). No difference in the glucose yield was observed after 72 h enzymatic digestion when EG was hydrolyzed prior to the experiment. This indicated that the incorporation of EG into carbohydrates has a negligible effect on the activity of the enzymes (Figure S39).

Mass balance at optimized conditions

The mass balance was evaluated using results obtained under optimized conditions (Figure 9). Lignin was converted to a single monophenolic product (G-C2-acetal) in 9 wt% yield (Fraction 3), whereas 31 wt% of lignin was converted into lignin-derived oligomers (Fraction 4) and approximately 23 wt% of lignin remained in the solid residue. These results indicated that delignification needs to be improved to better exploit lignin. Approximately 52% of the initial hemicellulose content was preserved, of which, 30% was isolated as a water solution and 22% remained in the solid residue. Additionally,

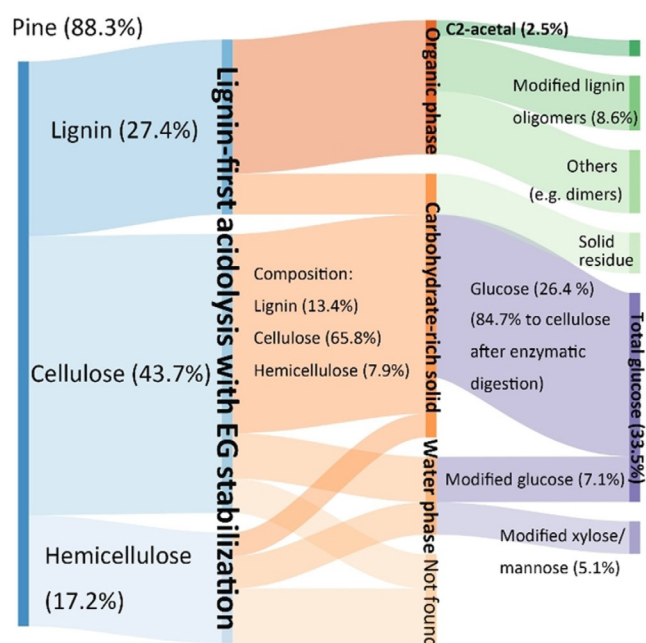


Figure 9. Product distribution, including mass balance for lignin and carbohydrates. Numbers are reported as percent relative to pinewood. Optimized reaction conditions: Pine lignocellulose (1.5 g), EG (5.4 mL, 400 wt% to pine), DMC (24.6 mL), H₂SO₄ (30 mg, 2 wt% to pinewood), 140 °C, 30 min (excluding 10 min to reach 140 °C from room temperature).

sugar derivatives in the organic phase most likely stem from hemicellulose. Cellulose also underwent partial dissolution, because the water phase contained 16% of the initial cellulose as glucose derivatives. The main portion of cellulose, approximately 72%, remained in the solid residue. The solid residue was converted to glucose in 85% yield. Overall, this signified 77% cellulose conversion. Taking into account the initial biomass composition and the yields of all the fractions, 56% of the lignocellulose was valorized.

Conclusions

A mild lignin-first depolymerization process was developed by using sulfuric acid as a catalyst and ethylene glycol as a stabilization agent in the green solvent DMC. Overall, high lignin depolymerization efficiency to G-C2-acetal was reached without the need to isolate the lignin. A high aromatic monomer yield of 77–98% (based on DFRC) was achieved. The relationship between the G-C2-acetal yield and solvent parameters indicated that solvents with low relative permittivity ($\epsilon_r < 5$) and moderate dipole moments (μ) were most beneficial.

The system was tunable depending on the EG and catalyst content. The optimum EG concentration of 400 wt% (to pine wood) resulted in the maximum delignification and G-C2-acetal yield. The structures of the aromatic dimers and the modified sugars dissolved in the liquor were identified by a detailed characterization of the depolymerization oil. A partial loss of DMC owing to its reaction with EG was detected but the effect of this on downstream processing needs to be evaluated.

In summary, a promising single aromatic compound (G-C2-acetal) and specific dimers and acetal-functionalized oligomers were obtained, which can be potentially used for the manufacture of various biobased products or in polymer chemistry. Notably, the process allows effective fractionation of softwood biomass preserving cellulose, as evidenced by a glucose yield of 84.7% after enzymatic hydrolysis. In terms of mass balance, a total glucose yield of 87.8% was reached together with 51.7% of hemicellulose and 63.8% of lignin. Softwood typically delivers a low yield of aromatic monomers, albeit with high selectivity. The use of hardwood to obtain a higher yield of S- and G-C2-acetals will be the subject of future studies.

Experimental Section

General procedure for lignin first acidolysis in conjunction with EG stabilization

In a typical experiment, a 100 mL Parr reactor (material: Alloy 20; maximum temperature: 350 °C; maximum pressure: 200 bar) with a glass insert was charged with 1.500 g lignocellulose, 0.015 g octadecane as an internal standard (0.50 mL of a stock solution in DMC 0.03 g mL⁻¹), 5.4 mL EG as stabilization agent (400 wt% to pinewood), 24.6 mL DMC as solvent and 30 mg sulfuric acid (1.6 mL of a stock solution in DMC 0.019 g mL⁻¹, 2 wt% to pinewood). After sealing the reactor, the mixture was heated to 140 °C at a heating rate of 12 °C min⁻¹ under vigorous stirring. After cooling the reaction mixture for 10 min with an ice-bath, 1 mL was filtered through Celite and used for GC-FID or GC-MS analysis. The carbohydrate-rich solid residue (pulp) was collected by filtration and washed either with only acetone (20 mL) and dried at RT (dry pulp) or acetone (20 mL) and then water (20 mL) and kept wet (fresh pulp) for enzymatic digestion.

Volatile products analysis and characterization

The liquid phase was analyzed by a Shimadzu GC-2014 equipped with a FID detector using helium as a carrier gas. Standard settings: 1 μL injection (260 °C), split ratio 50:1, helium flow 0.95 mL min⁻¹. The GC apparatus was equipped with a HP5 column (30 m × 0.25 mm × 0.25 μm). The following temperature profile was used: 5 min 60 °C isotherm followed by a 10 °C min⁻¹ ramp for 20 min to 260 °C. The detector temperature was 260 °C. The quantification of the G-C2-acetal was based on a calibration curve performed using G-C2-acetal synthesized and purified using a modified reported procedure^[59] versus an internal standard (octadecane). The calibration curve was used as follows:

$$m_{\text{G-C2-acetal}} = \left(\frac{\text{Area}_{\text{G-C2-acetal}}}{\text{Area}_{\text{Octadecane}}} \times 2.5386 \right) \times m_{\text{Octadecane}} \quad (1)$$

The G-C2-acetal yield was calculated as follows (wt% to lignin content):

$$\text{Yield}_{\text{G-C2-acetal}} = \frac{m_{\text{G-C2-acetal}}}{m_{\text{biomass}} W_{\text{lignin}} W_{\text{extractives at 105 °C}}} \times 100\% \quad (2)$$

The calculated G-C2-acetal yield includes the weight added by EG. The liquid phase was analyzed with a Shimadzu GC-MS equipped with a HP5 column (30 m × 0.25 mm × 0.25 μm) using the same method as described for GC-FID.

Pinewood fractionation procedure

To gain additional insight into the remaining components in the oil residue, a fractionation procedure was applied under optimized conditions (Figure 6). After filtering off the residual carbohydrate-rich solid, 15 mL of buffer solution K₂HPO₄/KH₂PO₄ pH 8 was added to the DMC phase (typically 30 mL) to neutralize the catalyst and extract the water soluble compounds and EG. DCM (5 mL) was added to help the separation. Two fractions were obtained: Fraction 1 consisting of the organic phase and Fraction 2—the aqueous phase. Fraction 1 was characterized by GC-MS (before and after silylation), HSQC/HMBC NMR, SEC analysis. After characterization, Fraction 1 was extracted with toluene (5 mL × 3) resulting in 2 additional fractions (Fraction 3: toluene soluble, Fraction 4: toluene insoluble) which were analyzed by the same techniques. Fraction 2 was characterized by HSQC/HMBC NMR and GC-MS analysis after acetylation. To quantify carbohydrates, Fraction 2 (aqueous phase) was subjected to hydrolysis to release native glucose, xylose, and mannose (5 wt% aqueous H₂SO₄, 120 °C, 1 h).

Acknowledgements

K.B. is grateful for financial support from the European Research Council, ERC Starting Grant 2015 (CatASus) 638076. This work is part of the research program Talent Scheme (Vidi) with Project Number 723.015.005 (KB), which is partly financed by The Netherlands Organisation for Scientific Research (NWO). The work performed by P.J.D. and C.W.L. has partly been conducted within the framework of the Dutch TKI-BBEI project "CALIBRA", reference TEBE117014.

Conflict of interest

The authors declare no conflict of interest.

Keywords: acidolysis • biomass valorization • depolymerization • dimethyl carbonate • lignin

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Manuscript received: December 23, 2019

Accepted manuscript online: February 26, 2020

Version of record online: March 31, 2020