




Cellulosic glycols: an integrated process concept for lignocellulose pretreatment and hydrogenolysis

Thimo D. J. te Molder, Sascha R. A. Kersten , Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands

Jean-Paul Lange , Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands; Shell Global Solutions International B.V., Shell Technology Centre Amsterdam, Amsterdam, The Netherlands

M. Pilar Ruiz , Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands

Received March 08 2021; Revised June 23 2021; Accepted June 28 2021;

View online at Wiley Online Library (wileyonlinelibrary.com);

DOI: 10.1002/bbb.2269; *Biofuels, Bioprod. Bioref.* (2021)



Abstract: Lignocellulose is the most abundant source of saccharides and it is therefore a promising feedstock for glycols, such as ethylene-glycol, via catalytic hydrogenolysis of the polysaccharides that it contains. However, this catalytic hydrogenolysis step is hampered by the presence of lignin and other biomass contaminants, such as ash, which need to be removed in a pretreatment step. We propose an organosolv-like pre-treatment that can delignify and de-ash lignocellulose to a level that allows it to be upgraded to glycol with comparable yields to pure cellulose under demanding hydrogenolysis conditions. This work identifies the main design constraints of the integrated process and provides an initial experimental validation of it. Pretreatment of biomass in water/ethanol/acetic acid solutions at 180–200 °C can reduce the lignin content of the solid residue to ≤ 6 wt%. The addition of an organic acid, such as acetic acid, appears important to improve the removal of the recalcitrant Ca^{2+} , which is a known inhibitor of the tungstate catalyst typically used in this process. The pretreatment medium is designed to use the by-product(s) of the process as organic solvent, to reduce the need for fresh solvent input. However, the process still needs a high solvent recovery (between 93.5 and 99.9 wt%). This can be achieved by selecting volatile component as organic solvent, as it allows recovery by evaporation from the dissolved lignin and ashes. © 2021 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

Supporting information may be found in the online version of this article.

Key words: ethylene glycol; hydrogenolysis; lignocellulosic biomass; pretreatment; solvent recovery; organosolv

Introduction

Ethylene glycol (EG) is a bulk chemical with an annual production of 20 million tons by 2010,¹ which is traditionally produced via the partial oxidation of ethylene to ethylene oxide, followed by thermal hydrolysis to ethylene glycol.² In an alternative and more sustainable route, it can also be selectively produced from (poly)-saccharides, such as cellulose, with a high atom-economy via bi-catalytic hydrogenolysis.³ The hydrogenolysis requires two catalysts, typically a homogenous tungstate for the retro-aldol condensation of glucose to glycolaldehyde, and a heterogeneous metal catalyst for hydrogenation of the glycol aldehyde (e.g. Raney nickel). The present case further requires the cellulose to be depolymerized to glucose in acidic conditions, e.g. hot compressed water (245 °C).⁴

Most studies within this field used pure microcrystalline cellulose as model feedstock and demonstrated the viability of the process to produce EG under diluted feed concentrations. However, direct hydrogenolysis of untreated lignocellulose appeared indeed problematic,^{5–8} in particular when feed concentrations^{6,9} were raised from 1 wt% to more practical though still modest levels of 5–10 wt%. For example, Fabičovicová *et al.*⁹ reported an EG yield of only 2 C% for untreated barley straw, whereas they achieved an EG yield of 36 C% for pretreated barley straw.

The origin of these low yields is probably related to the presence of catalyst poisons within the biomass. In this context, we have previously reported that lignin deactivates the hydrogenation catalyst.⁸ The hydrogenation catalyst is highly sensitive to components that interfere with its surface (*viz.* physisorption and chemisorption). Lignin, which is after holocellulose the major biomass constituent, is poorly soluble in water, *i.e.* the hydrogenolysis solvent, and, therefore, likely to foul the hydrogenation catalyst. Unfortunately, no quantitative relationship between these poisons and the catalyst stability is available. However, in our previous work⁸ we did not observe a decrease in hydrogenation activity for feeds with a lignin content lower than 5 wt%. Lignin content of the solid residue should therefore be kept below 5 wt%.

Besides lignin, inorganic compounds, *i.e.* ash, that are present in biomass¹⁰ are preferably removed during pretreatment as well. The alkaline ash neutralizes the acids needed to run the catalytic hydrogenolysis at its optimal, mildly acidic condition (pH 3–5).¹¹ More importantly, it is also known that the homogenous tungstate catalyst is prone to deactivation by divalent cations, *e.g.* calcium and magnesium, through the formation of insoluble tungstate mixed oxides.^{11,12} Indeed, Pang *et al.*¹¹ showed that the EG yield plummeted for cellulose hydrogenolysis ($Y_{EG} = 60$

C%) under the addition of divalent chloride salts of calcium ($Y_{EG} = 23$ C%), magnesium ($Y_{EG} = 46$ C%) and indeed observed CaWO_4 in the spent catalyst. A test with CaWO_4 as retro-aldol catalyst showed that it was not catalytically active as the EG yield (11 C%) was not significantly higher than what was previously reported for cellulose conversion without tungsten species.¹³

Based on these observations, it is clear that pretreatment is a prerequisite, in particular when considering that a low-catalyst consumption of <1 kg/tonne product is key for the process viability.¹⁴ Such pretreatment requirements mainly deviate from those of traditional pretreatment processes on three key points:

- 1) The aim of pretreatment is to remove selectively potential catalyst poisons present in biomass, in particular lignin and ash, rather than increasing the accessibility or liberating the fibers, which are typical aims for pulp and papermaking¹⁵ and for microbial upgrading¹⁶ of cellulose to fuels and chemicals.
- 2) Furthermore, the addition of inorganic acids and/or additives, such as HCl and H_2SO_4 , to the solvent mixture, which is a popular practice in existing literature, should be averted as these inorganics generally inhibit metal-based catalysts.
- 3) The by-products (*e.g.* light alcohols) that are formed during the hydrogenolysis step (*e.g.* excessive hydrogenation of EG yields ethanol) can be recycled to the pretreatment reactor to serve as a make-up for organic solvent losses.

In this context, the main goal of this study is to develop an integrated process of biomass pretreatment followed by catalytic hydrogenolysis of the saccharide-rich residual solid. We first derived the design criteria for the pretreatment based on heuristics, calculations, and knowledge obtained from the literature. The pretreatment step was explored experimentally and the solid residue was characterized and subjected to catalytic hydrogenolysis. We also experimentally estimated the net size of the solvent make-up stream by identifying and quantifying consumption and production pathways of light alcohols and organic acids. These experimental outcomes were input for calculations to determine the required solvent recovery rate. We also performed preliminary calculations to estimate the viability of an evaporator operation for the solvent recovery. The purpose of this study is to provide an initial validation of the proposed process concept and to touch briefly upon all its various aspects. The lessons learned from this work may probably be applicable in other biomass valorization routes that rely on metal-based catalysts.

Experimental methods

Materials

Poplar wood was ground and sieved to obtain particle-size fractions of 1–2 mm and <53 μm . The <53 μm sieve fraction was used for hydrogenolysis and the 1–2 mm sieve fraction was used for pretreatment experiments. All chemicals were purchased from Sigma-Aldrich (USA), namely: glacial acetic acid ($\geq 99\%$), ethanol ($\geq 99\%$), Raney Ni (W.R. Grace and Co. Raney[®] 2800), sodium polytungstate ($\geq 85\%$ WO_3 basis), sodium hydroxide ($\geq 99\%$), barium carbonate ($\geq 99\%$) and microcrystalline cellulose (Avicel[®] PH-101, particle size $\sim 50 \mu\text{m}$). The poplar feed composition is displayed in Table 1.

Biomass pretreatment

The experimental procedure for biomass pretreatment is outlined schematically in Fig. 1.

In a typical pretreatment (PT) experiment, 10 g of biomass (oven dried at 105 °C) and 90 g of the desired solvent mix was charged to a 200 mL stirred autoclave. The solvent was composed of a mixture of water and/or ethanol and/or acetic acid. After a successful leak test, air was dissipated from the reactor by a three-time nitrogen flush, the autoclave was heated to the desired reaction temperature (e.g. 180–200 °C) and kept at this temperature for the desired reaction time (e.g. 1–5 h). After the desired reaction time, the reactor was cooled to room temperature by running water through the cooling jacket.

Table 1. Poplar (1–2 mm) composition on dry basis.

	Poplar
H ₂ O extractive* (wt%)	7.2 ± 0.3
EtOH extractive* (wt%)	1.8 ± 0.2
Lignin* (wt%)	21.4 ± 0.1
o-Acetylgroups* (wt%)	3.1 ± 0.1
<i>Saccharide composition</i>	
Glucan* (wt%)	38.7 ± 0.1
Mannan* (wt%)	2.6 ± 0.9
Galactan* (wt%)	0
Xylan* (wt%)	10.9 ± 0.3
Arabinan* (wt%)	0.5 ± 0.2
Total ash (wt%)	0.84 ± 0.07
Na (mg kg ⁻¹)	272 ± 25
K (mg kg ⁻¹)	1057 ± 109
Ca (mg kg ⁻¹)	173 ± 47
Mg (mg kg ⁻¹)	99 ± 25
*Previously published, ⁸ and measured in duplicate. Ash and AAEM quantification, n = 4, error = standard deviation.	

In the next step, the solid/liquid separator (S/L in Fig. 1), the reactor was opened and the slurry filtered over a 5 μm wire mesh. Additional spent solvent was recovered by compression of the wet solid residue in a pneumatic filter press under a pressure of ~ 10 bar. The solid residue was then dried under a N₂ stream at room temperature until no weight change of the solid residue was registered, see Dry in Fig. 1. The solid residue was subsequently washed with at 50/50 w/w water/ethanol mixture (Wash in Fig. 1) until the washing solvent showed no color change. The solid residue yield was calculated as the ratio of the dried solid residue after washing to the initial biomass fed – see Eqn (1):

$$Y_{SR} = \frac{m_{\text{solid residue}}}{m_{\text{biomass}}} \times 100 \quad (1)$$

Afterwards, the lignin content of the spent solvent and washing liquor were determined by precipitation with water in a 3:1 water-to-solvent ratio. Lignin, saccharide, acetyl and ash content of the solid residue were analyzed according to procedures described in the Analytical methods subsection. Retention is defined as the fraction of a component, for example lignin, which is left in the solid residue in comparison to the feed – see Eqn (2):

$$\text{Retention (wt\%)} = \frac{f_{X,\text{solid residue}} \times Y_{SR}}{f_{X,\text{Biomass}} \times 100} \times 100 \quad (2)$$

Catalytic hydrogenolysis

The experimental procedure for catalytic hydrogenolysis has been described extensively in our previous work⁸ and was optimized to be sensitive enough towards feedstock impurities that could deactivate the catalysts, and therefore, was not optimized with respect to the EG yield. Briefly, a 45 mL autoclave was loaded with 14.25 g of deionized water, 0.75 g of biomass, 0.02 g of retro-aldol catalyst (sodium polytungstate), 0.09 g of hydrogenation catalyst (Raney-Ni, dry basis) and 0.3 g of acetic acid together with NaOH to buffer the solution to pH 3.3. After a successful leak test, the reactor was pressurized with hydrogen to ~ 60 bar. The autoclave was submerged in the fluidized bed while stirring at ~ 1300 rpm and the timer was started once the reactor attained a temperature of 245 °C. After a typical reaction time of 1 h, the reaction was quenched by submerging the autoclave in a water bath. Hereafter gases were released and the liquid product collected and analyzed.

The hydrogenolysis product yields were calculated on the basis of biomass intake to the overall process, i.e. mass

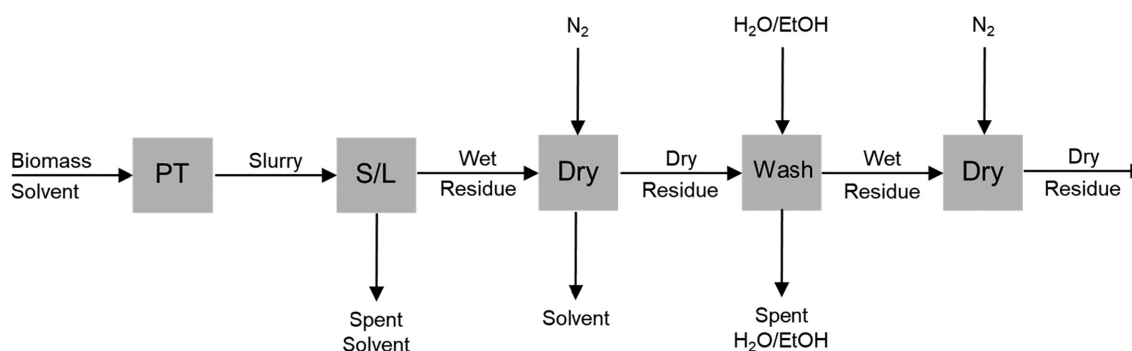


Figure 1. Schematic experimental pretreatment procedure.

of product obtained in the hydrogenolysis step divided by biomass fed to the pretreatment step – see Eqn (3):

$$Yield (wt\%) = \frac{m_{Product}}{m_{Feed}} \times 100 \quad (3)$$

Analytical methods

Biomass characterization

Saccharide, lignin, acetyl, and ethyl groups of the solid residues were quantified in duplicate according to a two-step sulfuric acid-based hydrolysis protocol.¹⁷ The solid residue ash content was determined by oxidation at 575 °C for 24 h¹⁸ and alkali and alkaline earth metal (AAEM) content by dissolution of ash in 0.01 mol L⁻¹ nitric acid followed by ion chromatography (IC). Ion chromatography was performed on a Metrohm 850 Professional IC operated on a Metrosep C6–150/4.0 column at 20 °C, running 0.1 mol L⁻¹ HNO₃ + 0.02 mol L⁻¹ dipicolinic acid mobile phase. Samples were filtered (Whatman 0.2 µm filter) prior to analysis.

High-performance liquid chromatography (HPLC)

Monosaccharides, acetic acid (acetyl groups), ethanol (ethyl groups) and hydrogenolysis products, such as EG, propylene glycol (PG), and sugar alcohols (SA), were quantified by HPLC analysis on an Agilent 1200 series. The machine was operated with a Hi-Plex-H⁺ column at 65 °C, running with 5 mmol L⁻¹ H₂SO₄ as eluent (0.6 mL min⁻¹) for the detection of acetic acid, ethanol, and hydrogenolysis products. For the detection of monosaccharides, and optionally ethanol, the machine was operated on a Hi-Plex Pb column at 70 °C with deionized water as eluent. The HPLC was equipped with a refractive index detector (RID) and variable wavelength detector (VWD) operated at 285 nm. Regular calibration curves were established for the components of interest and

samples were filtered prior to analysis (Whatman 0.2 µm filter).

Results and discussion

Process concept

The pretreatment goal is to retain the cellulose in the solid residue and maximize lignin and ash removal by dissolution. We envisage an organic solvent-based pretreatment process which utilizes *in situ* generated organic acid as catalyst. In fact, the organic acid (e.g. acetic acid) can act as both the catalysts and solvent.^{19,20} For this strategy to be successful, the solvent must be composed of three elements, namely; (i) water as a reactant to cleave lignin-carbohydrate bonds and lignin ether bonds, (ii) an acid catalyst for the cleavage reaction, and (iii) an organic solvent to facilitate dissolution of (depolymerized) lignin. A wide variety of organic solvent types has been successfully used to delignify lignocellulosic biomass, among them: alcohols, organic acids, esters, ketones, and phenolics.²¹ It is worth noting that the organic solvent to be used here is not limited to one organic component, but it will likely be composed of a mixture of light alcohols and light acids that are by-products of the pretreatment and hydrogenolysis steps.

Besides serving as a catalyst in the delignification reaction, the acid is also required to dissolve divalent cations (i.e. tungstate poisons), such as calcium and magnesium, from the biomass. Carbonates and oxalates of calcium and magnesium, which are typically present in lignocellulosic biomass,²² are poorly soluble in water (e.g. K_{sp} CaCO₃ (Calcite) = 10^{-8.5} mol L⁻², from Al Omari *et al.*),²³ Dissolution of these species can be achieved by acidifying the solution. Organic acids such as acetic acid and formic acid, which are typical by-products from biomass conversion, are suitable candidates as the solubility of their corresponding calcium and magnesium salts is sufficiently high. Moreover, these acids

are not poisonous to the hydrogenolysis catalysts, unlike for example hydrochloric acid²⁴ and H₂SO₄. Furthermore, they can be easily separated from lignin and ashes by evaporation.

A match in polarity of the solvent and lignin is also required to remove lignin successfully.^{21,25} The polarity of the solvent can be tuned by selecting an appropriate mixture of water and organic solvent. A solvent with a high share of water is desirable from an economic point of view, as organic solvents are more expensive than water.

In our process scheme, see Fig. 2, biomass is treated at elevated temperature (180–200 °C) in the presence of an organic solvent (e.g. ethanol/acetic acid) and water mixture to extract lignin and ashes (PT unit). The organic solvent is composed of organic acids (e.g. acetic acid) that are generated during the pretreatment, and light alcohols, which are by-products of the hydrogenolysis step. Preferably, the process produces its own solvent, but possibly an additional external solvent make-up is required (not displayed in Fig. 2). They are all recycled back to the PT step. As such, the separation infrastructure for glycols and by-products, such as light alcohols, after the hydrogenolysis step is already present.

The use of inorganic catalysts, such as Cl⁻, in the pretreatment solvent should be avoided, as they are typical poisons to metal catalysts. Moreover, the pretreatment is selected to run under acidic conditions, like the hydrogenolysis, to avoid a pH swing between the two steps. These considerations are important as biomass and its derivatives have the ability to hold vast amounts of liquid and thereby dragging pretreatment solvent and solutes to the hydrogenolysis reactor.

After pretreatment, the spent solvent and solid residue are separated (S/L unit, e.g. by a filter press), and the solvent is recovered by evaporation with an evaporator (Evap) unit from the dissolved biomass fraction, i.e. lignin and ashes. The combustion of lignin could provide heat to run

the evaporator. The recovered solvent is recycled to the pretreatment reactor and the solid residue enriched in cellulose is fed to the hydrogenolysis section and converted to ethylene glycol. Light alcohol by-products are separated from glycols by a separator (Sep) unit and utilized as a solvent makeup for the pretreatment step.

Experimental validation

In this work, we intend to give an initial experimental validation of this process concept (Fig. 2). The aim of pretreatment is to remove catalyst poisons such as lignin and ash selectively, i.e. to obtain a solid residue that is enriched in cellulose that can subsequently be fed to the hydrogenolysis section. We display here two examples of organic solvent based pretreatments to support the viability of our process concept, PT-A and PT-B. Pretreatment A was a classical organosolv pretreatment, 50 wt% H₂O and 50 wt% ethanol (EtOH), run at 200 °C for 3 h without acid. Pretreatment B was an acetosolv-type pretreatment that uses 70 wt% acetic acid (HAc) and 30 wt% H₂O, and was run at 180 °C for 1 h. The pH of the black liquors after the experiments was 4.2 for PT-A and 1.3 for PT-B.

The solid residue yields were 56 wt% for PT-A and 50 wt% for PT-B, which is typical for such pretreatments. As shown in Fig. 3(A), both pretreatments succeeded in selectively removing the lignin and ash fractions (>80 wt%), while preserving the cellulose, as indicated by the hexosan retention of ~100 wt%. The majority of the hemicellulose was removed as well: only 29 and 14 wt% was retained in the solid residue for PT-A and PT-B, respectively.

Besides silica, the majority of the inorganic components in biomass consist of alkali and alkaline earth metals (AAEM). Divalent ions, such as calcium and magnesium, form poorly soluble tungstates.^{11,12} More importantly, Pang *et al.*¹¹

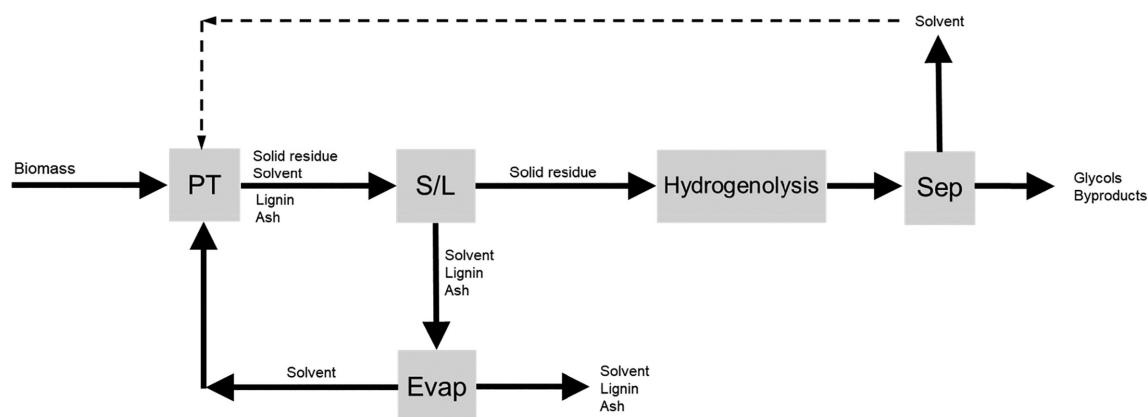


Figure 2. Simplified conceptual process scheme. PT, pretreatment; S/L, solid/liquid separation; Sep, separator.

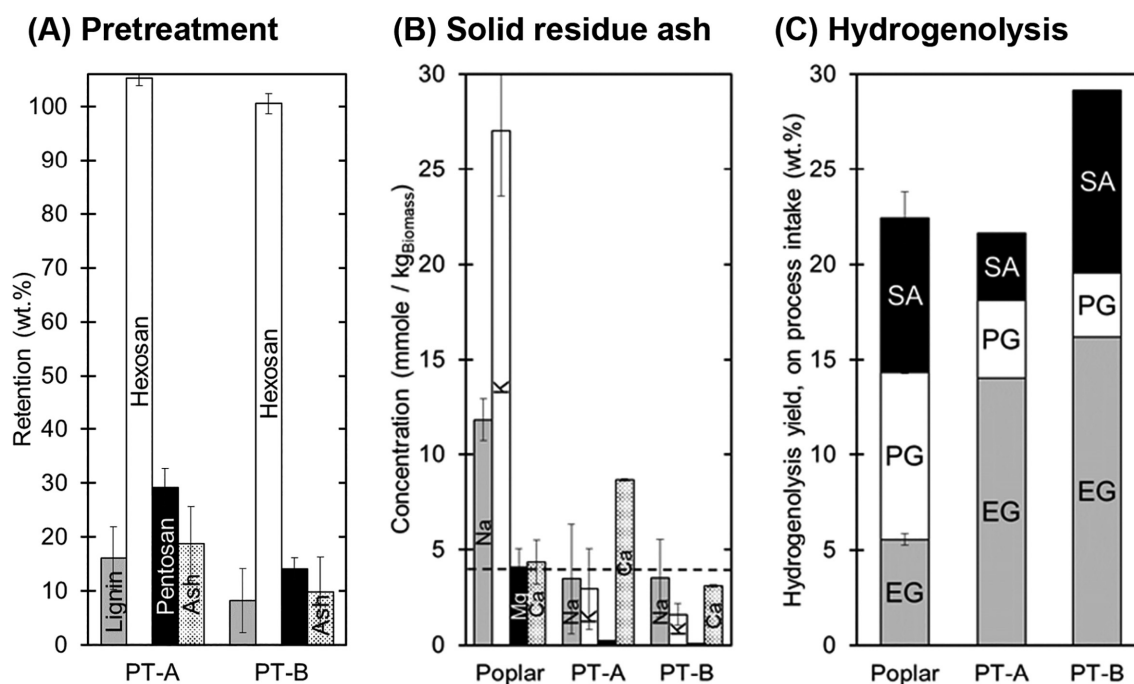


Figure 3. (A) Retention of biomass fractions after pretreatment, (B) alkali and alkaline earth metal composition of untreated poplar and pretreated samples A and B, and (C) hydrogenolysis yields on biomass intake to the overall process – see Eqn (3) for untreated poplar and solid residues obtained after pretreatments A and B. Pretreatment conditions: PT-A; 200 °C, 3 h, H₂O:EtOH 50:50 w/w, PT-B; 180 °C, 1 h, 30 wt% H₂O, 70 wt% HAc. Hydrogenolysis conditions: 5 wt% biomass loading, T = 245 °C, t = 1 h, P_{H₂} (initial) = 60 bar, pH_{initial} ~3.3, Ni-catalyst to biomass mass ratio 0.12, W-catalyst to biomass mass ratio 0.03.

previously showed that the EG yield dropped from 60 to 23 and 46 C% under the addition of calcium or magnesium respectively in the cellulose hydrogenolysis experiment. Assuming that deactivation (by precipitation) of tungstates occurs in a 1:1 M ratio, a maximum allowable concentration of undesirable divalent cations can be calculated to meet the maximum catalyst consumption (<1 kg/tonne_{product}²⁶), which boils down to <4 mmole (e.g. <161 mg Ca) per kg of biomass, see supporting information S1. Precipitation of tungstate species on the surface of the metallic hydrogenation catalyst poses an additional deactivation risk.

We studied the AAEM composition of the untreated poplar and pretreated substrates A and B, see Fig. 3(B). The poplar feedstock was relatively lean in calcium, 173 mg kg⁻¹ (4.3 mmole kg⁻¹), and magnesium, 99 mg kg⁻¹ (4.1 mmole kg⁻¹), but these levels are still higher than the target value of <4 mmole per kg of biomass. It turns out that an ethanol-water pretreatment, PT-A, successfully removes sodium, potassium, and magnesium (200 mg kg⁻¹), but falls short on the calcium removal. In fact, the solid residue calcium content of PT-A is higher than that of the feed, namely 346 mg kg⁻¹ (8.7 mmole kg⁻¹). This is explained by the mass loss during PT ($Y_{SR} = 56$ wt%), where Y_{SR} is solid residue yield after pretreatment (wt%), and hints that an organic

solvent- (e.g. ethanol)-based PT is not an effective tool for calcium removal, which is easily explained by the poor solubility of calcium salts, such as calcium carbonate,²⁷ in water-ethanol mixtures. The spent liquor was also only mildly acidic, pH = 4.2, whereas a pH < 3 is deemed necessary to remove calcium from biomass significantly.²⁸

In an attempt to improve calcium removal, we selected a more acidic pretreatment, PT-B, based on a solvent composed of 70 wt% acetic-acid, the remainder being water. Indeed, the calcium level was much lower for the solid residue of PT-B (3 mmole per kg biomass) than of PT-A and met the 4 mmole per kg biomass constraint. However, the calcium content of PT-B was not significantly different than the one of the feed, see Fig. 3(B). At the same time, PT-B delivered a solid residue with only ~4 wt% of lignin. Note that in PT-B the solid residue yield is 50 wt%, thus 50% of the calcium must also have been removed to end up with the same calcium content as the untreated feed. Nevertheless, this pretreatment also appears to be less effective in calcium removal than a wash of only 10 wt% acetic-acid water solution at 90 °C for 2 h, as was previously demonstrated by Oudenhoven *et al.*,²⁹ which reduced the pine calcium content from 1771 mg kg⁻¹ pine to 68 mg kg⁻¹ pine (1.7 mmole per kg pine) after acid leaching. This is well below the product constraint concentration of

4 mmole of divalent cations per kg of biomass. It thus appears that a high organic solvent share, which is believed to be necessary for delignification, hampers the removal of calcium.

We then performed hydrogenolysis of untreated poplar and the pretreated samples and chose demanding conditions developed earlier⁸ to verify whether the chosen pretreatment strategy was indeed successful. The pretreated substrates delivered higher overall glycol yields on process intake, despite the loss of hemicellulose during pretreatment, see Fig. 3(C). The EG yield on biomass intake to the overall process was 14 and 16 wt% for PT-A and PT-B, whereas it was only 6 wt% for untreated poplar. Note that the hydrogenolysis protocol was not tuned for maximum EG yield but for maximum sensitivity towards catalyst poisons; it should therefore be possible to raise the glycol yields significantly by optimization of the hydrogenolysis conditions.

Comparison of glycol yields for different studies is cumbersome as (i) different hydrogenolysis protocols⁸ are used, and (ii) the solid residue yield of the pretreatment step is often not reported.^{6,7,30} It is therefore more useful to compare the glycol yields obtained for treated biomass with a reference experiment with untreated and, importantly, microcrystalline cellulose, which has an extremely low content of potential catalyst poisons. Our demanding recipe applied high biomass loading and low catalyst W and Ni loading to exacerbate the sensitivity of the system towards catalyst poisoning. The pretreated samples delivered substantially higher glycol yield, expressed on holocellulose basis, than that of untreated poplar ($Y_{EG} = 8$ wt%) and very similar to pure cellulose ($Y_{EG} = 32$ wt%), namely 27 and 34 wt% for PT-A and PT-B respectively⁸ – see Fig. S9 in the supporting information. This is a clear proof that the proposed pretreatment strategy does remove undesirable catalyst poisons and deliver high overall glycol yields.

Despite the limitations, we calculated the process-based glycol yields for the studies by Fabičovicová *et al.*⁹ and Pang *et al.*⁷ on the pretreatment and subsequent hydrogenolysis of barley straw and corn stalk respectively. The process-based EG and PG yields for their best case scenarios were slightly higher, namely 17–18% EG compared to 14–16 wt% for this work, and PG yields of 8 C% (Pang *et al.*⁷), and 5 C% (Fabičovicová *et al.*⁹) compared to 3–4 wt% (this work) – see supporting information section S5.2. Although various pretreatments have been tried, we limit the discussion to successful approaches. Pang *et al.*⁷ used pretreatments based on solutions of ammonia, hydrogen peroxide, combinations thereof, and sodium hydroxide. Similar pretreatments in combination with ethanol as solvent were performed on *Miscanthus* in a different study by Pang *et al.*⁶

The alkaline pretreatment approaches require a pH-swap as the hydrogenolysis is run under acidic conditions and therefore requires extensive washing of the solid residue or neutralization of the alkali, whereas the hydrogen peroxide based approach is costly due to its single use. Our *in situ* produced organic-acid-based pretreatment avoids these issues. Fabičovicová *et al.*⁹ applied water-ethanol mixtures as a pretreatment protocol, similarly as this work, but merely focus their study on the hydrogenolysis outcome and not on the process considerations.

Solvent selection

The organic solvent needs to meet a number of requirements to be attractive for pretreatment. Due to the ability of treated biomass (e.g. cellulose) to retain vast amounts of liquids, a significant share of the pretreatment solvent inevitably ends up in the hydrogenolysis reactor. The acidity of the pretreatment solvent should therefore be compatible with the mild acidic (pH = 3–5) conditions required in the hydrogenolysis reactor. Furthermore, additives that are known catalyst poisons, such as hydrochloric acid,²⁴ cannot be part of the pretreatment solvent. Ideally, the solvent should be recovered without degradation to be recycled to the pretreatment. The solvent should therefore be resistant to high temperatures (~250 °C) and a reductive environment (i.e. not catalytically converted). For example, a ketone is easily converted to an alcohol during hydrogenolysis and therefore is not a preferred pretreatment solvent. Preferably, the pretreatment solvent would consist of a by-product or multiple by-products of the hydrogenolysis process. This gives two advantages: (i) the by-product stream can be utilized as make-up for losses in the pretreatment section, and (ii) the infrastructure to separate this solvent from the target product (EG) that is already present in the process.

We therefore selected light alcohols and organic acids in combination with water as pretreatment solvent, but, for the sake of simplicity, we centered our experiments around ethanol-water mixtures. Considering the pretreatment aims (high delignification, high sugars retention), from the results presented in Fig. 4, it can be concluded that the ideal solvent for delignification is composed of 50–60 wt% ethanol and the remainder being water. This is also reflected by the low residual lignin content of the solid residues, ~6 wt%, resulting from these experiments, see Fig. S1. To the best of our knowledge, the minimum share of organics in the pretreatment solvent to achieve deep delignification does not dramatically change for other light alcohols or light acids.^{19,25,31–33} It is therefore reasonable to expect that a

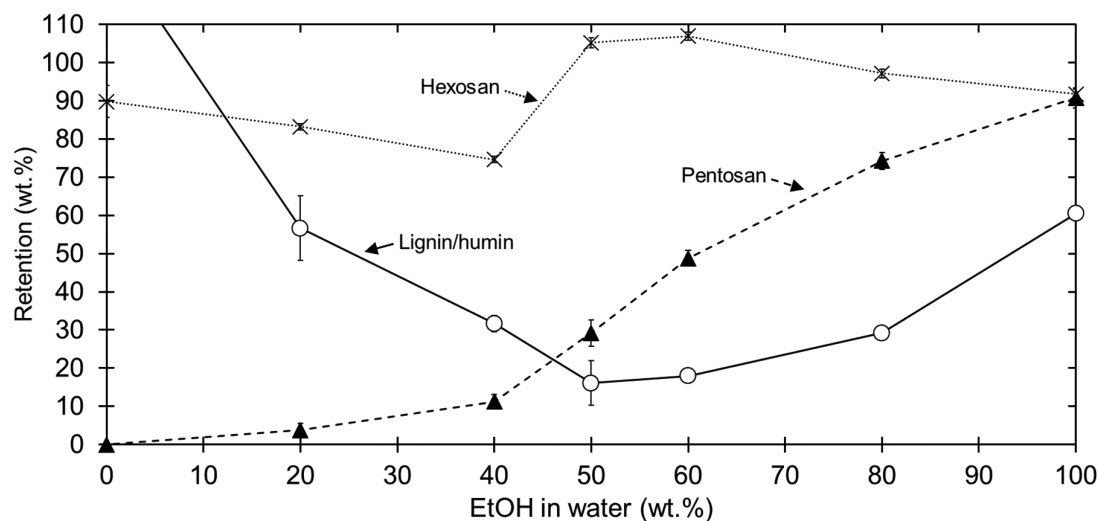


Figure 4. Pretreatment of poplar for 3 h at 200 °C for varying solvent composition (EtOH – water mixture), no acid was added. Note: Samples were washed prior to yield calculation and compositional characterization. The composition was determined in duplicate, except for the experiments with 20 and 40 wt% ethanol, where the sugar fraction was determined by a single measurement. The error in the solid residue yield, which is needed to calculate the retention, is unknown and therefore underestimated.

solvent with a minimum of ~50 wt% organics is needed to achieve deep delignification.

Note that the lignin retention for only water as solvent experiment was 131 wt%, indicating the formation of humins, which are perceived as lignin by our analytical procedure (i.e. it cannot differentiate between lignin and humins). This observation was further confirmed by a total lignin balance greatly exceeding 100% and the presence of 5-HMF and furfural in the black liquor (Fig. S2), which are known humin precursors.³⁴

The preservation of hexoses in the solid residue is high over the whole range of water-ethanol mixtures, indicating the recalcitrance of cellulose. The pentose content of the solid residue can be controlled by varying the water content of the solvent. This ultimately affects the EG (C₂) to PG (C₃) ratio in the hydrogenolysis product slate, as pentose (C₅) delivers 1 mol of EG (C₂) and 1 mol of PG (C₃), whereas hexose (C₆) can give 3 mol of EG (C₂). However, the majority of the hemicellulose is removed when delignification is maximized, i.e. for a solvent ethanol composition of 50–60 wt%.

Various aspects of this process advocate the use of a pretreatment solvent with high water content, as water (i) has a low cost, (ii) reduces organic solvent recovery rate, (iii) is a relatively good solvent for ashes, (iv) is already present in the feedstock, and (v) has a high compatibility with hydrogenolysis step. A high water-solvent share results in deep depolymerization of hemicellulose during pretreatment. This means that hemicellulose is not utilized for

the production of glycols and it will be present in the lignin downstream. Therefore, a separation step will be needed for further valorization.

***In situ* generation of organic solvent**

Our process relies on a solvent composed of water, light organic acids, and light alcohols. As these cost \$300–600 per ton, which is similar to the end products, EG and PG (~\$800 per ton), and vastly more than the feed price (~\$80 per ton),^{14,35} one intuitively feels that a loss of these organic molecules comes with a high economic penalty. We therefore envision producing these molecules *in situ* to compensate for losses. In this section we estimate the size of this make-up stream.

In situ organic solvent production mainly proceeds via (i) hydrolysis of acetyl groups during pretreatment; (ii) acid production via biomass degradation reactions, and/or (iii) light alcohol by-product formation during hydrogenolysis. The percentage of biomass acetyl groups is typically in the order of 1.2–4.4 wt%,³⁶ as is also reflected by the measured acetyl groups of three biomass archetypes in our previous work⁸ (1.4–3 wt%) and 3 wt% for poplar, used in this study (Table 1). These acetyl groups are easily liberated from the biomass to yield acetic acid.³⁷ Indeed, we found an acetic acid yield of 4–5 wt% on biomass intake, for the experiments depicted in Fig. 4, when the solvent was composed of at least 40 wt% water – see Fig. S3. Measurement of the residual *o*-acetyl groups of the solid residue confirmed that over 80 wt% of the *o*-acetyl groups

were hydrolyzed (Fig. S4). Besides liberation of the *o*-acetyl groups, degradation of the saccharide fraction can yield organic acids.^{34,38} We found that, next to acetic acid, minor fractions of formic, lactic, and glycolic acids were produced (3–4 wt% in total), see Fig. S5. Lactic and glycolic acid are of less interest as they cannot be recovered by evaporation. However, they could be valuable as chelating agents to trap the alkaline ash, thereby saving consumption of light acids, such as acetic acid.

During hydrogenolysis, roughly 3–5 wt% (in biomass intake to PT step basis) of light alcohol by-products are formed – see supplementary information S3.2.

To summarize, a total of 4–5 wt% of acetic-acid, 3–5 wt% of light alcohols and optionally 3–4 wt% of other organic acids is generated in the pretreatment and hydrogenolysis steps combined. In total, 10–14 wt% of organic molecules are produced *in situ*.

Besides production, a fraction of the organic solvent is consumed by (i) chemical bonding with a biomass fraction (e.g. cellulose or lignin) or, in the case of acids, (ii) by neutralization with basic ash.

Cellulose could be acetylated during the pretreatment step. However, we previously discussed that over 80 wt% of the *o*-acetyl groups were liberated for the experiments depicted in Fig. 4. Even for PT-B, in which the solvent was composed of 70 wt% acetic-acid (the remainder being water), 40 wt% of the *o*-acetyl groups was liberated, see Table S2. Thus, overall, the conversion of biomass to solid residue is a source of acetic acid. Furthermore, the solid residue is hydrolyzed in the hydrogenolysis step, thereby releasing chemically bound acetic acid and light alcohols, which can then be recycled to the pretreatment step. Note that this is a distinct advantage of this process compared to traditional organosolv aiming for pulp production, for these processes are truly losing the solvent in the final product.

Acetylation of lignin, however, would result in a loss of acetic acid, as lignin is either sold or combusted. Acid hydrolysis of lignin showed that acetylation of lignin for PT-A (EtOH) was negligible, namely 0.02 wt% on biomass intake, whereas it was significant for PT-B (HAc), 0.4 wt% on biomass intake, see Table S3. On the other hand, lignin bound some 0.3 wt% of ethanol (on biomass basis) for the ethanol-water experiment (PT-A) – see Table S4. Hence, lignin is a minor source of solvent loss.

Neutralization of poplar wood consumed 0.15 ± 0.01 mol H^+ $kg_{biomass}^{-1}$, which boils down to an acetic-acid consumption of 0.9 ± 0.07 wt% on biomass intake, see Table S5. Smit *et al.*³⁹ found a very similar value for poplar, namely 0.13 mol H^+ $kg_{biomass}^{-1}$. Typically, acid neutralization capacity (ANC) is around 0.1 mol H^+ per

kg of dry biomass for wood species, but can be up to 1 mol H^+ per kg of dry for herbaceous biomass (i.e. 0.4–6 wt% of acetic-acid on biomass intake).^{10,39} The measured ANC of poplar was roughly halved after water extraction, see Table S5. Optionally, a wash step prior to the pretreatment could be considered to reduce the need for acids. In general, the acid consumption by titration of the alkaline material is between 0.5 and 6 wt% of acetic acid on biomass intake.

Overall, 4–9 wt% of light organic alcohols and acids are net produced (Table 2). This value could be stretched to ~13 wt% when considering a biomass prewash to dispose of alkaline material or utilization of heavy acids (e.g. lactic and glycolic acid), that are formed within the process, as titrant of the basic ash.

Solvent recovery

Target

We previously discussed that biomass is a net producer of light organic molecules that can be utilized as process solvent. The absolute organic solvent loss is preferably, at maximum, equal to the absolute production. An organic solvent deficit could be compensated by additional solvent intake. However, this intake will come at an economic penalty, compared to the *in-situ* produced molecules. We derived an equation that describes the required organic solvent recovery rate (R) within the process – see Eqn (4) (see supporting information S4 for derivation). In this equation, Y_{Lights} is the conversion of biomass to light acids and alcohols, B/S is the biomass to solvent mass ratio, and $f_{organic}$ is the organic weight fraction of the solvent:

Table 2. Organic solvent production and consumption during pretreatment expressed on dry biomass intake.

	Yield (wt%, on biomass intake)
<i>Production</i>	
Acetic-acid (hydrolysis of acetyl groups + biomass degradation)	4–5
Other organic acids (biomass degradation)	3–4
Light alcohols (hydrogenolysis byproduct)	3–5
<i>Consumption</i>	
Lignin (acetylation or etherification)	–0.4
Neutralization	–0.5 to 6*
<i>Total</i>	4–13
*6 wt% HAc (on the worst-case scenario), 2.5 (pessimistic) and 0.5 (optimistic) are used for calculation.	

$$R(\text{wt.}\%) = \left(1 - Y_{\text{Lights}} \cdot \frac{B}{S} \cdot \frac{1}{f_{\text{organic}}} \right) \times 100 \quad (4)$$

A high recovery rate results in a stringent recovery specification, which would ultimately result in a high cost. The upper and lower boundaries for the recovery rate follow from Eqn (4). As discussed in the previous section, the conversion of biomass to lights is between 4 and optimistically 13 wt%. The biomass-to-liquid ratio in industrial reactors is, at a maximum, ~0.25,⁴⁰ but in academic studies it is typically 0.11. For successful delignification, the process solvent needs to be composed of a large fraction (≥ 50 wt%) of organic molecules, see Solvent selection subsection. Filling in Equation (4) with these numbers results in a recovery rate of 93.5 wt% (optimistic) to 99.9 wt% (pessimistic) – see supporting information S4 for details. Even the most optimistic scenario shows that high solvent recovery is pivotal to the viability of the process.

Although, in every scenario, a high organic solvent recovery rate is required, missing out on the recovery rate by 1 wt% (Eqn (4)), translates to an additional solvent make up cost, in an optimistic scenario, of 8 \$ dollar per ton biomass fed, whereas the margin, defined as ‘*product price* \times *product yield* – *biomass price*’, is roughly \$60 per ton biomass fed. Mitigating or avoiding the need for an external solvent make up therefore presents an important economic advantage. See supporting information S4 for details.

It is important to realize here that the recovery rate is a linear function of Y_{Lights} and B/S (note: non-linear with respect to biomass loading) but non-linear with respect to the organic fraction of the solvent. In a quest to reduce the necessary solvent recovery rate, finding chemistries that allow successful delignification while relying on a low solvent share of organics (e.g. ≤ 50 wt%) is much more beneficial than increasing the conversion of biomass to lights.

Evaporator

The stringent solvent recovery specification requires the selection of a robust separation technique that can fractionate the solvent and dissolved biomass fraction (e.g. lignin, ash, hemicellulose). We therefore chose to use an evaporator, which is commonly used in the pulp and paper industry.

The use of strong high boiling acids, such as sulfuric acid, should therefore be avoided. We observed a build-up of polymerized material that was insoluble in acetone and ethanol on the cooking flask wall during solvent recovery by evaporation. The acidity in the solvent increased due to the build-up of sulfuric acid and consequently enhanced unwanted polymerization reactions.

Table 3. Heat of vaporization of pretreatment solvent constituents and required energy duty per kg of biomass processed for a solvent to biomass ratio of 4 to 1 and 9 to 1.

	H_{vap} (MJ kg ⁻¹)	Q (MJ kg ⁻¹ _{biomass}) for S/B = 4/1	Q (MJ kg ⁻¹ _{biomass}) for S/B = 9/1
Water	2.4	9.6	21.6
Ethanol	0.9	3.6	8.1
Acetic acid	0.4	1.6	3.6

Furthermore, the process should run in an energy efficient manner. As a lower boundary for the available energy, we propose to combust all lignin, that has a higher heating value of ~25 MJ kg⁻¹⁴¹ which translates to ~5.4 MJ per kg of biomass processed. We calculated the required heat duties based on the heat of vaporization for a solvent to biomass ratio S/B of 4 to 1 and 9 to 1, see Table 3. It is evident that a low solvent-to-biomass ratio is imperative. But even for a solvent-to-biomass ratio of 4/1, the required energy duty largely surpasses the available energy in the case of water. Moreover, this is also the case for a 50/50 w/w ethanol/water scenario, which requires 6.6 MJ per kg biomass processed. This shows the need for reclaiming the energy lost by evaporation, for example by multiple-effect evaporation, which is common in the pulp and paper industry.

Conclusion

In this work, we propose a lignocellulosic biomass pretreatment process that is integrated with a subsequent catalytic hydrogenolysis step, to convert saccharides to ethylene glycol. The major target of this pretreatment is the selective removal of catalyst poisons, such as lignin and tungstate poisons (i.e. divalent cations), like calcium (≤ 4 mmole per kg biomass). After careful analysis, we have determined the specific design criteria required for the pretreatment step (Table 4).

We propose a solvent-based pretreatment utilizing light alcohols, organic acids, and water, which are by-products of the pretreatment and hydrogenolysis reactions, and could therefore compensate for losses in the system. In line with past research, it appeared that the pretreatment solvent should be at least composed of ~50 wt% of organic solvent to achieve deep delignification. However, such pretreatment did not remove sufficient calcium, a tungstate poison, from the biomass, and required the selection of a more acidic pretreatment solvent. Biomass pretreatment with a solvent composed of 70 wt% acetic-acid, the remainder being water, produced a solid residue with a calcium and magnesium

Table 4. Pretreatment design summary.

Consideration	Criteria
<i>Product composition</i>	
Lignin	<5 wt% in solid residue
Divalent ions (e.g. Ca)	≤4 mmole per kg solid residue
Alkaline ash	Preferably removed
<i>Pretreatment conditions</i>	
Biomass to liquid ratio	As low as possible e.g. 1:4 w/w
Solvent	Compatible with hydrogenolysis: Water + light alcohols + light acids
Solvent composition	50/50 w/w organic/H ₂ O
pH	Acidic
Inorganic additives	Prohibited (halogens, N, S components)
<i>Others</i>	
<i>In-situ</i> solvent generation	4–13 wt% on biomass intake
Solvent recovery	>93.5 wt%
Evaporator	Multi-effect or combined with energy efficient separator

content of 124 and 2 mg kg⁻¹ biomass respectively, thereby meeting the performance constraint of ≤4 mmole per kg biomass. Hydrogenolysis of this sample resulted in a higher glycol yield compared with untreated biomass, confirming the removal of catalyst poisons during pretreatment. Moreover, the overall process yields were higher, namely 16 and 3 wt% of EG and PG respectively compared with 6 and 9 wt% for untreated poplar.

We found that 4–13 wt% of the biomass can be converted to organic solvent, but it turns out that a high solvent recovery is still essential. In an optimistic scenario, a solvent recovery of 93.5 wt% is needed, which goes up to 99.9 wt% for a very conservative estimate. Despite the desired high recovery rate, *in situ* generation of solvent appears to present an important economic advantage. We suggest using an evaporator to recover the solvent, which is a robust separation technique, and likely to meet the required high recovery. However, preliminary calculations showed that there is a gap between the heat duty and the available heat that could be provided by the combustion of lignin.

Acknowledgement

The authors thank Shell Global Solutions International BV for funding this research, and Benno Knaken, Johan Agterhorst, Ronald Borst, and Erna Fränzel-Luiten for the technical support.

References

1. Yue H, Zhao Y, Ma X and Gong J, Ethylene glycol: properties, synthesis, and applications. *Chem Soc Rev* **41**:4218–4244 (2012).
2. Rebsdats S and Mayer D, *Ethylene Glycol*. Wiley-VCH Verlag GmbH & Co., Hoboken, NJ (2000).
3. Wang A and Zhang T, One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts. *Acc Chem Res* **46**:1377–1386 (2013).
4. Zheng M, Pang J, Wang A and Zhang T, One-pot catalytic conversion of cellulose to ethylene glycol and other chemicals: from fundamental discovery to potential commercialization. *Chinese J Catal* **35**:602–613 (2014).
5. Zhu Z, Toor SS, Rosendahl L, Yu D and Chen G, Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw. *Energy* **80**:284–292 (2015).
6. Pang J, Zheng M, Wang A, Sun R, Wang H, Jiang Y *et al.*, Catalytic conversion of concentrated miscanthus in water for ethylene glycol production. *AIChE J* **60**:2254–2262 (2014).
7. Pang J, Zheng M, Wang A and Zhang T, Catalytic hydrogenation of corn stalk to ethylene glycol and 1,2-propylene glycol. *Ind Eng Chem Res* **50**:6601–6608 (2011).
8. te Molder TDJ, Kersten SRA, Lange JP, Ruiz MP. Ethylene glycol from lignocellulosic biomass: impact of lignin on catalytic hydrogenolysis. (Research, I. E. C. (ed.)). 2021.
9. Fabricovicova K, Lucas M and Claus P, From barley straw to valuable polyols: a sustainable process using ethanol/water mixtures and hydrogenolysis over ruthenium-tungsten catalyst. *ChemSusChem* **9**:2804–2815 (2016).
10. Lange JP, Renewable feedstocks: the problem of catalyst deactivation and its mitigation. *Angew Chem Int Ed Engl* **54**:13186–13197 (2015).
11. Pang J, Zheng M, Sun R, Song L, Wang A, Wang X *et al.*, Catalytic conversion of cellulosic biomass to ethylene glycol: effects of inorganic impurities in biomass. *Bioresour Technol* **175**:424–429 (2015).
12. Cao C, Zhao Z and Chen X, Selective precipitation of tungstate from molybdate-containing solution using divalent ions. *Hydrometallurgy* **110**:115–119 (2011).
13. Pang J, Wang A, Zheng M, Zhang Y, Huang Y, Chen X *et al.*, Catalytic conversion of cellulose to hexitols with mesoporous carbon supported Ni-based bimetallic catalysts. *Green Chem* **14**:614 (2012).
14. Lange J-P, Catalysis for biorefineries – performance criteria for industrial operation. *Catal Sci Technol* **6**:4759–4767 (2016).
15. Biermann CJ, *Handbook of Pulping and Papermaking*, 2nd edn. Elsevier (1996).
16. Liao Y, de Beeck BO, Thielemans K, Ennaert T, Snelders J, Dusselier M *et al.*, The role of pretreatment in the catalytic valorization of cellulose. *Mol Catal* **487**:110883 (2020).
17. Sluiter A, Hames B, Ruiz R, *et al.*, Determination of structural carbohydrates and lignin in biomass, 2012.
18. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Determination of ash in biomass, 2008.
19. Vazquez G, Antorrena G and Gonzalez J, Kinetics of acid-catalysed delignification of *Euclalyptus globulus* wood by acetic acid. *Wood Sci Technol* **29**:267–275 (1995).
20. Vázquez G, Antorrena G, González J, Freire S and López S, Acetosolv pulping of pine wood. Kinetic modelling of lignin solubilization and condensation. *Bioresour Technol* **59**:121–127 (1997).
21. AZIZ, S. S., KYOSTI Organosolv pulping - a review, TAPPI J (VOL 72NRO 3, mar1989). 1989.
22. Nimz HH, Schmitt U, Schwab E, Wittmann O and Wolf F, *Wood*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2000).

23. Al Omari MM, Rashid IS, Qinna NA, Jaber AM and Badwan AA, Calcium carbonate. *Profiles Drug Subst Excip Relat Methodol* **41**:31–132 (2016).
24. Pattison JN and Degering EF, Some factors influencing the activity of Raney nickel catalyst. III. The poisoning of Raney nickel by halogen Compounds1. *J Am Chem Soc* **73**:611–613 (1951).
25. Huijgen WJJ, Reith JH and den Uil H, Pretreatment and fractionation of wheat straw by an acetone-based Organosolv process. *Ind Eng Chem Res* **49**:10132–10140 (2010).
26. Lange J-P, Fuels and chemicals manufacturing. *Cattech* **5**:82–95 (2001).
27. Gomaa EA, Solubility and solvation parameters of calcium carbonate in mixed ethanol-water mixtures at 301.15 K. *Sci Technol* **2**:51–52 (2012).
28. Chen D, Cen K, Chen F, Ma Z, Zhou J and Li M, Are the typical organic components in biomass pyrolyzed bio-oil available for leaching of alkali and alkaline earth metallic species (AAEMs) from biomass? *Fuel* **260**:116347 (2020).
29. Oudenhoven SRG, Westerhof RJM and Kersten SRA, Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: improved oil and sugar yields. *J Anal Appl Pyrolysis* **116**:253–262 (2015).
30. Zhou L, Pang J, Wang A and Zhang T, Catalytic conversion of Jerusalem artichoke stalk to ethylene glycol over a combined catalyst of WO₃ and Raney Ni. *Chinese J Catal* **34**:2041–2046 (2013).
31. Parajó JC, Alonso JL and Vázquez D, On the behaviour of lignin and hemicelluloses during the acetosolv processing of wood. *Bioresour Technol* **46**:233–240 (1993).
32. Chum HL, Johnson DK and Black SK, Organosolv pretreatment for enzymic hydrolysis of poplars. 2. Catalyst effects and the combined severity parameter. *Ind Eng Chem Res* **29**:156–162 (1990).
33. Wildschut J, Smit AT, Reith JH and Huijgen WJ, Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. *Bioresour Technol* **135**:58–66 (2013).
34. van Zandvoort I, Wang Y, Rasrendra CB *et al.*, Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. *ChemSusChem* **6**:1745–1758 (2013).
35. Lange J-P, Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels Bioprod Biorefin* **1**:39–48 (2007).
36. Pawar PM, Koutaniemi S, Tenkanen M and Mellerowicz EJ, Acetylation of woody lignocellulose: significance and regulation. *Front Plant Sci* **4**:118 (2013).
37. Chen X, Shekiro J, Franden MA, Wang W, Zhang M, Kuhn E *et al.*, The impacts of deacetylation prior to dilute acid pretreatment on the bioethanol process. *Biotechnol Biofuels* **5**:8 (2012).
38. Hu X, Wang S, Westerhof RJM, Wu L, Song Y, Dong D *et al.*, Acid-catalyzed conversion of C₆ sugar monomer/oligomers to levulinic acid in water, tetrahydrofuran and toluene: importance of the solvent polarity. *Fuel* **141**:56–63 (2015).
39. Smit A and Huijgen W, Effective fractionation of lignocellulose in herbaceous biomass and hardwood using a mild acetone organosolv process. *Green Chem* **19**:5505–5514 (2017).
40. Sävelin, P. *Digester developments*, 2014.
41. Demirbas A, Higher heating values of lignin types from wood and non-wood lignocellulosic biomasses. *Energy Sources A* **39**:592–598 (2017).



Thimo D. J. te Molder

Thimo te Molder is a PhD student at the Sustainable Process Technology group at the University of Twente. He holds a bachelor's degree and a master's degree in chemical engineering. His research interests focus on the fractionation of lignocellulosic biomass and its conversion to chemicals.



Sascha R. A. Kersten

Sascha Kersten is full professor and chair of the Sustainable Process Technology group at the University of Twente. His research focuses on the production of transportation fuels and bulk chemicals from biomass, energy storage in redox flow batteries, plastic recycling, plastic production from renewable feeds, and novel distillation and extraction concepts. He is also scientific director of the Dutch Institute for Sustainable Process Technology, the leading institute for open innovation in the process industry.



Jean-Paul Lange

Jean-Paul Lange is principal research scientist at Shell Projects & Technology in Amsterdam, and also professor in chemical biorefining at the University of Twente, working on novel catalytic processes for producing fuels and chemicals from different sources. His research embraces heterogeneous catalysis, chemical engineering, conceptual process design, manufacturing economics and technology strategy.



M. Pilar Ruiz

M. Pilar Ruiz is assistant professor at the Sustainable Process Technology group at the University of Twente. She has both academic and industrial experience in the areas of bioenergy and sustainability. Her research areas of interest include thermochemical and catalytic routes for biomass conversion to fuels, chemicals and materials, and plastic recycling.