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Cellulosic ethylene glycol-economic potential, contaminants and process concepts

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Ethylene glycol, an important commodity intermediate, could be readily made from carbohydrates. We review here recent developments to produce it *via* pre-treatment and hydrogenolysis of lignocellulose. We address the economic potential of this hydrogenolysis route *vs.* sugar fermentation to ethanol and *vs.* market prices. We review the detrimental impact of lignocellulose contaminants – lignin, ash and extractives – on the hydrogenolysis reaction. We then present two different process concepts with their strength, weaknesses and opportunities for improvement, namely a first concept based on thorough pre-treatment and cellulose hydrogenolysis in aqueous medium, and a second concept based on much simpler deashing and re-optimized hydrogenolysis in aqueous–organic medium.

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1. The perspective presents the role of contaminants on the hydrogenolysis of real lignocellulose to glycols. It then presents two archetype mitigations, one based on extensive pre-treatment to remove all contaminants, and the other based on minimal pre-treatment and modification of the hydrogenolysis to mitigate the accommodate residual contaminants, mainly the lignin.
2. This perspective provides a few general learnings on how to explore novel green chemistry processes. More specifically, it shows the importance of (1) running economic analysis early on, (2) considering real feedstock, (3) considering an integrated process beyond the simple conversion step and (3) using such integrated approach and technoeconomic analysis to identify the most critical opportunity for improvement to guide further research.
3. Lignocellulose will arguably be a critical feedstock for producing renewable oxygenated chemicals, particularly renewable glycols. This perspective shows the promises and of such process, how to explore the field to make green chemistry processes economically attractive.

1. Introduction

The exploitation of fossil resources has delivered unprecedented wealth in most part of the world. However, this progress also destabilized various fragile equilibria of the earth, most critically the global climate through the relentless release of CO_2 in the atmosphere. Most nations are now working at defossilising their energy system to limit the global warming. Much of their focus is on transitioning to renewable electricity, but a complementary transition to renewable carbon – CO_2, biomass and waste – will also be needed to supply the high duty-fuels and chemicals needed in the future.[1–4]

Such transition appears to be economically challenging.[3,5] For instance, the conversion of sugars to H_2, olefins and aromatics seems unaffordable while their conversion to oxygenated chemical intermediates looks more promising, as illustrated by Fig. 1.[5] Indeed, the economically viable selectivity (target selectivity) seems beyond reach for olefins and aromatics but achievable for various oxygenated chemicals by falling respectively above or below the theoretical selectivity. This trend can be rationalized by the (dis)similarity of O : C atomic ratio and of the overall oxidation state between product and the sugars they are derived from. Here, ethylene glycol (EG) stands out as being very promising as it could be manu-

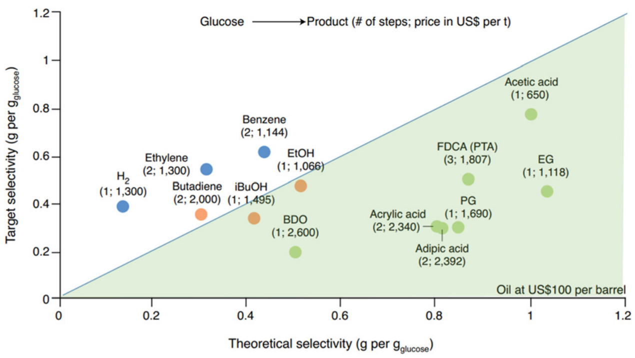

Fig. 1 Oxygenated chemical intermediates can potentially be produced affordably from glucose, with target selectivity below the stoichiometric one (adapted from ref. 5).

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factured affordably at about half the theoretical selectivity; hence the interest of industry for producing EG from sugars.

Ethylene glycol is a drop-in commodity with a mature market of 60 million tonnes in 2023[6] and an expected annual growth of 6.1% during 2021–2031.[7] EG is a versatile chemical used in several applications such as polyester textile (54%), PET bottles (26%), and antifreeze (9%). It is also used as a precursor for other applications such as resins, solvents, and plasticizers (11%).[8–10]

The main commercial process for EG production is based on fossil feedstock: the oxidation of ethylene to ethylene oxide, which is further hydrated to EG.[7] Its broad industrial application and its dependence on fossil feedstock call for more sustainable manufacturing routes. Among the various routes to renewable EG, we will here limit the discussion to its manufacture from sugar *via* fermentation to ethanol and hydrogenolysis.

A practical benchmark for sugar-to-EG starts with fermenting sugars to ethanol, followed by dehydration to ethylene, epoxidation to ethylene oxide, and hydration to EG (Fig. 2, upper route).[7] This four-step route appeals by relying on proven, industrial technology for all steps. Its drawbacks, however, include its large number of process steps, which leads to high investment cost, and its modest theoretical yield of 69 wt%, which results from CO_2 elimination during the fermentation step and leads to high sugar cost.

An alternative route is the one-step hydrogenolysis of sugars that could theoretically proceed with 103 wt% yield by simple addition of hydrogen (Fig. 2, lower route).[11–15] Hydrogenolysis operates with a bifunctional catalyst system, based on homogeneous WO_x species to catalyse the C–C cleavage *via* retro-aldol condensation, and on a supported hydrogenation metal to convert the glycolaldehyde intermediate to EG (Fig. 2, lower route). Foundational studies worked with cellulose as feedstock and proved high yield to EG (up to 74 wt%) over W-based catalysts promoted with Ni or Ru.

But real lignocellulosic biomass does not perform as well as do clean cellulose, an observation that is not yet properly understood despite extensive research.[7,16–23] For instance, various lignocelluloses deliver EG yields that vary between <10 C% and ~50 C%, depending on the type of lignocellulose, while clean cellulose delivers EG at 60 C% yield under similar conditions (Fig. 3, closed symbols – all yields are recalculated here as fraction of contained holocellulose).[23] The application of various pre-treatments occasionally enables high EG yields from poor feedstock such as pre-treated corn stalk but is not always efficient, as illustrated in Fig. 3 (open symbols).[22] Obviously, the WO_x/Ni catalyst system applied for hydrogenolysis differs markedly from the enzyme cocktail and the yeast applied for the hydrolysis and fermentation of cellulose to ethanol, for which the pre-treatments mentioned above were developed. Hydrogenolysis may then have different requirements to properly access the embedded crystalline cellulose and may also have different sensitivity to poisoning by contaminants present in the biomass. In short, the hydrogenolysis may require a different a pre-treatment, hopefully one that is cheaper than needed for fermentation to ethanol, which are notoriously expensive.[24]

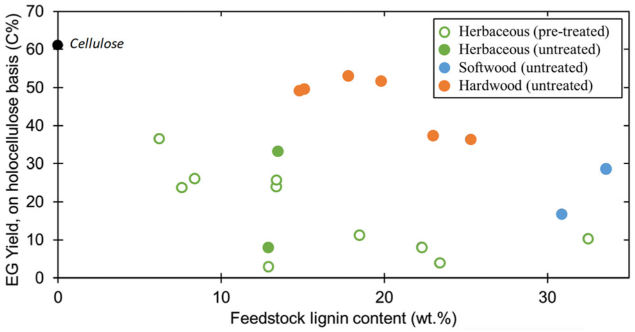


Fig. 3 EG yields reported for pure cellulose (at 0% lignin) as well as untreated and pre-treated lignocellulose (the original yield data from ref. 23 were recalculated on basis of holocellulose; figure adapted from ref. 18).

This perspective reports the studies run at the University of Twente in the Netherlands to tackle this challenge.[25–29] It first discusses the economic potential of cellulosic EG. It then investigates the role of lignin and other biomass components on the hydrogenolysis reaction. Thereafter, it investigates two approaches to mitigate the challenges of these contaminants. The first approach focuses on the pre-treatment step and designs it such as to produce clean holocellulose (cellulose + hemicellulose) at specification for the hydrogenolysis step. The second approach applies the simplest pre-treatment conceivable, a simple acid wash to remove ashes, and focuses on modi-

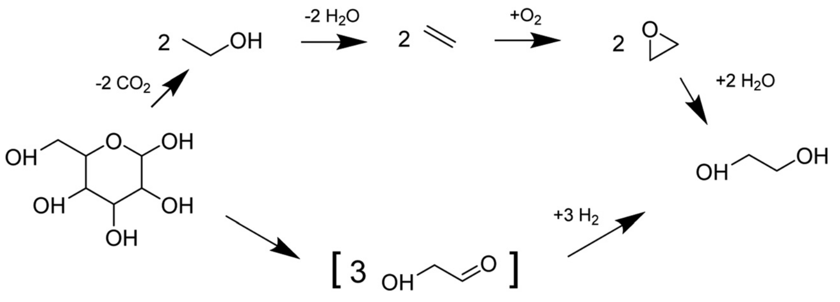


Fig. 2 Simplified ideal reaction scheme for converting glucose to ethylene glycol *via* fermentation (upper route) and hydrogenolysis (lower route).

fying the hydrogenolysis step such as to minimize the impact of lignin that is co-processed.

2. Economic potential of sugar-based EG

Both ethanol and hydrogenolysis routes have their strengths and weaknesses. The hydrogenolysis route promises higher yield and less process steps than the ethanol route. But it requires expensive renewable H_2. Could the cost of hydrogen overrule the benefits in yield and process simplicity? We can try to address this question without much technical information, by estimating the minimum selling price (MSP) using a simplified equation, eqn (1).[5,30] For multistep processes, the conversion cost of eqn (1) can be set as the number of steps × conversion cost per step, and the yield can be set as the overall yield achieved after the last step. It is however more accurate to use eqn (1) to calculate the fictive MSP of intermediates produced along the chain and use the resulting MSP as feed cost for the next step.[30] This results in the more elaborated eqn (2), which we will use below.

$$\mathrm{MSP} = (\text{feed price} + \text{conversion cost})/\text{yield} \tag{1}$$

$$\begin{aligned}\mathrm{MSP} = {} & \text{feed price}/(Y_1 \times Y_2 \ldots Y_n) + \mathrm{CC}_1/(Y_1 \times Y_2 \ldots Y_n) \\ & + \mathrm{CC}_2/(Y_2 \times Y_3 \ldots Y_n) + \ldots + \mathrm{CC}_n/Y_n \\ = {} & \text{feed price}/(Y_1 \times Y_2 \ldots Y_n) \\ & + \mathrm{CC} \times (1/(Y_1 \times Y_2 \ldots Y_n) + 1/(Y_2 \times Y_3 \ldots Y_n) \\ & + \ldots + 1/Y_n)\end{aligned} \tag{2}$$

Premises for bio-based glycol: glucose = \$300 per t, lignocellulose = \$50 per t with 60 wt% holocellulose, renewable H_2 = \$8000 per t, O_2 = \$50 per t, conversion cost (CC) = #step × \$200 per t or CC_i = \$200 per t; ethanol route: theoretical yield of 69 wt% in 4 steps with O_2 consumption of 0.18 t t^{-1} glucose (GLU); hydrogenolysis route: theoretical yield of 103 wt% in 1 step with H_2 consumption of 0.03 t t^{-1} GLU.

Based on eqn (2) and the premises reported above, the hydrogenolysis would be marginally cheaper than the ethanol route at comparable EG yield, as illustrated in Fig. 4(a). The cost of renewable H_2 at \$8000 per t offsets the lower conversion costs of the hydrogenolysis route. However, the hydrogenolysis route still has the advantage of allowing a higher theoretical yield of 103 wt%, *vs.* 69 wt% for the ethanol route.

But we could envisage running part of the ethanol route in existing equipment, namely the epoxidation and ethylene oxide hydration steps, and thereby lower the conversion cost of these steps from \$200 to \$50 per t to remove the investment contribution but still account for energy, catalyst, labour, *etc.* This does not dramatically change the picture as it lowers the MSP of the ethanol route from ~\$1100 per t to only ~\$950 per t at the theoretical EG yield of 69 wt% (Fig. 4a). The hydrogenolysis route remains favourable if it can deliver a higher overall mass yield, as promised. Notice that applying eqn (1) to the ethanol route would have delivered an MSP of ~\$1600 per t instead of the \$1100 per t reported above when using eqn (2). This confirms the conservative aspect of lumping the conversion cost of each step as number of steps × conversion cost per step.

We can apply the same economic screening for lignocellulose as done above for glucose. One needs to realize that lignocellulose is much cheaper, *e.g.* \$50 per t instead of \$300 per t, but contains less sugars, typically around 60 wt%, in the form of cellulose and hemicellulose. It therefore delivers a lower overall yield in glycols. One further needs to apply a pre-treatment process upstream of the hydrogenolysis route and apply a pre-treatment + enzymatic hydrolysis upstream of the ethanol route. Using the same logic and premises (incl. stoichiometric yield) as above for eqn (2), we find the hydrogenolysis route promising the same MSP for lignocellulose and glucose, while the ethanol route becomes more expensive with lignocellulose than it already was with glucose (Fig. 4b). The advantage can be related to the higher ideal yield and the simpler pre-treatment, *i.e.*, the absence of enzymatic hydrolysis. The advantage remains significant when we run the epoxidation and EO hydration steps of the EtOH route in existing equipment.

A preliminary sensitivity analysis of lignocellulose hydrogenolysis reveals that the glycol yield, the H_2 price and the conversion cost have a large impact on the EG MSP (Fig. 4c). Not surprisingly, the cost of lignocellulose is not as critical. Overall, numerous combinations could deliver glycols within the range of market price observed in 2018–2025.[31]

This analysis shows potential for the hydrogenolysis of glucose and lignocellulose to be cheaper than the ethanol dehydration route and competitive with, if not advantaged over fossil EG that dictates the market EG price.

But such economics only holds if we find an effective lignocellulose pre-treatment step that allows to reach high glycol yields upon hydrogenolysis, preferably higher than the ethanol route. The literature discussed above shows however much discrepencies in the effectiveness of the pre-treatments, with yield not exceeding 50 wt% of contained sugars. Furthermore, such high yields are generally achieved at high dilution, which leads to large equipment and expensive product work up.

3. Role of contaminants

3.1 Lignin

Lignin is often cited as a key obstacle for hydrogenolysis of lignocellulose due to the catalyst poisoning,[32,33] and to fouling of the reactors/equipment.[25] Delignification of lignocellulose has been perceived as crucial to make cellulose more accessible and, thereby, improve EG production.[7,16]

However, te Molder *et al.*[18] showed that lignin is not the primary obstacle of glycol formation. Across untreated feeds, pre-treated feeds, and physical mixtures of cellulose and lignin, EG and PG yields can be maintained at ~30 and ~10 wt%, respectively, irrespective of lignin content (Fig. 5, top and middle). In contrast, sugar-alcohol (SA) yield decreases monotonously with increasing lignin content of the feed

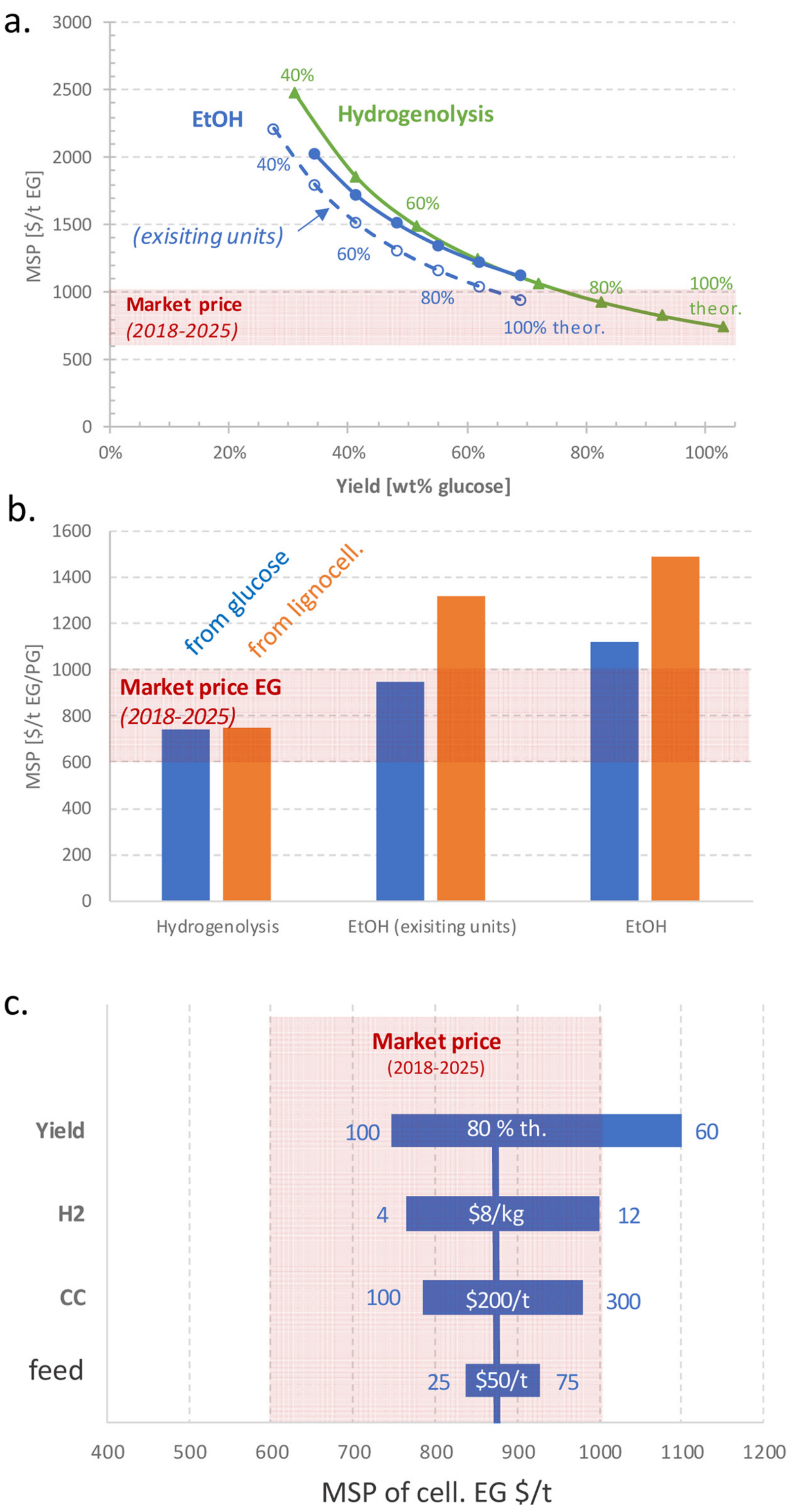


Fig. 4 Preliminary economic analysis of sugar-based ethylene glycol (EG) – a: minimum selling price (MSP) of EG produced *via* direct hydrogenolysis and *via* EtOH (ethanol); b: comparison of glycol MSP from glucose and lignocellulose produced *via* ethanol and hydrogenolysis at theoretical yield, optionally using existing units for Ethylene-EO-EG conversion, c: the MSP of cellulosic EG varies with varying yield, H_2 price, conversion cost per step and feed price.

(Fig. 5, bottom). This pattern suggests that lignin is mainly fouling the hydrogenation catalyst without affecting the retro-aldol condensation of the sugars.[18] The few low-EG points highlighted in the mid-lignin range (Fig. 5, top) likely result from other contaminants (*e.g.*, ash, S/N extractives to be discussed below).

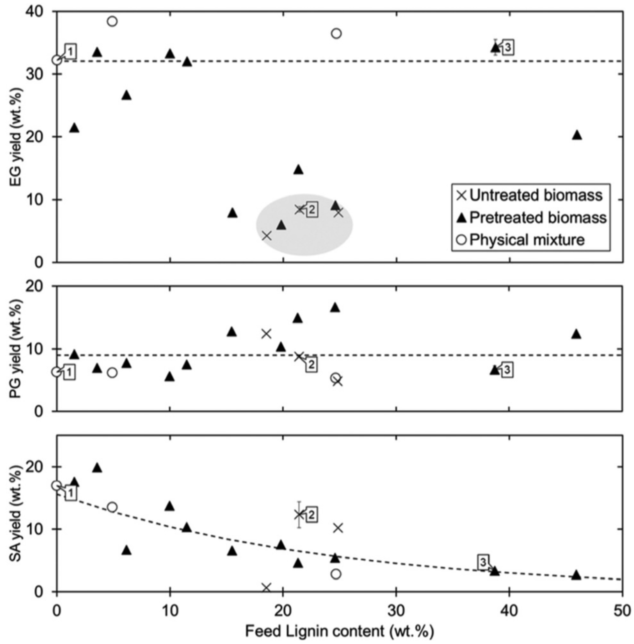


Fig. 5 No clear impact of lignin on the glycol yields of (ligno)cellulose hydrogenolysis of untreated and pre-treated lignocellulose as well as of physical mixtures of cellulose and lignin (data numbered 1,2,3 include duplicates with error bar occasionally smaller than the size of the symbol).[18]

3.2 Alkali earth metals and S, N components

Alkali-earth metals present in the ash of biomass, especially Ca^{2+} and Mg^{2+}, have been found to precipitate the WO_x species needed for catalysing the retro-aldol step during hydrogenolysis.[19,20,34] As shown in (Fig. 6a), the addition of ash to clean cellulose results in a steep drop in EG yield. This trend explains the modest EG of untreated poplar, wood based on nothing else than its ash content. Correspondingly, the EG yield of poplar can be increased by removing the ash with a mild acid leaching treatment.

Controlled additions of various salts show the same causality: divalent cations titrate WO_x out of solution, with Ca^{2+} forming insoluble $CaWO_4$ (equimolar Ca : W consumption) and driving the EG yield to drop.[19] In contrast, Na^+/K^+ addition does not precipitate WO_x nor affect the EG yield.[35] This has also been observed by Pang *et al.*[20] who found $CaWO_4$ in the spent catalyst, which is inactive for the aldol cleavage.

Herbaceous feeds such as hay lead to severe catalyst deactivation that cannot be explained by neither lignin nor Ca/Mg: low EG + PG yield are observed, even when sufficient soluble WO_x is found in the effluent. A detailed study assigned this low yield to poisoning of the hydrogenation catalyst with S/N-bearing extractives.[23,36] The presence of ~100 mmol of S and/or ~1000 mmol of N components per kg of Ni appeared to severely depress the glycol yield (Fig. 6b and c). Similar trend was found for cleaning hay by acid leaching or spiking cellulose with methionine (S + N) or glycine (N).[36]

In summary, to reach the level a catalyst productivity of >1 $t_{product}\ kg_{catalyst}^{-1}$ applied in the industry,[30] the pre-treatment should lower the alkali earth metals (AEMs), S and N content of the biomass down to 4 mmol AEMs, ~0.1 mmol S and 5 mmol N per kg biomass.[19,36] One could then envision either an extensive pre-treatment that delivers a clean holocellulose feed for hydrogenolysis, or a relatively simple pre-treatment such as acid deashing and deal with the presence of lignin in the hydrogenolysis process. This has been the starting point for the two process concepts discussed below.

4. Process concept 1 – with extensive pre-treatment

We first explored the potential of an extensive pre-treatment process to deliver a clean cellulose that meets the feed requirements mentioned above.[37] We based the pre-treatment on an acidic organosolv-like process to ensure proper removal of ash, S,N-extractives and lignin, without suffering the shortcomings of alternative delignification processes.[38] On the one hand, basic pulping processes such as Kraft or caustic pulping were parked because their high pH would command high washing and/or chemical costs to lower the pH to 3.5 for the subsequent hydrogenolysis step. Similarly, lignin-first processes, being reductive catalytic fractionation (RCF) or diol-/aldehyde-assisted fractionation, were parked because they either use an expensive metal catalyst that is sensitive to the biomass contaminants (*e.g.* ash and S,N-extractives) or they use and consume expensive diols or aldehydes as chemicals.[39] We realize that the choice for an extensive pre-treatment process, being our organosolv or any of the alternatives parked, will add significant costs to the manufacture of the glycols in concept 1.

For our organosolv-like pre-treatment, we selected light by-products of the hydrogenolysis, *e.g.*, light alcohol, as co-solvent to (1) allow recovering the lignin and ash by boiling the solvent and (2) compensate inevitable solvent losses by solvent produced by the process. The acidity of the medium would be secured by recycling the acetic acid generated during the pre-treatment step. The overall process would follow the scheme proposed in Fig. 7.

We evaluated this concept by running the pre-treatment under two typical conditions: (A) 50% ethanol in water at 200 °C and (B) 70% acetic acid in water at 180 °C. We then run the isolated pulp for hydrogenolysis in acidic water (pH = 3.3) at 245 °C and 110 bar H_2. Importantly, we purposefully used low catalyst loadings (Ni : WO_x : biomass = 0.6 : 0.15 : 5 wt% in solvent) to maximize the odds of detecting eventual catalyst deactivation, thereby accepting a sub-optimum glycol yield.

According to Fig. 8A, both pre-treatments succeeded in removing the lignin and the ash from poplar wood. They retained nearly all the cellulose in the pulp but dissolved most of the hemicellulose. Both pre-treatments delivered a modest improvement of the overall EG + PG yields on biomass intake, from ~14 wt% for untreated poplar to only 18–19 wt%, about half the >40 wt% (*i.e.* >60% of theory) needed for the affordable MSP discussed earlier (Fig. 8C). However, the yield

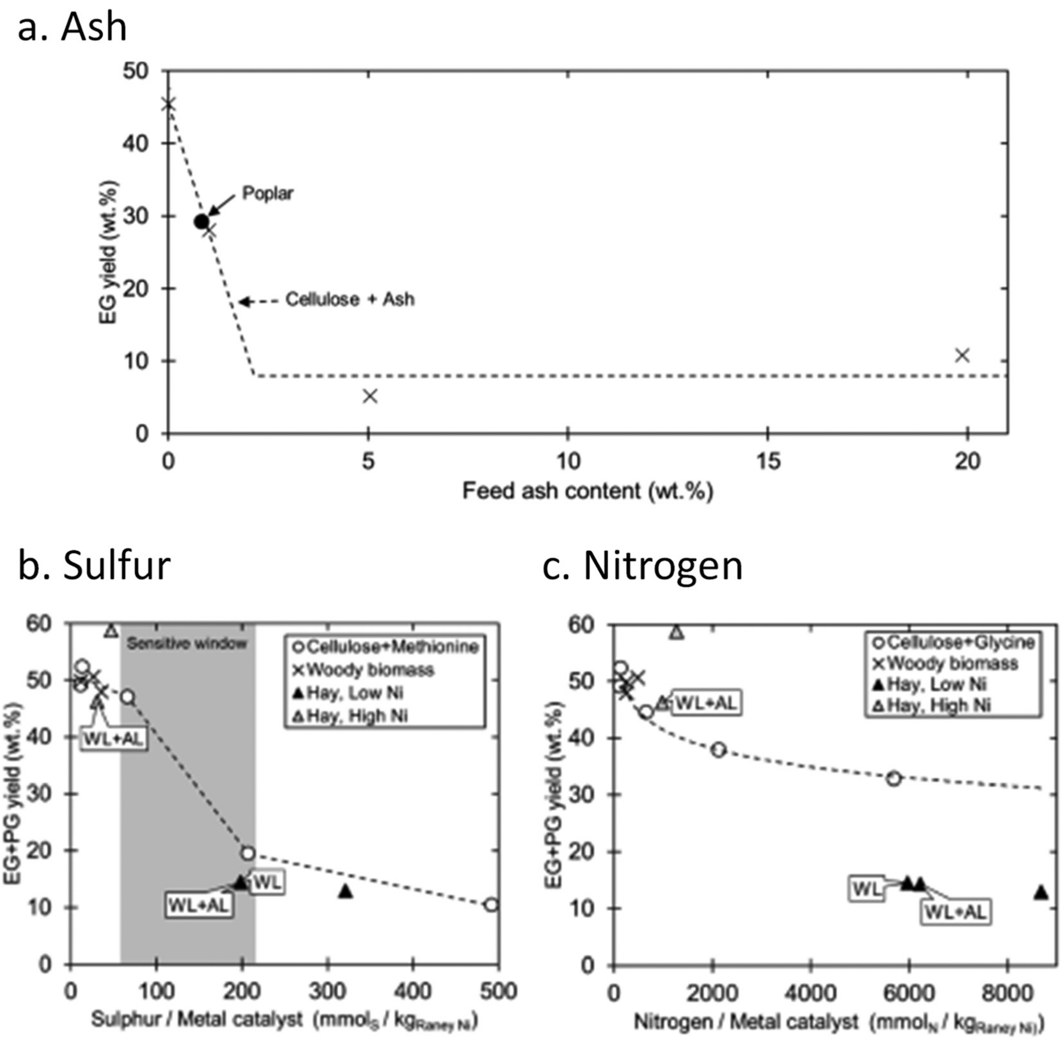


Fig. 6 Detrimental impact of Ash, particularly Ca^{2+} (a) and S or N components (b and c) on the yield of EG during (ligno)cellulose hydrogenolysis.[20,36]

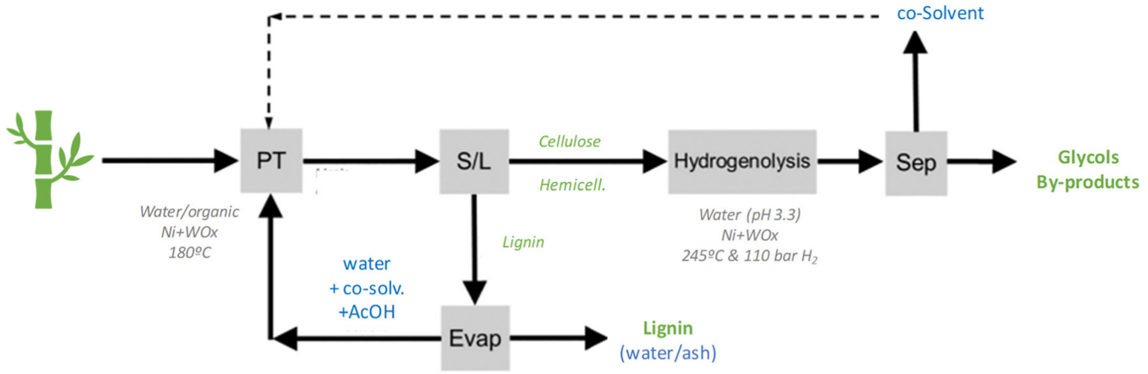


Fig. 7 Process concept for lignocellulose pre-treatment and subsequent hydrogenolysis of the holocellulose to glycols (adapted from ref. 37).

improvement was much more pronounced when expressed per holocellulose fed to the hydrogenolysis reactor, *i.e.* from 21 wt% to 35–42 wt% (Fig. 8C), and compares favourably with the ~38 wt% observed with pure cellulose under these conditions. Apparently, the improved quality of the pulp was largely offset by the losses of hemicellulose during the pre-

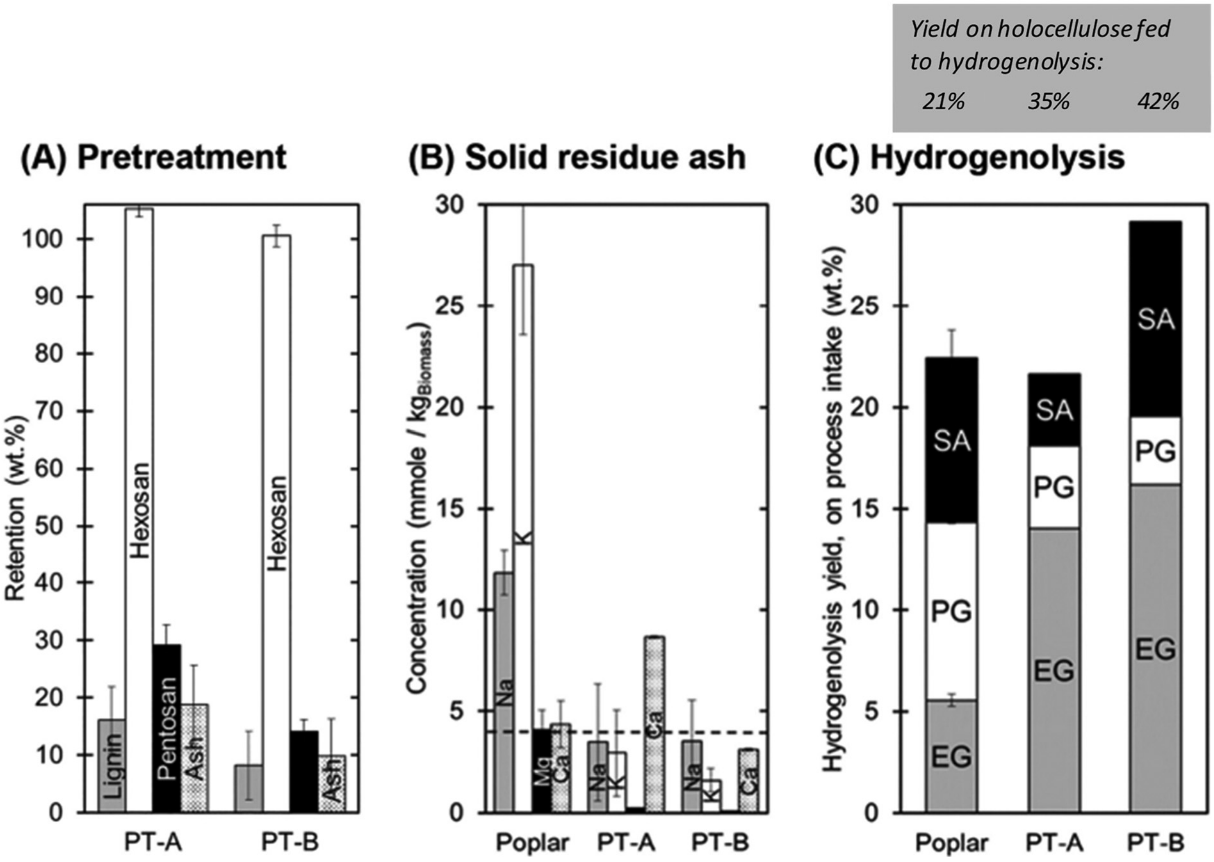


Fig. 8 Validation of extensive lignocellulose pre-treatments for hydrogenolysis to EG and PG (PT-A: 50% EtOH, 200 °C (no acidity), 3 h; PT-B: 70% acetic acid, 180 °C, 1 h; hydrogenolysis: water (pH 3.3), 245 °C, 110 bar H_2, 1 h, biomass : Ni : WOx = 5 : 0.6 : 0.15 wt%).[37]

treatment. It should be recalled that these yields are pessimistic, as they were measured with unfavourably low catalysts loading that was chosen to exacerbate their sensitivity to poisoning.

The removal of hemicellulose is a significant drawback in this specific case. Not only it discards a significant fraction (~20 wt%) of the carbohydrate feedstock, but it also contaminates and devalorise the co-extracted lignin. The removal of hemicellulose can potentially be reduced by optimizing the solvent composition. Running the pre-treatment with lower water content in the EtOH : water mixture, *e.g.*, from 50 to 40%, reduces the removal of hemicellulose but leaves also more lignin on the pulp.[37]

The solvent used above, EtOH and acetic acid, are representative for light alcohols and acids that are generated by the process. Such autogenous production reduces the need for purchasing solvent to compensate for the inevitable physical and chemical losses during the process. However, the autogenous production remains modest at 4–13 wt% on feed. Hence, the process still needs high solvent recovery (>94%), likely through extensive multi-effect evaporation, to minimize the cost of fresh solvent and energy.[37]

The process further needs to run the pre-treatment at fairly low solvent : biomass ratio, preferably <4 : 1, to minimize the energy consumed for solvent evaporation and minimize the solvent loss per kg of glycol produced. Such low solvent : biomass ratio appears to be within reach, *e.g.*, by operating the pre-treatment in counter-current mode; *i.e.* feeding the biomass at one end of the reactor and feeding the fresh solvent at the other end. A series of three stirred reactors operated counter-currently in was reported to extensively delignified the biomass (<5 wt% lignin on the pulp) at solvent : biomass ratio of 5.[25]

Interestingly, the process appeared not to require fine grinding of the wood particles prior to pre-treatment. Only minor reduction in glycol yields was observed for particles of 5 mm and 0.5 mm size.[25]

5. Process concept 2 – with minimal pre-treatment

The process concept discussed above puts all the effort onto the pre-treatment step by designing it such as to deliver the best possible pulp for the hydrogenolysis step. But the lignin was shown not to be critical for the hydrogenolysis. Hence, we considered the option to use the simplest and cheapest possible pre-treatment – a simple acid deashing step – and to shift the effort to the hydrogenolysis step by modifying it such that it can accommo-

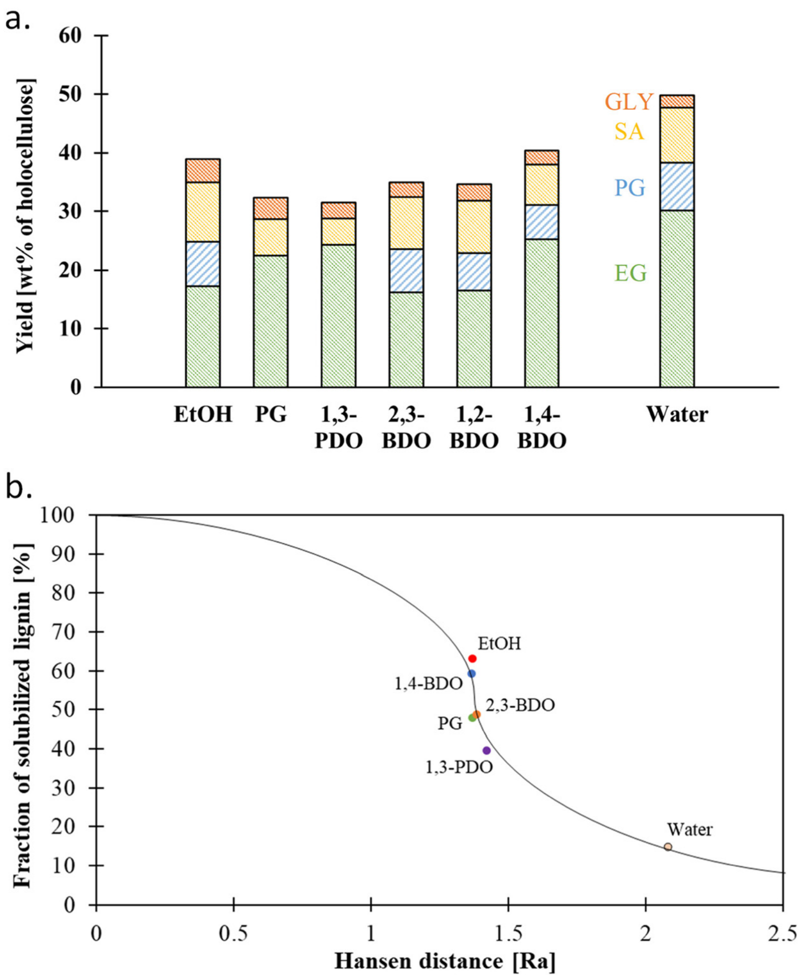


Fig. 9 Hydrogenolysis of deashed wood in water/diol media – yield to glycols (a), yield to soluble lignin (b), (reaction condition: biomass : Ni : W loadings of 5 : 0.6 : 0.15 wt%, 50 wt% organic phase in water, pH(initial) ≈ 3.3, T = 245 °C, t = 2 h, P_{H2} (initial) = 60 bar).[26]

date the deashed wood feed. This is our second approach discussed below. Notice that such process design may not be compatible with grasses and agro-residues as the acid-leaching does not remove the S- and N-contaminants that are present in the extractives and that can poison the Ni catalyst.[19,36]

To test the concept, we washed pinewood with a 10 wt% solution of acetic acid in water at 1 wt% solid loading for 24 h at room temperature. Optimization of this step was postponed to later, if we foresee a viable process. We then subjected the resulting deashed wood to hydrogenolysis in the presence of co-solvent to solubilize the lignin that remains on the pulp and could otherwise foul catalyst and equipment by precipitation. Ideally the hydrogenolysis co-solvent would consist of by-products of the hydrogenolysis reaction, *e.g.*, light alcohols or heavy polyols such as glycerol and heavier sugar alcohols. But it could also include crude glycol products. To ease the product analysis, however, we first considered model components, namely ethanol and various diols.[26]

Such modified hydrogenolysis shows similarities with the Reductive Catalytic Fractionation (RCF) process discussed elsewhere.[38,39] It nevertheless differs on two major points. Firstly, it is operated at higher severity to also hydrogenolyses the cellulose to glycols. Secondly, its acidity and hydrogenation catalyst are protected from ash by the acid-wash.

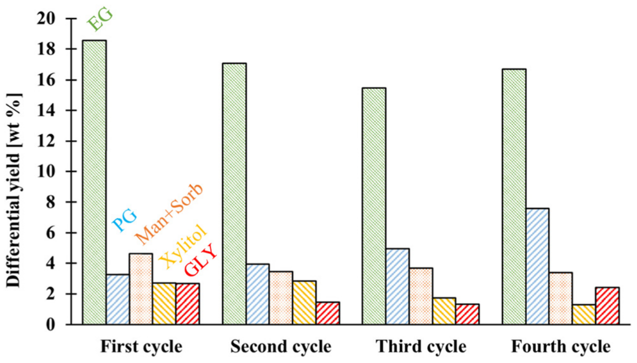


Fig. 10 Catalyst stability evidenced by stable glycol during successive hydrogenolysis of deashed pine wood in water/1,4-BDO solvent mixture performed by successive addition of fresh wood and H_2 to product/catalyst mixture (5 wt deashed pine in 1 : 1 water/BDO, 0.6 wt% Ni, 0.15 wt% W, pH 3.3, 245 °C, 110 bar H_2, 1 h).[28]

5.1 Co-solvent selection

The substitution of half the water with various co-solvents appeared to lower the glycol yields, *e.g.*, from ~38 wt% EG + PG in water to ~25–30 wt% in water/co-solvent (Fig. 9a; ref. 26). Notice that such modest yield is partly due to the high biomass loading (5 wt%) and the low catalyst : biomass ratio (0.12 and 0.03 w/w for Ni and WO_x) that was chosen to better detect eventual deactivation *e.g.* through fouling by lignin.

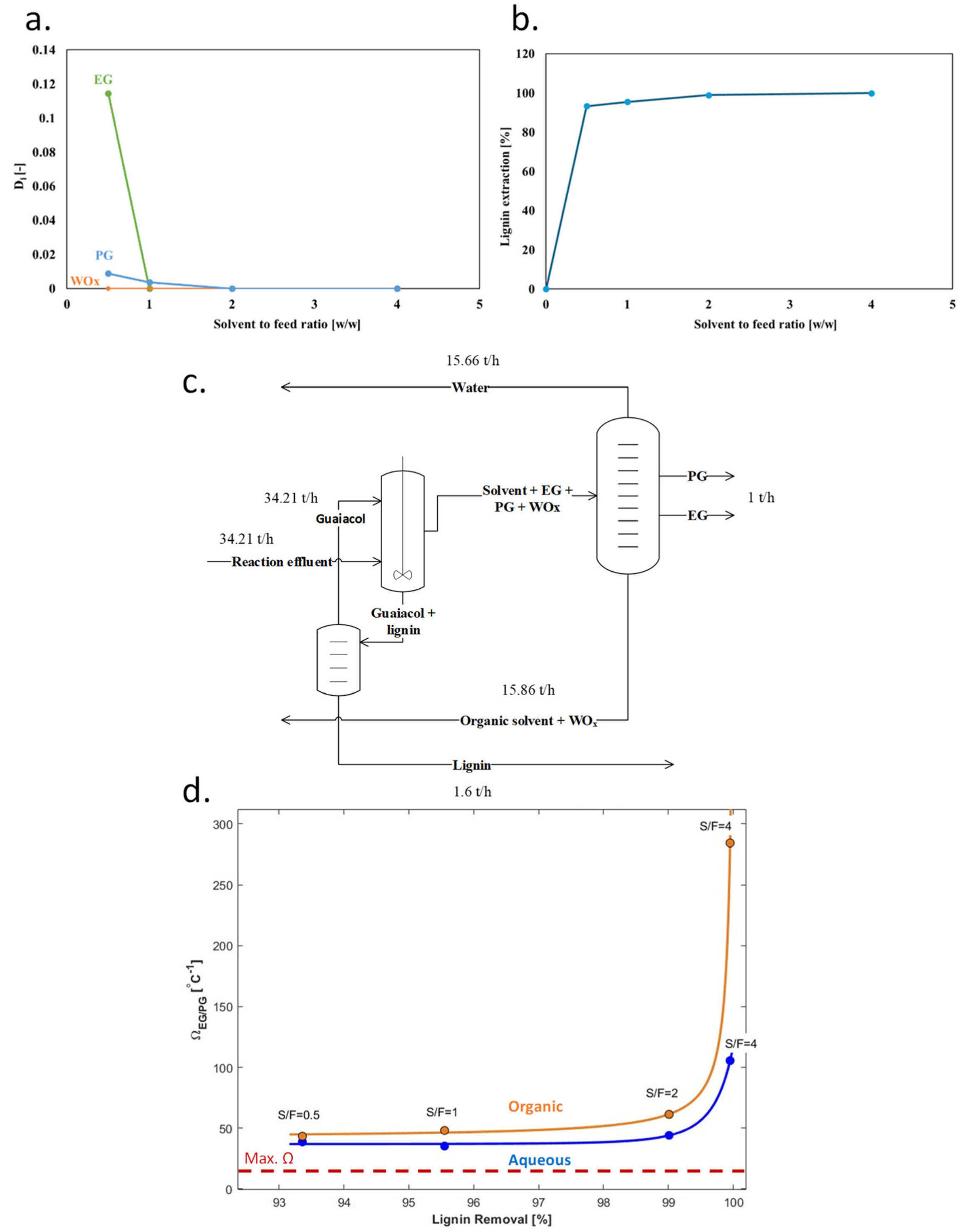


Fig. 11 Work-up of hydrogenolysis effluent by means of liquid/liquid extraction with guaiacol followed by distillation: a and b – lignin extraction efficiency; c – conceptual workup scheme; d: distillation resistance of aqueous and organic phases (hydrogenolysis reaction condition: 10 wt% biomass in 48 wt% 1,4-BDO/50 wt% water/2 wt% acetic acid loading, $pH_{initial} \approx 3.3$, WO_x : Ni : biomass = 0.112 : 0.12 : 1 w/w, 260 °C, P_{H2} (initial) = 60 bar, 1 h).[29]

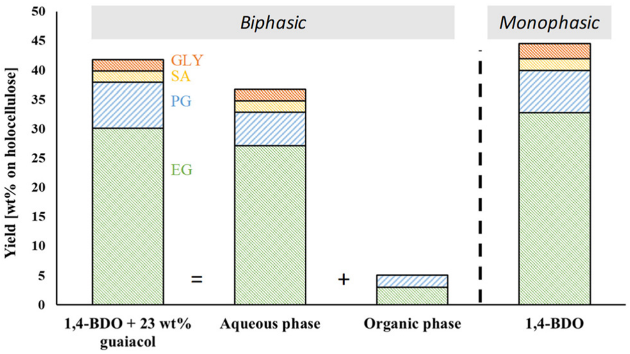


Fig. 12 Hydrogenolysis of deashed wood under bi-phasic conditions (10 wt% pinewood in 25 wt% 1,4-BDO/23 wt% guaiacol/50 wt% water/2 wt% acetic acid, $pH_{initial} \approx 3.3$, WO_x : Ni : biomass = 0.112 : 0.12 : 1 w/w, 260 °C, 60 bar H_2 at 20 °C, 2 h).[29]

Nevertheless, the use of co-solvent succeeded in solubilizing 40–60 wt% of the lignin in the liquid phase, thereby reducing fouling (Fig. 9b).[26] Intriguingly, the dissolved lignin was of sizable M_w, between 300 and 1000 Da, which indicates the absence of extensive depolymerization, in contrast with other studies on reductive catalytic fractionation.[27]

Attention was also paid to the fate of the homogeneous WO_x catalyst in the water/1,4-BDO medium.[28] WO_x appeared to largely (~86%) remain soluble in the water/organic mixture after reaction, with only minor fraction being detected in the solid phase after filtration and drying. The hydrogenolysis catalysts appeared to be fairly stable, even at such low loading, as we observed no severe drop in yields over 4 consecutive cycles of reaction.[28] According to Fig. 10, the EG yields initially dropped by 2% and then stabilized while the PG yields gradually increased.

5.2 Product workup

Obviously, this process concept is complicating the workup of the hydrogenolysis product by contaminating the valuable glycols with lignin. Contacting the reactor effluent with guaiacol appeared to allow for a selective extraction of the oligomeric lignin (M_w > 500 Da) with marginal extraction of glycol and the soluble WO_x catalysts species.[29] The partition coefficients exceeded 10 for the oligomeric lignin while remaining <0.2 for the glycols and <0.01 for WO_x (Fig. 11a and b).

These results open the possibility to work-up the reaction effluent though the following steps (see Fig. 11c):[29]

- Liquid–liquid extraction of the lignin with guaiacol.
- Distillation of guaiacol and co-extracted glycols from the lignin.
- Distillation of the water and glycols from the water-soluble heavy organic products (co-solvent, oxygenated by-products, residual lignin and soluble WO_x) and
- Recycling of water and the heavy organic products (+WO_x and soluble lignin) back to the hydrogenolysis reactor.

The distillation of both aqueous and guaiacol phases appeared to be very demanding, however: both showed a distillation resistance of ~50 °C^{-1} (Fig. 11d with S : F < 2), well above the industrial ceiling of 10–15 °C^{-1},[29] which is mainly due to the high dilution of both aqueous and guaiacol fractions.[29] It is therefore imperative to operate the process with more concentrated streams.

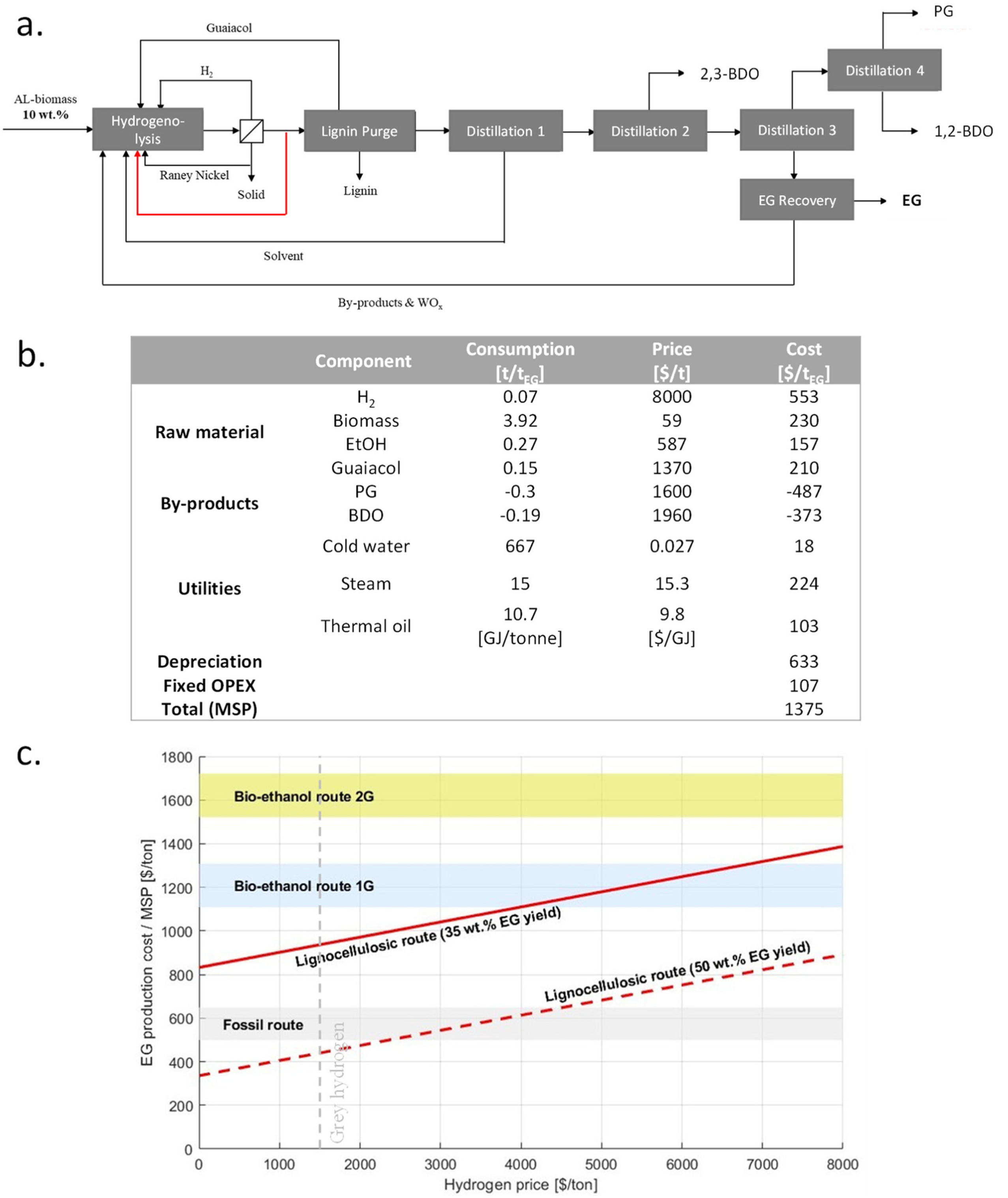
We could of course raise the glycols concentration by raising the wood loading beyond the 10 wt% used here, which is already much higher than used in many other reports. But the semi-batch operation reported earlier (Fig. 10) presents another complementary solution. We can build up the concentration of glycol and lignin in the reactor effluent by recycling the product stream back to the reactor prior to working it up, or by continuously feeding the biomass in a well-mixed tank and withdrawing the small fraction the liquid product for work-up (also called Continuous Stirred Tank Reactor, CSTR). The semi-batch operation indeed resulted to a gradual build-up of concentration of EG + PG from 0.8 wt% in the first run to 3.4 wt% in the fourth run, all without significant loss in glycol yields (Fig. 10).

But there is another way to increase the glycol yield, namely replacing a part of the BDO/water medium with guaiacol and running the process under biphasic conditions. This is the subject of the next section.

5.3 Biphasic hydrogenolysis

The various results discussed above clearly indicated the need to operate the hydrogenolysis at high glycol concentration. We explored the possibility to achieve that by adding guaiacol to the BDO/water medium and running the process under biphasic conditions.[29] Single batch experiments with half the BDO being substituted with Guaiacol slightly decreased the EG + PG yields from ~40 to ~38 wt% (Fig. 12). In fact, this biphasic operation produced less sugar alcohol and more PG than in the monophasic BDO/water mixture. Most of the glycols ended up in the aqueous phase upon cooling (Fig. 12). We further improved the biphasic operation by running four consecutive runs with fresh feed (semi-batch operation) to build up the EG + PG concentration from ~3 to ~11 wt%, thereby also building up the lignin concentration from ~1.5 to 3.8 wt%. Most of the glycols ended up in the aqueous phase after cooling, while most of the lignin was extracted in the guaiacol phase. Optimization of the medium composition, particularly the guaiacol and catalyst content, was not investigated but may further increase the product yields and concentration. The biphasic operation presents a drawback when run as described here: the guaiacol solvent undergoes partial hydrogenation upon recycling. This requires further optimising the reaction conditions and/or revisiting the choice of extraction solvent.

A process flow scheme was built in Aspen based on these results, and used to develop a preliminary economic analysis (Fig. 13a). The process was scaled to convert 1175 kt a^{-1} of biomass to 300 kt a^{-1} EG and ~150 kt a^{-1} of PG + BDO as by-product, which corresponds to an overall glycol yield of 38 wt% on biomass. The total investment cost was estimated at $950 Mill, based on energy transfer duties of the Aspen model. The resulting minimum selling price of EG amounted to $1375 per t (Fig. 13b). The economics appeared to be particularly sensitive to total investment cost (see depreciation in Fig. 13b), H_2 price, and overall Glycol yields, which includes the credit for PG and BDO by-products. Notice that this MSP does not dramatically deviate from those reported in the economic potential analysis, namely \$1000 per tonne for 60% of theoretical glycol yield or ~40 wt% on biomass intake.



	Component	Consumption [t/t_{EG}]	Price [\$/t]	Cost [\$/t_{EG}]
Raw material	H_2	0.07	8000	553
	Biomass	3.92	59	230
	EtOH	0.27	587	157
	Guaiacol	0.15	1370	210
By-products	PG	-0.3	1600	-487
	BDO	-0.19	1960	-373
Utilities	Cold water	667	0.027	18
	Steam	15	15.3	224
	Thermal oil	10.7 [GJ/tonne]	9.8 [\$/GJ]	103
Depreciation				633
Fixed OPEX				107
Total (MSP)				1375

Fig. 13 Conversion of lignocellulose to ethylene glycol (EG) *via* biomass deashing and biphasic hydrogenolysis – a: process flow scheme, b: economic analysis (for 300 kt a^{-1} EG), c: comparison with EtOH and fossil routes (EtOH price: \$500 (1G) or \$650 (2G) 1 per tonne and H_2 priced at \$8 per kg). Adapted from ref. 36.

This route appeared to be cheaper than the route based on cellulosic ethanol (Fig. 13c). It also showed good potential to beat the route based on 1G ethanol, and possibly the fossil route, after credible reduction in either of the key variables, *i.e.* H_2 price, total investment cost or glycol yields. Consequently, it could be wise to use cheap fossil H_2 in the first few plants and switch to more expensive green hydrogen at later stage, when the technology has been improved and made cheaper.

Further reduction in cost should be sought; *e.g.*, in raising the glycol yields beyond the 38 wt% assumed here, enabling the use of higher biomass loading than the 10 wt% used here and optimising the composition of the reaction medium to enable higher glycol concentration.

6. Conclusions

Ethylene glycol (EG) is arguably one of the most promising chemical intermediates to be derived from sugars. Its manufacture *via* hydrogenolysis of glucose and lignocellulose promises to be cheaper than the alternative fermentation route, provided it operates at high yield.

Lignocellulose is no suitable feedstock without pre-treatment, however, for the hydrogenolysis suffers from the presence of alkali earth, S and N in the feedstock, and to a lower extend from its lignin content. Two archetype mitigation approaches were investigated.

The first one was based on extensive and costly organosolv pre-treatment followed by conventional aqueous hydrogenolysis. The pulp produced by the pre-treatment appeared to be of good quality as it was efficiently converted to EG + PG: ~40 wt% yield on contained sugars, under demanding conditions of 5 wt% biomass loading and low catalyst loading. However, the pre-treatment already removed most of the hemicellulose, which led to a modest glycol yield of ~20 wt% when expressed on overall biomass intake. Improvements should be sought in (a) optimising to pre-treatment conditions to minimize the hemicellulose loss, (b) exploring strategies to raise the glycol yields and (b) exploring strategies to raise the glycol concentration in the product effluent.

The second approach used simple and cheap acid leaching followed by hydrogenolysis in an aqueous/organic medium to solubilized the residual lignin. The hydrogenolysis step appeared to run slightly less efficiently than in water, but used the full holocellulose of the biomass. It thereby delivered higher glycol yields of 30 wt% at 5 wt% biomass loading and low catalyst loading. Liquid extraction could remove the lignin from the hydrogenolysis effluent, while operation in CSTR and under bi-phasic conditions could increase the high glycol concentrations. A TEA analysis suggest that such operation could deliver EG at ~$1400 per tonne at measured performances, and could come close to the EG market price of $600–1000 per tonne with improved yield and cheap renewable H_2.

Conflicts of interest

The authors have no conflict of interest to report.

Data availability

The data are reported either in the perspective self, *e.g.* in tables, or in the papers referred to.

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