Letter

Interdependence of Solvent and Catalyst Selection on Low Pressure Hydrogen-Free Reductive Catalytic Fractionation

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ABSTRACT: Hydrogen-free reductive catalytic fractionation (RCF) is a promising method to produce aromatic compounds directly from native biomass without the use of external hydrogen gas. In this work, we show that by using high boiling point diols as a solvent in hydrogen-free RCF, reaction pressures can be reduced by an order of magnitude compared to conventional RCF with methanol and hydrogen gas, while still producing appreciable aromatic monomer yields. Importantly, the use of diols with secondary alcohol functional groups increases hydrogenation activity on Ru/C, Pt/C, and Ni/C, measured by the yield of aromatic compounds with saturated propyl side chains, compared to processing in ethylene glycol, indicating that the choice of solvent and catalyst together can be tuned to control product selectivity of aromatic monomers in RCF.

KEYWORDS: *Lignin, transfer hydrogenation, lignin-first biorefining, lignin valorization*
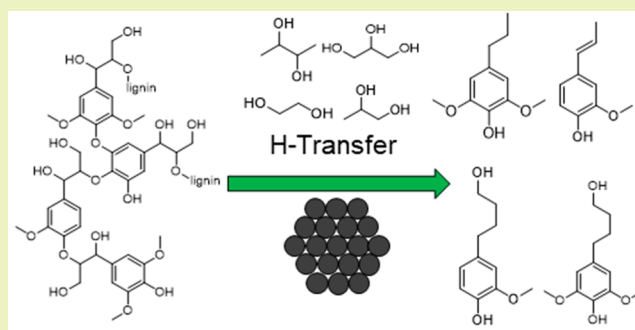
INTRODUCTION

The development of lignin-first biorefining processes has garnered significant attention in the past decade as a means to fractionate biomass and valorize both lignin and polysaccharides.[1−4] The intense global effort to this end includes the popular reductive catalytic fractionation (RCF) approach, where a polar protic solvent (often methanol) selectively extracts lignin from whole biomass, and the extracted lignin fragments are catalytically reduced with supported metal catalysts (Ru, Pd, Pt, Ni, etc.) to produce a stable lignin oil and a carbohydrate-rich, delignified pulp.[1−3]

In a recent techno-economic analysis (TEA) and life cycle assessment (LCA) of the RCF process, we highlighted critical steps to enable economic feasibility and to reduce environmental impacts.[5] Modeling methanol as a solvent and external H_2 as the hydrogen source, the reactor capital cost associated with the significant pressures arising from the methanol vapor pressure and H_2 gas was identified as a major economic driver. Two additional modeled cases to reduce the reactor pressure focused on hydrogen-free processing (i.e., without the use of external H_2 gas) and the use of ethylene glycol (EG) as an alternative solvent. It was estimated that the capital cost in these cases could be reduced by 24% and 28%, respectively, demonstrating the potential for both process options.

Processing either in hydrogen-free conditions or lower vapor pressure solvents than MeOH has been reported, but few studies to date have examined them in combination. Specifically, appreciable monomer yields in hydrogen-free

reactions have been reported over a variety of solvent−catalyst systems (e.g., MeOH-Ni/C, 2-propanol/H_2O-Raney Ni, EtOH/H_2O-Pd/C, and MeOH/H_2O-Pt/Al$_2$O$_3$).[6−9] EG has been the primary low vapor pressure solvent reported for RCF processes in the presence of external hydrogen gas, with multiple works reporting comparable monomer yields when processing in MeOH or EG.[10−12] To combine these two concepts, He et al. studied hydrogen-free reactions with EG, using sulfuric acid with Ru/C to obtain 27% monomer yields at 185 °C and atmospheric pressure.[13] They also observed significantly reduced monomer yields with Pd/C and Ni/SiO$_2$ catalysts at the same conditions. In addition, a recent study from our group demonstrated that catalyst choice must be considered when evaluating hydrogen-free reactions.[14] In combination with the results reported by He et al., it is likely the case that the solvent−catalyst pairing must be considered when evaluating these reactions.

In hydrogen-free RCF reactions, transfer hydrogenation is likely the mode by which the solvent contributes the hydrogen equivalents needed for reduction. To that end, transfer hydrogenation has been intensively studied among various
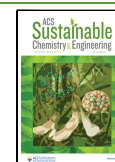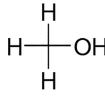
Table 1. Reichardt Parameter, Boiling Point, and Vapor Pressures of Studied Solvents at 225 °C[a]

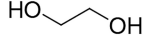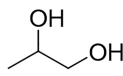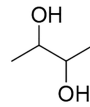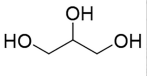| Compound & Structure	Methanol	2-Propanol	Ethylene Glycol	1,2-Propanediol	2,3-Butanediol	Glycerol
Reichardt Parameter (E_T^N)	0.76	0.55	0.79	0.72	0.65	0.81
Boiling Point (°C)	64.7	82.6	197.3	187.6	182.3	290.0
Vapor Pressure at 225 °C (Bar)	62.22	40.16	2.16	2.97	3.58	0.18

[a]Reichardt parameters values are from ref 18. Vapor pressures were calculated via the Antoine equation, with Antoine parameters taken from the NIST WebBook.

reactions pertinent to biomass conversion,[15,16] and a common theme in these studies is that secondary alcohols exhibit greater activity for transfer hydrogenation. For example, work by Vlachos et al. observed a greater than 2-fold yield improvement of 2-methylfuran in the hydrodeoxygenation of furfural over Ru-based catalysts when using 2-butanol or 2-pentanol as the solvent compared to the corresponding primary alcohols.[17] In the RCF literature, Rinaldi et al. pioneered the use of isopropanol as a hydrogen donor, which to our knowledge is the primary work reported to date describing the use of secondary alcohols for hydrogen-free RCF biorefining.[8]

RESULTS AND DISCUSSION

In the present work, we sought to examine hydrogen-free RCF with low vapor pressure solvents across a range of catalysts to validate if RCF reaction pressures can be significantly reduced while identifying solvent−catalyst combinations that promote transfer hydrogenation without jeopardizing monomer yield. Batch reactions were conducted with EG, 1,2-propanediol (1,2-PDO), 2,3-butanediol (2,3-BDO), and glycerol as low vapor pressure solvents. EG, 1,2-PDO, and 2,3-BDO were chosen as solvents to allow for comparison of diols with 0, 1, and 2 secondary alcohol functional groups, respectively (Table 1). We also included glycerol as it is a commonly used, biobased, low vapor pressure solvent that also contains a secondary alcohol group. Notably, a seminal study from Schutyser et al. reported birch delignification trended with the Reichardt parameter (E_T^N), which is an indicator of solvent polarity.[10] The solvents we investigated here from Table 1 exhibit E_T^N values similar to that of MeOH, which could suggest comparable delignification to MeOH, unlike secondary alcohols such as 2-propanol which have lower E_T^N values.[18]

To screen the performance of the high boiling point solvents, RCF experiments were conducted using 75 mL batch reactors at 225 °C, for 3 h reaction time after heat-up to the target temperature, with a 10:1 (w/w) biomass-to-catalyst ratio, and with a hybrid poplar feedstock used and characterized previously.[14] These conditions were chosen to compare with hydrogen-free results with MeOH.[14]

Reaction pressures for experiments under an inert or hydrogen atmosphere were recorded across all the experiments

conducted in this work. As expected, observed reactor pressures inside 75 mL batch reactors were significantly reduced processing in these solvents compared to in MeOH, both when initially charged with 30 bar of hydrogen or in hydrogen-free conditions (Figure 1). Hydrogen-free reaction
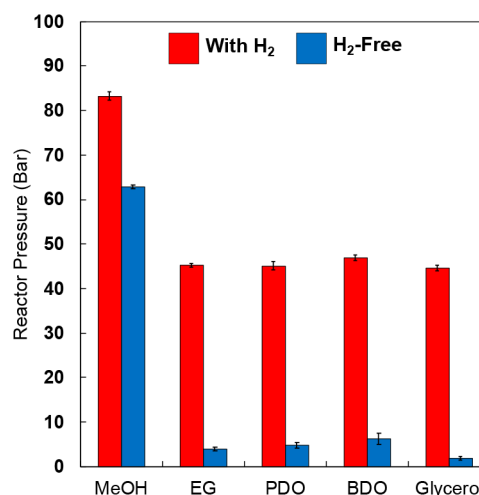
Figure 1. Observed RCF reactor pressure inside 75 mL batch reactors at 225 °C when initially charged with 30 bar of H_2 (red) or without hydrogen (blue). These reactions represent those from all four catalysts tested in this work; thus, each bar represents between 16 and 25 independent reactions. Reaction conditions: 1 g of biomass, 20 mL of solvent, and 100 mg of catalyst. Reactor pressure was recorded 1 h after reaching 225 °C. Error bars represent 95% confidence intervals. Tabulated values are reported in Table S2.

pressures ranged between 2 and 6 bar across these solvents after an hour of reaction, which is an order of magnitude less than those recorded in hydrogen-free reactions in MeOH (~60 bar). This also confirms that hydrogen-free RCF pressures are mainly controlled by solvent vapor pressure under typical laboratory conditions.

Initial catalyst−solvent performance studies for hydrogen-free reactions were conducted with EG as the solvent (Figure 2A). With external H_2, similar monomer yields were obtained for reactions with Ru/C, Pd/C, Pt/C, and Ni/C of ~21%,
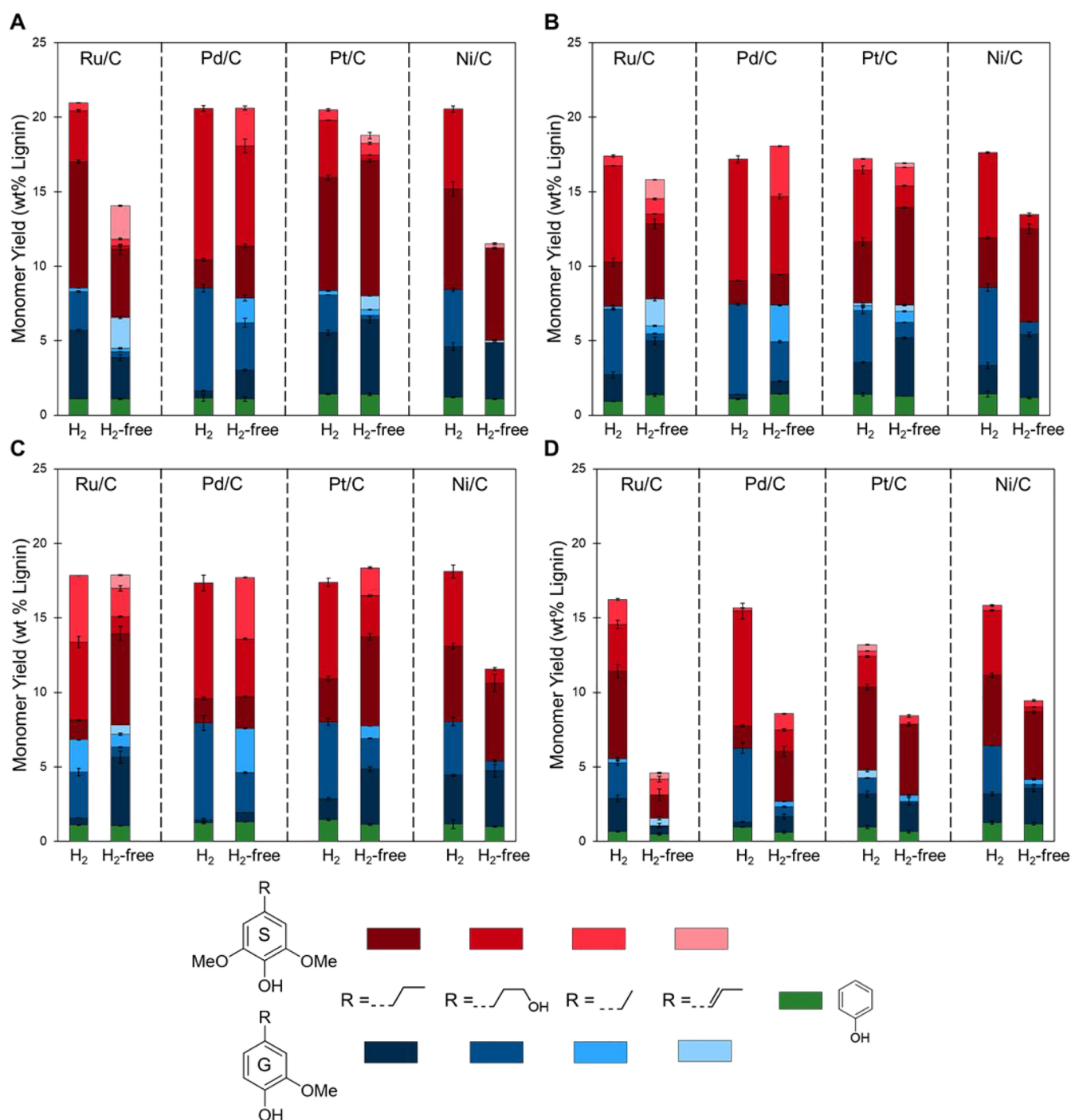
Figure 2. Monomer yields for reactions with external H_2 gas (left) and under H_2-free conditions (right) in (A) EG, (B) 1,2-PDO, (C) 2,3-BDO, and (D) glycerol as a solvent. RCF conditions: 1 g of poplar, 100 mg of catalyst, 20 mL of solvent, 225 °C, and 3 h. Reactions with H_2 were initially charged with 30 bar H_2. Reactions without H_2 were conducted under atmospheric He. Error bars represent the range of duplicate trials. Tabulated yields are reported in the Tables S3−S7.

which agree with previous reports that observe similar monomer yields with sufficient hydrogen pressure, regardless of catalyst choice.[14,19] In hydrogen-free reactions, similar monomer yields to reactions with external hydrogen were achieved with Pd/C and Pt/C, while reduced monomer yields were observed in Ru/C and Ni/C (14.1% ± 0.8% and 11.5% ± 0.3%). This follows trends for hydrogen-free reactions with MeOH from our previous work.[14]

Product distributions on all four of these catalysts differed from reactions with external hydrogen to hydrogen-free. While total monomer yield was retained, reactions with Pd/C exhibited increased yields of propyl and ethyl-substituted monomers, while those of propanol-substituted monomers were reduced, which is also consistent with reactions in MeOH.[14] Reactions with the 3 other catalysts exhibited near complete disappearance of propanol-substituted monomers,

while unsaturated isoeugenol and propenylsyringol products were formed, indicating low hydrogen transfer activity.

Reactions in 1,2-PDO (Figure 2B) with external hydrogen gas produced identical monomer yields with all four catalysts of ~17%. The lower apparent monomer yields follow with 1,2-PDO having a lower E_T^N than EG, which likely indicates lower lignin extraction with 1,2-PDO. However, hydrogen-free reactions in 1,2-PDO exhibited improved hydrogen transfer activity compared to EG. Hydrogen-free monomer yields in Pd/C and Pt/C matched the monomer yields with hydrogen, while hydrogen-free monomer yields with Ru/C fell just short of the value with hydrogen (15.8 ± 0.7%). Also, the hydrogen-free yields with both Ru/C and Ni/C exceeded those observed in EG (15.8% vs 14.1%) and (13.4% vs 11.5%) despite this likely lower lignin extraction. Improved hydrogen transfer, attributed to the secondary alcohol, is also seen in the functionality of monomers produced in hydrogen-free reactions where propanol-substituted monomers remain present in reactions with Ru/C, Pt/C, and Ni/C, unlike with EG.

With external hydrogen gas, reactions in 2,3-BDO (Figure 2C) exhibited similar performance with 1,2-PDO and produce similar monomer yields between all four catalysts of ~17.5%. Further improvement in hydrogen transfer capacity is likely observed with 2,3-BDO, as the hydrogen-free monomer yields with Ru/C, Pd/C, and Pt/C match those with external H_2 gas present, and selectivity to unsaturated monomers, especially with Ru/C, is decreased compared to reactions in EG and 1,2-PDO. Notably, the product distributions for reactions with hydrogen and Ru/C differ significantly between EG, 1,2-PDO, and 2,3-BDO. With EG, propyl-substituted monomers are the main product (62.4% ± 0.9% selectivity), while selectivity to propyl monomers decreased to 27.4%, and propanol-substituted monomers are the main products (62.5%) with 1,2-PDO. For 2,3-BDO, selectivity to propyl monomers is further decreased to 9.9%, with propanol monomers (46.7%) and ethyl-substituted monomers (37.2%) becoming the main products. The high selectivity to ethyl products is particularly noteworthy, as ethyl products are only produced in low amounts with ~4% selectivity with EG and 1,2-PDO and were not observed in our previous study for reactions with MeOH. This shift in selectivity from propyl-substituted monomers to propanol monomers is also seen with Pt/C. Reactions with EG produce propyl-substituted monomers with high selectivity (55.8%), while this decreases to 36.4% with 1,2-PDO and 24.7% for 2,3-BDO, and propanol monomer selectivities are 48.1% and 66.9%, respectively.

Reactions with glycerol (Figure 2D) show lower performance than the other three solvents. Reactions with Ru/C, Pd/C, and Ni/C with external hydrogen gas exhibited monomer yields of ~16%, while reactions with Pt/C produced 14% monomer yields. These yields are unexpected as glycerol exhibits a higher E_T^N value than EG, and following the trends observed with the other solvents, lignin extraction potentially should be higher and lead to higher monomer yields. Monomer yields for hydrogen-free reactions were reduced by at least 40% across all the catalysts, which indicate low hydrogen abstraction activity from glycerol.

Outside of the reduced lignin extraction capability with glycerol, the lower observed monomer yields could also arise due to mass transfer limitations with using glycerol as the solvent as glycerol has an order of magnitude greater viscosity than EG at 100 °C.[20,21] Reactions with 2 times Ru/C

(Supplemental Note 4 in the Supporting Information) produced increased monomer yields in glycerol both for reactions with external hydrogen and in hydrogen-free conditions, while reactions with external hydrogen gas added for EG, 1,2-PDO, and 2,3-BDO did not produce higher monomer yields with increased catalyst loading. This could be indicative of slow transport of lignin fragments to the catalyst surface in the glycerol solvent. Recent work by Epps et al. reported monomer yields between 10% and 40% for hydrogen-free reactions with glycerol on various isolated lignin substrates with Ru/C.[22] However, these reactions were conducted at 250 °C for 15 h and at a ~2:1 (w/w) lignin−catalyst ratio, making it difficult to directly compare why H-transfer is different between the two conditions.

■ CONCLUSIONS

RCF reactions were conducted with and without external hydrogen with EG, 1,2-PDO, 2,3-BDO, and glycerol to determine if RCF can be conducted at low operating pressures while maintaining appreciable monomer yields. Screening reactions were performed with four common catalysts to identify potential solvent−catalyst combinations that might improve hydrogen transfer. Hydrogen-free reactions with these four solvents at 225 °C reduced operating pressures by more than an order of magnitude compared to similar reactions in MeOH. In the presence of external hydrogen, these solvents produced comparable monomer yields regardless of catalyst choice, but a significant difference in performance was observed for hydrogen-free reactions. Hydrogen-free reactions with EG, 1,2-PDO, and 2,3-BDO retained identical monomer yield with Pd/C, but monomer yield and functionality varied significantly on Ru/C, Pt/C, and Ni/C between the three solvents. The presence of secondary alcohol groups with 1,2-PDO and 2,3-BDO led to incremental improvement in hydrogen transfer for hydrogen-free reactions with 2,3-BDO reactions producing identical monomer yield with hydrogen or without for Ru/C, Pd/C, and Pt/C. Hydrogen-free reactions in glycerol demonstrated significantly lower monomer yields, despite containing a secondary alcohol group. Ultimately, these results show that RCF can be conducted at near atmospheric operating pressures and that hydrogen-free performance can be improved by the choice of solvent−catalyst pairing.

The results from this work motivate further investigation of hydrogen-free processing of RCF, with consideration for both fundamental insights and process scale-up. The improved hydrogen-free monomer yields with 2,3-BDO prompt the need for fundamental insight into how the diol solvents improve hydrogen transfer, by detailing both the interactions between the catalyst and solven, and the mechanism of hydrogen transfer from the solvent to the aromatic fragments in RCF. While hydrogen transfer is commonly proposed to proceed either via metal hydride transfer or direct transfer such as the Meerwein−Ponndorf−Valley mechanism,[15] improvements on in situ characterization of the liquid phase during the reaction will be needed to confirm any potential mechanism. Furthermore, excellent hydrogen-free performance has been observed with Pd/C across multiple solvents (MeOH, EG, 1,2-PDO, and 2,3-BDO). While Pd/C may not ultimately be commercially viable for this process, fundamental understanding of these hydrogen-transfer mechanisms on Pd/C could provide insight into designing improved catalysts for hydrogen-free processing. From a processing point of view, further insight into the solvent's interactions with biomass,

such as quantification of delignification and stability of the carbohydrate fractions, is needed. This will require experimental systems capable of keeping the catalyst and biomass physically separated, such as a catalyst basket reactor.[23] Also, now that hydrogen-free RCF processing with high boiling point solvents has been effectively demonstrated, scale-up needs to be considered regarding how to effectively use these types of solvents.[24] These challenges include efficient separation of lignin oil from the diols, recovery of the diol solvent from soluble carbohydrate compounds formed during reaction, and regeneration of the solvent after dehydrogenation during hydrogen-transfer reactions, among others.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c07394.

> Materials and methods, tabulated data for figures in main text, reaction data with ethylene glycol at 200 °C, catalyst loading experiments, and solvent consumption during reaction (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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