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Research Article

Lignin-Derived Phenolic Compounds and Water Are Effective Cosolvents for Reductive Catalytic Fractionation

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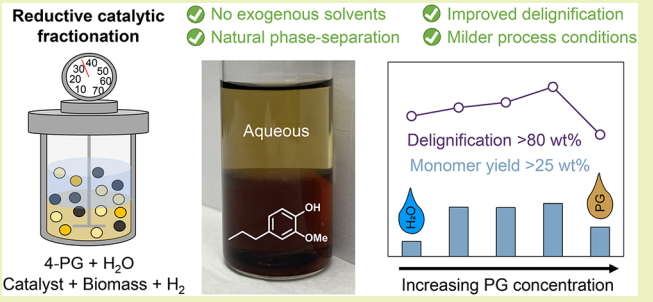
ABSTRACT: Reductive catalytic fractionation (RCF) is an effective lignin-first biorefining method to extract lignin as a stabilized oil from lignocellulosic biomass. To realize RCF at scale, process modeling has shown that minimizing the use of exogenous organic solvents is critical. To this end, here we investigate the ability of lignin-derived monomers to act as either solvents or cosolvents for RCF. We begin by examining the influence of lignin-derived aromatic compounds (4-propylguaiacol, 4-propylphenol, and propylbenzene) on RCF monomer yields and subsequently extend our analysis to mixtures of 4-propylguaiacol and either methanol or water. We demonstrate that 4-propylguaiacol is an effective solvent for lignin extraction and depolymerization during RCF, especially when used in combination with water as a cosolvent. Cosolvent mixtures of 4-propylguaiacol and water enable up to 81% lignin extraction, monomer yields up to 25 wt %, and postreaction phase separation. However, unlike methanol, water as a cosolvent fails to inhibit aromatic ring hydrogenation when conducted over Ru/C as a catalyst, potentially leading to excess hydrogen consumption in a process utilizing this approach. Nonetheless, these results suggest a promising strategy for eliminating external organic solvents from RCF by utilizing mixtures of lignin-derived compounds and water as alternative extraction solvents.



KEYWORDS: *reductive catalytic fractionation, lignin valorization, lignin, lignocellulose, biorefining*

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INTRODUCTION

Reductive catalytic fractionation (RCF) is a lignin-first biorefining technique that efficiently separates lignin from biomass polysaccharides while minimizing undesired condensation reactions, thereby generating a monomer-rich phenolic oil at high yields and a solid holocellulose pulp.[1−5] RCF involves processing raw biomass with a redox-active catalyst (e.g., Ru, Pd), an extraction solvent, and a hydrogen source under pressure to yield a depolymerized oil rich in aromatic monomers (e.g., 4-propylguaiacol (PG), 4-propylsyringol, etc.).[4] In the past decade, multiple studies have emphasized the role of solvent choice in influencing lignin extraction and the economic and environmental feasibility of RCF.[6−13] Unfortunately, many common RCF solvents, namely polar protic alcohols, have high vapor pressures under viable lignin extraction conditions, tend to undergo degradation, and exhibit significant cost and energy input for their separation from lignin-derived products.[9,14]

These inherent process limitations motivate technologies that either minimize or altogether eliminate the use of exogenous organic solvents in the RCF. A particularly promising candidate is water due to its abundance, low vapor pressure, and stability relative to common organic alcohols, such as methanol. Further, water exhibits limited miscibility with lignin-derived compounds at ambient conditions, often being utilized as a liquid−liquid extraction solvent for the separation of sugars and polyols from lignin-derived phenolics after RCF.[6−8,13,15] To these points, both pure water[6,15] and water/alcohol[7,8,13] mixtures have been previously examined for RCF, and generally promote increased extent of pulp delignification relative to alcohols alone.

Another promising strategy aimed at minimizing the use of exogenous organic solvents during RCF is known as "solvent looping," wherein depolymerized lignin oils are recycled and utilized as cosolvents for RCF to minimize solvent separation costs. Multiple groups have examined this concept utilizing both alcohols[16,17] and alcohol/water mixtures;[18,19] however, there has yet to be work conducted examining whether

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alcohols need to be present for efficient solvent looping RCF. This reveals a promising opportunity wherein the use of lignin-derived phenolic mixtures and water may help to eliminate the use of external organic solvents in RCF.

To this end, here we investigate a variety of aromatic model substrates [PG, 4-propylphenol (PP), and propylbenzene (PB)], meant to represent lignin-derived phenolic mixtures at varying levels of deoxygenation, as potential lignin extraction solvents. These models were initially used to probe the effect of aromatic solvent characteristics on monomer yields. Our results suggest some correlation between monomer yield and solvent polarity, suggesting this trend extends beyond traditional polar protic solvents to phenolic compounds as well.[6] In addition, we examined mixtures of PG and conventional RCF solvents (methanol and water) to improve lignin monomer yields. Notably, mixtures of water and PG result in increased biomass solubilization and monomer yields relative to methanol while enabling postreaction phase separation akin to that resulting for *n*-butanol/water mixtures.[8] However, this promising performance came at the cost of aromatic hydrogenation, which is not inhibited in cosolvent mixtures containing PG and water as in systems with protic alcohols, thereby motivating future work in designing selective hydrogenation catalysts for water-based RCF. Nonetheless, PG/water extraction mixtures have the potential to greatly improve one of the main techno-economic and environmental impact barriers toward the implementation of an RCF biorefinery by eliminating the requirement for exogenous organic solvents.

EXPERIMENTAL PROCEDURES

Materials. Poplar biomass was acquired from Idaho National Laboratory. It was milled and sieved <2 mm in size prior to use. Catalysts included 5 wt % Ru/C and 5 wt % Pd/C acquired from Sigma-Aldrich and were used as received. Solvents, including methanol (Fisher Scientific, ACS grade), ethanol (Koptec, 200 proof), tetrahydrofuran (Sigma-Aldrich, ≥99.9%), 2-methoxy-4-propylphenol (Sigma-Aldrich, ≥99%), 4-propylphenol (Tokyo Chemical Industry, >99.0%), and propylbenzene (Sigma-Aldrich, 98%), were also used as received. Ultra high purity nitrogen and hydrogen were both supplied by Matheson. The chosen external standard for monomer quantification was 1,3,5-tri-*tert*-butylbenzene (Tokyo Chemical Industry, ≥98.0%).

Biomass and Pulp Compositional Analyses. Compositional analysis of pre- and postreaction biomass/pulp samples was performed according to the relevant National Renewable Energy Laboratory (NREL) laboratory analytical procedures.[20,21] Prior to analysis, postreaction pulps were separated from catalyst powder via sieving between 105 and 140 mesh. Due to limited available pulp masses, postreaction compositional analyses were conducted using less solids than reported in the cited analytical procedure (100 mg vs 300 mg).

Reductive Catalytic Fractionation Experiments. Experiments were completed using 75 mL Parr autoclave reactors operated using a Parr 5000 Multiple Reactor System. In a standard reaction, a reactor was loaded with a Teflon stir bar, 150 mg of catalyst (wetted with 150 mg of water to prevent autoignition), a relevant quantity of poplar biomass, and 30 mL of total solvent. It was then sealed and pressure tested with nitrogen to 80 bar and subsequently depressurized. Magnetic stirring was then set to 700 rpm and the system was pressurized to 30 bar with hydrogen. The system was then heated to 225 °C over the course of 30 min and held for 3 h. Postreaction, each reactor was rapidly quenched to room temperature in ice. The postreaction pressures were measured at or near ambient temperature (<40 °C). Postreaction, each reactor was depressurized and unsealed. The solids were filtered through a tared polytetrafluoroethylene (PTFE) frit filter (Chemglass, 10 μm) with the filtrate being stored in a scintillation vial thereafter. Each phase of the resulting filtrate was then passed through a 0.2 μm PTFE syringe filter prior to subsequent analysis. The pulps were washed with ∼300 mL of ethanol and vacuum-dried overnight, followed by massing to determine pulp yields.

Quantification of Monomeric Products via Gas Chromatography (GC). Volumetric dilutions of the reaction liquors were made to analyze the compounds of interest at varying concentrations. Diluted samples were spiked using a concentrated solution of 1,3,5-tri-*tert*-butylbenzene to enable subsequent quantification.

Analysis was performed on an Agilent 8890 GC instrument equipped with a Flame Ionization Detector (FID) and a 5977B Mass Spectrometer Detector (MS) (Agilent Technologies). Agilent MassHunter Workstation GC/MS Data Acquisition Version 10.1.49 was used to collect data, and Agilent MassHunter Workstation Quantitative Analysis for GCMS and LCMS Version 10.2 Build 10.2.733.8 was used to quantitate analytes of interest against rigorous synthetic standards.

Samples were injected at 1.0 μL into the GC with a 20:1 split. The analytes were separated on an Agilent DB-624 UI 30 m x 0.250 mm x 1.4 μm film column with a constant flow of 3 mL/min using an inlet, transfer line, and FID temperature of 250 °C. The oven was held at 70 °C for 1 min then ramped to 260 °C at a rate of 20 °C/min and held for 5 min for a complete analysis run time of 15.5 min. The MS used a solvent delay of 1.70 min, which then began scanning from 10.0 to 250.0 *m*/*z*. A minimum of 5 standard calibration levels were made in methanol within a range of 10 to 1000 μg/mL. Resulting calibration curves had a minimum R^2 value of 0.995 across all analytes. A calibration verification standard was analyzed every 20 samples to ensure calibration integrity and monitor instrument performance and detector drift across the entirety of the analysis.

Solvent Miscibility Testing. Miscibility testing was conducted in a 10−20 mL Biotage microwave reaction vial (Part No. 354833) heated via a machined aluminum holder placed on a hot plate. The hot plate was controlled by a thermocouple slotted into the holder to ensure an accurate temperature measurement. The reaction vial was loaded with 5 mL of water and PG (each) and sealed. The vial was then progressively heated, removing the vessel and taking pictures at each temperature between ambient and 160 °C. A waiting period of 5 min from the block achieving temperature to taking the picture was applied to ensure equilibration.

Aqueous Sugar Analysis. Aqueous reaction liquors were analyzed using methods previously described in the corresponding NREL laboratory analytical procedure.[22]

Gel Permeation Chromatography with Ultraviolet Detection (GPC-UV). GPC characterization was conducted as previously reported.[23] Briefly, the resulting reaction liquors were diluted to their desired concentrations in tetrahydrofuran (20 mg/mL for organic phases, 200 mg/mL for aqueous phases) and filtered using a 0.2 μm PTFE syringe filter prior to analysis. A 20 μL injection volume was utilized along with a Hewlett-Packard 1100 series autosampler. Three 5 μm PLgel Agilent GPC columns (10^4, 10^3, and 50 Å) were arranged in series in order of decreasing pore size, and held at 26 °C for the duration of each measurement. Each run utilized a 0.3 mL/min carrier solvent flow rate and a total run time of 120 min. Eluents were characterized with a UV diode array detector at a wavelength of 260 nm, a reference wavelength of 360 nm, and a 4 nm slit.

Scanning Electron Microscopy (SEM). Postreaction pulps were washed with ∼300 mL of ethanol and vacuum-dried overnight prior to characterization. Samples were characterized using an FEI Quanta 400 FEG scanning electron microscope. Imaging was performed under low vacuum, at a beam accelerating voltage of 15 keV, and operated with the gaseous solid-state detector (GAD) to capture secondary electrons.

RESULTS

Neat Aromatic Solvents Fail to Achieve Equivalent Monomer Yields As Methanol during RCF. To probe the ability of aromatic lignin monomers to serve as RCF solvents,

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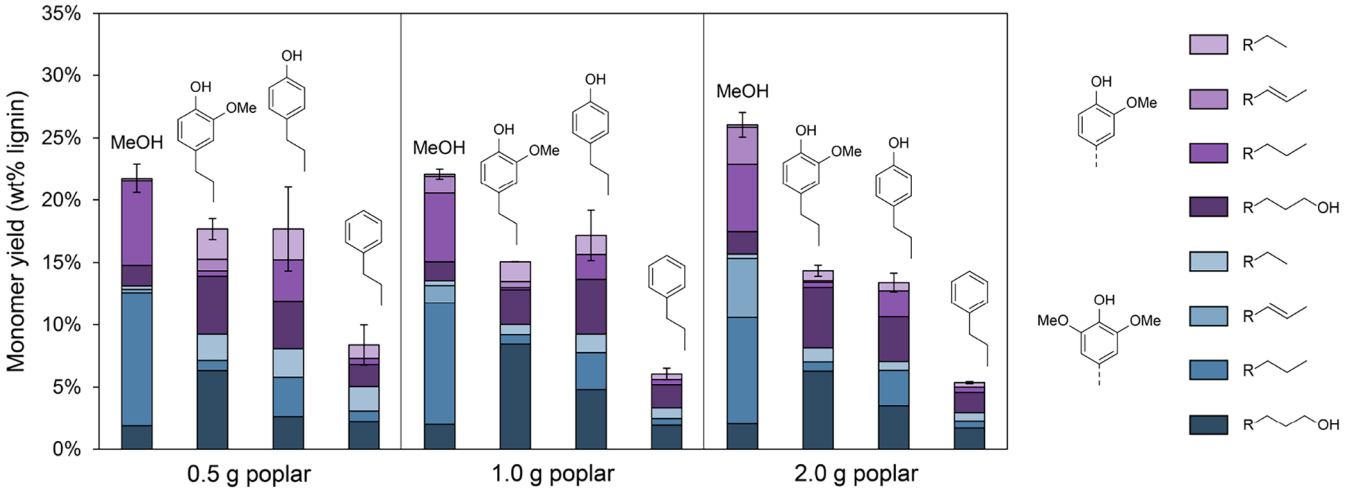

Figure 1. Monomer yields resulting from the use of neat propyl-aromatic solvents for RCF. Reaction conditions: 225 °C, 30 bar H_2, 150 mg Ru/C, 30 mL solvent, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). "*R*" in the legend refers to the 4-position of the aromatic ring. The structures shown above each bar refer to the utilized solvent. Error bars represent the range of cumulative monomer yields for duplicate experiments. Tabulated data are provided in Data S1.

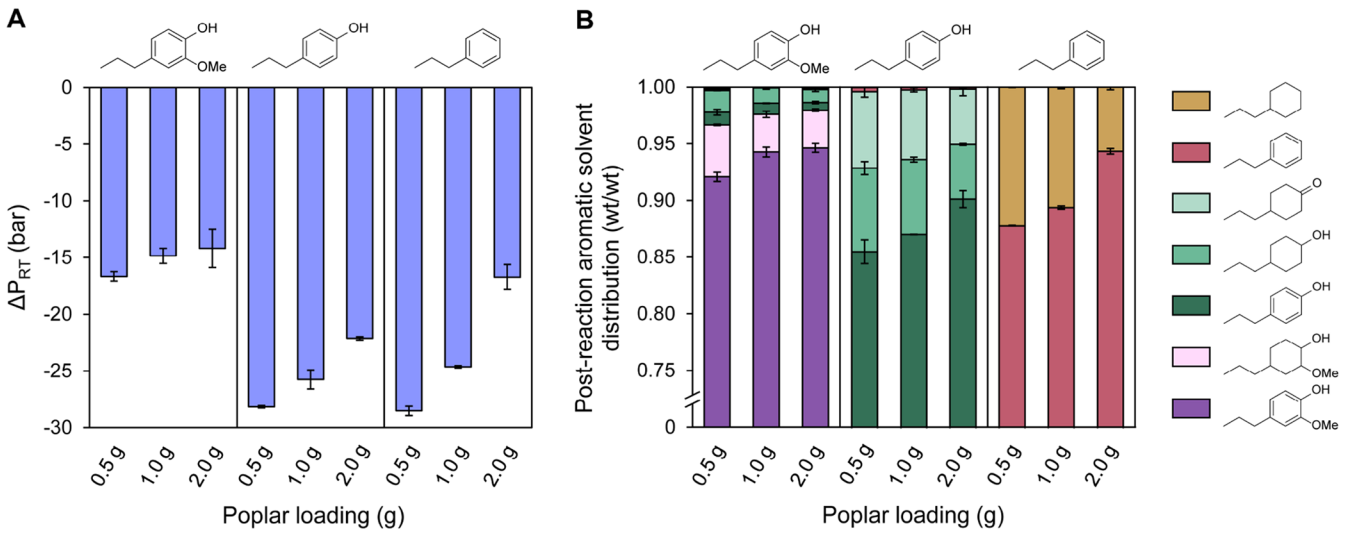

Figure 2. Effect of solvent identity and biomass loading on solvent reactivity. (A) Resulting differences in pressure pre- and postreaction (ΔP_{RT}) and (B) postreaction solvent composition for experiments utilizing neat propyl-aromatics for RCF. Reaction conditions: 225 °C, 30 bar H_2, 150 mg Ru/C, 30 mL solvent, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). The chemical structures shown above the outlined groupings refer to the solvent used in the given RCF reaction. Error bars represent the ranges for the duplicate experiments. Tabulated data are provided in Data S1.

we first conducted RCF on poplar biomass using neat propyl-aromatic compounds [PG, 4-propylphenol (PP), and propylbenzene (PB)] (Figure 1), chosen as surrogates for depolymerized lignin oils at varying stages of deoxygenation.[23,24] Extracted lignin monomers were quantified via GC-FID/MS with yields determined on a biomass lignin basis, assuming a product liquor volume equivalent to the initial solvent loading. This method was chosen as it allows for the determination of monomer concentrations without the need for distilling heavy aromatics such as PG. Furthermore, it helps to eliminate error resulting from attempting to recover all extracted lignin via biomass washing, which is challenging with viscous solvents. The concentration of PG was estimated based on molar S/G ratios calculated by tracking propanol monomers (dihydrosinapyl and dihydroconiferyl alcohol) due to peak convolution during analysis (Note S1) and showed reasonable agreement with concentrations directly measured for conventional methanol RCF (Figure S1).

Multiple biomass loadings were tested for each solvent to probe the effect of varying biomass-to-catalyst ratios on RCF with propyl-aromatic solvents. All tested biomass loadings and solvents failed to achieve monomer yields comparable to those obtained with methanol (22−26 wt %), with aromatic solvent polarity appearing to have some effect on yields, as illustrated by the low monomer yields obtained using PB (5−8 wt %). Meanwhile, PG (14−18 wt %) and PP (13−18 wt %) achieved similar monomer yields despite their functional differences, suggesting other factors besides polarity likely play a role in determining aromatic RCF performance. Interestingly, it appears that RCF conducted using propyl-aromatic solvents results in increased selectivities toward propanol side chains compared to RCF conducted with methanol, in which propyl

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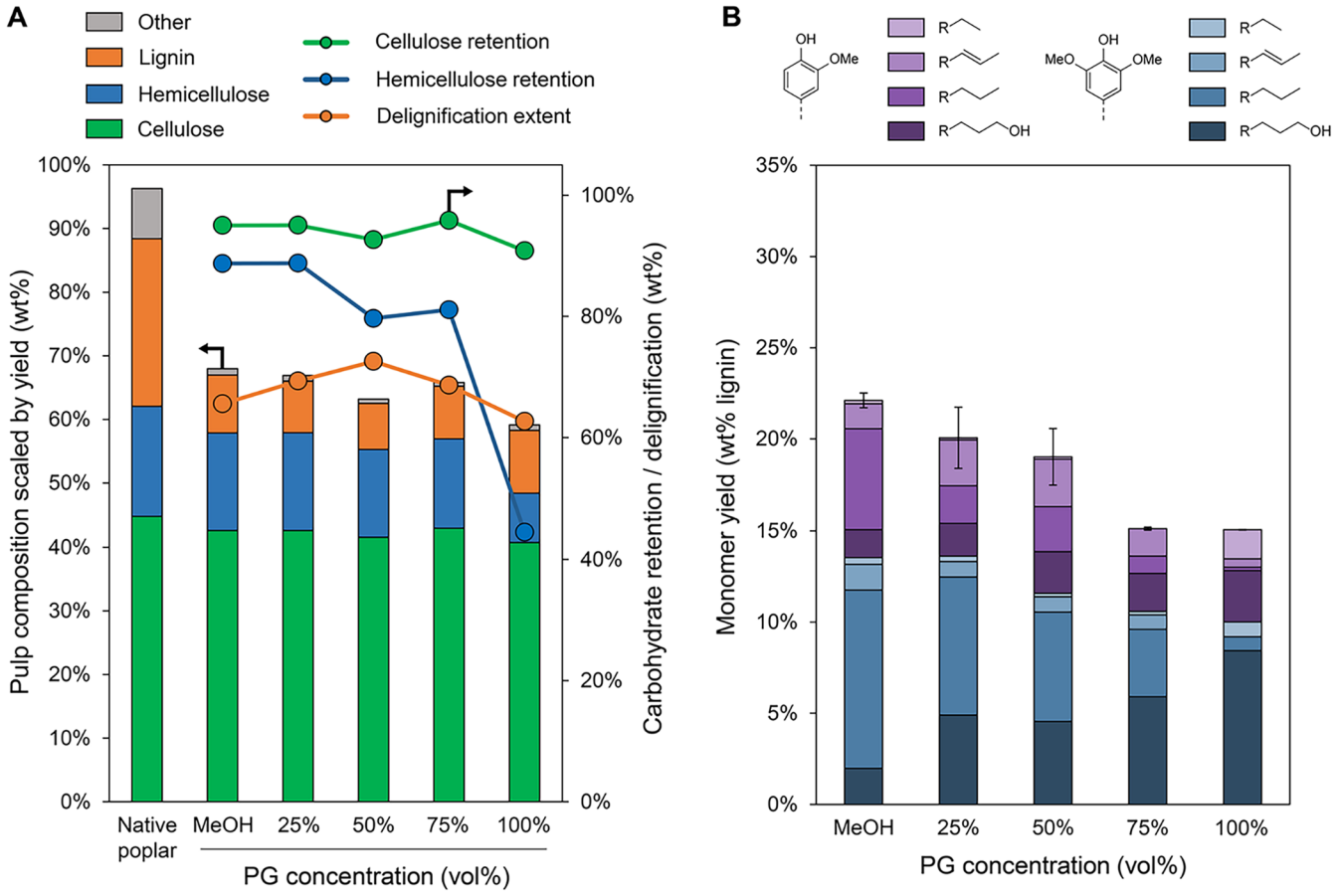

Figure 3. Effect of PG concentration on methanol-RCF performance metrics, including (A) biomass solubilization and (B) monomer yield. Reaction conditions: 225 °C, 30 bar H_2, 1 g poplar biomass, 150 mg Ru/C, 30 mL solvent, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). "*R*" in the monomer yield legend of panel (B) refers to the 4-position of the aromatic ring. Error bars represent the range of cumulative monomer yields for duplicate experiments. Tabulated data are provided in Data S1.

side chains tend to be favored. This aligns with our previous observations for nonvolatile RCF solvents and suggests that aromatic solvents suppress dehydration activity, thereby favoring the formation of propanol monomers.[12] The limited performance of neat aromatic solvents for RCF is likely due to a combination of factors, including their decreased polarity hindering lignin solvolysis, as well as their potential coordination with metal sites on the catalyst surface, thereby hindering lignin fragment adsorption and subsequent hydrogenolysis (*vide infra*).[4]

Metallic RCF Catalysts Drive Aromatic Solvent Hydrogenation. During RCF with aromatic solvents, substantial differences in initial and final reactor pressure at ambient temperature were observed (14−29 bar) compared with those that are typical for RCF in methanol (1−2 bar) (Figure 2A). These decreases can be attributed to aromatic ring hydrogenation and demethoxylation (in the case of PG) of the aromatic solvents under RCF conditions (Figure 2B). Moreover, it appears that increased biomass loadings led to decreased solvent hydrogenation extents, suggesting biomass derivatives reduce solvent hydrogenation during RCF. Furthermore, PG exhibited substantially lower extents of solvent hydrogenation than the other tested aromatic solvents, showing solvent hydrogenation/demethoxylation extents between 5 and 8 wt %, compared to 10−15 and 6−12 wt % for PP and PB, respectively. Owing to these reactivity trends, we compared the yields for two RCF catalysts, Pd/C and Ru/C (Figure S2). These systems achieved near-identical monomer yields and distributions, though Pd/C resulted in lower solvent hydrogenation/demethoxylation extents during reaction under identical conditions in a PG solvent (1−2 vs 5−8 wt % for Pd/C vs Ru/C, respectively), suggesting the potential for future catalyst development to overcome aromatic solvent stability constraints.

Methanol Cosolvent Experiments Reveal Lignin Depolymerization Is Hindered during Aromatic RCF. Because aromatic solvents alone achieved lower monomer yields than methanol, solvent mixtures were subsequently tested to promote higher extents of lignin extraction and depolymerization. PG was chosen as our model aromatic cosolvent based on its reduced consumption over Ru/C as well as its abundance in conventional RCF oils.[4] We began by mixing PG with methanol, as methanol generally achieves high monomer yields alone and has been the subject of multiple studies for the recycling of lignin-derived cosolvents for additional RCF reaction cycles (Figure 3).[16−19]

Mixtures of PG and methanol demonstrated similar extents of lignin extraction across all measured solvent compositions (Figure 3A), where delignification extents were between 63 and 73 wt %, reaching a maximum for the 50/50 (vol %/vol %) solvent composition. With regards to carbohydrate retention, while cellulose retention remained >90% for all solvent mixtures, hemicellulose retention decreased with increasing PG concentration, reaching a minimum of 45 wt

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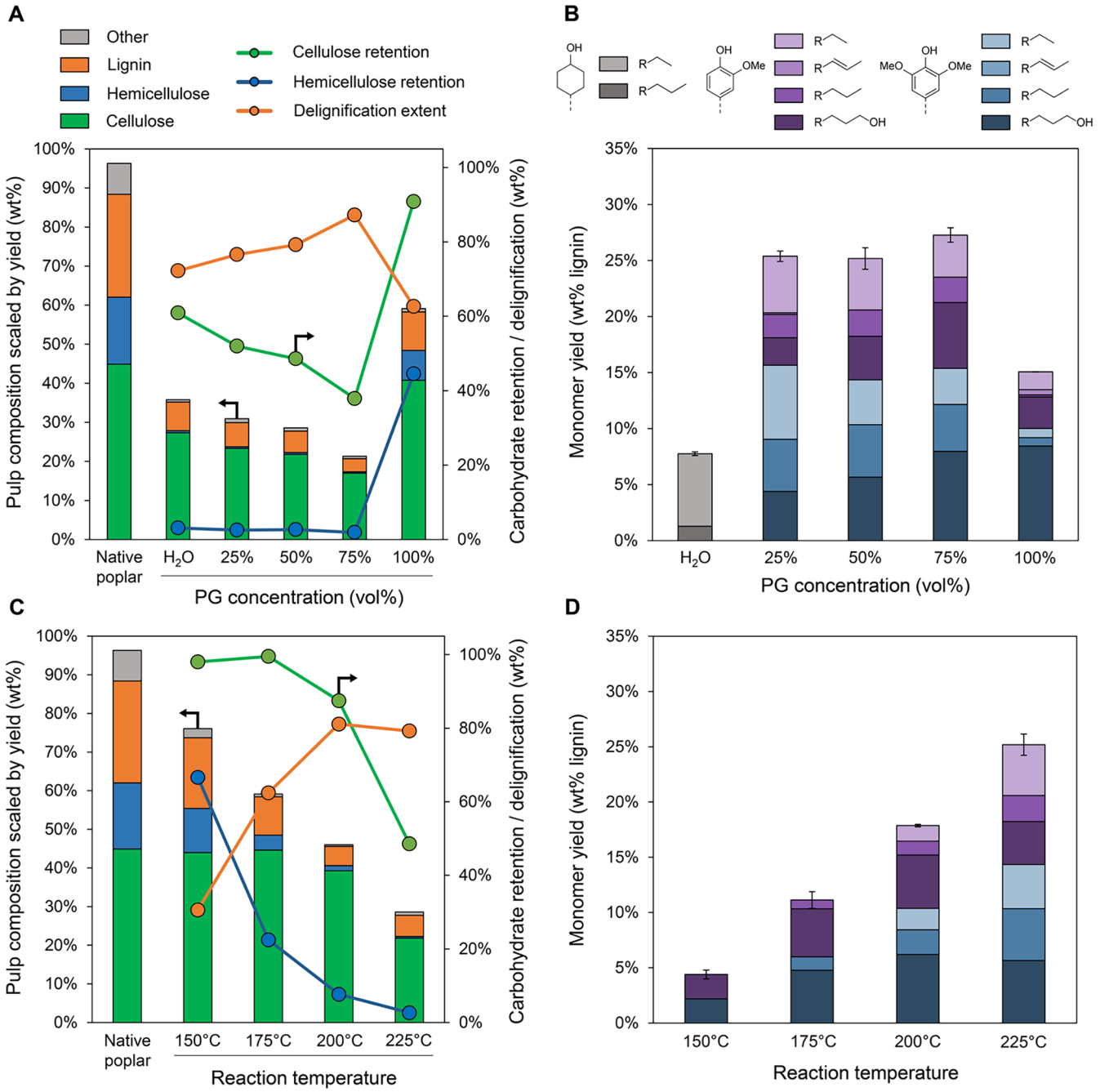

Figure 4. Effect of reaction conditions on PG/water RCF performance metrics. (A) Biomass solubilization extents at varying solvent compositions at 225 °C. (B) Resulting monomer yields at varying solvent compositions at 225 °C. (C) Biomass solubilization extents at varying reaction temperatures in 50 vol % PG. (D) Resulting monomer yields at varying reaction temperatures in 50 vol % PG. Constant reaction conditions: 30 bar H_2, 1 g poplar biomass, 150 mg Ru/C, 30 mL solvent, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). Note that lignin-derived hydrogenated analogues could only be quantified in the case of the water-only solvent composition due to convolution with solvent hydrogenation products. "*R*" in the monomer yield legends of panels (B, D) refers to the 4-position of the aromatic ring. Error bars represent the range of cumulative monomer yields for duplicate experiments. Tabulated data are provided in Data S1.

% for pure PG. This suggests PG to be better at solubilizing hemicellulose than methanol, potentially due to its higher acidity.[25]

Conversely, the resulting monomer yields from PG/methanol mixtures demonstrated similar behavior, as expected from our previous solvent screen, where increasing methanol concentrations led to increasing monomer yields (Figure 3B). This is in contrast to the measured delignification extents shown in Figure 3A, which could be a result of either decreased lignin stability in the presence of PG or impeded transport of reactive intermediates to the catalyst surface (e.g., by the competitive adsorption of aromatic solvent constituents to the catalyst inhibiting lignin fragment adsorption). The addition of methanol also significantly decreased solvent hydrogenation extents (see below) while shifting the resulting monomer selectivity toward propyl and propenyl side chains instead of propanol side chains, suggesting methanol tends to promote

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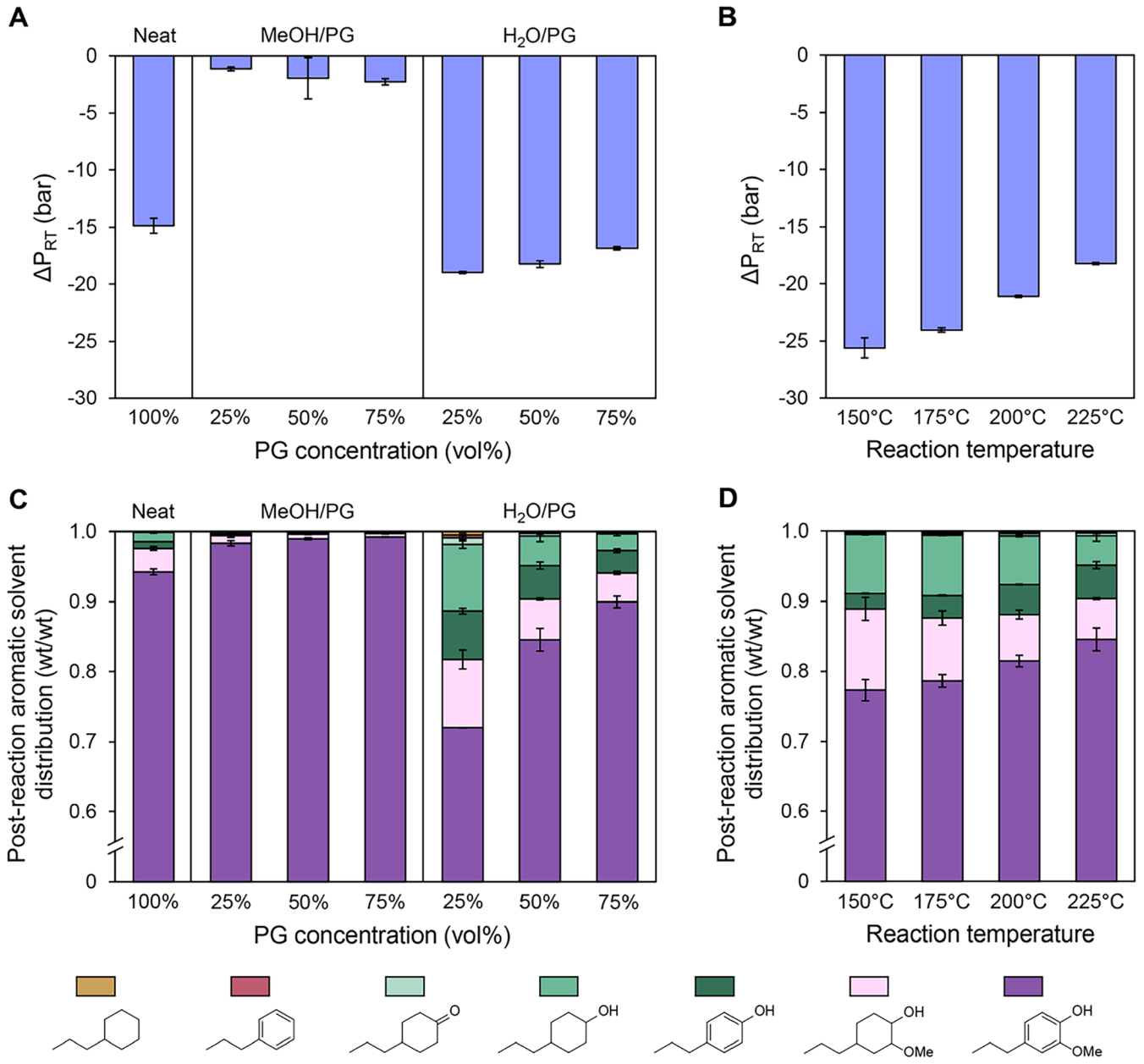

Figure 5. Effect of cosolvent identity and reaction temperature on solvent reactivity. (A, B) Resulting differences in pressure pre- and postreaction (ΔP_{RT}) for RCF conducted (A) in PG/methanol and PG/water mixtures at varying solvent ratios at 225 °C, or (B) in a 50/50 (vol %/vol %) PG/water mixture at varying reaction temperatures. (C, D) Postreaction solvent composition for experiments conducted (C) in PG/methanol and PG/water mixtures at varying solvent ratios at 225 °C, or (D) in a 50/50 (vol %/vol %) PG/water mixture at varying reaction temperatures. Constant reaction conditions: 30 bar H_2, 150 mg of catalyst, 1 g of poplar biomass, 30 mL of solvent mixture, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). Error bars represent the ranges for duplicate experiments. Tabulated data are provided in Data S1.

the dehydration of side chains as opposed to direct hydrogenation.[12]

PG/Water Mixtures Result in Increased Monomer Yields and Biomass Solubilization. Water was also tested as a cosolvent with PG owing to its promising lignin extraction capabilities, where it is known to achieve elevated extents of delignification during RCF relative to alcohols.[6−8,13,15] Broadly, PG/water mixtures demonstrated extents of delignification between 77 and 87 wt % (Figure 4A). However, this increased lignin extraction relative to PG/methanol came at the cost of carbohydrate retention, where measured PG/water mixtures retained negligible hemicellulose (2−3 wt %), as well as only 38−52 wt % of the initial cellulose. Interestingly, as PG concentration increased, the delignification extent also increased while cellulose retention dropped, suggesting PG, when in the presence of an aqueous cosolvent, aids in the solubilization of biomass. Increased biomass solubilization is further supported by decreased pulp structural integrity after treatment with aqueous cosolvents relative to pulps resulting from the use of pure PG or PG/MeOH cosolvent mixtures (Figure S3).

With regard to monomer yield, PG/water mixtures showed significant improvement compared to either solvent alone (Figure 4B). This performance extended across the range of solvent ratios tested (from 25 to 75 vol % PG), all of which generated yields >25 wt % (similar to those of pure methanol

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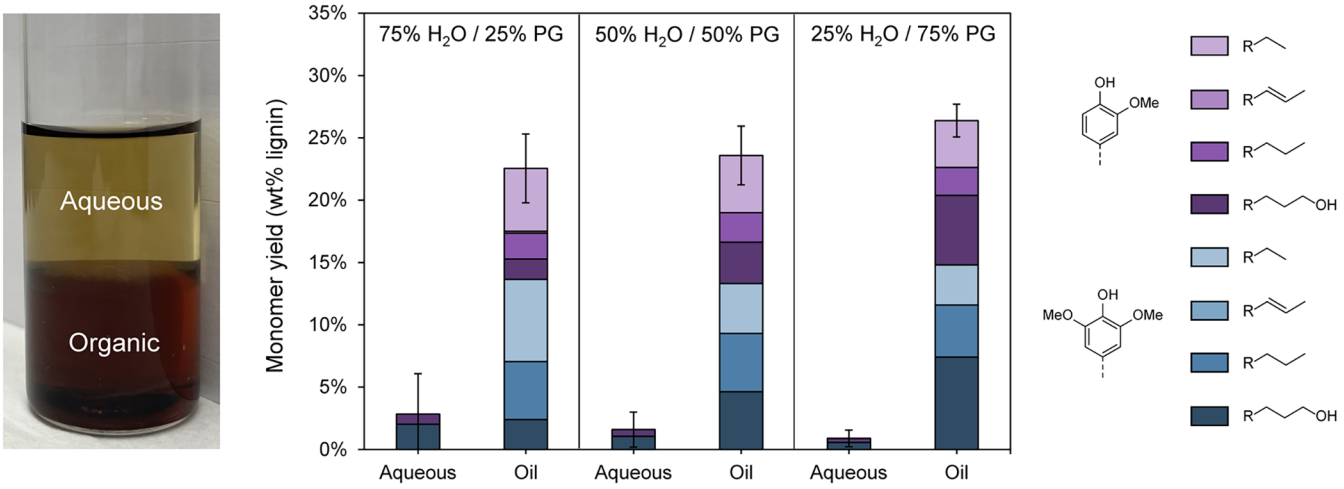

Figure 6. Resulting liquid−liquid fractionation of lignin monomers for varying PG/water solvent mixtures. Reaction conditions: 225 °C, 30 bar H_2, 1 g poplar biomass, 150 mg Ru/C, 30 mL solvent mixture, 700 rpm stirring, and 3 h reaction time (not including the 30 min heating ramp). "*R*" in the legend refers to the 4-position of the aromatic ring. Error bars represent the range of cumulative monomer yields for duplicate experiments. Tabulated data are provided in Data S1.

RCF). Higher water concentrations led to increased ethyl side chain generation while increased PG concentrations favored propanol monomers. The increased ethyl content when using water as well as a Ru-based catalyst for lignin deconstruction is in agreement with previous reports.[8,26] This observed selectivity could be due to either the subsequent dehydrogenation and decarbonylation of formed propanol side chains, or C−C bond hydrogenolysis reactions that are known to be prevalent over Ru/C (and may help to explain the decreased monomer yields for the pure water case).[27,28] Pure PG likely achieves lower monomer yields than PG/water mixtures in part due to its inability to free similar quantities of lignin from the carbohydrate matrix of biomass as well as its potential to inhibit mass transfer to and adsorption on the catalyst surface.

Owing to the poor carbohydrate retention at 225 °C using PG/water mixtures, we attempted milder reaction conditions (Figure 4C). As expected, at lower reaction temperatures, carbohydrate retention was improved, with a cellulose retention of 87 wt % at 200 °C relative to 49 wt % at 225 °C for a 50/50 (vol %/vol %) PG/water solvent mixture. Released carbohydrates were found to primarily be aqueous polyols (e.g., ethylene glycol, glycerol, propanediol) and ethanol (Figure S4). Promisingly, cellulose was nearly fully retained at temperatures ≤175 °C. Meanwhile, the delignification extent reaches a maximum of 81 wt % at 200 °C, failing to further increase at more severe reaction temperatures (225 °C). In contrast to improved carbohydrate retentions, decreasing reaction temperatures demonstrated depressed lignin monomer generation (Figure 4D), with monomer yields decreasing from 25 wt % at 225 °C to 18 wt % at 200 °C. This suggests lignin hydrogenolysis is inhibited at decreased reaction temperatures, as evidenced by decreased monomer yields at similar biomass delignification extents between 200 and 225 °C.

Reaction Conditions Play a Large Role in Defining Aromatic Solvent Stability. Notably, methanol use resulted in an aromatic hydrogenation/demethoxylation extent of <2 wt % for all solvent ratios tested relative to 6 wt % for pure PG (Figure 5A,C), suggesting that methanol is largely responsible for minimizing ring hydrogenation reactions during conventional RCF, in line with previous works utilizing methanol solvent systems with lignin oil.[16,17] Conversely, solvent hydrogenation for PG/water mixtures was promoted relative to pure PG, showing ambient reactor pressure decreases between 17 and 19 bar relative to 15 bar for pure PG (Figure 5A,C).[8] This could be in part due to the hydrophobicity of the carbon catalyst support, leading to increased aromatic adsorption at heightened water concentrations, or could be due to other promotional effects given by aqueous reaction media for aromatic hydrogenation over noble metal catalysts.[29,30] Interestingly, it also appears that decreasing reaction temperature promotes aromatic solvent hydrogenation/demethoxylation, with side product generation increasing from 15 wt % at 225 °C to 23 wt % at 150 °C (Figure 5B,D). This could also be due to catalyst partitioning, or it may be that liberated biomass derivatives act to inhibit solvent hydrogenation at increased reaction temperatures via either competitive adsorption or partial poisoning, thereby decreasing the solvent reactivity. Given these trends, it should also be noted that while not directly measured due to convolution with solvent byproducts, it is likely that some of the extracted lignin monomers are being hydrogenated and demethoxylated along with the PG solvent in experiments conducted with either neat PG or PG/water mixtures, potentially lowering the monomer yields reported here, which are limited to only aromatic products. However, it does appear that much of the hydrogenation activity tends to occur at lower temperatures during the reaction heating ramp (Figure S5), which likely limits these effects, while hydrogenation reactivity is highest, as the lignin has yet to be liberated from the biomass. This motivates future research to implement these systems in flow, where effects generated by transient heating ramps may be minimized or eliminated. Although some condensation of lignin-derived aromatics is possible at elevated temperatures, our data show that the PG solvent largely retains its molar mass over the course of reaction, as revealed by GPC (Figure S6). Regardless, these trends highlight the importance of future work in developing RCF catalysts that minimize aromatic ring hydrogenation and maximize solvent stability when utilizing water-lignin oil (co)solvent systems.

PG/Water Mixtures Enable Biphasic Liquid−Liquid Separation. Interestingly, for mixtures of PG and water,

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another inherent benefit apart from high monomer yields was the ability of PG and water to phase separate (Figure 6), thereby providing a means by which to fractionate generated lignin-derived products from the resulting aqueous phase, thus potentially avoiding/minimizing the need for distillation. Similar behavior has been seen previously for immiscible RCF systems, such as *n*-butanol/water as demonstrated by Renders et al.,[8] and could potentially help in lowering separation costs for a hypothetical biorefinery using this technology. To probe whether these two solvents are miscible at elevated temperatures, we conducted a series of tests in microwave reaction vials at 160 °C, where biphasic behavior was observed for all tested conditions (Figure S7). While increased solubility is expected at temperatures like those utilized for reactivity tests (225 °C), complete miscibility is unlikely. For comparison, 4-propylphenol, which is more polar than 4-propylguaiacol, exhibits a critical solution temperature with water >220 °C.[31]

As shown in Figure 6, most of the generated monomers selectively fractionate to the organic phase after reaction, potentially allowing for separation from the aqueous phase via liquid−liquid extraction. As opposed to most traditional aqueous/organic liquid−liquid extraction solvent systems (apart from halogenated systems), the organic phase tended to sit beneath the aqueous phase due to the higher density of PG compared to water. It was found that 94% of the generated monomers fractionated to the organic phase after reaction in a 50/50 (vol %/vol %) PG/water mixture, with higher water-to-aromatic ratios resulting in increased solubilization of aromatic products in the resulting aqueous phase. This effect was specifically prevalent for monomers containing propanol side chains (dihydroconiferyl alcohol and dihydrosinapyl alcohol), which have inherently higher solubilities in water than alkyl chain monomers owing to their increased polarity. Promisingly, it also appears that heavier lignin-derived substrates tend to selectively fractionate to the organic phase, as shown by GPC of the resulting reaction liquors (Figure S8).

DISCUSSION

Using PG as a model, we successfully demonstrated the efficacy of aromatics as both solvents and cosolvents for the extraction of lignin from biomass. While neat aromatic solvents alone showed modest aromatic monomer yields, the use of solvent mixtures greatly improved their performance. Specifically, mixtures of PG and water showed promise in that they displayed synergistic effects toward solubilizing and depolymerizing lignin, as evidenced by increased delignification extents and monomer yields for mixtures as compared with water or PG alone, although these improved metrics came at the cost of carbohydrate solubilization. These mixtures further enabled a viable phase separation, wherein lignin monomers selectively fractionated to the organic phase. This behavior should be investigated for other aromatic/water mixtures in the future as well as for real lignin-derived streams to determine if they show behavior similar to that achieved herein with the models.

Aromatic solvent hydrogenation is another major consideration when eliminating exogenous organic solvents from RCF, as water fails to inhibit aromatic hydrogenation like conventional RCF solvents (e.g., methanol, ethanol, etc.). In fact, water may actually play a role in promoting aromatic hydrogenation via either hydrophobic interactions with the utilized carbon support or by aqueous promotional effects with noble metal catalysts.[29,30] To this point, it fortunately appears that extracted biomass derivatives may act to decrease solvent hydrogenation to some extent, potentially limiting these effects for a system utilizing real lignin oils. However, should this not be the case, either catalysts that limit ring saturation or a sequential rearomatization step would be necessary to generate aromatic products. Otherwise, dependent on the process recycle ratio, extensive product hydrogenation would occur. Promising catalyst candidates for targeting selective RCF without hydrogenation include Mo_2C[32] and Pd/Nb_2O_5,[33] both of which have been shown to display metallic characteristics while limiting ring hydrogenation activity during hydrodeoxygenation. Conversely, by ring hydrogenating the RCF monomers, a similar process may be viable to target the hydrogenated analogues of RCF monomers, which could act as potential precursors to bioderived polymers,[3,34,35] or to cycloalkane-rich sustainable aviation fuel blends.[23,24,36−39] Aside from minimizing ring saturation extents, side chain selectivity also plays a large role in determining liquid−liquid fractionation efficiency, wherein ethyl and propyl monomers more readily fractionate to the organic phase during the natural phase separation that occurs relative to those possessing propanol side chains. Thus, a circular process that fully utilizes this biphasic behavior will require targeting molecules with nonpolar side chains. It should, however, be noted that the heightened viscosity of real lignin-derived bio-oils may act to slow phase separation or result in the formation of emulsions, wherein emulsion separation techniques may need to be employed.[40]

With respect to the future implementation of solvent looping processes, achieving viable recycle ratios will be critical to achieving feasible process economics, as high process recycle ratios contribute to increased operating and capital costs.[41] Achieving decreased solvent-to-biomass ratios during lignin-first biorefining has been a longstanding challenge, and has been previously investigated in multiple works.[9,16−19] Nonetheless, future studies should examine the effect of reducing solvent-to-biomass ratios during RCF utilizing aromatic-water mixtures. This also motivates the potential use of increased water loadings relative to lignin-derived aromatics in a process utilizing aromatic/water cosolvent mixtures. Regardless, process modeling and techno-economic analysis will be essential to understand the potential role that process recycle ratios play in defining the economics of solvent looping RCF.[9,17]

Carbohydrate retention will also be a key factor in advancing this technology, wherein the economics of a lignin-first biorefinery partially rely on the downstream upgrading of a purified holocellulose feedstock.[9] In this vein, while increased reaction temperatures tend to promote improved monomer yields, these depolymerization extents come at the cost of carbohydrate retention. Therefore, it may be beneficial to operate a process utilizing aromatic/water mixtures at conditions resulting in decreased monomer yields, wherein improved cellulose retentions can be achieved at lower reaction temperatures.

Beyond reactivity concerns, multiple separation challenges must be addressed when moving toward the implementation of such a solvent looping process. For instance, successful carbohydrate recovery and valorization is a critical aspect of lignin-first biorefining.[42−48] In this vein, pulp washing to avoid solvent retention in the holocellulose will be especially relevant when using aromatic compounds as cosolvents, considering that heavy aromatic solvents/products will likely be retained in

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the holocellulose pulp and cannot be removed easily via drying due to their low volatility. These challenges will be compounded when utilizing real lignin-derived bio-oils, which exhibit higher viscosities relative to the model aromatic monomers used here. One possibility could be to use water at elevated temperatures, as it is well-known that the dielectric constant of water shifts at elevated temperatures, significantly aiding in the solubilization of organic molecules.[31,49] Alternatively, exogenous solvents (e.g., methanol, ethanol, etc.) could also be used, as they are able to efficiently dissolve the majority of lignin-derived molecules while being volatile enough to be recovered via drying. However, unlike in traditional RCF, these washing processes would likely be done at mild to ambient conditions and could enable flexible solvent compositions, thereby eliminating concerns such as solvent losses to reforming reactions or high reactor pressures.[9] Beyond product recovery, catalyst/pulp separation will also be critical, which could potentially be conducted using a variety of established methods such as the use of a catalyst basket,[42,50] solvent separation approaches,[8,19,51] or use of flowthrough reactor configurations.[16,43,52]

Overall, mixtures of RCF-derived aromatics and water provide an interesting opportunity for the efficient extraction of lignin from biomass. In these systems, aromatic components help to solubilize extracted lignin, while the discrepancy in polarity between the two solvents enables a natural liquid−liquid separation for the recovery of aromatic products. This reveals a promising potential biorefinery concept in which both generated products and water can be utilized as cosolvents, thereby providing a potential path toward viable water-only RCF.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.5c08161.

Calculation of monomer yields, verification of PG concentration approximation, catalyst comparison for neat aromatic RCF, SEM micrographs for postreaction pulps, yields of aqueous-phase sugar derivatives after PG-H_2O RCF, reactor pressure transients, GPC comparing pre- and postreaction organic solvent composition, PG-H_2O miscibility testing, GPC probing dimer/oligomer fractionation in PG-H_2O mixtures (PDF)

Tabulated information for data reported in the manuscript (Data S1) (XLSX)

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Notes

The authors declare the following competing financial interest(s): M.S.W., J.H.J., M.L.S., D.G.B., G.T.B., and Y.R.-L. are inventors on a patent application which covers the use of lignin-containing mixtures for RCF.

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