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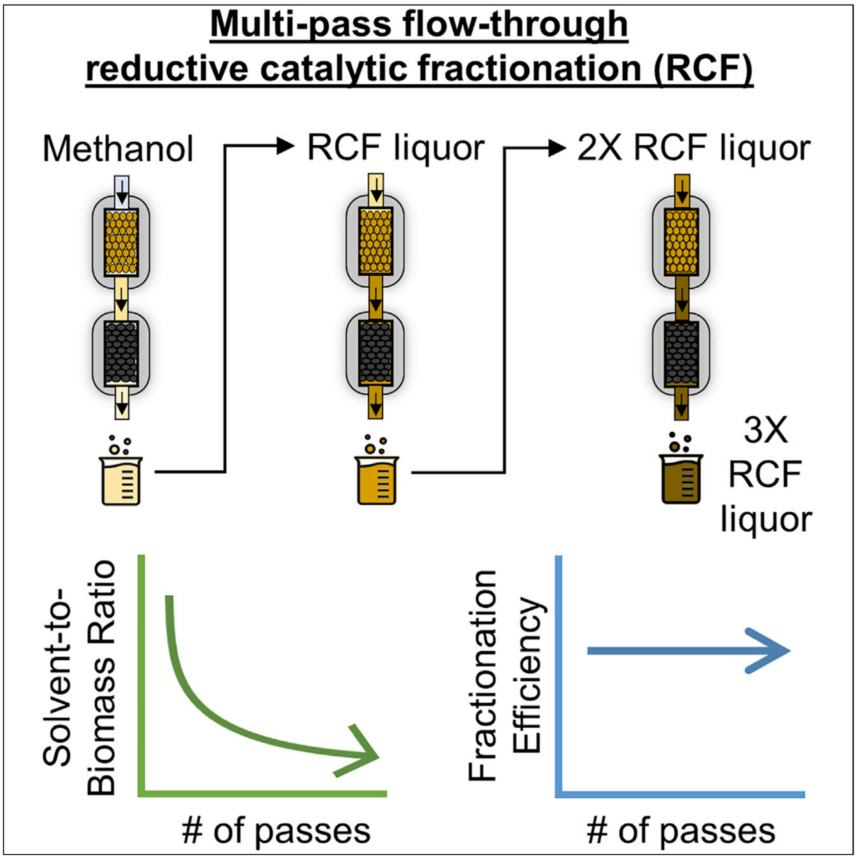

Lignin-first biorefining enables conversion of both lignin and carbohydrates to renewable fuels and chemicals, overcoming the limitations of traditional biorefineries that typically focus solely on polysaccharide valorization. However, a key challenge to enabling lignin-first biorefining at scale is high solvent usage. To that end, we introduce the concept of multi-pass flow-through lignin-first biorefining to minimize solvent usage without a detrimental effect on biorefining performance, with the aim to maximize the economic and environmental benefits of the process.

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Highlights

Multi-pass flow-through RCF significantly reduces the solvent usage in biorefinery

Fractionation efficiency is maintained during multi-pass flow-through RCF

Lignin and carbohydrate quality are invariant during multi-pass flow-through RCF

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Multi-pass flow-through reductive catalytic fractionation

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SUMMARY

Reductive catalytic fractionation (RCF) is a promising lignin-first biorefining strategy that selectively extracts and depolymerizes lignin from whole biomass. Flow-through (FT)-RCF enables physical separation of the biomass and catalyst, but this process configuration typically operates at high solvent-to-biomass ratios. Here, we demonstrate multi-pass FT-RCF, wherein the lignin-enriched solvent obtained after an initial FT-RCF step is recycled and used in subsequent FT-RCF without intermediate lignin recovery. Multi-pass FT-RCF reduces the solvent-to-biomass ratio from 48 to 1.9 L/kg, which is a lower solvent loading than is accessible in batch reactors, without negative impacts on delignification and monomer yield with up to 12 wt % lignin in the solvent. Overall, this work demonstrates that solvent demand in RCF processes, which is a key cost and energy driver to enable this process at scale, can be reduced by recycling lignin oil between RCF reactions.

INTRODUCTION

Reductive catalytic fractionation (RCF) is a prevalent lignin-first biorefining technique wherein lignin is extracted from native biomass with a polar protic solvent, and ether and ester bonds are cleaved in the presence of a metal catalyst and a hydrogen source to generate stable aromatic monomers and C–C linked oligomers.[1–10] RCF processes in batch reactors can produce lignin oil with near-theoretical maximum yields of lignin-derived monomers, based on the C–O–C inter-unit bond content of the substrate and a carbohydrate-rich pulp with high polysaccharide retention.[11–26] However, batch reactions commonly mix the catalyst and biomass physically, thus complicating studies of solvolysis and catalysis as well as catalyst recovery from the pulp.[27] Recently, several groups demonstrated flow-through (FT)-RCF processes wherein the biomass and catalyst are packed into separate beds, and a protic solvent is flowed over the biomass bed to extract lignin and send the solubilized lignin fragments to a catalyst bed for reductive stabilization. FT-RCF resolves the catalyst and pulp separation problem and enables intrinsic kinetic studies while achieving comparable lignin monomer yields and carbohydrate retention as batch RCF.[28–34]

For any RCF process configuration at scale, a key challenge is high solvent usage, which for FT-RCF has ranged between 90 and 360 L solvent/kg biomass. These values are drastically higher compared with those traditionally obtained in batch reactors, which range between 4 and 50 L solvent/kg biomass (Figure 1; Table S1).[10,27] High solvent usage substantially increases the energy demand, capital costs, and operating costs of the process.[35] In batch RCF, the impact of reduced solvent loadings

CONTEXT & SCALE

Lignocellulosic biomass is a promising renewable carbon feedstock for fuels and chemicals. Although lignin is a major biomass component (15–30 wt %) and the largest source of renewable aromatics, traditional biorefineries have primarily focused on the conversion of polysaccharides. Recent advances in lignin-first biorefining can now enable simultaneous valorization of lignin and carbohydrates to valuable products, but solvent usage in lignin-first biorefining is a key parameter for biorefinery economics and sustainability. Here, we demonstrate the concept of multi-pass flow-through reductive catalytic fractionation, which significantly reduces overall solvent usage for lignin-first biorefining while maintaining effective biomass fractionation and lignin oil quality.

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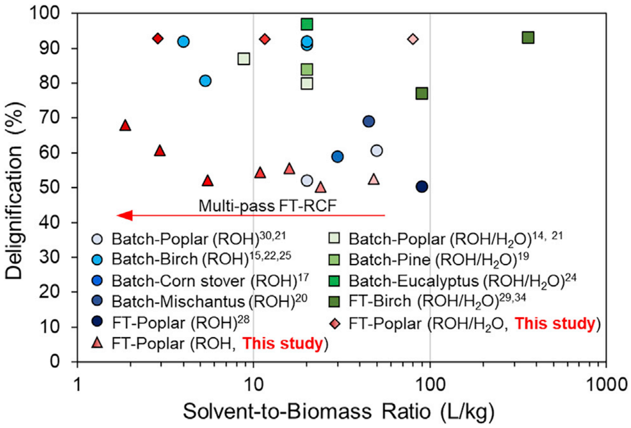

Figure 1. Delignification extent as a function of solvent usage on a biomass basis in batch and FT-RCF in previous studies and this work

The reported delignification varied with feedstocks, solvents, and reaction conditions. ROH denotes RCF reactions with alcohol solvents and ROH/H_2O are RCF reactions in alcohol-water mixtures. The superscripts are reference numbers. Table S1 contains the quantitative information for this figure.

have been examined by Sels et al., wherein they varied the solvent-to-biomass ratio from 4 to 20 L/kg for batch RCF of birch in methanol and confirmed similar delignification and monomer yields regardless of the tested solvent loadings.[15] Additionally, Samec et al. recirculated the product and solvent mixture multiple times to reduce solvent usage for solubilization of birch bark in a batch system.[36] Three consecutive recycles of the solubilized bark and solvent reduced the solvent-to-biomass ratio from 10 to 3.3 L/kg, which did not affect the solubilization efficiency of new portions of bark. Recent process modeling and life cycle assessment from our group estimated that reducing solvent loading from 9 to 4 L/kg would reduce the overall energy demand for the RCF process by 15% and the minimum selling price of RCF oil by 20%.[35] Additionally, this extent of solvent loading reduction would result in a net negative greenhouse gas (GHG) process wherein the potential for GHG uptake in growing biomass is greater than GHG emissions within the biorefinery life cycle.[35] However, the high solids content (26%) at a solvent loading of 4 L/kg in a batch system approaches the intrinsic limit of lignin extraction due to mass transfer limitations.[35]

Here, we investigate the concept of multi-pass FT as a means to study lignin oil recycling and solvent reduction in RCF processes. Reuse of FT-RCF effluent without additional separations, other than recovery of the gases including H_2, CO, and CO_2, could lead to a net solvent reduction on a per mass of biomass basis. Specifically, if effective, each pass through the FT-RCF system without lignin-solvent separation would increase the effective concentration of RCF-derived lignin oil in the solvent, thus decreasing the solvent-to-biomass ratio. Compared with reducing solvent loads in batch RCF, we hypothesized that multi-pass FT-RCF would enable reaching a solvent-to-biomass ratio below 4 L/kg without the process challenges associated with slurries. Furthermore, this multi-pass concept could be extended to other RCF process configurations including batch reactions with a catalyst basket and truly continuous reactions.

RESULTS

To evaluate the ability to recycle lignin oil using the multi-pass FT-RCF concept, we first prepared seven feed solutions of varying lignin oil concentrations from 0 to 12 wt %, conducted tandem solvolysis and catalysis reactions with the feed solutions in

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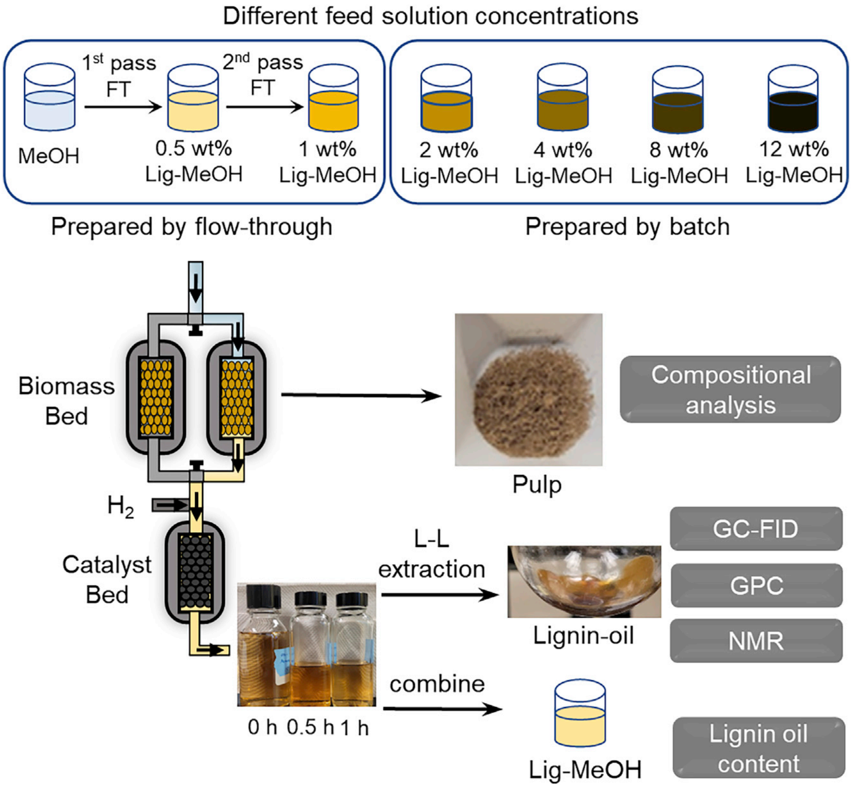

Figure 2. The experimental scheme of poplar FT-RCF with methanol or Lig-MeOH (0.5, 1, 2, 4, 8, and 12 wt % lignin oil) and analyses of liquid and solid streams

a FT reactor, and characterized the lignin oil and pulp from each FT-RCF reaction (Figures 2, S1, and S2). For all flow reactions in this work, we used a custom-built flow reactor consisting of two biomass beds (5/8″ ID) and one catalyst bed (9/32″ ID).[28,33] For each experiment, we packed 5 g of hybrid poplar (26% lignin) and 0.9–1.2 g of 15 wt % Ni/C in the biomass and catalyst beds, respectively. The tandem solvolysis and catalysis reactions were conducted at 225°C in flowing methanol or a lignin oil-containing methanol solution (denoted hereafter as "Lig-MeOH") as a solvent. All experiments and analyses were conducted in duplicate, and the error bars in figures are the range of duplicates, unless stated otherwise. The materials and methods are detailed in the supplemental information.

Thermal stability of lignin oil

In a multi-pass FT-RCF process, the lignin oil obtained from a typical RCF experiment, including monomers, dimers, and oligomers as well as solvent, and any extracted carbohydrates extracted from the biomass and stabilized in the metal catalyst are recycled without further modifications and contacted with a new biomass bed in a subsequent cycle. Thus, first understanding the stability of the lignin components in the RCF effluent at the reaction temperature (here, 225°C) is critical to ensure that no deleterious reactions can impart yield losses. To examine this, we first prepared stabilized lignin oil in methanol via FT-RCF of poplar and heated the lignin-rich solution to 225°C in a pressurized batch reactor. Gel permeation chromatography (GPC) traces were collected as a function of time at 225°C. In the first hour, modifications were observed in the molecular weight (MW) range of 600–1,500 Da, with an increasing trimer peak (470 Da) and higher MW oligomers (1,500–4,000 Da). Then, the GPC traces were mostly invariant until 6 h (Figure S3),

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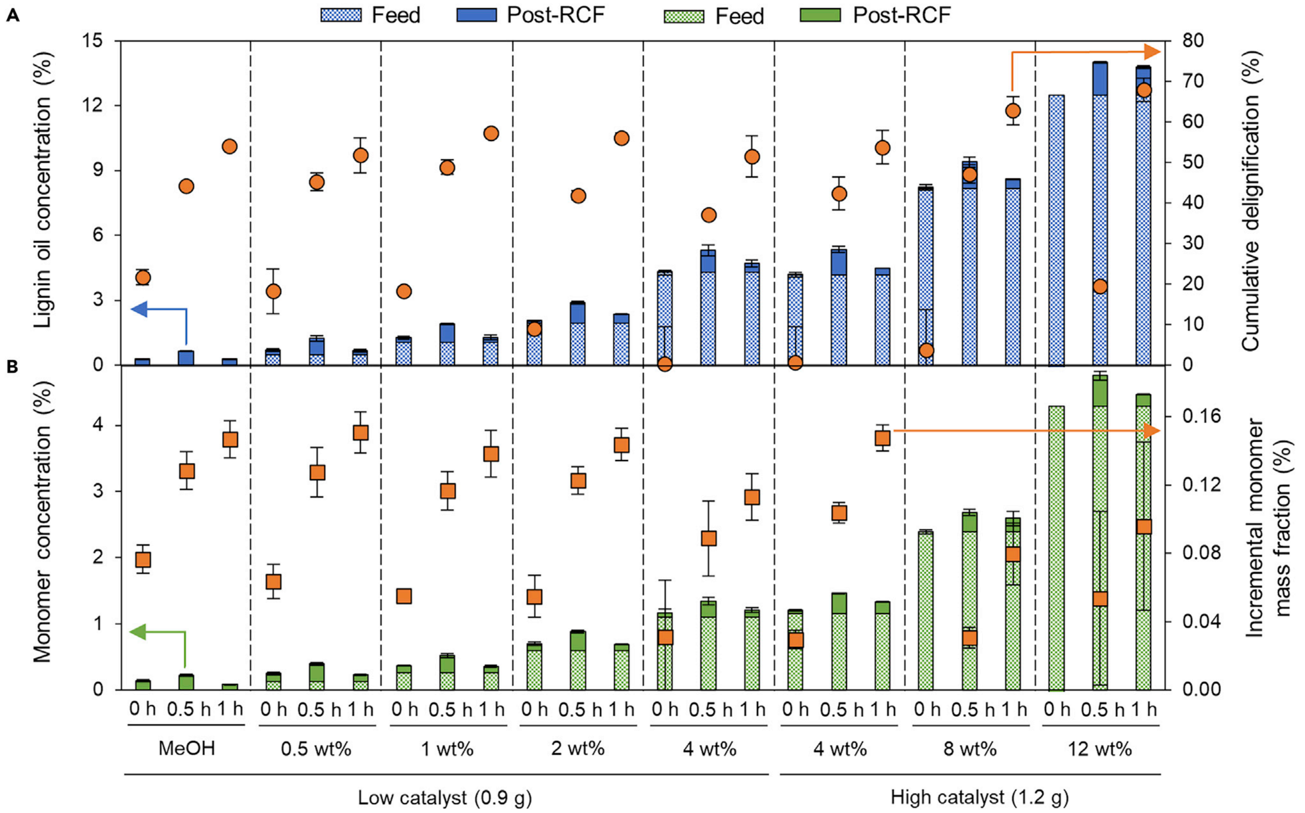

Figure 3. FT-RCF reaction of poplar with various feed concentrations (methanol and 0.5, 1, 2, 4, 8, and 12 wt % Lig-MeOH)

(A) Lignin oil concentration in each sample and calculated cumulative delignification.

(B) Monomer concentration and calculated incremental monomer mass fraction. Each experiment with different feed concentrations is separated by a dashed line. For each FT-RCF experiment, pooled samples were collected at 0 (after a 1 h bed heating ramp), 0.5, and 1 h. The secondary x axis labels (below the time points) indicate the lignin oil concentration in the feed and the catalyst loading for each experiment. The light patterned bars show the lignin oil or monomer concentration in the feed, and dark solid bars represent the additional concentration of lignin oil or monomers that were added over that time. Feed-solution preparation methods are described in the supplemental information (Figures S1 and S2). Reaction conditions: 2 mL/min feed solution, 5 g poplar, 0.9 or 1.2 g 15 wt % Ni/C (diluted with 2.1 or 2.8 g of fused silica), 1,600 psig, 200 sccm H_2, 225°C, and 1 h heating ramp and 1 h run. Table S2 contains the quantitative information for the data shown here.

and slight changes in the low MW peaks were apparent only after 18 h. The reactor operating conditions here resulted in a residence time of 30 min, such that the lignin components in RCF solution will be stable across multiple passes in the FT reactor.

Single-pass FT-RCF with methanol

As a first step, we conducted single-pass FT-RCF with methanol (denoted "1^{st} pass FT-RCF"), which selectively extracted lignin from the biomass and exhibited an expected time profile of cumulative monomer production and delignification (experiments with MeOH in Figure 3).[28,33] With a fixed amount of biomass, lignin extraction rates and the resulting lignin oil concentration in the effluent decreased as the reaction time increased (Figure S4). Thus, to prepare a more concentrated lignin oil solution for the purposes of testing the multi-pass FT-RCF concept, we stopped the reaction at 1 h. We note that the 1 h time for delignification was chosen for experimental convenience, and as described below, we also ran several additional experiments with higher delignification extents.

Pooled samples were collected at the 0 (sampled when the beds reached reaction temperature after a 1-h heating ramp), 0.5, and 1 h time points and were subjected

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to solvent removal and liquid-liquid extraction to isolate lignin oil from methanol and any extracted carbohydrates. Based on the mass of the collected sample and the isolated lignin oil, the lignin oil concentration of each sample was calculated and is shown in Figure 3A. The higher lignin oil concentration of the 0.5 h sample (0.65 ± 0.02 wt %), compared with those of the 0 and 1 h samples (0.28 ± 0.01 and 0.29 ± 0.01 wt %, respectively), indicates a higher lignin extraction rate in the first half-hour at 225°C (Figure 3A; Table S2). The cumulative delignification, which is equivalent to lignin oil yield, during the 1 h heating ramp and the 1 h run reached 54.0% ± 0.9%. The average lignin oil concentration of the collected samples was 0.38 wt %. We note that while a 3 h reaction reached 63% cumulative delignification, the average lignin oil concentration decreased to 0.22 wt % (Figure S4).

The monomer concentration of the samples was analyzed by gas chromatography with flame ionization detection (GC-FID) and is shown in Figure 3B. Here, to track the monomers, we use a metric of "incremental monomer mass fraction," defined as the mass of monomers added by each experiment per total mass of product solution. In the case of FT-RCF with Lig-MeOH, monomers could be generated from the lignin oil solubilized in feed solution as well as from the fresh biomass. Thus, the metric of incremental monomer mass fraction reflects both monomers from the feed solution and from fresh biomass. We note that the commonly reported metric of monomer yield represents only monomers from fresh biomass. The incremental monomer mass fraction during the 1st pass FT-RCF was 0.147% ± 0.011%. This value corresponds to a 22% monomer yield.

FT-RCF with 0.5 and 1 wt % feed solutions

To test the multi-pass FT-RCF concept, we produced 1.1 L Lig-MeOH at a 0.47 wt % lignin oil concentration (0.13 wt % of monomers) by combining five consecutive 1st pass FT-RCF runs, switching biomass beds and maintaining the same catalyst bed (denoted as "0.5 wt % Lig-MeOH," detailed in Figure S1). We used this product as a solvent in the FT-RCF reactor with fresh poplar and fresh catalyst for a second pass (denoted as the "2nd pass FT-RCF"). Compared with the lignin oil concentration from a single run of the 1st pass FT-RCF (i.e., 0.38 wt %), consecutive runs resulted in a higher lignin oil concentration because the remainder of Lig-MeOH in the reactor system between runs was collected in the subsequent run. It is worth noting that the 0.5 wt % Lig-MeOH did not undergo separation, thus it included lignin monomers and oligomers, soluble sugars, acetate, water, and extractives from biomass during the 1st pass.

The concentration values of the 0.5 wt % Lig-MeOH, 0.47 wt % of lignin oil, and 0.13 wt % of monomers were used as feed concentrations of the 2nd pass experiments (light patterned bars of experiments with the 0.5 wt % feed in Figures 3A and 3B, respectively). During the 2nd pass with the prepared 0.5 wt % Lig-MeOH feed, additional lignin oil was extracted from fresh poplar and depolymerized, leading to increased lignin oil and monomer concentrations. The increased lignin oil concentration from the feed concentration was used to estimate the cumulative delignification in this pass (51.8% ± 4.3%). Importantly, the similar delignification extent in the 1st and 2nd passes are indicative of an equivalent solvolysis ability of the recycled methanol in 0.5 wt % Lig-MeOH relative to pure methanol. In addition, a similar temporal profile of the incremental monomer mass fraction suggests the same rate of depolymerization of the extracted lignin in methanol and 0.5 wt % Lig-MeOH. The incremental monomer mass fraction in the 2nd pass FT-RCF was 0.151% ± 0.012%.

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Similarly, we conducted the 3rd pass FT-RCF with the 1 wt % Lig-MeOH feed, including 1 wt % lignin oil and 0.27 wt % monomers, which was obtained from two consecutive runs of the 2nd pass FT-RCF. The 3rd pass FT-RCF achieved 57.3% ± 0.8% cumulative delignification and 0.137% ± 0.014% incremental monomer mass fraction with similar time profiles observed in the 1st and 2nd passes. By using three consecutive passes, total solvent usage was reduced from 48 to 16 L solvent/kg biomass (Table S2).

FT-RCF with 2, 4, 8, and 12 wt % feed solutions

Inspired by the promising results of the three consecutive FT-RCF passes, we subsequently conducted FT-RCF with more concentrated feed solutions. Namely, 2, 4, 8, and 12 wt % Lig-MeOH feed solutions were prepared by diluting or concentrating 2.7 wt % Lig-MeOH that was collected from 3 L batch RCF reactions (Figure S2).

Interestingly, FT-RCF reactions with the prepared 2 and 4 wt % solutions extracted lignin to a similar extent (56.0% ± 1.1% and 51.5% ± 5.1%, respectively), and reactions with 8 and 12 wt % solutions exhibited slightly higher delignification (62.8% ± 3.5% and 67.9% ± 2.8%, respectively). We posited that the improved delignification with higher feed concentrations could be due to accumulated components in the feed solutions, including carboxylic acids, extractives, and water, which may promote improved lignin extraction. Acetic acid extracted from hemicellulose was converted to methyl acetate in these conditions, and during the workup, we confirmed that methyl acetate dissolved in the 2.7 wt % Lig-MeOH was evaporated when the solution was concentrated to the 8 and 12 wt % Lig-MeOH (Figure S7). Therefore, the increased delignification values at 8 and 12 wt % lignin in the feed solutions are likely not due to the presence of acetic acid and methyl acetate.

Higher lignin concentrations of the feed resulted in slightly different time profiles (orange circles in Figure 3A). Namely, when the concentration of the feed increased, delignification during the heating ramp (0 h sample) decreased. This effect might be due to the physical attachment of lignin components in the feed solution onto the biomass at low temperature. The attached lignin components could potentially then be released at reaction temperature, resulting in the sharp increase of lignin oil concentration in the 0.5 and 1 h samples and a similar cumulative delignification across the reaction duration.

In terms of the incremental monomer mass fraction, the FT-RCF reaction with 2 wt % Lig-MeOH exhibited a value of 0.145% ± 0.001%, similar to those observed in FT-RCF reactions with 0–1 wt % Lig-MeOH (orange squares in Figure 3B). However, a lower incremental monomer mass fraction (0.112% ± 0.012%) was observed with a 4 wt % feed solution while the delignification extent did not significantly change. We hypothesized that the reduced incremental monomer mass fraction was because the lignin oil in the feed solution competed for adsorption sites on the catalyst surface with lignin extracted from the biomass, thus inhibiting catalysis with the extracted lignin.

Overcoming catalyst-limited conditions in multi-pass FT-RCF

To avoid these catalyst-limited conditions, we increased the catalyst loading from 0.9 to 1.2 g and repeated the FT-RCF reaction with the 4 wt % Lig-MeOH feed. The incremental monomer mass fraction reached 0.151% ± 0.015%, demonstrating that a higher amount of catalyst is necessary to achieve a similar monomer production when using a higher concentration feed. Similarly, the 8 and 12 wt % lignin oil feeds resulted in only 0.083% ± 0.014% and 0.096% ± 0.049% incremental

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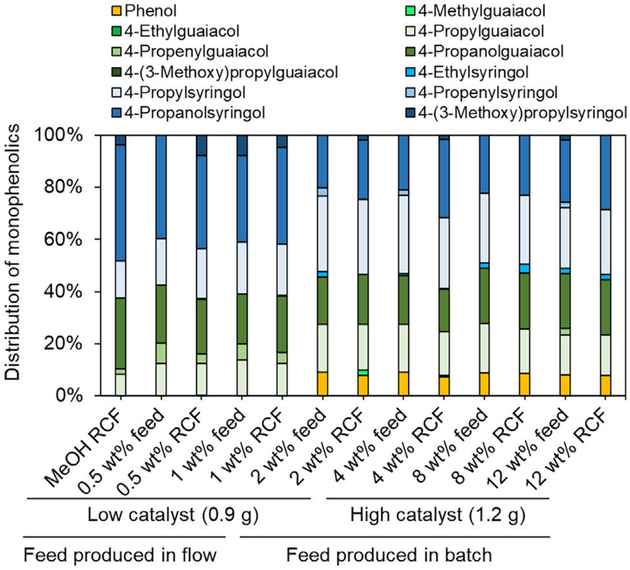

Figure 4. Distribution of monophenolics of feeds and post-RCF samples

The secondary x axis labels indicate the catalyst loading and the feed preparation method for each experiment. Table S3 contains the quantitative information for this figure.

monomer mass fractions, even with 1.2 g of catalyst. Due to physical limitations of our custom flow reactor system, catalyst loadings over 1.2 g could not be tested.

Instead, the samples from FT-RCF with the 8 wt % feed were combined and flowed through two additional catalyst beds to test whether the incremental monomer mass fraction increased. After the first additional catalysis step, the monomer concentration in the combined solution post FT-RCF increased from 2.38 to 2.65 ± 0.08 wt % (Figure S8A). Compared with 2.29 wt % monomer concentration of the 8 wt % feed, the estimated incremental monomer mass fraction was 0.356% ± 0.08%. The second additional catalysis step slightly further increased the monomer concentration to 2.71 ± 0.01 wt % and the estimated incremental monomer mass fraction to 0.422% ± 0.012%. A similar value (0.457% ± 0.044%) was observed when the FT-RCF samples underwent additional catalysis in a batch setup (Figure S9).

The high estimated incremental monomer mass fraction values after additional catalysis might be attributed to the cleavage of β-O-4 bonds that were in the 8 wt % feed. The β-O-4 peaks in the 8 wt % feed, which also remained after FT-RCF, were significantly reduced after two additional catalysis steps (Figure S15). Note that a hydrogenolysis reaction of the 8 wt % feed with fresh Ni/C in a batch setup exhibited 0.347% ± 0.058% incremental monomer mass fraction (Figure S9), indicating a significant amount of β-O-4 bonds in the 8 wt % feed. Thus, the cleavage of ether linkages in the feed, as well as depolymerization of lignin from fresh biomass, resulted in the high incremental monomer mass fraction values. This result indicates that higher catalyst loadings will be able to cleave C–O bonds both in the lignin extracted from the biomass and in the lignin oil solubilized in the feed solution.

Product distribution of monomers produced from multi-pass FT-RCF reactions

Lignin monomers produced via the 1st pass FT-RCF with pure methanol consist mostly of propanol-substituted syringol and guaiacol, followed by propyl-substituted monomers and propenylguaiacol (MeOH RCF in Figure 4). The 0.5 wt % Lig-MeOH solution—prepared via five consecutive 1st pass FT-RCF runs with five biomass beds and one catalyst bed—includes more propenylguaiacol, likely because of catalyst deactivation as previously observed in FT-RCF reactions.[28] Over the consecutive FT-RCF reactions with six fresh biomass beds and methanol, the catalyst was deactivated, evident from (1) the increase in propenyl chain monomers and (2) the decrease in the monomer mass fraction (Figure S10).[28] When 0.5 wt % Lig-MeOH was used as a solvent, slightly more rapid catalyst deactivation was observed in the presence of lignin oil in the feed. The fraction of the unsaturated monomers in the 0.5 and 1 wt % feed was reduced after FT-RCF with fresh catalyst. This observation suggests that the catalyst reacts with lignin components in the feed as well as in the extracted lignin from fresh biomass. Except for the changes observed in propenylguaiacol, other monomers did not change significantly after the FT-RCF reaction at 0–1 wt % concentration.

Compared with 0.5 and 1 wt % Lig-MeOH obtained via the FT-RCF setup, the feed solutions (2–12 wt %) from the batch reaction exhibited more propyl-substituted monomers and less propanol-substituted monomers (Figure 4). In addition, phenol- and ethyl-substituted monomers were also detected. At the higher feed concentrations (2–12 wt %), the distribution of monophenolic compounds remained similar after FT-RCF.

Stability of lignin monomers over multiple catalysis steps

In multi-pass FT-RCF, lignin monomers would be recycled, thus flowing over the catalyst beds multiple times. Therefore, changes in the monomer distribution over multiple catalysis steps are also worthwhile to investigate. We prepared and combined the 1st pass FT-RCF samples and flowed the combined solution over catalyst beds 8 times; specifically, after four catalysis steps, the spent catalyst was removed, and fresh catalyst was packed and used for an additional four catalysis steps. After each catalysis step, a sample was collected and the monomer distribution in each sample was analyzed. Even after eight additional catalysis steps, the distribution of monophenolics remained invariant (Figure S11). This indicates that the monomers stabilized during FT-RCF were not affected in the subsequent passes and remained stable over multi-pass FT-RCF. Consistently, the monomer distribution in the 8 wt % feed did not change when comparing compositions after the RCF reaction with those after two additional catalysis steps (Figure S8B), suggesting the stability of lignin monomers in Lig-MeOH over multiple passes. The monomer stability seems dependent on the reaction conditions and catalysts. Previously, more prolonged reactions led to partial changes of propyl monomers to ethyl monomers.[19]

Characterization of lignin oil

To characterize the lignin oil in the prepared Lig-MeOH feed solutions and post-FT-RCF samples, we isolated lignin oil from each sample through solvent removal and liquid-liquid extraction and analyzed the samples with GPC and 2D heteronuclear single quantum coherence (HSQC) NMR spectroscopy. The GPC trace of the isolated lignin oil from the 1st pass (MeOH RCF in Figure 5) showed three narrow peaks and two broad peaks. Peaks at 200 and 250 Da represent monomers including propanol- and propyl-substituted syringol and guaiacol, which were also detected in the NMR spectra (Figure S12). Three oligomer peaks at 310, 470, and 700 were assigned to dimers, trimers, and tetramers, respectively.[7,17,21,28,33]

Lignin oil in the 0.5 wt % feed showed not only monomers and low MW oligomers, but also high MW oligomer fragments up to 4,000 Da. The high MW values might

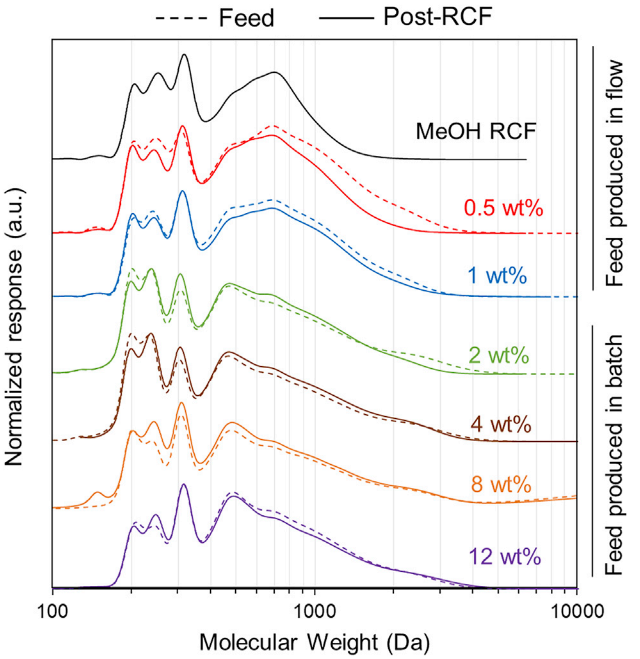

Figure 5. GPC traces of the isolated lignin oil of feeds and post-RCF samples
The right y axis labels indicate the feed preparation method for each experiment.

arise because the catalyst was deactivated throughout the five consecutive 1st pass FT-RCF runs.[28] This agrees with the higher β-O-4 peak intensity in the NMR spectrum of the isolated lignin oil from the 0.5 wt % feed (Figure S13) relative to lignin oil from a single run of the first pass FT-RCF (Figure S12). After the 2nd pass FT-RCF with the 0.5 wt % Lig-MeOH, fresh biomass, and fresh catalyst, the produced lignin oil exhibited reduced high MW oligomer fragments in the GPC chromatogram and a decreased β-O-4 peak intensity (Figure S13). These data suggest that in the 2nd pass, the fresh catalyst contributed to depolymerization of not only the extracted lignin from fresh biomass but also the high MW oligomers in the 0.5 wt % feed. It is noteworthy that the β-O-4 peaks in the 0.5 and 1 wt % feed exhibited much lower intensities than monomer product peaks (Figures S13 and S14), indicating a lower content of intact β-O-4 bonds in the feed solutions. This also suggests that the monomer addition during the 2nd and 3rd pass FT-RCF resulted primarily from depolymerization of the lignin extracted from fresh biomass and not from the cleavage of β-O-4 bonds in the lignin-enriched solvent.

Compared with the 0.5 and 1 wt % feeds, the 2–12 wt % feed solutions, prepared in batch reactions, showed slightly different chromatograms: a larger trimer peak at 470 Da than the tetramer peak at 700 Da (Figure 5). The similar overall GPC traces between the lignin oil in the feed and in the post-RCF sample suggest that the lignin oil in the feed is stable in the FT reactor and that a similar quality lignin oil could be extracted from fresh biomass added to the feed during FT-RCF. This excludes the possibility that the accumulated components in the high-concentration feeds promote the repolymerization of lignin oil. NMR spectra of lignin oil from each pass showed efficient removal of the aryl-ether linkage in poplar and production of monomers after FT-RCF or additional catalysis steps, suggesting that hydrogenolysis of the β-O-4 linkage of the extracted lignin was not affected by lignin oil concentration in feed solution under excess catalyst conditions.

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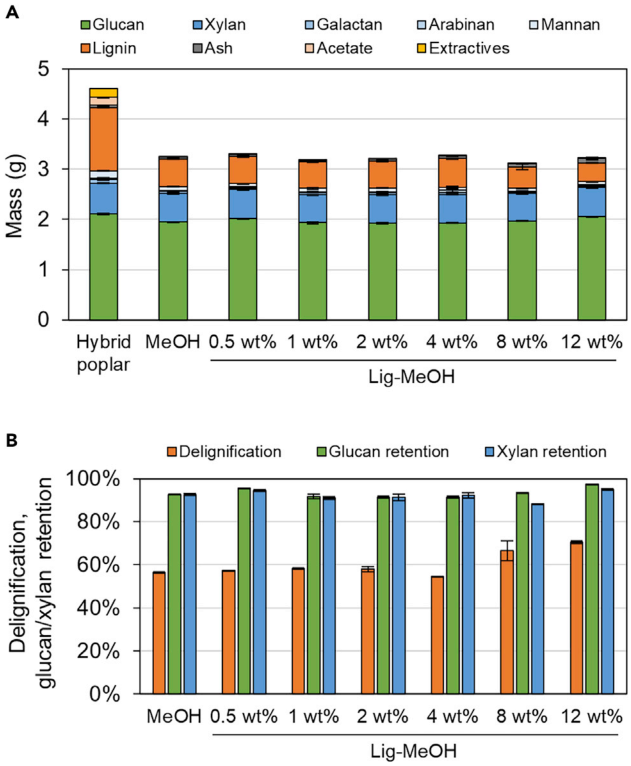

Figure 6. Composition and delignification extent over the FT-RCF reactions

(A) Compositional analysis of parent and post-RCF poplar in the different feed solutions.

(B) The calculated delignification and glucan/xylan retention using Equations S10–S12. Table S4 contains the quantitative information for the data shown here. Figures S5 and S6 present a general overview of the mass flow of the main lignocellulose components.

Characterization of carbohydrate pulp

Compositional analysis of the isolated residual pulp samples was also conducted to investigate the effect of the feed concentration on polysaccharide retention (Figure 6; Table S4). Compared with native biomass (hybrid poplar), the composition of the pulp residue after FT-RCF with methanol clearly showed a high selectivity for lignin removal with high retention of carbohydrates. The calculated delignification and glucan and xylan retentions were 56.4% ± 0.4%, 92.6% ± 0.2%, and 92.6% ± 0.4%, respectively. The small differences in the delignification values calculated based on the liquid sample and the solid residue likely arose because the liquid stream analysis did not include delignification by methanol remaining between the biomass bed and the sample collector. The use of 0.5–4 wt % Lig-MeOH solutions for FT-RCF instead of methanol resulted in similar delignification between 54.5% ± 0.1% and 58.4% ± 0.3%. With the 8 and 12 wt % feeds, FT-RCF reactions increased delignification values to 66.5% ± 4.7% and 70.6% ± 0.6%, respectively. This agrees with the higher delignification values from FT-RCF with the 8 and 12 wt % Lig-MeOH observed in the liquid stream analysis.

Glucan and xylan retentions were not significantly affected by the feed concentration of lignin. The glucan retention varied only from 91.4% ± 0.5% to 97.5% ± 0.3%, and xylan retention remained between 88.1% ± 0.1% and 95.0% ± 0.2% (Figure 6B). This solid stream analysis, combined with the liquid stream analysis, highlights the effectiveness of multi-pass FT-RCF.

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Multi-pass FT control experiments without stabilization

In addition to the multi-pass FT-RCF tests that reuse the Lig-MeOH solutions and undergo both solvolysis and catalysis, we conducted a control experiment to examine the multi-pass configuration in a solvolysis step only. Three consecutive solvolysis runs produced the 1st, 2nd, and 3rd solvolysis liquors (Figure S16). We previously reported that single-pass solvolysis produces native-like lignin with intact aryl–ether bonds.[33] Here, due to the considerably longer residence times than our previous work, the native-like lignin from the 1st solvolysis pass was repolymerized in the 2nd and 3rd solvolysis passes, evident from the increase in oligomer fragments (400–1,100 Da) and the decrease in the dimer peak (310 Da) in the GPC traces (Figure S17). Uncatalyzed lignin was likely recondensed with additional solvolysis time at 225°C during the 2nd and 3rd passes.[22] The prepared solvolysis liquors underwent a FT hydrogenolysis reaction separately, and the recondensation that occurred during multi-pass solvolysis resulted in the decrease of incremental monomer mass fraction from 0.123% to 0.09% (Figure S18). This control experiment indicates the importance of the catalytic stabilization in multi-pass FT-RCF to avoid repolymerization and reduced monomer yield.

Multi-pass FT-RCF at a higher delignification extent using methanol-water solvent mixtures

Methanol is a common solvent for RCF processes. The resulting delignification extent is in the 50%–70% range from FT-RCF with methanol or Lig-MeOH are close to the limit of methanol RCF that has been previously reported in batch and FT reactions (Figure 1).[21,28,30] To further examine the effect of recycling lignin oil, we were interested in studying the effect of higher levels of delignification. Thus, we additionally conducted FT-RCF with an equivalent 1:1 v/v methanol-water mixture (denoted as ''MeOH/H_2O'') and 2 and 8 wt % lignin oil-containing methanol-water solutions (denoted as ''Lig-MeOH/H_2O''). Previously, RCF of poplar with an alcohol-water mixture has been reported to achieve delignification extents between 70% and 90% (Figure 1).[14,21]

FT-RCF with MeOH/H_2O extracted both lignin and hemicellulose with a delignification extent of 92.9% ± 0.4% and a xylan retention of 20.0% ± 0.5% (Figure 7). Conversely, glucan was not appreciably extracted from poplar, exhibiting 93.4% ± 0.6% retention. The 2 and 8 wt % Lig-MeOH/H_2O feeds were prepared by batch RCF of poplar with MeOH/H_2O. Thus, the feeds include not only lignin components but also a more enriched hemicellulose content. After a 1 h heat ramp and a 1 h RCF reaction with the prepared 2 and 8 wt % solutions, similar extents of lignin extraction (92.6% ± 0.1% and 92.6% ± 0.6%, respectively) and glucan retention (91.9% ± 0.6% and 90.9% ± 0.2%, respectively) were achieved. This demonstrates that the recycled methanol-water mixture, with both enriched lignin and hemicellulose content in the feeds, could extract lignin and maintain glucan retention to a similar extent, compared with MeOH/H_2O. Xylan extraction was slightly different in the 2 and 8 wt % feeds, exhibiting xylan retention of 22.7% ± 0.2% and 27.9% ± 0.2%, respectively.

Concerning the incremental monomer mass fraction (Figures 7C and S19), to minimize the effect of catalyst-limited conditions, we reduced the biomass-to-catalyst ratio from 5 g biomass/1.2 g catalyst to 3 g biomass/1.2 g catalyst. The incremental monomer mass fraction value obtained via FT-RCF with MeOH/H_2O (0.071% ± 0.001%), which corresponds to a 19% monomer yield, was maintained in the reaction with the 2 wt % feed (0.080% ± 0.022%). A slightly higher incremental monomer mass fraction (0.108% ± 0.054%) from the reaction with the 8 wt % feed might result from the cleavage of C–O bonds both in the lignin extracted from the biomass and in the lignin oil solubilized in the feed solution.

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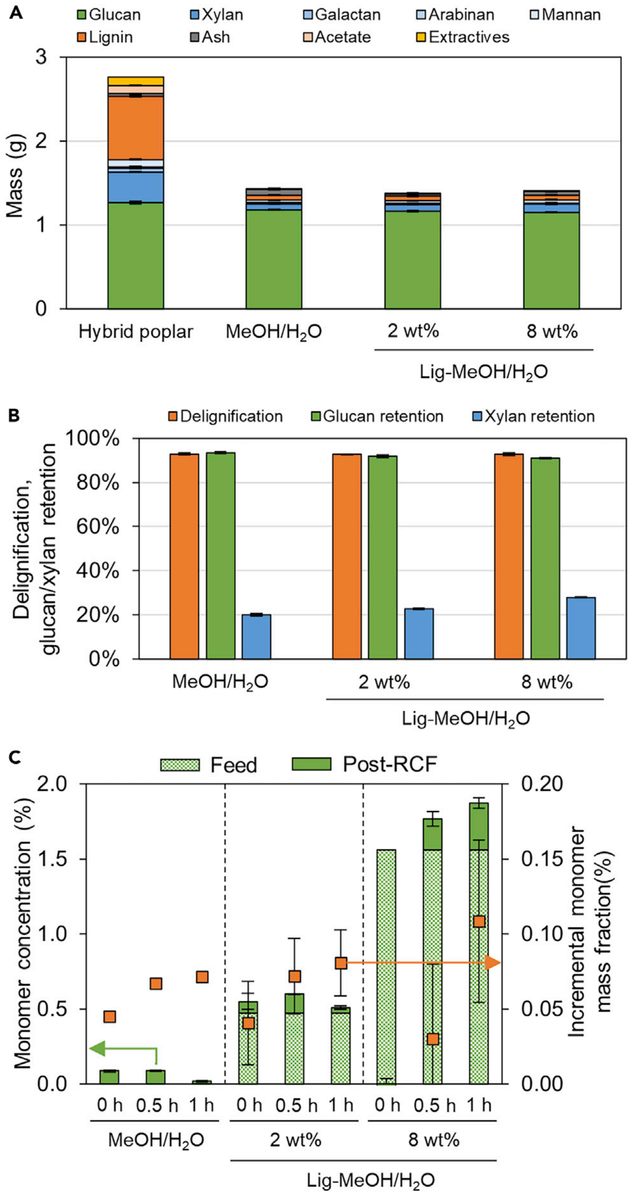

Figure 7. FT-RCF reactions with a methanol-water solvent system

(A) Compositional analysis of parent and post-RCF poplar in the different feed solutions.

(B) The delignification and glucan/xylan retention were calculated using Equations S10–S12.

(C) Monomer concentration and calculated incremental monomer mass fraction. For each FT-RCF experiment, samples were collected at 0, 0.5, and 1 h. The secondary x axis labels (below the time points) indicate the lignin oil concentration in the feed. The light patterned bars show the monomer concentration in the feed, and dark solid bars represent the additional concentration of monomers that were added over that time. Reaction conditions: 2 mL/min feed solution, 3 g poplar, 1.2 g 5 wt % Ru/C (diluted with 2.8 g of fused silica), 1,600 psig, 200 sccm H_2, 225°C, and 1 h heating ramp and 1 h run. Tables S5 and S6 contain the quantitative information for the data shown here.

DISCUSSION

As shown in this work, FT-RCF with 0.5–12 wt % Lig-MeOH feed solutions exhibited similar or higher lignin extraction and carbohydrate retention efficiency, compared with FT-RCF with pure methanol. FT-RCF with the 12 wt % feed solution resulted in the solvent-to-biomass ratio of 1.9 L/kg (Figure 1; Table S2), which is lower than the previously reported ratios in batch reactions (4–50 L/kg).[14–17,19–22,24,25,30,37] In batch RCF reactions, further reducing the batch solvent loading would likely encounter severe mass transport limitations in lignin solvolysis due to the high solid fraction.[35] By contrast, in multi-pass FT-RCF, the extracted lignin oil is solubilized, which avoids the use of high solid fractions and the resulting mass transfer issues. Because solvent usage linearly impacts energy demand, GHG emissions of RCF processes, and the minimum selling price of RCF oil, the multi-pass FT-RCF with solvent usage down to 1.9 L/kg is economically and environmentally more beneficial than single-pass batch or FT-RCF.[35]

The ultimate solvent-to-biomass ratio using the multi-pass concept could potentially be reduced further, but the 1.9 L/kg value reported shows the promise of this approach; however, it was not practical to continue carrying out more consecutive runs with our current FT reactor systems. Nonetheless, this initial study motivates additional efforts for further solvent reduction using multi-pass RCF configurations. When recycling the solvent with concentrated RCF oil, it will be critical to understand the effect of the accumulated components therein, such as acetate, water, extractives, and sugar-derived compounds. Compositional analysis (Figure 6A) revealed that acetate and extractives were extracted during FT-RCF and included in RCF oil. For example, a high concentration of acetic acid, hydrolyzed from hemicellulose side chains, could potentially promote the repolymerization of unstable lignin-derived intermediates.[5]

In addition to FT-RCF, the multi-pass concept can be extended to other reactor configurations to enhance industrial relevance. Similarly to multi-pass FT-RCF, a batch system with internal solvent recycles could also be considered. To this end, Samec et al. recently reported use of a high-pressure Soxhlet extractor wherein biomass is physically separated from a solvent and the solvent is refluxed, extracting lignin from biomass and washing the delignified biomass.[38] By adding a catalyst to the system, the extracted lignin could be depolymerized and stabilized. This system achieved 97% delignification in the presence of CO_2 with a solvent-to-biomass ratio of 6.6 L/kg. Additionally, traditional batch RCF processes, including via use of a catalyst basket,[22] could directly use the multi-pass concept, recirculating the RCF oil and solvent multiple times to reduce solvent usage.

Perhaps the most industrially favorable configuration would ultimately be a continuous RCF reactor configuration wherein biomass and solvent are continuously fed into and removed from the reactor. As a multi-pass approach, the RCF effluent from a continuous process, after solid-liquid separation, could be re-injected to the reactor to delignify fresh biomass, thus reducing net solvent usage. However, successful continuous RCF processes have not yet been reported to our knowledge.

In addition to the data presented here for the multi-pass FT-RCF concept, challenges common to most RCF processes reported in the open literature remain to be addressed in parallel.[10,27] Namely, catalyst deactivation during RCF has been observed in both batch and FT configurations.[22,28] However, there is still a lack of a comprehensive understanding of deactivation mechanisms like poisoning, fouling, leaching, or sintering during RCF. Besides, to maximize the value of RCF processes, the major cost and environmental contributors such as operating pressure and utilization of an entire slate of products in the RCF oil, including monomers, dimers, and oligomers, need to be further explored.[39,40] Breakthroughs to these ends could be simultaneously employed in multi-pass RCF reactor configurations to reduce overall solvent usage as well.

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Conclusions

In summary, we demonstrated that multi-pass FT-RCF could reuse RCF effluent without additional separation steps and extract lignin from biomass multiple times to a similar or higher extent (52%–68%). The incremental monomer mass fraction remained around 0.15% through multi-pass FT-RCF with feeds up to 4 wt % when the catalyst loading was adjusted for total lignin content. With the catalyst loading suitable for ≤4, 8, and 12 wt % feed solutions reduced the incremental monomer mass fraction to a range of 0.083%–0.096%, resulting from operating in catalyst-limited conditions. Additional catalysis steps cleaved C–O linkages both in lignin extracted from biomass and in lignin oil solubilized in the feed, increasing the monomer mass fraction to 0.422%. The extracted lignin oil from each pass exhibited similar monomer selectivity, GPC traces, and NMR spectra. These results suggest the reusability of the lignin oil-containing solution without a detrimental effect on RCF performance, including solvolysis, depolymerization, and stabilization, under excess catalyst conditions. A reduction in overall solvent usage to 1.9 L/kg, as achieved by the multi-pass FT-RCF concept, would reduce the energy demand and operating costs for solvent recovery as well as the net GHG emissions in the RCF process,[35] suggestive of the industrial potential for multi-pass RCF concepts.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Gregg T. Beckham (gregg.beckham@nrel.gov).

Material availability

This study did not generate new unique materials.

Data and code availability

The datasets in this article are provided in full in the supplemental information.

Methods

Methods for catalyst synthesis, feed-solution preparation, the FT reaction procedure, and characterization of liquid and solid streams are described throughout the main text and in detail in the supplemental information. Briefly, 5 g of poplar was packed in a biomass bed and 0.9 or 1.2 g of 15 wt % Ni/C catalyst, diluted with 2.1 or 2.8 g of fused SiO_2, was packed in a catalyst bed. The biomass bed was filled with the prepared feed solution to a pressure of 1,600 psig and the remainder of the reactor was filled with H_2 gas to 1,600 psig and heated to 225°C. Once the temperature of the catalyst bed reached 225°C, the reaction started by heating the biomass bed to 225°C and flowing the feed solution and H_2 gas with a flow rate of 2 mL/min and 200 sccm, respectively. The first sample was collected at the end of the 1 h heating ramp (denoted as 0 h) and samples at the reaction temperature of 225°C were collected at 0.5 and 1 h. The isolated lignin oil in each sample was characterized by GC-FID, GPC, and 2D HSQC NMR spectroscopy and the composition of the carbohydrate pulp residue was analyzed. The metrics used in this study including lignin oil and monomer concentration, delignification, incremental monomer mass fraction, and monomer selectivity are defined as the following equations.

$$\text{Lignin oil concentration } (\%) = \frac{mass_{lignin\ oil}}{mass_{solution}} \times 100 \qquad \text{(Equation 1)}$$

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$$\text{Delignification } (\%) = \left(\frac{mass_{\text{lignin oil in each sample}} - mass_{\text{lignin oil in feed}}}{mass_{\text{total lignin in fresh biomass}}}\right) \times 100 \quad \text{(Equation 2)}$$

$$\text{Monomer concentration } (\%) = \frac{mass_{\text{monomer}}}{mass_{\text{solution}}} \times 100 \quad \text{(Equation 3)}$$

$$\text{Incremental monomer mass fraction } (\%) = \left(\frac{mass_{\text{monomer in each sample}} - mass_{\text{monomer in feed}}}{mass_{\text{total solution of 0, 0.5, and 1 h samples}}}\right) \times 100 \quad \text{(Equation 4)}$$

$$\text{Monomer selectivity } (\%) = \frac{mass_{\text{desired monomer}}}{mass_{\text{total monomers}}} \times 100 \quad \text{(Equation 5)}$$

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.joule.2022.06.016.

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AUTHOR CONTRIBUTIONS

Conceptualization, J.H.J., D.G.B., J.R. Bielenberg, T.R., Y.R.-L., and G.T.B.; methodology, J.H.J., D.G.B., A.S.K., J.I.C., J.R. Bielenberg, Y.R.-L., and G.T.B.; validation, J.H.J.; formal analysis, J.H.J., D.G.B., L.M.S., and R.M.H.; resources, J.H.J., D.G.B., R.J.D., A.J.R., J.R. Bussard, and G.T.B.; data curation, J.H.J. and G.T.B.; visualization, J.H.J.; investigation, J.H.J.; writing – original draft, J.H.J.; writing – review & editing, J.H.J., D.G.B., R.J.D., A.J.R., J.R.B., L.M.S., R.M.H., A.S.K., J.I.C., J.R. Bielenberg, J.R. Bussard, T.R., Y.R.-L., and G.T.B.; supervision, Y.R.-L. and G.T.B.; funding acquisition, Y.R.-L. and G.T.B.; project administration, G.T.B. All authors approved the final version of the manuscript.

DECLARATION OF INTERESTS

J.H.J., D.G.B., Y.R.L., and G.T.B. have submitted patent applications on the multi-pass flow-through concept.

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REFERENCES

1. Rinaldi, R., Jastrzebski, R., Clough, M.T., Ralph, J., Kennema, M., Bruijnincx, P.C., and Weckhuysen, B.M. (2016). Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis. Angew. Chem. Int. Ed. Engl. *55*, 8164–8215.
2. Galkin, M.V., and Samec, J.S.M. (2016). Lignin valorization through catalytic lignocellulose fractionation: A fundamental platform for the future biorefinery. ChemSusChem *9*, 1544–1558.
3. Renders, T., Van den Bosch, S., Koelewijn, S.-F., Schutyser, W., and Sels, B.F. (2017). Lignin-first biomass fractionation: the advent of active stabilisation strategies. Energy Environ. Sci. *10*, 1551–1557.
4. Van den Bosch, S., Koelewijn, S.F., Renders, T., Van den Bossche, G., Vangeel, T., Schutyser, W., and Sels, B.F. (2018). Catalytic strategies towards lignin-derived chemicals. Top. Curr. Chem. (Cham) *376*, 36.
5. Schutyser, W., Renders, T., Van den Bosch, S., Koelewijn, S.F., Beckham, G.T., and Sels, B.F. (2018). Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem. Soc. Rev. *47*, 852–908.
6. Sun, Z., Fridrich, B., de Santi, A., Elangovan, S., and Barta, K. (2018). Bright side of lignin depolymerization: Toward new platform chemicals. Chem. Rev. *118*, 614–678.
7. Renders, T., Van den Bossche, G., Vangeel, T., Van Aelst, K., and Sels, B.F. (2019). Reductive catalytic fractionation: state of the art of the lignin-first biorefinery. Curr. Opin. Biotechnol. *56*, 193–201.
8. Sudarsanam, P., Ruijten, D., Liao, Y., Renders, T., Koelewijn, S.F., and Sels, B.F. (2020). Towards lignin-derived chemicals using atom-efficient catalytic routes. J. Trends Chem. *2*, 898–913.
9. Liu, X., Bouxin, F.P., Fan, J., Budarin, V.L., Hu, C., and Clark, J.H. (2020). Recent advances in the catalytic depolymerization of lignin towards phenolic chemicals: a review. ChemSusChem *13*, 4296–4317.
10. Abu-Omar, M.M., Barta, K., Beckham, G.T., Luterbacher, J.S., Ralph, J., Rinaldi, R., Román-Leshkov, Y., Samec, J.S.M., Sels, B.F., and Wang, F. (2021). Guidelines for performing lignin-first biorefining. Energy Environ. Sci. *14*, 262–292.
11. Yan, N., Zhao, C., Dyson, P.J., Wang, C., Liu, L.T., and Kou, Y. (2008). Selective degradation of wood lignin over noble-metal catalysts in a two-step process. ChemSusChem *1*, 626–629.
12. Song, Q., Wang, F., Cai, J., Wang, Y., Zhang, J., Yu, W., and Xu, J. (2013). Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation–hydrogenolysis process. Energy Environ. Sci. *6*, 994–1007.
13. Galkin, M.V., and Samec, J.S.M. (2014). Selective route to 2-propenyl aryls directly from wood by a tandem organosolv and palladium-catalysed transfer hydrogenolysis. ChemSusChem *7*, 2154–2158.
14. Ferrini, P., and Rinaldi, R. (2014). Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions. Angew. Chem. Int. Ed. Engl. *53*, 8634–8639.
15. Van den Bosch, S., Schutyser, W., Vanholme, R., Driessen, T., Koelewijn, S.-F., Renders, T., De Meester, B., Huijgen, W.J.J., Dehaen, W., Courtin, C.M., et al. (2015). Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. Energy Environ. Sci. *8*, 1748–1763.
16. Parsell, T., Yohe, S., Degenstein, J., Jarrell, T., Klein, I., Gencer, E., Hewetson, B., Hurt, M., Kim, J.I., Choudhari, H., et al. (2015). A synergistic biorefinery based on catalytic conversion of lignin prior to cellulose starting from lignocellulosic biomass. Green Chem *17*, 1492–1499.
17. Anderson, E.M., Katahira, R., Reed, M., Resch, M.G., Karp, E.M., Beckham, G.T., and Román-Leshkov, Y. (2016). Reductive catalytic fractionation of corn stover lignin. ACS Sustainable Chem. Eng. *4*, 6940–6950.
18. Ferrini, P., Rezende, C.A., and Rinaldi, R. (2016). Catalytic upstream biorefining through hydrogen transfer reactions: understanding the process from the pulp perspective. ChemSusChem *9*, 3171–3180.
19. Galkin, M.V., Smit, A.T., Subbotina, E., Artemenko, K.A., Bergquist, J., Huijgen, W.J., and Samec, J.S.M. (2016). Hydrogen-free catalytic fractionation of woody biomass. ChemSusChem *9*, 3280–3287.
20. Luo, H., Klein, I.M., Jiang, Y., Zhu, H., Liu, B., Kenttämaa, H.I., and Abu-Omar, M.M. (2016). Total utilization of miscanthus biomass, lignin and carbohydrates, using earth abundant nickel catalyst. ACS Sustainable Chem. Eng. *4*, 2316–2322.
21. Renders, T., Van den Bosch, S., Vangeel, T., Ennaert, T., Koelewijn, S.F., Van den Bossche, G., Courtin, C.M., Schutyser, W., and Sels, B.F. (2016). Synergetic effects of alcohol/water mixing on the catalytic reductive fractionation of poplar wood. ACS Sustainable Chem. Eng. *4*, 6894–6904.
22. Van den Bosch, S., Renders, T., Kennis, S., Koelewijn, S.-F., Van den Bossche, G., Vangeel, T., Deneyer, A., Depuydt, D., Courtin, C.M., Thevelein, J.M., et al. (2017). Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al2O3 catalyst pellets during lignin-first fractionation. Green Chem. *19*, 3313–3326.
23. Cao, Z., Dierks, M., Clough, M.T., Daltro de Castro, I.B., and Rinaldi, R. (2018). A convergent approach for a deep converting lignin-first biorefinery rendering high-energy-density drop-in fuels. Joule *2*, 1118–1133.
24. Renders, T., Cooreman, E., Van den Bosch, S., Schutyser, W., Koelewijn, S.-F., Vangeel, T., Deneyer, A., Van den Bossche, G., Courtin, C.M., and Sels, B.F. (2018). Catalytic lignocellulose biorefining in *n*-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose. Green Chem. *20*, 4607–4619.
25. Liao, Y., Koelewijn, S.F., Van den Bossche, G., Van Aelst, J., Van den Bosch, S., Renders, T., Navare, K., Nicolaï, T., Van Aelst, K., Maesen, M., et al. (2020). A sustainable wood biorefinery for low carbon footprint chemicals production. Science *367*, 1385–1390.
26. Muangmeesri, S., Li, N., Georgouvelas, D., Ouagne, P., Placet, V., Mathew, A.P., and Samec, J.S.M. (2021). Holistic valorization of hemp through reductive catalytic fractionation. ACS Sustain. Chem. Eng. *9*, 17207–17213.
27. Cooreman, E., Vangeel, T., Van Aelst, K., Van Aelst, J., Lauwaert, J., Thybaut, J.W., Van den Bosch, S., and Sels, B.F. (2020). Perspective on overcoming scale-up hurdles for the reductive catalytic fractionation of lignocellulose biomass. Ind. Eng. Chem. Res. *59*, 17035–17045.
28. Anderson, E.M., Stone, M.L., Katahira, R., Reed, M., Beckham, G.T., and Román-Leshkov, Y. (2017). Flowthrough reductive catalytic fractionation of biomass. Joule *1*, 613–622.
29. Kumaniaev, I., Subbotina, E., Sävmarker, J., Larhed, M., Galkin, M.V., and Samec, J.S.M. (2017). Lignin depolymerization to monophenolic compounds in a flow-through system. Green Chem. *19*, 5767–5771.
30. Anderson, E.M., Stone, M.L., Hülsey, M.J., Beckham, G.T., and Román-Leshkov, Y. (2018). Kinetic studies of lignin solvolysis and reduction by reductive catalytic fractionation decoupled in flow-through reactors. ACS Sustainable Chem. Eng. *6*, 7951–7959.
31. Anderson, E.M., Stone, M.L., Katahira, R., Reed, M., Muchero, W., Ramirez, K.J., Beckham, G.T., and Román-Leshkov, Y. (2019). Differences in S/G ratio in natural poplar variants do not predict catalytic depolymerization monomer yields. Nat. Commun. *10*, 2033.
32. Kumaniaev, I., Subbotina, E., Galkin, M.V., Srifa, P., Monti, S., Mongkolpichayarak, I., Tungasmita, D.N., and Samec, J.S.M. (2020). A combination of experimental and computational methods to study the reactions during a Lignin-First approach. Pure Appl. Chem. *92*, 631–639.
33. Brandner, D.G., Kruger, J.S., Thornburg, N.E., Facas, G.G., Kenny, J.K., Dreiling, R.J., Morais, A.R.C., Renders, T., Cleveland, N.S., Happs, R.M., et al. (2021). Flow-through solvolysis enables production of native-like lignin from biomass. Green Chem. *23*, 5437–5441.
34. Kramarenko, A., Etit, D., Laudadio, G., and D'Angelo, F.N. (2021). beta-zeolite-assisted lignin-first fractionation in a flow-through reactor. ChemSusChem *14*, 3838–3849.
35. Bartling, A.W., Stone, M.L., Hanes, R.J., Bhatt, A., Zhang, Y., Biddy, M.J., Davis, R., Kruger, J.S., Thornburg, N.E., Luterbacher, J.S., et al. (2021). Techno-economic analysis and life cycle assessment of a biorefinery utilizing reductive catalytic fractionation. Energy Environ. Sci. *14*, 4147–4168.
36. Kumaniaev, I., Navare, K., Crespo Mendes, N., Placet, V., Van Acker, K., and Samec, J.S.M. (2020). Conversion of birch bark to biofuels. Green Chem. *22*, 2255–2263.

Please cite this article in press as: Jang et al., Multi-pass flow-through reductive catalytic fractionation, Joule (2022), https://doi.org/10.1016/j.joule.2022.06.016

37. Subbotina, E., Velty, A., Samec, J.S.M., and Corma, A. (2020). Zeolite-assisted lignin-first fractionation of lignocellulose: overcoming lignin recondensation through shape-selective catalysis. ChemSusChem *13*, 4528–4536.

38. Di Francesco, D., Baddigam, K.R., Muangmeesri, S., and Samec, J.S.M. (2021). OrganoSoxhlet: circular fractionation to produce pulp for textiles using CO2 as acid source. Green Chem. *23*, 9401–9405.

39. Van Aelst, K., Van Sinay, E., Vangeel, T., Cooreman, E., Van den Bossche, G., Renders, T., Van Aelst, J., Van den Bosch, S., and Sels, B.F. (2020). Reductive catalytic fractionation of pine wood: elucidating and quantifying the molecular structures in the lignin oil. Chem. Sci. *11*, 11498–11508.

40. Dao Thi, H., Van Aelst, K., Van den Bosch, S., Katahira, R., Beckham, G.T., Sels, B.F., and Van Geem, K.M. (2022). Identification and quantification of lignin monomers and oligomers from reductive catalytic fractionation of pine wood with GC × GC – FID/MS. Green Chem. *24*, 191–206.