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Flow-through solvolysis enables production of native-like lignin from biomass†

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The inherent reactivity of lignin in conventional biomass processing commonly prevents isolation of native lignin and limits monomer yields from catalytic depolymerization strategies that target aryl-ether bonds. Here we show that flow-through solvolysis with methanol at 225 °C produces native-like lignin from poplar, enabling the study of intrinsic lignin properties and evaluation of steady-state lignin depolymerization processes.

Lignin valorization is important for the economics and sustainability of biomass conversion,[1,2] and catalytic deconstruction to valuable monomers is a common strategy to that end. The abundant aryl-ether linkage in lignin is the most frequent target of catalysis, but condensation reactions ultimately limit monomer yields from C–O bond cleavage.[3] To address this challenge, the lignin-first biorefining approach catalytically passivates reactive intermediates or uses stoichiometric reagents to functionalize the β-O-4 linkage.[3,4] Lignin-first strategies typically yield a narrow slate of aromatic monomers, bounded by the aryl-ether content of the lignin.[5]

Many lignin-first biorefining studies employ reductive catalytic fractionation (RCF) in batch reactors where biomass, a reducing catalyst, and a hydrogen donor are combined in polar protic solvents. Given the typical reaction times and temperatures of RCF processes, a catalyst must be present during reaction to prevent condensation.[6,7] However, physical mixing of the biomass and catalyst complicates kinetics studies and post-reaction analyses.

Recently, several reactor configurations have been applied to physically separate the biomass and catalyst for RCF processes, including conducting solvolysis and hydrogenolysis as separate batch reactions or in tandem flow-through reactors, or by using catalyst baskets in batch reactors.[8–13,19] In batch solvolysis reactions, the typical multi-hour residence time without catalytic stabilization results in lower monomer yields.[8,12,13] In flow-through RCF configurations (Fig. 1A), the catalyst performance is not measured at steady-state because lignin solubilization varies temporally. To overcome this, Lan *et al.* recently applied a protection-group method[14] to produce isolated lignin for subsequent depolymerization in a flow reactor.[15] Wang *et al.* also demonstrated that aqueous formic

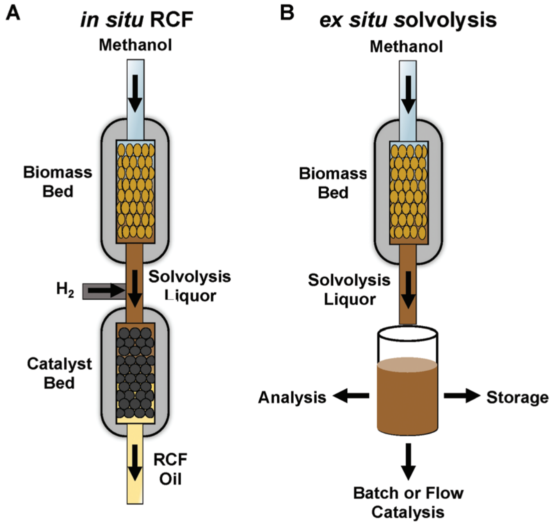

Fig. 1 Schematics of flow-through solvolysis and reductive catalytic fractionation (RCF) configurations used in the present study. (A) *In situ* flow-through solvolysis of biomass with methanol and hydrogenolysis with a Ni/C catalyst. (B) *Ex situ* flow-through solvolysis setup in flow, where catalysis is subsequently conducted in batch reactors or a flow reactor with isolated solvolysis liquor.

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acid extracts lignin from biomass, with an estimated 75% retention of aryl-ether linkages.[16] Generally, the ability to isolate native-like lignin for lignin property studies and to evaluate steady-state catalytic lignin depolymerization activity with intact C–O linkages would be useful, but with these few exceptions, the ability to isolate native-like lignin in a solubilized form has not been widely reported to our knowledge. In addition, reducing solvent usage in RCF is critical for process economics,[17] and the ability to isolate a native-like lignin may facilitate solvent recycling and enable more efficient use of a downstream catalytic step, thus reducing the costs in an RCF process.

In the present study, we hypothesized that solubilized lignin from whole biomass at typical RCF conditions must be rapidly exposed to a catalyst and hydrogen, otherwise it will undergo condensation.[6,7] To test this hypothesis, we conducted RCF reactions in either an *in situ* or *ex situ* mode with a multi-bed flow system (Fig. 1) and in batch reactors. Throughout, '*in situ*' denotes that the lignin is exposed to the catalyst directly after solvolysis (either in batch or flow), and '*ex situ*' denotes that lignin is first isolated, then in a separate processing step, subjected to hydrogenolysis. Throughout, we used methanol as a solvent, hybrid poplar as the substrate (Table S1†), a reaction time of 3 h, a reaction temperature of 225 °C, and 15 wt% Ni/C as the catalyst. The methanol-to-biomass ratio used in all batch and flow reactions was ~93 L kg^{-1}. All lignin monomer yields are reported on a wt% basis with respect to the total lignin content. The materials and methods are detailed in the ESI.†

We first benchmarked the aryl-ether bond content in poplar lignin based on aromatic monomer yield from *in situ* batch and flow-through RCF reactions. From these experiments, we obtained monomer yields of 36.8 ± 0.2% in a batch reaction and 31.6 ± 1.3% in a flow-through RCF experiment (Fig. 2 and Tables S1–S3†). For all flow-through reactions, we ran at temperature for 3 h, which resulted in a delignification extent of 63.1% ± 0.1%. A control *in situ* batch reaction with an activated carbon support alone resulted in a monomer yield of 11.3 ± 0.3%.

To compare the degree of lignin condensation without employing hydrogenolysis immediately upon extraction, we conducted an *ex situ* batch solvolysis reaction. The isolated lignin oil was then subjected to batch hydrogenolysis, where we obtained a monomer yield of 18.6 ± 0.2% (Table S2†). Relative to the *in situ* reactions, this result indicates that substantial lignin condensation (compared to 36.8 ± 0.2%, above) occurs over 3 h without catalyst and hydrogen.

To examine condensation extents when lignin is rapidly quenched, we produced solvolysis liquor with methanol over multiple biomass beds at 225 °C *via ex situ* flow-through solvolysis (Fig. 1B). We collected the solvolysis liquor in a knockout pot, pooled the liquor from 12 consecutive reactor beds (producing ~5.5 L total), and stored the sample at room temperature in a translucent LDPE bottle. After one week of storage at room temperature, we performed batch and flow-through hydrogenolysis on the solvolysis liquor, again using 15 wt% Ni/C at an equivalent catalyst to biomass ratio at 225 °C. Much to our surprise, the monomer yields from these experiments were 35.2 ± 0.0% and 32.3 ± 0.0%, respectively, similar to the *in situ* RCF results (Fig. 2 and Table S2†). A control *ex situ* flow-through experiment over the carbon support yielded 6.6 ± 0.4% monomer yield.

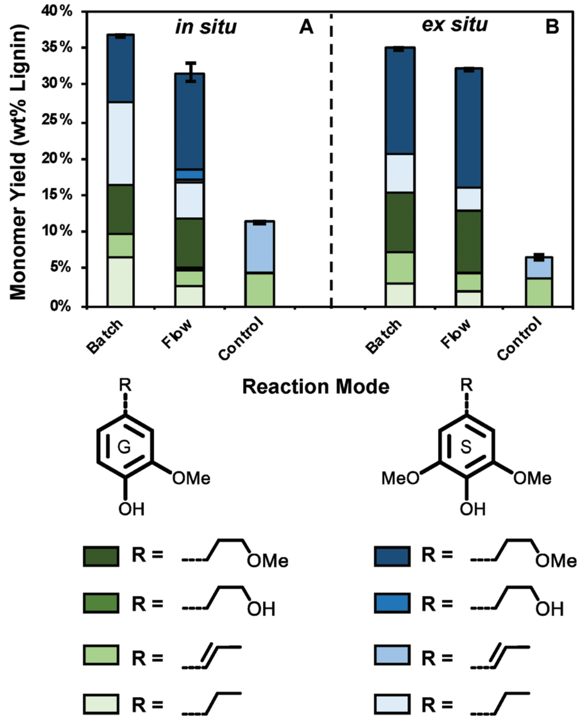

Fig. 2 Monomer yield and selectivity data from *in situ*, and *ex situ* RCF experiments in batch and flow-through modes. (A) Results from *in situ* batch and flow-through RCF experiments, including an *in situ* flow-through control reaction with biomass and carbon support in methanol. (B) Results from *ex situ* flow solvolysis and subsequent batch and flow-through hydrogenolysis reactions after 1 week of solvolysis liquor storage, as well as an *ex situ* control of solvolysis liquor run over carbon support only in flow. Product selectivity is shown for syringyl monomers in blue and guaiacyl monomers in green. These data are also provided in Table S2.† All experiments were conducted in duplicate, and the error bars are the range for total monomer yield. Batch reactions: either 30 mL (23.76 g) of *ex situ* solvolysis liquor or 0.313 g poplar in 30 mL methanol, 0.05 g catalyst (either 15 wt% Ni/C or activated carbon support), 30 bar H_2 at 225 °C, 3 h (exclusive of 30 min heating ramp). Flow reactions: 2 mL min^{-1} methanol or *ex situ* solvolysis liquor, 5 g poplar (*in situ*) or no biomass (*ex situ*), 0.9 g catalyst (either 15 wt% Ni/C or activated carbon support), 1600 psig, 200 sccm H_2, 225 °C, 3 h (exclusive of 1 h heating ramp for *in situ* runs).

The observation of similar monomer yields from *in situ* and *ex situ* RCF reactions suggests that flow-through solvolysis retains intact β-O-4 linkages in lignin. The *ex situ* liquor did not contain coniferyl alcohol, sinapyl alcohol, or any of the monomers shown in Fig. 2 at detectable levels, suggesting that flow-through solvolysis alone does not produce monomers. To ascertain the presence of intact aryl-ether linkages, we conducted 2D hetero-nuclear single quantum coherence (HSQC) NMR spectroscopy.[18] As shown in Fig. 3, the HSQC NMR

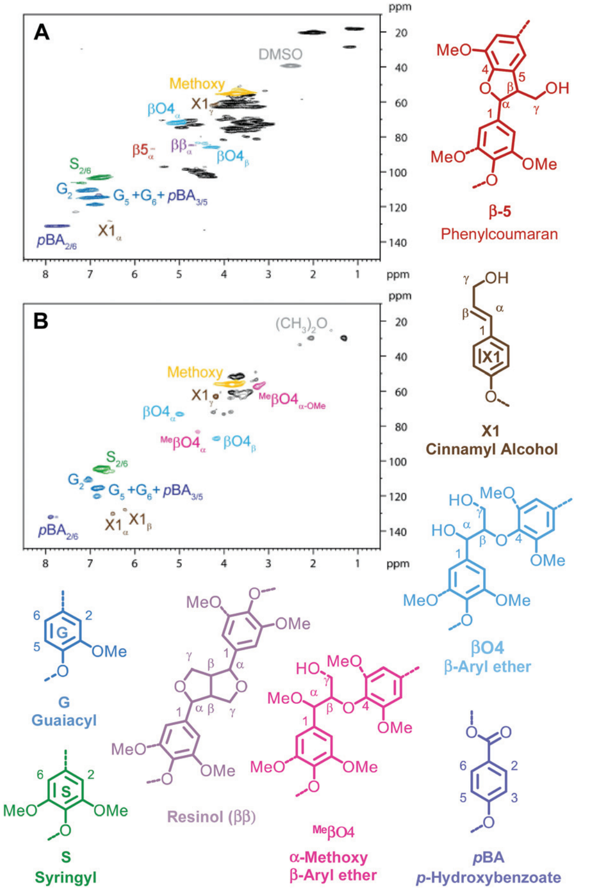

Fig. 3 NMR spectra of solvolysis liquor, demonstrating the production of native-like lignin. (A) 2D HSQC NMR spectrum of the native poplar biomass sample. (B) 2D HSQC NMR spectrum of the *ex situ* flow-through solvolysis liquor.

spectra of the *ex situ* flow-through solvolysis liquor exhibits intact aryl-ether linkages (blue). We note that partial methoxylation of the α-C (in the β-O-4 linkage) is observed, suggesting that methanol protection is occurring at this position.[8] Conversely, both the *in situ* flow-through RCF oil and the *ex situ* flow-through RCF oil exhibit complete disappearance of aryl-ether linkages (Fig. S2†). Overall, the lignin extracted by *ex situ* flow-through solvolysis produces similar RCF monomer yields and NMR spectra compared to the original poplar, suggesting that the extracted lignin is a "native-like" substrate.

We were additionally interested in the duration that the solvolysis liquor could be stored and to understand if the methanol could be removed from the solvolysis liquor without compromising lignin reactivity. These questions are relevant for downstream chemistries that require catalytic processing in different solvents, processing neat RCF oil, studies of lignin properties, and applications of native-like lignin in materials or other direct-use applications.

To address these questions, we conducted a 12-week experiment in which a fraction of the solvolysis liquor was maintained at room temperature in methanol, and duplicate *ex situ* batch RCF reactions were conducted after storage for 1 (*vide supra*), 2, 3, 5, 8, and 12 weeks. For a fraction of the solvolysis liquor, we used rotary evaporation to produce a methanol-free oil. At three time points over the same 12 weeks, we reconstituted a fraction of this solvent-less solvolysis liquor in methanol for conducting equivalent *ex situ* batch RCF reactions. Much to our delight, in both the stored samples in methanol and the reconstituted samples, the monomer yields are essentially invariant over the 12-week period, with only a 1.8 ± 0.1% and 2.0 ± 0.0% decrease in monomer yields in the 8- and 12-week reconstituted samples, respectively, as shown in Fig. 4 and Table S3.† We also characterized the molecular weight distributions of the *ex situ* flow-through solvolysis liquor after batch hydrogenolysis experiments as-made and reconstituted after 1, 5, 8, and 12 weeks (Fig. S3†). As shown, the post-hydrogenolysis molecular weight distributions are invariant as a function of storage time. Together, these data indicate that the solvolysis liquor is shelf-stable for at least three months.

One application of the *ex situ* solvolysis liquor is the ability to conduct flow experiments where the catalyst is subjected to a continuous feed of uniform lignin. As shown in Fig. 5, the *ex situ* solvolysis liquor, including a reconstituted sample and

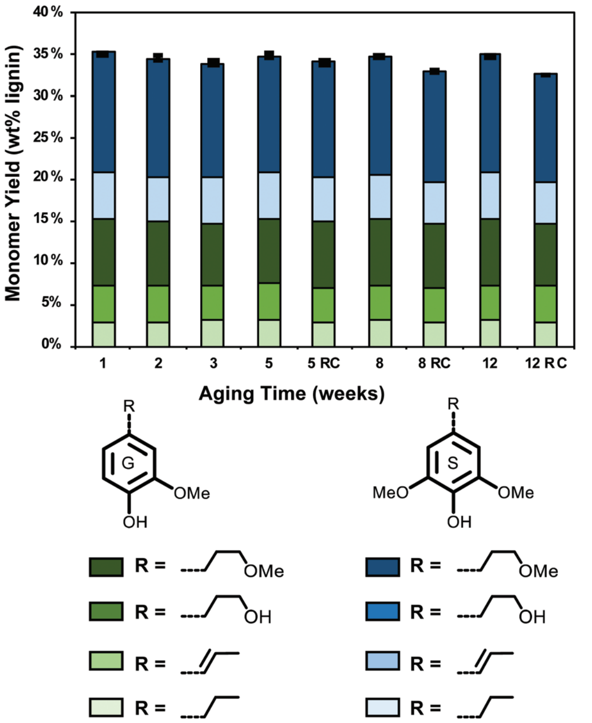

Fig. 4 Time-resolved study of *ex situ* batch RCF reactions on solvolysis liquor produced in flow and stored in methanol or reconstituted after solvent evaporation (denoted as RC). The monomer yield and selectivity for batch hydrogenolysis reactions of solvolysis liquor produced in flow. The as-made flow solvolysis liquor was tested at 1, 2, 3, 5, 8, and 12 weeks. Removing the methanol before aging was also tested at 5, 8, and 12 weeks. These data are also provided in Table S3.† All experiments were conducted in duplicate, and the error bars are the range of the total monomer yield. Reaction conditions: 30 mL *ex situ* solvolysis liquor, 0.1 g 15 wt% Ni/C catalyst, 30 bar H_2 at room temperature, 225 °C, 3 h (exclusive of 30 min heating ramp).

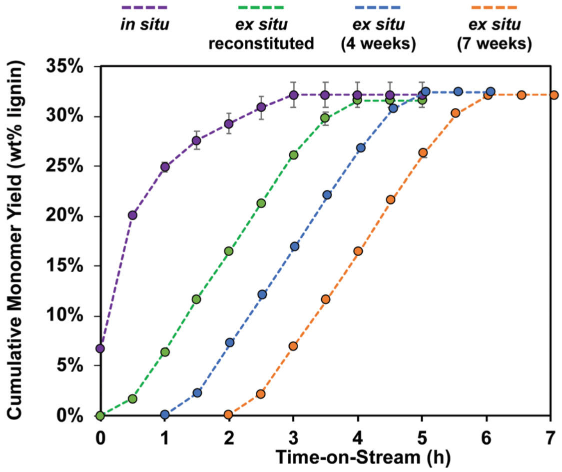

Fig. 5 Time-on-stream measure of cumulative monomer yields for *in situ* and *ex situ* hydrogenolysis. *Ex situ* flow-through RCF provides a consistent feed to the catalyst bed, resulting in a linear increase in monomer production, compared to the nonlinear, transient monomer production during *in situ* flow-through RCF. These data are also provided in Table S4.† All experiments were conducted in duplicate, and the error bars show the range. Reaction conditions: 2 mL min^{-1} methanol or *ex situ* solvolysis liquor, 5 g poplar (*in situ*) or no biomass (*ex situ*), 0.9 g 15 wt% Ni/C, 1600 psig, 200 sccm H_2, 225 °C, 3 h (not including 1 h temperature ramp for *in situ* runs). *Ex situ* runs included a 1.5 h methanol flush at the end of the reaction. 4-week and 7-week *ex situ* runs profiles are offset by 1 h and 2 h time-on-stream, respectively, for visual clarity.

two stored samples (4 and 7 weeks of storage in methanol), exhibits a linear increase in monomer yield (using the total lignin fed as the baseline for yield), while the nonlinear increase apparent for the *in situ* flow-through solvolysis indicates a transient lignin stream. As also noted by Lan *et al.*[15] and Wang *et al.*,[16] this feature will facilitate extended catalyst activity and stability studies.

While an in-depth exploration of solvolysis residence times is outside the scope of this work, it is worth considering the present results with respect to previous batch solvolysis work. Previous batch solvolysis residence times have been 2–3 h.[8,12,13] The flow-through solvolysis reported here employed a 5 g biomass bed centered inside a tube of approximately 35 cm total length and 1.6 cm inner diameter. The 5 g bed occupied approximately 10 cm in the axial dimension, thus the lignin traveled through a heated zone ranging between 12.5 and 22.5 cm in length, depending on where in the biomass bed it originated. At a 2 mL min^{-1} flow rate of methanol, the mean residence time for the lignin fragments to be quenched was thus ~17 min.

Additional studies will ascertain if this *ex situ* solvolysis approach to produce native-like lignin is sufficiently general. A system like that used here will be challenging to directly implement at scale, given that the solvent-to-biomass ratio is exceptionally high relative to the predicted range needed for industrially relevant operation.[17] However, these results suggest that native-like lignin extraction may be possible with appropriate reaction engineering measures to rapidly quench solvolysis liquor, which will be pursued in future studies. Also, the ability to isolate native-like lignin demonstrated here enables steady-state catalyst evaluation, potentially including neat lignin oil and in other solvents after methanol removal. Moreover, the current setup is a convenient approach to isolate native-like lignin from different feedstocks and with different solvents.

Conclusions

Overall, this study demonstrates that flow-through solvolysis can produce native-like lignin using poplar and methanol at 225 °C. Specifically, reductive catalytic treatment of the isolated lignin from a flow-through system produces monomer yields equivalent to a two-stage *in situ* flow-through setup, indicating that the aryl-ether bonds are conserved in the flow-based methanol extraction. From a lignin-first biorefining research perspective, these results demonstrate that immediate catalyst action is not necessary for passivation of reactive components of lignin, and that the lignin extract can be dried to an oil for storage or stored in methanol and processed later without losing substantial reactivity. Similarly, it may also be feasible to use the extracted lignin in materials. Taken together, these results suggest that lignin can be successfully isolated without significant chemical modification, which can enable both improved understanding of lignin structure and continuous catalytic processing of this important biopolymer.

Author contributions

DGB, JSK, NET, GGF, JKK, RJD, ARCM, TR, NSC, RMH, RK, TBV, and DGW executed the study. The paper was written by DGB, JSK, and GTB with contributions from all authors.

Conflicts of interest

Several authors have intellectual property filings related to lignin-first biorefining.

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