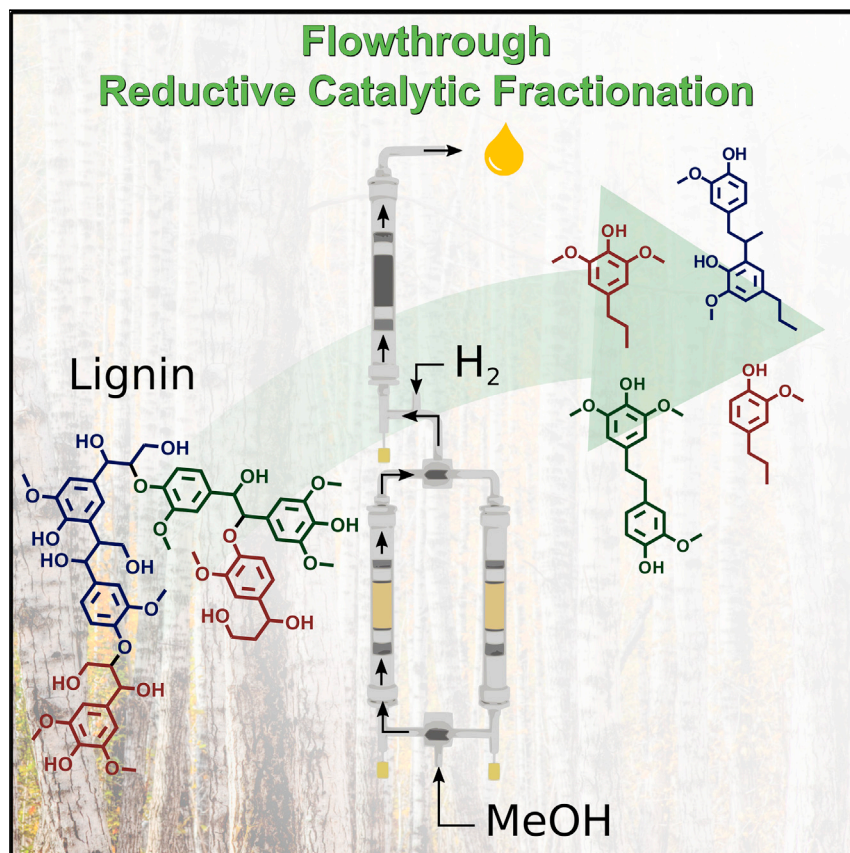


## Article

## Flowthrough Reductive Catalytic Fractionation of Biomass



Lignin, a major component of biomass, is typically treated as waste, squandering a natural source of aromatics for high-value chemical production. Here, we demonstrate the fractionation of biomass using flowthrough reactors to semi-continuously extract and depolymerize lignin into monomeric phenols. Flow processing allows for insights into the mechanistic steps of the lignin fractionation process, which are obscured in traditional batch processing. Lignin fractionation in flow will be essential for the integration of lignin processing in the complete utilization of biomass for chemicals production.

Eric M. Anderson, Michael L. Stone, Rui Katahira, Michelle Reed, Gregg T. Beckham, Yuriy Román-Leshkov

gregg.beckham@nrel.gov (G.T.B.)  
yroman@mit.edu (Y.R.-L.)

**HIGHLIGHTS**

Flowthrough studies allowed the observation of biomass extraction intermediates

Dual-bed reactor design allowed for the decoupling of solvolysis and hydrogenolysis

Semi-continuous RCF allows for facile catalyst recovery and recyclability

Semi-continuous flow elucidates catalyst deactivation mechanisms

## Article

# Flowthrough Reductive Catalytic Fractionation of Biomass

Eric M. Anderson,<sup>1,3</sup> Michael L. Stone,<sup>1,3</sup> Rui Katahira,<sup>2</sup> Michelle Reed,<sup>2</sup> Gregg T. Beckham,<sup>2,\*</sup> and Yuriy Román-Leshkov<sup>1,4,\*</sup>

## SUMMARY

Reductive catalytic fractionation (RCF) has emerged as a leading biomass fractionation and lignin valorization strategy. Here, flowthrough reactors were used to investigate RCF of poplar. Most RCF studies to date have been conducted in batch, but a flow-based process enables the acquisition of intrinsic kinetic and mechanistic data essential to accelerate the design, optimization, and scale-up of RCF processes. Time-resolved product distributions and yields obtained from experiments with different catalyst loadings were used to identify and deconvolute events during solvolysis and hydrogenolysis. Multi-bed RCF experiments provided unique insights into catalyst deactivation, showing that leaching, sintering, and surface poisoning are causes for decreased catalyst performance. The onset of catalyst deactivation resulted in higher concentrations of unsaturated lignin intermediates and increased occurrence of repolymerization reactions, producing high-molecular-weight species. Overall, this study demonstrates the concept of flowthrough RCF, which will be vital for realistic scale-up of this promising approach.

## INTRODUCTION

Growing concern over global climate change and continued reliance on petroleum has catalyzed increased demand for renewably sourced fuels, chemicals, and materials, driving significant innovations in the conversion of lignocellulosic biomass through biorefining.<sup>1–3</sup> Most commonly, the primary objective of biorefining is to develop and deploy efficient processes to convert plant polysaccharides to sugars, furans, or alkanes,<sup>4–6</sup> which can then be biologically<sup>7</sup> or catalytically converted to target fuels and chemicals.<sup>5,8–11</sup> In biorefining, however, the efficient production of valuable products from lignin, which is a complex, aromatic heteropolymer that accounts for 15–30 wt% of biomass and exhibits a higher energy density than polysaccharides, is a grand challenge that remains largely unsolved.<sup>3,12</sup> In plants, lignin is responsible for water transport in plant tissues and provides structure and defense against pathogens.<sup>13</sup> As such, lignin is a major contributor to biomass recalcitrance and severely inhibits access to the polysaccharide fraction of lignocellulose.<sup>1</sup> Thus, common biomass deconstruction processes rely on thermochemical pretreatments to either extract or redistribute lignin and facilitate the enzymatic depolymerization of polysaccharides.<sup>14–16</sup> These processes include steam,<sup>17</sup> organosolv,<sup>18</sup> acid,<sup>19</sup> and ammonia pretreatment,<sup>20</sup> all of which have been performed in flow. However, lignin can undergo considerable, deleterious modifications during some of these pretreatment processes, wherein labile ether bonds transform into an array of C-C linkages, producing a recalcitrant matrix that is quite challenging to process.<sup>21–24</sup>

## Context & Scale

As the environmental effects of mankind's energy use grow increasingly acute, economically viable and sustainable routes to carbon-neutral fuels and chemicals are critical. Biomass is an excellent feedstock for fuels and chemicals production because it is an abundant and renewable source of carbon. Biomass primarily consists of carbohydrates (cellulose and hemicellulose) and lignin. Carbohydrates have been studied and shown to be versatile feedstocks for the production of fuels and chemicals. Lignin, the largest source of natural aromatics, becomes highly recalcitrant during carbohydrate processing, hindering chemical production from lignin. Here, we demonstrate a flowthrough system for lignin fractionation from biomass into aromatics. Furthermore, flowthrough reactors allow for the measurement of critical parameters essential to the scale-up of lignin conversion, which is crucial for integration of lignin processing in the complete utilization of biomass for chemicals production.

In most modern biorefinery designs and in the established pulp and paper industries, chemically modified, residual lignin is typically burned for low-grade heat and power generation.<sup>3,12,25</sup> However, detailed techno-economic analyses have demonstrated that lignin valorization can offer substantial economic advantages to lignocellulosic biorefineries, including up to several dollars of positive revenue per gallon of hydrocarbon biofuel derived from sugars.<sup>26</sup> In addition, depending on the desired product from lignin, significant greenhouse gas offsets are possible as predicted by life-cycle assessment, even when importing fossil-based electricity to make up the loss in heat generation from lignin combustion.<sup>26</sup> Therefore, lignin offers significant valorization potential beyond its heating value for lignocellulose refining as long as processes can be developed that prioritize whole-biomass valorization rather than solely focusing on the polysaccharide fraction.

Given this emerging trend toward whole-biomass utilization, the last decade has witnessed a resurgence of lignin valorization research efforts. Multiple new solutions have been proposed to valorize biorefinery lignin. Monomeric species produced from lignin can be converted into polymer precursors either through thermochemical<sup>27,28</sup> or biological funneling processes.<sup>29</sup> In addition, thermochemical treatments can convert lignin into building block chemicals<sup>30</sup> such as alkylated aromatics,<sup>31,32</sup> cycloalkanes,<sup>33,34</sup> and aromatic ketones.<sup>35</sup> These processes all rely on an upstream step for the production of monomers from lignin.

A new class of lignin fractionation technologies, broadly characterized as employing active stabilization,<sup>36</sup> prevent undesirable lignin condensation by either the use of additives or reduction catalysts to stabilize reactive intermediates.<sup>23,37–39</sup> Reductive catalytic fractionation<sup>40</sup> (RCF) is an active stabilization technique that produces a narrow slate of phenols while preserving the biomass polysaccharides as a solid residue.<sup>40–46</sup> Specifically, RCF operates by way of a two-step process that involves an initial solvolysis step that extracts lignin fragments from biomass, followed by a stabilization step wherein these intermediates react with a hydrogen donor over a redox-active catalyst via hydrogenolysis and hydrogenation pathways.<sup>44,47–49</sup> This simultaneous extraction and stabilization results in a narrow distribution of monomers with yields approaching the theoretical limit of plausible monomeric units resulting from  $\beta$ -O-4 bond cleavage (e.g., 22%–49% for hardwoods assuming a 47%–70%  $\beta$ -O-4 linkage content and complete lignin extraction).<sup>50,51</sup>

To date, essentially all RCF studies reported in the open literature have employed liquid-phase batch reactors. Typical temperatures used range from 180°C to 250°C for 2–12 hr, at reaction pressures of 5–15 MPa, using a solid catalyst mixed with biomass in a 0.5–2:10 mass ratio, a polar protic solvent such as alcohol or water, and a reductant (e.g., H<sub>2</sub>).<sup>52–54</sup> Harsher RCF conditions result in high lignin extraction but also in the solubilization of carbohydrates, which can react further to form other products. Milder conditions extract less lignin, but preserve carbohydrates in solid form.<sup>47,55</sup> Although batch RCF processing is effective, it suffers from several inherent limitations. First, the long time-averaged nature of batch processes hinders the characterization of lignin intermediates and convolutes the analysis of the dynamics of lignin extraction and depolymerization. Second, rigorous catalyst stability and recyclability studies are more difficult to perform, with the best option being separating the catalyst from the biomass in a porous basket.<sup>49,56,57</sup> Lastly, the solvolysis and hydrogenolysis steps are subjected to the same reaction conditions and cannot be controlled and optimized independently to create an efficient process. In this respect, flow processing overcomes many of these limitations and also offers several unique advantages over batch processing. In addition, beyond the fundamental

<sup>1</sup>Chemical Engineering, Massachusetts Institute of Technology, 25 Ames St, Cambridge, MA 02142, USA

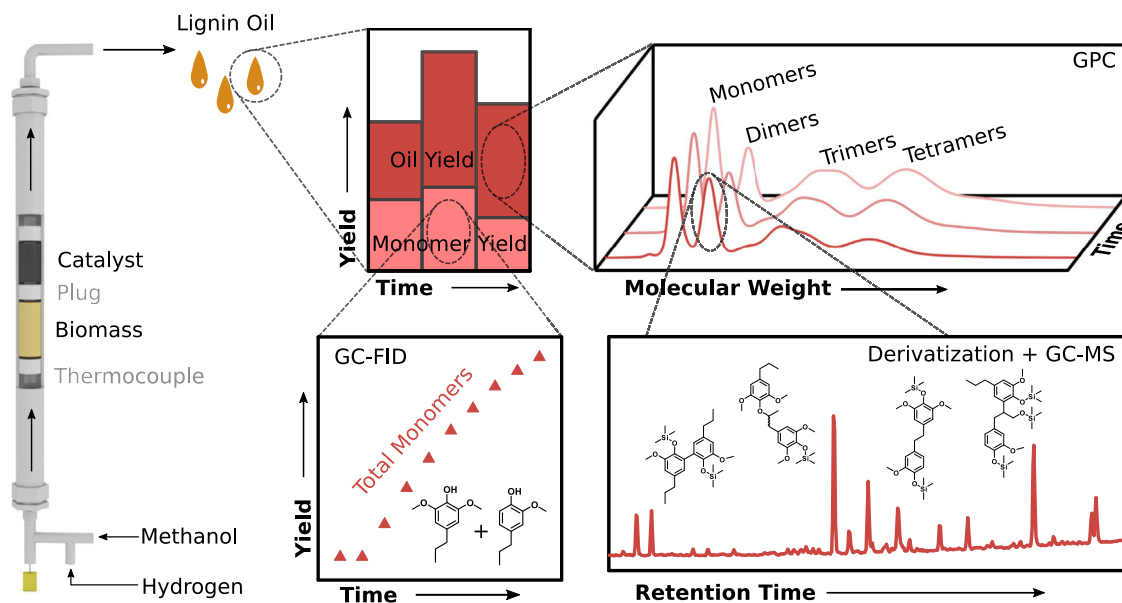
<sup>2</sup>National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO 80401, USA

<sup>3</sup>These authors contributed equally

<sup>4</sup>Lead Contact

\*Correspondence:  
gregg.beckham@nrel.gov (G.T.B.),  
yroman@mit.edu (Y.R.-L.)

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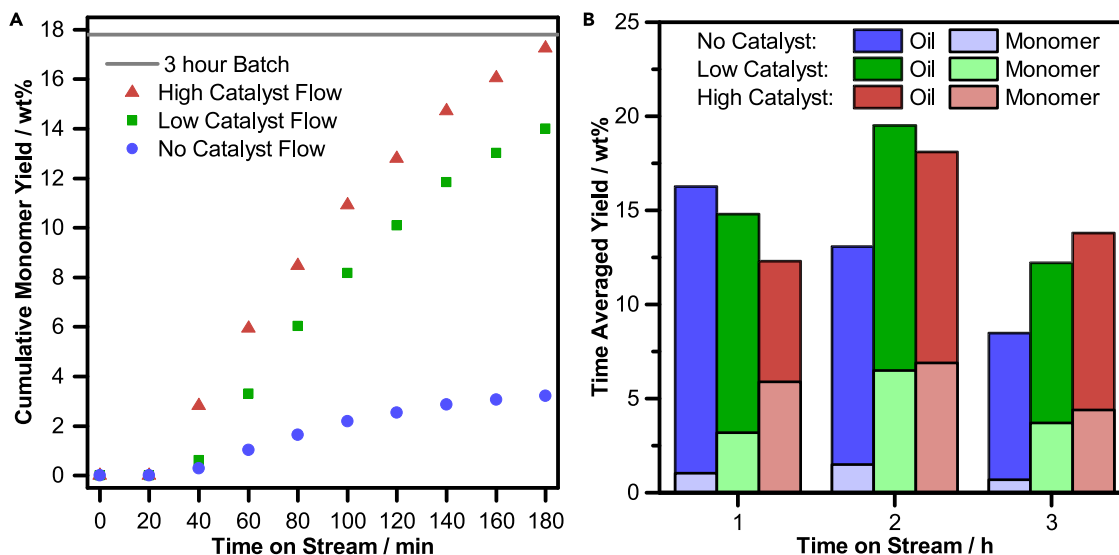
**Figure 1. Illustration of the Flowthrough Single-Bed Reactor for RCF, Highlighting the Different Analysis Techniques for Characterizing Lignin Oil at Different Extraction Times**

aspects of studying RCF, continuous RCF processing will likely be a necessity for robust, realistic scale-up of this promising approach.

Here, we investigated the RCF of poplar lignin in flow reactors. Two reactors were designed and built: a flowthrough single-bed reactor (FSBR) with a biomass bed located upstream from a catalyst bed (shown in Figure 1) and a flowthrough dual-bed reactor (FDBR) featuring switchable biomass beds physically separated from the catalyst in a separate upstream reactor allowing for uninterrupted biomass processing. Figure 1 depicts how flow systems allow us to access unique information about and gain fundamental insights into the RCF process. In contrast to batch processes, flow systems allow for facile collection of time-resolved data for both lignin extraction and hydrogenolysis products with independent control over the solvolysis and hydrogenolysis steps. In this respect, lignin solvolysis can be tuned by controlling the nature of the solvent, the extraction temperature, and the contact time. Further, near-instantaneous monomer yields are obtained at different extraction times due to rapid sampling of the effluent and rapid cooling of the products, which reduces side reactions and unwanted condensation. The molecular weight (MW) distribution of the extracted products can be obtained as a function of time by gel permeation chromatography (GPC). In turn, these fractions can be derivatized and identified via gas chromatography with mass spectroscopy (GC-MS). Lastly, flow systems are ideal to study catalyst stability and deactivation profiles, while also allowing for facile catalyst separation and post-reaction characterization.

## RESULTS AND DISCUSSION

Time-resolved data of both monomer and total lignin oil yields provide unique insights into the role of the catalyst in stabilizing RCF products. We performed flow reactions in the FSBR comparing high (300 mg), low (150 mg), and no loading of a 15 wt% Ni/C catalyst at 190°C for 3 hr on stream using 1 g of poplar containing 21% Klason and 5% acid soluble lignin (see Table S1 for compositional analysis). The high catalyst loading experiment produced a cumulative yield of 17.2 wt%



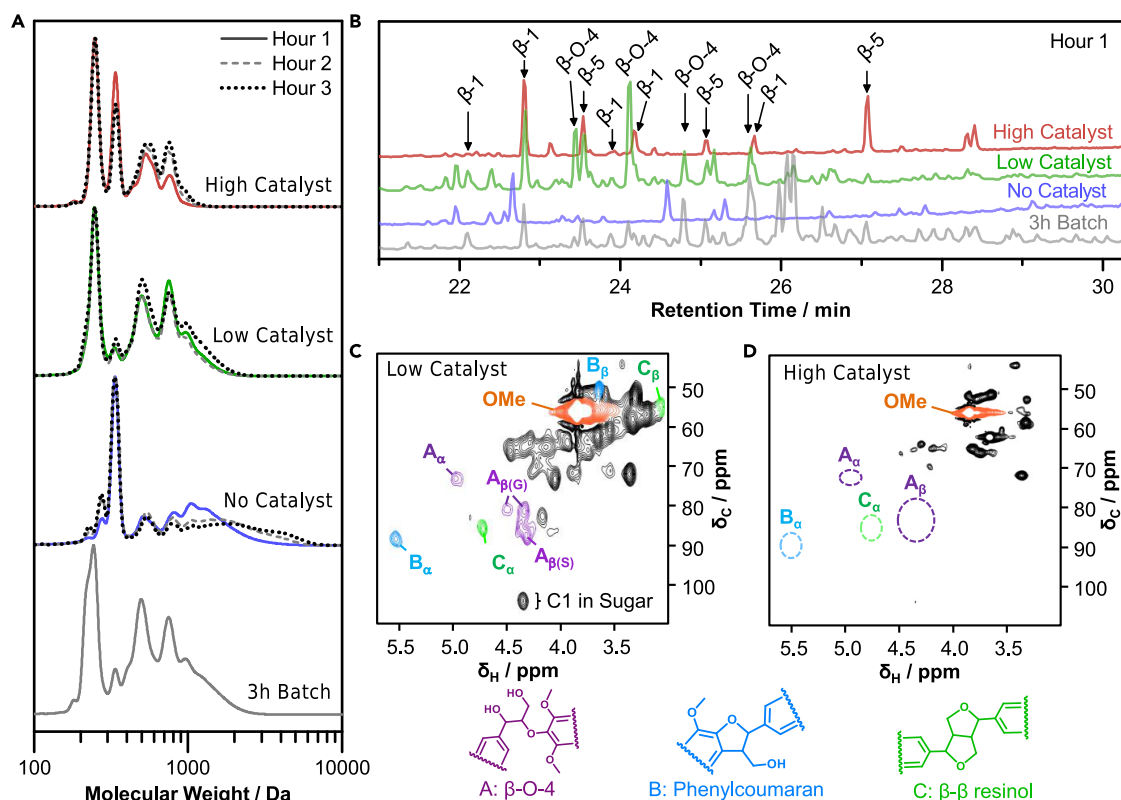
**Figure 2. Monomer and Oil Yields from Flow Reactions in the FSBR with Different Catalyst Loadings**

(A) On-stream cumulative monomer yields from the FSBR (outer diameter, 13 mm [0.5 inch]). Flow conditions: 1 g poplar, 0.6, 0.3, or 0 g (15% Ni/C mixed 50/50 SiO<sub>2</sub> 100–200 mesh, SiC diluted), 0.5 mL min<sup>-1</sup> MeOH, 50 mL min<sup>-1</sup> H<sub>2</sub>, 6 MPa, and 190°C. Batch: 1 g poplar, 0.3 or 0.15 g of 15% Ni/C, 3 hr, 3 MPa H<sub>2</sub> (STP), 190°C.

(B) Time-averaged lignin oil and monomer yields for different catalyst loadings.

monomers (normalized by total lignin content) that matches the yield produced in a 3 hr batch reaction under identical reaction conditions with either 300 mg or 150 mg of catalyst (Figure 2A). The monomer distribution was identical in both batch and flow experiments with a 12.1 wt% yield of propyl guaiacol and propyl syringol and 5.1 wt% of propanol guaiacol and propanol syringol (3 hr distribution shown in Table S2). However, the flow data revealed that the monomer distribution changes over the course of the reaction. Initially, equal amounts of guaiacol and syringol species were isolated, but the guaiacol species declined exponentially with time on stream while the syringol species decayed at a slower, linear rate (Figures S1 and S2). Time-averaged oil yields over each hour for the high catalyst loading experiment exhibited a monomer to oil ratio of 0.39 (Figure 2B), suggesting a higher degree of depolymerization than that observed in batch (monomer to oil ratio of 0.34). For the low catalyst loading experiments, a lower monomer yield of 14 wt% was obtained after 3 hr, with only 0.6 wt% of propanol guaiacol and propanol syringol. The selectivity toward monomers with a fully saturated propyl chain started at 90% and progressively decreased to 73% over the course of the reaction, along with a decrease of the monomer to oil ratio to 0.28 (Figures S3–S5). When no catalyst was used, the monomer yield was only 3.2 wt%, with a monomer to oil ratio of 0.08. The product distribution featured mainly coniferyl alcohol and sinapyl alcohol moieties with unsaturated propyl chains. In flow, it is clear that decreasing catalyst loading affects both reaction yield and product selectivity and leads to higher oligomer yields. A detailed analysis of higher MW products was necessary to determine if the decrease in monomer yields for the low catalyst loading experiment was the result of lignin condensation or incomplete conversion of lignin fragments generated from solvolysis.

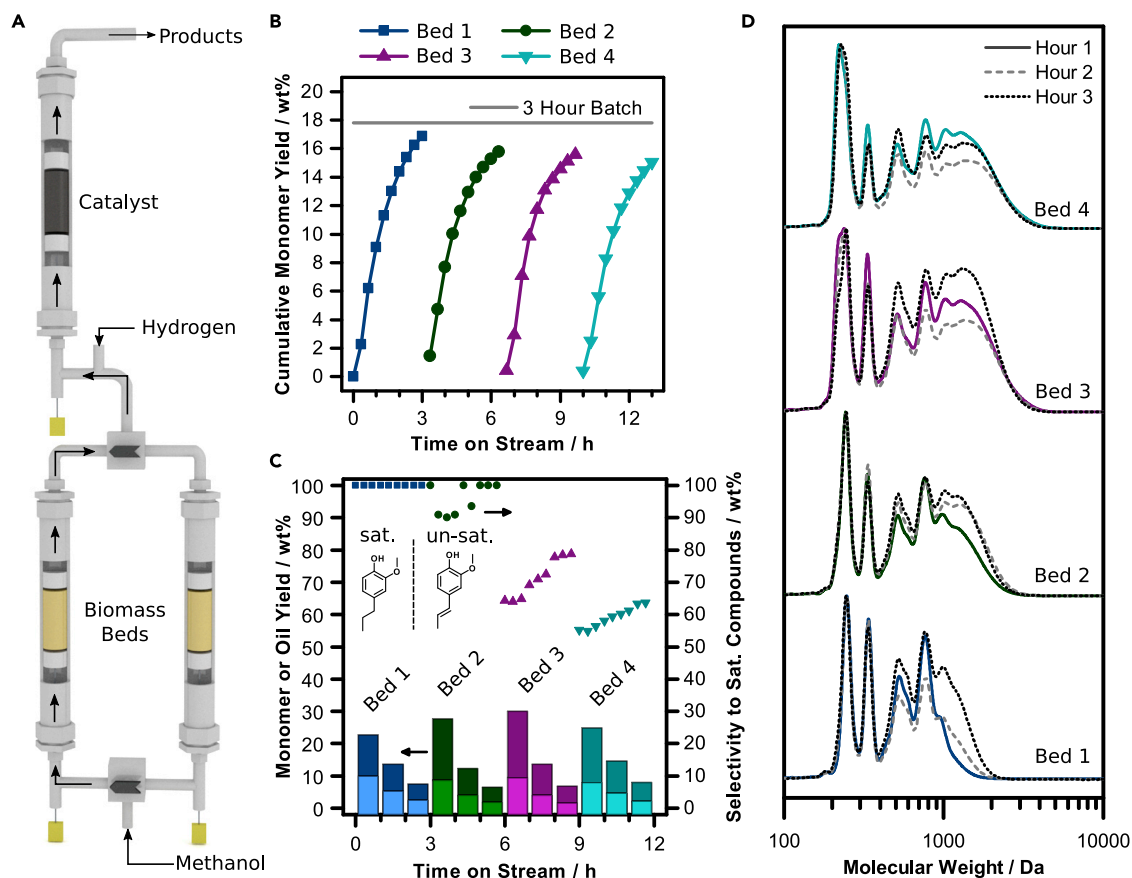
Characterization of the oligomer fraction of time-resolved lignin oil by GPC, heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectroscopy, and GC-MS of derivatized samples indicated that both repolymerization and partial lignin conversion affect monomer yields at 190°C. Normalized MW



**Figure 3. Characterization of the High-Molecular-Weight Fraction of Lignin Oil from the FSBR Catalyst Loading Studies**

(A and B) GPC traces (A) for different catalyst loadings with an overlay of longer extraction times for each flow reaction and a batch reaction for comparison (normalized to the largest peak in each sample). GC-MS chromatograms (B) of derivatized dimers at 1 hr extraction times. (C) 2D HSQC spectroscopy of the lignin oil obtained in the low catalyst loading experiment. (D) 2D HSQC spectroscopy of the lignin oil obtained with high catalyst loading.

distributions for the time-averaged oils from the high catalyst loading run exhibited a high extent of depolymerization with species in the tetramer weight range being the largest observable oligomers (Figure 3A). GC-MS analysis of the derivatized lignin oil from this experiment at 1 hr showed a small distribution of C-C linked  $\beta$ -1 and  $\beta$ -5 dimers (Figures 3B and S6–S9, and additional structural details in Data S1).<sup>52,58,59</sup> In contrast, when the low catalyst loading was used, new oligomers were observed with MWs extending past 1,000 Da, as well as new dimers with fragmentation patterns consistent with  $\alpha$ -deoxygenated and  $\alpha$ -methoxylated  $\beta$ -O-4 linked compounds. Data from 2D HSQC NMR performed on the oils obtained from high and low catalyst loading experiments corroborated these trends (Figures 3C and 3D). Peaks at  $\delta_c/\delta_H$  82–88/4.3–4.5 and 88/5.5 ppm corresponding to  $\beta$ -O-4 and phenylcoumaran species,<sup>13</sup> respectively, were present in the low catalyst loading oil but were absent in the high catalyst loading oil, confirming incomplete ether cleavage with decreased catalyst loading. Other studies have suggested that enol ethers formed from elimination of the  $\alpha$ -substituent are intermediates in the solvolytic cleavage of lignin.<sup>22,37,60</sup> These species, under our reaction conditions, would saturate to form the observed  $\beta$ -O-4 dimers. In the absence of catalyst, high MW fragments were observed up to 7,000 Da, with an altered dimer distribution containing new fragment patterns for syringol and guaiacol consistent with a double bond between the  $\alpha$  and  $\beta$  carbons (Figure S8). Van den Bosch et al.<sup>49</sup> showed in model compound and real lignin studies that the degree of unsaturation



**Figure 4. Semi-continuous Conversion of Lignin in the FDBR over a Single Catalyst Bed**

(A) Schematic of the semi-continuous dual-bed flow reactor (FDBR) (6.5 mm [0.25 inch] outer diameter catalyst, 13 mm [0.5 inch] outer diameter biomass). Conditions: 1 g poplar per bed, 0.3 g catalyst (15% Ni/C 50/50 SiO<sub>2</sub>), 0.5 mL min<sup>-1</sup> MeOH, 50 mL min<sup>-1</sup> H<sub>2</sub>, 6 MPa, 190°C (both beds).

(B) Cumulative monomer yields from four fresh poplar beds with the same catalyst bed.

(C) Hydrogenation selectivity (shown as data points) and the time-averaged monomer yields (light bars) and oil yields (sum of light and dark bars) at each hour.

(D) GPC traces of the lignin oils from the four poplar beds for each hour of extraction (see also Figures S15 and S16 for biomass compositional analysis).

in lignin compounds corresponds to repolymerization at 250°C with supercritical methanol. Furthermore, they suggested that the catalyst is solely responsible for the reductive stabilization of lignin intermediates by hydrogenation. Our results also indicate that unsaturated lignin compounds lead to repolymerization, but at a temperature of 190°C, the catalyst additionally performs hydrogenolysis as demonstrated by the absence of β-O-4 compounds in high catalyst loading experiments.

A modular FDBR featuring switchable biomass beds was used to investigate catalyst stability during RCF without interrupting the flow of lignin fragments to the catalyst (Figure 4A). The system was tested with four consecutive beds of poplar (1 g each, 26% lignin) and 150 mg of 15% Ni/C catalyst with otherwise identical conditions to those used in the FSBP experiments. The cumulative monomer yield for the first biomass bed was 16.9 wt%, which was nearly identical to a batch reaction yield at 3 hr. For the second bed, the monomer yield decreased to 15.5 wt% (Figure 4B). After this initial deactivation, the yields for the third and fourth beds remained constant at 15.6 and 15.1 wt%, respectively. Although the total monomer yields were similar across all beds, the product distributions varied considerably (Figure 4C).

Specifically, the first bed showed 100% selectivity for propyl chain saturation, but this value decreased steadily with each bed until it reached 55%–60% saturated and 45%–40% unsaturated propenyl chains in the fourth biomass bed (complete product distribution in [Figure S10](#)). In addition, the same unsaturated species and dimer distributions observed in the FSBR experiments with no catalyst began to appear for the third and fourth biomass beds ([Figures S11–S14](#)). The increased presence of unsaturated compounds led to a higher degree of repolymerization, as shown by GPC in [Figure 4D](#).

To investigate the mechanism of catalyst deactivation and poisoning, the particle size was measured by transmission electron microscopy, Ni content was measured by inductively coupled plasma atomic emission spectroscopy, and the presence of adsorbed organics was determined by thermogravimetric analysis (TGA). The physical separation of the solvolysis and hydrogenolysis reactors allowed for facile catalyst recovery and subsequent characterization ([Figure S17](#)). We observed that the particle size distribution ([Figures S18–S20](#)) increased from an average diameter of  $14 \pm 8$  nm before reaction to  $21 \pm 12$  nm after reaction, indicating that sintering occurred. In addition, elemental analysis showed that the Ni content decreased from  $13.5 \pm 0.7$  wt% to  $9.8 \pm 0.4$  wt% after the fourth biomass bed, indicating that leaching also occurred. To understand if leaching was influenced by biomass constituents, a control experiment was performed in which pure methanol and hydrogen were passed over the catalyst bed at reaction conditions for 12 hr. No significant change in Ni content was observed ([Table S3](#)), thus suggesting that the solvent alone is not responsible for leaching and that biomass components must influence Ni dissolution. In addition, a TGA of the post-reaction catalyst showed the presence of surface-bound species ([Figure S21](#)), in agreement with previous studies showing that lignin oligomers and sugars contribute to surface poisoning of the catalyst.<sup>49,61,62</sup> Taken together, these results suggest that sintering, leaching, and poisoning are all possible catalyst deactivation routes.

Clearly, further studies are required to optimize RCF in flowthrough reactors, as demonstrated by the moderate total lignin extraction values achieved here due to the mild solvolysis conditions used, as well as the catalyst instability over time. In addition, downstream process design will be critical for understanding solvent recovery, lignin oil fractionation, and oligomer valorization. Nonetheless, we envision that our reactor design and reactivity data in flow will be essential to start addressing these issues and further optimize the RCF process. To improve the lignin extraction, the solvolysis step could be altered through the use of solvent pairs and co-catalysts such as acid. Low residence times within the flow reactor could potentially limit the sugar decomposition rates that harsh fractionation strategies are known to cause. In flow, the solvent chemistry could be cycled at certain times on stream to allow for hemicellulose removal and increased lignin yields. The catalyst reactivity and stability can be studied in depth using the FDBR. The catalyst stability could be improved by exploring catalyst-support interactions to combat leaching and sintering, and creating bimetallic alloys that modify molecular surface adsorption to reduce catalyst poisoning. The flow reactor also allows for the development and optimization of other process parameters that would be useful for designing and implementing a full-scale system. The physical separation of the beds in the FDBR allows for independent tuning of reaction conditions for solvolysis and hydrogenolysis. The flow system is also amenable to direct integration of downstream processing such as sugar conversion and lignin upgrading. The near-instantaneous sampling of lignin products from the reactor makes kinetic studies on lignin conversion feasible. All of the flow data generated can be readily used for process design



and scale-up, bringing RCF closer to an integrated, scalable, and economically feasible process.

In summary, flowthrough reactors were implemented for the semi-continuous reductive catalytic conversion of lignin into low MW species. The short contact times and rapid cooling after reaction in these systems enabled the identification of lignin intermediates involved in specific reaction pathways associated with the solvolysis or hydrogenolysis steps of RCF. In addition, the time-resolved data obtained in semi-continuous flow highlight the impact of catalyst deactivation on the reaction selectivity to unsaturated compounds, and ultimately the increased yields of unwanted higher MW lignin oils over time. Overall, the results illustrate the advantages of a flowthrough setup over traditional batch reactors to further control and understand important aspects of the RCF process.

## EXPERIMENTAL PROCEDURES

Detailed experimental procedures for the catalyst synthesis, biomass characterization, and reactivity studies are provided in the [Supplemental Information](#). Briefly, the FSBR was packed with 1 g of poplar wood (<0.25 mm, 26% lignin) and the second bed (downstream of the biomass and separated by a glass wool plug) was packed with 0.0, 0.3, or 0.6 g of a 15% Ni/C catalyst mixed with SiO<sub>2</sub> (50/50) dispersed in SiC to a total mass of 2 g. The FDBR was packed with 1 g of poplar in the first reactor and 0.3 g of 15% Ni/C (50/50 SiO<sub>2</sub>) in the second reactor. Methanol and hydrogen flow rates were 0.5 mL min<sup>-1</sup> and 50 mL min<sup>-1</sup>, respectively. Reactions were run at 190°C and 6 MPa of total pressure. Products were quantified by GC with a flame ionization detector and characterized with GC-MS, GPC, and 2D HSQC spectroscopy.

## SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 22 figures, 3 tables, and 1 data file and can be found with this article online at <https://doi.org/10.1016/j.joule.2017.10.004>.

## AUTHOR CONTRIBUTIONS

The flow reactors were conceptualized by E.M.A. and constructed by E.M.A. and M.L.S. Experiments were performed by E.M.A. and M.L.S. NMR was performed by R.K., and compositional analysis was performed by M.R. The manuscript was written by E.M.A. and edited by E.M.A., M.L.S., G.T.B., and Y.R.-L.

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