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Rapid Flow-Through Fractionation of Biomass to Preserve Labile Aryl Ether Bonds in Native Lignin

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Abstract :Lignin is the second largest component of vascular plants and is the most abundant renewable aromatic polymer on our planet. The attractiveness of lignin valorization lies in the conversion into high value aromatic chemicals and biofuels through fractionation and upgrading. Literatures demonstrated the presence of aryl ether bonds in native lignin was a key factor for the conversion, while the conventional technical lignins from carbohydrate-first processes, e.g. pulp and cellulose ethanol production, are intensively condensed and lack these linkages due to the intense delignification conditions. Here, by using β -O-4 lignin model dimmer GG, we reveal the dramatic degradation of GG and the synchronous formation of ralatively stable intermediate β -O-4 dimers, C₆C₃ enol ether and the formylated enol ether, within the first 5 min under the condition of 72wt% aqueous formic acid and 130 °C, a condition suitable for biomass fractionation. Based on these findings, we propose a simple but effective strategy of rapid flow-through fractionation (RFF), which separates the dissolved lignin from reactor in time and space, thereby preserving these labile aryl ether bonds in native lignin. Application of RFF of poplar wood with a short residence time of 2.6 min attained 75% delignification with an equivalent of β -O-4 motif in native lignin. Structure-preserved lignins (75.0%-85.4% $\beta\text{-}$ O-4 retention) were also harvested from wheat straw with good lignin yields (61.7%-78.5%). Contrarily, batch fractionation acted as a protracted war and resulted in extensive cleavage of aryl ether bonds as suggested by 92%-100% loss of β -O-4 motif under the same conditions. Because of the well-preserved structure, RFF lignin can be used as good feedstock to boosting its downstream valorization, especially for hydrogenolysis into monophenolic

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chemicals and fuels. It is noteworthy that carbohydrate fraction from RFF retained structural integrity and almost reached theoretical yields for glucan and xylan.

Lignocellulosic biomass is a renewable organic resource from plants photosynthesis, and is chemically composed of cellulose, hemicellulose and lignin. Lignin is an aromatic polymer formed in nature by the radical polymerisation of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.^{1, 2} The radical polymerisation process leads to a variety of inter-unit linkages including the β -O-4, β - β , β -5, 5–5 and 4-O-5 structural motifs. Their relative abundance in native lignin varies from plant to plant but the β -O-4 aryl ether bond is typically predominant among these inter-unit linkages.^{3, 4}

Although a highly abundant aromatic feedstock, lignin is still treated as a waste product and commonly burned to supply heat and energy in carbohydrate-oriented processes, e.g. pulp, cellulose ethanol, xylose, and furfural production due to its chemical recalcitrance and structural complexity. Valorization of lignin is increasingly recognized as being crucial to the economic viability of integrated biorefinery. Transformation of lignin into aromatic chemicals and drop-in fuels through depolymerization and upgrading is now attracting much attention.5-7 Literatures demonstrated the presence of aryl ether bonds in native lignin was a key factor for the conversion of lignin to aromatic monomers.^{6, 8} Unfortunately, chemical structure of these technical lignins from the existing processes carbohydrate-oriented is highly modified. Specifically, under the intense delignification conditions, lignin aryl ether bonds are cleaved, and stable carbon-carbon bonds are formed as result of condensation.²

In response, biomass fractionation strategies that are capable of preventing structural lignin degradation are being developed with the expectation of efficient and selective lignin-to-aromatic conversion. A new liquid ammonia pretreatment methodology called extractive ammonia (EA) was developed by Costa Sousa et al., ⁹ which can produce lignin with well preserved functionalities but limited lignin yield lower than 50%. Study from Huy Quang Lê et al. showed the delignification is more than 90% from a γ-valerolactone (GVL)/water binary mixture treatment. However, the isolated

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lignin only contain 12% β-O-4 per C9 motif.¹⁰ These passive strategies demonstrate trade off between lignin yield and structure integrity, which means that high aryl-ether bond contents go hand in hand with low isolated lignin yields, and vice versa.¹¹ An alternative concept of particular interest, called active stabilisation, is emerging, that relies on active lignin stabilisation and thereby prohibits the problem of lignin condensation during biomass fractionation. Shuai et al. reported a novel lignin stabilization strategy by applying formaldehyde during an acid-catalysed delignification process to form relatively stable acetals (i.e., 1,3-dioxane structure) with lignin's α - and y-OH side-chain groups.¹² Deuss et al. reported an elegant solution to suppress lignin condensation by capturing lignin-derived unstable aldehyde products by reaction with diols to form acetal structures.^{13, 14} Two step of strategies consisting oxidation and depolymerization/hydrogenation also succeed in attaining remarkable aromatic monomers yields due to effective suppressing the undesired condensation reactions.¹⁵⁻¹⁷ However, these active lignin stabilization strategies require extra chemicals or catalysts. Downsides also include underside side reactions, i.e. grafting of formaldehyde on carbohydrate in the case of formaldehyde stabilization and formation of alkyl sugars.

Different from the previous defending strategies, i.e. lignin stabilization using capping agent, here we contemplate a simple but effective strategy to preserve lignin structures by employing rapid flow-through formic acid on the basis of the plethora of information about formic acid fractionation over the last few decades.¹⁸⁻²² Rapid flow-through fractionation (RFF) offers a large surface-to-volume ratio, good mixing and heat transfer properties, and therefore can accelerate the speed of delignification and reduce the lignin condensation.²³⁻

The most important is the ability of RFF in separating the formic-acid-dissolved lignin fraction in time and space, thereby quenching lignin condensation reaction and protecting liable aryl ether bonds. Expanding the arsenal of biomass fractionation methods could play an important role in developing viable lignin valorization method within future biorefinery. Here, we describe the significance of RFF for lignin valorization via revisiting the cleavage of aryl ether bonds in aqueous formic acid, evaluating time effect on lignin degradation, and our successful application of RFF in extracting high quality lignin with good yields.

Guaiacylglycerol-β-guaiacyl ether (GG), a phenolic model lignin dimer with a methoxy substituent on each of the phenyl rings, was used to investigate the cleavage of β -O-4 aryl ether bond and the formation of intermediate dimmers and lignin monomers in 72wt % aqueous formic acid at 130 °C for different time. The conditions were chosen because it is suitable and widely applied for biomass fractionation and Organosolv pulping.^{18, 28, 29} Reaction pathways were proposed based on analysis of resultant products from GC/MS determination (Fig. 1, Fig. S5). The acknowledged acid catalytic mechanism was confirmed that the aryl ether bond cleaves along with the formation of a new-formed phenolic compound GOH and Hibbert's ketone-type substructures, PHHM and

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HMV (Fig. 1A, Fig. S5, S8). C_6C_3 enol-ether (EE), $3-(A_{-}hydroxy_{-}3_{-})$ methoxyphenyl)-2-(2-methoxyphenoxy)-2ିମ୍ମାର୍ଟଡିମିଟି(^{C9GC02}ଐରିଂଶ identified by GC-MS as the primary β -O-4 intermediate dimer of GG acidolysis according its mass spectrum (Fig. S9). EE was reported by Satoshi Kubo and Shuji Hosoya as a stable product from GG degradation in ionic liquid ³⁰. Formylation of EE occurred at y-OH as verified by the formation of 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol methyl ester (f_v-EE) from analysis of mass spectrum in Fig. S10. This finding is consistent with the study of Stahl et al ¹⁵. The time course study demonstrated a quick degradation of GG with a reduction of 58 % in 5 min, and a complete consumption in 60 min (Fig. 1C), as determined by GC-MS (Fig. S5). The intermediate dimer EE and f_v-EE were stable in aqueous formic acid as indicated by the yield of 38% at 5 min and 50% at 60 min (Fig. 1C). Degradation of GG consists of synchronous formation of β -O-4 intermediate dimmers, depolymerization into monomers, and repolymerization into condensed products. Yields of monomers, dimmers, and condensed products were quantified using peak area of GPC (Fig. 1 C, Fig. S4). Time course study showed that approximately 80% β -O-4 bonds (sum of GG and EE) were preserved at first 5 min. The quantity of β -O-4 decreased further to 44% at 60 min, as suggested by the yields of GG and EE dimmers (Fig. 1C). The gradually decrease of β -O-4 dimers is ascribed to depolymerization and condensation reactions. Condensation reaction was aggressive and accounted for 8% and 35% of GG at 5min and 60 min, respectively. Condensation involves repolymerization of intermediate dimmers, monomeric products from acidolysis of GG *via* the α -benzyl carbocation by its electrophilic aromatic substitution on the electron-rich aromatic rings.^{31, 32} The condensation mechanism is verified by the formation of CD-I and CD-II as identified by 2D HSQC NMR (Fig. 2), and consistent with other studies.³³⁻³⁵ Theoretically, the above-discussed formylation at $C\alpha$ eliminates the possibility of carbon-carbon bonds formation at Ca. However, formylation is reversible, and the formyl group is not stable enough in acid condition. Besides acting as acidic catalyst in the depolymerization reaction, formic acid plays the role of reductant as indicated by the hydrodeoxygenation of PHHM into PMP (Fig. 1B). The mechanism of the reduction reaction of PHHM to PMP under treatment with formic acid can be interpreted by Eschweiler-Clarke reaction (Fig. S7a) or two steps reaction involving transfering hydride from formic acid to ketone and further reduciton of diols to PMP.³⁶ Oxidation reaction was observed that HMV was converted in to DMP with formaldehyde as by-product (Fig. 1B, Fig. S7b). The oxidation reaction could interpret the absence of HMV in products mixture from GG acidolysis using formic acid, while HMV was identified as the main product of GG acidolysis using sulphuric acid ³⁷ and hydrochloric acid.³⁵ Oxidative product DMP is then converted into BDME as result of adding a formaldehyde molecule (Fig. S7c), or converted into VAN as result of eliminating a formaldehyde molecule (Fig. 1B). Totally, the sum yield of all identified monomeric phenolics is approximately 21% at 60 min (Fig. 1C).



Figure 1. Possible Reaction pathways of GG in 72w% aqueous formic acid at 130°C, (A) Acid catalyzed cleavage of aryl ether bond and the formylation of GG at γ -OH, (B) Reduction and oxidation reactions of resultant monomers from acidolysis, (C) Yield of monomers, dimmers (GG + EE), and condensed compounds from GG degradation in time course.

2D HSQC NMR was used to study the cleavage of aryl ether bonds and synchronous condensation reactions (Fig. 2, Table S5). Cleavage product PHHM was identified by 2D NMR. The assignment of the Hibbert's ketone PHHM was made by the cross peaks at $\delta C/\delta H$ 44.5/3.67 ppm (α -position) and 67.1/4.19 ppm (γ -position) according to the study of Miles-Barrett et al.³⁸ It is worth noting that esterification reaction between GG and formic acid occurred to both aliphatic-OH at C_{α} and $C_{\nu}\text{,}$ and phenolic-OH at the first 5 min of reaction, leading to formation of totally formylated GG (f-GG), as revealed by 2D NMR. ³⁹ However, formyl groups at C_{α} and phenol- C_4 are not stable as indicated by the diminishing peaks at 2D NMR spectra (not shown). Consistent with GC-MS analysis, f_v-EE was identified again by 2D NMR with the assignment of $\delta C/\delta H$ 120.6/6.33 ppm at α position. Condensation products CD-I and CD-II were also unveiled by 2D NMR (Fig. 2) and LC-MS (Fig. S6). The structures of CD-I and CD-II are consistent with the wellacknowledged mechanism that condensation mostly occurred via the α -benzyl carbocation by its electrophilic aromatic substitution on the electron-rich aromatic rings, forming a new carbon-carbon linkage. The participation of GOH in formation of condensed products interprets the descending trend of GOH along with reaction (Fig. S11). The identification of condensation products brings new insight into the competition between the depolymerization and condensation via the α benzyl carbocation intermediate as catalyzed by aqueous formic acid. Carbon-carbon linkages in CD-I and CD-II show characteristic correlation signals from the $\alpha\text{-position}$ at $\delta C/\delta H$ 50.8/4.18 and 48.9/4.40 ppm, respectively. Signal intensity at α -position was used to quantify GG, f-GG, f_v-EE and CD-II during reaction with the normalization of untreated GG to 100 (Fig. 2). Quantity of GG decreases to 41.9 at 5 min of reaction. Products f-GG, f_v-EE and CD-II account 10.2%, 24.5% and 6.9%

for GG degradation at 5 min, respectively. Totally, GG, Arf. GG, If μ EE and CD-II kept 83% of β -O-4 in untreated GG are mainly consistent with the result in Fig. 1C from GPC analysis. 2D NMR confirmed the formation f-GG, f_{γ} -EE, CD-I, CD-II. Most importantly, the dependence of β -O-4 on treatment time was again verified.



Figure 2. HSQC NMR spectra of untreated GG, and reaction products at 5 min, 130 °C, 72wt % aqueous formic acid. Contours are colour coded according to the structure they are assigned to. Gray cross peaks correspond to currently unassigned signals.



Figure 3. Comparison of batch and flow-through reaction system in lignin chemistry, Top: homogeneous batch reaction of lignin model dimmer (guaiacylglycerol-β-guaiacyl ether) in 72wt% formic acid at 130 °C results in 20-57% cleavage of aryl ether bonds in 5-60 min; Bottom: heterogeneous rapid flow-through fractionation of lignocellulose in

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72wt% formic acid at 130 °C attains 50-94% lignin yield and 78-99% retention of aryl ether bonds due to the significantly reduced residence time of 2.6 min.

Lignocellulosic biomass is chemically composed by cellulose, hemicellulose and lignin. Components fractionation is the inevitable and crucial step for subsequent biorefinery upgrading. The conventional alkaline cooking for pulp production and dilute acid pretreatment for cellulosic ethanol production focus only on carbohydrate and therefore employ forcing conditions for a maximized delignification, which results in invertible degradation of lignin in terms of depolymerization and condensation. To facilitate the production of lignin monomer through reductive catalytic processes, extracting a stream of lignin with native uncondensed structure is very important. The above discussions suggest that the cleavage of aryl ether bonds is dependent on treatment time in homogeneous aqueous formic acid reaction system, with 20% loss at 5 min, 57% loss at 60 min (Fig. 1C). Furthermore, amount of new-formed condensed structures with carbon-carbon linkages increase with treatment time, with yields of 9% at 5 min, 35% at 60 min (Fig. 1C). For true biomass fractionation in heterogeneous system, our strategy is to attempt to shorten the residence time of lignin in reactor with an elaborate flow-through reactor, in which the flowing solvent takes the dissolved lignin from lignocellulose out of reactor in a really short time depending on flow rate (Fig. 3). The application of rapid flowthrough fractionation (RFF) using 72wt % aqueous formic acid as solvent with a residence time of 2.6 min and total running reaction time of 10 min demonstrates the ability of extract structure-preserved lignin from wheat straw with good yields from 61.7% to 78.5% (Table 1, Fig. S1). The lignin dissolution in flow-through reactor showed a rapid decline trend and almost finishes within 8 min (Fig. 3 bottom right). Noteworthy is the ability of preserving lignin structure as suggested by the good retention rates of β -O-4 aryl ether bonds from 75.0% to 85.4% compared with milled wood lignin (i.e. WS/MWL) depending on treatment severities (Table 1). In contrast, only 9.2% β-O-4 linkages retains for lignin from batch fractionation at the same conditions (WS/F72T130t10/Batch). RFF also showed excellent performance for poplar wood. Lignin yield attained 50.55~94.2% with remarkable retention rates of β -O-4 aryl ether bonds from 77.9~99.6% under various conditions (Table 1). By contrast, no β -O-4 aryl ether bonds survive for lignin from batch fractionation under the same conditions (Poplar/F72T130t30/Batch). Take delignification ability into account, formic-acid-RFF showed comparative performance to acid-hydrotrope-RFF⁴⁰ in protecting lignin structures from degradation (Fig. 4). This ability can be explained from multiple points of view. First, lignin dissolution is a fast diminishing process as indicated by the plot of reaction time against concentration of solubilized lignin in Fig. 3. This means a majority of lignin flows out of reactor and therefore suffers less degradation than lignin in batch reactor. Second, residence time of the solubilized lignin in flow reactor can be infinitely shortened to reduce lignin degradation in reactor by increasing the flow rate, while the residence time for batch reactor is fixed and equal to the reaction time whild of or heterogeneous reaction, mass transfer of flow reactor is much more efficient than batch reactor due to the elevated concentration gradient in the surface of solid reactant.²⁷ The advantage of RFF in preserving lignin structures was confirmed by a comparison with lignins from batch treatments using alkali ⁴¹, ethanol ², and formic acid ^{41, 42} (Fig. 4). Last but not least, esterification reaction between lignin and formic acid leads to formation of -O-formyl group at C α , eliminating the possibility of the acidolysis reaction and the subsequent cleavage of β -O-4. Formation of -O-formyl group at C α also suppresses condensation reactions at C α . Clearly, if the goal of lignin valorizaiton is production of aromatic hydrocarbon,^{43, 44} lignin from RFF is a good alternative for an easier catalytic upgrading.

Fig. 5 shows the comparison of HSQC spectra of the milled wood lignin (MWL), and lignins from RFF and batch fractionation under the same conditions. Main inter-unit lignin linkages (A: β -O-4, B: β - β , C: β - 5) and substructures (I, FA, PCA, G, H, S, PB, T) are assigned to correlation peaks accordingly.^{17,} $^{45,\ 46}$ MWL is obtained by solvent extraction (dioxane:H_2O, 96v:4v) and commonly used as a representative of native lignin.⁴⁷ There are no obvious difference between MWL and RFF lignin (WS/F72T130t10/RFF, Poplar/F72T130t10/RFF) in aryl ether linkages (A, A'). However, crosspeaks of aryl ether linkages (A, A') decreased significantly or dispeared for lingin treatments (WS/F72T130t10/Batch, from batch Poplar/F72T130t30/Batch). Signals from guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units are observed almost equivalently in the spectra of the MWL and RFF lignin. In contrast, strong correlation peaks of condensed S were observed for lignin from batch treatment of Poplar/F72T130t30/Batch, which means formation of carboncarbon bonds. Formyl groups were identified both for lignin from batch and flow-through reaction system using formic acid, but not for native MWL lignin (Fig. 5). Formylation makes lignin soluble in formic acid and accelerates the delignificaiton process.

Table 1. Lignin yield and amount of β -O-4 aryl ether bonds of MWL, RFF lignin and batch lignin from wheat straw and poplar wood under various conditions

Samples	Lignin yield (%) ^b	β-Ο-4 (Α/Α') ^c
WS/MWL		44.4
WS/F72T120t10/RFF ^a	61.7	37.9 (85.4) ^d
WS/F72T130t10/RFF	72.4	36.5 (82.2)
WS/F72T140t10/RFF	78.5	33.3 (75.0)
WS/F72T130t10/Batch	73.8	4.1 (9.2)
Poplar/MWL		46.1
Poplar/F72T130t10/RFF	50.5	45.9 (99.6)
Poplar/F72T120t30/RFF	76.0	42.2 (91.5)
Poplar/F72T130t30/RFF	90.3	38.4 (83.3)
Poplar/F72T140t30/RFF	94.2	35.8 (77.7)
Poplar/F72T130t30/Batch	91.7	ND ^e

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[a] WS is wheat straw; numbers after F, T, t are concentration of formic acid, treatment temperature, and total running time, respectively. [b] lignin yield is calculated using the equation '100 - $100 \times Lsr \times Ysr / L_{ub}$ ', where *Lsr* is lignin content in solid residue, *Ysr* is yield of solid residue, and L_{ub} is lignin content in untreated biomass. [c] Expressed per 100 Aromatic units based on the relative volume integrals of characteristic peaks in 2D-HSQC spectra using computational formula in Table S1 and Table S2. [d] Numbers in parentheses are retention rate of β-O-4 on basis of MWL. [e] Not detected.



Figure 4. Correlation between delignification and β -O-4 linkages.

Continuous RFF showed nearly theoretical recovery of carbohydrate from the mass balance analysis (Fig. 6). No dehydration products of carbohydrate, e.g. furfural from pentose and 5-hydroxymethylfurfural from hexose, were

observed due to the short residence time of soluble sugars in reactor. The majority of xylan is dissolved but of abiomass anto liquor as indicated by the xylose yield of 88.3% and 79.4% for poplar wood (Poplar/F72T130t30/RFF) and wheat straw (WS/F72T130t10/RFF), while more than 95% glucan remains in solid. The delignification ability of RFF is reflected by the soluble lignin yield of 90.3% and 72.4% for poplar wood and wheat straw, respectively (Fig. 6). The mass balance data for other treatment conditions were provided in Table S3 and Table S4. Due to the good selectivity toward non-cellulose components, the cellulose-rich solid residue from RFF treatment can be utilized for paper and paperboard production. The soluble substances, e.g. xylose and lignin, can be separated from solvent by spray dry. The condensed solvent can be reused for RFF. Powders from spray dry process mainly consist of sugars and lignin. These sugars can be converted selectively to biofuels through biotransformation or furfural through dehydration, or purified for sugars production through redissolution-crystallization in water since lignin is water insoluble. The structure integrity of sugars and lignin from RFF ensures good compatibility to current biorefinery schemes. The obtained lignin can then be converted to high value dispersant or surfactant through sulfonation, or low molecular phenol compouds by catalytic hydrogenolysis. These flexible lignin valorization appoaches will enhance the process economic competitiveness of RFF.



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Figure 5. HSQC spectra of the milled wood lignin (MWL), and lignins from RFF and batch fractionation. Main structures present are: (A) β-O-4' alkyl-aryl ethers; (A') β-O-4' alkyl-aryl ethers with acylated and formylated γ-OH; (B) phenylcoumarans; (C) resinols; (F) spirodienones; (I) cinnamyl alcohol end-groups; (FA) ferulates; (PCA) p-coumarates; (G) guaiacyl units; (H) p-hydroxyphenyl units; (S) syringyl units. (S') oxidized syringyl units with a Cα ketone; (T) tricin. (PB) p-hydroxybenzoate substructures. See Table S1 for details of signal assignments.

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Figure 6. Mass balance of polysaccharide (glucan and xylan) and lignin fractions of biomass. (A) Poplar wood (B) wheat straw, the standard deviation of determination is ±2%.

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Experimental Section

Degradation of GG in aqueous formic acid

Stock solution of GG was prepared by dissolving GG (10 mg) in acetone (10 ml). Stock solution (1.0 ml) was introduced into a glass vial. Solvent acetone was evaporated using stream of N₂. Aqueous formic acid (2 ml, 72wt %) was added to the vial to dissolve GG, which gives a GG concentration of 0.5 mg /ml. The vial was sealed, and incubated at 130 °C for 60 min in an oven. Reaction was stopped at pre-set time by taking the vial out from the oven and placing it in icy water. The resultant products were dried through evaporation of aqueous formic acid using stream of N₂. Acetone (1.0 ml) was added to the vial to dissolve the resultant products for GC/MS analysis.

Flow-through and batch fractionation of biomass

The RFF system consists of a solvent bottle, an HPLC pump (LC-10AT, Shimadzu, Corp. Japan), an extraction column (300 mm length \times 8 mm diameter, 15 ml volume), a temperature adjustable silicone oil bath, a bottle for liquid sample collection, and stainless steel tubes connecting them, as illustrated by Fig. S1. Aqueous formic acid (72wt%) was used as solvent. Biomass (3.0 g) was loaded in the extraction column. The remaining space of the extraction column for flowingsolvent after biomass loading is 13 ml since biomass takes up approximately 2.0 ml (solid density of biomass 1.5 g/ml). After end-fittings installation and tubes connection, pump was started at 10 ml/min for a fast filling-in of the extraction column with solvent. Pump was then stopped, and the extraction column was placed in an oil bath at pre-determined temperature for 5 min to allow heat transfer and liquid diffusion. RFF of biomass was conducted at a flow rate of 5 ml/min (residence time 2.6 min) for 10 min, or at a flow rate of 1.67 ml/min (residence time 7.8) for 30 min. RFF consumes totally 63 ml (50 ml +13 ml) solvent, which corresponds to solid/solvent of 1:21. Extract was collect from the outlet of RFF reactor at room temperature. Solid residue of biomass in the column was washed by pumping 100 ml of water through the column, and then taken out of column. stored at 4 °C for further analysis.

Batch fractionation was performed in a 120 ml pressure flask in an oil bath at temperatures of 130 °C. Biomass (3 g) and 72wt % aqueous formic acid (63 ml) were introduced into the flask with a biomass/liquid of 1/21 (w/v). The flask was shaken every 5 min during fractionation. At the end of batch fractionation, flask was taken out from the bath and placed in icy water to quench the reaction. Extract was then separated from solid residue of biomass by vacuum filtration through a filtering crucible. Solid residue and extract were collected for further analysis.

Conflicts of interest

There are no conflicts to declare

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Graphical Abstract



Effective isolation of Lignin Containing Native Aryl Ether Linkages

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Rapid Flow-Through Fractionation of Biomass to Preserve Labile Aryl Ether Bonds in Native Lignin