Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Highly selective reductive catalytic fractionation at atmospheric pressure without hydrogen

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1. Chemicals and materials

All wood substrates used in the work were crashed and sieved. The part of 20 – 60 mesh was used for reaction. Below is the source information and lignin content of each wood substrates.

Table S1 Source and Klason lignin content of wood substrates.

Wood substrates	Source	Klason lignin content (wt.%)
Poplar	Taian, Shandong Provence, China	21.0
Birch 1	The greater hinggan mountains, Heilongjiang Provence, China	21.2
Birch 2	The greater hinggan mountains, Heilongjiang Provence, China	18.4
Beech	Lishui, Zhejiang Provence, China	21.5
Eucalyptus	Yulin, Guangxi Provence, China	29.0
Willow	Anyang, Henan Provence, China	23.7
Cypress	Shanghai, China	34.2
Pine	Uruguay	27.7

All chemicals were used without further purification. The solvents including methanol, ethylene glycol (EG), dichloromethane, glycerol and 1,2-propylene glycol (all in AR grade) and tetrahydrofuran (HPLC) were purchased from Tianjin Concord chemical corporation. Diethylene glycol (99%), p-propylguaiacol (G-3, 98%), dibenzyl ether (95%), 5% Ru/C and 5% Pd/C were purchased from Aladdin industrial corporation. Note that: the two catalysts contain 50 wt.% water and the mass of the catalysts presented in the manuscript are based on the dry weight. p-propenylguaiacol (G-3ene, 97%) was purchased from Heowins chemical corporation. Benzyl phenyl ether (98%), 2-(benzyloxy)phenol (98%), 2-phenoxyethylbenzene (97%) and 2-phenoxyphenol (98%) were purchased from Bide pharmatech corporation. Guaiacylglycerol-β-guaiacyl ether (97%) was purchased from 9ding chemical corporation. Sulfuric acid (97%) and phosphoric acid (AR) were purchased from Tianjin Jiangtian chemical corporation.

Synthesis of 25% Ni/SiO_2 (by incipient-wetness impregnation method): 3.71 g $Ni(NO_3)_2 \cdot 6H_2O$ (AR, Tianjin Jiangtian chemical corporation) was dissolved in 4.05 g water, followed by pouring the solution into 2.25 g SiO_2 (60–100 mesh, Qingdao Haiyang chemical industry). The mixture was well stirred and dried at 110 °C for 2 h, followed by calcination at 450 °C for 2 h. The as-formed mixture was crashed and sieved to 200 – 300 mesh. Before reaction, the precursor was reduced in flowing H_2 (60 mL/min) at 450 °C for 1 h.

2. Experimental procedures

2.1 Determination of Klason lignin content

About 1.0 g wood substrate was hydrolyzed by 16.4 g (~10 ml) 72% H_2SO_4 solution for 2 h at room temperature (15-20 °C). The mixture was magnetically stirred at 200 rpm to ensure mass transfer. Afterwards, the mixture was transferred in a 500 ml flat-bottomed flask followed by adding ~280 ml water. The acid concentration was, therefore, diluted to ~4%. The mixture was refluxed for 4 h at 500 rpm. Then, the Klason lignin was filtered and washed with water and dried at 100 °C to constant weight.

2.2 Reaction procedures and calculation

Typical procedure of traditional RCF reaction: Poplar sawdust (2.0 g) and 5% Ru/C (0.100 g) were put in 50 ml methanol or EG. The mixture was transferred to a stainless-steel reactor. After replacing the air with pressured hydrogen for 3 times, the mixture was pressured with H_2 at the designated pressure and room temperature. Then, the mixture was heated in an oven to 230 or 185 °C and stirred at 500 rpm, and the temperature was maintained for 3 h. During the reaction, the working pressure was measured by a high-precision pressure gauge. Then, the reactor was removed from the oven and cooled to room temperature. After filtering the mixture, about 0.1 g of o-isopropylphenol (internal standard) was added into the filtrate before analysis by gas chromatograpgy-flame ionization detector (GC-FID) and GC-mass spectrometer (MS).

Typical procedure of ARCF reaction (10 ml): About 10 g of EG was added into a glass bottle and acidified to the desired level with 5 g/L sulfuric acid solution in EG. The final mass was fixed at 11.1 g (the density of EG is 1.11 g/ml). Then, 0.5 g poplar sawdust, 0.050 g 5% Ru/C, and a magnetic stir bar were put into the acidified EG. The mixture part of the bottle was immersed in an oil bath (190 °C), and the mixture was stirred at 500 rpm. The bottle was sealed after ~3 min to prevent the loss of products. The gauge pressure inside the bottle was estimated to be between 0.1–0.5 bar.

After a designated reaction time, the bottle was quenched in cold water. The mixture was filtered, and ~10 ml methanol was used to wash the inside of the bottle and then the residual. Next, 60 ml water and 20 ml dichloromethane (DCM) were added into the combined filtrate to extract the lignin monomers. The DCM phase was separated, and 10 ml fresh DCM was added into the aqueous phase to extract the monomers again. The combined DCM phase was rotary-evaporated to obtain the product oil. Then, 2.000 ml methanol containing the internal standard was accurately measured and added to dissolve the oil. The mixture was analyzed by GC-FID and GC-MS.

Calculation of yield and selectivity: Since the G and S monomers with the same substituent group are produced simultaneously and the mass ratio of G/S is fixed at around 2, we combined them in the calculation. Thus, the yield results are presented as G/S-X (X = 3, 3ene, 3OH, and total, Fig. 1); where G/S-total represents the total amount of G/S-3, G/S-3ene, and G/S-3OH.

Each compound was quantitatively analyzed by GC-FID (Agilent 7890B). Injector temperature: 300 °C; detector temperature: 300 °C; column: HP-5 (30 m×0.320 mm×0.25 μm); column temperature: 70 °C-2 min-8 °C/min-150 °C-15 °C/min-300 °C-8 min. The relative response factor was determined by the effective carbon number method. The yields were based on the mass of Klason lignin in the substrate:

$$Y_{G/S-X} = \frac{mass\ of\ G-X + mass\ of\ S-X}{mass\ of\ Klason\ lignin}$$

If the peak of one compound is so small that its yield is below 0.1 wt.%, it is "under detection limit" and we did not calculate them.

The selectivity of lignin monomers is used to analyze their relative content in the product. So, only the six lignin monomers were considered in selectivity:

$$S_{G/S-X} = \frac{mass\ of\ G-X + mass\ of\ S-X}{mass\ of\ G/S-total}$$

Typical procedure of model compounds reaction: 250 mg model compound was completely dissolved in 50 ml EG. The mixture was divided into 5 part (10 ml for each) and transferred into glass bottles for the reaction. Adding 0.025 g 5% Ru/C to bottle 1 and 2 and acidifying EG in bottle 1 and 3 to 0.2 g/L using sulfuric acid. The fourth bottle was used as a blank sample and the fifth was used to analyze the starting concentration. Putting the magnetic stir bar into the four bottles which were then sealed. Putting the four bottles into the oil bath at 185 ^{o}C, stirring at 500 rpm and reacting for 30 min. In some cases, 50 mg model compound was used for the tests and reacted for 20 min due to lack of sufficient substrate.

After the reaction, the bottles were cooled and the mixtures were filtered. The samples in each bottle were directly analyzed by GC-FID and GC-MS. The GC-FID condition was that: Injector temperature: 260 °C; detector temperature: 270 °C; column: Innowax (30 m×0.320 mm×0.25 μm); column temperature: 50 °C-5 min-20 °C/min-150 °C-10 °C/min-250 °C-8 min. To analyze dimers, some samples were also analyzed using the method described above. Conversion and yield of each product are calculated based on the GC peak area of each compound. Conversion=$A_{\text{substrate, after reaction}}$/ $A_{\text{substrate, before reaction}}$; Yield=$A_{\text{product, after reaction}}$/$A_{\text{substrate, before reaction}}$.

2.3 Determination of carbohydrate content in residual

0.25 – 0.30 g poplar or residual were torn to small pieces (if the residual was in the shape of tightly heaped filter cake) and immersed by 4.92 g (~3 ml) 72%H_2SO_4. The mixture was stirred at 200 rpm for 1 h at room temperature (15~20 °C). After that, the mixture was transferred to a 150 ml autoclave followed by adding 84 ml water. The autoclave was sealed and heated in an oil bath at 121 °C for 1 h and stirred at 500 rpm. Then, transfer the autoclave to cold water. After cooling, the mixture was filtered. The filtrate was collected for determination of carbohydrate content, and the solid was washed with water and dried to constant weight. When the poplar was analyzed, the percentage of the solid (i.e., Klason lignin) was 5% higher than its Klason lignin content determined by Section 2.1.

The content of sugar in the filtrate was analyzed by using a home-made HPLC system equipped with a RID detector. HPLC conditions: column: Biorad Aminex HPX-87H; column temperature: 65 °C; sample volume: 20 μL; mobile phase: 0.005 M sulfuric acid; flow rate: 0.6 mL/min; RID temperature: 40 °C.

The content of glucose, xylose and cellobiose in the filtrate were determined using corresponding standard substances. The content of glucan equates to the content of glucose × 0.9 plus the content of cellobiose × 0.9474. The content of xylan equates to the content of xylose × 0.88.

2.4 Determination of polymers in the products by gel permeation chromatography (GPC)

All GPC samples were prepared from GC samples. Thus, all GPC sample contained a certain amount of GC inner standard. Each GC samples (introduced in the main text of the manuscript) was rotary-evaporated to remove the solvent, followed by adding 2 ml tetrahydrofuran (THF) to dissolve the product. The mixture was filtered through a 0.22 μm syringe filter and ready for the test.

GPC was performed on a Shimadzu Prominence Modular HPLC system equipped with a RID detector. HPLC conditions: column: Agilent PLgel 5 μm MIXED-C; column temperature: 40 °C; sample volume: 20 μL; mobile phase: THF; flow rate: 1.0 mL/min; RID temperature: 40 °C. Polystyrene (PS) standards (370 – 4830 g/mol) were used for calibration. Note that the nominal molecular weight (MW) range for this column is 200 – 3,000,000 Da, so the MW of mono-, di- and trimers reach its limit. This made the MW of monomers and di- and trimers did not match PS standard to some extent. Thus, our result presented in the function of time instead of MW.

2.5 Observation of sawdust and the residual

Polarizing microscope: the images were observed using a Sunny CX40P polarizing microscope. Small pieces of residual were carefully taken using a tweezer to a glass slide which was subsequently put under the objective of the polarizing microscope. The polarizing microscope was operated in transmission mode. And the polarizer was rotated to 10° to pass some non-polarized light to make the background of the image bright.

Scanning electron microscope (SEM): the images were observed using a Regulus 8100 field emission SEM using 3 kV accelerating voltage. Small pieces of residual were carefully taken using a tweezer to a conducting resin on specimen stage. The stage was spayed metal film before observation. All samples were slightly pressed to tightly stick to the conducting resin and not to drop out in the observation.

2.6 Procedures for scale-up experiments (100 and 300 ml)

In 100 ml scale tests, 5 g sawdust and 0.5 g 5% Ru/C were well mixed in an EG solution of 0.4 g/L sulfuric acids. The mixture and a magnetic stir bar were transferred into a 250 ml three-neck round-bottom flask. The three necks were used for 1) sampling and adding acid; 2) connecting to air (185 °C) or a condenser (Reflux) or a tube to a bottle to collect distilled liquid and 3) measuring the internal temperature of the reaction mixture using a K-type thermocouple. After connecting corresponding accessories, the reactor was fixed into the oil bath and started the reaction.

In 300 ml scale (semi-continuous) test, 300 ml EG solution of 0.4 g/L sulfuric acids was prepared in a 500 ml beaker, followed by adding 15 g sawdust and 1.5 g 5% Ru/C. The mixture was well mixed using a magnetic stir bar. To start the reaction, the beaker was put in an oil bath (220 °C) with a cold trap on the top to condense the vapor. At beginning of the reaction, appropriately remove the cold trap and release vapor to control the reaction temperature above 190 °C. After 6 h, stop heating and remove the cold trap. The fibers were taken out using a strainer (60 mesh). Similarly, part of the catalyst was removed simultaneously. Afterwards, 15 g sawdust, 1.5 g 5% Ru/C and 2.4 ml EG solution of 50 g/L sulfuric acids were added into the reaction system and the reaction re-restarted. The acid and catalyst were necessary at the present stage because the acid was rapidly consumed (Section S3.6) and the catalyst was unable to be separate from the fibers (Section S3.3). The residual just taken out was immediately filtered and washed with methanol. The methanol filtrate was rotary-evaporated to remove methanol. Then, the combined EG was added back to the reaction system.

During the reaction, aliquots of ~1 ml reaction mixture were sampled at the appropriated time. The sample was cooled down and transferred to a syringe. Then, the mixture was filtered using a 0.22-μm syringe filter. The filtrate was collected in a 10 ml centrifuge tube containing 5 ml water and weighed. 2 + 1 + 1 ml dichloromethane (DCM) were separately added to extract lignin monomers in the aqueous phase. The combined DCM phase was rotary-evaporated and 1 ml methanol containing inner standard was added to dissolve the product oil. Then, the mixture was analyzed by GC-FID.

Besides, the conversion cannot treat a twofold amount of sawdust in one reaction for the substrate was too much to magnetically stir, and thus, the total yields were lower (Fig. S12).

2.7 Reaction temperature in reflux attempt and ASPEN simulation of EG's boiling point

The reaction temperature in reflux attempt (boiling point of the reaction mixture) decreased from 192 °C to 184 °C during reflux. This is because of the accumulation of low boiling point substances, such as water and some impurities. To achieve better conversion, the decrease in reaction temperature should be avoided. Thus, we studied the boiling point of EG by simulation (Fig. S11).

ASPEN plus V10 was used for simulating the binary diagram of EG and water. EG and water were chosen in the database. The property method was NRTL. Binary analysis module was used for the calculation. The calculation varied based on the mass fraction of water in EG from 0 to 0.01 at 50 intervals.

2.8 Enzymolysis of residual of ARCF

5 g origin poplar sawdust or final residual of semi-continuous operation were well dispersed in 100 ml citrate buffer (0.05 M, pH 4.8) at 50 °C. Then, 1.8 mg cellulase (biological reagent, 50 u/mg, Shanghai Yuanye biological technology corporation), 50 mg β-glucosidase (biological reagent, 100 u/g, Shanghai Yuanye biological technology corporation) and 15 mg hemicellulose (biological reagent, 20000 u/g, Shanghai Yuanye biological technology corporation) were added into the mixture. The mixture was shaken at 150 rpm using a shaking table at 50 °C. 1 ml of the mixture were sampled for analyzing carbohydrate content at the appropriate time. The samples were filtered using a 0.22 μm syringe filter before analysis by HPLC. The HPLC condition wathe s same with that in Section S2.3.

3. Further discussion

3.1 Discussion on lignin content in residual

The content of lignin of the residuals was unable to be determined through methods in Section S2.1 and S2.3 due to the existence of catalyst to be introduced in Section S3.3 and possible existence of by-product impurities. After hydrolyzing the residuals, the mass of the remained solid were among 55–76 mg (which is 21.0–25.4 wt.% of the corresponding residual), in which the mass of catalyst was 50 mg (if no catalyst was lost in the reaction). After hydrolyzing at 121 °C, we found the remained solid was dark-brown if the residual was in the form of sawdust; or pure dark if the residual was fibers. The brown solid was believed to be Klason lignin (same with Klason lignin of poplar); while the dark solid was 5% Ru/C. Thus, the fiber residual contained few amounts of lignin.

Moreover, we tested ARCF of a fiber residual (reaction conditions: 10 ml EG, 0.1 g/L sulfuric acid, 185 °C, all residual of 0.4 g/L at 1 h (~ 0.34 g), 10 wt.% (0.05 g) 5% Ru/C, 1 h and 500 rpm), and obtained just 2.3 wt.% of the total yield of lignin monomers. Thus, most lignin (estimated to be over 85%) on sawdust was transferred into EG within the first hour of reaction.

Therefore, we estimate the lignin content in the fiber-like residual is less than 3 wt.%, and the rest part of the remaining solid after hydrolysis may be impurities formed in ARCF. So, it was very difficult to identify the 3 wt.% lignin within the 21.0–25.4 wt.% solid.

3.2 Discussion on mass transfer in sawdust and fibers

Sawdust can easily adsorb EG and swell. Thus, lignin inside sawdust can be cleaved due to heat and solvolysis. However, the as-formed fragment is difficult to be transferred to the bulk solvent and converted to lignin monomers.

In another test of 0.4 g/L at 1 h, after filtrating the product mixture, the fiber residual was not washed by methanol as in a normal procedure but squeezed to collect the product inside the fiber. 0.4309 g liquid was obtained. It was redder and darker than the main filtrate, indicating more polymers. The total content of lignin monomers of the liquid was 1.0 mg/g while the value of the main filtrate was 1.9 mg/g. We believe the difference would be bigger if the substrate is in the form of sawdust. This indicates EG inside the substrate contained more polymers and fewer lignin monomers. Thus, a better mass transfer (e.g., the transformation of sawdust to slender fibers) will benefit to the conversion.

We also tested the conversion of small-sized sawdust and found the total yield was higher (Table S2). This also demonstrates that better mass transfer benefits to the conversion.

Table S2 Comparison of ARCF with different substrate size.[a]

Substrate size (mesh)	Selectivity (%)		Yield (wt.%)
	G/S-3	G/S-3ene	G/S-total
20-60	89.3	10.7	24.1
60-100	91.5	8.5	26.2

[a] Reaction conditions: 10 ml EG, 0.4 g/L sulfuric acid, 185 °C, 0.5 g poplar sawdust (with different size), 10 wt.% (0.05 g) 5% Ru/C, 3 h and 500 rpm.

3.3 Discussion on the separation of catalyst in residual

If the residual is in the form of sawdust, it is easier to separate the catalyst for 5% Ru/C is much smaller than the sawdust. When the residual is filtered, 5% Ru/C deposits on the bottom of the filter cake while sawdust residual on the top (e.g., Fig. S7 shows the residual just after filtration). Even so, we believe a small part of the catalyst was still mixed with the sawdust residual.

If the residual is in the form of tightly heaped filter cake (i.e., sawdust is converted into fibers), the catalyst and fibers are not able to be separated by filtration mentioned above because the fiber has similar size with the catalyst. They cannot be separated by liquid-liquid separation proposed by Sels' group either.[1] We tried to disperse the residual in methanol or water, and extracted with decane. But no 5% Ru/C could be extracted. However, 5% Ru/C in the residual of traditional RCF can be extracted. This is another difference between traditional RCF and ARCF.

Therefore, in the analysis of carbohydrate, all sample were not separated and the actual retention of glucan and xylan should be higher.

3.4 Discussion on the synergistic effect of EG, acid and catalyst in ARCF

Catalyst (5% Ru/C) is very important in ARCF. Only 0.2 wt.% of total yield was obtained without the catalyst. Similar results were obtained in traditional RCF.[1-2]

Without a catalyst, EG with 0.4 g/L sulfuric acids was unable to transfer poplar sawdust into fibers (185 °C, 1 h and 500 rpm). The residual looked identical with the original poplar, and few celluloses shined in the polarizing microscope (fewer than the residual of 0.2 g/L at 1 h with catalyst). Obviously, most lignins remained on the sawdust without the catalyst. Thus, we believe that the transformation of sawdust to fibers is realized by the synergistic effect of EG, acid and catalyst.

3.5 Discussion on the heating rate

In 10 ml scale tests and the first attempt of 100 ml scale, the oil bath temperature was set to 190 °C. The temperature of the reaction mixture reached 170 °C at around 3 min for 10 ml tests while, in the first attempt of 100 ml scale, it needed 14 min. So, the yield of the first attempt of 100 ml scale was lower. In the following tests of 100 ml scale, the temperature of the oil bath was set to 220 °C. Thus, the heating rate was faster than the first attempt, reaching 170 °C at around 9 min. So, the total yields were closer to the results of a 10 ml scale.

Given that the cleavage of lignin and hemicellulose and consumption of acid happened at the beginning of the reaction, we speculate that heating rate is more important for scale-up and determines the scaling effect to a large extent.

3.6 Discussion on the acid corrosion

Sulfuric acid is not a homogenous catalyst in ARCF. It rapidly consumed. In the conversion in 0.8 g/L sulfuric acids at 0.5 h (i.e., highest concentration and shortest time in this work), part of the reaction mixture was diluted with 5 times of water, and the aqueous phase was tested with precision pH test strips and $BaCl_2$ solution. The aqueous phase was neutral and no sediment formed, indicating sulfuric acid was rapidly and completely consumed. We speculate the acid may react with the sawdust and incorporate into the lignocellulose matrix, just as the formation of lignosulfonate in the paper-making industry. It needs further characterization and investigation which does not belong to this work. Since it rapidly consumed, reactor and facilities after it can be prevented from corrosion. And if the acid is added during the reaction, facilities before reactor (e.g., pipes and storage tank) can be protected too.

4. Figures and Tables

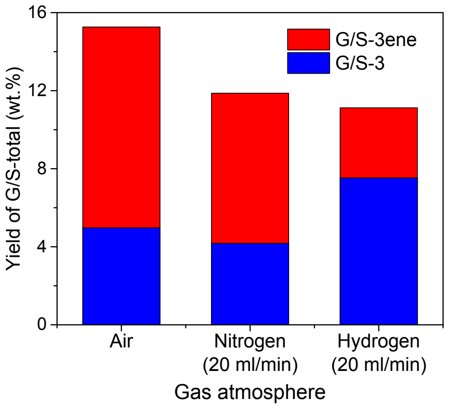


Fig. S1 Influence of flowing gases. Reaction condition: 190 °C, 10 ml EG, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C, 4 h and 500 rpm.

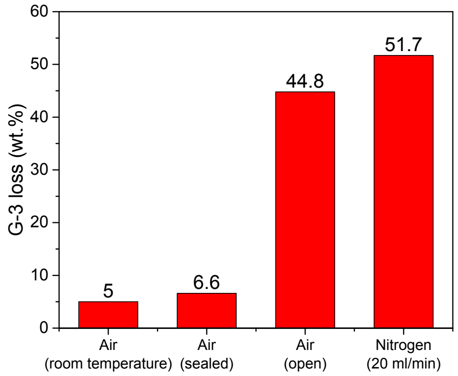


Fig. S2 Effect of gas atmosphere on the loss of G-3. Reaction conditions: 10 ml EG, 185 °C or room temperature, 1 h, 0.1 g G-3 and 500 rpm.

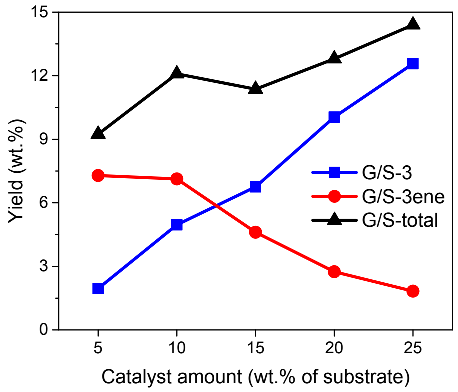


Fig. S3 Influence of catalyst amounts. Reaction condition: 185 °C, 10 ml EG, 0.5 g poplar sawdust, 5-25 wt.% (0.025–0.125 g) 5% Ru/C, 3 h and 500 rpm.

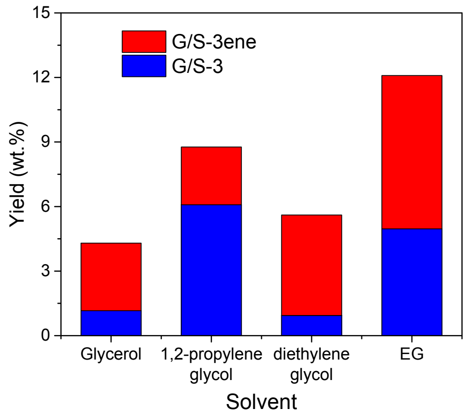


Fig. S4 Influence of solvents. Reaction condition: 185 °C, 10 ml solvent, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C, 3 h and 500 rpm.

Discussion for Fig. S4: Solvent is an important factor for ARCF. The solvent should have a high boiling point because it is conducted at atmospheric pressure and the hydroxy group which is the key for the reduction.[3] Glycerol, 1,2-propylene glycol and diethylene glycol were chosen as the solvent to test and compare with EG. As shown in Fig. S4, EG is the best among the four solvents. This is probably because EG can more effectively cleave and dissolve lignin from the substrate for more lignin oligomers were detected in the product by gel permeation chromatography (GPC) (Fig. S5).

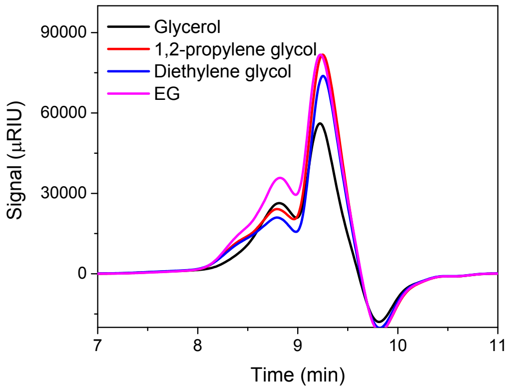


Fig. S5 GPC spectra of ARCF products obtained in different solvents. Reaction conditions: 10 ml solvent, 185 °C, 3 h, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

Table S3 Yield data of products of atmospheric RCF reaction with sulfuric acid addition.[a]

Reaction time (h)	Acid concentration (g/L)	Selectivity (wt.%)		Yield (wt.%)		
		G/S-3	G/S-3ene	G/S-total	Other phenolics	Impurities[b]
0.5	0.2	37.6	62.4	6.6	0.5	0.3
	0.3	40.7	59.3	8.6	0.4	0.5
	0.4	55.4	44.6	13.3	0.7	0.7
	0.5	64.3	35.7	14.7	0.7	0.9
	0.6	77.9	22.1	14.8	1.4	1.2
	0.7	73.8	26.2	10.5	3.2	2.0
	0.8	74.3	25.7	7.4	5.6	4.2
1	0.2	38.8	61.2	10.5	0.7	0.5
	0.3	48.5	51.5	12.9	0.6	0.6
	0.4	55.0	45.0	18.7	1.0	1.3
	0.5	77.1	22.9	18.5	1.2	1.1
	0.6	84.1	15.9	19.2	1.9	2.1
	0.7	85.9	14.1	13.5	4.2	3.2
	0.8	80.1	19.9	7.9	6.5	5.0
3	0.2	63.7	36.3	15.7	1.1	0.7
	0.3	80.4	19.6	21.4	1.2	0.9
	0.4	89.3	10.7	24.1	1.6	1.5
	0.5	90.5	9.5	23.5	2.9	3.3
	0.6	92.1	7.9	20.6	4.4	6.0
	0.7	90.1	9.9	15.2	5.8	6.8
	0.8	79.2	20.8	8.0	7.8	15.4
6	0.2	85.5	14.5	20.3	1.2	0.9
	0.3	93.0	7.0	22.9	1.4	1.1
	0.4	95.2	4.8	26.8	2.6	2.4
	0.5	95.6	4.4	23.7	4.0	6.2
	0.6	94.7	5.3	21.9	4.7	7.4
	0.7	89.7	10.3	16.0	6.9	13.6
	0.8	77.6	22.4	9.2	7.8	17.1

[a] Reaction conditions: 10 ml EG with designated concentration of sulfuric acid, 185 °C, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

[b] Impurities are non-phenolics compounds whose GC peaks are in the range of phenolic monomers. Impurities include ethers (from the polymerization of EG), furans and furfural (from the degradation of hemicellulose) and undetermined substances.

Table S4 Conversion of G-3ene as model compound under ARCF conditions.[a]

Acid concentration (g/L)	Selectivity (wt.%)		Yield (wt.%)
	G-3	G-3ene	G-total
0	21.6	78.4	42.3
0.1	56.7	43.3	21.3

[a] Reaction conditions: 10 ml EG with designated concentration of sulfuric acid, 185 °C, 1 h, 1.0 g G-3ene, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

Discussion for Table S4: In fact, most G-3ene in both tests were converted to dimers. The results indicated that G/S-3ene can easily polymerize. And acid promoted the polymerization as well as the saturation of double bond.

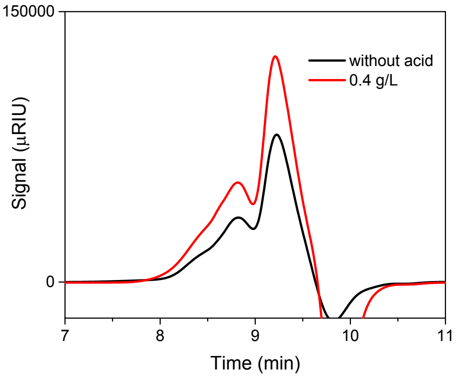


Fig. S6 Comparison of GPC spectra between the products with 0.4 g/L sulfuric acid (1 h) and without acid addition (3 h). Note that the curve without acid addition is the same with the purple curve in Fig. S2.

Fig. S7 Image of residual of traditional RCF on 5% Ru/C. Reaction conditions: 230 °C, 3 MPa H_2, 3 h, 2.0 g poplar sawdust, 5 wt.% (0.1 g) 5% Ru/C and 500 rpm.

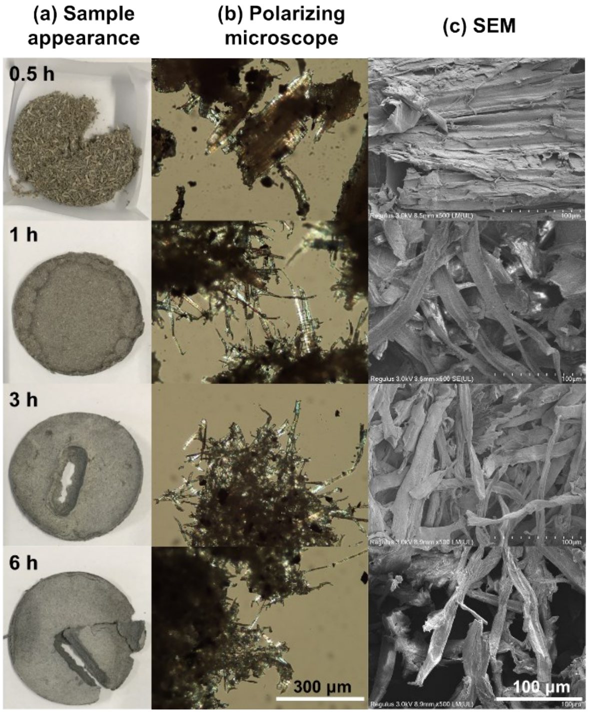


Fig. S8 Images of the wood residual of atmospheric RCF with 0.4 g/L sulfuric acids at different reaction time. Reaction conditions: 10 ml EG with 0.4 g/L, 185 °C, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

Table S5 Yield results of ARCF with the addition of phosphoric acid. [a]

Acid concentration (g/L)	Selectivity (wt.%)		Yield (wt.%)		
	G/S-3	G/S-3ene	G/S-total	Other phenolics	Impurities
0.4	66.3	33.7	20.9	0.9	0.8
0.8	84.0	16.0	24.4	1.3	1.0
2	91.9	8.1	17.4	1.7	2.0

[a] Reaction conditions: 10 ml EG with designated concentration of phosphoric acid, 185 °C, 3 h, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

Table S6 Acid concentration screen of ARCF of different wood substrates.[a]

Entry	Substrate	Acid concentration (g/L)	Selectivity (wt.%)		Yield (wt.%)	
			G/S-3	G/S-3ene	G/S-total	Other phenolics
1	Birch 1	0.4	81.7	18.3	10.4	4.5
2		0.3	78.8	21.2	16.8	2.9
3		0.2	41.2	58.8	15.6	0.7
4	Birch 2	0.4	82.7	17.3	12.7	4.2
5		0.3	69.8	30.2	17.6	1.4
6		0.2	53.6	46.4	17.9	1.0
7		0.1	46.3	53.7	13.1	0.1
8	Beech	0.5	86.9	13.1	12.2	3.7
9		0.4	78.8	21.2	18.5	1.7
10		0.3	30.9	69.1	13.9	0.5
11	Eucalyptus	0.4	76.3	23.7	9.5	3.2
12		0.3	68.8	31.2	14.0	1.7
13		0.2	50.0	50.0	13.3	1.0
14		0.1	41.4	58.6	12.1	0.4
15	Willow	1.2	73.5	26.5	4.4	6.1
16		1.0	76.3	23.7	9.7	3.0
17		0.8	35.5	64.5	10.6	0.9
18		0.4	32.3	67.7	6.9	0.3
19	Cypress[b]	1.2	73.2	26.8	1.5	4.3
20		0.8	49.7	50.3	2.8	1.0
21		0.4	41.6	58.4	2.3	0.3
22	Pine[b]	0.8	89.3	10.7	1.2	5.7
23		0.4	72.0	28.0	4.2	0.8

[a] Reaction conditions: 10 ml EG with designated concentration of sulfuric acid, 185 °C, 3 h, 0.5 g poplar sawdust, 10 wt.% (0.05 g) 5% Ru/C and 500 rpm.

[b] Only G units were detected in the products of cypress and pine.

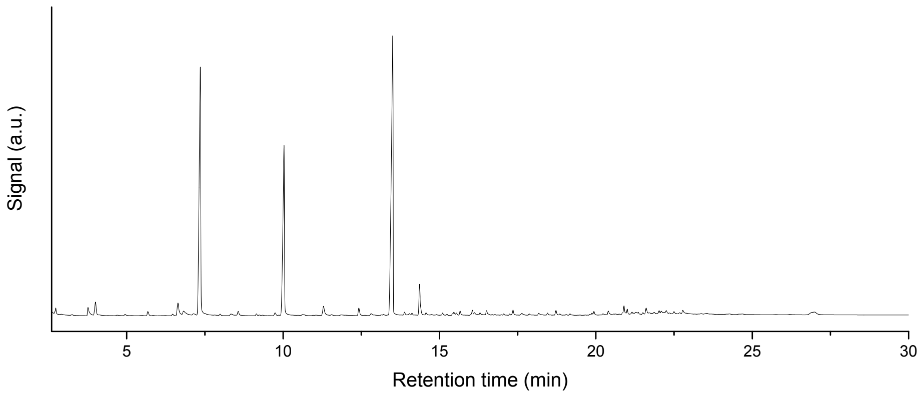


Fig. S9 GC spectrum of the final product of ARCF at 100 ml scale. Reaction conditions: 100 ml EG with 0.4g/L sulfuric acid, 195 °C (boiling), 6 h, 5 g poplar sawdust, 10 wt.% (0.5 g) 5% Ru/C and 500 rpm.

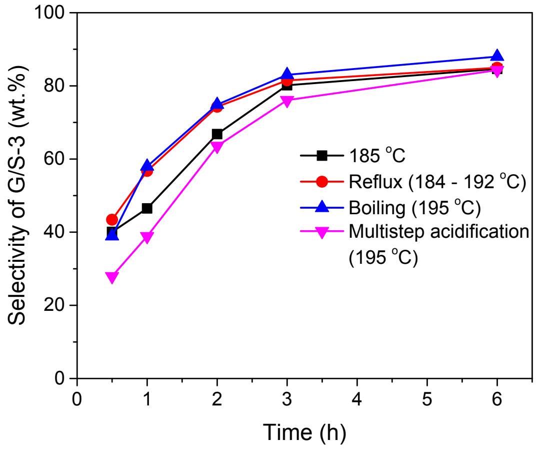


Fig. S10 Selectivity of G/S-3 in scale-up experiment (100 ml) in function of time. Reaction conditions: 100 ml EG with 0.4g/L sulfuric acid, 6 h, 5 g poplar sawdust, 10 wt.% (0.5 g) 5% Ru/C and 500 rpm.

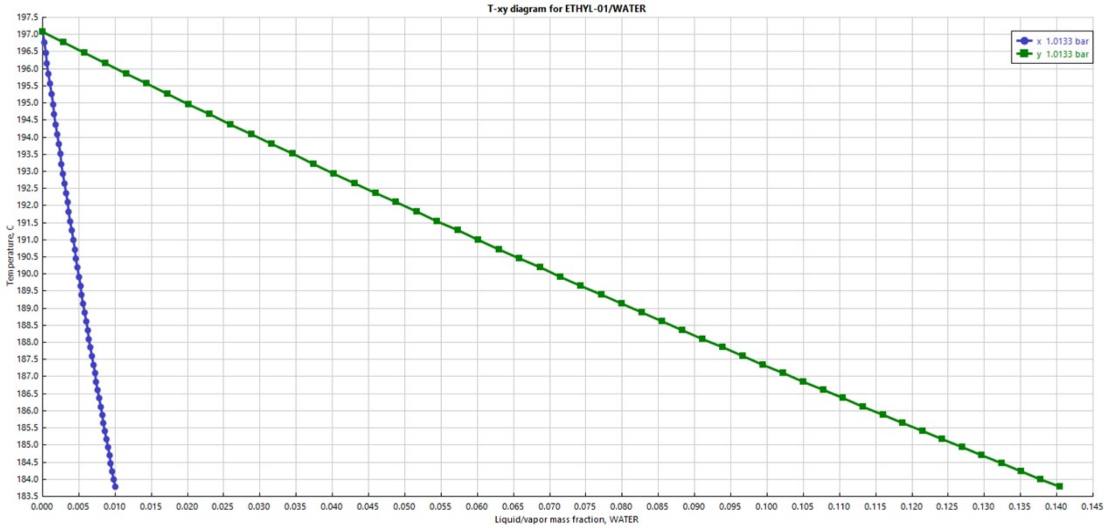


Fig. S11 Simulation and calculation of the boiling point of EG containing water. Blue line: bubble point line; green line: dew point line.

Discussion for Fig. S11: The content of water and other impurities with low boiling points influence the boiling point of the reaction mixture. For example, 1 wt.% water (i.e., 1.11 g water in 100 ml tests) leads to 183.7 °C of the boiling point. And the starting water content is estimated to be 0.82 g (0.5 g in catalyst and 0.32 g in sawdust). Thus, to operate at the higher temperature, part of water and other low boiling point impurities should be distilled out.

Table S7 Analysis of distilled liquid in 100 ml ARCF.

Operation condition	Mass of distilled liquid (g)[a]	Mass (mg) and proportion (%)[b]				
		G-3	G-3ene	S-3	S-3ene	G/S-total
Boiling (195 °C)	3.3	4.66 (6.7)	0.45	0.40	0.00	5.50 (2.1)
Multistep acidification (195 °C)	12.0	12.41 (18.0)	2.21	2.89	0.53	18.05 (6.8)

[a] The mass of distilled liquid is controlled by the reaction temperature. The higher the temperature, the more liquid distilled out. There would be plenty of EG distilled out if the reaction temperature maintained at 196 – 197 °C for a long time.

[b] Mass of lignin monomers in the distilled liquid and their proportions to the corresponding parts in the reaction.

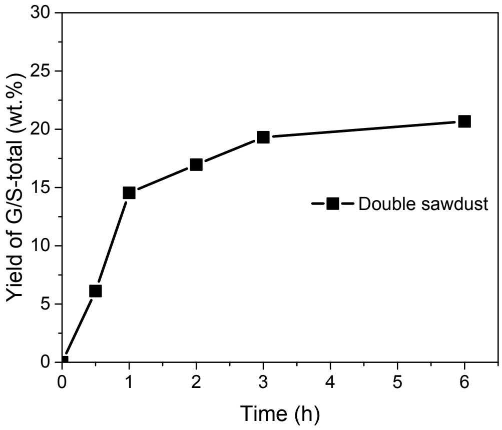


Fig. S12 Yield results of 100 ml ARCF test with double amount of sawdust. Reaction conditions: 100 ml EG with 0.4g/L sulfuric acid, 6 h, 10 g poplar sawdust, 10 wt.% (0.5 g) 5% Ru/C and 500 rpm.

Discussion for Fig. S12: The conversion cannot treat the twofold amount of sawdust in one reaction for the substrate was too much to magnetically stir, and thus, the total yields were lower (Fig. S12).

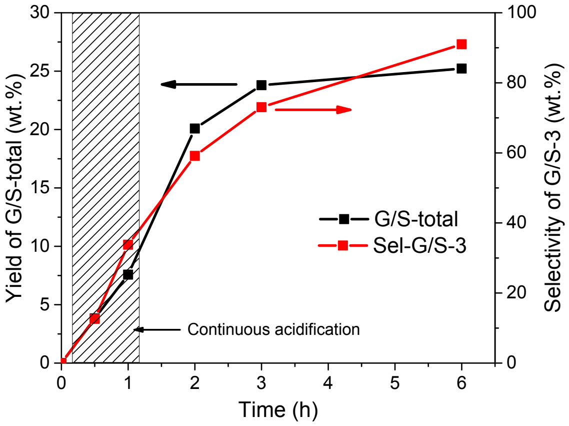


Fig. S13 Continuous acidification in ARCF at 300 ml scale. Reaction condition: 290 ml EG, 15 g poplar sawdust, 10 wt.% (1.5 g) 5% Ru/C, 6 h, 500 rpm, 10 ml EG solution of sulfuric acid was continuously pumped into the reactor over 1 h from 10 min, and the final sulfuric acid concentration added is equal to 0.4 g/L. Detail procedures and analysis of the product are similar to the semi-continuous experiment presented in Section S2.6.

Discussion for Fig. S13: The most extreme state of multistep acidification is continuous acidification. In this test, sulfuric acid was added using a separated tube and controlled by a pump. At the beginning of the reaction, the total yields were lower than 100 ml tests and small scale tests due to less acid in the reaction mixture. However, after adding all the acid and enough reaction, the total yield return to normal level at 3 h. The experiment indicates that the way of adding acid is not that important. So, acid can be added separately to avoid corrosion.

Table S8 Model compounds studies and the functions of 5% Ru/C and sulfuric acid.[a]

Table S8-1 Model conversion of eugenol.

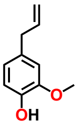
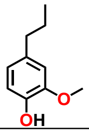
Conditions	Conversion (%)	Yield (wt.%)	
			Dimers
Ru/C and acid	100	88.6	3.1
Ru/C	100	96.5	0.5
Acid	18.2	0	2.9
Blank	1.2	0	0.7

Table S8-2 Model conversion of isoeugenol (G-3ene).

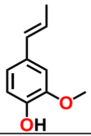
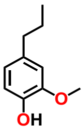
Conditions	Conversion (%)	Yield (wt.%)	
			Dimers
Ru/C and acid	100	96.0	8.2
Ru/C	100	93.9	1.2
Acid	72.8	0	35.6
Blank	13.6	0	3.6

Table S8-3 Model conversion of benzyl phenyl ether (α-O-4).

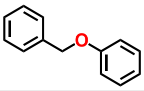
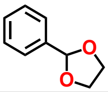
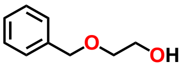
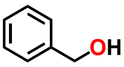
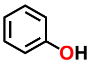
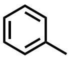
Conditions	Conversion (%)	Yield (wt.%)				
						
Ru/C and acid	93.3	1.5	5.3	0	33.8	33.4
Ru/C	58.6	0	0	1.2	16.3	15.7
Acid	46.2	5.3	20.7	0	19.6	0
Blank	7.5	0	2.9	0	2.8	0

Table S8-4 Model conversion of 2-(benzyloxy)phenol.

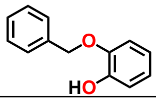
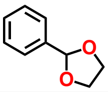
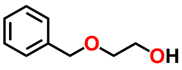
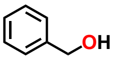
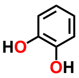
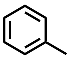
Conditions	Conversion (%)	Yield (wt.%)				
						
Ru/C and acid	100	0	1.8	1.1	37.8	39.6
Ru/C	66.9	0	0.6	1.3	23.8	24.1
Acid	87.7	3.0	49.8	0	25.7	0
Blank	1.5	0	0	0	0	0

Table S8-5 Model conversion of dibenzyl ether.

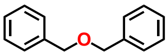
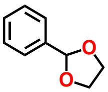
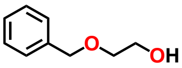
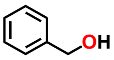
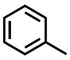
Conditions	Conversion (%)	Yield (wt.%)			
					
Ru/C and acid	98.2	8.7	20.1	7.0	49.8
Ru/C	70.6	8.1	0.9	14.6	25.1
Acid	60.2	23.1	18.6	5.7	6.7
Blank	5.0	1.8	0	1.2	0

Table S8-6 Model conversion of 2-phenoxyethylbenzene (β-O-4).

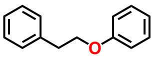
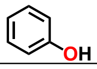
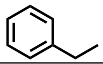
Conditions	Conversion (%)	Yield (wt.%)	
			
Ru/C and acid	65.4	16.1	21.0
Ru/C	48.5	12.5	15.0
Acid	9.0	0	0
Blank	9.4	0	0

Table S8-7 Model conversion of 2-phenoxyphenol (4-O-5).

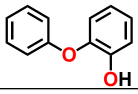
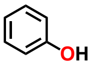
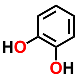
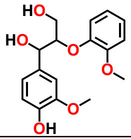
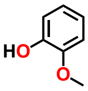
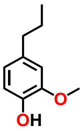
Conditions	Conversion (%)	Yield (wt.%)	
			
Ru/C and acid	64.4	7.9	10.7
Ru/C	42.2	3.2	4.3
Acid	33.5	3.6	0
Blank	2.3	0	0

Table S8-8 Model conversion of guaiacylglycerol-β-guaiacyl ether (β-O-4).

Conditions	Conversion (%)	Yield (wt.%)	
			
Ru/C and acid	-[b]	28.1	17.5
Ru/C	-[b]	27.0	23.0
Acid	-[b]	24.7	0
Blank	-[b]	18.2	0

[a] Reaction condition: Table S8-1-6: 10 ml EG (0 or 0.2 g/L sulfuric acid), 50 mg substrate, 0 or 25 mg 5% Ru/C, 185 °C, 30 min and 500 rpm; Table S8-7 and 8: 5 ml EG (0 or 0.2 g/L sulfuric acid), 10 mg substrate, 0 or 25 mg 5% Ru/C, 185 °C, 20 min and 500 rpm. Conversion and yield of each product are calculated based on the GC peak area of each compound. Conversion=$A_{\text{substrate, after reaction}}/A_{\text{substrate, before reaction}}$; Yield=$A_{\text{product, after reaction}}/A_{\text{substrate, before reaction}}$. In all dimer experiments, the mass of components was not well balanced before and after the reaction, perhaps because of adsorption on 5% Ru/C and oxidation and polymerization due to acid.

[b] The substrate cannot be detected by GC, so the conversion is not calculated. Since the substrate concentration of Table S8-7 and 8 are the same, the product yield in Table S8-8 is roughly calculated based on the peak area of the starting substrate of Table S8-7.

Discussion for Table S8: In Table S8-1 and 2, all substrates were hydrogenated when 5% Ru/C were used. However, although eugenol and isoeugenol (G-3ene) have similar structures, G-3ene is much easier polymerized under acidic environment. This is also proven by the results in Table S4. Thus, the hydrogenation (stabilization) of G/S-3ene is very important to achieve high yield.

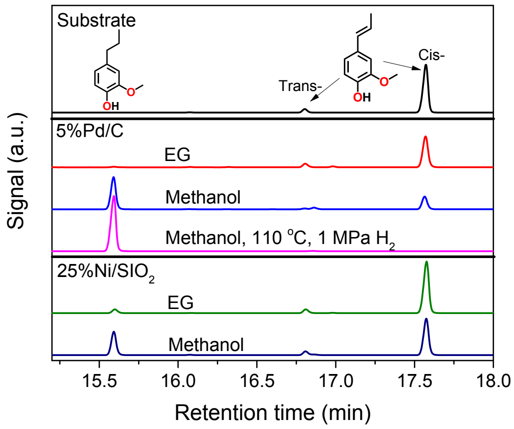


Fig. S14 GC spectra of model conversion of G-3ene in EG and methanol over 5% Pd/C and 25%Ni/SiO$_2$. Reaction conditions: in EG: 185 °C, 10 ml EG, 0.05 g G-3ene, 5% Pd/C (0.025 g) or 25% Ni/SiO$_2$ (0.05 g), 0.5 h and 500 rpm; in methanol: 185 °C (or as specified), 40 ml EG, 0.2 g G-3ene, 5% Pd/C (0.1 g) or 25% Ni/SiO$_2$ (0.2 g), 0.5 h, 500 rpm with or without hydrogen.

Discussion for Fig. S14: The model conversion (in Fig. 5) were further tested in methanol. More G-3 were formed in methanol over 5% Pd/C and 25%Ni/SiO$_2$, indicating that methanol is more reactive to serve as a hydrogen source. If the reaction started with 1 MPa hydrogen, almost all G-3ene was hydrogenated over 5% Pd/C at as low as 110 °C. It shows that, with hydrogen, Pd/C shows strong hydrogenation ability. Thus, Pd/C has high reactivity in traditional RCF. The results (including Fig. 5) indicate that an effective hydrogen source and a highly reactive catalyst are important in RCF and ARCF.

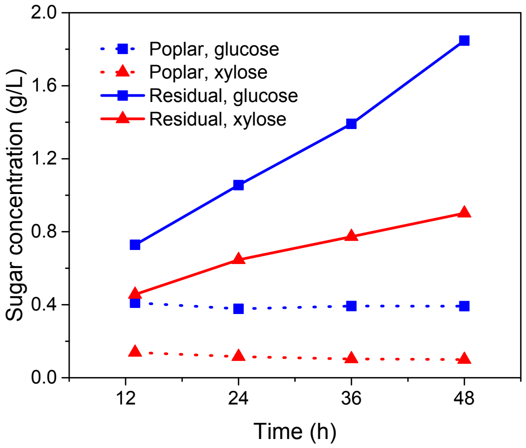


Fig. S15 Enzymatic hydrolysis of poplar and residual. Enzymolysis conditions: 5 g residual of semi-continuous operation or original poplar, 100 ml citrate buffer (0.05 M, pH 4.8), 50 °C and a mixture of cellulase, β-glucosidase and hemicellulose.

Discussion for Fig. S15: After removing most lignin, the residual of traditional RCF can effectively produce monosaccharide by enzymolysis and even ethanol by simultaneous fermentation.[2] Thus, we also investigated the enzymolysis of residual of ARCF. As shown in Fig. S15, the yields of glucose and xylose gradually increased over time by enzymolyzing the final residual of semi-continuous operation of ARCF; while in the case of enzymolyzing poplar, the yields of both sugars were not changed. At 48 h, the concentration of glucose and xylose in the case of enzymolyzing residual were 4.7 and 9.0 times of those of enzymolyzing poplar, respectively. This shows the residual of ARCF can be effectively enzymolyzed as well. The original wood substrate is hard to be enzymolyzed because lignin hinders enzyme contacting cellulose and hemicellulose.[4]

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