Electronic Supporting Information

Reductive catalytic fractionation of lignocellulose: when should the catalyst meet depolymerized lignin fragments?

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A. Experimental method

Determination of the Klason lignin content

The determination of the Klason lignin content was performed base on the procedure from Lin & Dence.[1] The beech wood was extracted with toluene and ethanol (2:1) by Soxhlet extraction method for at least 3 h. After cooling, the solid was washed with ethanol and dried at 80 °C overnight. Then, the solid (0.6 g) was put into 72 wt% sulfuric acid (15 ml) for 2 h with mixing. Afterwards the slurry was diluted with 290 ml water until the H_2SO_4 reach to 3 wt%. The solution was heated with reflux for 4 h. After filtration of the solution, the acid insoluble residue was retained and dried in an oven overnight. Klason lignin content was determined gravimetrically and corrected for the weight from extractives.

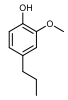
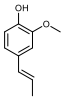
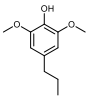
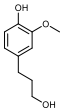
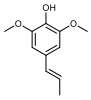
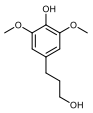
Calculating lignin oil yield

$$DCM\ extracted\ lignin\ oil\ (DELO)\ yield = \frac{mass\ of\ DELO}{wt\%\ Klason * mass\ of\ dry\ biomass}$$

$$Methanol\ soluble\ lignin\ oil\ (MSLO) yield = \frac{mass\ of\ MSLO}{mass\ of\ dry\ biomass}$$

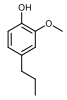
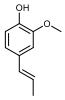
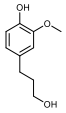
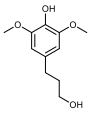
B. Tables

Table S1. Yields of lignin monomers of all reactions (wt%) described in the article in Table 1 [a]

											Total
Before reaction	0.6	1.6	12.7	0.7	1.9	2.4	21.3	0.7	0.3	1.9	44.1
140°C	0.5	2.4	12.4	0.8	1.8	2.6	19.5	1	0.5	2.1	43.6
200°C	0.5	0.8	11.6	1	2.2	2.5	18.4	0.7	0.5	2.1	40.3
250°C	2.1	1.1	8.7	0.7	0.3	2.6	12.7	0.7	-	2	30.9
250°C for 0.5h	2.6	1.6	5.9	0.7	-	2.2	5	-	-	0.8	18.8
250°C for 1h	1.5	1.3	5.7	0.6	0.2	2	5.9	-	-	0.4	17.6
250°C for 2h	-	0.6	3.9	0.3	0.7	1.3	5.5	-	1.2	1	14.5
None	-	1.4	0.6	0.2	1.2	0.4	0.6	-	1.0	-	5.4

[a] Reaction conditions: 2 g of beech wood (particle size <40 mesh), 0.3 g of Ru/C, 100 mL of methanol, 1 MPa H_2 at room temperature, 250 °C, and 310 min in total. Reaction pressure is approximately 9 MPa.

Table S2. The lignin monomer selectivity (%) of all reactions described in the article in Table 1 [a]

										
Before reaction	1.4	3.6	28.8	1.6	4.3	5.4	48.3	1.6	0.7	4.3
140°C	1.1	5.5	28.4	1.8	4.1	6.0	44.7	2.3	1.1	4.8
200°C	1.2	2.0	28.8	2.5	5.5	6.2	45.7	1.7	1.2	5.2
250°C	6.8	3.6	28.2	2.3	1.0	8.4	41.1	2.3	-	6.5
250°C for 0.5h	13.8	8.5	31.4	3.7	-	11.7	26.6	-	-	4.3
250°C for 1h	8.5	7.4	32.4	3.4	1.1	11.4	33.5	-	-	2.3
250°C for 2h	-	4.1	26.9	2.1	4.8	9.0	37.9	-	8.3	6.9
None	-	25.9	11.1	3.7	22.2	7.4	11.1	-	18.5	-

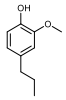
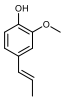
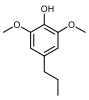
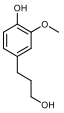
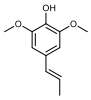
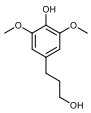
[a] Reaction conditions: 2 g of beech wood (particle size <40 mesh), 0.3 g of Ru/C, 100 mL of methanol, 1 MPa H_2 at room temperature, 250 °C, and 310 min in total. Reaction pressure is approximately 9 MPa.

Table S3. Depolymerization of beech wood without catalyst at different stop times [a]

Entry	Stop time	Monomer yields (wt %)	MSLO yield (wt %)	DELO yield (wt %)
1	140 °C (55 min)	-	3.4 ± 0.2	5.7 ± 0.2
2	200 °C (85 min)	-	7.3 ± 0.3	13.8 ± 0.3
3	250 °C (130 min)	2.0	18.8 ± 0.2	50.1 ± 0.5
4	250 °C for 0.5 h (160 min)	2.8	19.4 ± 0.2	52.5 ± 0.3
5	250 °C for 1 h (190 min)	4.1	20.9 ± 0.3	58.9 ± 0.4
6	250 °C for 2 h (250 min)	5.0	22.8 ± 0.5	60.3 ± 0.6

[a] Reaction conditions: 2 g of beech wood (particle size <40 mesh), 0.3 g of Ru/C, 100 mL of methanol, 1 MPa H_2 at room temperature, 250 °C, and 310 min in total. Specially, reaction is stopped and cooled as fast as possible prior to catalyst addition.

Table S4. Yields of lignin monomers of reactions (wt%) without catalyst at different stop times [a]

											Total
140°C	-	-	-	-	-	-	-	-	-	-	-
200°C	-	-	-	-	-	-	-	-	-	-	-
250°C	-	0.5	-	-	0.5	0.1	-	-	0.9	-	2.0
250°C for 0.5h	-	0.7	-	-	0.7	0.2	-	-	1.1	-	2.8
250°C for 1h	-	1.1	-	-	0.9	0.3	-	-	1.8	-	4.1
250°C for 2h	-	1.0	-	-	0.8	0.3	0.7	-	-	-	5.0

[a] Reaction conditions: 2 g of beech wood (particle size <40 mesh), 0.3 g of Ru/C, 100 mL of methanol, 1 MPa H_2 at room temperature, 250 °C, and 310 min in total. Reaction pressure is approximately 9 MPa. Specially, reaction is stopped and cooled as fast as possible prior to catalyst addition.

Table S5. Effective carbon number (ECN) for lignin monomers used in this study

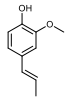
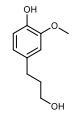
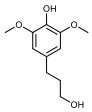
Lignin monomer structure	Effective carbon number
	7
	5
	6
	8.25
	7
	8
	7.4
	7.4

Table S6. Mn, Mw and PD calculated from GPC results for each lignin oil obtained from reductive catalytic fractionation of beech wood with Ru/C added at different times or not.

Time of adding catalyst	Mn	Mw	PD
Before reaction	414	498	1.2010
140 °C	417	506	1.2123
200 °C	429	533	1.2428
250 °C	430	550	1.2805
250 °C for 0.5 h	457	619	1.3532
250 °C for 1 h	480	691	1.4394
250 °C for 2 h	498	752	1.5108
-	574	1027	1.7900

C. Figures

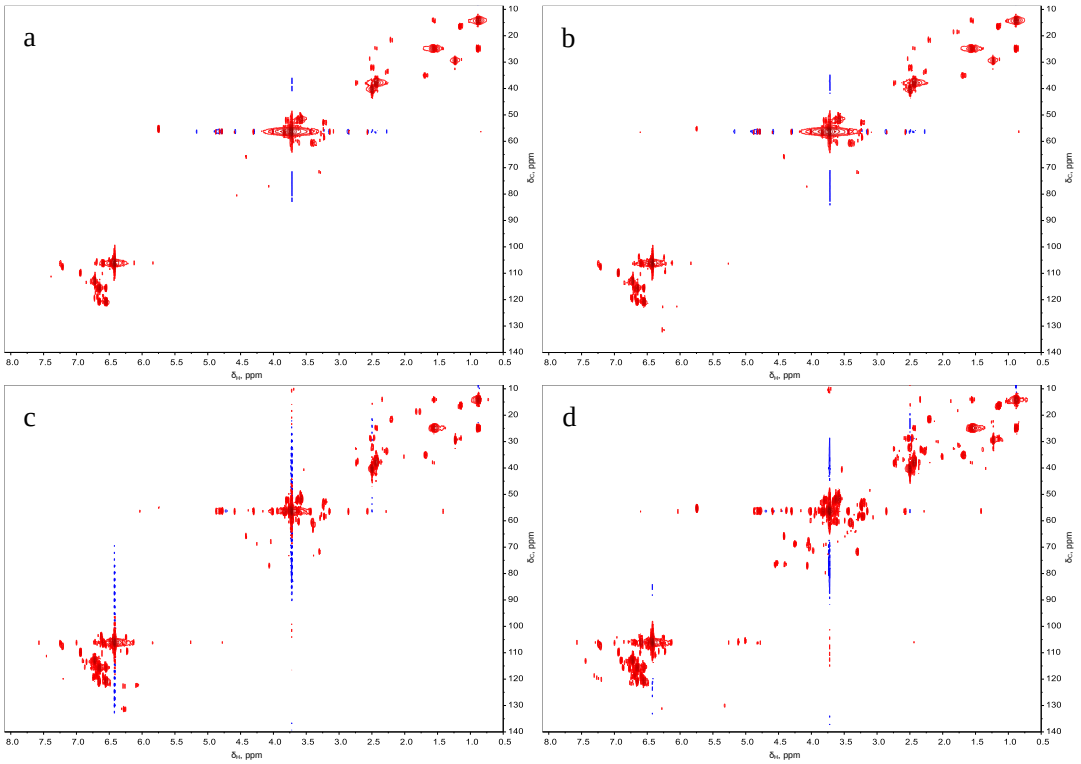


Figure S1. 2D HSQC NMR spectra of the lignin oils obtained from reductive catalytic fractionation of beech wood with Ru/C (a) before reaction, (b) added at 140 °C, (c) added at 200 °C and (d) added at 250 °C.

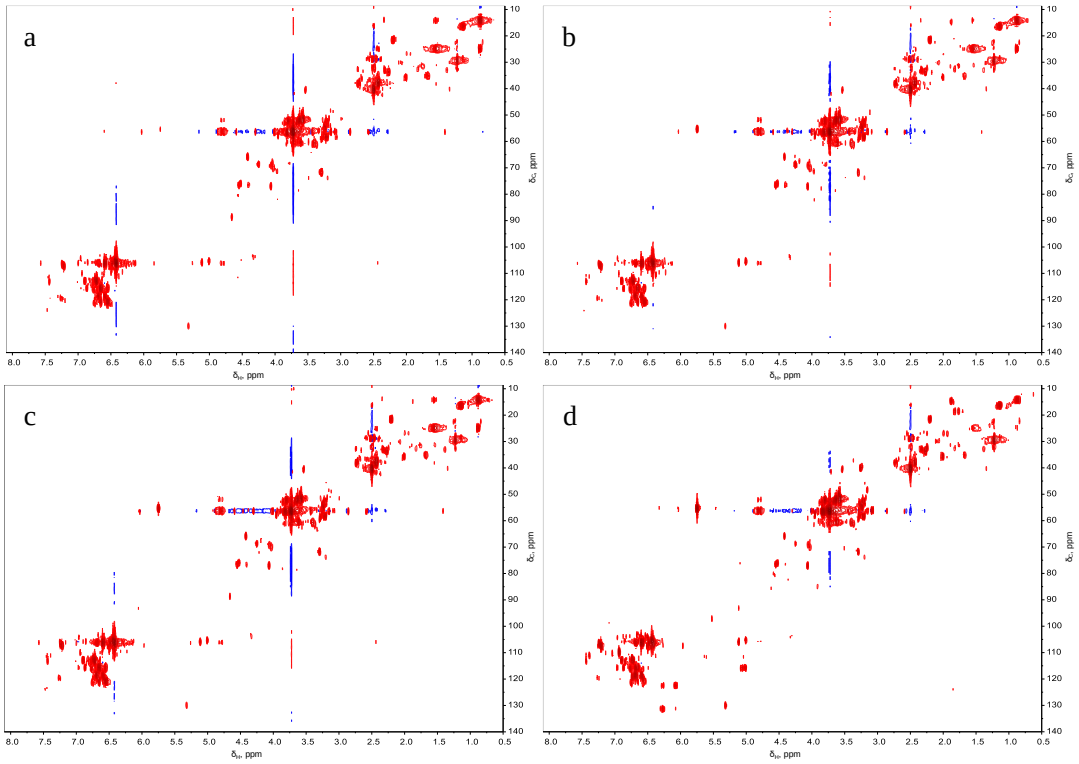


Figure S2. 2D HSQC NMR spectra of the lignin oils obtained from reductive catalytic fractionation of beech wood with Ru/C added after 250 °C for (a) 0.5 h, (b) 1 h, (c) 2 h, and (d) without Ru/C.

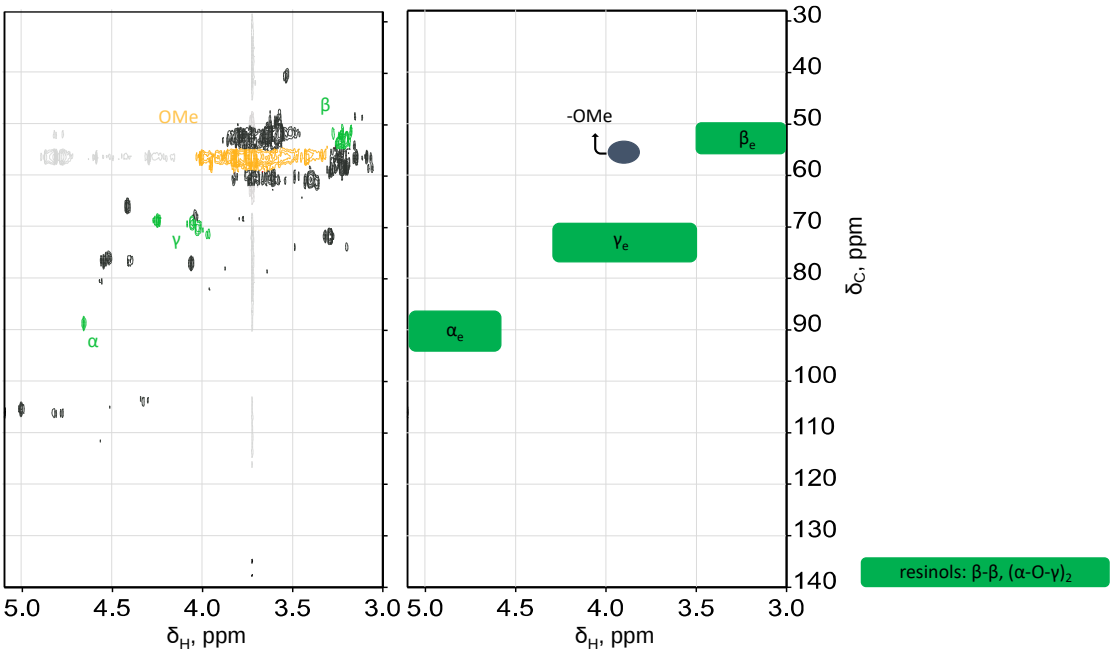


Figure S3. 2D HSQC NMR spectra of the typical lignin oils and the artificial HSQC spectrum (with related information) from the study reported previously[3]. The signals of side-chains involved in ether-bonds are indicated with an "e" in subscript. The analysis results also correspond to the reported study for lignin structures[4].

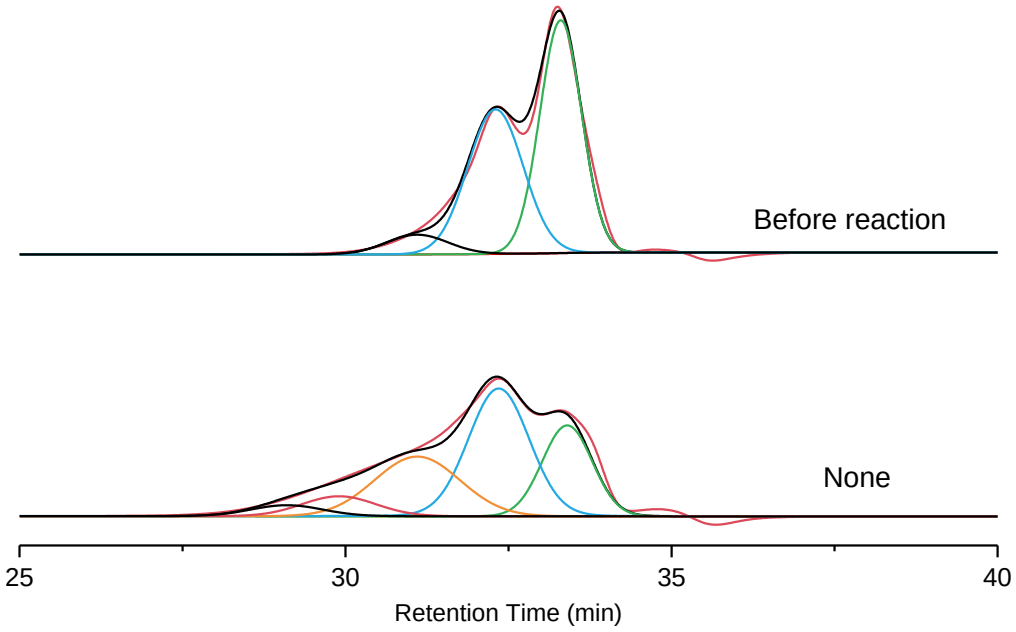


Figure S4. The deconvolution for gel permeation chromatograms (GPC) of the lignin oils obtained from reductive catalytic fractionation of beech wood with Ru/C added before reaction or not.

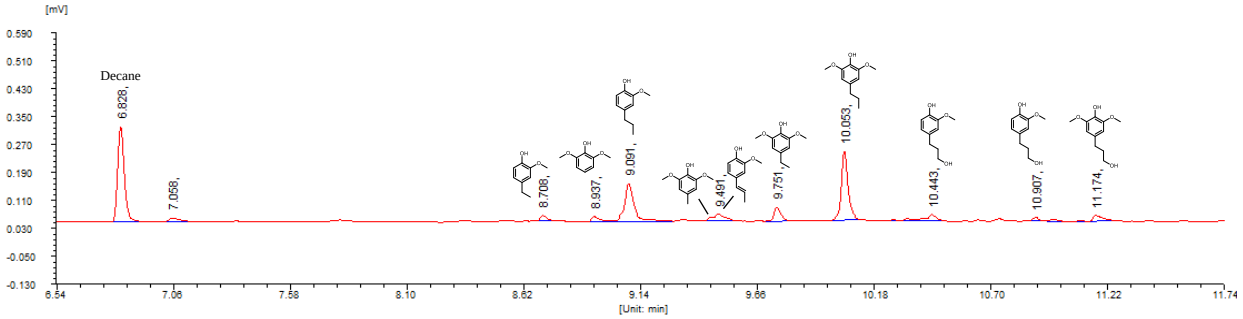


Figure S5. GC spectrum of product mixtures with decane obtained from typical reductive catalytic fractionation of beech wood with Ru/C.

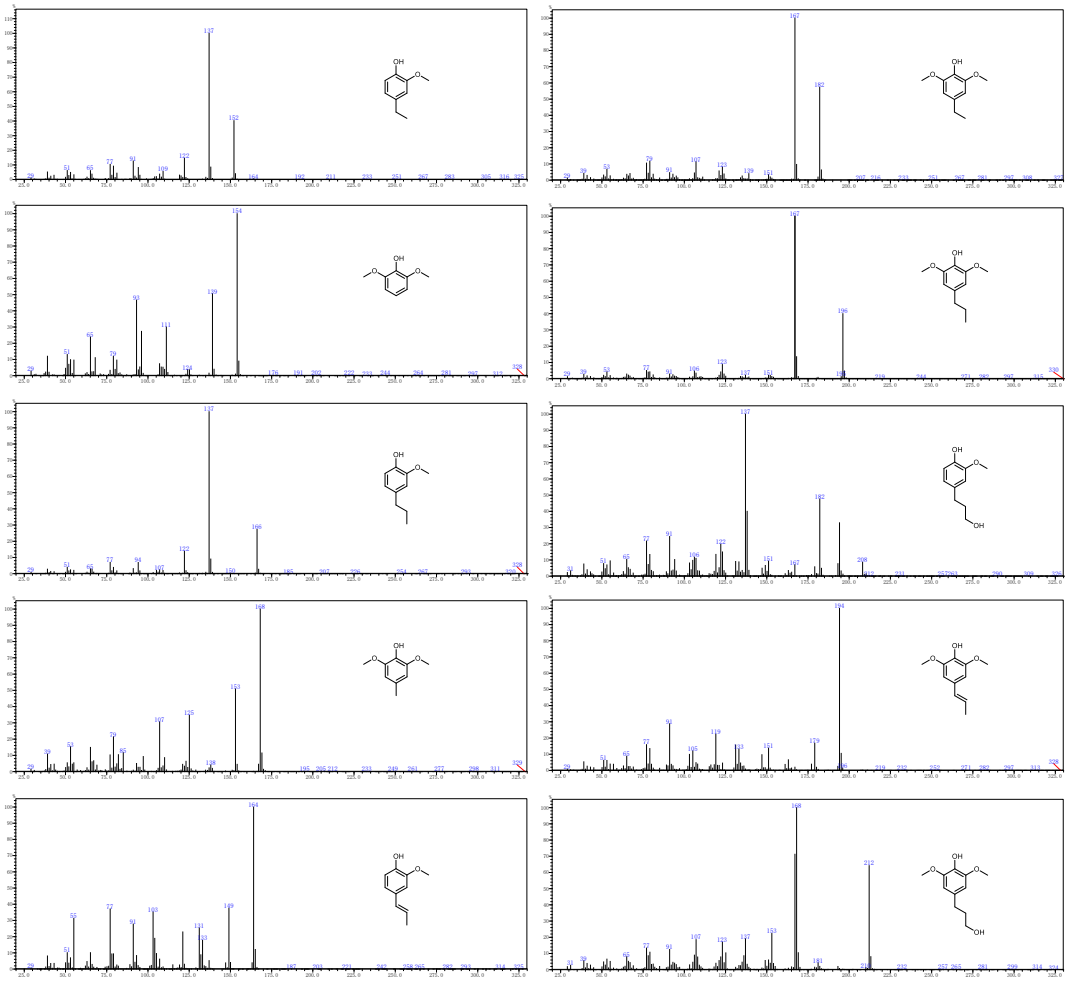
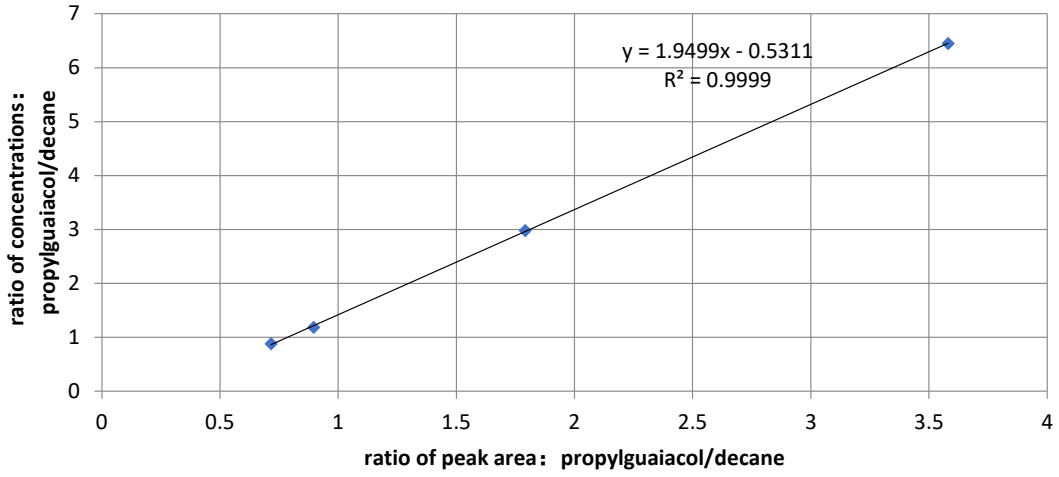


Figure S6. GC-MS spectra of products resulting from typical reductive catalytic fractionation of beech wood with Ru/C.



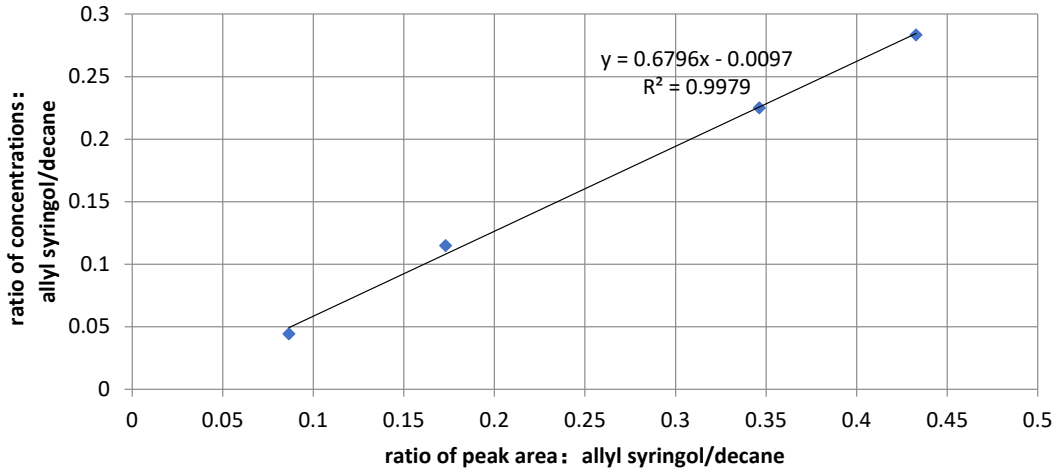


Figure S7. Calibration curves for GC determination of two lignin monomers (propyl guaiacol and allyl syringol). Decane was used as internal standard.

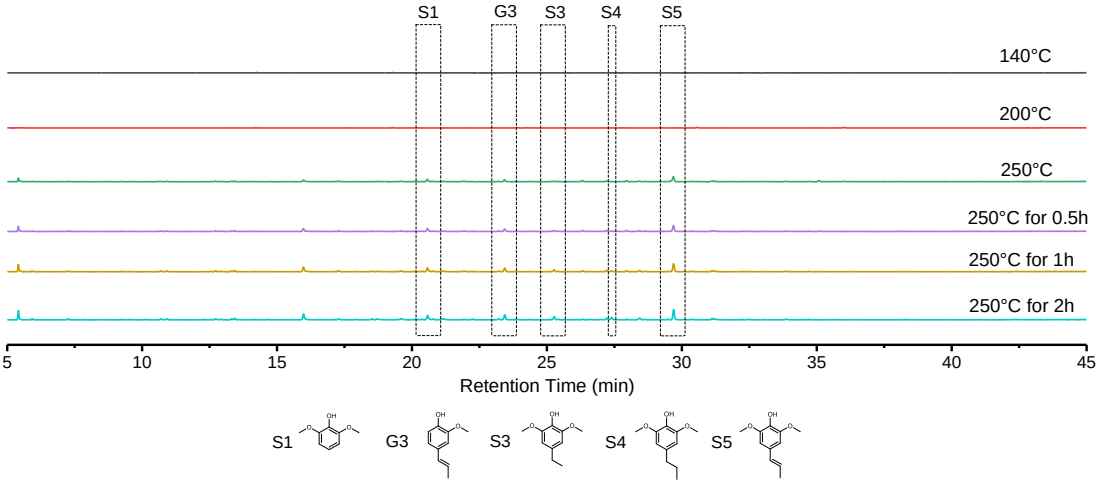


Figure S8. Total-ion chromatograms (TICs) of lignin oils obtained from reductive catalytic fractionation of beech wood without catalyst at different stop times.

D. References

1. C. W. Dence, in *Methods in Lignin Chemistry*, eds. S. Lin and C. Dence, Springer Berlin Heidelberg, 1992, ch.3, pp. 33-61
2. X. Wu, X. Fan, S. Xie, J. Lin, J. Cheng, Q. Zhang, L. Chen, Y. Wang, *Nature Catalysis*, 2018, 1, 772-780
3. S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy Environ. Sci*., 2015, 8, 1748-1763
4. T. Q. Yuan, S. N. Sun, F. Xu and R. C. Sun, *J. Agric. Food. Chem.*, 2011, 59, 10604-10614.