Supplementary Material

Effects of metal site and acid site on the hydrogenolysis of cornstalk in supercritical ethanol during lignin-first fractionation

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Table S1 The retention rate of cellulose and hemicellulose over different catalysts.

Catalyst	Retention rate (%)
Ru/Al_2O_3	74.8
Ru/C	80.4
Ru/C-acid (5)	76.1
Ru/C-acid (10)	69.2
Ru/C-acid (20)	60.5

Note: Retention rate is calculated based on the weight change before and after hydrogenolysis reaction. The weight of cellulose and hemicellulose is measured concentrated sulfuric acid hydrolysis according to the National Renewable Energy Laboratory (NREL) procedure.

Table S2 Acid amount of the different catalysts derived from NH_3-TPD profiles.

Catalyst	Total acid (mmol g^{-1})
Ru/Al_2O_3	4.78
Ru/C	2.19
Ru/C-acid (10)	6.44

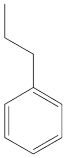
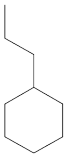
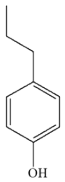
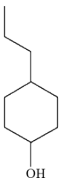
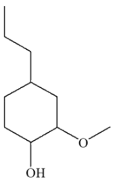
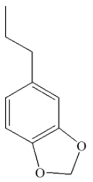
Table S3 The main components of the monomers.[a]

Component	Yield[b] (wt%)		
	Ru/Al_2O_3	Ru/C	Ru/C-acid (10)
Phenols	**11.6**	**12.5**	**19.3**
Phenol, 4-ethyl-	4.1	3.0	4.5
2,5-Diethylphenol	0.4	1.3	1.8
Methyl 4-hydroxybenzoate	0.0	1.0	1.7
3-(4-Hydroxyphenyl) propanoic acid	2.9	4.1	5.7
Benzenepropanoic acid, 4-hydroxy-, methyl ester	4.2	3.1	5.6
Guaiacols	**7.3**	**14.7**	**15.5**
Phenol, 2-methoxy-4-methyl-	0.5	0.7	0.0
Phenol, 2-methoxy-4-ethyl-	2.6	2.9	3.0
Phenol, 2-methoxy-4-propyl-	3.1	9.3	9.3
Methyl 3-(4-hydroxy-3-methoxyphenyl) propionate	1.1	1.8	3.2
Hydrogenated products	**4.8**	**5.7**	**3.5**
Cyclohexanol	1.7	2.3	0.4
Cyclohexanol, methyl-	1.2	1.5	2.1
2-(2-Methylcyclohexyl)-2-propanol	0.0	1.2	0.0
Cyclohexanepropionic acid	1.4	0.0	0.0
Cyclohexanepropanoic acid, methyl ester	0.5	0.7	1.0
Other aromatic compounds	**0.9**	**3.2**	**4.6**
1-Propanone, 1-(2,4-dimethoxyphenyl)-	0.0	1.7	0.7
1,3-Benzodioxole-5-propanoic acid, ethyl ester	0.9	1.5	3.9
Total	**24.6**	**36.1**	**42.9**

[a] Condition: 0.5 g cornstalk, 0.2 g Ru/C-acid (10) catalyst, 15 mL ethanol, 3 MPa H_2, 260 ^oC, 4 h.

[b] Measured by GC-MS, where acetophenone was used as internal standard chemical. Components listed were those represented by more than 0.5% of yield determined by GC-MS.

Table S4 Hydrogenolysis of 4-propyl guaiacol and product distribution over different catalysts.

Catalyst	Conversion (%)	Product selectivity (%)							
		1	2	3	4	5	6	2 + 4 + 5 Hydrogenated products	5 + 6[a] -OCH_3 products
									
Ru/C	23.8	12.1	22.5	2.3	20.4	38.1	4.5	81.0	42.6
Ru/C-acid (5)	28.4	17.9	33.0	3.1	16.5	24.2	5.2	73.7	29.4
Ru/C-acid (10)	35.5	20.7	36.7	1.5	15.8	19.3	5.9	71.8	25.2
Ru/C-acid (20)	39.1	24.3	41.4	0.8	12.6	10.5	10.3	64.5	20.8

[a] Compound 6 accounts for the –OCH_3 products due to the existence of –OCH_2– group.

Condition: 0.1 g 4-propylguaiacol, 0.05 g catalyst, 15 mL ethanol, 3 MPa H_2, 260 °C, 4 h.

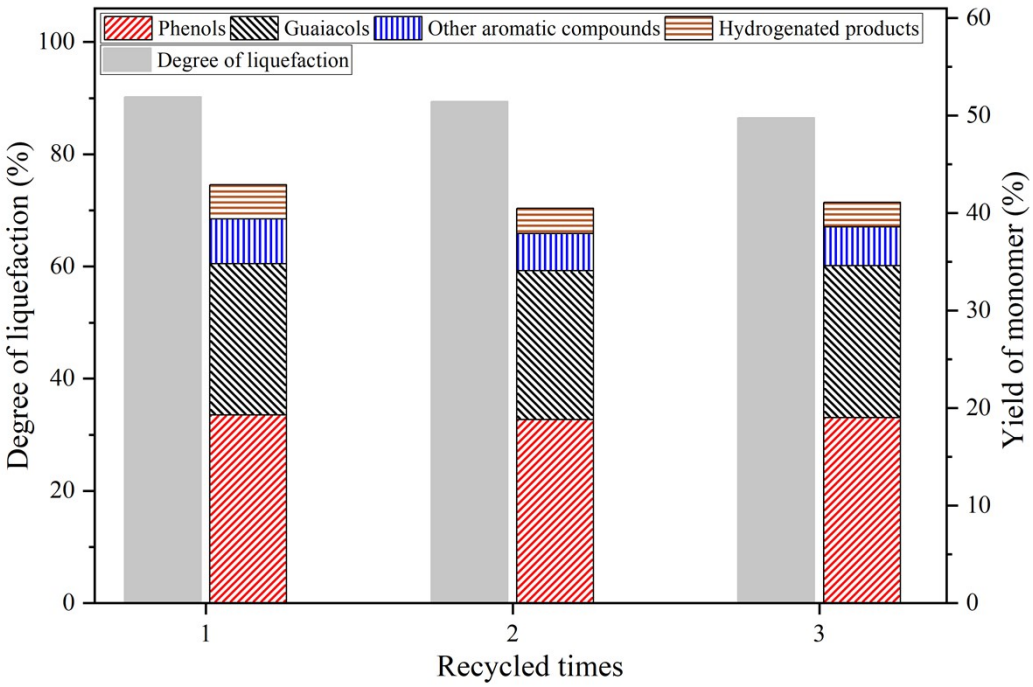


Fig. S1. The recyclability of the Ru/C-acid (10) catalyst. Condition: 0.5 g cornstalk, 0.2 g Ru/C-acid (10) catalyst, 15 mL ethanol, 260 °C, 4 h.

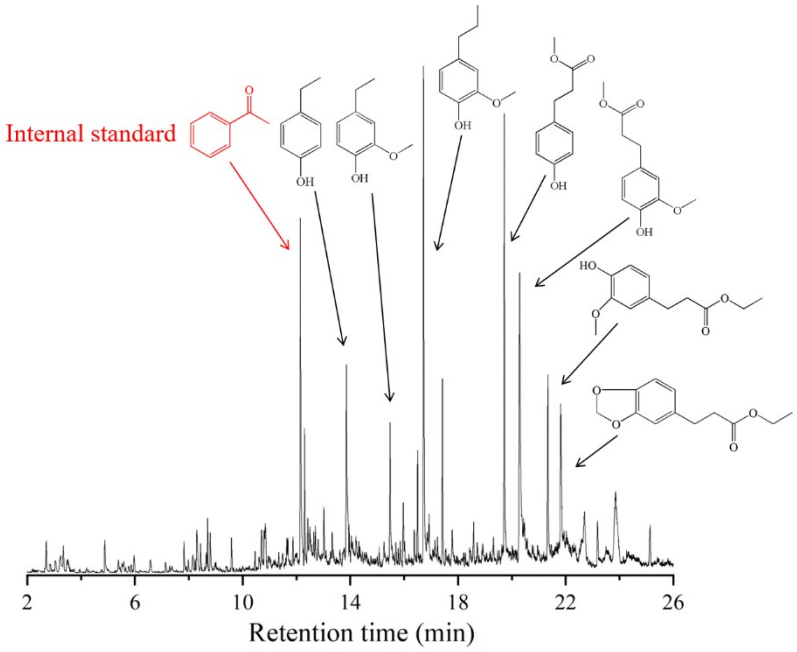


Fig. S2. GC-MS chromatogram of the volatile products after hydrogenolysis with Ru/C-acid (10) catalyst.

Condition: 0.5 g cornstalk, 0.2 g Ru/C-acid (10), 15 mL ethanol, 260 °C, 3 MPa H_2, 4 h.

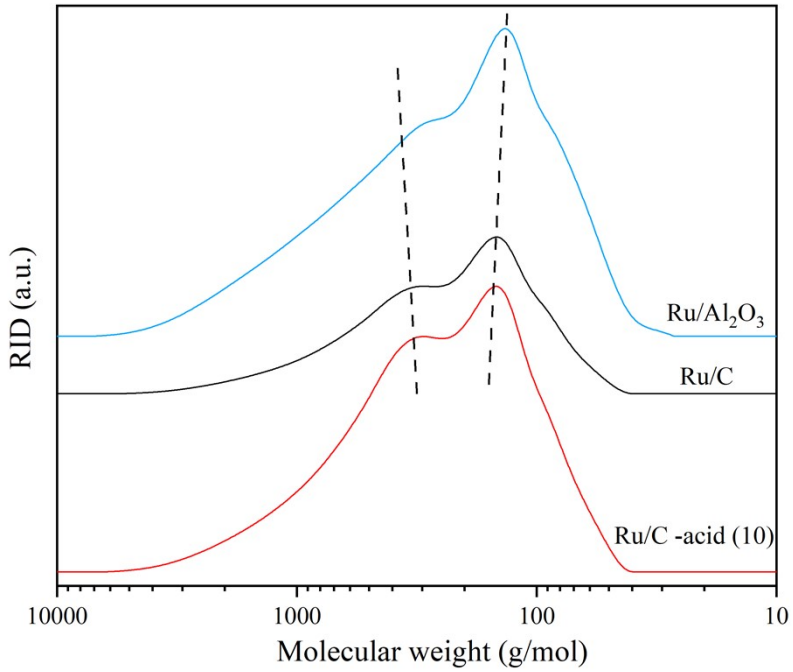


Fig. S3. GPC analysis of the nonvolatile products with different catalysts.

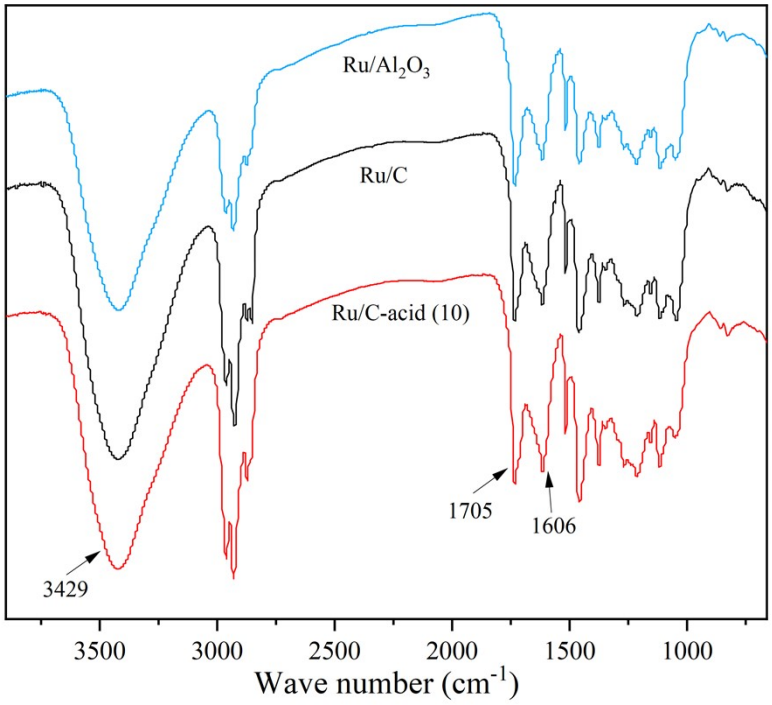


Fig. S4. FT-IR spectra of the nonvolatile products with different catalysts.