

## Electronic Supplementary Information

### Depolymerization of lignin via a non-precious Ni-Fe alloy catalyst supported on Activated Carbon

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#### Birch sawdust preparation

Dry birch wood was milled to get a sawdust fraction with a size of ca.40 mesh. Fats, waxes, resins and terpenoids/steroids, which may influence the determination of Klason lignin, were removed by a Soxhlet extraction. The extractant was a 2:1 toluene: ethanol mixture. After 3 h of standard Soxhlet extraction, the obtained samples were washed with ethanol and dried at 378 K for 12 h.

#### Determination content of lignin in birch

The yields of monophenols in raw biomass reaction were based on the content of Klason lignin in birch sawdust. The content of lignin was determined based on a method reported by Lin & Dence.<sup>1</sup> 2 g birch sawdust was added to a 100 mL beaker and 30 mL of 72% H<sub>2</sub>SO<sub>4</sub> solution was subsequently added to the beaker. The mixture was stirred for 3 h at room temperature. Then the mixture was slowly transferred into a 1 L breaker with 200 ml water. The diluted solution was added to a 1 L round bottom flask and the final concentration of H<sub>2</sub>SO<sub>4</sub> was 3%. The flask was heated for 4 h under reflux condition. The hot solution was filtrated and the filter residue was washed with hot water. Then the residue was dried in an oven at 373 K for 24 h. The lignin content is obtained by comparing the quantity of the dry residue and the original birch sawdust.

## Elemental analysis

**Table S1** C, H, O, N, S content in organosolv lignin

C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)
53.56	6.22	35.38	0.09	0.08

## Partial 2D HSQC NMR spectra of the organosolv lignin

A 2D HSQC NMR technique following previously reported works<sup>2, 3</sup> has been used to determine the linkages and structure of the organosolv lignin. Semi-quantification of the ratios of lignin linkages and aromatic units was calculated by using the guaiacyl G<sub>2</sub> and syringyl S<sub>2,6</sub> cross-peaks as the reference (100 C<sub>9</sub> units).<sup>3, 4</sup>

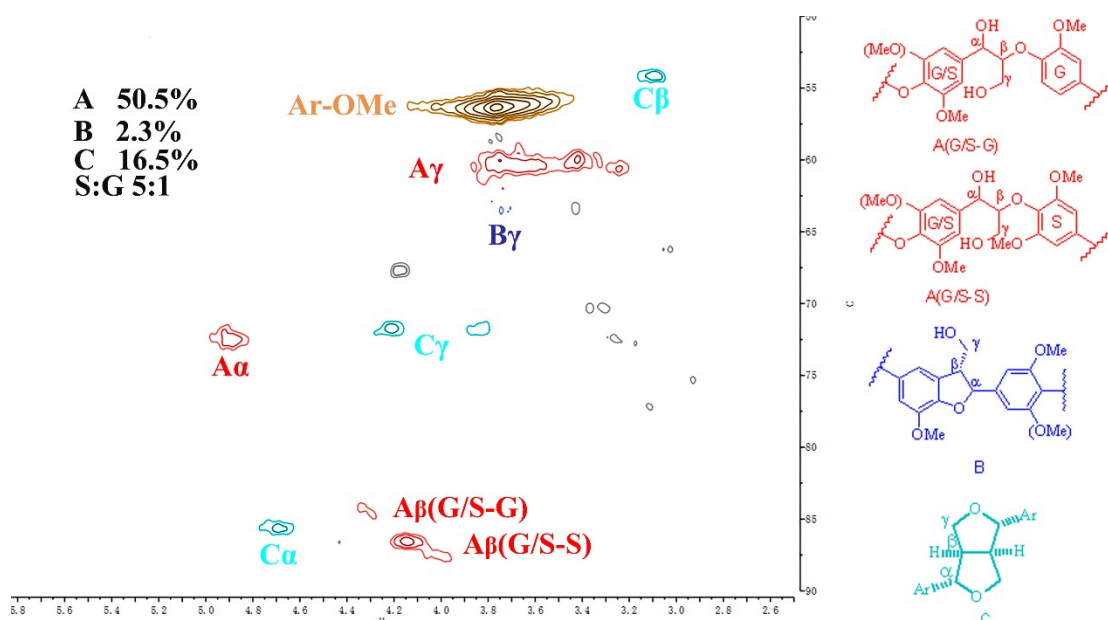


Figure S1. Partial 2D HSQC NMR spectra of organosolv lignin

## Acetylation of organosolv lignin and lignin depolymerization products

The molecular weight distribution of the organosolv lignin and lignin depolymerization products were analyzed by gel permeation chromatography (GPC). Acetylation of the free hydroxyl groups<sup>5</sup> has to be done before GPC analysis. Acetylation was performed by using acetic anhydride and pyridine (2 mL each for 30 mg dry sample) at room temperature. After 48 h, the reaction mixture was diluted with ethyl alcohol, concentrated under vacuum and dried in vacuum drying oven.

### Mass balance and char content

The char was measured in hydrogenolysis reaction of organosolv lignin. The mixture of catalysts and char was collected and dried in an oven for 24 h. The dry mixture was weighted and the mass of char was calculated by subtracting the mass of catalyst from the dry mixture. When Fe/AC catalyst was used, the char was 32 wt%. There was almost no char formed by using Ni-Fe/AC catalyst at 200 °C, 2 MPa H<sub>2</sub>. However, 10% char was detected at 240 °C.

$$\text{Char (wt\%)} = \frac{\text{weight of catalyst and char mixture} - \text{weight of catalyst}}{\text{weight of lignin}} \times 100\%$$

**Table S2.** Mass balance of the lignin depolymerization products

Entry	Catalyst	Temperature	Methanol-soluble	THF-soluble	Char	Mass balance
1	Ni <sub>1</sub> -Fe <sub>1</sub> /AC	200 °C	60.01mg	22.19 mg	trace	82.2%
2	Ni <sub>1</sub> -Fe <sub>1</sub> /AC	240 °C	46.50 mg	21.71 mg	10.03 mg	78.24%

### Catalysts recycle

Catalyst recycle was conducted by adding the mixture of collected catalysts and 10 mg of fresh catalyst to new reaction. After each recycle, the total yield of monomers decreased. The catalyst was regenerated before the fourth recycle.

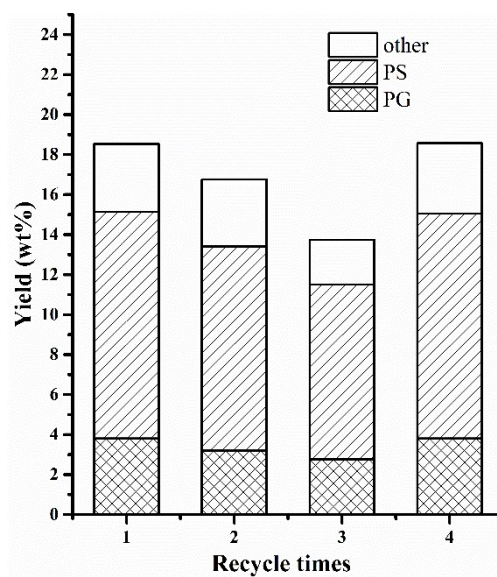
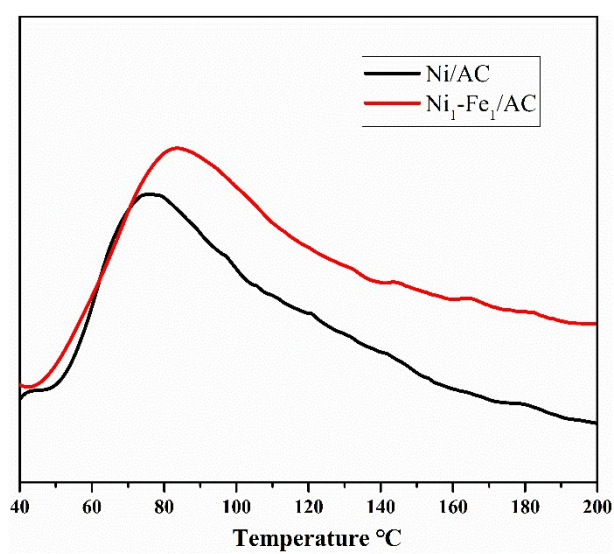


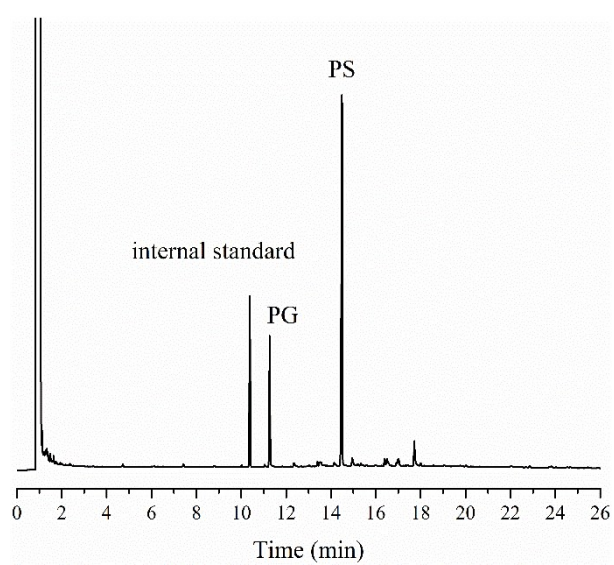
Figure S2. Recycle of catalysts (Reaction condition: 100 mg organosolv lignin, 10 ml methanol, 2 MPa H<sub>2</sub>; 200 °C; 6 h; 800 rpm)

### NH<sub>3</sub>-TPD

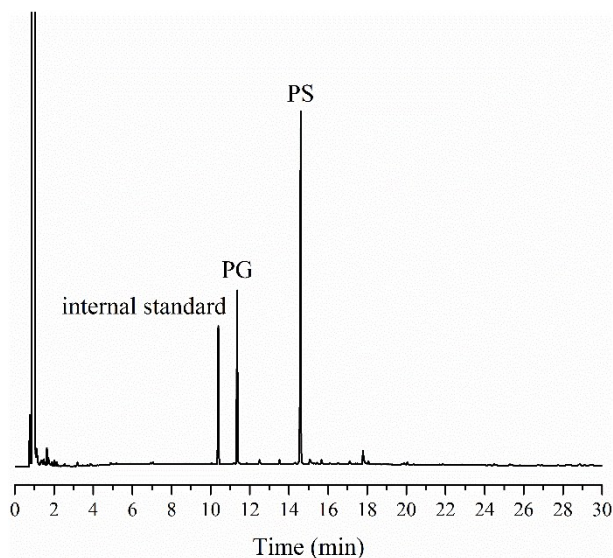


**Figure S3.** NH<sub>3</sub>-TPD profiles of Ni/AC and Ni<sub>1</sub>-Fe<sub>1</sub>/AC catalysts

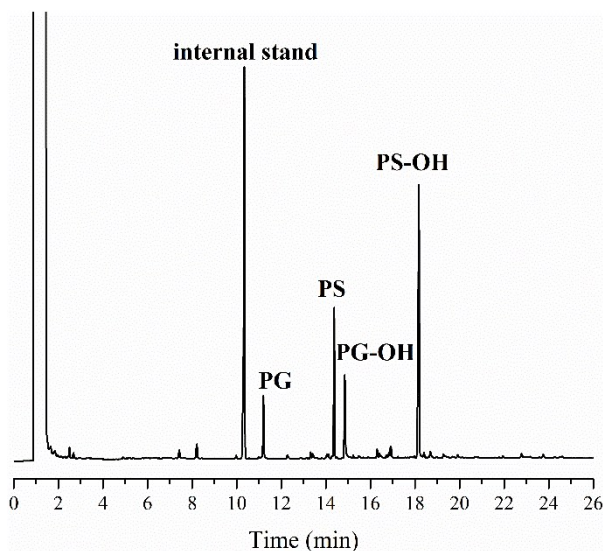
### GC results



**Figure S4.** GC result of Ni<sub>1</sub>-Fe<sub>1</sub>/AC catalyzed organosolv lignin depolymerization

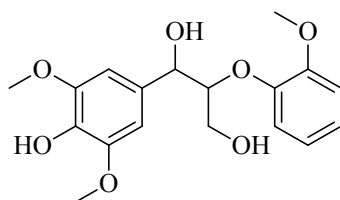


**Figure S5.** GC result of Ni<sub>1</sub>-Fe<sub>1</sub>/AC catalyzed organosolv lignin depolymerization



**Figure S6.** GC result of Ni/AC catalyzed birch sawdust depolymerization

**1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (1):**



The β-O-4 lignin model compound was synthesized according to reported paper.<sup>6</sup> It was a mixture of diastereomers, erythro: threo (2:1) and used without separating the diastereomers.

**Reference**

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