

Supporting Information

In Situ Reactor-Integrated Electrospray Ionization Mass Spectrometry for Heterogeneous Catalytic Reactions and Its Application in the Process Analysis of High-Pressure Liquid-Phase Lignin Depolymerization

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GC-MS analysis procedures

The collected samples were centrifuged and analyzed by GC-MS system (Agilent Technologies 7890B-7000D) equipped with a DB-5ms capillary column (30 cm×250 μm ×0.25 μm). The naphthalene was added into the sample for the quantitative analysis. The oven temperature was programmed as 50 °C hold for 3 min and ramped up to 280 °C with 8 °C/min and hold for another 10 min. The injector was kept at 280 °C in split mode (5:1) and the injection volume was 1 μL . A solvent delay of 4 min was used to protect the detector. The structure information of detected compounds was obtained by the matching with NIST database. The calibration factors of phenolic monomers were calculated from the commercial standards.

Supplementary Note 1

In this work, the diffusion limitation was reasonably neglected during online MS monitoring research of lignin depolymerization for the following reasons. First, the reaction system is very close to the supercritical condition, permitting excellent mass transfer properties such as large diffusion coefficient and small viscosity. Second, in this work the formic acid was used an in-situ hydrogen source, the diffusion limitation for hydrogen and lignin could be neglected. Similarly, during the reaction of lignin depolymerization under the catalysis of Ni/Al₂O₃, the varieties of depolymerization products under static condition is almost the same to that under stirring condition (750 rpm), and the difference of monomer yield was less than 15%.¹

Supplementary Note 2

As a typical batch mode reaction, the pressure inside the reactor will be increasing during the heating process, so the flow rate generated for the ESI needle was changing as illustrated in the Experimental Section. The differences between the spray form in Figure S1c and Figure 2c as well as the TIC in Figure 4a show the effect of pressure change. To make sure that the signal intensity of online MS could have the comparability, the intensity of signal was divided by the total intensity for normalization. In addition, the use of appropriate internal standards will be the appropriate solution for quantification in this method. However, it is hard to find an inert internal standard compound for now because the reaction during online monitoring is quite severe under high temperature.

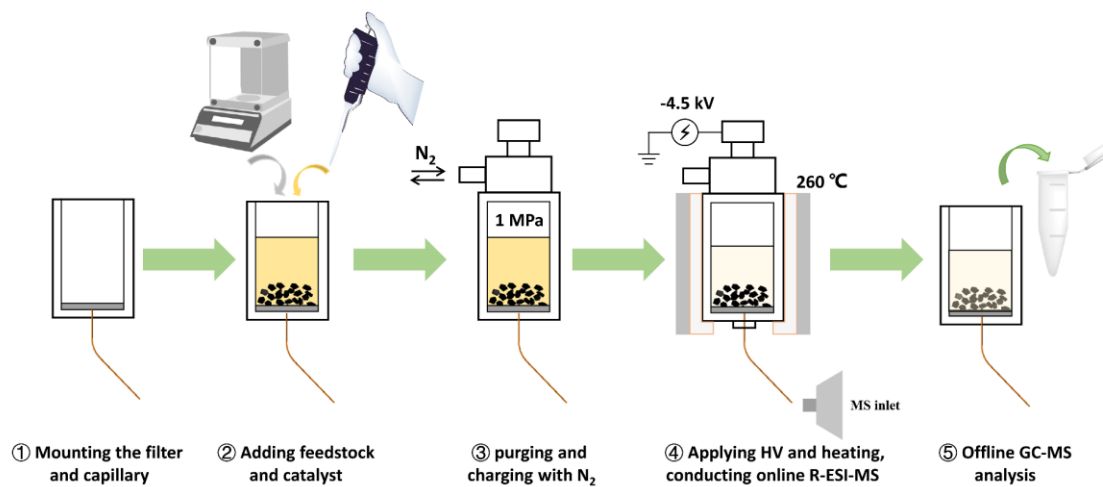


Figure S1. Schematic diagram for the workflow of R-ESI-MS.

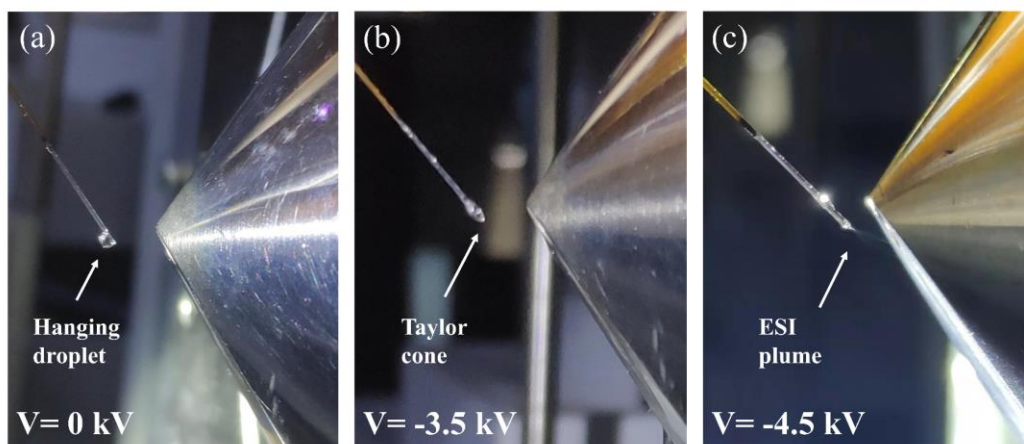


Figure S2. Photographs of R-ESI applying a high voltage of 0 kV, -3.5 kV, and -4.5 kV under room temperature.

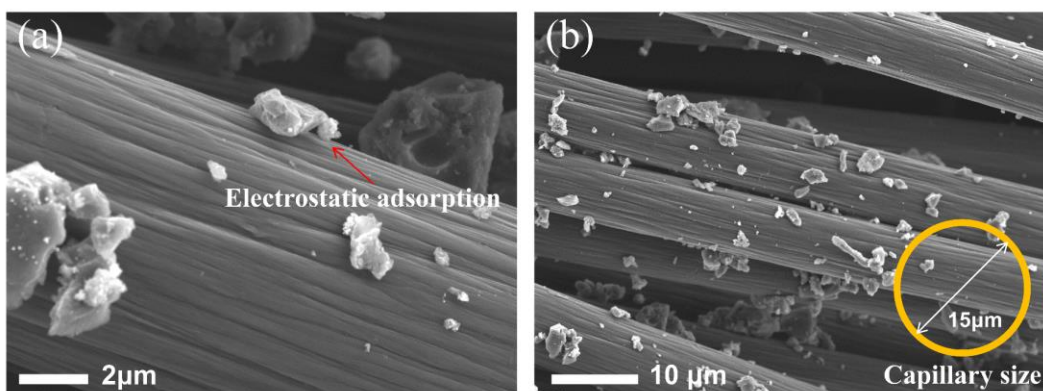


Figure S3. SEM images of carbon cloth filter after reaction. (a) Illustration of electrostatic adsorption of catalyst particles on the surface of carbon fiber; (b) the comparison between capillary inner diameter and particle size of catalyst.

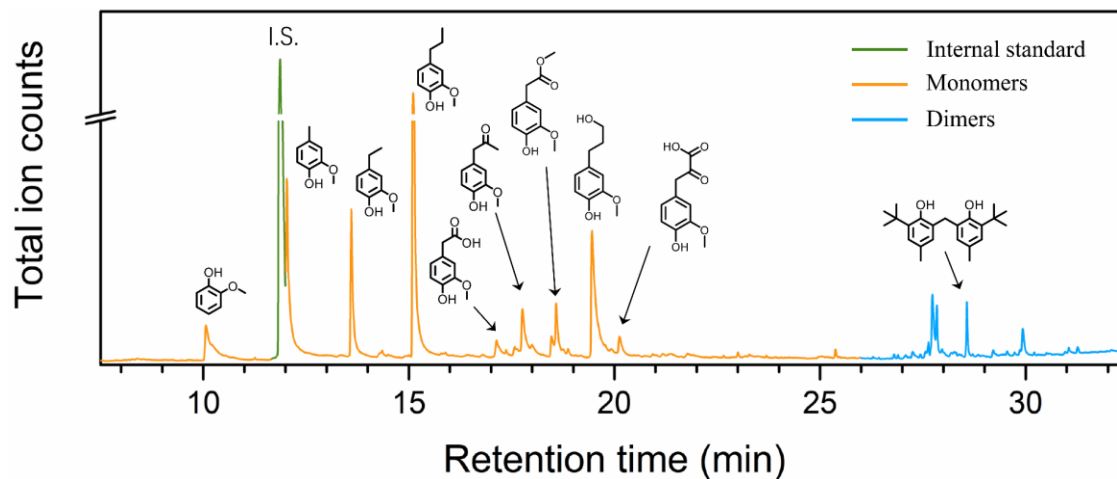


Figure S4. GC-MS analysis of final products of alkali lignin depolymerization. The naphthalene was used as the internal standard for quantitative analysis of monomers. The total monomer yield was as about 6.59 wt% and the yield of phenolic monomers was about 5.70 wt%.

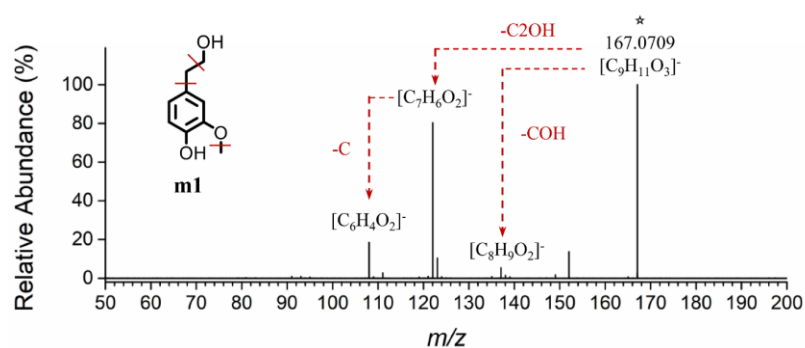


Figure S5. MS/MS spectrum of monomer compound **m1** $C_9H_{12}O_3$ (homovanillyl alcohol, m/z 167.0709) with collision energy of 30%.

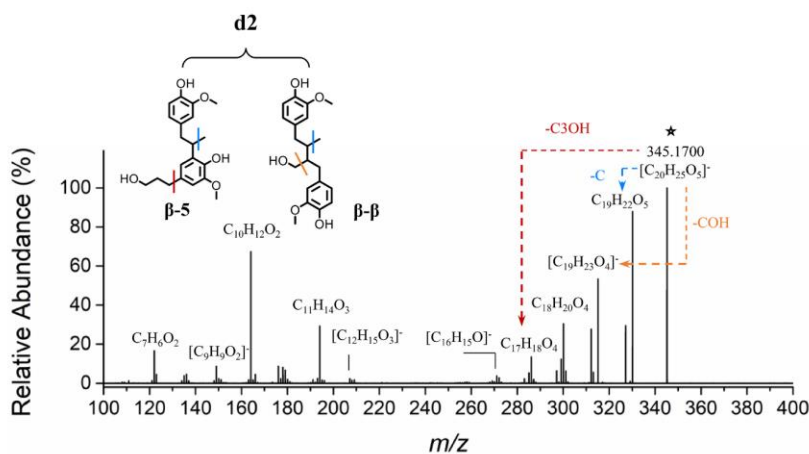


Figure S6. MS/MS spectrum of dimer compound **d2** $C_{20}H_{26}O_5$ (m/z 345.1700) with collision energy of 30%.

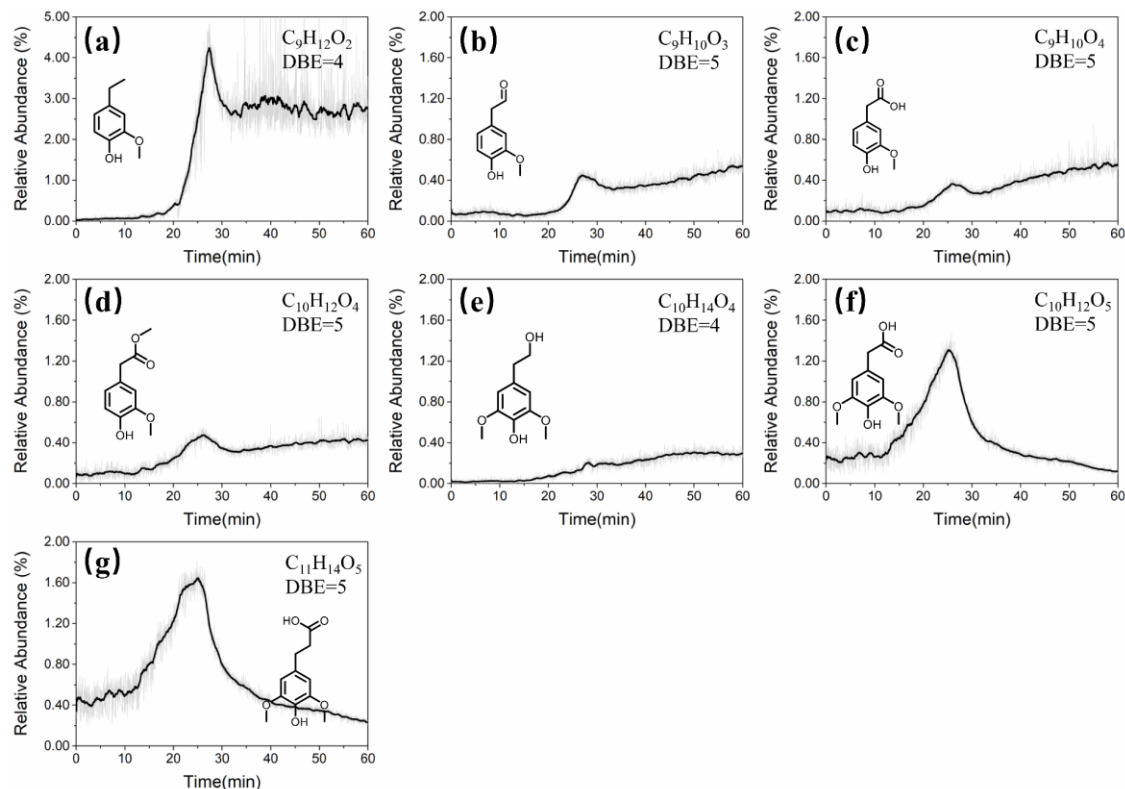


Figure S7. The real time evolution curves of typical monomers.

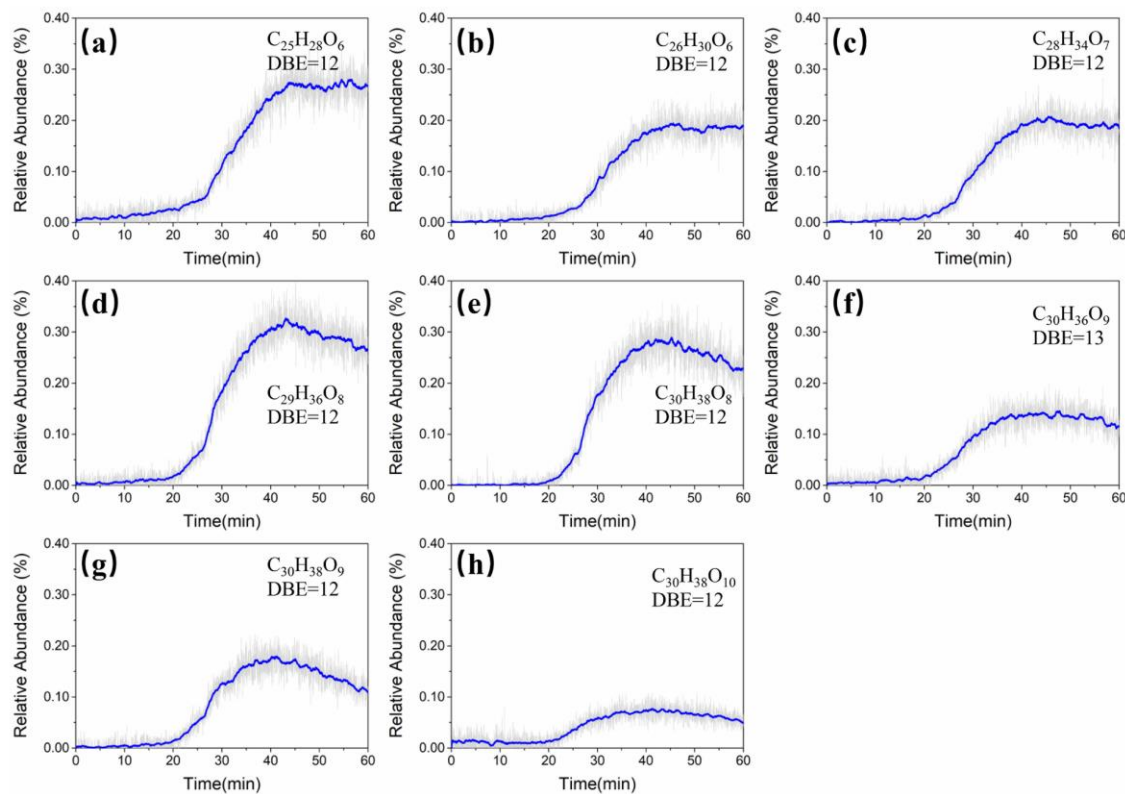


Figure S8. The real time evolution curves of typical trimers.

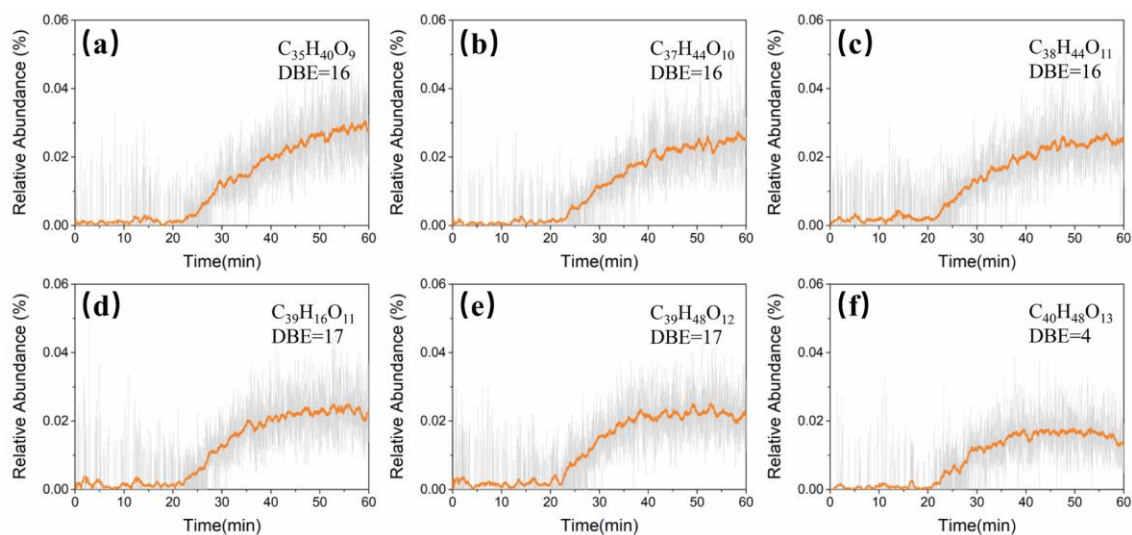


Figure S9. The real time evolution curves of typical tetramers.

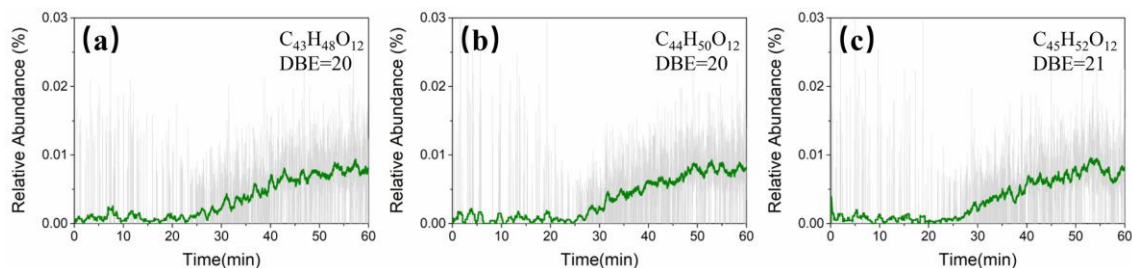


Figure S10. The real time evolution curves of typical short oligomers.

Reference

(1) Van den Bosch, S.; Renders, T.; Kennis, S.; Koelewijn, S. F.; Van den Bossche, G.; Vangeel, T.; Deneyer, A.; Depuydt, D.; Courtin, C. M.; Thevelein, J. M.; Schutyser, W.; Sels, B. F. Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al₂O₃ catalyst pellets during lignin-first fractionation. *Green Chem.* **2017**, *19* (14), 3313-3326.