Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 76–77

Steam reforming of lignin modified with iron

Leonid M. Kustov, Andrey L. Tarasov and Alexander L. Kustov

Hydrolysis lignin powder with a bulk density of 0.38–0.4 g cm^{-3} was used (Biocorb, Rechitsk, Belarus). The element composition of the dry substance (wt%): N, 1.6; C, 60.9; H, 5.5; O, 27.8; S, 0.8; the rest, 3.3. The calculated formula was $CH_{1.09}O_{0.35}$. Mineral ash content was 8.6%.

Iron-containing samples were prepared *via* an impregnation of lignin with an aqueous solution of $Fe(NO_3)_3 \bullet 9H_2O$. The samples were dried after the impregnation in air at 120 °C without calcination in order to avoid lignin ignition in air. The iron loading in the samples was 5–10 wt%.

Lignin and iron-containing lignin samples (0.4 g, particle size of 0.1-–0.5 mm) were loaded in a flow reactor (a quartz tube with the internal diameter of 7 mm) and heated in N_2 flow to 200 °C to decompose supported iron nitrate. A trap for collection of liquid products was placed at the reactor outlet. After purging the samples with N_2 (600 cm^3 h^{-1}) at 200 °C for 1 h, water was supplied into the reactor with a pump at atmospheric pressure with the flow rate 0.8 cm^3 h^{-1}, and the system was kept for 15 min; then temperature-programmed heating of the samples from 200 to 900 °C was switched on with a step of 50 °C. The temperature increase by 50 °C was performed during 5 min at the rate of 10°C min^{-1}, and then the sample was kept at the chosen temperature for 10 min, and gaseous probes were collected at the reactor outlet for the chromatographic analysis. The overall duration of the experiment during the heating from 200 to 900 °C was 3.5 h.

Analysis for CO, CH_4, and CO_2 was carried out using a HayeSep-Q (2 m) packed column at 60 °C equipped with a thermal conductivity detector. Gaseous probes were introduced using a loop with a fixed volume and a 6-way valve. The hydrocarbon-containing part of the gas was analyzed at 60 °C using the same 3700 chromatograph (Granat, Russia) equipped with a SE-30 (25 m) capillary column and flame-ionization detector. The liquid reaction mixture was extracted with benzene or chloroform and analyzed using an SE-30 capillary column in a temperature-programmed mode (60 °C, 7 min, then heating at the rate of 7 °C min^{-1} to 240 °C).

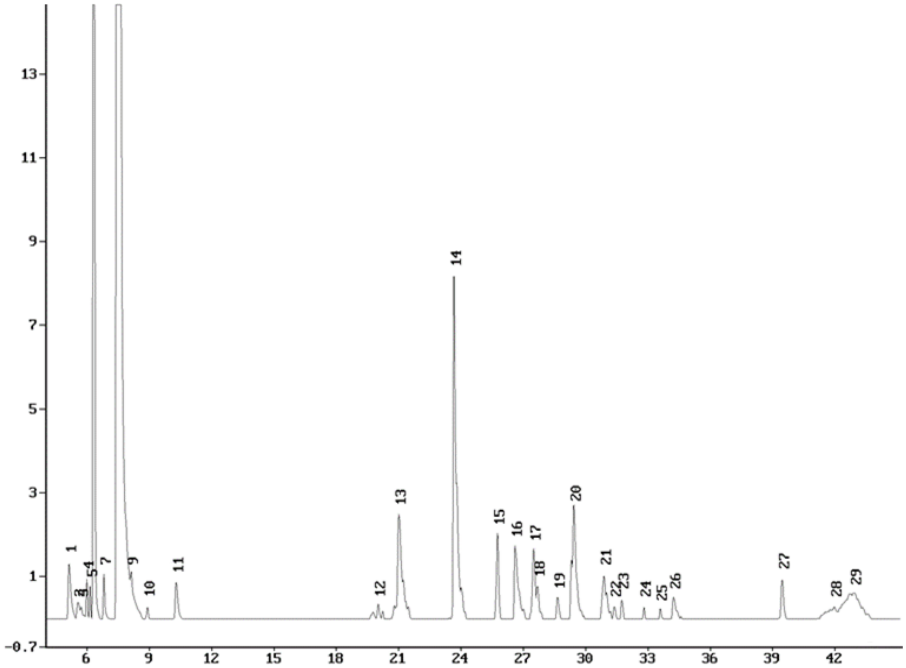

Figure S1 Chromatogram of liquid products (extracted with benzene) recorded during the steam lignin conversion in the temperature range of 350–500 °C for the sample of initial hydrolysis lignin. The peaks 1–10 are assigned to light C_1–C_3 aliphatic products (hydrocarbons and alcohols) of cracking, the peak 11 corresponds to phenol, the peak 12 to cresols, the peak 13 to anisol, the peaks 14–26 to unidentified isomers of methoxy- and dimethoxyphenols, and the peaks 27–29 to alkoxyphenols.

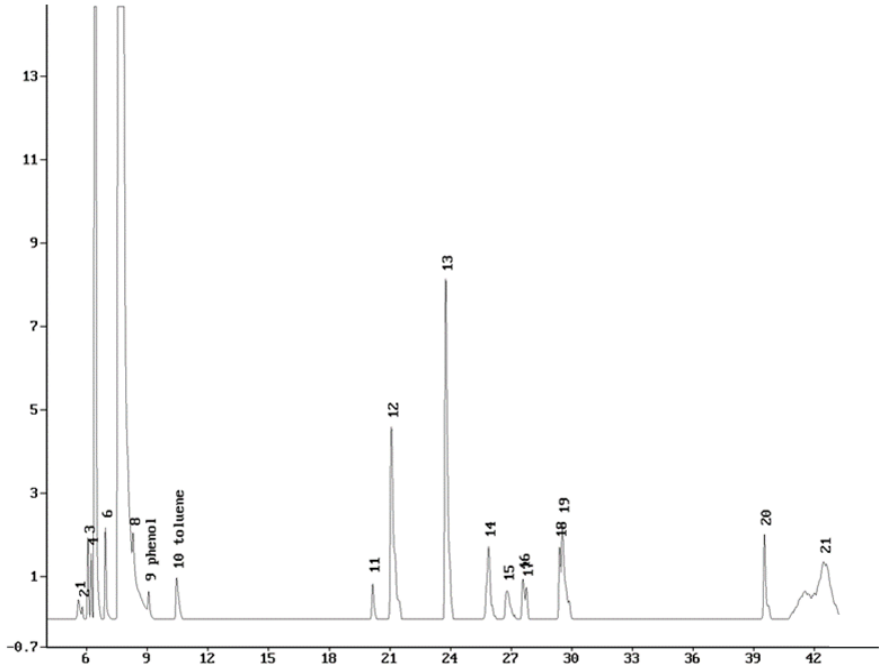

Figure S2 Chromatogram of liquid products (extracted with benzene) recorded during the steam lignin conversion in the temperature range 350–500 °C for Fe(10%)/HL sample. The peak assignment is the same as presented in Figure S1.