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Mendeleev Commun., 2020, **30**, 76–77

Mendeleev Communications

Steam reforming of lignin modified with iron

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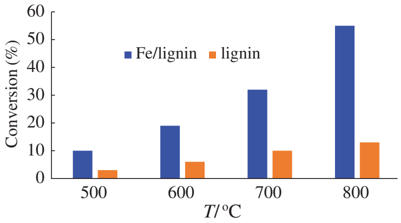
DOI: 10.1016/j.mencom.2020.01.025

Steam reforming of lignin was performed in the presence of catalytic amounts of iron introduced into lignin *via* an impregnation from a $Fe(NO_3)_3$ solution. Organic products with low molecular weights formed in the low-temperature region included aromatic, aliphatic and phenolic compounds. The high-temperature processing of lignin in H_2O vapors resulted in the formation of CO and H_2 as the major products.



Keywords: lignin, carbon-containing materials, carbon monoxide, steam reforming, hydrogen, iron catalyst.

Recently, a search for efficient methods for a biomass conversion into valuable products became one of the main research trends. Lignin is a class of complex organic polymers present in plants. A promising way of the lignin conversion is its catalytic depolymerization to produce low-molecular-weight compounds that could replace products of the petrochemical synthesis. The major problem in the development of such methods for the lignin processing is a fair stability of the major components of biomass, *i.e.* cellulose and lignin, towards any depolymerization. Lignin possesses a network polymer structure composed mainly of phenylpropane units linked *via* C–O bonds.

One of the approaches to lignin utilization is its high-temperature decomposition (pyrolysis) resulting in the formation of a coal-like product and tars. Pyrolysis processes in the absence of oxygen and thermal degradation in organic solvents lead predominantly to the high-boiling compounds containing increased amounts of oxygen.[1–5] To produce motor fuels, such products should be subjected to catalytic cracking and hydroreforming. It has been demonstrated[6] that the lignin hydroprocessing at 350–390 °C and the H_2 pressure of 133–196 atm in the presence of supported catalysts containing cobalt, nickel, ruthenium, platinum, iron, rhenium, palladium, or chromium results in the formation of mono-, di-, tri- or tetraalkylcyclohexanes, cycloheptanes, C_7–C_{10} paraffins, alkylbenzenes, *etc.*

This work was aimed at revealing effects of lignin-supported iron on the activity and product distribution during the steam reforming of lignin, *i.e.* the process occurring in the presence of H_2O vapors. We have earlier reported that the temperature of coal gasification significantly decreases if various metals (Fe, Ni) are supported onto the carbon materials.[7]

In the course of lignin conversion in the presence of steam, the temperature rise above 350 °C results in the formation of dark-brown liquid in both the cases of initial non-modified lignin sample and Fe-modified lignin. The product composition for both samples was practically the same (see chromatograms of the mixtures in Figures S1 and S2, Online Supplementary Materials).

At the temperatures above 500 °C and after the thermal lignin decomposition with the formation of oxygenates (phenolic products), the remaining carbon-containing residue was transformed *via* the pathways similar to the steam gasification of coal. Figure 1 shows thermodynamic equilibrium amounts of the reagents and products in this process.

The steam reforming of lignin and Fe(10%)/lignin samples at the temperatures higher than 500 °C in the flow containing water vapor results in an intense formation of gaseous products. According to the thermodynamic calculations (see Figure 1), the major products should be H_2 and CO at the temperatures above 600 °C. However, in our experiments, the major products were H_2 and CO_2, which is due to the occurrence of water gas shift reaction in the flow containing an excess of water vapor. This reaction is in the equilibrium with the reverse process of CO_2 hydrogenation according to the thermodynamic calculations (Figure 2).

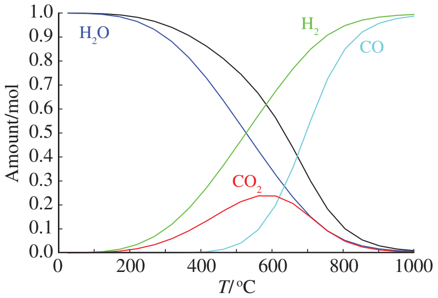


Figure 1 Temperature dependences of thermodynamic equilibrium concentrations of reagents and products in the reaction of steam gasification of coal.

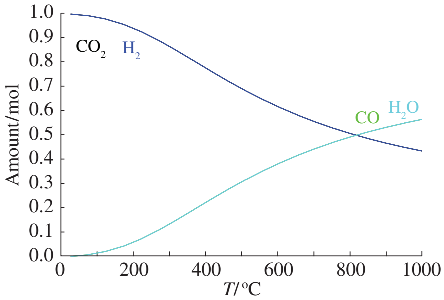


Figure 2 Temperature dependences of thermodynamic equilibrium concentrations of the reagents and products in the water gas shift reaction.

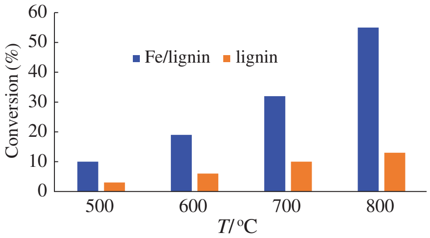


Figure 3 Conversions of lignin and Fe-modified lignin in the steam reforming as a function of the reaction temperature.

Figure 3 shows the lignin conversion measured as the weight loss during its steam reforming. This diagram clearly demonstrates that there is a promoting effect of Fe additives on the lignin conversion. A considerable enhancement of the lignin decomposition into light products was observed for the entire temperature range, and the conversion ratios for the Fe/lignin *vs.* lignin reforming as high as 3–5 are clearly seen at the temperatures above 600–700 °C. The distributions of gaseous products in the steam reforming of lignin and iron-containing lignin are shown in Figures 4 and 5. The product distribution at the temperatures above 500 °C is most interesting due to the acceleration of process in this temperature range. It should be noted that the major products at lower temperatures are mostly H_2 and CO with a shift towards CO_2 upon decreasing temperature, which is in agreement with the thermodynamic analysis of possible products.

As one can see, the experimental data acquired at the temperatures above 500 °C are still not very close to the thermodynamic equilibrium, and a reduction of the gas flow rate will probably result in a further increase of the conversion. The comparison of Figures 4 and 5 shows that the modification of lignin with iron affects the selectivity of CO, CO_2 and H_2 formations. For both samples, the maximum selectivity towards the CO_2 formation was observed at 600 °C, which is also in agreement with data of the thermodynamic calculatons (see Figure 1). Evidently, a higher selectivity towards CO (reaching 60%) is observed for Fe(10%)/lignin sample at a fairly low temperature (500 °C), whereas it does not exceed 45% in the case of pure lignin sample. Most probably, the iron species present in lignin catalyze the reaction of hydrogenation of formed CO_2. This hypothesis is confirmed by our recent data demonstrating that a melted Fe–K catalyst is active in the reaction of CO_2 hydrogenation to CO and exhibits the maximum selectivity towards CO at 500 °C unlike the catalysts containing other reduced metals.[8]

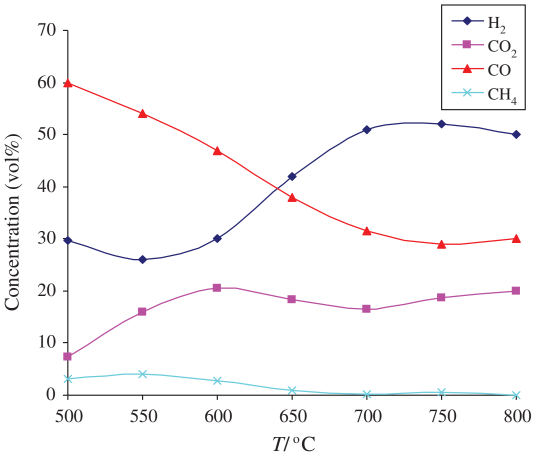


Figure 4 Concentrations of the products in the gas phase *vs.* the reaction temperature for the steam reforming of Fe(10%)/lignin sample.

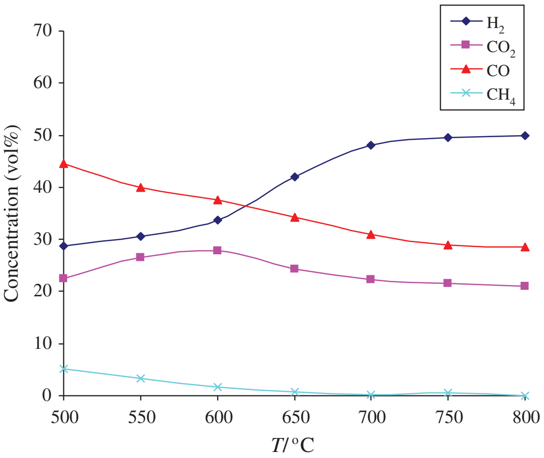


Figure 5 Concentrations of the products in the gas phase *vs.* the reaction temperature for the steam reforming of lignin.

It should be noted that the CO_2 production is not practically valuable, while the synthesis of CO and H_2 is an important way of lignin utilization, since synthesis gas can be used downstream for methanol synthesis and other hydroformylation or carbonylation processes. However, the acquired data (see Figures 3 and 4) indicate that the gas composition in the process of high-temperature steam reforming of lignin or Fe/lignin materials is not quite suitable for the consequent Fischer–Tropsch conversion or methanol synthesis, because it contains significant amounts of CO_2.

The number of published reports on the lignin conversion in the presence of iron compounds is very limited. For instance, a method of conjugated lignin conversion into synthesis gas coupled with an iron reduction from iron ore was developed; however, this process occurs at very high temperatures, up to 1060 °C.[9] There are also some reports on a two-step scheme of lignin conversion including lignin depolymerization in the presence of strong acids or bases at the first step and a deeper processing of the oligomers and phenolic products formed at the first step *via* cracking, hydrocracking, or gasification for the synthesis gas production.

In conclusion, the present work is the first account of the catalytic effect of iron on the lignin conversion into valuable products under the conditions of steam reforming.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-29-24182).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.025.

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Received: 18th June 2019; Com. 19/5956