Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2021, **31**, 376–378

Mendeleev Communications

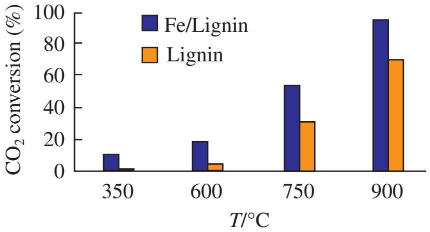
Dry reforming of lignin: the effect of impregnation with iron

Leonid M. Kustov,[*a,b] **Andrei L. Tarasov,**[a] **Vera D. Nissenbaum**[a] **and Alexander L. Kustov**[a,b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: lmk@ioc.ac.ru*

DOI: 10.1016/j.mencom.2021.05.031

Dry reforming of lignin was carried out in the presence of a catalytic amount of iron introduced into lignin by impregnation with a solution of iron(III) nitrate. Organic products with low molecular weight have been obtained at lower temperatures, including aromatic, aliphatic and phenolic compounds.



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

Developing practical approaches to converting biomass into valuable products is extremely important. The conversion of lignin by catalytic depolymerization with the formation of low molecular weight compounds is the first stage. The main problem with lignin processing is that the main components of biomass, cellulose and lignin, are highly resistant to depolymerization. Both the pyrolysis of lignin in the absence of oxygen and its thermal conversion in organic solvents lead to the production of high-boiling compounds with high oxygen content.[1–4] It was shown[5] that the hydroprocessing of lignin at 350–390 °C and 133–196 atm of hydrogen 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 tetraalkyl cyclohexanes, cycloheptanes, C_7–C_{10} paraffins, alkylbenzenes and other products.

Lignin gasification is studied to a much lesser extent, especially dry reforming, that is, the conversion of lignin with CO_2. We have previously investigated the conversion of lignin in the presence of hydrogen by hydrogenolysis and hydrogenation using Pt/C catalysts[6] and the oxidative conversion of lignin to synthesis gas using a V–Mo–Nb–Te–O_x mixed metal oxide catalyst with oxygen as an oxidant.[7] In both processes, *in situ* microwave activation has reduced the process temperature and increased catalyst activity. Also, steam reforming of lignin has been studied using iron and nickel species supported on lignin.[8] Even though liquid products obtained from non-catalytic or catalytic pyrolysis of lignin may have some value, they are usually formed as a mixture that cannot be separated into individual components, which reduces the value of the process and the resulting products. Gasification provides a more efficient way of utilizing lignin by converting it almost completely to synthesis gas in oxidative conversion or steam reforming, or predominantly to CO in dry reforming.

This work aimed to reveal the effect of iron supported on lignin on the activity and distribution of products during dry reforming of lignin under the action of carbon dioxide. We have previously found that various metals (Fe, Ni) deposited on carbon materials significantly reduce the coal gasification temperature.[8] An attempt to use additives of catalytically active metals (nickel, zinc and their oxides) to coal to improve the gasification performance[9] showed that the mechanical mixture does not provide this. The same authors found[10] that nickel deposited on activated carbon exhibits the highest activity in converting CO_2 at 600–800 °C compared to the non-catalytic process. It was also interesting to investigate whether the incomplete oxidative or reductive conversion of lignin with supported different metals (Fe, Ni, *etc.*) could lead to novel carbon-based materials with supported metals, which could be useful in various catalytic processes.

Samples of iron-containing lignin were prepared by impregnating lignin with an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$. Then the samples were dried in air at 120 °C. The iron content in the samples was 5–10 wt%. Samples of lignin and iron-containing lignin were preheated in a nitrogen flow at 200 °C to decompose the supported iron nitrate. Then, CO_2 was fed into the reactor at atmospheric pressure with programmed heating to 900 °C for 3.5 h (for details, see Online Supplementary Materials).

Figure 1 presents the dependences of CO_2 conversion in the reaction of dry reforming of initial lignin and Fe(10%)/lignin samples on the process temperature. For the initial lignin, a smooth increase in the CO_2 conversion is observed with increasing temperature. For the Fe-containing sample in the temperature range of 300–450 °C, there is a noticeable increase in the CO_2 conversion. In this case, along with unreacted CO_2, the gaseous reaction products contain carbon monoxide, water, gaseous C_1–C_4

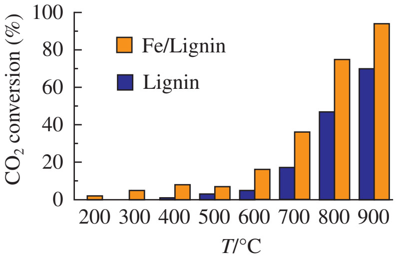


Figure 1 Dependences of the CO_2 conversion in the reaction of dry reforming of initial lignin and Fe(10%)/lignin samples on the process temperature.

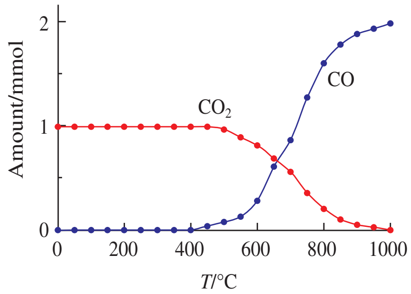


Figure 2 Temperature dependences of thermodynamic equilibrium amounts of the reagent (CO_2) and product (CO) in the reaction of coal gasification with carbon dioxide.

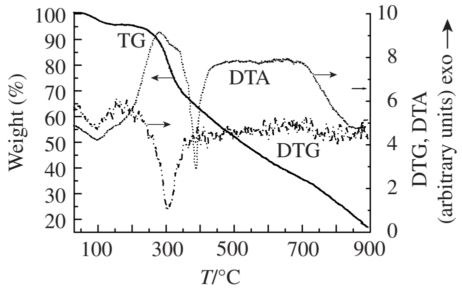


Figure 4 TG, DTG, DTA curves for the initial lignin sample in the air atmosphere.

hydrocarbons, oxygenates (methanol, ethanol) and C_{5+} hydrocarbons, including aromatic hydrocarbons (benzene). A comparison of the chromatograms (Figures S1 and S2, see Online Supplementary Materials) shows that methane begins to prevail in the hydrocarbon gas when the temperature rises from 300 to 450 °C. In our opinion, the increase in CO_2 conversion is associated with iron-catalyzed oxidation of lignin already at moderate temperatures, causing partial destruction of the complex structure of lignin.

During the dry reforming of a Fe(10%)/lignin sample in a CO_2 flow at a temperature of about 360 °C, an intense release of dark brown liquid begins, consisting of water and high-boiling products formed during the thermal (pyrolytic) destruction of hydrolytic lignin. A typical chromatogram of products is shown in Figure S3. According to mass chromatographic analysis, the products of pyrolytic destruction of hydrolytic lignin in the low-temperature range (300–450 °C) at low conversions of lignin contain aromatic hydrocarbons (ethylbenzene), phenol, methoxyphenols, as well as high-boiling derivatives of various alkyl (methyl, ethyl, propyl)-substituted methoxyphenols. It should be noted that for a sample of pure lignin that does not contain iron, an intense release of dark brown liquid is also observed, but this process begins at a higher temperature (above 400 °C). The product composition is similar to that obtained from the Fe(10%)/lignin sample, but the product distribution is shifted towards lower molecular weight methoxyphenols and their alkyl derivatives.

In the higher temperature range, CO is abundant. Notably, the carbon-based CO selectivity was close to 100%. Only minimal amounts of CH_4 (below 0.1%) can be found in the gas mixture leaving the reactor. The second important product, of course, was water. Thus, at lignin conversion close to 95–100%, at temperatures of ~900–950 °C, the mixture contained more than 80 mol% CO and less than 20 mol% H_2O. Obviously, due to this degradation, the lignin structure ($CH_{1.09}O_{0.35}$) is further depleted in hydrogen and oxygen and turns into semi-coke. In this regard, during the subsequent conversion of the lignin and Fe(10%)/lignin samples with carbon dioxide at temperatures above 500 °C, other mechanisms of converting carbon materials with carbon dioxide begin to prevail. It should be noted that in this high-temperature region, carbon monoxide (CO) is the main product of carbon dioxide-assisted gasification of both the initial lignin and Fe(10%)/lignin sample.

Since carbon is more than 60 wt% of the lignin composition, we assumed that it might be plausible to consider the thermodynamics of coal gasification with CO_2 as an approximation of the lignin behavior. Figure 2 shows the thermodynamic calculation results for the reaction of coal gasification with carbon dioxide, carried out using the HSC-4 computer program. According to the thermodynamics of the process, the conversion of coal only begins at temperatures above 500 °C, and 50% conversion of CO_2 is achieved at 710–720 °C (see Figure 2). For the Fe(10%)/lignin sample, the temperature of the 50% CO_2 conversion in the gas flow practically coincides with the thermodynamic data calculated under static conditions. As one can see for the Fe(10%)/lignin sample, a shift in the conversion curve towards lower temperatures is observed compared to the pure lignin sample. This indicates an intensification of the catalytic gasification process in the presence of iron in the sample. Similar patterns were obtained[9] when studying the carbon dioxide-assisted conversion of various activated carbons (such as SKT-6A).

In our case, after completing the runs of carbon dioxide-assisted conversion of samples (initial loading 0.4 g) in the mode of increasing the temperature to 900 °C followed by cooling the samples in a flow of N_2, we unloaded 164 mg of the residue from the lignin sample and 78 mg of the residue from the Fe(10%)/lignin sample, which initially contains about 40 mg of iron, *i.e.*, lignin in the Fe(10%)/lignin sample was almost completely converted into low-molecular products. Thus, when iron is supported on lignin, it intensifies carbon dioxide-assisted conversion of the carbon material (semi-coke) formed from lignin.

The DTA/TG data for the Fe(10%)/lignin sample in a CO_2 flow (Figure 3) show the maximum of the DTG (mass loss) curve at 360 °C, which closely coincides with the data obtained during the catalytic conversion of lignin using carbon dioxide in the increasing temperature mode. The data from DTG/TG analysis of the initial lignin and Fe(10%)/lignin samples in the air atmosphere are presented in Figures 4 and 5. A comparison of the figures shows that differential maxima of mass loss appear at 300 °C on the DTG curves of the initial hydrolyzed lignin, while for the Fe(10%)/lignin sample, two maxima are observed at 210

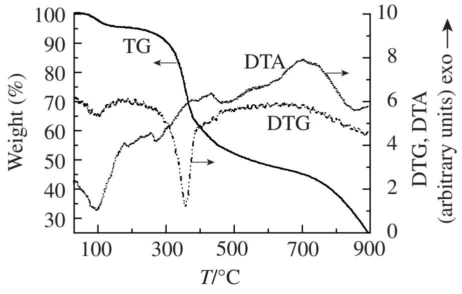


Figure 3 TG, DTG and DTA curves for the Fe(10%)/lignin sample in a CO_2 atmosphere.

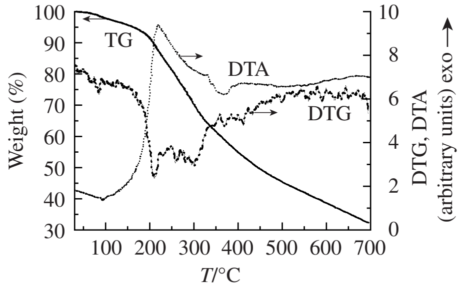


Figure 5 TG, DTG and DTA curves for the Fe(10%)/lignin sample in the air atmosphere.

and 290 °C, which are shifted to lower temperatures, *i.e.*, the effect of iron additives on the oxidative conversion of lignin is obvious.

Knowledge of the state of iron species in composite lignin samples with iron additives is essential for understanding the role and catalytic effect of iron on the dry reforming of lignin. The nature of iron species in materials of this type (lignin impregnated with iron salts) was studied by diffuse reflectance IR Fourier-transform spectroscopy.[11] It has been shown that the samples contain both reduced (metal) species and oxidized particles (Fe_3O_4).

The number of publications on the conversion of lignin and carbon in the presence of iron compounds is minimal.[12–14] A method was described for the conjugated conversion of lignin to synthesis gas combined with the reduction of iron from iron ore. However, the process occurs at very high temperatures, up to 1060 °C.[14]

Thus, this work discloses the catalytic effect of iron on the conversion of lignin into valuable products under dry reforming conditions.

This work was supported by the Russian Science Foundation (project no. 20-73-10106, synthesis of materials) and the Russian Foundation for Basic Research (grant no. 18-29-24182, characterization of materials and catalytic testing).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.031.

References

1 *Biomass Pyrolysis Liquids Upgrading and Utilization*, eds. A. V. Bridgewater and G. Grassi, Elsevier Applied Science, London, 1990.
2 J.-M. Ha, K.-R. Hwang, Y.-M. Kim, J. Jae, K. H. Kim, H. W. Lee, J.-Y. Kim and Y.-K. Park, *Renewable Sustainable Energy Rev.*, 2019, **111**, 422.
3 A. Kumar, Anushree, J. Kumar and T. Bhaskar, *J. Energy Inst.*, 2020, **93**, 235.
4 C. Liu, S. Wu, H. Zhang and R. Xiao, *Fuel Process. Technol.*, 2019, **191**, 181.
5 J. S. Shabtai, W. W. Zmierczak and E. Chornet, *US Patent 5959167*, 1999.
6 L. M. Kustov, A. L. Tarasov and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2015, **51**, 1677 (*Zh. Org. Khim.*, 2015, **51**, 1711).
7 L. M. Kustov and A. L. Tarasov, *Russ. Chem. Bull., Int. Ed.*, 2015, **64**, 2963 (*Izv. Akad. Nauk, Ser. Khim.*, 2015, 2963).
8 L. M. Kustov, A. L. Tarasov and A. L. Kustov, *Mendeleev Commun.*, 2020, **30**, 76.
9 N. A. Kurbatova, A. R. El'man and T. V. Bukharkina, *Kinet. Catal.*, 2011, **52**, 739 (*Kinet. Katal.*, 2011, **52**, 753).
10 N. A. Kurbatova, A. R. El'man and T. V. Bukharkina, *Uspekhi v Khimii i Khimicheskoi Tekhnologii*, 2011, **25** (5), 30 (in Russian).
11 O. P. Tkachenko, A. L. Tarasov, I. V. Mishin and L. M. Kustov, *Russ. J. Phys. Chem. A*, 2020, **94**, 725 (*Zh. Fiz. Khim.*, 2020, **94**, 550).
12 A. L. Tarasov, E. M. Kostyukhin and L. M. Kustov, *Mendeleev Commun.*, 2018, **28**, 530.
13 L. M. Kustov and A. L. Tarasov, *Mendeleev Commun.*, 2014, **24**, 349.
14 R. Wei, S. Feng, H. Long, J. Li, Z. Yuan, D. Cang and C. Xu, *Energy*, 2017, **140**, 406.

Received: 12th January 2021; Com. 21/6417