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# Gasification of hydrolysis lignin with $CO_2$ in the presence of Fe and Co compounds

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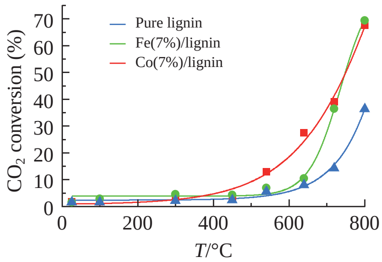
**The effect of the nature of the metal (Fe and Co) deposited on the surface of hydrolysis lignin, as well as the metal content (1, 3, 5 and 7 wt%), on the process of dry catalytic lignin reforming has been studied. The use of the catalyst led to a twofold increase in the conversion of carbon dioxide at temperatures of 500–800 °C, while both metals showed similar activity. The maximum specific catalytic effect is achieved when supporting 7 wt% of active metals.**




*Keywords*: lignin, carbon materials, carbon dioxide, carbon monoxide, $CO_2$ conversion, gasification.

The development of methods for using and utilizing carbon-containing wastes, such as low-quality coals, woodworking waste and heavy oil residues, with the formation of products with a higher added value, is an urgent global challenge. One such carbon material is hydrolysis lignin. The use of lignin as a precursor is complicated by its low reactivity, but recently a number of chemical methods have been found for processing this carbon material.[1,2]

Pyrolysis,[3,4] alkaline or acid hydrolysis[5,6] and conversion of materials under supercritical conditions[7–9] are among the most widely used chemical methods for the disposal of such carbon-containing materials using catalysts. Particular attention is paid to the reforming of lignin into valuable chemical products under the action of microwave heating using catalysts containing transition metals.[10–14]

The current trend is also associated with the utilization of carbon dioxide,[15] which can be used in various ways, such as obtaining synthesis gas in the process of $CO_2$ hydrogenation on various catalysts,[16,17] reacting with carbon-containing materials to form carbon monoxide[18,19] and using it as a mild oxidant in various catalytic reactions.[20]

One way to use a renewable carbon-containing raw material such as lignin is to gasify it with carbon dioxide to obtain higher value-added gaseous products. The most important product of lignin gasification is carbon monoxide. Carbon monoxide can be used both for direct combustion to generate electricity and to produce valuable chemical products.[21]

The gasification reaction of carbon material (for example, graphite) is highly endothermic [reaction (1)] and proceeds with quantitative conversion at temperatures of about 1000 °C:

$$CO_2 + C \rightleftarrows 2CO, \Delta H = 176 \text{ kJ mol}^{-1}. \quad (1)$$

The use of carbon materials (particularly lignin) for gasification leads to a significant decrease in the process temperature.

Transition metal compounds, as well as compounds of alkali and alkaline earth metals,[22–25] exhibit catalytic activity in such processes. In our opinion, the use of transition metal compounds, in particular elements of the iron triad, is especially promising due to their low impact on the Earth's ecosystem, as well as the low cost of such compounds. In addition, these metals are easily recovered after gasification and are recyclable. This article presents the results of our research on the catalytic conversion of hydrolysis lignin with carbon dioxide using various supported catalysts.

Figure 1 presents XRD patterns of lignin samples with deposited iron and cobalt compounds after the catalytic reaction. The XRD patterns of all samples contain peaks at 26.60° and 26.64° corresponding to the (004) reflection of carbon (JCPDS card no. 00-026-1080) and the (011) reflection of quartz (JCPDS card no. 01-085-1053), respectively. The diffraction pattern of a sample of lignin with deposited iron compounds after catalytic tests contains reflections (112), (103), (004) and (321) of magnetite (JCPDS card no. 01-075-1609) at 30.12°, 35.54°, 43.12° and 57.09°, respectively. Peaks at 36.49° and 42.39° in the XRD pattern of the sample with deposited cobalt compounds correspond to reflections (111) and (200) of cobalt(II) oxide (JCPDS card no. 00-048-01719), respectively.

The analysis of reflections shows the presence of carbon and quartz in all samples. The presence of quartz in samples of hydrolysis lignin is confirmed by other researchers using various physicochemical methods.[26] According to XRD data, iron in the Fe(7%)/lignin sample after the catalytic reaction is in the form of magnetite, while cobalt in the Co(7%)/lignin sample exists as cobalt(II) oxide.

Samples with a metal content of 7 wt% were studied by scanning electron microscopy and X-ray spectral microanalysis (EDX analysis). EDX mapping showed an average uniformity of the distribution of metal atoms for the Co(7%)/lignin sample and

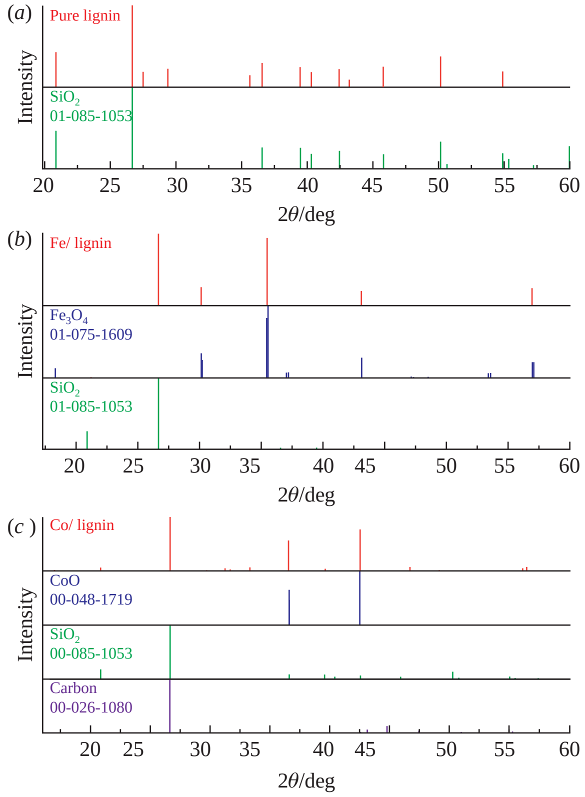



**Figure 1** X-ray diffraction patterns of (*a*) initial lignin, (*b*) Fe(7%)/lignin and (*c*) Co(7%)/lignin samples after catalytic testing, as well as reference XRD patterns of pure phases with corresponding JCPDS card numbers.

a high degree of dispersion of metal deposition for the Fe(7%)/lignin sample.

Catalytic studies were carried out in a flow quartz reactor at atmospheric pressure in a carbon dioxide atmosphere. The efficiency of the catalyst was evaluated by the conversion of carbon dioxide at various temperatures. The conversion was calculated using the equation:

$$C_{CO_2} = (0.5\ n_{CO})/(n_{CO_2})\ 100\%.$$

Figure 2 shows the temperature dependence of carbon dioxide conversion during gasification of initial lignin samples, as well as samples with deposited iron and cobalt compounds at a metal content of 7 wt%. The use of such catalysts makes it possible to shift the conversion curve to lower temperatures, and at temperatures of 500–800 °C, the conversion of carbon dioxide for samples with a catalyst is almost two times higher than the conversion of $CO_2$ for the sample without a catalyst. The use of iron and cobalt

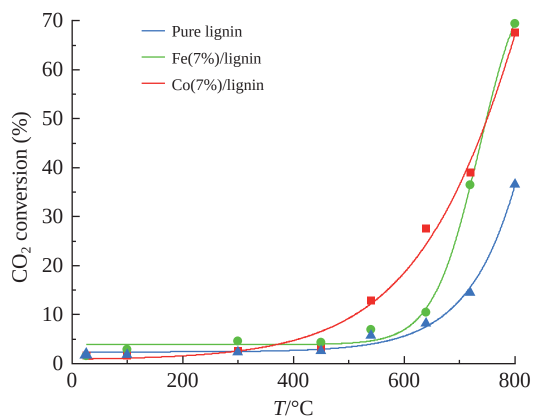



**Figure 2** Temperature dependence of carbon dioxide conversion during gasification of initial lignin samples and lignin samples with deposited iron and cobalt compounds.

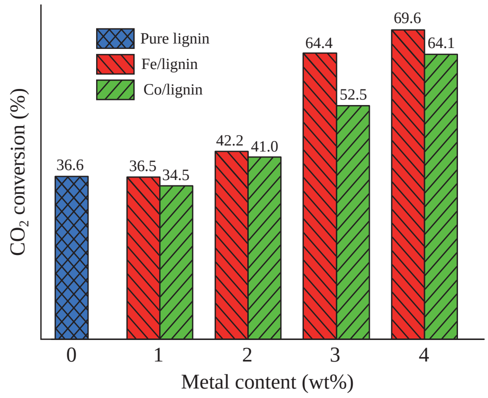



**Figure 3** Dependence of carbon dioxide conversion at 800 °C on the content of deposited metals.

catalysts makes it possible to achieve close values of carbon dioxide conversion.

Figure 3 shows the values of carbon dioxide conversion at a temperature of 800 °C for Fe- and Co-containing catalysts depending on the content of the supported metal. The maximum specific catalytic effect of the metal for both elements is achieved at 5 wt%, which is especially pronounced for Fe-containing samples.

In summary, systems containing iron and cobalt are promising for the utilization of carbon dioxide and lignin to produce carbon monoxide for further use in the synthesis of compounds with a higher added value.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.038.

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