



## **THE CATALYTIC OZONATION OF THE LIGNIN RELATED MATERIAL**

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The plant biomass is considered as the renewable sources of the valuable organic products. Many of the modern methods for the conversion of natural lignocellulose materials involve the use of ozone, which has high reactivity and does not form toxic side products. At the same time, in the area of ozone technologies, studies of ozone catalytic processes are being intensely developed. This contributes to increasing the effectiveness and selectivity of the ozonation of various organic compounds.

In this work we studied the influence of iron(III) and manganese(II) homogeneous catalysts on the rate of ozonolysis of several lignin (technical sulphate lignin, soluble liginosulphonate), its model compounds (phenol, guajacol, 2,6-dimethoxyphenol, veratrol -derivatives) and their oxidation short-chain byproducts (glyoxal, maleic, glyoxylic, oxalic, formic acids).

Ozonation was performed at room temperature in aqueous solutions acidified to pH 1.5 by adding H<sub>2</sub>SO<sub>4</sub>. A bubbling reactor was used. Ozone was obtained from air. Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•9H<sub>2</sub>O and MnSO<sub>4</sub>•5H<sub>2</sub>O were used as the source of metallic ions.

The kinetics of reactions was studied by keeping track of the ozone absorption, as well as organic substrates transformation. The values of ozone consumption were estimated from the experimental time dependences of ozone concentration in the gas phase at the outlet of the reactor. The reactions rate constants were calculated on the basis of the film theory.

It follows from the experimental data that Fe(III) and Mn(II) do not influence the initial rate of the reactions between aromatic model compounds and ozone, but accelerate the degradation of intermediate reaction products and thereby increase the depth of organic matter mineralization. It was found that catalytic effect of transition metals is observed at the stages of oxidation of short chain C<sub>2</sub>-C<sub>1</sub> carbonic acids and aldehydes.

The mechanism of the Fe(III) and Mn(II) catalytic action was investigated by the example of the ozone reactions with glyoxal, glyoxylic, oxalic and formic acids.



The results obtained led us to assume that Fe(III) is effective on the organic acids and aldehydes which form a stable complex (chelate) with metallic ion. At acidic pH the catalytic reaction pass through the direct oxidation of substrate in its complex with the Fe(III) by molecular ozone without change in the oxidation state of the metal.

In the case of manganese different mechanism is valid. Mn(II) catalytic action is due to Mn(II)/Mn(III) cyclic oxidation/reduction transformations. The reaction starts with Mn(II) oxidation by ozone to Mn(III), which further oxidize organic substrate in its complex, giving Mn(II).

The application of methods including ozone and catalysts combination could be aimed for solving the problems of delignification, pulp bleaching and treatment of waste of pulp and paper industry.