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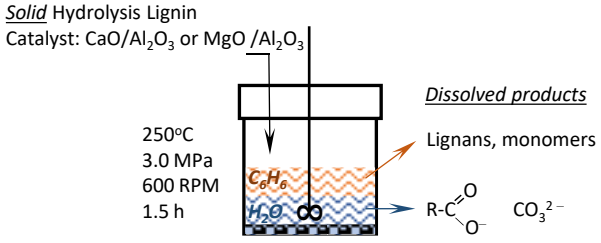
Depolymerization of hydrolysis lignin over Ca- or Mg-containing catalysts supported on alumina: IR analysis of products separated by benzene extraction

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FTIR-spectroscopy was applied to study the conversion of hydrolysis lignin into light aromatic products soluble in benzene with carbonates and organic acids soluble in water. Alumina supported Na-, Ca- and Mg- catalysts in the water-phase medium were used and extraction of products by benzene was continuously maintained in the course of the reaction. The activity of a Mg-containing catalyst in the formation of products soluble in benzene was two times higher than that of other alumina-supported systems studied.



Keywords: hydrolysis lignin, depolymerization, hydrolysis, Na_2O, CaO, MgO, aluminates, lignans, benzene, multiphase separation.

The main process of chemical wood conversion is the separation of solid cellulose from lignin and hemicelluloses by converting the latter into water-soluble forms.[1] The most commonly applied version of this process is wood cooking in alkaline aqueous solutions at 150 — 170°C. Cooking in an alkaline medium with the addition of sulfur-containing compounds (Kraft process) to form a water-soluble Kraft lignin is one of the most effective processes. A less known process of chemical wood processing is the hydrolysis of hemicellulose and cellulose to produce furfural. Wood hydrolysis is carried out by steam treatment at 170 — 230°C. The method involves pretreatment of the raw material with a solution of diluted sulfuric acid. Both procedures yield the byproduct that contains a significant portion of lignin composed of polyphenols. Also in both cases, in addition to lignin, the by-product contains a considerable amount of cellulose and hemicellulose. The average weight of lignin particles transferred to solution depends on the treatment method[2] and usually ranges from 1 to 10 kDa (~ 1.4 — 3.0 nm). A common feature of cooking processes is the use of homogeneous catalysts, which creates a large amount of aggressive liquid wastes that require neutralization. In addition, depolymerization products formed from both carbohydrates and lignin components exist in the same liquid phase. Various solvents for extraction of technical lignin components were described,[3,4,5,6] mainly water soluble oxygenates: dioxane, alcohols, ethers, and acids. Aromatic solvents, first of all toluene[7] are used in rare cases. It has been shown[5] that as the solvent molecular weight increases from methanol to butanol, the particle size of lignin transferred to the solution decreases.

Base-catalyzed lignin hydrolysis (depolymerization) is typically performed at temperatures 240 — 330°C more often in aqueous solutions of NaOH or $Ca(OH)_2$.[8,9] Despite the interesting catalytic behavior of catalysts based on CaO and/or MgO, there are only a few original reports on the biomass heterogenous hydrolysis over these oxides[10,11,12]. More often a positive effect of basic oxides was reported for biomass catalytic pyrolysis.[13,14] A promising approach to simplify the product separation and the technique of biomass conversion may be the use of less aggressive homogeneous catalysts or heterogeneous catalysts, as well as processing of biomass in heterophase media with inherent affinity for individual products.

The purpose of this work is to evaluate the efficiency of solid supported basic catalysts (CaO, MgO) in hydrolysis of technical lignin components accomplished with product separation in a water-benzene heterophase system. In this work, we used hydrolysis lignin produced by the Fuel and Technology Complex company, Belarus, TU BY 490822905.001-2015, obtained from waste of the furfural production from oak and elm wood at the Rechitsa Pilot Hydrolysis plant (Belarus), which is similar to hydrolysis lignin studied before.[15] In our previous study,[16] it was shown that the carbohydrates to lignin ratio is close to ~1:1 for this material. The results of elemental analysis and thermogravimetric measurements (TGA) of the parent hydrolysis lignin are given in Table S1 and Fig. S1. Hydrolysis lignin starts to degrade rapidly at temperatures above 250°C. That was the reason why the temperature of 250°C was chosen for hydrolysis in the present study. This temperature is higher than the temperature of the previous treatment used in the factory technology, but lower than the thermal degradation temperature.

Spherical alumina A204 (produced by La Roche) with a particle size of ~2 mm was used for catalyst preparation. Metals (Na, Ca, Mg) were supported by incipient wetness impregnation using the corresponding nitrate. The metal concentration in supported samples was ~2.25 mmol/g_{cat}. The impregnation step

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was followed by calcination at 1100°C for 3 hours in an air flow. The treatment of the samples with supported active components at a high temperature was chosen to facilitate the formation of new aluminate phases. The treatment reduced the specific surface area by an order of magnitude as compared with the surface area of the pristine support (A204, see Table S2). Since in the process under study the interaction between two solids (catalyst and lignin) are developed, it can be expected that the main contribution in the reaction rate increase comes from the external rather than from internal pore surface. Accordingly, a consideration of the specific surface area cannot be important for the formation of the active surface. The catalysts were studied using BET and XRD methods and the formation of new aluminate phases has been shown. Details can be found in the Supplementary Materials (Figs. S2 — S8). The main parameters of the catalysts are shown in Table 1.

Table 1 Support and Catalysts main properties

Entry	*Catalyst*	*XRD phase**	*Surface area, m^2/g*	*Metal loaded to reactor, mmol*
1	NaOH solution	—	—	12
2	Al_2O_3	Corundum	27	0
3	Na_2O/Al_2O_3	$NaAl_7O_{11}$	22	9
4	CaO/Al_2O_3	$CaAl_4O_7$	6	9
5	MgO/Al_2O_3	$Mg_{0.388}Al_{2.408}O_4$	26	9

*Details can be found in Figs. S5 — S8.

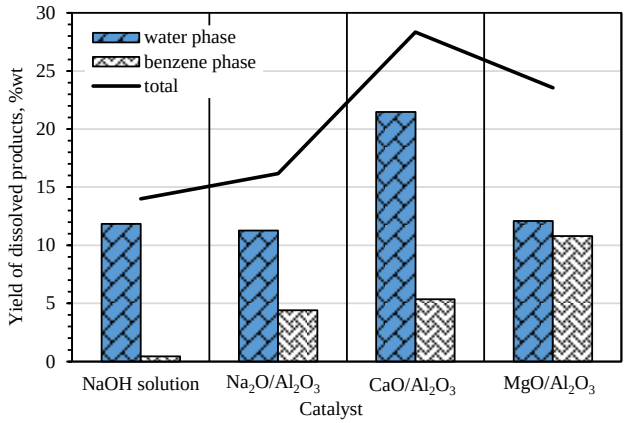


Figure 1 Products distribution between water and benzene phases. Product yields are given as weight percent of the hydrolysis lignin load.

Hydrolysis was carried out in an autoclave (300 ml) at 250°C for 1.5 hours at a pressure of ~3.0 MPa corresponding to benzene vapor pressure at this temperature. In all experiments, the autoclave was loaded with 1 g of hydrolysis lignin, 50 ml of distilled water, and 20 ml of benzene. In experiments with solid catalysts, 4 g of a catalyst (~5 ml) was added in the autoclave, whereas 0.5 g of NaOH was added in the experiment with the homogeneous alkaline catalyst. It should be noted that due to sodium aluminate formation at the catalyst preparation step, the evaluation of the amount of sodium hydroxide leached from the Na_2O/Al_2O_3 catalyst and dissolved in water at the reaction conditions is nearly impossible. After cooling and depressurizing the autoclave, the benzene and water phases were filtered with a syringe filter (0.8 μm) and analyzed. IR spectra of the products were measured as described earlier[17]. In accordance with the procedure, 0.1 ml of the solution was deposited on a KRS-6 glass disk (Thallium Bromo Chloride) using an automatic pipette and after drying at 60°C in air, transmittance spectra were then recorded. In order to estimate the amount of dissolved substances, 10 ml of the filtered solution was deposited on a weighing aluminum boat, dried at 60°C in a drying chamber and weighted again (accuracy ±0.0001 g). The amount of a dissolved product was found as a difference in the weight between the empty vessel and that containing dried products. An attempt to carry out the hydrolysis over calcined unmodified alumina was unsuccessful, because a single-phase mixture with dispersed unreacted solids was obtained rather than individual phases of water and benzene. The products obtained in this experiment were not studied.

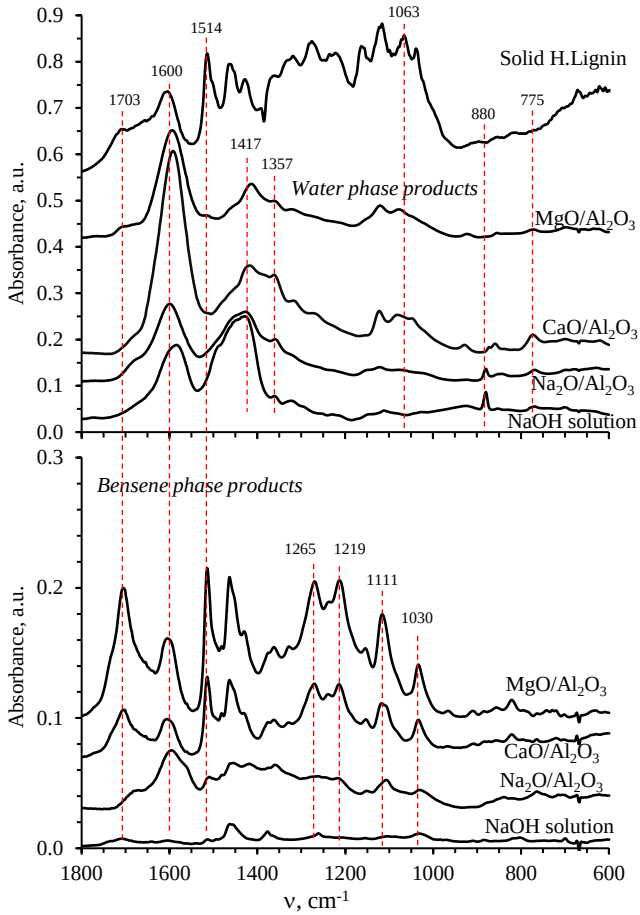


Figure 2 FTIR-spectra of the hydrolysis lignin conversion products. The top part corresponds to water-phase products, the bottom part corresponds to benzene phase products.

When hydrolysis was conducted in the presence of the homogeneous catalyst, products making up as much as 11.9 wt%. of the loaded hydrolysis lignin were accumulated mainly in the water phase. The use of the Na_2O/Al_2O_3 system increased the yield of products soluble in benzene up to 4.4 wt%, while the yield of products in the water phase (11.3 wt%) remained nearly unchanged. (Fig. 1). The use of the CaO/Al_2O_3 catalyst resulted in a significant increase of water-soluble products to 21.5 wt% but the yield of products soluble in benzene (5.4 wt%) showed a negligible change. Over the MgO/Al_2O_3 catalyst, the yield of water-soluble products was close to the yield found for the Na-containing system (12.1 wt%), but the yield of the benzene-soluble products nearly doubled (10.8 wt%). These results provide the evidence that both the nature of the supported metal and the presence of the support have a significant impact on the distribution of reaction products between the water and benzene

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phases. The Mg-containing catalyst seems to be the most suitable system to produce aromatic products.

Products of both phases were studied by FTIR spectroscopy. The assignment of absorption bands is based on the previous studies[18,19]. A number of strong absorption bands were found in the IR spectra of water phase products. A broad absorption band with the maximum in the region 1590 to 1605 cm^{-1} can be assigned to anions of various organic acids. Vibrations near 1457 and 880 cm^{-1} can be attributed to carbonates, the band at 1417 cm^{-1} can be ascribed to acetates, the bands at 1357 and 775 cm^{-1} can be related to formates, whereas bands in the region 1047 to 1112 cm^{-1} are characteristic of the ether and alcohol groups of sugars and their derivatives. The results obtained are consistent with the literature data, which repeatedly reported that carboxylic acids are formed from cellulose during wood cooking with NaOH[20]. The IR spectrum of water-phase products in the range of 3700 — 2700 cm^{-1} (Fig. S9) contains low-intensity bands in the C-H groups vibration region and a wide absorption band of perturbed OH groups. Comparison of the water-phase products spectra with spectra of selected substances taken from the database[21] is presented in Fig. S10.

A number of bands were identified in the FTIR spectra of products in the benzene phase. The band at 1703 cm^{-1} is attributable to aliphatic acids carbonyl -COOH groups, the bands at 1600 and 1514 cm^{-1} can be related to skeletal vibrations of the aromatic ring, the band at 1460 cm^{-1} is assigned to bending vibrations of CH_3, antisymmetric and scissor vibrations of CH_2. The bands at 1265 and 1219 cm^{-1} are related to compound vibrations of the aromatic ring with the C–O group, the band at 1111 cm^{-1} belongs to bending vibrations of C–O bonds in aliphatic alcohols and esters, the band at 1030 cm^{-1} is assigned to in-plane bending vibrations of aromatic C–H bonds and the band at 827 cm^{-1} is the result of out-of-plane bending vibrations of C-H bonds in the aromatic ring. The FTIR spectra of the benzene phase products in the range of 3700 — 2700 cm^{-1} (Fig. S9) contain the following main bands: a wide 3412 cm^{-1} band of perturbed OH groups, a shoulder at 2952 cm^{-1} of antisymmetric stretching vibrations in the group -CH_3, 2925 cm^{-1} – antisymmetric stretching vibrations in the group -CH_2. 2852 cm^{-1} – symmetric stretching vibrations in the -CH_2 group.

Comparison of spectra of the water-phase products (Figs. 2 and S10) with IR spectra taken from the spectroscopic database[21] suggests that the use of CaO and MgO as catalysts leads to a higher yield of sugar acid salts and a lower yield of carbonates, acetates, and formates. Analysis of the IR spectra of obtained products (Figs. 2 and S10) including the presence of characteristic patterns in the regions of 1600, 1417 and 1063 cm^{-1} provides an additional evidence to suggestion that fragments of water-soluble carboxymethyl cellulose over Ca and Mg catalysts are also formed.

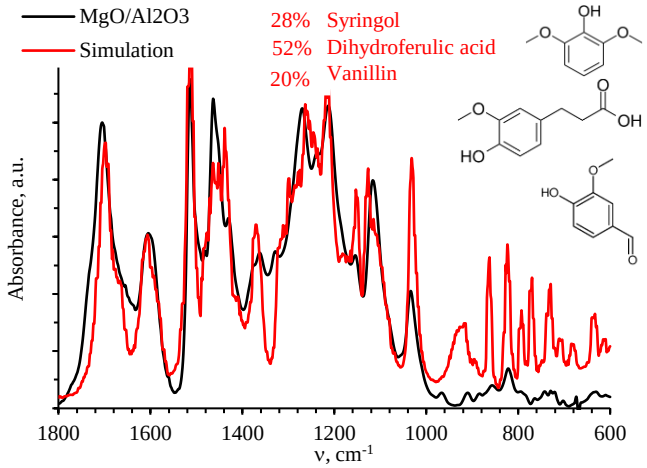


Figure 3 Comparison of simulated and experimental FTIR-spectra of benzene-phase products for the MgO/Al_2O_3 catalyst.

Comparison of the spectra of benzene phase products (Figs. 2 and S11) indicates that the main products formed in the presence of the homogeneous catalyst are aliphatic acids that enter into the benzene phase. The IR spectra of the product obtained over Na_2O/Al_2O_3 consist of numerous poorly resolved absorption bands, which makes the product spectrum similar to spectra of parent hydrolysis lignin. This can be interpreted as evidence of relatively large fragments of lignin formed. The IR spectra of benzene phase products obtained over Ca and Mg catalysts are characterized by the presence of narrow absorption bands, and the most of them correspond to the spectra of guaiacil and syringyl rings, aliphatic fragments, and carboxyl groups (Fig. S11). The IR spectrum of the product obtained over MgO/Al_2O_3 was simulated by the previousl data[16] as a linear combination of the syringol, dihydroferulic acid, and vanillin spectra taken from the spectroscopic database[21] (Figs. 3 and S12). It should be noted that the model spectrum agrees with the measured spectral picture. This observation can serve as an argument for the suggestion that the product consists of a mixture of monomers. In addition, a comparison of the measured spectrum with the experimental spectrum of the β-O-4 dimer synthesized in the previous study[22] (Figs. 4 and S13) allows us to conclude that the product contains a substance similar to a B-O-4 dimer, since the patterns of absorption bands in the region around 820 cm^{-1} are similar. This region is attributable to skeletal vibrations and is sensitive to vibrations of the molecular structure.

Thus, analysis of obtained products using FTIR spectra provides the basis for the conclusion that the water phase contains carbonates and organic acid salts, whereas the benzene phase contains small lignin derivatives. In order to determine more precisely the distribution of the obtained products, additional analytic techniques should be used.

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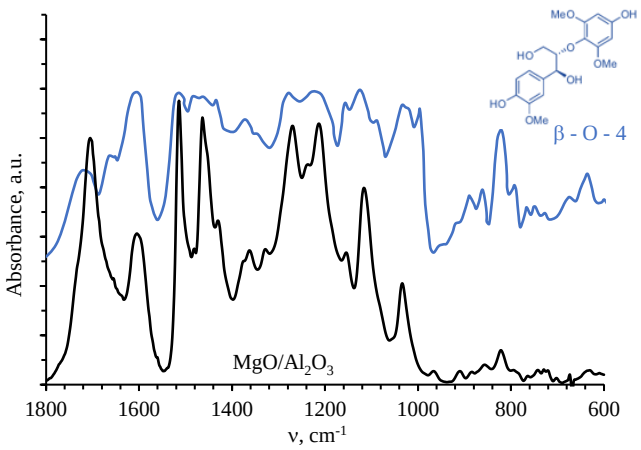


Figure 4 Comparison of the experimental FTIR spectra of the MgO/Al_2O_3 catalyst benzene-phase products with the experimental spectrum of a dimeric β-O-4 lignin fragment (lignan)[22].

From the data described above it can be inferred that alumina-supported basic metal oxides CaO, MgO are active in biomass components hydrolysis. CaO/Al_2O_3 is more active in carbohydrates conversion with predominant formation of the water-soluble products (organic acids and carbonates). MgO/Al_2O_3 demonstrated a higher activity toward lignin conversion to aromatic benzene-soluble products. The use of a heterophase liquid medium (water-benzene) makes it possible to easily separate the reaction products.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8109

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