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The hydrogenolysis of the protolignin of rice husks in the presence of a polymetallic catalyst that is used in the hydrocracking of petroleum has been investigated. The dependence of the yield of low-molecular-mass compounds on the reaction conditions has been found. It has been established on the basis of experiments with model compounds that on hydrogenolysis with the use of the polymetallic catalyst both alkyl-aryl C-O-C and C-C bonds are cleaved.

The study of the structure of lignin is one of the most important problems of the chemistry of natural polymers. The structure of natural lignin can be established with the aid of hydrogenolysis - the cleavage of lignin under the action of H_2 . By the hydrogenolysis method, Japanese scientists have succeeded in isolating and demonstrating the structures of 28 dimeric and several trimeric compounds from spruce lignin [1]. A combination of these compounds gave a fragment of the possible structure of lignin.

A number of studies devoted to the hydrogenolysis of lignin have been reported in the literature. Salts and alloys of various metals are frequently used as catalysts [2, 3].

We have studied the hydrogenolysis of the protolignin of rice husks in the presence of a polyfunctional catalyst that is used in the hydrocracking of petroleum. In the first place, it was of interest to follow the action of this catalyst in the hydrogenolysis of lignin because it had not been used for this purpose previously. In the second place, it was desirable to follow the dynamics of this process and to know how the reaction conditions affect the yield and composition of the reaction products.

The process was carried out under various conditions, with changes in the temperature, the pressure of H_2 , the duration of the reaction, and the amount of catalyst used (Table 1).

As was found, the yield of cleavage products depended greatly on the reaction temperature. The highest yield of dioxane-soluble products was observed at 250°C. A moderation of the reaction conditions led to a sharp decrease in the yield of products. At a higher temperature (300°C) a fall in yield was observed which was probably connected with condensation processes, and then a slight rise in the temperature (315°C) led to the cleavage of some C-C bonds, as a result of which the yield of product increased.

We have calculated the influence of the duration of the reaction on the yield of products. Performance of the process for 1 h was clearly insufficient to obtain a good yield, while 4 h was already too long - after this time the products formed underwent condensation and the yield decreased. The yield of products was highest for a two-hour reaction.

The influence of the pressure of hydrogen (2.5, 5.0, and 10.0 MPa) was studied. A halving of the pressure (from 5.0 to 2.5 MPa) led to a 1.5-fold decrease in the yield of dioxane-soluble products. A doubling of the pressure to 10.0 MPa likewise led to a fall in yield, since in this case degradation processes were suppressed.

Another of the reaction parameters is the amount of catalyst used. When the amount of catalyst was lowered from 20% to 10% there was a slight decrease in the yield of dioxane-soluble products, while the use of 5% of catalyst on the weight of the raw material now led to a substantial fall in the yield of desired products.

Thus, the highest yield of dioxane-soluble products was achieved with the following reaction parameters: temperature) 250°C; pressure of hydrogen, P_{H_2} , (initial)) 5.0 MPa; time) 2 h; amount of catalyst) 20% on the weight of raw material.

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TABLE 1. Conditions for Performing the Hydrogenolysis of Rice Lignin

Expt. No.	Temperature, °C	P_{H_2} , MPa	Time, h	Catalyst, %	Yield of dioxane-soluble products, % on the raw material
1	200	5,0	2	20	25,7
2	250	5,0	2	20	54,0
3	300	5,0	2	20	34,4
4	315	5,0	2	20	47,8
5	170	5,0	2	10	9,8
6	200	5,0	2	10	13,2
7	250	5,0	2	10	51,7
8	250	5,0	2	5	12,3
9	250	5,0	4	20	35,3
10	250	10,0	2	20	38,3
11	250	2,0	2	20	35,7
12	250	5,0	1	20	42,0

TABLE 2. Yields of Phenolic Substances, % on the Komarov Lignin

	Experiment No.							
	1	2	3	4	5	6	7	8
Hexane extract	4,4	10,2	14,7	12,3	1,6	1,4	8,6	7,3
Ether extract	24,6	47,9	40,3	46,1	4,6	8,2	49,5	46,1
Hydrol lignin	24,0	40,0	44,1	39,5	6,6	14,2	40,8	43,4
Σ	53,0	98,8	99,1	97,9	12,8	23,8	98,9	96,8

Attention must be directed to the fact that we performed the hydrogenolysis of rice husks, and not of pure lignin. This means that the dioxane-soluble product contained not only substances of lignin nature but also the products of the degradation of the carbohydrate components of the rice husks. We therefore separated the products of phenolic nature (i.e., the products of the cleavage of the initial lignin) from the other components of the dioxane-soluble product. For this purpose, the total dioxane-soluble product was dissolved in 2% aqueous NaOH solution, and, after acidification to pH 3, the phenols were extracted with hexane and ether. So far as concerns the yield of phenols, the same tendencies were observed here as for the dioxane-soluble products as a whole (Table 2).

We investigated the hexane and ether extracts of the lignin cleavage products with the aid of GLC. While the ether extracts consisted mainly of the lower phenols (phenol, guaiacol, cresol, and creosol) the hexane extracted represented a more diverse mixture of substances (Table 3).

In a comparison of the hexane extracts obtained under various conditions, the following facts were established:

- the hexane-soluble products obtained at the lower temperatures were the richest in phenols; here substances belonging to all three types of structural units of lignin were present;

- with a rise in temperature, guaiacyl compounds with hydroxyls in the side chain disappeared;

- with a rise in temperature the yield of such compounds as cresol and creosol increased, which is connected with an intensification of the cleaving action of the catalyst on the C-C bonds of the side chain and, at the same time, with the hydrogenation of some reaction products; and

- in all the experiments except those at low temperatures substances with a syringyl structure were absent, which is probably due to a property of the catalyst of promoting the partial demethoxylation of syringyl derivatives.

In the course of the isolation of the phenolic substances, hydrol lignins, consisting of the product of the incomplete decomposition of the lignin by hydrogenolysis, were obtained. The IR spectra of these hydrol lignins exhibited bands characteristic of a benzene ring with substituents ($1510, 1600, 1470 \text{ cm}^{-1}$), and of hydroxy (3450 cm^{-1}), carbonyl (1720 cm^{-1}), methoxy (1330 cm^{-1}), and ether ($1280, 1230, 1040 \text{ cm}^{-1}$) groups. On the basis of elementary analysis and a determination of the amount of methoxy groups short empirical formulas of the phenylpropane structural unit of the lignins obtained were calculated: $L_1-C_9H_{7.52}O_{3.62}(OCH_3)_{0.75}$ L_2-C_9-

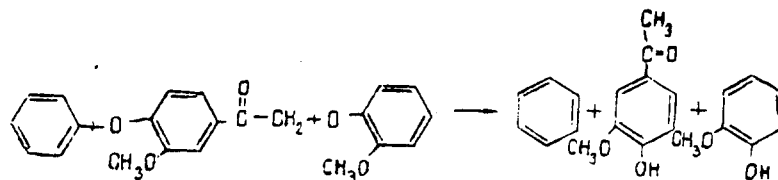
TABLE 3. GLC Analysis of the Hexane Extracts, % on the Total

Substance	Experiment No.							
	1	2	3	4	5	6	7	8
Phenol	0.8	1.2	1.0	0.5	1.8	1.8	2.3	2.9
m- + p-Cresols	4.1	5.6	17.7	16.0	5.8	9.3	9.3	3.2
Guaiacol	0.9	10.1	15.5	8.6	10.4	7.3	22.8	—
p-Hydroxyphenylethane	3.2	19.9	5.5	21.2	7.2	25.8	27.5	41.5
Creosol	15.6	1.8	24.6	15.6	23.2	19.0	14.0	10.3
p-Hydroxyphenylpropane	2.0	14.3	2.4	5.9	9.6	16.8	11.3	8.6
Guaiacylpropane	3.2	3.8	15.0	17.1	5.0	9.5	5.5	11.5
Guaiacylpropane	14.0	13.6	14.1	15.1	6.3	8.1	5.0	22.0
Guaiacylpropan-1-ol	30.1	11.3	—	—	13.2	—	—	—
Guaiacylpropan-1-ol	19.2	10.6	—	—	11.3	—	—	—
Syringylpropane	4.4	—	—	—	—	—	—	—
Unidentified	2.5	6.8	4.2	—	6.2	1.4	2.3	—

$H_{7.94}O_{3.12}(OCH_3)_{0.34}$; $L_3-C_9H_{7.56}O_{4.45}(OCH_3)_{0.35}$; $L_4-C_9H_{8.43}O_{2.96}(OCH_3)_{0.07}$; $L_5-C_9H_{9.69}O_{4.39}(OCH_3)_{0.74}$; $L_6-C_9H_{9.62}O_{4.46}(OCH_3)_{0.65}$; $L_7-C_9H_{9.52}O_{4.10}(OCH_3)_{0.48}$; $L_8-C_9H_{7.67}O_{3.84}(OCH_3)_{0.48}$.

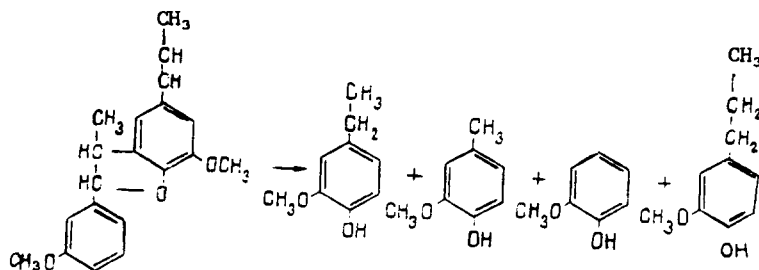
It is clear from these formulas how greatly the methoxyl content decreases with a rise in the temperature. In the lignin obtained at a temperature of 315°C (L_4), the number of methoxy groups calculated to one phenylpropane structural unit was only 0.07. When the amount of catalyst used was 10% of the weight of the raw material (L_5 , L_6 , and L_7), the H_2 content increased in comparison with the lignins obtained on hydrogenolysis with the use of 5% and 20% of catalyst. It is probably just this concentration of catalyst that is most favorable for hydrogenation. At higher or lower concentrations of catalyst the H_2 content remained at approximately the same level.

To elucidate the mechanism of the hydrogenolysis reaction in the presence of the polyfunctional catalyst, we carried out experiments with model compounds of lignin under the conditions selected for natural lignin (see Tables 1 and 2). As the models we used phenolic substances with alkyl-aryl C-O-C and C-C bonds that were in our possession. The reaction products were identified by GLC under the conditions described in [4]. The first substance subjected to hydrogenolysis was the trimer



The hydrogenolysis of this substance yielded benzene, guaiacol, and acetoguaiacol, which indicated the cleavage of the C-O-C alkyl-aryl bonds.

The second substance was a dimer with C-C bonds - dehydrodiisoeugenol. After hydrogenolysis a mixture of new substances was formed, among which the following predominated (in decreasing sequence): guaiacylpropane, creosol, guaiacol, and guaiacylpropane. On the basis of the results obtained it is possible to speak of the cleavage of C-C bonds under the action of hydrogenolysis in the presence of the catalyst used.



Thus, on the hydrogenolysis of lignin in the presence of a catalyst, alkyl-aryl C-O-C and C-C bonds are cleaved.

EXPERIMENTAL

Rice husks (50 g) that had been ground, washed with hot water, and extracted with ethanol-benzene were charged into a 1-liter rotating autoclave, the catalyst (5-20% on the weight

of the raw material) and 500 ml of dioxane were added, H₂ was pumped in to a pressure of 10.0 MPa, and the whole was heated at 170-315°C for 1-4 h. After the end of the reaction, the mixture was cooled to room temperature and was filtered from the solid residue, and the dioxane was distilled off. The resinous dioxane-soluble product was dissolved in 2% aqueous NaOH and the solution was acidified to pH 3 and extracted with hexane and ether. The resulting extracts were analyzed by GLC on a Chrom-4 instrument under the conditions described in [4]. The hydrol lignin that had deposited when the alkaline solution was acidified was centrifuged off, dried, dissolved in dioxane-water (9:1), and reprecipitated in absolute ether.

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APPLICATION OF IR SPECTROSCOPY IN THE ANALYSIS OF THE WOODY-FIBROUS MASS IN THE PROCESS OF HYDROLYSIS

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The possibility has been shown of using IR spectroscopy in the investigation of the changes in the polysaccharide component of wood in the process of acid hydrolysis. The method of determining the relative optical density (ROD) was used for the quantitative evaluation of the changes in the functional groups of the lignocellulose.

In the investigation of the structure of polysaccharides, the results obtained with the aid of chemical methods of analysis are represented most fully. However, the detailed elucidation of complex questions of the morphology of fine structure, the conformations of chains, and the determination of the ratios of the components of wood after chemical treatment, and also a number of other not less important questions require the use of a set of physical and physicochemical methods of analysis. Extremely useful in this respect are the results obtained by IR spectroscopy.

In the IR spectrum of cellulose, as for the majority of organic molecules, the predominant absorption bands relate to the 3600-660 cm⁻¹ region. The cellulose spectrum permits the isolation of approximately 30 absorption bands of different intensities. The presence of lignin in wood samples leads to the appearance of a number of new absorption bands that are absent from the IR spectra of cellulose and to a rise in the intensity of those absorption bands the frequencies of which coincide.

In the present paper we give an analysis of the IR spectra of the woody-fibrous mass (WFM) after acid hydrolysis and we also study the link between the changes in the relative optical density (ROD) at certain wavelengths and the amount of free sugars.

The hydrolysis of the WFM with sulfuric acid leads to an increase in the intensity and a broadening of the absorption band in the 3600-3000 cm⁻¹ region with an intensity maximum at 3400 cm⁻¹. This region of the IR spectrum characterizes the presence in the wood sample under investigation of hydroxy groups involved in both intermolecular and intramolecular hydrogen bonds. An intramolecular hydrogen bond can exist between adjacent units of the cellulose chain and, in particular, between the hydroxyl at C₃ of one glucose residue and the ring oxygen of a neighboring one [1]. Furthermore, the hydroxy groups of the lignin present in

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