of the raw material) and 500 ml of dioxane were added, H_2 was pumped in to a pressure of 10.0 MPa, and the whole was heated at 170-315°C for 1-4 h. After thee nd 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

V. A. Strel'skii and T. P Belova*

UDC 634.0.813.1:543.422.4

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 predominating 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 C_3 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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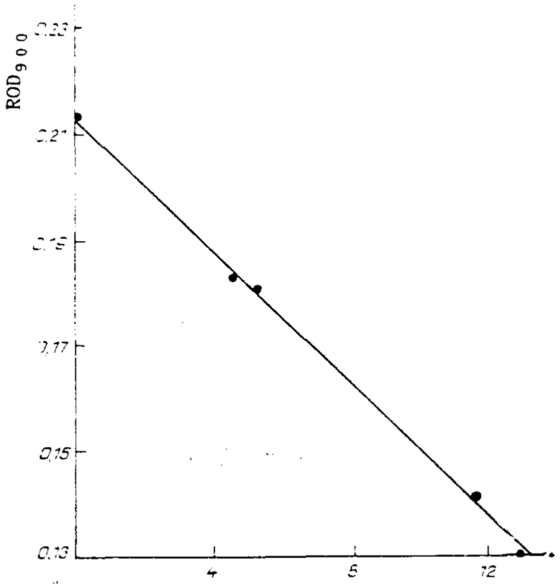

Fig. 1. Dependence of ROD_{900} on the amount of reducing sugars in the woody-fibrous mass.

TABLE 1. Changes in the RODs of the Absorption Bands of WFM as a Function of the Temperature of the Process

Sample	ν, cm^{-1}				
	3400	2900	1720	1505	890
A_0	1,6	0,62	0,275	0,56	0,22
A_1	1,8	0,70	0,20	0,49	0,18
A_2	2,0	0,71	0,15	0,47	0,13
A_3	2,2	0,70	0,17	0,49	0,14

Conditions of hydrolysis: sulfuric acid concentration: 0.5%; duration of the process; 60 min; temperatures: A_0) initial (unhydrolyzed WFM); A_1) 100°C; A_2) 120°C; A_3) 140°C.

the WFM and consisting of a reticular structure may also be bound by both intra- and intermolecular hydrogen bonds. The formation of hydrogen bonds between the lignin and the polysaccharide molecules in the process of the hydrolytic degradation of the plant raw material cannot be excluded, either.

The hydrolysis of the WFM in the presence of sulfuric acid at an elevated temperature leads to a change in the ratio of the bonds with maxima at 2910 and 2870 cm^{-1} due to the symmetrical stretching vibrations of $>CH_2$ groups. These absorption bands undergo the greatest changes after the treatment of the WFM at 100°C, and then, with a rise in the temperature of hydrolysis, the relative intensity of the 2910 cm^{-1} band does not change, while the intensity of the 2870 cm^{-1} band falls, and in the spectrum of the WFM after treatment at 140°C it appears only in the form of a shoulder.

In the absorption spectrum of lignocellulose materials, the 1720-1730 cm^{-1} region is interpreted as the appearance of the vibrations of acetyl groups in cellulose [2] and of carboxy groups in the lignin macromolecule [3].

A band with a maximum at 1635 cm^{-1} is connected with the presence of water adsorbed on the cellulose and may also be due to the presence of the carbonyl (more accurately, quinoid) groups of the lignin that are formed in the hydrolysis of the woody raw material.

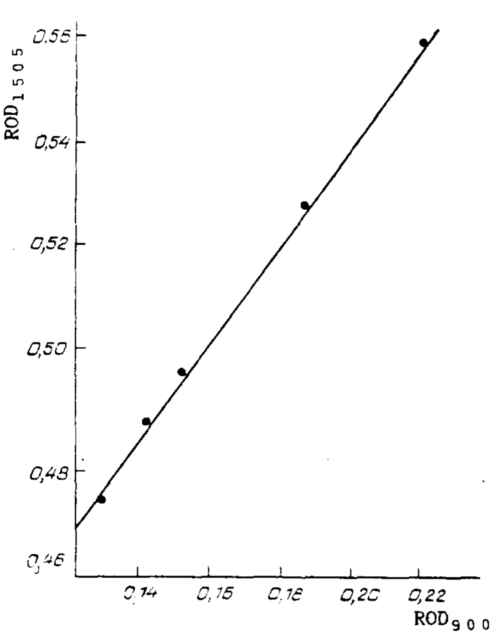

Fig. 2. Correlation relationship between ROD_{1505} and ROD_{900}

The vibrations of the aromatic ring of the lignin molecule appear in the IR spectra in the 1600-1500 cm^{-1} region. However, while the band at 1505 cm^{-1} is represented by an intense isolated line, the band with its maximum at 1600 cm^{-1} is more diffuse.

The band at 898 cm^{-1} has been assigned to the antisymmetrical vibrations of the glucose ring taking place in antiphase. Its assignment to the C_1 atom and the four atoms linked to it is in good agreement with the idea of the characteristic nature of this band for β-glucosidic binding. In a study of different types of cellulose and of model compounds it was concluded that the band at 900 cm^{-1} was due to two different vibrations, one of which resulted from the glucosidic bond. This vibration was assigned to a combination of the symmetrical stretching vibration of the glucosidic bridge with the deformation vibrations of the C_1H group [4].

For the quantitative evaluation by means of IR spectroscopy of the change in a particular functional group of WFM that has been subjected to acid hydrolysis use has been made of the method of determining relative optical densities [2]. As the internal standard we have used the 1150 cm^{-1} band. The relative optical densities (RODs) of a number of absorption bands of WFM after hydrolysis are given in Table 1.

Particular interest is presented by the existence of a link between the RODs of some absorption bands of the hydrolyzed WFM and the amount of free sugars in it. During the hydrolysis of the fibrous mass a fall in ROD_{900} is observed, with a rise in the amount of reducing substances (RSs) in the sample. The relation ROD_{900} = f[RSs] bears a linear nature with an increase in RSs from 0 to 12-13% (Fig. 1). An intensification of the conditions of hydrolysis and the increase in the amount of sugars connected with it ([RSs] > 13%) does not lead to a further fall in ROD_{900}. This phenomenon can be explained from the point of view of the cleavage of the glucosidic bonds of the readily hydrolyzable carbohydrates. With an increase in the concentration of catalyst and a rise in the temperature it is not only the readily hydrolyzable but also the difficultly hydrolyzable part of the WFM that undergoes hydrolysis, and this compensates the fall in the ROD, the process becoming an equilibrium one. The establishment of an equilibrium cannot be connected with the breakdown of the sugars to furfural, since the formation of the latter has not been detected chemically. Consequently, in the process of hydrolyzing the WFM the equilibrium is due to the cleavage of the glucosidic bonds of the difficultly hydrolyzable part of the wood with the formation of oligomeric structures. ROD_{900} is only a function of the concentration of RSs and does not depend on the conditions of their formation (changes in the concentration of catalyst and the temperature and time of hydrolysis). With a statistical set of results it is possible to determine the RSs in the mass of hydrolysate from the linear graph of ROD_{900} = f[RSs] when the concentration of reducing substances is in the range of 0-13%.

In the hydrolysis of the WFM, in parallel with formation of RSs there is a decrease in the concentration of lignin in the mass of hydrolysate. The connection between the fall in the amount of lignin and the cleavage of glycosidic bonds can be judged from the relation $ROD_{1505} = f[ROD_{900}]$, which is represented by a straight line (Fig. 2). It may be assumed that in the hydrolysis of the WFM a cleavage of the bonds between the readily hydrolyzable carbohydrates and the lignin takes places, as the result of which part of the lignin passes into the soluble state and is eliminated from the wood. However, this hypothesis requires additional investigations and more reliable proofs of the existence of a bond between the lignin and the readily hydrolyzable part of the wood.

As mentioned above, in the hydrolysis of the WFM an increase in the amount of hydroxy groups involved in inter- and intramolecular hydrogen bonds is observed. ROD_{3400} rises from 1.6 to 2.2 with a change in concentration of RSs from 0 to 30%. However, the dependence of ROD_{3400} on the amount of sugars is not linear but practically repeats the kinetic curve of the formation of the RSs under analogous conditions of hydrolysis. According to a comparison with other relationships, the function $ROD_{3400} = f[RSs]$ most fully reflects the dynamics of the formation of RSs in the hydrolysis of the WFM. With a change in the sugar content from 0 to 30% there is an inversely proportional relationship between ROD_{3400} and ROD_{900}, which permits the formation of monosugars to be linked with the cleavage of glycosidic bonds.

Thus, on the basis of results obtained by IR spectroscopy, a relationship has been established between changes in individual absorption bands and the amount of reducing sugars in WFM subjected to acid hydrolysis.

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KINETICS OF THE HYDROLYSIS OF WOODY-FIBROUS MASS

V. A. Strel'skii, T. P. Belova,*
and M. L. Skandrova

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The possibility has been shown of obtaining fodder additives by the hydrolysis of woody-fibrous mass with dilute sulfuric acid solutions. The kinetics of hydrolysis have been studied, a calculation has been made of the effective rate constants of hydrolysis of the polysaccharide part of the woody-fibrous mass, and the range of variation of the effective activation energy of the process has been determined.

At the present time, the production of fodder yeast from woody-fibrous mass has become common. Fodder saccharified woody-fibrous mass (KODVM) is being produced in the Arkhangel'sk, Kotlas, and Bratsk pulp and paper combines and is providing collective farms with fodder yeast containing 10% and more of sugars.

The technology of the production of KODVM is based on the impregnation of the chips with acid and subsequent heat and pressure treatment in hot-grinding machines of the UGR-03 and RT-50 types [1, 2]. However, the presence of a catalyst in the steam chamber of the grinder may lead to irreversible corrosion of the metal and, as a result, to its failure. In addition

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