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Abstract

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ON THE BONDING OF CELLULOSE WITH ASSOCIATED SUBSTANCES IN PLANT TISSUE

Many investigators, in particular Freudenberg, Hess, and others, deny the presence of a chemical bond between lignin and cellulose in plant tissue; in essence, they adhere to the hypothesis first advanced by Payen, who isolated cellulose, that cellulose is not chemically bound to its associated substances; the various components making up the woody complex are only mechanically and intimately intermixed during the growth of plant tissue. Some investigators hold the supposition that cellulose is joined in plant tissue with noncellulosic substances chemically, in the manner of esters. P. P. Shorygin pointed out that even if lignin is not chemically combined with cellulose, nevertheless its bond with cellulose is fairly strong, since the reactivity of cellulose containing lignin is in many cases greatly reduced compared with pure cellulose. Shorygin, however, allows for the existence of a bond of the type of mutual adsorption of colloidal gels, which is also distinguished by considerable strength and in many cases differs from a true chemical bond only by the absence of exact stoichiometric ratios (^1).

In the present communication we give the results of experiments carried out with the aim of clarifying the presence of a bond between individual components in the woody complex, and also of elucidating the individual processes occurring during alkaline cooking of cellulose. For this purpose experiments were performed to obtain cellulose with the use of NaOD from certain samples of lignified plant materials and to cook cotton cellulose with the same NaOD solution, as the purest cellulose, containing 99.8% cellulose.

The NaOD solution was prepared from heavy water and sodium peroxide according to the reaction

$$\mathrm{Na_2O_2 + 2D_2O \rightarrow 2NaOD + D_2O_2}$$

Deuterium peroxide was decomposed by prolonged (24 hr) boiling in a flask with a reflux condenser. The cellulose was cooked in a steel autoclave with a 12.06% solution of NaOD in heavy water. Dried over P_2O_5 samples of pine wood of different ages were subjected to delignification: June shoots, mature wood of one-hundred-year age, fossil wood of thousand-year age, wood of interglacial age, and decorticated flax-fiber wastes (^2). The liquor-to-wood ratio of the cook was $1:6$, $t=160^\circ$, and the cooking time, including heating to temperature, was 5 hr 40 min. After cooking, alkali was pressed out from the isolated cellulose, and heavy water was distilled from it. The distillation of heavy water was carried out in a somewhat modified apparatus described in the literature (^3). The distillate was oxidized twice with $KMnO_4$ to remove organic substances and was subjected to an additional double distillation.

Isotopic analysis of the distillate was carried out by the pycnometric method using a glass precision pycnometer according to the method described by I. Kirshenbaum (^4); the isotopic composition of the distillates was calculated by the procedure described in work (^3). The results of the study of the isotopic composition of the distillates and the yields of deuterium celluloses are presented in Table 1.

Table 1

Sample name	Cellulose yield, %	Distillate density d_{20}^{20}	Desired deuterium concentration, mol. %	D_2O entering into exchange with 100 g of wood (cellulose), g
Initial cooking liquor	–	1.10773	100.484	–
June pine shoots	20.55	1.10139	94.460	32.61
Mature pine wood	31.10	1.10178	94.825	30.63
Fossil pine wood from a peat deposit	24.81	1.10486	97.605	12.14
Fossil wood from a peat deposit of the interglacial period	11.20	1.10253	95.527	27.42

Sample name	Cellulose yield, %	Distillate density d_{20}^{20}	Desired deuterium concentration, mol. %	D_2O entering into exchange with 100 g of wood (cellulose), g
Decorticated flax-fiber waste	46.0	1.10143	94.498	33.39
Cotton cellulose, grade "Ts"	–	1.10190	94.938	32.8

As is seen from Table 1, some part of the OH groups of the wood complex, in the process of alkaline cooking of cellulose, enters into isotopic exchange and is replaced by OD groups.

From the same table it is evident that the amount of D_2O that interacted with the components of the wood during the cooking of wood celluloses is greatest for young wood. The smallest amount of D_2O for the fossil wood of the peat deposit should apparently be explained by the presence of a considerable amount of resins (17%) in this sample (5). The number of OH groups participating in the reactions during cellulose cooking depends on the origin of the wood complex and also, probably, on its age, chemical composition, and structure.

The isolated deuterium-cellulose was studied by infrared spectroscopy. The cellulose samples were kept (for a long time) in a vacuum desiccator over P_2O_5. Preparation of semitransparent films for analysis according to the described procedure (6) was carried out under dry conditions. Before the investigation, the films were also kept for a long time in vacuum over P_2O_5. The spectra were recorded in a special cell without direct contact with the atmosphere.

To obtain the spectra, a recording spectrophotometer UR-10 was used. Measurements were made in three regions: 3600–2100 cm^{-1} (LiF prism), 2000–700 cm^{-1} (NaCl), and 700–400 cm^{-1} (KBr).

Figure 1 shows: the spectrum of deuterium-cellulose obtained from mature pine wood (sample No. 1); the spectrum of cellulose obtained by cooking with a 12% NaOH solution (sample No. 2), and the spectrum of cotton cellulose treated with a 12% NaOD solution under the conditions of cooking cellulose from wood (sample No. 3).

As is seen from the figure, the spectra of all the investigated samples are characterized by the presence of an intense band in the region of the OH group—3600–3100 cm^{-1}. For the spectra of samples Nos. 1 and 3, a band of the OD group in the region 2600–2400 cm^{-1}, of lower intensity, is characteristic. For sample No. 3 the OD band is formed as a result of direct isotopic exchange and has a clearly expressed structure, apparently characteristic of OD groups

Fig. 1. Spectra of cellulose

Figure 1: Fig. 1. Spectra of cellulose

in three possible positions. In the spectrum of sample No. 1 no such structure is observed, which indicates a different mechanism of formation of OD groups.

For the spectra of celluloses obtained by cooking with a 12% NaOD solution in D_2O (sample No. 1), a considerable decrease in the intensity of the 1340 cm^{-1} band and disappearance of the 1320 cm^{-1} band are characteristic in comparison with the spectra of celluloses isolated by cooking with a 12% NaOH solution in H_2O (sample No. 2). As established (7,8), the bands 1370, 1340, 1320 cm^{-1}

in the spectrum of cellulose should be attributed to deformation vibrations of primary hydroxyls of different rotational isomers. Therefore, the differences observed in this spectral region on passing from the second sample to the first should be attributed to the formation of OD groups at the sixth carbon atom. The latter cannot be attributed solely to isotopic exchange.

Indeed, the spectra of cotton cellulose subjected to alkaline treatment under the conditions of deuterium boiling, and of wood cellulose obtained

Fig. 1. Spectra of cellulose obtained by boiling with 12% solutions of NaOD in D_2O (1), NaOH in H_2O (2), and of cotton cellulose treated with a 12% solution of NaOD in D_2O under boiling conditions (3)

by ordinary sodium-hydroxide boiling are approximately identical in the region 1300–1400 cm^{-1} and differ strongly from the spectrum of wood cellulose isolated by deuterium boiling. The differences in the spectra are easily explained if it is assumed that, in the wood complex, there are chemical bonds between cellulose and its companions at the 6th carbon atom of some of the elementary units of the cellulose macromolecule. In the process of boiling wood cellulose with NaOD, the formation of OD groups occurs not only as a result of isotopic exchange, but also because of rupture of the chemical bond. The spectrum of linen cellulose obtained by boiling with NaOD is close to the spectrum of sample No. 1. This indicates that cellulose in the structure of flax fiber is not in the free state, but is to some extent chemically bound to components of the plant tissue.

It is possible that such bonds are also present in other positions. At the same time, the bulk of the hydroxyl groups of the cellulose macromolecules of the wood complex is not bound to its companions, which is confirmed by the presence of a very intense OH band in the spectrum of sample No. 1.

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Note: Figure translations are in progress. See original paper for figures.