Cellulose Hydrolysis After Combined Action of High Pressure and Shear Deformation

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INTRODUCTION

An apparatus of Bridgeman anvil type stands out among different types of high-pressure devices since it allows the exposure of solid materials to the combined action of uniaxial compression (up to pressures of about 20 GPa) and shear deformation. Under such action of high pressure (HP) and shear deformation (ShD), sample material is in the plastic flow state, the value of plastic flow (degree of deformation) being practically unlimited.

Using the anvil apparatus, a number of regularities in the behavior of solids at the moment of plastic flow under pressure were established. Thus, in Reference 1 it was shown that by varying the value of pressure one could change the direction of some chemical reactions in organic solids. It turned out that under HP and ShD, the reactions, which had not been observed before, took place[2-4] and under pressures of 0.2–0.4 GPa, the formation of diamondlike structures in graphite was found.[5,6] It was established that, under HP, all solids at the moment of plastic flow were characterized by a sharp acceleration of mass transfer processes displayed in the mixing of solid components at the atomic-molecular level for several tens of seconds. This was shown, for example, by molecular crystals during the study of copolymerization and polycondensation reactions.[7,8] In the case of metals under HP and ShD conditions, at room temperature one can observe the formation of solid solutions.

As for polymers, it has been established that at plastic flow under HP, the formation of cocrystals may take place in the mixture of semicrystalline polymers,[9] and polymers, normally thermodynamically incompatible, may become compatible in the amorphous phase at the segmental level.[10-12]

Spectral analysis of a number of polyolefins shows that HP and ShD action can transform polymers into another crystalline structure and induce conformational changes in macromolecules.[13] This may lead to changes in the properties of the polymers themselves, as well as in polymer compositions. In Reference 14, the oxidation properties of pure polypropylene and of polypropylene with a low-molecular additive were studied. It was established that as a result of treatment under HP and ShD the induction period of thermal oxidation increased, but the rate of the oxidation process decreased. According to Reference 15, after HP and ShD action, the strength of the electric field of polypropylene increases.

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During the study of the plastic flow mechanism of polymers under HP, it has been found[16] that mechanisms of plastic flow are similar for flexible polymers (polyolefins) and for rigid polymers. This suggests that, as a result of treatment under HP and ShD, one can also change certain properties of rigid polymers.

Of the greatest interest in a series of rigid polymers is cellulose, which is widely used in chemical engineering, which is why it is very important to study new ways of processing and application of this product.

One of the most important properties of cellulose is its hydrolyzability at the cleavage of 1,4-β-glucosidic bonds in the presence of acid catalysts. It is known that the content of a readily hydrolyzable fraction (RHF) in cellulose increases owing to the fracture of densely packed structures as a result of grinding or the action of ionizing radiation[17, 18] accompanied by degradation of polymer chains.

Our aim was to study the effect of treatment under HP and ShD on cellulose hydrolyzability and to estimate the relationship between hydrolyzability and the value of degree of polymerization (DP).

EXPERIMENTAL

Treatment of samples under pressure was carried out in a pressure range from 0.5 to 2 GPa at room temperature with a help of an apparatus of Bridgeman anvil type with hardened steel anvils (diameter of the working surface of anvils, 20 mm). Ashless wood cellulose with DP = 700 was used as
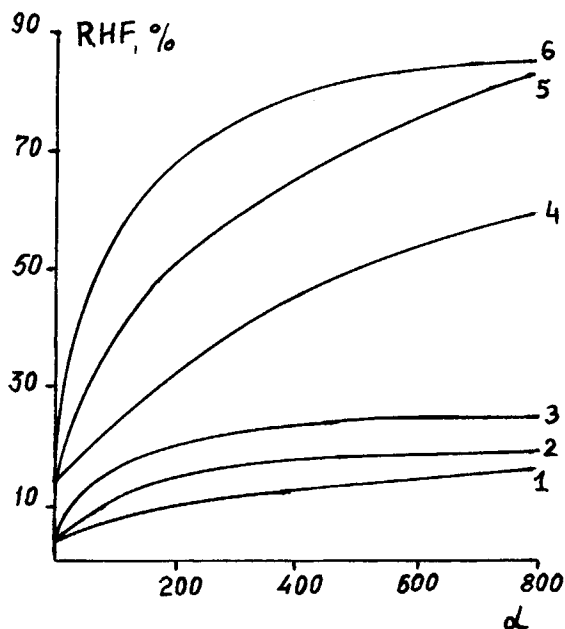

Fig. 1.   Effect of HP and ShD on RHF yield. Cellulose, treated under pressure: (1) 500 MPa; (2) 1000 MPa; (3) 2000 MPa. Cellulose + 1% H_2SO_4, treated under pressure: (4) 500 MPa, (5) 1000 MPa, (6) 2000 MPa.

the subject of investigation. After HP and ShD action, the samples were crushed in a mortar.

The degradation degree of cellulose macromolecules was estimated by the change in intrinsic viscosity of cellulose solutions according to Reference 19.

After treatment of samples under pressure, we obtained transparent films. In the central part of the sample one could see a muddy spot with a diameter of 2–3 mm. This was the part of the sample that took part in the process of plastic flow to a lesser extent than the border zone. X-ray diffraction analysis of the transparent part of the samples showed that crystallinity peaks characteristic of untreated samples were absent, whereas one could observe two wide halos, indicating that cellulose crystallites were intensively grounded and saturated with structural defects.

Compared with untreated samples, no marked changes were found in infrared (IR) spectra of the cellulose samples after HP and ShD action in the frequency range from 2000 to 400 cm^{-1}. However, we did observe a certain decrease in absorption at 1429 cm^{-1} and a simultaneous increase in absorption
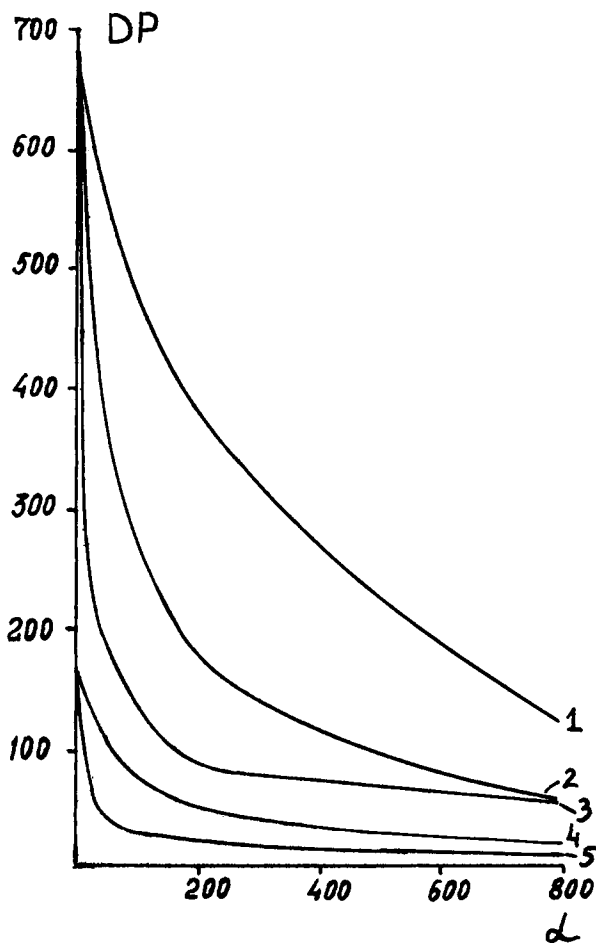

Fig. 2. Effect of HP and ShD on DP. Cellulose, treated under pressure: (1) 500 MPa, (2) 1000 MPa, (3) 2000 MPa. Cellulose + 1% H_2SO_4, treated under pressure: (4) 500 MPa, (5) 2000 MPa.

at 897 cm^{-1}. According to Reference 17, the ratio of the band intensities may be considered the value of the degree of crystallinity.

As is known,[20] decomposition of polysaccharides proceeds more rapidly in the presence of concentrated sulfuric acid during grinding in ball or vibrating mills. Cellulose samples, containing from 0.2 to 2% sulfuric acid, were also exposed to HP and ShD action. The acid was introduced by soaking the samples with dilute solutions with subsequent drying at 105° for 2 h. Afterward, all reagents were introduced in a similar way.

RESULTS AND DISCUSSION

In Figure 1 are given the results illustrating the effect of HP and ShD on RHF content in the samples. After treatment of cellulose under HP and ShD conditions, RHF content increases three to five times compared with untreated samples. The larger the applied pressure and the rotational angle, the higher is the content of RHF. This dependence is the most clearly pronounced for the samples containing sulfur acid. In this case, the RHF content reaches 80%.

Simultaneous measurements of DP of the samples showed that, after treatment under HP and ShD, intensive degradation of the cellulose macromolecules took place (Fig. 2). After such treatment acid-containing samples acquired the ability of being partly dissolved in cold water. After boiling in 2% hydrochloric acid, the unhydrolyzed residue was poorly filtered out, since it formed on a filter a sticky gellike film. Acid-free samples treated under similar
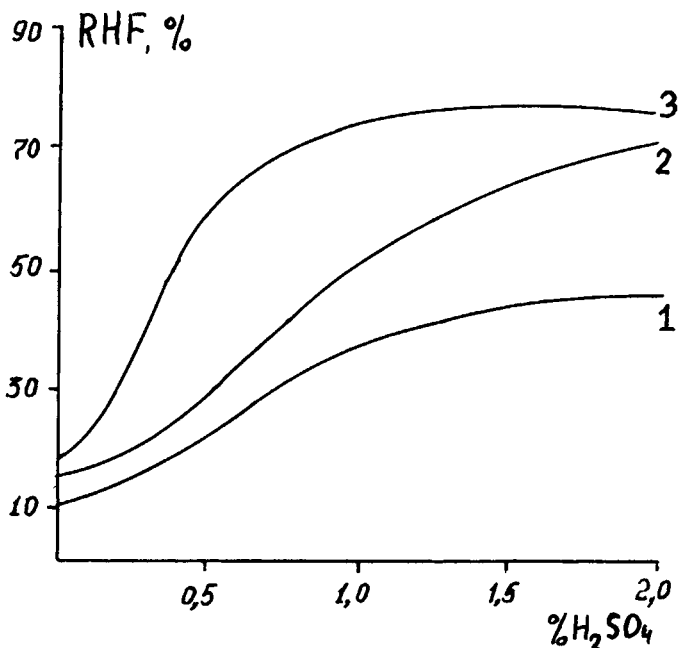

Fig. 3.   Effect of acid amount c on RHF yield under pressure: (1) 500 MPa, (2) 1000 MPa, (3) 2000 MPa (rotation angle = 400°).
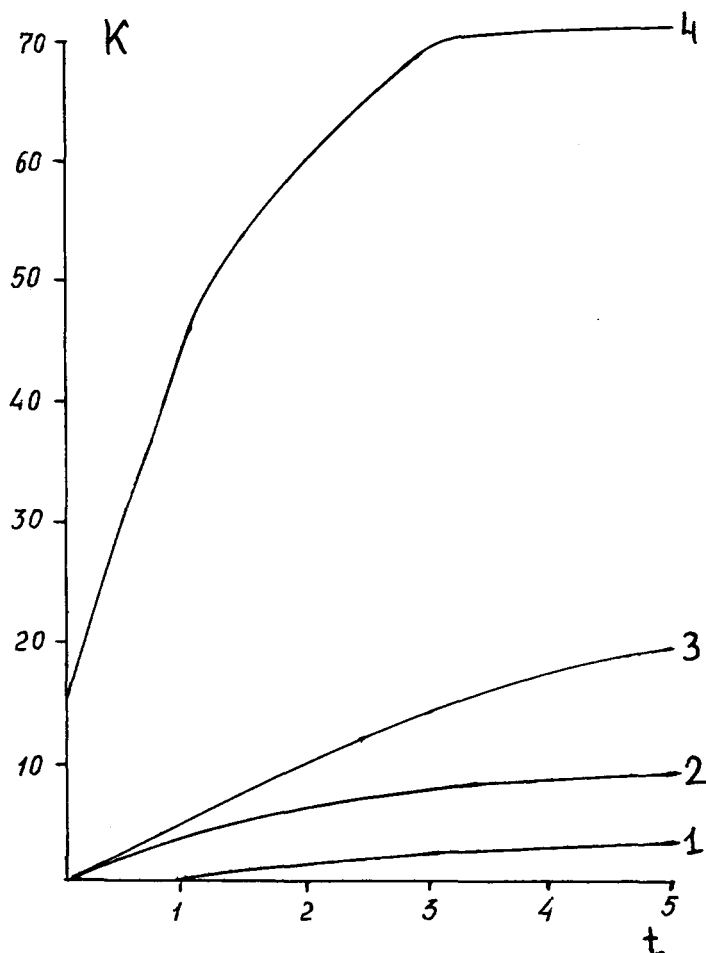
Fig. 4. Effect of stationary hydrolysis time t on reductant yield K (modulus of 2% HCl 40; temperature 98°C). Untreated cellulose: (1) without acid, (2) with 1% H_2SO_4. Treated on anvils with a diameter of 30 mm at pressure 1000 MPa and rotation angle of anvils, 400°: (3) without acid, (4) with 1% H_2SO_4.

conditions were not dissolved in cold water, and after hydrolysis, on the filter there remained an easily filter-passing free-flowing powder.

In Figure 3 are given the dependencies, illustrating the change in RHF content under HP and ShD conditions with the amount of sulfuric acid introduced. The increase in the amount of acid up to 1% led to considerable growth of RHF yield. Further increases influenced the yield of RHF only slightly. This is why further experiments were carried out with samples containing 1% H_2SO_4.

It was interesting to study the dependence of the yield of reductants on the time of hydrolysis. The data given in Fig. 4 indicate that the yield of reductants in acid-containing samples treated under pressure is higher than in acid-free samples.

The primary object of the study was to find out why RHF content increased after HP and ShD action. The data given in Figures 2 and 3 were
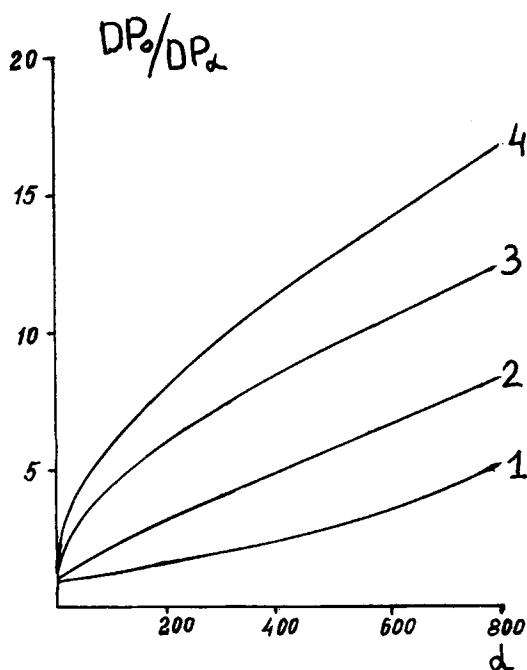
Fig. 5. Relative change of $\overline{DP}$ with a rotation angle (α) of anvils. Cellulose treated under pressure: (1) 500 MPa, (2) 2000 MPa. Cellulose + 1% H_2SO_4 treated under pressure: (3) 500 MPa, (4) 2000 MPa.

used for plotting in relative coordinates. In Figures 5 and 6 is shown the relative change of DP and RHF with the rotation angles of anvils at different pressures. One can see that the character of DP change for both acid-containing and acid-free samples is the same. Slightly smaller molecular masses in the acid-containing samples may be due to intensive interaction between acid and cellulose.

To clarify the mechanism of breaking 1,4-β-glucosidic bonds, cellulose was exposed to HP and ShD action in the presence of anhydrous sulfates of various metals. The sulfate content was 1% SO_4^{2-} from the cellulose mass.

From Table I it is clear that under HP and ShD conditions sulfate ions do not influence cellulose, but in the presence of aluminum ions the degradation of macromolecules is sharply intensified.

The data given in Figure 6 show that, during the process of stationary hydrolysis of both acid-containing and acid-free samples, pretreated under HP and ShD, the breaking of 1,4-β-glucosidic links takes place and the process does not depend on sample prehistory.

In Figure 7 is given the dependence of RHF yield on DP, which indicates the absence of a linear relationship between these parameters, especially in the region of small DP. The linear relationship between the amount of RHF and DP is also not held for the samples not pretreated with acid.

It is known that HP action increases the mobility of an acid proton, thus leading to an increase in the acid strength.[21,22] It was interesting to study the
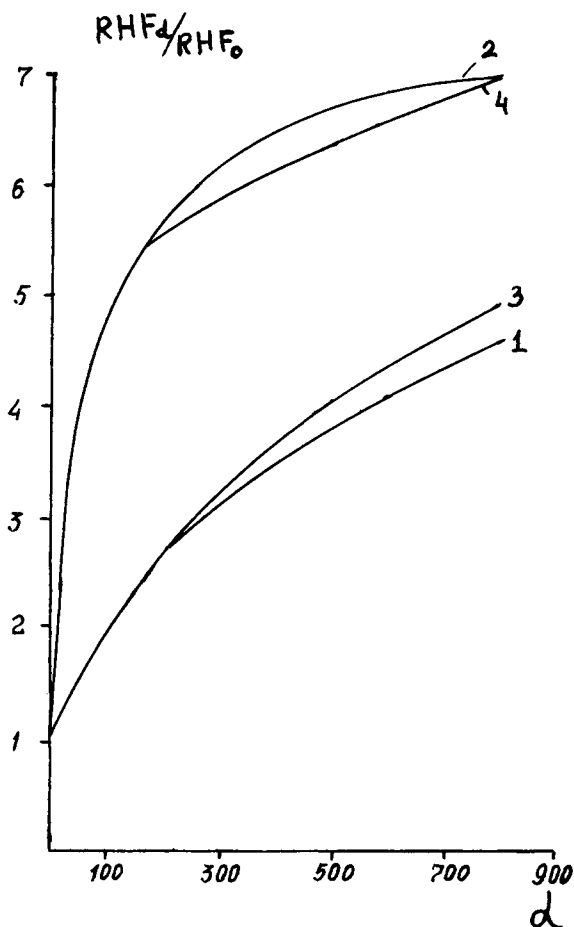
Fig. 6. Relative change of $\overline{RHF}$ with a rotation angle (α) of anvils. Cellulose treated under pressure: (1) 500 MPa, (2) 2000 MPa. Cellulose + 1% H_2SO_4 treated under pressure: (3) 500 MPa, (4) 2000 MPa.

effect of weak organic acids of different strength on cellulose degradation during the treatment under HP and ShD.

To this purpose, such acids as oxalic, malonic, and succinic, which belong to the same homologous series but have different values of dissociation constants, were used. The content of an oxalic acid was 5% from the cellulose mass. Other acids were taken in equimolar ratio. After the introduction of the

TABLE I
Effect of Sulfates on DP and RHF[a]

Sample	Without sulfates	With K_2SO_4	With $ZnSO_4$	With $Al_2(SO_4)_3$
DP	162	160	113	36
Content of RHF	12.7	12.0	14.3	36.2

[a] Pressure, 1000 MPa; rotation angle of anvils, 400°; diameter of anvils, 30 mm.
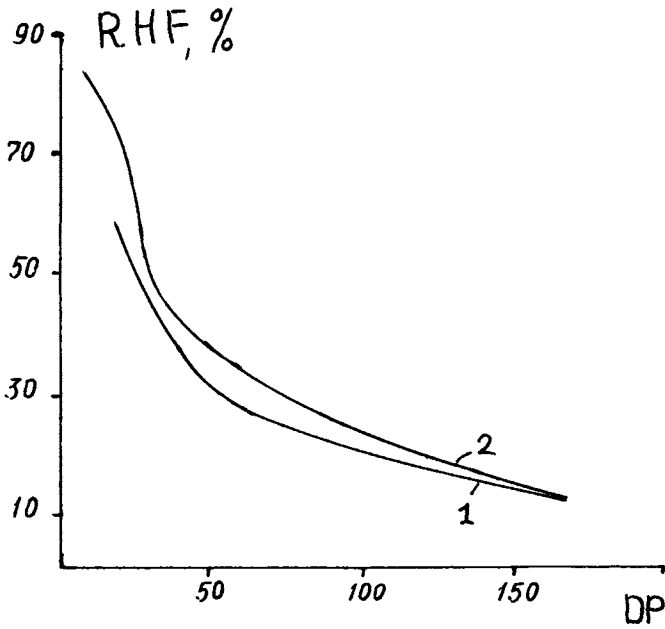
Fig. 7.   RHF yield versus DP. Cellulose + H_2SO_4 treated under pressure: (1) 500 MPa, (2) 2000 MPa.
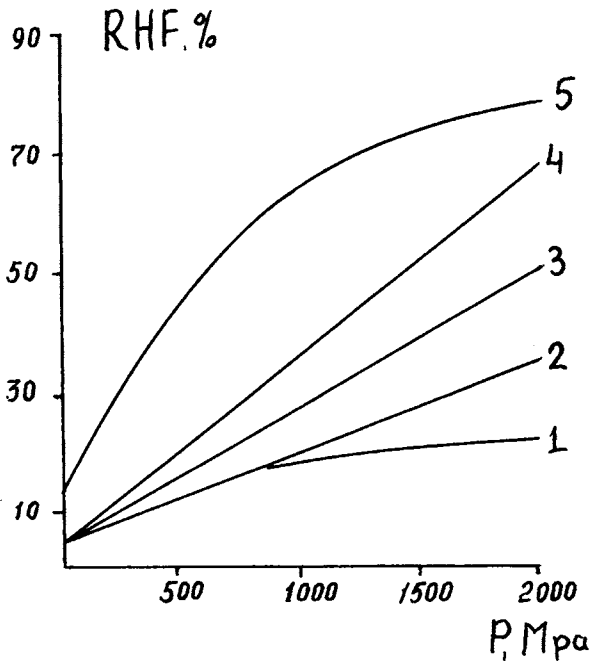

Fig. 8.   Effect of weak organic acids on RHF yield under HP and ShD conditions (diameter of anvils, 20 mm; rotation angle of anvils, 400°): (1) acid-free cellulose, (2) cellulose + succinic acid, (3) cellulose + malonic acid, (4) cellulose + oxalic acid, (5) cellulose + 1% H_2SO_4.

TABLE II
Effect of Weak Organic Acids on Cellulose DP under HP and ShD Conditions[a]

Sample	pK_α	Pressure (MPa)	DP
Acid-free		500	240
sample		1000	114
		2000	
With an oxalic	(I) 1.27	500	62
acid	(II) 4.27	1000	42
		2000	34
With a malonic	(I) 2.86	500	107
acid	(II) 5.70	1000	38
		2000	35
With a succinic	(I) 4.21	500	205
acid	(II) 5.64	1000	119
		2000	

[a] Diameter of anvils, 20 mm; rotation angle of anvils, 400°.
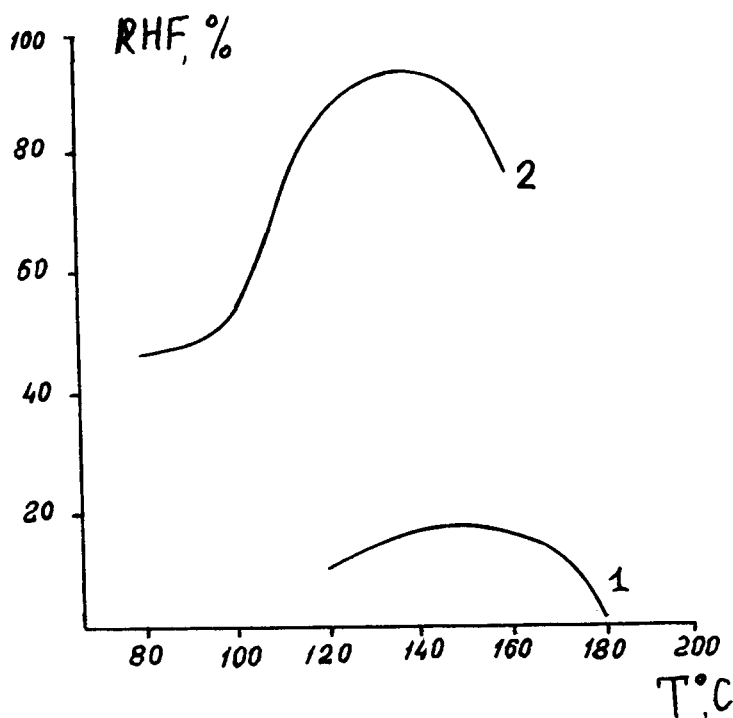

Fig. 9. RHF yield versus heating for samples pretreated under HP and ShD conditions. Cellulose + 1% of H_2SO_4 (time of heating—10 min.): (1) untreated, (2) pretreated under HP and ShD conditions (pressure 1000 MPa, anvils diameter 30 mm, rotation angle of anvils 400°).

acids and complete dehydration of the samples, the DP and RHF content in cellulose remained unchanged at DP 700, and RHF 2.5%.

However, after treatment under HP and ShD, the RHF yield in the acid-containing samples was higher than in the acid-free samples (Fig 8), and DP sharply decreased (Table II). The larger the constant of acid dissociation, the more pronounced is the effect observed. For a weak succinic acid, a marked increase in RHF was observed only at pressures of 200 MPa, compared with an acid-free sample.

Since the introduction of an acid does not influence DP and the yield of RHF in the samples that were not exposed to the action of HP and ShD, one can conclude that the effect of acids on the change in cellulose properties is displayed at the moment of HP and ShD action. The mechanism of this action is likely to be connected with the increase in the acid strength under HP. In Table II are given the values of DP obtained for the samples containing organic acids. These values indicate that, in the case of stronger acids, the decrease of DP is more pronounced. These results also agree with the data on the strengthening of acid properties of weak organic acids under HP and ShD conditions.

It is known[23] that breaking the packing density of cellulose macromolecules by introducing liquid ammonia or NAOH leads to an increase in glucose yield during hydrolysis. During our study, acid-free and acid-containing (1% H_2SO_4) samples of cellulose, pretreated under HP and ShD conditions, were exposed in sealed ampuls to heating at different temperatures. In Figure 9 are given the dependencies of RHF yield on the temperature of heating. From these dependencies it is clear that one can observe a sharp increase in RHF content in the acid-containing samples. Heating the acid-containing sample for 10 min at 140° led to an increase in RHF content from 46.6 to 93%, but DP decreased from 34 to 12, respectively.

The data in Table III show the changes in DP and RHF content in the acid-free samples with the time of heating at different temperatures. From these data, it follows that, as a result of HP and ShD action, the thermal stability of cellulose macromolecules sharply decreases. The decrease in DP is accompanied (as in the previous cases) by an increase in RHF content.

During boiling in 2% hydrochloric acid, the acid-free samples may form hydrogels with the increase in temperature and time of heating.

TABLE III
Dependence of DP and RHF Yield for Acid-Free Samples on the Time of Heating

Temper- ature (°C)	Time of heating (min)							
	10		20		40		90	
	RHF (%)	DP	RHF (%)	DP	RHF (%)	DP	RHF (%)	DP
160	10.2	160	10.5	160	12.6	107	—	—
180	13.6	130	14.3	90	19.4	64	32.5	—
200	16.3	—	20.3	68	29.2	47	35.6	41
220	—	—	35.3	53	—	—	—	—

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