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

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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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to this, the production of KODVM is connected with an interruption in the main stream of the manufacture of wood-fiber boards, which affects the profitability of the enterprise.

One of the methods of eliminating these deficiencies is the separation of the main stream of the manufacture of wood-fiber boards and the production of the KODVM. The woody-fibrous mass (WFM) after grinding can be fed directly to the hydrolyzer where its saccharification will be performed. In comparison with the existing scheme of producing KODVM, the proposed changes affect only the unit for feeding sulfuric acid, and the cyclone is replaced by a hydrolyzer of the corresponding throughput. The neutralization of the finished product can be carried out directly in KODVM-discharging worm conveyor.

The main parameters determining the hydrolysis of plant raw material are the temperature and time of hydrolysis and the concentration of catalyst. By varying these parameters it is possible to obtain a KODVM with a given sugar content, which is difficult when chips are impregnated with acid and are then subjected to heat and pressure treatment.

In the present paper we give the results obtained in a study of the kinetics of the hydrolysis of WFM after the grinding of the chips in a RT-50 machine under the conditions of a wood fiber board factory.

The WFM obtained in the cooking and grinding process consisted of a partially degraded lignocarbohydrate complex containing 19.9% of readily hydrolyzable and 38.7% of difficultly hydrolyzable polysaccharides. The hydrolysis of the initial mass was performed in 0.5-liter laboratory autoclaves with the use of 0.3-0.75% sulfuric acid as catalyst in the temperature interval of 100-140°C at a liquor ratio of 1:8, the time of hydrolysis being varied from 30 to 120 minutes.

The hydrolysis process was monitored from the amount of reducing substances (RSs) formed, this amount being recalculated to sugars by Bertrand's method. Table 1 gives the yield of sugars as a function of the conditions of hydrolysis. Analysis of the results presented shows that with a rise in the temperature of hydrolysis from 100 to 140°C the yield of sugars increased from 0 to 30%. Thus, at 130°C, a hydrolysis time of 120 min and an acid concentration of 0.75%, the amount of sugars in the mass became equal to the initial amount of readily hydrolyzable polysaccharides (19.9%). A rise in the temperature of hydrolysis led to a partial degradation of the difficultly hydrolyzable polysaccharides. The changes in the polysaccharide content during the hydrolysis of the WFM are given below:

Monosaccharide, %	Readily hydrolyzable polysaccharides, %	Difficultly hydrolyzable polysaccharides, %
Less than 1	19.88	38.73
3.62	13.37	38.51
9.51	8.33	38.15
13.65	5.36	37.42
26.43	0	36.31

With an increase in the amount of monosaccharides in the hydrolyzed WFM the amount of readily hydrolyzable polysaccharides fell and when there was more than 20% of sugars in the mass such polysaccharides were practically absent. The high yield of sugars (more than 20%) was apparently due to the fact that under high-temperature conditions the acetyl groups of the hemicelluloses were split out, leading to the formation of acetic acid, which additionally catalyzed the hydrolysis. Under these conditions the dissolution and partial hydrolysis of a certain part of the amorphous cellulose, the amount of which was 2.5-3.5% on the weight of the wood, is possible [3].

For a more complete kinetic characterization of the process, a calculation was made of the effective rate constants of the hydrolysis of the polysacccharides. For calculation at a low degree of hydrolysis we used the equation of a first-order reaction [4]:

$$K = \frac{2.3}{t} \lg \frac{C_0}{C},$$

where K is the rate constant, min^{-1}; t is the reaction time, min; C_0 is the initial amount of readily hydrolyzable polysaccharides (19.9%); and C is the residual amount of polysaccharides in the WFM after time t.

TABLE 1. Dependence of the Yield of Sugars on the Conditions of Hydrolysis

Time of hydrolysis, min	H_2SO_4 concentration, %	Yield of sugar (%) at the given temperature, °C				
		100	110	120	130	140
30	0,3	0,8	1,8	3,1	5,8	11,4
	0,5	1,3	2,2	3,1	7,3	11,7
	0,75	2,2	4,0	5,4	10,0	—
60	0,3	1,3	2,5	4,7	10,1	16,4
	0,5	2,1	3,7	6,1	10,7	17,1
	0,75	3,3	7,4	11,4	15,0	—
90	0,3	2,2	3,7	6,8	13,0	19,4
	0,5	2,8	5,7	7,2	15,1	23,8
	0,75	5,0	9,7	14,4	17,8	—
120	0,3	2,7	4,8	9,1	16,4	22,5
	0,5	4,4	6,9	11,5	18,0	29,6
	0,75	6,1	10,3	16,2	19,6	—

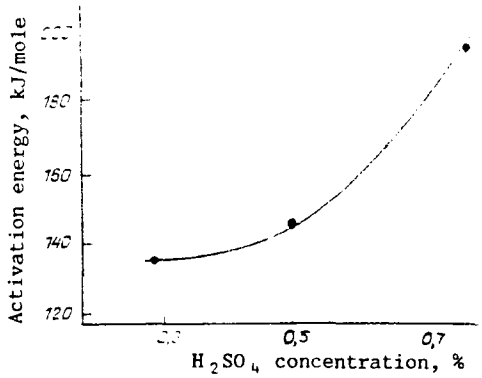

Fig. 1. Dependence of the activation energy on the concentration of catalyst.

The calculations showed that the rate constants of the hydrolysis of the WFM were $0.35 \cdot 10^{-3}$ min^{-1} at 100°C and $2.9 \cdot 10^{-2}$ min^{-1} at 140°C. Thus, the range of variation of the rate constants of the hydrolysis of the WFM is in the region of 10^{-4} to 10^{-2} min^{-1}

An investigation of the hydrolysis of the WFM at various temperatures permitted the effective activation energy of the process to be calculated. It must be mentioned that the activation energy depends strongly on the concentration of catalyst and varies between 135 and 200 kJ/mole. The calculations were made from the formula

$$E = \frac{R \ln K_2/K_1}{T_1^{-1} - T_2^{-1}}$$

where E is the effective activation energy, kJ/mole, R is the universal gas constant, T_1 and T_2 are the absolute temperatures of the reaction, K; and K_1 and K_2 are the hydrolysis rate constants at temperatures T_1 and T_2, respectively, min^{-1}.

The investigations performed showed a rise in the activation energy with an increase in the concentration of sulfuric acid in the system (Fig. 1). The change in E_{eff} as a function of the catalyst concentration is apparently connected with the nonuniformity of the polysaccharide part of the WFM. With a rise in the temperature and an increase in the catalyst concentration there is a breakdown of the difficultly hydrolyzable polysaccharides that is associated with a higher activation energy than that for the readily hydrolyzable carbohydrates. To all appearance, it is just the degradation of the difficultly hydrolyzable part of the plant raw material that makes the main contribution to the change in the effective activation energy.

In spite of the high temperature of hydrolysis (140°C), no formation of furfural (a breakdown product of sugars) was observed in the system. This was confirmed both by chemical methods and by the analysis of kinetic curves. If furfural had been formed, the kinetic curves would have revealed a fall in the yield of sugars as a result of their decomposition, and this was not observed in our case.

The proposed scheme of the hydrolysis of woody-fibrous mass in order to obtain fodder yeast with a regulable and increased sugar content can be used both under the conditions of the manufacture of wood-fiber boards and also directly in the enterprises of Agroprom. The kinetic curves shown make it possible to give a regime for obtaining fodder saccharified woody-fibrous mass.

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