AMMONOLYSIS OF TECHNICAL LIGNINS

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The oxidative ammonolysis of hydrolysis lignin, cellolignin, and lignosulfonate takes place effectively with the greatest formation of a water-soluble fraction at 140-150°C in 2 h. On oxyammonolysis, cellolignin forms approximately twice as much water-soluble fraction as hydrolysis lignin, while lignosulfate desulfonates under conditions exceeding the optimum. The maximum amount of nitrogen in the water-soluble fraction of lignin (nitrogen-containing lignin) amounts to 9.0% for cellolignin and is 2-3% less for the others.

The problem of utilizing the chemical processing of plant raw material and in particular, lignin is one of the most complicated in modern technology [1].

Every year, hydrolysis-yeast and biochemical factories discharge to dumps several million of tons of hydrolysis lignins (HL) and cellolignin (CL), while pulp and paper combines dump approximately the same amount of lignosulfates (LS) [2].

It is usually considered that after the "introduction" of nitrogen into the lignin macromolecule the possibility exists of the wide use of such modified lignin as a fertilizer or a raw material for the growth of food yeasts and for other purposes.

The most technologically feasible method of introducing nitrogen into lignin is oxidative ammonolysis. For this reason, much attention has been devoted to the question of the oxyammonolysis of HL [3-8], CL [9], and LS [1, 7]. The most diverse nonsystematic information on the conditions of performing the process, the amount of so-called organically bound nitrogen, and also the percentage content of the water-soluble fraction (WSF) of the lignin has been given.

We have performed the comparative oxyammonolysis of HL, CL, and LS under identical conditions with the aim of determining the amount of WSF formed and also the amount of nitrogen in the water-insoluble fraction (WISF) of the lignin.

The quantitative dependence of the formation of the WSF of LH and CL on the temperature and time of the process was determined (Fig. 1a). The maximum in the solubility was reached

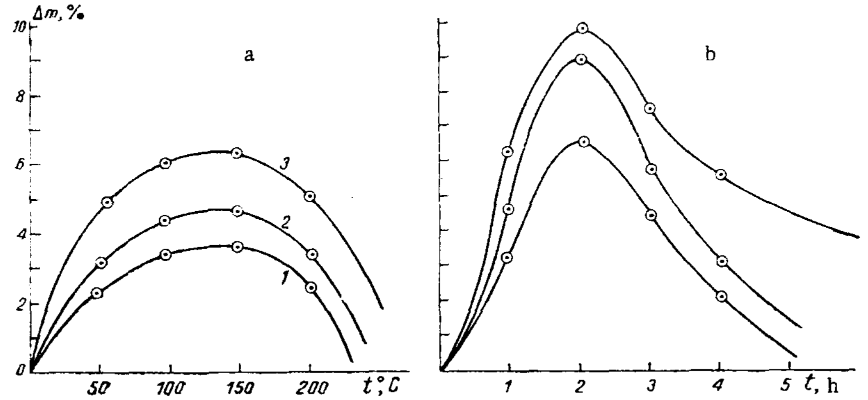

Fig. 1. Yield of the water-soluble fraction of the lignins as a function of the temperature in 1 h (a) and in oxyammonolysis at 150°C (b): 1) HL; 2) CL; 3) LS.

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TABLE 1. Oxyammonolysis of Technical Lignins with 25% Aqueous Ammonia

Substance	Conditions of synthesis		Water-insoluble fraction of the lignin		Water-soluble fraction of the lignin	Total yield, %	Nitrogen in the unseparated oxyammonolysis product
	temperature, °C	time, h	yield % of total	nitrogen, %	yield, % of total		
Ammoniated hydrolysis lignin							
1- HLA	50	1	104,2	2,62	2,5	106,7	9.08
2- HLA	100	1	105,3	3,18	3,2	108,5	12,60
3- HLA	200	1	103,4	4,74	2,4	106,0	14,32
4- HLA	150	1	104,5	5,12	3,4	107,9	19,20
5- HLA	150	2	105,2	7,40	6,7	111,9	21,18
6- HLA	150	3	105,5	7,26	4,7	110,2	20,90
7- HLA	150	4	105,7	7,20	2,6	108,3	20,86
Ammoniated cellolignin							
1- CLA	50	1	105,2	3,14	2,9	108,1	9,85
2- CLA	100	1	106,4	4,05	4,1	110,5	13,62
3- CLA	200	1	103,4	5,84	3,0	106,4	17,12
4- CLA	150	1	105,5	6,37	4,6	110,1	18,30
5- CLA	150	2	106,2	8,18	9,0	115,2	23,18
6- CLA	150	3	106,7	8,15	5,7	112,4	22,85
7- CLA	150	4	107,0	8,10	3,3	110,3	23,02
Ammoniated lignosulfonate*							
1- LSA	50	1	—	—	104,9	104,9	7,32
2- LSA	100	1	—	—	106,1	106,1	12,18
3- LSA	200	1	—	—	105,2	105,2	20,52
4- LSA	150	1	—	—	106,3	106,3	17,30
5- LSA	150	2	—	—	109,8	109,8	21,74
6- LSA	150	3	—	—	107,6	107,6	21,30
7- LSA	150	4	—	—	105,7	105,7	21,06

*The lignosulfonate and the products of its ammonolysis had no water-insoluble fraction.

at 140-150°C, after which it fell sharply, since the water-soluble fraction of the lignin, containing products with a lower molecular weight than the initial LH or the CL, took part in a secondary polycondensation process occurring particularly actively at 200-210°C. The greatest solubility of the lignin was achieved at 140-150°C in two hours (Fig. 1b). Subsequently, with an increase in the time of the process, the amount of WSF decreased for the reason given above.

Cellolignin formed approximately twice as much WSF as hydrolysis lignin (Table 1). This is explained by the fact that CL is obtained in industry [10] under less severe conditions than HL, i.e., it contains a larger amount of lignin that has not been subjected to processes of intramolecular cross-linking.

It follows from the results of this investigation (Fig. 1a, b, and Table 1) that the performance of the oxyammonolysis process for more than 2 h at temperatures above 140-150°C is undesirable, since after this the yield of the WSF from the HL and the CL decreases. This conclusion is not in harmony with Rosmarin's results [8], who states that a time of the process of from 2 to 4 h leads to an increase in the yield of WSF by 2-3%.

In our opinion, the amount of nitrogen should be determined only in the WISF, i.e., the part of the macromolecule retaining the lignin matrix which in some degree actually corresponds to the term "nitrogen-containing lignin."

This term is inapplicable to the WISF, which consists of a mixture of various lignin cleavage products with considerable amounts of low-molecular-weight carboxylic acids present in the form of ammonium salts and amides [4, 6, 11]. A determination of the total amount of nitrogen in the oxyammonolysis products does not give a real idea of the amount of the nitrogen "introduced" into the macromolecule and leads to a definitely exaggerated index, as is reflected in a number of publications [5, 7].

For this reason, we determined the nitrogen introduced only into the WISF of the lignin after it had been washed with dilute acid (see Table 1), and we called the product obtained

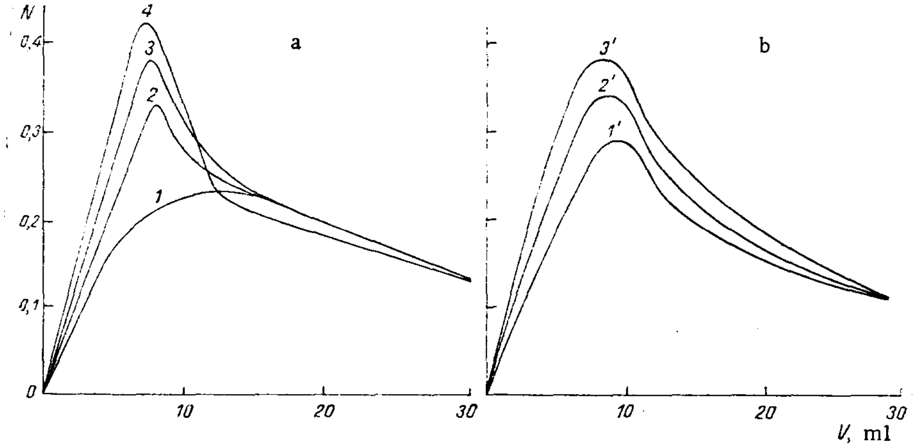

Fig. 2. Comparison of the peaks of high-molecular-weight compounds in hydrolysis lignin obtained under various conditions (a) and in that obtained in 2 h at 150°C (b): 1) 50°C, 1 h; 2) 100°C, 1 h; 3) 150°C, 1 h; 150°C, 3 h; 4) 150°C, 2 h; 1') HL; 2') CL; 3') LS.

in this way "nitrogen-containing lignin". For clarity, we also determined the nitrogen in the unseparated lignin oxyammonolysis product (see Table 1).

The IR spectra of the WISF showed pronounced diffusional scattering which is characteristic for condensed high-molecular-weight compounds.

The absorption bands of the stretching vibrations of C=O groups appearing in the 1610-1765 cm^{-1} region underwent the greatest changes on oxyammonolysis [6]. The band at 1720-1740 cm^{-1} was retained but its intensity had decreased considerably. According to the statements of a number of authors [12], it relates to the carboxy group. The presence of this band after the treatment of the lignin with ammonia shows that it also relates to the C=O groups of ketones or esters.

Considerable interest is aroused by the change in the region of the deformation vibrations of the LS at 665 cm^{-1}, which characterize the SO$_3$H group: its intensity decreased with a rise in the temperature and a lengthening of the time of ammonolysis of the LS and it disappeared completely at 200°C, i.e., desulfonation took place.

EXPERIMENTAL

As technical lignins we used hydrolysis lignin from the processing of sunflower husks in the Zaporozh'e hydrolysis-yeast factory, cellolignin produced by the hydrolysis of tan waste by the acidless method in the Shumerlya chemical factory, and lignosulfate produced by the Kamo pulp and paper combine.

The lignin and cellolignin were washed with water until the reaction was neutral and SO$_4^{2-}$ ions were absent, were dried in a vacuum desiccator to constant weight, and were ground in a ball mill. Samples weighing 10 g of lignins with a particle size of not more than 1 mm were taken and were treated with 25% aqueous ammonia in a solid:liquid ratio of 1:5. The oxyammonolysis reaction was performed in an autoclave heated by means of a heating mantel regulated with an accuracy of ±3°C. The conditions of the process are given in Table 1.

The water-soluble and water-insoluble fractions were separated on a glass filter with suction. The solid phase was washed with 5% aqueous HCl solution followed by washing with water to pH > 7 and was dried at 105-110°C.

The IR spectra of the samples were measured on a UR-20 spectrophotometer in KBr tablets (3 mg of substance and 300 mg of KBr). Nitrogen was determined by the Kjeldahl method [13].

SUMMARY

1. The oxidative ammonolysis of hydrolysis lignin, cellolignin, and lignosulfate takes place effectively with the greatest formation of a water-soluble fraction at 140-150°C in 2 h.

2. On oxyammonolysis, cellolignin forms approximately twice as much water-soluble fraction as hydrolysis lignin, while lignosulfonate is desulfonated under conditions above the optimum.

3. The maximum nitrogen content of the water-insoluble fraction of lignin (nitrogen-containing lignin) amounts to 9.0% for cellolignin and is 2-3% less for the others.

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DEVELOPMENT AND COMPARATIVE EVALUATION OF METHODS FOR THE MICRODETERMINATION OF IODINE IN DRUGS OF NATURAL ORIGIN

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Investigations have been made with the aim of drawing up a new and all-sided comparative evaluation of various known methods for the microdetermination of iodine in order to select the optimum procedures for the quantitative analysis of this element in materials of animal and plant origin. The efficacy of the use of the method of combustion in a flask with oxygen in the analysis of thyroidin and laminaria has been shown, and a new procedure for the microdetermination of iodine based on the combustion of a sample in oxygen and the determination of the iodine formed photometrically and by the starch-iodide reaction has been proposed.

Iodine-containing drugs of natural origin (thyroidin — a powder of the thyroid glands of animals, and laminaria — sea kale) have long been widely used in medical practice. Their therapeutic effect is due in part, to the presence of iodine [1]. Therefore, in the standardization of such raw material for medical purposes and also its prepared medicinal forms and in biochemical investigations various methods for the quantitative determination of this element are used that are based on the employment of several variants of the mineralization of the sample [2, 3], iodine-selective electrodes, differential pulsating polarography, kinetic methods, etc. [4, 5]. However, the determination of iodine in such specific material is a complex analytical problem. This is due to the small amount of iodine in materials of natural origin, the complexity of their chemical compositions, the volatility of iodine, and the possibility of its passage during mineralization into compounds with different degrees of oxidation.

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