

ELECTROHYDRAULIC EFFECT IN HETERODISPERSE WATER-PLANT SYSTEMS.

II. CHEMICAL NATURE OF THE SUSPENDED PARTICLES

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On the basis of the results of acid hydrolysis, chromatographic analysis of the hydrolysates, and a study of IR spectra, it has been established that the suspended particles liberated under the action of electrohydraulic shocks on heterodisperse water-plant systems consist of small fragments of the lignocarbohydrate complex of the plant tissue.

In the electrohydraulic (EH) treatment of heterodisperse water-plant systems, the main components of the plant tissue (cellulose, carbohydrates, lignin) undergo partial degradation. Part of the carbohydrates of the plant specimen pass into solution in the form of free monosaccharides, while substances of the *p*-hydroxyphenyl and guaiacylpropane series have been identified among the fractions of phenolic substances and phenolcarboxylic acids formed by the decomposition of the lignin component [1].

However, under the action of electrohydraulic shock (EHS) on heterodisperse water-plant systems, so-called "suspended particles-lyophilic colloids" separate out and deposit, and the formation of these products has not previously been discussed. In the present communication we give the results of a study of the chemical nature of these particles and discuss the pathways of their formation. It is known that the electrohydraulic effect (EHE) is a multifactorial physicochemical process in which shock waves with hydraulic pressures of 10^2 - 10^3 MPa, plasma with a temperature of up to 10^4 K, a pulsed electromagnetic field, and x-ray, luminous, and thermal radiations participate [1]. Each of these factors makes its own contribution to the EHE, during which mechanochemical, plasmochemical, polymerization, and degradative processes may take place in the heterodisperse system.

The suspended particles formed as the result of the the action of the EHS on the heterodisperse water-plant system consist of a light brown amorphous powder insoluble in water and organic solvents and sparingly soluble in alkalis. There are reports that in the EHS process polymeric compositons undergo mechanocracking with the formation of macroradicals under the action of flows with high velocity gradients arising in the motion of the shock waves [2]. On the basis of what has been said above, and also in the light of the multifactorial nature of the EHE process, it may be assumed that the suspended particles could be formed as a result of the mechanocracking of the lignocellulose components of the plant and are, probably, small fragments. The lignin component of the plant — in this case, the stems of the cotton plant — may be dispersed both in the form of small particles and in the form of particles of fairly large dimensions (high polymer or colloid).

With the aim of studying the chemical nature of the suspended particles we subjected them to acid hydrolysis with 2 N sulfuric acid at 100°C for 48 h. From 19.0 to 73.0% of the mass of the suspended particles underwent hydrolysis (Table 1).

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TABLE 1. Acid Hydrolysis of the Suspended Particles

Sample	No. of EHSs	Medium	Yield of hydrolysate, % on the initial mass of suspended particles
1. Cottonplant stems	50	H ₂ O	50.0
2. "	100	H ₂ O	73.0
3. "	500	5% H ₂ O ₂	71.7
4. "	1000	5% H ₂ O ₂	26.2
5. Kenaf tow	50	H ₂ O	19.0
6. "	100	H ₂ O	22.0
7. "	1000	H ₂ O	21.0

The presence of carbohydrates in the hydrolysates was established with the aid of the phenol/sulfuric acid test. Paper chromatography was used to determine the qualitative compositions of the hydrolysates. The main component identified was glucose, with trace amounts of xylose and arabinose, and also noncarbohydrate substances appearing on the chromatogram in the form of a "tail." To elucidate the nature of the unseparated substances, the hydrolysates of the suspended particles of some samples (5, 7) were hydrolyzed for another 6-8 h. Glucose and galactose were identified by the paper chromatography of these samples. Thus, the hydrolyzable part of the suspended particles had a carbohydrate nature.

The presence of lignin in the suspended particles was shown with the aid of the color reaction with phloroglucinol (red coloration) [11].

When wood is subjected to prehydrolysis with water, suspended particles are produced that pass into solution in the form of lyophilic colloids. They consist of low-molecular-mass fragments of lignin [3]. The colloidal state of the lignin fragments is stabilized by the protective action of polysaccharides [4]. It may be assumed that during the EH treatment of heterodisperse water-plant systems, in addition to dissolution, there is a production of partially degraded fragments of lignin and carbohydrates in the form of lyophilic colloids-suspended particles. There are reports that the colloidal state of the suspended particles is eliminated on acid inversion and cryogenic treatment of the aqueous phase [5]. In our case, on acidification to pH 1-2 and cryogenic treatment (freezing at -5°C) of the liquid phase of heterodisperse water-plant systems that had been subjected to EH treatment, the total separation and deposition of the suspended particles took place. Consequently, the suspended particles under investigation were lignin fragments, and their colloidal state was stabilized by polysaccharides.

The IR spectra of the suspended particles (Table 2) contained all the main absorption bands that are characteristic for lignin preparations and carbohydrates: $840\text{--}860\text{ cm}^{-1}$ (β -glycosidic bond), and $815\text{--}829\text{ cm}^{-1}$ (pyranose ring) [7].

As compared with the IR spectra of isolated lignins, the IR spectra of the suspended particles had a more "diffuse" form because of the superposition of the signals of the lignin and the carbohydrate components of the sample under investigation. This was shown in the broadening of the absorption bands of the common OH groups from a range of $3200\text{--}3600\text{ cm}^{-1}$ to one of $3100\text{--}3700\text{ cm}^{-1}$.

Absorption bands at $1735\text{--}1760\text{ cm}^{-1}$ were assigned to the vibrations of C=O groups in esters [6]. The IR spectra of specimens of the suspended particles contained absorption bands in the $1730\text{--}1760\text{ cm}^{-1}$ region, which may witness the presence of an ester bond between the lignin and carbohydrate fragments.

It must be mentioned that the samples of suspended particles investigated were not isolated without the application of mechanical, radiant, and ultrasonic energies (all these being components of the EHE), and this in itself is an indication of the existence of chemical bonds between the lignin and carbohydrates in the plant tissue.

Analysis of the elemental composition and OCH₃-group content of the suspended particles (Table 3) showed that the carbon and hydrogen contents were in the ranges of 32.0-41.0% and 4.0-5.7%, respectively. An increase in the number of EHS to 100 led to a fall in the OCH₃-group content in systems with an aqueous phase. The explanation of this phenomenon is that, as the result of the EH treatment, and, in particular, the mechanochemical effect [8], the lignin underwent demethylation and the products obtained contained ortho-quinoid and quinomethide structures, the presence of which may be judged from the IR spectra of the suspended particles ($1650\text{--}1670\text{ cm}^{-1}$).

In systems where the EHE process was carried out in hydrogen peroxide solution, an increase in the number of EHS to 1000 led to a rise in the OCH₃-group content. This is possibly connected with a higher content of the lignin component in the sample under investigation (sample 4, Table 1). Thus, after the acid hydrolysis of sample 4 the unhydrolyzable part amounted to 73.8%.

TABLE 2. IR Spectra of the Suspended Particles from Cottonplant Stems and Kenaf Tow

Absorption band, cm^{-1}	Suspended particles from the stems					Suspended particles from the tow				Stem DLA [4]	Tow DLA, [10]
	50 EHS	100 EHS	500 EHS	1000 EHS	50 EHS	100 EHS	50 EHS	100 EHS	1000 EHS		
C-H deformation vibrations in OCH_3 and an aromatic nucleus	1170	1170	1040	1030	1160	1160	1160	1160	1160	1035	1035—1040, 1125
Stretching vibrations of C—O—C bonds	1260—1280	1260—1280	1240—1250	1230—1250	1240—1250	—	1240—1250	—	1240	1225	1225
Vibration of phenolic OH groups	1335	1335	1335	1335	1330	1320	1330	1320	1320	1325	1330
Deformation vibrations of OCH_3 or CH_3 in acetyl groups	1430—1450	1450—1470	1420—1430	1420	1480	1480—1485	1440—1470	1440—1470	1440—1470	1460	1425, 1460
Skeletal vibrations of an aromatic nucleus	1510, 1535	1550—1560	1530	1520—1560	1550	1520—1570	1555	1555	1555	1520	1510, 1590
Stretching vibrations of CO groups in quinoid structures	1670	1670—1680	1650—1670	1650—1670	1660—1670	1660	1670	1670	1670	1640	—
Stretching vibrations of CO groups	1730—1740	1730—1745	1760	1745	—	1735	1740	1740	1740	1720	1725
Stretching vibrations in $-\text{CH}_3$ and $-\text{CH}_2$ groups	2940	2940—2950	2930—2940	2930	2945—2965	2945	2930	2930	2930	2920	2925
Stretching vibrations of OH groups involved in hydrogen bonds	3100—3700	3100—3700	3100—3650	3100—3650	3150—3700	3100—3700	3000—3600	3100—3700	3100—3700	3100—3700	3100—3600

TABLE 3. Elemental Compositions and Methoxy-Group Contents of the Suspended Particles Formed under the Action of EHS on Heterodisperse Water-Plant Systems (E = 500 and 2500 J), %

Sample	Number of EHS	C	H	N	OCH ₃
1. Cottonplant stems	50	40.9	4.6	3.7	2.2
2. "	100	40.3	4.0	4.3	1.7
3. "	500	40.2	5.5	0.8	0.95
4. "	1000	38.0	5.7	0.8	1.7
5. Kenaf tow	50	34.4	4.3	4.1	2.8
6. "	100	32.2	4.0	2.8	1.8
7. "	1000	39.3	5.0	2.9	3.5

Hence, on the basis of the results of acid hydrolysis, a comparative study of IR spectra, and the results of elemental analysis and of OCH₃-group determination, it may be concluded that the suspended particles formed under the action of EHS on heterodisperse water-plant systems are split-out fragments of the lignocarbhydrate complex of the plant tissue.

EXPERIMENTAL

Paper chromatography was conducted in the butanol-pyridine-water (6:4:3) system on FN II paper with the revealing agent aniline phthalate.

IR spectra were taken on a UR-20 instrument in tablets with KBr. C, H, and N, contents were determined on a CHN analyzer (Czechoslovakia), and OCH₃ groups by a standard method [11].

Acid Hydrolysis. A mixture of 0.1 g of suspended particles and 4.0 ml of 2N H₂SO₄ was heated in sealed tubes in the water bath at 100°C for 48-54 h. Then the tubes were opened and the contents were centrifuged. The supernatant - the hydrolyzed part of the suspended particles - was evaporated in a rotary evaporator to 1.0 ml.

The Phenol/Sulfuric Acid Test. The diluted hydrolysate of suspended particles (0.5 ml) was treated with 0.5 ml of 0.5% phenol and 2.5 ml of conc. sulfuric acid. The brown coloration characteristic for carbohydrates appeared.

The color reaction for the presence of lignin in the suspended particles was conducted with phloroglucinol [11]. A red coloration was observed.

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