

ELECTROHYDRAULIC EFFECT IN WATER-PLANT HETERODISPERSE SYSTEMS.

IV. ALKALINE HYDROLYSIS OF A SOLID RESIDUE.

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The alkaline hydrolysis of plant material subjected to electrohydraulic shock leads to an increase in the yield of phenolcarboxylic acids. This may be a consequence of the cleavage of ester and ether bonds in the lignins of the samples investigated.

A characteristic feature of the lignins of herbaceous plants is the presence in them of 5-10% of phenolcarboxylic acids bound with the lignin by ester and ether bonds [1]. The formation of phenolcarboxylic acids, aromatic aldehydes and ketones as the result of alkaline hydrolysis and nitrobenzene oxidation performed under severe conditions is known [2, 3].

The formation of phenolcarboxylic acids is also observed under the action of the factors of an electrohydraulic effect (EHE) — mechanochemical, plasmochemical, ultrasonic, etc. — on water-plant heterodisperse systems [4]; however, the yields are low (0.08-0.17% of the plant).

In order to determine the degree of influence of the EHE on the quantitative and qualitative composition of the phenolcarboxylic acids of heterodisperse systems with cottonplant stems and kenaf tow we have carried out the alkaline hydrolysis of the solid residue remaining after the action of electrohydraulic shocks (EHSs).

From 34.0 to 60.0% of the plant underwent hydrolysis.

With an increase in the number of EHSs from 500 to 1000 the amount of plant hydrolyzed rose. One of the main components — lignin — passed into a soluble state, as was shown by a difference in the amount of Komarov lignin in the solid residue before and after hydrolysis. When the aqueous phase — the hydrolysate — was acidified, a microdisperse brown precipitate of so-called "lignin substances" deposited. A determination of their elemental composition and a study of their IR spectra permitted the assumption of their lignocarbohydrate nature (Table 2).

As can be seen from the samples subjected to a greater action of EHSs, phenolcarboxylic acids were also extracted in larger amount, with the exception of the sample of cottonplant stems subjected to 1000 EHSs. The comparatively low content of phenolcarboxylic acids in this case can be explained by possible polymerization processes during the electrohydraulic treatment.

It must be mentioned that the action of EHSs on water-plant disperse systems followed by the alkaline hydrolysis of the solid residue leads to the liberation of a larger proportion of phenolic acids.

The methylated total phenolcarboxylic acids were analyzed by gas-liquid chromatography (Table 3). Acids belonging to the *p*-coumaryl, guaiacyl, and syringyl structural units of lignin were identified,

The formation of phenolic acids with an unsaturated propane side-chain (ferulic and *p*-coumaric) shows that during alkaline hydrolysis rupture of the ester bond takes place in which the carboxy groups are involved, while the formation of phenolic acids without a side-chain (vanillic, *p*-hydroxybenzoic, and syringic) may be a consequence of the rupture of aryl-alkyl ether bonds.

Thus, under the conditions of alkaline hydrolysis of the solid residue of a plant subjected to EHSs, the ether and ester bonds between the lignin and the phenolic acids are weakened, which leads to the comparatively easy liberation of these acids. The alkaline hydrolysis of the solid residue forms not only phenolcarboxylic acids but also other substances of phenolic nature,

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TABLE 1. Result of the Alkaline Hydrolysis of the Solid Residue, % on the Plant

Sample	No. of EHSs	Amount of plant hydrolyzed, %	Komarov lignin, %		Lignin substances	Phenol-carboxylic acids
			before hydrolysis	after hydrolysis		
Cotton plant stems	50	52.4	27.3	21.3	11.6	0.4
	100	50.0	26.2	21.0	14.0	1.8
	500	60.0	15.5	14.6	9.1	1.9
	1000	55.5	22.8	21.0	10.0	1.1
Kenaf tow	50	33.6	25.8	22.7	17.9	1.2
	100	35.0	24.7	23.0	9.1	1.8
	1000	42.8	24.6	22.8	10.6	2.8

TABLE 2. Composition of the Lignin Substances, %

Sample	No. of EHSs			OCH ₃	Ash
1. Cotton-plant stems	100	43.5	6.8	3.1	4.5
2 "	500	50.3	6.9	5.7	8.5
3 "	1000	41.0	6.1	6.0	6.5
4. Kenaf tow	100	55.5	6.5	4.6	5.3
5 "	500	35.6	5.2	4.9	7.1
6 "	1000	43.2	6.0	5.3	5.5

TABLE 3. GLC Analysis of the Total Phenolcarboxylic Acids, % in the Mixture

Substance*	Cotton plant stems				Kenaf tow		
	No. of EHSs				No. of EHSs		
	50	100	500	1000	100	500	1000
Vanillic acid	17.6	23.4	36.3	15.3	18.5	12.8	9.8
<i>p</i> -Hydroxybenzoic acid	9.9	11.5	6.1	2.3	1.8	1.5	2.1
Ferulic acid	33.0	19.5	19.9	41.4	28.0	29.5	32.0
<i>p</i> -Coumaric acid	5.8	5.6	6.4	2.3	1.6	4.4	5.6
Syringic acid	1.2	5.8	8.9	10.4	15.4	13.0	6.6

*Analyzed in the form of methyl esters.

which we do not consider in the present paper. We therefore believe it premature to draw conclusions concerning the behavior of the whole lignin macromolecule of a plant sample subjected to EHSs followed by alkaline hydrolysis.

EXPERIMENTAL

IR spectra of the lignin substances were taken on a Perkin-Elmer model 2000 IR spectrometer (Sweden).

GLC Conditions. The methylated total phenolcarboxylic acids were analyzed on a Chrom-41 instrument using a stainless steel column (0.3 × 200 cm) filled with Chromaton N-AW-DMCS bearing the stationary liquid phase 15% of Carbowax-20M. The rate of flow of the carrier gas (helium) was 40 ml/min, the thermostat temperature 190°C, and the column temperature 210°C.

The Komarov lignin content was determined as described in [5].

The methoxy group content was determined by the method of Vieböck and Schwappach, as given in [5].

Electrohydraulic treatment was carried out as in [4].

Alkaline Hydrolysis of the Solid Residue. To 5.0 g of the solid plant residue remaining after EH treatment was added 100 ml of 1 N NaOH, and the mixture was boiled under reflux for 1 h. After the lapse of this time the contents of the flask were filtered, and the plant was washed with water to neutrality. The filtrate and the wash-waters were combined. The resulting hydrolysate was acidified with 2 N hydrochloric acid to pH 1-2, whereupon a precipitate of "lignin substances" deposited, and this was centrifuged off, washed with water, dried in a desiccator over P₂O₅, and used for further analysis.

The acid supernatant was extracted with ether (3 × 300 ml), and the ethereal extract, after concentration to a volume of 200-250 ml, was extracted with saturated sodium bicarbonate solution.

The soda solution was acidified to pH 2-3 and extracted with ethyl ether (3 × 300 ml). The extract was dried over anhydrous magnesium sulfate, evaporated to small volume, and methylated with a freshly prepared solution of diazomethane.

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