

# INFLUENCE OF DEMETHYLATED LIGNIN ON THE ALKALINE HYDROLYSIS OF COTTONPLANT LIGNIN

V. E. Madzhidova and B. Kh. Pulatov

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*This paper gives information about the influence of demethylated lignin on the alkaline hydrolysis of the natural lignin of the cotton plant under various conditions.*

On being added to the cooking alkali, demethylated lignin (DML), just like anthraquinone (AQ), accelerates the delignification of wood. In its efficacy, DML approximates to that of AQ, and on its addition to the alkali the yield of cellulose increases by 2% [1]. It is also known that DML is a polydisperse product containing condensed quinone structures. The mechanism of their action in delignification is similar to the mechanism of the action of the AQ-anthrahydroquinone system [2], in which, on the addition of the AQ, the creation of a redox cycle takes place during which the anthraquinone is reduced to anthrahydroquinone by the carbohydrates of the wood and is then reoxidized to AQ as a result of a reaction with the quinonemethide structures of the lignin, promoting its dissolution [3].

In view of the shortage and high cost of AQ and its analogs, we have set ourselves the task of studying how DML affects the yield and composition of the low-molecular-mass phenols during alkaline hydrolysis.

TABLE 1. Yield of Low-Molecular-Mass Products of the Destruction of Lignin as a Result of the Alkaline Hydrolysis of Cottonplant Stems Catalyzed by DML (% on the amount of Komarov lignin)

Reaction conditions	pH 7—8	pH 2	Total yield
<i>T=60°C</i>			
Without DML	1.9	2.1	4.0
+0.5% DML	3.4	3.9	7.3
+1.0% DML	3.2	5.0	8.2
+2.0% DML	4.2	3.2	7.4
<i>T=100°C</i>			
Without DML	2.4	3.9	6.3
+0.5% DML	6.1	8.4	14.5
+1.0% DML	7.3	11.7	19.0
+2.0% DML	6.6	9.8	16.4
<i>T=160°C</i>			
Without DML	4.5	5.1	9.6
+0.5% DML	12.0	10.0	22.0
+1.0% DML	13.0	10.9	23.9
+2.0% DML	11.1	12.2	23.3

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TABLE 2. Qualitative and Quantitative Compositions of the Monomeric Phenols in Ethereal Extracts

Substance	Composition (% of the total) at the given DML concentrations								
	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
	60°C			100°C			160°C		
Phenol	0.96	7.13	3.00	3.11	2.45	5.22	3.83	7.61	8.92
Guaiacol	3.18	9.16	0.96	3.18	4.90	6.70	3.72	3.34	3.57
<i>p</i> -Hydroxyphenylethane	10.79	2.37	8.77	7.12	8.91	10.06	7.48	12.35	12.81
<i>p</i> -Hydroxyphenylpropane	11.60	3.95	13.56	8.81	10.50	11.38	6.89	14.61	13.64
Guaiacylthane	11.60	22.09	14.97	18.51	21.63	17.93	25.73	15.99	17.18
Guaiacylpropane	16.34	20.46	23.54	22.63	22.15	15.40	20.20	18.14	16.15
Vanillin	5.06	3.33	2.99	4.90	2.81	5.38	3.93	1.89	2.34
1-Guaiacyl ethanol	3.11	—	2.88	—	3.04	5.38	2.01	3.15	4.43
1-Guaiacylpropanol	15.59	11.60	9.84	7.01	3.61	6.84	—	4.27	3.19
Syringylpropane	1/11	16.40	16/5	23.50	20.00	10.76	18.40	4.89	4.46
3-Guaiacylpropanol	3.60	3.50	2.74	1.23	—	—	—	—	2.54
Unidentified peaks	1.06	—	—	—	—	5.25	6.81	13.76	10.15
Ratio:									
<i>p</i> -coumaroyl	0.39	0.19	0.43	0.33	0.37	0.46	0.32	0.74	0.70
guaiacyl	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
syringyl	0.29	0.23	0.29	0.40	0.34	0.18	0.32	0.10	0.09

Hydrolysis was conducted in an 8% solution of NaOH in an atmosphere of nitrogen for 4 h at various temperatures and concentrations of DML (Table 1). To facilitate the identification of the low-molecular-mass products formed, the reaction mixture was reduced with Raney nickel. The monomeric fraction of the products of alkaline hydrolysis was extracted with ether at pH 7-8, and other low-molecular-mass substances with ethyl acetate at pH 2.

The amounts of DML added were 0.5, 1.0, and 2% of the weight of the initial plant, which are 10 times more than the amounts of AQ used in the analogous reactions. It is known [4, 5] that the increased consumption of DML as an additive is due to the lower mobility of the semiquinone radical fragments of the DML molecule than of anthrasemiquinone radicals.

It can be seen from Table 1 that on the use of DML as additive the yields of low-molecular-mass phenols increased. With a rise in the temperature, for all the concentrations of DML used the yield of low-molecular-mass products gradually increased, reaching 23.9% of the Komarov lignin. The figures given in Table 1 show an ambiguous influence of a change in the concentration of DML at different temperatures of the process. Thus, at 60°C the total yield of hydrolysis products rose slightly on passing from 0.5 to 1.0% of DML (7.2 and 8.2%), but there was a slight fall again with a further increase in its amount to 2.0% (7.4%). At 100°C this tendency to a change in yield was retained and became more pronounced (from 14.5% to 19.0% and 16.4%), but with a further rise in temperature to 160°C the influence of the concentration of DML on the total yield of products leveled out.

A change in the concentration of DML had no appreciable effect on the relative amounts of the product fractions. With a rise in the temperature to 160°C the proportion of low-molecular-mass products rose, while at lower temperatures oligomeric hydrolysis products predominated in the majority of cases. This showed an intensification of degradative processes.

A lengthening of the time of hydrolysis from 4 to 6 h at 1% of DML also led to a rise in the total yield of low-molecular-mass phenols, to 32.2%, while a shortening of the reaction time to 2 h was accompanied by the opposite effect (22.6%). A rise in temperature 180°C led to a fall in the yield of products (20.2%). This situation is probably explained by the fact that with a rise in temperature to 160°C degradative process predominate in the system, while at temperatures above 160°C condensation processes exert a considerable influence on the yield of products.

Gel-chromatographic analysis of ethyl acetate extracts obtained at 160°C and 180°C showed an increase in the proportion of substances with higher molecular masses in the case of the experiments at 180°C.

The activity of DML in the alkaline hydrolysis of natural lignin is possibly due to the fact that the demethylation and destruction of hydrolysis lignin by pyridine hydrochloride in an alkaline medium at 180°C leads to products with a considerable amount of quinone-containing structures which, together with readily oxidized pyrocatechol structures, form a redox system [8, 9].

The alkaline hydrolysis of the demethylated lignin itself at 160°C also formed low-molecular-mass phenols (15.5%). When 10% of DML was used as catalyst the total products of alkaline hydrolysis due to the DML itself increased by 0.64%, calculated on the Komarov lignin, which amounts to 22.9% in ripe cottonplant stems.

The monomeric fractions of the products of the hydrolysis of lignin in the presence of DML were investigated by GLC (Table 2). On analyzing the ratio of the structural units, it may be noted that the total monomeric products of alkaline hydrolysis (pH 7-8) at low temperatures (60°C) contained a larger amount of syringyl structures. With a rise in the temperature of hydrolysis in the presence of 2.0% of DML, the proportion of syringyl derivatives fell, while at other concentrations of the catalyst it reached a maximum at 100°C. It is obvious that with a rise in the temperature the lignin underwent demethoxylation, which was possibly promoted, to some degree, by the presence of the DML, and in this process syringyl nuclei proved to be less stable than guaiacyl nuclei. A partial demethoxylation of lignin and substances modeling it on heating with alkali has also been shown by other facts reported in the literature [6, 10].

## EXPERIMENTAL

The demethylated lignin was obtained by the method described in [11].

**Alkaline Hydrolysis of Cottonplant Stems in the Absence and in the Presence of Demethylated Lignin.** Cotton-plant stem sawdust (10 g) was treated with 100 ml of 8% NaOH solution. DML was added in an amount of 0.5, 1.0, or 2.0% of the weight of the plant material and the mixture was heated with stirring in an atmosphere of nitrogen for 4 h. The solid matter was separated off by centrifugation and was washed first with 8% NaOH solution and then with distilled water to neutrality. The combined alkaline solutions were reduced with 20 g of Raney nickel in an atmosphere of nitrogen for 6 h. Then the reaction mixture was brought to pH 7-8 by the addition of dilute (1:1) HCl, and the monomeric fraction of lignin hydrolysis products was extracted with ether (1 liter), after which the pH was brought to 2 and the remaining low-molecular-mass products were extracted with ethyl acetate (1 liter). When the experiments were conducted in an autoclave, the reaction mixture was first purged with nitrogen.

GLC analysis was conducted on a Chrom-41 chromatograph. The total phenols were analyzed in a glass column (3 mm × 2.5 m) filled with 15% of Apiezon L on Chromaton N-AW-MCS (0.16-0.20 mm) at 205°C and a rate of flow of helium of 35-40 ml/min, with a flame-ionization detector [6].

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