Thermal Depolymerization of Cellulose

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Abstract

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The results of a study of the thermal decomposition of cotton cellulose and hydrate cellulose led us to the conclusion that the mechanisms of this process for the two structural modifications of cellulose are different ([1]). Further investigation of the question showed that, by reducing the ash content from 0.2 to 0.09%, it is possible to direct the thermal decomposition of hydrate cellulose according to the mechanism previously observed only for cotton cellulose, namely toward the formation of 1,6-anhydro-1,5-glucopyranose (levoglucosan) in an amount of 40-50%.

Freeing cotton cellulose and hydrate cellulose from ash to analytically undeterminable amounts, i.e., to a value on the order of $< 0.001\%$, leads to the most complete decomposition of cellulose at the C—O—C bonds. Thus it becomes possible to study the thermal depolymerization of both structural modifications of cellulose. For this purpose we investigated the levoglucosan content in the volatile products of thermal decomposition of cellulose, the rate of the process, and the regularity of the change in the degree of polymerization of cellulose during the process. The conditions for carrying out the thermal decomposition and the methods of investigation have been described previously ([1]).

Table 1 presents data on the yields of volatile products obtained from de-ashed* samples of cotton cellulose and hydrate cellulose at different degrees of decomposition, in comparison with the results of decomposition of the same cellulose samples containing 0.07-0.09% ash.

As follows from the data in Table 1, when the ash content in cellulose changes from 0.07-0.09% to analytically undeterminable amounts, the yield of tar-like distillate increases from 30-74% to 78-88%, while the levoglucosan content in it increases from 33-66%** to 75-83%. Thus, over the course of the decomposition process studied within the range from 12 to 95% loss in weight, the yield of levoglucosan is, for both cotton cellulose and hydrate cellulose, 65-73% of the weight of the decomposed cellulose. In addition, the data in Table 1 indicate a sharp decrease in the yields of products of deep decomposition of cellulose at the C—C bonds.

The rates of the process were measured with the aid of MacBain spring balances. For each sample, 3-10 curves were taken (see Figs. 1, 2).

Curves 1 in Figs. 1 and 2 characterize the rates of decomposition of cotton

cellulose and hydrate cellulose in the presence of 0.22-0.26% ash. The thermal decomposition of these cellulose samples proceeds with the formation, chiefly, of products of deep decomposition of cellulose at the C–C bonds; levoglucosan is formed in an amount of 4-10% ([1]). The process is characterized by a high

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* For brevity, cellulose samples with an ash content < 0.001% are referred to as de-ashed.

** The lower value of the first figure characterizes the decomposition of the first 5-10% of cellulose in the presence of 0.07-0.09% ash; because of the high rate of the process for de-ashed cellulose samples, this stage of decomposition cannot be observed.

initial rate, which decreases by half when the samples have decomposed by 15-20%. With further decomposition, a slower decrease in the rates is observed.

Curves 2 in Figs. 1 and 2 characterize the rates of decomposition of cotton cellulose with an ash content of 0.06% and of hydrate cellulose with an ash content of 0.09%, which upon decomposition form levoglucosan in yields of up to 45%.

Table 1

Yield of volatile products of the thermal decomposition of two structural modifications of cellulose

Degree of decomposition of cellulose, in % of dry charge	Yield of levoglucosan, in % of decomposed cellulose	Yield of liquid volatiles, in % of decomposed cellulose	Yield of reducing substances in the paste-like distillate before hydrolysis, in % of paste-like distillate	Yield of other products in the paste-like distillate, in % of paste-like distillate	Yield of paste-like distillate, in % of decomposed cellulose	Levoglucosan content in the paste-like distillate, %
Cotton cellulose, ash content <0.001%	**Cotton cellulose, ash content <0.001%**	**Cotton cellulose, ash content <0.001%**	**Cotton cellulose, ash content <0.001%**	**Cotton cellulose, ash content <0.001%**	**Cotton cellulose, ash content <0.001%**	**Cotton cellulose, ash content <0.001%**
12	64	15	9	No	78	82

Degree of decomposition of cellulose, in % of dry charge	Yield of levoglucosan, in % of decomposed cellulose	Yield of liquid volatiles, in % of decomposed cellulose	Yield of reducing substances in the paste-like distillate before hydrolysis, in % of paste-like distillate	Yield of other products in the paste-like distillate, in % of paste-like distillate	Yield of paste-like distillate, in % of decomposed cellulose	Levoglucosan content in the paste-like distillate, %
17	70	14	8	No	84	84
31	65	14	10	3	82	79
46	67	13	10	1	84	80
95	64	14	12	5	85	75
Cotton cellulose, ash content 0.07%	**Cotton cellulose, ash content 0.07%**	**Cotton cellulose, ash content 0.07%**	**Cotton cellulose, ash content 0.07%**	**Cotton cellulose, ash content 0.07%**	**Cotton cellulose, ash content 0.07%**	**Cotton cellulose, ash content 0.07%**
3–4	20	30–40	14	23	30–40	57
7	35	52	13	17	56	63
28	45	25	11	15	68	67
36	41	27	16	18	70	59
58	45	27	15	13	70	65
86	35	27	17	22	64	54
Hydrate cellulose, ash content <0.001%	**Hydrate cellulose, ash content <0.001%**	**Hydrate cellulose, ash content <0.001%**	**Hydrate cellulose, ash content <0.001%**	**Hydrate cellulose, ash content <0.001%**	**Hydrate cellulose, ash content <0.001%**	**Hydrate cellulose, ash content <0.001%**
23	69	12	9	2	86	80
37	73	10	7	1	88	83
59	71	11	6	3	87	82
95	65	13	13	No	84	79

Degree of decomposition of cellulose, in % of dry charge	Yield of levoglucosan, in % of decomposed cellulose	Yield of liquid volatiles, in % of decomposed cellulose	Yield of reducing substances in the paste-like distillate before hydrolysis, in % of paste-like distillate	Yield of other products in the paste-like distillate, in % of paste-like distillate	Yield of paste-like distillate, in % of decomposed cellulose	Levoglucosan content in the paste-like distillate, %
Hydrate cellulose, ash content 0.09%	**Hydrate cellulose, ash content 0.09%**	**Hydrate cellulose, ash content 0.09%**	**Hydrate cellulose, ash content 0.09%**	**Hydrate cellulose, ash content 0.09%**	**Hydrate cellulose, ash content 0.09%**	**Hydrate cellulose, ash content 0.09%**
13	15	47	33	30	47	33
23	47	25	25	–	71	66
40	49	22	20	–	74	66
53	37	23	22	18	70	53
67	31	21	23	22	63	49
76	36	22	27	21	64	50

From a comparison of curves 1 and 2 it is evident that, on going from ash contents in cellulose of 0.20% to 0.06–0.09%, the character of the decomposition-rate curves changes sharply. These curves have a maximum at 20–30% decomposition of the sample.

The thermal decomposition of ash-free samples of cotton cellulose and hydrate cellulose is characterized by a similar course of the curves, with a maximum in the same range of decomposition, but in this case the decomposition proceeds at considerably higher rates (curves 3 in Figs. 1 and 2).

It should be noted that the rate of decomposition of all samples of hydrate cellulose is higher than that of the corresponding samples of cotton cellulose (Figs. 1 and 2).

Fig. 1. Rates of thermal decomposition of cotton-cellulose samples with ash content: *1*–0.22%, *2*–0.07%, *3*–0.001%

Fig. 2. Rates of thermal decomposition of hydrate-cellulose samples with ash content: *1*–0.26%, *2*–0.09%, *3*–0.001%

Fig. 1. Rates of thermal decomposition of cotton-cellulose samples with ash content: 1–0.22%, 2–0.07%, 3–0.001%

Figure 1: Fig. 1. Rates of thermal decomposition of cotton-cellulose samples with ash content: 1–0.22%, 2–0.07%, 3–0.001%

Fig. 2. Rates of thermal decomposition of hydrate-cellulose samples with ash content: 1–0.26%, 2–0.09%, 3–0.001%

Figure 2: Fig. 2. Rates of thermal decomposition of hydrate-cellulose samples with ash content: 1–0.26%, 2–0.09%, 3–0.001%

The pattern of change in the degree of polymerization of ash-free cellulose samples during decomposition is analogous to that described previously ([2]). However, the two structural modifications of cellulose that we studied differ in the limiting value of the degree of polymerization. This value is about 200 for cotton cellulose and 30-40 for hydrate cellulose.

The high rates of the process at a high yield of 1,6-anhydro-1,5-glucopyranose and the preservation of a constant degree of polymerization of cellulose throughout the entire decomposition after the sharp initial drop to a limiting value allow us to classify cellulose as a polymer capable of thermal depolymerization.

From a comparison of the absolute values of the maximum rates of thermal decomposition of cotton cellulose and hydrate cellulose and the limiting values of their degrees of polymerization, it follows that the macromolecules of cellulose in both of its structural modifications are in different energetic states.

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Note: Figure translations are in progress. See original paper for figures.