Cellulose destruction by electron-beam-induced heating

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An efficient method for producing furfural and other furan derivatives from cellulose was proposed. Radiolytic destruction of cotton cellulose, sulfate and sulfite pine celluloses, and carboxymethylcellulose was studied under electron-beam-induced distillation conditions. The yield of the liquid distillate from cellulose of various origin was about 60%. Furfural and its derivatives with the molecular weight up to 140 were the predominant products. Grinding and preheating of cellulose increase the fraction of furan derivatives in the condensate. The liquid products are partially transformed into high-molecular-weight compounds that are distilled with difficulty and that are involved in the formation of wood charcoal in the yield of about 20%.

Key words: cellulose, radiolysis, electron-beam-induced distillation, radiation-induced heating, destruction, furans, furfural.

Electron-beam-induced distillation (dry distillation using radiation-induced heating with a beam of accelerated electrons) seems interesting as a productive method for conversion of lignocellulose raw materials to furans, phenols, and acyclic carbonyl compounds demanded in various fields of chemistry and fuel industry.[1] Elucidation of regularities of destruction of cellulose, which is the most important structural cell component of all plants,[2] is of key significance for the solution of the problem of deep processing of renewable plant raw materials. In particular, any wood consists of cellulose by nearly 50%. In this work, we studied for the first time the efficiency of electron-beam-induced conversion of cellulose to liquid organic compounds depending on temperature, the degree of grinding, and types of the starting raw materials.

Experimental

Cotton cellulose (C1) (GOST 5556-81), pine sulfate unbleached cellulose (C2) (GOST 12765-88), pine sulfite bleached cellulose (C3) (GOST 3914-89), and carboxymethylcellulose (C4) (CP Kelco ApS) were used. The samples were dried at 107 °C and deaerated. Depending on the degree of grinding, electron-beam-induced distillation was studied for samples C2 with a specific surface of 49—104 $cm^2\ g^{-1}$ (grinding was carried out by cutting EKB-1 cardboard sheets). The influence of the type and initial temperature was studied for the samples with the specific surface $S = 104\pm4\ cm^2\ g^{-1}$.

Distillation was initiated by radiation-induced heating of the samples with accelerated electrons (without nuclear reactions) generated by an UELV-10-10T linear accelerator (energy 8 MeV, pulse duration 6 μs, pulse repetition frequency 300 Hz, average beam current ≤800 μA, scan width 245 mm, and scan frequency 1 Hz). The chart of a laboratory setup for electron-beam-induced distillation is shown in Fig. 1. Irradiation was carried out under atmospheric pressure with exclusion of air in 100-mL quartz cylindrical vessels (*2*). The reaction vessels were filled by 60% at an average packing density of 0.15 g mL^{-1}. The electron beam (*1*) was scanned along the vertical axis of the vessel. Vapor was condensed in air (*3*) (at 17±2 °C) and water (*4*) (at 15±2 °C) condensers outside the irradiation zone. Gaseous products were separated in an inertial separator *6* and blown-off with gas blower *8*. This unit is designed for decreasing the vapor and gas pres-

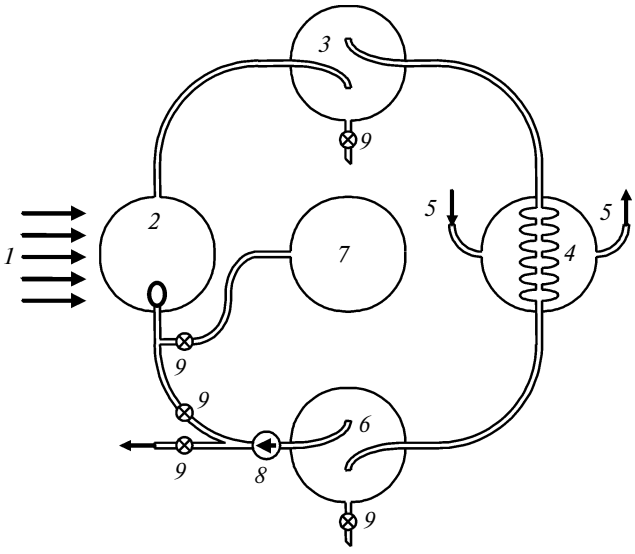

Fig. 1. Scheme of the laboratory setup: *1*, accelerated electron beam; *2*, quartz reactor; *3*, air condenser; *4*, water condenser; *5*, cooling water; *6*, inertial gas—liquid separator; *7*, cylinder with an inert gas; *8*, gas blower; *9*, valves.

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sure in the reactor over the period of very vigorous chain destruction of cellulose. The more efficient gas and vapor removal, the larger the amount of the condensate obtained and the weaker secondary irradiation of the condensate components. The setup was pre-filled with an inert gas (argon or nitrogen) from cylinder *7*. The direction of gas flows in different experimental steps was controlled by valves *9*. Experiments were carried out at an ambient air temperature of 16 °C.

The study of the temperature dependence was performed for samples C2 preheated at a constant temperature in a muffle oven for 30 min. The preheating temperature was at most 250 °C in order to avoid the initiation of pyrolytic dry distillation of the samples. The preheating stage was directly followed by the stage of electron-beam-induced heating. Electron-radiation dosimetry was effected using a copolymer with phenazine dye SO PD(F)R-5/50 (GSO 7865-2000). The average dose power (P) was 2.1 kGy s^{-1}. Vaporous products distilled off upon cellulose destruction were condensed outside the irradiation zone and analyzed with a Perkin Elmer AutoSystem XL GC-MS spectrometer (helium as a carrier gas, glass capillary column 60 m long with the inner diameter 0.25 μm, mass spectrometer and katharometer as detectors) using the Q-Mass program package including the NIST mass spectra library. The microscopic images of the starting samples and wood charcoal were obtained on JEOL JSM 6490 LV and Philips PSEM-500 scanning microscopes.

Results and Discussion

Telemetric observation revealed no substantial differences in electron-beam-induced distillation of samples C1, C2, and C3. At a dose of ~250 kGy, heavy steam fog rises from the reaction vessel and gradually flows into the condenser. Its color changes from the initial white to bright yellow. A condensate appears in the receiver, its level increases as the irradiation proceeds. Vapor formation and the rise of the condensate level cease at a dose of ~500 kGy. The condensate is formed in a yield of ~60% (Table 1), being a homogeneous odorous brown liquid. The condensate is characterized by high density, viscosity, and refractive index, which is not typical of water-organic solutions formed upon pyrolysis.[2] A dry black powder (wood charcoal) with a smaller volume than that of the starting sample remains in the reaction vessel after distillation. Carbon (89.1 at.%) and oxygen (10.6 at.%) are its prevailing structural elements. Mineral admixtures are also observed: Ca, 0.07; Cu, 0.10; Zn, 0.13 at.%. The coal yield is about 20% of the dry cellulose weight.

Table 1. Yield (G), refractive index (n_D^{18}), density (ρ^{18}), and viscosity (η_0) of the condensates ($S = 104$ cm^2 g^{-1})

Sample	G (wt.%)	n_D^{18}	ρ/kg dm^{-3}	η_0/mPa s
C1	63	1.4479	1.1639	5.96
C2	58	1.4479	1.1560	5.67
C3	60	1.4455	1.1594	5.79

Electron-beam-induced distillation of carboxymethylcellulose sodium salt C4 occurs with vigorous formation of dense white smoke. The solid dry residue (yield 56%) is a foamed dark brown mass, whose volume was approximately twice as large as that of the starting material. The condensate (yield ~15%) is separated into two liquid phases: brown organic tar (~1/10) and a faintly colored water-organic solution. The main organic components of the condensate are acetic acid, methyl formate, butane-2,3-dione, vinyl acetate, and hydroxyacetone. The overall yield of liquid organic compounds does not exceed 6%.

The content of the main components in the condensates obtained from cellulose samples C1, C2, and C3 are presented in Table 2. All components are of the same type and include more than 40 organic compounds with the molecular weights from 32 to 140. Furans are predominant liquid products, and furfural, furfuryl alcohol, 5-methyl-2-furaldehyde, and 3-furaldehyde prevail among them. The water content in the condensate does not exceed 8%. Similar results have been obtained earlier[3] in the study of distillation of cotton and sulfate celluloses in a flow of gaseous alkanes.

Grinding of cellulose C2 exerts no appreciable effect on the duration and intensity of electron-beam-induced distillation. The condensate yield remains unchanged: 58±1%. However, there is a tendency to decrease the yield of the dry residue and increase the yield of low-boiling-point fragmentation products (by approximately 2—3 wt.%) with an increase in the degree of grinding. In addition, the composition of the condensate changes: the finer the raw materials, the higher the density, viscosity, mean molecular weight, refractive index, and absorbance

Table 2. Average content (m) of the main components in the condensates obtained from cellulose samples C1, C2, and C3 ($S = 104$ cm^2 g^{-1})

Component	m (wt.%)		
	C1	C2	C3
Methyl formate	0.9	0.8	1.3
Acetone	4.9	2.7	3.4
Formic acid	5.0	5.2	3.6
Butane-2,3-dione	1.6	3.5	1.7
2-Oxopropanal	3.4	0.6	0.8
Acetic acid	7.3	6.0	3.1
Hydroxyacetone	7.3	10.7	1.5
sec-Butyl acetate	1.8	0.9	2.0
Furfural	40.4	42.4	48.2
3-Furaldehyde	2.1	1.9	2.8
Furanmethanols	2.0	2.8	4.7
Methylfuraldehydes	9.4	13.3	17.3
Furfuryl acetates	1.2	1.6	2.8
2,2-Dimethyl-3(2*H*)furanone	1.4	1.7	0.9
Overall furans	*62.5*	*64.4*	*79.0*

of the condensate (Figs 2 and 3). The following tendencies were revealed by the comparison of the component composition of the condensates obtained with an increase in the degree of powdering of cellulose:

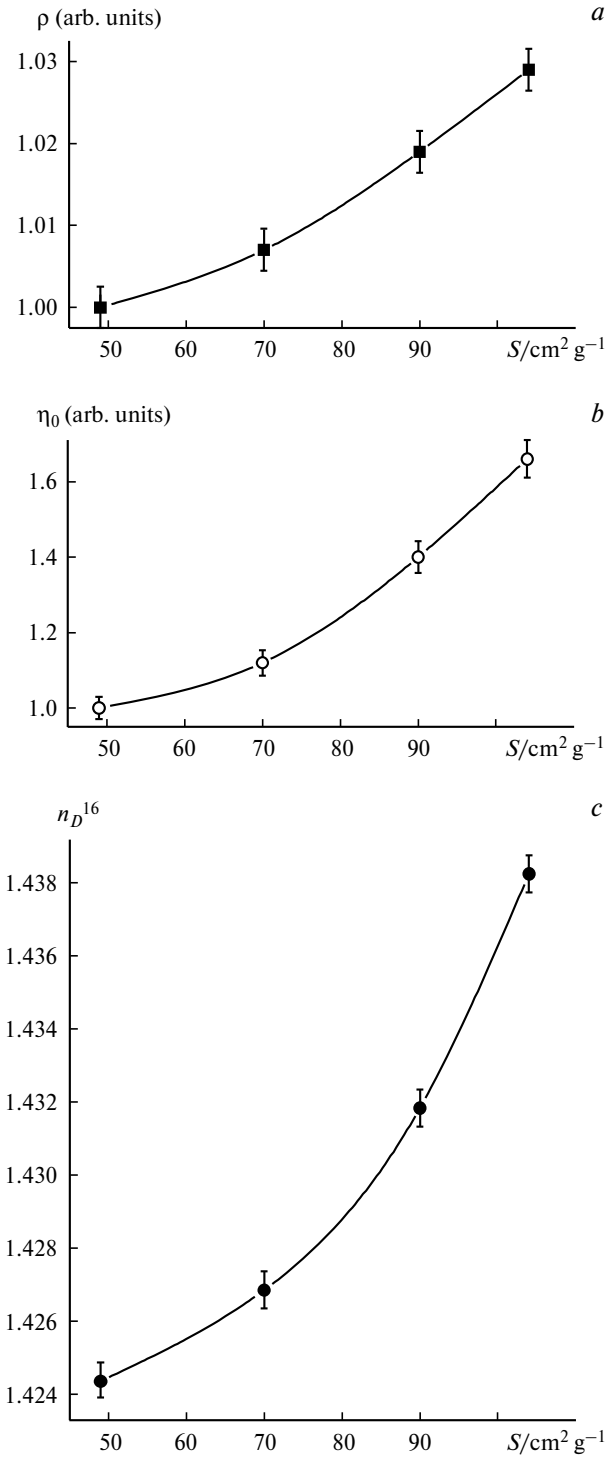


Fig. 2. Influence of the specific surface (S) of samples C2 on the density ρ (*a*), viscosity η_0 (*b*), and refractive index n_D^{16} (*c*) of the condensate.

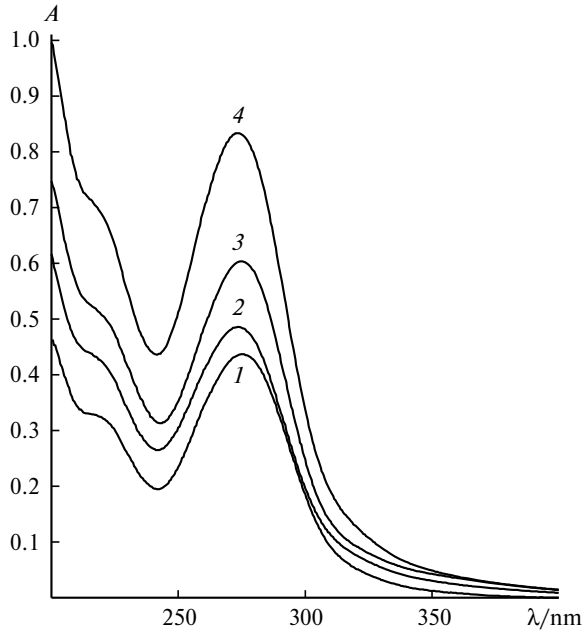


Fig. 3. Absorbance spectra (A) of the condensates distilled from C2 at the initial temperature 16 °C (*1*—*3*) and 230 °C (*4*) for the samples with the specific surface S = 49 (*1*), 70 (*2*), and 104 $cm^2\ g^{-1}$ (*3*, *4*).

(1) the fraction of "heavy" furan derivatives, being products of relatively non-deep cellulose fragmentation (such as furaldehydes, furanmethanols, furanones) increases;

(2) the fraction of deeper (secondary) cellulose fragmentation products (such as hydroxyacetone, acetic and formic acids) decreases;

(3) the fraction of "heavy" products (such as furfuryl acetates) formed in secondary reactions of the predominant primary products also decreases.

Evidently, the products of radiolytic cellulose fragmentation are formed both on the surface and in the bulk of solid particles. Time is required for the migration of fragmentation molecules from the bulk of the solid particle to the surface (into the mobile vapor phase). This increases the probability of additional radiolytic destruction of the primary fragmentation products or their reactions with other products to form "hybrid" compounds. It is most likely that an effect of this kind can explain the difference in composition of the condensates obtained upon distillation of the samples with different degrees of grinding.

The influence of preheating of the sample to temperatures not higher than 250 °C (to avoid cellulose pyrolysis before irradiation[2,3]) on electron-beam-induced distillation was studied. No noticeable temperature effect on the condensate was observed. According to the telemetric data, the time of distillation onset somewhat decreased for the preheated samples, but the time of distillation completion was independent of the initial temperature. This indicates that radiolysis and radiation-induced heating rather than

the temperature of the starting raw materials are the predominant factors determining the dynamics of electron-beam-induced distillation. The yield of the condensate in the studied temperature range from 16 to 250 °C was 58.0±1.5 wt.%.

The usual process of dry distillation is initiated at ~270 °C. Seemingly, the radiation-induced heating of more hot samples would result in faster distillation. However, this is not the case. In the temperature range from 230 to 270 °C, irradiation did not increase the rate of cellulose heating. The temperature rise is retarded, indicating the initiation of an efficient endothermic process. The boiling point of the major part of liquid radiolytic destruction products lies within the range 100—250 °C. The heats of vaporization is 30—46 kJ mol^{-1} (see Refs 4 and 5). Energy expenses to evaporation several times exceed the heat storage acquired by cellulose during preheating (about 3.1 kJ mol^{-1} based on one glucopyranose unit). The temperature in the reactor during distillation is determined by the yield, composition, and heat of vaporization of the radiolytic products.

Figures 3 and 4 indicate that preheating favors the formation of a heavier condensate: its density, viscosity, and refractive indices increase with the rise of the initial temperature (see Fig. 4). The molar weight of the condensate increases smoothly from ~87 to ~94 g mol^{-1}. The absorbance at the band with λ_{max} = 275 nm characteristic of furans increases (see Fig. 3). The overall fraction of furan derivatives in the condensate increases from 60 to 72 wt.% with an increase in the initial temperature. Furaldehydes (about 75% of which are represented by furfural) remain to be the predominant component of furans. At the initial radiolysis stages where the influence of preheating is most significant, the fast migration, distillation of light fragmentation products, and decomposition of thermally unstable fragments occur. This prevents their influence on the subsequent radiolysis stages and involvement in reactions with heavier products. Preheating reveals the predominant significance of radiolytic processes in the formation of the final products. The vigorous formation of CO_2 and a whole series of other radiolytic products in a chain process prevents excess warming of cellulosic raw materials, thus avoiding the development of destruction and distillation according to an unfavorable pyrolytic mechanism.

The major gaseous destruction products are CO_2, H_2, and CO. Carbon dioxide and dihydrogen are formed in approximately equimolar amounts, whereas the yield of CO is lower by an order of magnitude. The weight fraction of the fragments —O—C—O— (probable precursors of CO_2) as determined stoichiometrically in the ring $C_6H_{10}O_5$ is ~27 wt.%. At the same time, the experimental total yield of CO_2 and CO is ~20% of the dry weight of cellulose. There are several possible reasons for the difference between the calculated and experimental yields of CO_2.

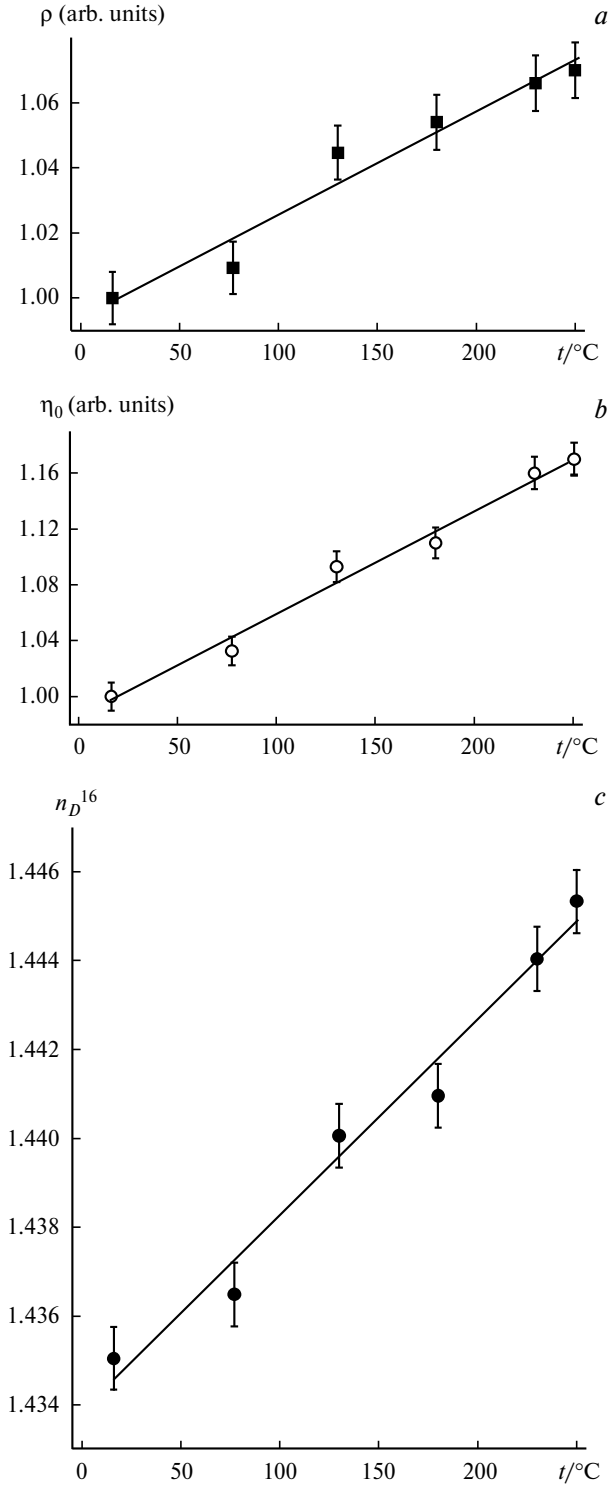


Fig. 4. Influence of the initial temperature of samples C2 (S = 104 cm^2 g^{-1}) on the density ρ (*a*), viscosity η_0 (*b*) and refractive index n_D^{16} (*c*) of the condensate.

Among them are incomplete cellulose destruction, competitive processes of formation of carboxyl compounds occurring without CO_2 elimination, and inconsistency

between the real composition of the samples and the classical formula of cellulose. The latter can be due to technological factors: bleaching, sterilization, *etc*. (they require special investigation). For example, elemental analysis of sample C1 indicated that the real initial oxygen content was 10% lower than the theoretical value. In addition, sample C1 contained about 1.8 wt.% of mineral components. Thus, in the samples under study, a part of carbon is contained in the units depleted in oxygen. Probably, this part of wood charcoal could be formed due to the condensation of the destruction products with the formation of high-boiling-temperature compounds, whose distillation from the reaction zone is impeded. The dry residue obtained from samples C1—C3 consisted of two fractions: a fiberous soft (by touch) mass (resembling in structure the starting cellulose; atomic ratio C/O ≈ 8.4, Fig. 5, *a*) and solid inclusions (frozen melt as balls and plates, atomic ratio C/O ≈ 6.4, see Fig. 5, *b*) with the porous structure. The second fraction is present on the charcoal surface and, most likely, forms in condensation reactions. In particular, under dry distillation conditions, condensation reactions are characteristic of furfural and a series of its derivatives.[6] In an acidic medium, furfural was shown[6] to decompose rapidly to yield formic acid and humic substances (50 g of formic acid and 41.5 g of humic substances are formed from 100 g of furfural). Refractory humic compounds and similar condensation products are retained in the irradiation zone, undergo caking, and, most likely, form the second fraction of a coal-like residue. Probably, the main route of reducing the yield of condensation products is faster distillation of furfural homologs from the reactor.

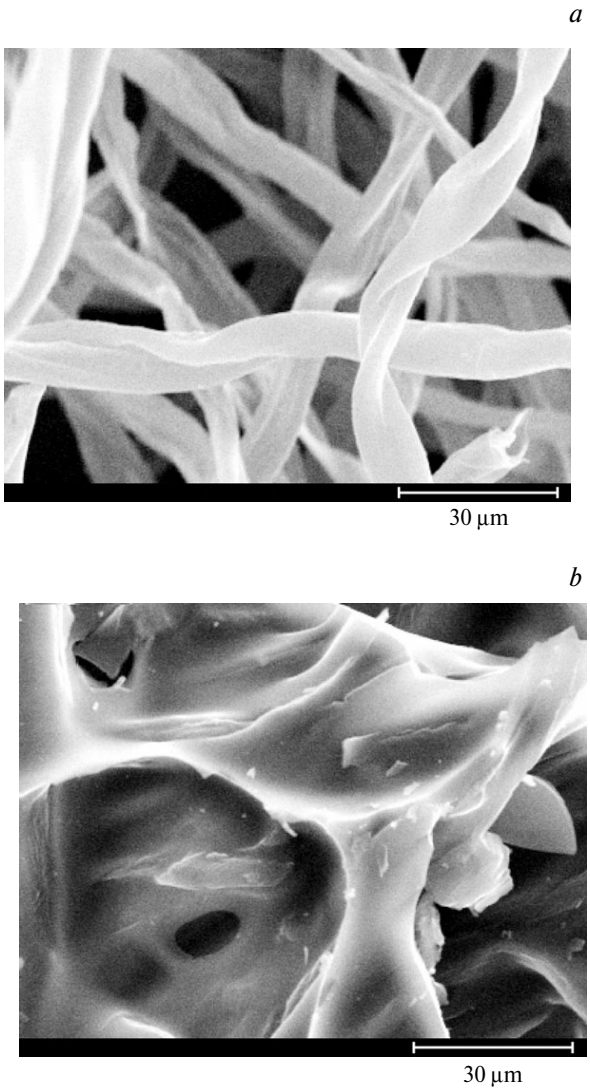


Fig. 5. Structures of the bulk (*a*) and surface (*b*) wood charcoal fractions obtained from sample C3 (scanning electron microscopy, microimage size 105×80 μm).

In practice, furfural is synthesized by the acid-catalyzed hydrolysis of pentosans, which are the components of easily hydrolyzable plant hemicelluloses[2,6]

$$(C_5H_{10}O_5)_n - 3\,H_2O \longrightarrow C_5H_4O_2.$$

Both the hydrolysis and pyrolysis of cellulose, unlike hemicelluloses, are characterized by the low probability of furfural formation.[1,2,6] In the present work, we used the samples depleted in hemicelluloses. Therefore, the high yield of furfural is due to the destruction of the cellulose itself.

The experimentally observed yield of CO_2 with allowance for the real composition of the samples indicates that the predominant majority of or almost all glucopyranose units undergo decomposition upon electron-beam-induced distillation. The radiolytic action consisting of the ionization and excitation (Scheme 1, reactions *1* and *2*) of cellulose macromolecules results, most likely, in the cleavage of the weakest C—H bonds in positions 1 and 4 of the glucopyranose ring[7] (reaction *3*). The formed radicals $^{\bullet}H$ dehydrogenate other cellulose fragments in the same positions (reaction *4*).

Scheme 1

$$RH \longrightarrow RH^+ + e^- \longrightarrow RH^* \qquad (1)$$

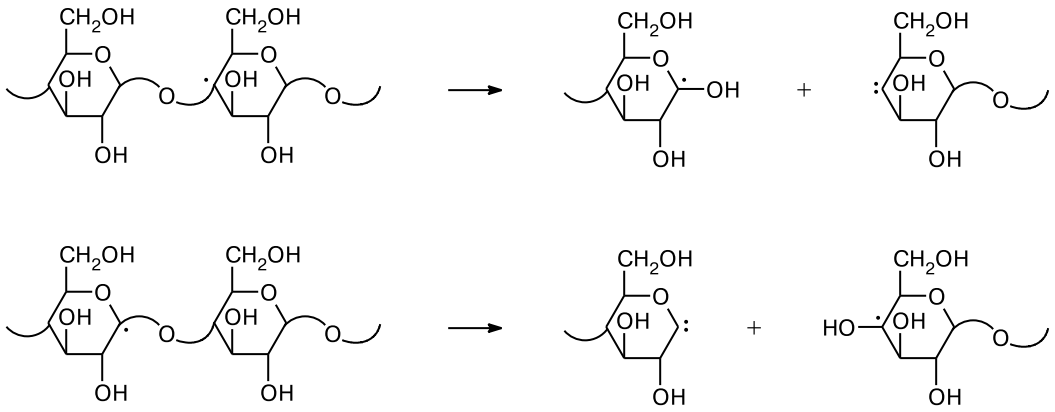
$$RH \longrightarrow RH^* \qquad (2)$$

$$RH^* \longrightarrow R^{\cdot} + {}^{\cdot}H \qquad (3)$$

$$RH + {}^{\cdot}H \longrightarrow R^{\cdot} + H_2 \qquad (4)$$

It is most likely that the primary radicals $R^{\cdot}$ are unstable and decompose already at ambient temperature with the glycosidic bond cleavage[7,8] (Scheme 2) due to considerable strains caused by inconsistency of the electronic configurations of the formed radical center

Scheme 2



(sp^2-hybridization) and the initial fragment (sp^3-hybridization).

It is most likely that the intermediate products formed upon electron-beam-induced distillation are thermally unstable and decompose following the chain mechanism with the predominant evolution of CO_2, H_2O, and an organic fragment (mean formula $C_5H_6O_2$). The decomposition stage of the glucopyranose rings can be written as a balance equation

$$C_6H_{10}O_5 \longrightarrow CO_2 + H_2O + H_2 + C_5H_6O_2.$$

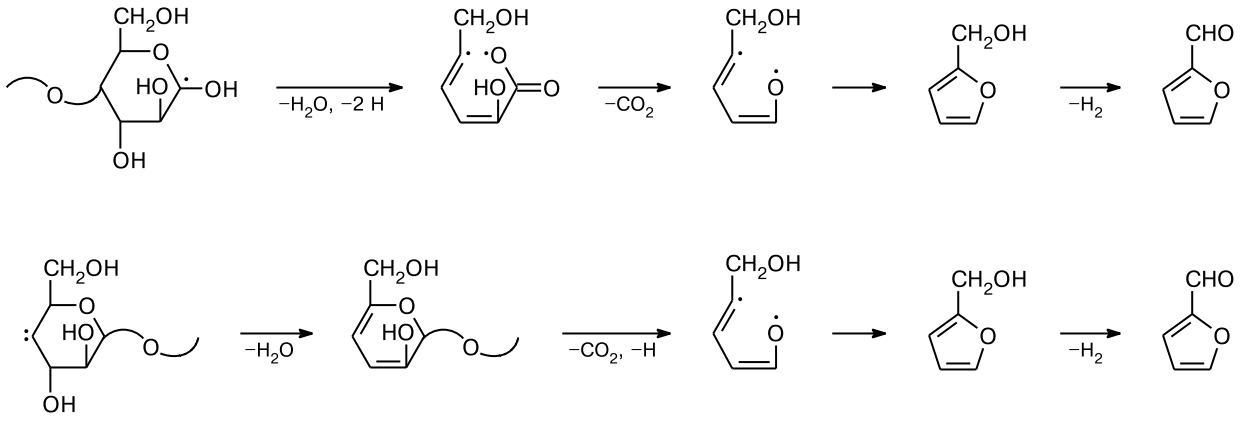
In particular, the formation of furfuryl alcohol and furfural can be due to the thermostimulated β-cleavage[9,10] of skeletal bonds, which is characteristic of radicals (Scheme 3).

The organic fragments R liberated from the glucopyranose ring can exist in several configurations determined by a series of factors: the site of primary cleavage of the C—H bond; the site of localization of an unpaired electron upon organic radical transformation; the position of the double bond formed due to the dehydration or dehydrogenation of the radical; excessive energy and temperature; the presence and structure of a system of hydrogen bonds; steric factors controlling the removal of the fragmentation products from the site of their formation, and some other. The possibility of several forms of the liberated fragment predetermines the probability of various routes of its stabilization or transformation into the final low-molecular-weight products. The chain development of cellulose destruction is due, most likely, to both the liberation of H atoms and thermal instability of shorter radicals that are formed during the decomposition of the primary radical intermediates.

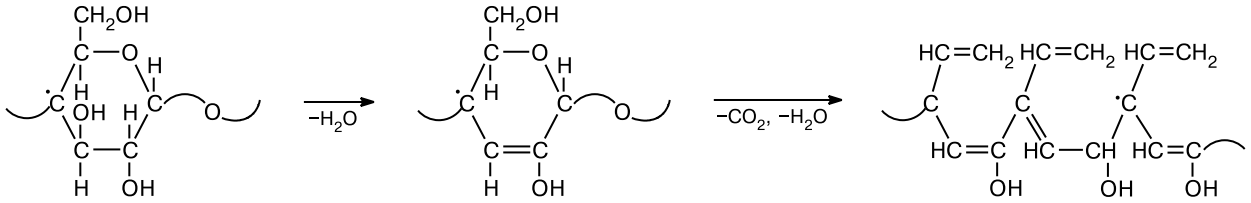
Obviously, the dense packing of cellulose molecules in fibrils[2,7] can prevent the removal of the formed fragmentation products. This increases the probability of transformation of allylic radicals into more stable polyene radicals[11] (Scheme 4), preceding coal-like residue formation.

Some organic fragments, such as furfural, being active acceptors of radicals and excessive energy,[6,10] are involved

Scheme 3



Scheme 4



in fast reactions with other fragmentation products or decompose, which enlarges the set of final products.

When irradiation is performed at a lower dose power (~0.15 kGy s^{-1}), which is insufficient for efficient heating and initiation of distillation, cellulose turns yellow but remains in the solid state. For the post-radiation dry distillation of sample C2 (dose 500 kGy), the yields of the condensate and wood charcoal are 47 and 32 wt.%, respectively. A substantial decrease in the condensate yield compared to electron-beam-induced distillation additionally indicates an important role of the processes that occur directly during radiolysis. Post-radiation dry distillation is accompanied only by the thermal destruction of stable molecular cellulose fragments with a reduced degree of polymerization. Probably, the intermediates formed and decomposed upon pyrolysis differ from the products of radiolytic reactions (see Scheme 2). This determines the difference in yields of the condensate and wood charcoal.

The differences in yields and compositions of the condensates distilled from pine cellulose C2 and C3 are determined, most probably, by the distinction of methods of chemical treatment of pine wood used for cellulose extraction. The residual content of lignin and polysaccharides is determined, to a great extent, by the method applied to pulping and bleaching of raw materials.[2]

Carboxymethylcellulose C4 differs from samples of cellulose C1—C3 in chemical composition and low molecular weight. The more vigorous evolution of CO_2 upon electron-beam-induced distillation of C4 indicated the predominant localization of excessive energy on the additional carboxyl group. The carboxyl groups easily evolve CO_2 and thus provide the protection of the remained molecular framework from decomposition.

Thus, about 60 wt.% of the liquid condensate are formed due to the electron-beam-induced distillation of cellulose of different origin. Furfural and its derivatives predominate among the liquid products. Grinding and preheating of the starting raw materials favor an increase in the fraction of furfural and its derivatives in the condensate. Radiolysis of carboxymethylcellulose, unlike that of cellulose, is accompanied by a more vigorous evolution of CO_2 and a low yield of liquid organic products. The used regime of electron-beam-induced distillation seems to be a promising method for production of furfural and other furan derivatives. Unlike the traditional methods based on extraction and conversion of hemicelluloses, this method makes it possible to use most abundant plant materials (including wastes) rich in cellulose as raw materials.

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