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RADIATION CHEMISTRY

Formation of Furans upon Electron-Beam Heating of Cellulose

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Abstract—Similarity between cotton cellulose and sulfate and sulfite pine celluloses in degradation during electron-beam distillation has been shown. The yield of the distillate liquid slightly depends on the type of cellulose and makes up ~60 wt %. The product liquid contains organic compounds with molecular masses of 32 to 128, of which furfural and its derivatives prevail. Electron-beam distillation can be used as an effective method for the manufacturing of furfural and other furan derivatives from cellulose (along with the traditional pentosan conversion processes). It has been shown that grinding and preheating of cellulose lead to an increase in the proportion of furfural and other furans in the condensates.

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INTRODUCTION

Destructive distillation initiated by radiation heating with a fast-electron beam (electron beam distillation) is of interest as an efficient means of conversion of lignocellulose raw materials into furans, phenols, and acyclic carbonyl compounds demanded by a variety of chemical and fuel industries [1]. Concerning the problem of deep processing of renewable raw materials, it is of primary importance to reveal of the basis features of degradation of cellulose, which is the key structural component of cell walls in all plants [2]. In this work, we investigated the efficiency of electron-beam conversion of cellulose into liquid organic compounds, depending on temperature, degree of comminution, and the type of feedstock.

EXPERIMENTAL

Cotton cellulose (O1) according to GOST (State Standard) 5556-81; pine unbleached sulfate pulp (O2), GOST 12765-88; and pine bleached sulfite pulp (O3) according to GOST 3914-89 were studied. Cellulose samples were dried at 107°C and deaerated. To study the dependence of electron-beam distillation on the degree of grinding of raw materials, O2 samples with a specific surface area of 49–104 cm^2/g (shredding by cutting sheets of EKB-1 cardboard) were used. The effect of the type and the initial temperature of cellulose was studied using samples with a specific surface area of 104 ± 4 cm^2/g. Distillation was initiated by the radiation heating of samples with fast electrons generated by a UELV-10-10T linear accelerator (energy 8 MeV, pulse duration 6 μs, pulse repetition frequency of 300 Hz, average beam current ≤800 μA, sweep width 245 mm, scanning frequency of 1 Hz). Irradiation was carried out at atmospheric pressure without air in 100-ml cylindrical quartz vessels. The reaction vessels were filled to 60% of their volume at an average packing density of 0.15 g/ml. The electron beam was scanned along the vertical axis of the vessel. The vapors were condensed in the air and water-cooled condensers (at 16 ± 2°C and 15 ± 2°C, respectively) outside of the irradiation zone. To study the temperature dependence, the O2 samples were preliminary thermostated in a muffle furnace over 30 min. To avoid the initiation of pyrogenetic dry distillation of the samples, the preheating temperature was maintained not higher than 250°C.In this case, the preheating step was immediately followed by electron-beam heating. Dosimetry was performed with the use of a copolymer containing a phenazine dye SO PD(F)R-5/50 (GSO (State Standard Sample) 7865-2000). The average dose rate P was 2.1 kGy/s. Distillation products were determined chromatographically on a "Perkin Elmer AutoSystem XL" instrument (the carrier gas helium, glass capillary column of 60 m length and an internal diameter of 0.25 μm, mass spectrometer and thermal conductivity detectors).

RESULTS AND DISCUSSION

According to telemetric observation data, the O1, O2, and O3 samples do not significantly differ in the dynamics of electron-beam distillation. Heavy vapor begins to flow from the reaction vessel to the condenser and the receiving container at a dose of ~250 kGy. Its color varies from the original white to bright yellow. The formation of vapor and the rise of the condensate level in the receiver cease at a dose of ~500 kGy. The condensate is formed with a yield of ~60 wt % (see table). It is a homogeneous brown liquid with high density, viscosity, and refractive index values, a fact that is not typical of pyrolytic aqueous–organic solutions [2]. The distillation residue is a dry black powder (charcoal) with a volume smaller than that of the original sample. The yield of the charcoal is about 20% of the mass of dry cellulose. The elemental composition of the charcoal is characterized by a predominance of carbon (89.1 mol %) and oxygen (10.6 mol %). Mineral impurities are Ca (0.07 mol %), Cu (0.10 mol %), and Zn (0.13 mol %) compounds.

The composition of the condensates is of the same type (see table) and includes more than 40 organic compounds with a molecular mass in the range of 32 to 128. The amount of water in the condensates varies from 8 to 10 wt %. The main liquid products are furans, such as 2-furaldehyde (furfural), 2-furanmetanol, 5-methyl-2-furaldehyde, and 3-furaldehyde. Some differences in yield and composition between the condensates distilled from pine cellulose O2 and O3, apparently stem from differences between the processes of the chemical treatment of wood used for the extraction of cellulose. A similar condensate composition has been observed previously [3] in the study of distillation of cotton cellulose and kraft pulp in a stream of gaseous alkanes.

The shredding of O2 results leaves the condensate yield almost unchanged, 58 ± 2 wt %. There is a tendency toward a fall in the yield of the solid residue and a rise in that of volatile fragmentation products (about 2–3 wt %). The condensate composition changes in this case, the smaller the particle size of the raw material, the higher the density, viscosity, average molar mass, refractive index, and optical absorption values of the condensate (see Figs. 1, 2). As the degree of comminution increases, the fraction of heavy furan derivatives, which are the products of relatively slight fragmentation of cellulose (such as furaldehydes, furanmethanols, and furanones) increases. At the same time the proportion of products of deeper (secondary) fragmentation of cellulose (such as 1-hydroxy-2-propanone and acetic and formic acids) is reduced, as well as the relative amount of heavy products (such as furanmethanol acetates) resulting from secondary processes of interaction between the prevalent primary products.

The products of radiolytic fragmentation of cellulose are probably formed both on the surface and in the bulk of solid particles. The migration of fragment molecules from the bulk of a solid particle to the surface (in the moving vapor phase) takes time, thereby allowing for the secondary radiolytic and thermal degradation of the primary fragmentation products or their

Yield G (wt %, on a dry cellulose basis) and properties of condensates (refractive index n_D^{18}, density ρ^{18}, viscosity η_0) and average content of their major components

Sample ($S = 104$ g/cm^3)	O1	O2	O3
G, wt %	63	58	60
n_D^{18}	1.4479	1.4449	1.4455
ρ, kg/dm^3	1.1639	1.1560	1.1594
η_0, mPa s	5.96	5.67	5.79
Amount of major components in condensate (wt %)			
Methyl formate	0.9	0.8	1.3
Acetone	4.9	2.7	3.4
Formic acid	5.0	5.2	3.6
2,3-Butanedione	1.6	3.5	1.7
2-Oxopropanal	3.4	0.6	0.8
Acetic acid	7.3	6.0	3.1
1-Hydroxy-2-propanone	7.3	10.7	1.5
1-Methylpropyl acetate	1.8	0.9	2.0
2-Furaldehyde	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
Total furans	62.5	64.4	79.0

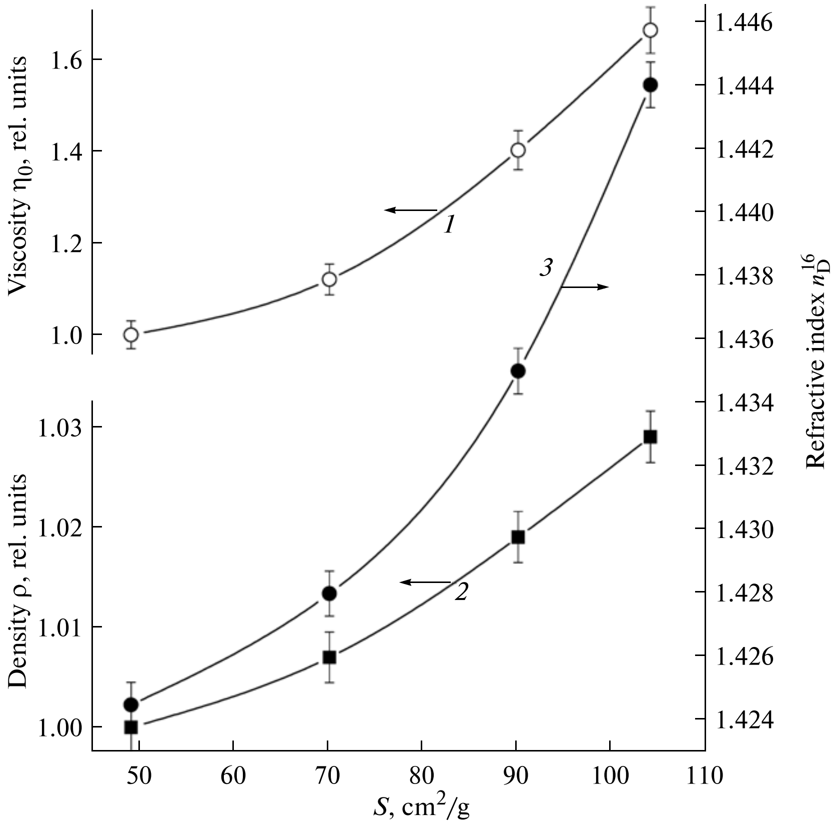


Fig. 1. Influence of the specific surface area of O2 samples on the (*1*) viscosity η_0, (*2*) the density ρ, and (*3*) the refractive index n_D^{16} of the condensate.

reaction with other products yielding the 'hybrid' compounds. It is effects of this kind that seem to be responsible for the influence of the degree of comminution on the composition of the distillates condensed.

To preclude the pyrolytic decomposition of cellulose before irradiation [2, 3], the dependence of electron-beam distillation on the severity of preheating was investigated at a temperature T_0 no higher than 250°C. In the preheated samples, the distillation onset time decreased somewhat, but the time of its completion was not dependent on the initial temperature T_0. This implies that the radiolysis and radiation heating determine the dynamics of electron-beam distillation to a greater extent than does the feedstock temperature. The yield of condensate was 58.0 ± 1.5 wt % in the examined temperature range of $T_0 = 16–250°C$. Most liquid products of radiolytic degradation have a boiling point in the range of 100–250°C. Their heat of vaporization is 30–46 kJ/mol [4, 5]. The consumption of energy for evaporation is several times greater than the amount of heat received by cellulose during preheating (about 3.1 kJ/mol per glucopyranose cycle).

At the same time, preheating facilitates the formation of a heavier condensate (see Figs. 2, 3); namely, as the initial temperature T_0 increases, a rise in its density, viscosity, and refractive index is observed. The molar mass of the condensate smoothly increases from ~87 to ~94 g/mol. The absorbance at the band with λ_{max} = 275 nm characteristic of all furans increases (see Fig. 2). The total amount of furan derivatives in the condensate increases from 60 to 72 wt % with the increasing initial temperature. In this case, furaldehydes remain the dominant furan species (of which about 3/4 is made up by furfural). It is likely that preheating promotes more rapid migration and distillation of light fragmentation products on one hand and the degradation of thermally unstable fragments at the initial stages of radiolysis on the other hand. Being distilled off, the primary products are eliminated from the subsequent stages of radiolysis and do not participate in secondary reactions. The results of experiments with preheating indicate the predominant role of radiolytic processes in the formation of the final products. The violent chain formation and vaporization of a large mass of radiolytic products prevents the excess heating of the cellulose feedstock, thereby precluding the development of degradation and distillation via the unfavorable “pyrogenetic” mechanism.

The main gaseous degradation products are CO_2, H_2, and CO. Carbon dioxide and hydrogen are formed in about equimolar amounts, whereas the yield of CO is an order of magnitude lower. The stoichiometrically determined mass fraction of the –O–C–O– fragments (probable precursors of CO_2) in the $C_6H_{10}O_5$ cycle is about 27 wt %. However, the experimental total yield of CO_2 and CO is approximately 1/5 of the dry cellulose mass. The formation of charcoal and the low gas yield suggest the existence of competitive cellulose degradation processes. In particular, the decrease in the yield of gases can be due to the processes of formation of carboxyl and carbonyl compounds, which do not involve the elimination of CO_2 or CO. A part of the charcoal may result from chemical condensation of degradation products when high-boiling-point compounds, which are difficult to distill from the reaction zone, are formed. As shown in Fig. 4, the dry residue of samples O1–O3 was composed of two factions, the soft fibrous matter (resembling the original cellulose in structure; C/O atomic ratio ≈ 8.4, see Fig. 4a) and solid inclusions (in the form of beads and plates, the C/O atomic ratio ≈ 6.4, see Fig. 4b) with a porous structure. The second fraction occurs on the charcoal surface and seems to be produced via condensation and secondary transformations of heavy vaporous products. In particular, condensation processes under dry distillation conditions are characteristic of furfural

$$2C_5H_4O_2 \rightarrow C_{10}H_6O_3 + H_2O \qquad (1)$$

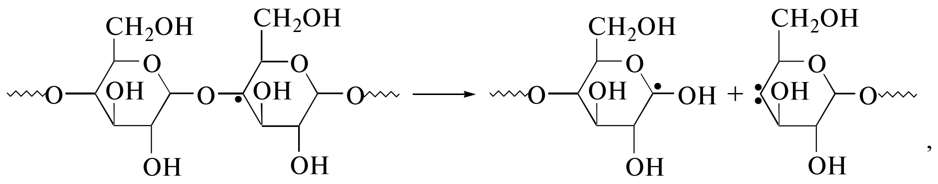
and some of its derivatives. It was shown [6] that furfural rapidly degrades in an acidic medium, yielding formic acid and humic substances (100 g of furfural gives 50 g of formic acid and 41.5 g of humic substances). The formation of macromolecular products due to furfural interaction with intermediate compounds can play a significant role as well [6].

In practice, furfural is produced by acid hydrolysis of pentosans, which are components of the composition of easily hydrolysable plant hemicelluloses [2, 6]

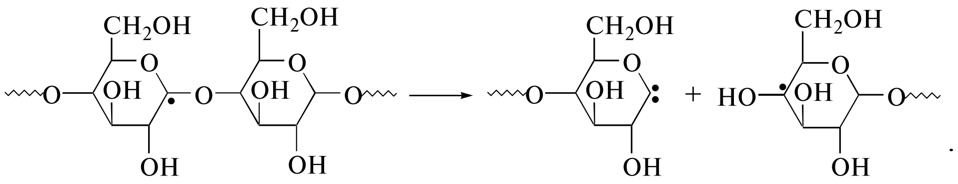
$$C_5H_{10}O_5 - 3H_2O \rightarrow C_5H_4O_2. \qquad (2)$$

Both the hydrolysis and pyrolysis of cellulose, in contrast to hemicellulose, is characterized by a low furfural formation probability, ~10 wt % [1, 2, 6]. In this study, we used hemicellulose-depleted samples. Consequently, the high yield of furfural is due to the degradation of the cellulose itself.

The primary radicals of cellulose (generated mainly via the abstraction of H atom in the 1- or 4-position of the glucopyranose cycle [7]) are unstable and, as a result of significant strain caused by the mismatch of electron configurations of the radical center produced (sp^2 hybridization) and the initial fragment (sp^3 hybridization) decompose even at room temperature with a cleavage of the glycosidic bond [7, 8]:



(3)



(4)

Apparently, the intermediate products of reactions (3) and (4) are thermally unstable and decompose via a chain mechanism, releasing prevalently CO_2, H_2O, and an organic fragment R (average formula $C_5H_6O_2$). The stage of decomposition of glucopyranose cycles can be written in the form of balance equation:

$$C_6H_{10}O_5 \rightarrow CO_2 + H_2O + H_2 + C_5H_6O_2. \qquad (5)$$

In particular, the formation of furfuryl alcohol and furfural can be due to the thermally stimulated β-cleavage of skeletal bonds typical of radicals [9, 10]:

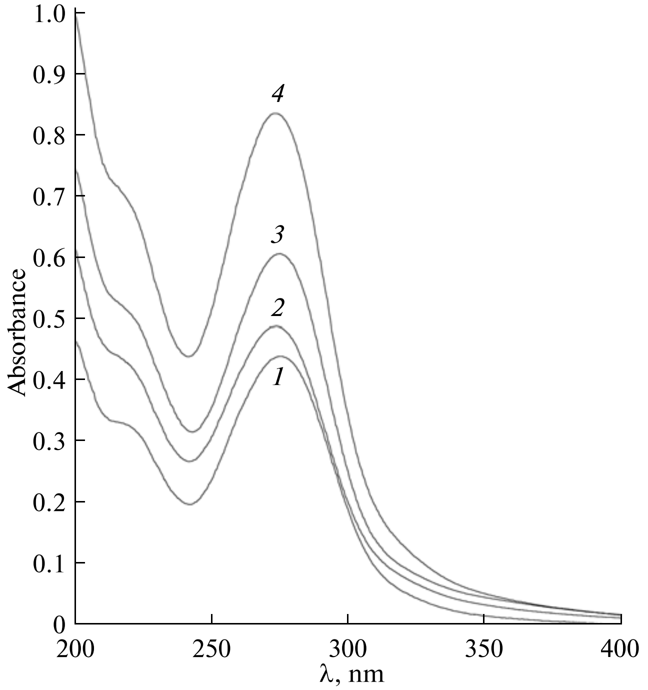
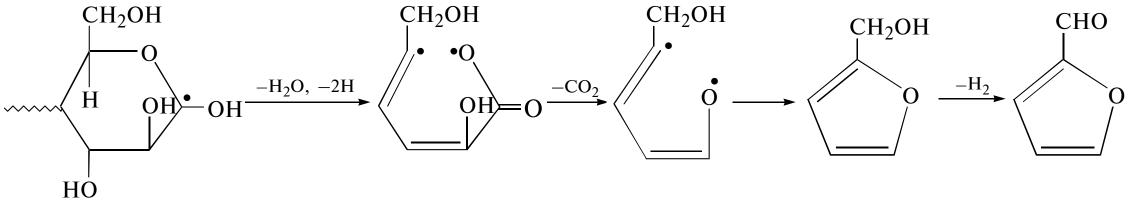
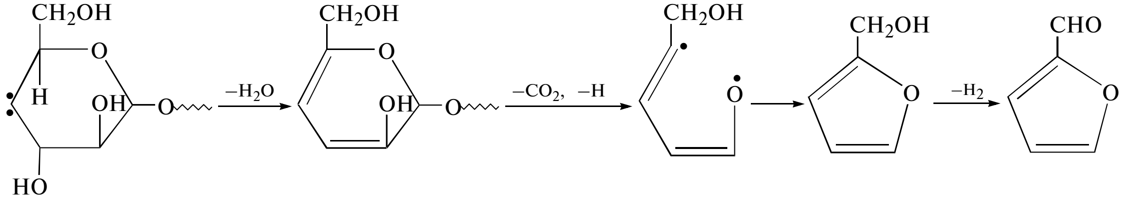


Fig. 2. Electronic absorption spectra of the condensates distilled off O2 at initial temperatures of 16°C (*S* = (*1*) 49, (*2*) 70, and (*3*) 104 cm^2/g) and 230°C ((*4*) *S* = 104 cm^2/g).



(6)



(7)

The organic fragment R released from the glucopyranose cycle in reactions of type (6) and (7) can have several configurations determined by a number of factors: the site of the primary C–H bond rupture, the place of localization of the unpaired electron during the transformation of the organic radical, the position of the double bond formed as a result of dehydration or dehydrogenation of the radical, the excess energy and temperature, the presence and structure of the hydrogen bond system, steric factors controlling the detachment of the fragmentation products from their formation place, and some others. The possibility of existence of a few forms for the released fragment determines the likelihood of different ways of its stabi-

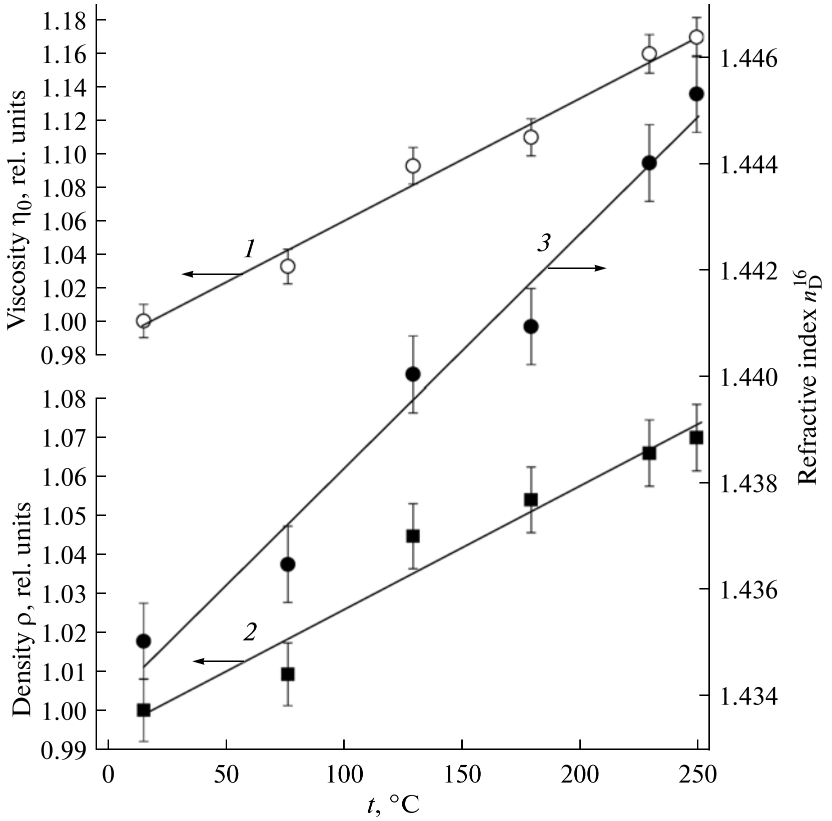
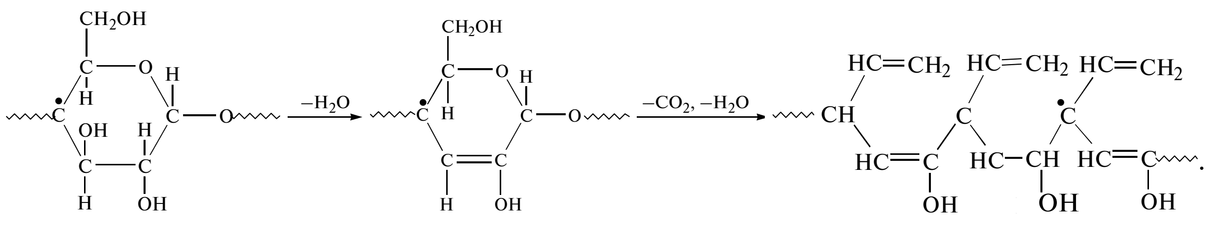


Fig. 3. Influence of the initial temperature of O2 samples (S = 104 cm^2/g) on (*1*) the viscosity η_0, (*2*) the density ρ, and (*3*) the refractive index n_D^{16} of the condensate.

lization or transformation into final low-molecular-mass products. The chain mode of cellulose degradation is apparently due to both the release of H atoms and the thermal instability of shorter radicals resulting from the decay of the primary radical intermediates. Obviously, the close packing of molecules in cellulose fibrils [2, 7] can impede the removal of the fragmentation products. This increases the probability of conversion of allyl radicals into more stable polyene radicals [11]



(8)

which precede the formation of the coal-like residue.

A part of the organic fragments, such as furfural, being effective of radical scavengers and acceptors of excess energy [6, 10], are involved in rapid reactions with other products of the fragmentation or decay, thereby extending the range of end products.

In summary, the electron-beam distillation of cellulose of different origin gives about 60 wt % of liquid condensate. The liquid products are dominated by furfural and its derivatives. Their proportion in the condensate distilled off is facilitated by shredding and preheating of the feedstock. The electron-beam dry distil-

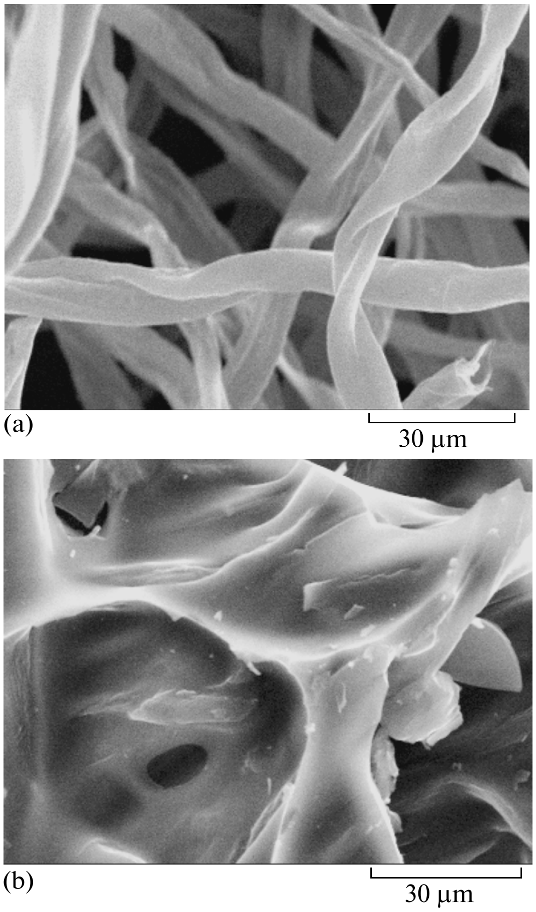


Fig. 4. Structure of the (a) bulk and (b) surface charcoal fractions (105 × 80 μm).

lation mode holds promise as a method for obtaining furfural and other furan derivatives. Unlike the conventional methods based on the extraction and conversion of hemicelluloses, this process can make use of the most widespread cellulose-rich plant materials (including waste) as feedstock.

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