Russian Chemical Reviews **81** (10) 918 – 935 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n10ABEH004266

Fundamental aspects of radiation-thermal transformations of cellulose and plant biomass

A V Ponomarev, B G Ershov

Contents

I.	Introduction	918
II.	Radiation techniques and processing of renewable plant biomass	918
III.	Destruction of cellulose at moderate absorbed dose rates	920
IV.	Radiation-thermal transformations of cellulose at high dose rates	922
V.	Radiation-thermal transformations of lignin	928
VI.	Electron-beam distillation of wood	929
VII.	Conclusion	932

Abstract. The results of radiation-thermal transformations of cellulose are generalized. It is shown that an event of radiation chemical destruction of polymeric cellulose chain involves local 'explosion' of the glucopyranose ring, resulting in carbon dioxide and compounds with terminal carbonyl and carboxyl groups. Effects of the absorbed radiation dose rate and heating conditions on the product composition and yields are analyzed. It is shown that at high dose rates ($\geqslant 1$ kGy s^{-1}), instantaneous and uniform heating of the whole sample promotes high-energy processes with distillation of liquid condensate mainly composed of furfural and other furan derivatives, which are considered among the most promising components of alternative engine fuels. The mechanism of the radiation-thermal transformations comprising the formation of terminal radical and dehydration, elimination and decomposition of the glucopyranose unit of cellulose to give furfural and formaldehyde is discussed. It is substantiated that utilization of accelerated electrons could provide implementation of direct one-step transformation of cellulose and lignocellulose biomass into components of liquid engine fuel and intermediates for large-scale chemical synthesis. The bibliography includes 99 references.

I. Introduction

Cellulose and wood products find wide use in everyday life. Processes that include radiation treatment of wood materials are also known.[1–3] Examples are sterilization of medicines and bandaging materials; destruction of lignocellulose raw materials to intensify its hydrolytic processing into food, forage and technical products; production of explosives, lacquers, viscose, various monoses and feed for farm animals; radiation pretreatment of cellulose for production of its esters (nitrates, xanthates, *etc*.) and so on. It is also important to emphasize that cellulose, lignin and other components of wood material represent convenient models for the analysis of effects of irradiation on biological systems. All these issues stimulate interest in the study of mechanisms of radiolytic transformations of wood and its components and elucidation of effects of temperature, raw material characteristics (composition, state) and other factors on the efficiency of radiation destruction of the plant materials.[4–7]

Initially, studies of cellulose destruction with cleavage of the polymer chain were mainly carried out at room and moderate temperatures when pyrolytic processes related to the raw material distillation do not occur. The situation has changed considerably in the past few years when it was shown[8,9] that the radiolysis of cellulose and wood materials at higher temperatures (> 190 °C) results in deeper transformations with formation of liquid organic products and gases. It has become apparent that radiation techniques may play an exceptional or even revolutionary role in solving the problem of processing renewable plant biomass into components of liquid engine fuel and intermediates for large-scale chemical synthesis.

A V Ponomarev, B G Ershov A N Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation.
Fax (7-495) 335 17 78, tel. (7-499) 234 62 44,
e-mail: ponomarev@ipc.rssi.ru (A V Ponomarev),
tel. (7-495) 333 95 67, e-mail: ershov@ipc.rssi.ru (B G Ershov)

Received 25 August 2011
Uspekhi Khimii **81** (10) 918 – 935 (2012); translated by S E Boganov

II. Radiation techniques and processing of renewable plant biomass

The renewable plant lignocellulose raw materials may become a principal resource of chemical industry and the fuel industry in this century.[10–13] The global energetic and ecological crisis, largely caused by growing demand of energy resources and simultaneous inventory reduction of fossil fuel, dictates the need for using alternative energy

sources.[12–14] The trends of major economic and ecological indicators show that the future need of the mankind in energy and materials cannot be satisfied if the present pattern of the energy budged is preserved. At the same time, approximately 200 billion tons of biomass are reproduced annually; this is enough to meet the needs of the world population in the fuel and chemical and agricultural products.

Russia is the world' lead in forest area (> 850 million hectares). Wastes of wood processing and agricultural production (straw, husk, *etc.*) represent a substantial reserve of raw materials for manufacture of valuable products. Wood is important renewable resource, which will undoubtedly play a key role in the future strategy for energy security and sustainable human development. Conversion of the plant biomass to liquid and/or gaseous organic products can be considered as a promising way of raw material supply for the alternative energy sector and heavy chemical industry.[10, 12–14]

Comprehensive investigation of direct transformation of biomass into fuel or fuel components is a global and highly topical problem. Researches aimed at the development of efficient and profitable methods of utilization of the renewable plant raw materials in power engineering and chemical industry are actively carried out in all advanced countries. The methods based on bioprocessing and pyrolysis of the raw materials, resulting in production of producer gas, coal, liquid biofuel of various types and some additional products are being mainly developed.

According to our opinion, the radiation techniques also have a large potential in this area and can be considered as promising and innovative. The radiation techniques utilize penetrating and ionizing γ-radiation emitted by radioactive isotopes (mainly by ^{60}Co and ^{137}Cs) or high-energy electrons (usually of $\geqslant 200$ keV) generated in accelerators. At present, electron accelerators are used most widely as radiation sources due to economic and ecological reasons.[3] The cost of irradiation by accelerated electrons is significantly lower than by γ-quanta. In addition, the use of radioactive isotopes is associated with the risk of their emission to the environment, whereas electron accelerators are environmentally safe. They only emit electron radiation when connected to a power source. An additional substantial advantage of electron accelerators becoming more and more apparent is the possibility of radiation treatment at high temperatures. This advantage is fully employed in the plant biomass processing. If high absorbed doze rates are used, the accelerated electrons not only initiate chemical processes in the bulk of the irradiated material, but also heat it. As a result, both radiation-induced chemical and thermal processes are proceed in parallel on exposure to an electron beam, resulting in transformation of the lignocellulose raw material into stable liquid fuel (or fuel components).[15–17] Thus, an almost direct conversion of the plant biomass to fuel occurs in a single-step process.

There are three fractions of products of the electron-beam distillation of lignocellulose raw material that can be used as fuel:

1) liquid condensate (~60%);

2) gas (~20%) containing large amounts of hydrogen and carbon oxides and if mixed with gaseous alkanes, can be used as synthesis gas;

3) charcoal (~20%), which can also be converted to synthesis gas.

Thus, the degree of radiation conversion of lignocellulose to liquid fuel products can be approximately 60% to 90% of the dry plant material.

The quality of the liquid fuel and the proportions of components corresponding to the engine, diesel, jet engine fuels or fuel oil are controlled by varying the conditions of electron-beam distillation of the biomass and subsequent processing of the gas–vapour mixture. A typical evaporation curve of such a condensate obtained from birchwood in the methane flow is shown in Fig. 1 (the average content of vapour at the final stage is 1.7 mass %). As it is seen, the

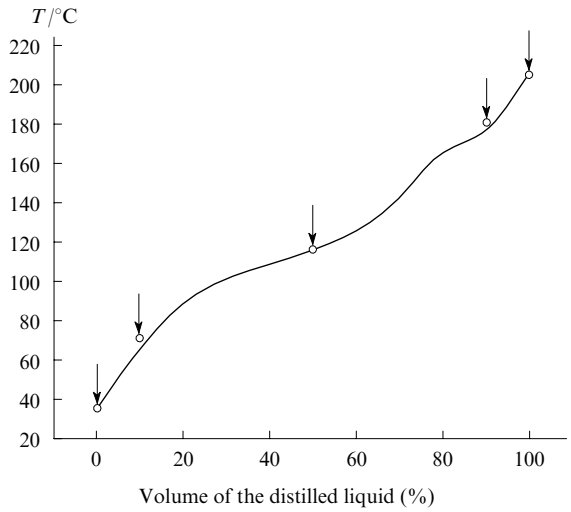


Figure 1. Evaporation curve of the product obtained from birch.[16]
The standard limits for fractional composition of motor fuel are indicated by dots and arrows.

formed liquid corresponds to the standard requirements to the fractional composition of the engine fuel.

Another important characteristic of fuels is their antiknock stability expressed in the octane number. Mixtures prepared from the vapour products of dry distillation of birchwood (at 1.5 mass % to 3.5 mass % vapour concentration in the gas–vapour mixture)[16] have octane numbers of more than 95.The average molar mass of the mixtures does not exceed 115 g mol^{-1}. It is also important that the heat of combustion of the obtained fuel exceeds more than three times the energy expenditure for its production.

The electron-beam conversion is waste-free and environmentally safe, which could become an important argument for its implementation. In addition to the liquid fuel, this may give high-quality charcoal, which can be used for the manufacture of effective sorbents or as conventional solid fuel.

Thus, the use of electron-beam distillation in plant biomass processing is of unquestionable practical value. Elucidation of the mechanism of biomass transformation under the simultaneous influence of radiation and heat is of a primary importance for the purpose of optimization of this process.

III. Destruction of cellulose at moderate absorbed dose rates

To understand the mechanism and efficiency of the processes occurring in plant materials exposed to ionizing radiation, we will consider cellulose. It is the major structural component of plants forming their cell walls.[1,2] Along with lignin, cellulose is the basis of plant biomass (50 mass % – 80 mass %). The major steps of the mechanism of the cellulose radiolysis and quantitative ratios of the formed products have now been established. The ways for intensification of the cellulose destruction by combined treatment of cellulose with ionizing radiation (at moderate absorbed dose rates) and heat (using supplementary heating devices) have been identified.[5,6,18,19]

1. Regularities in the cellulose destruction and its products

The action of ionizing radiation on cellulose, as on other polysaccharides, mainly results in its destruction. This process changes all the physicochemical properties of the material: its structural state, mechanical strength, solubility in various fluids, reactivity and so on. The change in the degree of polymerization of cotton cellulose (P_v is the average number of units in the polymer chain) depending on the absorbed dose (D) of γ-radiation is shown below:[3]

D /kGy	0	5	10	32	170	480
P_v	2537	827	723	314	138	32

It can be seen that the degree of polymerization reaching ~2.5 thousand units in the initial material decreased to almost 30 after irradiation to 480 kGy (1 kGy = 1 kJ kg^{-1}), *i.e.*, the average chain length decreased by a factor of approximately 80. The material was extensively destroyed. The destruction process is adequately described by equations based on random cleavages of a polymeric chain.[6] The dependence of the degree of polymerization of cellulose (P) on the dose (at $D \leqslant 200$ kGy) is linear and obeys the equation

$$\frac{1}{P} + \frac{1}{P^0} = \frac{1.62\,G^0 D}{N_A k}, \qquad (1)$$

where P^0 is the initial degree of polymerization of cellulose, k is an auxiliary coefficient, N_A is the Avogadro number. The radiation chemical yield of the destruction (below called the destruction yield, G^0) is 6 bonds per 100 eV of the absorbed radiation energy (~0.6 μmol J^{-1}), it almost does not depend on the dose rate of γ-radiation or accelerated electrons, on the starting degree of polymerization or microcrystallinity of the initial celluloses, or on whether irradiation was carried out in vacuum, under inert gases or in air. The lack of visible effect of air on the efficiency of cellulose destruction is a result of the dense crystal packing of cellulose, which hampers the diffusion of oxygen to reaction centres.

Application of higher doses (≥200 kGy) reduces the destruction rate. This effect is caused by accumulation of destruction products in the material. Intermediates of radiation chemical transformations and final products of radiolysis accept electrons, radicals and excitation energy, thus retarding further degradation of the biopolymer. For very high doses (>1 MGy), the cellulose destruction may be described by empirical equation (1), in which the D parameter is replaced by D^q, where exponent q is equal to 0.83 (Refs 20 and 21) or 0.73 (Ref. 22). Oxygen participates only in the surface radiolytic oxidation, resulting in the formation of carbonyl and carboxyl groups on the polymer surface. Destruction of cellulose becomes much slower upon moistening.[23,24]

Radiation at room temperature at low dose rates leads to deep chemical transformations of cellulose.[25–29] Among water-soluble products, cellobiose, glucose, arabinose, glyoxal and 2-keto-gluconic and some other acids were detected. Hydrolysis of the water-soluble fraction results in the formation of xylose, arabinose, glucuronic and formic acids, malondialdehyde, *etc*.

The effect of irradiation at room temperature on the concentration of the carbonyl and carboxyl groups in the cotton cellulose is illustrated in Fig. 2. The data show that the cellulose destruction gives mainly carbonyl compounds. The carbonyl group yield is equal to 6.5 ± 0.5 per 100 eV of absorbed radiation energy, whereas that of carboxyl groups is from 0.9 to 1.8.[22,30–35] Radiolytic formation of both carbonyl and carboxyl groups is almost independent of their starting concentration in the initial sample, and is determined by the absorbed dose. For instance, ~3 mmol of C=O and 1 mmol of CO_2H are formed in 100 g of cellulose at 50 kGy. The type of cellulose and the initial concentration of carbonyl and carboxyl compounds in it do not affect the product yields noticeably (Table 1).

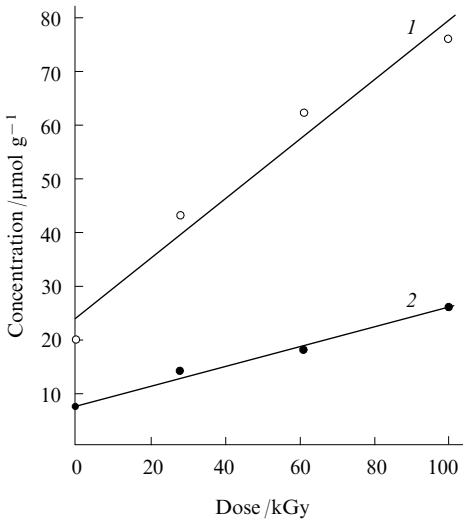


Figure 2. Accumulation of carbonyl (*1*) and carboxyl (*2*) groups during radiolysis of cotton cellulose.[24]

The concentrations of the carbonyl and carboxyl groups at high radiation doses are described by the non-linear dependence

$$c = BD^q,$$

where coefficient B is 6.8×10^{-7} for carbonyl groups and 1.8×10^{-7} for carboxyl groups,[20] the exponent q is equal to 0.50 – 0.69 for both groups.[22,30] It is obvious that upon cellulose destruction at high absorbed doses, carbonyl and carboxyl compounds are formed and then involved in subsequent radiolytic transformations.

Table 1. Initial concentrations and radiation chemical yields of oxygen-containing groups upon the cellulose γ-radiolysis.[33]

Cellulose type	Concentration /mmol per 100 g		Yield /mmol per 100 eV	
	CHO	CO_2H	CHO	CO_2H
Sulfite cellulose	0.13	0.24	6.0	2.0
High-viscosity sulfite cellulose	0.53	3.16	5.4	1.8
Cotton cellulose	0.10	0.45	5.9	2.5

Carbon monoxide, carbon dioxide and hydrogen are the major volatile products of cellulose radiolysis.[27,29,31,36–40] Their yields in vacuum at doses of ~ 300 kGy are 6.0, 0.9 and 3.2 molecules per 100 eV of absorbed radiation energy, respectively. Methane was also found among the volatile products.

2. The destruction mechanism

According to the generally accepted ideas about the nature of free radicals,[24,41–56] the radical states (unpaired electrons) in irradiated cellulose are predominantly located in positions 1 and 4 of the glucopyranose rings of the polymer. The probabilities of the C(1)–H and C(4)–H bond cleavages are rather similar at the liquid nitrogen temperature. Irradiated samples of frozen cellulose are dark blue-coloured due to optical absorption of electrons captured by cellulose. Wet samples have more intense colour.

The radiolytic destruction of cellulose (RH) is based on ionization, neutralization of ion–electron pairs and decay of excited states:

$$RH \longrightarrow RH^+ + e \quad (2)$$

$$RH^+ + e \longrightarrow RH^* \quad (3)$$

$$RH^* \longrightarrow R^\bullet + H^\bullet \quad (4)$$

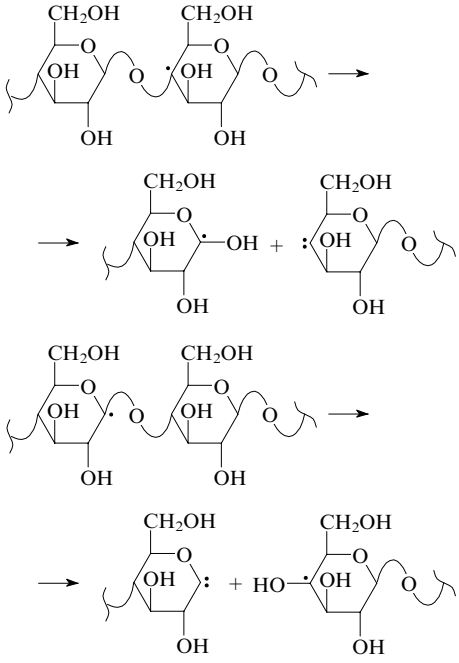
The excited states mainly decay with cleavage of the C(1)–H or C(4)–H bonds in the glucopyranose rings to give the $R^\bullet$ radicals (no $RO^\bullet$ radicals were detected in the irradiated cellulose samples). Free hydrogen atoms abstract glucopyranose hydrogen atoms giving the same $R^\bullet$ radicals.

$$RH + H^\bullet \longrightarrow R^\bullet + H_2 \quad (5)$$

The radiation chemical event in the cellulose polymeric chain occurs as a local 'explosion' of the glucopyranose ring. Destruction of the ring is a consequence of the fact that cellulose is a rigid-chain polymer, and the metastable radical centre formed upon its irradiation can be transformed into a stable radical only if the polymeric chain is cleaved and the monomeric (glucopyranose) unit is destroyed. The primary radicals $R^\bullet$ are unstable due to substantial deformations caused by mismatch between the electron configurations of the radical carbon atom (sp^2 hybridization, planar structure) and the starting macromolecular unit (sp^3 hybridization with the tetrahedral structure). Even at room temperature, the radicals $R^\bullet$ dissociate with cleavage of the glycosidic linkage (Scheme 1).[5]

Further decomposition of the fragments formed in these reactions (see Scheme 1) gives stable low-molecular-mass products. Thus, the cleavage of the cellulose polymeric

Scheme 1



chain results in elimination of a CO_2 molecule and formation of substances containing carbonyl and carboxyl groups. As noted above, the yields of carbonyl groups and CO_2 are rather close to the yield of polymeric chain destruction. This means that each cellulose chain cleavage event is accompanied by formation of a CO_2 molecule and a carbonyl group.

Decrease in the irradiation temperature from 300 to 77 K results in almost twofold reduction of the cellulose destruction yield and the yields of carbonyl compounds, CO_2 and CO. It is important to emphasize that the H_2 yield remains unchanged. Hence, the process of C–H bond cleavage is not temperature-dependent, whereas the glucopyranose ring decomposition may be retarded on cooling.

3. Effect of temperature

The radiation destruction of cellulose is a temperature-dependent process.[18] As the temperature at which irradiation is carried out increases, the degree of polymerization rapidly decreases. The temperature effect on the yield of radiation chemical destruction of cellulose is shown in Fig. 3. One can distinguish two temperature ranges differing by the efficiency of the radiation destruction of the biopolymer. Temperature rise from room temperature to ~100 °C has little effect on the destruction yield, while higher temperatures result in its significant increase. For example, the efficiency of radiation fragmentation at 190 °C is 6 times higher than at room temperature (see Fig. 3).

The temperature effect on the cellulose destruction is caused by the chain mechanism of this process. The destruction is initiated by radicals formed upon irradiation. The activation energy of the chain process[18] is 23.4 ± 1.6 kJ mol^{-1}. Such a value is typical of radical diffusion in a polymer and corresponds to the energy of conformational oscillations in the glucopyranose unit.[57] Increase in temperature initiates the transfer of the radical centre to a nearby polymeric chain, thus causing its destruction. Analogous radical chain transfer and destruction processes further propagate through the polymer bulk.

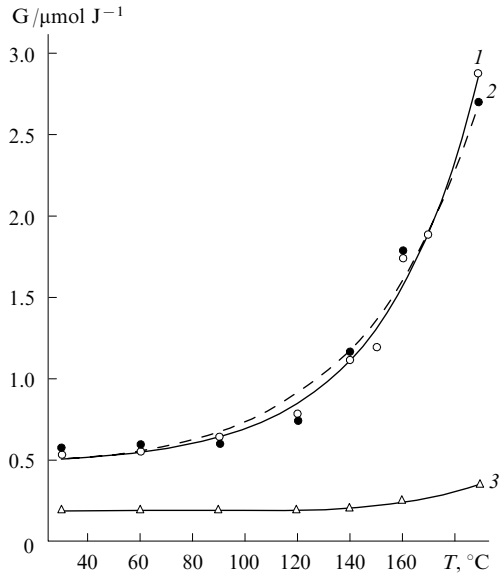


Figure 3. Temperature dependences of yields of the cellulose destruction (*1*) and formation of carbonyl (*2*) and carboxyl groups (*3*).[21]

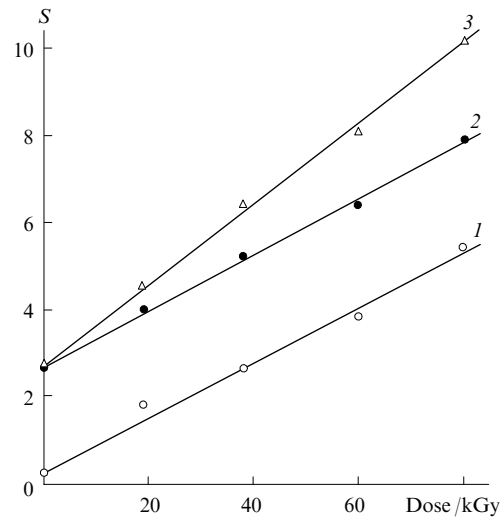


Figure 4. Dependences of the number of bond cleavages (S) on the dose for radiolysis of wood cellulose at various combinations of radiation and heating (3 h at 190 °C): (*1*) irradiation, (*2*) heating → irradiation, (*3*) irradiation → heating.[60]

The ratios of the major product yields remain the same as upon irradiation at room temperature (see Fig. 3). This fact evidences that the low- and high-temperature processes are the same, being accompanied by destruction of glucopyranose rings and elimination of CO_2 to give compounds containing carbonyl and carboxyl groups. The cellulose destruction at high temperatures is also characterized by increase in the yields of hydrogen and carbon dioxide.

The efficiency of the cellulose destruction depends on the succession of application of irradiation and heating.[58] Both irradiation and heat treatment decrease the degree of cellulose polymerization and increase the yield of hydrolytic sugar formation. The number of bond cleavages per cellulose macromolecule upon two-stage treatment in the sequence heating → irradiation obeys the equation

$$S_{(T\rightarrow R)} = S_T + S_R \qquad (6)$$

where S_R is the number of cleavages upon single-stage radiolysis, S_T is the number of cleavages upon single-stage heat treatment. Therefore the succession heating → irradiation is characterized by an additive effect.

On the other hand, the sequence irradiation → heating results in superadditive number of cleavages:[28, 59–61]

$$S_{(T\rightarrow R)} = S_R + S_T + \beta D, \qquad (7)$$

where β is a coefficient reflecting the increase in efficiency of thermal destruction of the irradiated cellulose at dose D. The sequence irradiation → heating also has superadditive effect on the yield of hydrolytic formation of sugar from the treated cellulose.[60]

The dependences of bond cleavage numbers on the absorbed doses are shown in Fig. 4 for some combinations of irradiation and heating procedures. The same slope of straight lines *1* and *2* implies that a preliminary heat treatment has no effect on the efficiency of the subsequent radiation destruction. At the same time, the larger slope of line *3* evidences more effective destruction of cellulose upon the succession irradiation → heating. The coefficient β correlates with the slopes of the dose dependences at the treatment temperature used. At 150, 170 and 190 °C, the values of β are equal to the following bond cleavage numbers per kGy: 0.004, 0.02 and 0.038.[28, 60]

IV. Radiation-thermal transformations of cellulose at high dose rates

The use of accelerated electrons at high dose rates makes it possible to implement the direct single-step conversion of cellulose into the liquid condensate (electron-beam distillation mentioned above). It is established[62, 63] that at dose rate of $\geqslant$1.5 kCy s^{-1}, such a treatment is accompanied by strong cellulose decomposition, which gives charcoal in addition to the liquid condensate.

1. Electron-beam distillation

The typical dynamics of electron-beam heating of cellulose (or wood) at dose rate of 2.5 kGy s^{-1} is shown in Fig. 5. The most active condensation of vapours in the condenser is observed 3 min after the start of irradiation, whereas wthin 6 min, vapour generation is completed.

The feebly marked step on the plot at 100 °C is caused by evaporation of the residual water and water formed during radiolysis. In the temperature range of 230–250 °C, the sample decomposes with rapid production of gaseous low-molecular-mass products. Then the temperature rise becomes slower (the shaded step on the curve, see Fig. 5) due to endothermic evaporation of the destruction products. The observed yield of condensed products of the cellulose distillation at this stage is $\geqslant$15 μ mol J^{-1}, this implies that the destruction proceeds according to the chain mechanism. When the formation of gaseous and liquid products is finished, charcoal is produced in the residue. Further irradiation is accompanied by warming-up of the charcoal residue.

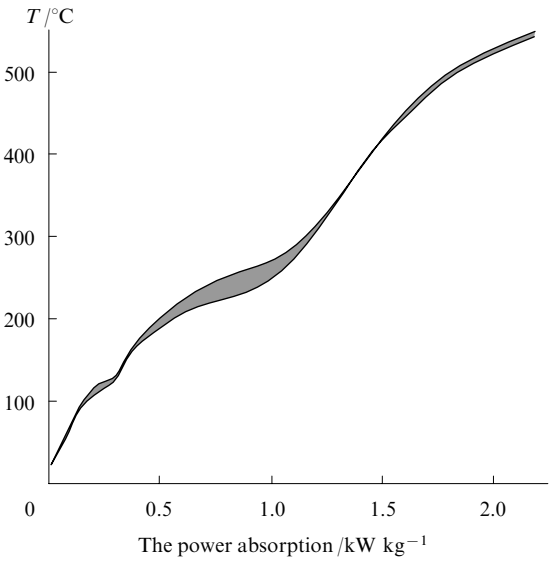


Figure 5. Dynamics of electron-beam heating of cellulose at the dose rate of 2.5 kGy s^{-1} [the specific surface area of the material (Z) is 105 cm^2 g^{-1}; the volume density is 150 g dm^{-3}].[9]
The temperature region of distillation of decomposition products is shaded.

The efficiency of the electron-beam conversion of cellulose to liquid organic products was studied depending on the initial temperature and the dispersion degree (specific surface area, Z) and the type of starting material.[62–64] Cotton cellulose (C1), unbleached pine sulfate cellulose (C2) and bleached pine sulfite cellulose (C3) were chosen for the comparison. Telemetry revealed no noticeable difference in dynamics of the electron-beam distillation of samples C1, C2 and C3 in the pressure range of 730–740 mm Hg in the absence of air. Irradiation with the dose of ~250 kGy is accompanied by formation of heavy fog slowly overflowing from the reactor to the condenser, its colour gradually changing from white to bright-yellow. The condensate is collected in a receiver flask, its amount increases in the course of irradiation. The vapour formation and the production of condensate ended at the dose of ~500 kGy. The condensate is a homogenous odorous brown liquid, its yield amounts to ~60 mass %. The physicochemical characteristics [refractive index (n_D^{18}), density (ρ) and relative viscosity (η_0)] of the condensates obtained from samples C1, C2 and C3 are summarized in Table 2.

Table 2. Yield of condensate [G (%) of cellulose dry mass] and physicochemical characteristics of condensates (Z = 104 cm^2 g^{-1}).[62]

Cellulose	G	n_D^{18}	ρ /kg dm^{-3}	η_0 /mPa s
C1	63	1.4479	1.1639	5.96
C2	58	1.4449	1.1560	5.67
C3	60	1.4455	1.1594	5.79

As mentioned above, a dry black residue (charcoal) remains in the reactor after distillation. Its volume is smaller than that of the starting material, its yield being ~16%–20% of the initial dry cellulose weight. Therefore most of the glucopyranose units are destroyed during the electron-beam distillation.

2. Products of electron-beam distillation

The major components of the condensates obtained from celluloses C1, C2 and C3 and their relative contents are shown in Table 3. All the condensates have similar composition and include more than 40 organic compounds with molecular masses from 32 to 165 The major liquid products are furans among which furan-2-carbaldehyde (furfural), 2-furylmethanol, 5-methylfuran-2-carbaldehyde and furan-3-carbaldehyde predominate. The content of water in the condensates is ~8 mass %. Analogous results were obtained earlier [15] in the studies of electron-beam distillation of cotton wool and sulfate cellulose fibres in a gaseous alkane flow. The fact of formation of furfural and other furan derivatives as predominant products of cellulose decomposition upon electron-beam distillation is unexpected because these products are formed in quite low yields upon radiolysis at temperatures below 190 °C (see Section III) and upon cellulose pyrolysis.[65]

Table 3. Contents (mass %) of major compounds in the condensates obtained upon radiolysis of cellulose samples (Z = 104 cm^2 g^{-1}).[62]

Compound	Cellulose		
	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
1-Hydroxypropan-2-one	7.3	10.7	1.5
sec-Butyl acetate	1.8	0.9	2.0
Furancarbaldehydes	42.5	44.3	51.0
Furylmethanols	2.0	2.8	4.7
Methylated furancarbaldehydes	9.4	13.3	17.3
Furans [a]	72.5	64.4	79.0

[a] The total amount is indicated.

Grinding of cellulose C2 has practically no effect on the duration and intensity of the electron-beam distillation. The condensate yield remains unchanged, being 58% ± 1% of the cellulose weight. However, some tendency to decreasing yield of the charcoal residue and increasing yield of gaseous products (approximately by 2 mass %–3 mass %) was observed for more finely ground samples C2. The condensate composition also changed: the more finely ground is the starting material, the higher are the density, viscosity, average molecular mass and refractive index (Fig. 6).

As the cellulose specific surface area increases, the absorption band of the condensate at 275 nm becomes more intense (Fig. 7). This band is due to absorption of furan derivatives, its increase indicates that the yields of these compounds increase with increase of dispersity of the starting material.

Thus, the following trends for condensate composition are observed with increase in the cellulose specific surface area:

— the content of the fraction of furan derivatives, which represent large fragments of glucopyranose (furancarbaldehydes, furylmethanols, furanones, *etc.*), increases;

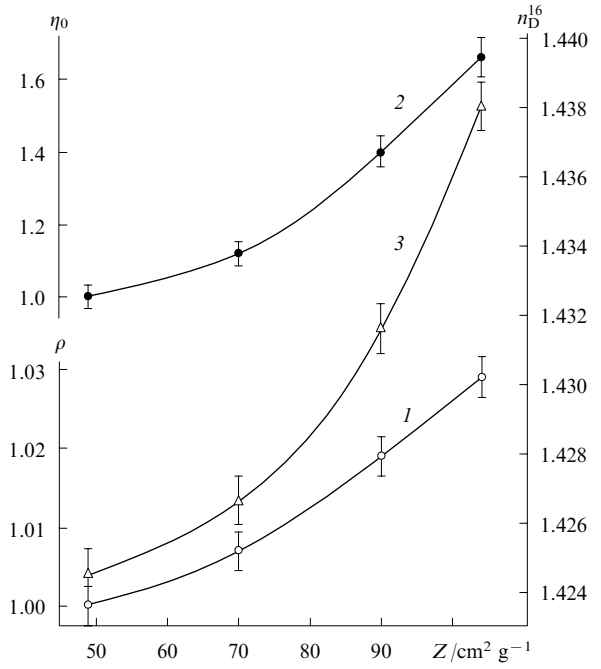


Figure 6. Effect of the specific surface area of cellulose C2 samples on density (*1*), viscosity (*2*) and refractive index (*3*) of condensates.[62]
Here and in Fig. 8, the relative changes in the density and viscosity are shown (these parameters of the sample with $Z = 48$ cm^2 g^{-1} are taken to be unity).

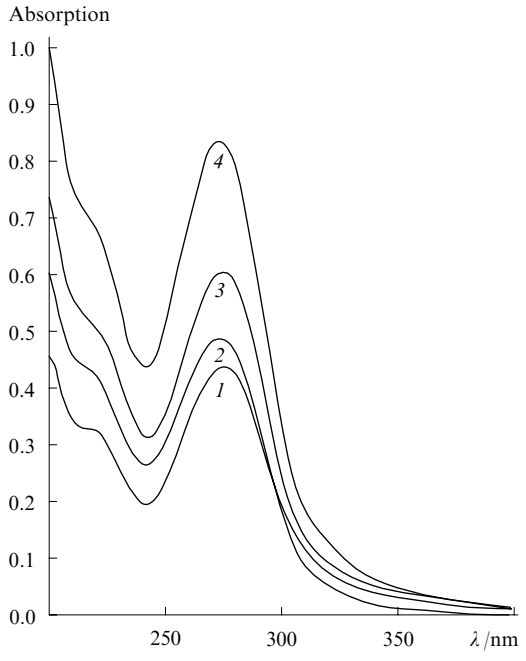


Figure 7. UV spectra of condensates obtained from cellulose C2 samples with specific surface areas of 49 (*1*), 70 (*2*), 104 cm^2 g^{-1} (*3*) at starting temperature of 16 °C, and also for a sample with $Z = 104$ cm^2 g^{-1} (*4*) at 230 °C.[18]

— the content of the fraction of small fragments of glucopyranose (1-hydroxyacetone, acetic and formic acids) decreases;

— the content of the fraction of heavy products (furylmethyl acetates), which are formed apparently in the secondary reactions between the major primary products, also decreases.

The products of radiolytic fragmentation of cellulose are formed both on the surface and in the bulk of the material. Migration of the fragments from the bulk to the surface (into the mobile vapour phase) takes some time, thereby the probability of a secondary radiolytic or thermal decomposition of the primary products and their reactions with other products (to give 'mixed' compounds) increases. Apparently, all this changes the composition of condensates obtained from samples with different degrees of grinding.

To estimate the contribution of pyrolytic decomposition of samples,[1] the effect of cellulose preheating (before irradiation) on the electron-beam distillation at ~250 °C was studied. It was found that the change in the initial temperature affects insignificantly the condensate yield. According to the telemetry data, the time elapsed before vapour appeared in the heated samples was slightly reduced but the time of completion of the distillation did not depend on the starting temperature. This fact indicates that the dynamics of cellulose decomposition is controlled by radiolysis and radiolytic heating stages but is not determined by the temperature of the raw material. The condensate yield was 58.0 ± 1.5 mass % when the temperature of the raw material was varied from 16 to 250 °C. Pyrolysis of cellulose is usually initiated at ~270 °C. It may seem that radiation heating of hotter samples should result in faster distillation; however this is not the case.

The data shown in Fig. 8 indicate that preheating favours the formation of heavier condensate: when the initial temperature of the raw material before irradiation was increased, the resulting condensate had higher density, viscosity and refractive index. The average molar mass of the condensate increases monotonically from ~87 to ~94 g mol^{-1}. The optical density at $\lambda_{max} = 275$ nm (characteristic band of furans) also increases as it is seen in Fig. 7. The furan derivative fraction in the condensate grows from 60 mass % to 72 mass %, being mainly composed by furancarbaldehydes (furfural content is ~75%).

The effect of preheating is most significant at initial steps of radiolysis: faster migration and removal of primary destruction products and thermal destruction of labile fragments take place. This precludes participation of the primary products in further radiolytic transformations. The sample preheating experiments reveal the predominant influence of radiolytic processes on the formation of final products of the distillation. The vigorous chain formation of carbon dioxide and other products and their release into the gas–vapour phase prevent cellulose overheating and thus divert its decomposition and distillation from the unfavourable pyrogenetic mechanism.

As mentioned above, preheating of cellulose has no significant effect on its electron-beam distillation. Nevertheless, the auxiliary heating during irradiation increases the yield of liquid products almost up to 70 mass % and decreases the yields of charcoal and gases. As shown in Fig. 9, with increase in the power of an auxiliary electrical heater, the condensate being distilled becomes heavier. due to increase in the fraction of furan derivatives. This is

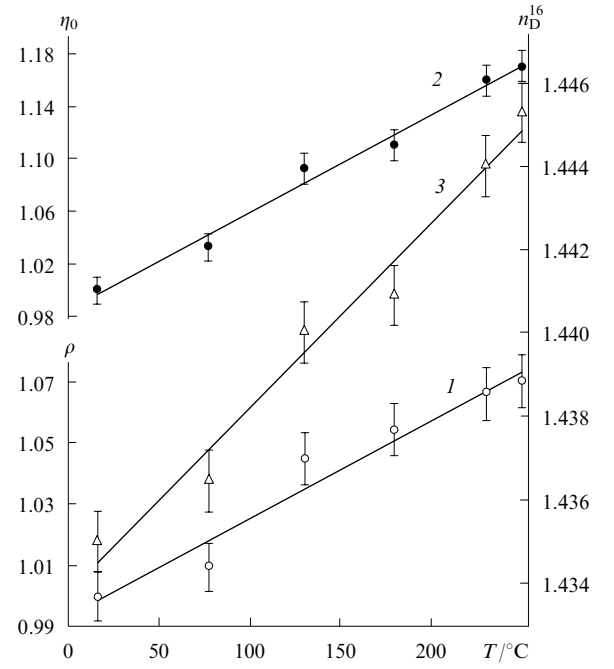


Figure 8. Effect of the starting temperature of radiolysis of C2 samples (Z = 104 cm^2 g^{-1}) on the density (*1*), viscosity (*2*) and refractive index (*3*) of condensates.[18]

observed only if the simultaneous radiation and auxiliary electrical heating maintain a temperature of the cellulose sample (during distillation of low-molecular-mass products) of up to 270 °C (the onset of pyrolysis). If the auxiliary heating is too intense, conventional pyrolysis (dry distillation) starts to prevail, the sample is fast heated to the pyrolysis onset temperature, the yield of the distilled condensate decreases, and water becomes the predominant component in the condensate (the viscosity and the refractive index decrease, see Fig. 9).

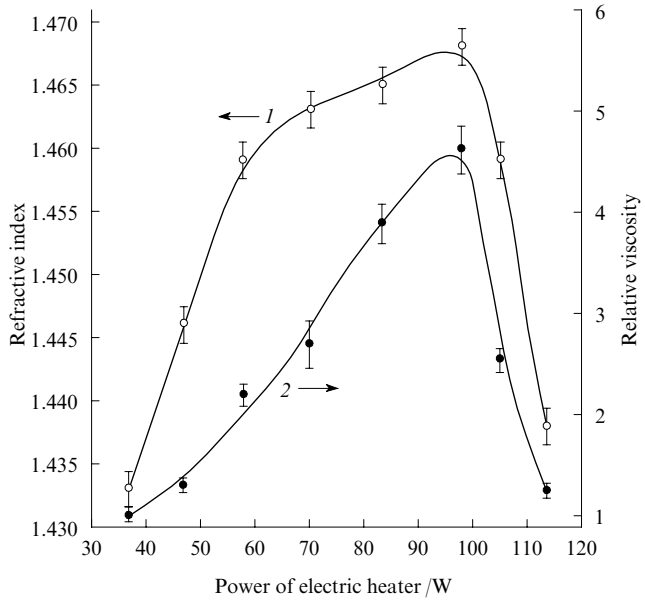


Figure 9. Effect of additional electric heating on refractive index (*1*) and relative viscosity (*2*) of the condensate distilled from microcrystalline cellulose at dose rate of 0.42 kGy s^{-1} and starting temperature of 80 °C.[19]

The major gaseous products of cellulose decomposition formed upon electron-beam distillation are CO_2, H_2 and CO. Equimolar formation of carbon dioxide and hydrogen is observed, while the CO yield is lower by an order of magnitude. Stoichiometrically, the fraction of the $-O-CH-O-$ groups (CO_2 precursor) in the glucopyranose $C_6H_{10}O_5$ unit is ~27 mass % of the starting cellulose dry weight. At the same time, the experimentally observed $CO_2 + CO$ total yield from cotton cellulose is almost twice lower. Therefore there is deficiency between the amounts of eliminated carbon dioxide and decomposed glucopyranose units.

Recall that if cellulose is irradiated at temperatures below the pyrolysis temperature range ($\leqslant$ 190 °C), the yields of compounds containing carbonyl group and CO_2 coincide within the experimental error (see Section III) with the yield of polymeric chain destruction. This indicates that each cellulose chain cleavage event is accompanied by decomposition of a glucopyranose unit to afford CO_2 and a carbonyl group. In the course of electron-beam distillation, the glucopyranose ring destruction provides a lower yield of CO_2. Thus, under these conditions, decomposition of glucopyranose units, resulting mainly in formation of furan derivatives, is most likely not always accompanied by elimination of CO_2.

The charcoal residue from the C1, C2 and C3 cellulose samples consists of two fractions, namely, long fibres (their structure is similar to that of initial cellulose; the atomic ratio C : O = 8.4; Fig. 10 *a*) and foam inclusions (as drops and films; the atomic ratio C : O = 6.4; see Fig. 10 *b*). The oxygen depleted components could be rather important precursors of charcoal remaining at the end of distillation and forming the first fraction. A part of charcoal can be formed in condensation reactions of destruction products resulting in high-boiling compounds, whose evaporation from the reaction zone is difficult. The second fraction occurs on the charcoal surface and is obviously formed in the condensation. Particularly, condensation processes are typical of furfural (the empirical formula is $C_5H_4O_2$) and some of its derivatives under the dry distillation conditions, for example, by the equation [1, 66]

$$2\,C_5H_4O_2 \longrightarrow C_{10}H_6O_3 + H_2O \qquad (8)$$

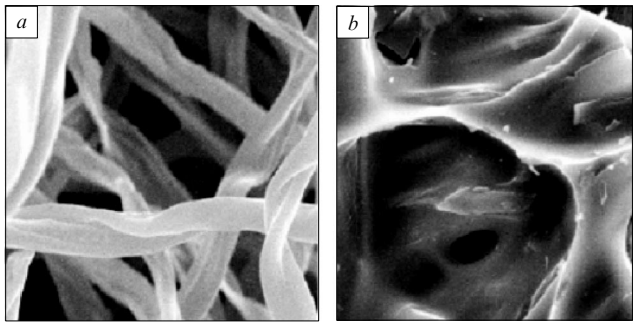


Figure 10. Photomicrographs of two structural modifications of charcoal (the scale is 105 × 80 μm) (see text).[18]

As it was shown,[66] furfural quickly decomposes in an acid medium yielding formic acid and humic compounds (50 g of formic acid and 41.5 g of humic compounds are formed from 100 g of furfural). The formation of high-molecular-mass products upon reactions of furfural with other intermediates could also promote an additional carbonization of the initial material. Evidently, fast removal of vapours from the irradiation zone is a major way to decrease the yield of high-molecular-mass products and to minimize the loss of furfural homologues.[66]

In practice, furfural can be formed upon acid hydrolysis of pentosanes, which belong to easily hydrolyzable vegetable hemicelluloses of the general formula $C_5H_{10}O_5$.[66]

$$C_5H_{10}O_5 - 3\ H_2O \longrightarrow C_5H_4O_2 \qquad (9)$$

In contrast to hemicelluloses, hydrolysis and pyrolysis of cellulose has a low probability of formation of furfural and furylmethanol.[1,2,6,66] Moreover, as we pointed out above, no formation of furan derivatives was observed upon irradiation of cellulose at temperatures of $\leqslant 190$ °C. Therefore, the high yield of furans observed in the electron-beam distillation is due to the specificity of the cellulose decomposition mechanism involved in this unusual radiation-thermal process.

Thus, the main result of the electron-beam distillation of cellulose of various types is formation of liquid organic condensate. Furylmethanol, furfural and their derivatives are the major liquid products. Grinding and preheating of the starting material promote an increase of the furan fraction in the condensate. The electron-beam distillation process could be a key to development of promising methods of production of furans from widespread plant materials and wastes of their processing.

3. The mechanism of radiation-thermal transformations

The procedure of electron-beam distillation of cellulose (or wood) could be conditionally divided into two phases. The first phase is radiolytic destruction independent of temperature, which gives radical fragments with unpaired electron being located at the chain end. This phase smoothly transforms into the subsequent phase, the high-temperature (220–250 °C) decomposition of such fragments. At the dose rate of the electron-beam treatment of 2–3 kGy s^{-1}, vapours start to condense in the condenser ~ 3 min after the beginning of irradiation (conditionally, the first phase proceeds during this period), and the vapour generation is finished 6 min later (the second phase is completed).

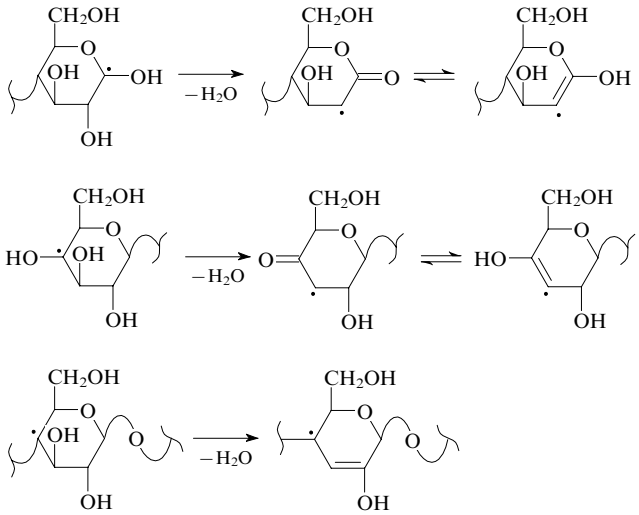
The vast majority of low-molecular-mass products of the distillation have 1 to 6 carbon atoms. Analysis of their composition shows that their common precursor is the glucopyranose unit ($C_6H_{10}O_5$). It is important to emphasize that the major products of the high-temperature radiation destruction are furfural (or furylmethanol) and other furan derivatives. This set of products is untypical of both cellulose radiolysis at moderate temperatures and cellulose pyrolysis without irradiation. Therefore, a specific mechanism of transformations operates during the electron-beam distillation of cellulose (or wood). Below we consider and discuss this mechanism.

As we have already stated, at moderate temperatures ($\leqslant 190$ °C), during the first phase, radiation initiates the destruction of cellulose with formation of oligosaccharides and radicals. The primary radicals are produced according to reactions (2)–(7) upon C–H bond cleavage mainly in positions 1 and 4 of glucopyranose. These bonds are unstable because of mismatch of electron configurations of the radical centre and the initial glucopyranose unit (see above),[3,5,6] which is secured by hydrogen bonds in the rigid framework of cellulose. The radical transforms into the stable configuration with the flat sp^2 hybridization of the carbon atom upon decomposition of the glucopyranose unit and rupture of the polymer chain. As a result, the stable radical states in the irradiated cellulose are located at the terminal fragments of the polymer chain (see Scheme 1).

The second phase is decomposition of cellulose fragments into low-molecular-mass compounds upon high-temperature radiolysis (radiation pyrolysis) in the range of 220–250 °C. Processes that occur under these conditions are determined by the intensive dehydration of cellulose and, especially, its shorter fragments formed upon destruction. In the course of dehydration of a polysaccharide, consecutive elimination of water molecules may finally result in carbonization of the material. Glucopyranose undergoes deep chemical transformations and structural reorganization, *viz*., double bonds appear and conformations of polymer units change.

Note that dehydration of radicals starts at substantially lower temperatures than that of molecules. For instance, transformations of terminal radicals in positions C(1) and C(4) in the irradiated cellulose into allyl type radicals is already observed at ~ 100 °C and above, whereas water molecule elimination during the cellulose pyrolysis starts above 200 °C (Refs 67–69). During the thermally stimulated dehydration, the terminal radicals at the C(1) and C(4) acquire an allylic structure as shown in Scheme 2.

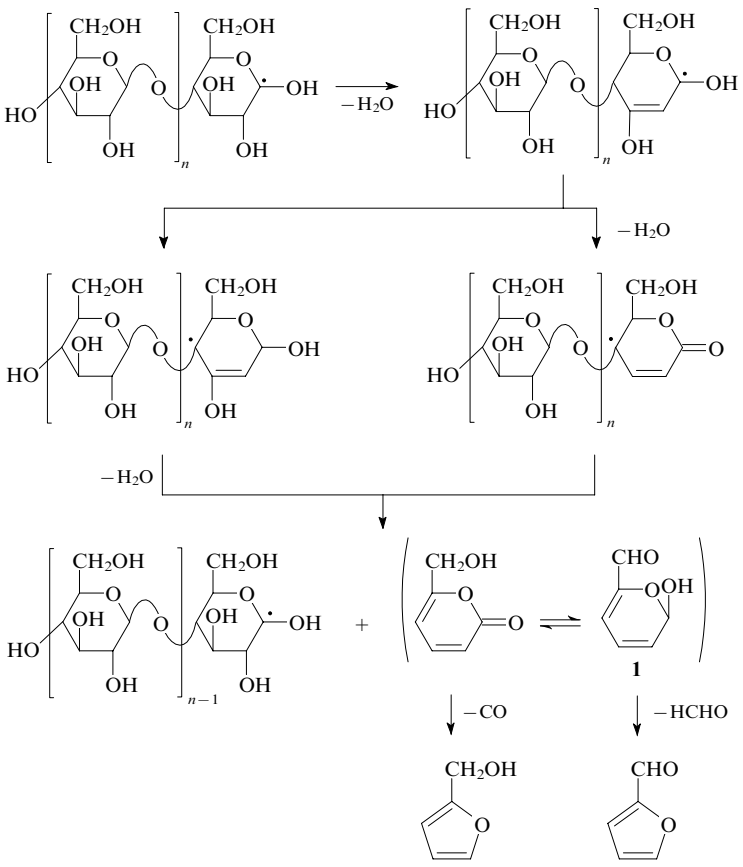
Scheme 2



This process was detected using EPR spectroscopy.[5,25,70] In turn, conjugation of the C=C bonds destabilizes the C–C and C–O bonds, thus facilitating the opening of the glucopyranose ring and/or elimination of some fragments from it.

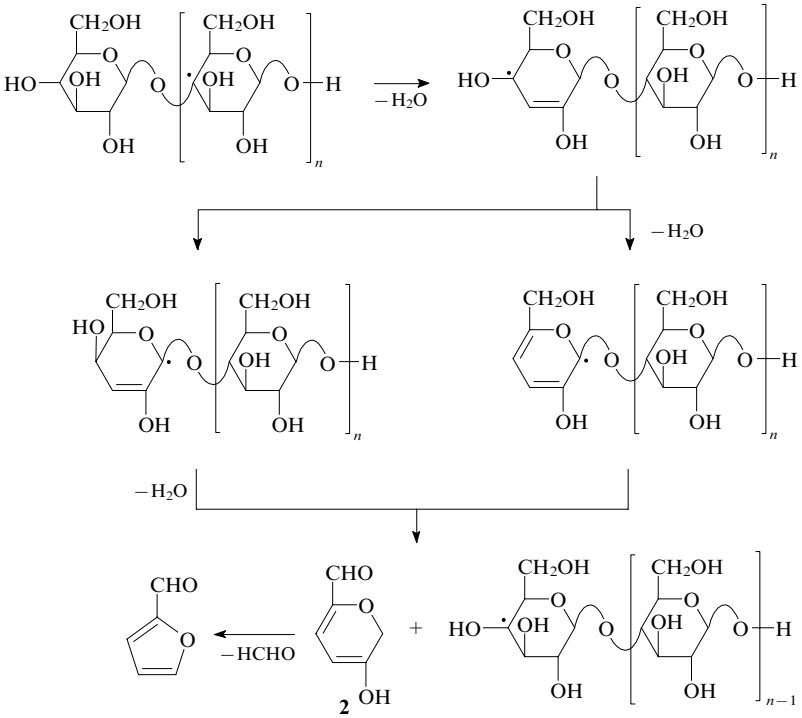
In our opinion, the radiation-thermal 'pyrolysis' occurring during electron-beam distillation of cellulose can be described by the mechanisms of transformations of terminal radicals at C(1) and C(4) shown in Shemes 3 and 4, respectively.

Scheme 3



According to the proposed mechanism, the deep radiation-thermal transformations of cellulose are initiated by dehydration of glucopyranose units with participation of the C(1) and C(4) terminal radicals. The 'catalytic' effect of the radicals is manifested as accelerated dehydration at temperatures lower than those typical of the conventional pyrolysis. The formed system of conjugated bonds favours the radical centre and hydrogen atom transfer along the polymer chain. Owing to these reactions, the radical centre migrates to the next fragment unit, while the terminal

Scheme 4



fragment gets detached and decays to give furylmethanol or furfural molecules and other smaller decomposition products (formaldehyde, formic acid, CO, CO_2, *etc.*). The decomposition is favoured by the structural strain caused by the presence of double bonds (sp^2 hybridization and the planar structure) and the CH(OH) or CH_2 groups (sp^3 hybridization and the tetrahedral structure) in the intermediate.

Formic acid and formaldehyde are chemically reactive and prone to condensation and reactions with carbonyl or carboxyl compounds. Apparently, they are precursors of other low-molecular-mass products formed in the electron-beam distillation of cellulose. Radiation- and heating-induced chemical transformations of furans, formic acid and formaldehyde result in a variety of final products of radiation-thermal decomposition of cellulose. Being active acceptors of radicals and excess energy, these compounds participate in fast reactions with other fragmentation products or decompose.

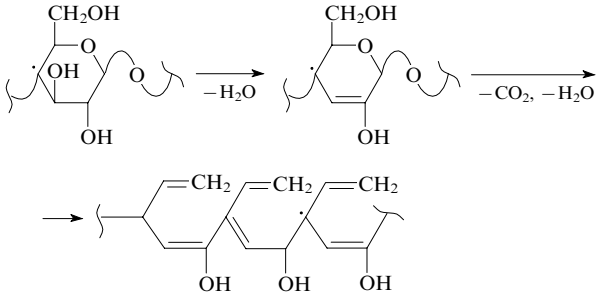
The predominant formation of furan derivatives, CO_2 deficiency indicating that decomposition of the glucopyranose unit is accompanied by elimination of some other compound (formaldehyde in this case) and a substantially lower yield of water in the polysaccharide destruction confirm this mechanism of radiation-thermal transformations of cellulose in the electron-beam distillation. Particularly, in the course of the electron-beam distillation of cellulose, according to Schemes 3 and 4, two water molecules are eliminated due to dehydration, while approximately five water molecules should have formed upon predominant decomposition of glucopyranose unit to charcoal in the course of dry distillation. Indeed, water is formed in approximately such ratio in the processes under comparison. This also clarifies why cellulose preheating has no significant effect on the electron-beam distillation process. Indeed, according to the stated mechanism, a stage consisting in the destruction of cellulose with formation of fragments with terminal radical centres should precede its radiation-thermal decomposition.

Perhaps, the mechanism of radiation-thermal transformations of cellulose upon its electron-beam distillation is not exhausted by suggested Schemes 3 and 4. For example, intermediates **1** and **2** might eliminate either HCO_2H and H_2 or CO_2 and $2\,H_2$ molecules (these correspond to the stoichiometric composition of $H_2O + HCHO$ in Schemes 3 and 4); this elimination would also results in the formation of furfural as a final product. However, the release of substantial amount of molecular hydrogen would be observed in these cases. In the whole, further investigation of cellulose transformations in the process of electron-beam distillation is required.

The chain radiation-thermal decomposition of cellulose propagates through the entire material. The close packing of surrounding molecules may prevent the removal of formed radical and molecular fragments. Allyl radicals are capable of rearranging into polyene type radicals,[25] which are more stable and can be precursors of charcoal (Sheme 5).

At low dose rates (~ 0.15 kGy s^{-1}) insufficient for efficient heating and launch of distillation, cellulose remains solid and becomes yellow. The yields of condensate, in which water prevails, and coal upon post-radiation (~ 500 kGy dose) dry distillation are ~ 47 mass % and

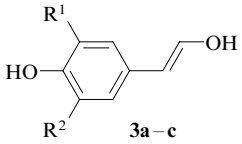
Scheme 5



32 mass %, respectively. The substantial reduction of the yield of the condensate as compared with the electron-beam distillation indicates the importance of the reactions occurring during radiolysis. Only thermal degradation of stable molecular fragments of cellulose with reduced polymerization degree occurs in the post-radiation dry distillation. This fact confirms the conclusion that the intermediates participating in radiation-thermal cellulose decomposition differ from those in conventional pyrolysis. Accordingly, the yields of the electron-beam distillation products differ from the yields observed in post-radiation distillation.

V. Radiation-thermal transformations of lignin

Lignin (Lig) is the second most abundant plant polymer. In contrast to cellulose and proteins, lignin is a branched polyphenol polymer without regular alternation of structural units; therefore, it is one of the objects most difficult to study. The primary structural units of lignin are *p*-hydroxycinnamic alcohols: *p*-coumaric (**3a**), coniferyl (**3b**) and sinapic (**3c**).[1]



3a–c

$R^1 = R^2 = H$ (**3a**); $R^1 = H$, $R^2 = OMe$ (**3b**), $R^1 = R^2 = OMe$ (**3c**)

The lignin molecular chain is mainly a combination of four types of phenoxyl radicals, among which most important is the radical with the unpaired electron located on phenolic oxygen.[1] Lignin is used less frequently than cellulose and it is often considered as an unavoidable waste product of the cellulose manufacture. The annual world production of lignin is more than 50 million tons.[1, 2, 71]

The protective effect of lignin on wood was demonstrated in studies of qualitative and quantitative contents of radiolytic radicals.[72, 73] Irradiated wood contains two types of radicals formed from cellulose (like those formed in fibres of purified cellulose) and phenoxyl radicals formed from lignin. The signal of the lignin radicals is most intensive in the EPR spectra of hardwood irradiated at 77 K at dose rate of 60 kGy, although $\sim 70\%$ of wood pulp is composed of carbohydrates (cellulose and hemicellulose). In the case of aspen wood, the radiation chemical yield of the phenoxyl radicals formed from lignin is equal to 1.7, whereas the yield of cellulose radicals is 0.8. On the other hand, the yield of cellulose radicals from purified aspen cellulose is 2.7.

1. Electron-beam distillation of lignin

In electron-beam distillation experiments, hydrolytic lignin containing 10 mass % cellulose was used. The compositions of tars obtained upon conventional dry distillation (pyrolysis) and electron-beam distillation of lignin [74–76] are shown in Table 4. The tar obtained upon heat treatment contains a large fraction of various aromatic compounds, the GLC chromatogram containing ~50 peaks. The major components are toluene, xylenes, phenol, guaiacol and creosol. The dry distillation products also include furfural, 5-methylfurfural and furylmethanols. Apparently, their formation is due to cellulose impurity in the used lignin samples.

Table 4. Major products of dry (*T* mode) and electron-beam (*R* mode) distillation of lignin (mass %).[74]

Product	Mode (dose /kGy s^{-1})		
	T	*R* (4.8)	*R* (3.6)
Charcoal	56.1	48.8	46.8
Gas	20.5	15.8	18.9
Water–organic fraction	16.2	16.8	15.3
Tar [a]	7.2	18.6	19.0
including:[b]			
methanol + ethanol	0.5	1.0	0.4
benzene	0.8	–	–
toluene	8.7	0.2	0.2
furfural	0.5	0.1	0.2
furylmethanols [a]	0.8	0.2	0.1
ethylbenzene	0.6	0.1	0.1
dimethylbenzenes [a]	9.7	0.1	0.1
isopropylbenzene	1.1	–	–
phenol	12.4	3.6	2.9
ethyl(methyl)benzenes [a]	2.2	0.1	0.1
4-methyl-1-methoxybenzene	0.3	0.1	0.1
1,3-dimethyl-2-ethylbenzene	1.1	0.1	0.1
methylphenols [a]	2.7	1.1	0.9
dimethylphenols [a]	2.5	2.2	1.8
methoxyphenols (guaiacol and others) [a]	38.6	57.7	60.2
4-methyl-2-methoxyphenol (cresol)	5.8	19.8	21.3
4-methyl-3-methoxyphenol	0.4	3.9	2.8
dimethoxyphenols [a]	0.5	3.9	2.3
2-methoxy-4-ethylphenol	0.8	3.0	3.8

[a] The total amount is indicated; [b] below, contents of components relative to the mass of tar are presented.

The number of products is smaller in the case of electron-beam decomposition of lignin: there are 35 peaks in the tar chromatogram, only 27 of them coincide with the peaks of the chromatogram of dry distillation tar.[74,75] Two compounds, guaiacol and creosol, prevail in the radiolytic tar. The total yield of the tar after the electron-beam distillation is three times as high as that after pyrolysis. Note that the content of alkylbenzene fraction is reduced in the radiolysis products. Phenols and alkoxyphenols prevail among liquid radiolysis products, while methane is the major gaseous product. The formation of stable products of radiolytic fragmentation of aromatic macromolecules is mainly determined by radical processes.[1–3] In the first place, radiolysis results in abstraction of hydrogen atoms from saturated substituents in the lignin molecules.

2. Mechanism of radiation-thermal transformations of lignin

Under the action of ionizing radiation on lignin, most of hydrogen atoms arise from dissociation of phenolic hydroxyl groups,[1–3] giving rise to phenoxyl radicals ($ArO^{\bullet}$).†

$$Lig(ArOH) \longrightarrow ArO^{\bullet} + H^{\bullet} \quad (10)$$

Analogous radicals can also be formed upon cleavage of ether bonds.

$$Lig(Ar-O-Ar) \longrightarrow ArO^{\bullet} + Ar^{\bullet} \quad (11)$$

Hydrogen atoms readily react with aromatic compounds with formation of H-adducts (σ-complexes).[1,3,77] It is likely that thermal stability of the aromatic H-adducts is not high and they decay with cleavage of side C–C bonds to give stable aromatic molecules ArH and secondary radicals $R^{\bullet}$.

$$Lig(ArR) + H^{\bullet} \longrightarrow LigH^{\bullet} + ArR \longrightarrow Lig + ArH + R^{\bullet} \quad (12)$$

This reaction was observed for toluene:[77] methylcyclohexadienyl radicals easily dissociate to benzene and methyl radical at elevated temperatures (< 500 °C). In addition, it is known [3] that in radiolysis of alkylbenzenes, the yield of dealkylation products is higher than the yield of alkylation products.

Recombination of methyl and phenoxyl radicals gives methoxy derivatives.

$$^{\bullet}CH_3 + ArO^{\bullet} \longrightarrow ArOMe \quad (13)$$

In turn, the methyl radical gives methane by abstracting hydrogen atom from lignin according to the following equation:

$$^{\bullet}CH_3 + Lig \longrightarrow CH_4 + Lig^{\bullet} \quad (14)$$

or forms heavier hydrocarbons upon radical recombination as in the following example:

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow C_2H_6 \quad (15)$$

The tar distilled off upon electron-beam heating is distinguished by high antioxidant activity, particularly in inhibition of styrene thermal polymerization. It was found [76] that other examined phenolic inhibitors are inferior to the reference stabilizer, the Mannich base 2,6-di-*tert*-butyl-4-dimethylaminophenol. The high inhibiting activity can indicate the presence of polyatomic phenols in the tar. These components prevail in the fraction boiling at about 235 °C. Therefore, the tar formed upon electron-beam distillation of wood or lignin can be utilized for the production of polymerization inhibitors.

VI. Electron-beam distillation of wood

Radiolytic destruction of cellulose as a component of wood (*i.e.*, without isolation) is less efficient than destruction of isolated and purified cellulose fibres.[78–80] Evidently, protection of cellulose against radiation in the wood bulk is due

† The designation Lig(X) means compound X present as a lignin component.

to excitation energy transfer from cellulose to lignin containing more stable aromatic fragments.[1, 72, 81]

The high yield of conversion of cellulose to organic liquid with suppression of dehydration processes has become a basis for development of electron-beam technology of processing of the lignocellulose material into liquid fuel and valuable chemicals. The processing of wood material aimed at production of liquid fuel mixtures includes conversion of lignocellulose material to low-molecular-mass gaseous and/or liquid compounds (dry distillation) and further transformation of these compounds into stable liquid products possessing acceptable fuel characteristics (the proper production of fuel).[8, 9, 16]

The effect of the wood type on the phase composition of products formerd upon electron-beam distillation is demonstrated by the data of Table 5. Softwood gives somewhat more charcoal in comparison with hardwood.[17] Simultaneously, the amount of charcoal remaining after radiation heating is lower than after pyrolytic treatment. The conventional dry distillation of pine, spruce, alder and birch produces charcoal and non-condensing gases in amounts of approximately 33 mass % – 36 mass % and 15 mass % – 17 mass %, respectively; almost a half of the liquid condensate is water.[1, 74]

Table 5. Phase composition (mass %) of products of electron-beam distillation of wood material in isobutane flow under atmospheric pressure ($Z = 40 \pm 5$ cm^2 g^{-1}, bulk density is 150 g dm^{-3}).[9, 17]

Wood material	Latin name	Products		
		charcoal	gas	liquid
Alder	*Alnus*	25.4	18.0	56.6
Aspen	*Populys tremula*	25.4	16.7	57.9
Birch	*Betula*	23.7	14.7	61.6
Larch	*Larix*	28.9	14.5	56.6
Lime	*Tilia*	23.5	15.1	61.4
Juneberry	*Amelanchier*	25.0	17.1	57.9
Eucalyptus	*Eucalyptus*	28.5	14.0	57.5
Pine	*Pinus*	29.6	13.3	57.1
Poplar	*Populus*	25.5	16.5	58.0
Spruce	*Picea*	29.5	15.9	54.6

The yields and composition of the products of conventional dry distillation and electron-beam distillation differ owing to different mechanisms of wood decomposition and different conditions of distillation of low-molecular-mass compounds formed. Whereas the start of pyrolytic destruction is mainly related to destruction of the least stable ether bridges (the C—O bonds) between the monomeric units of macromolecules, the initial radiolytic process consists in hydrogen atom abstraction (cleavage of the C—H bond) inside monomeric units. In the course of irradiation, the wood fragmentation products are formed and accumulated long before the temperature of the onset of pyrolysis is reached.

An important advantage of electron-beam treatment consists in simultaneous and fairly uniform heating of the whole bulk of the irradiated material. During pyrolysis, heat is transferred from the surface to the centre, which is associated with increased non-productive heat loss and high probability of material overheating with formation of charcoal. The consequence of the activation of free-radical reactions and more favourable heating conditions is higher yield of liquid products upon electron-beam distillation of plant material and twofold decrease in the energy consumption as compared with pyrolysis.

The differences between various sorts of wood already appear during condensation of the vapour formed upon radiation heating. Almost half of the vapour produced from softwood is condensed in the air condenser, whereas in the case of hardwood, this is less than one-third.[17, 82] The fresh condensate does not contain much water ($\sim$8 mass % – 10 mass %). The water fraction increases during storage of the condensate, especially in the case of warm storage where the formation of water accelerates. The condensate instability indicates that its dilution or reprocessing would be expedient. In this case, stabilization of low-molecular-mass products of distillation is achieved during vapour removal from the reactor.[17, 19]

The component composition of condensed products of electron-beam distillation strongly depends on the type of wood used (Table 6). The condensates obtained upon softwood distillation are enriched in phenol derivatives. They are formed from lignin and other aromatic macromolecular components of wood.[1] Aromatic compounds exhibit antiradiation and antioxidant properties;[3, 76] therefore, their high concentration predetermines several significant features of softwood decomposition. The condensates from softwood contain a smaller amount of low-molecular-mass products having 1 – 3 carbon atoms. That indicates that fragmentation of wood enriched in aromatic compounds is somewhat less extensive. Hence, the average molar mass of pine and spruce condensates is larger than that of hardwood condensates (see Table 6). The mixtures of liquid products of electron-beam distillation of softwood are usually more stable to storage and heating. However, higher yield of charcoal is, perhaps, also related to higher concentration of aromatic compounds in raw softwood material.

The radiation-thermal decomposition of both softwood and hardwood produces a large furan fraction (see Table 6). As noted above, the major source of furans is cellulose. Furancarbaldehydes prevail among furan derivatives. The electron-beam heating of hardwood results in the formation of both furan-3-carbaldehyde and furan-2-carbaldehyde (furfural). Furfural is a dominant compound of the furancarbaldehyde series upon decomposition of softwood. The condensates from aspen and alder have a larger fraction of furylmethanols, whereas the pine condensate is relatively enriched in 5-methylfurfural. The condensates obtained from softwood contain more diverse furans than hardwood condensates. For instance, the pine condensate, in addition to aldehydes, contains furan, 2-methylfuran, 2,5-dihydrofuran, 2,5-dimethylfuran, 2,5-dihydro-3-methylfuran and 5-methylfuran-2(3*H*)-one. The wide variety and the high total yield of furans obtained from softwood may be due to lower fragmentation capablity of cellulose in the presence of aromatic compounds.

The most abundant components of the condensates are low-molecular-mass oxygen compounds. Oxygen atoms are present in various functional groups contained in acids, aldehydes, ketones, alcohols, esters and ethers. The relative abundance of these compounds among oxygen-containing components is shown in Table 7. Three-quarters of the hardwood condensate weight are represented by carbonyl compounds, although their fraction is significantly lower in softwood.

Table 6. Composition and characteristics of condensates obtained upon wood radiolysis in isobutane under atmospheric pressure ($Z = 90 \pm 5$ cm^2 g^{-1}, bulk density is 150 g dm^{-3}).[82]

Parameter	Wood material				
	birch	aspen	alder	spruce	pine
Contents of major components (mass %)					
methanol + methyl formate	10.1	10.9	13.9	12.7	9.8
acetone + propanal	4.3	2.4	3.4	3.4	2.3
butane-2,3-dione	5.9	9.9	7.2	3.8	4.5
2-oxopropanal	3.0	3.7	4.9	1.2	1.2
acetic acid	26.1	28.0	23.5	15.1	10.6
1-hydroxypropan-2-one	6.1	6.2	4.9	9.7	8.6
furfural	13.1	11.1	11.2	15.6	16.1
furan-3-carbaldehyde	9.5	2.9	4.8	0.3	0.1
furylmethanols	1.6	9.0	6.7	3.3	3.1
5-methylfurfural	0.5	0.3	0.8	0.8	2.0
4-methylphenol	0.1	0.6	0.2	0.1	0.3
2-methoxyphenol	0.1	0.1	1.5	3.7	6.1
creosol	0.1	0.1	0.2	0.7	4.0
furans [a]	24.7 ± 2.1	24.9 ± 2.3	24.8 ± 2.9	24.9 ± 3.9	28.4 ± 5.1
aromatic compounds [a]	0.3	2.2 ± 0.9	2.6 ± 1.0	13.9 ± 3.0	18.4 ± 6.2
Average density /kg m^{-3}	1141	1122	1119	1138	1125
Average molecular mass /kg mol^{-1}	73.8 ± 1.1	73.6 ± 0.7	75.8 ± 1.4	79.4 ± 1.6	81.2 ± 1.4

[a] The total amount is indicated.

Table 7. Distribution of components (mass %) in the oxygen-containing fraction of condensates obtained upon wood radiolysis in isobutane under atmospheric pressure ($Z = 90 \pm 5$ cm^2 g^{-1}, bulk density is 150 g dm^{-3}).[82]

Compound	Wood material				
	birch	aspen	alder	spruce	pine
Alcohols and phenols	13.8	12.3	8.4	20.2	28.1
Carboxylic acids	41.3	35.8	35.6	22.4	17.8
Ketones	11.6	23.1	18.5	19.5	17.0
Aldehydes	17.6	16.2	21.3	18.1	22.4
Ethers	10.5	10.7	12.9	15.1	22.2
Esters	5.2	1.9	3.3	4.7	0.4

As a rule, cellulose radiolysis is carried out in a reactor filled with a light alkane, for instance, isobutane. This alkane also participates in the process, being a precursor of liquid alkanes. The liquid alkane fraction in the condensates amounts to ~ 2 mass % and is mainly composed of octane isomers. On the other hand, butyl alcohols and some ethers, which are untypical for electron-beam distillation of proper wood material, are observed among oxygen-containing compounds. Obviously, these compounds are formed upon radiolytic transformations of isobutane used as the carrier gas. Note that the procedure of electron-beam distillation of wood under a light alkane atmosphere provides a gaseous alkane binding yield an order of magnitude higher than radiolysis of the dry or wet gas without addition of wood.[9,83] This may be based on charge and energy transfer from low-molecular-mass products of chain fragmentation of wood to the alkane molecules. As a consequence, more active gas decomposition increases the probability of participation of the radical intermediates thus formed in the formation of liquid alkanes, alcohols and ethers.

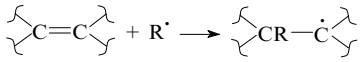
The natural ageing of wood affects [82] the composition of electron-beam distillation products. The condensate contains less light products resulting from cellulose fragmentation, while the content of fractions of aromatic compounds and furans increases. For instance, relative amount of aromatic compounds and furans in the condensate after electron-beam distillation of rotten pine dust amounts to 65 mass % – 70 mass %. The total yield of the condensate decreases to 40 mass %, whereas the yields of charcoal residue and gases increase to 42 mass % and 18 mass %, respectively. These changes indicate that aromatic compounds are more stable against processes of natural biochemical ageing of wood.

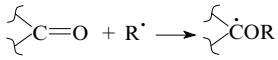
Liquid products of electron-beam distillation cannot be directly used as fuel. The presence of unsaturated bonds and active functional groups gives rise to undesirable chemical reactions (dehydration, polycondensation and so on) between condensate components. Alkanes, benzenes, aliphatic alcohols, ethers and esters are usually considered as suitable components of liquid fuel.[12] Tetrahydrofuran derivatives are also considered as satisfactory components of high-octane motor fuel.[12,84]

Comprehensive studies show that hydrogenation and/or alkylation of organic vapours obtained in electron-beam distillation of plant biomass give stable mixtures, which can be used as engine, diesel, jet engine fuels or fuel oil. A radiolytic version of such transformation can be seen from the observed influence of the gas flow rate on the condensate composition.[85,86]

When gaseous alkanes or hydrogen are utilized in the radiation chemical processing of lignocellulose material, several important effects are observed. The gas flow facilitates the removal of fragmentation products from the irradiated raw material. Strong dilution of vapour products

of electron-beam distillation with the gas flow prevents secondary processes of their fragmentation and undesirable reactions between the vapour components. In the presence of hydrogen-containing molecules (RH) utilized as a carrier gas, the probability of radiolytic formation of hydrogen atoms and alkyl radicals [according to reaction (4)] increases.[3,87] These species initiate both chain destruction of the starting plant material and hydrogenation and alkylation of the fragmentation products, for instance


(16)


(17)

As a result, the hydrocarbon backbone of gaseous compounds is elongated, the degree of unsaturation of the molecules in the vapour decreases, and the stability of molecules increases. Besides, radiolysis of the gas enriches the condensates with valuable fuel components, *i.e.*, with branched alkanes.[85,86,88] The radical intermediates formed from the carrier gas react mainly with unsaturated compounds in the vapour. As a result of this process, the yield of the gas utilization also increases due to the suppression of regeneration of its components.

It was demonstrated earlier[16] that the birchwood can be transformed in a methane flow into liquid motor fuel having a suitable fractional composition and octane number of >90. High dose rate (to prevent the formation of high-molecular-mass compounds) and low vapour concentration in a gas – vapour mixture (to avoid polycondensation) are important requirements necessary for production of high-quality fuel.

It is ascertained[89,90] that electron-beam treatment of natural bitumen and high-viscosity crude oil in the presence of lignocellulose can also be used in the fuel production. Lignocellulose has a combined influence on destruction of heavy hydrocarbons under these conditions, increasing the yield of light fractions at rather low heating.

Thus, the use of electron-beam technique for plant biomass processing into valuable products has several undoubted advantages, among which the simplicity and versatility, waste prevention and environmental safety of this technique are in the first place. The most important innovative feature of this technique is the fact that, in contrast to existing processes, it gives a possibility to convert plant biomass to liquid fuel and other valuable products practically in a single-stage process. The heat of combustion of the obtained fuel is more than three times higher than the amount of the energy consumed in its synthesis.

VII. Conclusion

As follows from the presented material, the use of high-energy accelerated electrons makes it possible to implement a direct single-stage conversion of cellulose biomass into liquid condensate. In comparison with pyrolysis, electron-beam distillation has several advantages: it hampers water formation, halves the accumulation of charcoal and increases $\sim$6-fold the yield of liquid organic products.[9,16,17,91] Such high performance of the process is related to the specific mechanism operating upon simultaneous action of ionizing radiation and heating.

An accelerated electron loses its energy in a condensed medium in small portions ($\sim$20 eV on average), thus forming spurs (*i.e.*, isolated areas of ionization and excitation) of 2–5 nm size.[3,92] The typical distance between the spurs is hundreds of nanometres. Recombination of ion and radical pairs in a spur is accompanied by energy release, which is equivalent to fast local temperature increase. Due to this, a sequence of high-temperature 'nano-reactors' isolated from each other is rapidly formed along the accelerated electron trajectory. In contrast to pyrolysis, irradiation predominantly generates excited and super-excited molecules, in which the carbon skeleton bonds are easily cleaved. Usually, compounds in their singlet excited states decay to molecular products, whereas their triplet states dissociate with formation of radicals.[3] The energy excess is dissipated by the cold macromolecular chains, promoting further destruction of unstable intermediates.

At a certain absorbed dose rate, the rate of radiation heating of the material can exceed the rate of heat dissipation. As a result, the temperature of the reaction mixture increases. Under atmospheric pressure, pyrolysis of plant biomass occurs at >270 °C.[1] However, during electron-beam distillation of biomass, the probability of undesired pyrogenetic decomposition mechanism is minimized. The process is self-regulated due to initiation of efficient endothermic process consisting in evaporation of liquid products of radiolysis. Thus, a relatively steady mode of radiation-thermal decomposition is sustained in the temperature range of 200–260 °C. The energy of the accelerated electron beam is consumed for the fragmentation of the starting material and evaporation of radiolytic products, which does not result in further heating. A noticeable increase in the temperature occurs only after completion of the distillation process and charcoal formation.

Under these conditions, the mechanism of radiation-thermal transformation of cellulose is implemented; it is initiated by dehydration of a radical localized at the terminal glucopyranose unit. Thus, a consecutive decomposition of the polymer chain occurs, resulting in the formation of furfural and formaldehyde. This process is typical of neither pyrogenetic nor radiation-induced cellulose decomposition. This is because there are no radicals required for this mechanism during pyrolysis and no total dehydration of glucopyranose occurs upon radiolysis. Two facts support the proposed mechanism: (*i*) an essential deficiciency of carbon dioxide and water formation in comparison with the number of decomposed glucopyranose units and (*ii*) the lack of influence of cellulose preheating to 250 °C on the subsequent electron-beam treatment. Indeed, radiation destruction of cellulose involving cleavage of polymeric chain and decomposition of glucopyranose units with formation of terminal radicals and H_2O molecules is a necessary condition for implementation of further steps in glucopyranose unit decomposition to give furylmethanol (or furfural) and formic acid (or formaldehyde) molecules. The pretreatment of cellulose at 250 °C initiates its partial dehydration; however, it does not result in the appearance of radicals which should catalyze the polymer chain decomposition. At the same time, preliminary irradiation of cellulose resulting in its destruction and formation of terminal radicals facilitates its subsequent thermal decomposition with formation of furans.

The charcoal yield upon conventional dry distillation is 38 mass %.[1] It is close to the theoretical yield (45 mass %) expected of dehydration mechanism of glucopyranose decomposition according to the equation

$$C_6H_{10}O_5 \longrightarrow 6C + 5H_2O \quad (18)$$

Thus, only ~7 mass % of carbon is consumed for formation of organic compounds and gaseous CO_2 and CO.

The charcoal yield in electron-beam distillation of cellulose [15, 62, 93, 94] does not exceed 20 mass %. Therefore, the degree of carbon conversion to liquid organic compounds amounts to ~25 mass %, which is a consequence of glucopyranose unit decomposition mainly according to the reaction

$$C_6H_{10}O_5 \longrightarrow C_5H_4O_2 + HCHO + 2H_2O \quad (19)$$

Optimization of radiation-thermal decomposition of lignocellulose material could result in the decrease in charcoal yield and, therefore, in the increase in the yield of the desired liquid condensate. The loss of carbon at the first, 'incubatory' step of radiation destruction giving carbon dioxide is unavoidable. Estimates show that the carbon loss at this step does not exceed 3 mass % – 5 mass %. Therefore, there is a substantial reserve for process optimization. In our opinion, to optimize the process, it is necessary (i) to reduce the temperature of distillation; (ii) to achieve the most complete removal of products of primary decomposition from the irradiation zone; (iii) to use gases and additives for activation of decomposition of lignocellulose material; (iv) to optimize irradiation conditions; (v) to enhance the degree of dispersion of the raw material, *etc*.

Recently, the US Department of Energy has published [12] the list of ten key products the production of which by plant biomass processing is most desirable: ethanol, furans, glycerol and its derivatives, hydrocarbons (first of all, isoprene), lactic acid, succinic acid, hydroxypropionic acid (or aldehyde), levulinic acid, sorbitol and xylitol. Almost all of these compounds could be obtained with the use of electron-beam technologies. Furans take a top place in this list. Along with the application in fuel production, they are considered as promising substitutes for oil stock in production of a series of valuable products. However, methods of large-scale industrial production of furan have not been developed so far. As mentioned above, electron-beam distillation of cellulose and lignocellulose material is characterized by a high yield of furans and could serve as such desired method.

The above described procedure of electron-beam processing can be considered as a method for refinement of bio-oil (pyrolysis oil). The pyrolysis oil is an intermediate product in the process of transformation of biomass into stable fuel. Upon the fast pyrolysis,[65] biomass is heated to ~500 °C for less than a second and then is quenched to stop the reaction. The liquid product known as bio-oil is obtained in a yield up to 75% of the the dry raw material weight. Bio-oil consists of carbonyl compounds and other unsaturated components, which are active radical acceptors.

Most of unsaturated components in bio-oil are high-molecular-mass compounds. Pyrolignin and solid fragments of cellulose (cellobiose, for instance) dominate in the organic fraction of bio-oil.[65] Catalytic transformation of these components into commercial fuel is difficult. High-boiling oxygen-saturated solid particles cause fast decrease in the activity of a catalyst. Many research groups endeavour to improve catalysts and catalytic methods for bio-oil processing. The desired transformation of pyrolysis oil consists in its cracking and hydrogenation leading to stable high-quality fuel.

Bio-oil vapours possess low stability against radiation. Their destruction is initiated thermally. The chain decomposition of heavy components of bio-oil can be initiated by radiation at low dose rates and gentle heating. The pyrolignin destruction gives mainly guaiacol and creosol, while cellobiose transforms predominantly into furans. Saturated derivatives of furan are considered as very promising components of alternative motor fuel.[12, 84]

In addition to destruction, electron-beam treatment of bio-oil vapours under the atmosphere of gaseous alkane results in alkylation and hydrogenation of radiolytic products.[16, 19, 95, 96] Strong dilution of the vapour by the gas facilitates the increase in the alkylation and hydrogenation degree. On the other hand, the elevated temperature causes intensive dehydration and decarboxylation of the fragments due to thermal instability of radicals.[3]

The conditions of electron-beam conversion supress the carbonization processes, simultaneously the bio-oil oxidation degree decreases owing to removal of water and carbon dioxide. Therefore the electron-beam treatment of gaseous alkanes in the presence of organic vapours can be a final step of bio-oil processing into liquid fuel.

Thus, a direct transformation of bio-oil into valuable chemicals can be performed using electron-beam distillation. The high performance of the method [16, 17] is a key characteristic for development of waste-free technologies for the transformation of biomass into alternative fuel and other popular products. Its industrial use seems highly promising, taking into account the fact that electron-beam distillation has highly significant advantages: chain mechanism, high yield of organic condensate, selectivity, quite low power consumption, and, what is especially important, a possibility of implementation of a commercial process resulting in conversion of lignocellulose material into popular and valuable products in a single stage without waste formation. The electron-beam conversion of biomass into an organic liquid may be of interest as an initial stage of subsequent industrial production of various products: active polymerization inhibitors; monomers and other reagents for production of polymers, alternative liquid fuel, charcoal of special types and some other compounds.

The above described thermally stimulated radical processes are not specific to the radiation-chemical biomass processing. There is a high probability that they occur in the bowels of the Earth and on its surface. Light, ultrasonic, plasmochemical and other types of treatment may activate similar transformations of plant macromolecules.[1–3] Particularly, very similar mechanochemical processes of bond cleavage, fast local heating, formation and decomposition of radicals with formation of liquid, gaseous and solid fragmentation products occur during various mechanical treatments of biomass, including its grinding, pressing, surface treatment.[97–99] The noted versatility of the transformations considered in the present review indicates the possibility of further substantial extension of methods and techniques for efficient conversion of renewable plant material into fuel and valuable intermediates of organic synthesis.

References

1. Von D F'engel, G Wegener *Wood. Chemistry, Ultrastructure, Reactions* (Berlin, New York: W de Gruyter, 1984)
2. B G Ershov *Kormoproizvodstvo i Radiatsionnaya Tekhnologiya* (Fodder Production and Radiotechnology) (Moscow: Radiatsionnaya Tekhnika, 1985)
3. R J Woods, A K Pikaev *Applied Radiation Chemistry: Radiation Processing* (New York: Wiley Interscience, 1994)
4. *Cellulose and Cellulose Derivatives* Vol. 2 (Eds N Bikales, L Segal) (New York: Wiley, 1974)
5. B G Ershov, A S Klimentov *Russ. Chem. Rev.* **53** 1195 (1984) [*Usp. Khim.* **53** 2056 (1984)]
6. B G Ershov *Russ. Chem. Rev.* **67** 315 (1998) [*Usp. Khim.* **67** 353 (1998)]
7. V Ya Kabanov, V I Fel'dman, B G Ershov, A I Polikarpov, D P Kiryukhin, P Yu Apel' *Khim. Vys. Energ.* **43** 5 (2009) [a]
8. RF P. 2338769 (2008); *Byull. Izobret.* (32) (2008)
9. A V Ponomarev *Radiat. Phys. Chem.* **78** 345 (2009)
10. I I Moiseev, N A Plate, S N Varfolomeev *Vestn. Russ. Akad. Nauk* **76** 427 (2006) [b]
11. M Mascal, E B Nikitin *Green Chem.* **12** 370 (2010)
12. J J Bozell, G R Petersen *Green Chem.* **12** 539 (2010)
13. G J Kramer, M Haigh *Nature (London)* **462** – **463** 568 (2009)
14. B N Kuzyk *Al'ternativ. Energ. Ekol.* **67** 353 (2008) [c]
15. A V Ponomarev, A V Bludenko, V N Chulkov, I G Tananaev, B F Myasoedov, A Yu Tsivadze *Khim. Vys. Energ.* **43** 404 (2009) [a]
16. A V Ponomarev, A Yu Tsivadze *Dokl. Akad. Nauk* **424** 57 (2009) [d]
17. A V Ponomarev, B G Ershov, in *Wood Types, Properties and Uses* (Ed. L F Botannini) (New York: Nova Sci. Publ., 2010) p. 41
18. E M Kholodkova, A V Ponomarev *Khim. Vys. Energ.* **45** 21 (2011) [a]
19. A V Ponomarev, E M Kholodkova, B G Ershov, in *Proceedings of the 12th Tihany Simposium on Radiation Chemistry, Zalakaros, Hungary, 2011* Vol. 1
20. V B Komarov, A V Gordeev, S D Samuilova, A V Fadin, B G Ershov *Khim. Vys. Energ.* **33** 189 (1999) [a]
21. R Imamura, T Uena, K Murukami *Bull. Inst. Res. Kyoto Univ.* **50** 51 (1972)
22. K Sultanov, U A Azizov, Kh U Usmanov *Dokl. Akad. Nauk SSSR* **309** 907 (1989) [d]
23. I Sakurada, T Okada, K Kaji *J. Polym. Sci., Part C: Polym. Lett.* **37** 1 (1972)
24. Y Kusama, E Kageyama, M Shimada, Y Nakamura *J. Appl. Polym. Sci.* **20** 1679 (1976)
25. S I Kuzina, A I Mikhailov *Zh. Fiz. Khim.* **80** 1874 (2006) [e]
26. B G Ershov, S D Samuilova, G A Petropavlovskii, G G Vasil'eva *Dokl. Akad. Nauk SSSR* **274** 102 (1984) [d]
27. B G Ershov, O V Isakova, E P Matyushkina, S D Samuilova *Cellul. Chem. Technol.* **21** 331 (1987)
28. B G Ershov, V B Komarov, S D Samuilova *Cellul. Chem. Technol.* **21** 457 (1987)
29. A S Klimentov, G A Petropavlovskii, N E Kotel'nikova, S V Skvortsov, L A Volkova *Cellul. Chem. Technol.* **19** 251 (1985)
30. B G Ershov, O V Isakova, E P Matyushkina, S D Samuilova *Khim. Vys. Energ.* **20** 142 (1986) [a]
31. F A Blouin, J C Arthur *Textile Res. J.* **29** 198 (1958)
32. J Arthur, F A Blouin, R J Demint *Am. Dyes Rep.* **49** 383 (1960)
33. K Burczak, W Pekala, J Rosiak *Wiad. Chem.* **37** 193 (1983)
34. B Bludovsky, V Duchacek *J. Radiochem. Radioanal. Lett.* **38** 21 (1979)
35. V Duchacek, R Bludovsky *J. Radiochem. Radioanal. Lett.* **38** 31 (1979)
36. R Bludovsky, M Prochazka, J Kopoldova *J. Radioanal. Nucl. Chem.* **87** 69 (1984)
37. V B Komarov, S D Samuilova, L S Kirsanova, V A Morozov, T M Kuleshova, A G Smirnov, B G Ershov *Zh. Prikl. Khim.* **66** 393 (1993) [f]
38. M Horio, R Imamura, K Murukami *Bull. Inst. Res. Kyoto Univ.* **43** 117 (1965)
39. S Dilli, J L Garnet *Chem. Ind. (London)* 409 (1963)
40. A D Nekhaichuk, A M Evdokimov, S Kh Kitaev, V E Moskaleva, A A Yatsenko-Khmelevskii *Khim. Drevesiny* (1) 32 (1974)
41. A S Freidin *Deistvie Ioniziruyushchei Radiatsii na Drevesinu i ee Komponenty* (Effect of Ionizing Radiation on Wood and Its Components) (Moscow: Nauka, 1961)
42. R Florin, L Wall, D Brown *Trans. Faraday Soc.* **56** 1304 (1960)
43. V N Makatun, A K Potapovich, N N Ermolenko *Vysokomol. Soedin., Ser. A* **5** 467 (1963) [g]
44. P J Baugh, O Hinojosa, J C Arthur *Appl. Polym. Sci.* **11** 1139 (1967)
45. J C Arthur, O Hinojosa, V W Tripp *J. Appl. Polym. Sci.* **13** 1497 (1969)
46. J C Arthur, T Mares, O Hinojosa *Textile Res. J.* **36** 630 (1966)
47. S Dilly, J T Ernst, J Garnet *Aust. J. Chem.* **20** 911 (1967)
48. K Worlungton, P Baugh *Cellul. Chem. Technol.* **5** 23 (1971)
49. O Hinojosa, Y Nakaraura, J C Arthur *J. Polym. Sci., Part C: Polym. Lett.* **37** 27 (1972)
50. C Siraionescu, R Butnaru, G Rosmarin *Cellul. Chem. Technol.* **7** 153 (1973)
51. D S Khamidov, U A Azizov, V K Milinchuk, Kh U Usmanov *Vysokomol. Soedin., Ser. A* **14** 838 (1972) [g]
52. M Shimada, Y Nakamura, T Kusama, O Matsuda, E Kageyama *J. Appl. Polym. Sci.* **18** 3387 (1974)
53. I S Gaponova, G P Pariiskii, D Ya Toptygin *Vysokomol. Soedin., Ser. B* **19** 706 (1977) [g]
54. B G Ershov, A S Klimentov *Vysokomol. Soedin., Ser. A* **19** 808 (1977) [g]
55. A S Klimentov, B G Ershov, A E Bykov *Khim. Drevesiny* (2) 74 (1977)
56. O V Plotnikov, A I Mikhailov, E L Rayavee *Vysokomol. Soedin., Ser. A* **19** 25 (1977) [g]
57. O P Golova *Russ. Chem. Rev.* **44** 687 (1975) [*Usp. Khim.* **44** 1454 (1975)]
58. S Takeshi, K Shosaki *Nucl. Eng. (Jpn.)* **23** 41 (1977)
59. B G Ershov, V B Komarov *Vysokomol. Soedin., Ser. B* **27** 132 (1985) [g]
60. B G Ershov, V B Komarov, S D Samuilova *Vysokomol. Soedin., Ser. B* **27** 430 (1985) [g]
61. B G Ershov, V B Komarov, S D Samuilova, in *Vsesoyuznaya Konferentsiya po Teoreticheskoi i Prikladnoi Radiatsionnoi Khimii (Tez. Dokl.)* [All-Union Conference on Theoretical and Applied Radiation Chemistry (Abstracts of Reports), Moscow, 1984] p. 183
62. E M Kholodkova, A V Bludenko, V N Chulkov, A V Ponomarev *Izv. Akad. Nauk, Ser. Khim.* 1778 (2010) [h]
63. A V Ponomarev, E M Kholodkova, A K Metreveli, P K Metreveli, V S Erasov, A V Bludenko, V N Chulkov *Radiat. Phys. Chem.* **80** 1186 (2011)
64. E M Kholodkova, A V Bludenko, V N Chulkov, A V Ponomarev, I G Tananaev, in *Aktual'nye Problemy Khimii Vysokikh Energii (Materialy 4-i Vseros. Konf.)* [Actual Problems of High Energy Chemistry (Proceedings of the Fourth All-Russian Conference), Moscow, 2009] p. 96
65. S B Jones, C Valkenburg, C W Walton, D C Elliot, J E Holladay, D J Stevens, C Kinchin, S Czernik *Pacific Northwest National Laboratory Report, PNNL-18284, Richland, WA, 2009*
66. A A Shcherbakov *Furfurol* (Furfural) (Kiev: Gos. Izd. Tekhn. Lit. USSR, 1962)

67. S Ya Pshezhetskii, A G Kotov, V K Milinchuk, V A Roginskii, V I Tupikov *EPR Svobodnykh Radikalov v Radiatsionnoi Khimii* (EPR of Free Radicals in Radiation Chemistry) (Moscow: Khimiya, 1972)
68. R Livingston, H Zeldes *J. Am. Chem. Soc.* **88** 4333 (1966)
69. V A Sharpatyi *Radiatsionnaya Khimiya Biopolimerov* (Radiation Chemistry of Biopolymers) (Moscow: Energoatomizdat, 1981)
70. S I Kuzina, A I Mikhailov *Zh. Fiz. Khim.* **79** 1115 (2005) [e]
71. G F Zakis *Funktsional'nyi Analiz Ligninov i ikh Proizvodnykh* (Functional Analysis of Lignins and Their Derivatives) (Riga: Zinatne, 1987)
72. B G Ershov, O V Isakova, V B Komarov, E P Matyushkina *Khim. Drevesiny* (1) 6 (1986)
73. S I Kuzina, S V Demidov, A Yu Brezgunov, O G Poluektov, O Ya Grinberg, A A Dubinskii, A I Mikhailov, Ya S Lebedev, in *Fizika i Khimiya Elementarnykh Khimicheskikh Protsessov (Tez. Dokl. 5-i Vseros. Konf.)* [Physics and Chemistry of Elementary Chemical Processes (Abstracts of Reports of the Fifth All-Russian Conference), Chernogolovka, 1997] p. 310
74. A V Bludenko, V N Chulkov, A V Ponomarev *Khim. Vys. Energ.* **41** 459 (2007) [a]
75. A V Ponomarev, A V Bludenko, V N Chulkov, A G Liakumovich, I A Yakushev, R S Yarullin *Mendeleev Commun.* **18** 57 (2008)
76. D P Shalyminova, E N Cherezova, A V Ponomarev, I G Tananaev *Khim. Vys. Energ.* **42** 388 (2008) [a]
77. A Amano, O Horie, N H Hanh *Int. J. Chem. Kinet.* **8** 321 (1975)
78. I N Arnapal'skii, A I Skrigan, N S Kuprina *Khim. Drevesiny* (1) 126 (1975)
79. V N Sergeeva, Z N Kreitsberg, M Ya Yakobsone *Khim. Drevesiny* (5) 58 (1976)
80. K Ficher, W Goldberg, M Wilke *Lenzinger Ber.* 33 (1985); *Chem. Abstr.* **104** 11607 (1986)
81. F J Campbell *Radiat. Phys. Chem.* **18** 109 (1981)
82. A V Bludenko, A V Ponomarev, V N Chulkov *Khim. Vys. Energ.* **43** 125 (2009) [a]
83. A V Ponomarev, B G Ershov, in *Aktual'nye Problemy Khimii Vysokikh Energii (Materialy 4-i Vseros. Konf.)* [Actual Problems of High Energy Chemistry (Proceedings of the Fourth All-Russian Conference), Moscow, 2009] p. 31
84. US P. 5697987 (1997)
85. A V Ponomarev *Radiat. Phys. Chem.* **78** 48 (2009)
86. A V Ponomarev *Mendeleev Commun.* 256 (2006)
87. G Cserep, I Gyorgy, M Roder, L Wojnarovits *Radiation Chemistry of Hydrocarbons* (Budapest: Akademiai Kiado, 1981)
88. A V Ponomarev, A Yu Tsivadze *Dokl. Akad. Nauk* **411** 652 (2006) [d]
89. V N Chulkov, A V Bludenko, A V Ponomarev, I A Yakushev, R S Yarullin, in *Tezisy Dokladov XVIII-go Mendeleevskogo S'ezda po Obshchei i Prikladnoi Khimii* (Abstracts of Reports of the XVIIIth Mendeleev Congress on General and Applied Chemistry) (Moscow: Granitsa, 2007) Vol. 4, p. 447
90. A V Bludenko, A V Ponomarev, V N Chulkov, I A Yakushev, R S Yarullin *Mendeleev Commun.* **17** 227 (2007)
91. V N Chulkov, A V Bludenko, A V Ponomarev, B G Ershov *Khim. Vys. Energ.* **43** 478 (2009) [a]
92. V M Byakov, F G Nichiporov *Vnutritrekovye Khimicheskie Protsessy* (Intratrack Chemical Processes) (Moscow: Energoatomizdat, 1985)
93. E M Kholodkova, I G Tananaev, A V Ponomarev, in *V Yubileinaya Konferentsiya 'Yaderno-Promyshlennyi Kompleks Urala: Problemy i Perspektivy' (Tez. Dokl.)* ['The Fifth Anniversary Conference 'Ural Nuclear Industrial Complex: Problems and Perspectives' (Abstracts of Reports), Ozersk, 2009] p. 57
94. A B Sazonov, A D Tkhun, E P Magomedbekov, A V Ponomarev, I G Tananaev, B F Myasoedov *Ros. Khim. Zh.* **54** (3) 94 (2010) [i]
95. A V Bludenko, A V Ponomarev, V N Chulkov, B G Ershov *Khim. Vys. Energ.* **43** 516 (2009) [a]
96. A V Ponomarev, E M Holodkova, B G Ershov, in *Trombay Symposium on Radiation and Photochemistry (Abstracts of Papers), Trombay, India, 2010* p. 22
97. P Yu Butyagin, G V Abagyan *Vysokomol. Soedin.* **7** 1410 (1965) [g]
98. P Yu Butyagin, G I Gorokhov, G V Abagyan *Izv. Vyssh. Ucheb. Zaved., Lesnoi Zh.* **6** 135 (1965)
99. P Yu Butyagin *Khimicheskaya Fizika Tverdogo Tela* (Chemical Physics of Solid) (Moscow: Moscow State University, 2006)

[a] — *High Energ. Chem. (Engl. Transl.)*
[b] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[c] — *Int. Sci. J. Altern. Energ. Ecol. (Engl. Transl.)*
[d] — *Dokl. Phys. Chem. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem., Ser. A (Engl. Transl.)*
[f] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[g] — *Polym. Sci. (Engl. Transl.)*
[h] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[i] — *Mendeleev Chem. J. (Engl. Transl.)*