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Radiation-thermal decomposition of lignin

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The radiation-induced decomposition of lignin was studied using both radiation heating and dry distillation.

Lignin and cellulose are reproducible raw materials. Lignin is a waste of cellulose production and the annual world output of lignin exceeds 50 million tons.[1,2] Both lignin and cellulose easily decompose with heating. Dry distillation[1,2] (thermal decomposition without access of air) is suitable to obtain high-quality charcoal for metallurgy and valuable chemicals such as acetone, methanol, acetic acid and phenols.

The degradation of lignin and cellulose can be provoked by ionizing radiation.[3,4] In this work, the dry distillation of lignin was performed by conventional heating in a muffle furnace [thermal initiation (TI)] and by electron-beam heating[3,4] [radiation initiation (RI)]. In RI mode, lignin was processed only by a powerful electron beam without additional heat sources.

Natural hydrolytic lignin containing 8.5 wt% cellulose and 1.5 wt% mineral impurities was studied. Lignin was initially exposed to vacuum degassing at 105 °C. The samples were irradiated at atmospheric pressure in cylindrical quartz vessels 300 mm in height and 40 mm in inner diameter (degree of fullness, 60%). The radiation source was a U-003 linear accelerator (energy, 8 MeV; pulse duration, 6 μs; pulse repetition frequency, 300 Hz; average beam current, 800 μA; scan width, 245 mm; and scan frequency, 1 Hz). Dose rates were 2.0 and 2.8 kGy s^{-1}. Film dosimetry with the phenazine dye-doped copolymer standard reference material SO PD(F)R-5/50 [GSO (Certified Reference Material) no. 7875-2000] was used. During irradiation, distilled vapours were condensed in a water condenser at 15±1 °C. At a dose rate of 2.0 kGy s^{-1}, the temperature of samples increased to 400 °C during the first 4 min of irradiation and then changed slowly to 440 °C. The yield of lignin decomposition was above 15 kg kW^{-1} h^{-1}, which indicates the chain mechanism of this process. The volatilization was terminated at about 900 kGy. Comparative experiments were performed, in which a similar dynamics of heating was modeled by a muffle furnace. The role of admixed cellulose in lignin was assessed on the basis of experiments on dry distillation of EKB-1 sulfate brown pulp. The liquid products were analysed with a Q-Mass Perkin-Elmer AutoSystem XL gas chromatograph–mass spectrometer (carrier gas helium, a 60 m glass capillary column 0.25 μm in inner diameter).

Dry distillation gives gas, water, tar and coal products. Average compositions of the tar obtained from lignin in TI and RI modes are shown in Figure 1. In TI mode the tar includes a broad set of aromatic compounds with a rather high partial concentration; the chromatogram contains about 50 significant peaks. The most significant components are toluene, xylenes, phenol, guaiacol and creosol. The tar also contains furfural, furanmethanols and 5-methylfurfural. Probably, these products are formed by the destruction of cellulose. The total yield of formation of furfural, furanmethanols and 5-methylfurfural from cellulose EKB-1 is about 90 wt% in both TI and RI modes. However, in RI mode the relative concentration of furfural in tar was twice lower than that in TI mode.

The range of destruction products narrows in the case of the radiation heating of lignin. The chromatogram of the tar contains 35 peaks, of which only 27 coincide with peaks of products detected in TI mode. Guaiacol and creosol are the main components of the tar in RI mode. However, the total yield of tar in RI mode is almost three times higher: 24–27 wt% *versus* 8 wt% in TI mode.

Note that the fraction of alkylbenzenes among the products of radiolysis is lowered. Phenols and alkoxyphenols are the predominant radiolytic products. The formation of stable products of radiolytic fragmentation of aromatic macromolecules is determined mainly by radical processes.[4,5] In addition to the radiolytic cleavage of C–C bonds and the thermal decomposition of lignin molecules, radiolysis results in the efficient elimination of hydrogen atoms from lateral substituents.[1,4,5] The essential part of H atoms is formed *via* the cleavage of hydroxyl groups with the production of phenoxyl radicals[1,4] ArO·.

$$\text{Lig} \rightarrow \text{H}\cdot + \text{ArO}\cdot \qquad (1)$$

The H atom, easily reacting with an aromatic ring, is being transformed into an H-adduct.[4,5] Probably, aromatic H-adducts

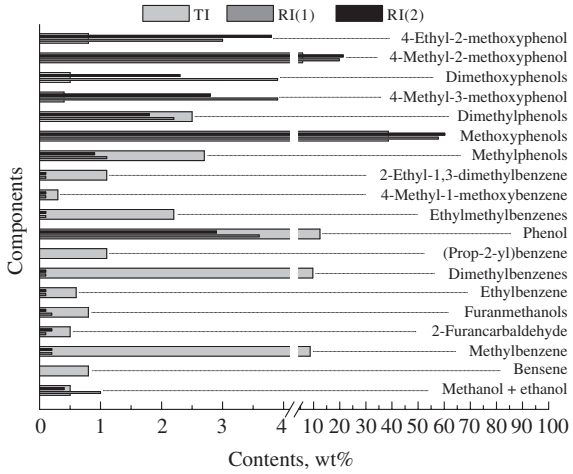

Figure 1 Contents of the basic components in the tar obtained by dry distillation in TI and RI (1 – 2.8 kGy s^{-1}, 2 – 2.0 kGy s^{-1}) modes.

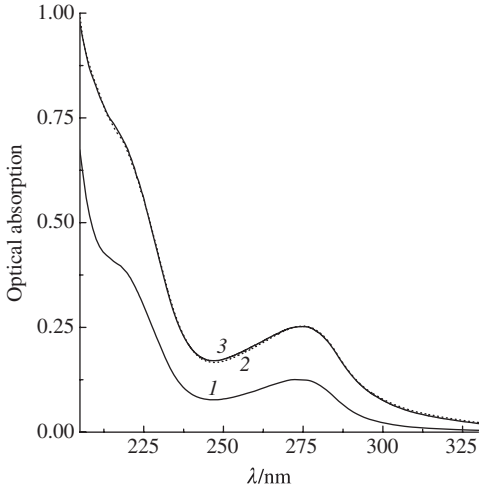

Figure 2 Optical absorption spectra of the aqueous fraction obtained by dry distillation in (*1*) TI and RI modes: (*2*) 2.8 kGy s^{-1}; (*3*) 2.0 kGy s^{-1}.

have a low thermal stability. The decay of H-adducts takes place *via* the cleavage of a lateral C–C bond. As the result, stable aromatic molecule M_i and secondary radical R· are formed.

$$\text{Lig} + \text{H}\cdot \rightarrow \text{LigH}\cdot \rightarrow \text{M}_i + \text{R}\cdot \quad (2)$$

Such an effect was observed in toluene:[6] alkylcyclohexadienyl radicals easily dissociate and turn into benzene and an alkyl radical at increased temperature (< 500 °C).

Methyl groups are dominant lateral alkyl substituents in lignin intermediates. Therefore, the probability of formation of ·Me radicals *via* the decay of H-adducts in reaction (2) is high. The recombination of methyl and phenoxyl radicals gives methoxy derivatives:

$$\cdot\text{Me} + \text{ArO}\cdot \rightarrow \text{ArOMe}. \quad (3)$$

In turn, the ·Me radical is transformed into methane, eliminating hydrogen from lignin

$$\cdot\text{Me} + \text{Lig} \rightarrow \text{CH}_4 + \text{Lig}\cdot, \quad (4)$$

or forms larger hydrocarbon

$$\cdot\text{Me} + \cdot\text{Me} \rightarrow \text{C}_2\text{H}_6. \quad (5)$$

Owing to such processes the essential concentrating of methoxy compounds in tar is observed, as well as the concentrating of light alkanes in gas. It is known[4,5] that the radiation-chemical yields of dealkylation products of alkylbenzenes are higher than the yields of alkylation products. The recombination of alkyl and phenoxyl radicals can increase the relative yield of alkoxy derivatives. It is supposed[1,2] that the formation of methanol during dry distillation takes place, mainly, by the elimination of methoxy groups from lignin molecules. Therefore, the low yield of methanol in RI mode points to the relative stability of methoxy groups.

A small part of the organic products of dry distillation is water soluble. The yield of an aqueous fraction in both modes is about 15–16 wt%. The aqueous fractions have a brown colour and a high acidity. In TI mode, the pH of an aqueous fraction is about 3.3, whereas in RI mode pH ≤ 3.0. The optical absorption spectra in aqueous fractions, being in equilibrium with tar, are demonstrated in Figure 2. Almost twice more of water soluble organic products are formed in RI mode. It is demonstrated by the fractional distillation of aqueous solutions.

There are differences in composition and structure of charred residues remaining after dry distillation in RI and TI modes. The carbonization is incomplete in both modes. The atomic composition of the charred residue includes ~90% C and ~10% O

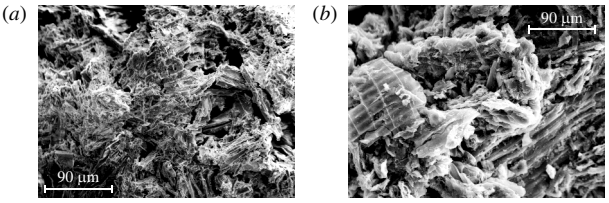

Figure 3 Typical structures of the charred residues obtained by dry distillation in (*a*) TI and (*b*) RI modes.

in the RI mode, but ~83% C and ~16% O in the TI mode. The RI mode provides conservation of ordered structure being characteristic of initial fibrils of cellulose and aggregates of lignin. In turn, the TI mode results in the deformation and compaction of charred residue (Figure 3). The yield of charred residue in the RI mode is 43–45 wt%, while in the TI mode it is 55–56 wt%. In turn, the RI mode yields less gaseous products (on 4–6%); however, this gas is triply rich by light alkanes.

The applied RI mode of dry distillation is not optimum. At first, the removal of destruction products from a hot irradiation area can delay by sorption in a bulk of lignin packaging. As a result, there is a high probability of subsequent thermal and/or radiation destruction of distilled off products. The increase of the yield of liquid products in TI and RI modes can be realized by means of vacuum pumping-out[1,2] of formed vapours or by means of removal of vapours into a flow of carrier gas.

Radiation-chemical processes in lignin can be accompanied by a 'cage effect': radical pairs formed by the dissociation of a single molecule may be prevented from moving away from each other by the surrounding molecules.[4] As a consequence, there is a high probability of geminate recombination of the radicals. Accordingly, stable products of the unimolecular decomposition or disproportionation of radicals prevail in tar.

The RI mode gives simultaneous and rather uniform heating of all volume of lignin, which is distilled. Inside of a muffle furnace, the heating in the TI mode goes from periphery to centre of a sample; that increments unproductive thermal losses and raises probability of overheat of a material (formation of charred residue). The RI mode intensifies free-radical reactions[1,5] and creates more favourable conditions of heating, therefore the yield of liquid products of dry distillation of lignin increases, while the energy inputs drop twice.

The new procedure of the radiation-induced decomposition of lignin integrates both radiation heating and dry distillation. The explored procedure yields remarkable features of the products: the gas is enriched in light hydrocarbons C_1–C_4; the charred residue conserves structure of initial fibrils and has a large free surface; the tar contains a narrow assortment of phenols. The productivity of the procedure is above 15 kg kW^{-1} h^{-1}, which indicates the chain decomposition of lignin.

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