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## MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

# Potential Activity of Hydrolytic Lignin in Copolymerization Reactions

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**Abstract**—Structural-molecular characteristics of hydrolytic lignin samples from various factories were studied and their potential activity in copolymerization with polyacrylonitrile was determined.

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In preceding papers, the effect of thermochemical interaction between lignin (LG) and polyacrylonitrile (PAN) was observed [1, 2]. The choice of samples was governed by application-related goals of the study: industrially manufactured PAN fibers and ordinary hydrolytic lignin, a product of a domestic pulp-and-paper combine, were used.

Because the principal characteristics of the starting polymers strongly depend on the prehistory of their formation, studies of particular representatives of each kind of macromolecular compounds are of indubitable scientific and practical interest. For this purpose, we made in this communication a prospective analysis of probable pathways of interaction of various LG samples with PAN, depending on the chemical composition and structure of hydrolytic lignin from various factories.

It is well known [3, 4] that lignin is a large 3D macromolecule constituted by phenylenepropane units with various spatial orientations. This is a product of a biological genesis of plants, which forms, in the course of complex competing reactions, a substance binding two other components of the vegetable mass, cellulose and hemicellulose. According to a figurative expression of a lignin researcher [5], this natural polymer plays, together with hemicellulose, the role of a cement in the “reinforced vegetable concrete”, in which cellulose serves as the reinforcement. Hence follows the conclusion about the low molecular mass of LG, the growth of whose macromolecule is limited by termination reactions at hemicelluloses and cellulose. As a rule, MM values are limited to $20–30\times10^3$; however, the 3D nature of the LG structure is beyond any doubt. This specific feature presents certain difficulties both in interpretation of the structure of each separately taken sample and in determination of various functional groups present in LG, in relation to its formation in the nature and methods of its recovery from wood. As a result, we still have no reliably determined characteristics of lignin, in general, with only some parameters of particular samples available, which is indicated by numerous reports of researchers from the Riga scientific school, concerned with wood and its products [6, 7].

It is also known that the thermal stability of wood components is rather low, especially for cellulose and hemicellulose. On their background, LG possesses an enhanced thermal stability because of the high aromatization of its structure. In this regard, it can be compared to phenolphthalein resins; however, the natural indeterminacy of the LG structure hinders purposeful control over its properties, especially in carbonization. Moreover, the low thermal stability of cellulose favors development of destructive processes precluding carbonization.

Hence follows that attempts to replace cellulose macromolecules with more thermally stable macromolecular formations are promising as regards the improvement of deformation-strength parameters of carbon compounds based on LG at a preserved or increased coke number (CN). First experiments on cocarbonization of LG with polyacrylonitrile [1, 2] demonstrated perceptible changes in the kinetics of thermochemical reactions and revealed new properties in analysis of cocarbonization products. This fact makes it possible to outline ways to optimize the cocarbonization of PAN with LG and to choose the best suitable LG and PAN samples for accomplishing this goal.

The choice of PAN samples was based on results of preceding studies [8–10], in which it was shown that, among three PAN samples synthesized in different ways (anionic, radical, and partly cyclized), the first (A-PAN) is the most thermally stable. The original choice of this polymer was due, in addition to the enhanced thermal resistance, to the higher strength of carbon materials based on A-PAN [11]. A thermal analysis of three A-PAN samples with different MM (38 to 440 103) in air and in a vacuum demonstrated a fairly identical nature of thermochemical reactions in the temperature range 20–900°C. The main carbonization criterion, CN, is within the range 34–38%.

By analogy with [1], we used in the study of cocarbonization of A-PAN with LG the same sample of hydrolytic LG at a 25 : 75 mass ratio, and the temperatures of isothermal keeping in the atmosphere of argon were raised to 500°C. Figure 1 shows how the loss of mass by an A-PAN–LG sample depends on the temperature of isothermal keeping according to TGA data obtained in a self-generated atmosphere and TVA data in a vacuum. The observed extremal dependence of the loss of mass on the thermal keeping temperature is accounted for by the difference between the thermal degradation mechanisms of both LG and A-PAN in the temperature range 250–400°C. It is known that, in this temperature interval, A-PAN undergoes thermocyclization to give a compound more thermally stable than the linear A-PAN. As for LG, the nature of its thermal degradation in the presence of PAN is changed in the same temperature range and leads to predominance of the competing reaction of cross-linking of unstable fragments of the LG macromolecule.

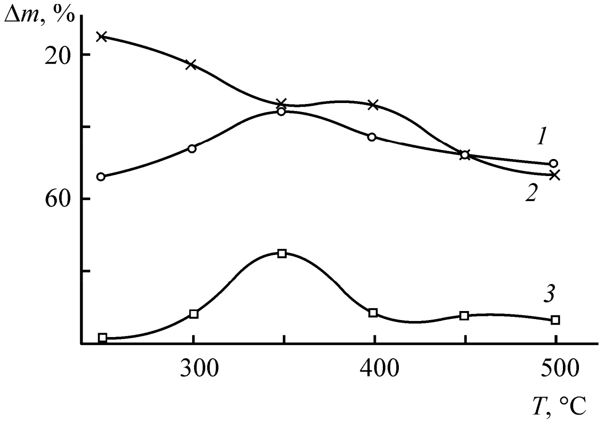

**Fig. 1.** TG curves for isothermal keeping of an A-PAN–LG blended formulation, 25 : 75 wt %. (Δ*m*) Loss of mass and (*T*) temperature; the same for Fig. 2. (*1*) Thermal treatment in a vacuum at 400°C; keeping in a self-generated atmosphere at a temperature (°C): (*2*) 400 and (*3*) 500.

To verify this conclusion, we made a comparative thermal analysis of LG samples isolated in different

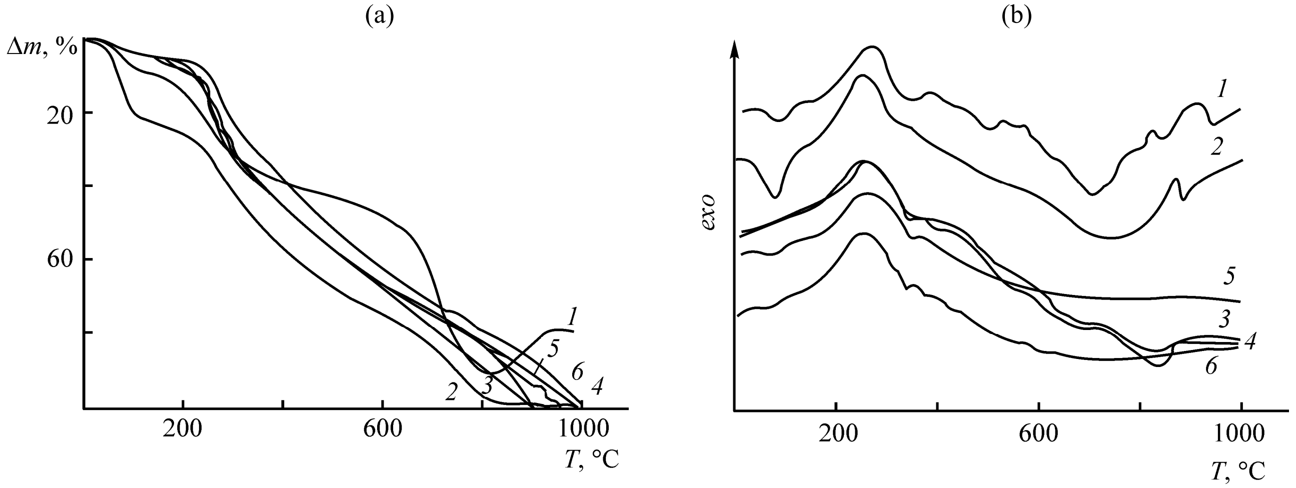

**Fig. 2.** (a) TG and (b) DTA curves for thermooxidative destruction of LG samples. (*1*) Lignosulfonate; hydrolytic LGs: (*2*) Syktyvkar HP, (*3*–*5*) Tavda HP, and (*6*) Kirov HP.

**Table 1.** Results of a chromatographic analysis of soluble fractions of LG samples

| Sample no. | Interval | | | | | Content of the soluble part, % |
|---|---|---|---|---|---|---|
| | >5000 | wt % | 600–5000 | wt % | 0–600, wt % | |
| | | | DMSO | | | |
| 2 | 5000–30000 | 9.7 | 600–5000 | 87.6 | 2.6 | 15.5 |
| 4 | 5000–30000 | 18.3 | 600–3200 | 76.6 | 5.1 | 10.5 |
| 6 | | | 600–30000 | 73.5 | 26.5 | 9.2 |
| 1 | | | 1300–8000 | 36.7 | 63.3 | 100 |
| | | | Pyridine | | | |
| 2 | 5000–100000 | 27.3 | 600–5000 | 62.7 | 10.0 | 8.8 |
| 4 | 5000–100000 | 27.1 | 600–5000 | 63.3 | 9.6 | 13.0 |
| 6 | 5000–100000 | 35.1 | 600–5000 | 56.1 | 8.8 | 9.5 |
| | | | Dioxane | | | |
| 6 | 1000–30000 | 6.36 | 600–5000 | 41.2 | 52.4 | 9.4 |

ways. Figure 2 shows TG and DTA curves for LG samples isolated by hydrolysis of wood pulp at different pulp-and-paper combines by different methods. Sample no. 1 is Na lignosulfonate manufactured by Stephan Europe NCA; sample no. 2, hydrolytic LG produced by sulfate cooking at Syktyvkar hydrolysis plant (HP). Samples 3–5 are hydrolytic LG manufactured at Tavda HP: no. 3, untreated; no. 4, the same sample, fraction with a diameter less than 1 mm; and no. 5, sample no. 4 extracted with toluene. Sample no. 6 is hydrolytic LG from Kirov plant.

The thermal analysis data show certain differences in the thermal degradation kinetics of the samples under study. The kinetics of thermooxidative degradation of lignosulfonate noticeably differs from that of hydrolytic lignin samples. In the low-temperature stage of composition below 200°C, a noticeable loss of mass (12%) is observed, accompanied by an endothermic effect peaked at 106°C (Fig. 2b, curve *1*). In this temperature range, it would be expected that, in this temperature range the reaction occurs of splitting-off of sulfoxy groups at the α-carbon atom of the side propane chain of the lignin structural fragment. It is known that that the content of sulfoxy groups in lignosulfonate is within 12–14% [12] and they are distinguished by high reactivity in position α [13]. Consequently, the splitting-off of sulfoacid groups or low-molecular-weight fragments containing these groups occurs in the sample under study in the early stage of composition. This assumption is in agreement with the results of chromatographic analysis (Table 1) performed as follows.

A 10-mg portion of lignin and 2 mg of an organic solvent were placed in a hermetically sealed vessel. The vessel was thermostated at 65°C for 8 h, with agitation at regular intervals of time. The oversediment fluid (1 ml) was dried in a vacuum and then dissolved in 0.2 ml of a mixture of DMF and 0.2 M of trifluoroacetic acid. Soluble fractions were analyzed on a chromatographic system with a Test-900 refracttometric detector (St. Petersburg) and a column packed with styrogel (Phenogel MXL). The concentration of soluble lignin was determined using the calibration dependence $S = kc$, where $S$ is the peak area, and $c$, lignin concentration in the calibration solution. The calibration dependence was constructed using chromatograms of Björkman lignin, which is fully soluble in the eluent. The mass m of soluble lignin was calculated by the formula $m = 0.2c$.

The analysis demonstrated the presence of a considerable amount of DMSO-soluble fractions with MM of 100 to 600. According to solid-state $^{13}$C NMR data, these fractions contain ester and carbonyl groups at nearly equal amounts of syringyl and guaiacyl moieties (Table 2). In addition, elemental analysis data indicate that, on heating sample no. 1 to 200°C, the amount of sulfur decreases by more than a factor of 2. Another specific feature of lignosulfonate is noteworthy. A region of comparatively high thermal stability (320–680°C) is well seen in the TG curve (Fig. 2a). In this region, the loss of mass is substantially decelerated and the coke number has rather large values. For example, the loss of mass at 500°C is about 40%, and the CN50 temperature is 650°C. Probably, this effect is due to the presence of residual sulfoxy groups, in which sulfur acts as an inhibitor of thermooxidative degradation.

The thermooxidative degradation of hydrolytic LGs (sample nos. 2–6) occurs by a similar mechanism, with minor distinctions related to methods of LG recovery from wood. For example, the loss of mass by sample no. 2, which is 24.1% in the temperature range 20–140°C, is probably due to removal of low-molecular-weight substances remaining in hydrolytic lignin before its extraction. In this parameter, this sample markedly differs from other hydrolytic LG samples, which lose 7–8% of the initial mass below 250–266°C. Apparently, specific features of wood cooking at various HPs affects the amount of low-molecular-weight impurities in lignin and the content of reactive groups thermally unstable in this temperature range. According to the exothermic effects (Fig. 2b) accompanying the decomposition of LG samples, peaks of heat release in thermal oxidation are concentrated within a narrow temperature range for hydrolytic LG and are somewhat shifted to higher temperatures for sample nos. 1 and 5. The reason is that lignosulfonate is different from hydrolytic lignin (Fig. 2b, curve *1*) and sample no. 5 is extracted with toluene (Fig. 2b, curve *5*).

For hydrolytic lignins, the coke number does not exceed 40–50% above 500°C. The run of the TG curves suggests that, above 400°C, the kinetics of thermochemical reactions in the samples studied is consistent with the specific features of carbonization of cellular macromolecular compounds with a heterocyclic structure [14]. The same is indicated by the heat effects noticeable in the carbonization region, especially for lignosulfonate, and comparable with the endo- and exothermic effects previously observed in carbonization of polyacrylonitrile [15].

Additional information about thermochemical reactions occurring in treatment of the samples under study at up to 800–1000°C can be obtained from results of a thermal analysis in a vacuum and inert or self-generated atmosphere. Of particular interest is a comparison of the loss-of-mass curves in the differential form in the temperature range 20–400°C, where the reactivity of the lignin samples is the highest.

**Table 2.** Results of solid-state $^{13}$C NMR spectroscopy of the samples

| Sample no. | Ar/Al[a] | Content, wt % | | S/G[b] |
|---|---|---|---|---|
| | | cellulose | COOR group | |
| 1 | 1.2 | 0.0 | 3 | 0.9 |
| 2 | 1.6 | 1.9 | 1 | 4.6 |
| 3 | 1.4 | 2.1 | 1 | 1.3 |
| 4 | 1.3 | 2.0 | 1 | 1.4 |
| 5 | 1.6 | 2.9 | 1 | 1.1 |
| 6 | 1.0 | 1.0 | ~0 | 0.4 |

[a] Ar/Al is the ratio between aromatic and aliphatic groups. [b] S/G is the ratio of syringyl and guaiacyl moieties.

Figure 3c shows as an example DTG curves for sample nos. 1, 2, 4, and 6. As is known [4, 16], the chemical and thermal treatment of wood raw materials is accompanied by physicochemical reactions leading to partial destruction and structuring of lignin. The formation of a considerable amount of a water-soluble product is characteristic of lignosulfonates; hydrolytic lignins mostly contain products of deep structuring, which have an increased molecular mass.

Analysis of thermograms in Fig. 3 shows that lignosulfonate decomposed in stages. The number of stages and their parameters depend on the thermal treatment conditions of the samples. The largest number of stages is observed in the case of heating in a vacuum, which is well explainable by the permanent shift of the degradation ↔ structuring chemical equilibrium toward decomposition as a result of the continuous removal of thermal degradation products from the reaction zone. This process is particularly noticeable in the initial stage of carbonization above 400°C, when several peaks indicating that the decomposition reactions continue are observed at 490, 665, and 715°C in the TVA curve (Fig. 2, curve *2*). In addition, the coke number does not exceed 20% in a vacuum thermolysis of lignosulfonate at 800°C, which is two times smaller that that in thermooxidative degradation (Fig. 3, curve *3*) and thermal degradation in an inert atmosphere (Fig. 3, curve *1*).

In these experiments, a certain comparability in the loss-of-mass kinetics is observed along the temperature

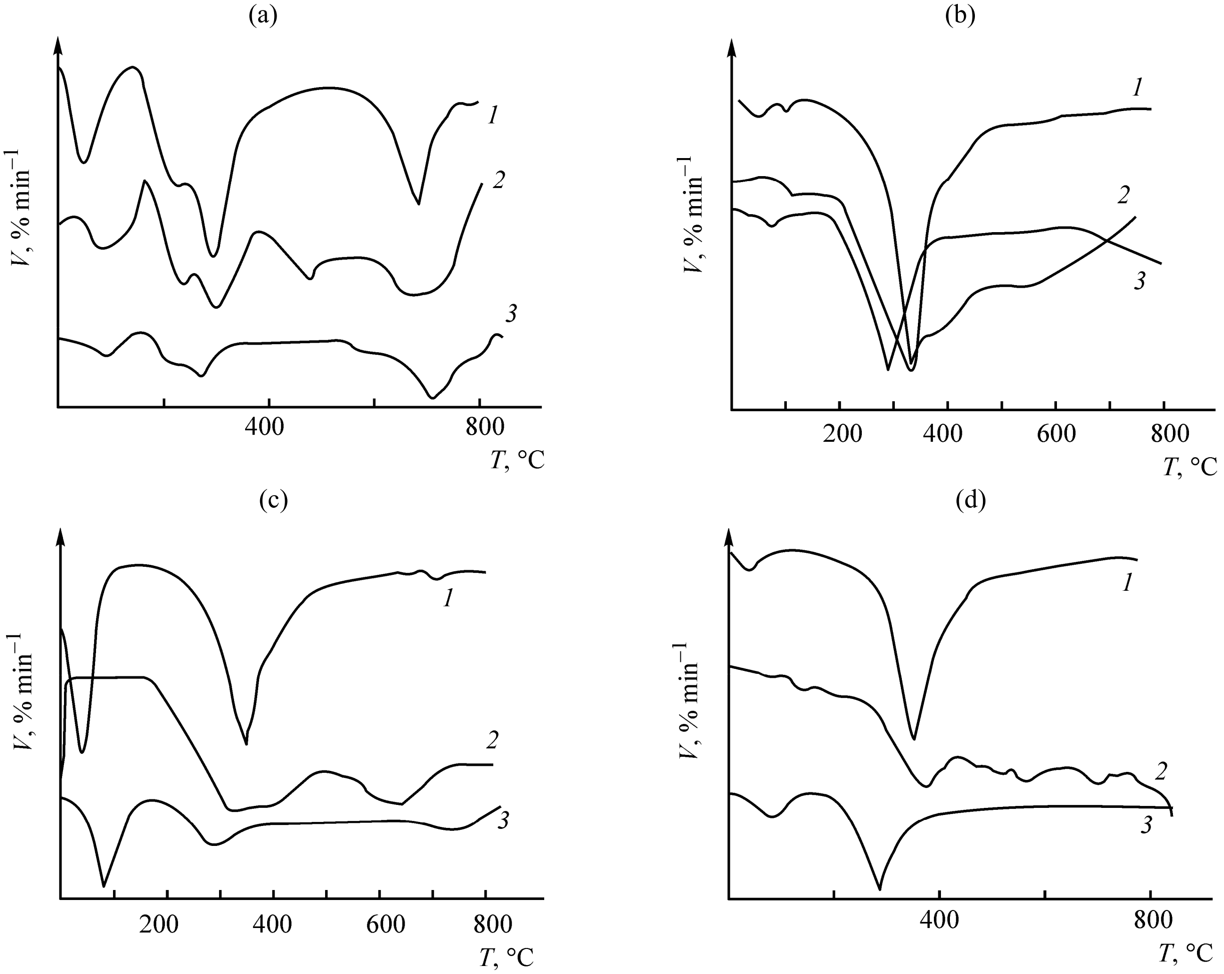

**Fig. 3.** Differential curves of release $V$ of products in (*1*) thermal, (*2*) vacuum, and (*3*) thermooxidative degradation of LG sample nos. (a) 1, (b) 2, (c) 3, and (d) 4. (*V*) Release rate and (*T*) temperature.

scale. There only exist some quantitative differences in the temperature parameters of the peaks; however, these values fit a three-stage scheme of thermal transformations of lignosulfonate in the temperature range 20–900°C. In heating under dynamic conditions to a temperature of 170–180°C, low-molecular-weight products of thermal decomposition are released, with a peak at 73°C in an inert medium and at 110 and 115°C in an oxidizing atmosphere and in a vacuum. Depending on the composition of the ambient atmosphere, lignosulfonate loses 5 to 10% of its mass below 180°C. According to DSC calorimetric data, the loss of mass is accompanied by a considerable endothermic effect peaked at 84°C in an inert atmosphere and at 106°C in an oxidizing atmosphere.

Results of chromatographic and spectral (solid-state $^{13}$C NMR) analyses of sample no. 1 suggest that thermal degradation products formed in the first stage of lignosulfonate decomposition contain low-molecular-weight products leaving the reaction zone in the temperature range 50–180°C. To these products belong dimeric derivatives of guaiacylpropane diol β-guaiacyl ether and also of veratrylpropanediol, whose volatile products are released at 165 and 210°C, respectively [17]. In addition, predominance of ali-phatic units is observed, compared with sample nos. 2–5 (Table 2). The presence of ester groups and their low-temperature decomposition favor formation of peroxide radicals, which accelerate thermal oxidation to give aromatic alcohols and aldehydes.

In contrast to other LG samples, the initial thermal stability of lignosulfonate is limited by a temperature of 200°C (Fig. 2), above which a noticeable loss of mass is observed up to 340°C. Probably, this process is associated with the considerable polydispersity of sample no. 1, which is confirmed by the data for lingosulfonates obtained in various ways [18]. As the temperature of thermal treatment of sample no. 1 is raised further, the decomposition reactions associated with release of volatile products are markedly decelerated. As a result, the CN increases at 600°C to appro-ximately 60%, in contrast to other samples.

The comparison of the kinetic curves of thermochemical reactions for hydrolytic lignins, sample nos. 2, 4, and 6, shows that differences are only observed in the low-temperature region of thermal degradation. These differences reflect specific features of thermal treatment of wood at HPs and also changes in treatment stages in a single process. For example, sample nos. 2 and 4 were isolated at Syktyvkar and Tavda HPs without (no. 2) and with subsequent extraction of the raw material. As a result, the TG curve of sample no. 2 shows a significant loss of mass (~25%) below 100°C, which is not observed for sample nos. 4 and 6, subjected to a preliminary extraction to remove low-molecular-weight impurities (water, tars, extractive substances).

As the temperature is raised further, the shapes of the kinetic curves describing the loss of mass for all the samples almost coincide at temperatures within the thermal degradation and carbonization zone. As in the case of sample no. 1, the differences between the kinetic curves of thermal degradation depend to a greater extent on the TGA conditions (Figs. 3a–3d). A thermal treatment in a vacuum leads to a nearly complete decomposition of all the LG samples. In this case, the CN at 900°C does not exceed 15–20%. In an inert atmosphere, the CN reaches values of 40–43% for some samples (Table 3). These data demonstrate that hydrolytic lignins are promising as precursors for production of carbonized materials in combination with certain thermally stable polymers.

It is well known that the side three-carbon propane chain of the aromatic ring of lignin is a most important reaction group responsible for intra- and intermolecular reactions with LG. Depending on the technology of wood processing at various pulp-and-paper combines, the isolated lignins may contain a rather wide variety of low- and high-molecular-weight compounds. Samples may contain fragments with various molecular masses: beginning from the simplest phenylpropane single-ring derivatives of guaiacyl, coniferyl and oxybenzaldehyde; products of their oxidation (hemipinic acid derivatives); as well as di-, tri-, tetra-, and other *n*-dimensional compounds formed in cleavage of a “large” LG macromolecule based on the known Freudenberg formula and its modifications.

**Table 3.** Results of TGA of LG samples in an inert atmosphere[a]

| Sample no. | $P_{on}$, % | $\tau_0$, °C | $\tau_5$, °C | $\tau_{10}$, °C | $\tau_{max}$, °C | $\tau_{50}$, °C | CN, % |
|---|---|---|---|---|---|---|---|
| 1 | 5 | 194 | 235 | 269 | 310 | 592 | 43.0 |
| 2 | 13 | 195 | 293 | 330 | 360 | – | 43.5 |
| 3 | 2 | 200 | 276 | 312 | 360 | 438 | 34.3 |
| 4 | 2 | 175 | 270 | 307 | 350 | 467 | 36.5 |
| 5 | 3 | 160 | 271 | 294 | 310 | 548 | 40.5 |
| 6 | 2 | 220 | 302 | 334 | 365 | 524 | 39.8 |

[a] $P_{on}$ is the loss of mass by a sample before the onset of decomposition of a macromolecule (before temperature $\tau_0$); the CN is given for 800°C.

Because all the lignin samples under study are rather low-molecular-weight products of deep degradation (group IV of methods by classification [16]) of natural lignins, it is of interest to identify the main compounds promising as agents of polymer-analogous reactions with polyacrylonitrile.

Preliminary chromatographic studies of the chosen LG samples demonstrated that, despite the rather severe thermohydrolytic treatment of wood, which eliminates qualitative compositional differences, there exist certain indications distinguishing each of the five samples from one another.

Analysis of the data in Table 1 shows that the amount of soluble fractions conditionally divided by molecular masses into three regions depends both on the nature of the solvent used and on technological features of LG isolation from hydrolysis products. For example, for sample no. 6 (LG from Kirov HP), the total amount of the soluble fractions is approximately 10 % relative to the initial mass of the sample. As for the MMs of the fractions, this sample contains a noticeable amount of low-molecular-weight fractions with MM 100–500. The largest amount (26.5%) passes into the DMSO solution, and approximately 10%, into each of the pyridine and dioxane solutions. Dioxane extracts the largest amount of compounds with *MM* 250–300, which can be attributed to dimeric structural units of lignin. According to $^{13}$C NMR data, these structures may be derivatives of ferulic acid and its oxyesters, for which dioxane may be the most suitable solvent.

Thus, we can conclude that the soluble part of sample no. 6 is composed of a set of low-molecular-weight products containing a certain amount (~7%) of fragments with *MM* > 10 000. A larger amount of macromolecular products with *MM* < 100 000 can be extracted from sample no. 6, with pyridine used as the solvent. As for dimethyl sulfoxide, two soluble parts of lignin no. 6 were found in this solvent: low-molecular-weight (26.5%) and medium-molecular-weight (73.5%). The first of these belongs to mononuclear substituted phenylpropane moieties with equal amounts of aromatic and aliphatic carbons. The second is probably a mixture of di-, tri-, and oligomeric fragments with aromatic-to-aliphatic component ratios in the lignin structure of 4.6, 1.4, and 0.4.

Noteworthy is the high activity of pyridine in recovery of the highest-molecular-weight compounds with *MM* up to 100 000 from all of the hydrolytic lignin samples studied (nos. 2, 4, 6). Probably, this effect is due to a specific feature of pyridine: it is well mixes with water, which enables its use for hydrophilic media. In addition, the basicity of pyridine enables formation of complexes with carboxy and carbonyl groups of separate fragments of lignin, which facilitates formation of solutions of macromolecular compounds.

For DMSO, we observed a similar (to pyridine) activity in partial dissolution of sample no. 6, with the only difference that the *MM* of the highest-molecular-weight fragments did not exceed 30 000. For both the solvents, the ionization energy is approximately 9.34 and 9.1 eV for pyridine and DMSO, respectively, and the donor numbers (138.5 and 124.7) exceed the acceptor numbers by more than an order of magnitude. Apparently, these specific features predetermine the potential activity of polar solvents in the transformation of the molecular structure of lignin in its fractionation. In addition, it is known that, under certain conditions, DMSO can exhibit electron-donor and electron-acceptor properties [19]. Therefore, with the redox characteristics of lignin taken into account, DMSO can act as a versatile solvent whose applicability can be controlled by technological means. It should be noted that, similarly to pyridine, DMSO is of interest as a solvent initiating low-temperature reactions with polyacrylonitrile and, in particular, those ending in chain rupture. From this standpoint, these solvents are promising for performing joint reactions of hydrolytic LG with PAN.

The specific features of the interaction with pyridine and DMSO, noted for LG no. 6, are about the same for hydrolytic lignin sample nos. 2 and 4. However, the ratio between the high- and low-molecular-weight fractions in DMSO for sample no. 2 is strongly shifted to the region of macromolecular fragments. Moreover, the total content of the DMSO-soluble part of sample no. 2 exceeds by almost 30% that of sample no. 6. Probably, the method used to isolate sample no. 2 noticeably differs in technological parameters. The solubility parameters of sample no. 4 are on the medium level as regards the fractional and quantitative composition of separate fractions and also reflect the specificity of delignification of wood raw materials at different plants. This conclusion is confirmed by NMR spectroscopic data, which indicate that the ratio between the aromatic and aliphatic components (Ar/Al) decreases in sample nos. 2, 4, and 6 in the order 1.6–1.3–1.0. This tendency is observed in a comparison of the ratios between the guaiacyl and syringyl fragments (G/S) in the samples under study: 4.6, 1.4, and 0.4.

## CONCLUSIONS

(1) The results of thermal, chromatographic, and NMR spectral analysis were used to evaluate the reactivity of a number of hydrolytic lignin samples in polymer-analogous transformations in a thermochemical interaction with polyacrylonitrile of varied composition.

(2) It was shown that the solubility of separate hydrolytic lignin fractions in organic solvents depends on a method used to recover lignin from wood.

## ACKNOWLEDGMENTS

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