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Depolymerization of Alkaline Lignin in the Medium of Supercritical 2-Propanol

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Abstract—The results of optimizing the conditions of alkaline lignin depolymerization in a medium of supercritical 2-propanol in order to obtain low molecular weight aromatic compounds, which are potential renewable raw materials for organic synthesis, production of various products and materials, are presented. The designed experiment was applied, based on a central composite rotatable uniform plan design of the second-order for three variables (temperature, process time, liquid module) varied at five levels. The target parameters for optimization were the degree of conversion of lignin to soluble products and their molecular weight. Based on the obtained dependences the optimal depolymerization conditions (450°C, 8 min, liquid module 20) were determined, which ensured the degree of lignin conversion at the level of 73%. Using high-resolution mass spectrometry, it was shown that the resulting depolymerization products have an extremely complex component composition, which includes mainly monomeric and dimeric phenols.

Keywords: lignin; supercritical fluid; 2-propanol; depolymerization; planned experiment

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Lignin is the second most abundant biopolymer in nature after cellulose and accounts for up to a third of plant biomass [1]. This makes it the most important promising renewable source of various organic compounds and raw materials for the production of a wide range of products, alternative to fossil hydrocarbons. Of particular interest in this regard are technical lignins formed during the production of cellulose, as well as biofuels (ethanol, butanol) from plant feedstock [2]. One of the important reasons for the weak involvement of technical lignins in the production activities (in addition to combustion) is the lack of effective technologies for their conversion into low molecular weight aromatic compounds, which are of the greatest value as raw materials for organic synthesis, production of various products and materials. So, even without preliminary separation into individual components, complex mixtures of low molecular weight phenols obtained from lignin can be used to produce phenol-formaldehyde resins with improved consumer properties and low formaldehyde emission [3]. In this regard, active searches are being made for ways of lignin depolymerization, among which the largest number of publications is devoted to pyrolysis, catalytic hydrogenolysis and oxidation, acid and alkaline hydrolysis [4–12].

Application of supercritical fluids seems to be very relevant and promising as solvents and depolymerizing agents to achieve a high degree of lignin conversion due to harsh process conditions. [13, 14]. The use of supercritical water, methanol and ethanol, and water-alcohol mixtures as depolymerizing agents was reported in literature, schemes of the course of solvolytic processes in such media were suggested, and some products of lignin conversion were established [6, 13, 15–18]. A disadvantage of supercritical water is its low dissolving ability with respect to lignin and its degradation products, as well as the occurrence of undesirable condensation processes that reduce the yield of low molecular weight compounds [19]. An important aspect of the use of organic solvents in supercritical technologies is their thermal stability: Lower alcohols and aprotic solvents with a high dissolving ability with respect to lignin under supercritical conditions form a significant amount of liquid and gaseous degradation products [20–22]. In this regard, the most preferred depolymerizing agent is 2-propanol, which has a high dissolving ability with respect to lignin [23] and the highest stability among lower alcohols under supercritical conditions necessary for depolymerization of lignins [20]. In addition to affordability and low cost, a significant advantage of 2-propanol is also its ability under supercritical conditions to act as a hydrogen donor for the implementation of reductive hydrogenation depolymerization of lignin [2] to produce many valuable products. In solving this problem, 2-propanol is able to compete with such well-known and more expensive hydrogen donors as formic acid and tetralin [24, 25]. The use of 2-propanol with the addition of water and a heterogeneous catalyst based on rhodium and rare earth oxides allowed the authors of [19] to achieve 80% conversion of kraft lignin into low molecular weight products with a high proportion of alkyl phenols. Despite this fact, the processes of lignin depolymerization in 2-propanol medium are still insufficiently studied, which is associated with a large number of parameters that affect the yield of the target products.

The aim of the study was to optimize the conditions for the depolymerization of alkaline lignin in the medium of supercritical 2-propanol to achieve the maximum yield of low molecular weight products under technologically acceptable conditions. Taking into account the complexity of the system under study, methods for active planning of a multifactor experiment were used to solve the problem, which made it possible to obtain a quadratic regression model of the influence of at least three factors on the process [26–29].

EXPERIMENTAL

A sample of alkaline lignin, one of the most typical of technical lignins, obtained as a result of alkaline delignification [30] of spruce wood (sawdust) under laboratory conditions, was used as an object of study. Delignification mode: raising the temperature of the cooking solution to 100°C for 30 min, the isothermal stage 100°C for 90 min, raising the temperature to 180°C for 60 min, the isothermal stage 180°C for 240 min. The ratio of liquid and solid phases (liquid module) is 5, the content of active alkali (NaOH) is 120 g L^{-1}. The resulting cooking solution was filtered off from the fibrous cellulose residue after cooling to 50°C and acidified with sulfuric acid to pH 3. The settled lignin was separated by centrifugation and washed with distilled water until there was no sulfate ion in the washings. The resulting product was dried in vacuum at 40°C.

The moisture content of the alkaline lignin preparation was 3.5%, and the ash content was 0.1%. According to elemental analysis performed with a EuroEA-3000 CHNS analyzer (Eurovector, Italy), the carbon and hydrogen contents were 63.1 and 6.94%, respectively. The polysaccharide fraction was not detected. The empirical formula of the structural unit based on the guaiacylpropane structural unit was $C_{10}H_{13.4}O_{3.61}$, and its molecular weight was 191 Da.

Lignin was treated with supercritical 2-propanol using a TI-LabSys-100 Control laboratory reaction system manufactured by TOP Industrie (France), which was a 100 mL heated autoclave made of a corrosion-resistant Inconel-718 alloy equipped with a magnetic stirrer, temperature and pressure control, and control unit. The maximum allowable temperature and pressure were 700°C and 800 atm, respectively.

An exact lignin sample weighing 1 g was placed in an autoclave, and the required volume of 2-propanol (chemically pure grade, Component-Reaktiv, Russia) was added to obtain a desired liquid module, and after sealing, the temperature was raised (~15 deg $\min^{-1}$) until the required value was reached. After keeping for a predetermined time with constant stirring, the reaction system was cooled, the gaseous products formed were blown off, and the contents of the autoclave were quantitatively transferred to a porous glass filter (POR 160). The solid residue was separated, washed with 2-propanol to obtain colorless washings, dried and its yield was determined by the gravimetric method.

The degree of lignin conversion (K) was calculated from the weight difference of the initial lignin (m_{lig}) and solid residue (m_{s}):

$$K = \frac{m_{lig} - m_s}{m_{lig}} \times 100. \tag{1}$$

The number average (M_{n}) and weight average (M_{w}) molecular weights of the soluble depolymerization products were determined by size exclusion chromatography [31] using an LC-20 Prominence chromatographic system (Shimadzu, Japan) with a SPD-20A spectrophotometric detector. The separation was carried out at 40°C on a column MCX 300 × 8 mm with a pore size of 1000 Å (PSS, Germany) for the analysis of water-soluble polymers. Detection was carried out at a wavelength of 275 nm. A 0.1 M sodium hydroxide solution was used as the mobile phase and solvent of the sample. The system was calibrated using standard monodisperse samples of sodium poly(styrene sulfonate) (PSS, Germany).

High resolution mass spectra of lignin depolymerization products were recorded using a Q Exactive Plus Orbitrap mass spectrometer (Thermo Scientific, USA) at a resolution of 70 000 ($M/\Delta M$). Acetone-doped photoionization at atmospheric pressure in the negative-ion generation mode was carried out [16, 32] using an Ion Max ion source equipped with a krypton lamp as a radiation source. The parameters of the ion source were the following: pressure of the sheath gas 20 arb. units, flows of Aux and sweep gases were 5 and 2 arb. units, respectively, the temperature of the desolvation line was 250°C, the vaporizer temperature was 500°C, the S-lens radio frequency voltage was 55 conv. units. A solution of lignin depolymerization products (5 μL) with a concentration of 50 mg L^{-1} in an acetone–water mixture (9 : 1) was introduced into the solvent flow (200 μL min^{-1}), followed by subtraction of the background signal of the solvent from the mass spectrum of the sample. The error in determining the masses of ions did not exceed 3 ppm. Based on the exact masses, the elemental compositions (empirical formulas) of the lignin depolymerization products were determined.

The planned experiment to optimize the conditions of lignin depolymerization was implemented with the rotatable composite uniform plan design of the second order [29]. The temperature (T), the treatment duration (D), and the liquid module (Z) were chosen as independent variables, with the output parameters being the degree of lignin conversion and the number average molecular weight of the products of depolymerization. The general form of the regression equation is a mixed second order polynomial:

$$K = b_0 + b_1t + b_2d + b_3z + b_{12}td + b_{13}tz + b_{23}dz + b_{11}t^2 + b_{22}d^2 + b_{33}z^2, \tag{2}$$

$$M_n = b_0 + b_{1t} + b_2d + b_3z + b_{12}td + b_{13}tz + b_{23}dz + b_{11}t^2 + b_{22}d^2 + b_{33}z^2, \tag{3}$$

where $t = (T - 300)/100$; $d = (D - 210)/120$; $z = (Z - 25)/10$; b_i are coefficients characterizing the effect of the corresponding process parameters on the degree of lignin conversion.

When designing the plan, T, D, and Z were chosen as the main level: 300°C, 210 min, and 25, respectively. The variation intervals were 100°C, 120 min, and 10. The star point (α) of the plan was 1.682. Processing the results of the planned experiment with obtaining regression equations and response surfaces was carried out using Microsoft Excel 2016 software.

RESULTS AND DISCUSSION

Table 1 demonstrates the planning matrix in natural and encoded form as well as the obtained values of the degree of conversion of lignin and molecular weights of the resulting products with varying experimental conditions.

Based on M_n value, the formal degree of polymerization of the products (N) was calculated using the molecular weight of the structural unit determined according to the elemental analysis. The parameter N allows to formally identify the conditions for the depolymerization process, leading to the formation of predominantly monomeric products.

The obtained experimental data were used to calculate the coefficients of the regression equations (Table 2) within the framework of the adopted model (2), (3), which relates the values of the degree of conversion and number average molecular weight with the process conditions. The statistical adequacy of the obtained regression equations is confirmed by the high convergence of the experimental results and the calculated data (Fig. 1): the correlation coefficients for the parameters K and M_n were 0.84 and 0.96, respectively.

A comparison of the absolute values of b_i coefficients (Table 2) indicates that the operating parameters to varying degrees affect the values of the degree of conversion and molecular weights of lignin depolymerization products.

The values of the coefficients b_1, b_3, and b_{23} are positive in the regression Eq. (2) for the degree of conversion, which reflects an increase in the fraction of lignin converted to a soluble state with an increase in temperature and liquid module (Figs. 2, 3). An increase in Z (b_3) leads to a decrease in the concentration of lignin degradation products in a supercritical fluid and, as a consequence, reduces the probability of their condensation. The significant positive effect of elevated temperatures (b_1) on the value of K indicates a higher value of the temperature coefficient of the destruction processes in comparison with the condensation processes. There is a

Table 1. The matrix of the experimental design and the obtained values of the degree of conversion of lignin, number average molecular weight and the formal degree of polymerization of products depending on the conditions of the experiment

Factor value			Factor value in coded form			K, %	M_n, Da	N
T, °C	D, min	Z	t	d	z			
200	90	15	–1	–1	–1	41.9	726	3.8
400	90	15	+1	–1	–1	60.5	266	1.4
200	330	15	–1	+1	–1	26.1	656	3.5
400	330	15	+1	+1	–1	60.0	210	1.1
200	90	35	–1	–1	+1	20.9	805	4.2
400	90	35	+1	–1	+1	75.0	281	1.5
200	330	35	–1	+1	+1	47.2	696	3.7
400	330	35	+1	+1	+1	57.8	196	1.0
132	210	25	–α	0	0	39.5	777	4.1
468	210	25	+α	0	0	60.5	208	1.1
300	8	25	0	–α	0	56.6	341	1.8
300	412	25	0	+α	0	54.5	325	1.7
300	210	8	0	0	–α	46.4	207	1.1
300	210	41	0	0	+α	60.9	290	1.5
300	210	25	0	0	0	56.3	300	1.6
300	210	25	0	0	0	63.0	313	1.7
300	210	25	0	0	0	58.7	316	1.7
300	210	25	0	0	0	66.5	313	1.7
300	210	25	0	0	0	60.5	286	1.5
300	210	25	0	0	0	56.0	302	1.6

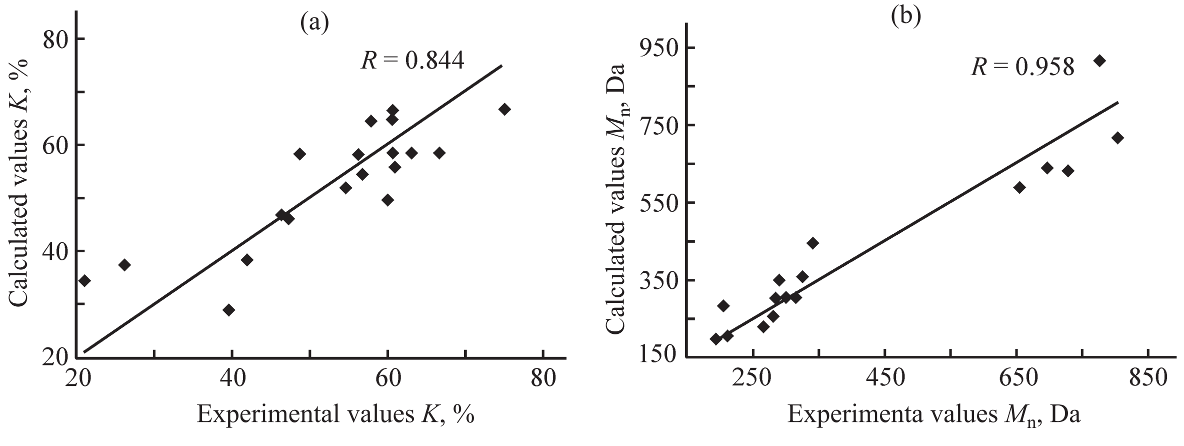

Fig. 1. The convergence of experimental and calculated values of (a) the degree of conversion and (b) number average molecular weight.

Table 2. The regression equations coefficients for the dependence of the degree of conversion of lignin and the average molecular weight of the resulting depolymerization products on temperature, the duration of supercritical treatment, and the liquid module

Output parameter	Coefficient										R	δ, %
	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{11}	b_{22}	b_{33}		
K, %	59	11.2	–0.8	2.7	–3.5	0	3.2	–3.8	0	–2.6	0.83	15
M_n, Da	301	–211	–25.4	19.0	0	–14.8	0	91.4	35.0	0	0.95	10
N	2.4	–1.7	–0.2	0.15	0	–0.12	0	0.73	0.28	0	0.95	10

mutual influence of factors, both positive $b_{23} > 0$ (a joint change in the treatment duration and the liquid module), and negative $b_{12} < 0$ (a joint change in temperature and treatment duration). In other words, there is an increase in the effect of the liquid module of the process with an increase in the duration of supercritical processing, which contributes to the development of destructive processes, as well as a weakening of the effect of temperature with an increase in the duration, which indicates the possibility of lowering the temperature of the process with its longer duration to achieve a preset value of the degree of lignin conversion. The quadratic coefficients b_{11} and b_{33} have a negative value, which means that the response surfaces in terms of temperature and liquid module will be convex and there are optimal values of T and Z at which the maximum degree of conversion can be achieved. On the whole, an increase in the fraction of lignin that has passed into solution is facilitated by a fast high-temperature regime with a high value of the liquid module, in which the destruction processes of lignin macromolecules proceed more intensively than the condensation processes of the resulting low molecular weight compounds.

Accounting for that the conversion of lignin to soluble products is primarily due to depolymerization, considering the molecular weight of the resulting products as an output parameter in Eq. (3) allows to draw similar conclusions. As for the well-known industrial methods of wood delignification (alkaline, sulfate, sulfite), an increase in temperature positively affects the accumulation of the lowest molecular weight degradation products ($b_1 << 0$) due to the intensification of the reactions of the destruction of ether bonds in the lignin macromolecule (Figs. 4, 5). Therewith the temperature increase affects slightly the condensation transformations of lignin degradation products. The effect of duration and liquid module is weakened compared to the number average molecular weights of products (b_2, $b_3 << b_1$ in absolute terms). At the same time, a comparison of this effect with the results of regression analysis for the degree of conversion draws attention to the opposite effect of the duration and the

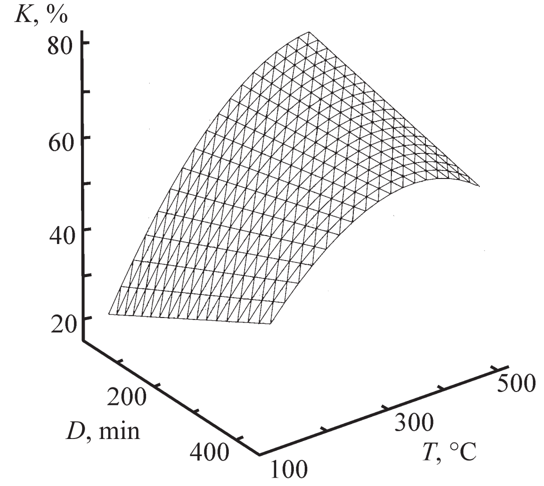

Fig. 2. The effect of temperature and treatment duration on the degree of lignin conversion.

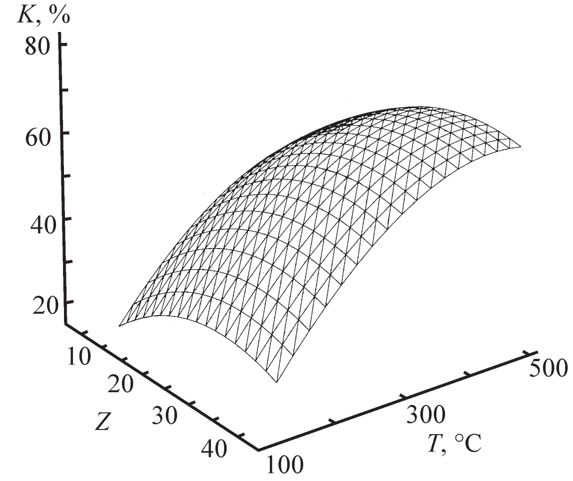

Fig. 3. The effect of temperature and liquid module on the degree of lignin conversion.

Table 3. Optimization results of the supercritical treatment conditions of the alkaline lignin to achieve the maximum degree of conversion and the minimum degree of polymerization of the resulting products

Target parameter	Optimal conditions			Calculated values of the parameters under optimal conditions		
	T, °C	D, min	Z	K, %	M_n, Da	N
K, %	468	8	20	78.5	349	1.8
M_n, Da	402	253	8	50.4	169	0.9

liquid module on the values of M_n and K: an increase in D simultaneously leads to a decrease in both the fraction of the lignin that has passed into the solution and the molecular weight of the resulting products. Similarly, a large excess of supercritical fluid with respect to lignin leads both to an increase in the degree of conversion and as a result of supercritical treatment to the production of larger soluble oligomers (dimers, trimers) instead of monomeric phenolic compounds. This fact reflects the significant difference between M_n and K as output parameters during optimization of the depolymerization process and, accordingly, the difference in optimal conditions ensuring the maximum conversion of lignin to soluble products or the production of target monomers. There is practically no pairwise mutual influence of factors on the number average molecular weights of the lignin degradation products: the coefficients b_{23} and b_{33} are equal to zero, and the coefficient b_{23} has a minimum absolute value.

As can be seen from Figs. 4, 5 the response surfaces are extreme (concave) in nature (coefficients b_{11} and b_{22} are positive) due to the predominant effects of temperature and the treatment duration. Thus, in order to obtain the most low molecular weight products (primarily monomers), supercritical treatment should be carried out at high temperatures and moderate duration.

As a result of the study of the obtained regression equations (2) and (3), the optimal conditions were determined for the conversion of alkaline lignin in supercritical 2-propanol, which correspond to the highest degree of conversion of the original lignin and the achievement of the lowest degree of polymerization of the obtained products (Table 3).

If the temperature values that are optimal for both output parameters are quite close and can be taken equal to 450°C, then, as was shown above, the optimal parameters of the treatment duration and the liquid module, providing a high degree of conversion and low molecular weight values of the products, differ greatly. Considering the priority the maximum yield of soluble depolymerization products, supercritical treatment is rational to carry out with the liquid module of 20 and the duration of 8–10 min. Under these conditions an additional verification experiment was carried out in three

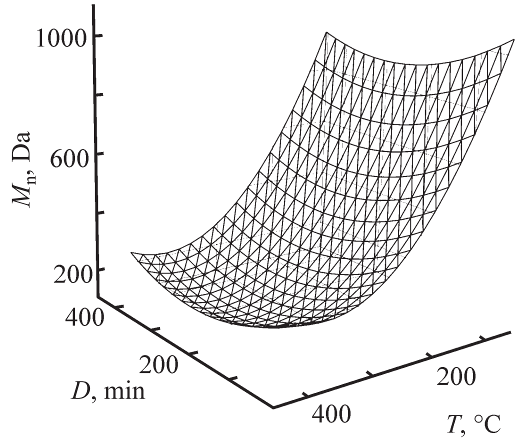

Fig. 4. The effect of temperature and treatment duration on the number average molecular weight of lignin degradation products.

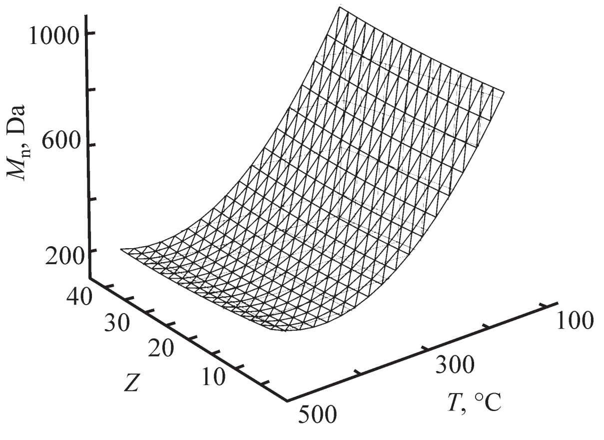

Fig. 5. The effect of temperature and liquid module on the number average molecular weight of lignin degradation products.

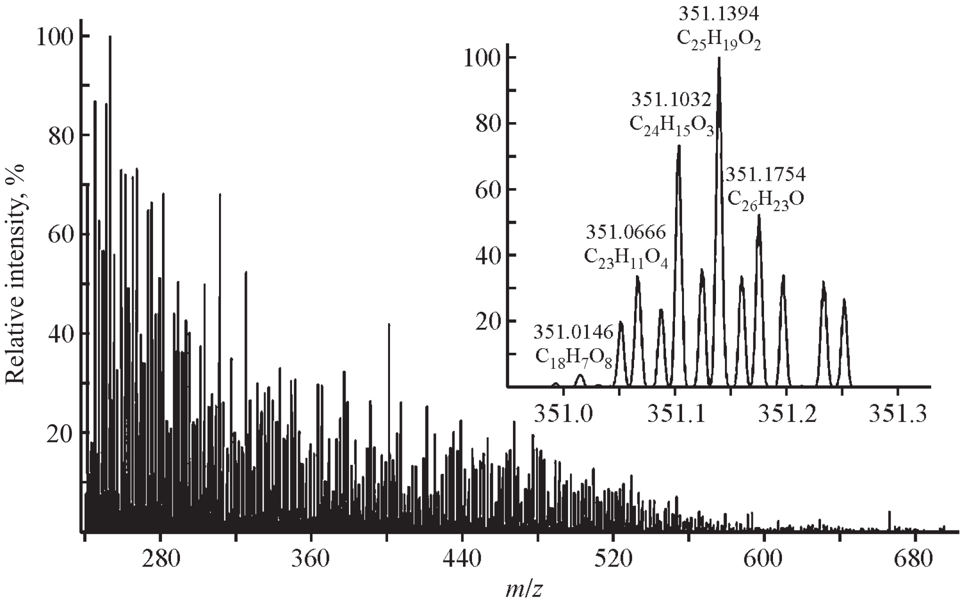

Fig. 6. The mass spectrum of the products of depolymerization of alkaline lignin obtained in the regime of photoionization doped with dioxane at atmospheric pressure.

repetitions (Table 4) and fully confirmed the efficiency of the model used and the correctness of the calculations.

The selected conditions for the depolymerization in 2-propanol medium made it possible to ensure the transition to the dissolved state of 73% of the original alkaline lignin at fast processing. The achieved degree of conversion is comparable with the results described in the literature for the approach to lignin depolymerization based on the use of expensive catalytic systems [19].

High resolution mass spectrometry with acetone-doped photoionization at atmospheric pressure was applied for a more detailed description of the lignin depolymerization products formed under the proposed optimal conditions. The resulting mass spectrum (Fig. 6) shows the predominance of monomeric and dimeric compounds (*m/z* 150–380), as well as the presence of a small number of trimers (*m/z* 400–600), which is in good agreement with the data of size exclusion chromatography (Table 4)

The chemical composition of depolymerization products is extremely complex: in total about 3 000 peaks of deprotonated molecules $[M–H]^–$ of aromatic compounds with a relative intensity of more than 0.1% are detected in the mass spectrum. Among the monomeric products of lignin depolymerization, the highest relative intensity in the mass spectra was observed for ions with *m/z* 93.0343 $[C_6H_5O]^–$ (45%), 107.0502 $[C_7H_7O]^–$ (75%) and 121.0659 $[C_8H_9O]^–$ (100%), which relate to phenol, methyl and dimethyl phenols, respectively. The predominance of these compounds indicates the occurrence of processes of deep degradation of lignin in the supercritical 2-propanol medium, accompanied not only by breaking bonds between phenylpropane structural units of macromolecules, but also by further degradation of the resulting fragments with cleavage of functional groups.

CONCLUSIONS

The application of the method of the actively planned experiment made it possible to optimize the conditions for the depolymerization of alkaline lignin in the supercritical 2-propanol medium both from the point of view of achieving the maximum conversion of the biopolymer to soluble low molecular weight products, and in order to obtain predominantly monomeric aromatic compounds. It was found that the optimum temperature lies in the range of 400–470°C, therewith in the first case, fast (8–10 min) supercritical treatment should be carried out with a high value of the liquid module (20), and in the second case, a moderate treatment duration (~4 h) when the ratio of solvent and lignin is 8 : 1. The degree of conversion of alkaline lignin under optimal conditions achieved 73%. The resulting depolymerization products have an extremely complex chemical composition (up to 3000 compounds), in which monomeric and dimeric phenols predominate, which are products not only of the breaking of bonds between phenylpropane structural units of lignin macromolecules, but also of degradation of the latter by cleavage of functional groups.

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CONFLICT OF INTERSTS

The authors declare that there is no conflict of interest requiring disclosure in this article.

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