CELLULOSE CHEMISTRY AND TECHNOLOGY

LIGNIN SEPARATED FROM THE HYDROLYZATE OF THE HYDROTHERMAL TREATMENT OF BIRCH WOOD AND ITS SURFACE PROPERTIES

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The chemical composition, structural features and surface active properties of alkali lignin, separated from the hydrolyzate of the birch wood sawdust treatment in a moderately alkaline water solution at a temperature below 100 °C, were studied. The separated lignin was rich in p-oxyphenylpropane fragments and carbonyl groups, but contained a relatively low amount of aliphatic hydroxyl and methoxyl groups. The carboxyl groups were weaker than those in kraft lignins. The lignin aqueous solutions were structured, containing both nano- and micro-sized colloidal particles. The pronounced amphiphilic character of the lignin molecules governed their low critical micelle concentration (CMC) values and enhanced the surface activity at the water-air and liquid-liquid interfaces. When decreasing the pH and increasing ionic strength, the surface activity of lignin at the air-water interface grew, while that at the oil-water interface dropped. Scanning electron microscopy (SEM) images revealed that the microstructure of the lignin surface consisted of globules, forming extended clusters of the "grape-bunches" type.

Keywords: alkali lignin, globular structure, hydrolyzate, nanoparticles, oil-in-water emulsion, polyelectrolyte effect, stabilization, surface tension, wood hydrothermal treatment

INTRODUCTION

As known, the thermal treatment of hardwood is widely applied in wood processing for many purposes.[1] The hot-water treatment of wood, intended for the disintegration and separation of the wood components, is the main stage of wood biorefining for obtaining lignocellulosic biomass, used for producing bioenergy[2,3] and value-added bioproducts.[4] Prehydrolysis of wood is also used to enhance the efficiency and increase the cellulose yield in kraft[5] and thermomechanical pulping.[6] For these purposes, as a rule, elevated temperatures (>100 °C) and high pressures are applied.

In Latvia, as well as in many other countries of Eastern Europe, the hydrothermal treatment of hardwood in special water basins at $T < 100$ °C and normal pressure is an important stage employed prior to wood mechanical processing, for the production of veneer, matches, parts of furniture, etc. The wastewater of the hydrothermal treatment of wood is dramatically polluted with wood components, so that the wastewater precipitate formed after flocculation is commonly burned. Considering the presence of soluble lignin in wastewater, as well as the volume of wastewater annually formed during industrial wood treatment, it may be concluded that waste lignin may serve as a local feedstock for obtaining new value-added products, taking into account the traditional use of lignin as an ingredient of composite materials,[7,8] binders,[9,10] surface active agents,[11] etc.

Researches on lignins, separated from the wood hydrolyzates obtained through enzymatic[12] and steam explosion treatments,[13] are known. At the same time, comparatively very few studies have been devoted to the identification of lignin separated from the wood hydrolyzates formed in mild alkaline aqueous solutions at a temperature below 100 °C.

The aim of the present study was to characterize – based on chemical and spectroscopic methods – the lignin separated from the hydrolyzate obtained by hardwood treatment under mild alkaline conditions at a temperature below 100 °C, as well as to investigate the surface activity of this lignin at different interfaces. The obtained information may be also useful for enhancing the efficiency of waste lignin precipitation with flocculants from wood hydrolysis wastewater.

EXPERIMENTAL

Materials

Characteristics of initial wood

For alkali hot-water hydrolysis, birch wood sawdust with particle sizes below 1.00 mm, but over 0.25 mm, was used. The composition of sawdust was determined according to analytical chemical procedures[14] – Klason and Kürschner – for lignin and cellulose, respectively. The content of extractives in the sawdust represented the sum of the content of wood substances dissolved in acetone, using a Soxlet extractor, and in hot water (100 °C), for 3 h. The found content of cellulose, lignin and extractives in birch wood was of 40.3, 25.2 and 3.9%, respectively.

Obtaining of the hydrolyzate

The hydrothermal treatment of sawdust was performed with 0.01M NaOH at a 1/50 (mass ratio of the oven dry sawdust to water) hydromodulus and a temperature of 90 °C for 4 h, using a 5 L three-neck flask equipped with a return condenser, a thermometer and a stirrer. After hydrolysis, the hydrolyzate was separated from the sawdust treated through filtration. The yield of the solid biomass was of 7.1% from the mass of the oven dry sawdust. The elemental composition of the solid biomass was the following: 37.75% C; 4.78% H; 56.69% O; 0.30% N; 0.14% S; 0.34% ash.

According to the data listed in Table 1, the obtained hydrolyzate is characterized by a moderate alkaline pH value, a low content of dry matter, which represents the sum of water-soluble lignin, hemicelluloses and extractive substances passing to the hydrolyzate, a moderate value of chemical oxygen demand (COD),[15] as well as by a high surface tension at the air-water interface and a relatively moderate value of dynamic viscosity.

Lignin separation from a model solution

Lignin was separated from a concentrated solution of the hydrolyzate by precipitation with 20% sulphuric acid, followed by filtration, washing with distilled water and subsequent drying of the formed precipitate – at first, at room temperature and then at 40 °C, in a thermal vacuum chamber. After the first precipitation with sulphuric acid, the content of Klason lignin in a lignin sample did not exceed 75%, which pointed to the presence of hemicellulose admixtures. For their removal, purification of the precipitated lignin through its thrice repeated dissolution with 0.1M NaOH, and subsequent precipitation with concentrated sulphuric acid according to the method recommended by Kim *et al.*,[16] were carried out. Each time, the precipitate obtained on the filter was carefully washed with diluted sulphuric acid (1%) and hot water. After triple dissolution/precipitation, the content of Klason lignin in the sample increased up to 88.84%, while the content of acid-soluble lignin[14] was of 5.11%. The total yield of (Klason and acid-soluble) lignin amounted to 0.57 and 2.37% relative to the absolutely dried wood and native lignin, respectively.

Methods

The elemental composition of lignin was determined on an Elementar Analysensysteme GmbH (Germany). The chemical composition of lignin (methoxyl groups, hydroxyl groups, carbonyl groups, as well as phenolic hydroxyl groups and carboxyl groups) was analyzed by the Fibok-Shvappakh method, acetylation, interaction with hydroxylamine hydrochloride, and potentiometric and conductometric titration (InoLab level 3), according to Zakis.[17] For identifying the functional groups, UV-spectroscopy was employed, with a UV-VIS Spectrometer Genesys^{TM} 10 (Thermo, USA)[18] and a FTIR spectrophotometer (Perkin-Elmer Spectrum One, USA), using tablets with KBr.

Table 1
Parameters of the obtained hydrolyzate

Sample	pH	Dry solids, g l^{-1}	COD, mgO l^{-1}	Density, kg m^{-3}	Dynamic viscosity,* mPa s	Surface tension,* mN m^{-1}
Hydrolyzate	9.12	1400	1285	0.998	1.030	63.2

*c = 1.0 g l^{-1}, 25 °C

Surface tension (σ) at the water-air interfaces, measured by a Wilhelmy plate, using a K9 tensiometer (KRUSS, Germany), was studied in lignin aqueous solutions, over the $3.2 \cdot 10^{-4}$-$2.0 \cdot 10^{-2}$ g dl^{-1} concentration range. The preparation of samples and the measuring procedure were similar to those described by Shulga *et al.*[19] Critical micelle concentration (CMC) was defined from the dependence of σ on the logarithm of lignin concentration. Reduced viscosity (η) was determined with an Ubellohde capillary viscometer, at 25.00 ± 0.01 °C, with the flow time of distilled water (specific conductivity $1\cdot10^{-6}$ s cm^{-1}) close to 300 ± 0.01 s, using a visco-bath (JULABO Labottechnik GmbH, Germany) after 24 h of lignin solution preparation. The measurements, including viscometric and surface tension determinations, were repeated in triplicate, the indicated values of surface tension and viscosity representing their average arithmetic means.

The stabilizing action of the lignin solution with a 0.01-1.00 g dl $^{-1}$ concentration in terms of volume (H) and time (t) of water separation was studied in a rapeseed oil-in-water emulsion (40/60, v/v), prepared with a Disperser T10 (IKA, Germany) (γ = 9500 rpm), for 1 min. The full time of testing was 120 min. The lignin content in the emulsion varied from $6\cdot10^{-3}$ to $6\cdot10^{-1}$%. The measurements, repeated in triplicate, represented their average arithmetic means.

The size and zeta-potential of the lignin particles were determined in aqueous solutions, using a ZETASIZER NANO ZS Malvern Instrument (Malvern, United Kingdom), at 23 °C. The samples were prepared by dissolving the dry lignin powder in 0.1M and 0.01M NaOH solutions, with and without 0.1M NaCl and 1M NaCl. Changing of the pH of the lignin alkaline solutions was made by adding 1M HCl solution under stirring (80 rpm), after which the solutions were left to stabilize for 24 h at room temperature. To achieve a good quality of the colloidal dispersion, prior to the measurements, the samples with a concentration of 1 g dl^{-1} were ultrasound-treated for 10 min at room temperature. The obtained size distribution graphs represented the dependencies of the relative intensity of scattered light on the hydrodynamic diameter of lignin particles. The intensity area (%) shows the contribution of a particle size mode to the intensity of scattered light.

The microstructure of the separated lignin surface was examined by scanning electron microscopy (SEM), using a scanning electron microscope (Tesla, Czech Republic). The sample was prepared by casting a 0.1 g dl^{-1} lignin solution with pH 5.5 onto a flat substrate, with subsequent evaporation of water at room temperature.

RESULTS AND DISCUSSION

Chemical and spectroscopic characterisation of lignin

It is known that the spectroscopic methods, supported by analytical chemical analysis, are the main tools to characterize the chemical composition of lignin. In its FTIR spectra (Fig. 1), typical bands can be seen, common for hardwood lignins, namely the bands at 1323 cm^{-1} and at 821 cm^{-1} are assigned to syringyl rings; the latter band is characteristic also of the C–H vibration in syringyl units. A band at 3410 cm^{-1} is attributed to the hydroxyl groups in phenolic and aliphatic structures, while those at 2917 cm^{-1} and 2847 cm^{-1} are caused by C–H stretching vibrations in methoxyl, methyl and methylene groups. The bands at 1591 cm^{-1}, 1503 cm^{-1} and 1417 cm^{-1} are assigned to skeletal vibrations and C=O group stretching in the syringyl and guaiacyl aromatic rings. The relatively higher intensity of the band at 1591 cm^{-1}, in comparison with that of the band at 1502 cm^{-1}, may be caused by the presence of a considerable amount of p-oxyphenyl fragments, as well as of some condensed aromatic structures, favouring an increase in the intensity of this absorption band.[20] The broad band in the 1715-1625 cm^{-1} range may be assigned to the presence of unconjugated and conjugated carbonyl and aromatic carboxyl groups in lignin macromolecules. A shoulder at 1378 cm^{-1} may be caused by the presence of phenolic hydroxyl groups and aliphatic C–H in methyl groups. The higher intensity of the band at 1219 cm^{-1}, comparatively with that of the band at 1262 cm^{-1}, may be determined by the presence of both p-hydroxyphenyl derivatives and guaiacyl-containing fragments.[21,22] A very strong band at 1121 cm^{-1} may be caused by the C–H deformation in syringyl units and secondary alcohols, or by C=O stretching vibrations. The weak band at 1084 cm^{-1} may be related to the deformation vibrations of C–O in secondary alcohols and aliphatic esters. The strong band with a maximum at 1036 cm^{-1} is complex and may be governed both by the deformation vibrations of C–H in the aromatic structures with predominating guaiacyl units, and by the deformation vibrations of C–O in the primary and stretching vibrations of unconjugated C=O groups.

The UV curves of the separated lignin (Fig. 2) exhibit a pronounced maximum at 276 nm only in weak acidic media. In alkaline media, they represent the integrity of the absorption bands in the form of strongly or weakly pronounced shoulders, reflecting the presence of different phenyl propane units in the lignin macromolecules. The pronounced shoulders at 242, 257, 280 and 312 nm on the lignin ionization curve in strong alkaline medium indicate the presence of biphenyl derivatives, as well as aromatic structures, containing non-etherified hydroxyl groups, conjugated carbonyl groups and aromatic carboxyl groups in lignin macromolecules. The values of the extinction coefficient (ε) of the separated lignin, calculated from the obtained spectra, vary from 13.5 l $g^{-1}cm^{-}$

[1] (λ = 276 nm) to 16.8 l $g^{-1}cm^{-1}$ (λ = 280 nm) at pH 5.3 and 12.7, respectively. They are lower than the values of the extinction coefficients for softwood kraft and organosolv lignins, but somewhat higher than those for hardwood lignins at these pH values.[14,22]

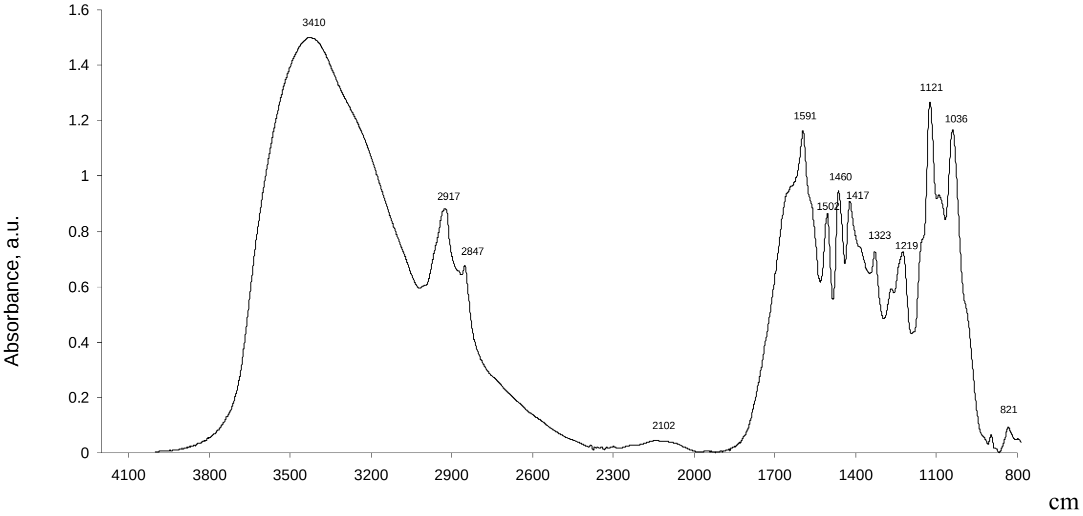

Figure 1: FTIR spectrum of separated lignin

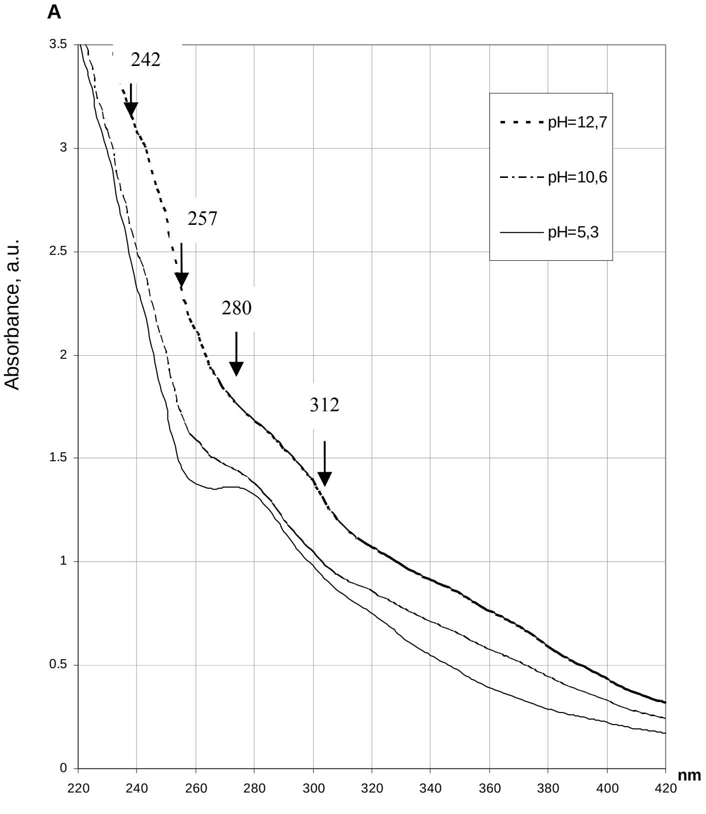

Figure 2: UV spectra of separated lignin at different pH values

Table 2
Chemical characteristics of lignin separated from the hydrolyzate

C, %	H, %	O, %	N, %	S, %	OCH_3, %	CO, %	$OH_{tot.}$, %	OH_{aliph}, %	OH_{ph}, %	COOH, %
54.13	6.47	38.61	0.52	0.27	16.25	4.52	7.98	5.04	2.94	2.03

The results of the chemical analysis given in Table 2 agree with the data on the obtained FTIR and UV spectra. According to these data, lignin macromolecules are characterized by a relatively high O/C ratio, which may be associated with the essential content of oxidized groups, namely, hydroxyl, carbonyl and carboxyl groups. It is known that kraft and soda lignins, derived from hardwood, are characterized by an increased content of methoxyl groups (18-22%).[14,22] The relatively low content of methoxyl groups in the lignin composition may be explained by the presence of a considerable amount of aromatic fragments, containing p-hydroxyphenyl derivatives, according to the FTIR spectrum (Fig. 1). It is known[23,24] that the methoxyl groups of syringyl derivatives are easily hydrolyzable and less stable against alkaline hydrolysis than the guaiacyl ones. Besides, it is also known[25] that the low molecular water-soluble fragments of lignin, passing into alkaline aqueous solutions, are characterized by a moderate content of methoxyl groups.

According to Table 2, the content of aliphatic hydroxyl and phenolic hydroxyl groups in the separated lignin is lower than in kraft lignins,[26] which may be governed by the peculiarities of the chemical conversions of the native lignin structure during alkaline hydrolysis.[27]

The analysis of the potentiometric and conductometric titration curves[17] (Fig. 3) shows that the common content of the acidic groups, namely the phenolic hydroxyl and carboxyl ones, from lignin, is close to 4.97%; in this case, the amount of phenolic hydroxyls is 1.5 times higher than the content of carboxyl groups (Table 2). The discrepancy between the amount of phenolic hydroxyls found in lignin and the relatively high value of the extinction coefficient of its solution at pH 12.7 ($\varepsilon = 16.8$ l $g^{-1}cm^{-1}$) may indicate that the main part of the phenolic hydroxyl groups in the isolated lignin has $pK_a \geq 10$, and thus cannot be quantitatively titrated in the aqueous medium. This means that the amount of phenolic hydroxyl groups present in the lignin sample is higher than that shown in Table 2. The carboxyl groups present in lignin are also rather weak. The profile of the curve of the dependence of apparent pK_a of the carboxyl groups on the degree of their dissociation is demonstrated in Figure 4. According to Nyman and Rose,[28] the decrease of pK_α, with increasing the dissociation degree to 0.2, may be attributed to the starting dissociation of the lignin macromolecules incorporated in the associates; the increase of pK_a, with further enhancing the dissociation degree to 0.5, shows the classical polyelectrolyte behaviour of lignin macromolecules within the still existing associates, while lowering of pK_a at $\alpha > 0.5$, and the further increase in pH practically demonstrate full ionization of the lignin carboxyl groups. The extrapolation of the curve profile (Fig. 4) to the zero value of the dissociation degree of the carboxyl groups gave a value of "intrinsic" $pK_o = 5.32$, which is essentially higher than the same index found for the same groups in kraft lignins and lignosulphonates.[28]

It is also known that the phenolic hydroxyl and carboxyl groups are responsible for the polyelectrolyte behaviour[29] of lignins in aqueous solutions, which manifests itself in an increase of the reduced viscosity of the solutions with decreasing lignin concentration. According to Figure 5, polyelectrolyte swelling of birch lignin macromolecules occurs both in the saltless solution and in the presence of 0.1M NaCl in a strongly alkaline medium (pH 12.8). Obviously, the presence of 0.1M NaCl cannot suppress the swelling of macromolecules in the alkaline solution with a lignin concentration below 0.06 g dl^{-1}. The increase of only the content of the salt up to 1M NaCl results in a full inhibition of the polyelectrolyte effect. At the same time, as shown in our experiment, in weakly alkaline media (pH $\leq$ 8.0), a concentration of 0.1M NaCl was sufficient to suppress lignin swelling over the entire concentration range under study.

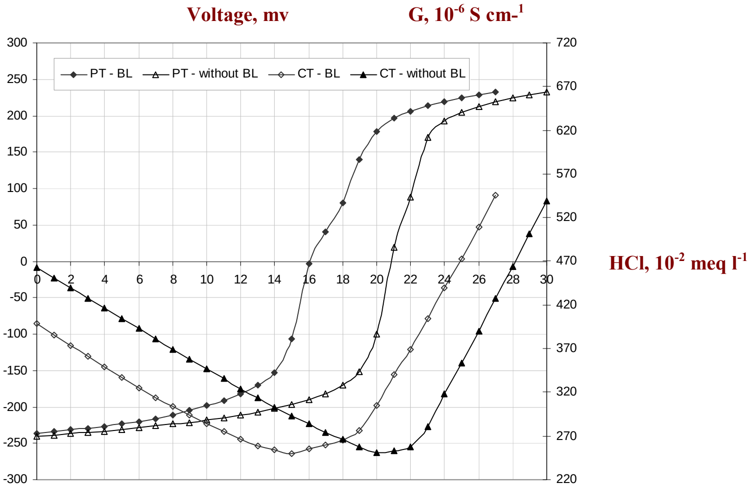

Figure 3: Potentiometric (PT) and conductometric (CT) titration curves for an alkaline solution of birch lignin (BL) with the concentration of 0.01 g dl^{-1} and an alkaline solution without lignin

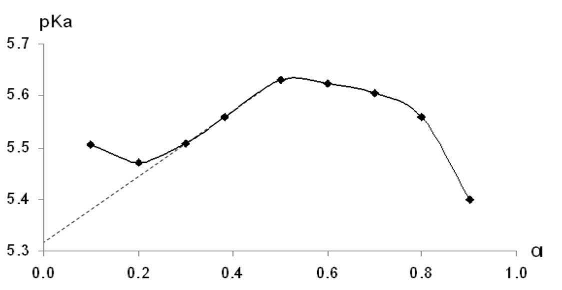

Figure 4: Dependence of pK$_{\alpha}$ on the dissociation degree of the separated lignin

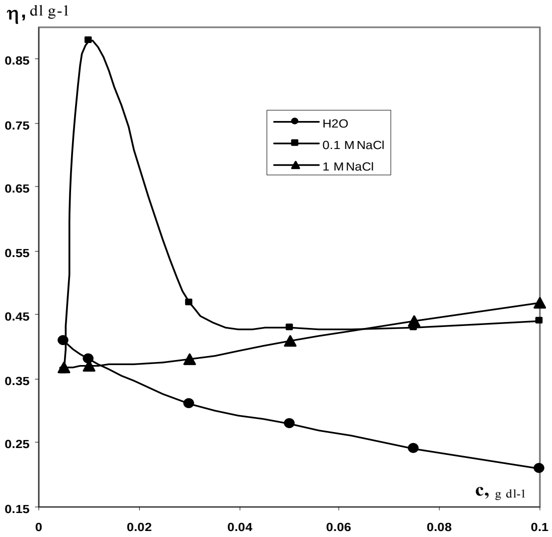

Figure 5: Dependence of the reduced viscosity of the separated lignin on its concentration in strong alkaline solutions with different ionic strength

Self-aggregation and surface properties of lignin

The simultaneous presence of pronounced hydrophilic and hydrophobic structural constituents in the lignin macromolecule, represented by aromatic structures and ionized groups, governs its amphiphilic character and tendency for self-aggregation. Opinions differ[30-32] as to the driving force of the association of lignin molecules in solutions, namely the H-bonding between the functional groups of lignin, such as hydroxyl, carboxyl and ether oxygen ones, van der Waals interactions among the lignin molecules, orbital interactions among the lignin aromatic rings, etc. However, due to the complex mechanism of self-aggregation of the lignin macromolecules, no consensus of opinion on this phenomenon has been reached.

According to the obtained results, the tendency of birch lignin macromolecules to associate in a strongly alkaline medium is indicated by an increase of its reduced viscosity in the presence of 0.1M NaCl in the concentration range of 0.06 g dl^{-1}-0.1 g dl^{-1} (Fig. 5), within which the polyelectrolyte effect is practically suppressed, so that it cannot influence the viscosity values of the lignin solutions. The pronounced association of the lignin macromolecules may be governed through screening their surface charge with sodium counter-ions, present in excess, which intensifies the associative interactions among the macromolecules. At the same time, the effect of increasing NaCl concentration up to 1M on the reduced viscosity values of the lignin solutions in the specified concentration range is slightly manifested.

In more detail, self-aggregation of the lignin particles was studied in 1 g dl^{-1} lignin aqueous solutions, depending on pH, using dynamic light scattering. As shown in Figure 6, irrespective of pH, the lignin solutions are highly structured systems which contain both nano- and microsized particles. In an alkaline medium at pH 12, the measured sizes of the lignin particles have a bimodal distribution, with an average diameter of 67 and 702 nm, respectively. At pH $\leq$ 8, the lignin particles show a polymodal distribution. Polymodality and the presence of small particles (2-3 nm in size) at pH 8 (Fig. 6) may indicate rearrangement of the lignin particles in the solution and the formation of new self-assembled structures, which are thermodynamically more stable in this environment. One of the reasons of this rearrangement may be the loss of the charge by the main part of the phenolic hydroxyl groups, having pK$_a$ $\geq$ 10, with pH values of the lignin solution decreasing from 12 to 8. According to the light scattering intensity, the highest quantity of nanoparticles with an average diameter < 100 nm is observed at pH 12; at the same time, the highest sizes of the lignin associates with an average diameter of 1426 nm are characteristic of the solution with pH 5. With a decreasing pH from 8 to 5, the sizes of the large and medium lignin associates slightly change, and only their mutual distribution and quantity vary, which may testify that lignin association was practically completed in a weakly alkaline medium.

The pronounced tendency of self-aggregation of the lignin separated in aqueous solutions is also testified by its reduced values of CMC and surface tension at the air-water interface, which achieve $1\cdot10^{-3}$ g dl^{-1} and 31.5 mNm^{-1} in acidic media, respectively (Fig. 7). With a decreasing pH from 12.7 to 5 (Fig. 7) and in the presence of 0.1M NaCl (Fig. 8), both surface tension at the air-water interface and the CMC values significantly drop. This may be governed by the growing hydrophobicity of the lignin particles, due to both protonization of the ionic acidic groups and screening of the surface charge of the lignin particles. It should be noted that the decrease in pH from 12.6 to 8.0 favours an essential improvement of the surface-active properties of lignin at the air-water interface (Fig. 7), and a pronounced decrease in its CMC. However, when further lowering the pH values of the lignin solutions from 8.0 to 5.0, the values of CMC and the interface surface tension change insignificantly, confirming the weak strength of the main part of the phenolic hydroxyls, as well as the carboxyl groups of birch lignin.

It is known that lignins are used as emulsifiers and stabilizers of different emulsions and dispersions.[11] Figure 9 shows the dependencies of the separation volume and time on the pH of the aqueous phase, containing lignin in different concentrations, for the rapeseed oil-in-water (O/W) emulsion. It can be seen that, with increasing the lignin content in the O/W emulsion, the stability of the emulsion remarkably increases, as indicated by a decrease in the value of the separation volume, and an increase in the separation time occurs. Birch lignin in the aqueous alkaline phase (pH 12.8) is characterized by the highest stabilizing properties. The decrease in the pH of the aqueous phase from 12.8 to 8.0 results in an increased separation volume of the emulsion, by 14-16% on the average, and in a notable decrease in its separation time, by 60-70 min on the average, most pronounced at low concentrations of lignin in the aqueous phase. With further decreasing the pH of the aqueous phase from 8.0 to 5.5, the stability of the O/W emulsion slightly changes. The presence of 0.1M NaCl in the lignin-containing strong alkaline aqueous phase still to a greater extent decreases the separation volume (by 10-12% on the average) and increases the separation time (by 30-40 min on the average), with increasing lignin concentration relative to the saltless alkaline aqueous phase (Fig. 10). At the same time, 1M NaCl dramatically impairs the stabilizing action of lignin, expressed by the full separation of the emulsion already within the first 10 min, irrespective of the lignin content. Different stabilization mechanisms of the emulsions with lignin stabilizers at the liquid-liquid interface are suggested, especially the electrostatic and steric ones.[33]

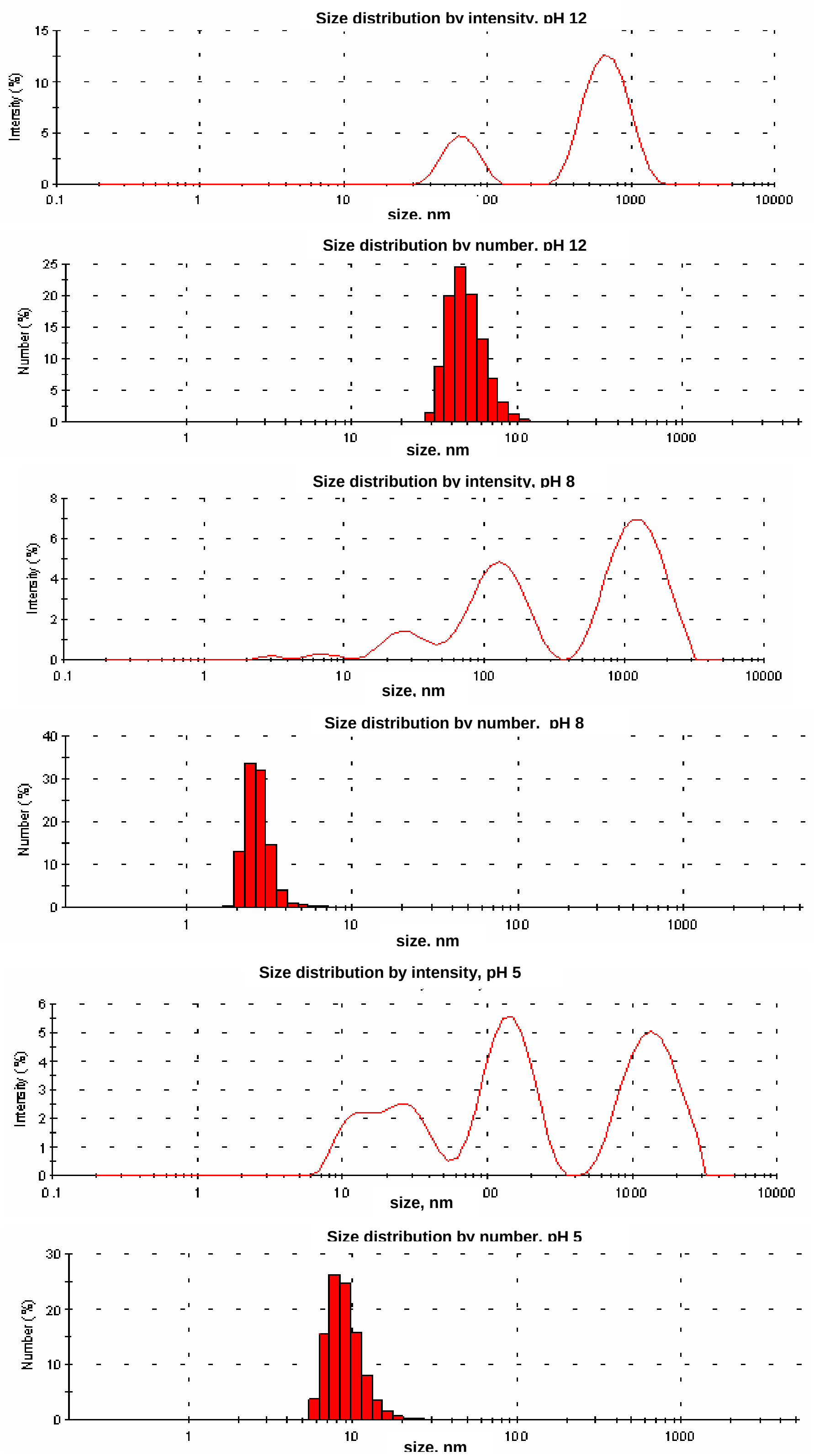

Figure 6: Particle-size distribution pattern of separated lignin particles depending on pH

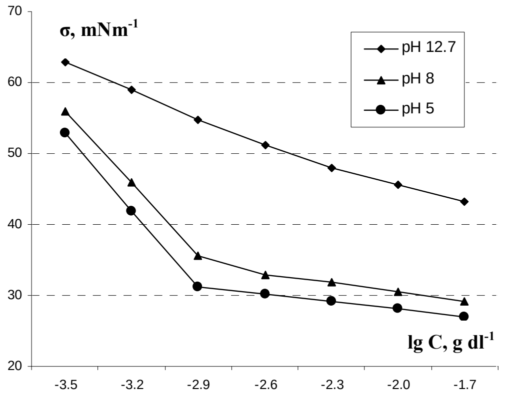

Figure 7: Surface tension at the air-water interface of lignin aqueous solutions with different concentration at different pH

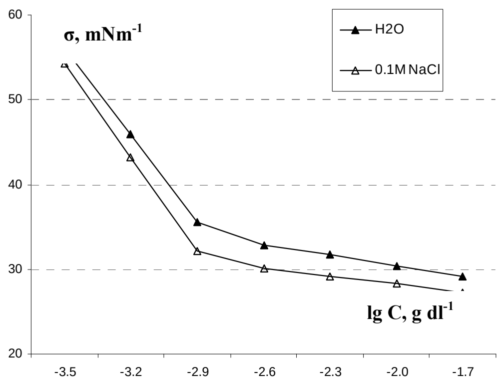

Figure 8: Effect of ionic strength on the surface tension at the air-water interface of lignin aqueous solutions at pH 8

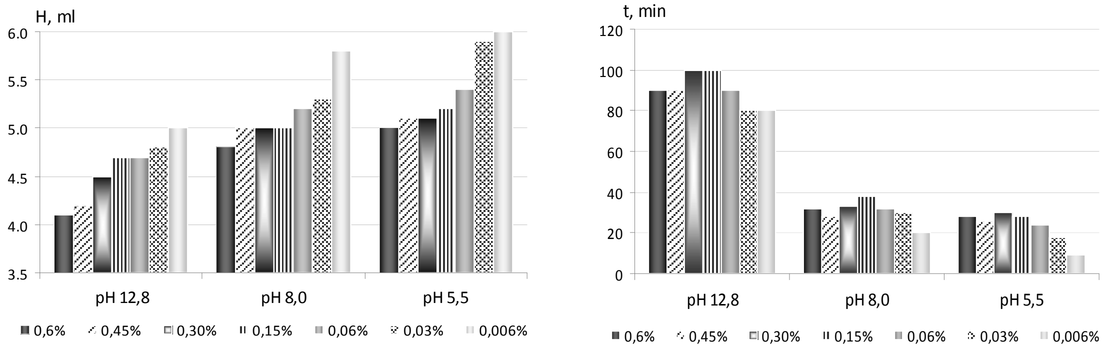

Figure 9: Volume and time of separation of rapeseed oil-in-water emulsion versus the pH value of lignin-containing aqueous phase

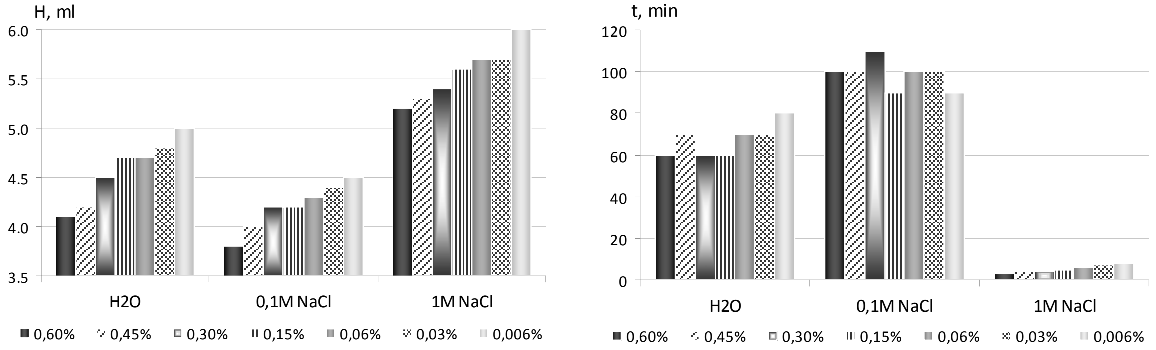

Figure 10: Volume and time of separation of rapeseed oil-in-water emulsion versus the concentration of NaCl in lignin-containing aqueous phase

Table 3

Average diameters of lignin particles in 0.06 g dl $^{-1}$ alkaline aqueous solutions

Solution	Size, nm	Intensity area, %
0.1M NaOH without NaCl	408	89
0.1M NaOH + 0.1M NaCl	859	84
0.1M NaOH + 1M NaCl	983	87

The study of lignin strong alkaline solutions by dynamic light scattering has shown that the lignin particles, characterized by the highest area of light scattering intensity in the presence of 0.1M NaCl, have an essentially larger average hydrodynamic diameter than those in a 0.1M NaOH solution without salts, at the same lignin concentration. For example, according to Table 3, the average sizes of the lignin particles with the highest intensity area in a 0.06 g dl^{-1} lignin solution in the presence of 0.1M NaCl, in which the polyelectrolyte effect is practically suppressed, exceed more than twice their average sizes in the saltless solution. In this case, the zeta potential and electrophoretic mobility of the lignin particles decrease from -34.1 mV and -2.671 μmcm/Vs to -19.3 mV and -1.516 μmcm/Vs, respectively. This may indicate strengthening of the association/aggregation interactions in the presence of salt, leading to the formation of lignin particles with less charge and larger in size than those from the saltless alkaline solution. However, the average sizes of the lignin particles having the highest value of the intensity area in the presence of 1M NaCl increase insignificantly (by only 14%), comparatively with the particle sizes in the 0.1M NaCl solutions. The insignificant enhancement of the particle sizes in the presence of 1M NaCl may be the reason for the negligible changes in the reduced viscosity values of the strong alkaline solutions with a lignin concentration ≥ 0.06 g dl^{-1}, *vs.* the viscosity values of the lignin solutions containing 0.1M NaCl (Fig. 5). Based on the obtained results, it is assumed that the marked enhancement of the stabilizing action of lignin in the strong alkaline medium in the presence of 0.1M NaCl may be caused by the realization of a complex mechanism of stabilization of the O/W emulsion, including electrostatic and steric one, through a predominantly electrostatic mechanism. The predominance of the electrostatic mechanism of emulsion stabilization may be confirmed by the decreasing stability of the O/W emulsion with lowering the pH values of the lignin-containing aqueous phase (Fig. 9).

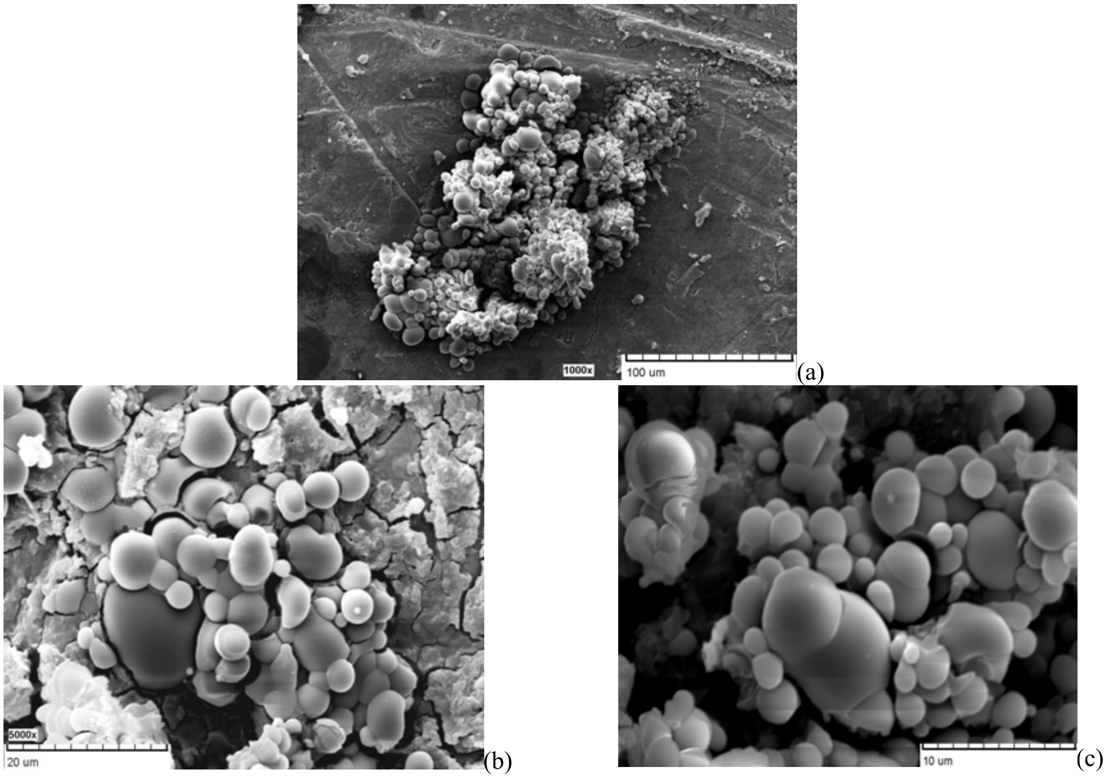

Figure 11: SEM images of the lignin film formed by evaporation of its aqueous solution with pH 5.5 at different magnification: (a) 1000 X, (b) 5000 X and (c) 10000 X

The SEM images plotted in Figure 11 reflect the morphological peculiarities of the microstructure of the lignin film, obtained by the evaporation of a 0.1 g dl^{-1} aqueous solution of lignin with pH 5.5, at room temperature. It can be seen that the formed supramolecular formations have a globular form, with different diameters, ranging from 500 nm to 10 mk. The mutual arrangement of the formed lignin globules represents extended clusters of the "grape bunches" type (Fig. 11a, b), similarly to the case of ethanol/water lignin.[34] Besides, at great magnification, in parallels with the typical globular structures, only particles of stretched form can be seen, formed by the interpenetrating globules (Fig. 11c).

CONCLUSIONS

The hydrolysis of birch wood sawdust was realized in a mild alkaline aqueous solution, at a temperature below 100 °C. The total content of lignin (Klason and acid-soluble lignin) in the separated alkali lignin, purified by multiple dissolution–precipitation, was of 93.9%, and its total yield was of 0.57% from the absolutely dry birch sawdust mass. The separated lignin was rich in p-oxyphenylpropane fragments and carbonyl groups, but contained a relatively decreased amount of aliphatic hydroxyl and methoxyl groups. The content of carboxyl groups found in lignin was 1.5 times lower than that of phenol hydroxyls. The observed discrepancy between the determined amount of phenolic hydroxyls in the lignin and the high value of its extinction coefficient in the strong alkaline solution indicates that most of the presented phenolic hydroxyl groups are weak and have $pK_a \geq 10$. The high value of "intrinsic" pK_o, determined for the carboxyl groups, testifies that they are weaker than those in kraft lignins and lignosulphonates.

The study of self-aggregation in lignin aqueous solutions, depending on pH, revealed highly structured systems containing nano- and microsized particles. In a strong alkaline medium, the sizes of the lignin particles had a bimodal distribution and showed the lowest values, comparatively with the case of weak alkaline and acidic media, in which the lignin associates had the greatest sizes and a polymodal distribution. The pronounced tendency of self-aggregation of lignin was testified by the relatively low CMC and surface tension values at the air-water interface of its aqueous solutions. A decreased pH and the presence of 0.1M NaCl significantly increased the surface activity of lignin at the air-water interface. The dependencies of the stability of the rapeseed oil-in-water emulsion on the pH values, and the ionic strength of the lignin-containing aqueous phase indicated a complex mechanism of emulsion stabilization, including the electrostatic and steric one, with a predominant electrostatic mechanism. SEM images demonstrated lignin globular supramolecular structures, forming extended clusters of the "grape bunches" type.

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