Electrochemical Oxidation of Hydrolytic Lignins in Fluoride-Containing Aqueous Electrolytes

O. V. Popova[a]*, T. A. Mal'tseva[a], E. A. Mar'eva[a]**, and K. S. Tarasenko[a]

[a] *Institute of Nanotechnology, Electronics, and Instrumentation, Southern Federal University,*
ul. Chekhova 2, Taganrog, Rostov oblast, 347922 Russia
e-mail: *ovpopova@sfedu.ru; **maryeva@mail.ru

Abstract—Electrochemical oxidation of hydrolytic lignins from different natural sources in fluoride-containing alkaline and acidic electrolytes was studied. An electrochemical method for the synthesis of oxidized lignins in hydrofluoric acid solutions was proposed. The products of modification of the lignins were examined using functional analysis, ^{19}F NMR, IR, and UV spectroscopy, and gel-chromatographic analysis.

Keywords: hydrolytic lignin, oxidized lignin, electrochemical synthesis, fluorination, fluoride-containing electrolyte

INTRODUCTION

Hydrolytic lignin (HL) is a large-tonnage waste of the hydrolysis industry whose main product is ethanol. In the Russian Federation hydrolytic lignin is used as fuel briquettes and also as *hydrocarbon feedstock for biofuels synthesis* [1]. At the same time, HL is a very valuable inexpensive renewable organic polymer, so the interest in finding effective ways of its application remains steady [2].

Chemical and physicochemical modification of lignin allows expanding the scope of application of lignin feedstock via significantly increasing the content of functional groups in lignin macromolecules. The most demanded are oxidized lignins. Highly oxidized lignins generated by electrochemical modification have various functional groups embedded in their structure and are suitable for preparing polymeric composite materials [3, 4].

Oxidized lignins are used as starting materials to synthesize sorbents for sequestering heavy metal ions from aqueous solutions [5], as enterosorbents in medicine [6–9, and as *fire extinguishing impregnation agents* for wood and pulp and paper products [10, 11].

The main process in the production of sorbing paste is alkaline treatment of hydrolytic lignin in a sodium hydroxide solution. Oxidized lignin can be produced as a water-soluble solid powder [12] by reacting lignin with nitric acid, followed by heating with a sodium hydroxide solution, whereupon the resulting reaction mass, after cooling, is mixed with isoamyl alcohol and 2-aminophenol-4-sulfonic acid diazonium salt. Alternatively, lignin can be oxidized in an alkaline medium in the presence of any oxidizing agent: hydrogen peroxide, oxygen, ozone, etc. [13]. The resulting product is proposed for use in the form of a liquid mixture of oxidation products of the lignin-containing substrate for surface or bulk flame-retardant treatment of combustible materials and also for fire seat suppression by flame retardant spraying.

Highly oxidized lignins can be obtained by oxidation with ozone or hydrogen peroxide [14–17] in various media in the presence of catalysts or at elevated pressure [18]. The use of different catalysts [19–22] enables oxidative degradation of lignins to low-molecular compounds.

Herein, we studied the products of synthesis of oxidized lignins in alkaline and acidic electrolytes and developed a method for oxidation of HL in hydro-fluoric acid solutions with the view of its application as a powder component of composite materials.

EXPERIMENTAL

In our study we used hydrolytic lignins derived from corn stalks (HLCS), cotton-seed husks (HLCH),

sunflower-seed hulls (HLSH), hardwoods (HLHW), and softwoods (HLSW). Solutions of electrolytes were prepared with distilled water and chemically pure reagents, and analyses were performed with analytically pure chemicals.

Electrochemical oxidation of the lignins in alkaline electrolytes was carried out in the potentiostatic mode at a potential of 2.0–2.2 V. A standard 100-mL electrochemical cell or diaphragmless electrolytic cells of up to 1000 mL capacity were used for the syntheses. Constant temperature was maintained by means of an ultrathermostat. Preparative syntheses in acidic electrolytes were carried out in the galvanostatic mode at current densities of 0.1–0.4 A/cm^2 in a 300-mL polyethylene electrolytic cell at ambient temperature. The electrolyte filling degree in the cells was 60–70%. The electrolytes were stirred with a magnetic stirrer at 120 rpm speed. The lignin sample (1–4 wt %) was loaded into the electrolytic cell and poured with the appropriate volume of the aqueous electrolyte containing 1–2 M KF and 1 M KOH or 40% KF·HF, or 15% HF. Platinum or platinized Ti anode and nickel cathode were used in the alkaline electrolyte. In 40% KF·HF or 15% HF electrolytes, glassy carbon SU-2000 was used as both anode and cathode; the anode surface area was 6 cm^2. Upon completion of the electrolysis the modified lignin was precipitated by adding 5–10% HF to the alkaline solution until pH 3–4 was achieved, whereupon the precipitate was filtered off. The modified lignin from the acidic electrolyte was filtered off, and the filtrate was used for the next synthesis run upon adding the missing volume of 15% HF (~5 mL). The products precipitated were rinsed with distilled water until neutral reaction of the medium was achieved and then dried in air and in a desiccator over CaCl$_2$ to constant weight.

Highly selective EK-040801 and ELIS-131F electrodes with membranes consisting of single crystal lanthanum fluoride were used for quantitative determination of fluorine in lignins by the analytical technique from [23]. The content of carboxy and other functional groups was determined by the appropriate procedures [24].

IR spectra of the oxidized lignin samples (suspension in Nujol or KBr pellets) were recorded on Specord IR-75 and Perkin Elmer 983 IR spectrophotometers in the 4000–400 cm^{-1} wavenumber range. The concentration of the samples was 1 wt %. UV spectra of the lignins were obtained with a Specord UV-VIS spectrophotometer. ^{19}F NMR spectra were recorded on a Bruker WP 80

instrument operating at the frequency of 75.4 MHz. The samples were dissolved in dimethylsulfoxide (DMSO-d_6); 3-chlorofluoromethane served an internal standard.

Gel-chromatographic analysis was carried out on a column packed with Sephadex G-50 using freshly distilled (in a vacuum) dimethylsulfoxide as eluent.

RESULTS AND DISCUSSION

According to relevant scientific data, oxidized lignin is typically synthesized in alkaline solutions, in which lignin dissolves. In case of a powdered material as the final product, synthesis of oxidized lignin in alkaline media under industrial conditions is accompanied by generation of a new waste, a salt solution resulted from neutralization of alkali with acid and filtration of the precipitated finished product. Therefore, the most expedient route to oxidized lignin is via oxidation in aqueous acidic media or in organic electrolytes in which lignin is insoluble. In this case the electrolyte solution is suitable for repeated use upon appropriate correction after the synthesis. However, in nonaqueous electrolytes it is impossible to obtain samples with a high content of oxidized groups [3, 25]. As to lignin oxidation processes run in an acidic (aqueous or organic) medium, the accumulation of functional groups (carboxy, hydroxyl, etc.) is paralleled by incorporation of the anions of these acids into the lignin macromolecule (sulfonation, nitration, chlorination, bromination, etc.) [3, 4]. The only exception is provided by modification in hydrofluoric acid solutions, since in aqueous medium hydroxylation dominates over fluorination.

Nevertheless, we succeeded in synthesized lignin samples containing up to 18.6% fluorine [4, 26] and thereby proved that lignins can be fluorinated in aqueous alkaline electrolytes in the presence of fluoride ions. We revealed the dependence of the maximum concentration of fluorine in lignins on their nature (Table 1), in particular, on the content of groups that underwent fluorination in the original lignins. According to the ^{19}F NMR spectroscopic data, electrochemical oxidation of lignin in an alkaline electrolyte (1 M KOH + 1 M KF) at controlled potentials (1.8–2.2 V) gave lignin sample containing fluorine in the nonaromatic part of the macromolecule.

The ^{19}F NMR spectrum of the modified HLCH containing 17.2% fluorine dissolved in DMSO exhibited signals at –150.3 ppm (d, J_{HF} = 74 Hz) and
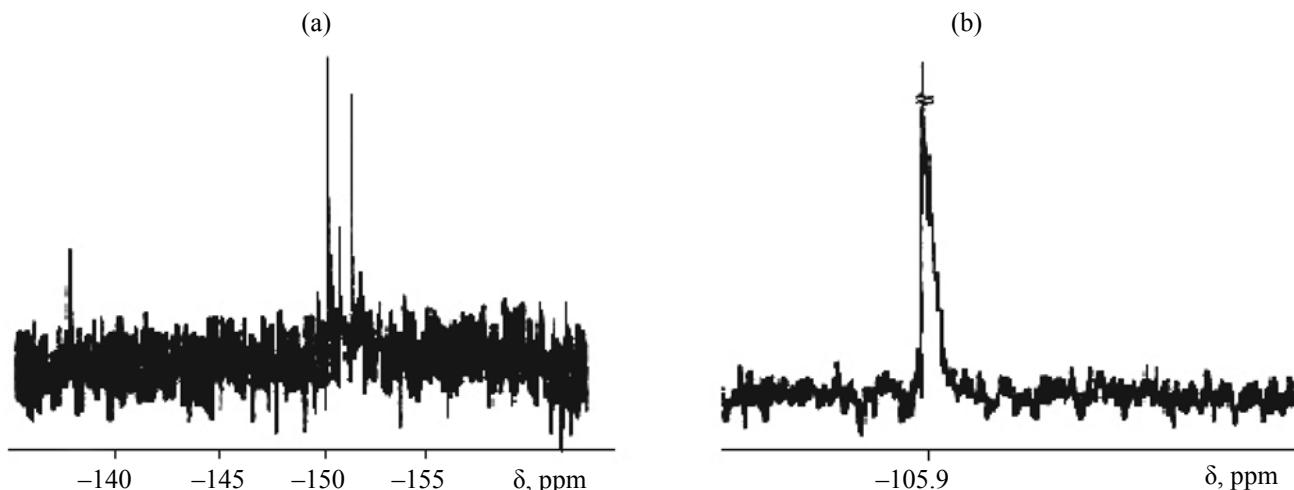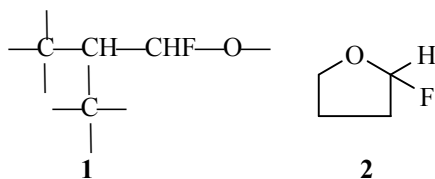
(a) (b)

Fig. 1. ^{19}F NMR spectrum of the oxidized HLCH containing 17.2% fluorine. Solvent: (a) DMSO-d_6 and (b) 4 M aqueous KOH. Internal standard: CFCl$_3$.

–150.8 ppm (d, J_{HF} = 71 Hz) (Fig. 1a), uncharacteristic for aromatically bound fluorine and for fluoride ion adsorbed by lignin [27, 28], whose chemical shift lies in a high-field region. The chemical shifts and splitting constants correspond to moieties **1** and **2** or to structurally close units.

Under identical conditions (current density i = 0.1 A/cm^2, amount of electricity passed Q = 3600 C/g), the largest amount of fluorine was introduced into the HLCH sample (Table 1). The lowest content of fluorine was revealed for the hydrolytic lignin derived from the HLHW and HLSH samples. The content of the –COOH, –OH, and =CO groups in the lignins modified in the aqueous alkaline fluoride-containing electrolyte (1 M KOH + 1 M KF) is indicative of modest degrees of oxidation of (Table 1).

The presence of these structures is also indicated by complete elimination of fluorine upon boiling in alkali. Based on the ^{19}F NMR spectroscopic data, the content of the resultant fluoride ion was estimated at 4.67 mmol (17.7%) of fluorine (Fig. 1b), which practically coincides with the quantitative analysis data for the same sample of the modified lignin.

Our attempts of electrochemical fluorination in an acidic medium, in 40% aqueous solution of KF·HF and 15% aqueous HF solution, revealed a similar dependence of the fluorine content on the nature of lignin, but the fluorine content in the modified lignins was minimal. The HLSW and HLCH samples were fluorinated to insignificant extent (typically of no greater than 2.5%); in the HLHW, HLSH, and HLCS samples no fluorine was detected after the syntheses.

Table 1. Results of fluorination in an aqueous alkaline medium in relation to the nature of the hydrolytic lignin[a]

Hydrolytic lignin[b]	F, %	COOH, %	OH$_{phen}$, %	OH$_{tot}$, %	CO$_{tot}$, %	CO$_{quin}$, %
HLSW	9.8	6.4	0.6	5.7	3.8	1.0
HLHW	1.1	5.4	0.7	5.0	4.6	1.2
HLCH	13.2	8.0	0.3	7.9	4.0	1.5
HLSH	3.3	7.1	0.9	6.1	4.4	1.3
HLCS	2.8	6.7	1.1	6.8	4.6	1.0

[a] Electrolyte 1 M KOH + 1 M KF; T = 25°C, Q = 3600 C/g.
[b] (HLSW) Hydrolytic lignin derived from softwoods; (HLHW) hydrolytic lignin derived from hardwoods; (HLCH) hydrolytic lignin derived from cotton-seed husks; (HLSH) hydrolytic lignin derived from sunflower-seed hulls; and (HLCS) hydrolytic lignin derived from corn-seed stalks.

Table 2. Gel-chromatographic analysis results for the lignins oxidized in 40% aqueous HF solution[a]

Sample	$M_N \times 10^4$	$M_W \times 10^4$	$M_Z \times 10^4$	M_W/M_N	M_Z/M_W
HLCS	2.10	4.79	6.61	2.27	1.37
Oxidized HLCS, Q = 3600 C/g	2.69	6.38	8.65	1.36	1.35
Oxidized HLCS, Q = 10800 C/g	2.80	6.71	9.70	2.34	1.44
Oxidized HLCS, Q = 21600 C/g	1.21	3.94	8.09	3.26	2.06

[a] M_N is the number-average, M_W is weight-average, and M_Z is average molecular weight.

Thus, the products of oxidation of these lignins in acidic fluoride-containing electrolytes contain only three elements: carbon, oxygen, and hydrogen.

The absorption band at 1512 cm^{-1}, which is observed in the IR spectrum of the original HLSW and confirmed the presence of aromatic rings in the lignin structure, was preserved in the spectrum of the HLSW oxidized in the 40% KF·HF solution (Fig. 2), but slightly decreased in intensity. The absorption band in the region of stretching vibrations of aliphatic hydrocarbons (2800–2950 cm^{-1}) noticeably increased in intensity. The ratio of the intensities of the bands at 1718 cm^{-1} (COOH group) and at 1636 cm^{-1} (CO group) changed; specifically, the content of carboxy groups increased, and that of carbonyl group, decreased, probably due to oxidation of carbonyl to carboxy groups. The intensities of the absorption band at 750 cm^{-1} (bending vibrations of carboxy group) and of the absorption bands in the 1000–1200 cm^{-1} region (bending vibrations of aliphatic hydroxyl and quinone groups) increased relative to the spectrum of the original HLSW, thereby evidencing intensive oxidation of HLSW.
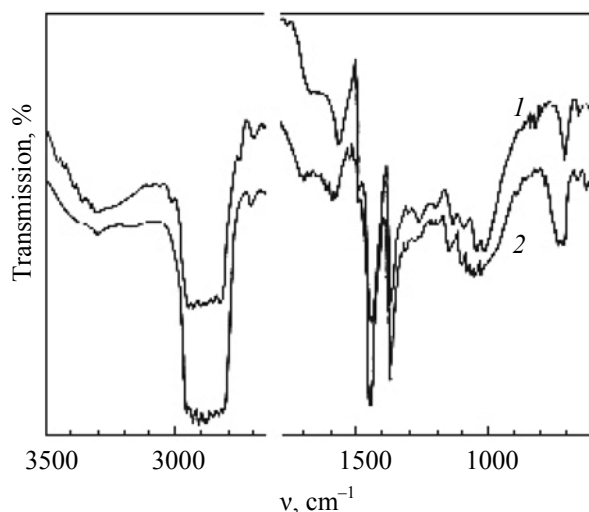
Electrochemical modification of lignins is typically performed at current densities of ~0.1 A/cm^2, under which conditions fairly mild oxidation proceeds. For example, gel-chromatographic analysis of the products of HLSW modification in 40% KF·HF solution showed that, before passing 3600 C/g electricity, the electrolysis was accompanied by polycondensation of the lignin macromolecules, probably owing to the oxidized groups. Next, the polycondensation slowed down; decreases in the average molecular weights of the lignins were achieved only after prolonged electrolysis [Q = 21600 C/(lignin g)] (Table 2), with the content of carboxy groups in the oxidized lignin samples reaching 38% (in terms of Klason lignin).

The HL oxidation at higher current densities (Table 3) was studied in 15% aqueous HF solution. As both current density and amount of electricity passed were increasing, the degree of lignin oxidation tended to rapidly increase, as evidenced by an increase in the content of carboxy groups (Table 3).

The IR spectra (Fig. 3) preserved the absorption bands at 1512 cm^{-1}, characteristic of vibrations of the benzene ring. At 4760 C/g electricity passed the absorption band attributable to benzene rings decreased in intensity, indicating oxidation-induced decomposition of the aromatic part of the lignin macromolecule. The absorption bands at 2925 and 2850 cm^{-1}, corresponding to the stretching vibrations of aliphatic hydrocarbons, by contrast, tended to increase in intensity with increasing amount of electricity passed. In the 1000–1200 cm^{-1} region (1035, 1014, and 1119 cm^{-1}, stretching vibrations of =CO bonds in carbonyl groups), the bands noticeably increased in intensity as well.

The absorption maxima observed in the UV spectra of the oxidized lignins at 280 nm (Fig. 4) correspond to aromatic structures and confirm that they were preserved until the content of carboxy groups in the oxidized lignin macromolecules reached ~40%. With increasing amount of the electricity passed the peaks near 280 nm tended to decrease in intensity.
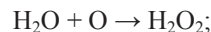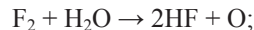

Fig. 2. IR spectra of (*1*) original and (*2*) oxidized HLSW. Electrolyte: 40% aqueous KF·HF.

Table 3. Results of HLCS oxidation in 15 % aqueous HF solution

Current density, A/cm^2	Electrolysis time, min	Amount of electricity passed, C/g	Content of COOH groups (in terms of Klason lignin), %
–	–	–	5.4
0.1	50	1800	7.2
0.1	100	3600	8.7
0.2	25	1800	7.5
0.2	50	3600	9.6
0.3	20	2160	31.1
0.3	25	2700	37.6
0.3	30	3240	39.8
0.3	40	4320	45.0
0.4	15	2160	29.2
0.4	25	3600	38.7
0.4	30	4320	45.8
0.4	40	5760	50.2
0.4	50	7200	Degradation

Oxidation of the HLCS in 15% aqueous HF solution at a current density of 0.4 A/cm^2 and at electrolysis times >40 min (Q = 5760 C/g) led to the degradation of lignin macromolecules, associated with complete loss of aromatic structures and a significant decrease in molecular weights.

In the processes performed at the current density of 0.1 A/cm^2 the electrode potential did not exceed 2–2.2 V. Oxidation of lignin occurred due mainly to the oxygen resulted from oxidation of water at the anode. The anode potential in the cells operating at the current densities of 0.3 A/cm^2 exceeded the standard oxidation potential of fluorine (2.87 V), and molecular fluorine was evolved at the anode, which made possible the following chemical reactions in the electrolyte solution:

$$F_2 + H_2O \rightarrow 2HF + O;$$
$$H_2O + O \rightarrow H_2O_2;$$
$$O_2 + O \rightarrow O_3.$$

In our opinion, the reaction with F_2 in the electrolyte solution gave other strong oxidants, H_2O_2 and O_3, which actively interacted with the lignin macro-
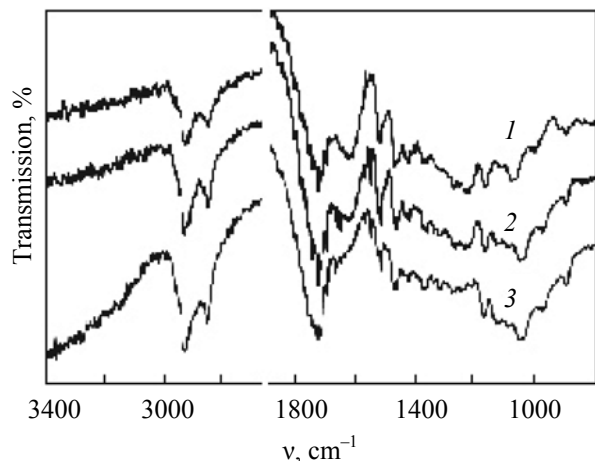

Fig. 3. IR spectra of (*1*) original and (*2, 3*) oxidized HLCS (electrolyte: 15% aqueous HF solution): (*2*) Q = 2160 C/g, i = 0.3 A/cm^2 and (*3*) Q = 3600 C/g, i = 0.4 A/cm^2.
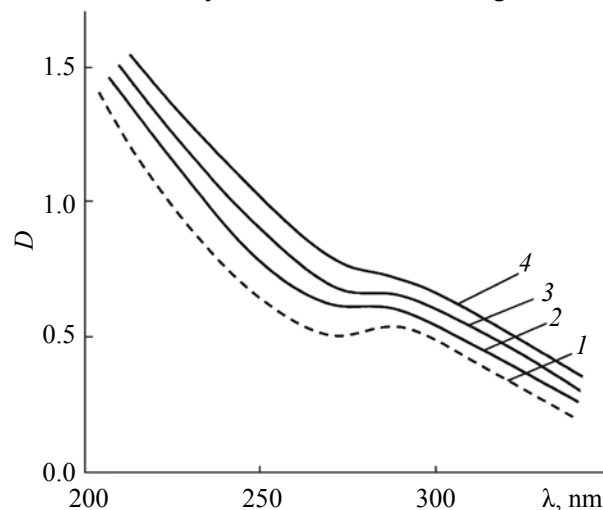

Fig. 4. UV spectra: (*1*) original and (*2–4*) oxidized HLCS (electrolyte: 15% aqueous HF solution). Q, C/g: (*2*) 2160, (*3*) 3240, and (*4*) 4320; i = 0.3 A/cm^2.

molecules. This led to formation of oxidized lignins characterized by a higher content of functional groups compared to that obtained at the current density of 0.1 A/cm^2 at identical amounts of the electricity passed ($Q = 3600$ C/g).

CONCLUSIONS

(1) It was demonstrated that modification of hydrolytic lignins in fluoride-containing aqueous alkaline electrolytes (1 M KOH + KF) led to in-corporation of fluorine into the nonaromatic part of the lignin macromolecule in the amount determined, above all, by the nature of lignin. For example, under identical experimental conditions the greatest amount of fluorine was introduced into the hydrolytic lignin derived from cotton-seed husks (18.6%). The lowest content of fluorine was found in the hydrolytic lignins derived from hardwoods and sunflower-seed hulls. The degree of oxidation of lignins after modification in the aqueous alkaline fluoride-containing electrolyte (1 M KOH + 1 M KF) at 25°C was relatively low, with carboxy and total hydroxyl groups being the most abundant in the HL derived from cotton-seed husks (8% and 7.9%, respectively).

(2) Modification of the hydrolytic lignins in acidic fluoride-containing electrolytes (40% aqueous solution of KF·HF and 15% aqueous HF solution) delivered significant degrees of oxidation of the lignin macro-molecule. During electrochemical oxidation of lignin in 15% aqueous HF solution at 0.3–0.4 A/cm^2 current density and 3600–5400 C/g electricity passed the content of carboxy groups in the modified lignins was ~40%. The aromatic structures of the lignin macro-molecules were partially preserved in the oxidation products.

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