Sulfation of ethanol lignin of abies wood by sulfamic acid in N,N-dimethylformamide medium

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The sulfation of ethanol lignin of abies wood by sulfamic acid–urea mixture in N,N-dimethylformamide (DMF) medium was studied for the first time. The effect of the duration of lignin sulfation process on the yield and sulfur content in resulted lignin sulfates was studied. It was shown that the reaction of ethanol lignin sulfation begins and ends in a homogeneous medium. At temperature 100 °C the sulfur content in lignin varies from 5.4 to 6.8 % mass, depending on the process time. The introduction of sulfate groups into the lignin structure was confirmed by FTIR and 2D NMR spectroscopy. It was found that both alcohol and phenolic hydroxyl groups of lignin enter the sulfation reaction. The molecular weight distribution of sulfated ethanol lignin was determined by gel permeation chromatography. The optimized method of synthesis allows to obtain sulfated ethanol lignin with low polydispersity (1.31) and narrow molecular weight distribution (3.25–3.75 kDa).

Keywords: abies ethanol lignin, sulfation, sulfamic acid, urea, N,N-dimethylformamide, sulfated ethanol lignin, degree of sulfation, molecular mass distribution.

1 Introduction

At the present time the traditional technologies for cellulose production – sulfate and sulfite cooking do not meet for modern environmental standards. The recently developed processes of organosolv cooking have a higher environmental safety. They are based on the use of low-boiling organic solvents – aliphatic alcohols, acetic acid, acetone, ethyl acetate, etc. – which can easily be regenerated by distillation [1,2].

One of the promising processes of organosolv delignification of wood is the process of alcohol cooking. Ethanol lignin obtained by alcohol cooking is soluble in acetone, tetrahydrofuran and ethyl acetate and insoluble in water [3,4].

One important direction of lignin processing is the production of its sulfated derivatives [5–7]. The presence of sulfate groups gives lignin the ability to dissolve in water and increases its biodegradability. Sulfated lignin derivatives can replace not only the widely used products of chemical modification of polysaccharides [8], but can also be used as antiviral drugs [9].

The traditional lignin sulfation methods [9,10] are based on the use of aggressive sulfating reagents (sulfuric and chlorosulfonic acids, oleum, sulfuric anhydride and its complexes

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with toxic pyridine and amines). The use of these sulfating agents can lead not only to sulfation of aliphatic and phenolic hydroxyl groups, but also to significant degradation of the biopolymer [10]. In this regard, it is necessary to search for new, less aggressive and more environmentally friendly reagents for lignin sulfation.

Compared to traditional sulfating agents, sulfamic acid is a stable, non-hygroscopic crystalline substance [11]. Sulfamic acid is produced commercially by the reaction of urea with oleum. As a sulfating agent, sulfamic acid is similar in properties to SO_3-tertiary amine complexes. Usually it is used when other sulfating agents do not lead to the desired result [12]. Sulfation reactions with sulfamic acid can be promoted by the addition of pyridine, other tertiary amines, and even such weak bases as urea and acetamide [12].

Previously, the authors [13] proposed a new method for producing water-soluble sulfated lignin, based on the interaction of abies ethanol lignin with sulfamic acid–urea mixture in 1,4-dioxane medium. However, the sulfated ethanol lignin is not dissolved in 1,4-dioxane. It is precipitated from the reaction solution during the sulfation process. As a result, sulfated ethanol lignin is formed in a heterogeneous medium with a low yield and a low degree of sulfation. Increasing the temperature of the sulfation process from 80 to 95 °C and the amount of the sulfating complex (sulfamic acid–urea mixture) does not significantly affect the degree of lignin sulfation.

In this work, it was proposed for the first time to carry out the sulfation of abies ethanol lignin with a mixture of sulfamic acid–urea in the medium of N,N-dimethylformamide (DMF). The sulfated ethanol lignin is dissolved in DMF, what makes it possible to carry out the sulfation process in a homogeneous medium. The optimal conditions of abies ethanol lignin sulfation in DMF medium have been established. They allow to obtain the sulfated lignin with rather high yield and degree of sulfation, with low polydispersity and narrow molecular weight distribution.

2 Experimental part

Ethanol lignin isolated from abies wood (Ábies sibírica) with water-ethanol mixture at a temperature of 185 °C by the method [14] was used as the initial material. The yield of ethanol lignin was 9.5% of wood mass (30% of the initial lignin content in wood), and its average molecular weight was 1.6 kDa.

The sulfation of ethanol lignin was carried out in a three-neck flask (100 ml) equipped with a reflux condenser, a thermometer and a mechanical stirrer. The N,N-dimethylformamide (40 ml), sulfamic acid (3.0 g), urea (2.0 g) were placed in a flask and stirred at 100 °C. Then 2.0 g of ethanol lignin isolated from abies wood was added to the flask. The ratio of lignin:sulfating complex (sulfamic acid–urea mixture) was 1:3 (g:mmol). The mixture was

intensively stirred at a temperature of 100°C for 0.5–6.0 hours. Then the reaction mixture was cooled to room temperature, diluted with 50 ml of water, neutralized with aqueous ammonia to pH 8 and filtered. To remove the excess of reactants, the product was dialyzed against water in a plastic bag of MF-503-46 MFPI brand (USA) with pores that pass molecules with a mass less than of 3.5 kDa. The water was changed every hour. After 8–10 hours of dialysis, an aqueous solution of sulfated lignin was evaporated in vacuum using a rotary evaporator to obtain a solid residue - sulfated lignin in the form of an ammonium salt.

Elemental analysis of sulfated lignin was performed on a FlashEA-1112 elemental analyzer (ThermoQuest, Italia).

The sulfur content in sulfated ethanol lignin was determined by burning the sample in a stream of oxygen at a temperature of 1000°C, followed by absorption of the combustion products by a 6% aqueous solution of hydrogen peroxide [13]. The resulting sulfuric acid was titrated with 0.01 N sodium hydroxide solution with methyl red as an indicator.

The FTIR spectra of initial lignin and sulfated lignin were recorded using a Tensor-27 FTIR spectrometer (Bruker, Germany) within the wavelength range of 400–4000cm^{-1}. The spectral information was analysed using the OPUS program (version 5.0). Solid samples for analysis were prepared in the form of pills in a KBr matrix (2 mg sample/1000 mg KBr).

NMR spectra were registered at 25 °C on a Bruker AVANCE III spectrometer (600 MHz (^{1}H) and 155 MHz (^{13}C)). 2D HSQC spectra were acquired using edited-HSQC pulse sequence from Bruker library (hsqcedgp). About 80 mg of lignin in 0.6 ml of deuterated dimethyl sulfoxide was set to dissolve for at least 12 hours. A solvent peak was used as an internal reference ($\delta^{13}C$ 40.1; $\delta^{1}H$ 2.5).

The weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (Đ) of sulfated ethanol lignin samples were defined by gel permeation chromatography using an Agilent 1260 Infinity II Multi-Detector GPC/SEC System chromatograph with triple detection: by a refractometer, by a viscometer and by light scattering. The separation was made on two Aquagel-OH Mixed-M columns using the solution 0.2M $NaNO_3$ + 0,01M NaH_2PO_4 in water (pH = 7) as the mobile phase. The column was calibrated using polydisperse polyethylene glycol standards (Agilent, USA). The flow rate of the eluent was 1 ml/min, the volume of the used sample was 100 μl. Before analysis, the samples were dissolved in the mobile phase (~5 mg/ml) and filtered through a 0.45 μm PTFE membrane filter (Millipore). Data collection and data processing were performed using Agilent GPC/SEC MDS software.

3 Results and discussion

The results of the study of abies ethanol lignin sulfation by sulfamic acid–urea mixture in the medium of DMF are presented in Table 1.

Table 1 The effect of time of ethanol lignin sulfation by a sulfamic acid-urea mixture in DMF on the sulfated lignin yield and on the sulfur content (temperature 100 °C)

№	Time, h	Yield*, g	Calculated yield, g	Sulfur content, % mass
1	0.5	2.34	2.40	5.47
2	1.0	2.56	2.41	5.61
3	2.0	2.63	2.42	5.74
4	3.0	2.69	2.45	6.05
5	4.0	2.84	2.48	6.38
6	5.0	2.73	2.52	6.83
7	6.0	2.64	2.51	6.75

* 2.0 g of ethanol lignin was sulfated in all experiments

The highest sulfur content (6.83%) was achieved after 5 hours of sulfation. When DMF is used as a solvent, the sulfation process begins and ends in a homogeneous medium. Some excess of the yields of sulfated lignins compared to calculated yields (Table 1) may be due to a side reactions, leading to the formation of carbamate groups during the sulfation [11]. The formation of carbomate groups may occur due to the reaction of hydroxyl groups and urea [15]. This assumption is confirmed by the appearance of an absorption band in the FTIR spectrum of sulfated lignin at 1719 cm^{-1}, which is characteristic of the valence vibrations of C=O groups.

Free hydroxyl groups in lignin have a different character [16]. They can be phenolic and alcohol nature. Hydroxyls located in the side chains of lignin are both secondary and primary (sometimes tertiary hydroxyl groups are also presented). In the lignin structural unit, the primary alcohol groups (–CH_2OH) are located in the γ-position of the propane chain, and the secondary alcohol groups (–CHOH) in the α-position. The content of secondary alcohol groups in the β-position is not large. The most reactive are the hydroxyl groups in the α-position, also called benzyl alcohol groups.

Among the main monomeric and dimeric structure-forming lignin units [9], the structures containing free alcohol and phenolic hydroxyl groups can undergo sulfation.

The substitution of hydroxyl groups with sulfate groups in the ethanol lignin during its sulfation with a sulfamic acid–urea mixture was confirmed by FTIR and 2D NMR spectroscopy.

In contrast to the initial ethanol lignin, in the FTIR spectra of the ammonium salts of sulfated ethanol lignin (Fig. 1), the new intense absorption bands corresponding to C–O–S stretching vibrations of the SO_3 group appear in the region of 803–861 cm^{-1}. Also the wide

absorption bands corresponding to asymmetric valence vibrations of the O=S=O group and skeletal vibrations of the guaiacyl ring appear in the region of 1219–1260 cm^{-1} [17]. In addition to the distinct bands of the sulfate group, the stretching vibration of the C=O groups was seen at the wavenumber of 1719 cm^{-1} [11].

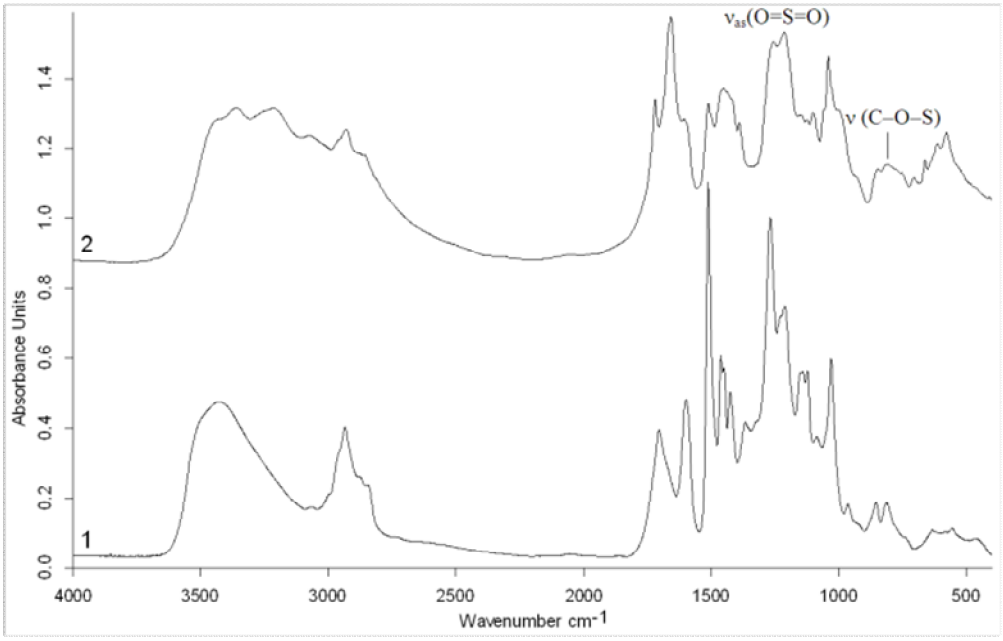

Fig. 1 FTIR spectra: 1 – sample of abies ethanol lignin, 2 – sample of ammonium salt of sulfated ethanol lignin (sulfur content 7.9 % mas.)

The HSQC 2D NMR spectrum of sulfated abies ethanol lignin is shown in Figure 2, and the spectrum of the initial ethanol lignin was previously described in [18]. The assignment of the main $^{1}H–^{13}C$ peaks in the HSQC spectra was performed using published data [19–21]. The table 2 presents the values of chemical shifts, including some of the low intensity peaks, the images of which are not shown in Figure 2. The main structural units and fragments of the initial and sulfated abies ethanol lignins are presented in Figure 3.

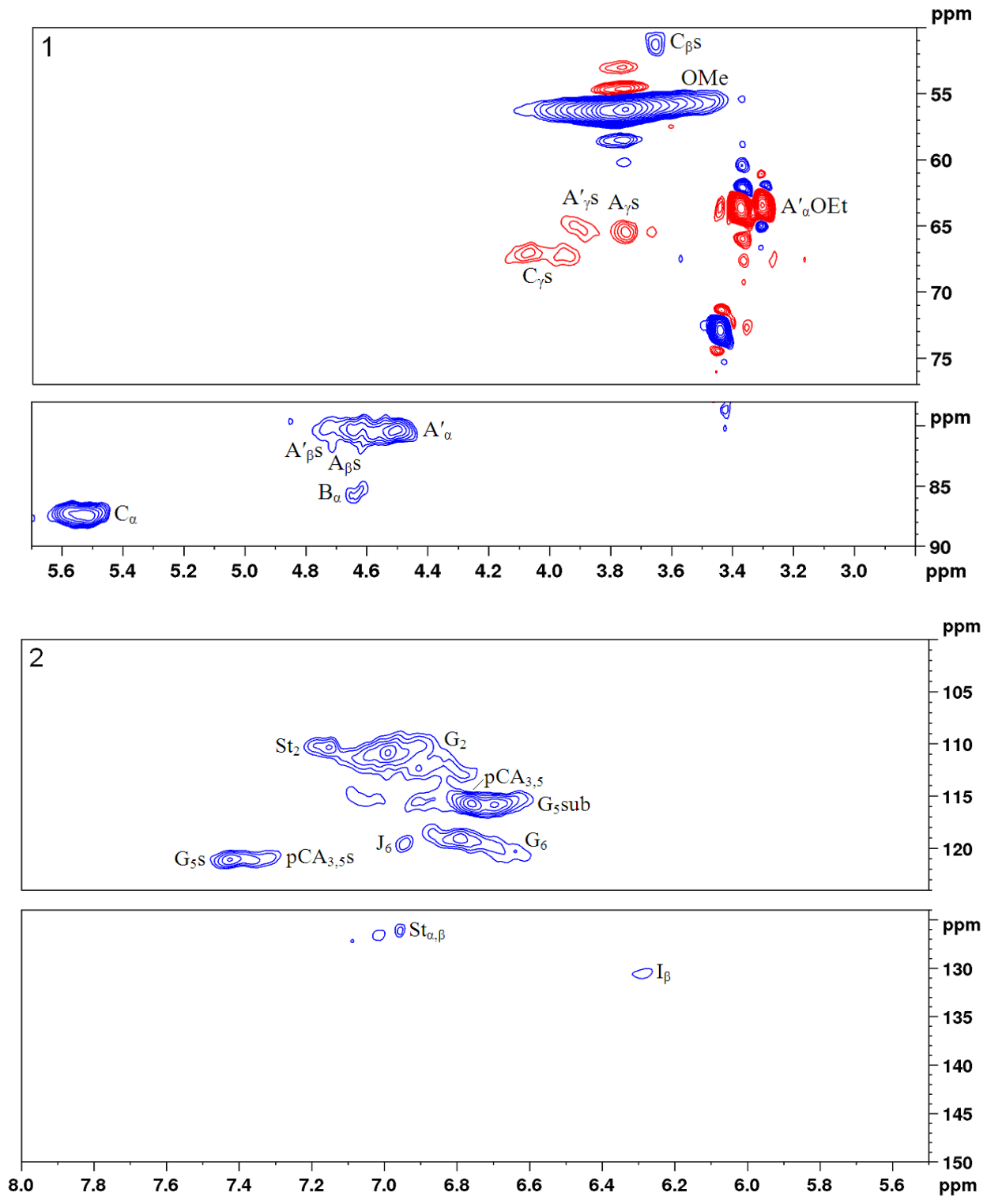

Fig. 2 HSQC spectrum of sulfated ethanol lignin (sulfur content 7.9 % mas): aliphatic oxygenated region (1), aromatic region (2). See Table 2 for signal assignment and Figure 3 for the main structures identified

Table 2 Assignments of the $^{1}H–^{13}C$ cross signals in the HSQC spectra of initial and sulfated abies ethanol lignins

Lable	δ_C/δ_H, ppm (initial lignin)	δ_C/δ_H, ppm (sulfated lignin)	Assignments
OMe	56.1/3.75	56.2/3.76	C−H in methoxyls (OMe)
A_γ and A'_γ	60.6/3.41 and 3.56	–	$C_\gamma–H_\gamma$ in β-aryl ether (β–O–4′) substructures (A) and in α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′)
A_γs and A'_γs	–	65.3/3.75 and 3.90	$C_\gamma–H_\gamma$ in γ-sulfated (γ-OSO_3NH_4) β-aryl ether (β–O–4′) substructures (As) and in γ-sulfated (γ-OSO_3NH_4) α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′s)
A_β and A'_β	83.9/4.31 and 83.1/4.39	–	$C_\beta–H_\beta$ in β-aryl ether (β–O–4′) substructures (A) and in α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′)
A_βs and A'_βs	–	80.6/4.73	$C_\beta–H_\beta$ in γ-sulfated (γ-OSO_3NH_4) β-aryl ether (β–O–4′) substructures (As) and in γ-sulfated (γ-OSO_3NH_4) α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′s)
A_α	71.6/4.76	–	$C_\alpha–H_\alpha$ β-aryl ether (β–O–4′) substructures (A)
A_αs	–	73.6/5.38	$C_\alpha–H_\alpha$ in α-sulfated (α-OSO_3NH_4) β-aryl ether (β–O–4′) substructures (As)
A'_αOEt	64.4/3.33	63.7/3.34	C−H of methylene group in α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′)
A'_α	80.3/4.48	80.2/4.51	$C_\alpha–H_\alpha$ in α-ethoxylated (C_αOEt) β-aryl ether (β–O–4′) substructures (A′)
B_β	54.3/3.06	–	$C_\beta–H_\beta$ in pinoresinol (β–β′) substructures (B)
B_γ	71.1/3.73 and 4.04	70.7/3.74 and 4.13	$C_\gamma–H_\gamma$ in pinoresinol (β–β′) substructures (B)
B_α	85.4/4.64	85.7/4.64	$C_\alpha–H_\alpha$ in pinoresinol (β–β′) substructures (B)
C_β	54.3/3.46	–	$C_\beta–H_\beta$ in phenylcoumaran (β–5′) substructures (C)
C_βs	–	51.1/3.66	$C_\beta–H_\beta$ in γ-sulfated (γ-OSO_3NH_4) phenylcoumaran (β–5′) substructures (Cs)
C_γ	63.5/3.70	–	$C_\gamma–H_\gamma$ in phenylcoumaran (β–5′) substructures (C)
C_γs	–	67.1/4.07	$C_\gamma–H_\gamma$ in γ-sulfated (γ-OSO_3NH_4) phenylcoumaran (β–5′) substructures (Cs)
C_α	87.6/5.44	87.4/5.53	$C_\alpha–H_\alpha$ in phenylcoumaran (β–5′) substructures (C_α)

I_β	130.9/6.33	130.6/6.29	C_β–H_β in cinnamyl alcohol end groups (I)
I_γ	60.2/4.04	60.2/4.03	C_γ–H_γ in cinnamyl alcohol end groups (I)
$I_\gamma s$	–	65.6/4.24	C_γ–H_γ in γ-sulfated (γ-OSO_3NH_4) cinnamyl alcohol end groups (Is)
J_6	119.6/6.95	119.6/6.95	C_6–H_6 in cinnamyl aldehyde end groups (J)
$pCA_{3,5}$	115.8/6.76	115.8/6.76	$C_{3,5}$–$H_{3,5}$ in p-coumarate (pCA)
$pCA_{3,5}s$	–	121.2/7.37	$C_{3,5}$–$H_{3,5}$ in 4-sulfated (4-OSO_3NH_4) p-coumarate (pCAs)
G_2	110.8/6.95	110.6/6.99	C_2–H_2 in guaiacyl units (G)
G_5	115.7/6.95	–	C_5–H_5 in guaiacyl units (G) with free hydroxyl in 4-position (4-OH)
G_5s	–	121.2/7.43	C_5–H_5 in 4-sulfated (4-OSO_3NH_4) guaiacyl units (Gs)
G_5sub	115.7/6.72	115.8/6.70	C_5–H_5 in 4-substituted (4-Sub) guaiacyl units (Gsub)
G_6	119.2/6.77	119.2/6.79	C_6–H_6 in guaiacyl units (G)
St_2	110.0/7.15	110.4/7.17	C_2–H_2 in stilbenes (St)
$St_{\alpha,\beta}$	126.2/6.97	126.3/6.96	$C_{\alpha,\beta}$–$H_{\alpha,\beta}$ in stilbenes (St)

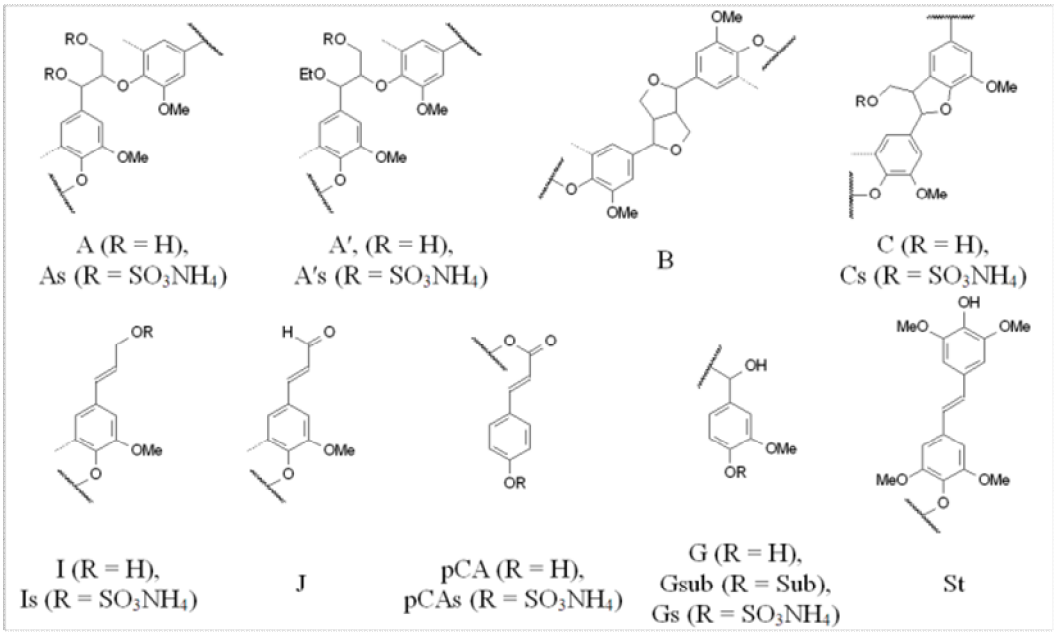

Fig. 3 Main structural units and fragments of initial and sulfated ethanol lignins: A – β-aryl ethers, As – α,γ-sulfated (α,γ-$COSO_3NH_4$) β-aryl ethers, A′ – α-ethoxylated (C_αOEt) β-aryl ethers, A′ – α-ethoxylated (α-COEt) β-aryl ethers, A′s – γ-sulfated (γ-$COSO_3NH_4$) α-ethoxylated (α-COEt) β-aryl ethers, B – pinoresinols, C – phenylcoumarans, Cs – γ-sulfated (γ-$COSO_3NH_4$) phenylcoumarans, I – cinnamyl alcohol end groups, Is – γ-sulfated (γ-$COSO_3NH_4$) cinnamyl alcohol end groups, J – cinnamyl aldehyde end groups, pCA – p-coumarates, pCAs – 4-sulfated (4-$COSO_3NH_4$) p-coumarates, St – stilbenes, G – guaiacyl units, Gsub – 4-substituted (4-COSub) guaiacyl units, Gs – 4-sulfated (4-$COSO_3NH_4$) guaiacyl units

A comparison of the HSQC spectrum of the initial ethanol lignin with the spectrum of the sulfated sample was carried out in the regions of chemical shifts of side chain atoms (δ_C/δ_H 50–90/3.0–5.6 ppm) and aromatic rings (δ_C/δ_H 100–150/5.5–8.0 ppm) lignin.

The group of peaks assigned to phenylcoumaran fragments (C) (Fig. 3) in the spectrum of sulfated ethanol lignin is characterized by a change in the position of the correlation signals C_γ–H_γ and C_β–H_β, which is caused by the effect of sulfation of OH groups in the γ-position (C_γ–H_γ is a shift to the down field $\Delta\delta_C \sim 4$ ppm, C_β−H_β – shift to a up field $\Delta\delta_C \sim 3$ ppm).

A comparison of the chemical shifts of β-aryl ether β–O–4′ (A) in the spectrum of sulfated ethanol lignin showed a similar change in the positions of the peaks along the axis of carbon atoms. In comparison with the initial lignin signals, the signals of C_γ–H_γ and C_α−H_α correlations of sulfated lignin are shifted to the down field by 5 and 2 ppm, respectively and the signal of C_β–H_β correlation is shifted to the up field by ~3 ppm. Such shift of signals in the spectra is probably due to the sulfation of OH groups of β-aryl esters of the lignin macromolecule in the γ- and α-positions. In the case of α-ethoxylated β-aryl ethers (A′), it seems that sulfation of free OH groups in the γ-position occurs, since there is a shift of the peaks C_γ–H_γ and C_β–H_β, and the peak C_α–H_α practically does not change its position.

A similar shift of signals in the aliphatic region of the spectrum of sulfated lignin in comparison with the initial lignin was also found for the C_γ–H_γ correlations of the cinnamyl alcohol end groups (I), which also indicates the sulfation of OH groups linked with the C_γ carbon atoms of this lignin fragment.

In the spectrum of the initial ethanol lignin, the group of peaks of pinoresinol (β–β′) substructure (B) is clearly distinguishable. However, in the spectrum of the sulfated lignin, a dramatic decrease in the intensity of the C_β–H_β, C_γ–H_γ peaks and practically unchanged intensity and position of the peak assigned to the C_α–H_α correlation (δ_C/δ_H 85.7/4.64 ppm) are observed. It is important to note that in the aliphatic region of the spectrum there is a peak at δ_C/δ_H of 72.9/3.44 ppm assigned to CH or CH_3 groups. It was not possible to establish an unambiguous assignment of this peak to any structural fragment.

In the aromatic region of the spectrum of the sulfated lignin there are the peaks assigned to CH groups of guaiacil units (G_2, G_5, G_6 in Table 2). Peaks of stilbene units ($St_{\alpha,\beta}$) and (St_2), as well as peaks of cinnamyl alcohol end groups (I_β) and cinnamyl aldehyde end groups (J_6) with chemical shifts similar to the initial ethanol lignin were assigned.

In addition, a new peak (121.2/7.43 and 7.37 ppm) was found in the spectrum of sulfated ethanol lignin, which indicates a possible substitution of phenolic hydroxyls with sulfate groups. Most probably, the hydroxyl groups of guaiacyl (G) and p-coumarate (pCA) structural units undergo sulfation, as a result the chemical shifts of positions 3 and 5 are observed. This

conclusion is supported by the expected effect of changing the nature of the substituent in phenol [22] and the disappearance of the cross signal at δ_C/δ_H of 115.7/6.95 ppm, which is typical for the C_5–H_5 correlation of guaiacyl units (G_5) with unsubstituted hydroxyl at the 4-position [23].

Based on these data, it can be concluded that the sulfation of available aliphatic hydroxyl groups in the γ- and α-positions of β-aryl ethers, in the γ-position of α-ethoxylated β-aryl ethers and phenylcoumaran substructures, as well as free phenolic hydroxyl groups in the 4-position of guaiacyl units and p-coumarates takes place. The hydroxyl groups in the γ-position of the cinnamyl alcohol end groups can also be sulfated.

The results of the study of molecular weight distribution (MWD) of the samples of the initial and sulfated abies ethanol lignin are presented in Table 3 and in Figure 4.

Table 3 Number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity ($Đ_m$) of the samples of the initial and sulfated abies ethanol lignin.

Sample	Sulfur content, % mas.	M_n, kDa	M_w, kDa	$Đ_m$
Abies ethanol lignin	–	0.95	1.83	1.95
Ethanol lignin sulfated 3 hours	6.05	2.45	3.82	1.56
Ethanol lignin sulfated 5 hours	6.83	2.48	3.26	1.31

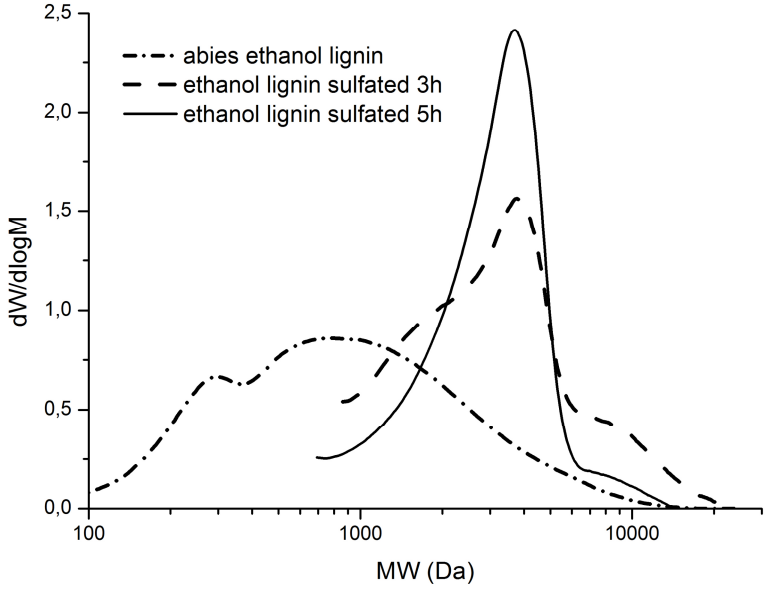

Fig. 4 Curves of molecular weight distribution of abies ethanol lignin and sulfated ethanol lignins

Compared with the initial ethanol lignin, the number average molecular weight (M_n) and weight average molecular weight (M_w) of sulfated lignin increase, and the polydispersity decreases from 2 to ~1.3. On the MWD curves of both initial and sulfated lignin, there is practically no region of high (up to 10.0 kDa) molecular weights. A significant increase in the proportion of high molecular weight sulfated lignin fraction is not observed due to the low reactivity in the sulfation reaction of large lignin molecules, which are insoluble in water due to the low degree of sulfation. The diameter of pores of the dialysis bag plays a decisive role in the shape of the molecular weight distribution curve: the fractions of sulfated lignins with low molecular weight are washed out during dialysis through pores that pass molecules with a mass less than 3.5 kDa. An increase in the time of the sulfation process from 3 to 5 hours reduces the polydispersity and content of low-molecular fractions of sulfated lignin and leads to an increase in the amount of fraction with a molecular weight of about 3.5 kDa. Thus, the sample of sulfated lignin with low polydispersity (1.31), narrow molecular weight distribution (3.26 kDa) and sulfur content 6.83 % mas. was obtained at the following process conditions: temperature 100 °C, time 5 hours, ratio lignin/sulfamic acid–urea = 1:3 (g:mmol) and a dialysis with a cut-off of 3.5 kDa.

5 Conclusion

For the first time it was proposed to carry out the sulfation of abies ethanol lignin by sulfamic acid–urea mixture in the DMF medium to obtain water-soluble sulfated ethanol lignin. The high sulfur content (6.83 % mass) was achieved at a temperature of 100 °C and a reaction time of 5 hours.

The introduction of sulfate groups into the structure of ethanol lignin was confirmed by elemental analysis, FTIR and NMR spectroscopy. Using 2D NMR spectroscopy, it was found that both alcohol and phenolic hydroxyl groups of ethanol lignin undergo sulfation with sulfamic acid–urea mixture in DFM medium.

By the use of gel permeation chromatography, it was found that the sulfation of ethanol lignin increases the average molecular weight and decreases the polydispersity of sulfated lignins. Under the selected conditions of sulfation and dialysis, the sulfated ethanol lignins with a narrow molecular weight distribution (3.25–3.74 kDa) and low polydispersity (1.31) were obtained.

Acknowledgements

The reported study was supported by Russian Science Foundation, grant N 16-13-10326. The devices of the Krasnoyarsk regional center of collective use of the Siberian Branch of the

Russian Academy of Sciences were used in the work. The authors thank Dr. I.V. Korolkova for recording FTIR spectra.

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