Research on Thermal Behaviour of Organosolv Lignins Isolated from Fir and Aspen Wood

N. M. MIKOVA, O. YU. FETISOVA, N. I. PAVLENKO, N. V. CHESNOKOV

Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia

E-mail: nm@icct.ru

Abstract

The composition and thermal behaviour of ethanol-lignins isolated by organosolv extraction from wood biomass of softwood and hardwood species were explored by non-isothermal thermogravimetric analysis (TG/DTG and DSC), FT-IR spectroscopy, elemental analysis, and scanning electron microscopy (SEM). Comparative analysis of IR spectra of the initial lignin and thermally treated lignin at 200 °C testifies the identity of their structural-group composition. The initial temperature of decomposition of fir lignin (252 °C) is about 10 °C higher than that of aspen lignin. It is determined that fir lignin is mainly decomposed in argon within a temperature range of 337–427 °C. The maximum degradation rate of the compound is −2.9 %/min; there is the maximal decomposition at 400 °C. Aspen lignin undergoes intense decomposition in a lower temperature range (327–400 °C) with a maximum mass loss rate of −3.1 %/min at 378 °C. Infrared spectral data for products of thermal transformation of fir lignin at 400 °C testifies a significant degree of lignin polymer decomposition to likely form guaiacol and phenol derivatives. The completion of thermal decomposition of lignins at 800 °C is accompanied by the formation of carbon residues in a 34 % yield of aspen lignin and 37% of fir lignin. The appearance of carbonized particles in the structure of the material, beginning with 240 °C followed by intensification of carbon matrix formation with an increase in pyrolysis temperature to 600 °C is proven by SEM. It is found that the maximum rates of aspen lignin degradation are higher than those for fir lignin in all conditionally isolated temperature ranges.

Keywords: organosolvent lignins, thermal decomposition, FT-IR spectra, surface morphology, carbonization

INTRODUCTION

Lignin finds applications for preparation of some synthetic products, hydrocarbon derivatives, or special agents, such as polymer compounds, carbon materials, adhesives, and resins [1–5]. Different methods for separation of macromolecular biopolymer components with a view to recovering lignin are aimed at limitation of condensation and oxidation reactions proceeding during its isolation from lignocellulosic materials. One of the preparation methods of production of high-quality lignin from lignocellulosic biomass is ethanol extraction [1, 6–9]. Due to the absence of reactive chemicals in organosolvent treatment with etha-nol, the cleaved lignin (ethanol-lignin) characterizing by minimum structural changes compared to lignins obtained by other methods is generated. Efficient method development for further research on lignins assumes research on structural features and thermochemical characteristics during their thermal transformation. A series of contributions are devoted to lignin pyrolysis, however, the data regarding the transformation of lignins isolated from lignocellulosic biomass are still incomplete, as thermal degradation of certain lignin-based compounds possess some individual features [10–12]. In this regard, in order to understand structural and chemical properties operated or controlled by the nature and the meth-

od of isolation from the wood matrix, it is required to explore in detail lignin behaviour during pyrolysis.

Thermogravimetric analysis of the pyrolytic behaviour of lignin polymers makes it possible to define such characteristics, as the range and main intervals of thermal decomposition, mass loss intensity in the corresponding stages of thermal decomposition, the temperature of mass loss maxima and other parameters. The methods of TGA using spectral analysis are widely used to investigate the pyrolytic behaviour of lignins and characteristics of the chemical structure of decomposition products [3–5, 9, 10].

This paper examines characteristics and the pyrolytic behaviour of ethanol-lignins from laboratory batches isolated using gentle ethanol organosolv lignin extraction from the wood of two types of trees typical for Siberia, *i.e.* fir (*Abies sibirica*) and aspen (*Populus tremula*).

The purpose of work was to explore the thermal behaviour of samples of softwood and hardwood lignins in an inert atmosphere, and also to compare the composition and properties of thermal decomposition products.

EXPERIMENTAL

Elemental analysis of C, H and N was performed using a FlashEA-1112 analyser (Italy).

Recording FT-IR absorption spectra was carried out in the 400–4000 cm^{-1} range using a Tensor 27 FT-IR spectrometer (Bruker, Germany) of the Krasnoyarsk Centre for Collective Use in KBr matrix (5 mg/1000 mg matrix). Spectral information is processed using the OPUS package (version 5.0).

Thermogravimetric (TG/DTG and DSC) analysis of samples of lignin, wood, and cellulose was carried out using a Netzsch STA 449F1 instrument (Germany) in an argon atmosphere. A sample of 5 mg was heated from room temperature to 800 °C with a rate of 10 °C/min. Measurement results are processed using Proteus Thermal Analysis software, Version 5.1.0.

Thermal treatment of lignin samples was carried out in a corundum crucible that was placed in a tubular electric furnace. Heating was carried out under pyrolysis conditions with a 10 °C/min rate of temperature elevation from the room temperature to the desired one (200–600 °C) with holding at the final point for 10 min. The samples were cooled under argon.

The surface morphological examination was carried out by scanning electron microscopy (SEM) and micro-X-ray spectral analysis of the chemical composition of samples using aTM-3000 Hitachi scanning electron microscope (Japan).

The experiments used fir ethanol-lignin (FEL) and aspen ethanol-lignin (AEL), ≤0.10 μm fractions, obtained by the organosolv method according to the procedure described in [6]. Table 1 gives elemental analysis data for samples of lignins per absolutely dry substance. Oxygen content was calculated according to the difference.

RESULTS AND DISCUSSION

As it follows from the data of Table 1, FEL and AEL samples have different average molecular mass but similar elemental composition. Moreover, AEL contains slightly less carbon and more oxygen compared to their content in FEL. The value of N/S and O/C ratios points to differences in the degree of aromaticity and the contribution of O-containing groups, respectively, in lignin samples. The higher O/C ratio in the AEL sample compared to FEL represents the ratio of guaiacyl and syringyl components, including elevated content of methoxyl groups in hardwood lignin than in softwood lignin.

In addition to the composition, FEL and AEL are different in the temperature of the beginning of softening and melting. It is 151–152 °C for aspen lignin, and 160–161 °C for fir lignin. The higher value of the softening point may be largely related to the formation of hydrogen bonds between phenolic hydroxyl groups in the main chain of pine lignins [7].

TABLE 1

Characteristics of initial samples of fir ethanol-lignin (FEL) and aspen ethanol-lignin (AEL)

Samples	Content, mass %			H/C	O/C	M_W, g/mol
	C	H	O_{dif}			
FEL	66.34	5.94	27.54	1.13	0.32	1740
AEL	63.90	6.61	29.40	1.24	0.35	2724

*Infrared spectroscopic analysis
of initial organosolv lignins*

Figure 1 presents FT-IR spectra of AEL and FEL (curves *1* and *2*, respectively). It can be seen that the samples have a similar functional composition. The observed absorption bands (AB) in spectra of organosolvent ethanol-lignins samples are due to vibrations in bonds of certain functional groups (aliphatic, carbonyl, hydroxyl, alkyl and aryl ether) and aromatic rings typical for the main building blocks (phenylpropanoids) of the lignin polymer [9, 13].

Nevertheless, in the IR spectrum, there appear typical features of softwood lignin (G-type): an absorption band near 1513 cm^{-1} corresponding to guaiacyl type aromatic structures, more intense compared to adsorption bands in the 1600 and 1423 cm^{-1} ranges typical for guaiacyl-syringyl type analogues (G- + S-type) of hardwood lignins [14]. A highly intense band corresponding to vibrations of the guaiacyl ring and a carbonyl group bound therewith appears near 1270 cm^{-1}.

The absorption band near 1032 cm^{-1} is of complex nature due to the contribution of different type vibrations into its intensity, such as aromatic C−H plane deformation vibrations of the guacyl ring and C−O−(H) vibrations of primary aliphatic alcohol and ether C−O−(C) groups in aromatic G-type structures [5].

The bands at 856 and 816 cm^{-1} caused by C−H out-of-plane deformation vibrations are typical for the guaiacyl aromatic ring structure [13].

Aspen ethanol-lignin (see Fig. 1, curve *1*) differs from fir ethanol-lignin only by the presence of syringyl rings and a lower number of guaiacyl rings in the composition. Absorption bands at 1514, 1270, and 1033 cm^{-1} are less intense due to competition between these compounds (S > G). Characteristic features of hardwood lignins are as follows: the band at 1328 cm^{-1} describing the skeletal ring together with C−O stretching vibrations, which is typical for syringyl compounds, the most intense peak at 1122 cm^{-1} driven by C−H in-plane deformation vibrations of syringyl compounds, and also C−O stretching vibrations in secondary alcohols [15, 16]. The separate band at 833 cm^{-1} characterizes C−H out-of-plane vibrations in the syringyl ring.

Distinctive features of the chemical nature and structure typical for lignins from different wood species may determine the diverse behaviour of fir and aspen ethanol-lignins during thermal degradation.

*Research on the thermogravimetric behaviour
of lignins*

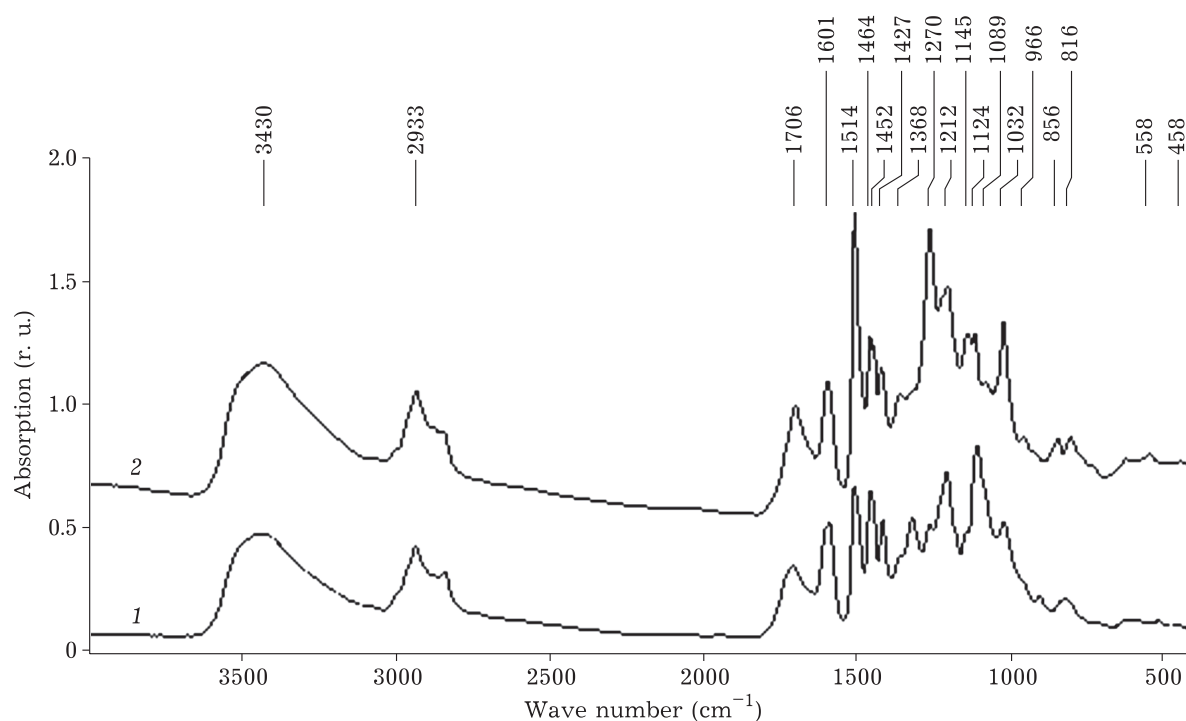The pyrolytic behaviour of organosolv lignins was investigated by thermogravimetric analysis

Fig. 1. IR spectra of samples of lignin samples isolated by organosolv extraction from fir (*1*) and aspen (*2*) wood.
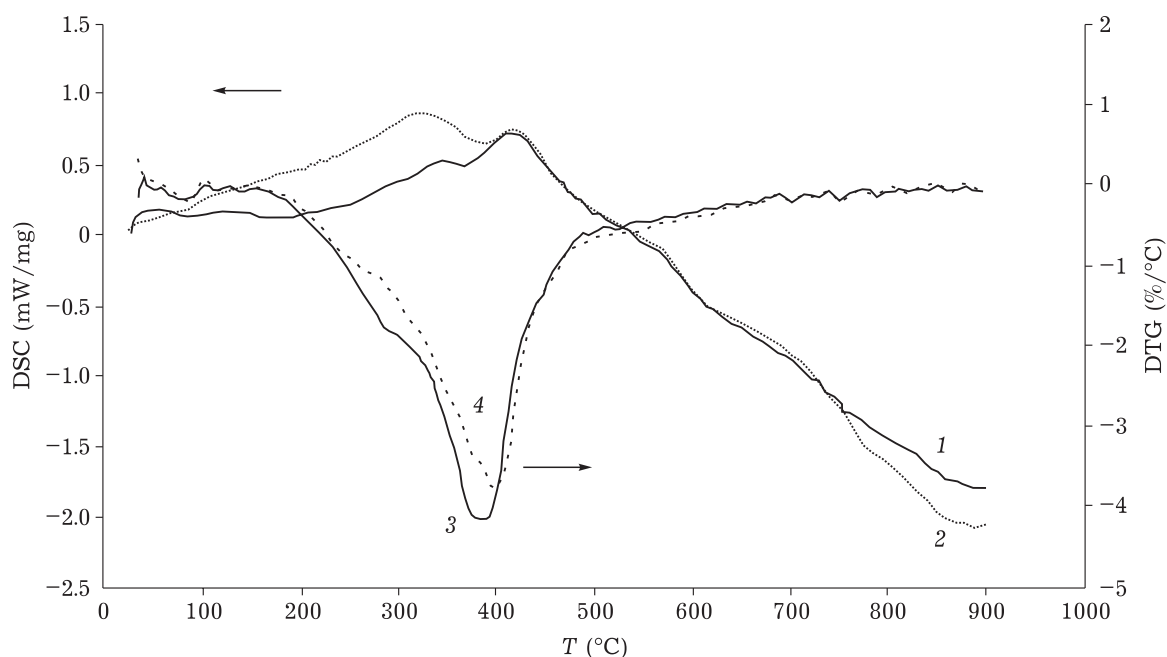
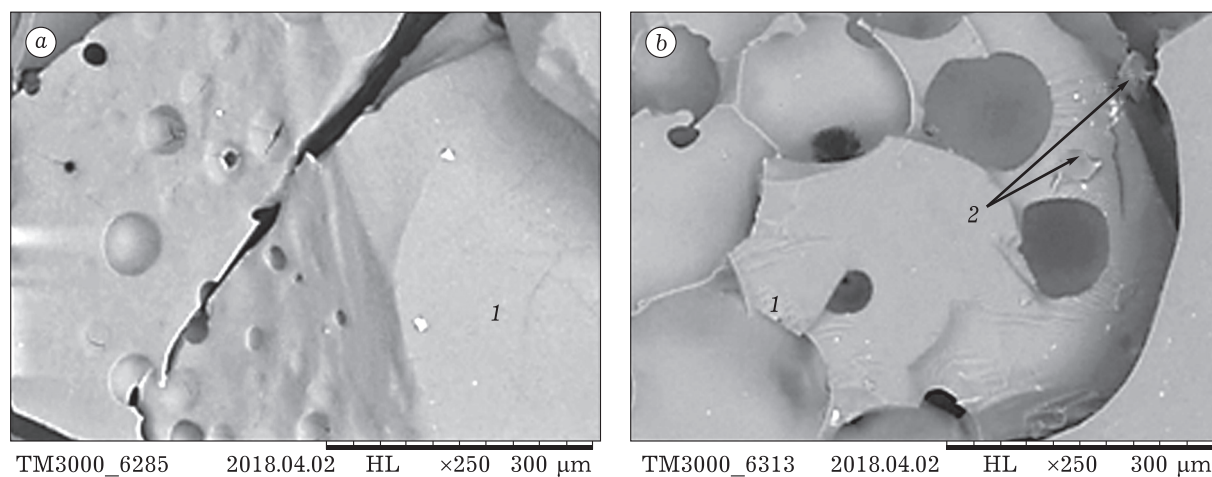Fig. 2. Results of thermal analysis (TG/DTG) of aspen (*1, 3*) and fir (*2, 4*) ethanol-lignin in inert atmosphere.

TM3000_6285   2018.04.02   HL   ×250   300 μm

TM3000_6313   2018.04.02   HL   ×250   300 μm

Fig. 3. SEM images of samples of fir (*a*) and aspen (*b*) lignin; lignin (*1*) and carbonized particles (*2*). Magnification of 250×.

(TG/DTG). The main decomposition of lignins of both types took place in a broad temperature range that was from 240 to 800 °C. The profile of differential thermogravimetric (DTG) curves (Fig. 2) has wide peaks that correspond to three not clearly separated mass loss steps, as indicated by bends in the differential curves.

In low heating temperatures, the mass loss by both samples was less than 2 % under low heating temperatures (30−200 °C) and was mainly related to the loss of moisture or adsorbed gases. A low endothermic peak corresponding to this range may also be due to lignin softening and melting [18]. The point, whereby the sample loses ~5 %

of its mass, is accepted as the temperature of the initial mass loss (T_i) [19, 20]. It was 242 and 252 °C, respectively, for AEL and FEL samples; in other words, fir ethanol-lignin is notable for higher thermal stability.

As demonstrated by SEM investigation of the surface of samples (Fig. 3), a dense homogeneous material based on particles of the initial lignin due to melting is generated in the initial step of decomposition of polymeric compounds (FEL-200 and AEL-240). The presence of cavities in the surface layer of lignin material points to emission of low-molecular-mass gaseous substances (H_2O, CO_2, *etc*.) formed resulting from the cleavage of ether
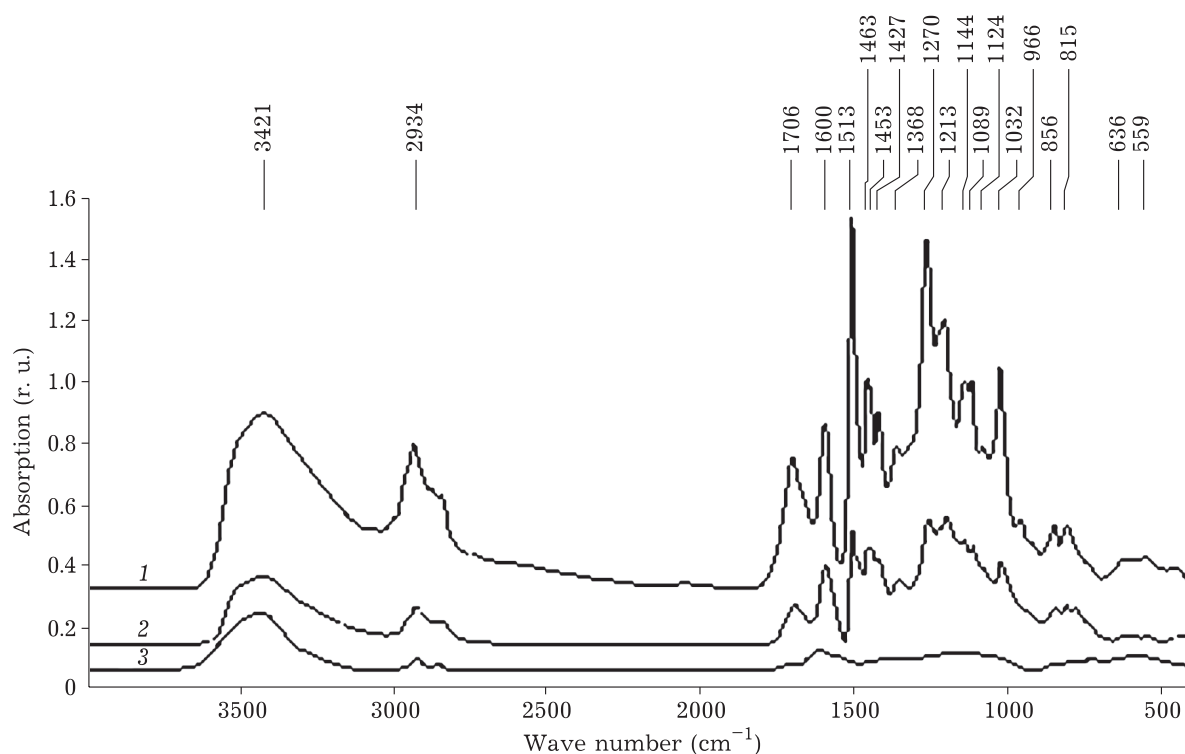
Fig. 4. IR spectrum of fir ethanol-lignin after thermal treatment at different temperatures (°C); 200 (*1*), 400 (*2*), and 600 (*3*).

bridges and weakly bound oxygen groups [21]. It can be seen (see Fig. 3, *b*) that the polymer structure of AEL is more liable to thermal changes. For example, local fragments made of particles of the generated coal appear on the surface of the sample AEL-240.

There are no noticeable changes in the composition of functional groups of fir ethanol-lignin (FEL-200) thermally treated at 200 °C (Fig. 4, curve 1). Its spectrum is almost identical to that of the initial fir ethanol-lignin; there is only a slight reduction in the intensity of the absorption band in the vibration range of alkyl ether bonds [18].

The main process of degradation of both lignins (the second step) proceeds in the 250–450 °C temperature range and is characterised by two exothermic maxima in the DSC curve: at ~345 and 415 °C for aspen lignin, and at 331 and 424 °C for fir lignin.

According to the literature data, the presence of an unapparent peak as a shoulder in the area of ~270 °C in both DTG curves may correspond to the initial decomposition of the polymer structure of the lignin to isolate phenol fractions (guaiacol and syringol compounds and/or their derivatives) [10, 12]. The main step of pyrolysis is preceded by this peak. The maximum mass loss rate (−3.11 %/min) was most clearly observed for AEL in the 357–437 °C temperature range with

the maximum decomposition at 378 °C. Herewith, the transformation degree of the substance was about 53 %.

Decomposition of the bulk of FEL is recorded in a broader range (337–437 °C) due to greater diversity and amount of thermally stable G-type phenol compounds than for syringol derivatives (substituted phenols) [5, 10, 21]. The mass loss rate is −2.9 %/min and the total mass loss is about 48 %; the maximum decomposition was reached at 400 °C. Pyrolytic degradation in this region involves secondary cracking of guaiacol derivatives, the fragmentation of intramolecular bonds, and the formation of phenol type compounds, the yield of which increases with temperature increasing [5, 12, 20, 22].

There is a substantial reduction in the intensity of absorption bands of almost all functional groups of −C−O−H, C−H, C−O, and C−C bonds, which points to a high degree of decomposition of the initial organic compound. Decomposition products of lignins in both types contain aromatic rings, hydroxyl, and alkyl groups and represent characteristic features of the structure of the initial lignin [12, 13, 21, 22].

A shift of the carbonyl band to a lower frequency range (from 1706 to 1699 cm^{-1}) may testify the appearance of C=O bonds involved into a conjugation system with unsaturated aromatic
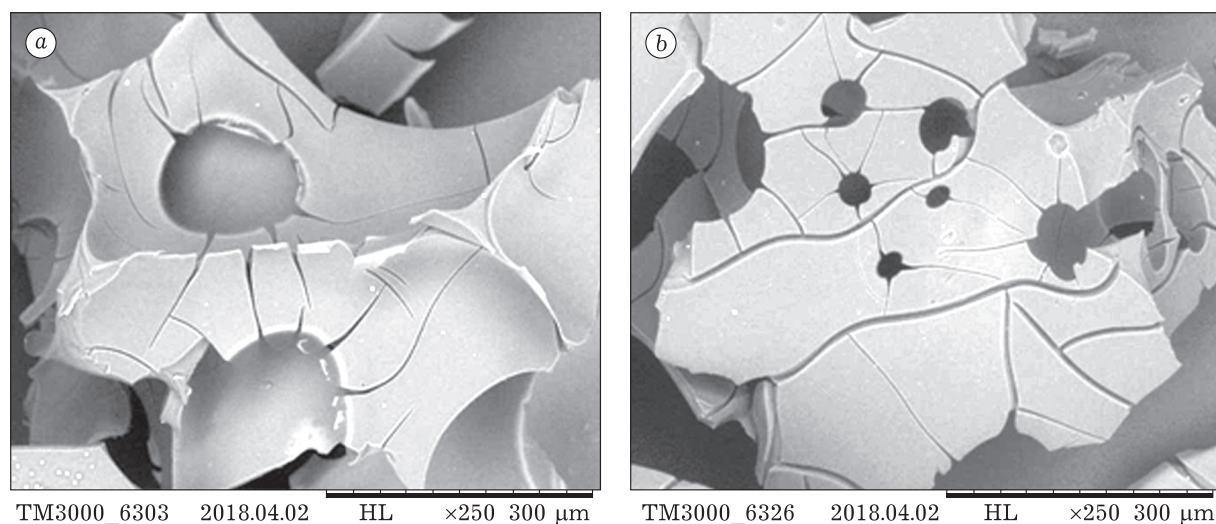
Fig. 5. SEM images of samples of fir (*a*) and aspen (*b*) lignin at 600 °C. Magnification of 250×.

bonds, which is proven by the presence of vibrations of skeletal C=C bonds inherent to conjugated aromatic systems. Likely transformation products of guaiacyl derivatives are compounds of methoxyphenol-type, typical products of lignin pyrolysis [13, 23].

The most probable directions of competing reactions at 350−400 °C is lignin decomposition to give aromatic the lower molecular mass products and their cross-linking followed by carbonization [24]. According to SEM data, changes in the chemical and phase composition of a carbonized matrix of products AEL-380 and FEL-400 are accompanied by the formation of a low-porous polymer aromatic product.

At temperatures above 437 °C, decomposition of compounds (the third phase) is characterised by a significant reduction in mass loss rate: as high as −0.6 mass %/min for AEL, and −0.7 %/min for FEL. Thermal decomposition is mainly completed by 600 °C to form coal products with a residual mass of 37 and 41 % for aspen lignin and fir lignin, respectively. The process is most likely related to slow degradation of aromatic fractions in lignin [5, 14], then in the region of 600 °C, there are aromatization and condensation of pyrolytic polymers to yield a product with an increased molecular mass, rich in carbon [25].

The almost complete disappearance of absorption bands in the IR spectrum of the sample FEL-600 (see Fig. 4, curve *3*) points to the lack of any functionalities and proves the formation of a polyaromatic condensed product with residual aliphatic particles and OH groups [26, 27].

As demonstrated by research on morphological features of samples of lignins pyrolyzed at 600 °C,

there is macroscopic decomposition in carbon residues to form cracks and large pores, by which the surface area is increased somewhat.

With an increase in temperature as high as ≈700 °C, the coal yield slightly decreases and then remains almost constant, whereafter a further slow rearrangement of matrix base and the additional release of volatile fractions result in the formation of coal residue at 800 °C in 34 and 37 % yields for aspen lignin and fir lignin, respectively.

Elevated product yield in the case of fir tree lignin is due to a higher trend of guaiacyl-propane units to condensation reactions with thermally stable products contained in coal residue [20, 26]. The findings make it possible to conclude that due to the higher thermal stability of guaiacyl units, fir tree lignin is more stable than aspen fur lignin and forms a product with a higher residual mass.

CONCLUSION

The differences in the behaviour of ethanol-lignins have been revealed during thermal decomposition depending on their origin. Furthermore, it has been determined that aspen lignin undergoes intense decomposition in the 242−400 °C temperature region with the maximum mass loss rate at 378 °C. It has been demonstrated that due to higher contents of guaiacyl units, there is a predominant thermal decomposition of fir lignin in an inert atmosphere within a larger temperature range, and the maximum rate of degradation is reached at 400 °C. It has been found that more coal residue is generated during thermal decomposition of ethanol-lignin compared to aspen eth-

anol-lignin (37 against 34 %). It has been determined that the maximum rates of decomposition of aspen lignin are higher than those of fir lignin.

REFERENCES

1 Audu I. G., Ziegler-Devin I., Winter H., Bremer M., Hoffmann A., Fischer S., Laborie M. P., Brosse N., *Green and Sustainable Chem.*, 2017, Vol. 7, No. 2, P. 114−140.

2 Suhas Carrot P. J. M., Ribeiro Carrot M. M. L., *Biores. Technol.*, 2007, Vol. 98, P. 2301−2312.

3 El-Mansuori N.-E., Salvado J., *Ind. Crop. Prod.*, 2006, Vol. 24, No. 24, P. 8−16.

4 Mikova N. M., Ivanov I. P., Chesnokov N. V., *Chemical Technology*, 2015, Vol. 15, No. 9. P. 528−535. (in Rus.).

5 Tejado A., Pena C., Labidi J., Echeverria J. M., Mondragon I., *Biores. Technol.*, 2007, Vol. 98, P. 1655−1663.

6 Weinwurm F., Drljo A., Silva T. L. S., Friedl A., *Chem. Eng. Transactions*, 2014, Vol. 39, P. 583−588.

7 Buranov A. U., Ross, K. A., Mazza G., *Biores. Technol.*, 2010, Vol. 101, P. 7446−7455.

8 Quesada-Medina J., Lopez-Cremades F. J., Olivares-Carrillo P., *Biores. Technol.*, 2010, Vol. 101, P. 8252−8260.

9 El-Mansouri N.-E., Vilaseca F., Salvado J., *J. Appl. Polymer Science*, 2012, Vol. 126, E214−E221.

10 Liu Q., Wang S. R., Zhen Y., Luo Z. Y., Cen K. F., *J. Anal. Appl. Pyrolysis*, 2008, Vol. 82, P. 170−177.

11 Sharypov V. I., Grishechko L. I., Tarasova L. S., Baryshnikov S. V., Celzard A., Kuznetsov B. N., *Journal of Siberian Federal University. Chemistry*, 2011, Vol. 3, No. 4, P. 221−232. (in Rus.).

12 Shen D. K., Gu S., Luo K. H., Wang S. R., Fang M. X., *Biores. Technol.*, 2010, Vol. 101, P. 6136−6146.

13 Faix O., Methods in Lignin Chemistry, S. Y. Lin, C. W. Dence (Eds.), Berlin: Springer−Verlag, 1992. P. 83−109.

14 Pandey K. K., *J. Appl. Polym. Sci.*, 1999, Vol. 71, P. 1969−1975.

15 Naron D. R., Collard F.-X., Tyhoda L., Gцrgens J. F., *Ind. Grops and Products.*, 2017, Vol. 101, P. 61−74.

16 Bonelli P. R., Cukierman A. L., *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2015, Vol. 37, P. 1534−1541.

17 Wang Sh., Wang K., Liu Q., Gu Yu., Luo Z., Cen K., Fransson T., *Biotechnol. Adv.*, 2009, Vol. 27, No. 5, P. 562−567.

18 Nassar M. M., MacKay G. D. M., *Wood and Fiber Science*, 1984, Vol. 16, No. 3, P. 441−453.

19 Poletto M., Zattera A. J., Forte M. M. C., Santana R. M. C., *Biores. Technol.*, 2012, Vol. 109, P. 148−153.

20 Poletto M., *Ciencia y Tecnología*, 2017, Vol. 19, No. 1, P. 63−74.

21 Brebu M., Vasile C., *Cellulose Chem. Technol.*, 2010, Vol. 44, No. 9, P. 353−363.

22 Ningbo Gao, Aimin Li, Cui Quan, Lin Du, Yue Duan., *J. Anal. Appl. Pyrolysis*, 2013, Vol. 100, P. 26−32.

23 Asmadi M., Kawamoto H., Saka S., *J. Anal. Appl. Pyrolysis*, 2011, Vol. 92, P. 88−98.

24 Nakamura T., Kawamoto H., Saka S., *J. Wood Chem. and Technol.*, 2007, Vol. 27, P. 121−133.

25 Kijima M., Hirukawa T., Hanawa F., Hata T., *Biores. Technol.*, 2011, Vol. 102, P. 6279−6285.

26 Faix O., Jakab E., Till F., Szekely T., *Wood Sci. Technol.*, 1988, Vol. 22, P. 131−137.

27 Evans R. J., Milne T. A., Soltys M. N., J., *Anal. Appl. Pyrolysis*, 1986, Vol. 9, P. 207−236.