

THERMAL PROPERTIES AND SIZE DISTRIBUTION OF LIGNINS PRECIPITATED WITH SULPHURIC ACID

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ABSTRACT

Dissolution and fractionation of lignocellulosic material is a critical step of valorisation of lignins. Precipitated lignin was isolated from black liquor by sulphuric acid at four levels of concentration (5, 25, 50 and 72 % wt). A comparison study was performed through thermal and size properties. The acid concentration influences of thermal properties of precipitated lignin. The acid concentration has an effect on changes in particle size of precipitated lignin. The results of thermogravimetric analysis indicated that the highest degradation of lignins appeared as an exothermic peak in range 470 - 650°C. The greatest weight loss in this section under an oxidation atmosphere was in the following order lignin 25 % wt (47.3 %), followed by lignin 72 % wt (45.0 %), lignin 5 % wt (43.6 %), and, smallest decline reached by lignin 50 % wt. The lowest temperature at the maximum degradation rate was determined for a sample of lignin 72 % wt at 488°C.

KEYWORDS: Selective precipitated lignin, black liquor, minerals acids, renewable raw materials.

INTRODUCTION

From an industrial point of view, there are various types of lignins, whose properties depend on the method of obtaining them (Chen et al. 1993; Jahan et al. 2012; Meng et al. 2012; Šurina et al. 2015; Zakharov and Lazareva 1992). Each of the methods has its own advantages and disadvantages. Since the mode of production of lignin are different further separation, purification and processing of lignins in derivatives and other chemicals. A simple and clean fractionation of the main components of biomass represents a very important step in the "clean", renewable carbon economy (Jablonský et al. 2015a; Šurina et al. 2015; Šutý et al. 2013). Fractionation on raw materials is an essential operation for almost all processes acquiring other products. If we

can easily separate the different components, we gain a significant source of raw material. These can be further used as a starting material for new composites, biopolymers, but also value-added chemicals as well as fuels (Capraru et al. 2009; Košíková et al. 2003; Monties 2005; Popa et al. 2011; Ungureanu et al. 2008, 2009). Many works related to the study of precipitate by organic or inorganic acids, polyelectrolytes and CO₂ and membrane processes and biodegradation for the recovery of lignin from black liquors have been published (Ammar et al. 2014; Antonovic et al. 2008; Garcia et al. 2009; Ibrahim et al. 2004; Mao et al. 2012; Minu et al. 2012; Nowaczyk-Organista and Pradzynski 2012; Puentes et al. 2012; Sun and Hughes 1999; Šutý et al. 2013; Šurina et al. 2015; Tejado et al. 2010, Toledano et al. 2010a, b; Tomani 2010, Wada et al. 1962; Zhou and Lu 2014). Understanding the thermal degradation of lignin substances is important to better understand the underlying processes and this information is a key-issue for an economic lignocellulosic biorefinery. Structure and functional groups, ether linkages in lignin precursors and essential presence in the structure affects their thermal degradation behaviour. Lignins with higher representation guaiacyl units have a higher activation energy and higher thermal stability (Brebú and Vasile 2012; Ružinská 2003). However, noncovalent interaction can affect the thermal properties of lignin (example hydrogen bonding) (Jakab et al. 1995, Poletto and Zattera 2013). The aim of the performed experiment was the thermal analysis of the nonwood lignin isolated from black liquor by different sulphuric acid at pH 5 and characterisation size of emerging particles.

MATERIAL AND METHODS

Material

Black liquor (soda-AQ pulping) characterization

The annual plants, hemp and flax, used for obtaining black liquor were kindly supplied by OP Papírna Ltd. (Olšany, Czech Republic). The cooking conditions: Active alkali sodium hydroxide and the presence of anthraquinone (AQ). The black liquor obtained had the following characteristics (Tab. 1): Dry matter 36.80 ± 0.62 % wt, pH of 12.9 ± 0.3 (determined by a digital Jenway (3510 pH-meter, UK), and density $1.242 \text{ g}\cdot\text{ml}^{-1}$, C 36.24 ± 0.09 % wt, H 4.93 ± 0.05 % wt, N 1.13 ± 0.01 % wt, S 0.24 ± 0.04 % wt, ash 45.75 ± 0.32 % wt and Klason lignin 21.23 ± 0.64 % wt.

Lignin recovery from black liquor

The precipitation of lignin from black liquor was initially studied as a single step process in which a dilute solution of sulphuric acid (5 % wt (1.05 N), 25 % wt (6.01 N), 50 % wt (14.22 N), and 72 % wt (23.99 N)) was added to the black liquor with the pH adjusted to the desired value at a temperature of 50°C. Then, 100 ml of the black liquor was treated with different amounts of diluted acid to obtain a final pH value of 5 while keeping the temperature constant at 50°C. After precipitation, the content of each flask was filtered through a pre-weighed oven-dried filter paper using a vacuum filtration unit. The precipitated lignin was washed twice with hot water (total volume 400 ml, pH= 6.8) to remove impurities. The lignin was then dried at 25°C under a pressure of 0.5 mbar using lyophilisation equipment (LYOVAC (GT2, Germany) until reaching a constant weight. Different techniques were used to establish the physicochemical characteristics of the obtained lignins (Tab. 1). These results were published in our paper (Jablonský et al. 2015a, b; Šurina et al. 2015).

Tab. 1: Characterization of precipitated lignin with solution sulphuric acids.

Concentration of sulphuric acid (% wt)	Elemental analysis (wt %)					Ash in precipitate % (w/w)	Purity (%)	Total amount of phenolic hydroxyl groups (mmol.g ⁻¹)
	N	C	H	S	O			
5	1.11	65.75	6.46	0.06	25.59	0.97 ± 0.2	85.1 ± 0.2	1.85 ± 0.4
25	1.12	63.64	6.54	0.07	26.95	0.66 ± 0.3	92.8 ± 0.1	1.91 ± 0.3
50	1.12	64.84	6.33	0.04	27.96	0.72 ± 0.3	90.6 ± 0.4	1.54 ± 0.6
72	1.18	64.90	6.42	0.07	25.66	0.85 ± 0.4	82.4 ± 0.4	1.19 ± 0.4

Methods

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of lignins was carried out using Mettler Toledo TGA/DSC 1 instruments. The analysis was performed in oxidation atmosphere keeping identical temperature regime for all samples. The atmosphere was ensured by air and flow rate 100 ml.min⁻¹. Argon plays the role of protection gas also in the balance space. The measurements were performed in the temperature interval of 30–800°C in three segments. At the beginning, the sample was conditioned at 30°C for 3 min. Subsequently, thermodynamic segment occurs increasing the temperature by 10 K.min⁻¹. After reaching 800°C, the measurement was concluded at 800°C for 3 min.

Size distribution of lignin particles

The size of the lignin particles was determined in water solutions, using a ZETASIZER NANO ZS Malvem Instrument, at 23°C. The samples were prepared by dissolving the dry lignin powder. The samples were prepared by dissolving the dry lignin powder in solution, with and without 0.1 M NaCl. To achieve a good quality of the colloidal dispersion, prior to the measurements, the samples with the concentration of 10 mg/ml were ultrasound-treated for 10 min at room temperature. The obtained size distribution graphs represented the dependencies of the relatively 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.

RESULTS AND DISCUSSION

The thermogravimetric analysis is widely used to study how the polymers decompose under helium or nitrogen and oxygen atmosphere (Baurhoo et al. 2008; Meister 2002; Tejado et al. 2007; Wormeyer et al. 2011). Thermal prosperity of lignin is very important for its utilization in thermochemical conversion into chemicals and energy. TG curves reveal the weight loss of substances in relation to the temperature of thermal degradation. The first derivative of that curve (DTG) shows the corresponding rate of loss. The peak of this curve (DTG max) may be expressed as a single thermal decomposition temperature and can be used to compare thermal stability characteristic of different materials (Wormeyer et al. 2011). TG was used to characterize the thermochemical properties and kinetics of thermal degradation of isolated lignin. Kinetic studies during the thermal degradation process have been used to acquire fundamental understanding of the structural changes in isolated lignin fractions. There are shown the differences in thermal stability. One possible explanation could be related to the lower molecular mobility of these isolated fractions to form crosslinking during fractionation, purity and isolation of lignins. This suggests that the isolation of these substances has an effect on thermal properties

of lignin (Baurhoo et al. 2008; Meister 2002; Tejado et al. 2007; Wormeyer et al. 2011). Another reason is the chemical composition of lignins. The DTG max appears between 105 and 470°C for all lignin samples analysed, as can be seen in Fig. 2 and Tabs. 2 and 3.

Tab. 2: Thermogravimetric analysis of preparations in oxidation atmosphere.

Precipitated lignin with solution of sulphuric acids (% wt)	Major degradation temperatures (°C)					Degradation at 200 – 650°C (%)	Charred residue at 800°C (%)
	0-105	105-200	200-470	470-650	650-800		
5	66.27	164.64	189.46	500.93	652.81	86.28	0.33
25	68.88	165.71	189.29	521.99	687.91	87.92	0.91
50	68.14	167.72	189.79	489.41	666.78	95.45	0.53
72	68.46	167.76	189.54	488.13	681.20	92.11	0.02

Tab. 3: The amount of degraded samples in temperature regions in oxidation atmosphere.

Precipitated lignin with solution of sulphuric acids (% wt)	Weight loss (%)				
	0- 100°C	100-200°C	200-470°C	470-650°C	650-800°C
5	2.15	2.06	42.65	43.63	9.18
25	2.23	2.14	40.65	47.27	6.81
50	1.77	2.17	52.41	43.04	0.08
72	1.56	2.23	47.11	45.01	4.08

The thermogravimetric as well as difference thermogravimetric analysis data are summarized in Tab. 3. The TG and DTG data show a higher thermal stability of lignin preparation. All these lignins have shown a wide variation in their thermal degradation phenomena. Lignin decomposition is a complex process involving several competing actions. During the reactions, various bondscissions within lignin molecule occur at wider ranges of temperatures based upon the bond energy. As can clearly be seen from Fig. 1 the difference between the curves is evident. TG analysis results Fig. 1b) showed five steps during sample degradation. The first one corresponded to the moisture removal (until 105°C), and the second and third one were related with the degradation of hemicelluloses (range between 160-300°C), it can be influenced by purity of isolated lignins (Tab. 1) (Domingues et al. 2008). Lignin sample prepared with 50 % wt H₂SO₄ has lower thermal stability than other samples. Progressive degradation of lignins is in range from 200 to 670°C. Complexity of lignin structure can be shown in differences in last two steps (450-670°C). This state is due to by content of linkages types and structures. At higher temperatures (> 500°C), was digested aromatic ring condensation occurs and releases hydrogen (Ferdous et al. 2002). In the first step (120-300°C), the products are formed as formic acid, formaldehyde, CO₂, CO, and water. The removal of the hydroxyl functional groups bonded at position β or γ atoms in the side aliphatic chain causes the release of water (dehydration), while the cleavage of the bond between the β-γ atoms in the alkyl side chains causes the release of formaldehyde. Aryl ether binding (or β-O-4-bonds) are also relatively easy cleavage. Ether bond to the γ carbon are relatively resistant and methoxyl groups are even more resistant to thermal stresses. This is due to the presence of hydrogen bonds, which generally increase the boiling points for pure substances and the total thermal resistance of cross-linked structures. While the general trend of degradation

is similar, yields of various products and the necessary temperature of fragmenting bonds vary according to the type of lignin and isolation conditions. By comparing all the samples in the first interval of 0-105°C, can we talk about the loss of moisture, which translates to the greatest extent in the sample 25 % wt with 2.15 %. The most interesting area in terms of organic matter was precisely the area from the first step to 470°C. The greatest weight loss in this section under an oxidation atmosphere was in the following order lignin 50 % wt (56.35 %), followed by lignin 72 % wt (50.89 %), lignin 5 % wt (46.86 %), and, smallest decline reached by lignin 25 % wt.

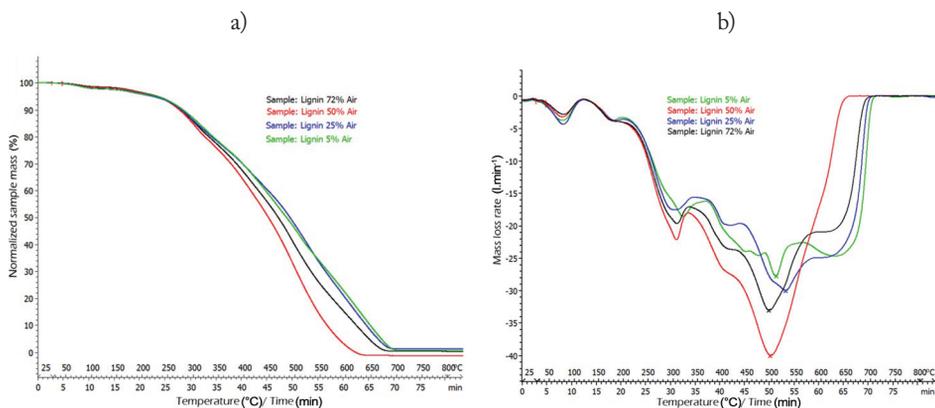


Fig. 1: TGA a) and DTG b) thermograms in oxidation atmosphere of isolated lignins by different concentration of sulphuric acid.

Aggregation of the lignin particles was studied in 10 mg/100 ml lignin aqueous solution with 0.1 M NaCl, using dynamic light scattering. A difference in particle size distribution between unground and ground material (Tab. 4 and Fig. 2) was clearly verified. As shown in Fig. 2, the lignin solutions are highly structured systems. At concentration 5 % wt, the measured sizes of the lignin have bimodal distribution, and contain nano- and microsized particles. The average diameter of the particles is 353 and 5478 nm, respectively. At 50 % wt concentration bimodal distribution occurs, with an average diameter of lignin particles 408 and 74 nm. Monomodal distribution was determined at 25 and 72 % wt concentration. Acid precipitation process is affected particle size of lignin colloid. The increase in particle size probably accelerates the coagulation of lignin colloids.

Tab. 4: Average diameters of lignin particles in lignin solution in 0.1 M NaCl.

Precipitated lignin with solution sulphuric acids	Size (nm)	Intensity area (%)	Size (nm)	Intensity area (%)
5 wt %	352.8	98.2	5478	1.8
25 wt %	279.2	100		
50 wt %	408.3	90.9	73.61	9.1
72 wt %	489.9	100		

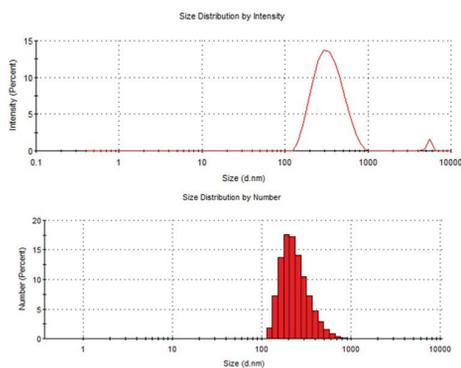


Fig. 2a: Size distribution diagram (sample lignin isolated by 5 % wt H_2SO_4 at pH 5).

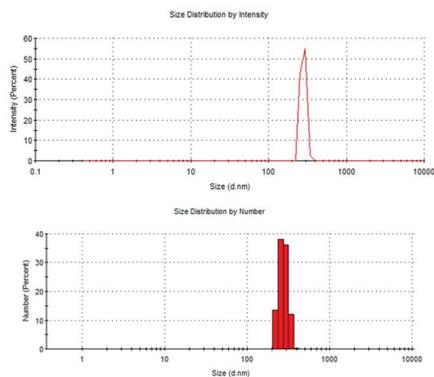


Fig. 2b: Size distribution diagram (sample lignin isolated by 25 % wt H_2SO_4 at pH 5).

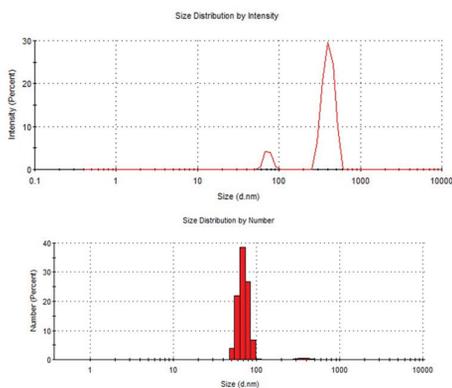


Fig. 2c: Size distribution diagram (sample lignin isolated by 50 % wt H_2SO_4 at pH 5).

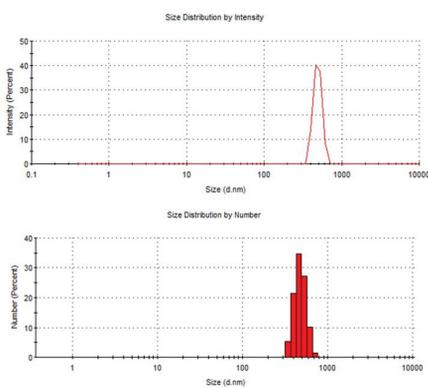


Fig. 2d: Size distribution diagram (sample lignin isolated by 72 % wt H_2SO_4 at pH 5).

CONCLUSIONS

Thermal properties and size characterization of precipitation lignin samples has been performed. It is possible to conclude that there are clear differences between the precipitates obtained at the pH 5 with different concentration of sulphuric acid, especially, to the content and properties of obtained lignin such as content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups for preparations, conductivity of preparations (Šurina et al. 2015), particle size and thermal properties. The thermal properties of isolated lignin fractions significantly depend on the way of lignin acquisition, purity and isolation. Dependence of thermal analysis can be evaluated by stability of isolated lignins; best thermal stability in this case was obtained by lignin precipitated by 5 % wt H_2SO_4 .

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