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RESEARCH ARTICLE

CHARACTERIZATION OF LIGNINS PRECIPITATED WITH NITRIC AND HYDROCHLORIC ACID

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ARTICLE INFO

ABSTRACT

Article History:

Dissolution and fractionation of lignocellulosic material is a critical step of valorization of lignins. Black liquor is very important stream in the production of kraft pulp and plays a key role in economic balance of lignocellulosicbiorefinery. Presented work deals with the isolation of the lignin from the black liquor by the precipitation method, using a variety of acids and different pH.

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lignin, isolation, UV/Vis, methoxy and hydroxyl groups, acids

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INTRODUCTION

Lignocellulosicsbiomass has been expected to be the most important resources in the second generation biomass industries. The majority of lignin available on an industrial scale is the byproduct of pulping processes and is used as fuel to obtain energy to operate pulping mills. A large number of studies propose the utilization of lignocellulosic biomass as a feedstock for producing of lignin. Lignin can be isolated from various raw materials, i.e. wood and black liquor. Lignin can be segregated by various methods. From an industrial point of view, there are various types of lignins, whose properties depend on the method of obtaining them. This is the reason why a large number of publications and patents aiming at studing the isolation and characterization of lignin from agricultural and silvicultural vegetation is available in the literature (Ibrahim et al., 2004; Tejado et al., 2007; Garcia et al., 2009; Toledano et al., 2010a, b; Minu et al., 2012; Surina et al., 2015). Depending on the structure of isolated lignin the different physical and chemical properties have been obtained. The structural differences between isolated lignins have been investigated using UV-Vis, FTIR, and NMR spectroscopies. The UV spectrum is one of the most characteristic features of a compound. According to Gosselink et al. (2004) the hydroxyl, methoxyl, carbonyl, and carboxyl groups are the most

important chemical functional groups in lignin, and they can be used for identification of lignin. Lignin functionality is a key factor for further applications. Sulphur-free high-quality lignins are suitable for further conversion to value-added products. In this study, the lignin from the black liquor from the cooking of annual plants (hemp and flax) was extracted using acidic solution at various acids and pH. The lignin preparations were further quantified and characterized by a comprehensive set of methods, including elemental analysis, FTIR, UV-VIS spectroscopy.

Experimental

Characterization of black liquor from modified alkaline anthraquinone cooking

Black liquor from the cooking of annual plants (hemp and flax) was kindly supplied by OP Papírna Ltd. (Olšany, Czech Republic). The black liquor had the following characteristics: pH of 12.9 ± 0.3 (determined by a Jenway Model 3510 pHmeter), density 1.242 g/mL.

Lignin recovery from black liquor

The precipitation of lignin from black liquor was initially studied as a single step process in which dilute acid solution (5

wt. %) was added to the black liquor with the pH adjusted to the desired value. 100 mL of the black liquor was treated with different amount of diluted acid (HCl or HNO3) to obtain a final pH value4, 3 and 2. After complete precipitation the content of each flask was filtered through a pre-weighed ovendry filter paper using a vacuum filtration unit. The precipitated lignin was twice washed with hot water to remove impurities. The lignin was then dried at 25°C for 24 hour, using a lyophilisation equipment (LYOVAC TG) up to reaching constant weight. Elemental analysis, UV/Vis spectroscopy were determined by a standard method. Details are given elsewhere (Kacik *et al.*, 1992, 1995, Jablonsky *et al.*, 2013, Surina *et al.*, 2015).

FTIR analysis

FTIR spectra of the different lignins were collected on a FTIR spectrophotometer (Bruker).

Pellets for IR analysis were prepared by mixing approximately 5 mg of sample with about 250 mg of potassium bromide (KBr), and then pressing the mixture in to a pellet. Spectra were recorded between 400 and 4000 cm⁻¹at a resolution of 4 cm⁻¹. The recorded spectra were the average of sixteen scans.

RESULT AND DISCUSSION

Elemental analysis and heating value

The weight percentages of elements C, H, N, O, S, OCH3 and ash of the isolated precipitate lignins are listed in Table 1. The results indicate that the elemental analysis of lignin is markedly affected by used acids. oxygen and less methoxyl groups than the lignin isolated by HCl. These differences indicate that lignin has undergone some modification which may include self - condensation, and or condensation at acidifications.

The content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups in lignins

It is known that when lignin is precipitated from kraft black liquor, the methoxyl content decreases, while the carboxyl and phenolic hydroxyl contents increase at a lower pH (Wada *et al.*, 1962). Since the objective of this work is the characterization of the content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups in monitored samples, samples of isolated lignins were not cleaned using ultrafiltration or solvent extraction. This method can be used for the determination of these groups with the satisfactory results which are in good agreement with the other reviews (Gartner and Gellerstedt, 1999). If it were used any of the methods for the purification such as ultrafiltration and solvent extraction, there would occur at the same time a change in the properties such as changes in the molecular weight and the change in the content of functional groups.

The results of content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups for these preparations are presented in Table 2. To compare the structural changes that occurred during the extraction process, difference UV/VIS spectra of preparations are shown in Figure 1. The difference spectra of the lignin preparations presented typical lignin absorption bands.

Sample	Ash	Ν	Н	S	С	0	OCH ₃	Higher heating value, calculated using
Lignin isolated by	(%)	(% wt)						HHV= 0.40659x(C) (MJ / kg)*
HNO ₃ at pH 4	1.79	1.67	5.89	0.00	62.68	27.97	15.0	25.5
HNO ₃ at pH 3	1.91	1.85	5.91	0.01	62.06	28.26	15.2	25.2
HNO ₃ at pH 2	1.98	1.10	5.74	0.01	60.54	30.63	15.3	24.6
HCl at pH 4	4.55	1.16	5.36	0.01	53.19	35.72	15.6	21.6
HCl at pH 3	2.13	1.20	5.72	0.01	58.69	32.24	15.8	23.9
HCl at pH 2	2.25	1.21	5.89	0.00	61.36	29.29	15.5	24.9

Table 1 Composition and properties of isolated lignins

*C is the carbon content (wt %) determinate by elemental analysis.

Methoxyl groups

Lignin contains functional groups such as methoxyl, phenolic hydroxyl, aliphatic hydroxyl and other carbonyl groups. In the paper Jablonsky *et al.*(2015b) was proposed a simple method for the prediction of methoxyl group's content in the lignin. The content of methoxyl groups (% wt) of lignin was calculated using the following equation: OCH3 = -18.5769 + 4.0658(H) + 0.34543(O), where the correlation coefficient was: 0.766.Table 1 shows the content of methoxyl groups in lignins. The highest content of these structures was found in lignin isolated HCl at pH 3, the lowest in lignin HNO3 pH 4 (15.0 % wt OCH₃). The content of methoxyl groups was ranges from 15.0 to 15.8 wt % OCH3. The results show that the content of methoxyl groups is very slightly affected by the acid used and the pH. As observed the lignin isolated by HNO₃ has more

Alkali neutral difference spectra exhibited three maximum at about 248-250 nm, 286-300 nm and 350-362 nm which indicate the presence of aromatic hydroxyl, a-conjugated hydroxyls, and conjugated carbonyl groups (Surina*et al.*, 2015). These lignins had absorption minima centred at 231, 278 nm. The spectral intensity at 280 nm is influenced to substantial extent by the presence of unsaturated substituents on -carbon of a side chain (e.g., carbonyl group, double bond) (Polcin and Rapson, 1969). The ratio of absorptivity of 282 nm and 280 nm peaks for the isolated lignins the ratio ranges from 1.02 to 1.12, and for lignin isolated HNO₃ pH 2 reached value 1.26. Lower values of the ratio would indicate the presence of the other chromophores, such as conjugated carbonyl and diphenyl which absorb more intensely.



Figure 1Ionization difference UV/Vis spectra of isolated lignins

From the results of Table 2 it can be shown that content of nonconjugated, conjugated and total amount of phenolic hydroxyl groups is different. This can be due to the method, and experimental conditions used in the method of lignin isolation and type of acids. The content of non-conjugated phenolic structures (I + III) ranges from 1.33 to 2.12 mmol/g. The content of conjugated phenolic structures (II + IV) is 0.17 -0.24 mmol/g and the total amount of phenolic hydroxyl groups (OH I + II + III + IV) is 1.52 - 2.43 mmol/g. As for isolated lignins, the highest content of these groups has lignin HNO3 pH 3(2.44mmol/g). When using HNO₃ (lignin isolated at pH 3), the total amount of phenolic hydroxyl groups (OH I+II+III+IV) is 2.36mmol/g, the use of HCl (lignin isolated at pH 2) led to 1.93 mmol/g. Isolation of lignin by different methods led to the evidence that the acid influenced both the content of individual groups and total content of the groups.

stretching of methyl and methylene group $(2842-3000 \text{ cm}^{-1})$ and methyl group of methoxyl (2689-2880 cm⁻¹) (Minuet al., 2012).



Figure 2 IR absorption bands for isolated lignin samples

The major peaks were the absorption at 2924 cm^{-1} originated from Csingle bondH stretching in methoxyl and methylene groups. The differences among lignin samples became more evident in the region below 1700.

Table 2The content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups for lignins

Sample Lignin isolated by	non-conjugated phenolic structures (I + III) (mmol/g)	conjugated phenolic structures (II + IV) (mmol/g)	total amount of phenolic hydroxyl groups (OH I + II + III + IV) (mmol/g)
HNO ₃ at pH 4	2.12	0.24	2.36
HNO ₃ at pH 3	2.20	0.24	2.44
HNO ₃ at pH 2	1.33	0.16	1.49
HCl at pH 4	1.73	0.20	1.93
HCl at pH 3	1.33	0.18	1.52
HCl at pH 2	1.94	0.23	2.17

IR analysis

To compare the structural changes that occurred during the isolation process (Table 3), FT-IR spectra of the lignin fractions were recorded (Fig. 2). The FT-IR spectra of the lignin fractions presented typical HSG lignin absorption bands (Saberikhah *et al.*, 2013).

Table 3 Type of vibration in different bands

Band location (cm ⁻¹)	Type of vibration						
3500 3000	Stretching vibrations of phenolic and alcoholic OH						
3300 - 3000	groups involved in hydrogen bonds						
2024	C single bond and H stretching in methoxyl and						
2924	methylene groups						
1655	Stretching vibrations of C=O bonds at and location						
1600, 15150-1500	Aromatic vibrations						
and 1430 - 1425	Aromatic vibrations						
1270 - 1210	Vibrations of guaiacyl rings and stretching vibrations						
	of C-O bands						

Every spectrum has a strong wide band between 3500 and 3000 cm^{-1} assigned to OH stretching vibrations (Ibrahim *et al.*, 2004; Toledano *et al.*, 2010a); and peaks corresponding to the C-H

The most characteristic vibrations of lignin correspond to those of aromatic rings at approximately 1600 cm⁻¹, 1516 cm⁻¹, and 1456 cm⁻¹(Boeriu *et al.*, 2004, Amar *et al.*, 2014). These bands were present in the spectra of all samples, although with different intensities. Band at 1516 cm⁻¹ are characteristic of aromatic rings due to aromatic skeletal vibrations. Band at approximately 1220 and 1120 cm⁻¹ are corresponding to syringyl unit, and small bands at 1270, 1036 cm-1 are assigned to guaiaxyl unit of lignin molecules (Amar *et al.*, 2014).

CONCLUSION

Lignin was efficiently separated from black liquor by using acids such as HCl and HNO_3 at different pH. The use of acidification prior to isolation of lignin isefficient and convenient method for obtain lignin. Lignin functionality is a key factor for further applications and better understanding of the lignin isolation process from black liquor. This information will be helped by the low marginal cost of producing lignin and will take advantage of its phenolic nature and reactivity with other compounds as well as of the properties that differentiate it from other lignins.

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