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CONTENT OF PHENOLIC HYDROXYL GROUPS IN LIGNIN: CHARACTERISATION OF 23 ISOLATED NON-WOOD LIGNIN WITH VARIOUS ACIDS

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ABSTRACT

Direct UV and difference spectra of alkaline and neutral solutions of isolated lignins are helpful in interpreting the chemistry of these fractions of biomass. UV ionization difference method has been used to determine the amount of free phenolic hydroxyl groups in isolated non-wood lignins from soda-antraquinone pulping with various acids (HNO₃, H₂SO₄, CH₃COOH and HCl). The content of free phenolic hydroxyl groups in lignin is important because of the reactivity of these groups and the effect they have on both chemical and physical properties of the lignin molecule.

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INTRODUCTION

Lignin is one of the three basic components of lignocellulosics feedstock, represents an important participant to the complex formation and transformation of organic material in the biosphere. (Rosas *et al*, 2004; Todorciuct *et al*, 2009). Lignins contain several functional chemical groups, such as hydroxyl (phenolic or alcoholic), methoxyl, carbonyl and carboxyl (Gosselink *et al*, 2014). The various chemical substituents confers unique functional properties to lignins, and in various amounts, depending on their nature and the isolation process (Ibrahim *et al*, 2004; Tejado *et al*, 2007; Garcia *et al*, 2009; Toledano *et al*, 2010a, b; Minu *et al*, 2012; Jablonsky *et al*, 2013, 2015a, 2015b; Surina *et al*, 2015; Jablonsky and Haz 2016). The structural differences between isolated lignins have been investigated using UV-Vis, FTIR, and NMR spectroscopies. One of the methods to characterize the properties of the lignin is UV techniques. The method is based on the findings that phenolic groups in non-ionized (i.e. in neutral media) and ionized (i.e. in alkaline media) forms differ in electronic absorption spectra. This difference can be used to estimate a ratio of various phenolic hydroxyl groups. Generally speaking the relative amounts of different chemical groups used will depend on the natures of all the chemicals involved and the operating conditions precipitating the generation of the precipitate. The presence phenolic hydroxyl groups which have an important influence on its solubility and reactivity of isolated lignins during other reaction in another application and

reactions. Lignin valorisation is a key factor for an economic lignocellulosicbiorefinery (Surina *et al*, 2015). Compounds potentially obtained from the guaiacyl units are as follows: apocynol, guaiacol, creosol, propyl guaiacol, eugenol, iso-eugenol, methoxyhydroxy phenyl glycol, 1-guaiacylethyl methyl ether, homovanillic acid, homovanillyl alcohol, vanillyl alcohol, vanillyl alcohol methyl ether, vanillic acid, vanillin, vanillic acid methyl ester, acetoguaiacone, α -carboxyvanillin, coniferaldehyde, coniferyl alcohol, α -hydroxypropiovanillone, propioguaiacone, α -hydroxyferulic acid, α -guaiacyl propanol, ferulic acid, and 4-hydroxy-3-methoxymandelic acid. Compounds potentially obtained from syringyl units are: syringic acid, sinapic acid, sinapaldehyde, syringeugenol, acetosyngone, methyl syringate, syringol, syringyl cresol, syringyl alcohol, syringaldehyde, and others. Dimeric structures derived from the guaiacyl units are very important, as this group is represented by more than 13 structures (Holladay *et al*, 2007). Most of this biomass is burned as fuel, and just a small portion is applied (Vishtal and Kraslawski 2011) as carriers for fertilisers and pesticides, carbon fibers, blends with thermoplastic polymers, ion-exchange resins, activated carbons, and chemical compounds such as vanillin, hydroxylated aromatics, quinones, aldehydes, and aliphatic acids, production of phenolic resins, animal nutrition, dispersants, new polymers, particleboards, detergents, glues, binders and resins, adhesives, feeds, and cement additives. Recent works of Hodosova *et al* (2015) showed the market potential of isolated lignins and their derivates or chemicals

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added value. The high potential of straw lignin lies in its phenolic content as a bio poly-phenol material. The quantification of those hydroxyls function groups becomes very interesting and essential on further lignin based materials (Delmas et al, 2011). Following their works, we report in this article analysis of function group of straw lignin isolated in acidic condition by the precipitated process.

MATERIALS AND METHODS

Characterization of black liquor from modified alkaline anthraquinone cooking

The annual plants, hemp and flax, used for obtaining black liquor were kindly supplied by OP Papirna 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 (Table 1): pH of 12.9 ± 0.3 (determined by a digital Jenway (3510 pH-meter, UK) and density 1.242 g/mL (determined by measuring the mass with the known volume of the black liquor).

Table 1 Characterization of black liquor

Dry matter (wt%)	36.80 ± 0.62
Elemental analysis of black liquor	
C (wt%)	36.24 ± 0.09
H (wt%)	4.93 ± 0.05
N(wt%)	1.13 ± 0.01
S(wt%)	0.24 ± 0.04
Ash (wt%)	45.75 ± 0.32
Lignin (wt%)*	21.23 ± 0.64
Carbohydrates (wt%)	33.02

*Klason lignin was determined according to TAPPI T 222 om-02

Lignin recovery from black liquor

The precipitation of lignin (dilution with water 1:10) from black liquor was initially studied as a process (normal and fractional precipitation (Fig 1 and 2) in which a dilute solution of acid was added (Table 2) to the black liquor with the pH adjusted to the desired value at a temperature of 50 °C. Then, 45 mL of the black liquor was treated with different amounts of diluted acid to obtain a final pH value, 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.

C, N, H, and S elemental analysis

Total nitrogen (N), carbon (C), hydrogen (H), and sulphur (S) content of all samples were determined by dry combustion using a Vario Macro Cube C/H/N/S-analyser (Elementar, Hanau, Germany). Two replicates were measured, and the mean standard errors were 0.35% for C, 0.04% for N, 0.05% H, and 0.01% for S.

Difference UV/VIS spectroscopy

After being dried overnight at 80 °C, a precisely weighed amount (5 mg) of lignin was dissolved in 5 mL of dioxane and 5 mL of 0.2 M NaOH. Some of the solutions were not quite clear and were filtered using a 0.45-µm PVDF membrane filter.

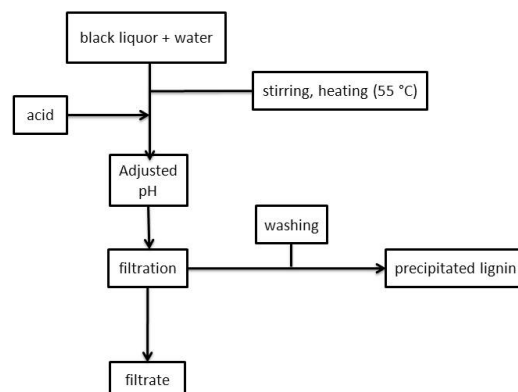


Figure 1 Scheme for normal precipitation of lignin

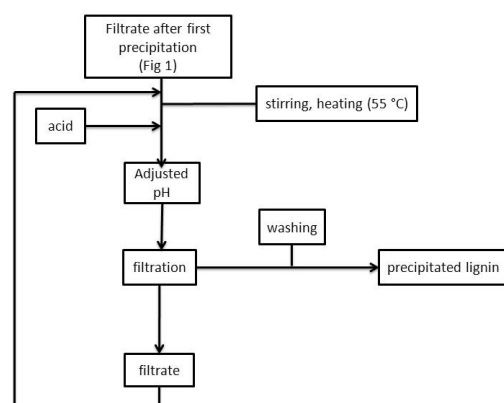


Figure 2 Scheme for fractional precipitation of lignin

Table 2 Elemental composition of isolated lignins

No.	Precipitated lignin with solution of acid (5 wt%)	pH of precipitation	Type of precipitation	Elemental analysis (wt%)			
				N	H	S	C
1	HNO3	5	normal	2.14	5.63	0.00	57.53
2	HNO3	4	normal	1.67	5.89	0.00	62.68
3	HNO3	3	normal	1.85	5.91	0.01	62.06
4	HNO3	2	normal	1.10	5.74	0.01	60.54
5	HNO3	5	fractional	1.44	6.00	0.00	62.35
6	CH3COOH	6.3	normal	1.08	5.74	0.03	57.21
7	CH3COOH	5.3	normal	1.21	5.80	0.03	63.16
8	CH3COOH	4.3	normal	1.21	5.93	0.00	62.48
9	H2SO4	6	normal	1.13	6.08	0.02	62.81
10	H2SO4	5	normal	1.13	5.52	1.04	57.41
11	H2SO4	4	normal	1.13	5.50	1.31	57.61
12	H2SO4	3	normal	1.14	5.50	1.68	57.88
13	H2SO4	2	normal	1.09	5.36	1.87	56.49
14	H2SO4	6	fractional	1.06	5.58	0.97	57.09
15	H2SO4	5	fractional	1.09	5.87	0.50	61.35
16	HCl	6	normal	1.06	5.87	0.03	59.42
17	HCl	5	normal	1.20	6.03	0.03	63.24
18	HCl	4	normal	1.16	5.36	0.01	53.19
19	HCl	3	normal	1.20	5.72	0.01	58.69
20	HCl	2	normal	1.21	5.89	0.00	61.36
21	HCl	6	fractional	1.13	5.95	0.01	59.41
22	HCl	5	fractional	1.21	6.00	0.00	60.63
23	HCl	4	fractional	1.36	6.04	0.00	62.54

From each lignin solution, 2 mL was further diluted to 25 mL using either a pH 6 buffer solution (citrate/NaOH, Merck) or 0.2 M NaOH (Gartner and Gellerstedt 1999). This gave each solution a final lignin concentration of about 0.04 g/L. The UV-VIS spectra were recorded on a Cecil spectrophotometer in the

absorption region from 200 to 450 nm, scan speed 5 nm/s, and 1nm resolution. The lignin solution with pH 6 was used as a reference, and the alkaline solutions were measured against it. From the difference spectra, the absorbance values at 300 and 350 nm, measured against the solution containing 0.2 M NaOH, were recorded. According to the original work of Gartner and Gellerstedt (1999), six structural types of phenolic structures exist (Figure2). Maxima at 300 nm and 350 to 360 nm can be assigned to unconjugated phenolic structures (I and III), and those at 350 to 370 nm can be assigned to conjugated structures (II and IV). According to Zakis (1994), the maximum at 360 nm is attributed only to IIa and IVa types of phenolic structures in lignin.

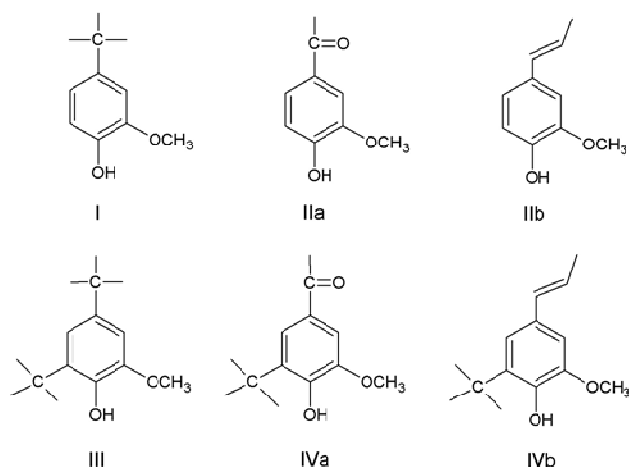


Figure 3 Type of phenolic structures determined by the UV method (Zakis 1994; Gartner and Gellerstedt 1999)

To obtain the concentration of individual phenolic structures in mmol/g, the following absorbance-based formulae were developed (Zakis 1994; Gartner and Gellerstedt 1999) and are applied in their original form also in this work (Eqs. 1-3):

1. Non-conjugated phenolic structures (I+III) OH (I+III) = $\{(0.250 \times A_{300\text{nm}}(\text{NaOH}) + 0.0595 \times A_{350\text{nm}}(\text{NaOH})) \times 1/(c \times d)\}$ (1)
2. Conjugated phenolic structures (II+IV)OH (II+IV) = $\{0.0476 \times A_{350\text{nm}}(\text{NaOH})\} \times 1/(c \times d)$ (2)
3. Total amount of phenolic hydroxyl groups OH (I+II+III+IV) = $\{0.250 \times A_{300\text{nm}}(\text{NaOH}) + 0.107 \times A_{350\text{nm}}(\text{NaOH})\} \times 1/(c \times d)$ (3)

where λ is the absorbance at a given wavelength divided by the corresponding molar absorptivity, c is mass concentration in g/L, and d is path length through the sample in cm.

RESULTS AND DISCUSSION

The weight ratio of oxygen to carbon (O / C) in all the analyzed samples is between the values of 0.35 to 0.46, wherein the ratio of the dispersion of the acid used for each was low. The ratio of hydrogen to oxygen (H / C) of all the samples, and also the dispersion of the acid have any value from 0.80 to 0.10. Content of nitrogen was highest at samples where nitric acid was used. The weight percentage is in range from 1.10% to 2.14%. The higher nitrogen content was caused by nitric acid, which bind the precipitation of nitrogen in its structure of the lignin molecule. Representation of hydrogen as the second the most contained component of elementary analysis, based on all of the analyzed samples was in ranges from 5.36 to 6.08%. The

amount of sulfur represents the expected change in sulfuric acid, which contributes structurally to increase the sulfur content of lignin which was precipitated by it. The sulfur content by using of sulfuric acid during precipitation was in range from 0.02 to 1.87 weight percent. Carbon was the most abundant element. Its amount contained by all precipitations with acids was from about 57 to 73 weight percent. When using hydrochloric acid, which precipitated lignin at a pH of 4 was the representation of the least carbon and 53.19%. Overall it can be said that hydrochloric acid and acetic acid somehow do not significantly affect the representation of primary elements. Sulfuric acid and nitric acid in a little affect the presence of sulfur (sulfuric acid) and nitrogen (nitric acid). It is clear from the nature of their structure which is attached to these elements. All precipitated lignins showed a low value of sulfur. This information makes it possible to use this lignin as a raw material for the production of value-added products or their use as biofuel.

Table 3 Content of non-conjugated, conjugated, and total phenolic hydroxyl groups

No.	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)
1	2.61	0.27	2.88
2	2.12	0.24	2.36
3	2.20	0.23	2.43
4	1.33	0.16	1.49
5	0.93	0.12	1.05
6	1.78	0.19	1.96
7	0.66	0.10	0.76
8	1.30	0.16	1.46
9	0.55	0.09	0.64
10	0.43	0.08	0.51
11	0.89	0.12	1.01
12	1.08	0.14	1.21
13	1.32	0.15	1.47
14	1.13	0.14	1.27
15	1.34	0.20	1.54
16	1.75	0.23	1.97
17	1.27	0.18	1.44
18	1.73	0.20	1.93
19	1.33	0.18	1.52
20	1.94	0.23	2.17
21	1.53	0.19	1.73
22	2.39	0.27	2.67
23	1.64	0.21	1.85

Two replicates were measured, and the mean standard errors were 2.1 % for the content of non-conjugated, conjugated, and total phenolic hydroxyl groups.

Depending on the amount of phenolic hydroxyl groups are changed and the possibility of using lignins in the rubber industry. Absorbance of phenolate ion of the non-conjugated phenolic hydroxyl groups at a maximum of 250 and 300 nm described by Gärtner and Gellerstedt, (1999) was recorded mainly at lignin precipitated with nitric acid (up to pH 5; 2.608mmol / g). The most represented conjugated structure of the phenolic and carbonyl (Sarkanen and Schuerch, 1955) absorbance at 250 and 350 nm was recorded by lignin precipitated by nitric acid (with highest amount at pH 5; 0.274 mmol / g). The overall representations of these structures are recorded in Fig 3. When comparing the representation of the phenolic hydroxyl groups either conjugated or unconjugated in lignins, most represented was in lignin precipitated by nitric acid. The presence of free phenol groups in them makes them useful for the production of phenolic

polycondensates, and as additives to rubber (Kubackova et al., 2013) and other polymers, where they act as stabilizers and antioxidants. In terms of antioxidant activity of lignin appears to be particularly important content of phenolic hydroxyl groups, which could contribute to increased stability of rubber compounds. Lignin efficiency is comparable to the commercial IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine). Isolated lignins can be used as a suitable replacement of commercial stabilizer IPPD (Haz et al., 2016). High potential of straw lignin lies its phenolic content of hydroxyl groups. The identification and quantification of those hydroxyls function becomes very interesting and essential on further lignin based materials (Delmas et al., 2011). Lignin has a great potential to replace phenolic compounds. However, its use in adhesive formulation is very dependent on its structural function characteristic and reactivity. Considering the fact that lignin is a polymer with a fair amount of hydroxyl and carboxylic groups that own reactive hydrogen, lignin has the potential to replace polyols in polyurethane production (Pan & Saddler, 2013). Very important for selective masking of the phenolic hydroxyl groups in technical lignins is known detailed chemistry and functionality of isolated lignins (Sadeghir et al., 2012). This information is crucial in determining their subsequent chemical and thermal reactivity and other additional polymerization or other side reactions using for prepare plastic materials. The knowledge of the concentration of the individual groups may be used to optimize the antioxidant activity of lignin itself and its derivatives (Pouteau et al, 2003, Faustino et al, 2010; Jablonsky et al, 2015a)

CONCLUSION

Lignin from grasses of annual plants was obtained with various acids, i.e. sulfuric acid, hydrochloric acid, nitric acid, and acetic acid. Isolated lignins were precipitated using normal and fractional way. The content of free phenolic hydroxyl groups in isolated lignin is a key factor for further applications of lignin for polymerization, plastic materials and application of lignin such as stabilizers and antioxidants in rubber materials.

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