Journal of Chemical Technology and Metallurgy, 48, 5, 2013, 524-529

BLACK LIQUOR LIGNIN PRODUCTS, ISOLATION AND CHARACTERIZATION

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Received 25 May 2013
Accepted 29 July 2013

ABSTRACT

By extraction with toluene and ethyl acetate monomeric lignin compounds: 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone, etc. were isolated from black liquor and sulfate lignin, and identified through GC/MS analysis. The identified low-molecular mass lignin compounds do not contain organic bonded sulphur. The sulfate lignin, separated from black liquor after acidification with acid was subjected to an alkaline treatment (4 h; 180°C; 5 % NaOH; lignin/NaOH ratio -1:8).

Keywords: black liquor, sulfate lignin, alkaline treatment, lignin compounds, extraction.

INTRODUCTION

Lignin is a widely spread, renewable, amorphous natural polymer, containing phenylpropane units. These units are derivatives of syringol, guaiacol and p-hydroxyphenol. They are interconnected through ether-and C-C bonds [1] forming thus a very complex three-dimensional polymer matrix [2]. They are in fact the source of low-molecular mass phenolic compounds (LMPC) [3 - 8]. In our previous investigations the alkaline hydrolysis of technical hydrolysis lignin [5] and poplar wood bark [6] under different conditions (temperature of 180°C; duration of 2, 4 and 6 h; 3, 5 and 7 % aqueous solution of NaOH; lignin/aqueous solution ratio of 1:6, 1:8 and 1:10) was studied. The liquid fraction containing the non-precipitated lignin after precipitation of the high molecular mass lignin fraction, is subjected to triple extraction with toluene. The following monomeric lignin compounds were isolated: phenol, 2-methoxyphenol (guaiacol), 2,6-dimethoxyphenol (syringol), 4-ethyl-2-methoxyphenol, 4-hydroxy-3,5dimethoxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone. These studies show that the response to the change in the experimental conditions is identical. The increase both of the duration and of the NaOH concentration leads to an increase of the LMPC yield. This is due to a great extent to the destruction of the lignin macromolecule. The most significant influence on the LMPC yield is the process duration, while the yield of precipitated activated lignin was influenced by NaOH concentration [5]. It was shown that the lignin derived monomer compounds can eventually be used as antioxidation additives to petroleum fuels [8, 9].

After the hydrolysis reaction of the organosolv black liquor, oil with a high concentration in guaiacol and syringol has been obtained. The liquor has been subjected to a liquid-liquid extraction with ethyl acetate [10].

Black liquor is produced as a by-product from the sulphate process when digesting wood into pulp, removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers with sodium-based alkali compounds, such as sodium hydroxide and sodium sulfide [11]. After precipitation with acid from the black liquor, sulphate lignin is separated.

The low-molecular mass lignin products which do not separate from the black liquor after precipitation by

acid, are obtained in quantities approximately 6 - 7 % of the initial wood mass [12]. The compounds are divided into 3 fractions each of them being about 2 % of the initial wood mass. The first fraction passes into solution as soon as the initial stage of boiling (at temperature about 100°C) is reached and possesses low content of methoxy groups. The second fraction are non-aromatic products of the lignin destruction and the third one are compounds which transfer/pass in solution at the maximum boiling temperature. It consists of two-dimensional phenyl propane units, a small quantity of vanillin acid, as well as simple methyl ketones of the type of acetoguaiacol. In the fraction of low-molecular mass lignin products obtained from the black liquor after sulfate boiling of wood, 2 - 3 % of sulfur is discovered but no compounds of organical bonded sulfur is isolated, except for dimethyl sulfide and mercaptan [11]. The sulfate lignin isolated from the black liquor contains 1 - 3 % strongly bonded sulfur. During the treatment the sulfate lignin undergoes processes of condensation and polymerization but to a considerably lower extent compared to the lignin from the alkaline boiling [11].

The aim of this study is to investigate the nature of the lignin destruction products which remain in the liquid phase after sulphate lignin precipitation from black liquor, and after an alkaline treatment of sulphate lignin.

EXPERIMENTAL

The black liquor, obtained as by-product during the production of cellulose from hardwood in the town of Svishtov, Bulgaria, was used in this investigation. The dry matter in the black liquor is 17.2 %. After precipitation with acid (2 mol/l HCl to pH1-2), from the black liquor sulfate lignin was separated. The sulfate lignin was washed and dried.

The principal scheme of the experimental processes is presented on Fig. 1.

The alkaline treatment of the sulphate lignin was carried out in stirred autoclaves made of stainless steel, heated in a bath of polyethylene glycol at 180°C for 4 hours.

Water solution of NaOH (5 %) was used as a depolymerization agent, at waste material/ water solution of NaOH in ratio 1:8. The destructed lignin suspension, obtained by the alkaline treatments, was filtered and the quantity of undissolved residue was determined. The dissolved part has been precipitated by acidification with HCl (2 mol/L) to pH ~ 1 - 2. The volume of the liquid part separated by filtration, under vacuum, has been reduced in a rotary vacuum vaporizer. A triple extraction has been carried out at toluene - water phase ratio of 1:5. The toluene extract has been dried up with anhydrous

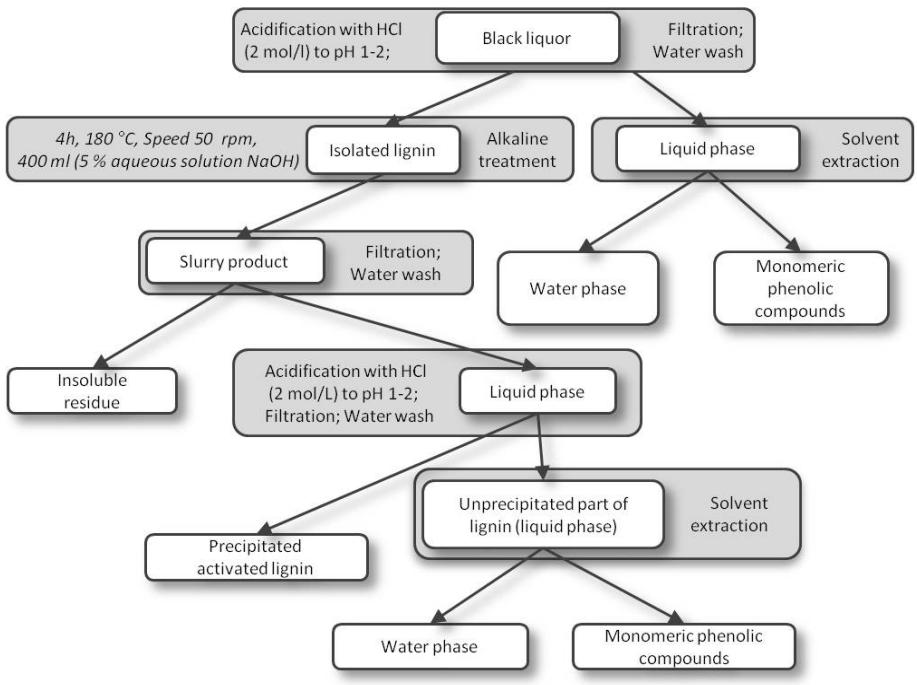

Fig. 1. Scheme for lignin compounds processing.

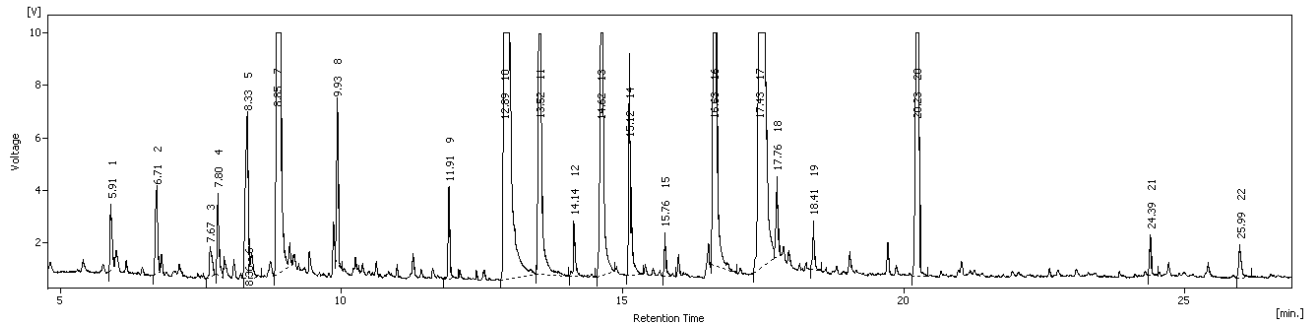

Fig. 2. Gas chromatogram of the toluene extract from black liquor.

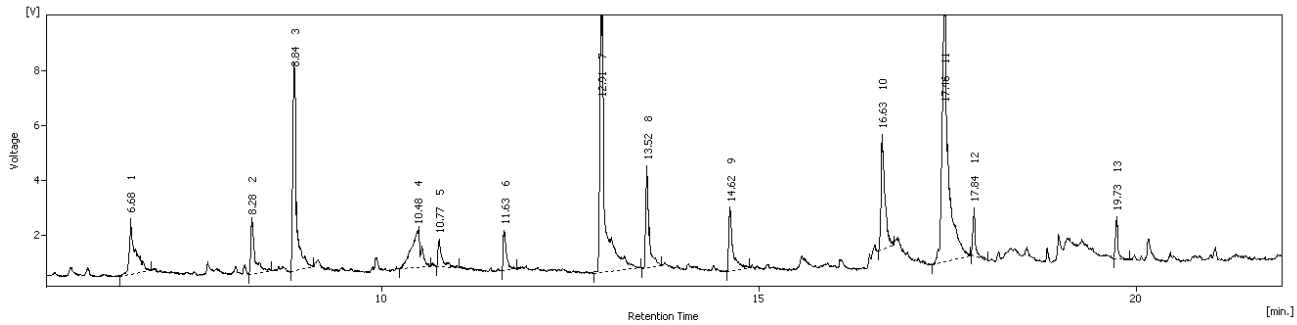

Fig. 3. Gas chromatogram of the ethyl acetate extract obtained after alkaline treatment of sulfate lignin.

Table 1. Sulphur content in the Black liquor and the Sulfate lignin.

Sample	Black liquor [%dry matter]	Sulfate lignin [%material]	ATSL [%material]	LMPC from black liquor [%material]	LMPC from ATSL [%material]
Sulphur content	3.48	1.9	2.1	8.5	2.4

Na_2SO_4 and then filtered. The liquid phase separated after the extraction with toluene has been subjected to double extraction with ethyl acetate at an organic-liquid phase ratio of 1:5. The amounts of obtained extracts, insoluble residue, precipitated and non-precipitated lignin were determined.

The obtained extracts were analyzed by GC-MS analysis with a KONIK gas chromatography unit, model HRGC 5000B, equipped with a mass selective detector, MS Q 12. A 15m x 0.25 mm I.D capillary column KNK 5 with a film thickness of 0.25 μm was used. The GC oven temperature was held at 40°C for 5 min and then programmed to attain a temperature of 270°C at 10°C/min. The injector temperature was 280°C with a split ratio 20:1. Helium was used as a carrier gas with a constant flow rate of 1.3 ml/min. The typical mass spectrometry operating conditions were as follows: temperature of transfer line, 250°C; temperature of ion source, 245°C; and electron energy, 70 eV.

RESULTS AND DISCUSSION

The sulphur content in the black liquor, sulfate lignin (SL), alkaline treated sulfate lignin (ATSL) and the obtained extracts was determined by the Elemental Analyzer Euro EA 3000. The results are presented in Table 1.

Table 2. Product yields after black liquor acidification.

Precipitated sulfate lignin [% dry matter]	Toluene extract [% dry matter]	Ethyl acetate extract [% dry matter]
25.15	0.26	0.16

Table 3. Yield of hydrolyzed products after alkaline treatment of sulfate lignin (SL).

Insoluble residue	ATSL	Unprecipitated part in the liquid phase after alkaline treatment	Toluene extract from the liquid phase	Ethyl acetate extract from the liquid phase
[%SL]	[%SL]	[%SL]	[%SL]	[%SL]
4.48	55.62	39.90	2.00	2.14

Table 4. Compounds Identified in Toluene Extracts

Compounds	Retention time, min	Sulfate lignin	Black liquor
		Area, %	Area, %
Unidentified compound	5.2	1.3	-
Benzaldehyde	5.9	9.4	1.0
Phenol	6.68	6.6	1.5
Unidentified compound	7.67	9.0	0.7
Unidentified compound	7.80	-	1.2
1,3-ciclopetanedione-2,4-dimethyl	8.32	-	3.0
Unidentified compound	8.36	-	1.2
2-methoxyphenol	8.85	17.5	12.3
1,2 cyclohexane dicarboaldehyde	9.93	-	2.2
4-ethyl-2-methoxyphenol	11.91	-	1.2
2,6-dimethoxyphenol	12.89	30.1	16.9
4-hydroxy-3-methoxybenzaldehyde	13.52	3.7	8.0
1,2,4- trimethoxybenzene	14.14	-	1.1
1-(4-hydroxy-3-methoxyphenyl) ethanone	14.62	4.1	8.0
1,2,3- trimethoxy-5 methylbenzene	15.12	-	4.0
1-(4-hydroxy-3-methoxyphenyl) propanone	15.76	-	0.6
4-hydroxy-3,5-dimethoxybenzaldehyde	16.63	6.6	9.2
1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone	17.43	11.7	16.7
Unidentified compound	17.76	-	1.2
Unidentified compound	18.40	-	0.7
Cyclic octaatomic sulfur	20.23	-	8.0
Unidentified compound	24.39	-	0.6
Unidentified compound	25.99	-	0.7

The lignin products obtained from the black liquor are presented in Table 2.

The amount of precipitated sulfate lignin is 25,15 % of the dry matter and this result is comparable with 27 % lignin content in dry matter of birch Kraft black liquors [13, 14].

Figs. 2 and 3 show gas chromatograms of the extracts, obtained with toluene and ethyl acetate.

Tables 4 and 5 present low-molecular mass compounds identified in the toluene and ethyl acetate extracts.

The following main compounds have been identified in both toluene extracts: 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone. Other lignin monomeric compounds as: 4-ethyl-2-methoxyphenol;

Table 5. Compounds Identified in Ethyl Acetate Extracts.

Compounds	Retention time, min	Sulfate lignin	Black liquor
		Area, %	Area, %
Phenol	6.68	5.7	7.0
1,3 ciclopentandione -2,4 -dimethyl	8.28	3.5	3.1
2-methoxyphenol	8.84	12.6	42.7
1,2 cyclohexane dicarboaldehyde	9.92	-	2.1
Benzoic acid	10.48	5.9	3.0
1,2-Benzenediol	10.77	1.8	3.0
3 methoxy-1,2 benzenediol	11.63	2.0	2.8
4-ethyl-2 methoxyphenol	11.91	-	4.6
2,6-dimethoxyphenol	12.91	21.5	1.8
4-hydroxy-3-methoxybenzaldehyde	13.52	5.2	3.1
1-(4-hydroxy-3-methoxyphenyl) ethanone	14.62	4.0	2.0
4-hydroxy-3,5-dimethoxybenzaldehyde	16.63	7.4	3.1
Unidentified compound	16.90	-	2.7
1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone	17.46	26.5	2.2
4- hydroxy-3,5 dimethoxybenzoic acid	17.84	2.1	5.9
Dibuthyl phtalate	19.73	1.8	3.2
Unidentified compound	22.21	-	1.8
Unidentified compound	26.278	-	1.4
Diisooctyl ester phtalic acid	26.583	-	1.6
Unidentified compound	29.64	-	1.5
Unidentified compound	36.00	-	1.4

1-(4-hydroxy-3-methoxyphenyl) propanone; 1,2,4-trimethoxybenzene; 1,2 cyclohexane dicarboaldehyde, 1,3-ciclopetanedione-2,4-dimethyl have been isolated from the toluene extract of black liquor. Only in this extract a sulphur-contained compound - cyclic octaatomic sulfur has been identified.

The main compounds extracted with ethyl acetate are: 2,6-dimethoxyphenol; 2-methoxyphenol and 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone. The ethyl acetate extracts contained also other ketones, aldehydes, and acids, which were not extracted by toluene.

The identified low-molecular mass phenol compounds, obtained by extraction with toluene and ethyl acetate from black liquor and sulfate lignin, do not contain organic bonded sulphur.

CONCLUSIONS

By the extraction with two solvents, the following lignin degradation products: 2-methoxyphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone were obtained from black liquor and after alkaline treatment of sulfate lignin. Organic bonded sulphur has not been found in the obtained extracts.

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