Chemistry of Natural Compounds, Vol. 44, No. 2, 2008

PRODUCTION OF PHENOL COMPOUNDS BY ALKALINE TREATMENT OF TECHNICAL HYDROLYSIS LIGNIN AND WOOD BIOMASS

S. Nenkova, T. Vasileva, K. Stanulov

UDC 547.99.992

Aqueous alkaline depolymerization of technical hydrolysis lignin (THL) was carried out with a 5% NaOH solution at a temperature of 180°C for 6 hours, the ratio between the biomass and depolymerizing agent being 1:8. The poplar wood sawdust was treated under the same conditions for 2 hours, where anthraquinone was added as a catalyst (0.5 wt %). The poplar wood bark was treated for 4 hours, without anthraquinone. Compounds contained in the aqueous phase were extracted three times by means of toluene for a ratio between the organic and aqueous phases equal to 1:5, 1:5 and 1:5. The compounds 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl)ethanone, 4-hydroxy-3,5-dimethoxybenzaldehyde, etc., were identified through GC-MS analysis in obtained extracts.

Key words: lignin, poplar wood, alkaline treatment, extraction, low-molecular phenol compounds.

There is a steadily growing need for novel alternative sources of chemicals and fuels [1]. One promising source is lignin, which is the main by-product of the cellulose and hydrolysis industry and has limited practical application.

Lignin is an amorphous three-dimensional natural polymer, consisting of phenyl-propane units linked through ether and C-C bonds [2]. These phenyl-propane units are sources of phenolic compounds. The alkaline depolymerization of lignin is achieved by tearing off the ether and C-C bonds that bind the separate phenyl-propane units together. This makes it possible to obtain low-molecular monomer phenols, which are relatively easy to separate and identify [3-8]. The catalytic hydrothermal treatment (Rb and Cs carbonates at 280°C for 15 min) of wood biomass produced mainly phenol compounds [9]. Alkaline-catalytic depolymerization of lignin has been carried out at 240–270°C with alcohol solution of bases (KOH, NaOH, $Ca(OH)_2$). The depolymerized product is subjected to selective hydrocracking during which the oxygen-containing functional groups are preserved, the C-C bonds are broken, and the output of monomer phenols is increased. Through a follow-up etherification, aromatic ethers with a high octane number are obtained, which may replace the present oxygen-containing additives to fuels [10].

The aim of this investigation is to apply aqueous alkaline treatment to technical hydrolysis lignin (THL) and sawdust and bark of poplar wood to obtain low-molecular phenol compounds which may be used as additives for chemical stabilization of fuel.

The chromatogram data are given in Table 1.

Gas chromatogram data of the extract obtained by the alkaline treatment of poplar wood sawdust and bark are given in Table 2.

The amounts of obtained products are given in Tables 3.

University of Chemical Technology and Metallurgy 8 Kl. Ohridski, 1756 Sofia, Bulgaria, e-mail: nusha_v@mail.bg.
Published in Khimiya Prirodnykh Soedinenii, No. 2, pp. 144-146, March-April, 2008. Original article submitted November 15, 2006.

TABLE 1. Compounds Identified in Toluene Extract of Depolymerized Lignin

Compound	Retention time, min	Area, %
Phenol	2.91	2.01
Unidentified compounds	3.51	2.59
2-Methoxyphenol	3.81	56.80
Unidentified compounds	4.28	1.43
2,6-Dimethoxyphenol	6.07	6.68
4-Hydroxy-3-methoxybenzaldehyde	6.53	18.48
1-[4-Hydroxy-3-methoxyphenyl]ethanone	7.26	10.96
Unidentified compounds	7.60	1.05

TABLE 2. Compounds Identified in the Toluene Extract of Piplar Wood

Compound	Retention time, min	Sawdust	Bark
		Area, %	
Phenol	2.91	2.58	3.85
Unidentified compounds	3.51	0.86	3.03
2-Methoxyphenol	3.82	0.94	16.44
Unidentified compounds	4.24	-	0.81
Unidentified compounds	4.29	0.26	2.86
Unidentified compounds	5.05	-	0.53
4-Ethyl-2-methoxyphenol	5.45	-	1.42
2,6-Dimethoxyphenol	6.08	13.75	37.84
4-Hydroxy-3-methoxybenzaldehyde	6.54	20.74	4.48
4-Hydroxy-3-methoxybenzoic acid	6.88	0.28	0.64
1-[4-Hydroxy-3-methoxyphenyl]ethanone	7.27	5.70	10.21
Unidentified compounds	7.53	1.23	3.97
Unidentified compounds	7.60	-	0.72
4-Hydroxy-3,5-dimethoxybenzaldehyde	8.77	39.50	1.92
1-[4-hydroxy-3,5-dimethoxyphenyl]ethanone	9.49	14.16	11.28

TABLE 3. Products Obtained from Alkaline Treatment

Raw material	Insoluble residue	Precipitated activated lignin	Low-molecular products	Extract from liquid phase
	% of initial weight			
Lignin	5.13	73.07	21.80	1.11
Poplar wood bark	28.98	17.79	53.23	1.40
Poplar wood sawdust	44.15	23.63	32.22	1.58

The alkaline treatment of THL and poplar wood leads to lignin destruction and as a result of this it becomes dissolved. Two fractions are separated from the lignin solution: a high-molecular fraction, precipitated after acidification, and a low-molecular one that remains in the liquid phase. By using extraction with toluene from the liquid phase, methoxyphenol compounds are isolated. The main products are: 2-methoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 2,6-dimethoxyphenol, and 1-(4-hydroxy-3-methoxyphenyl) ethanone. The high-molecular fraction precipitated after alkaline treatment of THL features a higher reactive ability compared to the initial hydrolysis lignin [11, 12] and can be used for obtaining azoic dyes [13], modifying wood [14], etc.

Treating poplar wood leads to a considerably higher yield of low-molecular compounds in comparison with that from THL treatment. This is due to the more condensed structure of THL.

The possibility of obtaining low-molecular phenol compounds through alkaline treatment of THL and poplar wood was investigated. It was found out that alkaline treatment is an effective process, in which the main part of the lignin is depolymerized, and as a result of this a high-molecular fraction, precipitated after acidification, and a low-molecular fraction, remaining in the liquid phase, are obtained.

By using extraction with toluene from the liquid phase, the following compounds were isolated: 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, and 1-(4-hydroxy-3-methoxyphenyl) ethanone.

EXPERIMENTAL

For the investigation, technical hydrolytic lignin, a secondary product of chemical processing of softwood and hardwood mixtures delivered from the town Razlog (Bulgaria), was used. The THL was previously washed and powdered, and the fraction <0.315 mm was selected.

The process conditions were determined based on a review of the available literature data as well as on the results of our earlier investigations [3].

The alkaline treatment of THL (50 g) was carried out in stirring autoclaves made of stainless steel and heated in a bath of polyethyleneglycol at 180°C for 6 hours and 50 rpm. The treatment of the poplar wood sawdust was performed under the same conditions for 2 hours, where anthraquinone was added as a catalyst (0.5 wt%). Anthraquinone is a delignifying agent, widely utilized in the production of technical cellulose for preserving the carbohydrate part [15]. In this case, its use will decrease the quantity of decomposed sugars in the alkaline lignin solution. The poplar wood bark was treated for 4 hours, without anthraquinone.

The low-molecular compounds obtained by alkaline treatment of THL and poplar wood were isolated by extracting three times with toluene for a ratio between the organic and aqueous phases equal to 1:5, 1:5, and 1:5. Extraction conditions were chosen bearing in mind the results of our previous investigations.

The compounds were identified by GC-MS analysis with a Hewlett-Packard gas chromatography unit, model 6890, equipped with a mass selective detector, model 5973. A 30 m × 0.25 mm ID capillary column HP 5 with a film thickness of 0.25 μm was used. The splitless injector was maintained at 280°C. High-purity helium at a constant flow rate of 0.8 $\mathrm{mL{\times}min^{-1}}$ was the carrier gas. The initial column temperature was set at 80°C and held for 1 min, after which the following temperature program was applied: at heating rate 15°C/min to 190°C, again heated at 5°C/min to 280°C, held for 10 min and cooled to 80°C.

The amounts of obtained extracts, insoluble residue, and precipitated and nonprecipitated lignin were determined.

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