Chemistry of Natural Compounds, Vol. 37, No. 1, 2001

PREPARATION OF N-CONTAINING LIGNOCARBOHYDRATES

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UDC 634.0.813.16

Oxidative ammonolysis of mechanicochemically activated lignocarbohydrates produces N-containing derivatives (5.98-7.45% N) with 15-35% readily cleaved N and 5.43-6.99% COOH.

Key words: lignocarbohydrates, oxidative ammonolysis.

N-containing lignin derivatives have great practical interest [1-3]. Some of them are biologically active [4] and have high sorption ability [5]. Organic and mineral fertilizers and sorbents are prepared from hydrolyzed lignin [6, 7].

We propose a method for preparing N-containing lignin via oxidation with ammoniacal solution of ammonium persulfate at 20°C [8]. The principal drawbacks of this method, in our opinion, are the high comsumption of N-containing reagents (ratio of 40) and the duration of the process (>100 h).

Available raw materials for the production of valuable high-molecular-weight N-containing materials, besides hydrolyzed lignin, are cheap wood (larch wastes) and various plant lignocarbohydrates (LC).

An advantage of using LC as raw material is that the processing is cheaper, the raw-material base is significantly expanded, and, finally, it is unnecessary to separate the LC into lignin and carbohydrate parts. Thus, the groundwork for establishing low-waste technology for chemical wood processing has been laid.

However, the principal components of LC, lignin and polyose, form a strong LC complex through chemical and physical bonds with a complicated structure, morphology, and supramolecular arrangement. Therefore, the activation by various chemical and physicochemical methods is a necessary step in the chemical modification of LC. Previous investigations [9] have shown that the most effective of all LC processing methods is mechanochemical activation.

Therefore, we studied the possibility of preparing N-containing derivatives of various LC by oxidizing them with ammoniacal solution of ammonium persulfate with preliminary mechanochemical activation to increase the effectiveness of the oxidative ammonolysis.

We used LC of aspen and pine wood, sunflower shell, and flax fiber as sources of lignin-containing raw material for the study of oxidative nitrogen fixation. The chemical compositions of the starting LC are given below.

LC	Content, %		
	cellulose	lignin	pentosan
Wood:			
aspen	49.6	21.2	22.8
pine	53.8	28.1	11.3
Sunflower shell	31.9	29.3	27.2
Flax fiber	36.3	30.3	30.7

A portion of LC together with ammonium persulfate (0.1 g O per g of raw material) was preliminarily mechanically ground in a ball mill for 0.5 h according to the literature method [10] and then treated with 25% aqueous ammonia (ratio 10) for 24 h at 20-25°C and periodically shaken [8] for the oxidation. The compositions of the resulting products are given in Table 1.

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TABLE 1. Properties of N-Containing LCs

LC	Yield, %	Content, %		
		N (total)	COOH	N (readily cleaved)
Wood:				
aspen	90.2	5.98	5.43	0.92
pine	91.3	7.18	6.62	1.81
Sunflower shell	89.2	7.24	6.87	2.18
Flax fiber	87.5	7.45	6.99	2.64

TABLE 2. Composition of Products from LC Oxidative Ammonolysis

LC	Content, %			N, %	COOH, %
	cellulose	lignin	pentosan		
Aspen wood	43.1	18.2	17.3	5.98	5.43
Flax fiber	31.7	24.2	26.5	7.45	6.99

The results (Table 1) show that all studied LC undergo oxidative ammonolysis. The products from oxidative ammonolysis of wood are obtained in slightly greater yield compared with those from annual plant sources (sunflower shell and flax fiber). This can be explained by the more extensive destruction of lignin and hemicellulose of nonwood LC during their oxidation in the ammoniacal medium. The use of preliminary mechanochemical treatment of lignin-containing raw material can reduce the overall duration of the oxidative ammonolysis from 100 to 24.5 h.

A comparison of the data shows that the content of bound nitrogen and carboxyls in the products of oxidative ammonolysis of LC that contains a larger quantity of lignin and pentosans (nonwood LC) is slightly greater than for the products isolated from wood (Table 1). It was found that the N-containing products include 15-35% N that is readily cleaved by alkaline hydrolysis with the remainder strongly bound to the LC.

IR spectra of the polymeric products contain a strong absorption at 1550-1730 cm^{-1} that is characteristic of carbonyl, quinone, amide, and carboxylic acids. Therefore, the main functional groups of readily cleaved N are ammonium and amide.

The resulting products were tested as N-containing organic and mineral fertilizers for bean culture. They were effective growth stimulators and increased the growth by ~1.5 times and the total biomass by 25-35% [10].

Thus, use of LC and hydrolyzed lignin to prepare N-containing fertilizers and sorbents can substantially expand the raw material base and provide the groundwork for low-waste chemical processing of plant material.

EXPERIMENTAL

The chemical composition of the starting LC was determined by the literature method [11]. For the mechanical treatment, a mixture (5.0 g) of air-dried LC (sawdust fraction 0.4-0.75 mm) and ammonium persulfate (0.1 g O per g raw material) was periodically ground in a ball mill with 12 steel balls with an accelerating rotor at 2000 rpm and a temperature of 20-25°C for 0.5 h [13].

The products were unloaded from the grinder and separated from the balls. Treatment with 25% ammonia (ratio 10) was carried out in a flask at 20-25°C with periodic shaking over 24 h.

The samples that were ammonolyzed were washed with water until the washings contained no ammonium ion according to Nessler reagent and dried in a drying oven at 60°C to constant mass.

The nitrogen content was determined by a semimicro Kjeldahl method [12]; the amount of COOH, by conductometric titration [13]. Hydrolysis of the ammonolyzed samples was carried out by boiling a sample (0.5 g) with NaOH solution (25 mL, 0.5 N). The content of readily cleaved N was determined by the Kjeldahl method from the amount of ammonia released on hydrolysis of the products from oxidative ammonolysis of LC [11].

IR spectra of the LC from oxidative ammonolysis were recorded on a Specord M-80 spectrometer as a mixture with KBr pellets (5 mg/150 mg) in the range 400-4000 cm^{-1}.

The products were tested as growth stimulators on sprouts of Sakhar peas and Altai-60 wheat. The studied fertilizers were applied in doses of 50 and 100 mg per 200 g of soil. The control was sprouts growing in water. The growth indicators were the length of the plants and their total biomass.

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