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AMMONIATED PRODUCTS OF ASPEN WOOD OXIDATION

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A high-molecular-weight product containing 10.9% organically bound N and 8.92% COOH groups is isolated after oxidation of aspen chips with an ammonia solution of ammonium persulphate. The product, which has ~25% readily assimulated N in the ammonium and amide forms, was proposed as a N-containing organo-mineral fertilizer.

Key words: wood, oxidative ammonolysis, new N-containing organo-mineral fertilizer.

Lignin is oxidized (demethoxylated) by soil microflora to form polyphenols that then undergo condensation-oxidation transformations into humic (biologically active) substances that fertilize the soil [1].

However, natural microbiological destruction of lignin that produces physiologically active humic substances is a rather prolonged process. It can be accelerated by oxidative destruction of lignin to form active (carboxylic and quinone) groups within its structure that can bind N upon reaction with ammonia.

Long-lasting N-containing humic fertilizers can be produced by changing the lignocarbohydrate material so that it contains groups with N in a slowly assimilated bound form (amines, imines, heterocycles). These can be formed in the lignin macromolecule by oxidative ammonolysis.

Various industrial methods of lignin oxidative ammonolysis by oxygen in ammonia media under forcing conditions (150-200ºC, 5-50 atm) have been described [2-4]. The main deficiencies of the proposed methods are the low product yield (25-30%), complexity, and duration of the industrial process.

Oxidation by an ammoniacal solution of ammonium persulphate at 20ºC has been proposed [5] for oxidative N fixation. However, this method also has serious industrial drawbacks, i.e., the duration >100 h and the high consumption of N-containing reagents. Only lignin was used as raw material.

In the present article, the oxidation of lignocarbohydrate materials (aspen wood) by ammoniacal ammonium persulphate is investigated and the properties of the obtained product are studied. The application of lignocarbohydrate materials as starting material significantly expands the raw-material base and economizes the industrial process [6].

Chemical analysis (Table 1) of the ammoniated product isolated from aspen wood chips (APW) shows it contains 10.9% organically bound N, 8.92% carboxylic, and 4.13% methoxy groups. Nitrogen binds to the wood with simultaneous oxidation, demethoxylation, and loss of free carbonyl groups (as determined by oxime formation) during oxidation of wood with ammoniacal ammonium persulphate. The N is probably bound during reaction of carbonyl and carboxylic groups of oxidized wood with ammonia.

An investigation of the effect of hydrolyzing reagents on the amount of N and carboxylic groups in the oxidized APW indicates that 15-35% of the bound N is released upon hydrolysis of the product of oxidative ammonolysis. The amount of COOH groups increases proportionally in the hydrolyzed samples (Table 2).

Ammonia is known to be released from R–$COONH_4$ and R–$CONH_2$ groups under these conditions for the hydrolysis of N-containing lignin derivatives [5]. As a result, free carboxylic acids (upon acid hydrolysis) or their salts (upon alkaline hydrolysis) are formed.

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TABLE 1. Properties of N-Containing Aspen Wood Derivatives (1 h Ammonolysis)

Sample	Amount, g/g wood		Yield, %	Content, %			
	NH_3	O		N	COOH	OCH_3	C=O
Starting wood	-	-	-	0.67	0.89	5.82	5.4
APW	10.0	0.05	81.5	10.9	8.92	4.13	2.1

TABLE 2. Nitrogen Release on Treatment of Oxidized APW with Hydrolyzing Reagents

Treatment method	Yield of solid, %	N in treated product, %	Amount of N released, of initial content, %	Content of COOH groups, %	Increased content of COOH groups, %
-	-	10.9	-	8.92	-
1N. NaOH, 3h 100°C	71.6	7.08	35.1	11.6	30.1
1N. H_2SO_4, 3h 100°C	83.4	9.25	15.2	10.1	13.2

Table 3. Nitrogen Uptake by Wheat and Fertilizer Recovery

Fertilizer type	N dose, kg/ha	N content, %		N Uptake, kg/ha			K_u, %	Recovery, kg grain/kg N
		Grain	Straw	Grain	Straw	Total		
Control	-	2.18	0.75	40.1	19.7	59.8	-	-
Ammonium sulphate	30	2.23	0.76	46.8	21.9	68.7	29.7	8.7
	60	2.37	0.86	56.4	27.5	83.9	40.2	9.0
	90	2.57	0.91	67.1	32.0	99.1	43.7	8.6
APW	30	2.27	0.74	45.4	20.5	65.9	20.3	5.3
	60	2.35	0.78	54.5	23.8	78.3	30.8	8.0
	90	2.38	0.86	61.2	29.2	90.4	34.0	8.1

Therefore, if ammonia release is due to the presence of these functional groups, then the content of carboxylic groups increases in the sample after hydrolysis. We did observe this experimentally. We previously studied the functional composition of N bound by wood and found that the obtained product contained 14% ammonium and 18% amide N of the total amount [8].

This means that the N-containing derivatives of wood contain 15-35% readily released N (average 25%) in the ammonium and amide forms. The remaining N is strongly bound to wood and is evidently slowly assimilated (Table 2). Thus, part of the N in the obtained product is readily available for plants (25%). The remainder is chemically bound to wood (75%). Apparently the N chemically bound by the principal components of the ammoniated wood converts to forms available to plants as the wood decomposes.

We previously performed field experiments [7] that showed that the products of oxidative ammonolysis of wood can stimulate the growth of leguminous plants. Field tests on the experimental plot of the Altai Scientific-Research Institute of Agriculture and Selection of the Siberian Division of the Russian Academy of Agricultural Sciences were carried out in May-September 2000. The effect of the oxidized APW on the harvest of grain and uptake (assimilation) of N by the plants was studied.

Adding the APW to soil at 60-90 kgN/ha increases wheat growth by 5.3-8.5% and enhances the accumulation of biomass by 19-47% more than the control. The final grain harvest increases by 4.8 and 7.0 centner/ha or by 26 and 47% compared with the control. Analogous results were obtained if ammonium sulphate was used in the corresponding doses.

However, it should be noted that APW at a dose of 30 kgN/ha is less effective than ammonium sulphate. This is apparently due to the fact that an insufficient amount of N reaches the plant in the initial growth period because most of the element is chemically bound to wood and can be used only after the wood decomposes in the soil.

The N concentration in both grain and straw increases with application of APW. Taken together with the increased biomass, this increases the transfer of N to the harvest by 10-50% depending on the fertilizer dose (Table 3). However, the organo-mineral fertilizer is somewhat inferior to ammonium sulphate in this respect at all studied doses. As a result, the coefficient of use of the fertilizer N by wheat averages 10% lower for APW than for ammonium sulfate.

The N is used slightly less than from ammonium sulphate but the additionally assimilated N is comsumed by the plants to a large extent to increase the harvest rather than increasing the N concentration in the biomass. Thus, the amount of recovery from the applied fertilizers is close to that of ammonium sulphate.

EXPERIMENTAL

The ammoniated product of wood was obtained from air-dried chips (1.0-1.5 cm, 1.5 kg) by treatment with ammonium persulfate (0.1 kg/kg wood) in ammonia (25% aqueous, 1:10) at 120-130°C for 1 h in an autoclave at 2.5 atm. The product was washed with water until a sulphate test was negative and dried in air to constant mass.

The N content was determined by a semimicro Kjeldahl method [9]. The amount of COOH groups was measured by conductometric titration by the literature method [10]. Methoxyls were determined by the Zeisel method using GLC; carbonyls, by oxime formation according to the handbook [9]. The properties of the obtained product are listed in Table 1.

The strength of the N bond was studied by heating the oxidized wood with NaOH (1 N) and H_2SO_4 (1 N) at the boiling point for 3 h. The content of N and COOH groups in the resulting solid were determined (Table 2).

The effect of the obtained fertilizer on agricultural harvests was studied in field tests using the Altai-region tender spring wheat variety. The soil of the experimental plot is black-earth with typical average clay content. The precursor was spring wheat. The content of nitrate N in the 0-40-cm soil layer before starting the experiment was 5.6-6.8 mg/kg. This is characteristic of low N availability to plants.

The experimental plan included a control (without fertilizer) and tests with increasing N content (30, 60, and 90 kgN/ha) applied as ammonium sulphate or N-containing wood derivative obtained by us (APW). Each experiment was repeated four times.

The height and biomass of the plants were determined during flowering. At maturity, the harvest of grain and straw were determined by a uniform method and the N content in the grain and straw was determined by the K'eldahl method [9]. The transfer of N to the harvest and its coffecient of use from fertilizers (by difference) were calculated [11].

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