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Reactions, characterization and uptake of ammoxidized kraft lignin labeled with ^{15}N

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Abstract

Ammoxidation of kraft lignin was carried out in a Parr reactor using $^{15}NH_3$ as the main nitrogen source. Reaction parameters were set up until a total nitrogen content of ≈13 wt.% in lignin was achieved, in accordance with conditions of previous studies. Analytical tools such as FTIR, Py-GC/MS, and solid state NMR were used in this research. The nature of nitrogen bondings is discussed. The incorporation of the ^{15}N from ammoxidized lignin was followed in pumpkins (*Zucchini cucurbita pepo* L.) by means of ^{15}N emission spectroscopy.

Keywords: Ammoxidation; Kraft lignin; Labeled-ammonia; ^{15}Nitrogen; Slow-release fertilizer

1. Introduction

The need for slow release organic fertilizers is widely recognized, not only because it is desirable to apply nitrogen in a rational and inexpensive way, but also because of the importance of improving soil fertility without polluting ground and surface water with harmful nitrates. The feasibility of using modified kraft lignin as a source of nitrogen in slow release fertilizers has been described in previous reports by our group and other authors. Ammoxidation was carried out both in a fluidized-bed reactor and a liquid-phase stirred reactor. Ammoxidized lignins may have an N-content between 2.8 and 31.8 wt.% depending on the raw material and process conditions. The absolute N-content has less relevance than the C/N-ratio which should be less than 25 in the final product to assure good biodegradability in soils (Schröder, 1984). Performance of ammoxidized lignin as a slow release fertilizer has been proven (Meier et al., 1992, 1994; Zúñiga et al., 1992, 1994; Martínez et al., 1993; Ramírez et al., 1993, 1997, 2001).

Liquid-phase ammoxidation starts as soon as lignin and ammonia are mixed in an aqueous medium under pressurized oxygen. Ammonification is almost instantaneous after the functional groups are oxidized (Meier et al., 1992). The reaction rate increases rapidly at temperatures above 130 °C. To achieve nitrogen contents above 10 wt.%, a temperature of around 150 °C and oxygen pressure of ≈15 bar have to be applied. Under such experimental conditions, (≈3 wt.% aqueous solution) NH_4OH is very stable and does not represent any explosive hazard under oxygen atmosphere. It is only recommended to avoid contact with metals like copper, copper alloys, galvanized iron and zinc (Material Safety Data Sheet).

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As reaction conditions become more drastic, lignin undergoes degradation. The moiety of the aromatic rings as well as ether and alcohol groups decrease while an increase in C=O, C–N and C–N–H bonds can be observed. This may be explained by the formation of amides in oxidized lignin structures.

The parameters of ammoxidation have been widely studied, and various applications have been devised for the reaction products. However, there is still a need to understand the type of N-bonds and the lignin modifications in order to predict better the behavior of the final product as a slow release fertilizer.

Only a few publications deal with structural modifications of lignin and the characterization of nitrogen bonds (Lapierre et al., 1994; Potthast et al., 1996; Wei and Elder, 1997). The results can be summarized as follows: (1) Ammoxidized products are more condensed than the parent lignin. (2) A large portion of the nitrogen occurs as ammonium salts and related compounds. (3) N-amides occur as of derivatives from vanillic acid and related compounds as well as nitriles from dehydration reactions.

The objective of this study is to contribute to the elucidation of chemical reactions occurring during ammoxidation of kraft lignin and monitoring the nitrogen uptake by plants. For this purpose, ^{15}N-labeled ammonia was applied for the first time in order to facilitate the interpretation of results from Py-GC/MS analysis and to improve sensitivity for solid state ^{15}N NMR.

2. Methods

2.1. Ammoxidation reactions

Ammoxidation was carried out in a 300 cm^3 Parr Model 4561 stirred mini-reactor, equipped with a heating jacket and temperature controller Model 4882. The reactor was connected directly to a reagent grade oxygen source and equipped with relief valves and a cooling system.

Basic ammoxidation reaction conditions were those reported previously by Meier et al. (1994), and were adopted to suit the particular conditions of this reactor. Black liquor from softwood kraft pulping was supplied by Compañía Industrial de Atenquique,[1] Mexico. Kraft lignin was prepared through precipitation by bubbling CO_2 until a pH of 8.5, followed by washings with diluted sulfuric acid and distilled water to reduce ash content.

Labeled ammonia gas (Aldrich, 99.9% ^{15}N-content) served as the ^{15}N source. The ampoules were broken and the gas was absorbed in degassed distilled water in a sealed apparatus. Concentration of the actual ^{15}N-labeled ammonia solution was determined by conventional micro-titration techniques.

In the course of ammoxidation runs, samples were taken from the ammonia solution of the reactor (10 ml each). The sample taken before heating, directly after mixing of the lignin with the ammonia solution, is identified as $L_{initial}$; the sample taken immediately after the desired reaction temperature was reached is identified as L_0, and for the other samples the reaction time in minutes is indicated by indices (Lx). The samples were dried at 60 °C under vacuum and pulverized prior to analysis.

^{14}N and ^{15}N ammoxidation experiments were conducted under conditions seen in Table 1.

2.2. Cultivation of pumpkins

The experiments were performed in black plastic pots (Table 2) of 23 cm in diameter and 40 cm high, with six holes at the bottom for water drainage. Each pot contained 12 kg agricultural soil (sandy clay loam), screened with mesh 10.

Four pumpkin seeds were placed in each pot at 3.0 cm depth and left for six days to complete germination. Thereafter, only one seedling was left in the pot for further growth.

The pots were arranged randomly, exposed to daylight during the day, and protected with a mesh overnight. Each pot was irrigated every other day with 0.6 l of tap water. The fertilizing formulation N–P–K was 130–80–60, respectively, in accordance with the agriculture methods used in the region, regardless of the nitrogen source used in the different experiments. The fertilizer was placed at a distance of 5.0 cm away from plant stem and at a depth of 3.0 cm into the soil.

According to the N–P–K formulation, the nitrogen dose for all plants was 540 mg per plant, using one of the following nitrogen sources (Table 2): ^{15}N-labeled kraft ammoxidized lignin (12 wt.% N), urea (46 wt.% N) and unlabeled kraft ammoxidized lignin (13 wt.% N). For supply of P and K, $CaHPO_4$ and KCl were used, respectively. All plants were harvested after 60 days, and biomass weight evaluated for all treatments. After harvest of pot number 1, a new seedling was placed in the same pot without adding any fertilizer. This follow-up trial is denominated, “harvest 2”.

2.3. Analytical characterization

Total nitrogen content was determined by elemental analysis using a Fisons instrument model EA1108. Analysis were done in duplicate, with 2.0 mg samples; oxygen was determined by difference.

FTIR measurements of ammoxidation products at different reaction times were made using a Nicolet instrument model 510 with detector DGTS, resolution of 4 cm^{-1}, gain 8. Determinations were made within a scan range of 4000–400 cm^{-1} at 200 scans per test, using 13 mm KBr pellets with 2.0 mg samples.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was carried out following the procedure described by Faix et al. (1990) for thermal degradation of lignin and

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