*Chemistry of Natural Compounds, Vol. 38, No. 6, 2002*

# NITRATION OF MECHANICALLY ACTIVATED SUNFLOWER SHELLS

**M. V. Efanov and A. V. Zabelina**

UDC 634.0.864.2:631.895

*Oxidative nitration of mechanically activated sunflower shells produces high-molecular-weight products containing 2.1-10.1% organically bound nitrogen and 3.6-13.7% carboxylic and 1.5-3.2% methoxyl groups. The products are proposed for using as N-containing organic fertilizers.*

**Key words:** sunflower shell, nitration, N-containing organic fertilizers.

The goal of this research was to develop an effective and ecologically safe method for oxidative nitration of wood and to study the properties of the nitrogenous organo-mineral fertilizers based on it.

We nitrated shells in order to introduce nitrogen (N) into the macromolecules of the principal components and to produce simultaneously more oxidized fragments of this plant raw material. Oxidized N-containing shell can be used as an organic fertilizer and applied to the preparation of ion-exchange materials. The starting material for the preparation of the organic fertilizers was sunflower shell, a multi-ton agricultural waste that has not yet found a qualified use. The raw material was analyzed by known methods [1]. The starting material contained (%): cellulose 31.9; lignin 29.3, hemicellulose 27.2, water-extractable substances 8.5, and ash 2.3.

Chemical analysis of the starting material showed that sunflower shell has a high content of lignin and hemicellulose and a rather low cellulose content. We studied the effect of various technical process parameters on the composition and properties of the products from oxidative nitration of sunflower shell by $HNO_3$ (100%) at 20°C for 0.5-3 h using preliminary mechanical activation in a ball mill.

Tables 1 and 2 contain the experimental results and show that nitration of sunflower shell is accompanied by oxidation. The content of C=O and COOH groups increases. Demethylation causes the loss of ~10-60% of the methoxyls compared with the starting value. The products contain 2.1-10.1% total N.

Increasing [$HNO_3$] from 15 to 100% gradually increases the content of bound N. Table 2 shows that the nitration time of shell by conc. $HNO_3$ has little effect on the N content and functional groups. The main amount of N (9.0%) is incorporated after 1 h.

The content of phenol hydroxyls in the shell decreases owing to their oxidation and formation of a significant quantity of carbonyl and carboxylic acid groups (Table 1). The IR spectra of the nitration products exhibit peaks near 1340 and 1530 $cm^{-1}$ that are characteristic of aromatic $NO_2$ and a peak (medium) near 1645 $cm^{-1}$ that is characteristic of $ONO_2$. The strengths of the absorption bands at 1705-1730 and 1675-1680 $cm^{-1}$ increase compared with the starting spectrum because of the presence of the carboxylic acid and carbonyl groups, which is consistent with the chemical analyses (Table 1).

Thus, nitration of mechanically activated sunflower shell causes its oxidation and demethylation. The high content of bound N in the product (up to 10.1%) and the IR spectra indicate that lignin and polysaccharide are nitrated.

The high content of N and carboxylic acids in the products enables their use as N-containing organic fertilizers. The plant height and leaf surface (Table 3) indicate that these products stimulate pea growth. Increasing the N content in the shell from 2.1 to 9.0% increases proportionally the main morphophysiological plant properties. Thus, preliminary growth tests recommend the products as fertilizers for grain and legume culture.

---

Altai State University, 656099, Russia, Barnaul, pr. Lenina, 61, fax (83852) 22 54 51, e-mail: efanov@chemwood.dcn-asu.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 482-483, November-December, 2002. Original article submitted October 23, 2002.

TABLE 1. Effect of $HNO_3$ Concentration on Functional Composition of Nitration Products of Sunflower Shell (Nitration time 1 h, Temperature 20°C)

| Concentration of $HNO_3$, % | Content, % | | | | |
|---|---|---|---|---|---|
| | N | COOH | $OCH_3$ | $OH_{phen}$ | C=O |
| - | - | 2.7 | 3.6 | 2.8 | 3.4 |
| 15 | 2.1 | 3.6 | 3.2 | 2.1 | 3.9 |
| 30 | 3.8 | 5.9 | 2.8 | 1.9 | 4.3 |
| 45 | 4.7 | 7.5 | 2.4 | 1.5 | 4.8 |
| 60 | 6.9 | 12.9 | 2.2 | 1.2 | 5.1 |
| 75 | 8.6 | 13.1 | 1.9 | 1.0 | 5.5 |
| 100 | 9.0 | 13.2 | 1.7 | 0.5 | 5.9 |

TABLE 2. Effect of Treatment Time by $HNO_3$ (100%) on Functional Composition of Nitration Products (Temperature 20°C) of Sunflower Shell

| Time, h | Content, % | | |
|---|---|---|---|
| | N | COOH | $OCH_3$ |
| 0.5 | 8.1 | 12.3 | 2.1 |
| 2 | 10.0 | 13.5 | 1.5 |
| 3 | 10.1 | 13.7 | 1.5 |

TABLE 3. Effect of N-Containing Derivatives of Sunflower Shell on Morphological Properties of "Sakharnyi" Pea Plants

| Sample | N content, % | Dose, g/500 g soil | Plant height, cm | Effect over control | | Leaf surface, $cm^2$ | Effect over control | |
|---|---|---|---|---|---|---|---|---|
| | | | | cm | % | | $cm^2$ | % |
| Control | - | - | 8.3 | - | - | 75 | - | - |
| 2 | 2.1 | 0.1 | 13.7 | 5.4 | 65 | 94 | 18 | 24 |
| 6 | 9.0 | 0.1 | 15.0 | 6.7 | 81 | 101 | 26 | 35 |
| Average | - | - | 14.4 | 6.1 | 73 | 98 | 23 | 29 |

## EXPERIMENTAL

The chemical composition of sunflower shell was determined by the usual methods described in a handbook [1]. For mechanical treatment, raw material (air-dried shell, 0.5-1.0 mm, 100 g) was thoroughly ground in a ball mill (industrial vibrator IV-98B) in a steel cylindrical reactor with 15 steel rods at 2800 $cm^{-1}$ for 30 min at 20-25°C. Then, the activated material was unloaded from the mill and separated from the grinders.

Activated shell was nitrated by $HNO_3$ (15-100%) at 20°C for 0.5-3 h (1:10 ratio) in a flask with a reflux condenser that was placed in a thermostat. The N content was determined by the Dumas method given in a handbook [2]; the carboxylic acid groups, by reverse conductometric titration; the methoxy groups, by the Zeitzel method using GC [3]; the phenyl hydroxyl content, by chemisorption on $BaCl_2$ [3], the carbonyl content, by a hydroxylamine method [2]. IR spectra of N-containing products were recorded in KBr pellets (5mg/150 mg KBr) on a Specord M80 spectrometer in the range 400-4000 $cm^{-1}$ with air background.

The effectiveness of the N-containing sunflower-shell derivatives for stimulating growth of Sakharnyi pea plants was tested in a growth experiment. Experiments with 30-day pea sprouts were conducted in 1-L polyethylene containers containing soil (0.5 kg) with addition of weighed portions of N-containing sunflower-shell nitration products (0.1 g per 0.5 kg soil) with N content 2.1 % (sample 2) and 9.0% (sample 6). Pea sprouts (20) were planted in each container in triplicate. After 30 days the growth was determined using the height, leaf area, chlorophyll content in the leaves, and absolute dry weight of the biomass. The controls were plants grown without fertilizers. We used biometric and gravimetric methods in addition to photocolorimetry in the experiments. The results were treated statistically using the Student method.

## REFERENCES


1. A. V. Obolenskaya, *Laboratory Studies of the Chemistry of Wood and Cellulose* [in Russian], A. A. Leonovich, ed., Ekologiya, Moscow (1991).
2. V. A. Klimova, *Principal Microanalytical Methods of Organic Compounds* [in Russian], Khimiya, Moscow (1975).
3. G. F. Zakis, *Functional Analysis of Lignins and Their Derivatives* [in Russian], Zinatne, Riga (1987).