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Hydrotropic Cellulose and Cellulose Nitrates from Fruit Shells of Oats

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Abstract

Major characteristics of cellulose obtained from fruit shells of oat by the hydrotropic method were studied. It was demonstrated that bleaching of pulp sample contributed to cellulose concentration and the removal of the bulk of noncellulosic compounds in the product. Samples of esters close by major characteristics to mastic-lacquer colloxylins were synthesised under conditions of preparation of highly soluble cellulose nitrates. Cellulose fibres of fruit shells of oat and cellulose nitrates obtained were characterized by scanning electron microscopy (SEM) techniques. It was found by IR spectroscopy that hydrotropic cellulose was identical to cellulose from traditional types of plant raw materials by major adsorption bands. It was demonstrated that the resulting esters were cellulose nitrates.

Key words: fruit shells of oat, hydrotropic cellulose, bleaching, nitration, cellulose nitrates, scanning electron microscopy, IR spectroscopy

INTRODUCTION

Currently, some advances have been made in complex refining of non-traditional plant raw materials: various methods of producing cellulose from agricultural wastes have been developed, the composition and properties of intermediates and target products have been studied [1–3]. Herewith, approaches meeting green chemistry principles are of special importance. As a result, such delignifying agents and reactants, as oxygen, hydrogen peroxide, and hydrotropic compounds have become most common [1–4].

It is hydrotropic reactants that allow maximally using plant raw materials, *i.e.* simultaneously obtaining cellulose and lignin from them [3, 4]. Advantages of hydrotropic method consist in the use of an environmentally sound compound that is sodium benzoate known as E211 Food Additive.

The opportunities of the further use of hydrotropic cellulose from non-wood plant raw materials in preparation of cellulose esters were studied [5, 6]. Cellulose was isolated from miscanthus by the hydrotropic method, its bleaching and further fusion were carried out to prepare cellulose nitrates with indicators close to high-viscous colloxylin [5].

The purpose of the present paper is isolation of hydrotropic cellulose from fruit shells of oat, its further nitration, and the study of major characteristics of the resulting products.

EXPERIMENTAL

Oat processing wastes from various husbandries of Biysk district presented by Biysk Elevator JSC were the research object.

Fruit shells of oat (*Avéna satíva*) are straw-coloured, surround the entire grain (seed), uni-

form in composition, and due to small particle size (10 mm), they can be used for isolation of cellulose without preliminary grinding.

Prior to work, raw materials were rinsed with hot water (50–60 °C) to remove wheat middlings, wringed out, and dried at room temperature to 9–10 % moisture content.

Fruit shells of oat have the following chemical composition (mass %): cellulose (by Kirchner) – 44.7, lignin – 18.1, pentosans – 30.8, ash – 4.6, extractive substances – 1.0.

Hydrotropic delignification was carried out in a universal thermobaric setup with reaction camera capacity of 2.3 L. The prepared sample weight of fruit shells of oat was laid in a reaction chamber of the apparatus and poured with a 35 % solution of sodium benzoate (Fooding Group Ltd., China). Process hydromodulus was 10 : 1. The setup was sealed, heated with stirring to a specified temperature. Delignification was carried out in the following mode: temperature rise to 180 °C – 40 min, boiling at 180 °C – 4 h. At the end of the boiling process, the reaction mass was cooled, unloaded from the chamber, wringed out from boiled-off liquor, washed with a fresh portion of a hydrotropic solution (hydraulic module is 20 : 1) and then with water until wash water bleaching. The product was dried at a temperature of 20–25 °C to 6–8 % moisture content. The yield and major physicochemical characteristics of pulp were defined after drying (Table 1).

Bleaching of pulp was carried out using H_2O_2 in alkaline medium (pH 10–11) [3]. Resulting bleached cellulose was dried at 20–25 °C temperature to 6–8 % moisture content and analysed by major characteristics (see Table 1).

The major characteristics of resulting cellulose samples (mass fractions of α-cellulose, pentosans, ash, and extractive substances) were defined by analysis standard methods [7].

Nitration of bleached cellulose in fruit shells of oat (with moisture content of no more than 5 %) was carried out in a mixture containing HNO_3 и H_2SO_4 with the addition of 14 % H_2O [5]. The yield and major characteristics, such as nitrogen mass fraction (by the ferrous sulphate method), viscosity of a 2 % solution of cellulose nitrates in acetone, solubility in an alcohol-ether mixture were defined for the resulting samples of cellulose nitrates by standards accepted in the industry.

All experiments were carried out from two to five times, the arithmetic mean of the carried out experiments was accepted for the final result.

Hydrotropic cellulose samples of fruit shells of oat and nitrates were studied by scanning electron microscopy (SEM) techniques using JEOL JSM-840 scanning electron microscope (Japan) after Pt spraying with 1–5 nm layer thickness and IR spectroscopy with Infralum FT-801 spectrometer (Russia) in the range 500–4000 cm^{-1} using KBr pellets (1 : 50 ratio).

RESULTS AND DISCUSSION

Fruit shells of oat are regarded as a pentosan-containing source, where pentosans mass fraction is 30 %. Nevertheless, cellulose content therefrom reaches 45 %, which also allows considering this type of raw materials as a source for cellulose production.

Hydrotropic delignification conditions contribute to ligno-carbohydrate matrix hydrolysis, with the result that pentosans mass fraction decreases from 31 % in initial raw materials to 7 % in pulp (see Table 1). Organic acids that are polysaccharide hydrolysis products of fruit shells of oat (pH of the process is changed from pH 8.6 to pH 4.9) are this process catalyst.

TABLE 1

Yield and characteristics of samples of technical and bleached cellulose from fruit shells of oats, obtained by the hydrotropic method

Cellulose	Yield*, %	Mass fraction, %				
		α-Cellulose	Lignin	Pentosans	Ash	Extractive substances
Technical	43.7	82.5	6.7	7.4	3.0	0.3
Bleached	37.9	91.6	1.5	5.6	1.0	0.1

* In terms of absolutely dry raw materials.

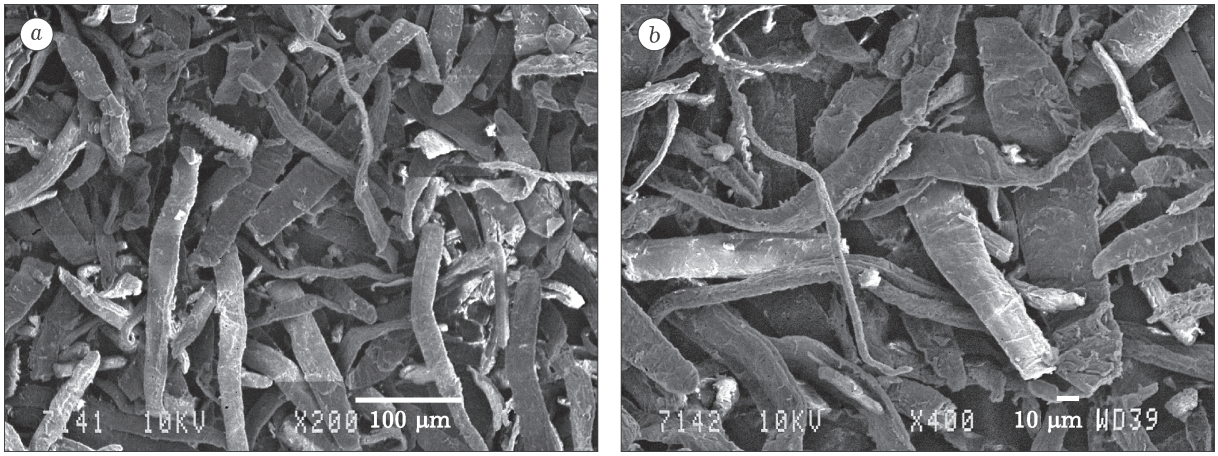

Fig. 1. Picture of scanning electron microscopy (SEM) of bleached cellulose fibres from fruit shells of oats. Magnification: 200× (*a*) and 400× (*b*).

Hydrotropic action of the reactant is directed at lignin; with the result that lignin mass fraction in the resulting cellulose reaches 7 %, ash – at 3 % level.

The bleaching action of hydrogen peroxide is based on electrolytic dissociation into ions [8]:

$$H_2O_2 \rightarrow H^+ + HO_2^-$$

It is supposed that hydroperoxyl anion (HO_2^-) is an active decolourant. Sodium hydroxide, sodium silicate, and magnesium sulphate are added during bleaching with hydrogen peroxide [8].

Bleaching with hydrogen peroxide allowed removing the bulk of non-cellulose components contained in pulp (see Table 1). The yield of cellulose was decreased by 13 %. Cellulose concentration to 92 % and a significant decrease in lignin mass fraction (to 1.5 %) occurred during bleaching.

By SEM data (Fig. 1), the bulk of bleached cellulose of fruit shells of oat is presented by ribbon-like fibres with a longitudinal size of the fibres from 80 to 300 μm, transverse – from 5 to 40 μm.

The study of cellulose by IR spectroscopy demonstrated that the IR spectrum of cellulose from fruit shells of oats contained the major absorption bands typical of traditional types of plant raw materials [9]: 3000–3700 cm^{-1} – stretching vibrations of hydroxyl groups includ-

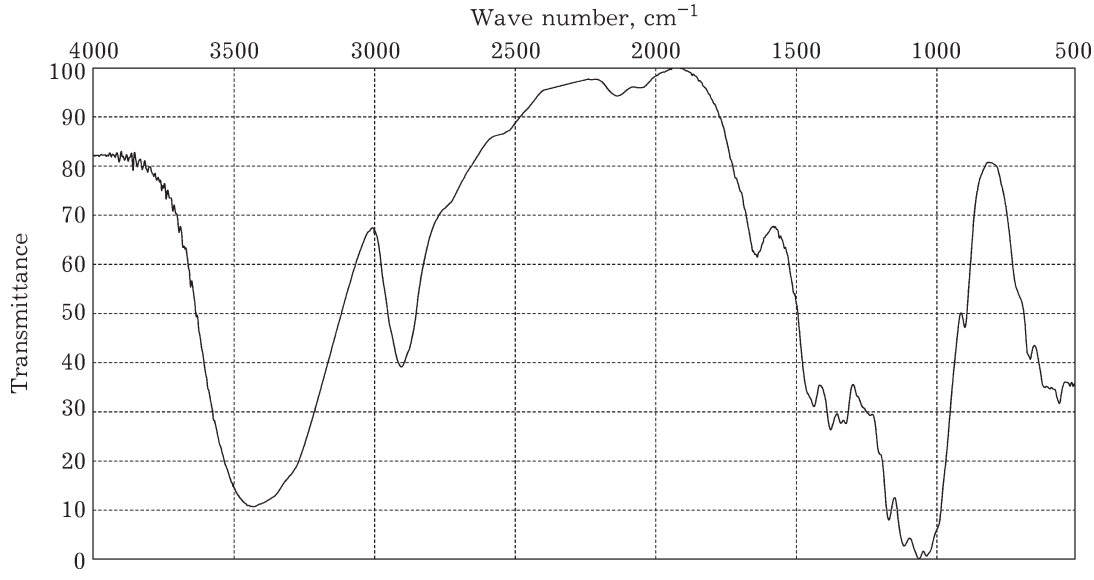

Fig. 2. IR spectrum for bleached cellulose of fruit shells of oats.

TABLE 2

Characteristics of samples of cellulose nitrate in fruit shells of oats and mastic-lacquer colloxylin

Samples	Nitrogen mass fraction, %	Viscosity, mPa · s	Solubility in an alcohol-ether mixture, %
Cellulose nitrates	11.45	4	93
Mastic-lacquer colloxylin	10.66–12.41	3.7–15.8	–

ed in the hydrogen bond; ~2900 cm^{-1} – asymmetric stretching vibrations of C–H bonds in methylene groups; ~1643 cm^{-1} – deformation vibrations of OH groups in water; 1300–1400 cm^{-1} – deformation vibrations of CH_2 and OH groups in CH_2OH; 1000–200 cm^{-1} – stretching vibrations of C–O groups; 600–700 cm^{-1} – vibrations of the pyranose ring (Fig. 2).

Nitration of samples of hydrotropic cellulose in fruit shells of oat was carried out under standard conditions for cotton cellulose [10]. Esterification reaction scheme may be presented as follows [9]:

$$[C_6H_7O_2(OH)_3]_n + xnHNO_3 \rightarrow [C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n + xnH_2O + Q$$

where x is the substitution degree (esterification) that is the number of nitrate groups per one elementary unit of the cellulose macromolecule.

To produce highly soluble cellulose nitrates from fruit shells of oat experiments on nitration of bleached cellulose samples of fruit shells of oat in a sulphuric/nitric acid mixture containing 14 % of H_2O were carried out. Characteristics of the resulting samples of cellulose nitrates are given in Table 2.

The resulting hydrotropic cellulose nitrates of fruit shells of oat are characterised by the complete solubility in a 2 % acetone solution. The yield of cellulose nitrates in fruit shells of oat was 130 %. Nitrogen mass fraction was 11.45 %, which contributed to substitution degree of 2.09.

In addition to characteristics for cellulose nitrates of fruit shells of oat, the data for mastic-lacquer colloxylin are given in Table 2 [9]. It can be seen that they are close between each other; therefore, the synthesized nitrates can be used in the production of mastic, nitro lacquers, nitrofilm, and construction linoleums.

A change in the structure of cellulose nitrate fibres (Fig. 3) compared to initial cellulose fibres (see Fig. 1) was demonstrated by SEM techniques. Cellulose nitrate fibres of fruit shells of oat retained a ribbon-like shape and increased in volume at the same time. The longitudinal sizes of cellulose nitrate fibres are found in the same range as cellulose fibre sizes that is from 100 to 300 μm, an increase in volume can be

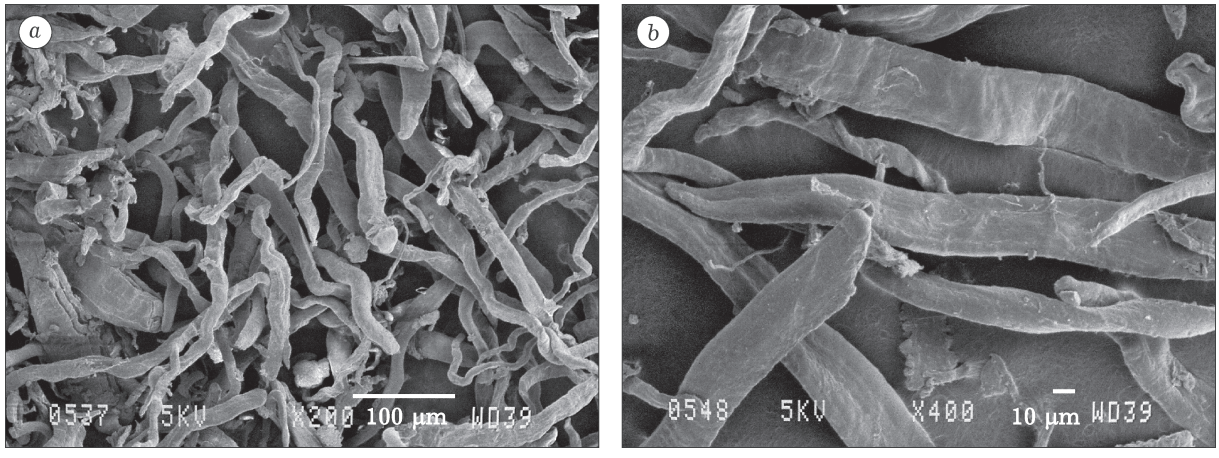

Fig. 3. Picture of scanning electron microscopy (SEM) of cellulose nitrate fibres from fruit shells of oats. Magnification: ×200 (*a*), ×400 (*b*).

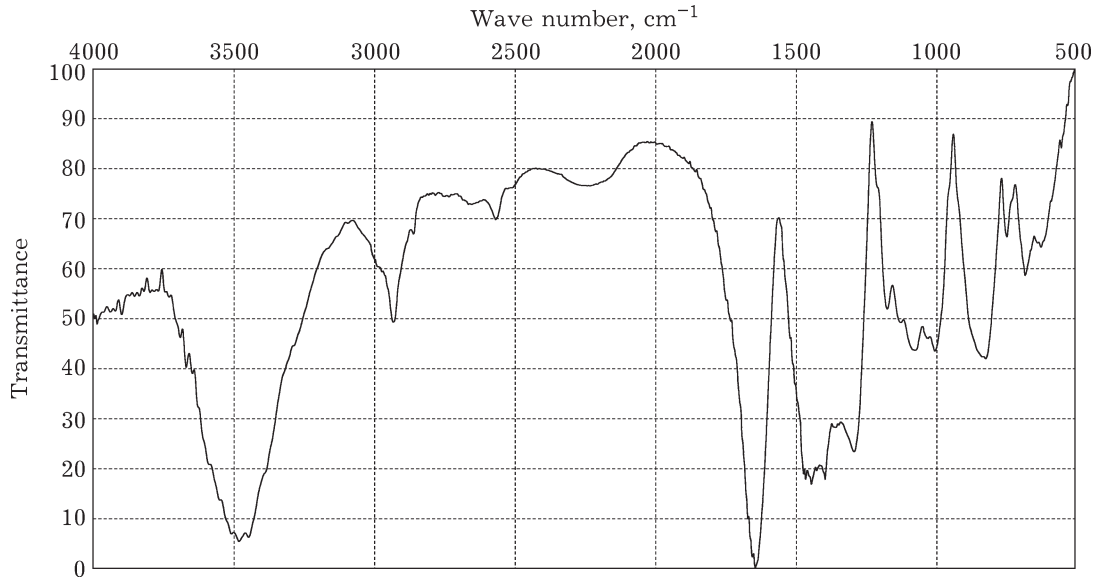

Fig. 4. IR spectrum of cellulose nitrates in fruit shells of oats.

traced by an increase in the longitudinal sizes of fibres that is from 10 to 60 μm.

Preparation of cellulose nitrates from fruit shells of oat was confirmed by the IR spectroscopy. Figure 4 presents the IR spectrum of cellulose nitrate in fruit shells of oat.

The IR spectrum of cellulose nitrates in fruit shells of oats contains the major adsorption bands typical for cellulose nitrates in cotton [9, 11]: 3200–3700 cm^{-1} – the adsorption bands of non-etherified hydroxyl groups, which indicates incomplete substitution of cellulose nitrate (substitution degree is 2.09); ~1632 cm^{-1}– asymmetric stretching vibrations of the nitro group of C_2 and C_3 in an the elementary glucopyranose fragment of a cellulose macromolecule; ~1279 cm^{-1} – symmetric stretching vibrations of NO_2 groups: ~677, ~743 and ~817 cm^{-1} – planar deformation, out-of-plane rocking and stretching vibrations of nitro ester groups, respectively.

CONCLUSION

Hydrotropic cellulose samples with lignin mass fraction to 7 % were isolated from fruit shells of oat resulting from the carried out studies. Subsequent bleaching of pulp samples resulted in cellulose concentration in the product to 92 % and reduction of lignin mass fraction to 1.5 %. Further cellulose nitration under conditions of preparation of highly soluble cellulose esters allowed synthesis of samples of cellulose nitrates close to mastic-lacquer colloxylins. Fibres of initial cellulose and cellulose nitrates of fruit shells of oat were characterised by scanning electron microscopy (SEM) techniques. Obtaining cellulose from fruit shells of oat and nitrates on its bases was confirmed by IR spectroscopy.

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