Highly soluble cellulose nitrates from unconventional feedstocks

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Abstract. Celluloses isolated by the nitric-acid process from domestic unconventional feedstocks such as *Miscanthus*, oat hulls, and intermediate flax straw were used herein to produce cellulose nitrates (CNs) with a high solubility. For the synthesis of CNs, a commercial technique was employed that involves nitration of cellulose with mixed acid containing 14 wt.% water followed by high-temperature treatment of the nitration product in acidic, alkaline, and neutral environments. The obtained CNs are similar in physicochemical attributes: 12.04–12.26% mass fraction of nitrogen, 10–14 mPa·s viscosity, and 98% solubility in alcohol–ester mixture. FTIR spectra of CNs had absorption bands (2559–2557, 1646–1631, 1277–1271, 825–812, 747–744, 683–680 cm⁻¹) typical of nitro group vibrations. ¹³C NMR spectra showed chemical shifts representative of 6-mononitrocellulose, 2,6-dinitrocellulose, 3,6-dinitrocellulose, and 2,3,6-trinitrocellulose. DSC revealed that the resultant CNs were highly chemically pure with an exothermic peak at 209–212°C. The CNs obtained from the said unconventional feedstocks were compared with a commercial, high-viscosity, lacquer-grade Colloxylin derived from cotton cellulose, as well as with other commercial Colloxylin, to show that the experimental CNs meet the requirements for commercial grades. Thus, the CNs obtained from the unconventional feedstocks are promising candidates as the component of composite explosives.

1 Introduction

Due to unique properties cellulose nitrates (CNs) are among the first and most important cellulose derivatives widely used in the manufacturing articles for defence and civil industrial sectors. Although NCs were discovered as early as the 18th century, they are still of interest. Nowadays, CNs are utilized not only to fabricate conventional products (gun powder, explosives, paints and lacquers), but also to make new rocket propellant types [1]. Wu et al. [2] reported results on improving the plasticizing ability of CN by incorporating promising energetic binders (GAP) into the formulation. The thermal decomposition kinetics of CN mixed with high-energy oxidizers was studied [3,4].

Young et al. [5] demonstrated the possibility of using nanosized aluminum mesoparticles with CN in rocket propellant formulations.

Along with that, CNs are finding new fields of application: for instance, they are used to prepare new filter membranes [6, 7] and a durable, room-temperature, curable, superhydrophobic, composite coating based on nitrocellulose lacquer [8]. Besides, different modifications of CN are tried to reduce its sensitivity to mechanical stimulus when used as a binder in insensitive high-energy propellants [9].

In Russia, research focused on expanding the assortment of civil Colloxylin by exploiting new cellulosic feedstocks is of special relevance [10].

CNs are typically produced from expensive cotton cellulose and scarce wood cellulose [11–13]. However, in recent years, the quality of products and stability of properties of cotton cellulose imported to Russia from near abroad countries (Uzbekistan and Kazakhstan) have deteriorated and the production of wood cellulose has been suspended because of environmental harm, difficult processing, and scarce forest resources.

To provide the nation with raw materials, preserve forests, and substitute imported high-cost cotton, an industrial base involving indigenous unconventional feedstocks needs to be developed. Fast-growing plants such as linen flax, hemp, melilot, hogweed, alfalfa, rape, and jute are especially attractive to scientists.

Overseas scholars consider esparto grass [14] and wood processing residues [15] as the potential source of cellulose and its nitrates. Not only plant cellulose but also bacterial cellulose as the promising source of CNs arouses interest of researchers. However, studies describing the synthesis of nitrates from those celluloses [16–18] give very little information on properties of CNs, making it difficult to assess their further application in practice.

Different advanced instruments are currently in use to evaluate the quality of CNs: scanning electron

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microscopy (Philips XL30, Quanta 600 W), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Stranton Redcroft STA-780), Fourier transform infrared spectroscopy (FTIR) (Nexus 670 FTIR, Shimadzu 8400S), diffractometry (multipurpose diffractometer with Cu-K α radiation), gas liquid chromatography (Agilent liquid chromatography series 1100), etc. [19, 20], as well as ^{13}C NMR spectroscopy [13].

At present, industrially important sources of feedstock with a high productivity are easily renewable crops and agricultural residues. *Miscanthus* is a fast-growing perennal crop with a high biomass yield of 10–15 ton/ha/year over a span of 15–25 years. Oat hulls and intermediate flax straw are large-tonnage agricultural residues whose disposal issue has not yet been resolved.

However, replacing elite cotton feedstocks by unconventional raw materials to produce high-quality CNs is still at a lab scale, and there is no information at all about the feasibility of utilizing *Miscanthus*-, oat hull- and intermediate flax straw-derived CNs as the component of composite explosives, making this research area undoubtedly topical.

The present study aimed to synthesize CNs from *Miscanthus*, oat hulls, and intermediate flax straw to explore whether the CNs could be used as the constituent of composite explosives.

2 Experimental part

The substrates for this study were celluloses isolated from *Miscanthus* (M), oat hulls (OH), and intermediate flax straw (IFS) by the nitric-acid method [21, 22] at the pilot production site of IPCET SB RAS.

The feedstocks prior to pulping were ground on a garden chaff cutter to at most 10 mm. The nitric-acid process for cellulose involved the following stages: step by step treatment at $94\pm 2^\circ\text{C}$ with 0.4% HNO_3 , 5% HNO_3 , 2% NaOH , and 0.8% NaOH prior to eventual decationation (souring) by treatment with 0.8% HNO_3 at 50°C to furnish the target cellulose.

Mass fractions of α -cellulose, ash, acid-insoluble lignin, pentosans were measured by standard procedures [23]. The cellulose degree of polymerization (DP) was determined from the viscosity of solutions in cadoxene on a VPZh-3 viscometer (ECROS, Russia) with a capillary of 0.92 mm in diameter [24].

A commercial nitration method was used to produce CNs from *Miscanthus*, oat hulls and intermediate flax straw. This method involved the treatment of celluloses with mixed acid containing 14 wt.% water in a solid-to-liquid ratio of 1:25 (w/v) at $33\pm 2^\circ\text{C}$ for 35 min. After the nitration was completed, the resultant CNs were washed with water until neutral reaction and treated in acidic, alkaline, and neutral medium under the following conditions: 1 h boiling in water at $85\pm 2^\circ\text{C}$; 1.5 h autoclaving in 0.3% HNO_3 at $130\pm 2^\circ\text{C}$; 3 h boiling in 0.03% Na_2CO_3 at $85\pm 2^\circ\text{C}$ followed by 1 h exposure to water at $85\pm 5^\circ\text{C}$ [21, 22].

The CN samples were dried at room temperature and then at $100\pm 2^\circ\text{C}$ for 1h until a moisture not above 5%, and were further characterized.

The commercial, high-viscosity, lacquer-grade Colloxylin made of cotton cellulose was used as the control.

The mass fraction of nitrogen was quantified by the ferrous sulfate method, which consisted in saponifying CNs with concentrated sulfuric acid and reducing the formed nitric acid with iron (II) sulfate to nitrogen oxide that generates, in excess of iron (II) sulfate, a $[\text{Fe}(\text{NO})]\text{SO}_4$ complex compound that turns the solution yellow-pink. This method is still in demand in the world practice [13].

The CN viscosity was determined by measuring the flow time of the 2% CN–acetone solution out of a VPZh-1 viscosimeter with a capillary diameter of 2.10 mm. The CN solubility in acetone was 100%.

The solubility of CNs in an alcohol–ester mixture was measured by filtration of the CN residue insoluble in the alcohol–ester mixture with subsequent drying and weighing. The CN solutions in the alcohol–ester mixture were poured into crystallizers, evaporated in a fume hood until thin films were formed, and the film transparency was evaluated macroscopically.

The information on the molecular structure of CNs was acquired by FTIR spectroscopy. IR spectra were recorded on an Infracum-801 spectrometer (NPF Simex, Russia) in the frequency range of $4000\text{--}500\text{ cm}^{-1}$. To take spectra, pellets were pressed in potassium bromide in an CN/KBr ratio of 1:150.

The CN samples were characterized by ^{13}C NMR spectroscopy on a Bruker Avance 400 MHz NMR spectrometer (Bruker, Germany) at 60°C with an operating frequency of 100.61 MHz, with $\text{DMSO-}d_6$ solvent.

Additionally, CNs were analyzed by DSC on a DTG-60 thermogravimetric analyzer (Shimadzu, Japan): 0.5 mg sample weight, $10^\circ\text{C}/\text{min}$ heating rate, 350°C maximum temperature, and nitrogen as inert medium.

All the reagents were manufactured in Russia: nitric acid (AO Azot), sulfuric acid (SigmaTec), sodium hydroxide (AO Kaustik), acetone (GC Titan), diethyl ether (Kuzbassorghim), ammonium ferrous sulphate (Khimreaktiv), ethylenediamine (Chemiline), mixed acid (Biysk Oleum Factory).

The analyses were done with instruments of the Biysk Regional Center for Shared Use of Scientific Equipment of the SB RAS (IPCET SB RAS, Biysk).

3 Results and discussion

In the manufacture of products for defense and civil industries, the highest quality CNs are produced from linter or wood cellulose having an α -cellulose content of 92–98% and the lowest overall content of non-cellulosics. The chemical composition of cellulose samples obtained from *Miscanthus*, oat hulls, and intermediate flax straw by the nitric-acid process at the pilot production site of the IPCET SB RAS are summarized in Table 1.

Cellulose samples isolated from the unconventional feedstocks by the nitric-acid process exhibit a high α -cellulose content of 88–94 % and a high degree of polymerization at 820–1420 (Table 1). The overall

content of non-cellulosic constituents of the *Miscanthus*, oat hull and intermediate flax straw celluloses is 3.43 %, 3.03 % and 5.0 %, respectively, which makes the preparation of CNs highly soluble in the alcohol-ester mixture, problematic.

Table 1. Chemical composition of cellulose samples obtained from *Miscanthus*, oat hulls, and intermediate flax straw by the nitric-acid process at the pilot production site of IPCET SB RAS.

Cellulose sample	Content, %				DP
	α -Cellulose	Acid-insoluble lignin	Pentosans	Ash	
<i>Miscanthus</i>	90.70	1.81	0.67	0.95	940
Oat hulls	94.29	0.32	2.30	0.41	1420
Intermediate flax straw	87.83	2.41	1.10	1.49	820

The comparison between the celluloses showed that the oat hull cellulose had the best quality (94 % α -cellulose and 1420 DP) together with a high natural homogeneity, and therefore the oat hull cellulose is preferred for preparing CN and making composite explosives.

Physicochemical characteristics of the obtained CNs and commercial, high-viscosity, lacquer-grade, cotton Colloxylin (CC) are listed in Table 2.

Table 2. Physicochemical characteristics of *Miscanthus*, oat hull and intermediate flax straw CNs and of cotton Colloxylin.

CN sample	Characteristics		
	Mass fraction of nitrogen, %	2% CN-acetone solution viscosity, mPa·s	Solubility in alcohol-ester mixture, %
M	12.26	14	98
OH	12.12	10	98
IFS	12.04	12	98
CC	12.34	15	98

It is seen from data in Table 2 that the CN samples from *Miscanthus*, oat hulls and intermediate flax straw have nearly the same parameters: 12.04–12.26% mass fraction of nitrogen, 10–14 mPa·s viscosity, and 98% solubility in alcohol-ester mixture. The comparison between the CN samples shows that they are comparable.

The high solubility values of the experimental CNs (98%) and the transparency of the CN films dried after analysis suggest that no nitrated hemicellulose residues are present in the CNs. The CNs obtained from the unconventional feedstocks are commensurable in properties listed in Table 2 with the commercial, high-viscosity, lacquer-grade, cotton Colloxylin and with other commercial Colloxylin, which indicates their further potential for use in composite explosives.

The assignment of bands in the IR spectra of the *Miscanthus*, oat hull and intermediate flax straw CNs and of the commercial, high-viscosity, lacquer-grade, cotton Colloxylin is set out in Table 3.

Table 3. Band assignment in IR spectra of *Miscanthus*, oat hull and intermediate flax straw CNs and of cotton Colloxylin.

Assignment	CN			
	M	OH	IFS	CC
	Frequency, cm ⁻¹			
$\nu(\text{OH})(\text{OH}\dots\text{OH})$ stretching	3569	3568	3564	3439
$\nu(\text{CH}_2)$ stretching	2925	2922	2921	2922
$2\nu(\text{NO}_2)$ stretching	2559	2558	2559	2557
$\nu_a(\text{NO}_2)$ stretching	1659	1660	1666	1660
$\sigma(\text{CH}_2)$ bending	1631	1639	1632	1646
$\sigma(\text{COH})$ bending	1435	1428	1444	1430
$\sigma(\text{CH})$ bending	1379	1379	1379	1381
$\nu_s(\text{NO}_2)$ symmetric valence	1275	1277	1275	1271
$\nu(\text{C-O})$ stretching	1164	1164	1165	1167
$\nu(\text{C-O})$ stretching	1071	1072	1074	1073
$\sigma(\text{CH})$ bending	1002	1000	1002	1001
$\nu(\text{NO}_2)$ stretching	822	825	823	812
$\gamma_w(\text{NO}_2)$ wagging	744	747	745	746
$\delta(\text{NO}_2)$ scissoring	683	681	680	680

All the IR spectra of the synthesized CNs show intrinsic frequencies indicating the structural features of CN macromolecules.

It follows from data in Table 3 that the IR spectra of the CNs have $\nu(\text{OH})$ stretching peaks as a broad band with complex contour around 3700–3200 cm⁻¹, which suggests an incomplete substitution of CN. Those peaks belong to CN hydroxyls involved in hydrogen bonding and are a fingerprint of the chemical inhomogeneity of CN.

The absorption band around 2925–2921 cm⁻¹ is responsible for CH stretching. Stretching vibrations of nitrate groups relate to the absorption band around 2559–

2557 cm^{-1} . Several bands are overlapped in the IR spectra of the CNs around 1700–1500 cm^{-1} .

The absorption band around 1666–1659 cm^{-1} was assigned to $\nu_a(\text{NO}_2)$ associated with CH groups of the glucopyranose rings of CN (position $\text{C}_{(2)}$ and/or $\text{C}_{(3)}$). The intense band around 1646–1631 cm^{-1} was attributed to $\nu_a(\text{NO}_2)$ associated with CH_2 groups of glucopyranose rings of CN (position $\text{C}_{(6)}$). This is in good agreement with assignment data of the $\nu_a(\text{NO}_2)$ band of primary and secondary alcohols. The substitution of OH group by NO_2 group is known to occur mostly at the $\text{C}_{(6)}$ position and inequally at positions $\text{C}_{(2)}$ and $\text{C}_{(3)}$, depending on the etherification degree.

The absorption band around 1444–1428 cm^{-1} was attributed to CH_2 sissoring vibrations. The IR spectra of the CNs have absorption bands around 1381–1379 cm^{-1} and 1277–1271 cm^{-1} , whose intensities markedly decrease as the mass fraction of nitrogen declined. The band at 1381–1379 cm^{-1} was assigned to bending vibrations of CH groups in CH_2ONO_2 . The absorption band at 1277–1271 cm^{-1} correspond to NO_2 symmetric stretch. The absorption band at 1167–1164 cm^{-1} refers to stretching vibrations of glycosidic linkage. In the region of 1100–1000 cm^{-1} , there is a band at 1074–1071 cm^{-1} relating to stretching of C-O bonds linking the pyranose rings. In the IR spectra of the CNs, there appear some bands due to the absorption of nitrate groups around 825–812, 747–744 and 683–680 cm^{-1} pertaining to N-O stretch, NO_2 out-of-plane pendulum vibrations and N-O in-plane bending, respectively [25].

The comparison between the IR spectra of the CNs obtained from the unconventional feedstocks and of the high-viscosity, lacquer-grade, cotton Colloxyline showed their likeness in terms of basic absorption bands corresponding to nitro group vibrations. The absorption bands of the *Miscanthus*, oat hull and intermediate flax straw CNs were also found to correspond to the reference data on commercial Colloxyline, validating CNs derived from the unconventional feedstocks.

^{13}C NMR spectra of the *Miscanthus*, oat hull and intermediate flax straw CNs and of the high-viscosity, lacquer-grade, cotton Colloxyline are given in Figure 1.

The ^{13}C NMR spectra of the synthesized CNs show chemical shifts representative of 6-mononitrocellulose at 102.1 ppm, 2,6-dinitrocellulose at 97.4 ppm, 3,6-dinitrocellulose at 82.8, 82.9 and 83.0 ppm, and 2,3,6-trinitrocellulose at 99.0, 99.2, 79.3 and 79.4 ppm [25].

The *Miscanthus*, oat hull and intermediate flax straw CNs were found to hold 6-mono-, 2,6-di- and 2,3,6-trisubstituted moieties of the pyranose ring, and most chemical shifts of the *Miscanthus*, oat hull and intermediate flax straw CNs match those of the high-viscosity, lacquer-grade, cotton Colloxyline, indicating that the chemical structure of the CNs obtained from the said unconventional feedstocks are identical to the cotton CN.

The TGA/DSC characteristics of the CNs obtained from *Miscanthus*, oat hulls and intermediate flax straw and of high-viscosity, lacquer-grade, cotton Colloxyline are given in Table 4.

DSC calorimetry revealed that all the CNs shared one narrow exothermic peak between 209°C and 212°C

accompanied by the sample weight loss to 82–91%. TGA curves of the CNs derived from the unconventional feedstocks coincide with those of the high-viscosity, lacquer-grade, cotton Colloxyline. The findings obtained herein suggest a high chemical purity of the synthesized CNs [14, 25]. The present exothermic peak and heat of decomposition in the range of 6–7 kJ/g in the inert medium indicate a highly energetic nature of the substance decomposition.

Fig. 1. ^{13}C NMR spectra of CNs obtained from (a) *Miscanthus*; (b) oat hulls; (c) intermediate flax straw and (d) high-viscosity, lacquer-grade, cotton Colloxyline.

Table 4. TGA/DSC characterization of CNs obtained from *Miscanthus*, oat hulls and intermediate flax straw and of cotton Colloxyline.

CN sample	Characteristics		
	Weight loss, %	Exothermic peak, °C	Heat, kJ/g
M	85	212	6,66
OH	91	211	7,54
IFS	82	210	6,28
CC	86	209	5,83

4 Conclusion

Cellulose nitrates (CNs) have been synthesized from domestic unconventional feedstocks such as *Miscanthus*, oat hulls and intermediate flax straw by an industrial technique using mixed acid, and exhibit similar physicochemical properties: 12.04–12.26% mass fraction of nitrogen, 10–14 mPa·s viscosity, and 98% solubility in alcohol–ester mixture. The IR spectra of the CNs derived from *Miscanthus*, oat hulls, and intermediate flax straw show basic absorption bands corresponding to nitro group vibrations: 2559–2557, 1646–1631, 1277–1271, 825–812, 747–744, and 683–680 cm⁻¹. The ¹³C NMR spectra of the synthesized CNs have chemical shifts typical of 6-mononitrocellulose, 2,6-dinitrocellulose, 3,6-dinitrocellulose, and 2,3,6-trinitrocellulose. DSC reveals that the prepared CNs have a high-temperature exothermic peak (209–212°C) with the weight loss to 82–91%, indicating that the CNs are high quality.

The comparison between the unconventional feedstock-derived CNs and high-viscosity, lacquer-grade, cotton Colloxylin shows that the experimental CNs match commercial Colloxylin in terms of basic properties and can therefore be advised as the component of composite explosives. Our suggestion to replace cotton nitrocellulose by CNs from alternative feedstocks is justified by their comparable basic properties but is not evident because the polymer inhomogeneity together with the considerable mass content of short fibers do not guarantee a high plasticizing ability of the experimental CNs. Nevertheless, the positive findings obtained in this study allow us to continue the started research.

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