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. \(^{13}\)C 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 Colloxylins, 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 Colloxylins 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 cellulosens [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-Kα radiation), gas liquid chromatography (Agilent liquid chromatography series 1100), etc. [19, 20], as well as 13C 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 perennial 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 about all 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±2°C with 0.4% HNO₃, 5% HNO₃, 2% NaOH, and 0.8% NaOH prior to eventual decationation (souring) by treatment with 0.8% HNO₃ 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±2°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±2°C; 1.5 h autoclaving in 0.3% HNO₃ at 130±2°C; 3 h boiling in 0.03% Na₂CO₃ at 85±2°C followed by 1 h exposure to water at 85±5°C [21, 22].

The CN samples were dried at room temperature and then at 100±2°C for 1 h 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 [Fe(NO)₃SO₄ 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 InfraLab-801 spectrometer (NPF Simex, Russia) in the frequency range of 400–500 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 13C NMR spectroscopy on a Bruker Avance 400 MHz NMR spectrometer (Bruker, Germany) at 60°C with an operating frequency of 100.61 MHz, with DMSO-d₆ solvent.

Additionally, CNs were analyzed by DSC on a DTG-60 thermogravimetric analyzer (Shimadzu, Japan): 0.5 mg sample weight, 10°C/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 (Kuzbasorghim), 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.

<table>
<thead>
<tr>
<th>Cellulose sample</th>
<th>Content, %</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Cellulose</td>
<td>90.70</td>
<td>940</td>
</tr>
<tr>
<td>Acid-insoluble lignin</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td>Pentosans</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>0.95</td>
<td></td>
</tr>
</tbody>
</table>

The comparison between the cellulosics 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 and with other commercial Colloxyliams, 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 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.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>CN</th>
<th>Frequency, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(ОН)(ОН…ОН) stretching</td>
<td>M</td>
<td>3569 3568 3564 3439</td>
</tr>
<tr>
<td>v(CH₃) stretching</td>
<td>OH</td>
<td>2925 2922 2921 2922</td>
</tr>
<tr>
<td>2v(NO₂) stretching</td>
<td>IFS</td>
<td>2559 2558 2559 2557</td>
</tr>
<tr>
<td>v_(NO₂) stretching</td>
<td>CC</td>
<td>1659 1660 1666 1660</td>
</tr>
<tr>
<td>v(CH₂) bending</td>
<td></td>
<td>1631 1639 1632 1646</td>
</tr>
<tr>
<td>v(COH) bending</td>
<td></td>
<td>1435 1428 1444 1430</td>
</tr>
<tr>
<td>v(CH) bending</td>
<td></td>
<td>1379 1379 1379 1381</td>
</tr>
<tr>
<td>v_(NO₃) symmetric valence</td>
<td></td>
<td>1275 1277 1275 1271</td>
</tr>
<tr>
<td>v(C-O) stretching</td>
<td></td>
<td>1164 1164 1165 1167</td>
</tr>
<tr>
<td>v(C-O) stretching</td>
<td></td>
<td>1071 1072 1074 1073</td>
</tr>
<tr>
<td>v(CH) bending</td>
<td></td>
<td>1002 1000 1002 1001</td>
</tr>
<tr>
<td>v(NO₂) stretching</td>
<td></td>
<td>822 825 823 812</td>
</tr>
<tr>
<td>γw(NO₂) wagging</td>
<td></td>
<td>744 747 745 746</td>
</tr>
<tr>
<td>δ(NO₂) sissoring</td>
<td></td>
<td>683 681 680 680</td>
</tr>
</tbody>
</table>

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 v(ОН) 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 \(v_3(\text{NO}_2)\) associated with CH groups of the glucopyranose rings of CN (position C\(_{12}\) and/or C\(_{13}\)). The intense band around 1646–1631 cm\(^{-1}\) was attributed to \(v_2(\text{NO}_2)\) associated with CH\(_2\) groups of glucopyranose rings of CN (position C\(_{19}\)). This is in good agreement with assignment data of the \(v_2(\text{NO}_2)\) band of primary and secondary alcohols. The substitution of OH group by NO\(_2\) group is known to occur mostly at the C\(_{40}\) position and inequally at positions C\(_{25}\) and C\(_{39}\), 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\(_2\)ONO\(_2\). 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 Colloxylins, 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 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 Colloxylins, 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 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 Colloxylins, validating CNs derived from the unconventional feedstocks.

The \(^{13}\)C NMR spectra of the Miscanthus, oat hull and intermediate flax straw 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 Colloxylin, 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 Colloxylin 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 Colloxylin. 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.

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

<table>
<thead>
<tr>
<th>CN sample</th>
<th>Characteristics</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Weight loss, %</td>
</tr>
<tr>
<td>M</td>
<td>85</td>
</tr>
<tr>
<td>OH</td>
<td>91</td>
</tr>
<tr>
<td>IFS</td>
<td>82</td>
</tr>
<tr>
<td>CC</td>
<td>86</td>
</tr>
</tbody>
</table>
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. The¹³C 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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