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Chemical Composition of Russian Miscanthus and the Quality of Cellulose Obtained Therefrom

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Abstract

Chemical compositions were determined for two miscanthus crops harvested from one-year-old and two-year-old plantations (the whole plant, stems and leaves taken separately). The content of non-cellulosic components (fat-and-wax fraction, ash, acid-insoluble lignin) in the leaves was revealed to be higher as compared with the corresponding parameters for the stems, whereas cellulose and pentosans in the stem are prevailing. It has been demonstrated that the cellulose species obtained with the help of a nitric-acid method from the leaves and stems, taken separately, are varying in quality and yield. The ash level and the residual lignin content inherent in the cellulose obtained from leaves is higher than that for the cellulose obtained from the stems, whereas the mass fraction of α-cellulose and the polymerization level of cellulose obtained from the leaves are lower as compared to those for the cellulose produced from the stems. It was found that the cellulose from the miscanthus stems taken from two-year-old plantations, is characterized by a high quality: the mass fraction of α-cellulose is equal to 94 %, PL 800, ash content 0.07 %, the mass fraction of residual lignin 0.5 %, that of pentosans amounting to 0.4 %.

Key words: Russian miscanthus, ash, fat-wax fraction, cellulose according to Kürschner, nitric acid method, α-cellulose, residual lignin, level of polymerization

INTRODUCTION

Cellulose-containing raw (CCR) is a valuable material for a number of industries, including pulp-and-paper industry, chemical industry, and energy production industry. From this standpoint, in the world nowadays there is only one significant source of industrial cellulose that is presented by wood [1]. However, in order to save the forest wealth as a promising CCR, researchers actively investigate non-arboreal plants [2].

One of such commercially important plants is presented by miscanthus (lat. *Miscanthus*), a perennial herbaceous plant belonging to Gramineae family. Currently, extensive studies are being performed abroad concerning the possibility of processing different miscanthus species: mainly *Miscanthus giganteus*, *Miscanthus sinensis* and *Miscanthus sacchariflorus* [3]. In Russia, at the Institute of Citology and Genetics (ICG) of the SB RAS (Novosibirsk) there has been an author's form of *Miscanthus sinensis* Andersson raised, with a restructured the root system that develops long shoots with growth buds to quickly colonize soil space, with a continuous and smooth (with no bumps) miscanthus plantation. The authors of [4] demonstrated that using conventional agricultural technologies, one could get 10–15 tons of dry miscanthus biomass from 1 ha per year [4].

In 2011 at the IPCET of the SB RAS (Biysk) there has been an experimental plantation of Russian miscanthus founded, whose planting material was provided by the researchers of ICG, SB RAS [5, 6]. The mentioned plant is positioned as a prospective CCR for the isolation of cellulose and for obtaining the products of the chemical modification thereof [7] as well as for the biochemical transformation into glucoseand-pentose hydrolysates with the subsequent conversion into ethanol, lactic acid, bacterial cellulose, *etc.* [8].

The purpose of this work consisted in determining the chemical composition of miscanthus grown on plantations of one (2011) and two (2012) years old in the Altai Territory, as well as in a comparative analysis of the quality of cellulose obtained from the miscanthus leaves and stems, taken separately, for the crop of 2012.

EXPERIMENTAL

The first object of our investigation was presented by a one-year-old *Miscanthus sinensis* Andersson, cultivar "Soranovskiy", harvested in 2011 grown on the experimental plantation at the IPCET of the SB RAS. In October 2011, we harvested all the plants *via* cutting, from the area of 61 m^2 we gathered 848 plants, 30 whereof had panicles (3.5 % of the total harvest). The average density of shoots amounted to 14 plants per 1 m^2. The mass of the total crop amounted to 2.8 kg, the mass of miscanthus without panicles being equal to 2.5 kg (91 %). The longest plant was 1.60 m high.

The second object of our investigation was presented by miscanthus harvested in 2012, grown on the same plantation after cutting the first harvest. Harvesting was carried out in the beginning of October, 2012. The mass of the total crop was equal to 12.3 kg (0.2 kg per 1 m^2), the density of shoots amounted to 39 plants per 1 m^2. The average length of a ripe miscanthus (with a panicle) is equal to 2.0 m, but some plants reached 2.40 m. The average mass fraction of leaves is equal to 0.539.

In order to study the chemical composition of miscanthus, we selected mature plants with a maximum height and inflorescence panicles, to investigate the composition of a plant as a whole, as well as leaves and stems taken separately. All the samples of miscanthus were minced with scissors. The determination of ash content (basing on absolutely dry raw material, a. d. r.), the mass fraction of the extractive substances such as fat-wax fraction (FWF) (extracting agent dichloromethane, a. d. r..), acid-insoluble lignin (a. d. r..) and cellulose (Kürschner method, a. d. r.) was performed by means of standard analytical methods for vegetable raw materials [9]. The fatty acid composition of FWF was analyzed in oil triglycerides according to the method described by the authors of [10], using gas chromatography method with the help of a Kristallyuks 4000M gas laboratory chromatograph (Russia, Yoshkar-Ola) with a flame ionization detector and programming the temperature. The humidity level was determined using a MB23/MB25 humidity analyzer (OHAUS, USA). The confidence intervals for determining the components in the raw material were as it follows: for determining the mass fraction FWF and ash content ±0.05; for determining the mass fraction of acid-insoluble lignin, cellulose according to Kürschner, pentosans ±0.5.

For obtaining the cellulose we used miscanthus harvested in 2012 from a two-years-old plantation. The cellulose was obtained using a nitric-acid method [11] that comprises the following stages: a preliminary hydrolysis by 0.5–1.0 % nitric acid solution to obtain a cellulose-containing product (CCP); nitric-acid cooking the CCP in 4 % nitric acid solution to obtain a lignin-cellulose material (LCM); a subsequent LCM processing with 2 % sodium hydroxide solution of at the temperature equal to 90–96 °C to produce technical grade cellulose (TGC); souring (decationation), the treatment with a solution of 1 % nitric acid to obtain target cellulose.

The analysis of the ash content, the content of residual (insoluble in acids) lignin and α-cellulose was carried out according to standard procedures for intermediate products and cellulose [9], the analysis of pentosans was performed using Fe orcinol reagent (Acros organics, Belgium) according to the procedure described by the authors of [9, 12], the polymerization level (PL) was determined with the use of a viscometry in cadoxen [9, 13].

RESULTS AND DISCUSSION

In the foreign literature there are no data available concerning the componential composition of miscanthus grown on a plantation of one year old. As far as the Russian literature is concerned, a quantitative composition is presented therein for one-year old miscanthus harvested from the plantation of the ICG of the SB RAS (Novosibirsk Region) in 2009 [14].

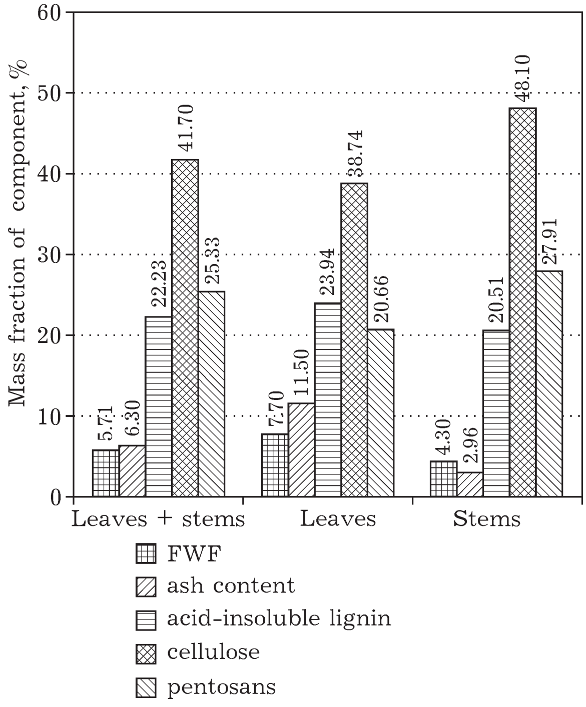

Fig. 1. Content of fat-and-wax fraction, of ash, acid-insoluble lignin, cellulose, pentosans in the whole plant of one-year-old miscanthus harvested in 2011, as well as in the leaves and stems taken separately.

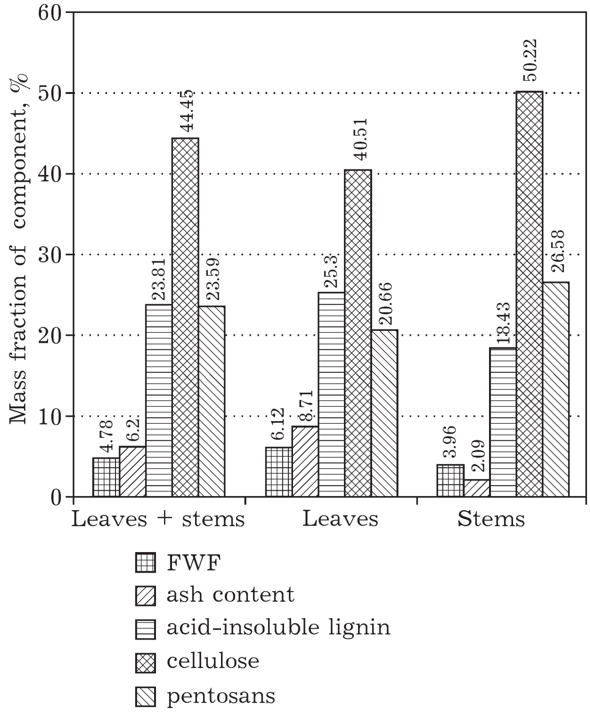

Fig. 2. Content of fat-and-wax fraction, of ash, acid-insoluble lignin, cellulose, pentosans in the whole plant of two-year old miscanthus harvested in 2012 from two-year-old plantation, as well as in the leaves and stems taken separately.

The chemical composition of one-year-old miscanthus harvested in 2011 from the plantations of the IPCET of the SB RAS (the whole plant, leaves and stems taken separately) is presented in Fig. 1. It can be seen that the plant as a whole is characterized by a satisfactory cellulose content amounting to 41.70 mass %. As to compare with the data obtained in [14], the plants harvested in 2011 are characterized by increased ash content and an increased mass fraction of acid-insoluble lignin: 6.30 *vs.* 5.56 % and 22.2 *vs.* 18.5 %, respectively. The mass fraction of FWF is also higher as to compare with similar data for the one-year-old plants grown within a colder area: 5.71 and 4.30 %, respectively [14]. The chemical composition of FWF involves 24 fatty acids, those are mainly non-identified, because they are absent in the Russian library database for edible and industrial oils. Among identified acids there are the following ones myristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, arachidic, behenic acid. The results concerning the identified acids are in a good agreement with data concerning the saturated and unsaturated fatty acids inherent in the FWF extracted by dichloromethane from a ripe miscanthus of European origin [15].

The comparative analysis of the chemical composition leaves and stems taken separately demonstrated that the leaves contain a higher mass fraction of non-cellulosic components: FWF (7.70 and 4.30 %, respectively), ash (11.50 and 2.96 %, respectively), and lignin insoluble in acids (23.94 and 20.51 %, respectively). Taking into account that this plant is was grown in unprepared soil with no fertilizing, a high value of ash content observed in the leaves of miscanthus could be explained only by the botanical characteristics of the plant (cereal). The mechanical strength of the leaves of miscanthus could be associated with a high content of lignin, which gives plasticity to the long flexible leaves of the plant. It should be noted that the difference between the cellulose content in the stems and leaves is significant amounting up to 10 %.

Data concerning the chemical composition of miscanthus harvested in 2012 from the two-years-old plantation (whole plant, leaves and stems taken separately) are demonstrated in Fig. 2. As to compare with the chemical composition of first-year plants, the mentioned chemical composition can be characterized by a slight decrease in the mass fraction of FWF (4.78 and 5.71 %, respectively) and a slight increase in the mass fraction of cellulose (44.45 and 41.7 %, respectively).

As far as the chemical composition of the leaves and stems taken separately is concerned, the leaves of miscanthus exhibit a higher mass fraction of non-cellulosic components as to compare with the stems, as it follows: FWF (6.12 and 3.96 %, respectively), ash (8.71 and 2.09 %, respectively), acid-insoluble lignin (25.3 and 18.4 %, respectively). In a similar manner, the chemical composition of the miscanthus harvested in 2011 exhibits the difference between the cellulose content in the stems and that in the leaves amounting up to 10 %. The mass fraction of pentosans is higher in the stems than in the leaves: 26.6 and 20.7 %, respectively.

From the comparison of the miscanthus harvested in 2011 and 2012, it can be noted that the cellulose is concentrated in the stems, whereas non-cellulosic components (except pentosans) prevail in the leaves. This regularity was described for the straw of cereals by the authors of [16, 17]. As far as the different genotypes of foreign miscanthus is just concerned, there is no information available about any quantitative difference between the componential composition of leaves and stems, and it was recommended to process the whole plant [18], without removing the leaves.

The dependence of the cellulose content on the age of plantations revealed by the authors of [14] can be observed also for the present samples of raw material: the cellulose content in the stem of mature plants is higher than that inherent in one-year-old plants (50.2 and 48.1 mass %, respectively). However, the cellulose content in the miscanthus harvested in 2012 could be even much greater if the weather conditions in the Altai Territory were not abnormal from early April to mid-September of 2012. Owing to rainfall deficiency in April, the quality of the seedlings of cultivated and wild plants was very low, whereas the aridity phenomena and abnormally hot weather observed in May and June led to withering the cereal crops already in the first half of the summer. Even perennial grasses suffered, which grasses began to ear already in early June, whereas further they withered.

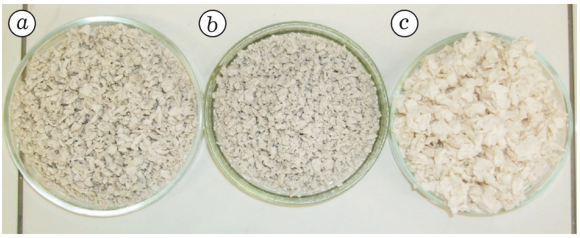

Fig. 3. Photographs of cellulose samples obtained using a nitric acid method from miscanthus harvested in 2012 (two-year-old plantation): *a* – from the whole plant (leaves + stems), *b* – from the leaves, *c* – from the stems.

Thus, as the result of determining the chemical composition of the Russian miscanthus taken from the one-year-old and two-year-old plantations, we found out a well-formed difference in the content of components for the leaves and stems, in favour of the latter, as well as an age-related pattern of changing the content of non-cellulosic components in the plant as a whole.

In this connection, we have obtained the samples of cellulose from the whole plant, leaves and stems taken separately (Fig. 3). They differ from each other in appearance, especially the cellulose samples obtained separately from leaves and stems: the former represents a gray powder with short fibres, the latter represents white "short cotton" (wadding) with long fibres difficult for grinding. Table 1 presents data concerning the yields and characteristics of cellulose samples produced using a nitric-acid method from the miscanthus harvested in 2012.

Foreign methods for miscanthus processing into cellulose involve sulphate and sulphite processes conventional for wood, soda cooking (alkaline delignification under pressure), bleaching by means of chlorine-containing agents and hydrogen peroxide, modified methods of using the anthraquinone catalyst, as well as so-called organosolv processes such as the treatment by a mixture of phenol with dilute hydrochloric acid (Battelle method) and by a mixture of acetic acid with dilute hydrochloric acid (acetosolv process) [3, 18]. The nitric-acid method for producing the cellulose from miscanthus

TABLE 1

Yields and characteristics of celluloses produced using a nitric-acid method from miscanthus harvested in 2012 (from the whole plant, leaves and stems taken separately)

Raw	Yield*, %	Ash content, %	Mass fraction, %			PL
			Lignin	α-Cellulose	Pentosans	
Whole plant	23.0±0.1	0.62±0.05	1.59±0.05	91.8±0.5	0.67±0.05	830
Leaves	20.3±0.1	1.01±0.05	1.51±0.05	91.7±0.5	0.43±0.05	580
Stems	28.7±0.1	0.07±0.05	0.45±0.05	94.4±0.5	0.40±0.05	800

* Calculated for a. d. r.

we developed [11] was first tested under the laboratory-scale and pilot conditions [7, 14, 19]. The yield of cellulose at the level of 23 % with respect to the mass of raw material or 52 % with respect to the mass of native cellulose therein is substantiated by complicated processes of lignin and hemicellulose oxidative destruction, as well as by decreasing the content of the amorphous part of cellulose in the product. Nevertheless, due to the high quality of cellulose obtained from miscanthus it can be used for further chemical modification, including for obtaining esters (cellulose nitrate) [20, 21]. It should be noted that a high α-cellulose content (92–94 mass %) and high PL (830) in the target product, (although the native PL of cellulose inherent in the miscanthus of separate genotypes is not higher than 1400 [3]), as well as a low total content of non-cellulosic impurities (ash, lignin and pentosans) lower than 3 mass % in the final product could be attained via miscanthus treatment with dilute solutions of nitric acid and sodium hydroxide, under the conditions and we sequence proposed using a standard equipment with a capacity of 250 L or more.

Comparing the sample of cellulose obtained from the leaves and stems demonstrate that the parameters for the samples prepared from the stems are better (see Table 1). Furthermore, the total content of non-cellulosic components in the sample obtained from the stem is three times lower than that in the sample of leaves: 0.95 and 2.95 mass %, respectively.

Thus, the stem of a rather young miscanthus (two-years-old plantation) could produce high quality cellulose with a 29 % yield that exhibits the mass fraction of α-cellulose 94 %, PL 800, ash content 0.07 %, the mass fraction of residual lignin 0.5 % pentosans – 0.4 %.

The most suitable raw material for obtaining the cellulose from miscanthus is presented by crop with a minimal mass fraction of leaves, *i. e.* that grown on the plantations with a maximum planting density [4].

Comparing the basic characteristics of the cellulose obtained from the stems of miscanthus with the elite cotton cellulose (the mass fraction of α-cellulose being at least 96 %, that of a residue insoluble in sulphuric acid (an analog of lignin) being lower than 0.5 %, the ash content being less than 0.3 %, the PL ranges from 300 to 2000 depending on grade), and the basic characteristics of wood cellulose (the mass fraction of α-cellulose being at least 92 %, that of lignin being lower than 0.4 %, the ash content being less than 0.3 %) indicates a high quality of the sample prepared basing on the miscanthus stems. The mentioned cellulose species are suitable for the preparation of nitrates with the properties required for implementation in the civil (lacquers, printing inks, different glue grades including medical ones) and defense (colloxylin powder) industries. It should be noted that combining the nitric acid method for producing cellulose from miscanthus and cellulose nitration in one processing line could allow simplifying significantly a general flowchart for obtaining the demanded cellulose nitrates from any alternative types of cellulose-containing raw materials.

CONCLUSION

Chemical compositions were determined for two miscanthus crops harvested from one-year-old and two-year-old plantations (the whole plants, stems and leaves taken separately). The content of non-cellulosic components (fat-and-wax fraction, ash, acid-insoluble lignin) in the leaves was revealed to be higher as compared with the corresponding parameters for the stems, whereas cellulose and pentosans in the stem are prevailing.

It has been demonstrated that the cellulose obtained with the help of nitric-acid method from the leaves and stems, taken separately, are varying in quality and yield: the ash level and the residual lignin content inherent in the cellulose obtained from leaves is higher than that for the cellulose obtained from the stems, whereas the mass fraction of α-cellulose and the polymerization level of cellulose obtained from the leaves are lower as compared to those for the cellulose produced from the stems.

It has been found that the cellulose from the miscanthus stems taken from two-year-old plantations, is characterized by a high quality: the mass fraction of α-cellulose is equal to 94 %, PL 800, ash content 0.07 %, the mass fraction of residual lignin 0.5 %, that of pentosans amounting to 0.4 %.

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