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Characteristics of Cellulose Produced Using a Hydrotropic Method in a Universal Thermobaric Unit

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Abstract

A process of cellulose producing from miscanthus by means of a hydrotropic method using a universal thermobaric unit was studied. An expediency of additional washing the technical grade cellulose by hydrotropic solution was vindicated. Main characteristics are presented for the products obtained depending on the conditions of delignification. The hydrotropic method for processing the cellulose-containing raw materials has been demonstrated to be universal with and the results being reproducible.

Key words: hydrotropic cooking, miscanthus, universal thermobaric unit, technical grade cellulose, lignin

INTRODUCTION

Known methods for processing cellulose-containing raw materials are characterized by the use of acidic or alkaline reagents, so current research works are aimed at reducing or avoiding the use of polluting chemical compounds [1, 2]. The hydrotropic processing plant raw materials belongs to neutral methods because it does not require for using sulphur- and chlorine-containing reagents. Cooking is carried out with a neutral solution of hydrotropic salt, consequently, the plant material undergo a softer impact as compared with acidic treatment under the conditions of the sulphite method or alkali treatment under the conditions of soda sulphate cooking [3]. Owing to this, there is increasing the yield of cellulose with a high content of α-cellulose (high polymer part), whereas plant tissue components themselves undergo minor changes as compared to the natural state thereof.

As hydrotropic reagents one uses sodium benzoate, xylene sulphonate or toluene sulphonate aqueous solutions Sodium benzoate is used in Russia and Europe as a food preservative, it is considered a safe product with a low price and unlimited availability. The other reagents are less common and less accessible.

The development of a hydrotropic method for processing a cellulose-containing raw material by the example of oat fruit coat [4, 5] and Russian miscanthus [6–8] represents one of the most important results of fundamental research for 2010–2012 conducted in the Siberian Branch of the RAS [9].

The purpose of this work consisted in studying the hydrotropic method for obtaining technical grade cellulose from miscanthus using a new type of equipment and in a qualitative analysis of the products.

EXPERIMENTAL

As the object of investigation, we used *Miscanthus sinensis* Andersson harvested in 2008 grown in the plantations of the Institute of

Cytology and Genetics of the SB RAS, the Novosibirsk Region [10]. Before starting the investigation, the miscanthus was ground into chaff, 10–15 mm in size.

The chemical composition of miscanthus, mass % as calculated for absolutely dry raw material, a. d. r.: cellulose (according to Kürschner) 57.4, pentosans 23.3, acid-insoluble lignin 19.1, ash 3.9.

The delignification was carried out using a universal thermobaric unit (UTU) [11], with the capacity of the reaction chamber equal to 2.3 L. The unit is purposed for carrying out the processes under excess pressure, so the body is made of a thick-walled cylindrical shell with upper and lower flat welded flanges. The temperature mode of cooking is initiated by external electrical heating tape elements located along the chamber. In the course of operating, the working chamber was swinged with high amplitude. This type of equipment is designed for the processing of vegetable raw materials in different media [12, 13].

The hydrotropic delignification process was performed as it follows. A weighed sample portion of the raw material (100 g) was placed into the UTU reaction chamber to add a 35 % solution of sodium benzoate (Fooding Group Ltd., China) with the modulus of 1 : 10. The chamber was sealed with further turning on the stirring and heating. The cooking mode was as it follows: increasing the up to temperature 180 °C during 40 min, boiling at 180 °C within the range of 3–5 h. The pressure in the reaction chamber in the course of cooking was equal to 1.0 MPa. Upon the completion of the cooking process the heating was turned off and the UTU was left for natural cooling the reaction mixture in the chamber to a room temperature. Thereafter, the reaction mass was discharged from the chamber with further squeezing and washing the cellulose to remove the spent cooking liquor.

The cellulose was washed with a fresh portion of 35 % sodium benzoate solution at 90–95 °C for 1 h under gentle stirring (module 1 : 20). Further, we performed squeezing the cellulose to remove the hydrotropic solution to repeat the washing with a 20 % solution of sodium benzoate under the same conditions. After squeezing, the technical grade cellulose (TGC) was washed with distilled water at a room temperature to obtain a colourless washing solution (three washing procedures, module 1 : 25), then it was squeezed and dried in air to reach a 7–10 % humidity level.

The content of acid-insoluble lignin, ash, cellulose according to Kürshner, α-cellulose, and pentosans was determined by means of standard methods for the analysis of raw materials and the products of processing thereof [14]. The humidity level was determined using an Ohaus MB 23 humidity analyzer (USA).

RESULTS AND DISCUSSION

Earlier it was established [15] that the dissolving ability of hydrotropic solutions exhibits an increase with increasing the concentration, so the hydrotropic cooking of miscanthus in the UTU was carried using a 35 % solution of sodium benzoate. Further increasing the concentration of the hydrotropic solution is impractical for economic reasons, besides, these results in the solution supersaturation to complicate the squeezing of cellulose. On the other hand, the solution with the concentration lower than 30 % loses the dissolving ability required for a more complete delignification of raw materials.

To prevent the loss of lignin and settling it on the cellulose fibres, we paid special attention to cellulose washing in the course of hydrotropic cooking [3, 6–8, 16]. In order to demonstrate the effect of washing by hydrotropic solution on the quality of the technical grade cellulose obtained we conducted an experiment wherein the washing was carried out with the use of water rather than the solution of sodium benzoate. For this purpose we performed a repeated cooking of miscanthus in the UTU at 180 °C for 3 h (module 1 : 10), but after discharging the pulp from the cooking apparatus and squeezing the product, it was washed with distilled water until the wash water discoloration. The sample was then dried at a room temperature to be analyzed for determining main parameters. Table 1 presents the characteristics of the cellulose species obtained via washing with water and hydrotropic solution.

The yield hydrotropic cellulose subjected to washing with sodium benzoate solution is somewhat lower as compared to the unwashed sam-

TABLE 1

Yield and characteristics of the technical grade cellulose obtained *via* washing with water and sodium benzoate solution

Washing solution	TGC yield, %	Mass fraction, %			
		α-Cellulose	Pentosans	Lignin	Ash
Water	49.7±1.0	82.6±0.5	9.7±0.1	10.6±0.1	4.1±0.05
Sodium benzoate solution	46.1±1.0	85.8±0.5	7.2±0.1	7.6±0.1	3.6±0.05

Note. Here and in the Tables 2, 3: the data are presented calculated for the initial raw material.

ple yield (46 and 50 %, respectively). This is connected with a more complete removal of lignin (7 %) and related impurities (pentosans - from 10 to 7 %, ash – from 4.1 to 3.6 %) from the cellulose, as confirmed by analytical data. Furthermore, the concentration of α-cellulose from 83 to 86 % is observed. Thus, the washing with sodium benzoate promotes obtaining better hydrotropic cellulose.

For the experiments, we used the aerial part of the plant as a whole. The miscanthus is presented by several morphological parts: stems with internodes, leaves, panicles, therefore in order to obtain a homogeneous composition of the product one needs "severe" enough conditions of cooking. Earlier studies concerning the cooking at the temperature of 140–160 °C and the duration of 3–5 h demonstrated that the fibrous products obtained contain undercooked feedstock inclusions [16]. The undercooking is presented by solid parts of the plant such as-stem with internodes. In order to reduce the fraction of the undercooking, the temperature in this experiment was increased up to 180 °C, the duration of the process remaining the same, and an additional washing with hydrotropic solution was performed. The results of the cooking procedures (yield and TGC characteristics) are presented in Table 2.

Technical grade cellulose represents a pulp with gray-brown colour. A high yield of the technical grade cellulose ranging within 43–46 % depending on the duration of the cooking procedure indicates the maximum preservation of cellulose. Because of releasing the organic acids from the raw material in the course of the cooking procedure, the acidity level of the cooking liquor hydrotropic varies from pH 10.3 to pH 5.0 (slightly acidic). The presence of weak acids in the cooking liquor, high temperature values and a long cooking time exert hydrolytic effect on the lignin-carbohydrate complex and readily hydrolyzed carbohydrates. As the result of hydrolyzing the pentosans in the course of delignification, during the mass fraction thereof decreases from 23 % in the feedstock to 7 % in the TGC. In the course of the hydrotropic cooking, a gas containing carbon dioxide is formed, which causes a slight increase in the pressure within the cooking apparatus. The gas bubbles can be observed in the reaction mixture after depressurization.

The samples of TGC obtained from the miscanthus with the help of UTU samples obtained at of miscanthus in appearance and qualitative characteristics are comparable with the samples obtained earlier from miscanthus under the same conditions with the use of other cooking equipment [16], which indicates the versatility of this delignification method.

In order to show the reproducibility of miscanthus hydrotropic delignification in the UTU

TABLE 2

Yield and characteristics of hydrotropic technical grade cellulose obtained using the UTU

Cooking duration, h	Yield, %	Mass fraction, %			
		α-Cellulose	Pentosans	Lignin	Ash
3	46.1±1.0	85.8±0.5	7.2±0.1	7.6±0.1	3.6±0.05
4	44.6±1.0	86.1±0.5	7.0±0.1	7.2±0.1	3.6±0.05
5	43.4±1.0	86.4±0.5	6.7±0.1	7.0±0.1	3.4±0.05

Note. For design., see Table 1.

TABLE 3

Yield and characteristics of hydrotropic technical grade cellulose obtained using the UTU at 180 °C, duration 5 h, module 1 : 10

Experiment No.	Yield, %	Mass fraction, %			
		α-Cellulose	Pentosans	Lignin	Ash
1	43.4±1.0	86.4±0.5	6.7±0.1	7.0±0.1	3.4±0.05
2	43.3±1.0	86.6±0.5	5.2±0.1	7.3±0.1	4.0±0.05
3	44.4±1.0	87.2±0.5	6.8±0.1	7.8±0.1	3.2±0.05
4	43.6±1.0	86.2±0.5	7.1±0.1	6.4±0.1	3.0±0.05
5	44.9±1.0	86.4±0.5	5.3±0.1	7.2±0.1	3.2±0.05

Note. For design., see Table 1.

we performed five cooks under identical conditions at the temperature of 180 °C, duration 5 h, module 1 : 10.

The TGC samples obtained (Table 3) are characterized by the yield within the range of 43–45 %. Under these cooking conditions, there occurs dissolving the lignin (lignin content in the TGC about 7 %) and readily hydrolyzed carbohydrate part of miscanthus (the mass fraction of pentosans decreased to 5–7 %). The hydrotropic action of sodium benzoate is directed primarily on lignin, whereas the cooking conditions (pH, temperature and duration) affect the hydrolysis of the carbohydrate part, in connection with which the ash content remains at the same level ranging from 3 to 4 %.

The cooking procedures performed exhibit a good reproducibility of the results for the hydrotropic delignification of miscanthus. The properties of cellulose obtained in the course of these processes are almost identical. The fluctuations observed could be to a considerable extent explained by inevitable mode deviations in the course of cooking procedures performed.

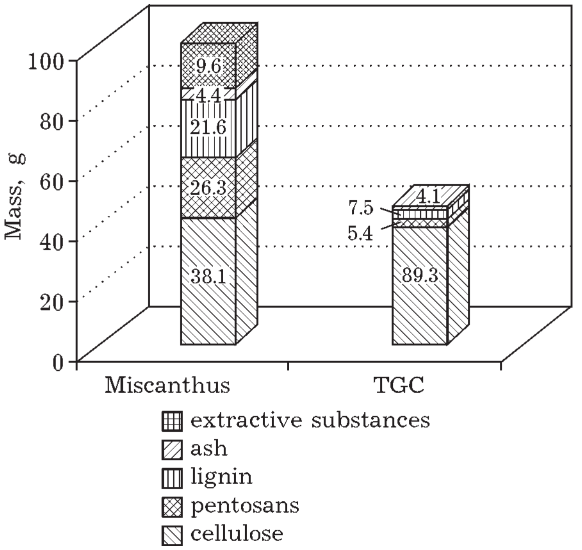

Fig. 1. Chemical composition of miscanthus and hydrotropic technical grade cellulose (TGC) obtained by using the UTU.

Figure 1 presents the chemical composition of the feedstock and the target TGC.

The hydrotropic cooking promotes the concentration of cellulose due to removing the impurities of non-cellulosic nature. Extractive substances are removed completely; the residual content of the components is as it follows (mass %): pentosans 5–7 %, lignin 6–7 %, ash 3–4 %.

In addition to the research works performed earlier concerning the hydrotropic cooking of non-arboreal raw materials in an autoclave [5–8], studying the hydrotropic cooking with the use of a new type of equipment (UTU) demonstrated that the TGC samples obtained are not worse in quality that the products resulted from autoclaving. Thus, the mentioned method for producing the cellulose is versatile.

The satisfactory quality characteristics of the hydrotropic TGC allow using it in the paper industry for producing different sorts of paper and packaging cardboard. The features of this method are they: no negative influence of hydrotropic solution upon cellulose; the possibility to reuse the same cooking liquor for hydrotropic cooking, and, consequently, a significantly lower water consumption as compared to the classical cooking procedures (sulphate and sulphite cooking); the absence of toxic residues of sulphur-containing reagents in air and in washing waters in the course of the hydrotropic cooking procedure. All this determines the

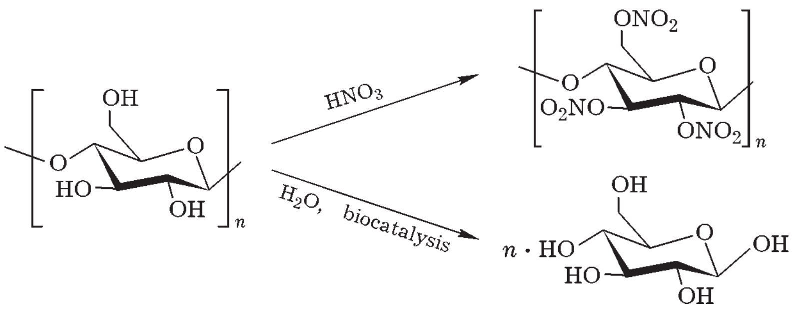

Fig. 2. Variants of processing the hydrotropic technical grade cellulose.

fact that using the method of hydrotropic cooking for semi-finished production of paper is promising [3].

The TGC obtained can be either ennobled for further esterification [17] or investigated as substrates for enzymatic hydrolysis into benign glucose hydrolysates [18]. The two lines of processing such as the transformation into esters and the biocatalytic hydrolysis with converting into monomers (Fig. 2) do not exclude but complement each other to extend the scope of the cellulose species produced *via* the hydrotropic method.

CONCLUSION

As the result of processing the miscanthus *via* the hydrotropic cooking with the use of the universal thermobaric unit, cellulose samples have been obtained with a high yield and satisfactory characteristics: the pentosan and lignin sum does not exceed 13 %. An additional washing of cellulose by hydrotropic solution has been vindicated. It is demonstrated that the hydrotropic method for the processing of vegetable raw materials is universal and it allows obtaining the products with a good reproducibility.

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