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RAPID COMMUNICATION

Pulps isolated from *Miscanthus*, oat hulls, and intermediate flax straw with sodium benzoate

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Abstract−To explore the susceptibility of herbaceous plants to delignification with hydrotropic liquors, the pulping of *Miscanthus*, oat hulls, and intermediate flax straw was performed with a concentrated sodium benzoate solution. The main characteristics of pulp samples derived hydrotropically from *Miscanthus*, oat hulls, and intermediate flax straw are given. *Miscanthus* was found to be more susceptible to delignification, with a pulp yield of 45% and lignin content of 7%. For oat hulls, the pulp yield is 31% and lignin content 9%. The cooking of intermediate flax straw affords a pulp in 51% yield but the lignin content is as high as 17%; further studies are needed. The pulps obtained from *Miscanthus* and oat hulls were confirmed by infrared spectroscopy.

Keywords: Hydrotropic Pulping, *Miscanthus*, Oat Hulls, Intermediate Flax Straw

INTRODUCTION

The hydrotropic processing of plant biomass currently arouses interest among researchers [1]. The hydrotropic processing implies delignification of the raw material using hydrotropic reagents (sodium, potassium or ammonium salts of xylene-, toluene-, naphtaline-, and cymolsulfonic acids as well as benzoates, salicylates, and thiocyanates of salts) to produce the two polymers, cellulose and lignin. The application of water-soluble and eco-benign hydrotropic agents as cooking reagents pertains to the principles employed in green chemistry. Utilizing easily renewable, herbaceous raw materials as a source of cellulose is a topical area in pulp and biotechnology industries [2-5]. *Miscanthus* [6], oat hulls [7], and intermediate flax straw [8] are regarded as promising, readily renewable sources of cellulose, but the isolation of cellulose therefrom by the hydrotropic process has not been reported in the literature. Pursuant to this method, a feedstock is subjected to pulping with a neutral concentrated solution of the hydrotropic salt, resulting in delignification wherein lignin is solubilized in the cooking liquor, cellulose remaining in the solid residue. Since the hydrotropic lignin can be separated upon diluting the spent cooking liquor, the hydrotropic process has great potential to simultaneously produce the two native polymers, cellulose and lignin, with a maximum utilization coefficient of biomass [9].

The aim of this study was to produce hydrotropic cellulose samples from *Miscanthus*, oat hulls, and intermediate flax straw and investigate their compositions.

MATERIALS AND METHODS

In the cooking, *Miscanthus* (*Miscanthus sinensis* Andersson) from Novosibirsk Oblast, oat hulls (*Avena sativa*) and intermediate flax straw (*Linum usitatissimum*) from Altai Krai, Russia, were used. The raw materials were analyzed for basic ingredients (Table 1) and then used in experiments. Before being cooked, *Miscanthus* and intermediate flax straw were chopped to a particle size of at most 10 mm. The feedstocks were hydrotropically cooked in a versatile thermobaric setup having a 2.3-L reactor with a 35% sodium benzoate solution at 180 °C for 3 h in a solid-to-liquid ratio of 1 : 10. The cooking was run as follows: temperature rise to 180 °C, 30 min, and then cooking at 180 °C for 3 h. Afterwards, the setup was cooled, the reaction mass was discharged, squeezed, and washed with a portion of the hydrotropic liquor to prevent lignin from precipitation onto the cellulose fiber, and then with water [10]. The hydrotropic liquor, 35% aqueous sodium benzoate solution, was prepared from the food additive. The yields and characteristics of the pulp specimens from *Miscanthus*, oat hulls, and intermediate flax straw are listed in Table 2. All calculated data was obtained as average from two to three measurements. The resultant pulps were analyzed for composition by commonly used procedures. The infrared spectra of the pulps were recorded on an Infralum FT-801 FTIR spectrometer (KBr pellets) in the frequency range of 4,000-400 cm^{-1}.

Table 1. Composition of *Miscanthus*, oat hulls, and intermediate flax straw

Ingredients[a], %	Miscanthus	Oat hulls	Intermediate flax straw
Kürschner cellulose	52.1±0.1	44.7±0.1	51.3±0.1
Klason lignin	18.6±0.1	18.1±0.1	15.6±0.1
Ash	4.83±0.05	4.62±0.05	2.30±0.05
Pentosans	21.3±0.1	30.8±0.1	21.2±0.1
Extractives[b]	2.1±0.1	1.0±0.1	9.5±0.1

[a]On oven-dry basis
[b]Methylene chloride extragent

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Table 2. Hydrotropic pulping results for *Miscanthus*, oat hulls, and intermediate flax straw

Yield and ingredients[a], %	Miscanthus	Oat hulls	Intermediate flax straw
Yield	45.2±0.5	30.9±0.5	51.3±0.5
α-Cellulose	77.8±0.1	71.9±0.1	69.3±0.1
Klason lignin	6.8±0.1	9.0±0.1	16.8±0.1
Ash	3.90±0.05	5.33±0.05	1.01±0.05
Pentosans	10.4±0.1	12.4±0.1	8.1±0.1
Extractives[b]	0.8±0.1	0.2±0.1	2.6±0.1

[a]On oven-dry basis
[b]Methylene chloride extragent

RESULTS AND DISCUSSION

The composition of the herbaceous raw materials used in the experiments is given in Table 1. All calculated data was obtained as average from two to three measurements.

The quantification results of the compositions of the raw materials used herein indicate that the pulp content is within 45-52%. *Miscanthus* and oat hulls have high ash content (5%) while the ash content of intermediate flax straw is only 2%. Oat hulls are a source rich in pentosans whose mass fraction amounts to 30%. Intermediate flax straw has the highest content of extractives, which is attributed to the nature of this raw material: straw is waste from flaxseed harvest.

Conducting the hydrotropic cooking at 180 °C facilitates the hydrolysis of carbohydrates and delignification of the feedstock. It follows from the findings that *Miscanthus* undergoes hydrotropic delignification easier and its pulp (yield 45%) is characterized by lignin and α-cellulose contents of up to 7 and 78%, respectively. Due to the hydrolysis of pentoses during the cooking of oat hulls, the pulp yield decreased to 31% and the residual lignin content of the sample was 9%. Delignification did not occur in the cooking of intermediate flax straw, the lignin content reaching 17% with the product yield of 51%. This is likely due to the high content of extractives in the feedstock.

The *Miscanthus*, oat hull, and intermediate flax straw samples and pulps obtained therefrom were characterized by infrared spectroscopy. Figs. 1 and 2 illustrate IR spectra of *Miscanthus* and its hydrotropic pulps, respectively. IR spectra of oat hulls and intermediate flax straw and pulps thereof are not shown herein.

The IR spectra of the hydrotropic pulp have absorption bands typical of wood pulp [11]. The absorption band at 3,000-3,700 cm^{-1} in the spectrum of the *Miscanthus* pulp is responsible for the stretching vibrations of the OH-groups involved in the hydrogen bond. The asymmetric stretching vibrations of the CH and CH_2 bonds in the methylene groups appear in the spectra at 2,900-2,920 cm^{-1}. The absorption bands at 1,630-1,650 cm^{-1} are for bending vibrations of the OH-groups attributable to the presence of the tightly bound water. The absorption band in the spectrum of *Miscanthus* in the region of C=O double bonds (1,736 cm^{-1}) indicates that *Miscanthus* has a significant content of carbonyl groups characteristic of hemicelluloses contained in the feedstock composition. The pulp spectrum does not have this band, suggesting the absence of hemicelluloses. Besides the absorption bands typical of cellulose in the IR spectrum of *Miscanthus*, the low-intensity bands at 1,607 cm^{-1}, 1,514

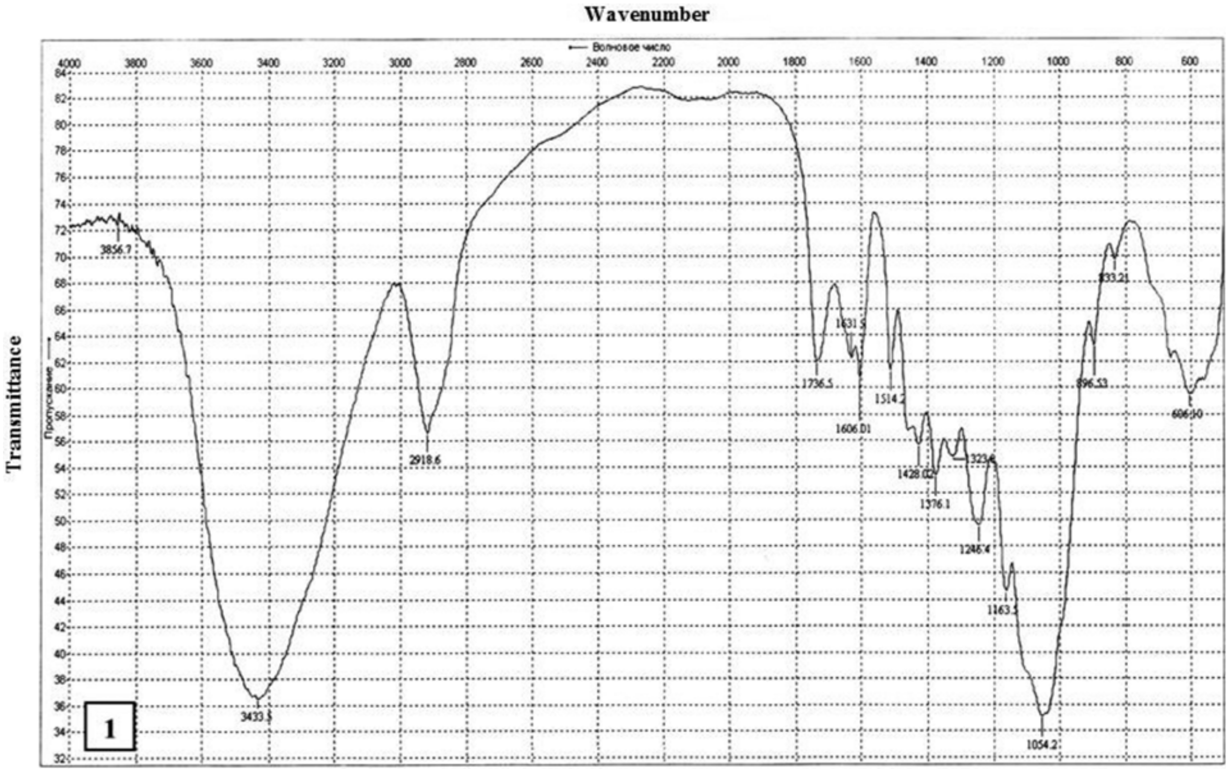

Fig. 1. IR spectrum of *Miscanthus sinensis* Andersson.

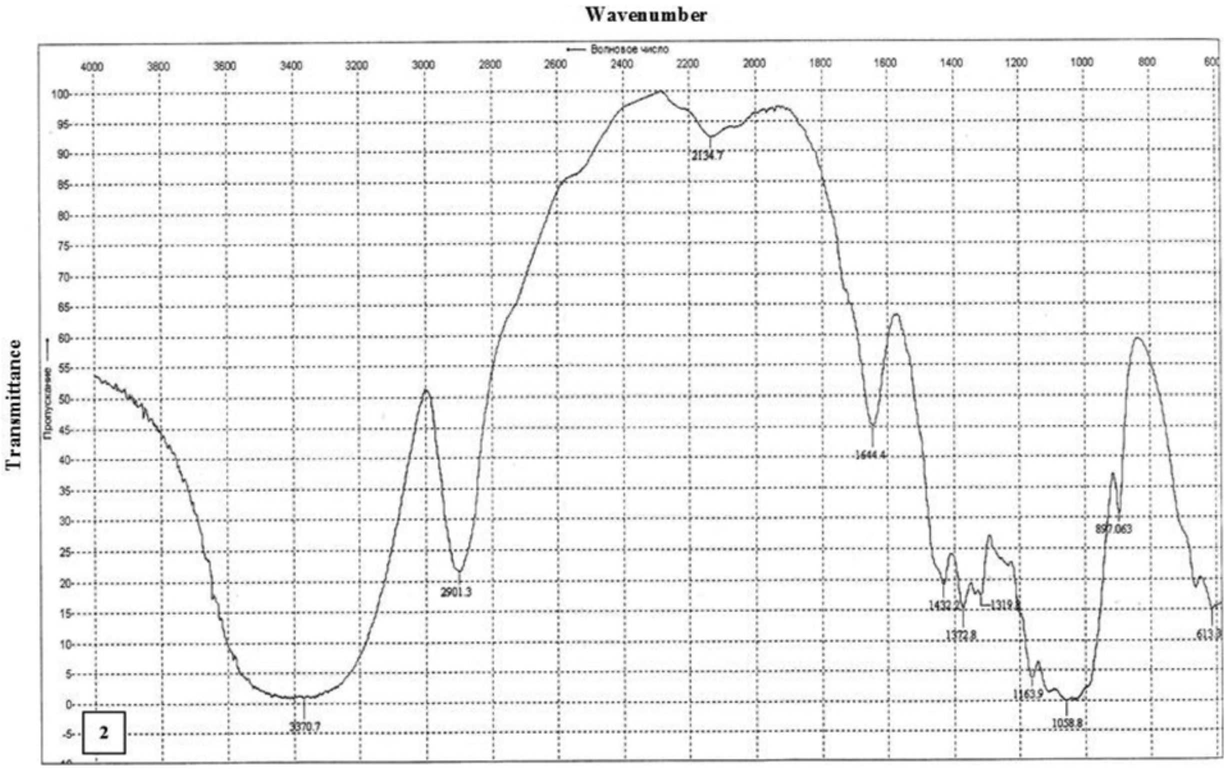

Fig. 2. IR spectrum of the hydrotropic pulp from *Miscanthus sinensis* Andersson.

cm^{-1}, and 1,462 cm^{-1} are observed and belong to vibrations of the aromatic moieties peculiar to lignin. In the IR spectrum of the pulp, the CH-group vibrations due to the presence of lignin were not detected. The bands at 1,300-1,400 cm^{-1} in the spectra of *Miscanthus* and the pulp correspond to the bending vibrations of the CH_2- and OH-groups in CH_2OH; 1,000-1,200 cm^{-1} is for the bending CO-group vibrations that are typical of polysaccharides and attributable to the existence of acetal C-O-C bonds and C-O bonds in alcohols. The absorption bands in the vicinity of 600-700 cm^{-1} correspond to the pyranose ring vibrations.

The IR spectrum of the oat hull pulp contains the same absorption bands as does the IR spectrum of the *Miscanthus* pulp (3,000-3,700 cm^{-1}, 2,900-2,920 cm^{-1}; 1,300-1,400 cm^{-1}; 1,000-1,200 cm^{-1}; 600-700 cm^{-1}); no absorption bands representative of the carbonyl groups of hemicelluloses and aromatic moieties peculiar to lignin are observed in the spectrum.

In contrast to the IR spectra of the *Miscanthus* pulp and oat hull pulp, the IR spectrum of the pulp obtained from intermediate flax has absorption bands characteristic of cellulose as well as bands typical of the feedstock: 1,740 cm^{-1} for the C=O bond of the carbonyl groups typical of hemicelluloses and 1,609 cm^{-1}, 1,511 cm^{-1}, and 1,465 cm^{-1} for vibrations of the aromatic moieties representative of lignin. Hence, it follows that the hydrotropic delignification of intermediate flax straw did not lead to the removal of hemicelluloses and lignin from the pulp.

Thus, the pulps produced hydrotropically from *Miscanthus* and oat hulls were spectroscopically confirmed according to the presence of the absorption bands typical of cellulose (3,000-3,700 cm^{-1} for the vibrations of the OH-groups involved in the hydrogen bond; 2,900-2,920 cm^{-1} for the vibrations of the CH and CH_2 bonds in the methylene groups; 1,300-1,400 cm^{-1} for the vibrations of the CH_2- and OH-groups in CH_2OH; 1,000-1,200 cm^{-1} for the vibrations of the CO-groups in the C-O-C and C-O bonds in alcohols; 600-700 cm^{-1} for the pyranose ring vibrations).

CONCLUSIONS

Miscanthus, oat hulls, and intermediate flax straw were pulped with 35% sodium benzoate to furnish pulp specimens. *Miscanthus* was found to be delignified better than other biomass feedstocks studied in this study and have the pulp yield and lignin content of 45% and 7%, respectively. The pulp yield and lignin content of oat hulls attain 31% and 9%, respectively. The pulp yield from the cooking of intermediate flax straw was 51%, but the lignin content was as high as 17%, necessitating further studies to lead to lower lignin contents in pulped biomass. The raw materials and hydrotropic cooking samples were studied by infrared spectroscopy, which confirmed the resultant celluloses from *Miscanthus* and oat hulls.

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