Vegetable raw materials for the production of fibrous semi-finished products

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Abstract. In the economic sphere, they envisage the creation of their own production facilities to produce fibrous semi–finished products - cellulose and its derivatives based on the wood of various hardwoods from the Central Asian region, whose plantations expand every year. Great attention should be paid to rice and wheat straw. Given that rice straw is not used as feed in animal husbandry and is simply burned, thus damaging the ecology of the country, we consider it necessary to carry out scientific work on the production of semi-finished modified fibrous products from local annual cellulose-containing plants. Waste generated by cutting poplar in the form of branches, sawdust, shavings, etc. can also serve as an additional source of raw wood materials to produce cellulose.

1. Introduction

There are several studies in the field of obtaining composite polymer materials based on cellulose worldwide in the following priority areas: improvement of the production system of thermal insulation materials; determining in advance of the factors affecting the synthesis of the material, maintenance of the process with high accuracy; cellulose and its derivatives with high molecular weight in various parameters, etc. Currently, demand is growing for cellulose esters and cellulose-based on cellulose and composite polymer materials based on them.

Currently, the demand for cellulose-based composite polymer materials, cellulose esters, and esters has increased. On the basis of the growing demand for esters of cellulose and esters in various industries, a high level of scientific research has been organized and certain results have been achieved.

In the third direction of the action strategy for the further development of Central Asia, important tasks are aimed at "further modernization and diversification of industry by transferring it to a qualitatively new level, aimed at advancing the development of high-tech manufacturing industries. First, for the production of finished products with high added value based on the deep processing of local raw materials. To expand the resources of cellulose and its esters based on local raw materials, there are annual and perennial plants and fiber waste from various industrial enterprises.

The main plant raw materials to produce cellulose are coniferous, hardwood, and cotton ribbons. However, over the past 20-30 years, annual plants have also become widespread: rye straw, barley, wheat, rice, and cane. Cellulose is also obtained from bamboo abroad [1].

In the work, methods for obtaining cellulose from the fast-growing cane were investigated. Reed (Arundodonax) is characterized by a large size and a high yield [2]. The experimental cooking of cellulose was carried out by sulfate and sodium methods using organic solvents, as well as by the alkaline-sulfite method with additives of anthraquinone and methanol. Cellulose was obtained, characterized by high yield, whiteness, and good paper-forming properties. It is recommended to use bleached cane cellulose to produce printed paper [3].

The paper considers the technologies of sulfate and sulfur-free cooking of cellulose from wheat and barley straw, sorghum or hemp stalks. It is shown that with alkaline cooking (1,3-19,7% NaOH; 0-0,7% hydroquinone, temperature 86-114 ^{0}C), the cellulose yield is 4-5% higher than with sulfate cooking.

In Canada, wheat straw waste is 3-6 million tons/g. The length of the straw fibers is 1,3 mm, the width is 13 microns. The cellulose content is 50%, the ash content is 6-11%. Sulfate, sodium, sulfite, and explosive methods were used to cook cellulose and semicellulose [4].

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The traditional raw material for pulp production is wood. The increasing demand for cellulose with a shortage of raw wood materials in sparsely wooded countries can be met using agricultural waste: straw and straw from cereals, reeds, cotton stalks, etc. [5].
In Central Asia, large-tonnage lignocellulose waste is wheat straw, which accumulates annually in volumes of more than 20 million tons. It is partially used to feed cattle and as bedding for animals, but the predominant part of the straw is burned.
Today, the use of agricultural waste such as rice, wheat, rye straw, husk, hemp, and many others is of great interest. The creation of technologies based on the processing of these types of agricultural waste will solve the problem of the base of raw materials for the pulp and paper industry [6].
Wheat straw is of great interest from agricultural waste. In our country, wheat straw waste amounts to more than 1 million tons/g. Processing such a large amount of straw will allow the production of up to 400 thousand tons/g of semifinished cellulose, which can be used successfully in the production of paper and cardboard, and will significantly reduce the import of cellulose from abroad, thus saving the foreign exchange reserves of our republic [7].

2. Materials and Methods

Fiber characterization included mechanical and thermal tests using thermogravimetric TGA analysis, infrared Fourier spectroscopy, and morphological analysis using optical microscopy (OM) and scanning electronics (SEM). The results show that one of the main changes caused by steam treatment was the removal of some substances present on the fiber surface. This can lead to weakening of the outer wall of the fiber, which will lead to a decrease in mechanical behavior. This indicates that this procedure effectively increases the fiber contact area and, therefore, can improve the mechanical adhesion of the polypropylene matrix now of manufacturing the composite material (Table 1).
As for the thermal behavior, a thermogram of the untreated fiber is shown (Fig. 1). Some thermal characteristics are indicated and the temperatures are the thermal fiber decomposition (Tmax) and maximum decomposition (Tmax) (Table 1). The fibers were completely saturated prior to thermograms.

Table 1. Thermal behavior of some fibers

Feature	Fiber Type Untreated	ST
Weight loss between 50-120 ^{0}C (%)	9,8	8,7
T_i (^{0}C)	205	350
T_{max} (^{0}C)	320	390

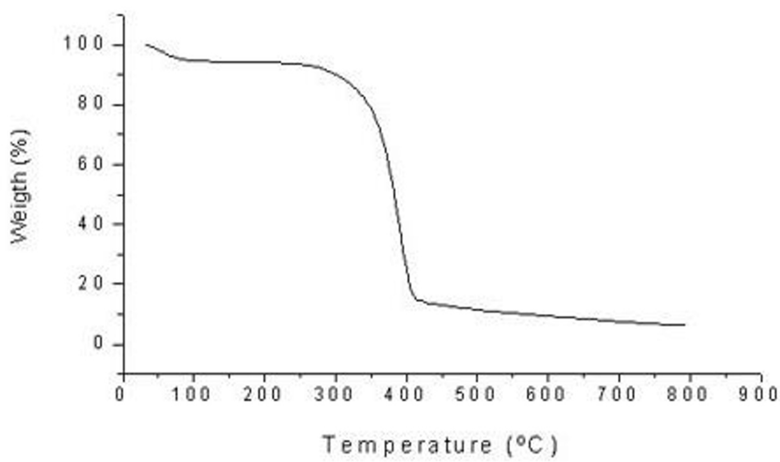

Fig. 1. Thermogram of untreated fiber

Between 50 and 120 ^{0}C, weight loss is observed in this area and summed (which was calculated using hardware-software), it may be related to moisture absorption by the fiber; it is clear that it decreases, indicating that the treated fiber has a lower affinity for moisture. This result may be associated with a possible decrease in the presence of components such as pectins and waxes, as well as parts of hemicellulose, which contribute to the absorption of moisture by the fiber. In addition, steam treatment can be assumed to reduce the hydrophilic tendency of the fiber, which improves the interfacial behavior of a natural composite made with a polypropylene matrix.

Between 300 and 400 ^{0}C, the fibers that have been treated have higher thermal properties than the untreated fibers, which is reflected in an increase in temperature. This result may also be associated with a decrease in some fiber components that have low thermal stability, such as hemicellulose. A modern trend in the chemistry of cellulose to produce products with new predetermined properties is its modification, which allows the elimination of the disadvantages inherent in natural cellulose.

The structural modifications of cellulose include microcrystalline cellulose (MCC), which has found the most diverse practical applications [8]. At the same time, the chemical derivatives of MCC, except for its nitrates and cellulose dialdehyde (DAT), have not actually been studied. At the same time, new cellulose derivatives with valuable properties such as biological activity, thermal stability, ion exchange, and others are synthesized through DAC, whose electrophilic groups can interact with a wide class of nucleophilic compounds. The modern theory of the structure of cellulose answers the following basic questions [9]. The structure of cellulose macromolecules is the chemical structure of the elementary link and the macromolecule as a whole; confirmation of the macromolecule and its links. The molecular weight of cellulose and its polydispersity. Cellulose structure: the equilibrium phase state of cellulose (amorphous or crystalline); types of bonds between macromolecules; molecular structure; structural heterogeneity of cellulose; structural modifications of cellulose.

The elementary link in the cellulose macromolecule contains three free hydroxyl groups. This is proved by the fact that during any cellulose esterification reaction, it is possible to obtain only three substituted cellulose esters as products of complete esterification. Hydroxyl groups in the elementary link of the macromolecule are found in the second, third, and sixth carbon atoms. This is proved by the identification of the main product obtained by hydrolysis of trimethylcellulose as 2,3-6-tri-0-methyl-0-glucose, as well as several other methods. It follows from this that glucose residues should be bound by 1,4 glycoside groups or 1,5-glycoside bonds [10].

Spontaneous ordering of macromolecules in amorphous cellulose preparations was found. The density of cellulose crystals can be calculated from the crystallographic data given above for various polymorphic modifications. It is 1.55–1.59 g/cm^3 and corresponds to the density values obtained (Fig. 2).

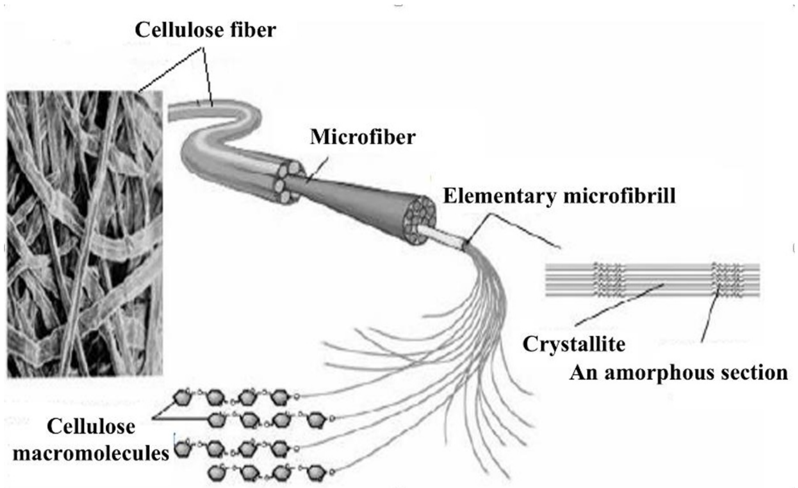

Fig. 2. The molecular structure of cellulose

3. Results and Discussion

Of all the methods of chemical processing of wood, the main one today remains the production of technical cellulose by cooking. The growing shortage of coniferous and deciduous wood resources creates the problem of expanding the base of raw materials in the pulp and paper industry. This problem can be solved by using annual plants as a raw material base. Waste from cereals and cereals is a valuable raw material for the production of cellulose, perfumery, and medical products (silicon dioxide, pigments, and dyes). The main advantages of this raw material are its annual production capacity, the possibility of processing with any cooking method, and its low cost. The distinctive characteristics of raw materials are a high content of hemicelluloses (pentosans); ash content (salts of silicic acid); heterogeneity of the fractional composition of fibers (the presence of non-fibrous cells); small fiber thickness; in some cases, a high content of dyes and pigments (for example, straw and buckwheat husks) [11]. The presence of such features creates problems in the production of technical pulp.

As a rule, non-woody vegetable raw materials are processed by traditional alkaline methods to obtain fibrous semifinished products. However, with these cooking methods, the mineral components of vegetable raw materials, mainly silicon dioxide, pass into the solution in the form of poorly soluble silicates. The formation of silicate scales on

the tubes of evaporation units and other heating surfaces of equipment reduces their heat transfer and reduces the productivity of installations. As a result, difficulties arise in the evaporation of lye, caustication, and calcination of lime sludge. In addition, the presence of silicate in the alkalis leads to a decrease in the degree of caustication. Therefore, when regenerating sulfate and sodium alkalis from annual plant brews, one of the main problems is the destination of the alkalis.
However, when silicon dioxide is removed from black liquor, its calorific value decreases, leading to difficulties during combustion [12].
Thus, when processing nonwoody vegetable raw materials by traditional methods, the main problems are low bulk weight and, as a result, a low degree of filling of the digester; low yield of the fibrous product due to the destruction of hemicelluloses; the presence of high content of inorganic components that make it difficult to process the fibrous semifinished product and the regeneration of alkalis.
Removal of excess lignin from annual plants containing cellulose to obtain high-quality cellulose intended for chemical processing requires the technology to produce cellulose using effective reagents and cooking modes.
According to the chosen research direction, it is advisable to use annual rice and wheat straw plants, as well as cotton lint, as raw materials to produce cellulose at lower economic costs.
The fiber of rice straw is similar in length, width, and structure to the fibers of rye and corn straw but differs from them and other cereals with a high content of silicic acid. The length of the rice straw fibers is 0.5-2.0 mm, the width is from 0.01 to 0.02 mm.
When studying the physicochemical composition of rice straw, the following indicators and their values were determined: stem length – 60-80 cm; dust content – 5-6%; grain content – 0.5-1.0%; bulk weight – 70 kg/m^3.
The physico-chemical composition of straw was determined, shown in Table 2.

Table 2. The Composition of Rice Straw

Components	Content, %
Fiber	40,14
Lignin	21,08
Pentosans	16,43
Ash	16,85
including silicon oxide	14,40
Protein	1,08
Pectins	3,53

Standard methods were used for rice straw analysis: humidity, ash content, lignin content, determination of the mass fraction of pentosans and content of the mass fraction of extractives soluble in organic solvents (alcohol-benzene mixture). To increase the yield of cellulose from annual plants, we have developed a technology for its processing in various modes of prehydrolysis and cooking.
To study and optimize the processing parameters of cellulose-containing raw materials for the production of semifinished cellulose products, prototypes of modified semifinished products from annual plants have been developed and their production modes have been worked out using the following technologies: crushing straw (cutting) into a 10--50 mm cross section by mechanical cleaning of raw materials; preliminary hydrolysis with an aqueous solution of chemical reagents using nitric acid; passing straw soaked with water through a meat grinder to soften and increase its bulk weight; alkaline cooking T = 98-105 ^{0}C for 1.5-3 hours; acidification, washing and drying of the resulting product.
As a result of the analysis of data on the technological mode of manufacturing modified semi-finished products and the study of their physicochemical properties, optimal parameters and conditions for their production were selected. Rice straw was used as a raw material to produce a semifinished cellulose product. The chemical preparation of raw materials must be preceded by mechanical preparation. Two of the most common types of dry straw preparation were selected, including cutting, dusting, removal of foreign inclusions, including metal ones, and straw sorting, which provides for the separation of grains and nodules, the presence of which reduces the yield of cellulose.
When chemical methods were developed for the preparation of annual vegetable raw materials, the primary focus was on processes that contribute to the effective removal of impurities contained in the raw materials of cellulose.
One of the features of non-woody vegetable raw materials is the presence of a fat wax layer on the outer and inner surface of rice straw, which has hydrophobic properties and performs a protective function. The presence of a hydrophobic layer prevents the penetration of chemical agents into the lignocarbon matrix and makes it difficult to extract other components. To remove the fat wax fraction, various organic solvents are used, such as acetone, ethyl ether, ethanol, benzene, or cellulose-containing raw materials are treated thermally by a mechanochemical method, etc. The yield of the fat wax fraction in rice straw is 4.5%.
After the separation of the fat wax fraction, it is advisable to extract a water-soluble one, which includes pectins, starch, and dyes, which together make up 12%. The extraction of the fat-wax and water-soluble fractions creates conditions for

the effective separation of silicon dioxide; therefore, the release of dioxide proceeds practically quantitatively with the complete extraction of the entire ash residue. It is known that the main components of vegetable raw materials containing cellulose are lignin and hemicellulose. Methods to produce cellulose for paper and cardboard to increase yield and quality ensure maximum preservation of hemicelluloses and removal of lignin [13]. Methods for obtaining cellulose for chemical processing (CMCs, acetates, viscoses, nitrates, etc.) provide for the removal of hemicelluloses from raw materials.
Table 3 shows the results of a study on the effect of pretreatment of rice straw with 2% nitric acid at room temperature and at a temperature of 95-98 ^{0}C with different cooking times in NaOH alkali on the yield of high quality cellulose.

Table 3. Effect of hydrolysis of water and cooking of rice straw in an alkaline solution on the yield and quality of the semi-finished product

Hydrolysis time in water, min	Boiling time in 2% NaOH solution, hour	Output, %	Indicators of cellulose		
			α-cellulose content, %	cellulose content, %	SP
30	0,5	24,12	66,4	16,45	920
Without a lock	0,5	22,06	64,7	21,67	980
30	1,0	24,58	68,55	15,97	900
Without a lock	1,0	23,67	66,43	20,67	950
30	1,5	25,83	69,56	13,25	900
Without a lock	1,5	24,34	67,03	19,50	920
30	2,0	28,65	69,84	10,68	860
Without a lock	2,0	27,40	67,87	16,75	890

From the above data, it can be seen that straw closure before cooking cellulose does not affect cellulose yield, and the content of hemicelluloses decreases, that is, locking increases the content of α - cellulose and reduces the content of hemicelluloses due to their hydrolysis. The process of cooking straw in a solution of nitric acid has another great influence on the quality of cellulose. In all cases, a high content of alpha–cellulose is observed (Table 4).

Table 4. Effect of hydrolysis and cooking time of rice straw in nitric acid on the yield and quality of cellulose

The soaking time in 2 % HNO_3, min	Boiling 2 % fluid HNO_3, min	Time of boiling 2 % fluid NaOH, hour	Output, %	Cellulose indicators		
				α-cellulose content, %	cellulose content, %	SP
5	20	0,5	37,52	76,4	8,75	950
Without soaking	20	0,5	37,76	76,06	15,02	990
5	20	1,0	35,32	78,24	7,97	1103
Without soaking	20	1,0	35,67	76,36	11,67	1256
5	20	1,5	33,89	79,08	7,05	1098
Without soaking	20	1,5	32,36	78,92	10,91	1092
5	20	2,0	32,78	79,44	6,34	1150
Without soaking	20	2,0	32,00	79,11	9,38	1050

Table 5. The effect of NaOH concentration on the parameters of cellulose obtained from rice straw

Alkaline cooking		Physico-chemical parameters of the semi-finished product					
Concentration NaOH, g/l	Time, min.	Outout, %	α - cellulose, %	Hemicellulose, %	SP	Whiteness, %	Ash content, %
5	180	-	-	-	-	-	-
10	180	-	-	-	-	-	-
15	180	57,9	45,8	24,4	-	50	11,7
20	180	52,7	51.3	24,0	-	51	9,2
25	180	49,8	62,7	23,6	-	53	8,7
30	180	45,7	73,2	23,2	1230	64	3,2
35	180	43,8	74,1	21,1	1180	67	2,4
40	180	39,7	79,2	17,4	1140	71	1,8
45	180	34,6	83,4	11,7	1080	73	1,3
50	180	32,1	87,7	9,8	1010	76	1,1

The method of obtaining cellulose from rice and wheat straw by acidic prehydrolysis will find application in the production of cellulose for chemical processing. Table 8 shows the results of the study of the effect of sodium hydroxide concentration on the physicochemical properties of cellulose. The results show that with an increase in the NaOH concentration when cooking cellulose obtained from rice straw, the yield of the semi-finished product decreases but the alpha cellulose increases. The concentration of NaOH has a positive effect on the hemicellulose content, i.e., with an increase in the concentration of caustic soda, hemicellulose decreases from 23,2 to 9,8%. In this case, the degree of polymerization of the joint venture decreases proportionally from 1230 to 1010. The effect on the whiteness of cellulose is greater than 50 to 76%. Composition 6 has the best physicochemical properties (Table. 5), which can be considered the optimal mode for cooking rice straw cellulose. In this mode, the alkali concentration is 2.0%, the cooking time is 180 min., at the optimal alkali concentration, cellulose was obtained with a high yield of 45,7% and 73,2% α-cellulose, and the whiteness had a sufficiently high content of 64%.

4. Conclusions

When the alkaline cooking of fibrous waste is done at different times and at different concentrations of alkali, the optimal process condition is selected. At the same time, the pulp yield was 91.6%. During the chemical processing of fibrous waste from the fiber composition, approximately 8.4% of various binders were converted into an alkaline solution. Such binders are considered to be various reagents that are used mainly in the process of chemical and mechanical processing of textile fibers for heating, winding, and increasing strength. Such reagents also include carboxylmethyl cellulose (CMC), because in the textile industry, in order to increase the strength of fibers during the application process, CMC is used in large quantities as an active substance.

The effect of the processing on a hydraulic dryer on the quality of cellulose is shown below. It is known from the initial task of the study that mechanical grinding has a positive effect on the process of cellulose delegitimization. Taking into account the above, in the following studies on the separation of cellulose from the WTO, a hydraulic desiccant was also used. Under the selected optimal process conditions and the optimal concentration of alkali at a set temperature, the WTO was treated in a hydraulic dryer for different times. With this in mind, based on the selected optimal conditions, the process of treating cellulose with water in a hydraulic dryer without the participation of alkali was carried out.

At the same time, the cellulose yield was 91.8%, α-cellulose - 98.3%, the degree of polymerization – 860 and swelling – 144. To separate the WTO-based pulp from various fillers and reagents, it is sufficient to process it in a hydraulic dryer for a certain time at the required temperature.

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