CELLULOSE CHEMISTRY AND TECHNOLOGY

PERACETIC ACID PULP FROM ANNUAL PLANTS

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The aim of this study was to carry out a comparative analysis of various kinds of annual plants and to investigate the process of obtaining pulp from these plants by a peracetic acid solution. The microscopic structure and chemical composition of the stalks of non-traditional annual plants for pulp and paper industry, such as wheat, rape, amaranth, lavatery, sverbiga and schavnat, were studied. It was established that their microscopic structure and chemical composition are similar to those of other kinds of non-wood plants, but are, nevertheless, different from those of softwoods and hardwoods.

The effect of the duration of oxidative-organosolvent delignification of these plants on the quality of peracetic acid pulp was investigated. It was shown that oxidation of lignin and its transfer into solution occurs with varying intensity for different annual plants. It was also evidenced that the peracetic acid pulps obtained from the investigated plants may be arranged in the following order, according to their physical and mechanical indices: wheat straw – rape – schavnat – sverbiga – amaranth – lavatera. They can be used for manufacturing various kinds of paper and cardboard. Black liquor composition was established after peracetic acid cooking of annual plants and the method to be used was suggested.

Keywords: non-wood, organosolv pulp, peracetic acid, black liquor

INTRODUCTION

Paper manufacture and consumption are continuously growing all over the world, especially in Western Europe and North America.[1] The world trend to improve the quality of paper and cardboard products and the increasing level of their consumption *per capita* testify the necessity to raise the volume of primary wood pulp for manufacturing quality paper and cardboard.

Among the methods of pulp manufacturing, those involving organosolvent delignification of plant materials drew the scientists' interest.[2,3] Organosolvent delignification is considered to be a promising direction for an ecologically safe pulp production, as it allows obtaining pulp with higher yield at the same lignin content, compared to the classical methods (kraft and sulphite) of cellulose production.[4] Different organic compounds are used as main components of the cooking solution in organosolvent delignification methods, such as alcohols, ethers, ketones and carboxylic acids. These compounds also include peracetic acid, which has a high delignification capacity and allows not only carrying out cooking at atmospheric pressure and low temperature, but also obtaining pulp with a comparatively high bleaching degree, which excludes an additional bleaching stage.[5]

The arrangement of additional equipment is not necessary for the technology of peracetic acid pulp manufacturing. The technological parameters of cooking are determined by the type of plant raw materials and by its actual composition.[6] Data on using oxidative-organosolvent delignification with solutions of peracetic acid for various kinds of softwood and hardwood are widely described in literature; however, information concerning cooking of non-wood materials by this method is not sufficient.[7] The main advantages of using non-wood materials include their annual renewal, their low cost in comparison with wood, the possible processing into pulp by both traditional and organosolvent methods.

EXPERIMENTAL

The non-wood raw materials most often used in the pulp and paper industry are stalks of cereals (wheat, rye, rice) and industrial plants (bagasse, flax, cotton, hemp). *Wheat straw* (*Triticum vulgare*) takes a leading position in the processing capacity among the other non-wood raw materials employed in pulp and paper industry. Wheat straw is an annual grass of the cereal family (*Gramineae*, *Poaceae*) widely used not only for fuel production, but also as feed, livestock bedding and fodder. On 1 ha of land, 1.4-3.5 tons of absolutely dry wheat straw may be collected, depending on the kind of wheat and on the conditions of its cultivation. Only on Ukrainian fields, up to 20 million tons of wheat straw remain unused annually.[8]

In the last few years, the cultivation area of industrial plants, such as rape, has increased. The oil of rape seeds is used for obtaining biodiesel fuel. Rape (*Brassica napus*) belongs to the herbaceous plants of the *Brassicáceae* family. It is an extremely important oil plant used mainly for obtaining biodiesel. The main producers of rape are the European Union, China, Canada, India and Ukraine. The rape straw that remains unused after harvesting can be considered as an alternative to wood raw materials for pulp production, and for the cardboard and paper products obtained from it.

Plant breeding scientists continue to work actively on breeding of new highly-productive plants with a crop yield of up to 15 t/ha. Crops of plants, such as amaranth, lavatera, sverbiga and schavnat, were obtained in the National Botanic Gardens of the National Academy of Sciences of Ukraine. *Amaranth* (*Amaranthus*) is an annual herbaceous plant, with a high crop yield of herbage (from 3.5 to 8.6 t/ha), used in fodder production, baking, pharmaceutical and perfume industries. *Lavatera* (*Lavatera*) is a grassy semi-bush plant of the mallow family (*Malvaceae*), growing abundantly in a black-earth zone of the European part of Ukraine, in northern Caucasus and southern Siberia; it includes approximately 25 species, among which: *Lavatera Thuringiaca*, used in the present research; *Sverbiga* (*Bunias orientalis L.*), a plant of the cruciferous family, growing as a one-/two-year, or long-term grass, with 1.5 m high stalks, also representing a valuable melliferous and feed plant, *Eastern Sverbiga*, also used in this research work; and *Schavnat*, a new species obtained at the National Botanic Gardens of the National Academy of Sciences of Ukraine by the hybridization and long-term selection of spinach and Tain-Shan's sorrel. It has a high stalk crop yield (10-15 t/ha of absolutely dry substance) and is suitable for complex uses. Also, it passed tests in Russia, Byelorussia, Kazakhstan, Czech Republic, People's Republic of China and Korea. The stalks of these plants can be also considered as an alternative to the wood raw materials for pulp production.

The present study performs a comparative analysis of the various kinds of annual plants, and investigates the process of obtaining pulp from them by a peracetic acid solution.

Wheat and rape stalks from the Poltavskiy region, and stalks of amaranth, lavatera, sverbiga, schavnat from the experimental areas of the National Botanic Gardens of the National Academy of Sciences of Ukraine were studied. Prior to initiating the research, the straw of annual plants was stripped of leaves and inflorescence, air-dried and cut to about 15-20 mm in length. The chaff obtained was stored in desiccators for maintaining permanent humidity, and then used for further investigations.

Microscopic analysis of the stalks of annual plants was carried out according to standard methods, *i.e.* by an M-10 microscope with an 8X10 zooming capacity. In this respect, the stalks of the studied plants were chopped and boiled for 15 min in a 1% sodium hydroxide solution. For achieving a neutral medium, they were washed with distilled water and then dispersed, for obtaining a homogeneous fibrous slurry, which was uniformly deposited on a glass slide area of approximately 1 cm^2. Further on, a solution of zinc-chloride-iodine was dripped on it, after which it was covered with a glass.

RESULTS AND DISCUSSION

The microscopic structure of the studied plants is shown in Figure 1. Microscopic results show that most of the anatomical elements of non-wood raw materials stalks are long, narrow, thin- and thick-walled fibers, *i.e.* sclerenchyma cells of fusiform shape with elongated pointed ends. The fibers of the studied annual plants are characterized by the presence of channels, the thickness and size of which varies from broad to narrow. In wheat, lavatera and schavnat, these channels are hardly observed. Typically, rape has uniform channels, while the channels of amaranth and sverbiga are non-uniform. The surface of sclerenchyma fiber is of transverse streak.

Similar with hardwoods, the stalks of non-wood plant raw materials also consist of vessels of different form and size. The main part of the vessels of all annual plants consists in narrow cells with oval ends which are 2-5 times wider than the fibers. A diagnostic feature of lavatera is the presence of only wide vessels, which are 8-10 times larger than the fibers. Compared to hardwood, which has only porous vessels, the plants here under study also consist of vessels with spiral and ringed thickening, which are destroyed during the heat treatment.

A distinctive feature of the non-wood plant materials is the presence of parenchima cells, occurring as short elongated casks. Wheat and amaranth stalks contain both small (up to 25 µm) and large (100 µm and above) parenchima cells, while those of rape, sverbiga and schavnat are characterized by the presence of small and medium-sized (up to 50 µm) parenchima cells. Lavatera contains only small parenchima cells. There are pores on the surface of parenchima cells of wheat, rape and lavatera. The presence of epidermal cells of one- or bifacial files form is typical for wheat stalks. Other epidermal cells of the studied plants have a low-grade file shape.

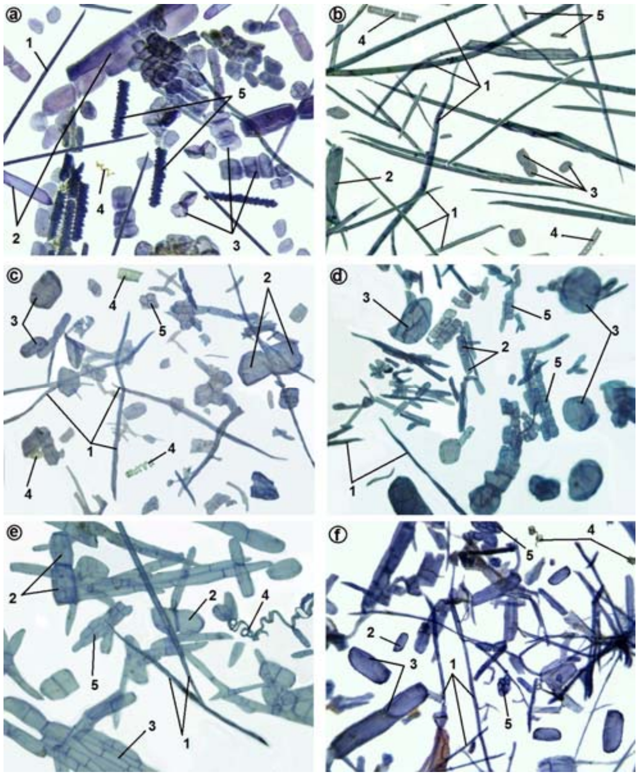

Figure 1: Microscopic structure of annual plants (a – wheat straw; b – rape straw; c – amaranth; d – lavatera; e – sverbiga; f – schavnat): 1 – sclerenchyma fibers; 2 – vessels; 3 – parenchima cells; 4 – vessels with spiral bulges; 5 – cells of epidermis (zooming: 8x10)

Table 1
Chemical composition of annual plants, pine and birch

Plant/tree species	Hot-water solubles, %	1% soda solubles, %	Ethanol-benzene extractives, %	Ash, %	Pentosans, %	Cellulose, %	Lignin, %
Wheat straw (*Triticum vulgare*)	6.0	36.2	4.6	4.2	26.4	46.2	18.6
Rape (*Brassica napus*)	10.1	24.2	3.6	3.2	29.6	37.7	26.4
Amaranth (*Amaranthus*)	17.9	35.6	0.4	3.7	19.8	31.9	26.5
Lavatera (*Lavatera*)	14.7	31.9	0.8	4.2	23.9	32.9	22.8
Sverbiga (*Bunias orientalis L.*)	25.4	35.7	1.4	5.1	19.9	34.3	22.0
Schavnat	14.2	26.0	1.4	3.5	21.9	37.8	21.4
Pine (*Pinus sylvestris L.*)	6.7	19.4	3.4	0.2	10.4	47.0	27.5
Birch (*Betula*)	2.2	11.2	1.8	0.5	28.0	41.0	21.0

Table 1 shows the results of the chemical analyses on the stalks of the studied non-wood raw materials, carried out according to the corresponding TAPPI standards for different components, namely T-257 for hot-water solubles, T-212 for 1% NaOH solubles, T-204 for ethanol-benzene extractives, T-222 for lignin and T-211 for ash. The content of hot-water solubles of the wheat straw stems is lower, compared to hardwoods and the other non-wood raw materials studied, but it is higher than that of softwoods. The hot-soluble substances present in the raw materials include starch and proteins, which consume the pulping reagents. Sverbiga has the highest content of hot-water solubles, compared to all other annual plants studied, and to pine and birch. The wood components soluble in soda solutions are components of the cell walls. The content of 1% soda solubles in the studied agricultural residues is twice higher than in softwoods, so that the pulp yield will be lower. The content of ethanol-benzene extractives in wheat straw is higher than in wood or in other annual plants, while amaranth and lavatera have the lowest content.

The ash content of all agricultural residues is higher than that of hardwoods and softwoods. The main part of the ash of all annual plants is silica, which causes difficulties in the recovery process. Sverbiga has the highest ash content among the studied annual plants, while rape stalks have the highest pentosans content. The pentosans content of the other studied plants is similar to that of softwoods, except for sverbiga and amaranth, whose pentosans contents are lower than that of softwood. The cellulose content of wheat straw is similar to that of wood, while amaranth, lavatera and sverbiga have a slightly lower cellulose content than those of softwoods and hardwoods.

The lignin content in wheat straw is lower than in softwoods, hardwoods and other annual plants. Based on this chemical composition, wheat straw can be expected to require a lower reaction time or to consume fewer reagents to yield pulp with a low lignin content.

Thus, it is possible to confirm that the chemical compositions of the studied plants are close to those of other representatives of non-wood plants (cotton, reed, sunflower, sorghum), but slightly different from those of hardwoods and softwoods.

Stalk delignification of the studied plant materials was carried out in heat-resistant glass flasks heated with hot water to a temperature of 95 °C, using return condensers to prevent losses of the cooking liquor components.

The preparation of the cooking solution was carried out by mixing 30% concentrated hydrogen peroxide pre-cooled at -2 °C with glacial acetic acid, at a 70:30 ratio by volume. The solution was subsequently kept in a dark and cold place, before attaining a peracetic acid concentration of 8% in the cooking solution and a concentration of hydrogen peroxide of 6%.

The delignification process of non-wood raw materials was carried out in a glass heat-resistant reactor by heating with hot water at a temperature of 95 °C, with the application of a condenser to prevent losses of the cooking liquor components. The liquid-to-solid ratio was of 10:1 and cooking time – from 60 to 180 min. At the end of the cooking process, the pulps were washed with water to remove the residual cooking liquor, and then dried in air, and the waste liquor was again collected in a separate container for subsequent analyses. Peracetic acid delignification of the studied stalk plants, at atmospheric pressure and low temperature, permitted to obtain pulp, whose quality indices are presented in Table 2.

The data presented in Table 2 show that the increase of delignification time from 90 to 180 min regularly leads to lower pulp yield and pulp residual lignin for all studied representatives of non-wood raw materials. This is related not only to the prolongation of lignin and polysaccharides oxidation, but also to the transition of low-molecular, mineral and extractive substances from the plant raw materials to the cooking solution. The pulps obtained are characterized by a higher bleaching degree, which is related to the ability of the peracetic acid of not only oxidizing lignin, but also of discoloring its chromophore groups.

The results of the study show that the oxidation of lignin and its transition to the cooking liquor for the above-mentioned types of non-wood plants occur at different intensity values. The differences observed in the delignification processes of the studied plant raw materials are conditioned both by their anatomic structure, which influences the process of impregnation (depth and rate of penetration of the delignification reagents into the intercellular space of the raw materials), and by the different chemical composition, which influences the reaction ability of lignin.

A longer duration of the peracetic acid delignification process influences in various ways the physical and mechanical indices of the peracetic acid pulps obtained from stalks of different annual plants. For example, an increase of the cooking time from 90 to 180 min promotes an increase of the quality indices of the peracetic acid pulps of wheat straw and amaranth, an increase from 90 to 120 min has the same effect on lavatera, and an increase from 90 to 150 min – on sverbiga. In the case of schavnat, a longer time of delignification leads to deterioration of the physical and mechanical properties. Such dependence on the quality indices of the peracetic acid pulp for the previously mentioned plants is explained by the predomination of the destruction reactions of polysaccharides hydrolysis over the delignification reactions with increasing the cooking time.

As shown in Table 2, the physical and mechanical properties of peracetic acid pulps obtained from the studied plants may be arranged in the following order: wheat straw – rape – schavnat – sverbiga – amaranth – lavatera. The values of the quality indices obtained from the peracetic acid pulp of the studied plants indicate their possible use in the pulp and paper industry, for the production of various kinds of paper and cardboard.

Table 3 lists the characteristics of spent liquors after oxidative organosolvent delignification of annual plants with solutions of peracetic acid at different durations. As obvious from Table 3, the increase of cooking time from 90 to 180 min regularly leads not only to the decrease of hydrogen peroxide content and peracetic acid in waste liquors, but also to the increase of its dry residues and to ash decrease. The observed decrease of hydrogen peroxide and peracetic acid concentrations in the spent liquors is associated with a more intensive delignification with increasing the cooking time.

The ash content in the spent liquors is defined as the ratio of mineral substances to dry residue. According to Table 3, the decrease in the ash content with increased cooking time is explained by a significant increase of the organic substances content in the dry residue.

The spent solutions contain reaction products with the compounds of cooking liquor, of lignin and of other components of the plant materials, which appear in the form of various organic compounds that can have a negative influence on the cooking process.

Table 2
Properties of peracetic acid pulps from different annual plants

Annual plants	Cooking time, min	Yield, %	Lignin, %	Breaking length, m	Burst index, kN/g	Tear index, mN m^2/g	Folding strength, double folds	Brightness, %
Wheat straw	60	69.4	3.6	5870	3.75	2.85	48	50
	90	65.1	2.7	6550	4.26	3.26	86	55
	120	54.0	2.4	7250	4.66	4.60	110	58
	150	51.2	2.1	7470	5.00	4.93	125	62
Rape	90	57.2	3.6	4200	5.43	2.93	156	52
	120	53.3	3.0	4800	5.94	3.46	448	54
	180	48.3	2.7	5150	6.07	3.66	380	57
Amaranth	90	51.8	1.4	2700	4.05	1.60	144	61
	120	51.2	0.7	3600	4.09	2.40	218	63
	150	50.0	0.2	4000	4.17	2.08	310	61
	180	48.8	0.1	4400	4.00	1.73	240	66
Lavatera	90	60.8	4.6	3100	3.63	1.44	204	58
	120	54.3	2.8	3300	3.60	2.93	215	64
	150	51.7	1.2	3200	3.45	2.08	176	60
	180	46.0	0.4	3100	2.67	1.43	124	61
Sverbiga	90	49.3	5.4	3700	3.06	2.00	97	58
	120	46.8	4.3	4300	3.73	2.03	119	58
	150	43.5	2.2	4700	4.00	2.51	189	59
	180	43.1	1.7	4500	3.87	1.41	148	64
Schavnat	90	57.0	3.1	4500	6.26	3.05	233	55
	120	53.9	2.6	4300	6.13	2.69	179	55
	150	45.1	1.1	3800	5.46	2.48	130	62
	180	44.6	0.9	3600	5.13	1.57	125	62

Table 3
Characteristics of spent liquors after peracetic acid pulping of annual plants

Annual plants	Cooking time, min	Concentration of H_2O_2, %	Concentration of peracetic acid, %	Dry residue, kg/dm^3	Ash, %
Amaranth	90	2.0	2.5	23.5	14.5
	120	1.8	2.5	25.8	13.1
	150	1.4	2.3	30.0	9.1
	180	1.0	1.5	42.2	7.5
Lavatera	90	2.5	2.5	14.1	14.0
	120	1.9	1,8	28.4	8.0
	150	1.7	1.6	30.0	6.8
	180	1.2	1.0	37.3	6.2
Sverbiga	90	3.9	5.8	23.2	8.5
	120	2.4	3.3	28.3	8.3
	150	1.8	1.8	28.5	7.6
	180	1.5	1.8	29.3	3.2
Schavnat	90	2.3	2.8	30.0	15.1
	120	1.2	1.8	35.6	11.1
	150	1.1	1.3	35.7	9.7
	180	1.1	1.0	42.8	8.6

In the process of peracetic acid cooking the acetic acid is spent on peracetic acid formation, being recovered during lignin oxidation, without participating at delignification reactions. It can be returned to the cooking process in a subsequent stage. Hydrogen peroxide is consumed in the formation of peracetic acid, nevertheless, it is simultaneously lost on decomposition, during cooking, which results in the release of molecular oxygen. Therefore, one of the options to fully use reagents of a waste solution is to return them into the cooking process. To this end, the separation of the excess quantities of organic substances by liquor ultrafiltration through the semipermeable membrane is recommended. The filtrate should be mixed with a fresh solution and returned to cooking.

CONCLUSIONS

1. Plants with a non-traditional microscopic structure and chemical composition for paper and pulp industry, but close to those of other kinds of non-wood plants, can be regarded as alternative wood sources for fibrous materials manufacturing.

2. For obtaining pulp by the peracetic acid method of delignification, a lower energy consumption is required than by the traditional methods of pulp production.

3. Judging by their physical and mechanical indices, the peracetic acid pulps obtained from non-traditional raw materials can be used in the composition of various kinds of paper and cardboard products.

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