AMMONIA-SULFITE-ETHANOL PULP FROM WHEAT STRAW

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The purpose of this study was to investigate the process of obtaining straw pulp by ammonia-sulfite-ethanol solution. The influence of the main technological parameters on the quality of the straw pulp obtained by this method was evaluated. A positive influence of anthraquinone on the delignification process of wheat straw and the strength properties of the pulp was found. The possibility of bleaching organosolv straw pulp by reagents without chlorine was evaluated.

The selectivity indexes of removing components from wheat straw and the kinetic characteristics of this process were determined. The activation energy values, which were calculated by analytical and graphical methods, indicate good coincidence of the results and the essential role of anthraquinone in decreasing activation energy. The possibility of using ammonia-sulfite-ethanol straw pulp for production of writing paper and container board was demonstrated.

Keywords: wheat straw, organosolv pulp, bleaching, selectivity index, kinetic characteristic

INTRODUCTION

The production of the pulp and paper industry has an exceptionally important role in the development of humanity and society. The consumption of paper and cardboard per capita is one of the life quality and development indexes of every country in the world. Only in 2009, on average about 54 kilos of paper were consumed per capita in the world.[1] According to Jaakko Poyry, by 2010 primary pulp fiber production was expected to reach 200 million tons for production of paper and cardboard.[2] The main raw material for manufacturing pulp in world's pulp and paper industry is wood. For the countries without large stocks of free wood, the search for alternative sources of pulp is a topical problem. Stems of non-wood plant materials, including wheat straw – one of the agricultural crops with the largest volumes of production, can serve as sources of pulp. Global wheat production in 2012 was expected to reach 665.33 million metric tons,[3] making it the third most-produced cereal after maize and rice.[4] 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*) and it is widely used not only for fuel production, but also as feed, livestock bedding and fodder. 1.4-3.5 tons of absolutely dry wheat straw may be collected from 1 ha, 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 annually unused.[5]

Among the methods of obtaining pulp for manufacturing paper and cardboard in world's pulp and paper industry, sulfate and sulfite methods prevail. They are one of the main sources of environmental pollution by getting mercaptans, hydrogen sulphide, dioxins, furans and derivatives of lignin into water reservoirs.[6] In order to reduce environmental load, scientists develop alternative methods of pulping, of which organosolv delignification methods are the most perspective. Organosolv processes have been applied with varying success to hardwoods and softwoods and also, to a lesser extent, to non-wood materials.[7] This process is also called low and non-waste technology.[8] Organosolv methods are characterized by the lesser environmental impact and power consumption, more selective effect on lignin, giving the possibility to increase the yield of pulp due to the greater polysaccharides (cellulose and hemicelluloses) preservation of plant materials, the higher ease of bleaching and solvent recovery.[9-11]

Organic solvents used in organosolv methods of delignification serve as chemical reagents and

medium, facilitating delignification of plant materials. As chemical reagents, organic solvents promote the destruction of lignin interacting with its reactive groups. As medium, they have positive influence on such physical and chemical processes as penetrating, swelling and solubility of lignin destruction products. A wide variety of organic solvents, including aliphatic and aromatic alcohols, esters and ketones, organic acids and peroxides, ammonia and amine bases, have been proposed for delignification of lignocellulosic materials in organosolv processes.[12-15] Aliphatic alcohols (ethanol, methanol) and different versions of their applications with the addition of mineral and organic compounds are among the solvents that are often used in organosolv pulping.[16] In our study, the possibility of using NH_3 and SO_2 solutions to accelerate the process of delignification of wheat straw was investigated. The selection of these components is made considering that sulfuric acid ions, which are present in the cooking liquor, contribute to the sulfonation reaction of lignin and NH_4OH shifts pH in the alkaline range, and thereby prevents condensation reactions of lignin. In addition, they will not cause problems with their recovery because of the low temperatures of the transition to a gaseous state (for ammonia it is – 33.6 °C, for SO_2 it is – 10 °C).

The objective of this work was to study one of the organosolv methods of obtaining pulp from wheat straw, namely, the ammonia-sulfite-ethanol (ASE) method, the effect of addition of anthraquinone (AQ) on the delignification process of wheat straw, to determine the indexes of selectivity of removing major straw components during ASE pulping, the kinetic characteristics of this process and the possibility of using ASE pulp for production of paper and cardboard.

EXPERIMENTAL

Wheat straw (*Triticum vulgare*) from Kyiv region was sorted out of leaves, ears of corn and grass, crushed to the size of 15-20 mm, stored in a desiccator for maintaining permanent humidity before pulping. The chemical composition of the raw material's main components was analyzed and used for further investigations.

The chemical composition for different components of wheat straw was determined in accordance with existing TAPPI standards,[17] namely: T 222 for lignin, T 257 for substances extracted with hot water, T 212 for substances extracted with 1% solution of NaOH, T 204 for substances extracted with alcohol-benzene solution, T 211 to determine ash content and cellulose by the Kűrschner-Hoffer method.[18]

Pulping of organosolv straw pulp was performed in acid proof steel autoclaves with 0.4 dm^3 volume, in a laboratory unit with glycerol heating, with a set temperature and liquor-to-solid ratio of 5:1. After pulping, the autoclaves were cooled under running water, the pulp was washed and dried to air-dry condition. Pulp yield was determined gravimetrically, after drying at 105 °C for 24 h. Residual lignin content related to absolutely dry raw material (a.d.r.m.) in the obtained pulp was defined according to standard techniques.[16] In order to determine the strength properties of the pulp obtained from wheat straw, it was refined in a centrifugal grinding machine achieving a beating rate of 60±2 °Shopper-Rigler (SR). The handsheets of organosolv pulp of 75±1 g/m^2 were formed on a Rapid-Kothen unit and their strength properties were evaluated in accordance with UNE standards: breaking length (57-054), burst index (57-028), tear index (57-058), folding strength (55-033) and brightness (57-062). The handsheets were conditioned at 20 °C and 65% RH for at least 24 h before testing.

Ammonia-sulphite-ethanol (ASE) pulping of wheat straw was performed in a cooking solution with the volume proportion of alcohol to water of 35:65%, consumption of NH_3 – 15% and SO_2 – 10% from the mass of a.d.r.m., at the temperature of 130-180 °C, duration of 30-120 min. In order to study ASE delignification under conditions of lower temperatures, a series of pulping experiments with anthraquinone (AQ) consumption of 0.1% from a.d.r.m. were performed. Specified values of ASE pulping technological parameters were identified as optimal from the point of view of chemical consumption after performing the set of previous investigations.

Bleaching of organosolv straw pulp using a less polluting reagent than the harmful chlorine containing products – namely, hydrogen peroxide – was performed. Hydrogen peroxide was used for bleaching pulp. In order to eliminate the problem of yellowing, an acid treatment stage was used in this study. In this work, the same bleaching scheme was used, identical for alkali-sulfite-anthraquinone-ethanol pulp from corn stalks:[19] chelating processing – hydrogen peroxide bleaching – acid processing. The first stage of bleaching, so called chelating cellulose processing, was carried out at a temperature 90 °C for 60 min, with the solution of 0.2% trilon B from the mass of a.d.r.m. and with the addition of $MgSO_4$, NaOH and Na_2SiO_3 directly before bleaching in order to create the required pH (9-10) and prevent the decomposition of hydrogen peroxide. Trilon B was used in this work as one of the most effective chelating agents and will be replaced by another reagent in the future. The second stage of bleaching was peroxide bleaching, which was carried out by H_2O_2 consumption up to 10% from the mass of the a.d.r.m. at a temperature of 90 °C during 60 min.

Acid processing was carried out to neutralize the small amount of alkali, which remains in the pulp after peroxide bleaching. Due to this processing, discoloring of the remaining highly colored compounds of iron, which are commonly found in bleached pulp, and stabilization of pulp brightness occurs. For this, ASE pulp processing was carried out by sulfite acid with the SO_2 consumption of 0.5% from the mass of a.d.r.m., at the temperature of 90 °C for 60 min. These values of technological characteristics were taken as optimal on the basis of previously performed investigations.[19] Each stage of pulp bleaching was completed by its washing with distilled water to neutral reaction. The yield and content of residual lignin of the bleached pulp and its brightness were determined according to standard techniques.

In order to determinate selectivity, the influence of the cooking solution on the components of wheat straw was calculated by such characteristics as: selectivity (SL), degree of carbohydrates removal (DCR) and degree of delignification (DD) using the following formulas:

$$SL = \frac{Y}{100 - \frac{A \cdot DD}{100}} \cdot 100 \quad , \% \tag{1}$$

$$DCR = 100 - \frac{Y \cdot (100 - C)}{100 - A} \quad , \% \tag{2}$$

$$DD = 100 - \frac{Y \cdot C}{A} \quad , \% \tag{3}$$

where: A – initial content of lignin in plant raw material, %; Y – yield of pulp from plant raw material, %; C – residual content of lignin in pulp, %.

For additional evaluating of the influence of technological parameters on the delignification of wheat straw by the ammonia-sulfite-ethanol method, such kinetic characteristics as reaction rate and activation energy were calculated. First-order (4) and second-order (5) kinetic equations were used for calculations:[20]

$$k = \frac{1}{t} \ln \frac{[A_0]}{[A]} \tag{4}$$

$$k = \frac{1}{t} \left(\frac{1}{[A]} - \frac{1}{[A_0]} \right) \tag{5}$$

where: k –reaction rate; t – duration of delignification process; [A] and [A_0] – original and current content of lignin in plant raw material, accordingly.

The Arrhenius Equation was used for calculation activation energy:[20]

$$k = k_0 \cdot e^{-E_a / RT} \tag{6}$$

where: k – specific reaction rate; k_0 – pre-exponential factor; E_a – activation energy; R – gas constant; T – temperature in Kelvin.

In order to study the influence of the organosolv straw pulping on the physical and mechanical properties of writing paper, handsheets with a mass of 80 g/m^2 (as required by the standard for this type of paper products) were formed on a Rapid-Kothen unit, with different fiber compositions: from 100% bleached ASE straw pulp to 100% sulfate coniferous bleached pulp. The beating rate of the pulps before handsheet formation was adjusted to about 45±2 °SR. Filler slurry 2.0%, rosin size 3% and aluminum sulfate 4.5% from mass of a.d.r.m. were added to the pulp suspensions. Also, handsheets of container board with a mass of 175 g/m^2 were formed on a Rapid-Kothen unit with different fiber compositions: from 100% ASE straw unbleached pulp to 100% waste paper grade 1.04 (EN 643). The beating rate of ASA straw unbleached pulp and waste paper before handsheet formation was adjusted to about 35 ± 2 °SR. The conditions of obtaining laboratory samples of cardboard were the following: white rosin size consumption 1.5%, clay soil 2.5% from mass of a.d.r.m. The strength properties of the obtained handsheets of writing paper and container board were evaluated in accordance with standard methods.

RESULTS AND DISCUSSION

Wheat straw has the following composition: 46.2% cellulose, 18.6% lignin, 33.8% substances extracted with 1% NaOH solution, 10% hot water solubles, 5.2% substances extracted with alcohol-benzene solution and 4.2% ash.

Wheat straw has a higher content of soluble substances in the stems, compared to that of the most common in Eastern Europe representatives of deciduous and coniferous wood. It means that the stems of wheat straw contain a large amount of components such as starch, dyes, cyclic alcohols, sugars and ash. Part of hemicellulose fraction and low molecular weight cellulose were additionally extracted from the plant material by an alkali solution. Stalks of wheat straw contain 2-3 times more substances soluble by an alcohol-benzene mixture and 8-20 times more ash than wood. Wheat straw with a comparable amount of pulp contains less lignin than representatives of softwood (21% for birch) and hardwood (28.5% for spruce) timber.[6] It suggests mild delignification of wheat straw compared to the delignification of wood.

In order to study the influence of temperature and duration of obtaining ASE pulp from wheat straw, a series of laboratory pulping experiments was performed. The results of ASE pulping of wheat straw using AQ and without AQ are presented in Table 1. As expected, the completed studies show that whether with or without AQ, if the temperature and duration of ASE pulping increased, lower yield of straw pulp and content of residual lignin were obtained. It is well known that the increase of cooking temperature and time

leads to the intensification of lignin destruction by splitting of α- and β-ether alkyl bonds within the lignin macromolecule and to a decreasing content of residual lignin in ASE straw pulp.[11,14,21] This relation of changes in the quality of straw pulp is also explained by the acceleration of dissolution of extractive substances, minerals and carbohydrates of the raw material and the process of their transferring to the cooking solution.

Table 1
Results of ASE pulping wheat straw with and without AQ

Cooking temperature, °C	Quality indexes of pulp with duration of cooking, min			
	30	60	90	120
Pulp yield*, % from a.d.r.m.				
130	86.1 / 88.1	81.1 / 83.0	79.2 /80.1	77.6 / 78.6
140	77.8 / 84.6	75.1 / 79.0	72.6 / 77.2	71.8 / 76.6
150	72.6 / 79.5	70.3 / 76.2	69.0 / 72.3	68.2 /69.3
160	70.3	67.4	67.0	66.7
170	67.9	66.9	66.6	66.2
180	61.2	60.7	59.0	58.8
Content of residual lignin*, % from a.d.r.m.				
130	11.0 / 9.1	8.6 / 6.7	7.2 / 6.0	6.3 / 5.6
140	8.4 / 7.8	7.0 / 5.9	6.4 /5.3	5.4 / 5.0
150	5.4 / 5.0	4.9 / 4.0	4.0 / 3.2	3.7 / 2.9
160	3.9	3.2	2.7	2.3
170	3.4	2.8	2.5	2.0
180	3.0	2.3	2.1	1.8
Breaking length, m				
130	6800 / 7000	7200 / 8550	8800 / 9650	8900 / 9900
140	6500 / 6600	7500 / 7800	8700 / 9400	8750 / 9700
150	6000 / 6400	7400 / 7600	8600 / 9200	8650 / 9400
160	5800	7200	8300	8200
170	5650	7000	7400	6800
180	5350	6800	6200	6000
Folding strength, double folds				
130	200 / 220	340 / 360	410 / 520	520 / 620
140	180 / 200	210 / 300	340 / 450	450 / 580
150	160 /180	190 / 210	220 / 440	420 / 500
160	120	170	300	310
170	90	160	200	190
180	70	120	100	90
Tear index, $mN \cdot m^2/g$				
130	5.3 / 6.8	6.3 / 8.4	7.8 / 9.4	9.1 / 10.5
140	5.1 / 5.6	5.7 / 8.3	7.4 / 8.6	9.0 / 10.2
150	4.9 / 5.5	5.4 / 6.8	7.3 / 8.4	8.0 / 9.8
160	4.5	5.3	6.6	6.7
170	4.3	4.8	4.3	4.2
180	4.1	4.6	4.,0	3.9
Burst index, kN/g				
130	5.1 / 5.4	5.7 / 6.5	6.7 / 7.5	7.1 / 7.7
140	4.8 / 5.3	5.4 / 6.1	6.6 / 7.2	6.8 / 7.6
150	4.5 / 5.1	5.3 / 5.6	6.4 / 7.0	6.6 / 7.5
160	4.1	4.7	6.1	6.5
170	3.8	4.5	4.5	4.0
180	3.0	4.1	3.7	3.3

*- in denominator are results with using AQ

A full factorial experiment type 2, which is widely used for designing experimental statistic mathematic models for objects of the technological parameters type, was used for

receiving mathematical dependencies of wheat straw organosolv pulp quality indexes from their main technological parameters as the mathematical method of planning. Pulping temperature (x_1) and pulping duration (x_2) were chosen as the main technological parameters impacting on ASE pulp quality indexes. The following characteristics of ASE delignification of wheat straw: Y_1 – yield of pulp; Y_2 – delignification degree; Y_3 – residual lignin content; Y_4 – breaking length; Y_5 – folding strength; Y_6 – tear index; Y_7 – burst index, were chosen as quality indexes. After coding the parameters x_i according to the formula $x_{icod} = (x_{inat} - x_{iav})/\Delta x_i$, where: x_{icod} – the value of parameter in coded form; x_{inat} – the value of parameter in natural units, x_{iav} – the average value of the parameter x_i; Δx_i – the interval of parameter variation x_i, and carrying out statistical processing of the experimental data by the algorithm of the full factorial experiment using criteria of Cochran, Student and Fisher, the following adequate regression equations for ASE delignification of wheat straw were received:

Yield of pulp, %:

$$Y_1 = 68.476 - 7.9285x_1 - 2.9159x_2 + 3.1215x_1x_2 + 0.4399x_1^2 + 0.9072x_2^2$$

Delignification degree, Kappa units:

$$Y_2 = 24.702 - 13.72x_1 - 9.2858x_2 + 5.9012x_1x_2 + 7.9216x_1^2 + 4.8745x_2^2$$

Residual lignin content, %:

$$Y_3 = 3.3971 - 2.8103x_1 - 1.2573x_2 + 1.1679x_1x_2 + 1.4741x_1^2 + 0.50899x_2^2$$

Breaking length, m:

$$Y_4 = 8400.4 - 930.98x_1 + 471.37x_2 - 1166.4x_1x_2 - 976.95x_1^2 - 713.43x_2^2$$

Folding strength, double folds:

$$Y_5 = 299.42 - 163.61x_1 + 113.09x_2 - 105.75x_1x_2 - 20.785x_1^2 - 48.184x_2^2$$

Tear index, $mN \cdot m^2/g$:

$$Y_6 = 487.18 - 152.54x_1 + 107.28x_2 - 112.02x_1x_2 - 50.929x_1^2 - 1.5262x_2^2$$

Burst index, kN/ g:

$$Y_7 = 442.91 - 114.15x_1 + 56.896x_2 - 56.77x_1x_2 - 51.979x_1^2 - 45.366x_2^2$$

The compromising area of carrying out ASA delignification depending on the main technological parameters (x_i) was identified by multicriteria optimization, using Harington's desirability function presented in Fig. 1 (interval in $x_1 - x_2$ area). The calculated value of generalized desirability function D equals 0.65, indicating good coincidence of quality indexes from the values of technological parameters. Such values of x_i wherein values of Y_i mostly satisfy the compromising area were defined as optimal point x_{iopt}. The values of x_1 and x_2 in the optimal point equal in code form $x_1 = -1$ and $x_2 = 0.69$, which corresponds in natural units to pulping temperature of 130 °C and pulping duration of 130 minutes. Straw ASE pulp quality indexes, which are calculated with the aid of the obtained equations, have the following values in the optimal point: yield – 73.0% from a.d.r.m.; residual lignin content – 6.2% from a.d.r.m.; breaking length – 9150 m; folding strength – 570 double folds; tear index – 9.8 $mN \cdot m^2/g$; burst index – 7.5 kN/g.

The defined adequate regression equations of ASA delignification of wheat straw with AQ have the following form:

Yield of pulp, %:

$$Y_1 = 77.005 - 3.5128x_1 - 5.1898x_2 - 0.7446x_1x_2 - 0.86284x_1^2 + 2.2317x_2^2$$

Degree of delignification, Kappa units:

$$Y_2 = 31.542 - 6.0388x_1 - 10.21x_2 + 0.8857x_1x_2 - 0.46386x_1^2 + 5.2134x_2^2$$

Residual lignin content, %:

$$Y_3 = 5.1764 - 1.4075x_1 - 1.4432x_2 + 0.4452x_1x_2 - 0,63252x_1^2 + 1.0378x_2^2$$

Breaking length, m:

$$Y_4 = 8880.7 - 259.23x_1 + 1590.1x_2 + 95.183x_1x_2 + 253.27x_1^2 - 809.15x_2^2$$

Folding strength, double folds:

$$Y_5 = 401.16 - 56.457x_1 + 200.88x_2 - 26.683x_1x_2 + 48.543x_1^2 - 45.485x_2^2$$

Tear index, $mN \cdot m^2/g$:

$$Y_6 = 603.3 + 0.88948x_1 + 209.27x_2 - 13.442x_1x_2 + 56.239x_1^2 + 33.485x_2^2$$

Burst index, kN/g:

$$Y_7 = 515.63 - 8.7959x_1 + 108.866x_2 + 10.,984x_1x_2 + 7.454x_1^2 - 20.207x_2^2$$

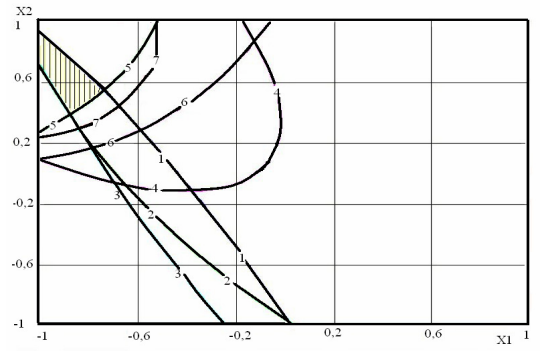

Figure 1: Compromising area of wheat straw ammonia-sulfite-ethanol delignification: 1 – yield of pulp, 2 – degree of delignification, 3 – residual lignin content, 4 – breaking length, 5 – folding strength, 6 – tear index, 7 – burst index

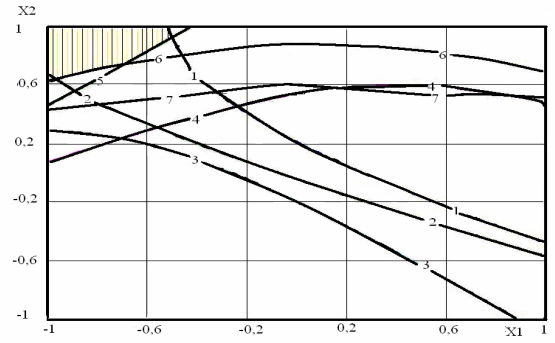

Figure 2: Compromising area of wheat straw ammonia-sulfite-ethanol delignification with the addition of AQ: 1 – yield of pulp, 2 – degreee of delignification, 3 – residual lignin content, 4 – breaking length, 5 – folding strength, 6 – tear index, 7 – burst index

The compromising area of carrying out ASE delignification with the addition of AQ in dependence of the main technological parameters (x_i) was identified by multicriteria optimization, using Harington's desirability function presented in Fig. 2 (interval in $x_1 - x_2$ area). The calculated value of generalized desirability function D equals 0.65, indicating good coincidence of quality indexes from the values of technological parameters. Such values of x_i wherein values of Y_i mostly satisfy the compromising area were defined as optimal point x_{iopt}. Values of x_1 and x_2 in the optimal point equal in code form $x_1 = -1$ and $x_2 = 1$, corresponding in natural units to a pulping temperature of 130 °C and pulping duration of 150 minutes, respectively. Pulp quality indexes calculated with the aid of the obtained equations, have the following values in the optimal point: yield – 77.4% from a.d.r.m.; residual lignin content – 5.1% from a.d.r.m.; breaking length – 10080 m; folding strength – 690 double folds; tear index – 12.2 $mN \cdot m^2/g$; burst index – 8.1 kN/g. The calculated optimal values of organosolv pulp quality indexes correspond to the obtained experimental data (Table 1).

It may be seen from Table 1 that the increasing cooking temperature in the investigated interval leads to the decrease of all quality indexes of organosolv pulp. The increasing duration of the cooking process in the temperature interval of 130-150 °C leads to increasing physical and mechanical characteristics, but at higher temperature (160-180 °C) the increasing of cooking time up to 90 min leads to decreasing quality indexes of the pulp. This was confirmed by the values of selectivity indexes of removing major components from the plant material in the organosolv pulping (Table 2), which are calculated by equations (1-3) for certain temperature and time intervals with and without AQ.

The data presented in Table 2 indicate that the increasing cooking temperature and duration decrease such selectivity indexes of removing components from wheat straw as selectivity and degree of carbohydrates removal, but increase the degree of delignification. The decrease of selectivity (SL) with increasing technological parameters of pulping is explained by a significant decreasing of pulp yield in accordance with equation (1), primarily due to the removal of carbohydrates, which is confirmed by the increasing values of the indexes in the studied temperature-time intervals (Table 2). It should be mentioned that the addition of anthraquinone in ASE pulping improves the selectivity of lignin removal from the wheat straw by 0.8-1.9%. Using ethanol as solvent, which modifies the solubilisation parameters of lignin and hemicelluloses, in ASE pulping, prevents lignin condensation and stabilizes the carbohydrate part of the plant material, thus contributing to a softer delignification and increasing the index of selectivity. It can be concluded from the obtained data that the delignification of wheat straw by the ASE method of pulping is characterized by high selectivity of lignin removal from wheat straw.

The present study (Table 1) shows that the addition of 0.1% AQ from a.d.r.m. leads to an increasing yield from 1 to 7% and reduces the content of residual lignin from 0.3 to 1.9%, compared with ASE pulping without AQ. The

pulp yield increase is explained by the usage of AQ, which leads to the oxidation of finite groups in carbohydrates (especially hemicelluloses) and their stabilization, and improves the delignification of wheat straw due to acceleration of lignin molecules fragmentation. Also, the physical and mechanical properties are higher for the pulp obtained with AQ.

Table 2
Indexes of selective effect of cooking solution on removing components from wheat straw by ASE methods of delignification

Cooking temperature, °C	Cooking duration, min	Selectivity, SL	Degree of carbohydrates removal, DCR	Degree of delignification, DD
130	30	98.6 / 99.2*	0.99 / 0.6*	61.9 / 64.5*
	60	98.7 / 98.8	1.4 / 1.0	71.8 / 77.8
	90	97.8 / 98.1	2.3 / 1.3	77.0 / 80.6
	120	96.8 / 97.7	3.3 / 1.3	80.2 / 82.2
	150	94.1 / 96.4	6.2 / 2.2	84.4 / 84.1
140	30	95.2 / 98.6	5.2 / 1.8	73.4 / 73.4
	60	92.2 / 97.9	8.4 / 2.1	78.9 / 81.2
	90	90.9 / 97.4	9.6 / 2.7	81.3 / 83.5
	120	90.8 / 96.9	9.7 / 3.2	84.4 / 84.4
	150	88.3 / 93.5	12.2 / 6.8	86.8 / 86.9
150	30	91.8 / 92.6	8.7 / 2.0	84.2 / 83.9
	60	89.4 / 91.8	11.1 / 3.2	86.1 / 87.4
	90	88.4 / 90.2	11.9 / 6.9	88.8 / 90.6
	120	87.7 / 89.7	12.7 / 8.6	89.8 / 91.9
160	30	90.2	10.2	88.9
	60	87.1	13.2	91.2
	90	87.0	13.3	92.6
	120	86.9	13.3	93.7
170	30	87.5	12.8	90.5
	60	86.8	13.5	92.5
	90	86.5	13.6	93.1
	120	85.3	13.7	94.5
180	30	79.5	21.1	92.5
	60	79.1	22.2	94.2
	90	77.2	23.1	95.1
	120	77.1	23.6	95.7

*- in denominator are results with using AQ

Table 3
Comparison between ASE, Kraft and soda-AQ pulps from wheat straw

Parameters	ASE	ASE-AQ	Kraft[11]	Soda-AQ[11]
Pulping temperature, °C	130	130	160	160
Pulping time, min	120	120	40	120
Time to max pulping temperature, min	-	-	55	60
Liquor/water	5/1	5/1	4/1	6/1
Kappa number	37.1	32.9	31	15.4
Yield, %	77.6	78.6	42	42.3
Breaking length, km	8.9	9.9	9.8	9.2
Burst index, kNg^{-1}	7.1	7.7	4.09	7.4
Tear index, mNm^2g^{-1}	9.1	10.5	4.57	7.5
Brightness, %	30	31	29	22.6

A small part of NH_3 and SO_2 solutions, which were not consumed during delignification, were subjected to the regeneration in the distillation column, trapped and saturated in the absorber and then sent in the necessary proportions to pulping. Alcohol was also recovered and partially returned

into pulping. An aqueous solution of lignin from the distillation residue was sent to centrifugation, separated and sent for further processing or incineration.

It can be concluded that the yield of pulp obtained by the ammonia-sulfite-ethanol method of delignification is higher than that for Kraft or soda-AQ straw pulps (Table 3) and is not worse than sulfate straw or wood pulp as to its quality parameters.[6,11] The advantages of using organosolv pulping, compared to other methods, were proved experimentally (Table 3). The protective action of the organosolv solution on wheat straw hemicelluloses, as opposed to traditional methods of obtaining pulp from plant raw materials, is one of the main reasons for developing organosolv pulping.

The kinetic parameters of ASE delignification process of wheat straw were defined for isothermal cooking conditions. After the analysis of the kinetic curve obtained by equations (4) and (5), it was established that organosolv delignification of wheat straw by the ASE method is described by a second-order kinetic equation, as the curves obtained by the second-order kinetic equation have a lower curvature and are described by linear dependencies with correlation coefficients 0.97-0.99 (correlation coefficients for first-order kinetic equation are 0.88-0.91). The results of calculating the kinetic characteristics of ASE delignification by equations (5-6) are presented in Table 4. As expected, the specific reaction rate of the delignification process of wheat straw increases with increasing cooking temperature. As seen from the data in Table 4, the addition of AQ accelerates the delignification of wheat straw, as evidenced by the specific reaction rate at the appropriate cooking temperatures and a lower value of the activation energy. The activation energy values calculated by analytical and graphical methods indicate good coincidence of the results and the essential role of AQ in decreasing the activation energy.

The results of the study on bleaching ASE straw pulp using hydrogen peroxide are presented in Table 5. As may be noted from Table 5, bleaching of organosolv straw pulp using just hydrogen peroxide with a consumption of 3% H_2O_2 from the mass of absolutely dry pulp gives the possibility to increase its brightness twice. A further increase in the consumption of hydrogen peroxide slows the increasing of straw pulp brightness. The application of a chelatic pretreatment stage using trilon B before hydrogen peroxide bleaching leads to increasing brightness up to 14% and preventing the decomposition of hydrogen peroxide. In general, the use of the bleaching scheme: chelating processing – hydrogen peroxide bleaching – acid processing, allows to obtain pulp with a brightness of about 86% ISO.

This organosolv pulp can be used for production of various kinds of paper and cardboard. The handsheets of writing paper, using different ratios of bleached ASE straw pulp to sulfate coniferous bleached pulp in the composition, meet the standard requirements and have a lower production cost. The results of the study have shown that the use of more than 25% organosolv straw pulp in composition along with waste paper allows improving the mechanical properties of container board and meets the standard requirements for this product.

Table 4
Kinetic characteristics of ASE straw pulping with and without AQ

Cooking temperature, °C	Analytical method		Graphical method	
	Reaction rate k, m^3/molecule·s	Activation energy E_a, kJ/mol	Reaction rate k, m^3/molecule·s	Activation energy E_a, kJ/mol
		ASE		
130	$7.61*10^{-4}$	45.5	$6.67*10^{-4}$	41.5
140	$8.85*10^{-4}$		$7.44*10^{-4}$	
150	$1.07*10^{-3}$		$1.20*10^{-3}$	
160	$1.77*10^{-3}$		$2.00*10^{-3}$	
170	$2.01*10^{-3}$		$2.33*10^{-3}$	
180	$2.27*10^{-3}$		$2.51*10^{-3}$	
		ASE-AQ		
130	$9.24*10^{-4}$	25.1	$7.12*10^{-4}$	24.7
140	$9.65*10^{-4}$		$1.00*10^{-4}$	
150	$1.25*10^{-3}$		$1.33*10^{-3}$	

Table 5
Results of bleaching ASE straw pulp by H_2O_2 solution

Characteristics	H_2O_2 consumption, % from mass of a.d.r.m.					
	0	1	3	5	7	10
Yield, %	100	98.5	96.7	95.8	95.6	95.3
Content of residual lignin, %	3	1.5	1.1	0.8	0.5	0.4
Brightness, %ISO	30	50	62	72	80	86

CONCLUSION

1. It was established that the use of anthraquinone in ASE wheat straw delignification increases the yield of pulp by 1-7%, reduces the content of residual lignin by 0.3-1.9% and increases the strength properties of pulp by 25-30%, compared to the pulp obtained by cooking without anthraquinone.

2. The increase of cooking temperature and duration leads to an increasing degree of delignification, but decreases such selective indexes of removing components from wheat straw as selectivity and degree of carbohydrates removal.

3. The activation energy values, which were calculated by analytical and graphical methods, indicate good coincidence of the results and the essential role of AQ in decreasing the activation energy.

4. It was proved that chelating processing using trilon B before hydrogen peroxide bleaching allows obtaining organosolv straw bleached pulp with a brightness of up to 86%.

5. Laboratory handsheets of writing paper and container board with ASE straw pulp in their composition correspond to the standard requirements.

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