PERFORMIC PULP FROM WHEAT STRAW

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Dedicated to the 70th anniversary of Acad. Bogdan C. Simionescu, a well-known expert in the field of chemical synthesis of polymers

This paper presents an efficient method for obtaining pulp from wheat straw. The influence of the chemical reagents used and of the duration of cooking in the formic acid–hydrogen peroxide solution on the quality of performic pulp was investigated. The selectivity indexes of lignin extraction from wheat straw by performic acid were calculated. The regression equations that described adequately the dependences of the straw pulp quality indexes on the key technological parameters were calculated. The optimal values of the technological parameters for the delignification process using performic acid were determined. The mechanical properties of organosolv straw pulp confirmed its suitability for being used in the production of paper and cardboard. A lignin–carbohydrate diagram, indicating the efficiency of different delignification methods for wheat straw, was proposed.

Keywords: wheat straw, performic pulp, catalyst, selectivity index, lignin–carbohydrate diagram

INTRODUCTION

The global trend of improving the quality of paper and cardboard products and increasing the level of their consumption indicates the necessity of increasing the volume of primary pulp. Wood is the main plant raw material for pulp production. In the countries with limited free timber resources, non-wood plant raw materials can be used to increase pulp and paper production.[1-3] Because of the constantly decreasing forest resources in different regions of the world, non-wood plant raw materials can serve as an effective alternative. In countries with a developed agriculture, millions of tons of bio-products, suitable for obtaining pulp, are produced during crop harvesting and cereal processing. Potential world resources of non-wood plant raw materials exceed 2.5 billion tons per year and renew annually.[4] Using non-wood plant raw materials in the pulp and paper industry is beneficial from environmental and socio-economic points of view.[5]

Processing of non-wood plant raw material into pulp for paper and cardboard production is closely related to the peculiarities of the anatomical structure and chemical composition of the plant material, the requirements for pulp quality and the main technical and economic indicators of the corresponding delignification method.[6]

A necessary condition for further development of the pulp and paper industry is to reduce the negative impact on the environment. Traditional cooking methods contribute to air and water pollution with sulfur and chlorine compounds.[7] One of the solutions to the environmental problems caused by the pulp and paper industry is to develop new pulping methods or to upgrade the existing ones. Of particular interest are the organosolv delignification methods, which are more environmentally friendly and allow obtaining higher yields of pulp, with relatively lower energy consumption and no sulfur emissions and industrial effluent.[8-9] Catalyzing oxidative delignification of plant raw material with hydrogen peroxide in an acid medium is an alternative to traditional methods of pulping.[10-11] Hydrogen peroxide is a weak oxidizer and is considered as one of the most acceptable reagents in terms of ecological impact for delignification processes.[12] Together with organic acids, it forms

peracetic and performic acids, which are characterized by high delignification activity. The use of organic peroxoacids with 4-10% concentration allows carrying out delignification of plant raw material at atmospheric pressure and a temperature of up to 100 °C, as well as reducing the consumption of fresh water.[13-15] The use of peroxoacids does not destroy the high molecular weight components of plant raw material. The pulp has a high brightness, allowing its use in the composition of paper and cardboard without application of additional bleaching agents. The cooking liquor of the process makes it possible to utilize the hemicelluloses of plant raw materials and to separate the lignin, which can be processed into valuable chemicals.[14]

One of the most frequently studied delignification methods of plant raw materials in a peroxoacid medium is the MILOX process. It uses concentrated solutions of performic and peracetic acids, is conducted in two or more stages, at high temperatures of up to 160-170 °C and requires longer cooking time.[15]

The technologies of oxidation pulping in organic solvents based on peracetic acid are quite widely covered in the literature,[14-18] unlike the process of obtaining pulp from wheat straw in a cooking solution of performic acid (PFA). Therefore, the purpose of this work has been to investigate the process of obtaining straw pulp in a PFA cooking solution and to determine its optimal technological parameters.

EXPERIMENTAL

Raw material

Wheat straw (*Triticum vulgare*) was obtained from the Kyiv region. Before pulping, it was sorted to remove leaves, ears and grass, crushed to the size of 15-20 mm, and then stored in desiccators for maintaining a constant level of moisture. The chemical composition of the wheat straw was determined in accordance with TAPPI standards,[19] namely: T-222 for lignin, T-257 for hot-water extractives, T-212 for extractives in 1% NaOH solution, T-204 for ethanol extractives, T-211 for ash content and T-264 for cellulose. The Wise method was used to determine the holocellulose.

Pulping process

The cooking liquor was prepared by mixing the solution of HCOOH, with a concentration ranging from 50 to 85%, and 30% solution of H_2O_2 with different HCOOH:H_2O_2 ratios: from 20:80 to 85:15 vol.% (Table 1). The wheat straw was cooked in a solution of PFA in heat-resistant flasks at a temperature of 90 ± 2 °C and a liquid-to-solid ratio of 10:1 during 60 to 120 minutes. To ensure the cooking process and to eliminate the loss of the cooking liquor solution, the flasks were connected to a reflux tube. The compounds of tungstate ($Na_2WO_4 \cdot 2H_2O$), molybdate ($MoWO_4 \cdot 2H_2O$) and titanium (TiO_2) were used as catalysts, in amounts of 1 to 5% based on the mass of absolutely dry material (a.d.m.). The pulp was washed with distilled water to achieve neutral pH, and air-dried.

Pulp properties

The pulp yield was determined by the gravimetric method. The content of residual lignin in the pulp was determined according to TAPPI method T-203os61. The obtained pulp was refined in a centrifugal grinding machine for achieving the freeness of 60±2 °SR. Then, handsheets of 75±1 g/m^2 were formed from the organosolv straw pulp on a Rapid-Kothen unit and their strength properties were evaluated in accordance with UNE standards: breaking length (57-054), tear index (57-058), folding strength (55-033) and brightness (57-062).

Table 1
Quality indicators of straw pulp (concentration of HCOOH – 85% and H_2O_2 – 30%, duration of cooking – 70 min)

Quality parameter	Ratio of HCOOH:H_2O_2, vol.%							
	20:80	30:70	40:60	50:50	60:40	70:30	80:20	85:15
pH of cooking solution*	2.5	2.3	2.1	1.9	1.7	1.5	1.3	1.1
Pulp yield, % on a.d.m.	57.1± 0.29	54.0± 0.34	53.1± 0.31	52.2± 0.34	51.3± 0.32	50.7± 0.31	50.9± 0.29	51.2± 0.32
Residual lignin, % on a.d.m.	2.38± 0.033	2.06± 0.032	1.85± 0.031	1.66± 0.033	1.74± 0.034	2.0± 0.035	2.19± 0.033	2.35± 0.034
Brightness, % ISO**	74	66	60	55	53	52	51	50

* standard deviation ±0.03; ** standard deviation ±0.56%

Scanning electron microscopy (SEM) analysis was performed using a PEM-106I microscope (SELMI, Ukraine) to observe the morphology of the PFA pulp.

To determine the mathematical dependencies of the straw pulp quality indicators on the main technical parameters, we used the method of full factorial experiments.[17] The optimum levels of the main technological parameters in the wheat straw PFA delignification process were determined. For this, multifactor optimization was carried out using the Gauss–Seidel method.[20]

RESULTS AND DISCUSSION

Chemical composition of wheat straw

As a result of the analysis, we obtained the following composition of the wheat straw: 45.6% cellulose, 16.5% lignin, 37.2% extractives in 1% NaOH solution, 10.1% hot-water extractives, 5.2% alcohol-benzene extractives and 6.5% ash. A part of the hemicelluloses fraction and the low molecular weight cellulose were additionally extracted by an alkali solution. The wheat straw has a higher content of soluble substances in the stalks than that of the most common representatives of deciduous and coniferous wood in Eastern Europe. It means that the stalks of wheat straw contain a large amount of components, such as starch, dyes, cyclic alcohols, sugar and ash. The stalks of wheat straw contain 2-3 times more alcohol-benzene soluble substances and 8-20 times more ash than wood. For a comparable amount of pulp, wheat straw contains less lignin than birch (21%) and spruce (28.5%). This suggests that mild delignification would be sufficient for wheat straw, compared to the delignification of wood.

Pulping process and properties of performic straw pulp

In order to determine the effect of the ratio of the cooking solution components on the wheat straw pulp properties, we carried out delignification, using a mixture of 85% formic acid and 30% hydrogen peroxide with ratios from 20:80 to 85:15 vol.% during 70 minutes. The quality parameters of the obtained straw pulp are shown in Table 1. The data in Table 1 indicate that while increasing the content of formic acid up to 70% in the cooking solution, the yield of the straw pulp is reduced. It is due to the intensification of lignin degradation, resulting from cleavage of α- and β-alkyl-aryl ether linkages of lignin macromolecules, dissolution of extractives, minerals and carbohydrates from the plant material and their transfer to the cooking solution.[12] Further growth of the HCOOH content increases the yield of the straw pulp through partial condensation of lignin. However, as can be seen from Table 1, with the increase of formic acid content in the cooking solution from 20 to 50 vol.%, the content of residual lignin decreases, but then the increase in the proportion of formic acid to more than 50% leads to the increase in the lignin content in the pulp. This dependence is explained by partial condensation reactions of lignin, which are activated with decreasing pH of the cooking solution.

The activation of condensation reactions with the increase of HCOOH content in the cooking solution is confirmed by the lower pulp brightness (Table 1). Therefore, the oxidation-organosolv pulping of the wheat straw should be performed with the following ratio of HCOOH: H_2O_2 = 50:50 vol.%, when the straw pulp has the least content of lignin. This ratio is confirmed by such indicators of lignin removal from the plant material, such as selectivity (SL), delignification degree (DD), degree of carbohydrates removal (DCR), and index of optimality (OPT), calculated by the following equations[17] (values are given in Table 2):

$$SL = \frac{Y}{100 - \frac{A \cdot DD}{100}} \cdot 100 \quad (1)$$

$$DD = 100 - \frac{Y \cdot C}{A} \quad (2)$$

$$DCR = 100 - \frac{Y \cdot (100 - C)}{100 - A} \quad (3)$$

$$OPT = DD \cdot SL / 100 \quad (4)$$

where A – original lignin content in plant, %; Y – yield of plant residue, %; C – residual lignin content in pulp, %.

As shown in Table 2, the optimal values of these indicators are achieved at the ratio of HCOOH:H_2O_2 = 50:50 vol.%.

Using of a high concentration of HCOOH, at a cooking temperature of 90 °C, creates technological problems because the temperature approaches the boiling point (100.8 °C). Therefore, the delignification of the wheat straw was investigated at lower concentration of formic acid in the cooking solution – from 50 to 85% with the ratio of HCOOH: H_2O_2 = 50:50 vol.%. The influence of the formic acid concentration on the quality parameters of the straw pulp is shown in Table 3.

Table 2
Selective indicators* of lignin dissolution by PFA cooking of wheat straw

Ratio of $HCOOH:H_2O_2$, vol.%	Delignification degree (DD), %	Selectivity (SL), %	Degree of carbohydrates removal (DCR), %	Index of optimality (OPT), %
20/80	92.7	69.4	31.4	60.0
30/70	94.1	68.1	35.3	62.0
40/60	94.7	66.8	35.6	63.2
50/50	95.4	65.3	35.8	63.9
60/40	94.9	63.9	36.4	59.1
70/30	93.8	54.6	45.9	51.3
80/20	92.7	54.2	46.5	50.3
85/15	92.2	53.5	47.4	49.3

*standard deviations: for DD ± 0.1%, for SL ± 0.07%, for DCR ± 0.05% and for OPT ± 0.06%

Table 3
Quality parameters of straw pulp obtained by PFA method with different acid concentration and duration of cooking (ratio of $HCOOH:H_2O_2$ = 50:50 vol.%)

Concentration of HCOOH, %	Duration of cooking, min	Pulp yield, % on a.d.m	Residual lignin, % on a.d.m
50	30	69.3 ± 0.36	5.9 ± 0.033
	60	63.2 ± 0.38	4.5 ± 0.033
	90	55.8 ± 0.41	3.5 ± 0.031
	120	51.7 ± 0.40	2.9 ± 0.032
60	30	60.2 ± 0.36	5.4 ± 0.033
	60	57.7 ± 0.38	3.6 ± 0.033
	90	50.9 ± 0.37	3.2 ± 0.032
	120	46.9 ± 0.37	2.7 ± 0.029
70	30	55.8 ± 0.38	4.6 ± 0.033
	60	52.3 ± 0.39	3.2 ± 0.029
	90	49.3 ± 0.38	2.7 ± 0.033
	120	43.3 ± 0.37	2.4 ± 0.032
85	30	53.6 ± 0.37	4.3 ± 0.031
	60	50.0 ± 0.38	2.8 ± 0.032
	90	45.0 ± 0.38	2.2 ± 0.027
	120	41.1 ± 0.39	1.9 ± 0.029

As can be seen from Table 3, the increase of formic acid concentration in the cooking solution and of the cooking duration leads to a decrease of the pulp yield in the range from 10.5 to 15.7%. The residual lignin content is reduced in the range from 1.0 to 1.6%, due to active conversion of lignin by the chain-radical mechanism and the degradation of polysaccharides with free radicals.[21] The obtained results allow asserting that the main amount of lignin is removed from the plant material in the first 30 minutes of the delignification process at a formic acid concentration of 50-60%. Therefore, carrying out PFA pulping of wheat straw with HCOOH concentration exceeding 60% is unreasonable.

The morphology of the PFA pulp was studied by means of SEM. Figure 1 presents electron micrographs of the surfaces of organosolv straw pulp prepared by the PFA method, using different concentrations of HCOOH in the cooking solution. As shown in Figure 1, an increase of formic acid concentration from 60 to 85% in the cooking liquor does not lead to a significant improvement in the structure of PFA pulps.

Mathematical modeling of delignification process

To obtain statistical models of the PFA delignification process of wheat straw, we carried out mathematical modeling of PFA cooking and sought to determine the optimal values for the parameters of this process. For this, the main technological parameters (X_i) that have an effect on the pulp quality (Y_i) were considered. After ranking them in a decreasing order of their impact on the pulp yield (Y_1) and on the content of

residual lignin (Y_2), we found the following sequence: X_1 – concentration of formic acid, %; X_2 – cooking duration, min; X_3 – pH of cooking solution; X_4 – liquid-to-solid ratio; X_5 – degree of compaction; X_6 – moisture and X_7 – chemical composition of raw material.

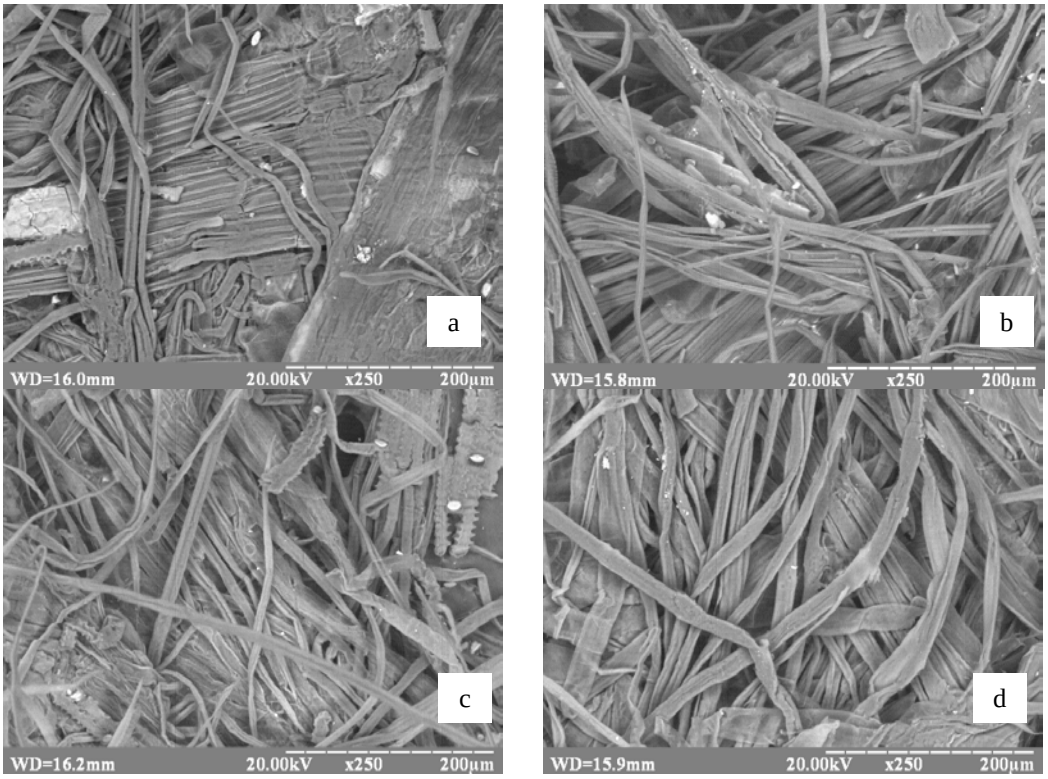

Figure 1: SEM images of PFA straw pulp obtained with different acid concentrations: 50% (a), 60% (b), 70% (c) and 85% (d)

The parameters X_3-X_7 are constant in the study and, therefore, are not considered in the calculation of regression equations, because we used for pulping wheat straw with the same moisture and chemical composition, as well as the same degree of compaction, liquid-to-solid ratio and pH of cooking solution. Coding the parameters X_i was carried out by the following formula:

$$x_{i\,cod} = (x_{i\,nat} - x_{i\,av})/\Delta x_i, \quad (5)$$

where $x_{i\,cod}$ – the value of parameter X_i in a coded form; $x_{i\,nat}$ – the value of parameter X_i in natural units, $x_{i\,av}$ – the average value of the parameter X_i; Δx_i – the interval of parameter variation X_i.

After coding the parameters X_i according to the formula (Eq. 5) and carrying out statistical processing of the experimental data by the algorithm of the full factorial experiment, using the criteria of Cochran, Student and Fisher, the following adequate regression equations for PFA delignification of wheat straw were received:

Pulp yield, %:

$$Y_1 = 51.4 - 5.6\ x_1 - 6.8\ x_2 + 1.7\ x_1x_2 + 2.8\ x_1^2 - 0.8\ x_2^2 \quad (6)$$

Residual lignin content, %:

$$Y_2 = 2.9 - 1.2\ x_1 - 0.67\ x_2 - 0.03\ x_1x_2 + 0.85\ x_1^2 + 0.17\ x_2^2 \quad (7)$$

The Gauss–Seidel method was used for multifactor optimization of the statistical regression equations (Eqs. 6 and 7). The optimal point was found to have the following values of parameters X_1 and X_2: concentration of formic acid – 50% and duration of cooking – 120 min, respectively. The quality indicators of the obtained straw pulp at the optimum point have the following values: yield – 51.9% and residual lignin content – 1.6% on a.d.m. Therefore, the delignification process can be considered as optimal when carried out under the following conditions: concentration of formic acid – 50%, duration – 120 minutes, temperature – 90 °C, the ratio of $HCOOH:H_2O_2$ = 50:50 vol.%.

Influence of catalyst on delignification process

According to the optimized technological parameters, a series of pulping runs were carried out using the catalysts Na_2WO_4•$2H_2O$, Na_2MoO_4•$2H_2O$ and TiO_2 to intensify the delignification process of the wheat straw. The impact of catalyst consumption on the quality indicators of PFA straw pulp is shown in Figure 2. As seen in Figure 2, the addition of various catalysts to the cooking solution accelerates the dissolution of lignin macromolecules and reduces the residual lignin content in the pulp in the range of 0.3-2.0% on a.d.m., and the yield is reduced from 1.5 to 10.9% on a.d.m. The obtained experimental data agree with those reported in the literature regarding the catalytic action of the studied catalysts.[22] They also indicate that, for this method of delignification, titanium oxide has the greatest selectivity relative to lignin. Using TiO_2 allows saving the pulp yield, but the residual lignin content is reduced by almost 3 times, compared to wheat straw cooking by the PFA method without catalyst. Maximum efficiency of titanium oxide is achieved at an amount of 2% on a.d.m. In this case, the maximum reduction of residual lignin in the obtained pulp was observed with minimal loss of yield (Fig. 2). Further increase of the catalyst addition up to 5% is economically inefficient, because it leads to no noticeable improvement of pulp quality indicators.

Under the above-mentioned optimum conditions, with the addition of an amount of 2% on a.d.m. of titanium oxide to the cooking solution, a series cooking runs were carried out to determine the effect of the catalyst on the mechanical properties of the PFA straw pulp. The quality indicators of the obtained organosolv straw pulp are shown in Table 4. The analysis of the data in Table 4 shows that the addition of TiO_2 catalyst to the cooking solution improves the mechanical properties of obtained straw pulp: breaking length increases from 10 to 21%, tear index increases from 5 to 11%, folding strength increases from 12 to 33%, compared to pulping without catalyst. In this case, the mechanical properties of the obtained pulp increase with increasing cooking duration due to better delignification process and saving of hemicellulose, which contributes to the formation of additional hydrogen bonds between the polysaccharides and the improvement of the pulp quality indicators.

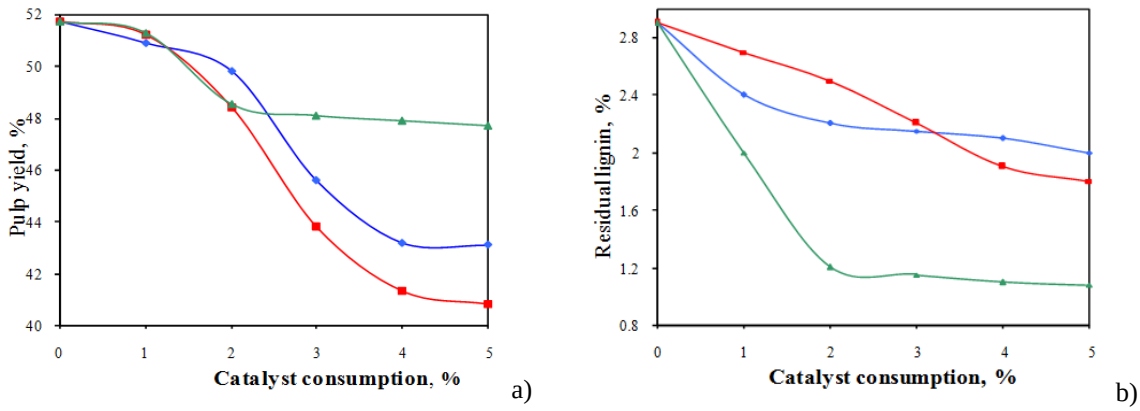

Figure 2: Dependence of PFA pulp yield (a) and residual lignin content (b) on amount of catalyst: ♦ Na_2WO_4·$2H_2O$; ■ Na_2MoO_4·$2H_2O$; ▲ TiO_2

Table 4
Mechanical properties of performic straw pulp obtained by the cooking process with and without TiO_2 (catalyst amount – 2% on a.d.m.)

Cooking time, min	Breaking length, m		Tear index, mN·m^2/g		Folding strength, double folds	
	-	TiO_2	-	TiO_2	-	TiO_2
30	3850 ± 30	4250 ± 30	3.8 ± 0.12	4.0 ± 0.11	300 ± 12	400 ± 13
60	4200 ± 34	5100 ± 35	4.2 ± 0.12	4.6 ± 0.12	550 ± 13	650 ± 14
90	4800 ± 40	5900 ± 40	4.6 ± 0.13	5.0 ± 0.14	700 ± 14	800 ± 15
120	5450 ± 45	6600 ± 50	4.9 ± 0.14	5.5 ± 0.16	760 ± 15	870 ± 16

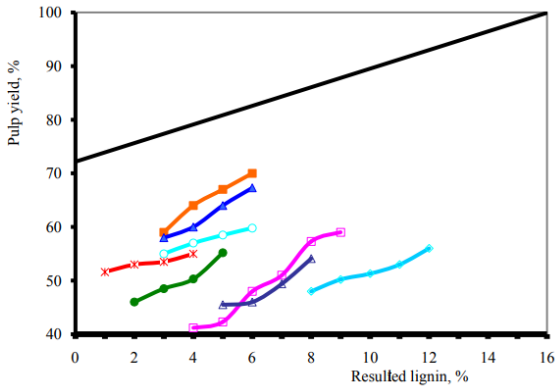

Figure 3: Lignin–carbohydrate diagram of wheat straw delignification by different methods: ■ ASE,[16] ♦ ASAE,[16] ○ PFA; * PFA+TiO_2, • PA + $Na_2WO_4 \cdot 2H_2O$,[12] □ PA,[12] Δ N-Su,[24] ◊ soda[23]

The mechanical properties of the obtained organosolv straw pulp are similar to those of kraft straw pulp, with a burst index of 4.09 kNg^{-1} and tear index of 4.57 mNm^2g^{-1}.[23] This indicates that PFA straw pulp can be used in the pulp and paper industry for the production of paper and cardboard.

Lignin–carbohydrate diagram

In order to compare the efficiency of the investigated PFA cooking process performed by various delignification methods for obtaining straw pulp, we constructed a lignin–carbohydrate diagram (Fig. 3). The proposed methodology for constructing the diagram differs from those of the known lignin–carbohydrate diagrams of Ross, Geertz and Schmidt, due to its simplicity of construction. In short, the method is described as follows. On the y-axis, the pulp yield is indicated starting from 40% (for better visualization of contents a few percent lower than those of cellulose in the raw plant material) to 100%. On the y-axis, the point corresponding to the holocellulose content is also indicated. On the x-axis, the percentage value of the lignin content in pulp is indicated from zero to its value in the raw plant material. The intersection of the horizontal axis at 100% yield and the vertical axis of the lignin content creates the point corresponding to the initial composition of all plant components (cellulose, hemicelluloses, lignin, resins, fats, waxes, mineral and other extractive substances). The line that links this point with the point of the holocellulose content in the raw plant material can be considered as the line of "ideal delignification". It characterizes the maximal polysaccharide content for certain residual lignin content in the pulp. The dependences of pulp yield on residual lignin content in the pulps obtained by different methods of delignification are further applied on the lignin–carbohydrate diagram. So, the closer the line of a certain delignification method is to the line of "ideal delignification", the higher is the polysaccharide yield in the obtained pulp and thus the delignification method is more efficient.

As can be noted from the diagram (Fig. 3), the different delignification methods can be arranged in the following sequence with regard to their closeness to the line of "ideal delignification", *i.e.* in the order of increasing efficiency in obtaining wheat straw pulp: soda – neutral-sulphite (N-Su) – peracetic (PA) – PA + $Na_2WO_4 \cdot 2H_2O$ – PFA – PFA + TiO_2 – alkaline-sulphite-anthraquinone-ethanol (ASAE) – ammonium-sulphite-alcohol (ASE).

Commercial aspects of PFA pulping

The high costs of peroxide and formic acid might be a restriction in using this process at an industrial scale. However, the proposed PFA process of plant raw material delignification is carried out in one stage at lower temperatures and at atmospheric pressure, in comparison with traditional sulfate, sulphite or MELOX cooking methods. The proposed method makes it possible to obtain hemicelluloses and lignin separately, which can be processed into valuable chemicals. For example, hydrolytic alcohol can be obtained from hexose sugars, and furfural from pentose sugars, while lignin can be used to obtain products used as liquid fuels or to separate individual organic compounds. In addition, from the spent liquors after regeneration, formic acid is returned to the technological cycle in quantities of up to 80%, which significantly reduces the total

capital costs for the production of organosolv straw pulp.

CONCLUSION

The obtained results show that PFA pulping is an efficient method of obtaining pulp from wheat straw. The following values of the technological parameters for PFA pulping are recommended: the ratio of HCOOH: H_2O_2 = 50:50 vol.%, the concentration of formic acid 50%, temperature 90 °C, 30-120 min duration. Titanium oxide has the highest catalytic effect on the delignification process of wheat straw among the investigated catalysts. PFA pulping of wheat straw with an amount of 2% on a.d.m. TiO_2 contributes to an increase in the mechanical properties of the obtained straw pulp from 5 to 33%, compared with pulping without catalyst. An indicator of lignin removal from the plant material, such as selectivity, decreases with increasing the content of HCOOH in the cooking solution, but the degree of carbohydrate removal increases. Other indicators, such as delignification degree and index of optimality, increase with increasing the content of HCOOH from 20:80 to 50:50 vol.%, but decrease with further increasing content of formic acid. According to their increasing efficiency of removing lignin from wheat straw, the investigated pulping methods can be arranged in the following sequence: soda – N-Su – PA – PA + $Na_2WO_4 \cdot 2H_2O$ – PFA – PFA + TiO_2 – ASAE – ASE. The mechanical properties of the obtained PFA pulp indicate the prospect of its use in the pulp and paper industry for the production of paper and paperboard.

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