Two-step straw processing – a new concept of silica problem solution

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ABSTRACT

Two-step wheat, and rice straw processing, as a new concept of agricultural by-product utilization, is presented. The first step includes wet removal of ash/silica, the second step includes conventional non-sulfur high-yield pulping. The strength properties are shown and compared with the properties of conventional hardwood high yield pulp (fluting). The beneficial effect of alkali pretreatment of straw on ash/silica removal was confirmed. Under the same experimental conditions of impregnation step, the desilication rate of the wheat straw sample (WS I) reached the value of 90.8%, based on acid insoluble ash (AISA) content, while the desilication rate of rice straw samples were determined to be 32.7% (RS I) and 51.0% (RS II) respectively. The lower number for RS I was caused, most likely, by a lower charge of impregnation chemical. Also, the positive effect of the impregnation, that causes more extensive combined degree of delignification and desilication, was demonstrated. The fact that the most of the strength properties of impregnated and delignified straw samples exceed the strength properties of commercial pulp, as well as the properties of the laboratory samples (red oak, wheat straw) processed without the impregnation, is another positive finding.

INTRODUCTION

Most of the non-wood fibers are derived from annual plants. The advantage of annual plants is that they can be grown on farmland and harvested each year with high yields (5-20 tone/ha depending on the crop). As a renewable resource they can be replaced annually, compared with the much longer growth cycle for wood.

Non-wood pulp production, which represents less than 10% of the total world's pulp source, is based primarily on straw (46%), bagasse (14%), and bamboo (6%). Agricultural by-products account for 73% of the world's non-wood capacity, while natural plants such as reed and bamboo account for 18%, and the remainder consists mainly of industrial crops *(1).*

In North America, there is over 200 million tons of agricultural residues, (wheat, rice, corn, flax, barley and other cereal grain straw) that are produced every year after harvesting. Although some of these residues must be left in the field for soil conservation purposes, the bulk of the residues are available for industrial use. The U.S. and Canada have an abundance of agricultural residues, which could be used for pulp and paper production. Wheat straw and corn stalks represent the most underutilized fiber resources in the U.S. *(2).*

Agricultural residues (straws) are primarily composed of cellulose, lignin and hemicelluloses. But straws also contain significant amounts of pectins, proteins and, most importantly, inorganic compounds (ash), most of which is silica *(3, 4.)* The ash component of plants varies greatly between families of plants as well as between individual species. The largest mineral component of ash, in perennial grasses, is silica. The main difference in silica contents between perennial grass species is often related to the photosynthetic mechanism of the grass, and to the amount of water being transpired by the plant *(5).* Within species, the water use efficiency will fluctuate depending on the region in which the crops are grown, and on the soil type *(6, 7).*

The total holocellulose content of wheat straw is similar to that in trees. In comparison with wood, straw contains less cellulose. The lignin content of wheat straw (16 - 21 %) is significantly lower than that of softwoods (26 - 34 %), and hardwoods (23 - 30 %). Cereal straws have relatively high silica and potassium content. Wheat straw contains 4-10% silica as small crystals embedded in the straw, rice straw has an even higher silica content of 9-14%, and other cereals such as barley, oat and rye straw have 1-6% silica. Wood on the other hand has silica content of less than 1%. Xylans are the principal hemicellulose of hardwoods and straws, analytically determined as pentosans.

Silica is distributed throughout the straw stem and is most concentrated in small bodies called phytoliths ("silica bodies", "silicophytoliths"), which cover the outer surface of the stem *(8)*. Studied phytoliths generally range from a few to several tens of micrometers. Silica deposits in terrestrial plants occur most commonly in the form of particles of characteristic shapes (dumbbells, saddles, bowls, boats, etc.), that are generally not diagnostic to the genus or species taxonomic level. Research efforts focused on biosilicification made by marine living sponges and unicellular algae have led to the finding of unique remarkably complex structures. Recent studies of silica structures made by living sponges show, that this remarkable annular substructure of demosponge biosilica spicules reveals that the deposited material is nano-particulate, with a mean particle diameter of 74 ±13 nm *(9)*.

The ash, and most specifically, the silica, remains the greatest impediment to the establishment of commercial straw pulping. Silica is extremely alkali soluble and its presence in spent liquors inhibits conventional chemical recovery process in three ways: 1/ by scaling multiple effect evaporators, 2/ by forming a colloid in the smelt tank reducing causticizing efficiency, and 3/ by forming glass in the lime kiln on lime particles. Therefore, as much silica must be removed from the recovery cycle as gets into the process with the raw material.

There have been many attempts made to resolve the silica issue, including black liquor desilication with carbon dioxide (flue gases), two-stage causticizing desilication method, green liquor desilication with lime, the incorporation of a sixth evaporator, used when an evaporator is being cleaned, and the use of ammonium- or potassium-based pulping with the liquor disposed of as a fertilizer *(3, 10)*. Also, incorporation of some of the pulping liquor into the product can partially avoid silica-related chemical recovery problems *(3)*. The appropriate pretreatment (dry cleaning) of straw is one of the solutions to minimize scaling problems in the recovery system. The dry cleaning system is fairly simple; it has low specific power consumption and its investment costs are rather low. Reductions in the silicon content from 20 to 50 % in straw have been reported *(10, 11)*.

The beneficial effect of sodium carbonate as a silica-leaching agent was studied *(12)*. Under the conditions of the experimental design, a desilication rate of 50-75 % can be reached. Sodium carbonate, with its additional hemicellulose conservation effect, might be an interesting impregnation agent.

Due to lower lignin content in annual plants and agricultural residues and their more open morphological structure, compared to hardwoods and softwoods, milder cooking conditions and a wider range of no-sulfur processes could be applied. Various chemical processes, including the mechanico-chemical process, are used for straw pulping. The lime or lime-soda processes are the classical methods for straw pulping and yield coarse pulps for the production of board, cheap packaging and wrapping papers, and corrugating medium. The soda, kraft and neutral sulfite processes are employed for producing various types of pulps, ranging from high-yield semichemical to soft bleached grades *(13-15)*.

In the present study, the concept of agricultural residue (straw) processing is submitted, including solubilization of nano/micro particles of silica deposits, and retention of silica-enriched calcium carbonate filler in papermaking furnish via a nano-particle retention system.

EXPERIMENTAL

Raw materials:

- **Wheat straw** (*Triticum Aestivum*) from the 1998 year collection (Michigan region)
- **Rice straw** *(Oryza sativa)* from the 2003 California harvest

Straw samples were cut into 15 to 20 mm long strips, hand cleaned of sand and dust prior to theexperiments. The straws, yellowish and greenish in color, were of high quality. They were stored at a dry-content of about 94 %. Whole stems including the leaves and rachis, were used.

Procedures and methods*:* Basic chemical analysis and moisture content in the both of the samples were performed according to TAPPI Standard Test Methods. The methods and results obtained are shown in **Table 1**

The scheme of whole process is depicted in the **Figure 1**.

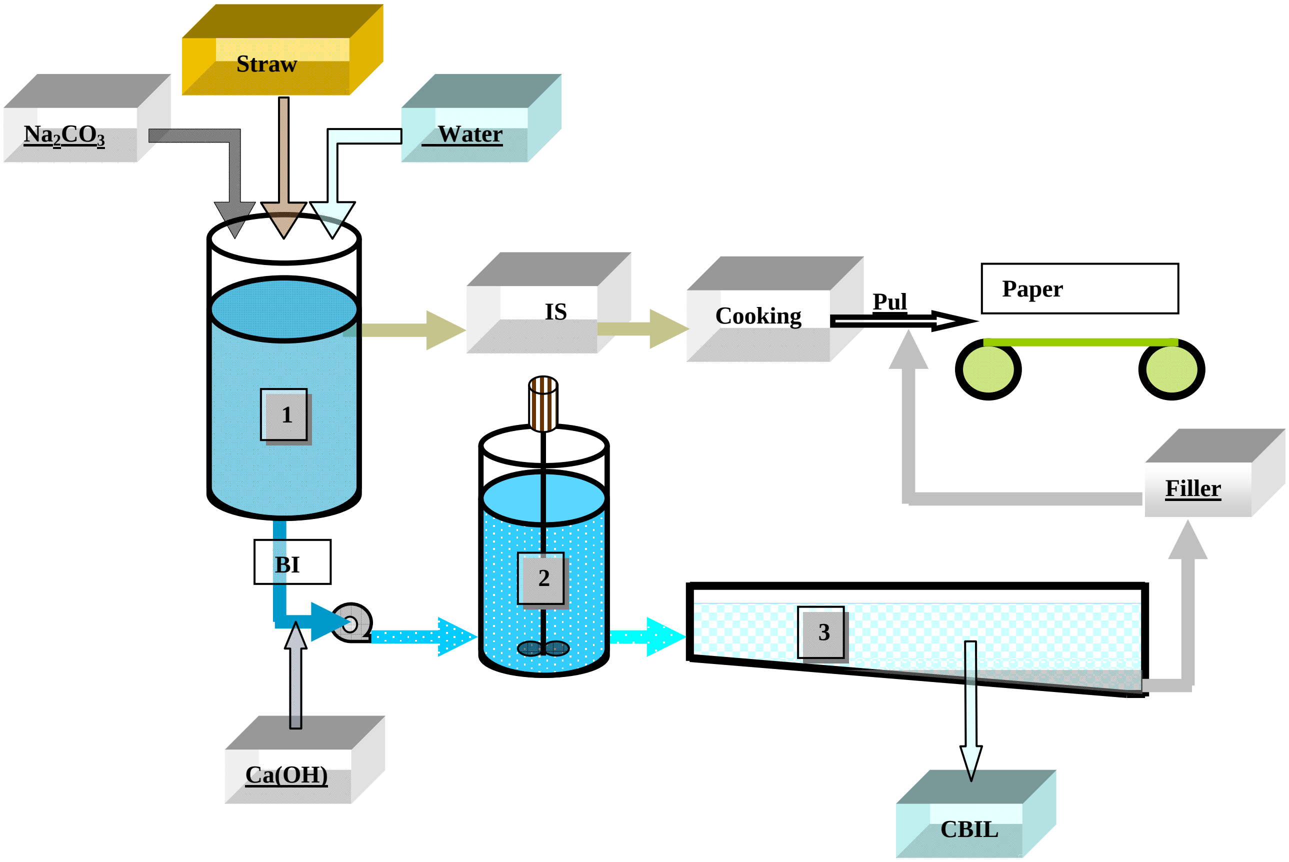

***Figure 1**. Simplified scheme of the concept – processing of agricultural residues*

Table 1. Chemical composition of wheat straw (WS) *(12)* and rice straw (RS)

Analysis	WS	RS	Test method (TAPPI)
Moisture content, %	5.4	7.6	T 208
EtOH-Benzene extract, %	3.8	2.9	T 204
Pentosans, %	22.2	20.6	T 223
Klason lignin, %	21.3	20.5	T 222
Ash in Klason lignin, %	5.6	24.1	T 211
UV lignin, %	2.0	2.3	UM 250
Total ash, %	3.0	9.7	T 211
Acid insoluble ash, %	1.2	5.0	T 244

Straw impregnation: Impregnation of wheat and rice straw samples were conducted in a 6.5 L stationary batch digester (M&K Systems Inc.) equipped with a electrical heat exchanger and a liquor circulation system.

The experimental conditions were maintained as follows:

160 grams of air-dried straw (159.6 g o.d.) with cca 6% of moisture content were soaked with 3,000 mL of cold tap water (ratio of straw to liquid equals to 1:20) at the ambient temperature. After the digester was heated up to the temperature of impregnation (90 or 95 ^{o}C), a calculated amount of anhydrous Na$_2$CO$_3$ was dissolved in a small amount of water and added into the digester. The time of the impregnation at the

controlled temperature and atmospheric pressure was 30 minutes for all experiments. Specific conditions for different impregnation experiments are described in **Table 2**:

Table 2. Experimental Conditions for Straw Impregnation

Sample	Temperature (^{o}C)	Reaction time (min)	Chemical Charge (%Na_2O)
WS I	95	30	15
RS I	90	30	7.5
RS II	90	30	15

At the end of the experiments, the pulps were washed copiously with fresh hot tap water to a neutral pH. For chemical analysis, the wheat straw and pulp was ground in a Wiley mill and the fraction smaller than 40 mesh was collected. After the impregnated samples were washed and air-dried, total yield, Klason lignin total ash, and acid insoluble ash were determined.

Delignification: Delignification of impregnated straw samples were performed in a 6.5 L stationary batch digester (M&K Systems Inc.) equipped with a electrical heat exchanger and a liquor circulation system. Delignification was maintained at the conditions as follows (**Table 3**):

Table 3: Experimental Conditions for Straw Delignification

Sample	Time to max. Temperature (min)	Max. Temperature (^{o}C)	Time @ max. Temperature (min)	Chemical Charge (%Na_2O)
WS I	25	174	30	5.0
RS I	15	145	15	5.0
RS II	25	174	30	5.0

Disintegration and refining: Immediately after the cooking, the next processing of pulp samples was carried out in 2 steps. The first step, disintegration of unwashed pulp, was performed in a laboratory blender (Waring) at medium speed for 15 seconds. The second step, fine refining (beating), was performed in the PFI laboratory mill (at the consistency of 10 %) to achieve desirable freeness. Counts of the revolutions were recorded. The degree of freeness was chosen depending on initial freeness obtained after the delignification step.

Screening. The pulps after 2^{o} refining were screened on laboratory vibration slot screener (0.006 in.), accept was collected on a 150-mesh screen and stored in cooling room at consistency ca. 30 %. Total yield, screened yield and screening (reject) respectively were determined.

Pulp testing. To evaluate the strength properties of the pulps, Tappi Standard handsheets with basis weight of 60 g/m^2 were prepared and conditioned at standard conditions. For ring crush test handsheets with the basis weight of 130 g/m^2 were prepared. All tests were performed according TAPPI Standard Methods.

RESULTS AND DISCUSSION

Chemical analysis

Before carrying out the impregnation and delignification experiments, chemical analysis of the wheat and rice straw was performed in accordance with TAPPI Test Methods. The results of analysis are listed in **Table 1**. The table contains also previously published results of wheat straw chemical analysis *(12).* The main difference in content of total and acid insoluble ash is evident. The total ash content in non-processed rice straw was 9.7%, and the acid insoluble ash was 5.0%. These not surprising much higher numbers (compared with the wheat straw) represent the average levels of the ash content in rice straw, while in some samples the content of total ash and acid insoluble ash can vary depending on the plant species and the type of the soil *(6).* Because acid insoluble ash, determined by any of the methods available, could contain mainly silica or silicates, not dissolved under acidic conditions, the term “desilication” instead of “deashing” was used.

Impregnation/Desilication

Results of the impregnation/desilication kinetics study were already published *(12)*. The temperature, time, and chemical charge were assumed to be the important parameters influencing the process of impregnation/desilication. The significance of these three parameters was analyzed with the central composite rotatable design method *(16)*. The first step was to define the range of every single variable. With the computer software, a set of 20 experiments was generated. Second-order polynomial analysis of the experimental data led to different quadratic (second-order) equations. Although the showing of the detailed experimental results was not the goal of this project, the strongest impact of temperature and time on the impregnation step was confirmed.

The statistical program allows displaying the effect of the single variables in 2-D or 3-D contour forms. The effect of wheat and rice straw impregnation/desilication step on total yield, degree of delignification, and degree of desilication is shown in **Figure 2-4**. Because the time and temperature of the impregnation was found as the parameters with the strongest influence on every single dependent variable (and the sodium carbonate with the lowest influence), the 2-D contours at constant charge of sodium carbonate (10% Na2O on raw material) are displayed.

Unfortunately, during the impregnation of wheat straw, a part of the organic compounds is also removed, while absolute selective leaching of silica is a problem not yet solved. Removal of the organic part of wheat/rice straw leads to a drop of total yield values. In the context of time and temperature, the effect of sodium carbonate has less importance.

The contour plot for yield (**Figure 2**) shows the same effect of temperature and time for a whole range of temperatures, until the time reaches approximately 30 min. After that time, at any level of temperature, increasing impregnation time doesn't affect the total yield, i.e., the solubilization (yield) is stabilized. This observation is identical to that obtained in other studies *(17)*.

For example, during the impregnation of wheat straw with Na_2CO_3 (10% Na_2O) at a temperature of 60 ^oC, the material loss after 30 min and 60 min reached 7.4% and 8.0%, respectively. Using NaOH as the impregnation chemical, a more effective desilication rate was obtained, but with significantly higher effect on solubility (lower yield) - 18.5%, and 22.3 % respectively. From the contours shown in the **Figure 2** is evident, that at the same conditions applied in the impregnation step rice straw gives 10-12 % lower yield compared with the wheat straw. This finding presented earlier is in good accordance with the results shown in the **Table 4**. Lower yield of the sample RS II is caused by the higher charge of impregnation chemical compared with the sample RS I.

Table 4. Experimental conditions for impregnation and pulping of straws. (KL - Klason Lignin, AISA - Acid Insoluble Ash, RM - Raw Material IRM - Impregnated Raw Material)

Step	Property	WS	WS I	RS I	RS II
Raw Material (RM)	Total Ash (%)	3,0	3,0	9,7	9,7
	KL (%)	21,3	21,3	20,5	20,5
	AISA (% on RM)	1,2	1,2	4,9	4,9
Impregnation	Total Yield (%)	/	88,1	81.7	76.6
	KL (% on RM)	/	16,9	16,5	14,3
	Total Ash (% on RM)	/	1,8	4,6	3,9
	AISA (% on RM)	/	0,11	3,3	2,4
Delignification	Total Yield (% on IRM)	59,3	69,8	56.6	42.1
	KL (% on pulp)	14,3	9,5		
	KL (% on IRM)	/	6,6		
	KL (% on RM)	8,5	5,8		
	Ash (% on pulp)	1,5	1,9		
	Ash (% on IRM))	/	1,3	Analysis in progress	
	Ash (% on RM)	0,9	1,1		
	AISA (% on pulp)	0,4	0,2		
	AISA (% on IRM)	/	0,1		
	AISA (% on RM)	0,2	0,1		

Extension of the lignin removal (delignification) during the impregnation step is shown in the **Figure 3**.

Again, the shape of the contours is very similar to that shown in the **Figure 2.** Results plotted in this figure are based on the determination of ash-free Klason lignin in the samples of impregnated straws. The delignification rate during the impregnation step is slightly higher in the case of rice straw. This fact was confirmed by the impregnation of the samples WS I, RS I, and RS II. The numbers valid for Klason lignin content (**Table 4**) are moderately lower for RS I and RS II samples, but they will be significantly lower, when the content of the ash in Klason lignin is taken into account.

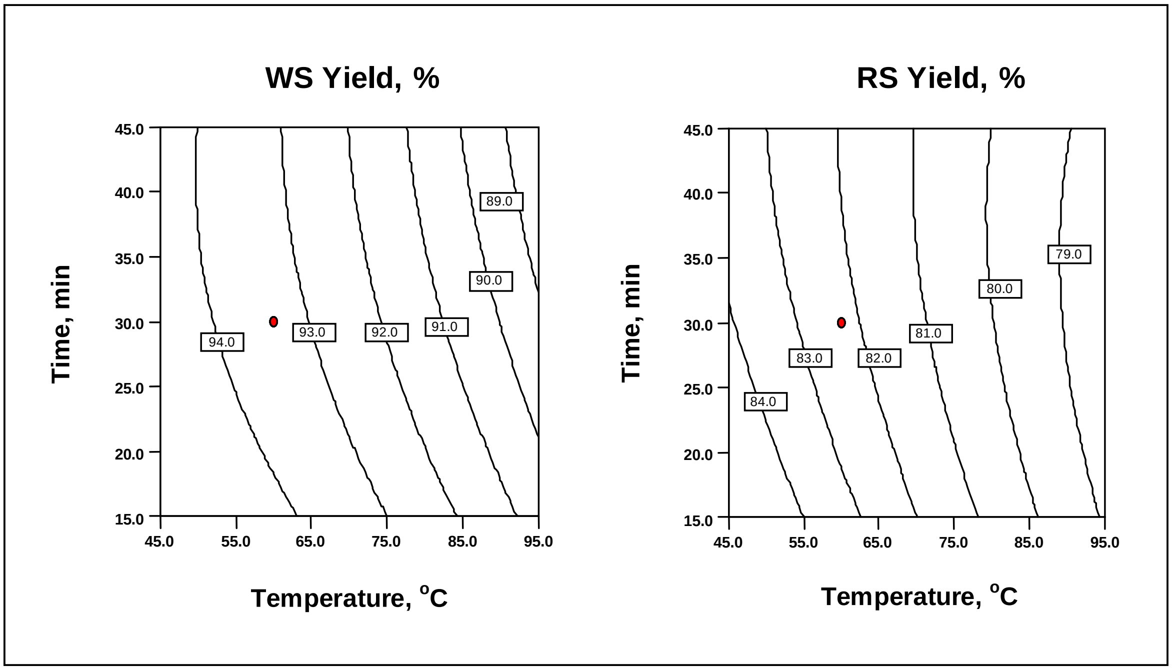

Figure 2. Contour plot of the wheat straw (WS) *(12)* and rice straw (RS) yield after **impregnation/desilication** as a function of time and temperature at constant charge of Na_2CO_3 (10% Na_2O on raw material)

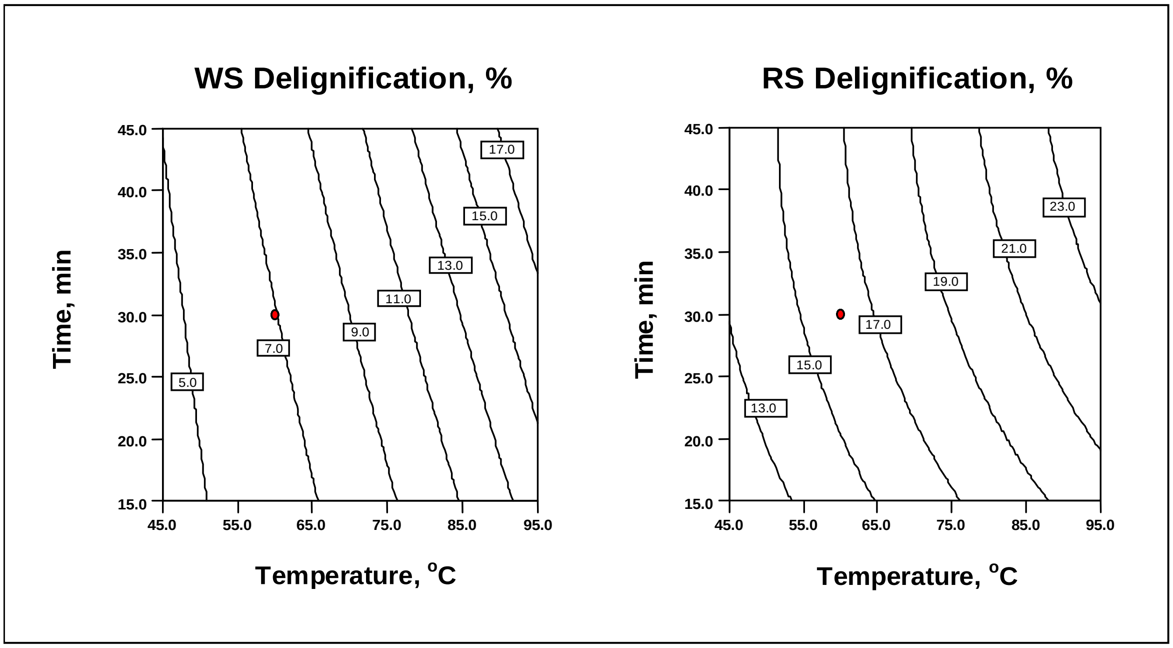

Figure 3. Contour plot of the wheat straw (WS) *(12)* and rice straw (RS) **delignification** as a function of time and temperature at constant charge of Na_2CO_3 (10% Na_2O on raw material).

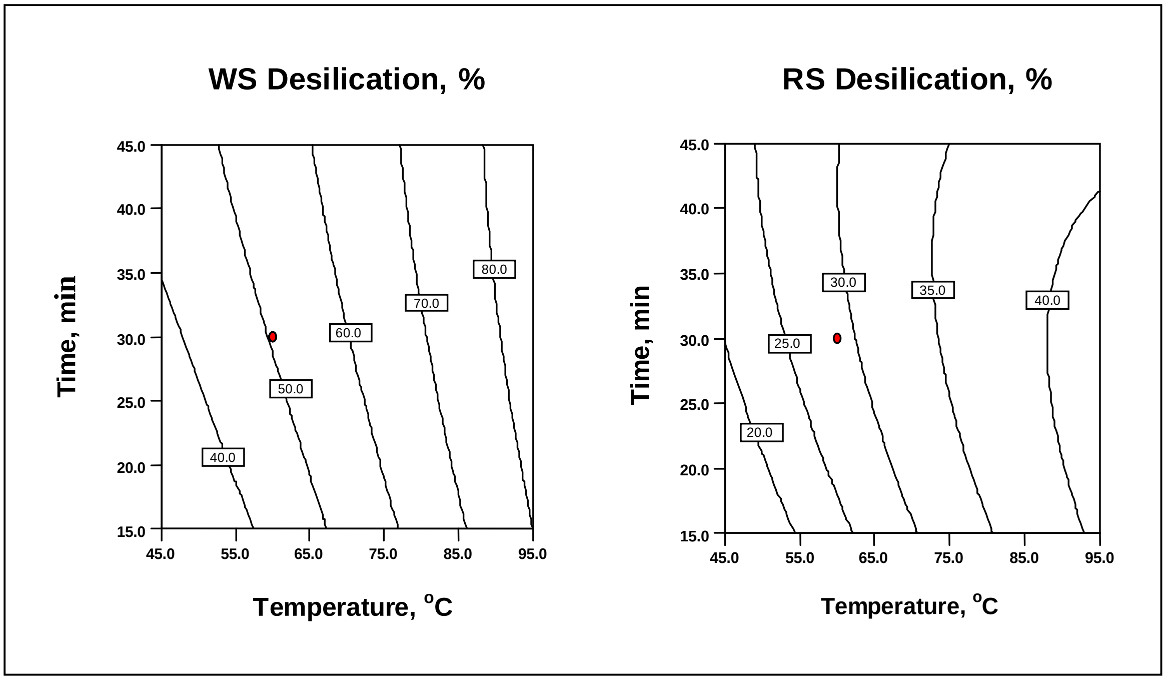

Figure 4. Contour plot of the wheat straw (WS) *(12)* and rice straw (RS) **desilication** as a function of time and temperature at constant charge of Na_2CO_3 (10% Na_2O on raw material).

The aim of the concept shown in the **Figure 1** is to evaluate the integral use of agricultural residues in the papermaking process, including the silica wet extraction/leaching in the impregnation step. Results of the wheat and rice straw desilication kinetics (**Figure 4**) show significant difference in the silica removal extent. In spite of the higher content of silica in rice straw raw material, significantly lower desilication rate for this material was observed. As seen in this contour, at the conditions of the central point of the experimental design, the desilication rate 50% for wheat straw and 27% for rice straw can be reached. At the higher temperatures, the desilication rate can reach 70 - 75%, and approximately 40%, respectively. Much lower desilication rate of rice straw raw material was observed during the impregnation of samples RS I, and RS (**Table 4**). While the desilication rate of WS I reached 90.8%, based on acid insoluble ash (AISA) content, the measured desilication rates were only 32.7%, and 51.0% for RS I and RS II, respectively. Lower number valid for RS I, was caused most likely by lower charge of impregnation chemical.

The most important fact is that even low levels of sodium carbonate charge causes leaching of silica (acid insoluble ash) from the raw material. The charge of sodium carbonate at the central points, even less, is sufficient to leach a significant quantity of ash/silica, in the first period of the impregnation phase of the process. It seems that part of the silica located on the surface of the stem is easily affected and removed. Prolonged processing could have a beneficial effect on deashing, but, on the other hand, could negatively influence other important process parameters, and therefore, the yield.

Delignification /Strength properties

At the delignification step of the concept presented here, thoroughly washed impregnated raw materials (to remove all dissolved ash/silica) was cooked under standard delignification conditions, applied for commercial non-sulfur pulping of hardwood. The reason of this decision was not to optimize delignification step, but to compare the characteristics and strength properties of laboratory samples with the commercial pulp used for corrugated medium production.

There are some reasons why sodium carbonate was chosen as the impregnation, and, at the same time, the delignification, chemical. The first reason comes from the fact, that sodium carbonate presents a beneficial effect on the silica leaching process. The effective impregnation/desilication of the wheat and rice straw can be carried out by sodium carbonate at a temperature up to 100 °C.

The second reason comes from industrial experience with sodium carbonate application in high yield pulping for fluting production. The process is well known as “non-sulfur pulping”, and is particularly suitable for either sole straw pulping or wood/wheat straw mixed pulping. Compared with sodium hydroxide, Na_2CO_3 with its hemicelluloses conservation effect may be a more interesting impregnation/desilication, and at the same time a delignification agent. Interest on sodium carbonate, rather than on sodium hydroxide, is also due to the fact that recovery of sodium hydroxide is more complex than that of sodium carbonate.

Results of chemical composition of laboratory prepared straw samples are shown in the **Table 4,** along with their strength properties listed in the **Table 5**. Based on the results in **Table 4**, we can consider that the combination of impregnation, and pulping of straw samples has impact on degree of delignification, as well as on that of desilication. At very similar total yield after delignification and the impregnation, respectively, (59.3% for WS and 61.5% for WS I), impregnation of WS I sample causes more extensive total/combined degree of delignification and desilication. This is not surprising, while partial lignin removal and silica leaching in the impregnation step was confirmed, lower total yields found during the impregnation, and delignification of rice straw (compared with the wheat straw) is again in good accordance with the results published earlier *(12).*

Table 5. Strength properties of unbleached pulps @ 60 g/m^2 (Ring Crush test @ 130 g/m^2)

Sample	Freeness mL CSF	Burst Index (kPa.m^2/g)	Gurley Stiffness (GSU)	Tear Tear (mN*m^2/g)	Tensile Index (N*m/g)	Stretch (%)	Folding Endurance ($\log_{10}$ of No.)	Ring Crush (kN/m)
WS I	400	3,5	79,7	6,1	49,9	2,69	2,1	2,2
	125	5,7	57,2	3,7	64,6	2,80	2,7	2,1
RS I	300	2,8	71,4	6,6	65,8	3,59	1,9	1,8
	172	3,5	61,4	5,5	71,7	3,39	2,2	2,0
RS II	235	2,7	75,8	6,0	40,3	2,57	2,1	2,3
	100	3,7	65,6	5,7	49,7	3,74	2,4	2,1
Red Oak *(18)*	400	3,5	81,4	7,2	45,6	2,71	2,0	1,5
WS *(18)*	400	2,0	68,0	4,6	32,6	2,00	1,7	1,4
	220	4,0	94,8	3,2	54,4	1,80	2,9	2,2
Commercial pulp *(18)*	400	1,8	80,2	4,7	33,2	2,00	1,1	1,4

Strength properties of the pulps prepared in the laboratory are shown in the **Table 5**, and are compared with the laboratory samples of red oak, wheat straw and commercial high yield pulp prepared by non-sulfur (sodium carbonate) delignification process, avoiding the impregnation step. To maintain the same freeness after the refining was difficult, which was caused by the different level of initial freeness of the pulp samples after screening (before the refining was applied). Therefore, every sample (WS I, RSI, and RS II) has just two levels of freeness – higher and lower.

The strength properties of the grass and agricultural residues pulps, with the exception of the comparatively strong bamboo pulps, are generally inferior to wood pulps. The pulp qualities naturally vary with the raw material, the pulping process and the conditions chosen. There are two major pulp categories within which several varieties can be discriminated. One is unbleached coarse semichemical pulp for cheaper grades of paper and boards, such as corrugating medium, egg case filler board, and cheap packaging papers, where strength in general is not essential. The other is semi-bleached/bleached semichemical or chemical pulp for glassine and fine papers. In the former category, the yellow-straw pulp made by the lime or alkali processes is dominating, and this is the largest use for straw pulp so far. In our study, delignification process for semichemical fluting production was evaluated. Therefore, especially the tests important for fluting quality evaluation were performed. They include mainly stiffness of the pulps and ring crush test. For the reason of general view to a quality of the pulps, hereby other strength properties important for chemical pulps were done.

From **Table 5**, it is evident that the refining of all samples of pulp increases their strength properties with the exception of tear strength, for which decreasing trend after additional refining is obvious, and is common phenomenon for most pulps. All results of the samples prepared in laboratory were compared with the strength properties of commercial pulp made from mixture of hardwoods. This pulp was taken after the brown stock washing (Chemiwasher), screened under laboratory conditions and refined to freeness of 400 mL CSF. Based on the results shown in the **Table 5** can be concluded, that commercial pulp shows lower values of all strength properties measured, compare with the properties of red oak laboratory pulp, and much lower that those of wheat straw pulp refined to a freeness of 220 mL CSF.

In general, there is no evidence of negative effect of straw impregnation/desilication on final strength properties, as most of the properties impregnated and delignified straw samples exceed the strength properties of commercial pulp, as well as the pulps (red oak, wheat straw) prepared under laboratory conditions without the impregnation step. Not significant, but still temperate higher values of Gurley Stiffness of commercial pulp are the exception.

CONCLUSIONS

This study was devised to investigate a comprehensive effect of impregnation and delignification of wheat and rice straw on the strength properties of the final pulps. Recovery of solubilized silica via causticizing reaction and retention of silica-enriched calcium carbonate filler in papermaking furnish are considered to be additional steps of this concept of agricultural residues processing.

Sample of wheat straw *(Triticum aestivum),* and rice straw *(Oryza sativa)* were processed. Much lower desilication rate of rice straw was confirmed during the impregnation of the samples RS I, and RS II. While the desilication rate of wheat straw (sample WS I) reached the value of 90.8% (based on AISA content) desilication rate of 32.7% for RS I, 51.0% for RS II, respectively. Lower number valid for the sample RS I was caused most likely by the lower charge of impregnation chemical (Na_2CO_3).

In the second step of the concept, impregnated /desilicated samples of the straw underwent the non-sulfur delignification. In the case of wheat straw samples, impregnation of WS I sample causes more extensive combined degree of delignification and desilication, compare with the sample of wheat straw, that was not impregnated, but were outright delignified.

Strength properties of all the samples were evaluated at two levels of freeness. Refining of all samples causes increasing strength properties in exception of tear strength. Results of strength properties of the samples prepared in laboratory (including red oak high yield pulp) were compared with the properties of commercial pulp. The commercial pulp presents lower values of all strength properties, compared with the properties of red oak laboratory pulp. In addition, much lower strength than those of wheat straw pulp refined to a lower value of freeness (220 mL CSF) was obtained. The positive finding is that the most of the strength properties of impregnated and delignified straw samples exceed the strength properties of commercial pulp, and at the same time, the properties of the laboratory samples (red oak, wheat straw) processed without the impregnation.

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