

# UPGRADING SPENT LIQUORS FROM NSSC PROCESS:

## IV. UTILIZATION OF SPENT LIQUORS AS PAPERMAKING ADDITIVES

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### Abstract

Hemicelluloses and NSSC spent liquors were studied as papermaking additives. Isolated NSSC hemicelluloses, and spent liquors from a previous work were used as raw materials. The preliminary trials consisted in different hemicelluloses and spent liquors dosages combined with cationic starch at pH = 7.5. Dynamic jar tests were performed and turbidity, cationic demand and conductivity were determined. The results were statistically analyzed using multifactor ANOVA tests and indicate that the pulps did almost not retain the hemicelluloses and spent liquors incorporated, and they remained as anionic trash. The influence of pH (4.5 and 7.5) was determined by a factorial design, with and without starch, at a hemicellulose concentration of 1.5%. A 2<sup>3</sup> factorial design was performed to see the influence of aluminum sulfate on retention. Variables studied in this case were aluminum sulfate, hemicelluloses or spent liquors and cationic starch. Alum sulfate does not have any significant influence on soluble substance retention. A strong interaction between starch and alum is evidenced; being starch more attached to fines. The best points were selected and additions of 1% of starch, and 1.5% of hemicelluloses, spent liquors and an ultrafiltration retentate of spent liquors were applied to pulp furnish. Britt jar tests for fines retention measurements, turbidity, and drainage of the filtrate were also executed. Physical tests on handsheets were made at standard conditions and at high humidity conditions.

### Keywords

Semichemical pulps - neutral sulfite pulps - paper properties - physical properties - board properties – cationic starch – hemicelluloses – additives – spent liquors.

### Introduction

Modern trends ask for the use of pulping processes friendlier to the environment. In the case of the NSSC process (Neutral Sulfite Semi-Chemical) there is a need for disposing spent liquors economically and ecologically. In many cases, NSSC spent liquors are sent directly to water courses as effluents. Despite great efforts from its beginning, spent liquors chemicals recovery is still to be addressed.

In previous works, we used a design of experiment approach (Central Composite Design: 29 cooks including five central points) to optimize operating conditions. First, we optimized physical properties of NSSC pulps (1). Spent

liquors containing the lowest ratio of inorganic/organic solids were obtained afterwards (2), their organic components were evaluated (3) and the average molecular weights (MW) and MW distributions of lignosulfonates and hemicelluloses obtained were determined (4). The last work focused on separation of spent liquor components by ultrafiltration (5).

The objective of the present work is to study the possible utilization of NSSC spent liquors and hemicelluloses separated from them, as papermaking additives in neutral sulfite corrugating medium. Trials were performed adding to pulp furnish hemicelluloses separated by a chemical laboratory method (3), NSSC spent liquors (2), and an ultrafiltration retentate of the spent liquor (5). This retentate represents an enriched natural polymer fraction that can be separated at industrial level from NSSC spent liquor.

Dry strength agents improve fiber bonding in the same sense as refining does (increasing tensile and burst strengths, and lowering tear). According to literature data, the use of hemicelluloses as a board additive proves to improve strength properties (6-8), especially wet stiffness of fluting of NSSC pulps for corrugating boards (9). Other authors found that addition of Na lignosulfonates (LS) and NSSC spent liquors significantly decreased brightness and enhanced slightly the tensile strength, ring crush and burst strength of dry handsheets (10). Hemicelluloses (11) and spent liquors were also tried as stock additives to increase filler retention. However, the problem is the retention of these soluble substances in the paper sheet. They tend to remain in the white waters as so-called anionic trash thus, modifying the ionic environment. The same effect may be observed in closing the water system in a paper machine, which increases soluble substance concentrations in white waters.

Retention of the various components of the stock in the final sheet is considered due to chemical, mechanical, or a combination of both mechanisms. While adsorption or chemical bonding to the suspended solids retains the dissolved materials, mechanical filtration or entrapment in the forming web of fibers retains the suspended solids.

The fine particles in a papermaking web can be retained (12) in two ways:

1. By attracting the fine particles into a macroparticle. This mechanism is known as flocculation (the destabilization of a particle suspension by bonding the particles together with long chain charged polyelectrolytes).
2. By attaching the fine particles to the large fibers that are retained at a 100% level by agglomeration (the destabilization of a particle suspension by adsorbing a new charge on the particles surface) or by coagulation (the destabilization of a particle suspension by changing the ionic characteristics of the particle suspension with salts).

While coagulation create small coagulated reversible structures which can give good drainage and formation but poor retention, macroflocculation creates large flocs which give high retention; but, can cause drainage and formation difficulties.

Chemical retention is obtained with the use of functional chemical additives. Retention aids are surface active materials which cause the fines fraction to flocculate either with themselves or by adsorption onto the long fiber portion of furnish; thus, bringing about greater retention by both chemical and mechanical means.

Dissolved and colloidal substances in the paper machine white water can destroy the electrokinetic equilibrium and reduce the effectiveness of cationic additives, particularly retention aids (13). In an acid papermaking system all fine particles that are to be retained (fines and fillers) are anionic. Therefore, the chemicals used to aid in the retention are generally cationic. To maximize the retention of fines the repulsive potential (a result of the electrical double layer or the protective colloid effect) between particles and fibers must be removed. The most effective flocculation of particles may theoretically take place at surface charge (zeta potential) and soluble charge (anionic demand) close to zero (14). These conditions can only be attained by the addition of cationic chemicals to the pulp, countering the particle's negative electrical double layer with positively charged ions (e.g., aluminum) or polymers. Dosing rates must be chosen in such a way that slight variations in the pulp system cannot cause a reversal of the surface charge during production.

Cationic polymers react preferentially with soluble charge (anionic trash) giving complexes, and not with surface charge. These complexes are called "simplexes" that are poorly retained. This lowers dewatering speed and causes increased energy consumption in the dryer section. Cationic wet end starches are not suitable "anionic trash catchers". For this purpose, low molecular weight, high charged polymers should be used. A suitable anionic trash catcher should be added before starch for improving starch retention. Poor starch retention is reflected by a higher turbidity of the filtrates.

Alum is an inexpensive retention aid, which can be efficiently used in some papermaking systems. It is the most important cationic coagulant used in acid systems, because of its high cationic charge density. The cationic polynuclear aluminum species reduce the anionic charge of furnish components and reduce the repulsive forces between them. This permits the furnish components to approach each other and increases the likelihood of aggregates forming and being retained in the sheet.

Even alum has been shown to possess a net cationic charge (at least initially) through the entire papermaking range (from acid to alkaline) (15), alum is poorly charged at pH above 7.0. In the range of pH from 4.5 to 5.5, free alum is available and the aluminum polymeric species are beneficial for small particle retention.

The use of aluminum salts for soluble substances retention is however controversial (16), and it was demonstrated that the concentration of alum in the system must be watched closely (17). Other studies demonstrated the detrimental effect of alum on all strength properties (18,19). Many paper mills have switched from acid to neutral papermaking, and have lowered alum usage.

Used alone, alum is a poor retention aid. A high molecular weight polymeric flocculant is usually required to achieve significant retention. An alum advantage is that it improves wet end performance of starches, both on acid and alkaline sides. However, alum will decrease the effectiveness of cationic and anionic retention aids if added in excess to that required to establish good sizing and to neutralize the effects of organic substances contaminants of the furnish.

In order to reduce our problems of poor soluble substances retention (lignosulfonates and hemicelluloses), the addition of an aluminum salt alone, and in presence of cationic starch was tried.

To measure retention of dissolved materials, different techniques are required. To establish the concentration of dissolved inorganic material, solution conductivity can be measured. In the case of organic soluble materials, the TOC (total organic carbon) technique is recommended; however, it correlates very well with the cationic demand of the pulp (20). Therefore, we decided to use this last technique.

## Experimental

The raw material used was the pulp corresponding to the central point of the experimental design performed in a previous work. The pulping procedure, pulp and spent liquors characteristics, and hemicelluloses isolation were described in previous articles (1-4). All pulping conditions generate soluble lignosulfonates having the same molecular weight distribution. Lignosulfonates presented average molecular weights of about 1030 and 235 for each fraction. Hemicellulose molecular weights distribution depends on pulping conditions. Under stronger cooking conditions higher molecular weight materials are dissolved. Hemicellulose average molecular weights vary between 8000 and 19600 for the first fraction, and it is 1000 for the second one. Spent liquor composition was 33% of LS, 12% of HC, 17% of acetic acid, and 37% of ash. Ultrafiltration retentate (URF) composition was 42% of LS, 29% of HC, 10% of acetic acid and 19% of ash. Ultrafiltration characteristics are described in reference (5).

The preliminary trials consisted in different hemicelluloses and spent liquors dosages (between 0 and 1.5%) at pH 7.5 combined with a cationic starch (dosages between 0 and 2%) having a degree of substitution of 0.024. Samples were prepared as 500 ml pulp suspensions at 0.5% consistency.

Dynamic jar tests were performed. Temperature was fixed at 50 °C and the mixing time was always 10 minutes. Turbidity (ntu), cationic demand, conductivity ( $\mu\text{S}/\text{cm}$ ) and soluble solids concentration in the supernatant were determined.

The cationic demand of the pulp was measured by colloidal titration (21) using the PCD laboratory method (Mutek PCD 02 Particle Charge Detector) (22) and a visual determination of the final point technique. The results of both methods were comparable.

The statistical analysis of these preliminary experiences was performed using multifactor ANOVA tests. Multiple range tests (a multiple comparison procedure to determine which means are significantly different from which others) were performed in all cases.

In order to study the effect of pH on our additives retention, a two variables (pH and starch dosage)  $2^2$  factorial design was applied at 1.5% on hemicelluloses.

As the best results obtained were at pH 4.5, it was possible to essay alum sulfate as a coagulant to increase retention. A 2<sup>3</sup> factorial design was executed studying aluminum sulfate, hemicelluloses or spent liquors and cationic starch as variables at pH 4.5.

The best points were selected. Additions of 1% of starch, and 1.5% of hemicelluloses, 1.5% of spent liquors and 1.5% of ultrafiltration retentate of spent liquors were applied to pulp furnish. Britt jar tests for fines retention measurements, turbidity, cationic demand and conductivity of the filtrate were also determined.

Pulps slurries were prepared at 0.5% consistency, heated to 50 °C, and additives were added as for doing jar tests. Handsheets of 120 g/m<sup>2</sup> (o.d.) were prepared at 0.15% consistency to avoid excessive dilution and they were dried with hot air. Physical tests on handsheets were determined according to TAPPI standard methods using T402 conditions (50% RH, 23°C) and high humidity conditions (75% RH, 27°C), to simulate real tropical environmental conditions.

## Results and discussion

The results of hemicelluloses, spent liquors and starch dosages in the preliminary trials (at pH = 7.5) are presented in tables 1 and 2.

Global means of turbidity, cationic demand, and conductivity are not statistically different when hemicelluloses or spent liquors were added, as shown by the **t** test. Their contribution to these system properties is therefore similar (both increase turbidity, conductivity and anionic charge of the system).

Figure 1 and 2 present turbidity and cationic demand variation of pulps for different starch, hemicelluloses and spent liquors dosages (pH = 7.5).

Table 1: Results of hemicelluloses and starch dosage

Hemicelluloses (% o.d. pulp)	Starch (% o.d. pulp)	Turbidity	Cationic demand (µeq/l)	Conductivity
0	0	35.90	-225	92.5
0	0.5	9.03	-130	111.9
0	1	5.00	-140	94.1
0	1.5	2.30	-80	83.7
0	2	0.86	-80	88.9
0.5	0	33.30	-500	104.5
0.5	0.5	16.80	-450	96.2
0.5	1	10.00	-440	92.0
0.5	1.5	7.00	-420	106.7
0.5	2	4.00	-350	102.5
1.5	0	30.60	-1230	109.8
1.5	0.5	21.00	-1130	115.0
1.5	1	18.70	-970	115.0
1.5	1.5	14.70	-1000	123.3
1.5	2	9.50	-1040	124.4

Table 2: Results of spent liquors and starch dosage

Spent liquor (% o.d. pulp)	Starch (% o.d. pulp)	Turbidity	Cationic demand ( $\mu\text{eq/l}$ )	Conductivity
0	0	35.90	-225	92.5
0	0.5	9.03	-130	111.9
0	1	5.00	-140	94.1
0	1.5	2.30	-80	83.7
0	2	0.86	-80	88.9
0.5	0	18.90	-430	107.7
0.5	0.5	15.90	-500	94.1
0.5	1	8.57	-460	108.7
0.5	1.5	4.83	-410	102.5
0.5	2	2.75	-400	109.8
1.5	0	27.60	-1060	162.1
1.5	0.5	16.50	-1010	156.9
1.5	1	13.10	-990	158.9
1.5	1.5	8.48	-1070	165.2
1.5	2	6.75	-960	156.9

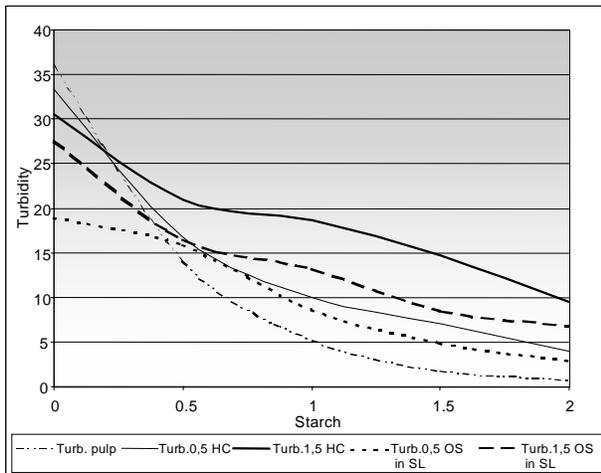


Figure 1: Turbidity of pulps with and without additives, at different starch dosages.

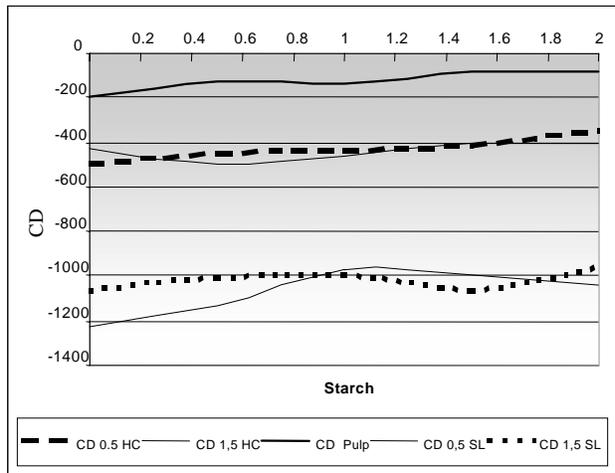


Figure 2: Cationic demand of pulps with and without additives, at different starch dosages.

The regression equations relating these properties at pH 7.5 are:

$$\text{Turbidity (with HC)} = 32.23 - 32.65 \cdot \text{Starch} + 8.10 \cdot \text{Starch}^2 + 4.74 \cdot \text{HC} \cdot \text{Starch} \quad (R^2 = 95.03)$$

$$\text{Turbidity (with SL)} = 27.13 - 27.05 \cdot \text{Starch} + 6.74 \cdot \text{Starch}^2 + 2.75 \cdot \text{SL} \cdot \text{Starch} \quad (R^2 = 88.48)$$

$$\text{Cationic demand (with HC)} = -197.05 - 633.43 \cdot \text{HC} + 75.33 \cdot \text{Starch} \quad (R^2 = 98.98)$$

$$\text{Cationic demand (with SL)} = -161.19 - 592.29 \cdot \text{SL} + 18.70 \cdot \text{Starch}^2 \quad (R^2 = 99.29)$$

$$\text{Conductivity (with HC)} = 93.53 + 15.75 \cdot \text{HC} \quad (R^2 = 65.42)$$

$$\text{Conductivity (with SL)} = 95.71 + 28.65 \cdot \text{SL}^2 \quad (R^2 = 94.69)$$

While turbidity is highly affected by HC addition, different applications of spent liquor do not have the same level of influence. Turbidity follows almost the same function in both cases, with a little effect of the interaction starch-additive. The ANOVA study shows that different dosages of starch change significantly the response ( $p= 0.0001$ ). Increasing starch reduces turbidity, as can be expected from its retention agent property. The multiple range tests show that there exist significant difference between 0,5 and 1.5% of HC dosage, increasing turbidity. For starch, differences are important between 0, 0.5, and 1%; but, greater additions do not affect turbidity. This conclusion can be better observed in Figure 1.

The same results than for turbidity are valid for the cationic demand of pulps, being stronger the influence of hemicelluloses ( $p= 0.000$ ) than that of starch ( $p= 0.0221$ ). The effect of HC on cationic demand is a little higher than that of SL. An almost negligible quadratic effect of starch is present in the last case. Figure 2 shows how of HC and SL addition increases cationic demand.

The conductivity of a system is related to the presence of monovalent or perhaps divalent ions (primary sodium, chloride, and sulfate) in a papermaking furnish. The higher the conductivity, the less will be the ionic attraction forces between a polymer and the components of the furnish, as the electrolyte concentration can suppress the charge onto the surface of the fiber and fillers. It is also probably that as the ionic interaction forces are diminished by conductivity, the conformation of polymers in the system may also be changed. Decreasing the repulsion forces within a polymer may also change its conformation from linear to globular. This effect decreases the surface area of the polymer available for interaction with the furnish components. The performance of the retention aids to use under conditions of low conductivity, (in particular medium or high charged polymers) is adversely affected when used under conditions of high conductivity.

In our case, conductivity values are generally low. The correlation coefficient  $R^2$  indicates that the model as fitted for conductivity with HC explains only 65.42% of the variability in the response. As inorganic matter is the principal responsible of conductivity, this variation with HC must be due to the contamination of these polymers during their separation from spent liquors. Spent liquor augments conductivity with a positive quadratic effect ( $p= 0.0000$ ) due to its high inorganic salt content.

A factorial design was applied to verify the effect of pH (4.5 – 7.5) and starch (0 – 1%) at 1.5% of HC dosage. The results are presented in Figures 3 and 4.

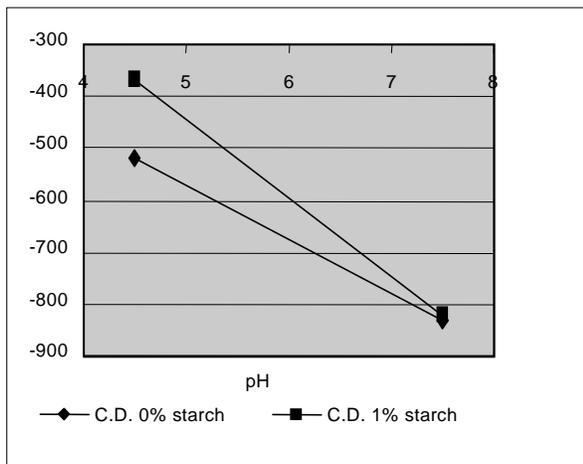


Figure 3: Charge of the system (C.D.) as a function of pH for different starch dosages (HC 1.5%).

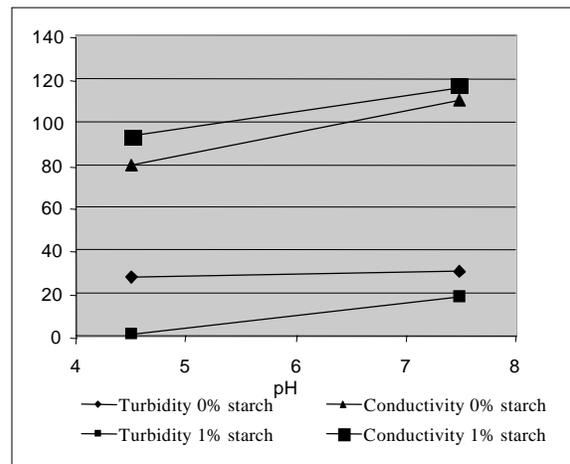


Figure 4: Turbidity and conductivity as a function of pH for different starch dosages (HC 1.5%).

Both, cationic demand and conductivity represent the system charge. The charged groups on fibers and the other organic materials of this system are mostly weak acids and their extent of ionization depends on the pH of the system (23). High pH values enhance the ionization of carboxyl groups in the different particle surfaces and in dissolved materials. Ionization varies from 40-45% at a pH of 4.5 to almost 100% at a pH of 7.5. This negative charged groups increase the cationic demand of the system. In this situation, the same starch dosage can not neutralize the global

charge of the suspension and therefore the turbidity increases. On the contrary, sulfonic acid groups are completely ionized at all pH values. Variation in the cationic demand at different pH in the system having spent liquors might be a result of their HC and other soluble anionic substance content.

The conductivity and the pH of the system also influence the conformation of the cationic polymer. At high conductivity, the average diameter of the molecule in solution diminished, thus influencing flocculation in a negative way. At alkaline pH cationic starch develops a globular configuration (due to the presence of hydroxide ion), while it develops a more linear configuration at acidic pH (due to the presence of hydrogen ions).

Table 3 presents the effects of significant factors (interactions were never significant). The effect of a factor is the variation produced on the response when it passes from the lower to the upper value.

The consequence of lowering the pH of the system is noticeable by the change in the variables measured. However, those changes can not attributed to changes in retention. They can be due to the protonization of anionic groups. Only for turbidity, the effect of starch is more important than that of pH.

To see if the retention of hemicelluloses could be increased, alum sulfate was added. Tables 4 and 5 present the results of aluminum sulfate, hemicelluloses, spent liquors and starch dosages in the factorial design (at pH = 4.5).

Table 3: Effects of pH and starch dosage at 1.5% of HC dosage on the studied variables.

Responses/effects	Average	pH (4.5 – 7.5)	Starch (0 – 1)
Turbidity	19.5	10.3	-21.7
C.D.	-635.0	-380.0	--
Conductivity	99.5	25.8	--

Table 4: Factorial design for  $Al_2(SO_4)_3$ , hemicelluloses and starch dosage.

$Al_2(SO_4)_3$	HC	Starch	Turbidity	C.D.	Conductivity
0	0	0	35.9	-225	40
0.5	0	0	21.1	-60	42
0	1.5	0	25.5	-520	80
0.5	1.5	0	24.4	-455	67.5
0	0	1	0.85	0	44.5
0.5	0	1	1	-150	50
0	1.5	1	0.95	-370	89
0.5	1.5	1	0.93	-605	91

Table 5: Factorial design for  $Al_2(SO_4)_3$ , spent liquors and starch dosage

$Al_2(SO_4)_3$	SL	Starch	Turbidity	C.D.	Conductivity
0	0	0	39.5	-220	40
0.5	0	0	21.1	-60	42
0	1.5	0	23.3	-400	100
0.5	1.5	0	26.9	-420	100
0	0	1	0.85	0	44.5
0.5	0	1	1	-150	50
0	1.5	1	0.91	-300	100
0.5	1.5	1	1.2	-660	100

Statistical analysis results showed that aluminum sulfate has no effect on the hemicelluloses retention. As the principal factors affecting alum charge decay are pH above 4, higher temperatures, high contact times and higher conductivity, is possible that our conditions were not adequate for the use of this coagulant. The presence of a counter ion like  $\text{SO}_4^-$  which significantly enhances the anionic charge can be another reason of its nonperformance.

Starch does not distribute itself equally among all components when added to mill furnishes. In general, it tends to adsorb more in high specific area components. Thus, fines and fillers will adsorb more starch than fibers (23). The relative adsorption intensity of cationic starch equals one for fibers and five for fines. In the case of alum, it became one for fibers and three for fines (23).

Therefore, starch has a great affinity for fines, and a lower one for soluble materials. Alum addition does not improve NSSC SL component retention. On the contrary, it presents a higher affinity for fibers and increases the supernatant anionic charge.

Tables 4 and 5 show the strong interaction between starch and alum in all cases (pulp without other addition, and with hemicelluloses or spent liquor added). The pulp alone presents the lowest anionic charge and the added starch neutralizes it totally. When hemicelluloses are incorporated to the system and alum is absent, starch neutralizes part of the anionic trash (charge passes from -520 to -370). In absence of starch, alum also acts as an anionic trash neutralizer (from -520 to -455). However, when both additives are present the anionic charge increases, it seems that it is due to the presence of  $\text{SO}_4^-$  ions.

Alum and cationic starch interact changing the system behavior. As starch is first added, it is attached directly to fines, lowering turbidity (this effect is independent of Al charge). When  $\text{Al}_2(\text{SO}_4)_3$  enters in the system (knowing that 90% exists as  $\text{Al}^{+3}$  at pH = 4.5), it goes directly to neutralize the fibers leaving the  $\text{SO}_4^-$  ions as additional anionic soluble charge. The total anionic charge equals therefore the initial one, plus the charge supplied by the  $\text{SO}_4^-$  anions (as cations do not remain in the soluble system). This effect produces also a conductivity augmentation (initial: 75  $\mu\text{S}/\text{cm}$ , after starch and alum additions: 90  $\mu\text{S}/\text{cm}$ ).

Table 6 shows drainage (CSF and Britt Jar) and fines retention data of pulp furnishes prepared for testing.

Physical tests on handsheets results at standard atmosphere conditions and at high temperature and relative humidity are presented in Table 7 and 8 respectively.

Percentages of drainage and retention properties variation from pulp without additives are presented in Figure 5. In Figures 6 and 7, the percentages of property variation having the properties of pulps without additives as reference (zero) values at both atmospheric conditions are shown.

Table 6: Drainage and retention results (CSF and Britt jar, pH = 4.5)

	Without additives	Starch	Starch – HC	Starch – SL	Starch – URF
CSF	300	475	475	475	475
Volume Britt (ml)	97	77	100	87	94
Turbidity Britt (ntu)	144.5	65.5	27.3	28.1	30.5

Britt jar test volumes show that starch and SL deteriorate drainage while hemicelluloses and UFR do not present significant differences with the pulp alone (Table 6, Figure 6). On the contrary, CSF increases in the same percentage with all additives. Fines retention is greatly increased with additives.

Dynamic turbidity values are greater than those obtained in static conditions (jar test) but results are coincident. Turbidity of the “white water” is positively affected by the incorporation of spent liquor components in these conditions (80% lesser turbidity than without SL additives). System conductivity could be the reason of this behavior (pulp alone: 40  $\mu\text{S}/\text{cm}$ , pulp with NSSC SL: 100  $\mu\text{S}/\text{cm}$ ). Increased concentration of salts reduces the electrical

double layer thickness and thereby enables fines particles to approach one another more closely which, in turn, decreases the bridging distance the starch must span in order to induce flocculation (23).

Table 7: Physical tests on handsheets with starch (1%), hemicelluloses (1.5%), spent liquors (1.5% of organic solids) and spent liquor ultrafiltration retentate (1.5% of organic solids) addition. Conditions: 23°C, 50% RH

	Without additives	Starch	Starch - HC	Starch – SL	Starch – URF
Humidity (%)	8.7	8.5	8.8	8.5	8.5
Bulk (cm <sup>3</sup> /gr)	1.60	1.54	1.55	1.60	1.59
Tear I. (mN m <sup>2</sup> /gr)	5.27	4.74	4.28	4.68	4.52
Burst I. (kPa m <sup>2</sup> /gr)	1.93	2.48	2.53	2.35	2.24
Tensile I. (N m/gr)	36.0	48.2	47.6	46.3	45.9
Stretch (%)	1.48	1.86	1.76	1.82	1.73
TEA I. (mJ/gr)	359	610	554	567	531
STFI I. (Nm/gr)	25.75	25.75	25.76	26.03	25.75
Permeability (μ-m/Pa.s)	1.59	1.62	1.67	1.76	2.20
Brightness	44.8	44.3	43.9	44.3	43.7
L*	81.3	80.9	80.5	80.8	80.4
a*	1.04	0.78	0.7	0.47	0.51
b*	15.3	15.3	15.0	15.0	15.1

Table 8: Physical tests on handsheets with starch (1%), hemicelluloses (1.5%), spent liquors (1.5% of organic solids) and spent liquor ultrafiltration retentate (1.5% of organic solids) addition. Conditions: 27°C, 75% RH

	Without additives	Starch	Starch - HC	Starch – SL	Starch – UFR
Humidity (%)	11.10	11.00	11.07	10.98	11.03
Bulk (cm <sup>3</sup> /gr)	1.60	1.60	1.58	1.59	1.57
Tear I. (mN m <sup>2</sup> /gr)	4.63	5.46	5.41	5.45	5.54
Burst I. (kPa m <sup>2</sup> /gr)	1.60	2.14	2.12	2.04	2.04
Tensile I. (N m/gr)	29.54	37.70	37.25	37.27	35.53
Stretch (%)	1.83	2.44	2.40	2.58	2.19
TEA I. (mJ/gr)	382	658	633	682	540
STFI I. (Nm/gr)	17.53	21.14	21.14	19.63	19.19
Permeability (μ-m/Pa.s)	1.59	1.82	2.10	1.42	1.82

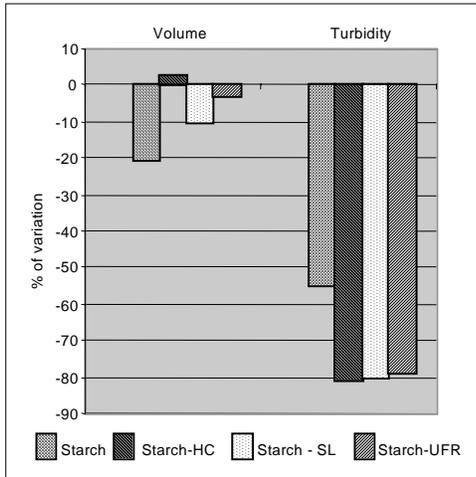


Figure 5: Percentages of drainage and retention variation (zero: properties of pulps without additives, Britt jar )

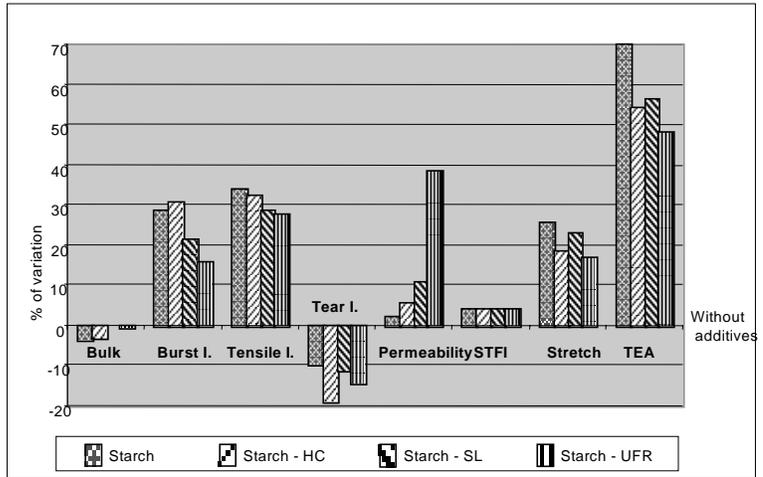
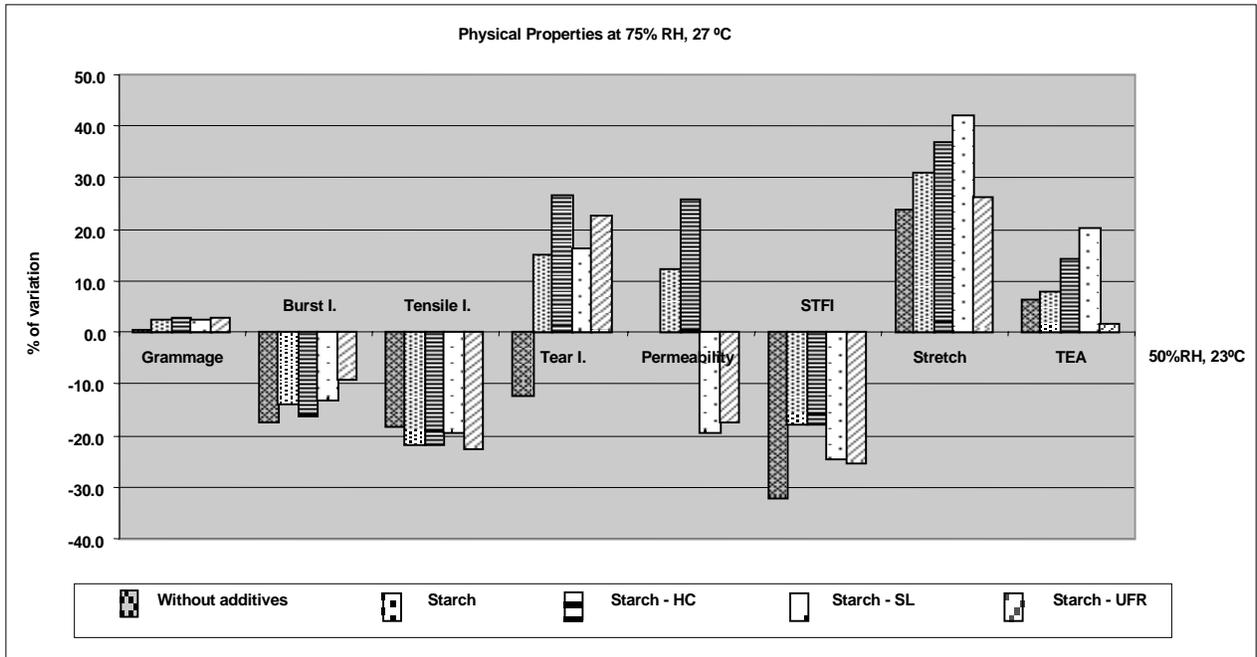


Figure 6: Percentages of property variation at 23°C, 50% RH (zero: properties of pulps without additives)



Figures 7: Percentages of property variation values at 75% RH, 27°C (zero: properties of pulps without additives at 50% RH, 23°C)

There exist significant differences between pulps with and without additives (23°C, 50% RH) in tensile, burst, stretch, STFI, and TEA. Differences between pulps with and without additives are about 30% for tensile and burst, 20% for stretch and STFI, and 50% for TEA. In tensile and burst there are no significant differences between starch alone or combined with hemicelluloses, but LS and UFR additions deteriorate these properties.

Results show that tear index suffered a significant diminution (10 to 20%) with all additions. Hemicelluloses produced the lowest value.

Pulps behavior at 50% RH presents little variations using starch alone or combined with HC or SL in all properties but air permeability. The presence of SL and UFR affect greatly this last property as is shown by the high values obtained.

Formation improvement in the presence of SL and UFR was noticeable (visual observation). Additives used as formation aids are generally natural or synthetic water-soluble polymers (anionic or non-ionic). Cationic polymers are a poor choice because they bridge the fibers resulting in the development of macro flocs, which would be detrimental to formation (24). In this case, anionic trash ameliorates formation, having therefore a detrimental effect on fiber bonding.

Air resistance measurements are commonly used as a control test for paper manufacture, because of its indirect correlation between porosity, formation, and strength of paper. As fiber bonding reduces permeability, its values increase when lignosulfonates content in the additive augments.

Optical properties are not really affected.

Pulps behavior at high relative humidity is on the contrary, very interesting (Figure 7). While tensile and burst responses at these conditions are almost the same than the pulp without additives, tear and stretch are positively affected as expected. In all cases, pulps with additives show a lower drop of STFI at high humidity. The effect of additives on air permeability at high humidity is reversed. Additives with high lignosulfonates content present an important drop of this property.

Tear, burst and STFI do not present differences with all additives, while tensile, stretch, TEA and permeability values are diminished in presence of UFR.

Globally, there are no statistical significant differences between starch alone and with the incorporation of hemicelluloses in physical properties. The presence of LS affects negatively some properties (burst, STFI), positively others (stretch, TEA) and produces great differences in permeability with the change of environmental conditions.

As there is no evidence of complete soluble substances retention, next trials could contemplate other cationic polymer incorporation with these additives, to see if they could be better retained and could be applied without starch.

## Conclusions

- Pulps furnish did almost not retain by themselves hemicelluloses and spent liquors incorporated, and they remained as anionic trash at pH 7.5.
- Substantial increases in soluble substance retention result at a pH of 4.5.
- Aluminum sulfate has no effect on the hemicelluloses retention at these conditions in our system.
- Pulp freeness augmentation is the same for all additives.
- Fines retention is greatly increased with all additives.
- There exist significant increases (20 to 50%) between pulps with and without additives in all mechanical properties but tear at standard conditions. At high relative humidity, these differences are vanished for tensile, burst and STFI. Stretch and TEA are on the contrary, greatly augmented.
- While tear index suffered a significant diminution with all additions at 50% RH, there is an important augmentation of this property with additives at 75% RH.
- Optical properties are not affected in a significant way in all cases.
- Globally, there are no statistical significant differences between starch alone and with the incorporation of hemicelluloses in physical properties.

- The presence of LS affects negatively some properties (burst, STFI), positively others (stretch, TEA) and produces great differences in permeability with the change of environmental conditions.
- There is no evidence of complete soluble substances retention. Other cationic polymer must be tested to see if these additives could be incorporated without starch.

## List of abbreviations

ANOVA: analysis of variance

C.D.: cationic demand

HC: hemicelluloses

LS: lignosulfonates

MW: molecular weight

NSSC: neutral sulfite semi-chemical

SL: spent liquors

STFI: short span compression test

TEA: tensile energy absorption

UFR: ultrafiltration retentate

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