

NSSC PROCESS OPTIMIZATION: II. SPENT LIQUORS

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Abstract.

Modern trends indicate the use of pulping processes that require less chemicals being friendlier to the environment. This is the case of NSSC (Neutral Sulfite Semi-Chemical) process where there is a need for disposing spent liquors economically and ecologically. The main objective this part of the project, using a design of experiments approach (Central Composite Design: 29 cooks including 5 central points), was to determine the operating conditions at which spent liquors containing the lowest ratio of inorganic/organic solids can be obtained. These operating conditions had to be such that they maintain at the same time the pulp quality. Hybrid poplar (*Populus deltoides*) was used as raw material. Minimum and maximum limits of the independent variables were established using mill conditions as set point values. Variables studied were: cooking time (10 to 30 minutes), cooking temperature (154 to 186°C), sodium sulfite (4 to 12% o.d.), and sodium carbonate charges on wood (0 to 3% o.d.). Each property was evaluated by comparison with the mill reference data (yield: 80%, pH: 7, IS/OS: 0.8). Optimum conditions minimizing the inorganic/organic solids ratio were: 26 min, 177 °C, 6.0 % Na₂SO₃, 2.54% Na₂CO₃. Spent liquors organic solids compositions were also determined. Time, temperature and sulfite charge showed the greatest effects on organic material dissolution. Carbonate charge acts through interactions.

Keywords.

Populus deltoides - semichemical pulps - neutral sulfite pulping – spent liquors properties - experimental design -.

Introduction.

Modern trends indicate the use of pulping processes that require fewer chemicals being friendlier to the environment. This is the case of NSSC (Neutral Sulfite Semi-Chemical) process where there is a need for disposing spent liquors economically and ecologically. The main objective this part of the project was to determine the operating conditions where spent liquors containing the lowest ratio of inorganic/organic solids can be obtained. These operating conditions had to be such that pulp quality is the same or better. Hybrid poplar (*Populus deltoides*) was used as raw material.

References of NSSC spent liquors characterizations are limited. In general, spent liquors have final pH varying from 6,5 to 8,5 and contain 10-13 g/l of sodium acetate and 8 to 22% of total solids. Their calorific capacity is rather low (6.3-12.7

GJ/t), (1). They contain hemicelluloses partially degraded having DP of 115-131 (2), being their viscosity proportional to the polysaccharide content (3).

Other work on eucalyptus NSSC spent liquor presents an ash content of 41,6% (4). They can only be evaporated to 50% because of their high viscosity (5). They are more corrosive than Kraft spent liquors, even after neutralization (6). The most used recovery system is the cross recovery with Kraft spent liquors (1), but some mills have fluidized bed combustion systems (7). Sulfur dioxide can be recovered from spent liquor by acidification, and recycled to the white liquor (8).

Experimental.

Pulping methodology.

Hybrid poplar (*Populus deltoides*) from the delta of Paraná River in Argentina is used as raw material. The wood chemical composition was:

- Cellulose Seifert: 41.8%
- Klason lignin: 24.2%
- Soluble lignin: 3%
- Hemicelluloses (difference): 26.1%
- Alcohol-benzene extractives: 2.6
- Hot water extractives: 2.3%
- Ash: 0.84%.

A Central Composite experimental design was used, studying four variables (29 cooks including 5 central points). The most important cooking parameters studied were: cooking time at maximum temperature, maximum temperature, sodium sulfite and calcium carbonate charges. The experimental design and the whole pulping procedure was described in the preceding article (9).

The volumes of all spent liquors were determined. The spent liquors were stored in glass containers over chloroform and under toluene.

In the organic fraction of the spent liquors the following measurements were performed: lignosulfonates and xylans concentrations, acetic and formic acids concentrations and sugar contents. Xylans were taking as representing hemicelluloses. Materials and methods were presented in a previous work (10).

Results and discussion.

Table I presents the cooking results and the composition of the organic solids in spent liquors. Table II shows the correlation coefficients between variables.

Figures 1 to 3 show the variation in organic materials dissolution at different pulping conditions (mean of all values for each point). Figure 4 shows changes of some spent liquor properties in function of cooking temperatures.

Table I: Cooking results and spent liquors characteristics and composition

Run	Initial pH	Yield (%)	Consumed SO ₃ ²⁻ (g/l)	Final pH	Total solids TS (g/100g s.l.)	Organic solids OS (g/100g s.l.)	Inorganic solids IS (g/100g s.l.)	IS/OS	Viscosity (mPa.s)	Lignosulfonates (g/100g s.l.)	Xylans (g/100g s.l.)	Acetic acid (g/100g s.l.)	Formic acid (g/100g s.l.)
1	10.8	92.0	6.13	5.90	2.07	0.990	1.080	1.091	1.093	0.867	0.081	0.250	0.027
2	10.8	90.8	6.57	5.71	2.40	1.320	1.080	0.818	1.178	0.948	0.136	0.297	0.032
3	10.8	88.5	8.28	5.47	2.92	1.840	1.080	0.587	1.228	1.176	0.302	0.264	0.025
4	10.8	86.2	8.60	5.39	3.45	2.370	1.080	0.456	1.482	1.307	0.49	0.302	0.023
5	10.7	87.2	7.46	6.20	3.26	1.630	1.630	1.000	1.348	1.340	0.222	0.380	0.028
6	10.7	85.9	8.02	6.13	3.49	1.860	1.630	0.876	1.701	1.500	0.237	0.402	0.035
7	10.7	83.5	9.10	6.02	3.95	2.320	1.630	0.703	1.706	1.621	0.469	0.414	0.037
8	10.7	81.8	10.23	5.95	4.57	2.940	1.630	0.554	1.365	1.756	0.606	0.398	0.036
9	10.9	91.4	6.26	6.70	2.58	1.270	1.310	1.031	1.300	0.895	0.117	0.292	0.021
10	10.9	88.2	7.59	6.42	2.98	1.670	1.310	0.784	1.305	1.188	0.229	0.374	0.030
11	10.9	85.2	8.46	6.23	3.79	2.480	1.310	0.528	1.506	1.362	0.496	0.383	0.043
12	10.9	82.3	9.28	5.87	4.33	3.020	1.310	0.434	1.659	1.723	0.589	0.364	0.042
13	10.9	91.1	7.27	6.88	3.35	1.490	1.860	1.248	1.397	0.952	0.029	0.360	0.032
14	10.9	86.0	8.34	6.70	3.66	1.800	1.860	1.033	1.483	1.340	0.313	0.460	0.044
15	10.9	82.1	9.91	6.73	4.67	2.810	1.860	0.662	1.323	1.826	0.459	0.426	0.045
16	10.9	79.9	11.05	6.52	4.96	3.100	1.860	0.600	1.952	2.039	0.576	0.422	0.049
17	10.8	90.2	7.84	6.32	2.89	1.420	1.470	1.035	1.299	0.941	0.208	0.316	0.042
18	10.8	86.1	8.91	6.13	3.55	2.080	1.470	0.707	1.598	1.252	0.412	0.425	0.044
19	10.8	93.9	6.20	6.53	2.34	0.870	1.470	1.690	1.149	0.558	0.077	0.280	0.024
20	10.8	82.1	11.11	5.79	4.87	3.400	1.470	0.432	1.972	1.715	0.66	0.342	0.039
21	10.9	91.0	5.89	5.91	2.46	1.545	0.915	0.592	1.021	0.887	0.208	0.260	0.030
22	10.8	84.4	9.72	6.62	4.52	2.500	2.020	0.808	1.641	1.563	0.393	0.406	0.041
23	9.7	88.8	7.71	5.60	2.97	1.740	1.230	0.707	1.219	1.160	0.222	0.308	0.033
24	10.9	87.1	8.85	6.60	3.68	1.980	1.700	0.859	1.659	1.296	0.356	0.295	0.036
25	10.8	86.3	8.09	6.26	3.36	1.890	1.470	0.778	1.552	1.360	0.344	0.354	0.043
26	10.8	86.8	8.15	6.15	3.47	2.000	1.470	0.735	1.441	1.378	0.232	0.387	0.041
27	10.8	87.6	8.15	6.26	3.78	2.310	1.470	0.636	1.412	1.389	0.304	0.372	0.034
28	10.8	86.4	8.28	6.20	3.48	2.010	1.470	0.731	1.493	1.417	0.292	0.371	0.044
29	10.8	86.2	8.09	6.14	3.63	1.94	46.6	0.66	1.485	-	-	-	-

s.l.: spent liquors

Table II: Correlation coefficients between evaluated responses

	Yield	Consumed sulfite	TS	OS	IS/OS	Viscosity	Lignosulfonates	Xylans	Acetic acid	Formic acid
Yield	1.00	-0.85	-0.79	-0.89	0.75	-0.62	-0.87	-0.89	-	-
Consumed sulfite	-0.85	1.00	0.95	0.93	-	0.79	0.91	0.89	0.61	0.63
Total solids	-0.79	0.95	1.00	0.94	-	0.79	0.92	0.86	0.70	0.66
Organic solids	-0.89	0.93	0.94	1.00	-0.73	0.73	0.91	0.95	-	-
IS/OS	0.75	-	-	-0.76	1.00	-	-0.67	-0.77	-	-
Viscosity	-0.62	0.79	0.79	0.73	-	1.00	0.75	0.70	0.70	-
Lignosulfonates	-0.87	0.91	0.92	0.91	-0.67	0.75	1.00	0.86	0.70	0.65
Xylans	-0.89	0.89	0.86	0.95	-0.77	0.70	0.86	1.00	-	-
Acetic acid	-	0.6	0.70	-	-	-	0.70	-	1.00	0.71
Formic acid	-	0.63	0.66	-	-	-	0.65	-	-	1.00

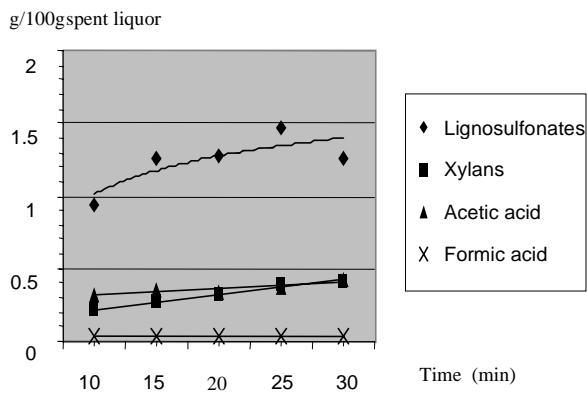


Figure 1: Organic components evolution in NSSC spent liquors vs. cooking time.

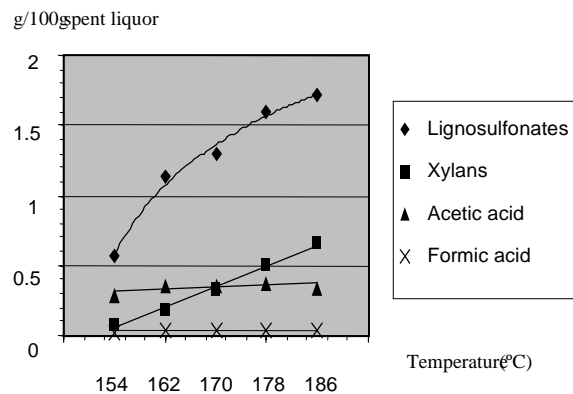


Figure 2: Organic components in NSSC spent liquors in function of temperature.

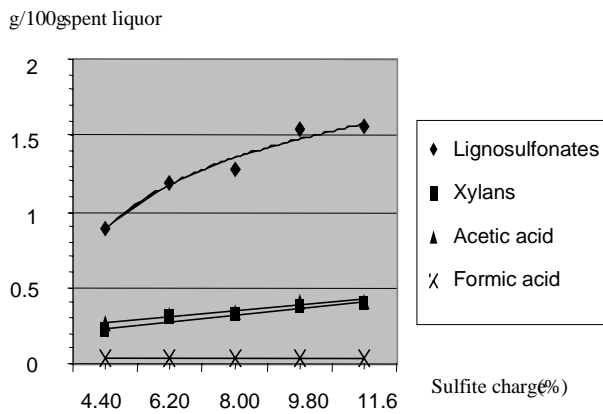


Figure 3: Organic components in spent liquors vs. sulfite charge.

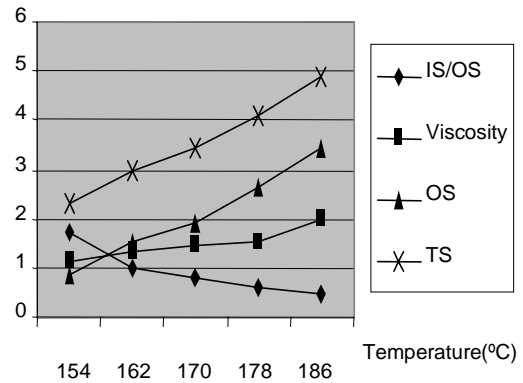


Figure 4: IS/OS ratio, TS, OS and viscosity vs. cooking temperatures

Figure 1 shows that organic acids are present in spent liquors since the early stages of NSSC cooking. While xylan concentration in spent liquor increases linearly during cooking, lignosulfonates concentration seems to stabilize at the end of the cooking.

Acid generation present similar pattern with temperature increase (Figure 2). Xylan dissolution at 154 °C is almost null, however it is important at 186°C. Lignosulfonates presence in spent liquors is high at 154 °C, and it seems to increase linearly toward higher ones.

While organic acids and xylans content in spent liquors present little modification with sulfite charge, changes in lignosulfonates concentration is high, showing an intermediate level between its variation with time and temperature (Figure 3).

The total solids increase with temperature is parallel to organic solids content in spent liquors (Figure 4). Their strong correlation can be also seen in Table II. Inorganic to organic solids ratio evolution is inversely proportional to viscosity increase.

The regression coefficients of the equations relating the properties of spent liquors with the variables studied are shown in Table III. Adjustments of all the equations are very good.

Table III: Regressions coefficients.

	Final pH	Consumed Sulfite	TS	OS	IS/OS	Viscosity	Lignosulfonates	Xylans	Acetic acid	Formic acid
Independent term	6.18	8.25	3.50	2.03	0.70	1.478	1.340	0.327	0.373	0.042
Time (A)	-0.08	0.37	0.19	0.19	-0.08	0.08	0.099	0.059	0.019	0.002
Temperature (B)	-0.16	1.13	0.58	0.58	-0.24	0.13	0.254	0.158	0.042	0.003
Sulfite (C)	0.20	0.74	0.48	0.20	0.06	0.12	0.177	0.035	0.043	0.003
Carbonate (D)	0.30	0.25	0.23	0.12	-	0.07	0.045	-	0.014	0.003
AB	-	-	-	-	-	-	-	-	-0.016	-0.002
AD	-	0.12	-	-	-	-	0.047	-	-	-
BC	0.07	-	-	-	-	-	-	-	-	-
BD	-	-	-	-	-	-	0.086	-	-	0.003
CD	-	-	-	-	-	-0.047	-0.058	-	-0.014	-
A ²	-	-	-	-	0.03	-	-0.033	-	-	-
B ²	-	0.11	-	-	0.08	-	-	-	-0.010	-0.003
C ²	-	-0.10	-	-	-	-0.038	-	-	-	-0.002
D ²	-	-	-	-	-	-	-	-	-0.012	-0.002
R ²	0.96	0.97	0.95	0.93	0.89	0.71	0.90	0.93	0.82	0.87

NSSC spent liquors characteristics results are presented in Figures 5 to 8.

Temperature and sulfite charges are the variables that show the greatest effect on consumed sulfite. Their influence is positive (Table III). Carbonate-Time interaction can be seen in Figure 5. At short cooking times, carbonate does not affect consumed sulfite, but its effect is strongly positive at long cooking times.

Inorganic solids and organic solids ratio has a minimum (optimum) value at 25 minutes and 181 °C (Figure 6). Time and temperature variables are the most significant ones, and act lowering the ratio. Sulfite charge increases IS/OS, while carbonate charge does not influence this ratio.

Dissolved lignosulfonates increase at higher temperatures and sulfite charges (Table III). The quadratic effect of time and its interaction with carbonate charge on wood is shown in Figure 7. While delignification reaches a limit value at short cooking times, it progresses continuously at longer times.

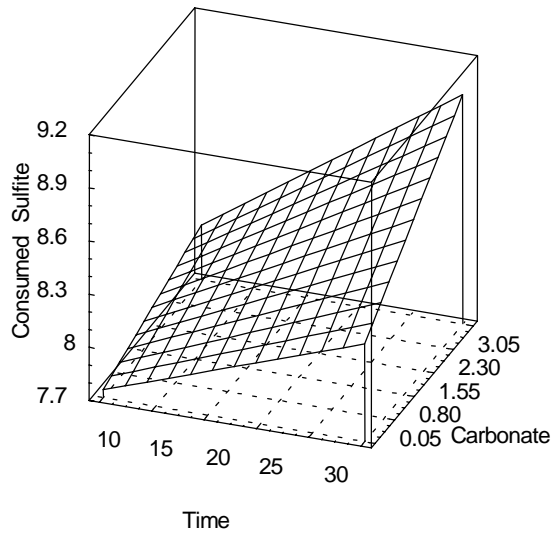


Figure 5 Consumed sulfite vs. cooking time and carbonate charge on wood (sulfite charge: 8% , temperature: 170°C).

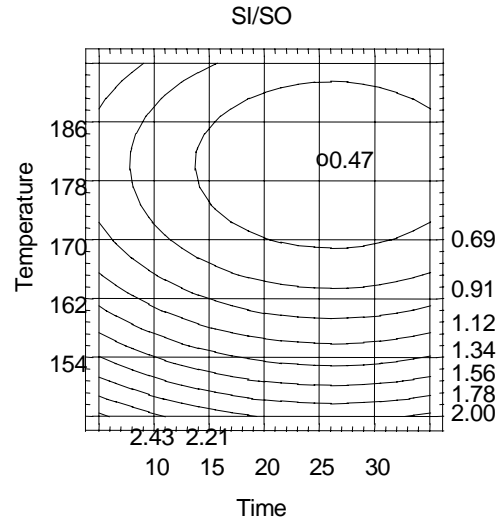


Figure 6: IS/OS ratio vs. cooking time and temperature (sulfite charge: 8% carbonate charge: 1.55%).

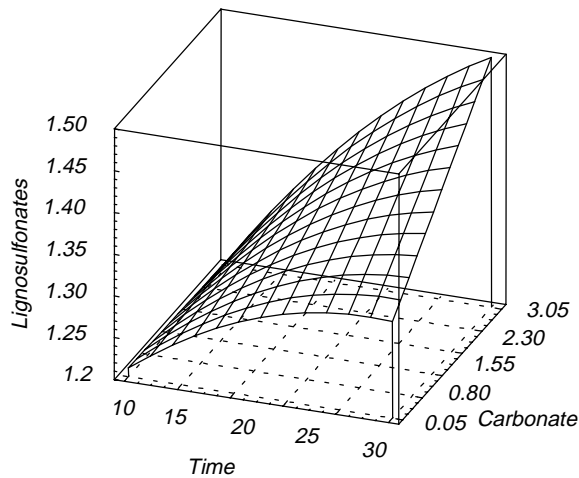


Figure 7: Lignosulfonates content in s.l. vs. time and carbonate charge. (sulfite charge: 8% , temperature: 170°C).

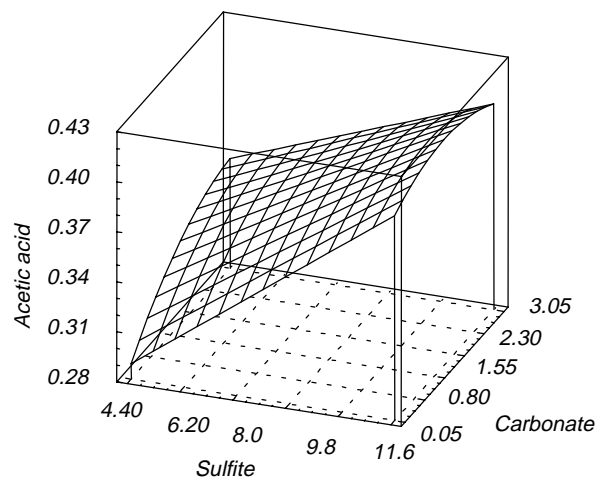


Figure 8: Acetic acid in spent liquors vs. sulfite and carbonate charges. (time: 20 min, temperature: 170°C).

Temperature and sulfite charge shows the greatest influence on acetic acid generation during the cooking (Table III). Again, carbonate charge acts through interactions, this time with sulfite charge (Figure 8). While carbonate charge

on wood exhibit an important effect on acetic acid formation, it does not evidence any effect at higher sulfite charges.

Chemical composition of several pulps were determined. Results show the selectivity of the process (Figure 9). This figure shows the typical curve for NSSC process selectivity (11). Lignin dissolution proceeds at a higher rate than hemicelluloses solubilization in the range studied. However, the graph indicate that NSSC is applicable only to the production of high-yield pulps, as the selectivity is very good at the beginning of the delignification.

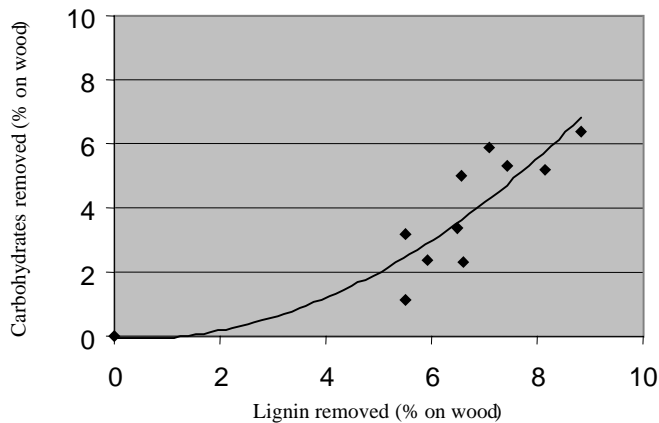


Figure 9: NSSC process selectivity.

Conclusions.

- Optimum conditions minimizing the inorganic/organic solids ratio were: 26 min, 177 °C, 6.0 % Na_2SO_3 , 2.54% Na_2CO_3 .
- Time, temperature and sulfite charge showed the greatest effects on organic materials dissolution.
- Carbonate charge acts principally through interactions.

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