

Nitric acid as pretreatment agent in the sugar cane bagasse chemimechanical pulping

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ABSTRACT

Chemimechanical pulps were prepared from sugarcane bagasse with nitric acid as a pretreatment chemical agent in a first step, and sodium hydroxide or ammonium hydroxide in a second step. The process variables were the chemical quantity, the temperature and the treatment time. Chemimechanical pulps with yield higher than 90%, 1.8—2.9 Km. tensile strength, and 52.2—57.7% Elrepho brightness with a 3% hydrogen peroxide were obtained.

INTRODUCTION

The sugarcane bagasse has been widely studied in Mexico and in other countries for the production of chemimechanical pulps using alkaline sodium sulphite as the main cooking agent (1—4). The pulp properties have been acceptable in strength but the pulp could be bleached only to a low brightness which is sufficient for newsprint and similar papers.

Bagasse chemimechanical pulps with sulphur free processes have been obtained (5—6) using alkaline peroxide as a pretreatment agent. The pulp characteristics were good enough to produce newsprint and similar papers but with a higher consumption of peroxide.

Another sulphur free chemimechanical pulping process promising good results with the sugar cane bagasse for the production of chemimechanical pulps is the nitric acid process (7). The pulp characteristics obtained are good but a high amount of hydrogen peroxide is required for bleaching. An advantage of this process is the possibility of using the waste liquor as fertilizer.

The objective in the present study is to find out the process parameters in the sugarcane bagasse nitric

acid pretreatment, prior to a sodium ammonium hydroxide treatment before defibration.

EXPERIMENTAL :

Depithing

Fresh dried bagasse was depithed by first screening it on a 8 wire/inch mesh and then treating in a sprout waldron disc refiner with water flow prior to another screening on the same mesh screen.

Cooking

The depithed bagasse was impregnated with dilute nitric acid at room temperature for 24 hours using a liquor to bagasse ratio of 3:1. The nitric acid quantity was varied from 1 to 5% based on the o.d. bagasse. The cooking was carried out in polyethylene plastic bags which were heated in a temperature controlled water bath. After the nitric acid cooking, the bagasse was washed with warm water (60°C) and then cooked again with sodium or ammonium hydroxide. The cooking conditions are given in Table—1.

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Defibration and Refining

The cooked bagasse was washed with warm water in a centrifuge and then defibrated and refined in a sprout-waldron 30 cm diameter disc refiner with disc pattern D2 A509 NH. The consistency was kept at 8% for defibration and at 5% for refining. The refined pulp was screened on a 0.15 mm wide slotted screen and it was screened on a 325 wire/inch mesh.

Pulp Evaluation

The Pulp properties were evaluated by measuring the strength and optical properties of the laboratory paper sheets in accordance with TAPPI and SCAN methods.

Bleaching

The bleaching was carried out on pulp samples of 10 g in plastic bags which were maintained at a given temperature in the water bath. The pulp before bleaching was pretreated with 0.3% DTPA at room temperature for 30 Minutes and 5% consistency. The bleaching liquor was composed of water with 0.1% magnesium sulphate, 5% sodium silicate 40° Be, 1% Sodium hydroxide, and 3% hydrogen peroxide. The bleaching conditions were : consistency 10%, temperature of 70°C and the bleaching time of 120 minutes. The bleached pulps were washed first with SO₂ water and then with hot water (50°C).

RESULTS AND DISCUSSION :

Yield

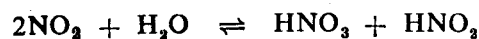
Table-2 shows the pulp characteristics of the pulps produced. The pulp yield values are more than 90% after the two treatment steps. The dissolved material depends on the action of nitrogen compounds which are present in the dilute nitric acid solution. The nitric acid presents a decomposition by the light action according to the following reaction :



In aqueous solution NO₂ is in equilibrium with the nitric acid according to the following reaction (8) :



The following reaction is also suggested for the aqueous NO₂ (9) :



The diluted nitric acid produces a higher proportion of nitric oxide, all the nitrogenous compounds have an oxidation or nitration action over the organic materials, producing nitrate compounds or some esterification (8).

The functional groups affected by oxidation are the final aldehyde groups and the hydroxyl groups, changing to aldehyde, ketone and carboxyl groups (10, 11).

The Chemical reactions in the nitric acid pulping are similar to the chloration reactions. They involve a fast electrophilic substitution of the lignin aromatic nuclei with nitro groups, similar to the one which occur in a phenol or phenolic ether treatment.

The nitric acid pulping process is a two step process as many of the lignin degradation products are not water soluble but they are alkali soluble (13).

The nitrolignin fragment as phenol or quinone are alkali soluble where posterior degradations occur, specially the nitro group elimination and the possible formation of hydroxinitroquinone configurations. The xylans are hydrolyzed to xylose (12). Even a high base concentration produces pulps with low glucomannan and xylan content (14).

The influence of treatment temperature on the yield is more clearer than the influence of reactants as shown in Figure-1. Increasing the temperature causes a continuous reductions in pulp yield both in the soda second step extracted and the ammonia second step extracted bagasse. The pulp yields are lower for the soda second step extracted bagasse. During the NO₂/O₂ chemical treatment prior to a warm alkaline treatment at 68°C a severe attack on the cellulose is caused (15). By reducing the temperature, a decrease in the delignification and in depolymerization is observed (16). Increasing the cooking time from 30 to 60 minutes in every step, the pulp yield is also slightly reduced.

TABLE-1

Pulping Conditions for the Nitric Acid Chemimechanical Pulping.
 Liquor to Bagasse Ratio 3:1 * Cooking Time for Every Step

SERIAL No.	CHEMICAL AGENTS			COOKING TEMPERATURE (°C)	COOKING TIME* (min.)
	HNO ₃ (%)	NaOH (%)	NH ₄ OH (%)		
1	1	1	-	80	30
2	1	-	1	80	30
3	2	2	-	80	30
4	2	-	2	80	30
5	3	3	-	80	30
6	3	-	3	80	30
7	4	4	-	80	30
8	4	-	4	80	30
9	5	5	-	80	30
10	5	-	5	80	30
11	-	5	5	80	30
12	5	5	-	EBULLICION	30
13	5	5	-	60	30
14	5	-	5	EBULLICION	30
15	5	-	5	60	30
16	5	5	-	60	60

TABLE-2

Characteristics of Pulp Obtained with the Nitric Acid Chemimechanical Pulping.
 After Two Cooking Steps * 3% Hydrogen Peroxide Bleaching

SERIAL No.	COOKING YIELD	BREAKING LENGTH		TEAR INDEX	UNBLEACHED BRIGHTNESS	LIGHT SCATT. COEFF.	BLEACHED BRIGHTNESS *
		50° SR	70° SR		50° SR	50° SR	50° SR
		m	m		mN.m ² /g	% ELREPHO	m ² /Kg
1	96.63	1519	1113	3.35	41.71	42.18	—
2	99.38	1078	1238	2.16	39.36	40.47	—
3	88.53	1105	1303	2.75	42.22	43.63	—
4	94.76	871	1033	2.19	41.62	42.53	—
5	94.72	1331	1742	2.43	38.71	42.79	—
6	91.31	687	1019	2.03	28.26	26.38	—
7	92.12	1464	1596	2.82	40.55	43.92	—
8	98.74	819	1159	2.07	40.26	43.87	—
9	92.48	2943	2329	4.87	36.18	42.78	52.26
10	95.25	800	1095	3.30	36.65	39.74	—
11	94.41	1757	1693	5.27	35.91	38.21	—
12	79.43	4308	4719	5.97	23.54	26.58	—
13	95.26	1835	1779	4.20	41.91	—	55.94
14	90.24	1697	1834	3.91	25.45	44.58	—
15	99.37	1012	938	3.29	41.17	—	—
16	94.47	2822	3062	5.66	41.79	—	57.72

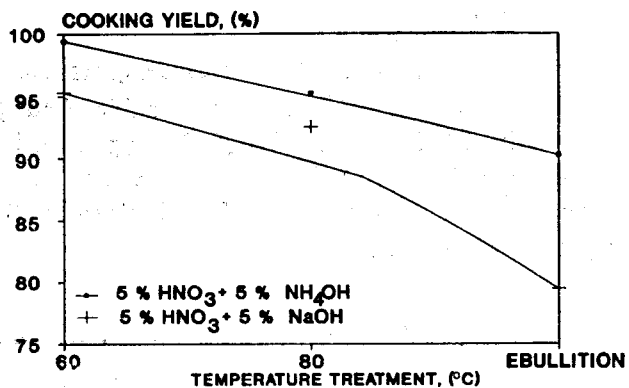


FIG. 1—CHEMIMECHANICAL PULP YIELD AS A FUNCTION OF THE TEMPERATURE TREATMENT.

Tensile Strength :

An increase in the amount of total reactants used in the two steps increases the tensile strength when soda is used in the second step cooking as shown in Figure-2. An increase of HNO₃ in the first step and NH₄OH in the second step do not have much effect on the pulp tensile strength and the values are clearly lower than the case when soda is used in the second step. The treatment temperature increment has an important influence over the tensile strength, specially when soda is used in the second step as can be seen in Figure-3. The temperature has less influence when NH₄OH is used in the second step. However, as can be seen in Figure-3, the tensile strength also increases, specially when ebullition temperature is used. Increasing treatment time from 30 to 60 minutes resulted in an increase of 84% in tensile strength thus reaching a more acceptable value from 1.8 to 2.8 km. as shown in Figure-4.

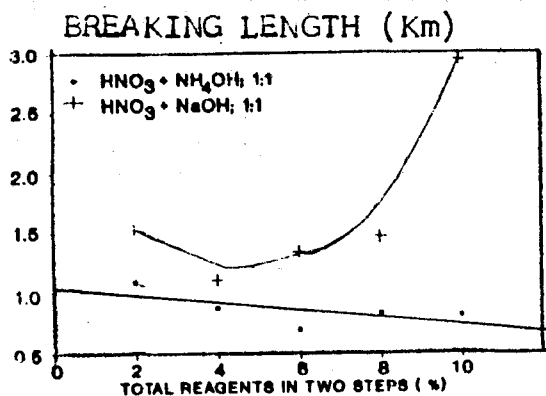


FIG. 2—BREAKING LENGTH AS A FUNCTION OF TOTAL REAGENTS USED IN TWO STEPS AT 50°SR FOR CHEMIMECHANICAL PULP,

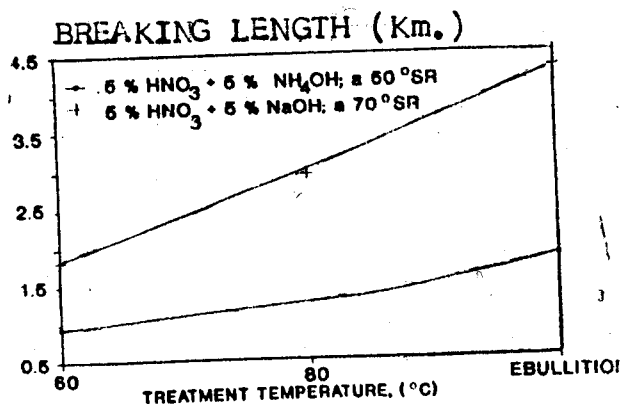


FIG. 3—BREAKING LENGTH AS A FUNCTION OF THE TEMPERATURE FOR 30 MINUTES TREATMENT TIME FOR CHEMIMECHANICAL PULP.

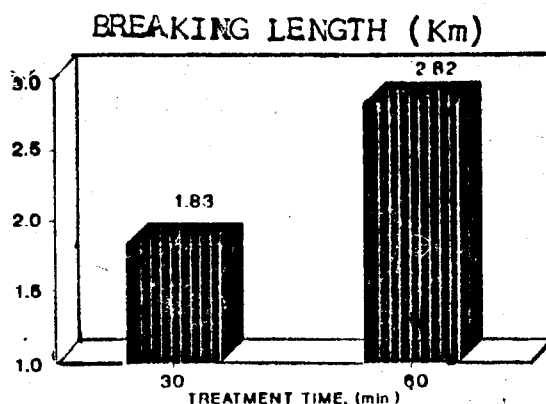
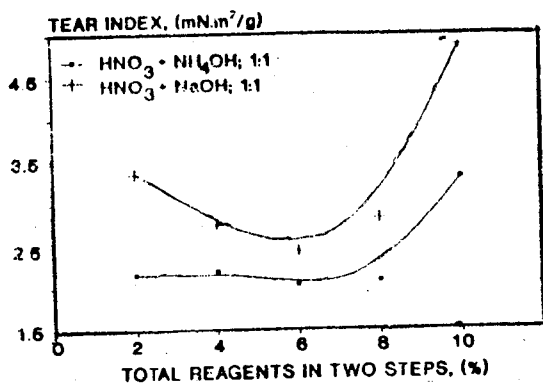


FIG. 4—BREAKING LENGTH AS A FUNCTION OF THE TREATMENT TIME, AT 60°C AND 50°C SR FOR CHEMICAL PULP.

TEAR STRENGTH :

The tear strength of bagasse chemimechanical pulp does not show a uniform behaviour with the increase in the amount reagents in two treatment steps. The increase in the soda content in the second cooking step does not increase the tear strength. In fact tear strength somewhat decreases until a 6% soda charge is used. After this level, higher soda charges results in pulps with higher tear as may be seen in Figure—5. Using NH₄OH in the second cooking step, the pulps are weaker in tear strength. Increasing NH₄OH charge does not increase the tear until more than 8% total reagents are used.

FIG. 5



TEAR INDEX AS A FUNCTION OF TOTAL REAGENTS USED IN TWO STEPS, AT 50 °SR FOR CHEMIMECHANICAL PULP.

The increase in treatment temperature increments shows an important influence on the pulp tear strength, when soda is used in the second cooking step, as shown in Figure-6. When NH₄OH is used as reagent in the second cooking step, no influence is observed at temperatures lower than the ebullition temperature. The treatment time increment from 30 to 60 minutes, produces a 36% increase in the tear strength, as may be seen in Figure-7.

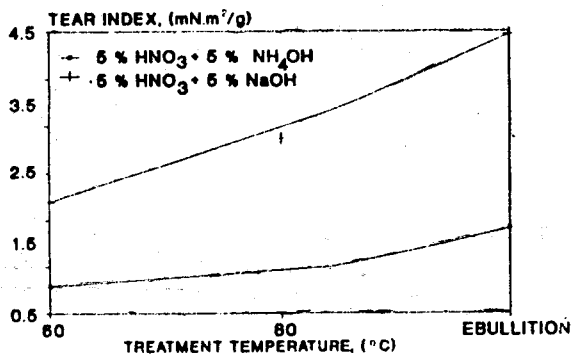


FIG 6.- CHEMIMECHANICAL PULP TEAR INDEX AS A FUNCTION OF TREATMENT TEMPERATURE, FOR 30 MINUTES AND 50 °SR.

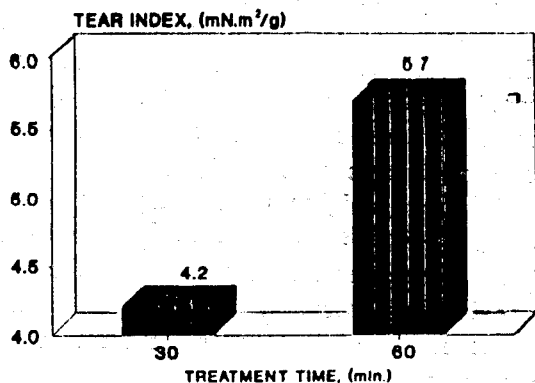


FIG 7.- CHEMIMECHANICAL PULP TEAR INDEX AS A FUNCTION OF TREATMENT TIME, AT 60 °C AND 50 °SR.

Brightness

Increasing the amount of total reagents causes a continuous drop in the brightness of unbleached pulp irrespective of NaOH or NH₄OH being used in the second cooking step. Figure-8 does not show a clear difference between the pulps obtained with the two type of reagents.

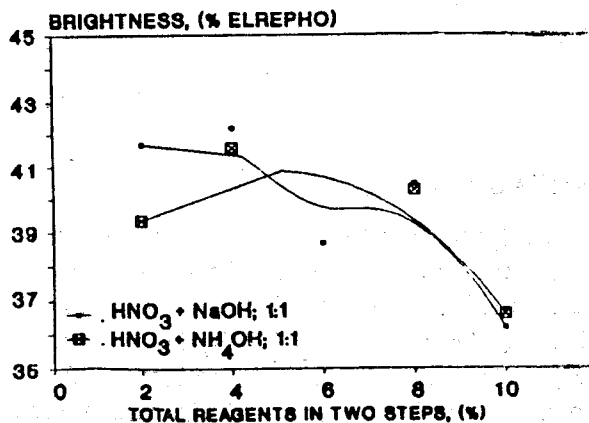


FIG 8.- UNBLEACH PULP BRIGHTNESS AS A FUNCTION OF TOTAL REAGENTS IN TWO STEPS, AT 60 °SR

The treatment temperature also shows a considerable influence over the brightness of pulps. As the temperature increases, the pulp brightness decreases and this is independent of NaOH or NH₄OH being used in the extraction step, as observed in Figure-9. The increase in treatment time from 30 to 60 minutes, does not show any difference in the pulp brightness, as shown in figure-10. However, the treatment time shows a clear difference in the response of pulp bleaching. A pulp obtained with 30 minutes cooking time by step

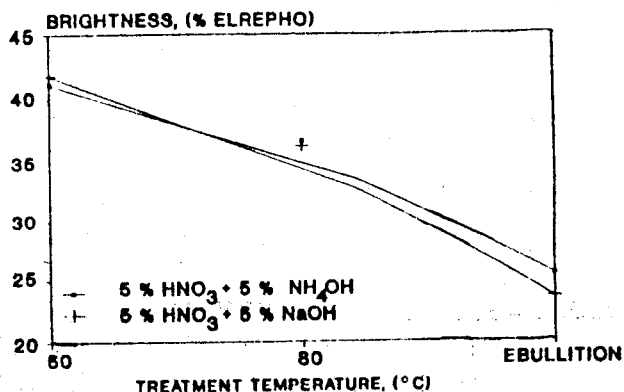


FIG 9.- UNBLEACHED PULP BRIGHTNESS AS A FUNCTION OF TREATMENT TEMPERATURE FOR 30 MINUTES AND 50 °SR.

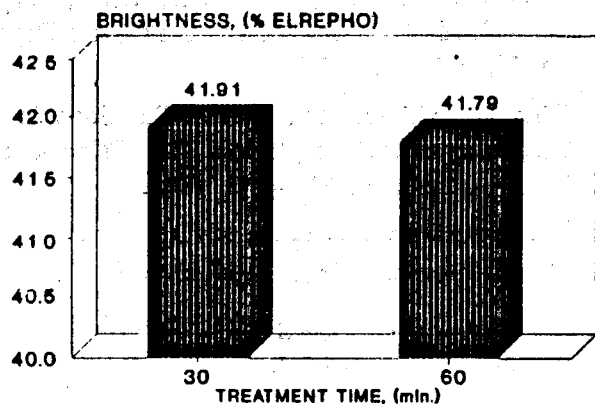


FIG 10.- UNBLEACHED PULP BRIGHTNESS AS A FUNCTION OF TREATMENT TIME, AT 60°C AND 50°SR.

results in the brightness gain of 14 points (55.9% Elrepho) with 3% H₂O₂ while the pulp obtained with 60 minutes cooking time by step gives a brightness gain of 15.9 points (i.e. 57.7% Elrepho) as shown in Figure—11.

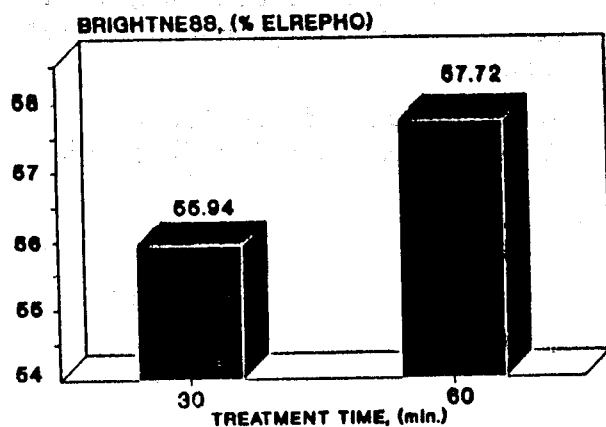


FIG 11.- BLEACHED PULP BRIGHTNESS AS A FUNCTION OF TREATMENT TIME AT 60°C AND BLEACHED WITH 3% PEROXIDE.

Light Scattering Coefficient :

An increase in total reagents presents a small positive influence on the light scattering coefficient when soda is used in the second cooking step, the scattering coefficient behavior is not uniform. Increasing the total reagents, the light scattering coefficient clearly increases until 8% of total reagents is reached. After this level, there is a sharp decrease in scattering coefficient as shown in figure—12.

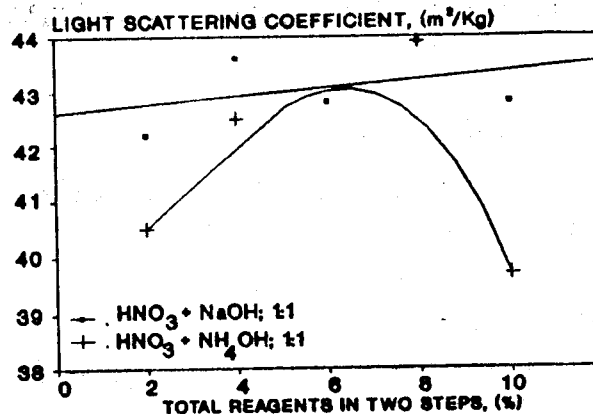


FIG 12.- PULP LIGHT SCATTERING COEFFICIENT AS A FUNCTION OF TOTAL REAGENTS USED IN TWO STEPS, AT 60°SR.

Conclusions :

- (i) The nitric acid process is promising for the sugarcane bagasse chemimechanical pulping, as the optical and physical properties of the pulp produced are adequate for producing some grades of paper.
- (ii) The pulp yield mainly depends on the total reagents used in the two cooking steps and also depends on the treatment temperature. The use of soda in the second cooking step produces pulp with yield lower than the case when NH₄OH is used.
- (iii) The pulp tensile strength is dependent on the amount of HNO₃ used. A 5% nitric acid produces a pulp with acceptable tensile and tear strength for some grades of paper. A 60°C temperature and one hour treatment time is found adequate for good pulp strength and the loss of the brightness was also at a low level.
- (iv) The brightness is negatively affected increasing the total treatment reagents with high temperatures. Increased treatment times do not seem to affect the brightness considerably if a temperature of 60°C is used but the peroxide bleaching response is improved.
- (v) A 5% of nitric acid at 60°C, one hour treatment time and refining to 50°C SR produce a 94% yield pulp with 2820 m of tensile strength, 5.7mN m²/g

of tear index and 57.7% final Elrepho brightness with 3% peroxide.

Acknowledgements

The financial support of the Jalisco state government is much acknowledged.

References

1. Ramos, J.; Y patt, R.; ATCP, Vol. XXIX, no.1; p 5-15; Enero-Febrero, 1989.
2. Ramos, J.; Tesis Doctoral; Universidad de Guadalajara; Mayo 1989.
3. Lopez, P.; Garcia, O.L.; y Rodriguez, L.; Tappi Non-Wood Plant Fiber Pulping; Progress Report no.15; p.13-17; 1984.
4. Nojima, S.; Umeda, K.; Sato, T.; and Yoshinaga, M.; Tappi Non-Wood Plant Fiber Pulping; Progress Report no. 15; p. 113-121; 1984.
5. Ramos, J.; Patt, R.; y Vargas J.; AmatI; Vol. III, no. 3 y 4; p. 10-15; Julio-Diciembre 1989.
6. Ramos, J., Vargas, J., Y Patt, R., 22 Congresso Anual de Cellulose e Papel, ABTCP; Sao Paolo, Brasil, p. 535-549, Novembro, 1989.
7. El-Taraboulsi, M.A., and Hurter, A.M., Tappi Non-Wood plant Fiber pulping, Progress Report no. 16, P. 27-46; 1986.
8. Kirk, R.E.; Y Othmer, D.F., Enciclopedia de Tecnologia Quimica, Tomo XI; Primera ed. Espanol, Uteha, p. 245-248, 1962.
9. Lachenal, D., Choudens, C. de, and Monzie, P., Svensk Papperstidning, no. 17, P. 494-497, 1980.
10. Ridholm, S.A., pulping Processes, Intercience, N-Y, P. 130-148, 1965.
11. Casey, J.P.; Pulp and Paper; Chemistry and Chemical Technology, Third Edition, Vol. 1, p. 21, 1980.
12. Ridholm, S.A., Ob. Cit. p.674-675.
13. Wither, R.P., and Captein, H.A., Forest Products Journal; 10 (3), p. 174-177, March, 1960.
14. Godsay, M.P., and Mac Donald, D.M., U.S. Patent, no 3578553, May 11, 1971.
15. Abrahamsson, K., and Samuelson, O.; Svensk Papperstidning; Vol.85, no3; p.R.27-R32; March, 1982.
16. Samuelson, O.; and Sjoberg, L.A.; Svensk Papperstidning; no. 6 p. R30-R35; 1984.