

Explosion pulping of jack pine: hydrogen peroxide and hydrosulfite bleaching of pulp

AZIZ AHMED* AND BHOUSLAV V. KOKTA*

ABSTRACT

Jack pine, in general, yield pulp of low brightness. The brightness of jack pine explosion pulp can be raised to 60.9% from the initial 38.9% by applying 4% H_2O_2 in a single stage H_2O_2 bleaching. By adding 5% H_2O_2 in a single stage hydrogen peroxide bleaching, the pulp brightness can be raised to 62%. The brightness gain obtained by adding a second stage hydrosulfite bleaching is only 2 points. The bleaching chemicals, except NaOH, have little or no effect on the physical properties of the pulp. Both breaking length and burst index increase and tear index decreases with the increase of %NaOH in bleaching liquor.

INTRODUCTION

The ultra-high-yield explosion pulp is expected to become an attractive alternative to the well-known CMP or CTMP in near future. The physical properties of explosion pulp is equivalent or superior to those of CMP or CTMP. Above all, the defibration energy demand of explosion pulp is about 30-50% less than that of CMP or CTMP for a similar CSF value (1).

In explosion pulping process (1-5), wood chips were impregnated with chemicals and then cooked in a saturated steam at a temperature between 180 to 210°C corresponding to a pressure between 12 to 15 atmosphere for a period of 2 to 6 minutes. At the end of the cooking period, the chips were exploded by sudden release of reactor pressure to atmospheric pressure. The exploded chips were then washed and refined to prepare pulp for paper making. Generally, the yield range of the pulp was around 85-94% and brightness level around 40-70% depending on the wood species and pulping conditions.

In a recent study of jack pine explosion pulping (6), we have reported the effect of operating conditions on resulting pulp properties.

Jack pine, generally, gives pulp of low brightness. The high resin content of jack pine is partly responsible for this initial low brightness (7). The response of jack pine mechanical and chemi-mechanical pulp towards H_2O_2 and hydrosulfite bleaching has been studied previously (8,9).

The primary objective of this work is to study the H_2O_2 and hydrosulfite bleaching of ultra-high-yield jack pine explosion pulp. The effects of operating conditions and of different bleaching chemicals on pulp brightness have been examined.

EXPERIMENTAL

Materials

Jack pine was supplied by Syndicate des producteurs de bois de la Mauricie en Shawinigan, Quebec. The freshly cut trees of average diameter 6" were debarked manually, chipped and screened at la Station Forestiere Duchesnay, Quebec. All chips were shredded in Centre de Recherche et Developement, Consolidated-Bathurst, Grand Mere to obtain thin chips. The shredded chips were then sieved in a classifier. The average

*Centre de Recherche en Pate et Papiers
University du Quebec a Trois-Rivieres
Trois-Rivieres, Quebec

chips thickness, width and length were respectively as follows: 1 to 9 mm, 1 to 2 cm and 2.5 to 3.75 cm. Technical grade bleaching chemicals are used in this studies.

Impregnation

150g of chips (=50% siccity) were mixed in plastic bag with solution made up of 8% Na_2SO_3 and 0.5% NaOH . The weight ratio of liquor/chips during impregnation was 6. The temperature and time maintained during impregnation were respectively 60°C and 24 hours.

Cooking

Cooking was performed in a laboratory batch reactor of 350 ml build by stake Tech. Co by using saturated steam. The cooking was done at 190°C for 4 minutes. Each cooking was preceded by one minute steam flushing at atmospheric pressure. After cooking, the pressure was released suddenly and the chips which exploded into the release vessel were washed in a washing machine with tape water. The washed exploded chips were then stored in a cold room and refined later on.

Refining

Laboratory refining was done using a domestic blender Osterizer B-8614 at 2% consistency level. The CSF of the pulp used for bleaching experiment was about 250 ml.

Bleaching

The peroxide bleaching liquor was prepared by mixing DTPA, magnesium sulfate (MgSO_4), sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2). The percentage of each component is given in table-1. The peroxide liquor and a certain amount of distilled water (to attain desired pulp consistency) were poured in polyethylene bags containing the unbleached pulp and the bag was then sealed after removing the air as much as possible. The bleaching liquor and the pulp in the bag were then thoroughly mixed by hand before unsealed the bag to measure the initial pH of the liquor. Then the bag was sealed again as before by removing the air as much as possible and mixed again by hand before immersing the bag in a thermostatic bath at desired temperature and time. A mixing of the contents in the bag in of 15 minutes periods is necessary to have uniform heat and mass transfer

during the bleaching period in the thermostatic bath. At the end of the peroxide liquor treatment the reaction mixture was neutralized with sodium metabisulfite to pH 5.5 and washed well with distilled water before proceeding further in order to evaluate the pulp yield, optical and physical properties. Pulp brightness was measured on 3.5g handsheet, The pulp bleaching conditions along with the variation of liquor composition was presented in Table-1.

Hydrosulfite bleaching of the pulp was performed by using sodium hydrosulfite of percentages varying from 1 to 4 with 0.5 sodium tripolyphosphate. The results are presented in Table-2.

In two stage bleaching, the peroxide stage was followed by a second stage hydrosulfite bleaching. The operating conditions and liquor compositions were presented in Table-3.

Property Evaluation

Paper sheets were prepared and tested according to CPPA standard methods.

The brightness (Elrepho) was measured on 1.2g or 3g handsheet prepared using demineralized water. The brightness stability of the unbleached and bleached pulp was evaluated after exposing the pulp in an oven at 105°C for 60 minutes.

RESULTS AND DISCUSSION

Hydrogen Peroxide Bleaching

Bleaching of ultra-high yield pulps with hydrogen peroxide removes very little lignin in contrast to conventional bleaching chemicals. Alkaline hydrogen peroxide probably cleaves some of the phenyl propane groups of lignin, resulting the destruction of chromophore and prevents regeneration of color (10).

Prevention of Hydrogen peroxide and heavy metal interaction :

The hydrogen peroxide used for pulp bleaching can be wasted as water and oxygen by the catalytic action of heavy metals such as iron, manganese, copper, lead etc. Generally, the chelating agent (DTPA) and/or Silicate (Sodium silicate) are used to control the heavy metals. These additives effectively prevent the chemical interaction of the metals and the peroxide.

TABLE -1

HYDROGEN PEROXIDE BLEACHING OF JACK PINE EXPLOSION PULP

Code No.	0	2	4	5	5a	6	7	8	9	10	11	12	13	14	15	16	17	18
DTPA, (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MgSO ₄ , (%)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
NaOH, (%)	4	2	2	1	2	2	2	2	2	2	2	2	2	2	1	2	2	2
Na ₂ SiO ₃	5	5	5	5	5	10	3	10	10	10	10	10	10	10	10	10	10	10
H ₂ O ₂ , (%)	3	3	3	3	4	4	4	4	4	4	4	4	4	4	4	4	2	1
Temperature (°C)	80	80	80	80	80	80	80	70	60	80	80	80	80	90	80	80	80	80
Time (minutes)	150	150	150	150	150	150	150	150	150	200	100	100	100	100	100	100	100	100
Consistency, (%)	20	20	20	20	20	20	20	20	20	20	20	15	25	25	25	25	25	25
Initial PH	13	12.5	12.5	11.6	12.6	12.4	12.4	12.5	12.4	12.5	12.4	12.4	12.5	12	12	12	12	12
Final PH	12.5	10.6	10.6	10.2	10.4	10.6	10.6	10.9	11.1	10.5	10.7	10.8	10.5	9.6	10.2	10.7	10.9	9.8
Yield, (%)	96.7	98.5	98.5	99.1	97.9	99.2	98.1	99.2	98.9	97.4	98.2	99.1	99.9	98.2	96.8	98.8	97.9	98.5
Residual H ₂ O ₂ , (%)	0	0.1	0.1	0.06	0.23	0.27	0.01	0.6	0.98	0.1	0.2	0.7	0.26	0.2	0.6	0.2	0.1	0.5
Brightness (%)	38.9	39.4	54.6	49.4	57.7	59.6	49.9	57.3	56.2	59.1	59.5	57.2	60.9	61.1	60.2	55.9	48.2	62.0
Burst index, (KPa.m ² /g)	3	3.3	3.1	3.2	3.3	3.2	3.1	3.3	3.1	3.1	3.0	2.8	2.7	3.1	3.3	2.9	2.7	3.2
Tear index, (mN.m ² /g)	9.2	8.5	8.0	8.3	8.9	8.7	8.9	8.54	8.7	8.1	8.8	9.5	9.1	8.2	8.3	9.67	10	8.5
Breaking Length, km	4.5	5.7	4.9	5.1	5.0	5.2	5.2	5.2	5.2	5.6	5.4	5.0	4.9	5.4	5.4	4.8	4.4	5.4
Stretch, (%)	2.1	2.9	2.5	2.8	2.6	2.4	2.4	2.5	2.5	2.5	2.3	2.4	2.4	2.6	2.6	2.6	2.2	2.7

Experimental conditions of hydrogen peroxide bleaching of jack pine explosion pulp and properties of resulting bleached pulp.

TABLE-2

HYDROSULFITE BLEACHING OF JACK PINE EXPLOSION PULP

No. of experiments	1	2	3	4
Sodium tripolyphosphate (%)	0.5	0.5	0.5	0.5
Sodium hydrosulfite (%)	1	2	3	4
PH	5.5	5.5	5.5	5.5
Consistency (%)	4	4	4	4
Temperature, (°C)	60	60	60	60
Time, min.	60	60	60	60
Yield (%)	99.6	98.6	100	99.7
Initial brightness (%)	38.9	38.9	38.9	38.9
Final brightness (%)	44	44	45.1	43.7
Burst index, (KPa.m ² /g)	2.67	2.72	2.97	2.56
Tear index, (mN.m ² /g)	8.9	9.41	8.81	9.36
Breaking length, km	4.76	5.04	4.95	4.89
Stretch (%)	2.24	2.41	2.37	2.38

Experimental conditions of hydrosulfite bleaching of jack pine explosion pulp and properties of resulting bleached pulp.

TABLE-3

TWO STAGE HYDROGEN PEROXIDE AND HYDROSULFITE BLEACHING OF JACK PINE EXPLOSION PULP.

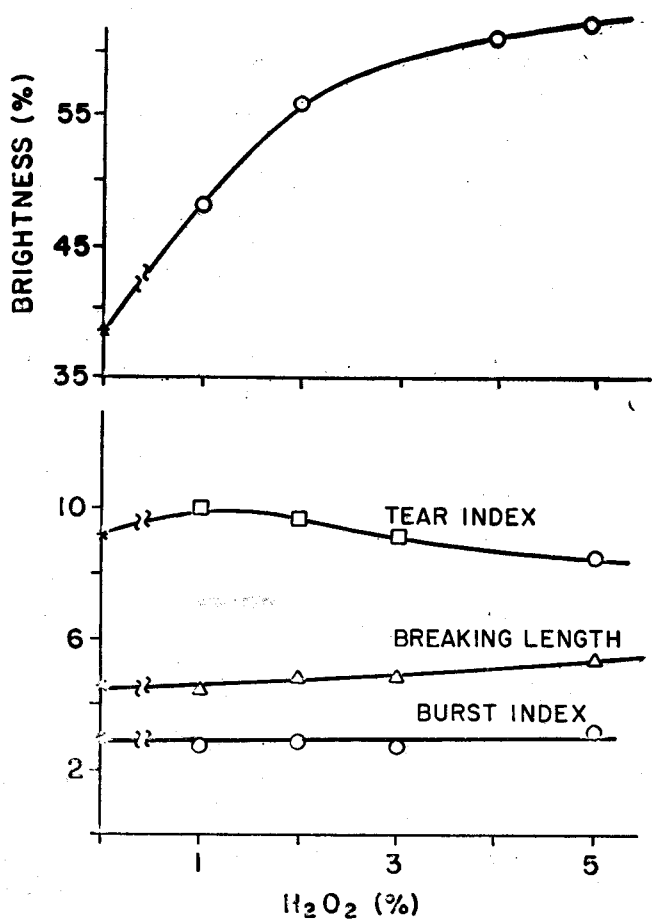
Hydrogen peroxide bleaching	
DTPA (%)	0.5
MgSO ₄ (%)	0.05
NaOH (%)	2
Na ₂ SiO ₃ (%)	10
H ₂ O ₂ (%)	4
Temperature, (°C)	80
Time, (min)	100
Consistency (%)	25
Initial PH	12
Final PH	9.95
Yield (%)	99.97
Residual H ₂ O ₂ (%)	0.27
Initial Brightness (%)	38.9
Final Brightness (%)	60.9
Hydrosulfite bleaching	
Sodium tripolyphosphate (%)	0.5
Sodium hydrosulfite (%)	3
PH of bleaching liquor	5.5
Consistency (%)	4
Temperature (°C)	60
Time, (min.)	60
Yield (%)	97.8
Brightness from 1st stage (%)	60.9
Final brightness (%)	63

Experimental conditions of two stage hydrogen peroxide and hydrosulfite bleaching of jack pine explosion pulp and properties of resulting explosion pulp.

The actual amount of DTPA is a function of the amount of heavy metal present. Magnesium sulfate acts as stabilizer presumably forming insoluble flocs to absorb or coprecipitate heavy metal ions. Usually 0.05% MgSO₄ (based on o.d. pulp) is sufficient for such a function (11).

Effect of Hydrogen peroxide concentration :

The effects of the variation of H₂O₂ concentration in hydrogen peroxide bleaching liquor on the resulting pulp brightness and physical properties are presented in Table - 1. This table also presents the bleaching conditions as well as the proportion of different chemicals present in hydrogen peroxide bleaching liquor. Percentage of brightness are plotted in Figure-1 as a function of %H₂O₂ applied. The brightness of jack pine explosion pulp increases with the increase of H₂O₂ concentration in bleaching solution. Brightness increased from 38.9 to 60.9% sharply with the addition of 4% H₂O₂ in bleaching liquor. With the addition of 1 more percentage of H₂O₂, brightness increased only by 1 point. Therefore, the use of H₂O₂ above 4% is not economically feasible. The bleaching process has little effect on the physical properties of the bleached pulp. Both burst index and stretch remain nearly same, whereas tear index decreases and breaking length increases with the increase of H₂O₂ concentration.

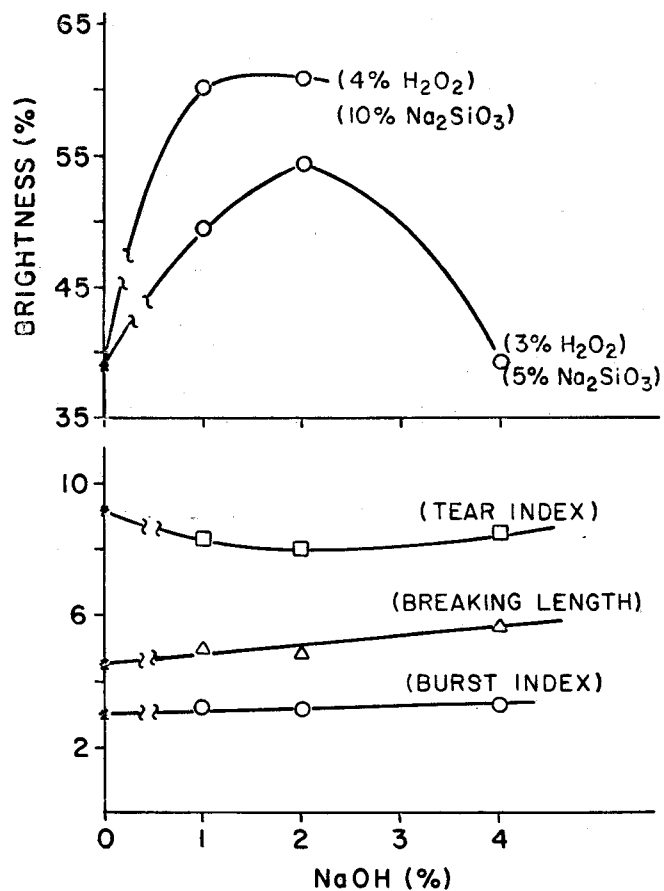


1. Effect of H₂O₂ concentration present in bleaching liquor on pulp brightness and properties like tear index, burst index and breaking length.

Concentration of NaOH in Hydrogen peroxide bleaching :

Sodium hydroxide is a source of alkali required to prepare hydrogen peroxide bleaching liquor. Total alkali content and hydrogen peroxide content of bleach liquor must be balanced so that residual amounts of both are present at the end of the bleaching reaction. If total alkali is exhausted very soon, there will be no driving force producing the perhydroxyl ion, resulting no more bleaching action. If hydrogen peroxide is exhausted while alkali remains, brightness reversion will occur. The effects of the variation of NaOH concentration in bleaching liquor on the resulting pulp brightness and physical properties are presented in Table-1. Pulp brightness and physical properties are plotted respectively in Figure-2 as a function of %NaOH. The pulp brightness increases sharply from the initial brightness of 38.9 to as high as 54.6% with the increase of

2% NaOH. The addition of 4% NaOH in bleaching liquor increases the brightness from 38.9 to 39.4% only. In this condition, the percentage of H₂O₂ and Na₂SiO₃ used was 3 and 5 respectively. By increasing the percentage of H₂O₂ by 4% and Na₂SiO₃ by 10%, it is observed that with 2% NaOH in bleaching liquor, the brightness of the pulp increases to 60.9% in comparison to the 60.2% brightness obtained by 1% NaOH present in bleach liquor. The increase of %NaOH in bleach liquor is efficient to the development of mechanical properties, as evident in Figure-2.

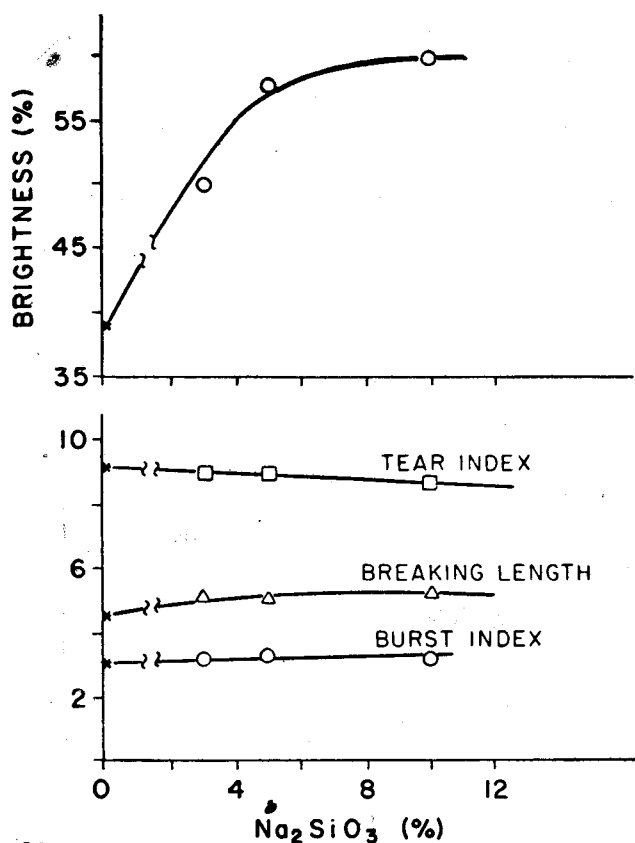


2. Effect of NaOH concentration present in bleaching liquor on pulp brightness and physical properties like tear index, burst index and breaking length.

Effect of Sodium silicate concentration :

Sodium silicate was used as a source of alkali and as a buffering agent (12) for hydrogen peroxide bleach liquor. It also has a third function as a stabilizer for hydrogen peroxide in the presence of heavy metals (13-15). It forms insoluble heavy metal silicates or adsorb these metals in calcium and magnesium silicate

flocs. This reduces catalytic hydrogen peroxide decomposition. The effects of the variation of Na_2SiO_3 concentration in bleaching liquor on pulp brightness and physical properties are presented in Table—1. The brightness and the physical properties of the bleached pulp are presented in Figure—3 as a function of percentage of Na_2SiO_3 present in bleaching liquor. The brightness of the pulp increases with the increase of Na_2SiO_3 in bleaching. With 5% Na_2SiO_3 the brightness of the pulp increases from initial brightness of 38.9% to final brightness 57.7%. With 10% Na_2SiO_3 in bleaching liquor, the brightness increases to 59.6%. The physical properties of bleached pulp remain unchanged with the variation of Na_2SiO_3 proportion in bleaching liquor.

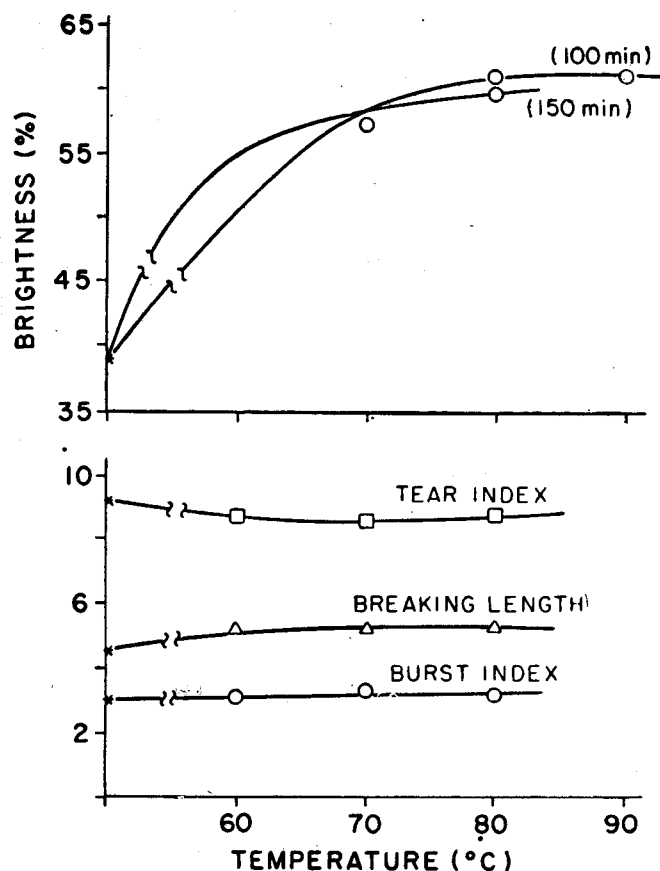


3. Effect of Na_2SiO_3 concentration present in bleaching liquor on pulp brightness and physical properties like tear index, burst index and breaking length.

Effect of bleaching temperature :

The rate of bleaching with hydrogen peroxide increases as the temperature increases. The decompo-

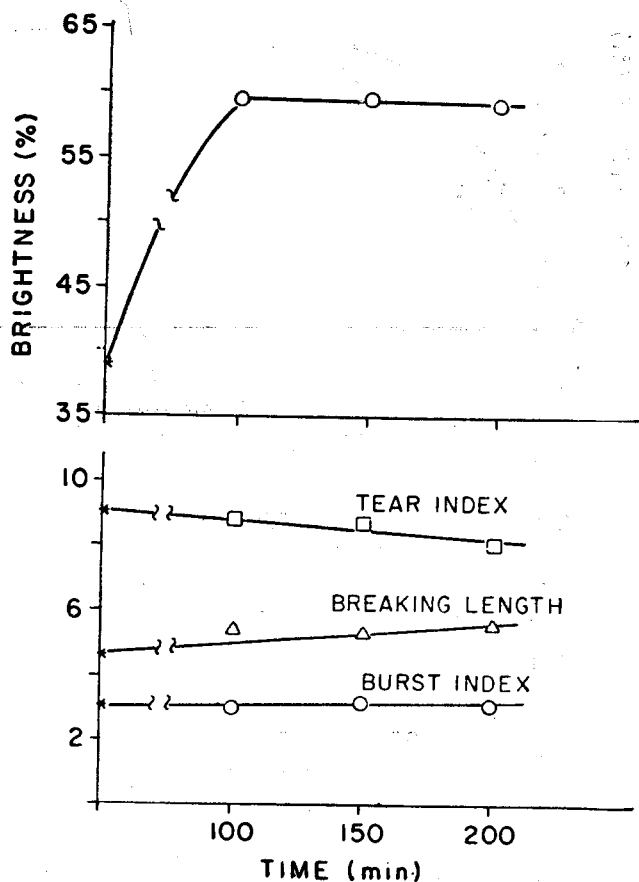
sition rate of hydrogen peroxide also increases as the temperature increases. For most practical purposes, bleaching is usually performed at temperatures between 70 to 80°C. When bleaching is performed at temperatures above 80°C, good control of the total alkali/hydrogen peroxide ratio becomes increasingly important. If the total alkali is too high, rapid decomposition of the peroxide occurs; if the total alkali is too low, the bleaching reaction slows down. The data relating the effects of temperature on hydrogen peroxide bleaching are presented in Table—1. The bleached pulp Brightness and the pulp physical properties are plotted in Figure 4. The pulp brightness increases with the increase of bleaching temperature, however, the physical properties of the pulp remain unchanged.



4. Effect of temperature during hydrogen peroxide bleaching on pulp brightness and physical properties like tear index, burst index and breaking length,

Effect of bleaching time :

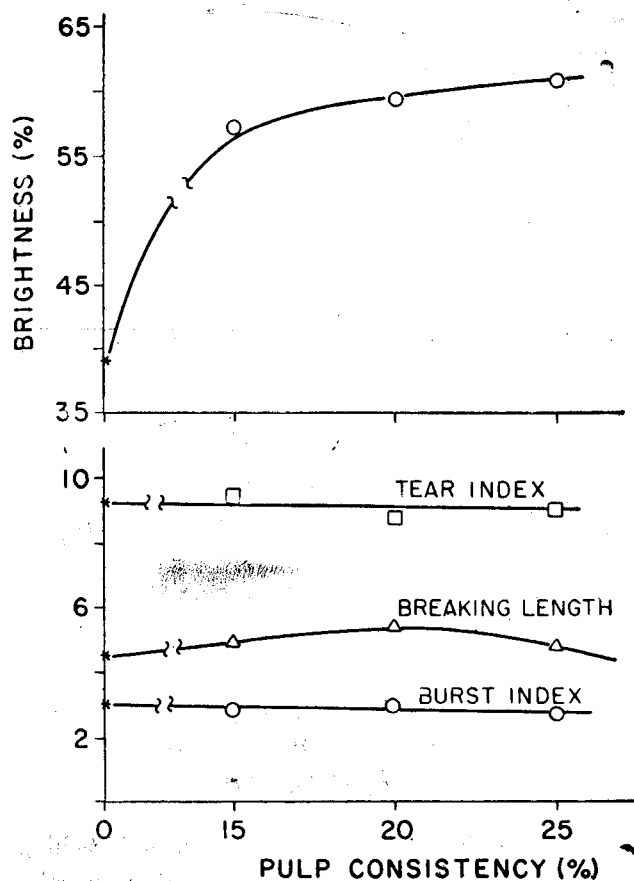
Bleaching time and temperature are complementary to each other. Low bleaching temperature needs more time for bleaching reaction and high bleaching temperature needs less time for bleaching reaction. There should be always a balance between time and temperature. The data relating the effect of bleaching time at constant temperature 80°C are presented in Table-1. The pulp brightness and the physical properties of the bleached pulp are presented in Figure-5 as a function of bleaching time. The pulp brightness increases sharply with the increase of time up to 100 minutes and then remain nearly constant with further increase of time up to 200 minutes. The pulp brightness drops below 150 minutes level for the bleaching time of 200 minutes. Breaking length of the pulp increases and tear index decreases slightly with the increase of bleaching time. Burst index and stretch are remain nearly constant.



5. Effect of bleaching time on pulp brightness and physical properties like tear index, burst index and breaking length.

Effect of pulp consistency :

Consistency of pulp during bleaching is important in terms of bleaching chemical requirements as well as the mixing problems. The data relating the effects of pulp consistency on hydrogen peroxide bleaching are presented in Table-1. The pulp brightness and the physical properties are plotted in Figure-6 as a function of pulp consistency. The pulp brightness increases with the increase of pulp consistency during hydrogen peroxide bleaching. The change in physical properties is insignificant.

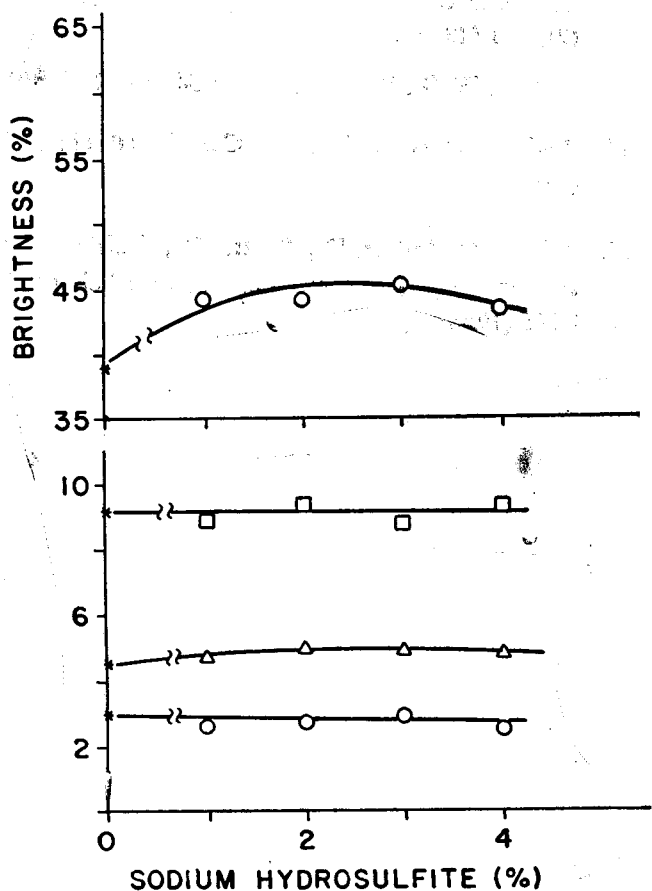


6. Effect of pulp consistency maintained during hydrogen peroxide bleaching on pulp brightness and physical properties like tear index, burst and breaking length.

The optimum condition of hydrogen peroxide bleaching of jack pine explosion pulp, as appeared from the analysis of bleaching results, is as follows: DTPA 0.5%, $MgSO_4$ 0.05%, NaOH 2%, Na_2SiO_3 10% H_2O_2 4%, bleaching temperature 80°C, bleaching time 100 minutes and consistency 25%. In this optimum conditions, 60.9% brightness can be obtained.

Hydrosulfite bleaching of jack pine explosion pulp :

Hydrosulfite bleaching is less effective than hydrogen peroxide bleaching. The hydrosulfite bleaching condition as well as the optical and physical properties of the bleached pulp for various concentration of sodium hydrosulfite are presented in Table-2. The brightness and the physical properties of the bleached pulp are plotted in Figure-7 as function of sodium hydrosulfite percentage in bleaching liquor. Sodium hydrosulfite



7. Effect of sodium hydrosulfite concentration present in hydrosulfite bleaching liquor on pulp brightness and properties like tear index, burst index and breaking length.

bleaching increases the pulp brightness from the initial 38.9% to final 45.1% for 3% sodium hydrosulfite in bleaching liquor. The increase in percentage of sodium hydrosulfite to 4% gives the pulp of 43.7% brightness which is even below the brightness (44%) obtained by using 1 or 2% sodium hydrosulfite in the bleaching liquor. The physical properties are more or less remain same.

Second stage hydrosulfite bleaching :

When two stage bleaching is used, the first stage should be the hydrogen peroxide bleaching. The reason is two fold. 1. Although hydrogen peroxide and hydrosulfite react chemically to destroy one another, when hydrogen peroxide is the first stage this problem can be overcome by the addition of aqueous sulfur dioxide at 3-5% consistency to neutralize the pulp. 2. This sequence simplifies equipment needed for the hydrosulfite bleaching in second stage. Moderate density pulp is usually used in hydrogen peroxide bleaching, while low density pulp is used in hydrosulfite bleaching. Thus, neutralization and dilution are only steps necessary to prepare hydrogen peroxide bleached pulp for hydrosulfite bleaching.

In two stage bleaching, the best condition of hydrogen peroxide bleaching is used in the first stage and the best condition of hydrosulfite bleaching is used in second stage bleaching. The operating conditions as well as the pulp brightness obtained by two stage bleaching is presented in Table - 3. The brightness gain obtained by second stage hydrosulfite bleaching is only 2 points.

CONCLUSION :

The brightness of jack pine explosion pulp can be raised to 60.9% from the initial 38.9% following the hydrogen peroxide bleaching process. The process conditions were optimized for bleaching the jack pine explosion pulp up to 62% brightness level. By adding a hydrosulfite bleaching stage after the hydrogen peroxide bleaching stage, an additional 2% brightness gain can be obtained. Except NaOH, the bleaching chemicals have very little or no effect on the physical properties of the pulp. Both breaking length and burst index increase whereas tear index decreases with the increase of NaOH proportion in bleaching liquor.

REFERENCES :

1. Kokta, B.V. and Vit, R. "New Ultra-High Yield V-Pulping Process." 73rd CPPA Annual Meeting, (Jan. 1987).
2. Kokta, B.V., "Process for Preparing pulp for Paper Making" *Can. Pat.* 1,230, 208 (Dec. 15, 1987).
3. Kokta, B.V. "Process for preparing pulp for paper making." *U.S. Pat.* 4, 798, 651 (Jan. 17, 1989).
4. Kokta, B.V., "Improved Process for Preparing Pulp for Paper Making. *Can. Pat. Appl.* 542,643 (May 1987).
5. Kokta, B.V. Chen, R., Zhan, H. Y, Baarrette, D. and Vit. R., "Pate a tres haut rendement: Mise en Pate-V et blanchiment a partir de tremble" *Pulp and Paper Can.* 89 (3) : T91-T97 (1988).
6. Ahmed, A. and Kokta, B.V.. "Explosion Pulping of Jack Pine: Effect of Operating Conditions on Explosion Pulp Properties." Submitted to: *Investigacion Y Tecnica del Papel.*
7. Jossart, D., Barbe, M.C., Lapointe, M. and Law, K. N. "Properties of Mechanical and Chemi-mechanical Jack Pine Pulps, Part-1, Thermo-mechanical Pulp." *Pulp and Paper Canada*, 89 (4), P. T115-T122. (1988).
8. Gagne, C, Barbe, M. C., Remillard, B and Lapointe, M. "Properties of Mechanical and Chemi-mechanical jack pine pulps. Part-IV. Bleaching Studies." 75th. CPPA Annual Meeting, Montreal, Quebec, Canada. pp. B273-B283.
9. Andrews, D.H. and Desrosiers, P., "The Influence of wood components on the Bleach Response of jack pine groundwood to peroxide." *Pulp and Paper Magazine of Canada*, 67 (c), T119-128 (1966).
10. Reeves, R.H. and Pearl, I.A. *Tappi* 48 (2) : 121-125 (1965).
11. Kokta, B.V. and Daneault, C., *Tappi*, 69 (9), 130-133 (1986)
12. Ali, T., Fairbank, M., McArthur, D , Evans, T.D. and Whiting, P., *J. Pulp and Paper Sci.* 14 (2), J23 (1988).
13. Strunk, W.G , *Pulp and Paper* 54 (6): 156 (1980).
14. Andrew. D.H., *Pulp Paper Canada*, 60 (11); T273 (1968).
15. Ali, T., McArthur, D., Scott. D., Fairbank, M. and Whiting, P., *J. Pulp and Paper Sci.* 12 (6); J 166 (1986).