Development of a Volatile Sulfur Recovery Process for Kraft Pulping

H. VEERAMANI,
K. V. SARKANEN and
L. N. JOHANSON

The limitations of current devices for reducing sulfur losses and kraft mill odour indicate the potential promise of an alternate process to recovery sulfur as hydrogen sulfide from unoxidized weak black liquor. The volatile sulfur recovery process developed from preliminary laboratory experiments would add four major steps to the conventional chemical recovery operations in a kraft pulp mill These steps include (a) precarbonation of unoxidised weak black liquor, (b) recovery of hydrogen sulfide from precarbonated black liquor by further carbonation, (c) recovery of carbon dioxide from carbonated black liquor by steam stripping and (d) absorption of hydrogen sulfide from $H_2 S{\cdot}CO_2$ *mixture using green liquor* (sodium carbonate). The odour release from evaporators and recovery furnace treating desulfurized black liquor may be expected to be quite small.

The multiple effect evaporators, flue gas evaporator and the recovery furnace contribute most to the well-known kraft mill odour problem. The digester relief and blow gases and condensates, pulp washer vent and to a lesser extent the smelt dissolver vent and the lime kiln stack gases account for the minor sources of sulfur loss and odour.

Sulfur losses from many effluent locations and the extremely low odour threshold levels of the malodorus chemicals has been a constant challenge to chemical engineers engaged in developing odour control techniques. Some of the methods available for reducing the kraft mil odour problem include oxidation of black liquor, combustion of noncondensable gases from digester, blow tank and evaporators, steam or air stripping of condensate streams and the efficient control of the recovery furnace operating conditions. The limitations of some of these methods were discusser earlier[1].

The removal of sulfur compounds from weak black liquor could considerably reduce the emission of odorous constituents from the evaporators and the recovery furnace. Sarkanen[2] has proposed a process for the transfer of sodium sulfide from black liquor to green liquor by passing the recovery furnace, this may be one of the several possible ways in which new process technology could markedly improve kraft odour control facilities.

Volatile Sulfur Recovery Process :

The principle of the method consists in recovering sulfur as a volatile stream from unoxidised black liquor prior to evaporation. Sodium hydrosulfide in unoxidised black liquor can be displaced as hydrogen sulfide by acidification with carbon dioxide. The black liquor relatively free of sulfides, could be concentrated and burned to yield smelt containing mainly sodium carbonate. The resulting basic smelt may be recombined suitably with sulfur constituents for the regeneration of pulping liquor.

The principal reaction of interest is the recovery of sodium hydrosulfide in black liquor as hydrogen sulfide, as represented by the equation (1).

$$NaHS + CO_2 + H_2O = NaHCO_3 + H_2S \quad \ldots \quad (1)$$

Other chemicals present in a commercial black liquor sample, such as sodium carbonate, sodium hydroxide and sodium phenolates of lignin contribute to the following set of reactions during carbonation.

$$OH^- + CO_2 = HCO_3^- \qquad (2)$$

$$HCO_3^- + OH^- = CO_3^{--} + H_2O \qquad (3)$$

$$CO_3^{--} + CO_2 + H_2O = 2\ HCO_3^- \qquad (4)$$

$$\text{Lignin-O}^- + CO_2 + H_2O = \text{Lignin-OH} + HCO_3^- \qquad (5)$$

These reactions are incidental to the carbonation process and must be considered in an evaluation of the principal reaction (1) leading to the recovery of hydrogen sulfide. The residual hydroxyl ions in the high pH black liquor react with carbon dioxide to form carbonate ions, reactions (2) and (3); these together with carbonate ions initially present in the black liquor carbonate further to bicarbonate ions, reaction (4). The phenolic groups of lignin with a pH value of 10.9 (3) also consume carbon dioxide resulting in bicarbonate ion and precipitated lignin product, reaction (5). With a further lowering of the pH by carbonation, hydrosulfide ion is released as hydrogen sulfide with further consumption of carbon dioxide and formation of bicarbonate ions, reactions (1).

The technical feasibility of this proposed process was evaluated considering the following major factors :

1. The yield of hydrogen sulfide obtainable by carbonation.
2. Carbon dioxide requirements of the process and sources available for supplying carbon dioxide.
3. Establishing the process flow path and material and energy balance during carbonation.
4. Handling of the lignin precipitate incidental to the carbonation process.

Pure carbon dioxide was used for the batch carbonation experiments with unoxidised weak black liquor (obtained locally from a kraft mill pulping Douglas Fir chips). The results of the ex-

H. Veeramani*, K. V. Sarkanen and Johanson, Department of Chemical Engineering, University of Washington, Seattle Washington.

*** Present Address : Indian Institute of Technology, Kanpur, U.P.**

periments and the role of the several factors included in the development of the volatile sulfur recovery process are discussed below.

RECOVERY OF HYDROGEN SULFIDE BY CARBONATION:

The hydrosulfide ions will be the dominant sulfur species over the pH range, 10.5-13.0, of weak black liquor. Sulfur will be present to a minor extent as sulfite, thiosulfate, sulfate, polysulfide, etc. depending upon sulfur make up chemical, recycle practices and the exposure of black liquor to the atmosphere. The controversy over the presence of sulfur in organic combination with lignin, 1.7 per cent of organically combined sulfur according to Enkvist[4] and Ekman[5] and some tenths of one per cent according to Zhigalvo and Tischenko[6] has been clarified by Mckean et. al.[7]. Mckean et. al. have shown that part of the hydrosulfide added in white liquor is utilised in dimethylation reactions and that essentially no hydrosulfide is consumd irreversibly by reaction with lignin.

The results of preliminary experiments (Table 1) show that upto 97.0 per cent of the sodium hydrosulfide in black liquor may be recovered as hydrogen sulfide by carbonation. The yields of hydrogen sulfide obtained by carbonation are comparable to the yields resulting from the addition of 1.0 N HCl for the acidification. A known quantity of white liquor was added to carbonated black liquor and the concentration of sodium sulfide in the mixture was determined by Tappi standard procedures[3]. The residual sodium sulfide in carbonated black liquor was approximately 1.5 per cent of the original sulfide concentration in black liquor. Quantitative yield of hydrogen sulfide was also obtained in similar experiments using white liquor and carbon dioxide.

It was observed that a pH level of about 7.8 was reached by carbonation and that this was sufficient to recover essentially all of the sulfidic sulfur from unoxidised black liquor. A pH value of 9.2 was reached in black liquor carbonation experiments before the release of hydrogen sulfide started. The corresponding value of pH = 9.5 observed in white liquor carbonation tests is in good agreement with the value pH = 9.5 reported in the literature for green liquor carbonation[9]. During this carbonation to pH = 9.5, excess alkalinity and some of the phenolic groups of lignin molecules are neutralised without the release of measureable amounts of hydrogen sulfide.

Mai's results[10] establishing the operating path followed in actual carbonation of Na_2S-Na_2CO_3 brines is reproduced in Figure 1. Carbon dioxide was bubbled through a solution containing sodium carbonate (0.06 geq/l) and sodium sulfide (0.04 geq/l), designated as point A in Figure 1. The change in composition with time for batch carbonation at 35°C is shown as a dotted line in Figure 1. This shows that the actual path may be closely approximated by assuming the carbonation reaction to follow the path ABD. Segment AB represents carbonation of carbonate ions to bicarbonate according to reaction (4) and segment BD describes carbonation of sodium hydrosulfide ion to form bicarbonate ion with the release of hydrogen sulfide, reaction (1). This approximation should simplify the treatment of practical carbonation processes since it assumes that the carbonation proceeds in two steps.

UTILISATION OF CARBON DIOXIDE:

The progress of the carbonation process may be followed with the balck liquor titration curves in Figure 2, obtained

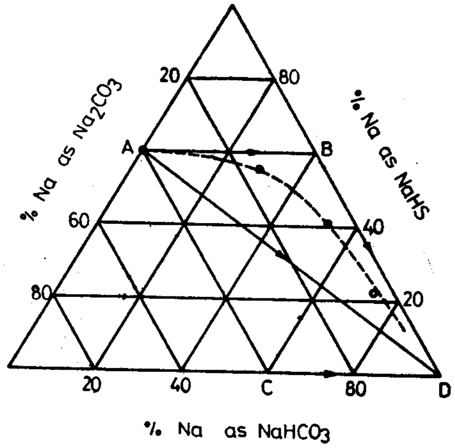

Fig. 1: Batch carbonation of Na_2S-Na_2CO_3 solution (Sodium ion = 0.1N) Mai (10)

by observing the change in pH values on acidifying 50 ml black liquor samples with 1.0 N hydrochloric acid. Acid consumption at various pH levels may be expressed in equivalent amounts of carbon dioxide required; carbon dioxide consumed at any desired level of carbonation can be easily obtained from these plots.

It can be shown from these curves that nearly three-fourth of the total carbon dioxide requirement (total corresponding to pH = 7.8) will be utilised in lowering the alkalinity of the kraft

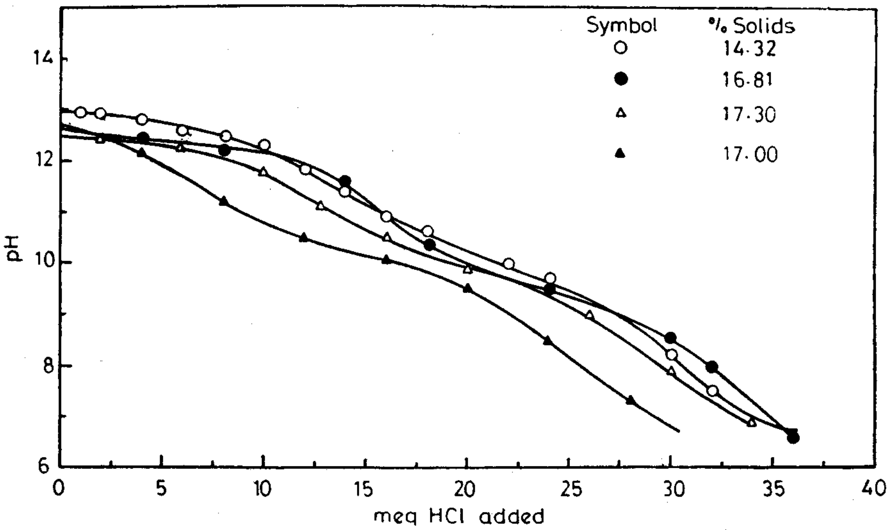

Fig. 2: -pH variation with the addition of 1.0 N HCl to 50 ML of unoxidised industrial black liquor at 23°C.

black liquor to pH = 9.5. This change in black liquor pH from an initial value of 11.0-13.0 to 9.5 will be referred to as the precarbonation step. This critical value of pH = 9.5 will facilitate the possible use of flue gas for the precarbonation step and permit the use of a smaller quantity of relatively pure carbon dioxide to recover a gas mixture rich in hydrogen sulfide. Also, elimination of inert nitrogen gas here will reduce the volume of gases to be handled in subsequent operations. Steam stripping of carbonated black liquor should give pure carbon dioxide which could be utilised to strip out hydrogen sulfide from precarbonated black liquor. The carbonate-bicarbonate equilibrium is such that the temperature attainable by steam stripping in an atmospheric pressure tower will release nearly all the bicarbonate carbon dioxide in accordance with the reverse of equation (4), (11, 12).

Batch experiments were conducted to establish a material balance for carbon dioxide during carbonation and steam stripping operations. Unoxidised black liquor samples (500 ml) were carbonated until all the hydrosulfide was displaced from the solution. Addition of carbon dioxide was stopped and a liquor sample withdrawn for analysis; The carbonated black liquor was heated to boiling and the carbon dioxide released collected in sodium hydroxide absorbent solution. The boiling was continued for 6-8 hours; at the end of the heating period the final black liquor and absorbent solution were analysed for their carbon dioxide concentration. Analysis was performed by adapting the Tappi standard procedure for sodium carbonate in white liquor and green liquor (13). The suitability of this procedure to black liquor was established independently. It was also observed that the black liquor titration curves of Figure 2 would predict the concentration of carbon dioxide in precarbonated black liquor to within 10.0 per cent.

The results of these experiments are given in Table 2. The total concentration of carbon dioxide present as carbonate and bicarbonate is expressed as gram moles of carbon dioxide per litre of black liquor. The sum of carbon dioxide present in the final black liquor and the amount released in the steam stripping step agrees well (98.0 per cent average) with the amount of carbon dioxide added during the carbonation step.

Nearly 40.0 per cent of the carbon dioxide present in carbonated black liquor may be recovered in the stripping operation, accompanied by a proportionate increase in sodium carbonate concentration in the final black liquor. This indicates that about half of the total carbon dioxide added during carbonation remains behind in the steam stripped black liquor; the relative amounts of sodium carbonate and bicarbonate will depend upon the final pH, temperature and ionic strength of the solution.

The changes in pH accompanying the carbonation and stripping steps are also included in Table 2. The pH of carbonated black liquor 7.9 @ 47°C increased to a maximum of 9.53 @ 98°C; the corresponding values of pH at room temperature are 8.00 and 10.55 respectively.

The influence of Lignin on Black Liquor Carbonation.

The main alkali consumption in kraft pulping is caused by the peeling reactions, hydrolysis of glucosidic bonds and acetyl groups in the carbohydrate chains of wood chips. However, it can be shown that lignin reaction utilise about a quarter of the total alkali consumption[14]. Delignification, in kraft pulping proceeds with the caustic soda reacting with phenolic hydroxyls (either present initially or formed by hydrolysis of ether linkages) of the hydroxy phenyl-propane structural units in lignin forming soluble lignin phenolates. The dissolved lignin has about 0.8 phenolic groups per monomer unit whereas the protolignin contains only 0.3 phenolic groups per monomer unit[14]. By equilibrium sedimentation methods, Marton and Marton[15] have found the weight average molecular weights for pine and hardwood kraft lignins recovered by partial acidification of industrial black liquors to be 3,560 and 1,900 respectively; an average pine kraft lignin is composed of 20 building units and an average hardwood kraft lignin molecule contains 15 structuarl units. Alkali lignins and kraft lignins in sodium hydroxide and buffer solutions have pH values of 11.0 and 10.9 respectively[3].

Sodium phenolate groups in lignin molecules participate in the carbonation reactions resulting in lignin precipitate as a product, reaction (5). Lignin precipitation accompanying carbonation is perhaps undesirable but unavoidable. Lignin may precipitate out as a lump with poor mixing but with good agitation may be maintained as a slurry in carbonated black liquor.

Weak black liquor samples were carbonated at various temperatures and carbonation terminated either when hydrogen sulfide evolution commenced (determined qualitatively with cadmium chloride solution) or when hydrogen sulfide recovery was complete. The yields of lignin precipitate obtained under these conditions and the behaviour of the lignin product observed in the carbonated black liquor are summarised in Table 3. Lignin yields obtained with the addition of hydrochloric acid alone to lower pH levels are also included in Table 3.

It may be inferred that about one-fourth of the total lignin precipitated during precarbonation; granular lignin separated in the overall carbonation process accounted for half the amount obtained from acid addition. Average lignin yields corresponding to about one-third and one-half of the total lignin in black liquor was reported by Merewether[16 17] on carbonating black liquor (wood species used-Eucalyptus regnans and Eucalyptus siberiana) to pH levels of 9.5 and 8.0 respectively.

Temperature sensitivity of the lignin product would also play an important role in the carbonation process. Lignin precipitate obtained around 70°C remained as a slurry in black liquor carbonated with agitation; the precipitate settled on standing and facilitated decantation and easy filtration. At 84°C, lignin precipitated out as lumps even with mixing. At lower temperature, 23°C, filtration was extremely slow.

Some tests were performed with a commercial black liquor sample pulping predominantly alder, a hardwood species. The temperature sensitivity of the hardwood lignin product during carbonation was more pronounced. Lignin precipitate remained as a slurry at 52 and 70°C facilitating fairly rapid filtration. However, carbonation at 84°C gave a liquid lignin product. The molten liquid lignin phase solidified on cooling; the supernatent liquor was clear. Quantitative results were not obtained for hardwood black liquor. Tomlinson and Tomlinson[18] carbonated aspen (hardwood) soda black liquor in a spray tower at 70°C and separated the precipitated lignin as a liquid phase by heating the carbonated black liquor to 85°C.

A comparison of the yields of precipitated lignin from carbonation and stripping operations discussed earlier (36.4 and 15.4 g of lignin per litre of black liquor respectively) indicated that about half of the precipitated lignin may be redissolved in the carbon dioxide recovery process.

The concentration of sodium phenolate groups in lignin molecules may be estimated indirectly from a knowledge of the initial composition of the black liquor (NaOH, Na_2CO_3, Na_2S) and the total consumption of carbon dioxide in the carbonation process. An average value of 0.64 phenolic units per monomer units is obtained from the results in Table 3 for Douglas fir black liquor; the calculation is for a pulp yield of 45.0 per cent assuming 17.0 per cent solids in the black liquor, molecular weight of lignin monomer of 175 and a typical softwood composition. This value compares reasonably well with the published value of 0.8 phenolic groups per monomer unit for dissolved kraft lignin[14].

PROPOSED VOLATILE SULFUR RECOVERY PROCESS :

The results of the preliminary studies on the black liquor carbonation concept suggest four major steps for a potential sulfur recovery scheme outlined in Figure 3. In the precarbonator, excess alkalinity in black liquor is neutralised whereas in the hydrogen sulfide generator hydrosulfide is displaced as hydrogen sulfide with further carbonation. Hydrogen sulfide leaving the H_2S generator with the excess carbon dioxide used will be absorbed in sodium carbonate solution. Steam stripping of carbonated black liquor in the CO_2-generator should give a pure stream of carbon dioxide for use in the H_2S-generator.

Precarbonator : Black liquor after separation from the pulp is passed downward through a packed or plate tower counter-current to a gas steam rich in carbon dioxide; in Figure 3 this a portion of the lime kiln stack gases. Black liquor will leave the precarbonator at pH=9.5.

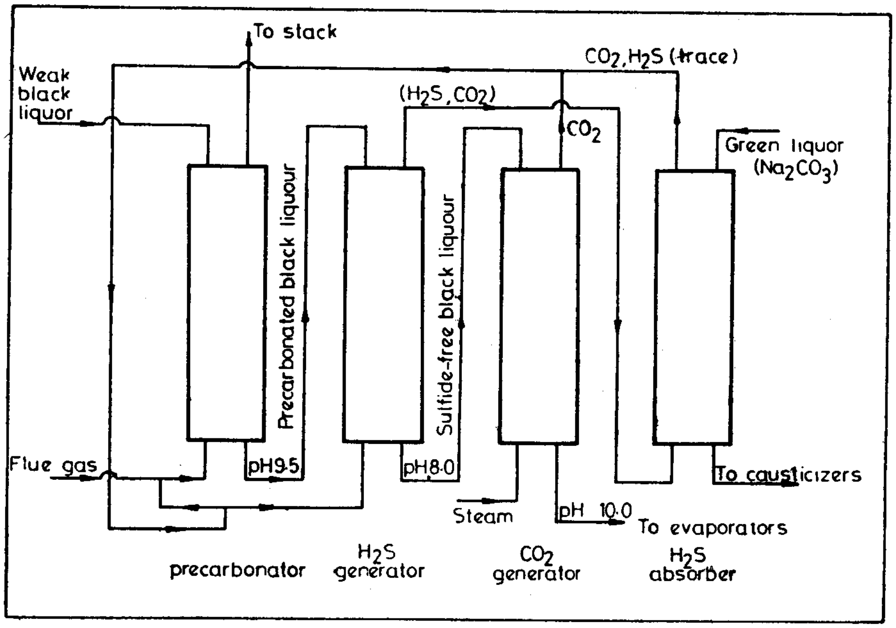

Fig. 3 : Proposed volatile sulfur recovery process.

H_2S-Generator : Precarbonated black liquor is contacted with an almost pure carbon dioxide gas in counter-current operation. Hydrogen sulfide will be stripped from the solution in this tower and leave the column with the excess carbon dioxide used. The residual sodium hydrosulfide concentration in the carbonted black liquor should be quite low.

CO_2-Generator : Carbonated black liquor (pH near 8.0) now essentially free of sulfide sulfur is steam stripped in a tower in counter-current operation. Carbon dioxide released here is sent to the H_2S generator, for carbonating the precarbonated black liquor. The steam stripped black liquor is sent to the evaporators.

H_2S-Absorber : The gas mixture leaving the H_2S-generator contains hydrogen sulfide and carbon dioxide; hydrogen sulfide in this gas will be selectively absorbed in green liquor (mainly sodium carbonate) in a packed tower. Carbon dioxide and residual hydrogen sulfide leaving the absorber are sent to the H_2S-generator or black liquor precarbonator. The liquor effluent is sent to the causticizer.

Black liquor from the CO_2-generator is subsequently concentrated in multiple effect evaporators together with a direct contact evaporator if desired, prior to burning in the recovery furance. The resulting sodium carbonate smelt after dissolution is partly utilised in hydrogen sulfide absorption. White liquor is prepared through the usual causticizing and clarifer operations. The bulk of the green liquor and the portion of green liquor containing absorbed hydrogen sulfide from the H_2S absorber may be causticized separately, since the causticizing efficiency at equilibrium is about 2.0 per cent higher for a solution of zero sulfidity compared to a solution corresponding to 30.0 per cent sulfidity[19]. The lime kiln operation remains unchanged except for the small additional lime required for neutralising the bicarbonate ion formed in the H_2S absorber. The white liquor from the recovery operations is reused in the digester.

RELATED SULFUR RECOVERY PROCESSES :

Several related processes are in various stages of development for the recovery of chemicals from spent sulfite liquors. During the past ten years the following processes have been proposed. Mead[22 23], Rayonier[24], Sivola[20 21 25 27], Stora[20 28], Tampella[20 29 30], Crosby[31], Kubelka[20] and cross-chemical recovery[32 33] processes. Some of these processes such as Stora, Rayonier, Tampella and cross-chemical recovery schemes are in commercial operation today to a limited extent. All of these procees operate essentially on the same principle for recovering sulfur. The spent liquor is concentrated and burned in a kraft type recovery furnace to produce a smelt containing sodium carbonate and sodium sulfide. Sodium sulfide in the clarified green liquor is recovered as hydrogen sulfide by carbonation. There is no information available in the literature concerning the mass transfer characteristics or the kinetics of these processes. This is perhaps due to the proprietory nature of the work done by the commercial firms in developing these methods. These processes have the precarbonation and hydrogen sulfide recovery concepts similar to the volatile sulfur recovery process for a kraft pulp mill proposed in this investigation.

CONCLUSION

The proposed volatile sulfur recovery process will differ from the conventional chemical recovery operations in a kraft mill in that four additional absorption-stripping columns will be required. Also, processing sulfur free black liquor in the recovery furnace proper could eliminate the need to maintain a reducing zone in the furnace. Sulfur-free black liquor should also minimise malodorous emissions and sulfur losses from the evaporators and recovery furnace. However, sulfur losses from the lime kiln will not be influenced by the new process. A preliminary estimate of the potential sulfur losses in a pulp mill employing the proposed sulfur recovery process is given in Column C, Table 4. It may be observed from these values that the contribution of the evaporators and the recovery furnace to the overall kraft mill odour problem could perhaps be significantly reduced by the proposed modified sulfur recovery process.

Non-condensable gases from the evaporators and recovery furnace flue gases may need no further treatment while the evaporator condensates could be reused in the process. The presence of precipitated lignin in the steam stripped black liquor may be a disadvantage during concentration of the liquor in the evaporators; fouling of the evaporator tubes may necessitate more frequent cleaning.

An important factor in considering the proposed process for a pulp mill recovery operation is the capital requirement, which depends upon the sizes of the absorption and desorption columns recommended. Mass transfer coefficients necessary for a design of these columns are either non-existent or not well established for the systems under consideration. The details of the mass transfer experiments and the results for the carbonation and stripping processes[34] will be reported in forthcoming papers.

TABLE 1

RECOVERY OF HYDROGEN SULFIDE FROM BLACK LIQUOR BY ACIDIFICATION

Temp. °C	Acidifying media	Final pH	H_2S yield, expressed as Na_2S, g/l
22.0	1.0 N HCl	—	5.79
91.5	1.0 N HCl	—	5.76
22.0	CO_2	7.35	5.48
22.0	CO_2	—	5.81
	+ 10 ml 1.0 N HCl	—	Traces
	+ 10 ml 1.0 N HCl	—	None
100.0	CO_2	—	5.80*
80.0	CO_2	8.25	5.75

* Sample was under paraffin oil cover during carbonation.

Weak black liquor :

Total solids concentration, % = 15.3

Initial pH = 13.0

Initial concentration of sodium sulfide, g/l = 5.75

TABLE 2

MATERIAL BALANCE FOR CARBON DIOXIDE DURING CARBONATION OF BLACK LIQUOR AND RECOVERY OF CARBON DIOXIDE FROM CARBONATED BLACK LIQUOR

Temp. °C	pH @ T′ Carbonated liquor	Conc. of CO_2, gmol/l bl. carbonated bl. liquor	Stream stripped bl. liquor	CO_2 recovered	Bl. liq. final pH
50	7.85	—	0.450	0.404	9.35
63	8.00	0.877	0.471	0.352	9.82
					10.42
47	7.90	0.767	0.466	0.234	9.55
					10.55
48	7.82	0.822	—	—	—
57	—	0.814	0.443	0.432	—
Average	—	(0.820)	(0.457)	(0.357)	—

Black liquor type : Unoxidized industrial softwood black liquor from a batch digester.

Sample used for each experiment, ml = 500.

Initial conc. of sodium carbonate, gmol/l = 0.151.

Initial conc. of sodium sulfide, gmol/l = 0.154.

Initial pH = 13.0; Total solids conc. in black liquor, % = 17.0.

TABLE 3
YIELD AND BEHAVIOUR OF LIGNIN PRECIPITATE DURING CARBONATION OF BLACK LIQUOR

Acidifying medium	Temp. °C	pH @ T	Lignin g/l of bl. liquor	Remarks*
HCl	68	3.15	38.3	Fine ppt. lost in filtrate
HCl	72	0.60	48.0	(„ „)
CO_2	22	7.37	—	Very slow filtration
CO_2	85	9.05	12.4	Carbonation stopped when H_2S displacement started; ppt. in lumps
CO_2	82	9.10	12.7	(„ „)
CO_2	70	7.82	25.4	Lignin slurry, settles on standing, easy filtration
CO_2	73	7.88	26.8	(„ „)

Black liquor type — unoxidised industrial (Douglas fir) softwood black liquor. Initial pH = 13.0; Total solids conc. % = 15.3.

* All solutions stirred during carbonation.

TABLE 4
EMISSIONS OF SULFUR COMPOUNDS FROM A KRAFT PULP MILL* (1)

Source	A	B	C
Digester relief	1.0	0.2-0.5	0.2-0.5
Blow gas	1.0	0.2	0.2
Washer vent	0.25	0.0-0.1	0.0.1
Oxidation tower	—	0.1	—
Precarbonator	—	—	0.1
Evaporator	4-14	0.2-5	0.1
Contact evaporator and recovery furnace	5-12	4-7	0.1
Dissolver	0.1-0.2	0.05-0.1	0.01
Lime kiln	0.2-0.5	0.2-0.5	0.2-0.5

* Expressed as kg. of sulfur per ton of air dry pulp.

A — Pulp mill with no controls.

B — Pulp mill with odour control equipment.

C — Estimates for a pulp mill with the proposed volatile sulfur recovery process.

REFERENCES CITED

1. Veeramani, H., "Sources of odour and control in a kraft pulp mill" — Paper to be presented at IPPTA, 1971 conference.
2. Sarkanen, K. V., 'Effect of New Process Technology on Air Pollution Potential', Paper presented at the International Conference on atmospheric emissions from sulfate pulping, Sanibel Island, Florida, April 1966.
3. Shtreis, G. B. and V. M. Nikitin. Zh. Prikl. Khim. **40** (8) : 1814 (1967).
4. Enkvist, T., Paperi ja Puu **45** (11) : 649 (1963).
5. Ekman, K. H., Paperi ja Puu **48** (9) : 575 (1966).
6. Zhigalvo, Yu. V., and D. V. Tischenki, J. Appl. Chem. (USSR) **35** (1) : 130 (1962).
7. McKean, W. T., Jr. B. F. Hrutfiord and K. V. Sarkanen, Tappi, **51** (12) : 564 (1968).
8. Analysis of soda and sulfate black liquor, Tappi standards T-625 ts-64.
9. Mannbro, N. V., U.S. Patent 2,611,682 (Sept. 23, 1952).
10. Mai, K. L., Equilibrium studies of the system Na_2O-CO_2-H_2S-H_2O. Doctoral Dissertation, University of Washington, Seattle, Washington (1954).
11. Han, S. T., and R. B. Kesler, Tappi **46** (5) : 308 (1963).
12. Han, S. T., and L. J. Bernardin. Tappi **41** (9) : 540 (1958).
13. Analysis of soda and sulfate white and green liquors. Tappi Standards T 624 ts-64.
14. Rydholm, S. A., 'Pulping Processes', Interscience (1965).
15. Marton, J. and T. Marton, Tappi **47** (9) : 540 (1964).
16. Merewether, J. W. T., Holzforschung **15** (6) : 168 (1961).
17. Ibid; Tappi **45** (2) : 159 (1962).
18. Tomlinson, G. H., and G. H. Tomlinson II, U.S. Patent 2,406,867 (Sept. 3, 1946).
19. Whitney, R. P., Editor, 'Chemical Recovery in Alkaline Pulping Processes', Tappi Monograph Series No. 32 (1968).
20. Proceedings of the Symposium on Recovery of Pulping Chemicals, Helsinki, Finland, May 13-17, 1968, sponsored by IUPAC and EUCEPA, Kauppakirjapaino OY, Helsinki, Finland (1969).
21. Luthgens, M. W., Tappi **45** (11) : 837 (1962).
22. Markant, H. P., Tappi **43** (8) : 699 (1960).
23. Campbell, J., and P. E. Shick. Tappi **40** (9) : 202A (1957).
24. Petersen, R. E., and J. A. Krauth, Pulp and Paper **43** (10) : 133 (1969).
25. Pascoe, T. A., J. S. Buchanan, E. H. Kennedy, and G. Sivola, Tappi. **42** (4) 265 (1959).
26. Buchanan, J. S., and E. H. Kennedy, Tappi **42** (2) : 153A (1959).
27. Kennedy, E. H., Tappi **43** (8) : 683 (1960).
28. Cederquist, K. N. N. K. G. Ahlborg, B. Lunden and T. O. Wentworth, Tappi 43 (8) : 702 (1960).
29. Gullichsen, J., E. Saiha, E. N. Westerberg, Tappi, **51** (9) : 395 (1968).
30. Karhola, A. K., K. R. Kiminki, H. A. Klemetti, and E. V. Saiha, Paper Trade J., **151** (38) : 65 (1967).
31. Gray, H. R., H. L. Crosby, and J. C. Steinberg, U.S. Patent 2,772,965 (Dec. 4, 1956).
32. DeHaas, G. G., and L. C. Amos, Tappi **50** (3) : 75A (1967).
33. Williamson, D. F., G. W. Hough. and F. I. Mason, Tappi, **52** (11) : 2105 (1969).
34. Veeramani, H. Doctoral Dissertation, University of Washington, Seatle, Washington (1970).

Presented by Mr. H. Veeramani at the IPPTA Annual Meeting held at New Delhi on Nov. 8 & 9, 1971.