

Problems of Sulphate Black Liquor Evaporation

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Multiple effect evaporation plants are generally stated to be the backbone of modern soda recovery system. They are in general five to six stage vacuum evaporating units. The stage sequence in most of the mills is kept 3, 4, 5, 2, 1 or 4, 5, 6, 3, 2, 1. However, in many cases the sequence 3, 4, 5, 1, 2 have been found to be much more beneficial. Evaporation is one of the most important and the only method for concentrating the solutions. This process, as is clear from the facts and practice, starts with hot solution entry and its subsequent boiling by steam heating. The steam generated is consequently used, amount of solvent goes on reducing and the likewise concentration increases, process being continued till the required concentration is reached. But for efficient and smooth running, certain factors which affect the evaporator performance such as black liquor characteristics, (physical-chemical) rate of heat transfer and scale formation, temperature depression etc. are to be mastered.

Black Liquor Characteristics :- Black Liquor as such, is a complex material depending upon its constituents and characteristics of organic as well as inorganic types. The physical properties of Black Liquor

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Sulphate black liquor evaporation poses serious problems before the industry. Various factors affecting the evaporator efficiency and performance have been discussed. More emphasis has been laid on physico and physico-chemical properties of Black Liquor, heat transfer coefficients, scale formation and probable causes for the same have been discussed in detail.

Factors which affect the evaporator performance are density, viscosity, surface tension and boiling point rise. It has been found that the density of black liquors has direct relations with the dry solids it contains. As has been mentioned¹ the deviation is only $\pm 3\%$ i. e. negligible for all practical purposes. Viscosity shows more or less no change upto 30% d. s. for different Black liquors i. e. $\pm 5\%$. But at high d. s. of 55-60% the deviation rises to $\pm 25\%$. That clearly indicates the behaviour of a particular Black Liquor at high d. s. content. Such data are presented in Figure 1.

Heat transfer by vaporization without mechanical agitation is obviously a combination of ordinary liquid free convection and the additional convection produced by the rising stream of bubbles. The following factors are found to affect the rate of heat transfer by vaporization to a great extent and the possibility of obtaining one or two simple correlations applicable to majority of liquids² :

- 1) Nature of the surface and distribution of bubbles,
- 2) Properties of fluid such as

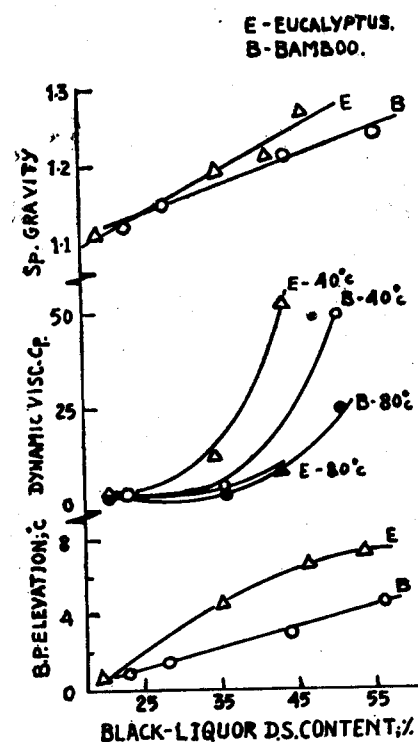


Fig. 1-Variation of Specific Gravity, Dynamic Viscosity & B. P. Elevation With D.S. Solid Content of Bamboo & Eucalyptus Black Liquors.

Surface tension, Coefficient of expansion and viscosity.

- 3) Influence of temperature difference on the evolution and vigour of bubbles.

It has been observed that surface tension of a solution at room temperature and at its boiling point are more or less the same. The mathematical relationship between surface tension and the density can be expressed as follows:³

$$\sigma = c \cdot d^4$$

where σ —surface tension,
dyne/cm.

d —density, g/cm³

c —coeff. of proportionality, depending only on composition of the liquor and not depending on temperature.

The values of surface tension for bamboo, eucalyptus and other local hardwood black liquors lie between 40–50 dyne/cm. while value for water being 75 dyne/cm.

As Black Liquor is a water solution of different organic and inorganic components, it causes temperature drop during evaporation, which in turn affects the flow pattern of the process. This calls for a knowledge of boiling point rise with concentration of B.L. At one and the same pressure, solutions boil at higher temperature than solvent. Higher the concentration of B. L. higher the difference in boiling point, which in turn is known as temperature depression. The values for a typical B. L. are shown in Fig. 1. A knowledge of foaming tendency of Black Liquors solves the problem of evaporation at the first stages. As is well known sulphate Black Liquors are prone to cause foams under certain compositions of Black Liquors depending on raw material used and the conditions

employed for pulping. It may even rise higher than the normal level during first stages of evaporation and come out with steam. At this stage loss of liquor and sodium may be noteworthy. This requires such technological improvements as good washing efficiency in pulp mill so that we may have a liquor of higher density as far as possible. The values of foam coefficients and foam indices for certain Black Liquors are as under :

Foam Characteristics of Black Liquors

	Bamboo	Pine
Foam No. %	5	9
Foam coeff.	15.5	18

These figures clearly indicate that the given pine liquor is more prone to foaming than bamboo black liquor.

Heat Transfer Coefficient :—Evaporator performances have indicated that the heat transfer coefficient decreases as dry content of the black mass increases; consequently the demand for boil out increases due to increased tendency for scaling. Heat transfer coefficient for evaporators is given by the general formula :

$$\frac{1}{U} = R_c + R_w + R_1 + R_s$$

where U = overall heat transfer coefficient, Btu/(ft²) (°F) (hr)

R_c = steam condensate film resistance

R_w = tube wall resistance

R_1 = stagnant liquor film resistance

and R_s = scale resistance.

Changes in temperature of steam condensate film have relatively little effect on the overall coefficient. The steam condensate film resistance, R_c , decreases only 20% if the temperature of the film increases from 200–300°F. Moreover this resistance is quite small when compared to the other resistances.

Because a B. L. evaporator is operated at a constant evaporation rate, the heat flux and the liquor composition remain essentially constant. Under these conditions the stagnant liquor film resistance, R_1 will remain constant. Hence, it is the resistance R_s due to scaling which is most important. Resistance due to scaling is given by the formula :

$$R_s = \frac{\delta s}{\lambda s}$$

where δs and λs are scale thickness and its heat conductivity respectively.

Total volume of scale formed on the tube surfaces depends on the utilization of the apparatus in terms of amount of water evaporated and can be given as under :

$$V_s = aW$$

where a —coefficient of proportionality

W —amount of water evaporated

$$\text{then } \delta s = \frac{V_s}{F}$$

where F —tube surface.

The general equation given by Kichigin and Kostenco⁴ is as follows:

$$R_s = \frac{\delta s}{\lambda s} = \frac{aW}{F\lambda s} = eS_T$$

where T —Time difference between two cleanings, hr

- S—Av. amount of water evaporated in Kg/M². hr during this period. whole process there on depends on characteristics and composition of processed black liquor.
- e—Coefficient of scale formation, depending on solution concentration. All the omissions and submissions in the pulp mill operations, directly

Rate of scale formation at various concentrations
is as shown under

Av. conc. %	15	20	25	30	35	40	45	50
e. 10 ⁶	0	0.1	0.2	0.35	0.55	0.85	1.125	2.0

This indicates clearly high rate of scale formation after 45% dry solids. For concentrations above 45% dry solids, we may have general formula as under :

$$e. 10^6 = 0.15 b - 5.5$$

where b — dry solid content of b. liquor.

Similarly scale thickness in turn depends on concentration of Black Lipuor and rate of evaporation. If in first effect scale thickness at any time is δ , and concentration and water evaporation x and W respectively, then scale thickness δ_1 in any other effect is given by

$$\delta_1 = \delta \left(\frac{x_i}{x} \right)^{3.4} \frac{W_i}{W}$$

where x_i and W_i are conc. and rate of evaporation in given effect. At constant value of scale-conductivity, similarly the scale resistance is proportional to scale thickness.

$$R_{s1} = R_s \left(\frac{x_i}{x} \right)^{3.4} \frac{W_i}{W}$$

Causes of Scale Formation— Thus

or indirectly affect the Black Liquor quality—and as a result the process of evaporation. This or that change from the normal working of the pulp mill may lead to operation troubles and sometimes we have to pay heavy dividends for the same. To mention a few of these troubles, which hinder evaporator performance, we may come across—(a) Intensive foaming, (b) Scale formation on evaporator tubes and frequent need for boil out, (c) Formation of lignin-origin precipitates and (d) Equipment corrosion (5).

As not much literature is available on this topic, but whatever is available clearly indicates that evaporator scales constitute of both inorganic as well as organic compounds.

The inorganics most commonly encountered in evaporator scales may be grouped in order as follows :

Sodium sulphate, Aluminium sili-

cate, Calcium and Sodium carbonate, Chromium oxide, Alumina, Sulphate-soaps and fibres³.

First three compounds start forming scales because their solubility falls with rising temperature and concentration. Sodium sulphate may give more trouble because of its varying amounts due to uneven working of the furnace and consequently due to formation of $2Na_2SO_4 \cdot Na_2CO_3$ complex¹. However the mention has been made that the amount of sodium sulphate in Black Liquor, in no case should go beyond 6% on dry solids^{6,7}. Of the organic compounds—it is the lignin precipitation due to shortage of Active Alkali in the Black Liquor, which when aggravated may lead to jamming of high dry solid evaporator tubes^{1,3}. A typical analysis of scale, the liquor forming that scale, and the liquor not forming the scale have been presented in Table 1. However it has been mentioned beyond doubts that a certain *minimum Active Alkali in the Black Liquor has to be maintained*; however this may vary from mill to mill and normally 7–8 gpl is maintained. Orr⁸ mentions that the activity of the black liquor in the range 20% of dry solids may keep the evaporators clean for longer times, thus resulting into economy and better performance. Mentions have also been made about sulphur dosing in digesters, high salt content, bad performance of causticizers and amount of lime make up in soda recovery as the causes for scale formation in the evaporator tubes⁶.

Table 1 : Analysis of Scale and Black Liquors

Compounds Analyzed	Compounds, Scale	% in the B. L. (A. D.)	
		Liquor giving Scale & ppt. (Sp. gr. 1.07)	Liquor not giving scale & ppt. (Sp. gr. 1.10)
Sodium sulphate	8.18	3.82	3.66
Sodium carbonate	16.01	5.53	7.00
Free caustic	0.56	0.27	0.85
Sodium sulphide	0.55	0.67	0.72
Org. bound sodium	8.64	10.84	9.82
Lignin	24.24	32.87	27.77
Soluble in Methanol	14.22	14.03	16.10
Insoluble in Methanol	10.02	18.84	11.67
Cellulose, fibres	0.92	0.59	1.65
Hemicellulose	1.32	1.04	1.13
Sugars	0.41	0.00	0.76
Ether extract	0.91	0.49	0.40
Acids	13.95	14.92	14.29
Other products of wood destruction	16.21	21.81	24.99
Unanalyzed materials	8.10	7.15	6.96

Silica, (HCl insolubles). . 45.66
% on O. D.

Mixed Oxides, % (on O.D.) 6.95

Calcium as CaCO_3 %
(on O.D.) 19.8

Total sodium as
 Na_2O , % on O D. . . 2.9

The above analysis clearly indicates that scales are chiefly of lignin-silica origin. Tests carried out in laboratory have demonstrated that formation of scales of lignin-silica origin is facilitated in high D. S. effect, if the residual active alkali in the black liquor is kept low.

A typical Black Liquor was obtained which was analyzed along with scale formed, for different constituents. The data are presented in Table 2.

At a first glance we can visualize the fact that the Active Alkali in scale forming Black Liquor was on the lower side (3.57 gpl). This black liquor on evaporation in Rotary Vac. Flash Evaporator to 50% dry solids, started precipita-

In above table two factors attract our attention.

1. Low content of free caustic.
2. High content of lignin for a liquor giving precipitate when the free caustic level was increased and the lignin content was reduced, a liquor giving no scale and precipitate was obtained.

Analysis of a regular bamboo sulphate liquor scale at WCP Mills Ltd. is as follows :

Moisture, % . . 65.9
Loss on ignition, % O.D. . 32.0

Table 2 : Analysis of the Scale Forming Weak Black Liquor & the Scale

	Weak Black Liquor	Scale
Total solids % w/w	19.7	72.0
Inorganics as NaOH %	31.4	54.5
Organics, %	68.6	45.5
HCl insolubles % on T. S.	5.0	44.8
*Silica as SiO_2 % " "	3.4	42.4
NaOH as Na_2O % " "	1.4	2.0
Na_2S " " " " "	0.23	0.15
Na_2CO_3 " " " " "	13.5	11.3
NaOH organically bound " "	4.5	8.1

Results of chemical analysis at the same dissolved solid content :

Total solids % w/w	19.7	19.7
Total alkali as Na ₂ O gpl.	43.0	47.2
Tappi Active Alkali,, "	3.57	4.70
Effective Alkali " "	2.00	3.95
Sulphur alkali " "	0.50	0.33
Phenolphthalein " "	14.8	16.4
NaOH as Na ₂ O, gpl.	3.10	4.37
Na ₂ S " " "	0.50	0.33
Na CO ₃ , " " "	29.6	24.8
+NaOH (organically bound) as Na ₂ O, gpl.	9.8	17.7

*Indicates separation of silica

+Indicates separation of lignin

ting out at even 32.5% d. s. and resulted in a very clumsy mass finally. Fresh caustic was added in different amounts to vary the alkalinity in steps to 7 gpl. The liquors were evaporated in RVF Evaporator, the findings are given in table 3.

tates out along with lignin even at a pH of 9.8 when plant bamboo black liquor was treated with acid. Furthermore pH of black liquor seems to be unreliable, when we are to control the B. L. originating from different raw materials and

Table 3. Evaporation of B. L. in Rotary Vac. Flash Evaporators

A. A. as Na ₂ O gpl	pH	Observations
3.56	10.4	Granulation started at 32.5% d. s. Very clumsy mass at 50% d. s.
4.20	10.5	Granulation started at 46.0% d. s. Mass a bit better than previous at 50%.
5.60	—	Granulation started at 49% d. s. Mass still better at 50% d. s.
6.80	10.75	No granulation upto 50% d. s. Mass fluidy and best.

This clearly indicates the importance of certain minimum active alkali in the Black Liquor for better and cleaner evaporator performance. Lesser A. A. in black liquor initiates the precipitation of lignin. Furthermore, it has been observed that lot of silica precipi-

varied pulping condition. Hence Black Liquor for evaporation must be controlled by A. A. in it rather than by pH value.

Thus any discussion of operating experience of Black Liquor evaporation to high dry solids must be based on a thorough and upto date

knowledge of the origin, back history and physico and physico-chemical characteristics of Black Liquor. Our present methods to characterize a black liquor can be improved upon, and such improvements seem to be must, if we ever want to master over an important process like evaporation.

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