Design data and correlations of waste liquor/black liquor from pulp mills

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ABSTRACT

An attempt has been made in this paper to review and to compile the information regarding the various physico thermal/chemical properties of black liquor/waste liquor required for engineering design of the equipments. Enormous volume of data are reported in literature for both woods and non-woods based liquors compared to little knowledge of mathematical models. On inspection it is found that data are scattered and proprietory in nature and strongly influenced by the type of raw materials, species, pulping process and parameters chosen, temperature, pressure, degree of concentration, nature of organic and inorganic constituents and sometimes the velocity gradients, shear stress, and duration of shear. Hence no two liquors are found to be identical with all those constraints The equations used for design should be carefully checked.

1.0 Introduction :

The chemical pulping of fibrous raw materials results in formation of pulp and paper and generation of liquors containing complex dissolved organic and inorganic compounds. Such liquors are termed as black liquor when the process used is soda/kraft or prehydrolysis kraft. On the other hand liquors obtained from sulphite or modified sulphite process are called waste liquor.

The economy of processing these liquors for recovery of chemicals and energy is strongly influenced by the nature of the liquors handled. The single most effective environmental management step for paper industry is the fullest recovery of organic and inorganic values of these liquors and not discharging them to receiving them to receiving water media as effluent waters, a practice followed by almost all the small mills in India. Thus it is important to evaluate the characteristics of black liquors and waste liquors for their efficient utilization.

In brief the entire process engineering calculations including the design of equipments are possible if the liquor properties are precisely predicted.

The above important design properties include liquor composition, total dissolved solids, ultimate chemical composition, specific gravity and density, viscosity and rheology, specific heat, thermal conductivity, boiling point elevation, surface tension, calorific value, latent heat of vapourization and solubility characteristics. Other properties mostly are qualitative in nature and not general and verv often used for comparison purposes are : precipitation point, swelling volume ratio, foam index, etc. As these characteristics are not universal, these will be discussed for a particular type of black liquor. The following paragraphs detail the quantitative information available on the aforesaid properties. However, all the physico-chemical

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properties are dependent on liquor temperature, concentration and the relative properties of the various dissolved organic compounds derived from wood during pulping and the residual inorganic chemicals of feed liquor to the digester. Black liquor may also contain some fiber fines and suspended matter escaping through digester house screening operations. Commercial black liquors can be expected to show a wide range of values of the above properties due to diversity of lignocellulosic materials and pulping conditions.

2 A. Some Salient Characteristics of Black Liquor :

2.1 Black liquor is distinctly alkaline (pH varies from 10 5 to 13.5) but not caustic owing to the fact that a large part of alkali is present in form of neutral compounds.

2.2 The lignin has an intense black colour, shading to reddish brown on dilution and retains a dark straw to yellow color even when diluted to 0.04% with water.

2.3 It is foamy at low concentrations. B/L from sulfate process is generally more foamy than that from soda process.

2.4 The foaming increases with an increase in resin content of wood used for pulping.

2.5 The amount of total solids in B/L depends on the quantity of alkali charged to the digester and the yield of pulp. Under average conditions B/L going to evaporators will contain 14–18% solids for wood and bamboo,

2.6 In general, the inorganic compounds in black liquor would tend to decrease specific heat and thermal conductivity, increase in density, specific gravity, viscosity, boiling point elevation and have practically no effect on surface tension.

2.7 The organic constituents of black liquor would tend to decrease specific heat, thermal conductivity and surface tension and increase density and viscosity values.

2.8 The complexity of the black liquor system precludes procedures adopted for the estimation of physical properties of simple aqueous solutions.

2.9 The data also shows that there are considerable differences amongst values for the different liquors attributed to the diversity of organic constituents in black liquors caused by the variation in pulping species, pulping conditions and pulp yields.

2 10 The black liquor obtained from agricultural residues. wheat straw, rice straw & bagasse, etc. are characteristically different.

2.B. Composition of Black Liquor

Black liquor is an exceedingly complex solution containing polydisperse lignins, a host of compounds from degradation reactions of lignins, polysaccharides and extractives and several inorganic compounds. The quantity of total dissolved solids in weak black liquor from digester operation is 1.3 to 1.6 tonne per tonne of pulp or approximately 15 m^3 per tonne of pulp. Various values of black liquor composition and its properties are evaluated by many investigators (1-17). The elemental composition of wood based black liquor is shown in Table-1.

Black liquor generally contains 50-70% organics and 30-50% inorganics. Table-2 shows the weak black liquor constituents for a typical wood based kraft mill. It also contains minor amount of impurities such as lime, iron-oxide, sodium chloride and alumina. The same from hardwood, bamboo, mixture of hardwood and bamboo, and that of bagasse are shown in Table-3. The composition of the non-wood b/l depends also on the pulping process followed and also on the type of nonwoods. A typical process conditions of straw pulping is listed in Table-4 and the corresponding black liquor characteristics is indicated in Table 5. Tables 6,7 compare the composition of bamboo black liquors and same from bagasse and straw respectively. The effect of anthraquinone in soda process on black liquor composition has been shown in Table-8. Table 9 shows the effect of storage time on pH of black liquor as a function of soda as Na_2O. The average values for non-wood black liquors are reflected in Table-10. Table-11 represents the composition between soda and alkaline sulphite rice and wheat straw black liquors. These values are exclusively typical and specified within a broad range.

Table—1 Elemental Composition Of Wood Based Black Liquors : (1,2)

In dry solids	Value	Max. value	Mean value	Standard deviation
Total C	35.4	41.2	38.3	1.15
Total H	3.43	4.40	3.87	0.23
Total S	3 19	5.97	4.58	0.71
Total Na	15.20	21.10	18.70	1.05

Table —2 : Weak Kraft Black Liquor Constituents (4)

A. Organic compounds

Alkali lignin and thio lignin
Isosaccharic acid
Low molecular weight polysaccharides
Resin and fatty acic soaps
Sugars

Constituents	Concentration g/l
Lignins	30—40
Carbohydrate degradation Products	45—65
Soaps	Small
Mercaptans	Small

B. Inorganic Compounds

Components	gpl	weak black liquor
NaOH	4—8	Constituent
NaHS/Na_2S	6—12	%dissolved solids=12-20
Na_2Co_3	6—15	pH of weak black liquor =10-5—13.2
$Na_2S_2O_3$	1—2	Temperature =50—90°C
NaSy	Small	
Na_2SO_4	0.5—1	
Elemental	Small	
Na_2So_3	Small	
SiO_2	Varying	

Table-3 Analysis of India Black Liquors (15)

Sl. No.	Particulars	Hard wood	Bamboo	40% hard wood+60% Bamboo	Bagasse
1.	Silica as SiO_2 gpl	0.97	1.25	1.07	0 95
2.	Na_2SO_4	4.7	4.4	1.8	0.85
3.	NaOH	3.9	4.3	6.6	5.90
4.	Na_2Co_3	16.5	21 0	8.7	35 5
5.	Na_5S	0.4	2.8	1 05	3.10
6.	pH	10.5	11.0	11.5	11.0
7.	Organic Inorganic ratio	55:45	46:54	55:45	44:56

Table - 4 Pulping Conditions of Rice and Wheat

Straw (7-10) Conditions	Rice Straw	Wheat straw
1. Cooking chemicals % as NaOH	8.0	12.0
2. Bath Ratio	1.4	1.4
3. Time to temprature hrs. 50 - 150°C	2.0	2.0
4. Time at temprature 150°C hrs.	2.0	2.0
5. Total pulp yield (unbleached)	58.0	53. 5
6. Kappa No.	15.0	20.0
7. Silica in Pulp	15.77	12.29

Table - 5 Black Liquor Characteristics

Particulars	Rice Straw	Wheat Straw
1. B/L pH	9.8	10.8
2. Total solids %	12.4	14.3
3. Free Residual Alkali gpl	0.8	3.2
4. Density at 80°C and 35% T.S. °TW	31	29

Table—6. Typical Composition of Non-Wood Black Liquors From Kraft Pulping of Bamboo (8,9)

Component	g/l	Component	g/l
Organics : Lignins	30—40	NaOH	4—8
Degraded	45—65	NaHS	6—10
Carbohydrates		Na_2CO_3	10—15
Soaps & Mercaptans	Small	Na_2SO_4	2—4
		SiO_2	4—8
		Na_2S, Na_2SO_3	Small

Table.—7. Composition of Soda B.L. From Straw and Bagasse (10)

Detail	Bagasse	Rice Straw
Alkali charge NaOH%	12	10
B L. generated m^3/t pulp	10.0	12
Inorganics%	29.9	22.8
Organics%	70.1	77.2
Lignin%	45.3	33.4

Table—8. Analysis Of Soda and AQ Rice Straw Spent Liquor

S. No.	Particulars	Soda as Na_2O			Soda-AQ as Na_2O		
		8%	10%	12%	8%	10%	12%
1.	pH	9.32	9.30	10.34	9.20	9.25	9.30
2.	RAA, mg/l	16	48	155	46.5	44.4	217
3.	ρ,g/cc	1.021	1.021	1.047	1.025	1.04	1.043
4.	TDS, g/l	85.98	86.70	130.18	79.40	109	114.65
5.	TDS,w/w	8.42	8.49	12.43	7.75	10.48	10.99
6.	Burnt Residues (based on % TDS)	18.28	20.6	28.30	18.41	20.81	29.68

Table—9. Effect Of Storage On Rice Straw Liquor

S. No.		Soda as Na_2O 8%	9%	10%	12%
1.	Initial, 0 day	9.32	10.4	9.45	10.5
2.	After 5 days	7.0	8.1	7.75	8.6
3.	After 10 days	6.6	7.75	7.35	8.25

Table—10. Characteristics Of Black Liquor From Small Non-Wood Fiber Pulp Mills in India. (5)

Parameter	Range (Average)	Remarks
pH	7—11(~9.0)	Based on 14 mills of capacity varying from 8 TPD to 30 TPD using rice straw, wheat straw bagasse, Sarkanda grass and other agriresidues.
Sp gr. at 20°C	1.01—1.05 (~1 02)	
Total solids, % (w/w)	4—10(~5)	
Residual alkali, g/l	0—7.32(~3)	Process : Soda pulping
Total alkali as Na_2O, g/l	7.5—18.5 (~11)	Bath ratio : 1:3 to 1;6 Alkali charge : 8 to 14% NaOH Cooking temperature : 150—170°C
Silica as SiO_2, %dry solids	0.73—12.85	
Inorganic/organic (IOM/OM)	1:2.1—1:3.5	
Calorific value, kcal/kg.	2900—3800	
Swelling volume Index, SVI, ml/g	3.0—16.0	

2B. 1 Silica in Black Liquor :

High silica content are major obstacles in any recovery process. The concentration of silica is particularly high in rice and wheat straw black liquors Presence of silica leads to problems related to scaling, clarification, and precipitation.

The non-wood fiber black liquors have a high percentage of silica, 4–6% (even more) in case of straw and 1-2% in case of bagasse. Silica enters both as intrinsic and external silica with raw material and cooking liquors. The magnitude of silica for different liquors are indicated in Tables-10-12. In black liquor it is present essentially as Na_2SiO_3 which undergoes hydrolysis to silicic acid as pH is decreased. This happens with dilution by wash water leading to silicic acid scale deposition on filters, wires screens and plates.

Black liquor becomes unstable and precipitates on standing This is prominent with pH falling to 10-10.6 In fact in 48 hours, with precipitation, pH goes down from 10 to 8. Silica contained in precipitated sediments settles down in the bottom of the black liquor tanks and become a very hard scale. Volume of such sludge is 10-30% of black liquor volume and most silica can be transferred to sludge from black liquor. The important parameters, thus influencing this, are pH and time of storage.

Semichemical pulps and high yield pulps have more silica in pulp and less silica in black liquor due to milder cooking. Higher alkali or pH in black liquor leads to greater dissolution of silica. The solubility of SiO_2 in rice and wheat straw black liquors with pH is given in Table-13.

Table—11. Composition Of Soda And Alkaline Sulphite Rice And Wheat Straw Black Liquors (12)

Details	Wheat Straw		Rice Straw	
	Soda	ASP	Soda	ASP
Chemical charge to digester				
(on O.D. raw materials)				
NaOH%	17	13	11	7
Na_2SO_3 %	—	3	—	3
Black Liquor Pentosans%	10.5	7.44	10.55	8.55
AA on total solids %	11.2	9.23	8.71	1.24
SiO_2 %	1.86	1.19	3.57	1.83

Table— 12 : Concentration Of Silica In Black Liquor Solids (4) :

Raw Material	Silica % (Range)
Rice Straw	3—16
wheat Straw	3—6
Bamboo	2—5
Bagasse	1—3
Eucalyptus	0.1—0.8

Table—13. Solubility Of SiO_2 in Straw Black Liquors (4,11)

pH of B L.	9	10	10.4	11	11.5	12
SiO_2 in B.L.	0.2	0 5	1	2.5	3-5	7

Swelling volume index (SVI), ml/g of dry BL solid roasted at 300°C, for I hour. High SVI value indicate a porous ignited bad with free air passage and complete incineration.

This clearly indicates that silica precipitation can be effected by lower pH while scale can be avoided by increasing pH with alkali addition. At higher availability of alkali (more than 5%), no hydrolysis of Na_2SiO_3 occurs. Result is reduced viscosity and avoidance of scaling. If pH is reduced to 10.3 or below, the silica content in B L. is less than 1%. This can be achieved by pulping process midification or by desilication. Thereafter elevating pH will ensure no precipitation of silica. For best precipitation of silica from black liquor the conditions are pH below 10.30. temperature around 80°C and time of storage around 8 hours.

The soluble silica in black liquor as weight % of black liquor solids (y) is related to active alkali in black liquor in g/l as NaOH (x) by the following relation for 6-10° Be B.L. at 20°C (11).

$$Y = 0.65 + 1.21 X \qquad ......(1.1)$$

The precipitated silica sludge from straw B L. in setting tanks can be separated. The volume of such sludge can be reduced from 30% of black liquor volume to 6-8% in 2 hours at 80°C. The sludge, dark yellow in colour, has more than 10 times SiO_2 than in clear black liquor. The black liquor with only 0.6% SiO_2 can be easily processed for recovery with proper alkali addition to ensure no precipitation in evaporators. The sludge on the other hand has almost 15% SiO_2.

In another study (11) it has been shown that silica in the rice straw soda black liquor reduced from initial value of about 9.3% to 7% in 5 days and 6.6% in 10 days due to setting of precipitates when the cooking liquor has 8% alkali. Soda black liquors will have more silica at high amount of alkali in cooking liquor. Under similar cooking condition soda AQ black liquor has less silica than soda black liquor for rice straw.

Straw black liquors have NPK. At lower pH and lower temperature they help in propagation of bacteria which drops pH further leading to lignin precipitation below pH of 8. This is one of the main causes of decay of straw black liquors.

3. Physico—Chemical/Thermal Properties Of Black Liquor :

3. 1 Specific Gravity or density of black liquor :

Density varies from species to species for both wood and non-wood materials.

The specific gravity of black liquor at any particular concentration and temperature depends upon the ratio of organic to inorganic matter and increases with an increase in inorganic matter and decreases with increase in temperature.

The density of black liquor can be found out by available graphs between concentration (of solid) and specific gravity. The higher the inorganic content, the steeper is the interacting slope of these isotherms. The dependence of density on temperature may be taken to be linear in the range from 60°F to the boiling point. The temperature effect increases the value slightly as concentration increases. Table—A shows expression relating to °Be, °Tw, G, and ϱ.

In the mill operation, the specific gravity is measured with a hydrometer which is often calibrated in degree Baume or degrees Twaddell and % solids is given by 1.5 times the Baume reading at 60°F.

Table—A Expressions For °Be, °Tw, Specific Gravity And Density.

$°Be = 140/G - 130 \ (G<1.0)$	.. (2.1)
$°Be = 145 - 145/Sp.Gr.(60°F/60°F) \ (G<1.0)$	...(2.2)
$G = 1 + 1/(145/Be - 1)$	
$°TW = Sp. gravity (60_oF/60_oF)/0.005 - 1$	...(2.3)
$°TW = 200 \ (G - 1.0)$	...(2.4)

From the above it is evident that a liquor of 11°Be at 60°F would contain about 11×1.5 = 16.5 % total solids by weight.

$$G = 1.012 + 0.763\times - 4.7 \times 10^{-4}t - 4.86 \times 10^{-4}xt \qquad ......(2.5)$$

valid for 15—55% solids at 30—90°C.

Hultin (2) has drawn graphs between tons of dry solids per ton of liquor, D.S. and density at 90°C, ρ_H in t/m^3 and suggested the following equation

$$\rho_{H90} = \rho_H t + \triangle P \qquad ..... (2.6)$$

$$d\rho_H/dt = 0.00065 \ t/m^3 °C \qquad ....(2.7)$$

For Black liquor :

$D.S.=1.77(p_{90}°C-0.963)$; for $S=10-25\%$ ......(2.8)

$D.S.=1.46(p_{90}°C-0.920)$; for $S=50-65\%$ ......(2.9)

For Sulfite spent liquor :

$D.S.=2.03(p_{90}°C-0.963)$; for $S=10-25\%$ ......(2.10)

$D.S.=1.79(p_{90}°C-0.937)$; for $S=50-65\%$, ...(2.11)

Registad (8,9) has expressed the density in terms of temperature and total dissolved solids.

$Pm=1007-0.495t+6S.$ ......(2.12)

$Sp\ gravity=(1.96/t_F{}^{0\ 11})\exp(0.03558.S/t_F{}^{0\ 296})$ (2.13)

$Log\ Pm= -1.0585 + 4.8 \times -0.0255tx^2+1.35462\times 10^{-3}t$ ......(2.13)

x ranging between 0.1—0.50.

The eq. 2.5 predicts specific gravity 1.45—1.40 at 60% solids whereas G becomes 1.07—1.40 at 90°C for the concentration range of 15% total dissolved solids. This equation predicts very well for bamboo and bagasse liquor within ±1.5% and also applicable to woody plants. The influence of proportions of organic compounds appears to be very small. Influence for organic matter (51%—61%) has been found to be small The eq.2.12 is found to be suitable for wood black liquors.

Sp. gravity is higher for Eucalyptus than Bamboo and density of Bamboo is higher than bagasse. Density is also higher at lower temperature for same solid concentration than at higher temperature.

Specific heat

Specific heat of black liquor, Cp, decrease as the solid content increases and increase with increase of temperature. The various correlations of specific heat of wood and nonwood black liquor are shown in Table—B. The specific heats of bamboo, pine, bagasse and straw have been experimentally determined by Viramani (8,9) and correlations are found out. Typical values of black liquor estimated from the above equation 3.8 are 0.93 and 0.77 for concentrations of 16.0 and 50.0 percent respectively at 80°C. The effect of temperature is found to be small. Data for bagasse, bamboo and pine black liquor has been shown graphically (8,9).

Table—B Correlations of specific haets

Harvin and Brown (1,2) by graphical method for wood liquors.

$CpF=0.99+8.0\times 10^{-5}tF-(0.639-6.4\times 10^{-4}tF)\times$ ....(3.1)

valid for temperature range of 4.9—52.6% of solids.

$Cp=0.990+4.44\times 10^{-5}t-(3.67\times 10^{-4}t)\times$ ......(3.2)

Kobe, Sorenson and Basberg (1,2) predicted Egs. 3.3 and 3.4

$Cpm=0.98-0.52S$ (25°C to 93°C) ....(3.3)

The eq 3.3 is less precise and valid within the temperature of 77°F to 200°F and works well at the mean temperature (150°F

$Cpt=0.96-0.45\ DS$ ......(3.4)

Kobe and Mc—cleve (1,2 for sulfite liquor (at 90°C)

$Cpt=0.97-0.40\ DS$ ....(3.5)

Following expression has been recommended in Tappi monograph

$Cp=1.0\ (1-Cps)s$;(in the absence of actual data...(3.6)

The value of Cps is 0.5 at 200°F.

For Bamboo and pine B/L (8,9):

Valid for 15—50% dissolved solids with ± 2% deviation.

$Cpm=(1.8\times 10^{-3}t-0.54)\times+1.0$ ..... (3.7)

and for Bagasse & Straw B/L (8,9)

$Cpm=(1.04\times 10^{-3}t-1.26)\times+=1.0$ ..... (3.8)

$Cp=1/G$;used for Rough calculation ......(3.9)

$Cp=1.00-3.234\ S/t_F$; also in Tappi .. ...(3.10)

$Cp=1.0\times 10^3\exp[2.118511-17.047481\times+3.67t+3.333t\times]$ ......(3.11)

Egs. 3.1 and 3.2 are the best correlations for wood liquors while the Egs. 3.7 and 3.8 can be applicable for nonwood liquors.

Thermal Conductivity

Thermal conductivity B/L can also be expressed as a function of % solids and temperature. Thermal conductivity k decreases from 0.56 to 4 47 k Cal/hr mK from concentration increase of 20% to 50% at 80°C linearly. With the increase in temperature, thermal conductivity increase non-linearity is reflected for 50%

solids. Harvin (1,2) plotted the thermal conductivity k as a function of temperature and concentration of solids for sulphite liquor and blackliquor. The results however, show that in technical calculations one can use the same values for both type of liquors.

The slope of the k versus concentration curver varies linearly with temperature. k is high at high temperature, Harvin's linear isotherm terminate at the conductivity of water. All avilable correlations are shown in Table—C. k is highest for bagasse and lowest for pine at same solid content.

Table—C Correlations of thermal conductivity

$dk/dx = m = slope = 0\ 21 - 3.38 \times 10^{-4} t_F$	......(4.1)
$m = 0.1992 - 6.08 \times 10^{-4} t$	......(4 2)
$k_F = 10.1992 - 6.08 \times 10^{-4} t_F$	......(4.3)
$k = 0.504 - 0.282 \times + 1.35 \times 10 - ^{3} t$	......(4.4)

Valid for % solid range of 15-55% and temperature range of 45°C—90°C. The deviation in values is ±2% for wood and non-wood fibres.

$k' = 0\ 598348 - 0.362045 \times + 0.00106012\ t$ ......(4.5)
valid for wood liquors.

Eq. 4.4 for nonwoods and Eq. 4. 5 for both species can be used.

5. Boiling point elevation

One of the most important parameters for determining the temperature gradient in each stage of multiple effect evaporator is the boiling point rise of the black liquor- BPR is smaller for lower inorganic contents and also becomes higher as the solids content increases.

Various graphs are available for the calculation of BPR as a function of specific gravity and temperature and the solid concentration. Durhing's plot is also available which states that the boiling point of a given solution is a linear function of the boiling point of pure water at same temperature. Thus if the boiling point of solution is plotted against that of water at the same pressure a straight line results. The pressure also influences on the boiling point rise. Studies indicate that 1°C rise of saturation temperature means about 0 6% rise in boiling point rise.

Heikel and Moore determined the value of $\triangle T$ b50% in eq. 5.3 for sulphite liquor to be 1.9°C and 1.70°C respectively whereas Hultin, Kobe, Keeneth & Sorenson presented the BPR data for black liquor to lie within the range of 6.5°C—7.5°C. Han (34) reported the data for N.S.S.C. liquor is 7.2°C.

The expressions for BPR as a function of concentration and other variable are given in Table-D.

Table—D Expressions For Boiling Point Rise

$\triangle T_b = 84C^2 - 107.5\ C^3 - 3.55\ C$; C in % solids ...(5.1)

where **C** is the mass fraction of solids.

valid for bamboo and bagasse, and at 100°C saturation temperature.

$\triangle T_b = [-3.55 \times + \%4 \times ^2 - 107.5 \times ^3]\ f$; f = correction factor ...(5.2)

valid for wood liquors.

$\triangle T_b 50 = T_{50} \times DS/W$ ...(5 3)

Pressure effect :

$\triangle T_b\ (P) = \triangle T_{760} \times 0.00387 (Tp^2/\lambda p)$ .. (5.4)
Hultin (1,2)

$\triangle T_b = kB \times /(1-x)$; KB = BPR at 50% solids
Tappi ...(5.5)

$\triangle T_{bF} = 41\ 4.(S/100 + 0.1)^2$ ...(5.6)

Veeramani (8,9) claimed that the boiling point elevation bata estimated from ep. 5.1 is in good agreement with the general purpose correlation of whitney based on softwood black liquors.

Eqs. 5.1, 5 2 and 5.3 are found to be fitted within their range of applicability.

In absence of any experimental data for black liquor the general equation applicable for non-elcetrolytic solution can be employed for preliminary estimaion for design. The equation is described as under :

$\triangle T_b = (RT_b^2/L_v)\, wM/wm = k_b x (1000) xw/mw$ ...(5 7)

6. Surface Tension ;

Surface tension is important parameter during formation drops of bubbles in spent liquor burners or in boiling heat transfer calculations. It is a function of dry solids content, temperature and the age of surface. The experimental data of surface tension for acid sulphite liquors and black liquor within the range of 11.6 to 60% dissolved solids and at temperature 20°C-90°C are available. Data for bamboo and bagasse black liquors upto concentration of 30% and temperature range of 30°C— 95°C. The data show that the effect of temperature is similar to its influence on the surface tension of water. The organic constituents of black liquor are all surface active and contribute to the observed decrease in surface tension values, the effect of inorganic is comparatively small.

No appropriate equation is available to predict the surface tension in terms of other parameters. However, the Table-E. indicates some equations which may be applied as a rough estimation in absence of any data.

Table—E Equations for Surface Tension

Mcleod Expression :

$$\sigma = cd^4 \quad \ldots\ldots(6.1)$$

Eotvos expression :

$$\gamma\ (M_v)^{2/3} = a - Kt \quad \ldots\ldots(6.2)$$

Ramsay and Shield expression :

$$\gamma\ (M_v)^{2/3} = t_o - b - t \quad \ldots\ldots(6.3)$$

7. Calorific Value and Elemental Composition :

Black liquor analysis shows that elemental analysis (Table-1)and calorifi cvalue(Table-14)are intimately related. To obtain a comprehensive picture of the influence exerted by the elements C,H,S, and Na upon the calorimeteric heat value, data were computer processed for regression analysis. The following regression equation was derived on the basis of the softwood black liquor analysis.

$$BHV = 53.31 + 94.59 \times C \quad \ldots\ldots(7.1)$$

where BAV=Calorimetric (bomb) heat value in kCal/kg dry solids & C=% of carbon in the black liquor solids. Only 64.6% of the total variation is explicable by this equation. It is interesting to note that the Carbon content is the only parameter which appears in the equation. Some data are shown in Tables 14A, 14B and 15. No equation has been predicted for nonwood black liquors.

8. Prandtl Numbers :

On the basis of data of density, viscosity, thermal conductivity and specific heat the Prandtl No. for acid spruce sulphite liquor have been calculated. Plot of log of Pr. Vs 1/t,(°C)and a function of solids content shows that with the increase of temperature, Prandtl No. decreases and at the same temperature Prandtl. No. increases as the % solid content becomes higher. The calorific value of non wood black liquor is shown in Table-15.

9. Viscosity :

As already said, viscosity or Rheology of black liquor is one of the most important properties controlling pressure drops, heat and mass transfer rates, mixing rates etc. and plays a vital role in the design of estimation of piping systems, selection of pumps and its efficiency, estimation of power costs for pumping

Table— 14A. Calorific value Of wood Based Black Liquors, kCal/kg Solids (1—3)

value	max. value	mean	deviation
3402	4039	3677	136

Table—14B. Comparison Of Calorific Value Of Black Liquors

Species	% C	Calorific value
Pine	42.1	4100
Eucalyptus	36.1	3550
Hardwood	38.6	3820
Bamboo	34.2	3300

Table—15 : Calorific Value of Black Liquors (13).

Material	Calorific Value (Range), Kcal/kg. Solids
Rice Straw	2600—2700
Wheat Straw	2800—3000
Bagasse	3200—3400
Bamboo	3200—3340

black liquor, deposition of scales in the evaporator tubes, diminishing the evaporation rate etc. and ultimately the overall economy and capacity of a recovery system. As an example, the high viscosity of strong black liquor can adversely affect the heat transfer rates and limit the number of units in a multiple effect systems requiring either a forced circulation evaporator or a direct contact flue gas evaporator to raise the concentration of liquor to 62—64% solids suitable for firing in the recovery boiler. The viscosity of strong black liquor(62—64% solids) is usually reduced by preheating to a temperature of 110—120°C before spraying in the recovery boiler. The size distribution of the droplets in the black liquor spray to the recovery boiler would depend upon viscosity characteristics of liquor, At lower temperature, storage and handling of strong black liquor poses a problem.

It would be desirable to operate the above equipments at near optimum conditions considering the high pumping costs versus preheating costs and auxiliary equipment cost for handling high viscosity black liquor. It has been reported that black liquor at a concentration above 50% solids is reported to exhibit Non Newtonian characteristics and would lead to high pressure drops even at low flow rates and is a major factor in the evaporation or flow through pipes and piping design. The fundamental difference between Newtonian and Non—Newtonian liquor characteristics is given elsewhere 18 – 21).

Several investigators (1-18, 24-35) have reported data on viscosity of black liquor from pine, Western Hemlock, Eucalyptus. Bamboo, Bagasse and straw. Various viscometers have been used for the above investigations. Several investigations have been conducted with a view to use in designing of black liquor processing system. These are shown in Table-16 and 17.

The characteristics of the hardwood as well as softwood at a high concentration have also been reported The liquors obtained from blending of hardwood and softwood are shown to be characteristically different from those of the individual raw materials (3,6).

9 1 Viscosity of Non-wood Agriresidues :

The rheological properties and viscosity of non-wood liquors. are very much different from those of woody and bamboo black liquors. The constitutents responsible for the rheological behaviour of these raw materials are pentosans, and polymers mainiy though silica-affects the property to a slight extent. However, no uniformity of data of viscosity of agri-based residues are reported whlch can be used uniquely in design calculations.

The bagasse black liquor has the highest viscosity compared to the other liquor system. For example at 60°C bagasse kraft black liquor viscosities in mPas are 4 8 (20% BLS), 35.5 (40% BLS) and 8800 (60% BLS) and the corresponding values at 90°C bagasse.

Table—16 Studies of Viscosity of Black Liquor (3)

Author	Study
1. Kobe & Mc-Cormack (1949)	—Soda, Sulphite & Sulphate Waste Liquors-solids Content at 65%, pulping of Western Hemlock.
2. Hedlund (1951)	—Kraft black liquors of different organic contents.
3. Han (1957)	—Spent Sulphite liquors from Neutral sulphite pulping of hard woods
4. Harvin (1965)	—Pulping of pine; kraft mill liquor.
5. Lengyel (1968)	—Pulping of Straw.
6. Hultin : (1968)	—Sulphite and black liquor.
7. Oyer, Langfors, Phillips & Higgins (1977)	—Pulping of eucalyptus.
8. Ghalke & Veeramani (1977)	—Pulping of Eucalyptus, Bamboo, Bagasse.
9. Albert (1982)	—Southern soft wood kraft spent liquors.
10. Sandquist (1982)	—Varo Birch, Varo-softwood, Skoghall soft wood. black liquor (solids 56—75% at 110°C & I15°C)
11. Ray etal. (1982)	—Pine & eucalyptus liquor.
12. Kulkarani A.G. etal. (1981)	—Hardwood lignins.

Table—17 Investigations on the Nature of Black Liquor (3,32)

Authors	Nature of Black Liquor
Han	Pseudoplastic time dependnecy at higher solids content.
Good Eve	Time Dependency $\mu = \mu_0 + \theta/\delta$; Newtonian at higher rates of shear.
Albert	Newtonian at low rates of shear and Non-Newtonian at higher shear rates.
TAPPI MONOGRAPH	New-tonian upto 50% solid content; time dependent for very concentrated Black Liquor.
Sanquist	Time Dependency & Pseudoplastic. (Solid content=65—75%)
Veeramani	Bingham Plastic
Ray et al.	Pseudoplastic and antithixotropic.
Buckman Laboratories, USA	Black Liquor; pseudoplastic & time dependent

kraft black liquor has a viscosity of 2.0 (20% BLS), 14.6 (40%BLS) and 1800 (60% BLS) mPas compared to the corresponding values of 0.84, 3·6 and 36.0 mPas for bamboo black liquors.

The higher viscosity of bagasse black liquor may be attributed to the high concentration of carbohydrate degradation products (mainly pentosans) and also the degree of pith removal in preparing the bagasse for pulping, since residual piths will be dissolved by the alkali and increase the organic consituents of black liquor.

Bamboo and bagasse black liquor are Newtonian upto a concentration of about 45-50% BLS and they exhibit Non-Newtonian behaviour (Bingham Plastic) above 45-50% BLS. The yield stress values for the Bingham plastic model increase with black liquor concentration and decrease with increase in temperature. During normal operation of chemical recovery units 45-65% BLS liquor is handled at 70-110° C. It is necessary to reduce or eliminate the yield stress values of strong black liquors by maintaining liquor temperatures about 90°C which will ensure Newtonian or a close approach to Newtonian conditions to avoid pressure drops and power consumption.

The viscosities of wheat and rice straw, bagasse, eucalyptus & pine are shown in Tables-18-24.

Table—18 : Viscosity of Straw Liquor

Particulars	Rice Straw		Wheat Straw	
Total solids	Temperature, °C			
%w/w	70	80	70	80
35	85	60	90	75
40	163	123	255	200
45	455	388	855	820
50	1650	1575	1675	1587

Table—19 : Effect of Free Alkali on Viscosity for soda Wheat Straw Pulp, 60% Solids Black Liquor (31)

Free alkali	Viscosity, in Centi Stokes	
g/lit.	Temp., 50°C	Temp., 90°C.
4.48	20,500	1430
8.00	8,000	660
12.80	6,000	570
15.83	5,700	75

Table—20 Effect of Active Alkali on Viscosity (28—29)

Residual active alkali as g/l as Na_2O	Brookefield viscosity, mPas		
	solids%		
	35	45	49/55
4.15/5,0	6	43	280
5.90	5	36	100
6.30	5	28	74
8.70	415	26	59

Table—21. Reduction Of Viscosity Using Busperse—47 (26)

A. Viscosity of hardwood B/L., mPas

Solids %	without chemicals	with addition
64.9	282	233
60.0	106	98

B. Viscosity of Softwood b/l.

Solids %	without chemicals	with addition
66.3	942	627
59.9	143	121

C. Industrial trial

Solids %	Before mixing tank		After mixing tank
65.6	380	345	298
64.2	260	239	257—202

Table—22. Viscosity Reduction Of Heavy Black Liquor Through Application Of 25 ppm Of Chemosperse—47. (27)

BLS (%)	Viscosity (mPas) without		Viscosity with chemoperse—47
65.0	1540	972	Average viscosity
67.0	906	786	
65.4	641	473	reduction of 55%
67.0	630	428	for BLS more than 60%
65.7	630	428	
67.5	740	604	
69.6	2420	1306	
66.7	1807	1050	

Doses : 25-50 ppm based on total weight of black liquor.

Table—23 : Viscosity of Black Liquors at 80°C in mPas (4)

Conc. of BL	Rice straw			Wheat Straw		Bagasse	
Wt%	Soda	A. sulphite	Kraft	Soda	Kraft	Soda	Kraft
35	57	15	8	58	—	35.5	16.7
40	125	26	13	105	20	50.1	31.6
45	316	45	23	251	—	105.0	50.1
50	1000	83	46	759	35	251.1	84.1
55	—	144	96	—	—	596	158.4
60	—	287	232	—	250	—	—
65	—	661	—	—	—	—	—
Pulping Condition	10% NaOH	3% Na_2SO_4 12% NaOH	12% No_2O 22% Sulphidity	10% Na_2O	18% NaOH	16% Na_2O Sulphidity	

Bath Ratio 1.5, Max. temp. 165° C. in al cases

Table 24-: Effect of Pulping Process and Temperature on Viscosity (11) of Black Liquor (30° Be liquor at 20°C), Viscosity in Centipoise

Temp. °C	Wheat Straw Soda CP	Wheat Straw GSP CP	Bagasse Kraft	Bagasse GSP CP	Bagasse Soda CP	Rice Straw GSP SCP	Rice Straw GSP CP	Rice Straw Soda CP
30	1270	630	1600	1900	78000	3200	760	—
60	300	170	500	850	8100	680	150	455(70°C)
90	80	50	50	96	360	240	50	388(80°C)

9.2 Reduction of Viscosity :

The reduction of viscosity is essential for optimal processing of black liquor through pipe lines, evaporator, oxidation tower, and in recovery furnace. Energy required to pump black liquor increases with increase of viscosity (29).

Therefore. it is evident that reduction of viscosity is very much necessary from energy conservation point of view. There are five ways of reducing viscosity both Newtonian as well as Non-Newtonian.

a) By increasing temperature of the liquor. Therefore in any case, strong black liquor temperature is not allowed to go below 90°C to avoid transport & storage problems. Normally 110°C 120°C is kept for spraying black liquor at recovery furnace.

b) Decrease of Concentration

The economy and efficiency of black liquor processing becomes higher as the solid content becomes higher and higher. Therefore decreasing solid content is not attempted with a view to decrease viscosity.

c) Increasing residual alkali ;

Work has already been done to increase the residual alkali of black liquor for straw and hardwood. The data as shown in Tables 19-20 indicate that how residue active alkali decrease the viscosity. It is also suggested that minimum residual active alkali to be maintained is 6 gpl. For black liquor obtained from agri-residues this is very much needed so that it can be processed without any problem.

(d) Removal of Polymeric and Gummy Materials:

The non-newtonian viscosity is normally due to the presence of the above materials. If the polymeric and gummy materials are be removed viscosity will be reduced significantly. This aspect has not been taken up till now for industrial practice. Normally if viscosity is below 4500 mPas the liquor is Newtonian and above 5100 mPas the liquor behaves Non-Newtonian. Molecular separation/Gel filtration before evaporation may be a solution.

e) Addition of Selective Chemical like Busperse-47 (25 ppm) or Chemosperse-47 (doses: 25-40 ppm) :

Experimental work and mill trial have been conducted by Beckman laboratories inc. before CE & B &W systems and before and after salt cake mixing tank (26). The above chemicals are nonionic in nature and a very good dispersing and penetrating agent. The data shown in Table-21 for hardwood as well as softwood show that there are 17% and 33% reduction in viscosity and in industrial trial 24% reduction after mixing tank has been possible. The data are shown in Table-21 Similarly application of chemosperse-47 has been shown in Table-22 (27).

However detailed experimental evaluation should be carried-out before drawing any final conclusion.

By measuring viscosity (Newtonian & Non-Newtonian) both thermal and electrical energy conservation is possible. Nature of black liquor at different stages should be known accurately. The first step in this energy conservation programme will be the selection of most suited apparatus followed by application of appropriate mathematical model which predicts accurate data.

Couette flow viscometer with provision of helical flow analysis will be the best choice for measurement of shear rate. The above mathematical model for computation purpose needs interrelationship with shear rate, sheaq stress, duration of shear in addition to temperature and solid concentration (18-22).

Reported data are probably not able to predict an unified correlations. Therefore, it should be experimentally measured at the factory conditions for accurate estimation of pump efficiency, pressure drop, heat transfer & evaporation.

At low concentrations, viscosity can be estimated at various solid content and at various temperatures.

At higher concentrations the viscosity increase in Proportion to the amount of organic matter in the total solids.

The viscosity of B/L may be measured with an Ostwald type capillary viscometer & μ can be plotted against % solids and temperature. These plots are known as Harvin's plots. For higher concentrations and time, the rheology instead of viscosity must be measured in a rotary viscometer such as cone plate, parallel plate, coaxial cylinder viscometer etc. The limitations of each and every viscometer is elaborated elsewhere (18—22).

Many expressions are also available for viscosity calculations. These are shown in Table-F.

Table—F Newtonian viscosity correlation

Gudmendson (33)

$$\ln \mu = a + bS + cS^2 + dS^3 \qquad \text{......(9.1)}$$

$$a = 0.4717 - 0.02472\, t + 0.7059 \times 10^{-5} t^2$$

$$b = 0.06973 - 0.5452 \times 10^{-3} t + 0.1656 \times 10^{-5} t^2$$

$$c = 0.002046 + 0.3183 \times 10^{-4} t - 0.976 \times 10^{-7} t^2$$

$$d = 0.5793 \times 10^{-4} - 0.6129 \times 10^{-6} + 0.1837 \times 10^{-8} t^2$$

Andrade's equation (32) :

$$\text{Ln}\, \mu = \ln A + E/RT = a + bX \qquad \text{......(9.2)}$$

Waterman's equation based on Cornelissen's and Waterman's experimental data (1,2).

$$\log \gamma = A/T^x + B; \text{ for water } x = 3 \qquad \text{......(9.3)}$$

or $\log \mu/p = A/T^x + B$; for B/L, $x = 3.5$

Walther's equation where Kinematic viscosity($= \gamma = \mu/p$) is expressed in terms of temperature.

$$\log [\log (\gamma + a)] = W - m \log T \qquad \text{......(9.4)}$$

Tappi :

$$\mu = 0.06198889 \exp [-0.0032563 (t_F - 460) + 0.10178S + 37.287 - 6 (t_F - 460)^2 + 0.0018003S^2 + 0.00049515 (t_F - 460) S] \qquad \text{......(9.5)}$$

valid for $S > 40\%$

$$\mu = \text{Exp}[-8.3 \times 10^{-3} - 6.55 \times 10^{-3} (S/100)^2 + 5.62 \times 10^{-2} (S/100)^2 (t_F - 460) + 5.7 (S/100) - 1.307] \qquad \text{......(9.6)}$$

valid for $S < 40\%$

$$\log \mu = 0.015 + 7.9x - 0.03125tx \;\; 5.75 \times 10^{-3} t \qquad \text{......(9.7)}$$

valid within the concentration range 0.1-0.50 and temperature 20-140°C.

In the linear range (6)

$$\text{Log}\, \mu/p = A + B/T^x; \; x = 2.0 - 3.5 \qquad \text{......(9.8)}$$

Eqs. 9.1,9.5 and 9.6 are applicable to wood liquors. For preliminary design estimates Eqs. 9.3 and 9.8 may be used.

Various experiments predict that

1. Viscosity of bagasse is 10 times that of bamboo at 45% solid.
2. Viscosity of eucalyptus and bamboo is equal at 45%.

Tables—23 and 24 reveal some interesting information. These can be summarized as under :

— In general viscosity of Rice Straw BL> viscosity of wheat straw BL> viscosity of bagasse B.L.

— In general viscosity of soda BL>viscosity of alkaline sulphite BL> viscosity of kraft BL. Bagasse appears not to follow this trend.

— For any BL, higher is the concentration, higher is the viscosity.

— Higher is the free alkali in BL, lower is the viscosity. This effect is more pronounced at higher temperatures.

— Green Liquor sulphite pulping black liquor viscosity is significantly lower than corresponding values for soda pulp for straws.

— Semi-chemical pulps black liquors have very high viscosity compared to chemical pulps.

One can grade B.L. from decreasing viscosity point of view as follows :

SCP Rice Straw> CP Rice Straw> CP Bagasse> CP wheat Straw> Bamboo CP> Wood CP.

Pulping process can be graded with respect to decreasing B.L. viscosity as follows :

Soda Pulp > Soda AQ > Alkaline Sulphite= Green liquor sulphite.

10 Some other properties :

This include colloidal stability, foam coefficient. swelling volume ratio (SVR), integral procedural decomposition temperature (IPDT), precipitation point & polymeric properties. These properties are specific for particular type of black liquor and hence universally not used for design purposes. These are used only for comparison purposes.

10.1 Colloidal Stability and Precipitation Point :

It is the indicator of solid concentration of black liquor at which colloidal instability of black liquors occurs resulting a precipitation. It is observed at low pH values of a black liquor having higher proportion of high molecular weight lignin macromolecules and the presence of organic acid and its salts. This is a phenomena reflected during concentration of black liquor. This is especially significant in case of hardwood & rice straw. Majority of hardwood black liquors show precipitation point in the solid concentration range of 30-40%which becomes thick granules at higher concentrations (say 50% solids). The probable cause for the above phenomena is due to condensation of alkali lignin and other macromolecules due to which molecular size increase affecting colloidal stability of the solution. The stability of this alkali lignin decrease with decrease of pH. Another cause may be due to higher chemical charges for hardwood pulping leading to the presence of higher salt in black liquor having inverted solubility characteristics.

10.2 Foam Coefficient & Foam Index :

Foam coefficient is mathematically expessed as

$K_f = V_{f/v};$ ....(10.1)

Foam index $= V_{i/v}$ .... (10.2)

Most of the black liquor contain significant proportion of organic acid salts or gums and other polymeric materials which have tendency to produce foam. The pH of the liquor also influences the foaming tendedcy of the black liquor. Some of the hardwoods also exhibits higher foaming tendency due to excess of resin salts. Foam affects the evaporation operation by entrainment resulting in liquor loss and washing of pulp.

Various kinds of oil, turpentine, kerosene, sulphonated castor oil, cotton seed oil or other vegetable oil or some silicones are used to control the foam. machanical foam breaker and thermal shock or impingement of streams are the proven technology of elimination of foam in industry.

Table—25 indicates the foaming characteristics, precipitation point, polymeric properties, and integral procedural decomposition temperature of rice straw, bagasse and hardwoods at different pH values. Qualitatively foam index is the percentage of volume of black liquor converted into foam and foam $V_{f/v}$ coefficient is the percentage ratio of volume of the foam to the volume of black liquor taken for test $_{fi/v}$. Foam coefficients of hardwood b/l is of the order of 12 as compared to bamboo 7.

Table—25 Foaming Characteristics, Colloidal, Stability, Precipitation Point and Polymeric properties of Black Liquors

Particulars		Rice Straw	Depithed bagasse	Mixed Hardwoods
1. Foam Coeff. at initial solids at 32 °C and				
pH	11.0	20.0	5.0	6
	10.0	14.0	5.0	—
	9.5	12.0	5.0	—
2. Foam Index 32°C and				
pH	11 0	18.0	10.0	19
	10 0	15.0	10.0	—
	9 5	15.0	10.0	—
3. Colloidal stability Precipitation Point at % solids		27	No pptn.	37
4. Polymeric properties Dialysis, % loss		74.9	81.0	65.2
Gel Filtration High/low Molecular Weight ratios		1.2	1.6	1.4
5. IPDT, °C		535	589	430

10.3 Dialysis, Gel Filtration & other Polymeric Properties :

Dialysis in cellulose membranes, molecular sieve chromatography (gel filtration) are widely used to find out the molecular size of the polymeric molecules present in black liquor. It is observed that bagasse black liquors have less permeable fraction compared to straw black liquor indicating higher molecular weight fractions in bagasse black liquor. Gel filtration studies also confirm above.

Bagasse spent liquor has higher proportion of high molecular weight lignin fractions compared to straw. Therefore the ratio of high to low molecular weight fractions is found to be higher in the case of bagasse black liquor. After dialysis the low molecular weight fraction disappears and only high molecular weight peak appears. Dialysis and gel filtration studies clearly indicate that higher viscosity of bagasse black liquor is attributed to high molecular wt. lignin fractions.

10.4 Swelling Volume Ratio (SVR)

Swelling volume Index/Ratio or volumetric isothermal expansivity (VIE), expressed as ml/g of dry black liquor solid roasted at 300°C for one hour is used for the assessment of the burning quality of the black liquors. High value indicates a porous ignited bed with free air passage and complete incineration.

A good burning black liquor has a fine homogeneous film during evaporation and has obviously more swelling volume ratio. Pine black liquor shows the highest swelling volume while the hardwood black liquors has the lowest value. It is a fact that hardwood black liquor forms hard impervious mass during burning and brittle incrustation are formed. As a result swelling tendency or in other words, the formation of porous mass as an outlet for the escape of the gases and vapours in the enterior reduces. Therefore, the raw materials like hardwoods, reeds and eucalyptus do not give satisfactory quality black liquor. Most of the hardwoods have swelling volume ratio in the range of 5—20 ml/g as compared to 40–50ml/g of softwoods. Rice straw black liquor (6.2) is found to have lower SVR values than those of depithed bagasse (15 5) and mixed hardwoods (13 0). Typical values are shown in Table—26.

Table—26 : SVI Values of Different Black Liquors (12,30).

Material	SVI ml/g
Rice Straw	3.13-6.2
Wheat Straw	5.05
70% wheat straw+30% Rice Straw	4.97
Bamboo	12
wood	26.77
Bagasse	15.5

Addition of alkali to black liquor first increases SVI values marginally and then decreases. Ratio of organic to inorganic matter in BL influences SVI value. SVI values decrease with increase in IOM/OM. The optimum values of IOM/OM for best SVI values for straw appear to be 4% active alkali in B.L. solids and they are in the range of 1 : 1.5 to 1 : 1.65· Decrease in silica improves SVI values. It also can be increased by reducing hemicellulose in B.L. It may be noted that a higher swelling volume index refers to better thermal decomposition of black liquor solids and better combustion. The straw BL decomposes slowly. Due to low values of SVI, proper height of charred black liquor solids is not formed in the combustion zone and unsteady combustion results. Though SVR and calorific values give prediction of combustion behaviour, the thermo analytical techniques like differential thermal analysis (DTA), thermo gravimetric analysis (TGA) are increasingly used to understand in detail regarding the combustion characteristics of organic substances. The % residue left at various temperatures say 100°C to 900°C is indicative of thermo gravimetric profiles. Integral procedural decomposition temperature(IPDT) is one such parameter which indicate the temperature at which half of the material is burnt. Both rice straw and bagasse black liquors showed higher IPDT values, compared to wood black liquor, indicating resistance to burning. Bagasse showed IPDT value higher than that for rice straw indicating the bagasse black liquor is relatively more difficult to decompose thermally. Resistance to thermal decomposition is attributed to higher proportion of higher molecular weight organic components.

11 Heat of vapourization

Clay(36)has reported eq. 11.1 which is found to be accurate.

$$H_V = 1086-0.448\ t_F - 4.6\times10^{-4}\ t_F{}^2$$

Conclusions

Data relating to almost all physico- thermal/chemical properties of black liquor as well as sulphite waste liquor have been collected for both wood and non-wood species. Possible equations of the above properties are also compiled and their applicability and limitations are examined. It is necessary that the equations and data available are to be checked before their use in design estimation. The conditions of pulping, species, and other factors must be compatible with the data given and equations proposed.

Nomenclature

T	Temperature, K; t, °C;F, oF.
x	Mass fraction of dissolved solids.
p	Density, H, t liquor/m³;m,kg/m³
D.S.	Tons solids/ton of liquor
S	% of dry solids;
Cp	Sp heat, kCal/kg°C;F,Btu/lb°F; 'MCal/ton°C; m, kCal/Kg°C;s for B/L solids (0.3—0.5 Btu/lb°F)
k	Thermal conductivity, Btu/hr.ft °C.; k also in kCal/hr°Cm, W/m°C
ΔTb	BPR, °C; (P), at any pressure; °C;760 at 760 mm Hg, °C.
TP	Boiling temperature Of solution, K; b50 at 50% Tds.
w	wt. of water, tons/ton liquor
d	Density, gm/cc
M_v	Molecular volume of B/L solids
V_f	Volume of foam
v	Volume of spent liquor taken for test (10 ml)
V_1	Volume of spent liquor converted into foam.
k_b	Ebulliopscoic constant (0.51°C for water)

a,b,A,B,c,t_o ,w,W,m Constants.

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