Sulphonation of Soda Bagasse Black Liquor

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ABSTRACT

This paper deals with the attempt of sulphonating the black liquor generated from bagasse pulping. Spent liquor generated in bagasse chemical and semichemical pulping processes were used for sulphonation using sodium sulphite. The variables affecting the degree of sulphonation reaction to get maximum sulphonation have been studied. The investigation revealed that the easy sulphonation conditions are required for semichemical spent liquor coupled with the achievement of higher degree of sulphonation, as compared to that of chemical spent liquor.

INTRODUCTION

The forest coverage in India has substantially reduced over the years. At the time of Independence the coverage was about 33% of the total area which has now declined to 11-12%. As a result of this the Indian pulp manufacturing units started looking at other fibre sources as an alternative means mainly in renewable form. Bagasse has emerged as a potential fibre source in this regard. Because of lower bulk density of the raw material there was however restriction on procuring the raw material from distant places adding exhorbitant cost of transportation to the production cost of pulp. This resulted into mushroom growth of small capacity pulp mills during 1970-1980's depending on the nearby availability of bagasse. The pulp per day production capacities of such mills were in the range of 30-70 TPD a size that precludes the economically viable recovery of chemicals from the spent liquor generated. During early phase of installation in seventies when the environmental considerations were not stringent, the pulp was produced profitably without the recovery and effluent treatment systems and the spent liquor so generated was discharged into down stream. Stoichiometrically 1.0 T of pulp generation leads to 1.2 T spent liquor solids which is sewered (1). The end of pipe treatment methods with low capital investment do not provide desired results because of non biodegradable lignin. In some instances the mills that were built in rural area due to fast urbanization of the surroundings over the years, the bread winning pulping operation had to be stopped or not allowed to expand to circumvent the problems of spent liquor discharges.

Either from the national perspective or from the point of environmental degradation or from the angle of cost of pulp production, a method wasting 1.2 Kg resources per Kg usable production calls for a total restructuring of the process to minimize such losses. In view of the same, an objective was set to examine the possibility of modifying these spent liquor solids to value added products of bulk industrial consumption.

Literature survey revealed that the organic matter of spent liquor solids comprises mainly lignin, a phenolic three dimensional polymer along with degraded celluloses and hemicelluloses. In the past, sulphite pulping liquor of soft woods of which the recovery system was not fully developed, has been directly used as dispersant/thinner in oil well drilling mud preparations. As on date this remained single largest use of sulphite spent liquors (2) but the alkali pulping process of bagasse does not produce in situ lignosulphonates. The alkali lignin needs introduction of sulphonate group in the phenyl propane moiety. Siso etal (3) have attempted the sulphonation of bagasse soda lignin and optimized the condition necessary for sulphonation, characterization of such sulphonated spent liquor is done and utility of bagasse lignosulphonate in plastifying action of cement as an aid in clinker grinding, its dispersion ability in oil well drilling cement has been studied.

Lan sojasheng, mainland China (4) have directly implemented this technique of sulphonation of bagasse soda lignin on a commercial scale. This product was markedly consumed in bulk at the nearby cement industries, resulting in not only avoiding the environmental problem of the wheat straw pulp manufacturing unit but also providing economy to pulp operation. An attempt was therefore made to evaluate the potentiality of sulphonated bagasse spent liquor. This paper deals with the characterization of bagasse spent liquor obtained from chemical and semichemical

processes, selection and optimization of proper sulphonation techniques and characterization of the sulphonated product.

EXPERIMENTAL

Spent liquors of chemical and semichemical pulping of bagasse received from Mysore Paper Mills, Bhadravati and Pudumjee Paper Mills, Pune respectively were filtered through a mat of glass wool to remove any suspended matter and used for further reaction and analysis. Both the liquors were analysed in accordance with the TAPPI Std method. T-625 and CM-85. Sodium was determined by Fame photometer using predried AR grade sodium chloride as standard. Lignin was determined gravimetrically by precipitation method at pH 1 (6).

The sulphonation reaction required varied initial concentration of the total solids in the spent liquor to maintain liquid : solid ratio during the reaction. Required concentration of the spent liquor was achieved using the rotary vacuum evaporator equipped with oil seal vacuum pump maintaining vacuum of 20 torr abs and water bath working between a temperature of 25°C and 100°C. The capacity of the evaporating still is 1 litre. Spent liquor of 40% total solids concentration was achieved by evaporating water at temperature 85-90°C and under vacuum of 150-250 torr abs.

a) Method of sulphonation

Sulphonation reactions using sodium sulphite in the presence of H_2SO_4 were required to be carried out under pressure at a temperature between120 to 160°C. So special type of stainless steel 304 quality bombs sustaining a working pressure 30 Kg/cm^2 were fabricated to run these sulphonation reactions. Wall thickness of bomb is 15 mm. The bomb is cylindrical type having 2 litres working volume and L/D ratio of about 4 : 1. After loading the bombs with the reactants spent liquor and sodium sulphite a tongue and groove type lid and Teflon gasket were used to seal the bombs. The sulphonation reaction was run by loading the bomb with about 1 litre spent liquor (Total solids 100-400 gms of desired concentration). The pH of the bomb content was adjusted to 9.0 using commercial grade H_2SO_4. Required dose of commercial grade sodium sulphite (of which the purity was determined by iodometric titration) was then added and the bomb was sealed as mentioned above. The bombs were then mounted on the wheels rotating in a oil bath. The reaction was continued under the predetermined set conditions. After completion of the reaction, the bombs were removed from the hot oil bath, cooled in waterbath and contents were transferred to a beaker by opening the lid, sulphonated product was then weighed and tested for residual sulphite and unsulphonated lignin.

b) Index of Sulphonation

Residual free sulphite content in sulphonated product was determined by iodometric titration. To circumvent the problem of dark colour during colour change of starch indicator, sulphonated product was sufficiently diluted. Despite these measures it was felt that the residual

Table 1 Characteristics of bagasse spent liquors under investigation.

Properties Pulping process employed	CP Spent Liquor Depithed Bagasse in the presence of 16% active alkali in pressure digester at temperature 145-155°C to get pulp of Kappa No. 22 and yield 45%.	SCP Spent Liquor Depithed bagasse in the presence of 10% Sodium hydroxide digested in open spherical reactor at temperature 95°C and then hot refined to get pulp of Kappa No. 50-55 and yield 60-65%.
PH	10.27	8.85
Total solids % w/w	11.50	8.14
Residual active alkali gpl (as Na_2O)	7.28	0.31
Sulphated Ash % on TS (as Na_2SO_4)	50.70	42.80
Organic matter % on TS (as Na_2SO_4)	49.30	57.20
Sodium % on TS	23.70	15.60
Lignin % on TS	30.0	35.0
Spent liquor solids (tonnes/tonne) of unbleached pulp.	1.22 : 1	0.9 : 1

sulphite cannot be measured accurately by the iodometric titration. Hence the extent of sulphonation was measured by determining the percentage of unsulphonated lignin. The unsulphonated lignin being water insoluble, will precipitate under acidic condition at or below pH 1.0, while sulphonated material will dissolve in water. The precipitated lignin was washed well with dilute acid and dried in oven and quantitatively weighed to constant weight.

RESULTS AND DISCUSSION

Characterisation of the bagasse spent liquor

Several types of pulping processes have been employed in pulping, most widely used among them are:

1. Chemical Pulping- in which active reactants are NaOH and Na_2S (Kraft) or NaOH and Anthraquinone (Soda)
2. Semi Chemical Pulping- which uses NaOH as active reactant and the pulp is further subjected to mechanical refining action.
3. Thermo mechanical- which uses thermal and mechanical energy for producing pulp. (Pulp yields are high-85% and above)

Due to very low solid contents in the spent liquor produced during thermomechanical pulp, sulphonation of the same is not contemplated. The first two liquors were only used in the study of sulphonation : the samples are collected from nearby mills and characterized.:

1. Spent liquor of chemical pulping (CP) was collected from Mysore Paper Mills Ltd., Bhadravati, Karnataka.
2. Spent liquor of semichemical pulping (SCP) was collected from Pudumjee Paper Mills Pune, Maharastra.

As can been seen from Table 1, the SCP liquor has more of organics and more lignin, less sodium and therefore it will be better suited for sulphonation reactions. However the SCP liquor needs more concentration and consequently the evaporation compared to CP spent liquor due to higher liquor to wood ratio used during pulping.

As the characteristics of spent liquor reveals the presence of sizable quantity of lignin a phenyl propane moiety, it is obvious that investigation is to be diverted towards exploiting the functional properties of phenyl propane moieties. It was possible to attempt some formaldehyde condensation products of the spent liquor that is generally used in wood adhesives but because of high inorganics in the spent liquors it is assumed that the latter would provide brittleness and weak bonding. Hence sulphonation products of spent liquors is contemplated to be a suitable mode of operation providing value to the spent liquor.

Selection of method of sulphonation

A number of sulphonating agents are used to sulphonate phenols and phenol model compounds. Among them notable are chlorosulphonic acid, oleum, sodium sulphite and / or sulphur dioxide in the presence of sulphuric acid depending upon the conditions of the reactants and quality of product required (5). However the objective of this investigation is to find a bare minimum value to the hitherto wasted byproduct in bulk. It is therefore hypothesized that the cost of production of the formed bulk product shall be minimum. In addition the lignosulphonate generated in the sulphite pulping process use cheap magnesium/ calcium/sodium sulphite. Therefore low cost sodium sulphite was used as the sulphonating agent for the sulphonation of spent liquor.

Sulphonation of spent liquor using sodium sulphite

Variables studied in the sulphonation reactions are:-

1. Reaction time and temperature.

Table 2 Preliminary experiments on sulphonation reaction and the study of variables- chemical bagasse black liquor

Experiment No Reaction parameters	1	2	3	4	5	6	7	8
Black liquor solids %	11.5	11.5	11.55	11.5	15	25	30	40
Sodium sulphite % on TS	12	12	15	15	20	20	20	20
Time Hrs	1.5	2.0	1.5	2.0	2.0	2.0	2.0	3.0
Temperature °C	140	140	140	140	145	145	145	155
pH 9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	
Results:								
Residual sulphite %	76.8	71.8	79.24	85.0	79.1	68.5	68.8	62.5
Unsulphonated lignin %	70.9	73.0	72.0	65.7	66.5	56.7	58.4	50.2

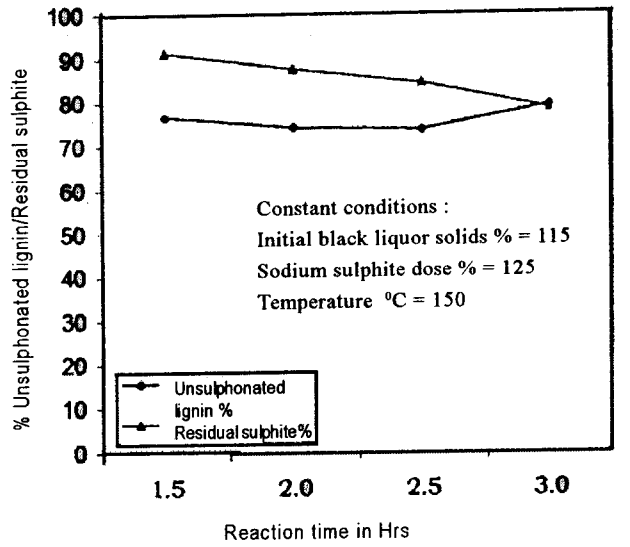

Fig. 1 Effect of Reaction time on sulphonation (CP spent liquor)

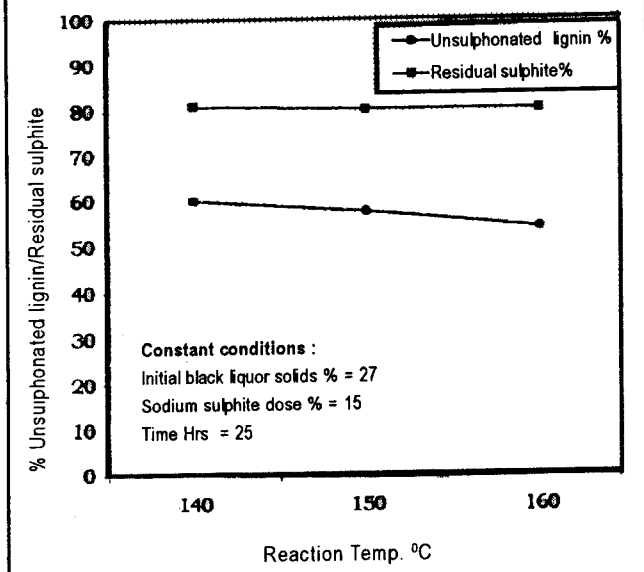

Fig. 3 Effect of Reaction Temp. on sulphonation (CP spent liquor)

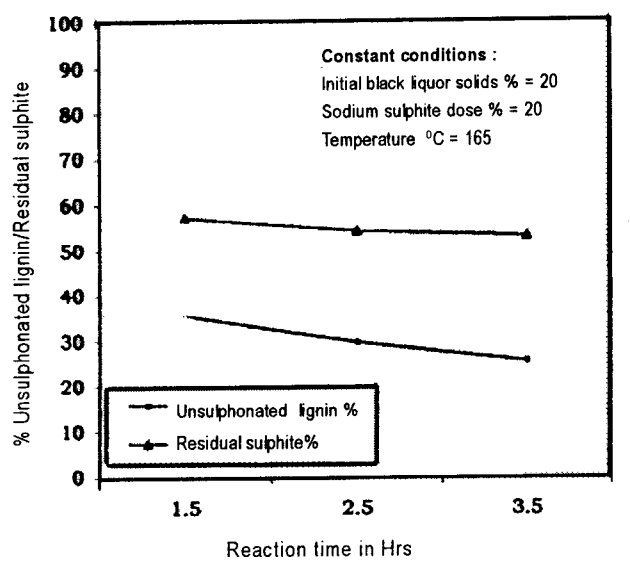

Fig. 2 Effect of Reaction time on sulphonation (SCP spent liquor)

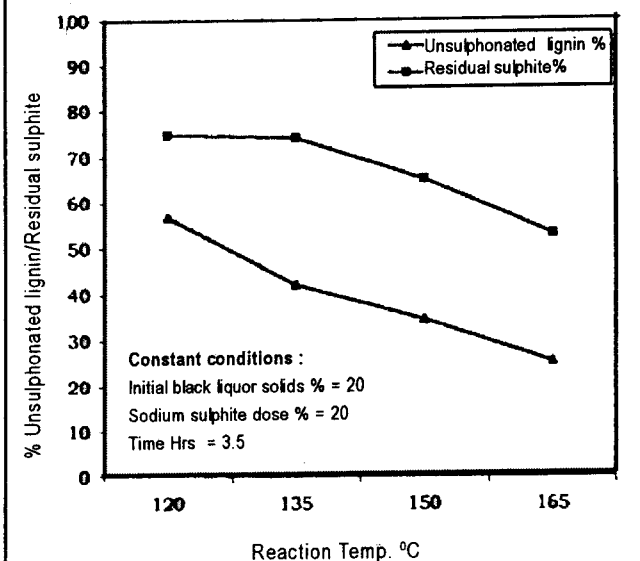

Fig. 4 Effect of Reaction Temp. on sulphonation (SCP spent liquor)

2. Liquid to solid ratio.
3. Dose of sodium sulphite.

To gauge the extent of sulphonation some analytical tools have been devised and employed and the indicators were,

1. To determine the residual sulphite in the reaction product.
2. To determine the percent unsulphonated lignin in the reaction product based on the fact that sulphonation provides solubility to lignin even under acidic conditions.

The extent of sulphonation can be deduced based on the analysis of residual sulphite and percent unsulphonated lignin.

A series of preliminary experiments conducted shown in Table 1 has allowed us to draw following inference:

1. The sulphonation in the range of 40-50% can be achieved by employing one of the above mentioned suitable reaction conditions.
2. The effect of variables such as dose of sodium sulphite and initial black liquor solids (ie. Liquid to solid ratio) are significant.

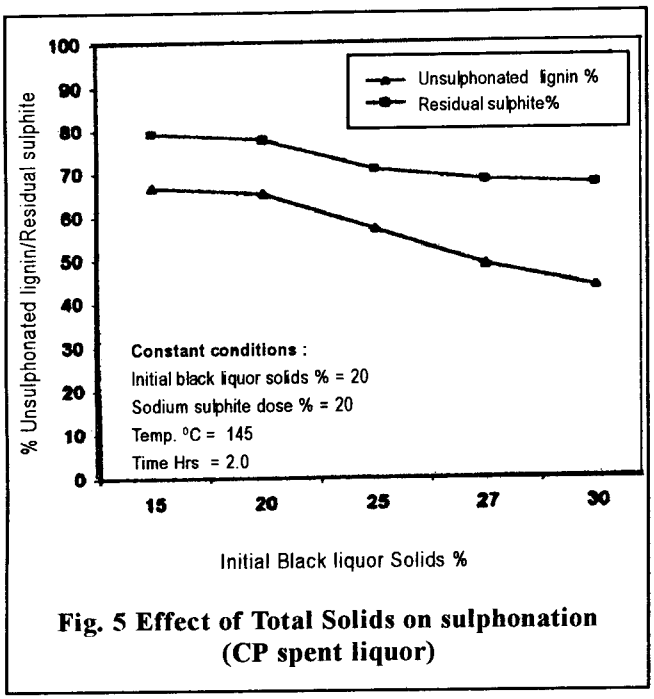

Fig. 5 Effect of Total Solids on sulphonation (CP spent liquor)

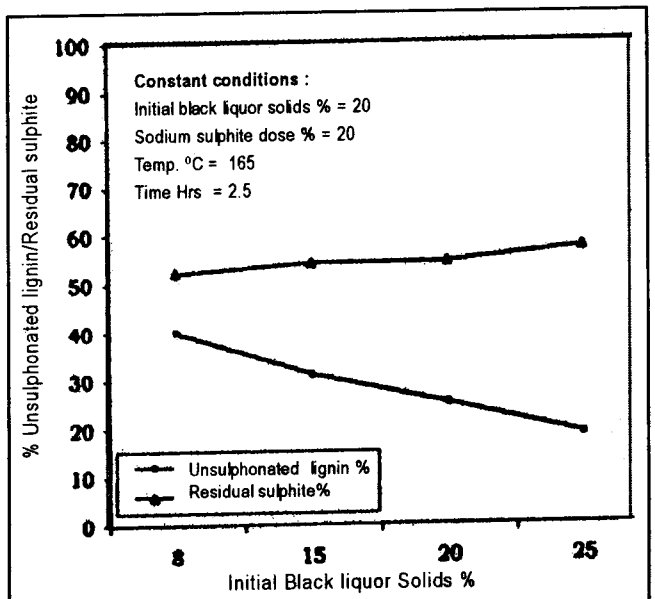

Fig. 6 Effect of Total solids on sulphonation (SCP spent liquor)

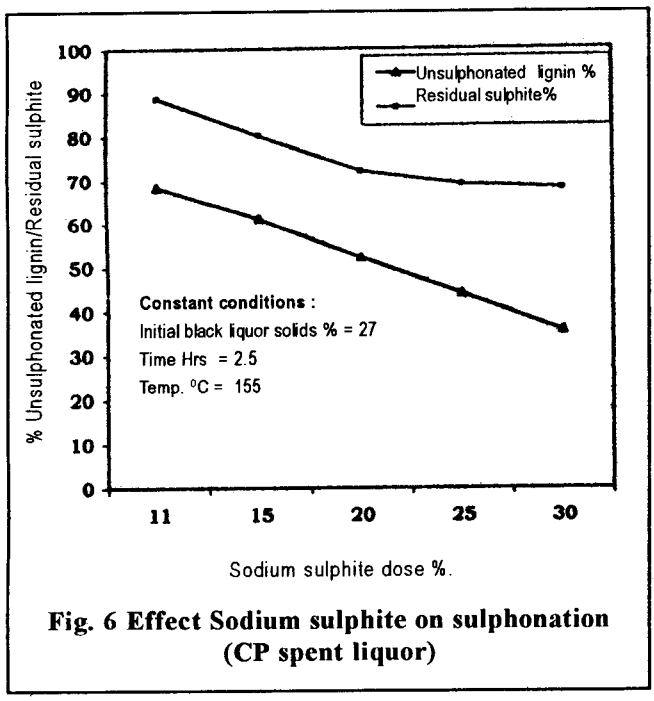

Fig. 6 Effect Sodium sulphite on sulphonation (CP spent liquor)

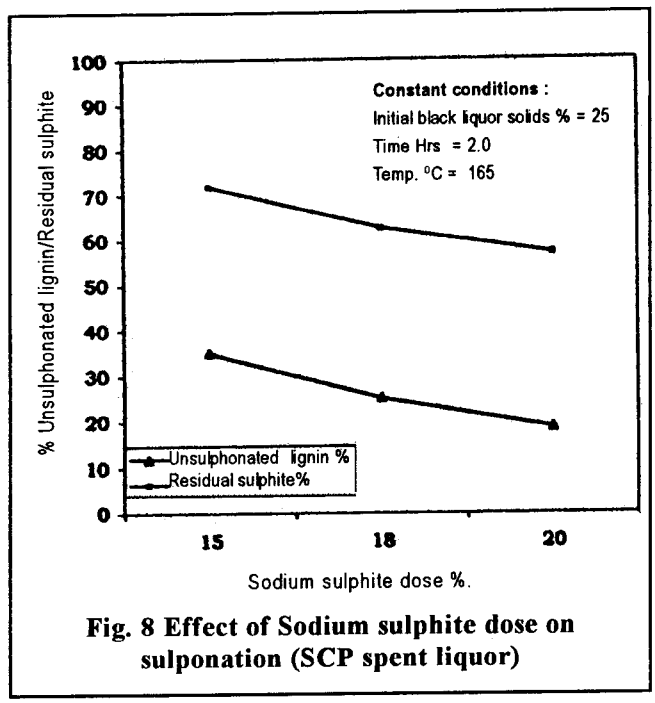

Fig. 8 Effect of Sodium sulphite dose on sulponation (SCP spent liquor)

3. The reaction conditions studied have revealed that the time and temperature do not significantly affect the sulphonation. It is possible that at higher temperature and for extended time the rate of decomposition of sulphite formed might compete with rate of formation of sulphonated product. These preliminary experimental findings coupled with the outcome of work elsewhere (3, 4) narrowed down the working range of variables of these sulphonation reactions as under:

a) Reaction time- between 1.0 and 3.0 hours.

b) Reaction tempertaure- between 130 and 160°C

c) Liquid to solid ratio- between 6.7 : 1 to 1.3 : 1 (in other words initial black liquor total solids content 11 and 40%)

d) Sodium sulphite dose on black liquor solids- between 5 and 30%.

a) **Effect of reaction time :** Figs. 1 and 2 provide effect of variation in reaction time on the sulphonation of CP and SCP spent liquor while holding other variables constant. No significant effect of reaction

Table 3 Selected sulphonation conditions for CP and SCP spent liquors

	CP Spent Liquor	SCP Spent Liqour
Initial Black liquor total solids %	25-30	22-25
Reaction temperature °C	150-160	160-165
Reaction time hours	2.0 - 3.0	2.0 - 2.5
Sodium sulphite dose % on TS	23 ± 3	18 + 2
Initial pH	9.0	9.0
Extent of sulphonation %	50-60	Above 90

time is seen for both the liquors. Under the conditions studied about 20-30% sulphonation occurs for the CP spent liquor while about 60-75% occurs for SCP spent liquor. Therefore a reaction time of 2 and 3 hours is considered adequate.

b) **Effect of reaction temperature:** Figs 3 and 4 depict the effect of reaction temperature during the sulphonation of CP and SCP bagasse spent liquors respectively. Almost horizontal line in Fig. 3 indicates insignificant effect of temperature for the sulphonation of CP liquor. However marked temperature effect is seen for the SCP spent liquor. The adequate reaction temperatures are 150 to 160 °C for CP liquor and 165°C for SCP liquors respectively.

c) **Effect of liquid to solid ratio:** As the percent total solids in the spent liquor alters the liquid to solid ratio of the sulphonation reaction this effect was studied for both the spent liquors in detail and shown in Figs 5 and 6. Based on the amount of residual unsulphonated lignin it is seen from Fig 5 that CP spent liqour can be sulphonated to a maximum of 50% whereas the SCP spent liquor (Fig. 6) responds more to the sulphonation. The observed sulphonation extends to almost 90% for the SCP spent liquor. The initial percent total solids to be maintained for the spent liquors to achieve maximum sulphonation are 25 to 30% and 20 to 25% respectively for CP and SCP spent liquors.

Table 4 Properties of Sulphonated bagasse spent liquor

Properties	CP	SCP
Spent liquor		
Solubility in water %	99.0	99.7
pH	8.78	9.5
Total solids %	32	29
Sulphated Ash %	38	32
Viscosity at 25°C	18	5.9
in cps of as such material		
Sodium %	25	24
Specific gravity at 25°C	1.258	1.213

d) **Effect of sulphite dose:** Figs. 7 and 8 respectively illustrate the effect of sulphite dose on the sulphonation performance of CP and SCP bagasse spent liquors. The increased dose of sulphite is conducive for the rapid increase in sulphonation of CP spent liquor; on the other hand with the SCP spent liquor marginal gain in sulphonation has been observed. The optimum dose of sulphite appeared to be 25 to 30% on spent liquor solids for the CP liqour while a dose of 15 to 20% is satisfactory for SCP spent liqour. One of the important observations in this study is that there is continuous improvement in sulphonation with the increase in the dose of sodium sulphite. However an increase beyond 20% dose, the residual sulphite content is increased. This is expected to increase the brittleness and ash content of the product due to which suitable industrial application may not be possible.

Response of spent liquors towards sulphonation and ideal conditions of sulphonation reactions to achieve maximum sulphonation

The above work revealed that both the spent liquors behave differently towards sulphonation using sodium sulphite. The conditions used for sulphonating the SCP spent liquor are mild and the sulphonation achieved is almost 90% when determined on the basis of precipitation of unsulphonated lignin at low pH. On the other hand the sulphonation reactions are sluggish with the CP spent liquor and the maximum sulphonation achieved is to the extent of 60%. This is probably because of the more reactive (open lignin structure) sites available in semichemical black liquor as compared to condensed nature of lignin in chemical black liquor. It can therefore be inferred that better sulphonated product is distinct possibility from semi chemical bagasse spent liquor. Selected sulphonation conditions for these liquors to achieve the maximum sulphonation are given in Table 3.

Characteristics of sulphonated product

The sulphonated product obtained in the above were in liquid form and such product is sold in China as dehydrating agent in the cement industry as well as binding agents for refractories and additives in various

industrial area (4). Preliminary study has been initiated to characterize the sulphonated product for its various chemical and physical properties. Analysis carried out so far is tabulated in Table 4.

In order to compare the properties of sulphonated spent liquor with that of commercially available lignosulphonates in powder form of sulphite pulp mill, it is desired to devise suitable method of evaporating the moisture from the slurried form of sulphonated spent liquor. The solids content of slurry is around 32%. Various methods have been attempted to demoisturize the product and spray drying is found to be effective method of producing free flowing powders with about 2-3% moisture. The prima-facie chemical properties of the sulphonated product indicate high sodium and ash content while the other properties such as water solubility and pH do fall in line. Further work to explore the potential of sulphonated bagasse spent liquor as clinker grinding aid in cement industry, in oil well drilling muds, as agricultural pesticide emulsifier and foundry core oil is in progress.

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