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by

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Ion Exchange Resin From Spent Sulfite Liquor*

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By heating spent sulfite liquor with formaldehyde and concentrated sulfuric acid a cation exchange resin was prepared and its operating charecteristics in the demineralization of water were investigated.

The possible effects which may improve the exchange capacity and the chemical stability of exchange resin were examined and the results obtained are presented.

INTRODUCTION

Large quantities of wood are consumed every year for the production of paper, cellulose and cellulose derivatives. However yields of chemical cellulose are less than 40 %. The other constituents of the wood, -viz., lignin hemicelluloses etc.,- constitute the spent liquors of the sulfite pulping processes.

In some locations the spent liquors from sulfite pulp mills are discharged into the sea. It has been agreed that fish have been damaged by the presence of these spent liquors.

Thus the desire to eliminate pollution and the incentive of economics are the basic reasons for the investigation of the utilisation of lignin. The utilisation of lignin presents difficulties. The major difficulty is due to the complexity of the chemical structure of lignin. The investigation of lignin is also complicated by the sensitivity of this polymer.

Most research concerning the utilisation of lignin has been carried out with the lignosulfonic acids which were present in the

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effluent stream from the sulfite pulping process. Although extensive research has been carried out, spent sulfite liquor still represents an important waste product of the pulp and paper industry. Lignosulfonates have found large uses in a variety of fields such as additives in the preparation of oil-well drilling muds, road binders, cement products, industrial cleaners, boiler scale inhibitors [1]. The preparation of cation exchange resins from spent sulfite liquor has also been reported in the literature [2,3,4,5].

In this paper various preparation of resin from spent sulfite liquor are described and the properties of these materials are investigated to see whether they would be useful as ion exchange resins. First of all, the resistance of the resins to different pH, was investigated since an ion exchange resin must be insoluble within very large intervals of pH. Secondly, their exchange capacity was determined since this has to be reasonably high if the resin is to be useful. Finally, the resin network must permit free diffusion of exchangeable ions so that columns may operate of reasonable flow rates. Consequently the resins should not be highly crosslinked. This requirement was investigated by testing the swelling properties of the resin.

Many cation-exchange resins containing different fixed ionic groups of various acid strengths are known. Strong acid resins generally contain sulfonic acid groups and because of the acid strength of this groups they possess a constant exchange capacity over a broad pH range. Even with only sulfonic acid groups, resins of various acid strengths can be prepared since the dissociation constants are affected by the nature and configuration of the units to which the groups are attached. For example arylsulfonic acids are stronger than alkyl sulfonic acids [7].

Since ligninsulfonates, Fig. 1, contain methylene sulfonic acid groups as the acidic exchange groups, it should be possible to prepare cation exchange resins merely by decreasing the solubility and increasing the chemical stability of the lignosulfonic acids. The sulfonic acid content of lignosulfonates present in SSL is usually about 0.5 per methoxyl [8], accordingly it was hoped to prepare cation exchange resin with a theoretical weight capacity of about 2.50 meq /g.

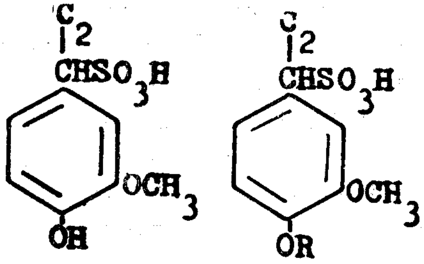

Fig. 1: Lignosulfonic acids

Description of spent sulfite liquor (SSL):

The spent sulfite liquor used in the investigations was obtained from the pulp and paper mill in İzmit. The spent sulfite liquor contained 15 to 16 % total solids [6] and about 58 to 60 % of these solids consisted of lignin sulfonates. The sulfur content of SSL was 1.08 %.

For the preparation of the cation exchange resin, SSL was first concentrated from 8–9° Bé to 16° Bé. During the concentration some of the calcium sulfate separated out as crystals.

EXPERIMENTAL

SSL contains sugars which may amount to 25 % of the total solids in the liquor. To establish whether SSL can be used directly for the preparation of the cation exchange resins and to what extent the sugars present have an influence on the exchange capacity of the resins obtained, two types of resins were prepared. One series of cation exchange resins were prepared directly using concentrated SSL. The second series of resins were obtained from the pure lignosulfonates which were separated from SSL by precipitation.

SSL (16° Bé) was first treated with concentrated sulfuric acid (9 g H_2SO_4/100 g SSL) and allowed to stand for two hours during which time calcium sulfate separated out as crystals. In this way it was possible to obtain an SSL solution with an ash content as low as 0.1 %. The clear solution obtained by centrifugation was then subjected to condensation as described below. Different resins were prepared by using different proportions of SSL /sulfuric acid /formaldehyde.

The mixture of SSL and formaldehyde was first heated both with and without sulfuric acid to 100–110°C in a steel bomb for two hours after which heating was continued in a beaker to higher temperatures and for different predetermined times.

For the investigation of cation exchange properties resin samples with an average particle size of 12 to 30 mesh have been used. The resin was washed first with a dilute solution of sodium hydroxide to remove the excess of sulfuric acid then with 2M hydrochloric acid and finally with distilled water to remove sorbed hydrochloric acid until the water remained free of chloride ions. Resistance to alkali was investigated by shaking the resins for ten days with aqueous solutions of alkali of different concentrations. The clear solution was removed after centrifugation and was evaporated and the residue ignited and weighed. The amount of the residue per gram of resin used was plotted as a function of the concentration of alkali.

For the determination of exchange capacity, about 15 g of ion-exchanger converted to the acid form by treating with 2M hydrochloric acid in a column. The resin is then washed with distilled water to remove sorbed hydrochloric acid until the water remains free of chloride ions. The adherent liquid is then removed by centrifugation in a tube fitted at one and with a sintered glass disk. After a known amount of the resin is placed in a laboratory column, 500 ml of 0.1 N NaOH is passed through the column at a flow rate of 200 ml per hour. After the column was washed with distilled water, the effluent was collected and the excess of sodium hydroxide was back titrated.

Another sample of resin was dried in an oven at 110°C until constant weight. The exchange capacity was calculated as a mEq NaOH used for 1 g dry resin.

Swelling of the resin was investigated by observing the volume changes of known amount of resins in water and different hydrochloric acids solutions.

RESULTS AND DISCUSSION

Preliminary tests showed that the resins obtained by heating 16 Be SSL with paraformaldehyde or with 40 % formaldehyde solution were not stable at high pH values. However, it was possible to obtain relatively stable resins by prolonged heating at higher temperatures. The effect of the temperature used during preparation on the stability of the resin is shown in Fig. 2. As can be seen from the figure, the resins were very slightly soluble even if they were prepared at temperatures as high as 250°C. It was for this reason that SSL and formaldehyde were condensed in the presence of sulfuric acid. Again the temperature used for the preparation of resins produced in the presence of sulfuric acid had an effect on their stability in alkali.

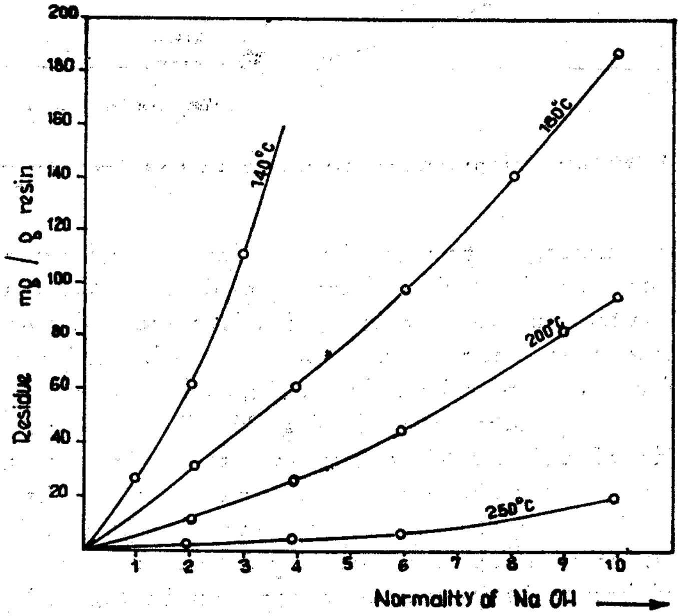

Fig. 2: Resistance of resins prepared at different temperatures

As can be recognized from Fig. 3 an increase on the stability of the resins was observed with an increase of the temperature to which the resins were subjected. According to the figure, resins prepared by heating at only 140°C for four hours were practically insoluble at high pH values.

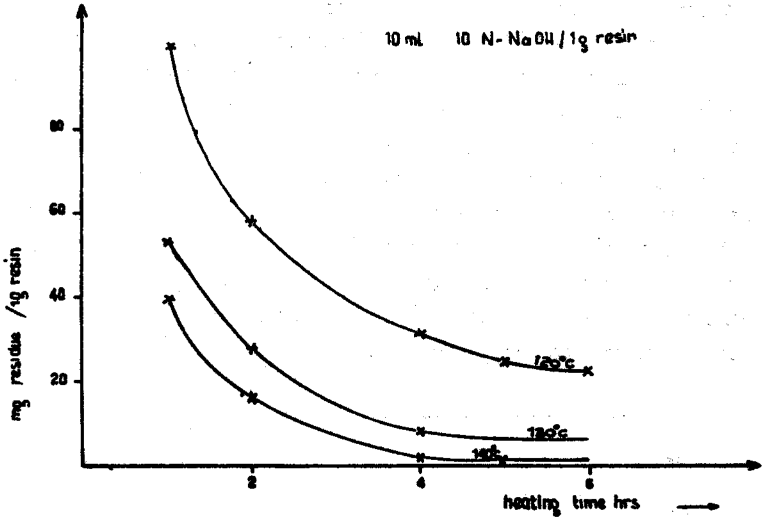

Fig. 3: Influence of temperature and the time upon the stability of the resin

The exchange capacities of the resins prepared using different amounts of sulfuric acid are reported in Fig. 4. As can be seen from the figure, as the amount of sulfuric acid used increased, a decrease in exchange capacity was observed. Similar results were also obtained with formaldehyde, Fig.5. According to Figures 4 and 5, resins prepared by condensing 100 g SSL with 5 g of 40 % formaldehyde and 9 g of 98%sulfuric acid had the highert exchange capacity. Therefore, the resin obtained using these ratios has been used for the determination of the exchange capacity and the pH titration curve. In Fig. 6 is shown the pH titration curve of 5 g of the acid form of the dry cation-exchange resin having the highest capacity with normal sodium hydroxide on a glass electrode in 25 ml of 0.1 M sodium chloride. Whereas between 0.2 and 0.43 free phenolic hydroxyl groups per methoxyl group have been reported in lignosulfonic acids [9,10,11], the shape and the low pH of the curve indicate that the exchange capacity of the resin is due only to sulfonic acid groups. This result may indicate that

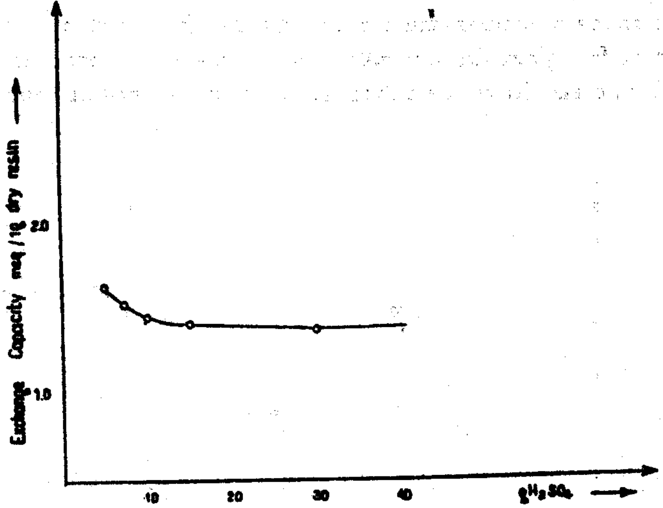

Fig. 4: The influence of g H_2SO_4 used for 100 g SSL + 20 g CH_2O on the exchange capacity of the resin

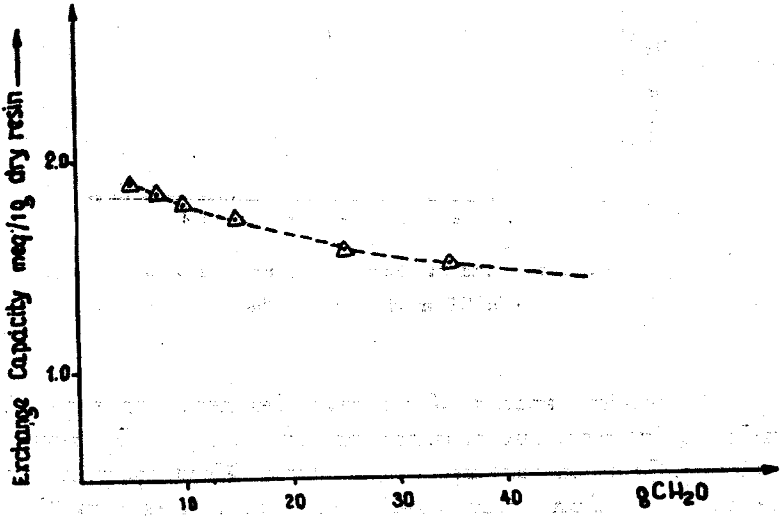

Fig. 5: Influence of g CH_2O used for 100 g SSL + 5 g H_2SO_4 on the exchange capacity of the resin

during prolonged heating the free phenolic hydroxyl groups undergo secondary condensation reactions. As the result of the low content of free phenolic hydroxyl groups, the resins are resistant to alkali and also have the advantage of being mono-functional.

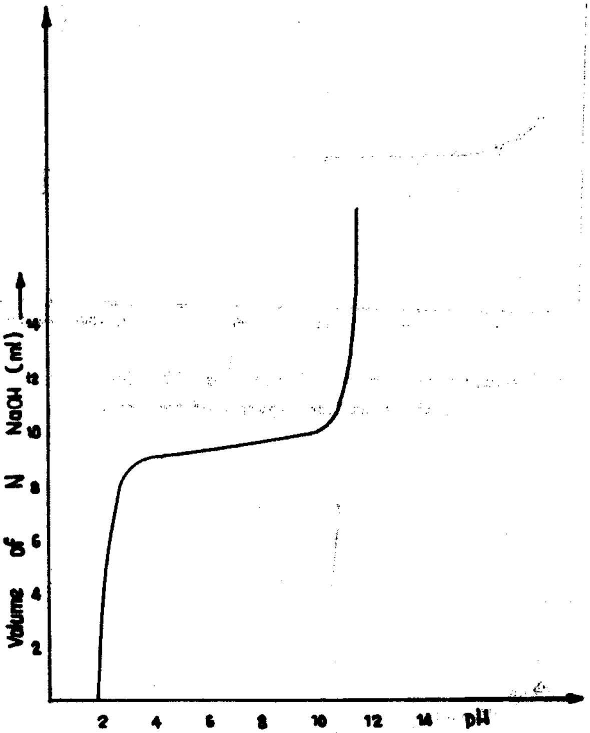

Fig. 6: pH Titration Curve of 5 g dry resin with N-Na OH in 25 ml 0.1 M NaCl

The weight capacity of the resin described above was 1.8 mEq /1 g dry resin, and its sulfur content was 4.1 %. The resins in hydrogen form can take up 35 % of water. When dry resin takes up water its volume increases 43 %. As can be seen from Fig. 7, the volume changes of the resin depends on the concentration of the electrolyte.

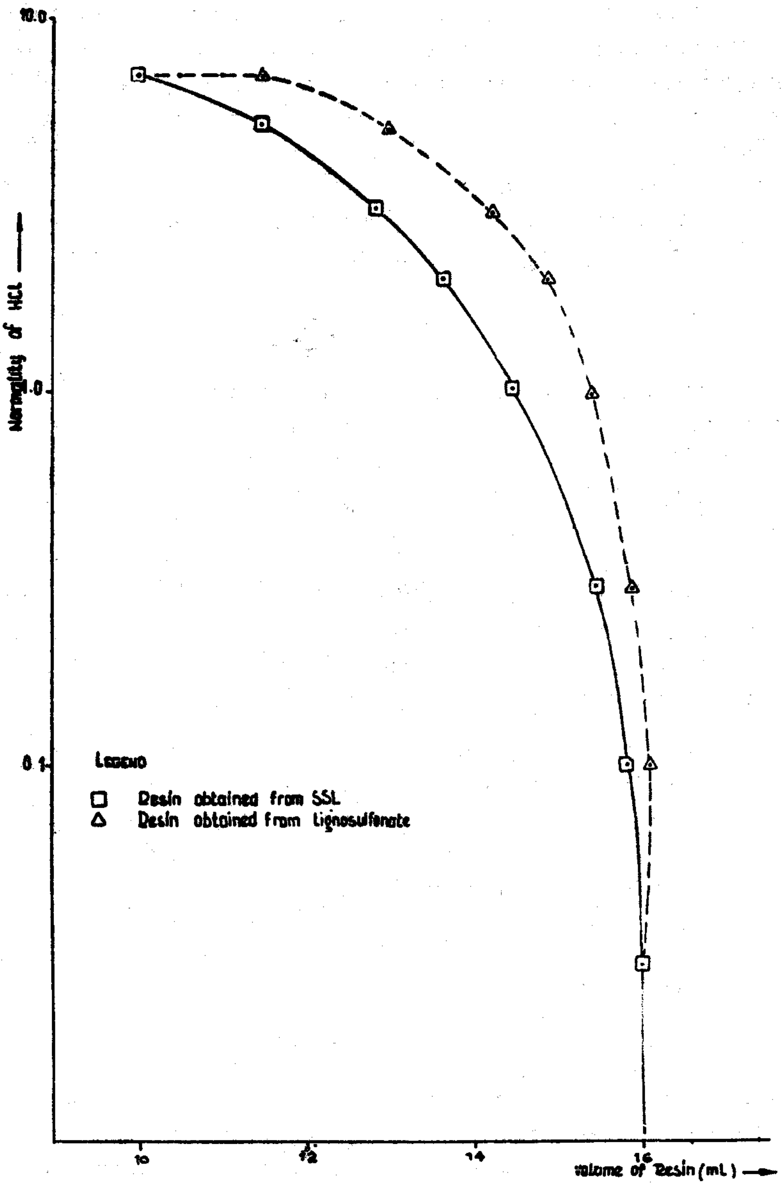

Fig. 7: Volume changes of 10 g resins in HCL - Solutions

The properties of the resins prepared under the above conditions from pure lignosulfonic acid were also investigated. The pH-titration curves of the resins were similar though their swelling properties and their exchange capacity were higher. The highest exchange capacity obtained was 2.34 mEq/1 g dry resin. Which agrees with the sulfonic acid content of the lignosulfonic acids. A cation-exchange resin with higher capacity cannot be obtained unless condensation of lignosulfonic acid is carried out with a component containing an ion-exchange active group.

CONCLUSIONS

The results obtained confirm that the sugar present in SSL does not contribute to the exchange capacity of the lignosulfonates. Therefore, resins prepared directly from SSL have lower exchange capacities then those prepared from pure lignosulfonates. However, sugars do not effect the stability of the resins. They have only a slight influence on the swelling properties. On the other hand in practice, resins with an exchange capacity of 2.50–9.0 mEq/1 g dry resin are pratically satisfactory. This means that the exchange capacity of the lignin (SSL) resins should be improved in order to prepare practically useful resins.

From the practical point of view, the tediousness and the expense of the processes involved in the separation of lignosulfonates from SSL should be taken into account; it is more reasonable, therefore, to investigate the possibility of increasing the exchange capacity of the resins prepared directly from SSL.

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ÖZET

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