Recent developments in characterisation and utilisation of black liquor lignins from small pulp and paper mills

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ABSTRACT

In India about 100 small pulp and paper mills are based on agricultural residues like wheat straw, rice straw and bagasse and are producing about 0.3 to 0.4 million tonnes of paper annually. Large paper mills have their own, well established chemical recovery units, but small pulp and paper mills due to high capital cost, chemical recovery becomes a bottleneck and the valuable chemicals are being discharged by these mills into stream causing severe stream pollution. The pollution treatment processes are also expensive for small scale pulp paper mills. The remedies to control the pollution caused by these mills includes either to develop a simple, adequate and cheap technology and methods for rapid characterisation of the black liquor or to utilize the black liquor as raw material for manufacturing various chemicals for industrial use.

Utilization of lignin, a brown gold, is now entering a new phase where active commercialization of lignin products and fundamental researches are being directed to the elucidation of property performance relationships of industrial lignins and development of new chemical processes for lignin modification and performance requirements of lignin chemicals for various industrial needs

In the present paper, some rapid method of analysis and factors influencing the properties of black liquor are reviewed and discussed.

It also gives an account of major advances that have been made in the area of upgrading the properties of industrial lignins for their applications as dye dispersent, adsorbent/desorbent, micronutrient for agricultural application, asphalt emulsion, cement dispersants, polymer application and oil-well field chemicals Researches carried out by the author and his co-workers at Cellulosa and Paper Branch, Forest Resesrch Institute. Dehradun on the modification of Industrial lignins (alkali, pulping sepent liquor lignins) for production of synthetic lignosulphonates for applicaticn as lignin solvent, aids in oil-well drilling and enhance oil recovery etc., has been reviewed and discussed.

To meet the growing needs of paper we have unique blend of large, medium and small pulp and paper mills in our country. These mills are utilizing variety of raw materials. Large paper mills are utilizing mainly Bamboo and hardwoods and have their own well established chemical recovery plant, whereas small pulp and paper mills are using agricultural residues like rice straw, wheat straw, bagasse and secondary fibre for producing pulp. High capital cost in establishing the conventional soda recovery chemical plants makes the small pulp mill economically unviable unit. Due to lack of suitably developed, economically viable chemical recovery unit for these small pulp and paper mills results in the drainage of valuable chemicals and causing severe stream pollution problems Now a days due to growing environmental awareness among the people and straingent pollution laws, it has become necessity for them to initiate chemical recovery unit. In the future Indian Pulp and Paper

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industry, it is envisaged that mostly non woody plant fibre will be available for the manufacture of pulp and paper, as forest based raw materials are in short supply.

The present paper gives an account of some of the recent developments (i) characterization of black liquor from pulping of agriculturai residues, so that suitable recovery plant may be designed in very near future and (ii) utilization of this black liquor as a raw material for the manufacture of most valuable lignin derivatives for various end uses.

Recent Developments In Characterization Of Black Liquor Analysis

There seems to be a demand for new methods for analysing spent black liquor from pulping of agricultural residues. We no longer have time for gravimetric manipulation or many hours of wet oxidation. In order to give a better and accurate description of liquor, some recent improvements in this area are :—

(a) Rapid determination of solids(1)

(b) Rapid determination of carbonate (2)

(c) Analysis of rheological properties (3,4)

In this article, the five most important characteristics of black liquor viz. calorific value, surface tension, foaming properties and ratio of inorganics to organics and colloidal and flow properties are discussed.

Calorific Value

Calorific value is an important property in evaluating the fuel value of the black liquor and in assessing the liquor producing process. There are new automatics devices in the market for determing the calorific value but the principle is still the same i.e. the sample (together with paraffin oil, if wet) is introduced into the autoclave (bomb) oxygen is added, the sample is ignited) and the heat evolved is recorded. The amount of energy thus measured per unit mass is the gross caiorific value from which the net calorific value is derived

Surface Tension

There is a little information available on the surface tension of black liquor. Measurements of surface tension of black liquor using a Do Nouy ring type tensiometer have recently been published by Deckwith et al[6]. The authors state that surface tensions could not be measured for solid contents about 45% because a tube of liquor was pulled away from the surface. The tensiometer method has several draw back including difficult thermostating, evaporation takes place at the surface and firm formation occurs on the surface. To overcome these defects, a glass vapour stalagmometer method has been developed.[5] The sample is introduced into capillary tube by suction. The valve is regulated to give steady flow of droplets and the number of drops is counted. The same procedure is repeated with a liquid of kn wn surface tension. Care should be taken that the liquid under reference should have surface tension close to liquid under test. For black liquor, acetic acid is generally taken as celebration liquid. The surface tension of black liquor is calculated by using formula :—

where,

$$\sigma_1 = \frac{n_2}{n_1} \times \frac{P_1}{P_2} \times \sigma_2$$

$\sigma 1$ and $\sigma 2$ are surface tension of black liquor and acetie acid, respectively.

n_1 and n_2 are number of drops of black liquor and acetic acid, respectively.

P_1 and P_2 are densities of black liquor and acetic acid. respectively.

The studies conducted by Soderhjelm[7] indicated that the surface tension decreases first rapidly with increasing dry solids but increases again when the dry solids content exceeds 30 to 50% .

Foam Properties

Due to presence of organic acid salts in different proportions and influence of pH, black liquor generates foam which creates problem in evaporator causing liquor loss, corrosion and scaling. Most of the methods for determining foam characteristics published so far are concerned with pulp washing and are based on the fact that a stream of air is passed through the liquor. The recent and quick method developed by Soderhjehm et al[5] is based on the generation of foam, in absence of air, under conditions where the gas phase consists of water vapour, methanol, terpentine etc. As the dynamic behaviour of foam is influenced by viscosity, a suitable care must be taken to control temperature. The apparatus used by the worker consisted to create mill situation by using an autoclave and applying a sudden release of pressure blowing and measuring the amount of foam at different solids and at different temperatures, studies conducted shows that foaming reaches a maximum at a certain solid content.

Ratio of inorganic to organics

Improper burning of black liquor in recovery boiler is often seen when the ratio inorganics/organics differ. Opinions differ on what are inorganics and what are organics ? The distinction between these two is not always defined in the same way. TAPPI method describes all the true inorganic compouds, organically bound sodium, potassium and organically bound sulphur all changed[8] to sulphates and then calculated as Na OH. Grace **et al**[8] include organically bound sodium but not sulphur within the category of inorganics.

J. villa [9] has studied the correlation between inorganic contents and sulphated ash and between organically bound sodium and total sodium. According to him, the true inorganics includes only true inorganic content measured by individual analysis and not organically bound sodium or sulphur.

Colloidal and Flow Properties

For an efficient and smooth operation of evaporator unit, it is necessary that the black liquor should be colloidally stable and free flowing. It has been discussed by kulkarni and Pant [10] that low PH, high proportion of high molecular weight lignin macromolecules and presence of organic acid salt in signicant proportion are responsible for colloidal instability of spent black liquor, results also in precipitation of lignin during concentration.

Flow behaviour in terms of viscosity is an important parameter for controlling pressure drop, heat and mass transfer rates, mixing rates etc. Knowledge of flow behaviour is desirable for piping design[11], selection of pumps and estimation of power costs,

To remove high molecular weight fraction of lignin, which is responsible for colloidal instability and high black liquor viscosity, can be removed by ultra filtration by using different sheives to some extent.

UTILISATION OF BLACK LIQUOR AS A RAW MATERIAL FOR VALUABLE PRODUCTS

A major expansion in lignin utilization has occurred in the last decade. Lignin hetrogenity plays a key role in defining the polymer performonce properties. The usefulness of industrial or technical lignins, especially isolated from spent black liquor generated from small pulp and paper mills has been demonstrated by the profitability of lignin chemicals business operated world wide. Industrial lignins are the single most widely available aromatic material obtained from the renewable forest resources. They are non-toxic and readily available at low costs. The prices of petroleum based chemicals for most industrial applications are 10 to 50 times higher the prices of lignin besed chemicals. There are various applications where the lignin a BROWN GOLD can be effectively utilized. Following are some of the potential areas of applications discussed in this paper.

Dye Dispersants

Rice straw and bagasse soda lignins show higher stability at elevated temperatures as compared to the wood based lignins indicating that rice straw and bagasse lignin decompose relatively slow as compared to wood based lignins. Based on this fact, the high performance dispersants containining lignosulphonates was introduced in 1960's. The lignosulphonates isolated/modified from soda black liquor, dispersants impart superior stability to dye formulations at elevated temperature. The tendency of lignosulphonate dispersants to stain textile fibres and reduce azo dyes are two main drawbacks which can be improved by blocking of free phenolic hydroxyl groups [12,13]. The tendency of lignin based dispersants to stain textile fibres Is related to the colour of lignin[14] which may be reduced as much as 44% by blocking the free phenolic hydroxyl groups with an alkylene oxide or halogen containing alkyl alcohol[15]. Lignin colour is reduced 80% by a combination of phenolic blocking and oxidation[13]. Thermal stability of lignin derivatives can be improved by (a) ultra filtration, (b) crosslinking, (c) condensation with formaldehyde, (d) oxidation in alkaline medium[16].

Adsorbent/Desorbent

A new process has been patented by Brown[17] in 1978 for making high molecular weight lignin gels in bead form. The process is an emulsion polymerisation technique similar to that used for producing the destran gel, sephadex. Lignin gel beads are rather uniform and spherical with good solvent regain property on swelling in Dimethyl formamide and dimethyl sulphoxide. The lignin gel is suitable for gel chromatography use and capable of separating polymers on the basis of molecular weight range 10^3 to 10^5 (18). Reversibly swellably lignin gels made by crosslinking an alkali lignin with epichlorohydrin or formaldehyde are claimed to be an improved carrier for organic pesticides.

Micronutrients for Agricultural Applications.

Certain groups like catacholic groups present in lignin are known to form a blue colour complex with ferrous ion[19]. Commercial lignin products which combine lignosulphonate with metal ions, such as Fe, Zn, Mg, and Mn are sold as micronutrients for agricultural applications.

Asphalt Emulsions

The emulsification of asphalt is an another area where lignin can be utilized by converting soda lignin into quarternary lignin amine (water soluble) after reacting with glycidylamine. Oxygenated alkali lignin in admixture with desulphonated lignin are used as an effective anionic lignin emulsifiers[16].

Cement Dispersants

Lignin derivatives especially lignosulphonates has a wider utilisation as a cement dispersant for increasing the compressive strength of cement concrete mixture[20]. A reduction in cement consumption by 3–10% without lowering the concrete strength was observed Lignosulphonates after treating with various aliphatic amines in ratios ranging from 1 : 1 to 50 : 1 and modified lignosulphonate were used as cement additive in 0.05–0.20% shows better strength properties, improved setting time as compared to corresponding properties to standard requirement[21-22].

Polymer Application

Polymer applications are considered one of the largest volume area for lignin utilization. Patel et al[23] Lin and Detroit[25], Gupta, and Sehgal[26], Singh and Joshi [27], Gupta Singh and Jolly[28], have made significant contributions on application of condensation products of lignin-phenol-formaldehyde mixtures as adhesives for plywood and other wood based panels. Researches of Singh and Joshi[27] have shown that 5% replacement of phenol with bamboo kraft black liquor lignin is possible for making boiled-water-resistant grade (BWR) plywood, having glue-adhesion properties as specified in IS 848-1974. Recent work is focused on structure-property relationship in Lignin-based phenol formaldehyde resins, seeking to enhance lignin reactivity in these resins. Glasser and co-workers[29,30,31] modified lignins by hydroxymethylation with formaldehyde. The resultant methylol substituents enhance lignin reactivity with phenol. It has also been shown by Glasser et al[31,32] that chemical modification by hydroxymethylation, forming hydroxy propyl lignin derivatives, reduces brittleness of lignin-derived polymers and improves their viscoelastic properties as propolymers for thermosat engineering plastics.

Oil-well field chemicals

Since 1974 a series of patents have been released on use of lignosulphonates and lignin derivatives as sacrificial agent to inhibit the deposition of the expansive surfactants like petroleum sulphonates on the reservoir matrix during secondary/tertiary oil recovery.

Work done ar Cellulose and Paper Discipline of Forest Research Institute, Dehradun on Lignin utilization

Considerable work has been carried out in Cellulose and Paper Branch of Forest Research Institute. Some of the Important findings are discussed here :-

Tewari and Singh[33], Singh and Singh[34] and Singh et al[35] have developed the following sequence for production of nuclear sulphonated derivatives of kraft/soda lignins for applications as dispresing agents, emulsifiers/gelling agents, surface active agents and solvents for lignin.

(i) Chlorination of lignin with molecular chlorine followed by reaction of chlorolignin with sodium Sulphite.

(ii) Nitration of lignin with nitric acid or sodium nitrite and hydrochloric acid followed by reaction of nitro-lignin with sodium sulphite.

The reactions were conducted between 30-90°C.

Highly water soluble nuclear sulphonated lignin derivatives were obtained by above methods. It has been observed that these lignin products possessess very high dissolving power for isolated industrial lignin (a 10g/1 solution of sulphonated lignin in 50% ethanol could produce a solutions of over 300 g/l concentration of industrial soda lignin (33). The standard dispersion number (SDN) calculated (0.02 to 1.50) for Blank/torque with sulphonated lignin using titanium dioxide-sodium chloride water system indicated that by changing the reaction conditions it is possible to produce sulphonated lignin having good dispersion properties as well as good emulsifying/gelling agents (31.32).

The presence of lignosulphonates in admixture with petrolium sulphonate surfactants increases oil recovery through reduced loss by absorption of the costlier petrolium sulphonate. The efficacy of the process for production of sulphonated kraft/soda lignosulphonates for application as an aid in secondary oil recovery was tested at Reservoir and Production Division of K.D.M., I.P.E, O.N.G.C., Dehradun by studying the interfaction tension of crude oil water emulsion by an addition of lignosulphonate. Interfacial tension (IFT) of crude oil water emulsion at 2.0% addition of sulphonated derivatives of lignin without addition of expensive petrolium sulphonate was found to be as low as 1.8 dynes/cm in comparison to 28.58 dynes/cm for blank and 10.00 dynes/cm for spent sulphite pulping liquor lignosulphonate (at 10% addition level) ([35]) indicating thereby the surface active properties for application as an additive for secondary/tertiary oil recovery. The reduction in the values of IFT indicates that the lignin derivatives can partially replace the costly petrolium sulphonates presently being used for secondary/teritary oil recovery. Surface active properties in terms of surface tension of the sulphonated lignin derivatives as evaluated by Singh and Singh ([34]) showed a reduction of about 29% in surface tension at pH 4 and 9.5. DTA (Differential Thermal Anaiysis) showed that sulphonated lignins are stable at 100°-120°C.

Rheological properties of sulphonated derivative of soda lignin were evaluated by Singh and Singh[34]. The apparent viscosity and the yield point values of the oil well drilling mud in fresh water were studied by Singh *et al*[36] indicated that these values decreased by about 49% and 59%, respectively at an additional level of 1.0% sulphonated soda lignin of bagasse. These results indicated the potential of sulphonated lignin prepared from bagasse soda lignin for application as an aid in oil well drilling mud system.

Conclusion

Lignin resecrch is no longer a laboratory chemistry. Lignin by products from commercial pulping processes-lignosulphonates and sulphonated soda lignin and lignin based prepolymers are being marketed in U.S.A. in a number of use areas. The potential for lignin chemicals is excellent. Markets could be identified as: Process fuel, oil.field chemicals, agricultural chemicals, asphalt extenders, speciality dispersants, adhesives, engineering plastics, enhanced oil recovery chemicals etc.

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