Better understanding of black liquor properties– A step towards innovative technologies

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ABSTRACT

Today, pollution control and better energy management have become major challenges before paper industry. With energy resources depleting, there is a greater awareness for cogeneration. Black liquor is one of the major fuel for cogeneration and considering the importance of black liquor as a source of energv and cooking chemicals. There is a need for better understanding of black liquor properties to enable to evolve the technology or modify the existing ones-with objectives to achieve higher chemical and thermal efficiencies. It is also important to understand the basic properties of spent lipuor for development of any treatment or chemical recovery process, particularly in context of small mills.

Introduction :

Spent pulping liquor is a complex colloidal system, which comprises of dissolved and colloidal organic residues and inorganic components. A wide variation in chemical composition of spent liquors is observed and the ultimate composition would depend on the type of fibrous raw material processed, conditions applied during cooking and the type of process selected for pulping. Knowledge of spe t pulping liquors is important not only for design of process equipments but also for monitoring the process parameters in chemical recovery systems.

In the paper industry, more importance is being given to the testing of the raw materials and of the end product— i.e. paper. The analysis of spent liquor is generally neglected. In the mills in Europe & U.S A the spent liquor processing for chemical recovery poses no special problem as often softwoods are used for pulp production. In India the basic raw material for large mills is bamboo and hardwoods and earlier work was directed towards these raw materials. However, with the advent of agricultural residues and non-wood fibres in the Indian raw material scenario, it is essential to collect a comprehensive data on the physico-chemical properties of spent liquors from agricultural residues. Studies conducted by researchers in different countries using non-woody materials have clearly indicated that the spent liquors from pulping of bagasse and straws differ substantially from those of woods (1, 2 3). Studies have been conducted in China (4,5) on various agricultural residue spent liquor and on their utilization. Interesting studies have also been carried out on thermal properties of spent liquors by Kellecher (5).

Lack of adequate knowledge on chemical nature of spent pulping liquors and its influence on important properties like foaming, viscosity, colloidal stability, rate of thermal decomposition etc. is one of the reasons why pulp mills based upon non-wood raw materials particularly small size units do not have suitable chemical recovery, treatment facility or black liquor utilization for generation of by-products. It has also been realised that existing test methods for wood black liquor testing are not adequate for non-wood black liquors and several tests are required to be standerdized for non-wood black liquors. The present paper highlights the modifications affected to the exist-

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ing test methods to suit the testing of non-wood spent liquors and also the use of modern testing methods to evaluate the spent liquors with high precision.

Results and Discussion :

Properties of spent pulping liquors can be studied under the following heads-Chemical properties, Physico-chemical properties and Thermal properties. It has been noted that method of evaluation of these properties are not standardized and there are variations in testing methods from mill to mill. In order to synchronise the testing procedures and to improvise the existing test methods CPPRI started a programme on spent liquor evaluation from various raw materials.

Improvisation of Testing Procedures :

Most of the methods developed abroad are based upon softwood spent liquors. They could also be applied to hardwoods which is pulped in the same fashion as softwoods by sulfate or kraft and sulphite processes. These analytical tests when applied to non-wood spent liquors sometimes showed certain anomalies. Tests include measurement of total solids, RAA & total alkali. Realising the importance of thermal properties of spent liquors, swelling volume ratio, thermogravimetry, differential thermal analysis, molecular weight distribution, CHN analysis and total carbon were included as the important tests.

Total solids estimation is an important test for black liquors. A slight deviation from the correct value may lead to appreciable changes in the steam requirement and final concentration of the spent liquor, which may result in excess consumption of steam in evaporators and supporting fuel in recovery boiler. Use of surface extender was introduced in the laboratory which enables the black liquor to be dried in the oven completely and more rapidly. Drying of black liquor with silica sand is practiced as standard method for solids determination.

Residual active alkali is also an important test which indicates the extent of pulping and helps in optimisation of dosage of cooking chemicals. It can also indicate the possible viscosity of the liquor after concentration.

For determination of residual alkali, the standard method involves neutralization of the black liquor after precipitation of lignin, with acid to pH 7. In the improved method graph is plotted between $\triangle pH/\triangle V$ and V (V is the volume of the acid). The volume of acid corresponding to first inflection point is taken for calculation.

Estimation of organic ratios in the spent liquors is often incorrectly measured. Generally ash content which is mainly sodium carbonate is taken as ash, which is misleading. The standard testing procedure used in CPPRI is conversion of ash to sodium sulphate by acid treatment and result is expressed as NaOH, which is in fact the real inorganic content.

Physico-chemical properties :

Viscosity :

In order to develop and design recovery boilers it is important to know the various engineering properties of the black liquor. Viscosity is important in atomising the black liquor during firing stage and governs size distribution of droplets in black liquor units like heat exchanger pumps, pipelines and oxidation tower. Viscosity of the liquors vary considerably with solids content and temperature and also depends upon the origin of the liquor and its organic to inorganic ratios. The viscosity of the black liquor from different pulp mills can vary considerably. The main limiting factor for reaching high solids content in evaporators is viscosity.

To study the flow behaviour of black liquors shear stress or viscosity has to be measured as a function of shear rate. Spent liquors behave as a Newtonian fluid below a certain shear rate value. The highly concentrated liquors behave as non-Newtonian fluid.

Flow behaviours of concentrated black liquors measured in terms of viscosity is an important parameter controlling pressure drop, heat and mass transfer rates mixing rate etc. It is also important from the view point of energy conservation. Extensive research on viscosity with various black liquors from bamboos, hardwoods and agricultural residues has shown that with rise in residual active alkali level, there is a decline in viscosity at all concentrations. There is a considerable viscosity drop at higher temperatures.

Molecular weight distribution studies on black liquor :

Spent liquor is a complex colloidal system containing nearly 10—40% of colloidal lignin macromolecules. Nature of these lignin macromolecules to a large extent is influenced by the important properties of black liquors like viscosity, rate of thermal decomposition etc. Gel filtration is an efficient technique for characterising molecules for their size. The crosslinked dextran gels have ability to separate complex mixture of macromolecules into fractions of varying molecular weights. In spent liquors, lignin is present as complex molecules which are distributed over a large molecular weight range (6).

Bagasse black liquor exhibit very high viscosity. On gel permeation studies of bagasse liquor, it was found that it contains high proportion of high molecular wt. fraction. It was found that these high molecular wt. fractions were lignin carbohydrate complexes (LCC). When the bagasse liquor was cooked at 120°C then some of the lignin carbohydrate bonds were cleaved and the resulting liquor showed lower proportion of high molecular wt. fractions. These liquor also exhibited lower viscosity.

Scaling tendency of black liquors :

The trend today is towards higher dry solids content in the black liquor fired into the recovery boiler. The limit to the dry solids content seem to be set by the physical properties of the liquor. The main problems encountered at high dry solids contents are the viscosity of the liquor and clogging of evaporator tube and spray nozzles. The extent of scaling of evaporators depends upon evaporation technique and nature of the liquor. Scaling may occur due to following reasons.

— high viscosity of the spent liquor, which slows down the liquor circulation rate causing local overheating and solidification on the surface of the tubes.

— the thermal characteristic of the liquor—the solubility limits of sodium sulphate and sodium carbonate are exceeded and crystallisation of Na_2SO_4. Na_2CO_3 salt occurs at higher dry solids.

It has also been suggested that some organic species play an important role in formation of calcium carbonate scale. Silica present in liquors of bamboo, grasses, straw and bagasse also causes serious scaling problems due to deposition of silica on the tube walls.

There are three types of scales which can influence evaporator or concentrator capacity :

1 Hard Scales—primarily insoluble, inorganic salts of calcium, silica, iron and magnesium.

2 Precipitated scales—primarily soluble inorganic salts such as sod. carbonate, and some black liquor solids.

3 Organic Scales—pulp attached to tubes by resinous compounds or attached to rough surfaces or to other types of scales.

Analysis of typical mill scales is given in Table—1.

TABLE—1

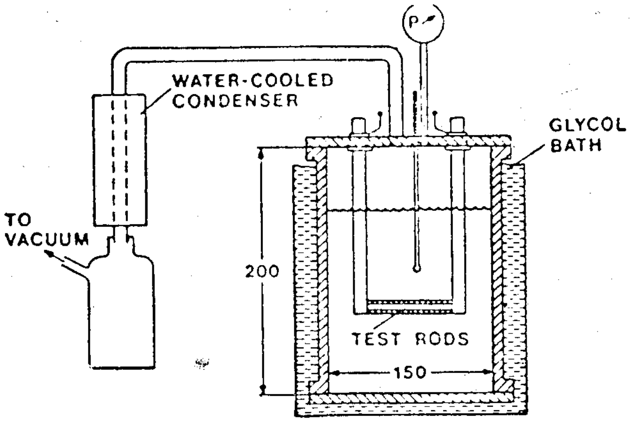
Analysis of Multiple Effect Evaporator Scale Deposits

Properties	Value
Ash,% w/w	84.97
Loss on ignition,% w/w	15.03
Hot water insolubles.% w/w	96.80
Silica, % w/w	58.49
Calcium, % w/w	11.09
Sodium, % w/w	0.52
Mixed Oxides, % w/w	2.61
Undetermined, % w/w	12.26

Methods to determine scaling tendency

An apparatus is being designed for this work, as shown in Fig 1. Black liquor is taken in a vessel and heated. The vapours are removed through a condenser. Over a period of time the liquor becomes concentrated and scales start to form which deposit on the test strip which serves as electrical bridge. The amount of scale deposited indicate the scaling tendency of the liquor.

Fig.1 - Test Assembly for Scaling Tendency



Control of Scaling :

1— Desilication :

An effective method to control scaling is reduction of silica in the liquor. A successful method of desilication has been developed by CPPRI/UNIDO/HNL using carbonation technique. Upto 90% silica can be removed by this method.

2— Control of soap content in the liquor :

Lower soap content is better for reducing gscalu tendency.

3— Control of organic and inorganic ratios of the liquor :

The high inorganic content results in increased formation of scales. So inorganic content should be regulated by proper addition of cooking chemicals and reduced dead load or inorganics.

Thermal Properties of black liquors — A tool in understanding combustion behaviours :

Steady combustion is one of the primary requirement in recovery furnace operation. Measurement of combustion heat is vital for the calorie measurement of the organics present in the black liquor. Though calorific value estimation is widely used method, it does not take into account the various stages involved in combustion like drying, pyrolysis, gasification and char burning. The thermal efficiencies as well as recovery efficiencies are determined by the way in which each step is accomplished under the conditions prevailing in the recovery furnace. It has been experienced on mill scale that black liquors from different raw materials exhibit different combustion behaviours in recovery furnace. It has been observed that even liquors having the same solids concentration and calorific values may perform differently in a furnace under similar operating conditions. Combustion in general is influenced by two factors-those arising from poor liquor quality and those attributable to incorrect operating variables. In the recovery furnace the burning process consists of several steps (I) Evaporation of water in the liquor, (2) Oxidative pyrolysis of the black liquor solids of char, and (3) Combustion of char. The burning mechanism of all organic solid fuels begins with oxidative pyrolysis. The volatile gases evolved during pyrolysis are responsible for flaming combustion, which is closely related to combustion of the char. The char burns without a flame, the mode is generally called glowing combustion. Two types of reactions with solid carbon take place in a burning char bed (i) Exothermic burning reactions with oxygen on the surface of the bed, and (ii) Endothermic gasification of the carbon inside the char bed by carbon dioxide.

Two properties which describe the behaviour of char particles at high temperature are (i) Ignition temperature and (ii) Integral procedural decomposition temperature (IPDT).

Ignition temperature (Tig)

When liquor chars are treated at sufficiently high heating rates in an oxygen-containing atmosphere in a temperature programmed furnace, it is observed that at a certain temperature there is a sudden change of slope on the thermogravimetric (TG) curve and a simultaneous release of heat on the differential thermal analysis (DTA) curve. The point, which signals the beginning of char combustion is denoted as Tig. Table—(2) shows the results of thermal analysis and it is noted that bagasse, rice straw and wheat straw have almost the same amount of volatiles. Higher ignition temperature shows slow thermal decomposition. From the DTA graphs in Fig. 2 & 3, it is evident that although all the spent liquors have more or less the same rate of thermal decomposition upto pyrolysis stage, but

TABLE—2
Thermal Properties Of Various Spent Liquors

Spent liquors	Carbon %	Organics %	Calorific value KCal/kg	IPDT °C	Tig °C
Bagasse	39.9	69.5	3600	574	722
Rice straw	39.6	79 2	3500	588	662
Wheat straw	37.4	78.6	3400	574	618
Hardwood (mixed)	35.6	70 2	3000	430	622
Reed	—	—	3200	445	600

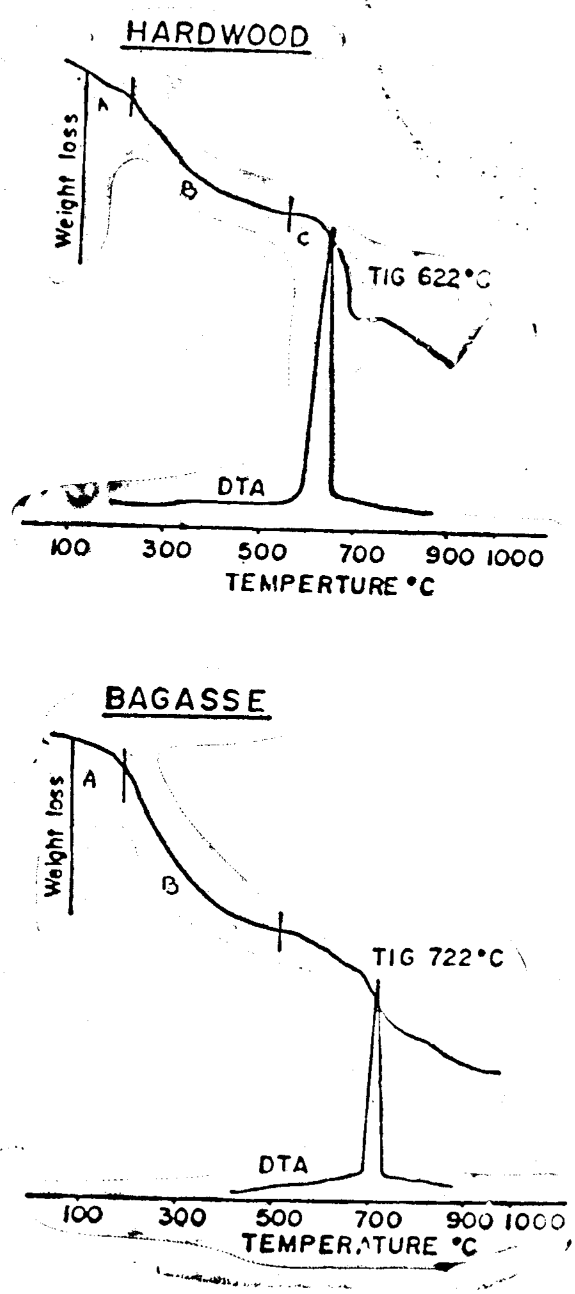


Fig 3—DTA & TG. Curve for Bagasse Black Liquor

the final char burning temperature differs significantly. From the above results, it is evident that bagasse spent liquor shows poor burning characteristics.

Integral procedural decomposition temperature or IPDT :

It denotes the temperature at which half of the material is decomposed. It is found from Table-2 that agricultural residues spent liquors show higher IPDT as compared to kraft spent liquor indicating their slow decomposition, though all the liquors contain almost the same amount of carbon. The results indicate that the combustion characteristics are not determined by carbon content or organics alone but also on the composition of lignin and carbohydrate macromolecule.

Conclusion

Black liquor is an important source of energy and chemicals and proper evaluation of its properties is essential for design of evaporators, reactors and furnaces and other processing equipments. It is necessary that basic and simple tests on black liquor properties like Total solids, Residual active alkali, Silica content, Inorganics, etc should be carried out at the mill with accuracy and standard methods should strictly be followed. The specialised properties like viscosity, scaling tendency, molecular wt. distribution and thermal properties should be carried out in the laboratories fully equipped with equipments and expertise. Proper evaluation of spent liquors can be a key to trouble free spent liquor processing, higher recovery efficiency and improved energy generation.

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