# Applications of modern analytical methods-a tool for predicting the behaviour of black liquors

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ABSTRACT

Processing of spent pulping liquors in pulp and paper mills in India, is not all that efficient as compared to those in developed countries. The primary reason for difficulties in processing of spent liquors has been the wide variations in properties due to changes in incomming fibrous raw materials composition. Due to lack of adequate knowledge on the behaviour of spent pulping liquors, at times, it becomes difficult for mill personnel to monitor the process conditions. Conventional testing procedures by and large, can meet only the requirements for running the plant and the data generated is inadequate to reflect spent liquor behaviour during various stages of chemical recovery operations. Now, with modern analytical tools available it has become possible to understand how the spent pulping liquors behave in evaporation and combustion stages. This paper highlights the efforts made by the Central Pulp & Paper Research Institute in adapting these modern techniques in studying spent liquor properties.

## INTRODUCTION

The major problem that Pulp & Paper Mills in India face today is the non-availability of raw material on sustained basis. As a result, the mills have to utilize raw material mixture in their furnish. Even the large paper mills utilize bagasse and eucalyptus alongwith bamboo. Due to changing raw material composition there is a wide variation in the properties of spent pulping liquors. The chemical recovery units in India have about 80% recovery efficiency as against 98% in the developed countries using softwoods. Softwood spent liquors show low viscosities, have high colloidal stability and exhibit good burning properties. The raw material available to our mills produce black liquors with diverse physico chemical properties[1] Overloading of chemical recovery units in India is also one of the reasons for lower recovery efficiencies. As a result the energy co-generation in Indian mills is about 30% as compared to 50%[2] in the mills abroad. Often improper monitoring of process parameters may also result in lower recovery efficiencies. For monitoring and controlling the process conditons the knowledge of properties of black liquor is essential. Today number of modern analytical tools are available for precise measurement of black liquor properties and subsequent predicting of behaviours of black liquors in various stages of chemical recovery operations.

Central Pulp and Paper Research Institute, has been doing research on black liquor properties since last 15 years. Institute with its experience, and looking into the needs of paper industry, aquired sophisticated instruments for research on black liquors. As a result of expertise gained with modern analytical tools it has become possible to understand black liquor properties and their behaviour during chemical recovery operation. The present paper highlights the major areas of applications of modern analytical instruments in chemical recovery and black liquor treatmen systems.

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The basic properties of spent liquor are broadly studied in the following heads—Physico chemical. Thermal and pollutional parameters.

**1. Physico–chemical properties of the spent liquor**: For design and development of process equipments, and monitoring and controlling of process parameters, the knowledge of physico-chemical properties like the chemical composition, colloidal state, elemental analysis, viscocity, specific gravity, boiling point rise and foaming tendency is very important. The Indian mills have experienced a wide variation in physico-chemical properties depending upon the raw material composition. A mill based on bamboo can process the black liquors without much problems, while the mills using Eucalyptus or mixed hardwoods have been facing problems particularly in evaporation and combustion stages of chemical recovery operations. Central Pulp & Paper Research Institute in the last 15 years has collected vast data both on laboratory and mill black liquors using modern analytical tools. The data collected has been highly useful in understanding the behaviour of black liquors. The conventional methods often are time consuming and sometimes may not give accurate results.

**Elemental Analysis** : For design and size of the chemical recovery boilers, the data on ultimate analysis of spent liquor solids is key stop. The conventional methods involves high temperature combustion and subsequent absorption of gases and often these methods give erroneous results. A modern analytical tool can give the carbon content to an accuracy level of $\pm 0.01\%$ in a short time. The accurate estimation will facilitate in designing the boilers and other heat recovery equipments. The Institute is equipped with a modern elemental Analyser for C, H, N & O. The estimation of C & H has been helping in carrying out the mass and heat balance.

**UV Visual spectrophotometer** : is a useful analytical tool which is used for qualitative and quantitative estimation of various components of spent liquors. It is also used for measurement of color of the sample. The organic matter in spent liquor is composed mainly of degraded lignin and aliphatic carboxallic acid, the later being degradation product of cellulose & hemicellulose. The lignin fraction, because of its aromatic character and of several chromophoric structural elements absorbs strongly in the ultraviolet range of the spectrum. UV spec tra of different analytical lignin preparations are quite similar, comprising a distinct absorption maximum near 205nm with a less pronounced flat shoulder at 280nm. The lignin estimation in spent liquor is carried out at 280nm. At this wave length only minor interference occur from carbohydrate degradation products[3]. The color of the spent liquors is measured at 465nm. The concentration of extractives mainly polyphenols is also measured at 465nm.

**Total solids Estimation** : Estimation of solids concentration of spent liquors is the primary step in all analytical exercises. The solids conc, results indicate the load on evaporators. Solids of liquor fired in recovery boiler are required to high accuracy level for economy & safety. Conventional methods of solids estimation by specific gravity measurement is influenced by surface tension, viscosity and is highly sensitive to temperature The oven drying method though accurate takes upto 24 hrs in case of black liquors For on line monitoring of the process conditions BLX solids analyser is employed.

**Viscosity** : Simple rotational viscometers were earlier used for the determination of viscosity of spent liquors. These viscometers had manual control of the shear rate which were fixed at various levels. The data obtained from these instruments was insufficient to predict the complete scene of the rheology of the spent liquors. With the introduction of computerised and programmable viscometers it is possible to understand the thixotropic nature of the spent liquors along with other properties like pseudoplasticity, delatency etc. The modern programmable Haake rotational viscometer is now used at the Institute. This has a searle system in which the inner cylinder—the rotor rotates at defined speed. The searle system also helps to accomplish good temperature control which is very important in case of spent pulping liquors.

The unit is used for measurement of viscosities of various samples of spent liquors The liquors exhibiting high viscosity were also studied. The viscosity curves obtained are shown in Fig. 1 and Fig. 2. The Fig. 1 shows the viscosity of bagas e black liquor at 45% conc at 93°C & 104°C The liquors show Newtonian behaviour at all shear rates (being a straight line relationship between shear rate & shear stress. Shown in Fig 2 are the viscosities of bagasse black liquor at

various temperature. At 55% solids and at 104°C, the pseudoplastic nature of bagasse liquor can be noted. On holding the liquor at maximum rotation (200RPM) for 6 secs. shear thining of the liquor is noticed resulting in reduction in viscosity. The 'down' curve exhibits lower viscosity due to this effect. One Important information gained from this experiment is that pumping of such liquors at high rates may result in encountering less viscosity or in other words energy on pumping can be saved when such liquors are pumped rapidly.

**Macromolecular properties of lignin employing gel filtration technique** : Spent liquor is a complex colloidal system containing nearly 30-40% of colloidal lignin macromolecules. Nature of these lignin macromlecules, to a large extent, is influenced by the important properties of black liquors like viscosity, rate of thermal decomposition etc. Gel filtration has become an efficient & simple tool for charaeterizing the lignin molecules for their size. The crosslinked dexran gels have ability to separate complex mixture of macromolecules into fractions of varying molecular weights. Institute is equipped with a modern gel chromatographic system. Number of black liquors have been characterized for macromolecular properties.

The experiments were conducted to note the changes in the bamboo spent liquor upon carbonation during the desilication process. The gel chromatograms of both carbonated and the original bamboo spent

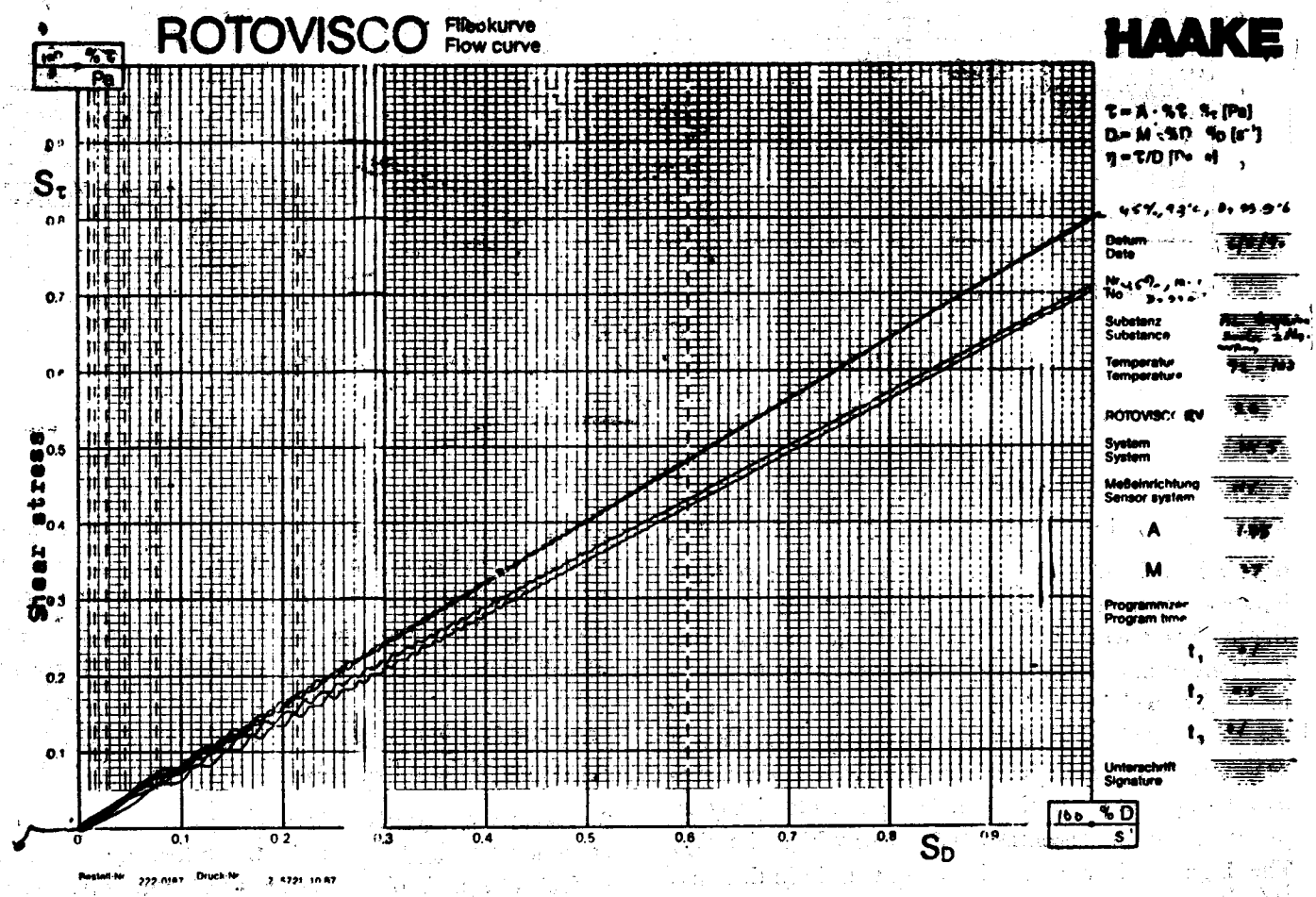


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Fig. 1 SHEAR STRESS VS. SHEAR RATE CURVE FOR BAGASSE SPENT LIQUOR AT LOW SOLIDS.

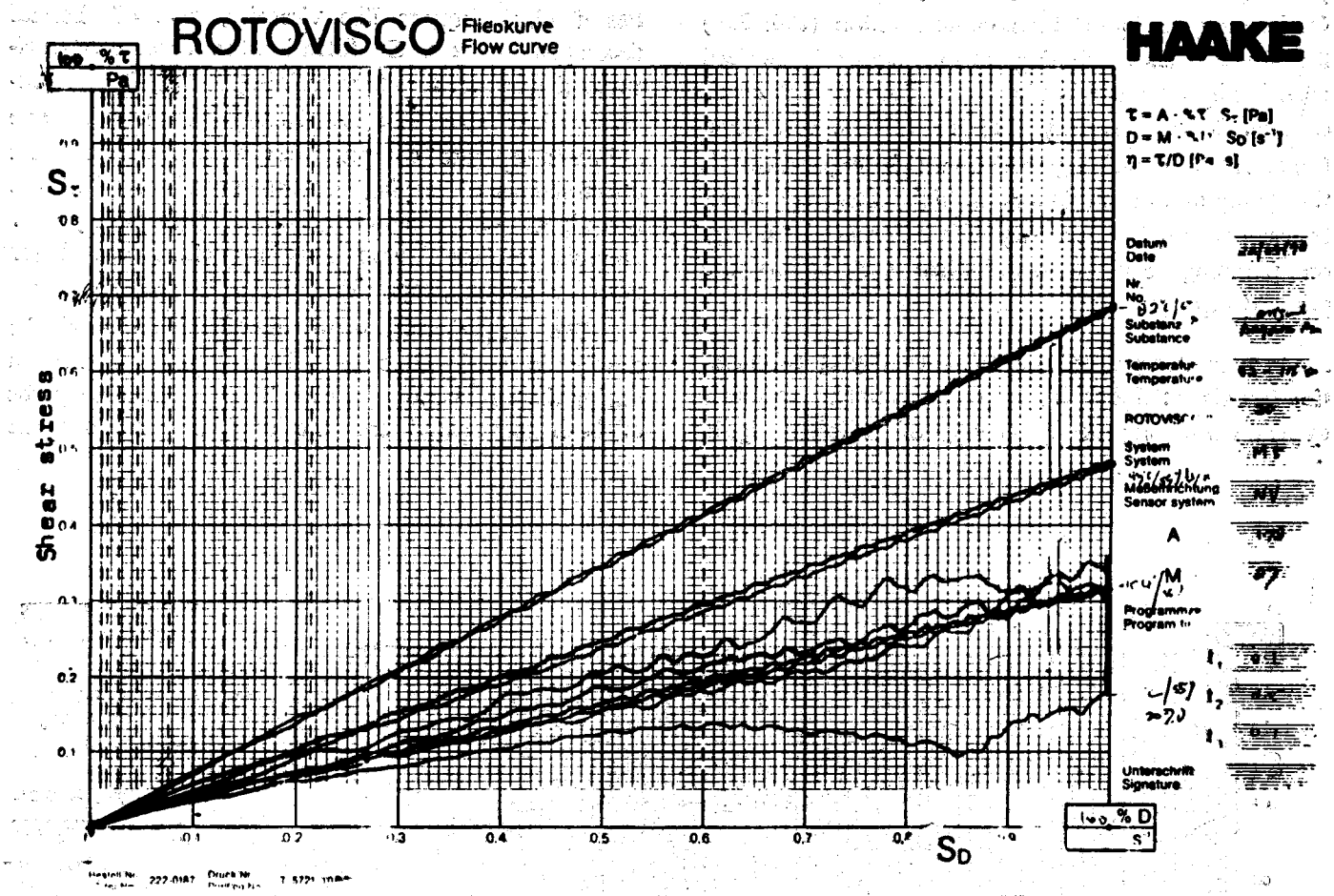


Fig. 2 SHEAR STRESS VS. SHEAR RATE CURVE FOR BAGASSE SPENT LIQUOR AT HIGH SOLIDS.

liquor obtained are shown in Fig. 3. The dotted line shows the gel chromatogram of the bamboo kraft black liquor & continuous line that of the carbonated black liquor. The two peaks in the original liquor show two fractions of molecular weights. The ratio of high to low molecular weight is 1.03. The gel chromatogram of the carbonated black liquor shows only one distinct peak depicting the condensation of lignin during carbonation, This explains the reasons for its tendency to precipitate upon concentration & for very high viscosity. The high to low moleculer weight ratio in this case is 6. 0.

In a spent liquor, lignin is present as complex molecules which are distributed over a large molecular wt. range. For development of lignin products, it is necessary to ascertain that high molecular weight fractions are present in adequate quantities. The fractionation of lignin on gel permeation chromatography unit gives an accurate picture of the high to low mole cular weight ratio. When compared to standard compounds it is also possible to predict the molecular wt. range of these fractions.

**2. Thermal Properties of black liquors :** Measurement of combustion heat is vital for the caloric measurement of fuels like coal, oil and spent pulping liquors. Conventionally, a manually operated bomb calorimeter is used to determine the calorific value of dried spent liquor. This method is time consuming and involves

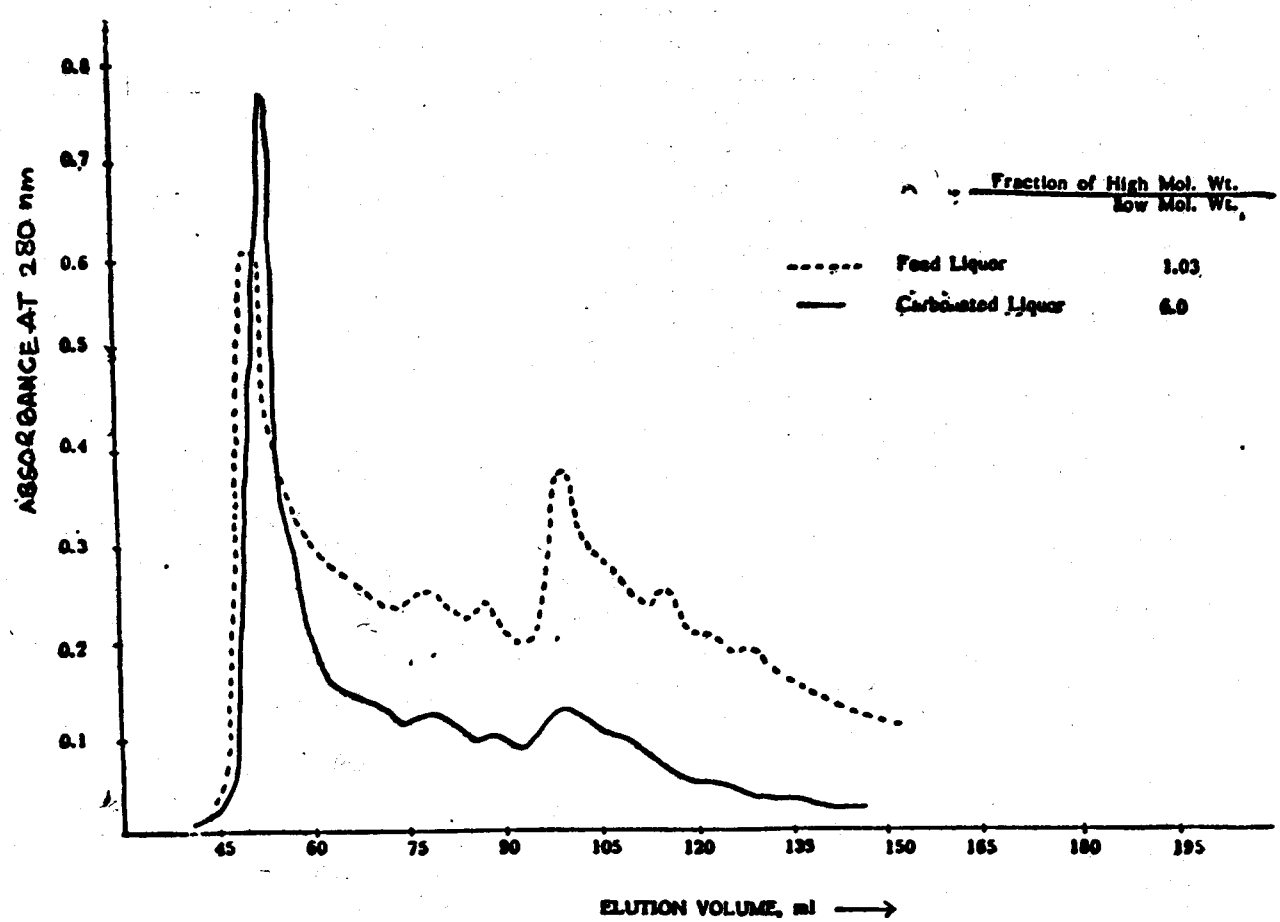


Fig 3 MOLECULAR WEIGHT DISTRIBUTION BY GEL CHROMATOGRAPHY

certain errors in temperature measurement which is manually recorded. The Institute has recently acquired an Autocalculating bomb calorimeter. The combustion heat is automatically measured and the results are calculated and printed. The results will be very useful for furnace design and for general operation of the recovery boiler.

**Black Liquor Combustion** : Combustion of black liquor is a complex step and involves stages like drying, pyrolysis and 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 experimenced on mill scale that black liquors from different raw materials exhibit different behaviours in recovery furnace. Combustion in general is influenced by two factors—those arising from poor liquor quality and those attributable to incorrect operating variables. The latter factor is largely determined by the former factor. The commonly measured properties like solids content, organic matter, carbon content, calorific values etc. have not revealed the reasons for poor combustion of the spent liquors. Recently, efforts have been made to correlate these properties with combustion behaviour using thermo-analytical tools. Institute had aquired an advanced thermal analysis STA-781 which is highly useful in characterising the various fuels like black liquor, furnace oil, coal and also other polymers. Wide range of data could be generated as the thermal analysis has facilities to conduct Thermogravimetric Analysis (TG). Differential thermal analysis (DTA), Temperature of Ignition (Tig) and Integral Procedural Decomposition Temperature (IPDT). These properties are helpful in predicting the combustion behaviour at different stages like drying, pyrolysis, gasification and char burning.

Thermogravimetric analysis, provides data on the change in weight of a sample when heated in a programmed fashion. Differential thermal analysis of a sample yields information on energy changes when a sample is heated ie. the heat released or heat absorbed. For instance, when a black liquor char burns, it is an exothermic reaction, but when suphates reduce to sulphides then it is an en endothermic reaction. The point corresponding to a DTA curve during char burning stage is taken as Ignition temperaturc or Tig. Integral procedural Decomposition temperature or IPDT is the temperature at which about half of the mass is burnt. Comparison of IPDT of various spent liquors explains the poor combusfion of some liquors.

**Thermogravimetric Anaiysis and Differential Thermal Analysis of spent liquors** : The thermogravimetric or T.G. curve of spent liquors is shown in fig. 4 Part A' of the curve shows Thermal drying of the sample. Part 'B' depicts the formation of char and part 'C' char burving. All the three stages show some loss in weight. During the drying of the sample, the energy is absorbed or it is as endothermic reaction and a negative DTA peak is observed. During the formation of char, Some heat is generated followed by an intense peak during char burning. At this point there is actual ignition taking place so this also indicates the temperature of igniton of Tig.

**T. G. and DTA of spent liquor-ferric oxide mixtures** : Heavy inorganic loading (with ferric oxide) was considered to be damaging for thermal degradation of the black liquor during ferrite recovery process. Samples of Bagasse Black liquor mixed with $Fe_2O_3$ in stoichiometric ratios were ignited using a normal heating programme and DTA & TGA curves were obtained. It was observed that in presence of $Fe_2O_3$, strong exothermic peak appears at about 300°C, 475°C and 750°C as against a normal peak in case of bagasse black liquor alone at 675°C. This indicates that $Fe_2O_3$ catalyses the thermal degradation of black liquor (Fig. 5.)

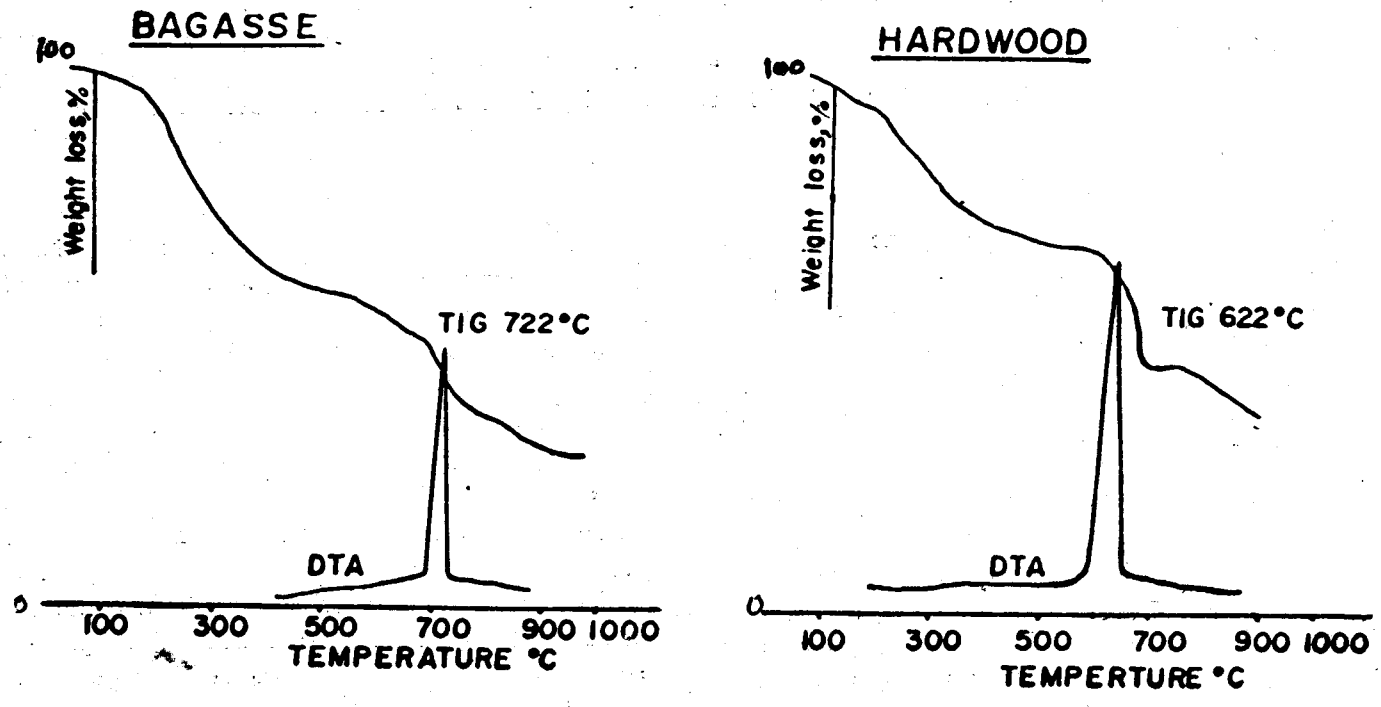


Fig 4 TG AND DTA CURVES

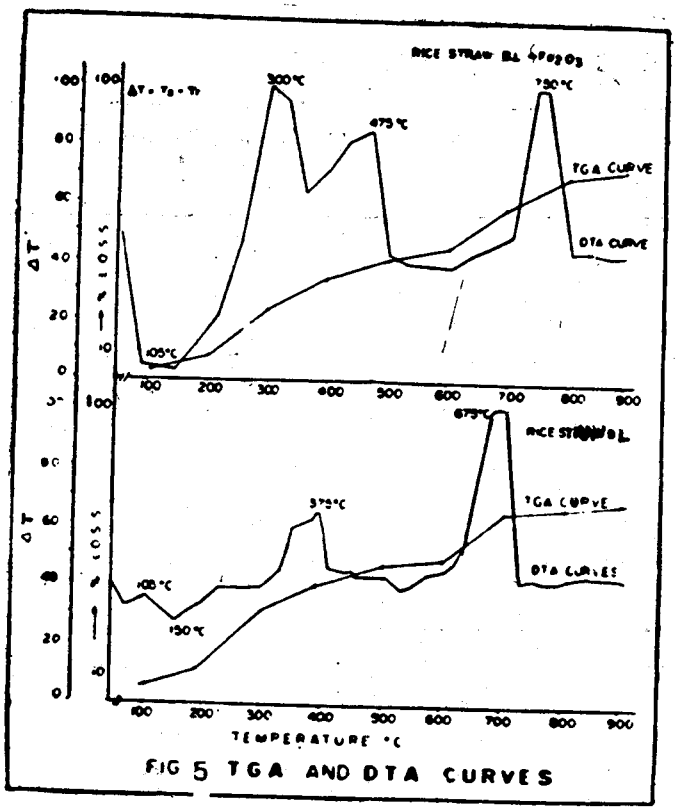

FIG 5 TGA AND DTA CURVES

**Integral Procedural Decompositon temperature (IPDT) and Ignition temperatue (Tig) of spent liquors** : Good combustability is highly essential for smooth operation of the recovery furnace. Thermal properties like. Burning profile (TG) Integral procedural Decomposition temperature, (IPDT) and ignition temperature (Tig) are very useful in predicting the combustion behavior of spent pulping liquors. IPDT is the temperature at which about half the mass is burnt. It was found that Bagasse and straw show higher IPDT values as compared to wood indicating their slow thermal degradation. When the liquor solids are heated at a sufficiently high heating in a temperature programmed furnace, there is a sudden change in slope of TG curve with simultaneous release of heat as observed on DTA curves (fig-4). The point corresponding to DTA signal is taken as Ignition temperature Tig. The table 1. shows the results of thermal analysis of various spent liguors.

**3. Pollution Parameters in Paper Mills** : A large quantity of effluent is generated in Paper mills which has to be discharged to the environment. Due to strict legistration mills have to treat their effluent to reduce BOD and COD load. Small mills, not equipped with chemical recovery have to discharge even spent pulping liquors which is rich in organic material. It is therefore desirable that extent of pollution generated should be known and efficiency of treatment plants closely monitored, for which modern analytical equipments are used.

**Total Organic carbon analysis** : The total organic carbon analyser is used to measure Total Carbon, Organic Carbon and Inorganic carbon in a sample. The unit TOC-500 uses a combustion signal processing system and high performancc catalyst. The combustion gas is detected by combustion-non dispersing infrared gas analysis method. The total organic carbon values can be used to estimate the COD values of the effluents. The table below shows the variation of COD with TOC.

TABLE—1
RESULTS OF THERMAL ANALYSIS OF BLACK LIQUOR

| | Sample | Carbon | Organics | Volatiles (400°C) | IPDT °C | Ignition Temp. Tig °C |
|---|---|---|---|---|---|---|
| 1. | Bagasse BL (mill) | 39.9 | 69.5 | 31 | 574 | 722 |
| 2. | Rice straw BL | 39.6 | 79.2 | 35 | 588 | 662 |
| 3. | Wheat straw BL | 37.4 | 78.8 | 35 | 574 | 618 |
| 4. | Hardwood (mixed) | 35.6 | 70.2 | — | 430 | 622 |

TABLE–2

RELATIONSHIP BETWEEN TOTAL ORGANIC CARBON & COD

| Sl. No. | Chem. oxygen demand % | Total organic carbon % |
|---|---|---|
| 1. | 122 | 36.80 |
| 2. | 110 | 36.40 |
| 3. | 103.7 | 36.84 |
| 4. | 97.62 | 33.70 |

TABLE–3

TABLE OF ANALYTICAL CONDITIONS

| Element | Wave length | Slit width | HC lamp current (mA) | Ashing & Atomising Conditions Ashing (stepwise heating) | Atomising (stepwise heating) |
|---|---|---|---|---|---|
| As | 193.7 | 0.6 | 6 | 300°C 20 sec | 2100°C 45 sec. |
| Fe | 248.3 | 0.2 | 8 | 500°C 20 sec | 2300°C 45 sec. |
| K | 766.5 | 0.5 | 5 | 500°C 20 sec | 2000°C 35 sec. |
| Pb | 217.0 | 0.3 | 7 | 300°C 20 sec | 1400°C 3 sec. |
| | 283.3 | 1.0 | 5 | — | — |
| Si | 251.6 | 0.2 | 10 | 900°C 20 sec | 2700°C 5 sec. |
| Hg | 253.7 | 0.7 | 2 | — | — |

The results depict that the relationship between COD & TOC are linear and it is possible to predict the COD values by knowing the TOC values. Total organic carbon values are also important for designing the wet air oxidation & wet cracking of spent liquors. These are the new emerging recovery technologies which have attracted a lot of attention lately.

The BOD load in effluents is mainly due to the presence of low molecular weight fractions of organic compounds. The gel chromatograms can predict the possible extent of BOD load as it fractioniates the various components of the effluent sample. The ones having higher proportion of low molecular weight fractions are expected to have higher BOD.

Various metallic ions are present in the spent pulping liquors originating from the raw material chemicals and material of construction of various handling equipments. These have tendency to accumulate to dangerous proportions in a closed cycle system in a mill. Non process elements like Iron, Chromium, Manganese Potassium, Mercury, Aluminium etc. are commonly present in spent liquors. In the ferrite chemical recovery process or DARS, which uses mineral haematite ore can carry a number of other non-process elements, which are derogatory to the various paper mill operations. Conventional volumetric and gravimetric methods are not only very time consuming but their accuracy for small concentration of these ions is also uncertain. The modern Atomic Absorption

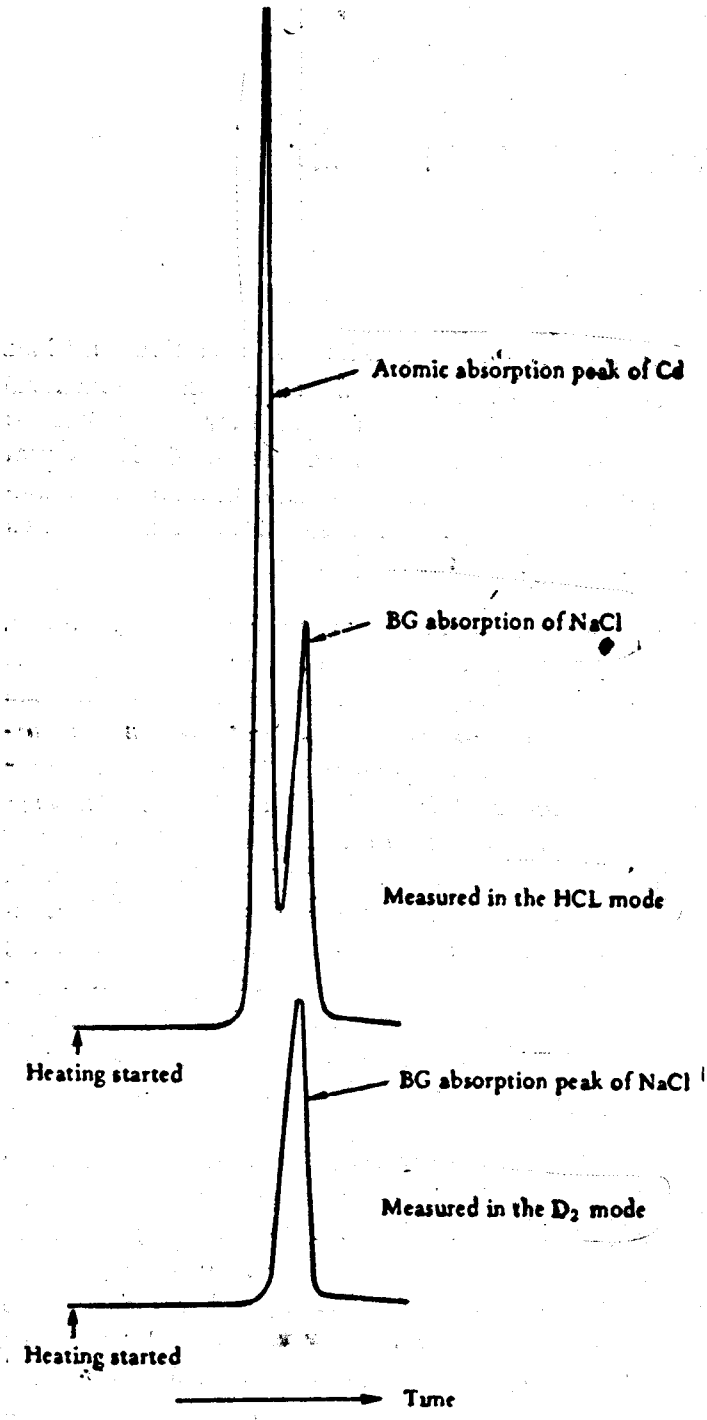


Fig 6 ATOMIC ABSORPTION PEAK OF CADMIUM IN PRESENCE OF SODIUM CHLORIDE

Spectroscopy is an invaluable tool in determining several metallic ions in minute concentration with high degree of precision. Flame emission and atomic absorption spectroscopy are complementry techniques which are both used in the system at the CPPRI laboratory. A graphite furnace is used to raise the temperature upto 3000°C for excitation and conversion of metallic elements to atomic vapours.

The table 3. depicts the conditions to be maintained in case of some of the metal ions of interest. Fig. 6 shows the peak obtained in case of cadmium when present along with Nacl. All other metal show similar peaks when required conditions of wave length, slit width, HC lamp current etc. are maintained.

Computrised Ionmeter uses various electrode to measure the concentration of ions like sulphide, chlorides, fluorides etc. These results are important for furnace design & for pollution control, Dionex Ion exchange system, based on the principle of HPLC is being used for measurement of various ions like sulphates, phosphates, chlorides, nitrates and metal ions like calcium, magnesium etc. Various organic ions like oxalates, lactates, formates can be determined. Sugars, alcohols etc can also be estimated with use of appropriate columns. All these are valuable results required for characterisation and utilisation of spent liquors and data is required to explain the various physico-chemical properties of the spent liquors.

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