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New treatment of the black liquor produced from pulping of rice straw

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ABSTRACT

Black liquor the main waste remained from paper industry composed mainly of some organic compounds as a soluble salts and a high portion of sodium silicate. The idea of this paper is to transfer the inorganic part from this waste into useful product (calcium silicate hydrate) which has a lot of known applications nowadays. The preparation of calcium silicate from black liquor was done through direct reaction between the black liquor, calcium carbonate and calcium hydroxide and boiling for about 2 hrs. This method was known as hydrothermal method. The obtained materials as well as the raw materials were investigated using both IR and XRD analyses.

Introduction

The environmental problems are more serious in small scale pulp and paper mills which lacks in infrastructure, technical manpower, research and development facilities and to top it the entire resource crunch. These small mills have poor machines and equipment with high energy consumption and more waste generation which results in high cost of conversion of raw material to paper. The major problem of small pulp and paper agro-based mills is from discharge of black liquor which contains highly polluting constituents in the form of lignin and cooking chemicals which are not recovered through chemical recovery prior to its discharge into the surface water or on land. Its discharge deteriorates the precious resource, like river water or land. The black liquor contains lignin along with pulping chemicals which is difficult to treat in effluent treatment plants (ETP) as the lignin is not easily bio-degradable. [1-3].

The black liquor consisting of water, chemicals and lignin up to 48%, resulting from washing is fed to evaporation plant where the water is evaporated. The black liquor, after water evaporation, is fed to the chemical recovery boiler where lignin is burnt and chemical (caustic) is recovered back. During the process of burning of black liquor, steam generation at 45kg/cm^2 passes through Turbine to generate power and steam at lower pressure i.e. 4Kg/cm^2 shall come out as bleed for the process i.e. evaporator. The recovered caustic, in molten form, is sent to re-causticising plant where lime, salt cake and caustic etc. are added whereby white liquor is formed, which is reused in the digester for cooking [4-6].

The loss of alkali in the un-recovered spent liquor is an economic burden because of the cost of chemicals as also for otherwise lost energy content of the spent liquor. It is possible to raise the profitability of a mill by lowering the chemicals and energy inputs to lowest levels by installing a chemical recovery plant [7, 8].

Chemical recovery plant mainly consists of the following three sections.

1. Storage and evaporation of dilute black liquor.
2. Burning of black liquor solids in recovery furnace.
3. Recovery of caustic by recausticising.

The semi concentrated black liquor from the evaporator plant is first taken to a direct contract evaporator to further concentrate to about 60 – 70 % of black liquor solids. It is then sprayed into the recovery furnace, where the black liquor gets dehydrated and drops to furnace hearth as dry solids. The combustion of organic compound of black liquor is controlled by the temperature of black liquor and air flow at primary and secondary levels. Inorganic compound come out from the bottom of furnace in the form of molten smelt. This smelt is dissolved with weak white liquor to form green liquor [9, 10].

The heat generated in combustion zone, goes in boiler zone with flue gases. In the boiler zone, steam is generated. After the boiler zone, flue gases pass through direct contact evaporator where balance heat is used to concentrate the black liquor further [11].

Green liquor is converted in to white liquor after the reaction with lime in causticising section. From causticising section white liquor (NaOH) goes to pulp mill and mud ($CaCO_3$) disposed off after its proper washing. Water comes out from mud washing is known weak white liquor. The recovery of chemicals can be as high as 98% on the total inputs of chemicals [12-15].

Experimental

Analysis of raw materials

Novel and non-polluting pulping processes suitable for rice straw are eagerly waited. Non-fibrous constituents, both hemicelluloses and lignin, could be recovered simply from waste liquors in large quantities by fractional precipitation. Results of isolation of both the organic content (lignin) and inorganic

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content (mainly sodium silicate) are considered.

Calcium silicate hydrate (CSH) was prepared by the reaction between calcium hydroxide CaOH and black liquor hydro-thermally as follows:

Solutions containing silicates were mixed with solutions containing calcium hydroxide and calcium carbonate in order to isolate calcium silicates as a precipitate, these precipitates were subjected to different analyses.

Compositions of calcium silicate hydrate (CSH) samples were confirmed by elemental analysis, IR and XRD spectra. The thermal studies were carried out using TGA-50 and DTA-50, Shimadzu Thermogravimetric analyzer (Japan), with the rate of heating 10 ^{o}C / min.

Results and discussion

Infrared spectral analysis investigation of calcium silicate hydrate (CSH) prepared from black liquor

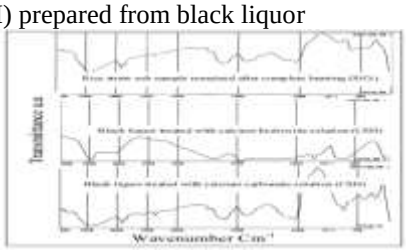

Fig 1 IR absorption spectra of calcium silicate hydrate samples

As shown in Fig. 1 the IR absorption spectra of samples prepared from black liquor, calcium carbonate and calcium hydroxide show three bands at 1100 – 1200 (broad), 800, and 463 cm^{-1} assigned to longitudinal SiO_2 lattice vibration, symmetric Si-O-Si stretching and Si-O-Si bending respectively. Weak absorption bands were also observed at 1790, 2335, and 2928 cm^{-1} which are assigned to symmetric (ν_s) and asymmetric stretching (ν_{as}) vibrations of Si-O-Si and Si-H respectively. The absorption bands at 3449 cm^{-1} are due to (νOH). The band at 1640 cm^{-1} is a combination tone due to (δOH), and the SiO_2 overtone [16]. The uniformity of the figure gives the indication that CSH prepared (with its type gained from the mode of vibration) depends mainly on the source of SiO_2 used.

Calcium silicate hydrates prepared have the same characteristic peaks at 221, 968, 1485, and 3427 cm^{-1} which are assigned to symmetric CaO stretching symmetric Si-O-Si stretching and Si-O-Si bending, respectively [17]. Weak absorption bands were also observed at 1790, 2335, and 2928 cm^{-1} which are assigned to asymmetric stretching vibrations respectively. Longitudinal SiO_2 lattice vibration at 454 cm^{-1} was observed as very week absorption. As can be seen from these results and from the literature some peaks disappear e.g. CaO stretching at 1410 cm^{-1} and CaO bending at 810 cm^{-1} some other peaks were shifted as CaO from 874 cm^{-1} to 810 cm^{-1} and SiO_2 from 1200 cm^{-1} to 968 cm^{-1}. Based on these changes in the IR band positions the formation of calcium silicate hydrates can be confirmed from the IR patterns. These results are similar to previous observations [18].

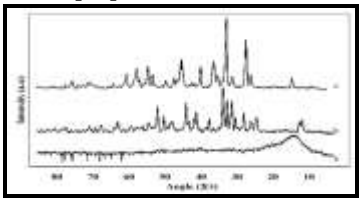

Fig 2 X-ray diffraction spectra of calcium silicate hydrate samples

Where:

a) the content of black liquor remained after complete vaporization.

b) CSH prepared from black liquor and calcium carbonates and

c) CSH prepared from black liquor and calcium hydroxide.

XRD measurements for the three samples prepared from black liquor were carried out in order to investigate the degree of change accompanied with the conditions of the reaction bath. Fig. 2 shows the result for these measurements.

The x-ray analysis of the samples prepared from black liquor with calcium hydroxide and calcium carbonate shows a similar spectrum as that of (CSH) in the literature, this means that we could decrease the viscosity of black liquor and prepare CSH which has many useful uses [19, 20].

TGA studies on silicate sample

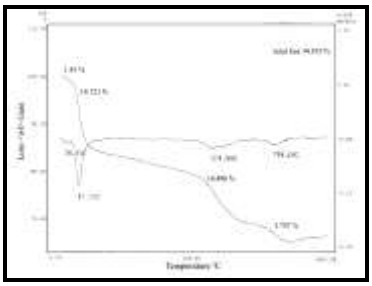

Fig 3 TGA thermograph of calcium silicate hydrate sample

The thermograph displays three stages at 38.35, 87.35 and 574.86 ^{o}C representing total weight loss 34.193 % and the remaining residue is more than 65 % from the initial weight and we can state from these results that calcium silicate can be separated from black liquor with this method.

Differential thermal analysis (DTA) of silicate sample

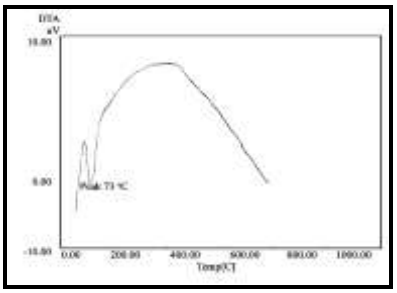

Fig 4 DTA thermograph of calcium silicate hydrate sample

Fig. 4 shows an endothermic peak at 73 ^{o}C which is due to moisture content loss, and there is no apparent peak but only the curve take the upper value all over its path, this is suggested to be due to oxidation of carbon content of the precipitated calcium silicates.

Conclusion

Using black liquor remained after pulping rice straw as well as many other cellulosic wastes for the production of paper and paper mill, according to its composition, could be used in many fields.

The newest one due to this paper is the isolation of calcium silicate as solid component from this liquor in order to reuse it in many applications and this will decrease the environmental effects.

Secondly, by using the IR and X ray diffraction analyses as well as TGA and DTA analyses for the investigation of the isolated and prepared calcium silicate are good manners as had been mentioned.

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Table 1 IR analysis of calcium silicate hydrate samples

Assignment	Si-O-Si bending	Si-O-Si stretching	SiO_2 lattice	-	H_2O bending	Si-H stretching	-	-	H_2O stretching
Calcium silicate hydrate	440	850	872	905	922	1035	1430	1490	-
Ref. data		790	1097	1650	Opal ($SiO_2.nH_2O$)				3480
1	475	621	-	-	790	-	-	1097	3429
2	471	-	-	-	787	-	-	1098	3443
3	462	-	668	-	790	-	2428	1038	3427