Role of Black Liquor Sulphidity In Dust Particles Formaion And Preventing Measures At Recovery Boilers



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ABSTRACT

Globally pulp and paper industries are moving to increase paper production and size, capacity of recovery boilers are escalating continuously as the rate of pulp production goes up. Due to the shortage of paper making raw materials the usage of twigs along with bark or without bark material for cooking is un-avoidable. It leads to poor pulping of wood species. To meet this all pulp mills are practiced to increase the sulphidity level of white liquor rather than increasing % AA addition .This causes the variation in Na_2/S ratio of black liquor and influence the flue gases and fume composition. In this research paper the role of black liquor sulphidity in dust formation has been analyzed in detailed manner and the preventive measure has been implemented at pulp mill, tertiary air port in recovery boiler at mill level.

Introduction

The primary functions of recovery boilers in pulp and paper mills are: 1) to recover inorganic chemicals; and 2) to transform chemical energy in the organic portion of black liquor to thermal energy for use in steam and power generation. In the combustion process, inorganic material is released from the fuel, incorporated into the combustion gases as both particles and vapors, and deposited on boiler surfaces or sometimes escapes to atmosphere. The energy efficiency, pulping capacity, and availability of kraft pulp mill recovery boilers are often limited by the ubiquitous problem of excessive deposit formation in the convection pass. Heat transfer distribution in furnaces depends in large measure on the overall quantity and thermal transport properties of the inorganic material present.

Deposit formation in the convection pass represents one of the major operation and design limitations for the boiler. Traditionally, deposition problems have been associated with two important classes of particles whose existence is readily apparent in the furnace flow: carryover particles and fume[1]. Carryover particles are generally considered to be 100 microns or greater in size and originate from black liquor droplets that burn out in flight or from entrainment of particles from the char bed at the bottom of the recovery boiler. Fume particles are less than 1 micron in diameter and form as a condensation aerosol from sodium that is vaporized during black liquor combustion.

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In recent years, several studies [2-7].have highlighted the potential importance of particles with sizes 1 to 100 microns, between the two well-studied classes, carryover and fume.

Particle Formation And Deposition Experiments

Some have reported the particle formation and deposition experiments by using multi fuel combustion chamber[8]. For this investigation, a new char bed burning facility was designed[9] as per Lien. The main section of the reactor was enclosed in a cylindrical furnace, allowing experiments to be performed with the char bed preheated to 1000 °C. The reactor shell was fabricated from stainless steel and the char and smelt were contained in a highdensity alumina crucible. The gas supply was mixed and heated in a separate gas pre-heater before entering the reactor. The gas was delivered through a nozzle or diffuser-type head several centimeters above the initial surface of the char bed. The char was prepared within the alumina crucible by pouring 400-800 ml of 65-70% d.s. black liquor into the cool crucible and then slowly heating it up to 1000 °C over the course of three hours, with a nitrogen purge of the reactor vessel. At the end of this char formation process, the gas mixture into the reactor was changed to O_2/N_2 with a prescribed oxygen level and char combustion commences.

10 different black liquors were investigated in this study. During char combustion, the char surface temperature is measured with a two-color pyrometer. The reactor exhaust gas flows to a hot cyclone with a bottom size cutoff of 5 µm, a gas cooler, and then to a micropore fume filter. A wet impinger is plumbed in parallel to the fume filter to collect hydrocarbons and tars evolved during the char formation process and to collect any overburden of fume produced during the char combustion experiments. The outlet gas composition (O_2, CO_2 and CO) is measured with standard continuous emission monitors to determine the rate of char combustion. The dust and fumes was collected for different S/Na_2 ratio black liquor.It was observed that black liquor which have high S/Na_2 ratio produce more amount of dust and fumes .

Black Liquor composition

Table -1 shows the black liquor elemental composition for a typical open cycle kraft process.Table-2 shows the black liquor sulphidity

Table: 1 Black liquor composition

Sl No.	Elements	% Dry Solid
1	C	38.0
2	H	3.6
3	O	32.0
4	N	0.1
5	S	5.0
6	Na	20.0
7	K	0.5
8	Cl	0.1
9	Others Ca, Si, Fe	0.7

S/Na_2 = 0.359

Table: 2 Black liquor S/Na_2

Black Liquor	1	2	3	4	5	6	7	8	9	10
sample Black liquor sulphidity	3	4	5	6	7	8	9	10	11	12
S/Na_2	0.34	0.45	0.54	0.67	0.78	0.87	0.98	1.02	1.23	1.34

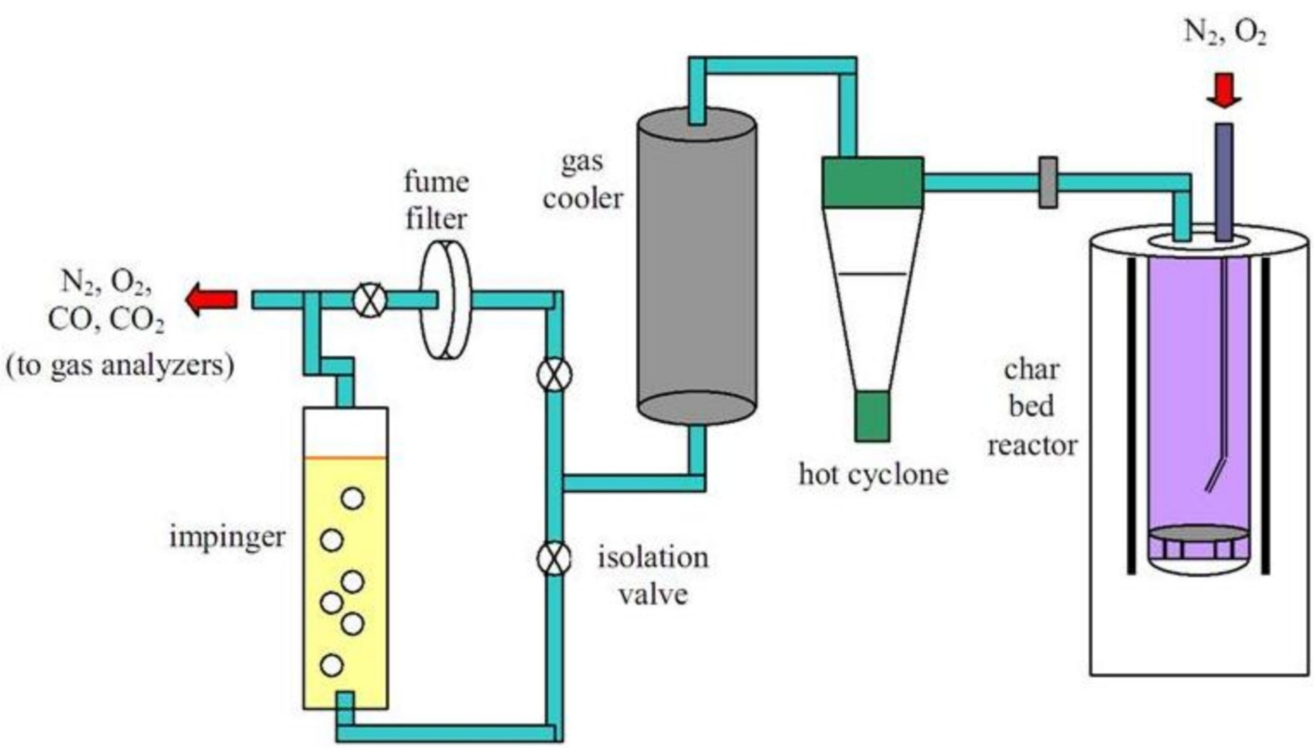


Figure: 1 Schematic diagram of char bed combustion facility, with particulate sampling and collection system.

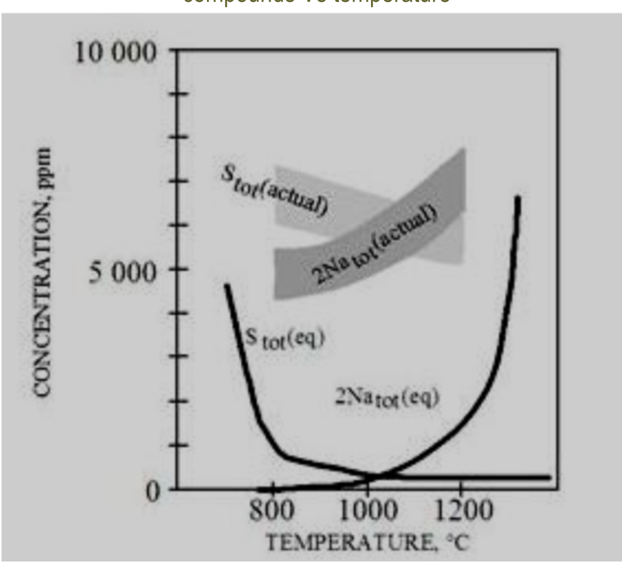
Result and Discussions

In an ideal recovery boilers process, all sulfur and sodium compounds would be transformed to sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3). The molar ratio of sodium to sulfur in black liquor determines the chemistry of sulfur and sodium in the flue gas of recovery boiler. From table 2 the variation in sulphidity leads to increase in variation sulfur to sodium ratio from 0.34 to 1.34.it was observed from the combustion character of black liquor that the carry over particle and fumes are more collected when the sulfur to sodium ratio varied from 0.64 to 1.34 and severe dust and fumes formation observed when the sulfur to sodium ratio exceeds one.

Plant Trial

Plant trail was conducted in a 200 tpd recovery boiler burning with 60-70% total solids. The black liquor having S/Na_2 ratio 0.98 supplied from the pulp mill where barked eucalyptus hybrid wood was used as a raw material. In the lower furnace, part of the sodium and sulfur is transferred into flue gases and does not return to the char bed. The most important sulfur compounds in the combustion gases are H_2S and COS.For sodium, the most important sodium compounds in the combustion gases are Na and NaOH.The main factor controlling the vaporization of sulfur and sodium compounds is temperature.

Fig No: 2, Vaporization of sulfur and sodium compounds Vs temperature



The figure.2 shows that the concentration of gaseous sodium compounds increases sharply with increasing temperature while the concentration of sulfur compounds decreases with increasing temperature. These two trends strongly affect flue gas and fume chemistry. The increasing and decreasing trends with rising temperatures for sodium and sulfur respectively have also been observed in operating boiler. It is generally known that when a boiler is operated at a low temperature the flue gases contain higher concentrations of sulfur gases. The low temperature may be due to low heat value of black liquor. From the field observations the amount of fine sulfate dust collected in the electrostatic precipitator was in the range of 12-18 grams per standard cubic meter of flue gas, equivalent to a total sodium concentration in the lower furnace of 4000 to 7400ppm.

Sodium was vaporized in the early phases of combustion, during pyrolysis. Char burning stage released a significant amount of sodium. Sulfur releasing mechanism entirely different than sodium. In an unoxidized liquor sulfur in the form of sulfide. This sulfur reacts with the liquor organic material releasing various mercaptans

Under the reducing conditions in the lower furnace, sulfur occurs in the form of hydrogen sulfide. Sodium occurs mainly as metallic sodium and sodium hydroxide .When the lower furnace gases rise to the upper furnace and their combustion was completed.

Preventive measure at Recovery boiler

The oxidation of hydrogen sulfide into sulfur dioxide takes place at the tertiary air level. The completeness of this reaction depends only on the efficiency of mixing the air with combustion gases .Any hydrogen sulfide not oxidized at this point will not be oxidized later on the cooling flue gases. Hydrogen sulfide reacts with sodium compounds yield sodium sulfate. To minimize the dust and fume generation secondary and tertiary air ratio was altered. Tertiary air was increased as 35% in total air supplied. Reduction in dust and fume formation was observed and the quantity collected in electrostatic precipitator was quantified that the amount of fine sulfate dust collected in the electrostatic precipitator was in the range of 6-9 grams per standard cubic meter of flue gas. Sulfate flew away and deposited around the recovery boiler area was absent.

Conclusion

Avoid cooking of wood with bark. It is only suitable for NSSC pulping where the cleanliness of pulp is not a matter because the NSSC pulp used only for making corrugated boards. S/Na_2 ratio affects the flue gas chemistry. Black liquor properties were mainly depending on the white liquor components. Increasing black liquor sulphidity causes variation in S/Na_2 ratio. This leads to the incomplete combustion and the formation of dust and fume particles. It can be eliminated by reducing the black liquor sulphidity, increasing the total solid content and finally increasing the tertiary air supply.

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