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EMISSION OF NON-CONDENSABLE GASES FROM A PULP AND PAPER MILL – A CASE STUDY

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ABSTRACT

In India nearly 40% of paper production is by big mills using sulfate process of cooking with emission of malodorous Non- Condensable gases such as methyl mercaptan, dimethyl sulphide, dimethyl disulphide and methanol. Most of the mills are in the vicinity of residential areas, so this odour source is a matter of great nuisance and no mentioned work has been done for the quantification, reduction and control of these gases. As per the literature these gases are highly toxic and affect the central nervous system. Though till date we don't have any limits on these malodorous gases, there will be growing resistance from public and NGO's in future for which industry will have to take appropriate steps. In this paper an attempt has been made for the quantification of these Non-Condasable gases from a mill based on hardwood and reduction in the malodorous gases due to the use of wet scrubber. The main aim of this study was to quantify amount of TRS gases so they can be completely reduced either by incineration or by other means.

INTRODUCTION

The Non-condensable gases like methyl mercapton (CH_3SH), dimethyl sulfide ($CH_{35}CHa$) and dimethyl disulphide ($CH_3S_2CH_3$) are formed through reactions between methoxyl groups of dissolved lignin and the hydroxyl ion present in the cooking liquor. During cooking methyl mercapton is formed and then dimethyl sulphide and dimethyl disulphides are formed.

Dimethyl sulphide is initially formed through the reaction of methyl mercaptide ion with the methoxy lignin component of the wood. Disproportion of methyl mercapton ion also results in the formation of dimethyl sulphide whereas formation of dimethyl disulphide takes place throughout the recovery system especially in the oxidation tower.

The mixture of hydrogen sulphide and mercaptants are responsible for the characteristic odor of Kraft process.

Hydrogen sulphide is formed in the stock washing and black liquor storage at the time when the pH of the black liquor decreases, however hydrogen sulphide is not formed during cooking this is due to the high pH value i.e., 7.0, but high amount of hydrogen sulphide is generated during black liqor evaporation because of the lowering of pH value. Formation of hy-

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drogen sulphide is also reported at the time of pyrolysis at the lower part of recovery boiler. A large amount of hydrogen sulphide is formed due to the reactions between water vapor from shatter steam jets and the presence of carbon dioxide.

MATERIALS AND METHODS

The BIS does not lay down any specific method (except for hydrogen sulphide) for the determination of these Non-Condensable gases till date. A method based on the absorption of methyl mercapton in a solution of mercuric acetate has been laid down by the American Society of Testing Materials- ASTM-D 2913-96 (3). However due to the non-availability of the standard compound (lead methyl mercaptide) problems are faced with this method, also this method does not quantify the individuals reduced sulfurs. Moreover, the methods given by BIS for hydrogen sulphide and ASTM for methyl mercaptan are only for the ambient air and there is no method available for stack sampling and analysis.

The three steps of every odor control solution are monitoring, data analysis and treatment. In this study we were involved in the monitoring. For this study detector tube method was used due to advantages over above methods. The GASTEC Model GV-100, gas sampling pump provided by Kangava 252-1103, Japan, was used for the study. The detector tubes for different Non-Condensable gases were also provided by the same company. For the dilution of gases, Gas sampling bags and syringe of 50 mL were used. Proper care had been taken while sampling of Non-Condensable gases to get rid off condensate by using condenser along with ice. Pyrotec pyrolyzer was used for the determination of dimethyl sulphide along with dimethyl disulphide.

RESULTS AND DISCUSSION

The study was done to determine following parameters viz. methyl mercaptan, dimethyl sulphide and dimethyl disulphide (co-reported), hydrogen sulphide and methanol. The determination of dimethyl sulphide and dimethyl disulphide was done with the help of pyrotec pyrolyzer kit.

Location of Sampling

The aim of this study was to evaluate the amount of total sulfur emitted from three main sources and reduction in the amount of Non-Condensable gases due to the use of wet scrubber. The points were;

1. **Evaporator Vent**

a. Evaporator surface condenser without scrubber
b. Evaporator surface condenser with scrubber

2. **Digester degassing**

a. Digester degassing without scrubber
b. Digester degassing with scrubber

3. **Digester degassing**

a. Digester blow after 2 minutes of blow
b. Digester blow after 4 minutes of blow

The study of NCG's was done at three different locations at different conditions. The results of study are tabulated in Table 1. The results of this study are discussed below:

1. Evaporator Vent

A. Evaporator surface condenser without scrubber

At this point dimethyl sulphide along with dimethyl disulphide was reported as 48,000 ppm while methyl mercaptan was found as 43,200 ppm and hydrogen sulphide was found as 22,500 ppm, while methanol was absent because of the type of the raw material used.

b. Evaporator surface condenser with scrubber

The objective of this study was also to crosscheck the viability of wet scrubbing of NCG's using alkaline liquid as scrubbing medium. It was found that there was reduction in the amount of all types of NCG's around 90%. The results of this location shows dimethyl sulphide along with dimethyl disulphide as 2500 ppm as compared to 48,000 ppm without scrubbing, concentration of methyl mercaptan was 4025 ppm while hydrogen sulphide was reported as 1850 ppm, The results at this location clearly reflects the advantage of wet scrubbing.

2. Digester degassing

A. Digester degassing without scrubbing

Monitoring of non-condensable gases was also performed at this location of all the parameters reported at earlier point. It was found that amount of dimethyl sulphide along with dimethyl disulphide is very much on lower side as compared to the evaporator vent and reported as 7500 ppm, concentration of methyl mercaptan was also on the lower side and recorded as

2937 ppm, while hydrogen sulphide was found as 4400 ppm, methanol was absent at this point.

B. Digester degassing with scrubbing

The results of this location after wet scrubbing are quite low and give weightage to the use of wet scrubber with alkaline medium. Concentration of dimethyl sulphide along with dimethyl disulphide was reported as 1000 ppm, while methyl mercaptan was completely reduced and reported in the not detectable range, whereas hydrogen sulphide was found in the range of 250 ppm, methanol was also found in the not detectable range.

3. Digester blow

To observe the change in the concentration of non-condensable gases during the blow, two samplings were done, one was done after two minutes of blow and another was done after 4 minutes of digester blow.

Comparison of results of digester blow recorded at different time intervals

The results of this study at this location shows that there was increase in the concentration of dimethyl sulphide along with dimethyl disulphide in the second sample i.e. after 4 minutes of digester blow and recorded as 35,000 ppm as compared to 17500 ppm

Table 1. Status of non-condensable gases and effect of wet scrubber

S.No.	Locations	Parameters Studied			
		H_2S	CH_3SH	$(CH_3)_2S$ & $(CH_3)_2S_2$	CH_3OH
1.	Evaporator vent from surface condenser without scrubber	22,500	43,200	48,000	N.D.
2.	Evaporator vent from surface condenser with scrubber	1850	4025	2500	N.D.
3.	Digester degassing without scrubber	4400	2937	7500	N.D
4.	Digester degassing with scrubber	250	N.D.	1000	N.D
5.	Digester blow after 2 minutes of blow	1050	9650	17,500	N.D.
6.	Digester blow after 4 minutes of blow	700	2000	35,000	N.D.

Note: All values are in ppm, N.D.: Not detected

Table 2. EPA standard for non-condensable gases

S.No.	Source Point	PPM (Vol.)	Condition
1.	Recovery furnace-old construction design (without welded wall or membrane wall construction or emission -control design air system).	20	12 hour average-corrected to 8% oxygen by volume.
2.	Recovery furnace-new design (with both welded wall and membrane wall construction or emission control designed air system).	5	12 hour average-corrected to 8%oxygen by volume.
3.	Lime kiln (a rotary or flu solid unit used to calcine calcium carbonate into calcium oxide).	20	Never to be exceeded-corrected to 10 % oxygen by volume
4.	Digester systems (condition or batch process for cooking wood chips in sodium hydroxide and sodium sulfide to produce cellulosic material).	5	Never to be exceeded
5.	Multiple effect evaporator system (Vapor heads, heating elements, hot wells, condensers and associated equipment used to concentrate spent pulp mill cooking liquid).	5	Never to be exceeded
6.	Smelt dissolving tank (the vessel used to produce an aqueous solution from the molten mixture discharged from the floor of a recovery furnace).	20	Never to be exceeded

Source : Downloaded through internet from the federal register online via GPO access (wais.access.gpo.gov) vol. 64, number 207, rules and regulations. 1999.

recorded just after two minutes of blow, while there is decrease in the concentration of methyl mercaptan and hydrogen sulphide collected after 4 minutes of blow. Methyl mercaptan was recorded as 9650 ppm in the first sample but it was only 2000 ppm in the second sample. Methanol was absent at this point also.

Control technologies of non-condensable gases

There are various technologies available for the control of non-condensable gases in the developed countries, but they are not feasible in India because of the size of paper mill and type of raw materials.

In the developed countries all the concentrated along with diluted NCG's containing reduced sulfur compounds are treated by collecting the gases into sealed systems and eliminating these malodorous compounds by converting them into non-odorous forms.

As per the literature the most efficient way for the treatment of these NCG's is thermal oxidation and lime kiln is the suitable choice for the thermal oxidation of concentrated NCG's.

In some literature use of recovery boilers for the burning of these malodorous gases are also reported.

Wet scrubber with alkaline medium are also frequently used for the reduction of non-condensable gases at different NCG's emissions sources like lime kilns, evaporator vents, digester degassing etc.

CONCLUSION

The problem of NCG's is a common problems for almost all the big mills using Kraft pulping. EPA has already submitted plan by the commonwealth of Pennsylvania for the purpose of controlling total reduced sulfur emissions from existing Kraft pulp mills. The plan was submitted to fulfill the requirement of the clean air act. EPA has already given emission standard for five source points i.e., recovery furnace, lime kilns, digesters, evaporators and smelt dissolving tanks tabulated in Table 2.

EPA has also recommended that these non-condensable gases are to be monitored continuously at the recovery furnace, digester systems, and multieffect evaporator unless emissions are incinerated at 12000F. Seeing the health effect of these malodorous gases sooner or later Central Pollution Control Board, New Delhi, will have limits on these non-condensable gases. As reported in some literature hydrogen sulphide causes headache, nausea, eye-nose-throat irritation. Hydrogen sulphide can cause respiratory and eye injury. Hydrogen sulphide is also corrosive to metals like iron, steel, copper and cement. The control of these gases are required immediately to provide healthier and aesthetic environment and three ingredients like monitoring, data analysis and treatment to control every odor are to be followed.

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