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Monitoring and Assessment of Heavy Metals In Agriculture Waste Used In Combustion Process

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ABSTRACT

The concentration of heavy metals like chromium, cadmium, mercury, arsenic, cobalt, copper, nickel, zinc, manganese, vanadium and lead has been analyzed in pre and post combustion process using ICP-AES technique for three seasons with the ambient air analysis and flue gas analysis. In the raw biomass the concentrations of Zinc and manganese were found in amplified whereas after combustion process that is in the fly ash the concentrations of zinc, manganese with cobalt and copper also found in higher state.

Keywords: Monitoring, Heavy Metals In Agriculture Waste, In Combustion Process.

INTRODUCTION

Industrialization and urbanization has led to rapid increase in energy demand. Power is the most important factor that influences economic development of the nation. With depleting fossil fuels, the renewable source of energy has gained importance world over. Biomass and waste –based renewable energy technologies can take a key role in combating global warming and other problems associated with fossil fuels [1]. Man’s activities through industrialization, urbanization, technological development and agricultural activities discharge heavy metals into the environment; water, land and air which has become a matter of concern over the past few decades, due to the characteristics of metals to cause objectionable effects by impairing welfare and reducing the quality of life in the environment [2]. Agri-residue has traditionally been a handy and valuable source of heat energy all over the world in rural as well as the sub urban areas. In spite of rapid increase in the supply of, access to and use of fossil fuels, agri-residue is likely to play an important role in developing countries in general and India in particular, in the foreseeable future. The agri-waste, like rice-straw, saw-dust, sugarcane-trash, coir-pith, peanut -shells, wheat-stalks and straw, cotton-seed, stalks and husk, soybean stalks, maize stalks and cobs, sorghum, bagasse and coconut husk can be fruitfully utilized in power generation.

For a comprehensive global assessment of waste biomass resources, including waste biomass generation and projection, as well as potential use and equivalent GHG reduction, please see the Report on the Global Assessment of Agricultural Biomass Waste Resources.

The major crops and waste utilized in the Compendium's technology entries are the following:

Crop	**Waste**
☐ **Coconut**	- Fronds, husk, shell
☐ **Coffee**	- Hull, husk, ground
☐ **Corn**	- Cob, stover, stalks, leaves
☐ **Cotton**	- stalks
☐ **Nuts**	- Hulls
☐ **Peanuts**	- Shells
☐ **Rice**	- Hull/husk, straw, stalks
☐ **Sugarcane**	- Bagasse
☐ **Agricultural Crops**	- Mixed agricultural crops, not limited to crop waste
☐ **Mixed type**	- Agricultural crops and waste including on-organic wastes

Due to improper sewage collection system, percolation of surface water and seepage to nearby ground water wells leading to environment pollution leading to degradation of surface and ground water used for agriculture which is containing heavy metals like As, Cd, Cr, Fe, Hg, and Pb have been reported as potential pollutants of both sources of water [5]. Depending on the chemical composition of the biomass and appropriate combustion process used to generate electricity may lead in generation of fly ash with major ash forming elements (Al, Ca, Fe,K,Mg, Na, P and Si) are of relevance for the ash melting behavior and deposit formation and volatile forming elements such as Cl, S,Na, Cd, As, Pb, Hg and Zn[6]. The others reported on this type of work [7-16].

MATERIALS AND METHODS

Proximate Analysis: Proximate analysis included Determination of moisture to check the loss in weight of solid waste by heating of weighted quantity of sample for an hour at 105 ^{0} C, volatile matter to check the loss in weight of moisture powder solid waste in muffle furnace at 950 ^{0} C for 7 min, ash to know the residue obtained after burning a weighted quantity of sample in an open crucible at 750^{0} C in a muffle furnace and fixed carbon which is sum total of moisture, volatile matter and ash percentage from 100. The achieved results of the proximate analysis are given in table 1.

Table 1

SNo.	**Characteristics**	**Values (%)**
1	Moisture content	4.60
2	Volatile Matter	58.90
3	Ash content	10.30
4	fixed Carbon	26.20
5	GCV	3462.00 k.cal \kg
6	PH	8.92
7	Carbon	46.56
8	Hydrogen	3.94
9	Sulphur	0.50
10	Oxygen	38.30
11	mineral matter	10.70

Ultimate Analysis: Determination of total carbon and hydrogen by burning of sample in dry oxygen and converting C and H of sample into CO_2 ($C + O_2 = CO_2$) and H_2O ($H+½O_2 = H_2O$) respectively and passing this in over weighted tubes of anhydrous calcium chloride and potassium hydroxide which absorbs H_2O and CO_2 respectively increase in $CaCl_2$ tube represents the weight of water (H_2O) formed while increase in the weight of KOH tube represents the weight of CO_2 formed, nitrogen by using Kjeldahal's method, oxygen and sulphur percentage in solid waste by burning the sample in bomb calorimeter in a current of oxygen. The obtained results are shown in table 1.

Analysis of Heavy Metals Using Icp-Aes: For Sample preparation followed wet digestion procedure. Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned to minimize the potential of cross-contamination. For each Digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed. For the digestion of samples for analysis by AAS or ICP, add 10 mL of 1:1 HNO_3 and10 mL of 1:1 HCl mix the slurry, and cover with a watch glass or vapour recovery device. Heat the sample to 95◦C ± 5◦C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the cover, and reflux for 30 min. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapour recovery system, either allows the solution to evaporate to approximately 5 mL without boiling or heat at 95◦C ± 5◦C without boiling for two hours.

Maintain a covering of solution over the bottom of the vessel at all times. After the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapour recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence heat, until effervescence subsides and cools the vessel. Continue to add 30% H_2O_2in 1mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total of 10 mL 30% H_2O_2. Cover the sample with a ribbed watch glass or vapour recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95◦C ± 5◦C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times. Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95◦C ± 5◦C in 6 minutes and remain at 95◦C ± 5◦C without boiling for 10 min. After cooling, dilute to 100 mL with water. Particulates in the digestate should be removed by filtration, or by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by AAS or ICP-AES.

RESULTS AND DISCUSSION

General Characteristics of Biomass

Physical analysis of the biomass (Agriculture waste): The proximate and ultimate analysis and the calorific value of the agro residues studied are included in table 1. As it can be seen, these agriculture wastes are characterized by low ash content and high combustibles content, indicating a good quality for these fuels. Also, sulfur content is very low, revealing that SO emissions during combustion are not of concern. The calorific value is considerably higher than that of most low rank coals.

Physical Characteristics Of Biomass Ash: The analysis of biomass ash after combustion studied is included in table 2. As it can be seen, these agriculture wastes are characterized by low ash content and low combustibles content indicating no re-burning capacity until it is mixed with some other material like using the ash content in brick manufacturing unit where it is mixed with sand, clay and other and burned in kiln for preparing bricks.

Table 2

SNo.	characteristics	values
1	Moisture content	1.40 %
2	Volatile Matter	0.90 %
3	Ash content	96.40 %
4	fixed Carbon	1.30 %
5	GCV	124.00 kcal./kg
6	PH	9.39
7	Carbon	1.50
8	Hydrogen	0.32
9	Sulphur	0.08
10	Oxygen	0.30
11	mineral matter	97.80

Heavy Metals Concentration in Different Seasons

Summer Season: The concentration of heavy metals during pre and post combustion in summer has been estimated and presented in the table 3

Table 3. Heavy metals during pre and post combustion process of agriculture waste

SNo	Heavy Metals	Pre combustion agri waste (ppm)	Post combustion agri waste (ppm)
1	Cadmium	<0.1	<0.1
2	Cobalt	2.6	18.6
3	Cromium	1.1	3.8
4	Copper	4.9	22.3
5	Arsenic	<0.1	<0.1
6	manganese	32.6	118.4
7	Nickel	1.3	6.9
8	Lead	5.3	28.4
9	Zinc	22.9	293.1
11	Mercury	<0.1	<0.1
12	Vanadium	4.1	28.6

The table shows that the concentration of heavy metals during pre combustion in summer was very low and highest concentration is observed in manganese at 32.6 ppm, zinc at 22.9 ppm, whereas lead at 5.3 ppm, copper at 4.9 ppm and vanadium at 4.1 ppm are at lower side of concentration. The zinc concentration abnormally increased from 22.9 ppm in pre combustion to 293.1 ppm in post combustion, manganese from 32.6 to 118.4, copper from 4.9 ppm to 22.3 ppm, lead from 5.3 to 28.4.

Winter Season: The concentration of heavy metals during pre and post combustion in winter has been estimated and presented in the table 4

Table 4. Heavy metals during pre and post combustion process of agriculture waste

Sl.No.	Heavy metals	Pre combustion agri-waste (ppm)	Post combustion agri-waste (ppm)
1	Cadmium	<0.1	<0.1
2	Cobalt	2.2	14.1
3	Cromium	0.8	1.6
4	Copper	3.2	17.6
5	Arsenic	<0.1	<0.1
6	manganese	27.6	98.4
7	Nickel	1.9	7.2
8	Lead	6.2	32.4
9	Zinc	29.6	342.8
10	Mercury	<0.1	<0.1
11	Vanadium	5.6	38.6

The table shows that the concentration of heavy metals during pre combustion in winter was very low and highest concentration is observed in manganese at 27.6 ppm, zinc at 29.6 ppm, and concentrations of copper at 3.2 ppm, nickel at 1.9 ppm and vanadium at 5.6 ppm which are at lower side. The zinc concentration abnormally increased from 29.6 ppm in pre combustion to 342.8 ppm in post combustion, manganese from 27.9 ppm to 98.4 ppm, lead from 6.2 ppm to 32.4 ppm, vanadium from 5.6 to 38.6. The concentration of majority the elements has been increased. On the contrary, the concentration of arsenic, mercury and cadmium didn't change but static at < 0.1 ppm.

Monsoon Season: The concentration of heavy metals during pre and post combustion in monsoon has been estimated and presented in the table 5.

Table 5. Heavy metals during pre and post combustion process of agriculture waste

SNo	Heavy metals	Pre combustion agri waste (ppm)	Post combustion agri waste (ppm)
1	Cadmium	<0.1	<0.1
2	Cobalt	1	8.6
3	Cromium	0.1	0.4
4	Copper	2.8	14.6
5	Arsenic	<0.1	<0.1
6	manganese	18.9	76.4
7	Nickel	2.2	9.8
8	Lead	4.1	24.1
9	zinc	21.2	246.2
11	mercury	<0.1	<0.1
12	Vanadium	3.6	27.4

The table shows that the concentration of heavy metals during pre combustion in monsoon was very low and highest concentration is observed in manganese at18.9 ppm, zinc at 21.2 ppm. The concentration of other elements is rather low. The copper concentration abnormally increased from 2.8 ppm in pre combustion to 14.6 ppm in post combustion, zinc from 21.2 ppm to 246.2 ppm, lead from 4.1 ppm to 24.1 ppm, manganese from 18.9 ppm to 76.4 ppm and vanadium from 3.6 ppm to 27.4 ppm. On the contrary, the concentration of arsenic, cadmium and mercury reminded unchanged at < 0.1 ppm.

Ambient Air Monitoring: Ambient air analysed in the biomass power plant in different locations are shown in the table 6 for 3 seasons.

Table 6. Ambient Air monitoring during three seasons

	Summer Season			**Winter season**			**Monsoon season**		
Location	**Near main gate**	**Near admin building**	**Near fuel yard**	**Near main gate**	**Near admin building**	**Near fuel yard**	**Near main gate**	**Near admin building**	**Near fuel yard**
Total suspended particulate matter (ug/m^3)	162	153	174	146	155	174	154	159	167
Sulphur dioxide concentration (ug/m^3)	10	12	08	11	08	07	08	13	06
Oxides of nitrogen (ug/m^3)	14	16	11	14	12	10	13	16	09
Respirable particulate matter concentration (ug/m^3)	57	48	68	43	56	72	49	55	70

The ambient air monitoring in the biomass based power plant in all the season are as per the standards given by regulatory authority and there are no variations seen in the reading which can affect the area surrounding the plant.

Stack Monitoring Data: The flue gases are analysed which is let out to the environment from the stacks how in table 7

Table 7

Particulars	**Summer season**	**Winter season**	**Monsoon season**
Suspended particulate matter (mg/Nm^3)	79	76	74
Sulphur dioxide (mg/Nm^3)	22	20	20
Oxides of nitrogen (mg/Nm^3)	34	28	29

The flue gases analysed in the biomass based power plant for the three seasons which are also as per the standards given by regulatory authority. This is achieved due to proper treatment of flue gases in Air Pollution Control Equipment (APCE) ie., Electrostatic precipitator and proper monitoring of the system by interlocking the ESP when it is not in work automatically the functioning of boiler stops by which the electricity generations also comes to stagnant.

The results show that the heavy metals in all the three seasons varies due to many reasons like: as to grow any crop macro and micro nutrients are supplied to crop as there are essential for the growth and good yield of the crop, due to soil texture the ability to absorb heavy metals increases, when the crop is grown surrounded by any industrial area then the chance of heavy metals entering in is possible, growing a crop in waste water is also one of the reasons for heavy metal presence, There is an inherent tendency of plants to take up toxic substances including the heavy metals, that are subsequently transferred along the food chain. Use of polluted land or water for cultivation of crops mainly accounts for decrease in the overall productivity and results in contaminated food grains and vegetables which adversely affects human health. The main advantage associated with study of plants including crops, is their ability to accumulate metals, if grown on metal polluted land or irrigated with polluted water. Thus, plants serve as a good tool for phytoremediation apart from this due to the technique applied to convert waste into energy is one of the causes for increase in the heavy metal in the post combustion and also due to use of coal as a support fuel for increasing the Gross Calorific Value can also cause the heavy metal increase after combustion.The highest change is observed in case of cobalt, manganese, zinc, lead and vanadium. On the contrary, there is no change in case of cadmium, arsenic and mercury which may be due to less existence in the areas where the biomass waste is selected for use in waste to energy process.

APPLICATIONS

This study is useful to assess the heavy metals which are present in bio-waste materials using for combustion and to suggest whether harmful or not due to presence of heavy metals.

CONCLUSIONS

The highest change is observed in case of chromium, copper and nickel. On the contrary, there is no change in case of cobalt, arsenic and mercury. There is an abnormal increase in cobalt, zinc, manganese, lead and vanadium in pre and post combustion process in all the seasons comparatively.

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