VOLATILE PRODUCTS AND TRACE METALLIC ELEMENTS DURING DRY DISTILLATION IN PAKISTANI COALS

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ABSTRACT: *The harmful trace metallic elements were investigated in two Pakistani coals (Lakhra & Hyderabad coal). Metals include silver, chromium, copper, lead, selenium, arsenic, nickel were determined by atomic absorption spectrophotometer. The dry distillation of these coals was performed recovering the low volatiles and heavy tar compounds. These coals contained significant amount of silver, arsenic, nickel, copper and lead. The GC-MS analysis of low volatiles showed the presence of organic acids, urea, phenols, and benzene types of compounds. It was observed that the harmful metals were present in low concentrations suggesting their suitability for direct industrial applications without effecting the* environment.

Key Words: Trace metals, Pakistani coals, Dry distillation, GC analysis, Spectrophotometer

INTRODUCTION

The estimated coal reserves in Pakistan are nearly 185 billion tones. Lakhra coal is the second largest coalfield in Pakistan with estimated deposits of 1328 million tons of coal located in Lakhra district of Sindh province. Lakhra and Hyderabad coals contain significant portion of sulfur and ash contents. Hyderabad coal is located at Hyderabad district of Sindh and contains significant portion of mineral ash and trace metals [1]. Lakhra coal and Hyderabad coals are recognized as lignite type coals containing sufficient quantity of ash and minerals. Pyrites, clays, and other organic compounds are part of coal and contain significant amount of metallic trace elements such as As, Cd, Hg, Cr, Ni, Pb and Se [2]. There are eleven elements including Hg, Pb, Cd, As, Sb, Ni, Co, Mn, Cr, and Be added in list of harmful metals under clean air act [3,4]. The presence of trace elements is expected to pollute environment during coal combustion and gasification processes.

The present study includes the estimation of metallic trace elements and products of dry distillation from the samples of coal and its possible implications on the environment. The proximate analysis of coals and their composition analysis for determination of specific compounds were investigated. The trace metallic elements in the samples chromium, copper, iron, and silver contents in coal samples were analyzed.

EXPERIMENTAL METHODOLOGY

Gross representative samples, weighing 40 kg each were collected from the stockpiles of Lakhra and Hyderabad coal reserves in the form of 3-4 inches coarser lumps with the help of mining engineers working at the respective mines according to ASTM method (D2234). The collected samples were stored in air tight bags. Samples were crushed by hammer crusher and were ground in an end roller mill (D2013). Then each sample was passed through 100 meshes (250 µm) following the standard procedure (D293-93). Ultimate analysis was carried out for determination of carbon, hydrogen, nitrogen, oxygen, and sulfur (D3176) . Proximate analysis was carried out to determine moisture, ash, volatile matter, and fixed carbon (D3172). Gross calorific value was determined by bomb calorimeter ((LECO AC 500)

To separate volatile and semi volatile organic compounds present in coal, 100g of prepared coal samples (Lakhra and Hyderabad) were first dried in an oven at 105°C for 1 hour, then dry distillation was performed in absence of air. As a result solid (residue), liquid/solution (ammonical solution, coal tar) and gas (coal gas) was obtained. Distillate (coal gases and liquids) was analyzed using gas chromatography-mass spectrometry (GCMS) (Agilent Technologies, USA). For identification of organic compounds, fractions of coal distillate were separated by using separating funnels. Condensed liquids were allowed to settle down into layers; upper layer of ammonical liquid and lower layer of coal tar were separated. Upper distillate fraction was directly filtered by using filtration assembly (0.2 µm pore size filter paper) while black viscous liquid fraction (coal tar) was first dissolved in ethanol, filtered and was tested in GC-MS. All of the samples were filtered in 0.45 45µm nylon filter before GC-MS analysis. GC-MS (Gas chromatography mass detector) analysis was carried out using column PAH 30 mm length 0.25 mm diameter at sample size of 2µg/mL. Temperature was ramped to 75°C (5 min), 100ºC/min (5 min), 190°C (5 min), 250°C (5 min), 360°C (3 min). Carrier gas was helium flow rate 1.5 mL/min [5].

Trace metals present in lignite were determined by atomic absorption spectrophotometer (Parkin Elmer). For this purpose 18 g of lignite and ash were treated with 4 N HCl for 1 hour and then it was filtered by using Whatman 0.45µm nylon filter paper. Acid treatment extracted metals from samples. Lignite and ash extracts were diluted 25 times (24 ml distilled water + 1 ml extract) by using distilled water. Standard solutions of silver, chromium, copper and iron of 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm were used for calibration curve for atomic absorption spectrophotometer. Metal ion concentration was determined by Eq (1).

$$\text{metal ion (ppm)} = \frac{R \times A}{wt. \times D.F} \qquad (1)$$

Where R is concentration of metal ions obtained from atomic absorption, A is the total volume of extract (mL), Wt is the weight of oven dry coal (g) and D F is the dilution factor

RESULTS AND DISCUSSION

According to proximate analysis (Table 1), the moisture contents were higher in Lakhra (13.9%) as compared to Hyderabad coal (6.2%). The volatile content, fixed carbon, and ash content for Lakhra coals were 37.92, 37.69, and 10.50% respectively. Similarly, for Hyderabad coal, volatile matter, fixed carbon, and ash contents were 30.4, 42.8, and 20.6. The calorific values were 5115.6 Kcal/kg and 5964.3 Kcal/kg for Lakhra and Hyderabad coals respectively. The composition of ash according to XRF analysis of coal is shown in Table 2. The significant amount of SiO_2, Al_2O_3, and Fe_2O_3 was present in both coals while MgO, KO and Na_2O were present in small amounts. The detailed analysis of samples indicates that both the Lakhra and Hyderabad coals belong to lignite rank.

Table 1 Proximate analysis of Lakhra and Hyderabad coal

Coal Type	Volatile matter	Ash	Fixed Carbon	Sulfur	GCV KCal/kg
Lakhra	37	10	33	5.6	5115.6
Hyderabad	30	20	50	3.7	5964.3

Table 2 Ash composition of Lakhra and Hyderabad Coal

Coal sample	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	KO %
Lakhra	41.6	15.0	17.7	5.1	1.42	0.39
Hyderabad	45.4	27.3	5.6	4.0	2.02	1.32

Results from dry distillation of Lakhra coal are shown in Table 3. The major compounds detected from GC-MS analysis were urea, phenols (phenol, 3-methyl phenol, 3-ethyl phenol, 2, 3-diethyl phenol, dioles (1, 2-bezenediol, 4-methyl 1, 2-benzendiol) and organic acids (n-hexadecanoic acid). The composition indicates that major components having low molecular weight compounds constitute the major portion of the volatile fraction. Moreover, the major part of constituents belongs to phenolic group compounds. The high concentration of phenolic constituents shows the presence of high phenolic groups in this coal [6].

Table 3 GC-MS analysis of volatile fraction of Lakhra coal

Organic Compound	Molecular mass	Formula
Urea	60	CH_4N_2O
Phenol	94	C_6H_6O
Phenol 3, methyl	108	$C_7 H_8O$
Phenol 3, ethyl	122	$C_8H_{10}O$
Phenol 2,3,dimethyl	122	$C_8 H_{10}O$
1, 2, Benzenediol	110	C_6 H6 O_2
1, 2, Benzenediol 4-methyl	124	$C_7 H_8 O_2$
1, 3, Benzenediol 4-ethyl	138	$C_8H_{10}O_2$
n-Hexadecanoic acid	256	$C_{16}H_{32}O_2$

Table 4 shows the results of dry distillation of products of Hyderabad coal. The volatile components in Hyderabad coal were not that significant compared to Lakhra possibility due to low volatile matter and high fix carbon in case of Hyderabad coal. The high carbon contents combined with high ash constituents in case of Hyderabad coal makes it a hard substance for dry distillation products [7]. The phenol derivatives were the major compounds found in volatile fraction of Hyderabad coal. From Hyderabad coal, the volatile fraction recovery was in smaller amount comparing to the fraction recovered from Lakhra coal. It may be seen from the proximate analysis of Lakhra and Hyderabad coals (Table 1) that Hyderabad coal contains low volatile matter, high fixed carbon and very high ash content. This composition makes Hyderabad coal much harder and difficult to decompose during dry distillation. Table 4 shows that major organic compounds in Hyderabad coal are phenol derivatives. It may be concluded that components in high volatile Lakhra coal are of different nature but in low volatile Hyderabad coal all organic compounds are phenol derivates. This is actually a distinct property of high volatiles and low volatile hard coals.

Table 4 GC-MS analysis volatile fraction of Hyderabad coal

Organic Compound	Molecular mass	Formula
Phenol 3, methyl	108	C_7H_8O
Phenol 4, methyl	108	C_7H_8O
Phenol 2,5,dimethyl	122	$C_8H_{10}O$
Phenol 2, ethyl 4, methyl	136	$C_9H_{12}O$
Benzyl alcohol alpha isobutyl 2,4,5 trimethyl	206	CH_4N_2O

Table 5 illustrates the metals found in Hyderabad and Lakhra coal. All of the tested metals were detected in both coal samples. The concentration of Se and Cr were high in Lakhra coal while that of Cu, Ag, Pb, and Ni were high in Hyderabad coal. The cleaning of two coals seems necessary before utilizing in combustion or gasification purposes. The metallic trace elements emissions are very common when coals are burned either alone or co-fired with biomass. There are standards formulated by international environmental agency which define limits beyond which trace elements emissions must be controlled before exposing to the atmosphere. Eleven metallic trace elements such as mercury (Hg), arsenic (As), selenium (Se), lead (Pb), and chromium (Cr) are very harmful if they exceed the specified limits [3]. There are a number of international reports which describes the harmful effects of these elements to human life and the environment [4,8]. Table 5 illustrates the metallic trace elements in Lakhra and Hyderabad coals. The quantities of trace elements have been determined by atomic absorption spectrophotometer in terms of ppm (parts per million). These quantities of trace elements are compared with international reports [9,10] which explains tolerable limits of the trace elements found in international coals. Comparing Table 5 with international reports, it may be mentioned that in Hyderabad coal the quantity of Cr, Hg, Pb, Se, and As are within acceptable limits whereas quantities of Cu, and Ni exceed the tolerable limits. In case of Lakhra coal, Cr, Pb, and As are within the acceptable limits but Cu, Se, and Ni exceed the standard limits. During the coal combustion process, some control devices may be necessary to check the release of trace elements which are beyond the acceptable limits. Measures may also be taken to clear the emissions before exposing these to the environment.

Table 5 Metals present in Lakhra and Hyderabad coals

Name of coal	Ag ppm	Cr ppm	Cu ppm	Pb ppm	Se ppm	As ppm	Ni ppm
Hyderabad	14.2	3.68	35.9	07.5	0.82	0.544	56.6
Lakhra	9.50	6.60	26.6	03.9	13.5	0.491	62.3

CONCLUSION

Two Pakistani coals were tested in this study to examine the trace metallic elements that may be harmful to the environment. The ash and volatile matter in Lakhra coal were 10% and 37% respectively and that for Hyderabad coal were 20% and 30% respectively. The calorific values of Lakhra and Hyderabad coals were nearly same 5515 K Cal/Kg and 6132 K Cal/Kg respectively. It was found that the chromium was slightly higher in Lakhra coal (6.6 mg/L) compared to Hyderabad (3.68 mg/L). The silver, iron, lead and copper were 9.5, 5250, 03.94, 26.5 mg/L for Lakhra coal and 14.25, 4345 35.9 mg/L for Hyderabad coal. The volatile products from dry distillation of Lakhra coals were significant that include urea, phenols, and organic acids. The volatile products in Hyderabad coal were similar; however, these products were low in concentration relatively. Overall, these coals were suitable that may inject low concentrations of harmful chemicals into the environment during combustion or during other relevant applications.

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