Pyrolysis–Gas Chromatography of Lakhra Coal: Effect of Temperature and Inorganic Matter on the Product Distribution

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ABSTRACT: *The objective of this article was to study the effect of pyrolysis temperature and mineral matter on the distribution of the product of C_1-C_6 hydrocarbons. Pakistani lignite named as Lakhra 6B was used to study the effect of inorganic substances on the reactivity of coal. The experiments were performed using pyrolysis gas chromatography to investigate the activity of virgin coal, HCl acid-washed coal and acid-washed coal with ($Ca(C_2H_3O_2)_2$, $Mg(C_2H_3O_2)_2$, $NaC_2H_3O_2$, $KC_2H_3O_2$), added respectively. The products obtained were monitored by a gas chromatograph. The main products identified were methane, ethane, ethylene, propane, 1-butene, n-butane, 1-pentene, n-pentane and benzene. The results showed that coal conversion to methane increased with an increase in temperature and the amount of this hydrocarbon was high among all the hydrocarbons formed. It was observed that the addition of metal ions affected the yields of the products in a selective manner. The yield of benzene was observed to be high in the case of calcium and magnesium form coals. The other cations form coals produced a smaller quantity of benzene in the temperature range studied. From the results, it can be concluded that metal ions played a selective role in controlling the yield of C_1-C_6 hydrocarbons from coal pyrolysis in general and benzene yield in particular.*

KEYWORDS: *Lignite coal; Pyrolysis-gas chromatography; Mineral matter; Temperature; Product distribution.*

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INTRODUCTION

Coal is a sedimentary rock formed million years ago by decomposition of dead plants. It is a complex matter that can be found in many forms i.e., anthracite, bituminous coal, lignite, and peat. It is an energy source and raw material for the production of different chemicals. In most countries, lignite is only used for power generation. Lakhra in Sind province is one of the major lignite coalfields in Pakistan. Hence, it necessitates the exploration, characterization, and utilization of these huge coal deposits for power generation. The coal reserves of Lakhra in Sind, Pakistan are estimated at 1328 million tonnes. Lakhra coal is lignite with a calorific value ranging from 5503-9158 Btu/lb. A feasibility study conducted in 1996 found Lakhra lignite suitable for power generation, however, high content of moisture, ash, and sulfur has made it unsuitable for direct combustion and hence its utilization is very slow in Pakistan [1-6]. This factor necessitates the needs for improving the quality of lignite for utilization as fuel, because lignite combustion before any treatment produces a large amount of dust leading to serious environmental contamination. Moreover, coal has plenty of inorganic material along with organic matter. The influence of the inorganic component on the pyrolysis of coal has been investigated by many researchers [7-26]. *Liu et al.,* [27] used two Chinese coals to study the influence of inorganic substances on the pyrolysis behavior of coal using thermogravimetry. The pyrolysis behavior was studied in virgin, acid-washed, and cations forms coals respectively. They observed that the addition of K_2CO_3, Al_2O_3 and CaO had enhanced the reactivity of coal resulting into a decrease in activation energy and a reduction in maximum degradation temperature. Previous results obtained from the pyrolysis of acid-washed coal with various cation exchanged form coals showed that the effect of minerals is very selective in nature. Only a few minerals were found to affect the pyrolysis behavior to a greater extent [28, 29]. *Wu et al.,* [30] examined the relationship between char reactivity and Na concentration in the reacting chars as well as the importance of char/carbon structure to the catalytic activity of Na using a set of NaCl-loaded Victorian brown coals, while in another investigation calcium was observed to have a pronounced effect on the pyrolysis of coal [31]. These inconsistencies in the results acquired by several investigators for coals obtained from different sites are due to differences in their composition and properties. Moreover, as no reports are available in the literature concerning the effect of inorganic matter on the pyrolysis behavior of Lakhra lignite, therefore, this fact motivated us to study the influence of cations on the rapid pyrolysis behavior of this specific coal from Lakhra mines. In this work, which is a continuation of previous work on the pyrolysis of indigenous coal [32, 33], the effects of sodium, potassium, calcium, and magnesium on the pyrolysis behavior of coal have been investigated.

EXPERIMENTAL SECTION

Materials

Lakhra 6B, low-rank coal from Lakhra in Sind province, Pakistan is used as a sample. Coal sample was ground to 100 mesh sizes. The coal was acid washed and then various inorganic substances were added to the acid-washed coal. The virgin, acid-washed, and acid-washed with the inorganic matter added were pyrolyzed over a wide range of temperatures in a pyrolyzer. The pyrolysates formed as a result of pyrolysis were injected into a gas chromatograph having a suitable column and detector for separation, identification, and quantization. The yields of these products not only depend upon the temperature of pyrolysis but also the inorganic matter present in the coal. The study is very helpful for investigating the effects of various mineral matters on the pyrolysis behavior of coal. The chemicals, hydrochloric acid (HCl) (37%), sodium acetate ($C_2H_3NaO_2$) (≥99.0%), potassium acetate (CH_3CO_2K) (≥99.0%), calcium acetate ($C_4H_6CaO_4$) (≥99%), magnesium acetate ($Mg(CH_3COO)_2$) (≥99%), ammonia (NH_3) (99.98%) and acetic acid (CH_3COOH) (≥99%) were purchased from Sigma-Aldrich through Scitech Services Providers (Pvt) Ltd., Peshawar, Pakistan. Standard hydrocarbon gases used were obtained from Matheson Company, through Allied Gases, Peshawar, Pakistan.

Formation of acid-washed and cation form coal

Virgin coal (50 g) was mixed with 300 mL of 2N hydrochloric acid; the mixture thus formed was stirred at room temperature for 24 hours. It was filtered, washed with de-ionized water unless no traces of chlorides were found. The acid-washed coal was dried at 80 °C in an oven and placed in a desiccator for further study.

Coals with the inorganic matter in the form of various metal contents (i.e. Na^+, K^+, Ca^{2+}, Mg^{2+}) were prepared from the acid-washed coal by shaking 1g of acid-washed coal with 100 mL of 1N solution of the corresponding metal acetate at pH 8.3. The extent of exchange was controlled by adjusting the pH with ammonia or acetic acid [31].

Pyrolysis procedure

The pyrolysis was carried out in an open tubular micro-furnace type pyrolyzer with a quartz reactor tube (Model Shimadzu PYR-2A, Kyoto, Japan). The furnace was electrically heated. The sample (2 mg) of approximately 100 mesh size was placed on to the reactor boat. The reactor was connected to a controller through a thermocouple. Nitrogen at a flow rate of 40 mL/min was flushed into the system to remove air in the reactor before pyrolysis. Three replicates were made for each sample.

Analytical Method

Analyses were carried out by Gas Chromatography using a gas chromatograph (Model Shimadzu GC-7AG, Kyoto, Japan) fitted with stainless steel column (6ft x 1/8 in); pre-packed with Porapak Q (80-100 mesh). A flame ionization detector was used for the qualitative and quantitative determination of the eluted compounds. Typical chromatographic conditions used in the present study were as: column oven temperature = 40 – 150°C, temperature programming rate = 11°C/min with initial time 2 min, carrier gas = N_2, flow rate of carrier gas = 40 mL/min, hydrogen pressure = 1 kg/cm^2, air pressure = 0.5 kg/cm^2, the injection port, detector and the interface (between pyrolyzer and GC) were kept at 150, 150 and 250°C respectively. The total pyrolysis time was 20 seconds. The recordings of the programs were carried out by the Spectra-Physics Model SP-4600 data jet integrator. The identification of the reaction products was confirmed from the comparison of retention time with standards of high purity gases and gas mixtures from Matheson Company.

RESULTS AND DISCUSSION

Precision

In order to assess the reproducibility of the pyrolysis gas chromatography system three precisely weighed samples were pyrolyzed at 650 °C. The data were processed to obtain the arithmetic mean of percent peak area and percent standard deviation. The results are listed in Table 1. The results show % standard deviation of 1.5 to 16.61. This level though not completely satisfying is in accord with similar work reported by *Awan et al;* [31] and in some cases better than the work reported by *Giam et al;* [34].

Effect of temperature on the product distribution

In order to evaluate the effect of temperature on the product distribution, the pyrolysis of coal samples in virgin, acid-washed, and cation forms was carried out in the temperatures range 500 - 800°C for a certain amount of coal (2 mg). The products formed were monitored by gas chromatography. The products identified were methane, ethane, ethylene, propane, 1-butene, n-butane, 1-pentene, n-pentane and benzene. A representative chromatogram from the pyrolysis of raw coal is given in Fig. 1.

The percentage yield of these products based on total organic volatiles detected from the pyrolysis of Lakhra 6B coal in raw, acid-washed and various cation exchanged form coals at various temperatures were quantitatively determined. The product distribution from the pyrolysis of these samples in raw, acid-washed and various cations exchanged form coals in the temperature range 500-800°C are presented in Tables 2-7.

The results show that coal conversion to methane increases with an increase in temperature and the amount of this hydrocarbon is high among all the hydrocarbons formed. The yield of CH_4 in raw coal (Table 2) increases from 18.8% at 500°C to 32.44% at 800°C. From de-mineralized coal (Table 3) it varies between 21.24–37.02% over a temperature range of 500–800°C. The yield of methane stays approximately constant at 500°C from sodium (Table 4) and potassium form coal (Table 5), as compared to demineralized coal. The %yield of methane from calcium (Table 6) and magnesium (Table 7) is low as compared to raw and demineralized coal. This is due to the higher yield of benzene from these coals. However, at high temperatures, the yield of CH_4 is nearly the same.

An increase in the yield of ethylene is also observed with an increase in temperature. The yield of ethylene is 4.9% (minimum) from magnesium form coal at 500°C. Ethane shows a maximum peak yield of 12.61% at 550°C and a minimum of 5.04% at 800°C from sodium form coal.

The propane yield remains unaffected over the temperature range 500- 800°C. The decreases in the yield of 1-butene, 1-pentene, and n-pentane are observed with an increase in temperature. This decrease in the yield of higher hydrocarbons may be due to the secondary

Table 1: Precision of pyrolysis of Lakhra 6B coal at 650 °C.

Peak	Methane	Ethylene	Ethane	Propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
% area of peak No.									
1.	24.88	18.04	11.04	19.28	6.62	10.23	1.62	4.79	2.15
2.	25.54	17.65	7.66	16.78	6.94	8.66	1.45	5.84	2.48
3.	25.79	20.09	9.44	18.70	7.09	8.56	1.05	5.77	2.20
Average % peak area	25.40	18.59	9.38	18.26	6.87	9.15	1.37	5.47	2.28
Standard deviation	0.39	1.07	1.38	1.07	0.20	0.87	0.06	0.48	0.38
% standard deviation	1.51	5.75	14.74	5.86	2.85	9.53	4.27	8.78	16.61

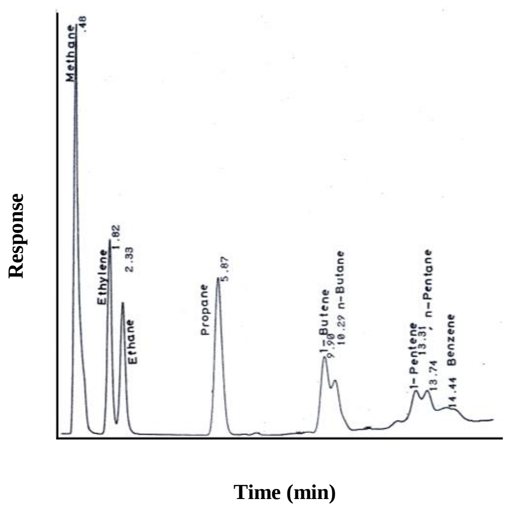

Fig. 1: A typical pyrogram from the pyrolysis of Lakhra 6B raw coal.

decomposition of these products to lower hydrocarbons at a higher temperature. A decrease in the yield of benzene with an increase in temperature is also observed, however, in the case of sodium and potassium, the yield is less affected.

Benzene shows a peak yield at 750°C in both calcium and magnesium form coals. By 800°C, the benzene drops to an insignificant level of 0.15% in raw coal. In the case of n-butane little is formed below 600°C in all forms of coals.

The fact that the formation of hydrocarbons in all coal samples improved with temperature rise shows that the bonds in coal break without any hindrance at high temperatures. This is consistent with the observation of *Mastral* [35]. Moreover, the decrease in the yield of higher hydrocarbons with increasing temperature was due to the secondary cracking reaction of pyrolytic vapors to lower molecular weight gaseous hydrocarbons. This causes the yields of low-molecular-weight hydrocarbons higher than those of high-molecular-weight [36].

Effect of inorganic matter on the product distribution

The yields of C_1-C_5 aliphatic hydrocarbons and benzene for each type of coal relative to demineralized coal are shown in Figs. 2-3. It can be concluded that benzene yield is 3-5 times higher from Mg and Ca exchanged coals compared to demineralized coal which in the presence of metal ion showed little or no effect on the yields of aliphatic C_1-C_5 hydrocarbons. This shows that Ca and Mg form coals have higher chemical activity than demineralized coal due to their enhanced positive catalytic effects on pyrolysis. The reason for this specific increase is quite obvious. Lakhra 6B which is low-rank coal exists in acidic functional groups in the form of phenols and carboxylic acids. This is due to the reaction of calcium and magnesium acetates with these groups, resulting in a higher yield of benzene [9]. *Zhang et al.,* [37] investigated the effect of foreign minerals on sulfur transformation in the step conversion of coal pyrolysis and combustion and concluded that increasing pyrolysis temperature enhances sulfur in the gas phase; however, the addition of Fe_2O_2 reverses the sulfur migration from gas to solid and has a positive effect on coal pyrolysis. *Kou et al.,* [38] studied the effects of mineral matter and temperatures on the conversion of carboxylic acids during the pyrolysis of brown coals and observed that cations promote the decomposition of COOH dimmers. *Li et al.,* [39] pyrolyzed raw, water-washed, and HCl-washed coal samples and observed that after treatments the larger aromatic hydrocarbons disappeared whereas a corresponding increase in smaller aliphatic compounds was observed.

CONCLUSIONS

From the results, it is clear that temperature is the key factor in determining coal behavior. The pyrolysis of coal enhanced with increase in temperature, showing rupture of bonds in coal more easily at elevated

Table 2: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B raw coal.

Pyrolysis Temp. (°C)	Product (%)								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	18.80	9.00	8.49	16.88	16.91	-	7.36	9.87	11.14
550	23.92	9.86	10.86	16.24	14.50	-	6.17	5.91	5.25
600	27.67	12.44	9.75	9.75	8.12	6.21	4.93	3.43	3.34
650	23.13	16.26	7.75	16.63	7.89	8.59	3.75	5.48	3.89
700	25.13	20.81	7.16	18.14	6.15	10.41	1.61	2.21	4.61
750	28.96	22.47	7.11	17.89	3.93	9.92	-	1.75	1.60
800	32.44	25.16	6.50	14.47	2.20	7.56	-	-	0.51

Table 3: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B demineralized coal.

Pyrolysis Temp. (°C)	Product (%)								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	21.24	8.76	9.66	17.06	17.24	-	6.19	8.06	9.71
550	25.95	9.53	11.75	15.97	14.12	-	4.64	4.29	4.07
600	31.52	12.36	10.58	15.46	8.23	5.03	4.21	4.04	3.40
650	28.49	15.78	7.81	15.52	7.39	7.90	3.58	3.62	4.90
700	26.73	20.32	6.59	17.89	6.21	11.04	0.26	2.14	2.76
750	30.31	20.97	6.97	16.18	3.59	9.54	-	1.40	1.25
800	37.02	22.41	5.62	11.58	0.01	6.85	-	-	1.57

Table 4: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B Sodium-form coal.

Pyrolysis Temp. (°C)	Product (%)								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	21.75	8.01	10.81	17.89	16.50	-	4.94	8.47	9.56
550	26.93	7.42	12.61	16.61	14.30	-	7.31	6.80	5.97
600	28.33	11.43	10.81	15.34	7.99	5.52	6.40	5.08	4.71
650	23.40	16.25	8.36	16.39	8.39	7.88	2.00	4.93	6.25
700	23.88	20.88	6.88	17.10	5.58	10.17	-	4.82	9.56
750	28.37	20.10	7.06	15.58	3.34	8.42	-	-	10.35
800	29.25	21.96	5.05	10.03	-	6.49	-	-	11.54

Table 5: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B Potassium-form coal.

Pyrolysis Temp. (°C)	% product								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	22.31	8.73	10.93	18.51	17.97	-	5.96	6.98	8.11
550	21.84	5.86	9.84	13.04	12.05	-	5.28	5.19	4.69
600	26.62	11.14	10.21	14.97	7.53	5.67	6.04	5.72	5.11
650	23.31	15.31	7.62	15.29	8.07	8.12	5.44	6.56	3.62
700	26.93	20.55	7.91	18.20	6.15	10.88	0.47	1.55	4.72
750	29.22	20.17	6.89	15.81	3.62	8.64	-	3.53	11.17
800	34.24	28.49	6.53	13.66	-	8.88	-	-	7.49

Table 6: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B Calcium-form coal.

Pyrolysis Temp. (°C)	% product								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	13.35	5.54	6.17	11.60	11.01	-	2.71	3.96	45.32
550	19.68	5.77	9.28	12.98	10.80	-	4.62	3.39	20.05
600	26.43	9.27	10.22	13.08	6.33	4.58	4.73	3.76	14.35
650	23.69	10.53	7.36	11.68	5.48	5.48	3.57	2.79	23.53
700	24.69	15.40	6.09	12.86	4.66	10.09	4.14	2.17	16.03
750	32.33	16.93	6.67	12.91	2.94	7.12	-	1.41	14.42
800	32.57	23.11	5.57	9.64	-	11.10	-	-	10.41

Table 7: Dependence of product yield on temperature for the pyrolysis of Lakhra 6B Magnesium-form coal.

Pyrolysis Temp. (°C)	% product								
	Methane	Ethylene	Ethane	propane	1-butene	n-butane	1-pentene	n-pentane	Benzene
500	9.97	4.90	4.20	9.23	9.04	-	0.14	13.09	47.00
550	16.44	6.75	7.73	11.97	10.08	-	3.74	3.89	24.06
600	25.97	8.83	9.01	11.08	5.89	4.06	3.49	2.82	18.47
650	24.38	12.58	6.72	12.09	5.90	7.57	5.10	4.57	12.95
700	27.36	17.81	6.05	13.76	5.05	8.14	0.20	1.57	13.90
750	30.22	17.36	5.86	12.21	2.71	7.11	-	0.92	16.77
800	32.75	24.31	5.33	9.79	-	6.96	-	-	13.39

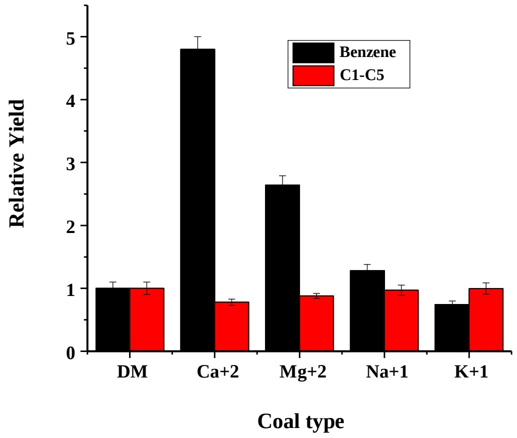

***Fig. 2:** Yields of benzene and C_1-C_5 hydrocarbons from various metal ions exchanged coals relative to demineralized coal at 650 °C.*

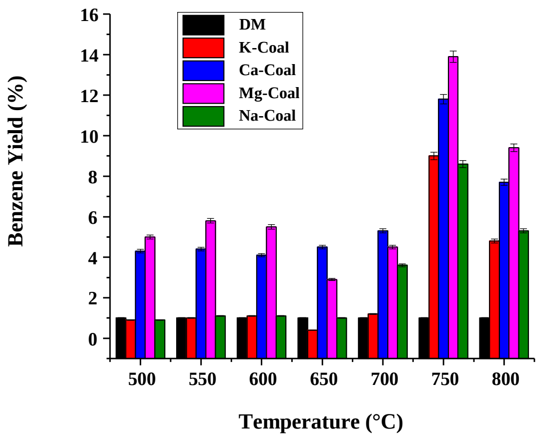

***Fig. 3:** Effect of temperature on the yield of benzene from cation exchanged coal relative to de-mineralized coal.*

temperature. Metal ions played a selective role in controlling the yield of C_1-C_6 hydrocarbons products from coal pyrolysis in general and benzene yield in particular. Over the temperature range 500 - 800°C the benzene yield was higher in the case of calcium and magnesium form coals than the raw, de-mineralized, potassium, and sodium form coals, showing the enhanced catalytic effect of calcium and magnesium on the reactivity of coal pyrolysis.

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