Pyrolysis of Metal Ions Exchanged Coal

I. A. AWAN* J. NISAR, A. YAMIN AND T. MAHMOOD
National Centre of Excellence in Physical Chemistry,
University of Peshawar, Peshawar, Pakistan

(Received 25th January, 2003, revised 10th April, 2003)

Summary: The influence of cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+} and Ba^{2+}) on the pyrolysis behavior of high volatile bituminous coal from middle seam Kost-Sharigh-Harnai coalfield Baluchistan under flash heating conditions was investigated using open tubular type pyrolyzer. Initial pyrolysis experiments were performed with de-mineralized and ion exchanged coal samples at 650 °C. The production of methane, ethane, ethylene, propylene + propane, 1-butene, n-butane, 1-pentene, n-pentane and benzene was monitored gas chromatographically. The addition of metal ions showed variable effect on the yield of pyrolysis products. The yield of benzene increased 5-6 fold for Ca and Mg exchanged coal compared to de-mineralized coal. Effect of temperature on the yield of benzene was explored over the temperature range 500-800 °C for the pyrolysis of Ca and Mg exchanged coal. The yield of benzene was higher than the de-mineralized coal at all temperatures and showed a decrease with increase in temperature.

Introduction

Coal pyrolysis is the first step of all coal conversion processes such as combustion, gasification and liquefaction and its understanding is essential for the effective use of coal. Yet coal exhibits a wide variation in pyrolysis behavior. The origins of these wide variations are for a given set of experimental conditions, both structural and compositional in nature. Because of its thermochemical and catalytic properties, mineral matter plays an important role both in the thermodynamic (product mixtures and activation energies) and kinetics of coal pyrolysis. The issue is further complicated by the manner in which mineral matters is distributed in various coals. While many classifications are possible, grouping into three classes is the most common. These classes are: (1) discrete mineral such as clays, oxides (basic and acidic) and sulphides; (2) organometallic matter as ion exchangeable cations; and (3) dispersed trace elements and compounds [1-4]. A considerable body of research exists for studying the effects of various forms of coal minerals on the pyrolysis behavior of coal [5-13].

In continuation of our work on the pyrolysis of indigenous coal [14-16], we studied the effect of individual mineral on coal pyrolysis by measuring the difference in the observed yield of C_1-C_6 hydrocarbons from demineralized coal and the coal which subsequent to demineralization was exchanged by cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+} and Ba^{2+}) using pyrolysis gas chromatography with flame ionization detector (Py-GC-FID). The metal cations selected for present study are known to be the major elements present in coal minerals. PY-GC-FID is a promising and widely used analytical technique for the characterization of coal as a source for volatile hydrocarbons and thus provides basic data for the development of commercial coal gasification processes such as Gasification Combine Cycle. The fresh coal sample used in present study was a high volatile bituminous from middle seam Kost-Sharigh-Harnai coalfield provided by Pakistan Mineral Development Corporation.

Results and Discussion

Pyrolysis of middle seam shariagh coal, after demineralization to remove the inherent mineral matters, was carried out at 650 °C. The main products identified were methane, ethane, ethylene, propylene + propane, 1-butene, n-butane, 1-pentene, n-pentane and benzene. A typical pyrogram is shown in Figure 1.To check the reproducibility of the peak area, three precisely weighed 1 milligram samples were pyrolyzed under identical conditions. The data was processed to obtain the arithmetic mean of percent peak area and percent standard deviation. The results are given in Table-1 and

*To whom all correspondence should be addressed.

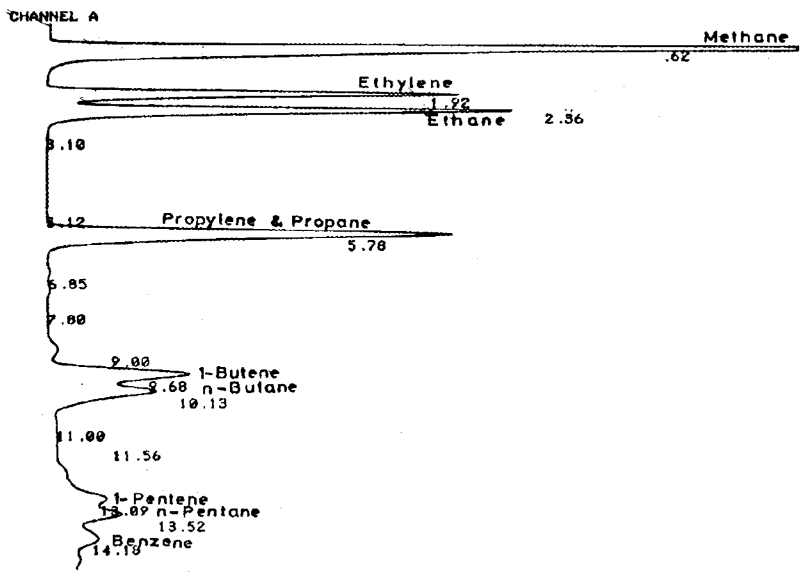

Fig. 1.: A typical gas chromatogram from the pyrolysis of de-mineralized middle seam Shariagh coal at 650 °C.

Table-1 .Precision of pyrolysis of middle seam coal (Shariagh) at 650 °C.

Peak	Methane	Ethylene	Ethane	Propylene &propane	1-butene	n-Butene	1-Pentene	n-Pentane	Benzene
%peak area No.1	28.58	11.56	13.83	15.89	5.77	6.07	6.84	3.64	2.49
No.2	30.95	12.71	14.20	16.94	5.98	5.68	5.16	4.54	2.35
No.3	32.70	13.67	15.23	17.50	5.89	6.41	5.21	3.87	2.01
Average%peak area(x)	30.74	12.65	14.42	16.78	5.88	6.05	5.73	4.02	2.28
Standard deviation	1.69	0.55	0.59	0.67	0.09	0.30	0.78	0.38	0.20
%standard deviation	5.49	4.32	4.12	3.98	1.48	4.92	13.61	9.55	8.93

Table-2.Reprudcibility of benzene injection

S.No	Peak area(x)	Average peak area(x)	x-x= dx	dx	Standard deviation	%standard deviation
1	15.90x10	1.72x10	1266667	1.6x10	5.45x10	3.17
2	18x10		-83300000	6.89x10		
3	17.6x10		-4300000	1.85x10		

show percent standard deviation ranging 1.48-13.61 %. This is consistent with the earlier work carried out in this laboratory [16] and the values(0.7-23 %) reported by G.S. Giam, et al from the pyrolysis of Texas lignites[17].

To check how much of this variation can be attributed to either the instrument or our technique and how much is attributable to heterogeneous nature of the coal, three 1 micro liter injections of benzene were made under the same conditions used for pyrolysis experiments. The data given in Table-2 indicates that a percent standard deviation up-to 3.17 can be taken as a maximum error in the reproducibility of the detector and the value exceeding 3.17 can be attributed to the heterogeneous nature of the coal.

Pyrolyses of various metal ion exchanged coals were performed under identical conditions as used for de-mineralized coal. The yields of C1-C5 aliphatic hydrocarbons and benzene for each type of coal relative to de-mineralized coal are given in Table-3 and results are shown in Figure 2. It can be seen from the results that the yields of C1-C5 hydrocarbons is higher from Fe+3, Al+3, Cu+2 and Ba+2-coal than the de-mineralized coal while a decease in the yields was observed for Na+, K+,

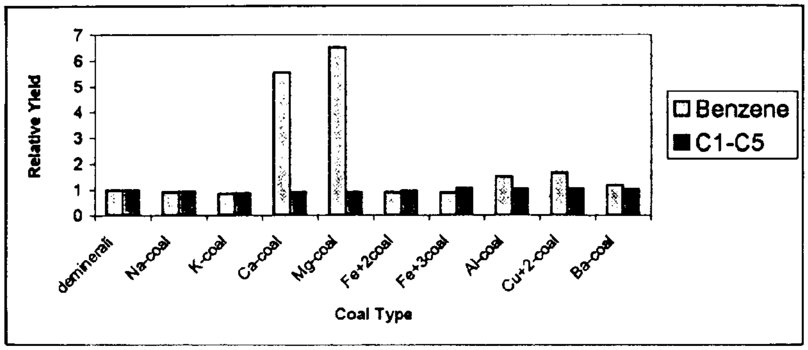

Fig. 2: Yields of benzene and C1-C5 hydrocarbons from various metal ions exchanged coals relative to demineralized coal at 650 °C.

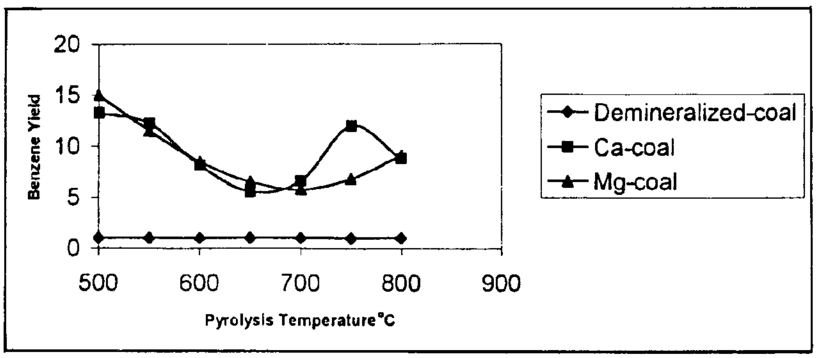

Fig. 3: Effect of temperature on the yield of Benzene from Ca and Mg exchanged coal relative to de-mineralized coal.

Table-3.Yields of hydrocarbon products from the pyrolysis of various metal exchanged Middle Seam Shariagh coal relative to de-mineralized coal at 650 °C.

Coal Type	Benzene	C1-C5 Hydrocarbons
De-miner-alized coal	1.00	1.00
Na-Coal	0.92	0.94
K-Coal	0.84	0.87
Ca-Coal	5.54	0.89
Mg-Coal	6.50	0.90
Fe+2-Coal	0.89	0.96
Fe+3-Coal	0.88	1.04
Al-Coal	1.51	1.02
Cu+2-Coal	1.66	1.02
Ba-coal	1.18	1.01

Ca+2, Mg+2 and Fe+2-coals. The Ca and Mg ions showed most appreciable effect on the yield of benzene. The benzene yield is 5-6 times higher from Ca and Mg exchanged coal compared to de-mineralized coal while the presence of metal ion showed little or no effect on the yields of aliphatic C1-C5 hydrocarbons. The general trend, which is observed for benzene yield from various metal ions coal samples at 650 °C is

K-coal < Fe+3-coal<Fe+ 2-coal<.Na-coal < de-mineralized-coal < Ba-coal < Al-coal < Cu+2-Coal <Ca-coal <Mg-coal

In order to see how benzene yield varies with temperature, pyrolysis experiments were conducted using Ca and Mg exchanged coal over the temperature range of 500-800 °C. The results are given in Table-4 and diagrammatically represented in Figure3. It can be seen from the results that for both the coal samples the yield of benzene is higher than the de-mineralized for all temperature and showed decrease with increase in temperature. This could well be due to the secondary decomposition of benzene at higher

Table-4. Effect of temperature on the yield of benzene from Ca and Mg exchanged coal relative to de-mineralized Middle Seam Shariagh coal.

Temperature °C	Ca-Coal	Mg-Coal
500	13.25	14.96
550	12.21	11.51
600	8.13	8.48
650	5.53	6.50
700	6.59	5.74
750	11.96	6.78
800	8.77	9.11

temperature. In a related study Cosway[18] when pyrolysed Wyodak sub-bituminous coal in its raw, de-mineralized, calcium, sodium and potassium form observed that metal ion exchanged coal gave lower yield of tar and gaseous hydrocarbon than did the acid form coal.

Experimental

Materials

Representative coal samples from middle seam Kost- Shariagh-Harnai coalfield Baluchistan were obtained from Pakistan Mineral Development Corporation (Pvt.) Ltd. Islamabad, in a sealed polythene bags. The sample was opened in the laboratory air and was ground in a grinder and sieved in 100 mesh size. The conventional analyses of coal sample used for pyrolysis studies are given in Table-5.

Preparation of de-mineralized and metal exchanged coals

De-mineralized coal was prepared from the raw coal by extraction with 2N HCl at room temperature [13]. A series of metal ions exchanged coals were then prepared from acid form coals. The sodium, potassium, magnesium and calcium exchanged coals were prepared by shaking 1g of de-mineralized coal with 100ml of 1N solution of the corresponding metal acetate at pH 8.3 [19]. The extent of exchange was controlled by adjusting the pH with ammonia or acetic acid. Ferrous, ferric, aluminum and copper exchanged coal samples were prepared by exchanging 1g sodium exchanged coal with 50 ml of 0.05 M solution of ferrous sulphate at pH 3.5, ferric chloride at pH 2, aluminum sulphate at pH 3.5 and copper sulphate at pH 4 respectively.

Barium exchanged coal was prepared by shaking 1g of de-mineralized coal with 50 ml of 0.3N solution of barium hydroxide at pH 3 and then

Table5. Conventional analysis of middle seam shariagh coal used for pyrolysis studies*

% Fixed Carbon	%Volatile Matters	% Suphure	% Moisture	% Ash	Calorific Value
43.48	41.25	5.11	4.23	5.93	6547 kcal/kg

* These analyses were carried out by Fuel Research Center, PCSIR, Karachi.

washed with 0.03N sodium hydroxide solution.. All the metal exchanged coals thus formed were recovered by filtration, washed, dried and transferred to labeled bottles for pyrolysis gas chromatography.

Pyrolysis gas chromatography system

The pyrolysis-gas chromatography system used has been described in detail previously [16]. It consists of a Shimadzu PYR-2A open tubular micro-furnace type pyrolyzer coupled to a Shimadzu gas chromatograph model GC-7AG, equipped with flame ionization detector. Coal samples were pyrolyzed at 650 °C for 20 seconds. The temperature of interface between the pyrolyzer and gas chromatograph was maintained at 250 °C. The analytical column was stainless steel (6ft x ¼"), which was packed with porapak Q (80-100 mesh).

The column temperature was maintained at 40 °C for the first minute and programmed to increase at a rate of 11°C /min upto 150°C. The nitrogen carrier gas flow rate was 40 ml/min (Table-6). The recording of the pyrograms were carried out by Spectra Physics model SP-4600 data jet recorder/integrator. Identification of product were done by comparison of the retention time of the peak of standard with those of samples programs.

Table-6. Instrumental operating conditions

Pyrolyzer	Shimadzu PYR-2A
Gas Chromatograph	GC-7AG
Column	Porapak Q (6ft x ¼") (80-100 mesh)
Oven temperature	40-150 °C
Temperature programming	@ 11 °C/min
Carrier gas	Nitrogen
Flow rate of carrier gas	40 ml/min
Detector	Flame Ionization
Air pressure	0.5kg/cm^2
Hydrogen pressure	1kg/cm^2
Pyrolysis Temperature	650 °C
Time of pyrolysis	20 seconds

Conclusions

The effects of adding various metal ions to de-mineralized middle seam shariagh coal on the production of volatile hydrocarbons were studied at 650°C. The general conclusions, which can be drawn from these results, are

1.. The choice of metal ions is one of the important factors to control the yield of C1-C6 hydrocarbons products from coal pyrolysis in general and benzene yield in particular.

2. The general trend observed for benzene yield from various metal ion exchanged coal samples at 650 °C is K-coal < Fe+3-coal<Fe+2-coal<.Na-coal < de-mineralized-coal < Ba-coal < Al-coal < Cu+2-Coal <Ca-coal <Mg-coal

3. Over the temperature range 500- 800 °C the benzene yield was higher than the de-mineralized coal at all temperature and tends to decrease with increase in temperature.

References

1. G.R. Gavalas, Coal Science and Technology 4 Coal Pyrolysis, Elsevier, New York (1982).
2. K.J. Voorhees, *Anal. Pyrol. Tech. And Appl;* Butter Worth, London (1984).
3. F. J. Tian, B. Q. Li, Y. Chen and C. Z. Li, *Fuel,* **81**(17), 2203 (2002).
4. Marsh, N.D., Zhu, D., and Wornat, M.J., Proceeding of Twenty-Seventh Symposium (International) on Combustion. Pittsburgh: The Combustion Institute, pp. 1897 (1998).
5. D. J Allardice, L.M. Clemow and W. R. Jackson, *Fuel,* **82** (1), 35 (2003).
6. T.Takarada, M.Matsuzawa and K. Morishita, Intl. Conf. On Clean Coal Technologies for our Future, Chia Laguna Conference Centre, Sardinia, Itlay, 21-23 October (2002).
7. W.P. Pan and G.N. Richards, *J. Anal. and Appl. Pyrol.,* **16,** 117 (1989).
8. W.P. Pan and G.N. Richards, *J. Anal. and Appl. Pyrol.,* **17,** 261 (1990).
9. G.N. Richards and G. Zheng, *J. Anal. Appl. Pyrol.,* **21,** 133 (1991).
10. W.F. DeGroot and G.N. Richards, *Fuel,* **67,** 345 (1988).
11. J. Wornat and R. Sakurovs, *Fuel* **75,** 867, (1996).
12 H.N.S. Schafer, *Fuel,* **58,** 673 (1979).
13 R.J. Tyler and H.N.S. Schafer, *Fuel,* **59,** 487 (1980).
14. I. A. Awan and Ikramullah, *Phy. Chem.Pak.* , **8**(1), 24 (1989).
15. I. A. Awan and Ikramullah, Sci. Intl., **4**(4), 367 (1992).
16. I. A. Awan and Ikramullah, *J.Chem.Soc.Pak.,* **18**(2), 64 (1996).
17. C.S.Giam, T.E. Goodwin, P.Y. Giam,, K.F. Rion and S.G.. Smith, *Anal. Chem.,* **49** (11), 1540 (1977).
18. R.G. Cosway, M. S. Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, M A , (1981).
19. H.N.S. Schafer, *Fuel,* **49,** 197 (1970).