

Analysis of Aliphatic and Aromatic Hydrocarbons Resulting From Pakistani Coals by Pyrolysis-Gas Chromatography

¹J. NISAR*, ²I. A. AWAN, ¹T. AHMAD AND ¹G. NAZ

¹National Center of Excellence in Physical Chemistry, University of Peshawar, Pakistan.

²National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

(Received 2nd December 2006, Revised 10th April 2007)

Summary: A gas chromatography-flame ionization detection procedure was developed for the analysis of individual hydrocarbon in a gaseous mixture resulting from the pyrolysis of a coal sample from Makerwal coalfields in Pakistan. The observed hydrocarbons were methane, ethene, ethane, propane, 1-butene, *n*-butane, 1-pentene, *n*-pentane, benzene, toluene and xylene. Total hydrocarbons yield is found to be characteristic of each sample indicating the structural and compositional variation. Such data may be useful for developing commercial coal conversion processes.

Introduction

On line pyrolysis gas chromatography with flame ionization (PY-GC-FID) is a powerful tool for the analysis of hydrocarbons mixture resulting from coal and other condensed phase fuels. Such analyses are important for assessing coal samples from different locations as a raw material for the production of gaseous fuel and chemicals.

Previously, we reported the pyrolysis of raw, demineralized and metal ion exchanged Pakistani origin coal from Lakhra (Sind) and Sharigh (Baluchistan) fields using pyrolysis gas chromatography with flame ionization detector [1-3]. Production of hydrocarbon was monitored over the temperature range 500-800 °C.

In this paper we report results obtained from the pyrolysis of raw and acid washed coal samples from Makerwal coalfields (District Mianwali, Punjab), using PY-GC-FID technique. Production of C1-C5 aliphatic and benzene, toluene and xylene (BTX) was monitored over the temperature range 500-800 °C. The effects of pyrolysis temperature and inherent mineral content on the yield of these products were investigated. The hydrocarbons yield increase with increase in temperature and passed through a maximum, which is characteristic of each sample.

Results and Discussion

Initial experiments were carried out at 600 °C with 1-milligram (150 mesh size) raw coal

samples. The main products identified were methane, ethane, ethylene, propylene + propane, 1-butene, *n*-butane, 1-pentene, *n*-pentane and benzene, toluene and xylene. The observed hydrocarbons were grouped as C1-C5 and BTX (benzene, toluene and xylene). The sum of integrated peak area for C1-C5 compounds was compared with that obtained from 1 microgram of *n*-pentane and that of BTX was compared with one microgram benzene to calculate the weight % yield.

To check the reproducibility of our procedure, three precisely weighed 1 milligram samples were pyrolyzed under identical conditions at 600 °C. The data was processed to obtain the arithmetic mean and percent standard deviation. The results are given in Table-1. Keeping in view the heterogeneous nature of the coal, these values are quite satisfactory.

Table-1: Precision of Pyrolysis of Makarwal Coal at 600 °C

S.No.	Peak Area x E5	
	C ₁ - C ₅	BTX
1	8.32	1.68
2	8.42	1.58
3	8.28	1.72
Average	8.34	1.66
Standard Deviation	0.0588	0.0588
% Standard Deviation	0.70 %	3.54 %

Effect of pyrolysis temperature on product yields was studied over the temperature range 500-800 °C. The results of these studies are shown in Fig. 1 and 2. As can be seen from the results, the

*To whom all correspondence should be addressed.

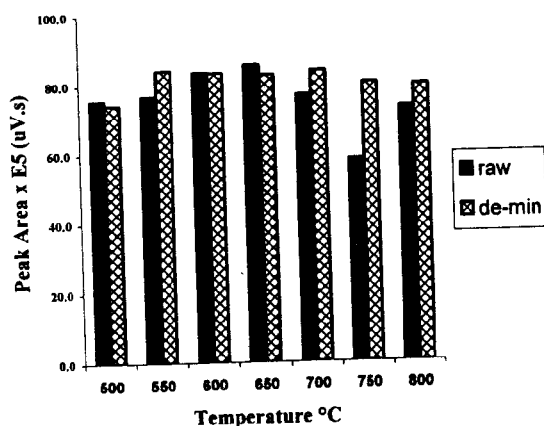


Fig. 1. Comparison of the yield of C1-C5 hydrocarbons released from the pyrolysis of raw and demineralized form coal samples at various temperatures.

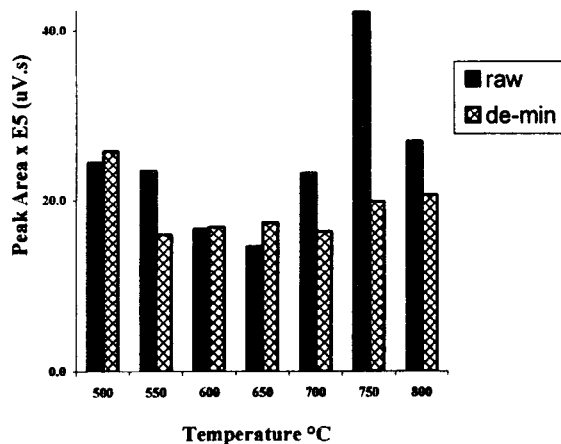
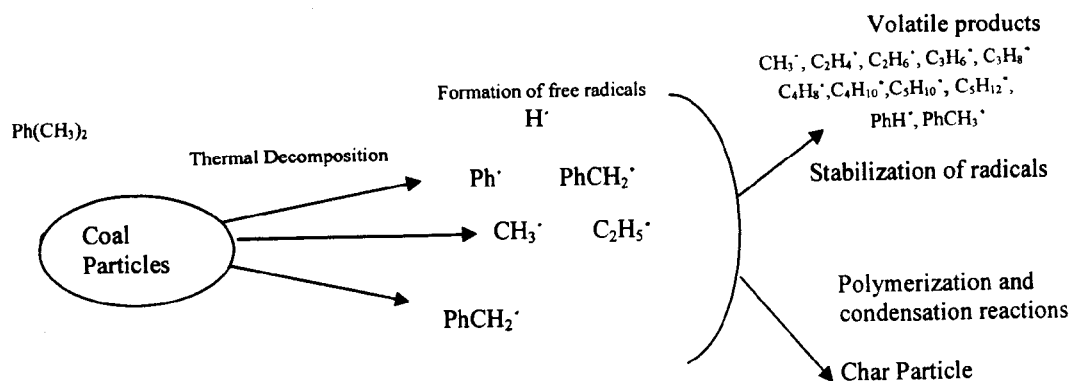


Fig. 2. Comparison of the yield of BTX released from the pyrolysis of raw and demineralized form coal samples at various temperatures.

yield of both C₁-C₅ aliphatic hydrocarbons and BTX showed an increase with increase in temperature with maximum yield in the range 700-750 °C. The fact that the conversion of organic matter in coal is increased with temperature increasing shows that the chemical bonds in coal break more easily at high temperature. This is consistent with the studies reported in the literature [4-5]. Bonfanti and co-workers pyrolyzed six coal samples with different origins and rank indexes at 250, 400, 550, 850 and 1000 °C. Production of *n*-alkanes was monitored gas chromatographically. For each single coal, the total amount of linear hydrocarbons tends to high with the temperature until a maximum. For coals samples of Poland, Columbia and Italia origin with code numbers of C04, C08 and C10 respectively, the temperature of the maximum was to be 550 °C, while for higher rank coal of USA (McCall), USA (Mapco) and South African origin having codes of C01, C02 and C0₃ respectively, it has raised to around 850 °C [6].

The observed hydrocarbons formed from the degradation of indigenous coal and its behavior with temperature clearly indicates the formation of free radical fragments from coal macromolecular structure by scission of cross-linking bonds. From the product analysis it is clear that H, [•]CH₃, [•]C₂H₃, [•]C₃H₇, [•]C₆H₃, [•]CH₂ and [•]C₆H₃ are the predominant radicals in our system. Once released from coal these radicals can either stabilize to give volatile products or can undergo polymerization and condensation reactions to form char. Scheme 1 summarizes the various processes occurring on coal pyrolysis.

Following reaction scheme summarizes the processes, which occur upon the flash heating of coal under study.



Scheme 1: Reactions and processes, which occur upon flash pyrolysis of Makerwal coal.

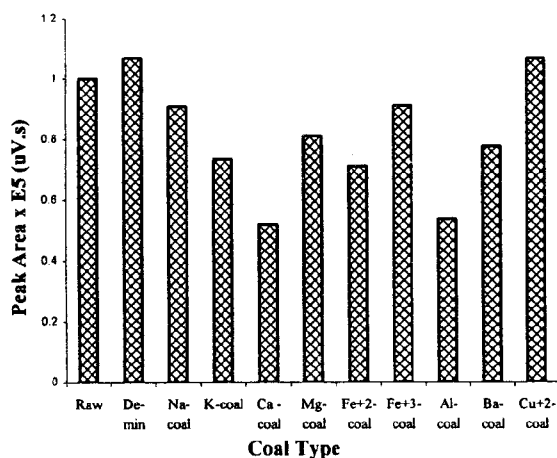


Fig. 3. Effect of different cations on the yield of C1 – C5 hydrocarbons released from the pyrolysis of cation exchanged form coal samples at 600 °C.

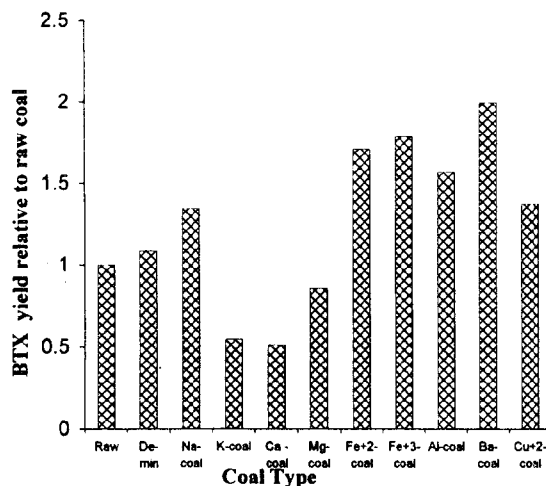


Fig. 4. Effect of different cations on the yield of BTX released from the pyrolysis of cation exchanged form coal samples at 600 °C.

In order to study the role of inherent mineral content of coal on pyrolysis, the coal sample under study was acid washed (de-mineralized). Pyrolysis of demineralized samples was conducted at 600 °C. The yields of C1-C5 and BTX were compared with raw coal. The results are shown in Fig. 3 and 4. Demineralization of coal increased the yield of C₁-C₅ by 6.8 % and BTX by 8.4 % as compared to raw coal. This is consistent with literature [7-15].

Experimental

A representative coal sample from Makarwal coalfields District Mianwali, Punjab-Pakistan was milled to obtain a particle size of 150 meshes. Acid form (de-mineralized) coal was prepared from the raw coal by extracting 100 grams of each sample with 2N HCl at room temperature [15]. After addition of acid the sample was kept in vacuum cupboard for three weeks. The sample was filtered, washed with demineralized water to remove last traces of acid from the treated samples and dried at 110 °C. The pyrolysis-gas chromatography system as described in our previous communication [1] 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 a particular temperature over the temperature range 500-800 °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 1/8 inch), 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 up to 150 °C. The nitrogen carrier gas flow rate was 40 mL/ min. The recording of the pyrograms was carried out by Spectra Physics model SP-4600 data jet recorder / integrator. Identification of products was done by comparison of the retention time of the peak of standards with those of samples pyrograms.

Conclusions

The effects of adding various metal ions to de-mineralized Makerwal 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⁺¹-coal < Fe⁺³-coal < Fe⁺²-coal < Na⁺¹-coal < de-mineralized-coal < Ba⁺²-coal < Al⁺³-coal < Cu⁺²-Coal < Ca⁺²-coal < Mg⁺²-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. I. A. Awan, T. Mahmood and J. Nisar, *J. Chin. Chem. Soc.*, **51**, 291 (2004).
2. I. A. Awan, J. Nisar, A. Yamin and T. Mahmood, *Jour. Chem. Soc., Pak.* **25**, 88 (2003).
3. I. A. Awan and Ikramullah, *Jour. Chem. Soc. Pak.* **18**, 64 (1996).
4. I. A. Awan, and Ikramullah, *Sci. Int. Lahore.*, **4**, 367 (1992).
5. H. Chen, B. Li and B. Zhang, *Fuel.*, **78**, 713 (1999).
6. L. Bonfanti, Ll. Comellas, J. Ll. Lliberia, R. Vallhonrat-Matalonga, M. Pich-Santacana and D. Lopez-Pinol, *J. Anal. Appl. Pyrol.*, **44**, 89 (1997).
7. P. Samaras, E. Diamadopoulos and G. P. Sakellaropoulos, *Fuel.*, **75**, 1108 (1996).
8. N.A. Oztas and Y. Yurum, *Fuel.*, **79**, 1221 (2000).
9. K. Miura, K. Hashimoto and P. L. Silveston, *Fuel.*, **68**, 1461 (1989).
10. K. Hashimoto, K. Miura and T. Ueda, *Fuel.*, **65**, 1516 (1986).
11. D. P. Ye, J. B. Agnew and D. K. Zhang, *Fuel.*, **77**, 1209 (1998).
12. H. D. Franklin, W. A. Peters and J. P. Howard, *Fuel.*, **61**, 155 (1982).
13. H. D. Franklin, W. A. Peters and J. P. Howard, *Fuel.*, **61**, 1213 (1982).
14. Q. Liu, H. Hu, Q. Zhou, S. Zhu and G. Chen, *Fuel.*, **83**, 713 (2004).
15. R.J. Tyler and H. N. S. Schafer, *Fuel.*, **59**, 487 (1980).