

Characterization of the Products Obtained in Coal Pyrolysis: A Case study of Some Pakistani Coals

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ABSTRACT: *Thermal decomposition of two coal samples obtained from Top Seam Sibi (TSS) and Sore Range Quetta (SRQ) coal fields in their raw and acid washed forms were carried out in an open type tubular pyrolyzer coupled to a gas chromatograph with FID. Elemental analyses were carried out with Scanning Electron Microscope-Energy Dispersive X-rays (SEM-EDX) analyzer. Effect of inherent mineral contents on the yields of pyrolysis products was investigated using acid washed coal samples. It was observed that total volatiles decreased as compared to raw form samples. Deductions in tar and liquid fractions were observed for both the acid washed Top Seam Sibi and Sore Range Quetta coals as compared to their raw forms where as an increase in the gas yield was noted in both the cases.*

KEY WORDS: *Coal Pyrolysis, Gas Chromatography, Demineralization, Characterization, SEM-EDX.*

INTRODUCTION

Pakistan has more than 185 billion tons reserves of coal giving her the seventh position in the list of twenty coal producing countries. Pakistan coal ranks from lignite to high volatile bituminous and thus offers a valuable raw material for power generation in view of the current shortage of electricity and frequent power outages. It can also replace kerosene, natural gas and firewood as domestic fuel and thus save the gas reserves and precious

forests wealth from further depletion. Top Seam Sibi (TSS) and Sore Range Quetta (SRQ) are among the few coal fields located in Baluchistan, Pakistan. Coal in Pakistan was not exploited for power generation for very long time. However, as a result of spending billion of dollars on import of oil and depleting reserves of gas at home, the policy makers are now seriously considering the use of indigenous coal for primary energy requirements

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in the coming decades. Though this switch over is difficult, however, it has certain advantages in terms of economic growth and self-sufficiency in energy sector.

Quality of coal can be characterized by a number of analytical tools such as Fourier Transform Infrared (FT-IR) spectroscopy [1-3], Electron Spin Resonance (ESR) [4-6], solid state ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) Spectroscopy [7,8], Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analyzer [9,10], X-ray Diffractions-GC-MS [11,12] Density fractionation methods [13,14] and Thermogravimetric Analysis (TGA) [15,16]. However, among the tools used, pyrolysis gas chromatography is the most widely used method.

EXPERIMENTAL SECTION

Materials

Two representative coal samples used in this study were collected in plastic bags from Top Seam Sibi and Sore Range Quetta open cut coalmines in Pakistan. Each coal sample was crushed in a grinder, and then passed through a mesh 85 sieve. The samples were dried at 150°C for 8 hours in an electric oven and then allowed to cool to room temperature in desiccators. In order to get consistent results these samples were allowed to achieve moisture equilibrium with the laboratory air. Acid washed coal samples were prepared from the raw coals by extraction with 2N HCl at room temperature. Both the raw and acid washed coal samples were stored in separate airtight polyethylene containers for further studies.

Apparatus and Procedure

The elemental analyses were carried out by using JEOL Model No. JSM-5910 Scanning Electron Microscopy (SEM) attached with Energy Dispersive X-rays analyzer (EDX) Model No. INCA-2000 at Centralized Resource Laboratories (CRL), University of Peshawar-Pakistan.

The experimental setup for pyrolysis studies was similar to that described in detail elsewhere [17]. The samples were pyrolysed in a pyrolyzer consisting of a main heater, pyrolysis chamber and operation rod. The temperature was controlled by a temperature control unit (PYR-2A No. 201177 U) over the temperature range $500\text{--}800^\circ\text{C}$. The products formed after pyrolysis are injected to a gas chromatograph GC-7AG coupled with FID. The column used was a stainless steel (1828mm x 3.175mm id) spiral

packed with Porapak Q (100-120 mesh). For the entire pyrolysis studies column temperature was programmed from $60\text{--}150^\circ\text{C}$ at the rate of $32^\circ\text{C}/\text{min}$ with initial time 2 minutes. The nitrogen was used as a carrier gas.

RESULTS AND DISCUSSION

Elemental Composition and SEM-EDX of Coal Samples

The composition of inherent minerals present was obtained by the elemental analysis of the representative samples in their raw and demineralized form. The results are shown in Tables 1 and 2. The results indicate that after demineralization carbon concentration is increased, whereas that of mineral contents decreased. Table 1 shows that after acid wash, sodium, calcium and magnesium have been completely removed from SRQ coal whereas iron has been extracted to a lesser extent. Table 2 shows results for raw and acid washed TSS coal samples. A complete removal of K is observed, where as Fe, Ca and Si are leached in large concentration. As these two fields are located at a distance of more than 100 kilometers, so the difference in their composition is quite evident. The results show that SRQ coalmines have traces of sodium and magnesium salts. The TSS coal does have traces of K salt but lacks Na and Mg salts.

On Line/Off Line Pyrolysis Gas Chromatography

Two distinct gas chromatographic procedures were adopted for analysis, online and offline pyrolysis gas chromatography. In the online method the volatiles formed from the pyrolysis of coal sample were inserted directly into the column with out any trap. In the offline method, there were two traps (made of Pyrex glass tubing) between pyrolyzer and GC. Trap-1 is placed in cold water (ca. 20°C) while trap-2 in methanol-liquid nitrogen slush bath (ca. -93.9°C). This set up helps in the separation and quantitative determination of tar, liquids and gaseous products.

In a typical experiment, 2mg, 85mesh size samples of raw and demineralized samples of both the coals were pyrolyzed at 690°C and their fractions (char, tar, liquid and the gases) were collected separately. Gaseous products leaving the traps were directly injected to gas chromatograph equipped with FID for compositional analysis. The results are shown in Table 3. These volatiles were lighter hydrocarbons of $\text{C}_1\text{--}\text{C}_5$. High yield of methane, ethane, propene/propane, and butene/butane

Table 1: Elemental Analysis of Raw and Demineralized form of Sore Range Quetta Coal.

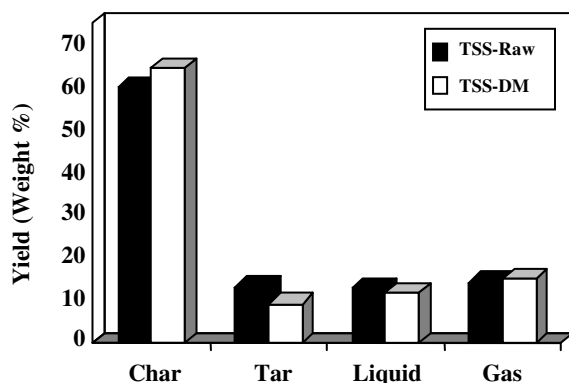
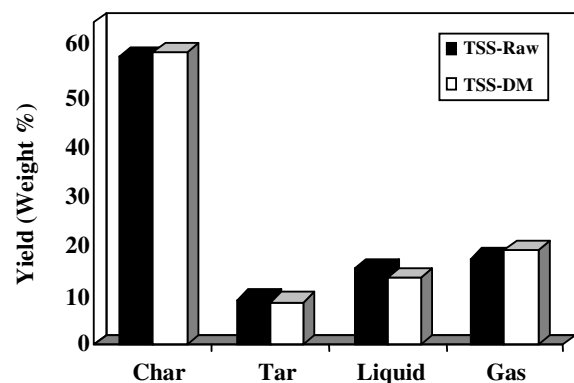
Sr. No.	Sample	Weight %						
		C	O	Na	Ca	Fe	Mg	S
1	Sore Range Quetta (raw)	68.48	25.11	0.21	1.85	1.09	0.13	1.69
2	Sore Range Quetta (demineralized)	70.39	24.95	-	-	0.77	-	1.52

Table 2: Elemental Analysis of Raw and Demineralized form of Top Seam Sibi Coal.

Sr. No.	Sample	Weight %						
		C	O	Si	S	K	Ca	Fe
1	Top Seam Sibi (raw)	65.04	26.57	0.75	5.00	0.08	0.46	1.69
2	Top Seam Sibi (demineralized)	69.94	26.94	0.63	1.82	-	0.04	0.13

Table 3: Composition of individual hydrocarbons released from pyrolysis of raw and demineralized samples at 690 °C.

Sample Type	Peak Area x E5 (μV. s)					
	Methane	Ethylene	Ethane	Propene /Propane	1-Butene /n-Butane	1-Pentene/n-Pentane
TSS-raw coal	45.28	71.26	20.85	29.84	13.78	5.89
TSS-DM coal	54.25	55.15	30.81	29.65	14.73	7.62
SRQ-raw coal	55.9	27.83	67.86	36.43	25.85	4.88
SRQ-DM coal	61.49	27.47	37.29	32.33	17.33	7.52

**Fig. 1: Comparison of the pyrolysates obtained from TSS Raw and DM form coal samples at 690 °C.****Fig. 2: Comparison of the pyrolysates released from SRQ raw and DM form samples at 690 °C.**

was observed from SRQ, while the yield of ethane and pentene/pentane was higher in case of TSS. In case of demineralized coal the yield of methane is more than the raw coal for both TSS and SRQ samples. As a whole the yield of gas was higher from SRQ than TSS coal. Much higher yields of aliphatic hydrocarbons to aromatic hydrocarbons from Sore Range Quetta coal sample suggest the abundance of alkyl chains in the macromolecule structure. The observations are in conformity with other reported results [18,19].

The results obtained from the pyrolysis of Top Seam Sibi and Sore Range Quetta coals at 690°C in raw and demineralized forms are graphically shown in Fig. 1 & 2. The figures show that in both the cases a decrease in tar and liquid yield was observed whereas the gas and char yields were increased after demineralization. This indicates that absence of mineral matter makes the coal sample porous, which can easily swell up, under high temperature resulting into more yields of gaseous fractions as compared to mineralized coal [20]. Moreover, the free radicals, which

have a leading role in the formation of tar and liquid, become unstable due to removal of inherent inorganic matter and hence recombine together to make more char [21].

CONCLUSIONS

This study suggests a novel approach for the demineralization of coal and reliable analyses of the pyrolysate. The quantitative information obtained through this technique may be very helpful for the effective use of solid fuels and its fragments. As the pyrolysis products (char, tar, liquid and gases) are collected separately so these can be used separately. It was concluded that demineralization has an appreciable effect on the yields of char, tar, liquid and gaseous fractions.

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REFERENCES

- [1] Öztas N.A., Yuda Y., Effect of Catalysts on the Pyrolysis of Turkish Zonguldak Bituminous Coal, *Energy Fuels*, **14**, p.820 (2000).
- [2] Geng W., Nakajima T., Takanashi H., Ohki A., Analysis of Carboxyl Group in Coal and Coal Aromaticity by Fourier Transform Infrared (FT-IR) Spectrometry, *Fuel*, **88**, p.139 (2009).
- [3] Painter P.C, Colman M. M., Application of Fourier-Transform Infrared Spectroscopy to the Characterization of Fractionated Coal Liquids, *Fuel*, **58**, p.301 (1979).
- [4] Khulbe K.C., Manoogian A., Chan B.W., Mann R.S., MacPhee J.A., Electron Spin Resonance Studies of Some Canadian Coals, *Fuel*, **62**, p.973 (1983).
- [5] Korkmaz S., Özbey T., Electron Spin Resonance in Some Turkish Coals, *Fuel*, **70**, 789 (1991).
- [6] Seehra M.S., Ghosh B., Free Radicals, Kinetics and Phase Changes in the Pyrolysis of Eight American Coals, *J. Anal. Appl. Pyrol.*, **13**, p.209 (1988).
- [7] Pan V.H., Maciel G. E., The Analysis of Three Representative Premium Coals by ^{13}C Nuclear Magnetic Resonance, *Fuel*, **72**, p.451 ((1993).
- [8] Newman R.H., Davenport S.J., Comparison of Australasian Tertiary Coals Based on Resolution-Enhanced Solid-State ^{13}C n.m.r Spectra, *Fuel*, **65**, 533 (1986).
- [9] Maes I.I., Gryglewicz G., Yperman J., Franco D.V., D'Haes J., D'Olieslaeger M., Van Poucke L.C., Effect of Siderite in Coal on Reductive Pyrolytic Analyses, *Fuel*, **79**, p.1873 (2000).
- [10] Domazetis G., Raoarun M., James B.D., Liesegang J., Pigram P.J., Brack N., Glaisher R., Analytical and Characterization Studies on Organic and Inorganic Species in Brown Coal, *Energy fuel*, **20**, p.1556 (2006).
- [11] Armanios C., Alexander R., Kagi R.I., Sobolev A.N., White A.H., The Molecular Structure of Sedimentary (22R) $17\alpha,21\beta(\text{H})$ -Homohopane from an X-ray Diffraction Study, *Geochemica et Cosmochemica*, **58**, p.2941 (1994).
- [12] Cappiello A., Mangani F., Bruner F., Bonfanti L., New Approach to the Characterization of Pyrolysis Coal Products by Gas Chromatography-Mass Spectrometry, *J. Chromatography A*, **736**, p.185 (1996).
- [13] Querol X., Klika Z., Weiss Z., Finkelman R.B., Alastuey A., Juan R., López-Soler A., Plana F., Kolker A., Chenery S.R.N., Determination of Elements Affinities by Density Fractionation of Bulk Coal Samples, *Fuel*, 2001, **80**, p.83.
- [14] Lu H., Chen H., Li W., Occurrence and Volatilization Behavior of Pb, Cd, Cr in Yima Coal During Fluidized-Bed Pyrolysis, *Fuel*, **83**, p.39 (2004).
- [15] Vijayakumar C.T., Vinayagamoorthis S., Fink J.K., Sivasamy P., haracterization of Low Rank Alpine Coals: Thermogravimetric Studies, *J. Anal. Appl. Pyrol.* **76**, p.191 (2006).
- [16] Rosenvold R.J., Dubow J.B., Rajeshwar K., Thermal Analyses of Ohio Bituminous Coals, *Thermochemica Acta*, **53**, p.321 (1982).
- [17] Ahmad T., Awan I.A., Nisar J., Amad I., Influence of Inherent Minerals and Pyrolysis Temperature on the Yield of Pyrolysates on Some Pakistani Coals, *Energy Convers Manage*, **50**, p.1163 (2009).
- [18] Bonfanti L., Comellas Ll., Lliberia J.Ll., Vallhonrat-Mataonga R., Pich-Santacana M., Lopez-Pinol D., Production of n-Alkanes and Polycyclic Aromatic Hydrocarbons in Coal Pyrolysis, *J. Anal. Appl. Pyrol.*, **44**, p.89 (1997).
- [19] Luce C.C., Humphery E.F., Guild L.V., Norrish H.H., Analysis of Polyester Resins by Gas Chromatography, *Anal. Chem.*, **36**, p.482 (1964).
- [20] Reucrafta P.J., Patel KB., Surface Area and Swellability of Coal, *Fuel.*, **62**, p.279 (1983).
- [21] McMillan DF., Malhotra R., Nigenda, SE., The Case for Induced Bond Scission Duirng Coal Pyrolysis, *Fuel.*, **68**, p.380 (1989).