Organic Geochemical Study of Lignite Coal from Salt Range Pakistan

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Summary: Coal sample from Salt Range-Pakistan has been analyzed to investigate its rank, hydrocarbon composition and most likely source of hydrocarbons. The rank of coal has been determined by general and chemical parameters. High percentage of volatile matter and sulfur content, low thermal characteristics and carbon and hydrogen content 62 and 5 respectively reveal that Salt Range coal is lignite in rank. In order to determine hydrocarbon composition, bitumen was extracted from the coal and was fractionated into saturated, aromatic and NSO (nitrogen, sulfur and oxygen containing compounds) fractions by liquid chromatography employing silica gel. Further fractionation of aromatic fraction by TLC yielded two sub fractions called aromatic fraction #1 and aromatic fraction #2 respectively. Analysis of these fractions by capillary GC-FID showed a profile with high abundance of peaks that were characterized as thiophenic compounds. The identifications were based on the comparison of GC retention data with the literature. Dibenzothiophenes are the most abundant compounds in the Salt Range coal. Their methyl– and dimethyl substituted derivatives are also present in high concentration. Naphthalene and phenanthrene are present in minor amount but their alkyl-substituted derivatives have relatively high concentration. The most likely source of aromatic hydrocarbons could be terpenoid precursors; however polynuclear aromatic thiophenes, could be formed from sulfur containing aromatic moieties of macromolecules during later stage of diagenesis of the sediments. The incorporation of hydrogen sulfide into the precursor molecules could not be ruled out which is abundant in reducing environment.

Introduction

Coal is a compact stratified rock containing more than 50% by weight and more than 70% by volume of macerals. The dominant coal macerals in order of decreasing hydrogen contents are liptinite, vitrinite and ineritnite. It also contains a variety of plant tissues at different stages of preservation. After preservation in the sediments, plant remains undergo a sequential physical, biochemical, chemical and thermal alterations referred to as diagenesis, catagenesis and metagenesis. Catagenetic changes in coal are basically a progressive elimination of less stable biological configurations, such as heteroatomic links, aliphatic chains and saturated cycles, in order to attain a more stable molecular configuration under higher temperature and pressure condition [1].

Regular polyaromatic hydrocarbons (PAH) in sub-bituminous and bituminous coal consist of naphthalene, biphenyl, phenanthrene, fluorine, fluoranthene, pyrene, chrysene, picene, perylene, coronene and their alkyl substituted derivatives. Brown coals and lignites are characterized by polycyclic aromatic terpenoid biomarkers [2-5]. A series of di- and sesquiterpenoid aromatic hydrocarbons with simonellite and dihydrocadinene predominance has been reported in Woyming lignite [6]. Chaffe and coworkers [7-9] identified various series of tri–, tetra– and pentacyclic aromatic biomarkers from the aromatic fraction of brown coals from Victoria, Australia. These compounds were suggested to be derived from triterpenoid precursors, especially the oleanane, ursane and lupane. Fan *et al* [10] analyzed the bitumen of a Chinese sphagnum coal in order to investigate the potential as oil source material. The aromatic hydrocarbons predominantly consist of the same tri- and tetra- aromatic, ursane and hopane skeletons. Polynuclear aromatic thiophenes were suggested as useful indicators for the evaluation of source rocks and diagenetic maturation [10-12]. High abundance of dibezothiohenes has been observed in marine sources than in non-marine. Moreover, dibenzothiophenes (DBT) and 4-methyl dibenzothiophenes (4-MDBT) have been suggested to be more abundant in type III kerogen [10, 13-15]. The ratio of 4-/1-MDBT was proposed as a maturity parameter for both marine and terrestrial organic matter [16].

The present study was undertaken to identify different classes of aromatic biomarkers and to infer

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most likely source of these compounds in a coal sample. The geochemical study of the type described in this paper has not been undertaken previously on any Pakistani coal.

Results and Discussion

Proximate and ultimate analysis

Proximate and ultimate analysis was carried out to assess the quality and rank of coal. The values are shown in Table 1. Coalification process decreases the moisture content and volatile matter with passage of time due to heat and pressure. A typical mature coal is anthracite. The moisture and ash contents in Salt Range coal sample are 5% and 27% respectively, which shows the large amount of minerals present in coal. The percentage of volatile matter is also quite high (23%). Fixed carbon value is 45%. These values suggest that Salt Range coal belongs to the category of higher volatile matter lignite coals as reported in the literature [17,18].

Table 1 Proximate and ultimate analysis data.

Test Parameters	Level (%)
Moisture content	5
Ash contents[a]	27
Volatile matter[b]	23
Fixed carbon[c]	45
Carbon[a]	62
Hydrogen[a]	5
Sulfur[a]	4
Nitrogen[a]	1

Calorific value: 4930 kcal/kg

a : Parameter calculated on moisture containing basis

b : Parameter calculated on dry moisture free basis in accordance with method D 3175

c : fixed carbon = 100 – [moisture+ash+volatile matter]

Maturation process increases the carbon contents relative to hydrogen and oxygen with the passage of time. Hydrogen content in peat bogs is high. Carbon and hydrogen content in Salt Range coal are 62% and 5% respectively. Francis [19] analyzed different Pakistani coals including Salt Range coal. These coals contain high proportion of organic sulfur. High sulfur content (3-5%) was suggested as a characteristic feature of carbonaceous products that have been accumulated and developed under marine conditions [14]. In Salt Range field, marine fossils, have been used to differentiate various seams, whilst the seam themselves contain frequent fossil containing marine limestone beds. The sulfur content is also high (4%), which signifies marine depositional condition. Percentage of nitrogen in Salt Range coal is one and its calorific value is 4930 kcal/kg (Table 1). Both proximate and ultimate analysis of sample reveals that the Salt Range coal deviate from a good quality coal and belongs to the rank of lignite coal [17].

Organic geochemical study

In order to determine hydrocarbon composition, soluble organic matter (SOM) from coal was fractionated into hydrocarbons types using column chromatography on silica gel. The saturated fraction represents low relative abundance than the aromatic fraction (Table 2). It is commonly believed that as a result of increased maturity from peat to anthracite, *n*-alkanes and cycloalkanes are converted to aromatic compounds. Cyclization, polymerization, aromatization and dehydration are the main reactions which bring about these changes with the passage of time, heat and pressure. Nitrogen, sulphur and oxygen containing compounds (NSO fraction) also represent a major fraction, which is a usual feature of high sulfur coals. Higher molecular weight compounds in Salt Range coal are plant resins.

Table 2 Geochemical data of the coal used in this study.

SOM	Relative Percentages				SOM
(%)	Saturates	Aromatics	NSO	Resins	Characteristics
0.45	6.9	19.1	28.3	44.7	Resinous

Gas chromatography

Aromatic fraction was separated into two subfractions (aromatic fraction # 1 & 2) by TLC and both the fractions were subjected to GC-FID analysis. Figures 1 and 2 display the gas chromatograms of these fractions. The identifications on both chromatograms have been made by comparing the elution order and retention data with the chromatograms published in the literature [13-16]. The relative concentrations of identified compounds have been calculated using peak area and are shown in Table 3.

The analysis of aromatic fraction # 1 revealed that benzene (B) and naphthalene (N) are the only mono- and di- aromatic compounds present in significant amount. Which represents 0.009% and 0.0083% of first aromatic fraction (Fig. 1). Their mono- and dimethyl- substituted derivatives were not detected, however, trimethylnaphthalenes (TMNs; 0.015%) and tetramethylnaphthalenes (TeMNs; 0.022%) are present in first aromatic fraction. It

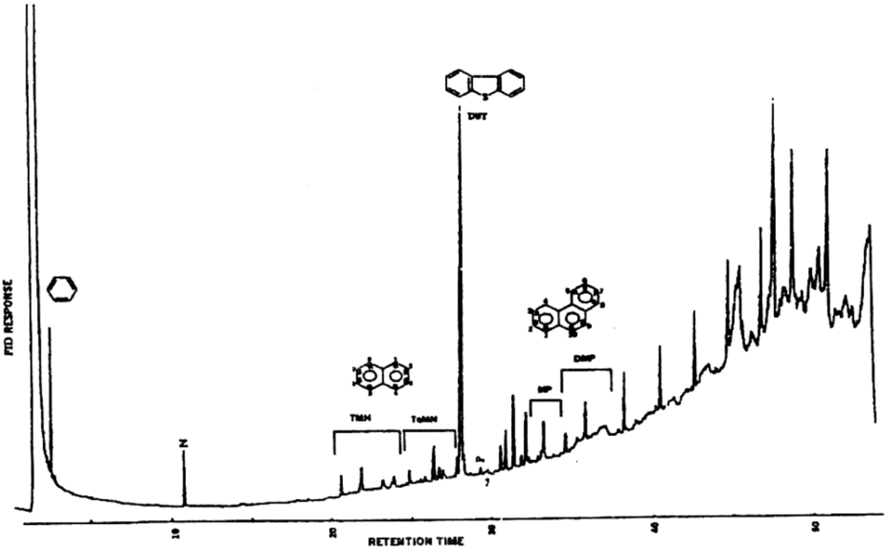

Fig. 1: Gas chromatogram of First Aromatic Fraction from Salt Rang coal sample.

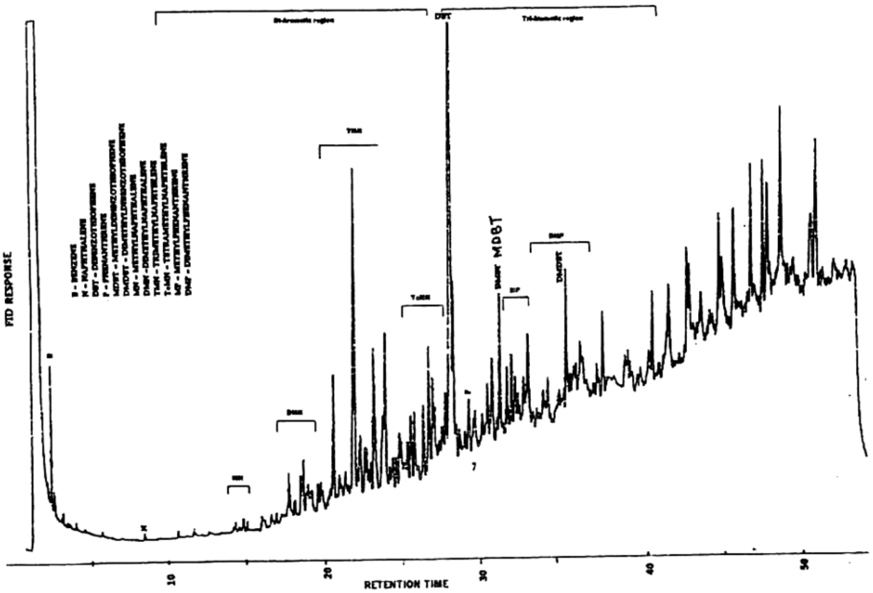

Fig. 2: GC analsysi of second Aromatic fraction from Salt Range coal sample.

shows that as the alkyl substitution increases from TMNs to TeMNs, its concentration also increases. Phenanthrene (P) is present in insignificant amount in first aromatic fraction, however alkyl-substituted phananthrenes, (MPs and DMPs) represent 0.0232% and 0.037% of the first aromatic fraction respectively. Tetra- and penta- aromatic hydrocarbons seems to be present but were not identified because of GC temperature limits. Thiophenes are the major compounds present in this fraction. Dibenzothio-

Table 3 Concentration of biomarkers in aromatic fractions of coal.

Aromatic fraction # 1 Identity	Conc. (%)
Benzene (B)	0.009
Naphthalene (N)	0.0083
Trimethylnaphthalenes (TMNs)	0.015
Tetramethylnaphthalenes (TeMNs)	0.022
Methylphenanthrenes (MPs)	0.0232
Dimethylphenanthrenes (DMPs)	0.037
Dibenzothiophene (DBT)	0.122
Aromatic fraction # 2	
Naphthalene (N)	0.0009
Methylnaphthalenes (MNs)	0.009
Dimethylnaphthalenes (DMNs)	0.0491
Trimethylnaphthalenes (TMNs)	0.244
Tetramethylnaphthalenes (TeMNs)	0.271
Phenanthrene (P)	0.025
Methylphenanthrenes (MPs)	0.0414
Dimethylphenanthrenes (DMPs)	0.13
Dibenzothiophene (DBT)	0.24
Methyldibenzothiophene (MDBT)	0.037
Dimethyldibenzothiophene (DMDBT)	0.038

phene (DBT) is the most abundant, its concentration is 0.122%. Presence of alkyl substituted DBT is also possible but they were not identified.

Gas chromatogram of aromatic fraction # 2 (Fig. 2) reveals that naphthalene is present in insignificant amount (0.0009%), while methynaphthalenes (MNs) and dimethynaphthalenes (DMNs) represent significant concentration (0.009% and 0.0491%). DMNs region may also contain ethylnaphthalene (EN). TMNs and TeMNs amounts are 0.244% and 0.271% respectively. Total diaromatics represent 0.67% of the second aromatic fraction. Multiple sources could be suggested for the origin of naphthylenes. For example, alkylnaphtha-lene have been reported to occur widely in ancient sediments and coals, where they are derived, at least in part, from degradation of natural terpenoids [13,14]. The presences of these compounds could also be related to precursor of natural products, which are characteristic of resins from *Araucariaceae*. In Salt Range coal, since these compounds are present in significant amount, they could have been derived from precursor molecules or by aromatization of bicyclic components of resins. Other sources of alkylnaphthalene are pentacyclic triterpinoids as proposed previously [5,20].

A relatively high concentration of triaromatic hydrocarbons is present aromatic fraction # 2, e.g. phenanthrene: 0.025%, and methylphenanthrenes (MPs) and dimethylphenanthrenes (DMPs) represent 0.0414% and 0.13% respectively. Higher alkyl substituted phenanthrenes may be present which were not identified because of GC temperature limits. The origin of methylphenanthrenes is abietic acid and sadarocopimaric acid type natural product precursors. These compounds are derived from natural product precursor by loss of isopropyl, or more generally by loss of CO_2 and alkyl substituents. It has also been suggested that MP is a likely aromatic biomarker for abietic acid-type natural products. Another source of MPs is the monoaromatic podocarpic acid, which is also a common constituent of conifer resins [21].

Dibenzothiophene (DBT) is the most abundant (0.24%) amongst the thiophenes in aromatic fraction # 2. Its alkyl substituted derivatives e.g. methyldibenzothiophene (MDBT; 0.037%) and dimethyldibenzothiophene (DMDBT; 0.038%) are also present (Figure 2). Higher alkyl substituted compounds of DBT are also expected but were not identified. Little is known about the precursors and pathway leading to formation of polynuclear aromatic thiophenes, although some studies have suggested that these compounds are formed by cyclization and aromatization of alkyl thiophenes. Other possible sources could be sulfur containing aromatic moieties of macromolecules formed either by incorporations of hydrogen sulfide or free sulfur species (which are abundant in marine/reducing environment) into the macromolecules and these compounds were formed from them during later stage of diagenesis of the sediments.

Experimental

Physico-chemical analysis

Physicochemical analysis including moisture and ash contents, volatile matter, fixed carbon, carbon and hydrogen, nitrogen, sulphur and calorific value determinations were carried out by ASTM standard methods [22-28].

Organic geochemical analysis

Organic Geochemical analysis was carried out according to previously published method [29]. In brief soluble organic matter (SOM) was extracted from the coal ultrasonically using dichloromethane as solvent. The SOM was separated into aliphatic, aromatic and NSO fractions by column chromatography employing silica gel. The aromatic fraction thus obtained was fractionated into sub aromatic fractions by thin layer chromatography using a TLC plate (8x8″) coated with 0.5 mm thick layer of alumina Naphthalene and phenanthrene were used as standards for the indication of di– and tri– aromatic fractions. Plates were developed using *n*-hexane as solvent in the chromatographic tank. After elution, the plates were observed under UV lamp long and short wave length. First and second aromatic fractions bands appeared at R_f values 0.82 and 0.40 respectively, were scratched off and analyzed by capillary GC-FID.

Capillary gas chromatography: Analysis of both aromatic fractions was performed on Shimadzu GC-14 series (Japan) gas chromatograph-FID with a 30m×0.25mm (i.d.) fused silica capillary column coated with methyl silicone (OV-1). Nitrogen was used as carrier gas at the rate of 28cm/sec. 1μg of aromatic sample in 1μL *n*-hexane was injected at 60°C. Detector (FID) and injector temperatures were 300°C and 280°C. The oven temperature was programmed from 60-250°C at 4°C/min. The final temperature was maintained for 5 minutes. The data was collected from retention time 0-55 minutes.

Conclusions

Organic geochemical study of aromatic fractions of coal sample from Salt Range Pakistan has revealed the following conclusions:

1. Salt Range coal belongs to the category of higher volatile matter lignite coals.
2. Dibenzothiophene, methyldibenzothiophene and dimethyldibenzothiophene are the most abundant compounds in the Salt Range coal which signifies marine depositional environment. Naphthalene and phenanthrene are present in minor amount but their alkyl-substituted derivatives have relatively high concentration.
3. The most likely source of naphthalene and alkylnaphthalene could be from the degradation of terpenoids precursors; however, the source of phenanthrene and alkyl phenanthrene is abietic acid and sadarocopimaric acid. These compounds could be derived from the precursor molecules by loss of alkyl substituents followed by aromatization and alkylation reactions in sediments.
4. The precursors and pathway leading to formation of polynuclear aromatic thiophenes, could be sulfur containing aromatic moieties of macromolecules, which release these compounds during later stage of diagenesis of the sediments. Another source could be incorporation of hydrogen sulfide (which is abundant in marine reducing environment) into the precursor molecules.

References

1. B. Durand, A. Marchand and A. Combaz, In: *Advances in Organic Geochemistry*, 753 (1975).
2. C. M. White and M. L. Lee, *Geochim Cosmochim. Acta*, **44**, 1825 (1980).
3. V. A. Garasimenko, A. V. Kirilenki and V. M. Nablvach, *J. Chromatogr.*, **208**, 9 (1981).
4. R. Gorchs, M. A. Olivella and F. X. C. de las Heras, *Organic Geochemistry*, **34**, 1627 (2003).
5. Jincai Tuo, Xianbin Wang, Jianfa Chen and B. R. T. Simoneit, *Organic Geochemistry,* **34**, 1615 (2003).
6. R. Hayatsu, R. E. Winans, R. G. Scott, I. P. Moore and M. H. Studrer, *Fuel,* **57**, 541, 2037 (1978).
7. A. L. Chaffe *Ph. D. thesis*, university of Melbourne, Melbourne, Australia (1981).
8. A. L. Chaffe and R. B. John *Geochim. Cosmochim. Acta* **47**, 2141 (1983).
9. A. L. Chaffe M. G. Strachan and R. B John *Geochim. Cosmochim. Acta* **48** . (1984).
10. P. Fan, R. P. Philip, Z. Li and G. Ying, *Org. Geochem.* **16**, 427 (1990).
11. A. Chakhmakhchev and N. Suzuki, *Org. Geochem.* **23**, 289 (1995).
12. C. M. Sandison, R. Alexander, R. I. Kagi and C. J. Boreham, *Org. Geochemistry*, **34**, 1081 (2003).
13. M. Radke D. H. Welte and H. Willsch *Geochim. Cosmochim. Acta* **46**, 1 (1982).
14. M. Radke H. Willsch and D. Leythaeuser *Geochim. Cosmochim. Acta,* **46**, 1831 (1982).
15. M. Radke, A. Hilkert and J. Rullkötter, *Org. Geochemistry*, **28**, 785 (1998).
16. M. Radke H. Willsch and D. H. Welte, *Org. Geochem.* **10**, 51 (1986).
17. B. P. Tissot and D. H. Welte, *Petroleum Formation and Occurrence*, Springer-Verlag, New York, 699 (1984).
18. Guijian Liu, Pengyue Yang, Zicheng Peng, Guiliang Wang and Wei Zhang, *Energy*, **28**, 969 (2003).

19. W. Francis *Coal, its Formation and Composition. Edward Arnold Publishers.* Page 287 (1961).
20. M. G. Strachan, R. Alexander and R. I. Kagi *Geochim. Cosmochim. Acta*, **52**, 1255 (1988).
21. R. Alexander, A. V. Larcher, R. I. Kagi and P. L. Price, In: Biological Markers in Sediments and Petroleum (J. Moldowan, P. Albrecht and R. P. Philp eds.) Prentice Hall Englewood Cliffs N. J., 221 (1992).
22. A.S.T.M. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, **05.05**, D 3173– 82.
23. A.S.T.M. Standard Test Method for Ash in the Analysis Sample of Coal and Coke, **05.05**, D 3174.
24. A.S.T.M. Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, **05.05**, D 3175.
25. A.S.T.M. Standard Test Method for Total Sulfur in the Analysis Sample of Coal and Coke, **05.05**, D 3177.
26. A.S.T.M. Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Coal and Coke, **05.05**, D 3178
27. A.S.T.M. Standard Test Method for Nitrogen in the Analysis Sample of Coal and Coke, **05.05**, D 3179.
28. A.S.T.M. Standard Test Method for Gross Calorific Value of Coal and Coke, **05.05**, D 3286.
29. T. Fazeelat, R. Alexander and R. I. Kagi, *Org. Geochemistry*, **21**, 257 (1994).