Chapter 1 Introduction

1.1 COAL

Coal is a heterogeneous and structurally complex material consisting of a large number of organic and inorganic compounds. It is mainly used as an energy resource and as a raw material for the production of chemicals. Coal is found and extracted in many different locations and its structure and composition record the geological history through which it was generated. Moreover, the composition of coal and its structure influence the combustion efficiency. Global environmental concerns require a careful examination of all steps involved in energy production, in the light of the fact that the emission of several pollutants appears to be linked to certain precursors originally present in the fuel. For all these reasons, coal characterisation is a source of valuable information [1].

In the structure of the earth the element carbon is hardly more than a trace element, its share in the total bulk being as small as 0.04 per cent. Even the carbon content of the earth's crust (down to a depth of about 5000 metres) does not exceed a mere 0.1 per cent. Only a scanty portion of this one part in 5000 occurs in a form capable of reacting with oxygen, and only this "dynamic " carbon is useful. The content of dynamic carbon in the total mass of our globe consequently amounts to one part in twelve and a half million [2].

1.2 BATU ARANG, SELANGOR.

The sequence underlying the Batu Arang area (Fig. 1.1) consist of Carboniferous-Permian metasediments unconformably overlain by tertiary sediments which are themselves overlain by younger semi-consolidated deposits of a probable Pleistocene age. The pre-tertiary sequence, composed mainly of argillaceous and arenaceous sediments, was deposited in a shallow marine environment while the sediments that make up the Tertiary coal measures sequence of sandstone, shales, and coal seams were laid down in a fresh water fluvio-lacustrine depositional setting [3]. Stauffer (1973) suggested that fault movement along Kuala Lumpur Fault Zone controlled the structure of Batu Arang Tertiary Basin [4]. Mahendran (1991) suggested that the Batu Arang Tertiary basin is possibly a half graben resulting from wrench faulting in the early Cenozoic [5]. Tjia (1978, 1995), however, believed that the basin was formed by gradual subsidence of its presumably calcareous basement and suggested that fault movement within the area only persisted until middle Eocene time [6,7]. Earlier workers, such as Scrivenor (1931) and Roe (1953) suggested a Miocene age for the Batu Arang coals [8,3], but a recent analysis of polymorph assemblages by Ahmad Munif (1993), suggests that the age of the Batu Arang coals is older, probably Eocene to Oligocene [9]

The Tertiary coal measures of Batu Arang comprises of two main coal seams: the upper seams averages 9 m and lower seam averages 6 m in thickness, and both thin westwards [4]. The coal was mined between 1915 and 1960 by open cast and underground mining methods, and a total of 13.2 million tonnes were produced [10]

In this study, eleven organic-rich Tertiary sediments, consisting of two shale, a coaly sandstone, a sandy base, three intercalation of coal with shale, and four coal samples, were examined by organic petrological method. All sediments samples are from the sampling station B (Fig. 1.2 - 1.3 (a) & (b)), however; they were sampled layer by layer.

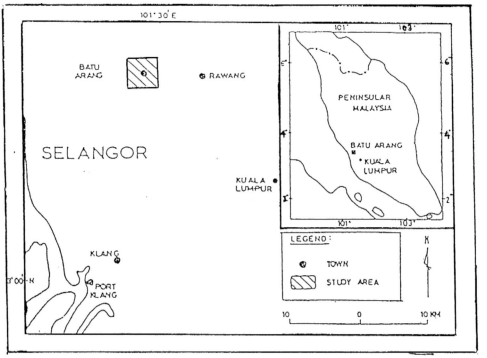


Fig. 1.1 *Locality map of study area*

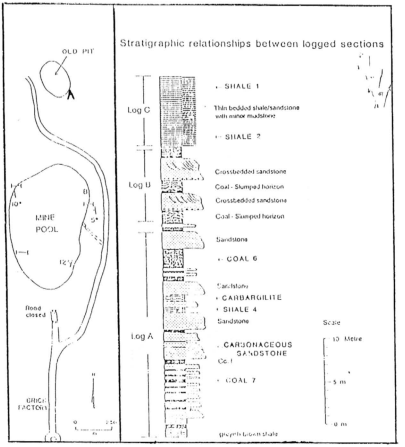


Fig. 1.2 *Batu Arang coal mine and stratigraphic relationship between logged section (Adapted from [13])*

Fig 1.3(a) *Photo taken of old mining pond in Batu Arang (near sampling station).*

Fig. 1.3(b)

Photo taken of sampling Station A shows the stratigraphic of different rock layers

1.3 COAL ANALYSIS

The characterisation of coal is a very complex matter and must take account of several aspects of its nature. Hence a large number of standard analyses and test have been developed [14]. Examples of conventional standard coal characterisation methods are proximate analysis (moisture, ash, volatile matter and fixed carbon content), elemental analysis (C, H, N, S and O content), petrographic analysis, calorific value and swelling index. On the basis of these methods, coals are classified according to a rank order. With increasing coal rank, coals are assigned to one of the following classes: peat, lignite, sub-bituminous coal, bituminous coal, anthracite and graphite.

More recently, the availability of modern investigation technique have oriented coal characterisation towards different strategies: electron spin resonance spectroscopy (ESR) [15], solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy [16-18], Fourier transform infrared (FTIR) spectroscopy [19-20] and Curie-point pyrolysis techniques [21-22]. Modern analytical strategies can provide a deeper and more accurate picture of the detailed coal composition.

Coal is made out of *aromatic* and *aliphatic* compounds. Aromatic compounds have structures in which carbon atoms are linked in closed rings; aliphatic compounds have carbon atoms in the form of open chains. Some of these compounds have functional groups (group that confer a characteristics type of reactivity) attached to those carbon atoms that are common to only one ring or that are at the end of a chain. The functional groups play an important role in the reactivity of coal during metamorphism and during the various processes involved in the economic use of coal (such as carbonization, gasification, and liquefaction) [23].

Among fuel sources being investigated as alternatives to petroleum, coal-derived liquids have generated considerable interest because of the abundance and low cost of coal feedstock. Various sources and processing methods produce coal liquids with different chemical compositions. When evaluating the overall usefulness and acceptability of these various coal liquids as fuel sources, it is important to include measurements of utile energy content and health risk assessment using

biological tests. The energy content of a fuel can often be determined using easily measured properties such as C/H ratios. However, biological testing to date has shown that in many instances only a few potent chemical compounds, present at trace levels in a coal liquid, account for most of the biological activity. Consequently, samples must be characterized extensively so that these species can be identified and determined. This task is made difficult, however, by the complexity of coal liquids; they are known to contain numerous hydrocarbon including, "simple" aromatics (including benzene and polycyclic aromatics), alkyl- and other substituted aromatics, hydroaromatics and heterocyclics. Therefore, a combination of several high-resolution analytical methods is usually required to characterise fully a particular coal liquid sample.

Prefractionation can both simplify and reduce the number of high-resolution analyses needed to characterise a coal liquid thoroughly. Prefractionation by normal-phase high-performance liquid chromatography (HPLC) using silica, amino and amino-cyano columns have been reported [24-26]. All the reported prefractionations however required the use of *back-flush* (refer Fig.2.1) in order to elute the aromatic fraction. Although the use of a back-flush is acceptable, a simplified prefractionation procedure that does not require the switching of valves in the middle of the chromatographic run would be of value.

In response to the limitations of existing polar stationary phases and liquid-solid chromatographic (LSC) adsorbents, a method employing isocratic normal phase will be investigated as a preliminary study to separated model compounds into aliphatic and aromatic fractions. In the study described here, the normal phase column was investigated further and used to fractionate coal liquid samples on a semi-preparative scale.

1.4 CHARACTERISTICS OF ORGANIC GEOCHEMISTRY: BIOMARKER

Biomarkers are individual organic constituent of sediments, sedimentary rocks and petroleum, which derive from biological precursor [27]. The constitute only a minor proportion of sedimentary organic matter, but their variety and structural diversity are invaluable aids to the decipherment and assessment of sediment maturity and depositional settings. The origins and sedimentary fates of biomarkers govern their occurrences, distributions and abundance, which can be determined by a variety of chromatographic and spectroscopic techniques. Biomarker assemblages provide a record of the environment in which they were deposited and the diagenetic processes that have subsequently influenced and modified them. Specific biomarker characteristics permit the differentiation of lacustrine and marine environments can aid the assessment of sea surface temperatures and salinity levels. Also, biomarkers undergo systematic and sequential transformations during diagenesis and the changes in their compositions can therefore be used as measures of the thermal history of sediments. Furthermore, the temperature range of biomarker transformations is sufficient that a combination of diagnostic reactions can quantify maturity changes from the earliest stages of sedimentation through the phases of petroleum generation by the thermal breakdown of organic matter. The varied evidence of environmental and thermal history contained in the biomarkers of sedimentary rocks typically survives within the compositions of their derived petroleums, thereby enabling correlation between oils and their source rocks. Under suitable conditions, however, reservoired petroleums can be degraded by aerobic bacteria, which selectively remove their biomarker components in an ordered sequence.

Biomarkers are discrete components within the solvent-soluble (or "lipid") portion of the organic matter of sediments, sedimentary rocks and petroleum. They differ in two respects:

(i) Their structural affinities

(ii) Their chemical functionality

In general, analytical procedures tend to separate biomarkers according to their functionality (see Table 1.1), but the generic affinities of biomarkers reside in their structures and it is therefore this characteristics which is most useful in their geochemical description. This preference also stems from the resilience of the structural skeletons of biomarkers as hydrocarbons compared to their functionalised counterparts, such as alcohols, ketones or carboxylic acids (Table 1.2). Specifically, the process of sediment diagenesis tend to modify the wide range of functionalised compounds synthesized by biota so that only their hydrocarbon counterpart survive in the ancient sedimentary record. However, it is important to recognise that comparatively few of the components are formed as hydrocarbons within living system. Yet the chemical nomenclature of biomarker types is based on their aliphatic hydrocarbon within living systems. Yet, the chemical nomenclature of biomarker types is based on their aliphatic hydrocarbon parent forms, which therefore serve as an appropriate basis for the description of the various important biomarker families.

Table 1.1 *Chemical aspects of the description of major functional groups in biomarkers.*

Group	IUPAC Name	Symbol	Suffix	Prefix
Alkene	alkene	>C=C<	-ene	-
Alcohol	alkahol	-OH	-ol	hydroxy-
Aldehyde	alkanal	-HC=O	-al	oxy-
Ketone	alkanone	-C=O	-one	oxy-
Acid	Alkanoic acid	-COOH	-oic acid	-
Ester	Alkyl alkanoate	-COOR	-oate	-

Table 1.2 *Chemical structures of major biomarker families.*

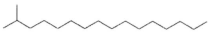
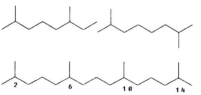
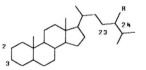
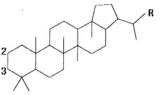
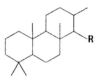
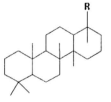
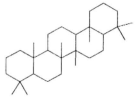
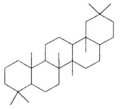
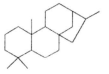
BIOMARKER FAMILY	STRUCTURES	CARBON NO RANGE	COMMENTS
n-Alkanes (tetradecane)		1-60	
Monomethyl branched alkanes (2-methylhexadecane)		4-40+	Branching can exist at any position
Acyclic isoprenoids (pristane - 2,6,10,14-tetramethyl-hexadecane		5-40	Compounds from isoprene units, either head-to-tail, tail-to-tail or head-to -head
Steranes R= CH_3, C_2H_5 or C_3H_7 (Methylsterane, at C-2, C-3 or C-4)		27-31	Various positions for methylation
Hopanes R= CH_3, C_2H_5 or C_3H_7 (Methylhopanes, at C-2, C-3 & Norhopanes at C-23 and/or C-28)		26-40	Various position for methylation of demethylation

Table 1.2 *Chemical structures of major biomarker families.*

(Continued)

BIOMARKER FAMILY	STRUCTURES	CARBON NO RANGE	COMMENTS
Tricyclic terpanes R= CH_3 - $C_{26}H_{53}$		19-45	Demethylated tricyclic terpanes also reported
Tetracyclic terpanes R= H, CH_3 - $C_{11}H_{23}$		24-35	C_{31} - C_{35} rare
Gammacerane		30	
Oleanane		30	Various structure for similar pentacyclic triterpenoids
Kaurane		20	Various similar structures for tetracyclic diterpane

We can study organic matters at its various structure levels and from diverse perspectives. At the *atomic* level, elemental and isotopic compositions are essential parameters that are used to determine mass transport, elucidate pathways, and construct inventories. At molecular level, the structure and stereochemical variations of individual organic compounds, *biological markers or biomarkers*, are important means of tracing source organisms, subsequent diagenetic affects, and thermal history [28]. For example, the C_{30} hydrocarbon squalene is a universal precursor molecule but, depending on the class of organism, can be transformed into a great variety of acyclic, tetracyclic, and pentacyclic product molecule (Fig.1.3).

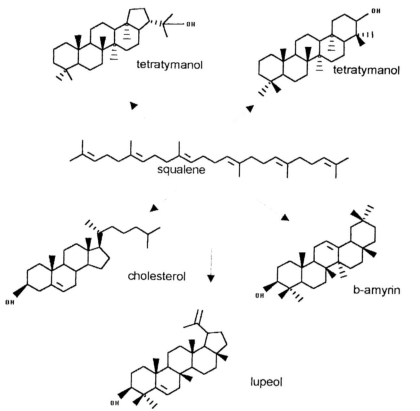


Figure 1.4 *An illustration of the varied structures, which can be produced when the ubiquitous precursor hydrocarbon squalene is cyclized by different classes of organism. Diplopterol is synthesized by Eubacteria, cholesterol by eukaryotes, and tetrahymanol by some protozoans and bacteria. Lupeol and β-amyrin are higher plant products. Cyclizations to diplopterol and tetramanoltake place anaerobically. The other transformations require molecular oxygen and are presumed to have appeared after the advent of oxygenic photosynthesis.*

1.5 OBJECTIVE OF PRESENT STUDY

Chromatography in reversed-phase systems is the most popular mode used in the contemporary practice of coal analysis by liquid chromatography. However, columns packed with polar adsorbents often show better separation selectivities than alklysilica column for various positional isomers of moderately polar compounds or for oligomers containing repeat polar groups. [29]

During gradient-elution chromatography in normal silica phase systems, the concentration of one or more polar solvent(s) in a non-polar solvent is increased. A disadvantage of this technique with respect to reversed-phase gradient elution is the possible preferential adsorption of more polar solvent(s) on the surface of the polar adsorbent, which may lead to important deviation of the actual gradient profile from the pre-set mobile phase composition program.

Reproducibility of gradient-elution retention data in normal phase systems with mobile phases composed of two organic solvents, a polar and a non-polar one, depends on a number of experimental factors that should be controlled. To obtain reproducible results, it is necessary to keep a constant adsorbent activity [30]. It is very important to work at a constant temperature and water content in the mobile phase. This can be achieved with dehydrated solvents that are kept dry over activated molecular sieves and filtered just before the use. Furthermore in predictive calculation of the gradient retention data in normal-phase gradient-elution chromatography, it is very important to account for the isocratic pre-elution before the start of the gradient, which is caused by the mobile phase of initial composition that is contained in the gradient dwell volume of the instrument. [31]

The objective of this study is to develop a suitable method for chemical class separation, namely aliphatic and polynuclear aromatic hydrocarbons (PAHs) by high-performance liquid chromatography (HPLC) isocratic elution. As this scheme is generally more reproducible as compared to gradient elution. The developed method is then applied to fractionate the coal extract, coal sampled from Batu Arang, Selangor.

We have therefore chosen for this study, standard commercial normal-phase (silica) HPLC columns to separate the coal rock (from Batu Arang) extracts. Two detectors will be used for this work, based on the fact that these are sensitive and that they complement one another in the type of information each provides. The first is a conventional UV absorbance detector operating at 254nm. This detector has demonstrated detectability in the nanogram range. The second is refractive index (RI) detector. The detection limits is not as low as UV. However the RI detector can be use to detect non-UV detectable compounds (i.e. *n*-alkanes) [38].

Several analytical method such as supercritical fluid chromatography (SFC), HPLC and GC have been used for coal characterization. GC has been successfully interfaced with appropriate identification technique such as mass spectroscopy. To date GC-MS has been extensively studied method of identification of individual components in a coal mixture. [36]

Planar chromatography is another popular method of coal characterization. One of the applications is preparative thin layer chromatography where fraction of material applied to the plate, can subsequently be recovered and examined by other micro-analytical techniques [40].