THE GEOCHEMISTRY OF MUKAH AND BALINGAN COALS: A NATURAL PRODUCT APPROACH

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THE GEOCHEMISTRY OF MUKAH AND BALINGAN COALS: A NATURAL PRODUCT APPROACH

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This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours (Resource Chemistry)

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DECLARATION

No portion of the work referred in this dissertation has been submitted in support of an application for another degree of qualification of this way or any other university or institution of higher learning.

__________________________________

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The Geochemistry of Mukah and Balingan Coals: A Natural Product Approach

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ABSTRACT

Balingan and Mukah coals were investigated for their organic geochemical contents. The coal samples were extracted sequentially on Soxhlet apparatus using dichloromethane and methanol. The crude extracts were subjected to fractionation on silica gel column chromatography into aliphatic hydrocarbon, aromatic hydrocarbon and polar organic compound fractions. These fractions were then analyzed on gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectroscopy (GC-MS). Analysis on aliphatic hydrocarbon fractions showed that both coals have been deposited under reducing or anoxic environment. Organic matters in Balingan and Mukah coals are thought to be originated from inland swamp and derived from marine environment. Polycyclic aromatic hydrocarbons (PAHs) data showed that both Balingan and Mukah coals are thermally immature. Several organic compounds have been successfully isolated and the significant organic compounds identified were grouped in fatty acid or ester compounds. Biomarker indices derived from distribution of hydrocarbons indicated that both coals were originated mainly from terrigenous higher plant with low thermal maturity.

Keywords: Organic geochemistry, gas chromatography, Soxhlet extraction, hydrocarbons, biomarkers, column chromatography.

ABSTRAK


Katakunci: Geokimia organik, kromatografi gas, pengekstrak Soxhlet, hidrokarbon, penandabio, kromatografi turus.
CHAPTER 1
INTRODUCTION

1.1 General Introduction

Coal is one of the world’s most important sources of energy, fuelling almost 40% of electricity worldwide. It also has been the world’s fastest growing energy source in recent years which is faster than gas, oil, nuclear, hydro and renewable (Schobert, 1989). The quality of each coal deposit is determined by temperature, pressure and by the length of time in formation, which is referred to as its organic maturity. There are coal types with low organic maturity which is call as lignite or brown coal. Lignite is quite soft and its colour can range from brown to dark black. When further chemical and physical changes occur these coals became harder and blacker, forming the bituminous or hard coals (Alpern et al., 1989).

Coal is form from fossilized plant remains in the swamps and coal is a complex heterogeneous mixture of macromolecular organic compound (Stach et al., 1975). It derived from the accumulation and also the alteration of the plant debris in the swamps area or the moist environments. Coal is a fossil fuel and generally hard, black coloured rock like substance. It is a combustible, sedimentary, organic rock, which is made up of carbon, hydrogen and oxygen, nitrogen and varying amount of sulphur.

The predominant elements in coal are carbon, hydrogen, and oxygen, with lesser amounts of sulphur and nitrogen (Schobert, 1989). So, it is true that coal was formed from components of plants such as pollen, which can be found in many coals. When coal is examined under a microscope, cellular structures similar in appearance to plant tissues can be observed.
Coals come from dead plant which have been buried and compacted beneath sediment. Coal formed from vegetation, which has been consolidated between other rock strata and altered by the combined effects of pressure and heat over millions of years to form coal seams. Coal is known as an organoclastic sedimentary rock, composed essentially of lithified plant debris. The initial sediment formed by this process is a moist, spongy material called peat but later it will compressed, dried and modified or change in both composition and texture due to diagnosis associated with burial and tectonic activity (Ward, 1984).

Coal can be also known as a heterogeneous mixture of organic compounds, together with certain amount of inorganic material in the form of moisture and minerals impurities. The properties of a coal depend on the nature of the various components in the original organic accumulation, including both the forms of vegetation represented and the degree of degradation or decay that they have suffered prior to burial.

The origin of coal is described in terms of the possible chemical constituents of the original plant material. Indeed, acknowledgement that the tissue of the original plants can themselves contribute to the physical structure of coal has led to the development of the area of scientific investigation known as coal petrography (Murchinson, 1968). Coal petrography is an investigation of the physical macrostructures and microstructures of coal and its subsequent identification in terms of those structures.

1.2 Statement of Problem

Coals are produce from many types of plant. It can be said that coal are produce from different types of sources and come from different types of origin. Each coal has different types of hydrocarbons and polar constituents. The amount of hydrocarbon inside
the hydrocarbon and polar constituents also differ from each other. This study will determine the chemical composition of the hydrocarbons as well as the polar constituent in the coals. In order to predict the accumulation history of organic matter and the sources of coal’s maturity during the coal formation in environment, the distribution of organic compound particularly biomarkers will be used.

1.3 **Objectives of the Project**

The objectives of this study are:

a) to extract the organic constituents from Mukah and Balingan coals using sequential Soxhlet extraction.

b) to isolate the organic components in crude dichloromethane and methanol extracts on silica gel column chromatography.

c) to determine the organic compositions of each fraction using gas chromatographic method.

d) to predict the source of organic matters and maturity based on organic geochemistry characteristics in coals.
CHAPTER 2
LITERATURE REVIEW

2.1 Formation of Coal

Coal forms from the accumulation of plant debris, usually in a swamp environment. When plant debris dies and falls into the swamp the standing water of the swamp protects it from decay. Swamp waters are usually deficient in oxygen, which would react with the plant debris and cause it to decay (Krevelen, 1993). This lack of oxygen allows the plant debris to persist. In addition, insects and other organisms that might consume the plant debris on land do not survive well under water in an oxygen deficient environment.

To form the thick layer of plant debris required to produce a coal seam the rate of plant debris accumulation must be greater than the rate of decay. Chemical and physical forces play an important role in the decay of plant materials. Once a thick layer of plant debris is formed it must be buried by sediments such as mud or sand. These are typically washed into the swamp by a flooding river. The weight of these materials compact the plant debris and aids in its transformation into coal. About ten feet of plant debris will compact into just one foot of coal.

The transformation of wood to coalified wood, or vitrinite, the major petrographically identifiable and volumetrically the most significant component of most coals, begins at the peat stage where cellulose is preferentially degraded and removed from the wood while the lignin, an aromatic wood biopolymer, is selectively preserved (Hatcher et al., 1982; Stout et al., 1988). Perhaps the most astounding aspect of this degradative process is the selectivity and structural precision with which it occurs.
Essentially the cellulose which is the major component of wood is lost. Apparently, the wood has been degraded by micro-organisms (bacteria and fungi) which use extracellular enzymes to enable destruction of the cellulosic materials. This process apparently does not involve physical maceration.

Shibaoka (1972) reported that the former type of coal seam was assumed to have been formed under conditions of relatively rapid regional subsidence with variable rates of local subsidence superimposed during the time of deposition (here designated "unstable" conditions), and the latter type of seam under conditions of relatively slow, uniform regional subsidence throughout the time of deposition (here designated "stable" conditions).

### 2.2 Classification of Coal according to rank

![Figure 2.1: Lignite Coal](image1)

![Figure 2.2: Bituminous Coal](image2)

![Figure 2.3: Anthracite Coal](image3)

The different grades or types of coal vary between relatively unchanged plant material and pure carbon. There are number of ways in which the different types of coal can be classified or rank. Some classifications rely on the use to which the coal is put but one common classification system divides coals into various rankings based on a range of properties which is based on the energy level from lower energy level to higher energy level or based on the moisture holding capacity.
There are three types of coals exist which are low rank coals, medium rank coals and higher rank coals. A ternary division of rank is maintained with the categories: low rank coal or lignite, medium rank coal or bituminous coal and high rank coal or anthracite (Alpern et al., 1989). The evaluation happened from peat stage into lignite coal is called coalification process and it is used to determine the rank of the coal. The coalification process occurs due to the high temperature and geological time (Stach et al., 1975).

Low rank coals, such as lignite and sub-bituminous coals are typically softer, friable materials with brown in colour. It is also known as brown coal. They are characterised by high moisture levels and low carbon content, and therefore have lower energy level. Higher rank coals, however, are generally harder and stronger and often black in colour. They contain more carbon, have lower moisture content, and produce more or higher energy. Anthracite is at the top of the rank scale and has a correspondingly higher carbon and energy content and a lower level of moisture.

2.3 Organic Composition of Coal

According to Speight (1994), coal can be defined as high molecular weight organic compound that composed of different and variety of carbon system. Coal can be classified with the general formula including carbon, hydrogen, nitrogen, oxygen and sulphur (Speight, 1994). Generally, coal is come from organic debris of plant because plant material consist the organic portions that include carbohydrates, lignin, proteins and also other polymer. The most abundant organic compounds inside coal are hydrocarbons and polar compound. Different coal contains different types of hydrocarbon and polar compound.
2.3.1 Hydrocarbons

Hydrocarbons (C\textsubscript{x}H) only consist of the elements carbon (C) and hydrogen (H). They contain a carbon backbone where hydrogen atoms are bounded. Schellenberger (2011) stated that methane is the simplest hydrocarbon and is also called swamp or marsh gas. It has one carbon atom and four hydrogen atoms (CH\textsubscript{4}). The recognition of the biomarkers in coal samples provides valuable information about the original organic matter and the transformation reactions that took place during sedimentation.

As stated in Van Krevelen’s (1993) book, structure of the parent biogenic macromolecules can determine the original biological markers and it can be called biochemical precursors. The organic molecules which have the skeleton that can be characteristic of certain groups of plants are called biological markers (Tissot and Welte, 1984). This biological markers or biomarkers such as hydrocarbon fraction can be used to determine the maturity of the coal or maturity indicator of the coal. Different hydrocarbon maturity determined different coal rank and type.

The distribution of n-alkanes in tertiary coals and lignites is generally characterised by a predominance of odd-carbon numbered homologues of high molecular weight, maximising at n-C\textsubscript{27}, n-C\textsubscript{29} and/or n-C\textsubscript{31} (Villar \textit{et al.}, 1988; Stout, 1992; Schoell \textit{et al.}, 1994). These hydrocarbons are considered to be derived from cuticular waxes of terrestrial plants (Tissot and Welte, 1984). In older coals the composition of n-alkanes may have a diverse fingerprint. In a Lower Carboniferous coal, the composition of linear alkanes is dominated by the C\textsubscript{20}–C\textsubscript{23} homologues, without any remarkable odd or even preference (Disnar and Harouna, 1994). According to the authors, these n-alkanes may
indicate the input of non-flowering plants which thrived at the time of the sediment deposition.

Conifer resin-derived tetracyclic diterpanes are other common constituents of coals (Villar et al., 1988; Haven et al., 1992). More recently, unexpected presence of ent-beyerane, phyllocladanes and kauranes in coal samples (Lower Carboniferous Gondwana) that predate the evolution of gymnosperms has led Disnar and Harouna (1994) to question the information and belief that they are only derived from such plants. Bacterially-derived hopanes, which have no age relationship, have been detected in several coal samples of different ages and degrees of thermal maturation. In many cases, the more abundant component is the C_{31} \( \alpha\beta \ 22R \) hopane, with secondary contributions of other \( \alpha\beta \) homologues, \( \beta\alpha \) and \( \beta\beta \) isomers (Hazai et al., 1988; Lu and Kaplan, 1992).

The distribution of aromatic hydrocarbons in coal and lignite extracts also reflects the origin and age of the sample. In this way, angiosperm-derived triterpenoids with oleanane and ursane skeletons may contribute significantly to Tertiary coals (Chaffee and Johns, 1983; Villar et al., 1988; Stout, 1992). Regardless of the sample history, alkylnaphthalenes and alkylphenanthrenes are usually present in coal extracts (White and Lee, 1980), (Villar et al., 1988; Vliex et al., 1994). Polycyclic aromatic hydrocarbons (PAHs) of pyrolytic origin such as pyrene and chrysene have also been detected in coal samples (White and Lee, 1980; Chaffee et al., 1986).

2.3.2 Polar Constituents

One of the most important polar constituents that will be found in coal is phenol compounds. The recovery of “natural” phenol from coal tar is still a fully operational
method to recover phenol. Coal tar is a complex mixture of condensable organic components, emerging from coal carbonization (Frank and Collin, 1968). During the fractionation of the coal tar, so-called carbolic oil fraction is separated and contains 30–35 wt% phenolic components. These phenols are called tar acids.

The carbolic oil is treated with diluted caustic soda to extract the phenols as sodium phenolate salts. The aqueous phenolate solution is then treated with carbon dioxide to liberate the phenols from the salts. This crude phenol fraction from carbolic oil consists of phenol, cresols, and xylenols. A typical composition is 30 wt% phenol, 12 wt% o-cresol, 18 wt% m-cresol, 12 wt% p-cresol, 8 wt% xylenols, 15 wt% water, and 5 wt% tar (Frank and Collin, 1968).

Besides coal tar, other sources of “natural” phenols are the liquid byproducts from gasification processes. Phenol, cresols, and xylenols are recovered from the aqueous phase by solvent extraction, for example with the Lurgi Phenosolvan process. A large source of natural phenols is the liquid by-products from Sasol’s gasification process in South Africa (Frank and Collin, 1968).

The phenols are produced and marketed by Merisol, a joint venture between Sasol and Merichem (USA), with a total production of phenols (phenol, cresols, xylenols) of about 110,000 metric tons per year in 2003 (Weber, 2010). Another large source is the recovery of phenols from the gasification process of lignite coal at Dakota Gasification Company (USA). The annual production of phenol there is about 20,000 metric tons.

2.4 Properties of Coal

There are various properties that provide even more valuable information about the potential of coal (Krevelen, 1993). Indeed, there are also properties of organic materials
that offer valuable information about environmental behaviour (Lyman et al., 1990). Four types of coal’s properties that have been found are physical properties mechanical properties, thermal properties and electrical properties.

The physical properties and behaviours of coal play an important part in dictating the methods by which coal should be handled and utilize. Physical properties consider properties such as density or specific gravity, in-place density, porosity and surface area, reflectance, and refractive index. There are three different density measurements: true density, particle density and apparent density (Speight, 1994).

True density of coal is determined by displacement of a fluid, the density data of varying with the fluids because of the porosity of coal and the physiochemical interaction. The true density also can be measure or determine by helium displacement. It is because helium can easily penetrate to the pores of the coal. The apparent density of coal can be determined by immersing a weighed sample of coal in a liquid and to get the accurate amount of liquid needed whereas place density can be defined as the coal in the seam can be expressed as tons per acre per foot of the seam thickness.

Coal porosity and surface area is influenced during the coal mining, preparation and utilization. Porosity influenced the rate of the methane can diffuse out of the coal and mineral matter removal during preparation. Coal reflectance is very useful because it indicates several important properties of coal. Coal reflectance is determined by the relative degree to which a beam of polarized light is reflected from a polished coal surface. Last but not least is the refractive index. Refractive index can be determined by comparing the reflectance in air with that in cedar oil.

The mechanical properties are important to predict the strength and the stability of the coal. The mechanical properties are included strength, hardness, friability, grindability, Dustiness index, Cleat structure, Deformation and flow under stress. The compressive
strength is decrease from the lower rank to the highest rank. The anthracite has a lower compressive strength than the lignite. The hardness of the coal also includes the friability and grindability of the coal.

Friability is the tendency towards breaking and depends on toughness, elasticity and fracture and also the strength. The grindability is a physical property but also have specific properties such as hardness, strength, tenacity and fracture. The dustiness index is the amount of dust produced by coal. In the coal formation, a system of joint planes is known as cleat joints. The cleat joints are affected by the properties of coal deposited (Speight, 1994).

The thermal properties are important to the combustion, carbonization, gasification and liquefaction process. The thermal properties are included Caloric value, heat capacity, and thermal conductivity. The caloric value is use to know the energy content and usefulness of coal. Heat capacity is the heat requires to raise the temperature of one unit weight of a substance by 1 °C. The specific heat of coal increases with the moisture and decreases with the carbon content, and also increase with the volatile matter content. Thermal conductivity is the rate of heat transfer by conduction through a unit area across a unit thickness for a unit difference in temperature. It is increase when the volatile matter content, ash content, and temperature increase (Carslaw & Jaeger, 1959).

The last properties of coal are the electrical properties. It is including specific resistance, electrical conductivity, and dielectric constant. The electrical conductivity of a coal is depending with temperature, pressure, and moisture content. The dielectric constant was varies with the different in the coal rank (Speight, 1994).
CHAPTER 3
MATERIALS AND METHODS

3.1 Sample Collection and preparation

Coals sample was collected from Mukah and Balingan of Mukah Division, Sarawak which are the well known area in production of coal as electric power plants in Sarawak. It is located at Matedang, Mukah Division about 550 km from Kuching. Prior to extraction, the coal was crushed into powder form with the size of < 1.0 mm/70 mesh. The coal was weighted about 55 g before placed inside a thimble for Soxhlet extraction.

3.2 Extraction of coal samples

Sequential extraction of coal samples were performed using Soxhlet extraction for 24 hours. The coal samples were first extracted with dichloromethane (DCM) followed by methanol to obtain dichloromethane and methanol extracts respectively. The extraction for each solvent was done in triplicate. The extracts were evaporated to nearly dryness (1-2 mL) using a vacuum rotary evaporator, redissolved with dichloromethane and then transfer to 10 ml-capacity vial using a Pasteur pipette. The extracts were then evaporated to dryness under gentle purified nitrogen stream and stored in dark and cold places until fractionation.
3.3 Fractionation of Crude Extracts

3.3.1 Crude dichloromethane extract

The fractionation of dichloromethane extract was performed according to procedure described by Buco et al. (2004) with a slight modification. The glass column (30 cm × 1 cm i.d.) was packed with 16 g of 70–230 mesh silica gels. The silica gel was deactivated with 5% of MQ water. An aliquot of the DCM extracts (30 mg in 1mL hexane) was placed on the top of the column and then fractionated into aliphatic hydrocarbons (F1) and aromatic hydrocarbons (F2) as shown in Table 3.1. All fractions were collected in pear-shaped flask. All the fractions were evaporated to near dryness using vacuum rotary evaporator. The fractions were then redissolved with 2-5 mL dichloromethane and transfer to a 10 mL-capacity vial using Pasteur pippete. The fraction was then evaporated to dryness under gentle nitrogen stream and was stored in dark places until further analysis. Prior to GC-MS analysis, the fractions were diluted with 200 µL of dichloromethane.

Table 3.1: Solvent system used to fractionate the dichloromethane extract

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Solvent system</th>
<th>Volume (mL)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Hexane</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>F2</td>
<td>Hexane: Dichloromethane</td>
<td>20</td>
<td>90:10 v/v</td>
</tr>
<tr>
<td></td>
<td>Hexane: Dichloromethane</td>
<td>40</td>
<td>80:20 v/v</td>
</tr>
</tbody>
</table>