HYDROCARBON BIOMARKERS IN COALS FROM SUNGAI MAS, MUKAH-BALINGIAN AND MERIT PILLA SARAWAK

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HYDROCARBON BIOMARKERS IN COALS FROM SUNGAI MAS, MUKAH-BALINGIAN AND MERIT PILLA SARAWAK

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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 Programme)

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DECLARATION

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

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Coal samples Merit pilla, Sungai Mas and Mukah-Balingian were studied qualitatively and quantitatively to determine the distribution of hydrocarbon. The coal samples were extracted with Soxhlett extraction method and fractionated on silica gel column chromatography to get the aliphatic (F1) and aromatic (F2) fraction. The aliphatic and aromatic fraction were analysed using gas chromatography/flame ionization detector (GC/FID) and gas chromatography/mass spectrometry (GC/MS). Proximate analysis showed that the organic matter and volatile for the Merit Pilla and Mukah-Balingian is more than 80% with a moisture content (11.77% for Merit Pilla and 24.64% for Mukah-Balingian) low volatile matter for Sungai Mas coal samples (45.57%) with a quite low of moisture content (2.79%). Biomarkers study based from the n-alkanes distribution, ratio of isoprenoids groups, isoprenoid/n-alkanes and CPI values gives the information to support the origin of these coal samples either from the higher terrestrial plants with the higher content of wax or evolved from algae, bacteria and zooplankton. The quantitative analysis were done to the aromatic hydrocarbon fraction (F2) to determine the distribution of aromatic hydrocarbon in the coal samples. The aliphatic fraction (F1) was further analysed by GC/MS to determine the quantitative distribution of n-alkanes, hopanes, diterpanes and triterpanes compound which are consistent to higher plants.

Keywords: Coal, aliphatic and aromatic hydrocarbon, biological markers, GC/FID, GC/MS
ABSTRAK

Sample arang batu Merit Pilla, Sungai Mas dan Mukah-Balingian telah dikaji untuk mengetahui taburan hidrokarbon secara kualitatif dan kuantitatif. Sample arang batu telah diekstrak menggunakan pengekstrak Soxhlet dan difraksikan pada turus kromatografi gel silika untuk mendapatkan fraksi alifatik (F1) dan aromatik (F2). Fraksi alifatik (F1) dan aromatik (F2) dianalisis menggunakan kromatografi gas/pengesan nyalaan ion (GC/PIN) dan gas kromatografi/spektrometri jisim (GC/MS). Analisis proksimat menunjukkan bahawa bahan organic dan bahan meruap di dalam sample arang batu dari Merit Pilla dan Mukah-Balingian melebihi 80% dengan kelembapan yang agak rendah (11.77% untuk Merit Pilla dan 24.64% untuk Mukah-Balingian) dan kandungan bahan meruap yang rendah bagi sample arang batu dari Sungai Mas (45.57%) dengan kandungan kelembapan yang rendah (2.79%). Analisis geokimia berdasarkan kepada nisbah kumpulan isoprenoids, taburan hidrokarbon, isoprenoids/hidrokarbon dan nilai CPI memberikan maklumat tentang asalan bahan organic dari setiap sampel arang batu samada berasal dari tumbuhan daratan tinggi dengan kandungan bahan berlilin yang tinggi atau daripada tindakan mikroorganisma seperti alga, bacteria dan zooplankton dengan kerogen adalah jenis marin satu. Analisis kuantitatif telah dilakukan kepada fraksi aromatik (F2) untuk mengetahui taburan hidrokarbon aromatik di dalam setiap sampel arang batu. Fraksi hidrokarbon alifatik (F1) dianalisis menggunakan GC/MS untuk mengetahui taburan hidrokarbon, hopana, diterpena dan triterpena dimana ia kekal di dalam tumbuhan daratan peringkat tinggi.

Kata kunci: Arang batu, hidrokarbon alifatik dan aromatik, penandan biologi, GC/FID, GC/MS
1.0 INTRODUCTION

Coal is an organoclastic sedimentary rock, composed essentially of lithified plant debris. The initial sediment formed by this process is a moist, spongy material called ‘peat’. However, it’s becomes compressed, dried and modified in both texture and composition due to diagenesis associated with burial and tectonic activity. The properties of coal depend on the nature of the various components in the original organic accumulation including types of vegetation represented and degree of degradation. Such components are analogous to the different mineral constituents found in inorganic sediments. They are organic materials and characterized by their botanic structure rather than their crystallographic properties. Thus, they are known to coal petrology as macerals.

Coal is made up of humic organic matter, which experienced several streps of devolatilization with increasing rank (Stach et al., 1982). It consist mostly of carbon with lesser amounts of water, nitrogen and sulfur (Arms, 1990). Coal is a brown or black carbonaceous deposit derived from the accumulation and alteration of ancient vegetation which originated largely in swamps or other moist environments. As the vegetation decomposed it formed peat layers, which were subsequently buried for example by marine sediments following a rise in sea level or subsidence of the land.

Coal can be classified into two types, i.e humic or woody coal that is derived from plant and sapropelic coal which are derived from algae, spores and finely divided plant material. The formation of coal from plant materials is shown in Figure 1.
Figure 1: Formation of Coal from compacted dead plant materials.
2.0 LITERATURE REVIEW

The Merit Pilla have a total coal potential of about 250 tonnes of low ash, low sulphur, high grade ortho-lignite with no coking property. Moisture is less than 20% and volatile matter between 35%-45%. The coal has a moderate calorific value of about 6,000 Kcal/kg (Chen, 1970).

Norgate et al. (1994) have studied the changes in hydrocarbon maturity indices with coal rank and type. The degrees of thermal alteration of organic matter in sedimentary basins can be estimated using the maturation indices which are based on the relative abundances of hydrocarbons. Alteration of organic matter during deposition and early diagenesis also imparts a chemical signature, which occurred at the later catagenetic stages. A better identification and relationships between hydrocarbon distributions, reliable thermal regime and the organic facies of source rocks required for maturity parameter.

The biological marker is the complex compound, which can be derived from the organisms, that have carbon, hydrogen and other substances that were from depositional and rocks showed the similar structure with the origin of organic matter in the organisms. The organic matter must have the component showed the structure of organisms, high abundance and distribution and also can be determined although occur in the complex mixture before it might used as the biological marker (Seifert & Moldowan., 1986). The aromatic hydrocarbon fraction can be used a biomarkers and also as maturity indicator for coals. The distribution patterns of several series of alkynaphthalenes, alkylphenanthrenes and benzothiophenes can be used for maturity measurement. Miranda et al. (1999) have studied the aliphatic and aromatic hydrocarbons in
Candiota coal samples. The biomarkers in coal samples provide a useful information on the origin of organic matter and transformation reaction that undergone during sedimentation.

The distribution of n-alkanes is describes by a predominance of higher molecular weight of molecules maximizing at n-C_{27}, n-C_{29} and n-C_{31} (Villar et al., 1988; Stout, 1992 and Schoell et al., 1994) and also derived from waxes of terrestrial plants (Tissot & Welte, 1984). The age and origin of the samples can be predicted based on the distribution of aromatic hydrocarbons in coal and lignite extracts. Pyrene is a major component identified in some Candiota bitumens, natural fires are the probable source of this component and other minor PAHs characterized in this coal.
3.0 OBJECTIVE

The main objective of this project is to characterize the composition of aliphatic and aromatic hydrocarbons in coals originated from three different locations in Sarawak. The information gathered are used to trace the origin of organic matters in coals and also to determines the maturity of coals. The hydrocarbon characterized are aliphatic and polycyclic aromatic hydrocarbon (PAHs).
4.0 MATERIALS AND METHOD

4.1 Sampling

Coal samples were collected from three different locations in Sarawak i.e Merit Pilla in Kapit Division, Mukah-Balingian in Mukah Division and Sungai Mas in Bintulu Division. The samples were kept in the cold place prior to sample extraction. Coal deposits in Sarawak are found in Mukah-Balingian, Sungai Mas Bintulu and Merit Pilla, Kapit. About 500 millions tones coal are reserve in Sarawak. Sarawak has three major coal field which are Silantek coal field, Merit Pilla coal field and Mukah Balingian coal field.

Merit Pilla is situated in the upper reaches of Batang Rajang which is about 75 km upstream of Kapit in the 7th Division (Liaw, 1983). Coals occur in this area are seams 1 to 3 m thick and possibly can be characterized as the sub bituminous b rank which having the high volatile matter, moderate ash content, low sulphur, moderate moisture and a gross calorific value about 5000 to 6000 kcal/kg. It is used as the power generation and in cement industry. The Merit Pilla coal field is the most of the main sources of coal supply in the country.
generally used a thermal or steam coal. Coal in Mukah-Balingian suitable used as fuel for an on-site or near-site power generating station to provide electricity to Bintulu or Sibu (Chen., 1970). Besides, it is also used to support a mine-mouth power plant according to its low rank and high moisture content.

4.2 Proximate Analysis

The proximate analysis of coal was carried out to determine distribution of product when coal was heated under the standard conditions. The proximate analysis are considered as determination of general properties of coal. These analyses includes determination of moisture content, ash content and volatile matter content. The objective of proximate analysis is to determine the content of volatile matter and moisture content which can be used determined the maturity of coal.

4.2.1 Determination of moisture content in Coal

Coal samples was pestled into powder and air dried at the room temperature. The coal powder was sieved. Approximately 10-15 g sample was weighted into a porcelain dish. The sample was placed in the furnace at 150°C for 1 hour. The dish was removed from the furnace and cool it in the room temperature. The dried sample are weighed and the total moisture content was determined based on the equation below.

\[ \% \text{ moisture content} = \frac{\text{total sample before dry} - \text{total dry sample}}{\text{total sample}} \times 100\% \]
4.2.2 Determination of Ash Content

Briefly, 5 g of coal samples with mesh size was weighted into a porcelain dish. The samples was dried in the furnace at 150°C for 4 hours. After four hours, the samples was cooled at room temperature. Then, 1 gram of sample was placed in the furnace for 3 hours at 827°C. The dish was removed after 3 hours and allowed it to cool at the room temperature. Then, the samples was reweighed accurately to get the ash content.

4.2.3 Determination of Volatile Matter

About 1 gram of coal samples in 70 mesh size was weighted into a porcelain dish. Then, the samples are placed in the furnace at 925°C for 7 minutes. At the end of heating period, the samples are removed from the furnace and cooled it quickly. The samples was reweighed again to get the total volatile matter.

4.3 Extraction and Fractionation

4.3.1 Soxhlett Extraction

The methods used for extract of hydrocarbon from coal was adapted from method used for sediment samples (Howsam, 2000). Before extraction, samples was pested intopowdered to increase the surface area and extraction efficiency (Hagemann & Puttman, 1989). The analysis was carried out for 24 hours by using dichloromethane (DCM) as an extracting solvent. Approximately 5 g of coal samples was weighted and into a preextracted tared cellulose thimble and put the timble into a clean soxhlet extractor. 50 mL of DCM was added to the clean 250 ml roundbottom boiling flask and attached to the flask to the base of the soxhlet extractor. The timble was spiked with the 50 μL each
of the octadecane and o-terfenil as an internal standard. 2 spatula of anti bumping granules was added to the roundbottom boiling flask and thimble was added into the condenser.

The condenser was attached to the soxhlet extractor. 150 mL of DCM are add into the condenser. Turn on the condenser cooling water and power to the heating mantle. The coal was allowed to extract for 24 hours. The extracted product are collected into the 100 mL pear flask for rotary evaporation. The extracted product are rotary evaporation from each pear flask until dry. The sample remained are diluted with 1 mL of DCM and transferred all the contents to 5 mL clean Teflon-caplined and clean glass pipette. The solvent in each vial was dried under a gentle stream of purified N₂. The organic residue that remained in the vial was total extractable lipids. The thimble containing solvent extracted coal was dried into the oven (60°C) and reweighed. The dry weight of thimble containing solvent extracted coal are calculated based from difference between this weight and tare weight for empty thimble.

4.3.2 Column Chromatography

The total extractable lipids (TEL) was then fractionated into aliphatic, aromatic and pdar fractions by using column chromatography (Stefanova et al., 2002).

Briefly, 5 g of silica gel was weighed and 15 mL of hexane was added to make it silica gel suspension. A small clean glass funnel put at the top of the column. The content was
swirled gently to suspend the silica gel and quickly pour the silica gel suspension into the funnel. 10 mL of hexane was added to assure all of the silica gel transferred from the beaker into the column. Carefully knocked the column to assure the silica gel was compacted in the column. The hexane was allowed to elute from the column until its level reached the top of the silica gel then closed the stopcock.

TEL in the vial was dissolved first with 1 mL of hexane and transferred into the silica gel column chromatographic by using a pasteur pipette. The vial was then rinsed twice with 1 mL of hexane and transferred it into the silica gel chromatographic column. The total aliphatic hydrocarbon (F1) was collected the eluant of 20 mL of hexane in the 50 mL pear flask. The polycyclic aromatic hydrocarbon (F2) fraction was then collected by eluting the column with 20 mL mixtures of methylene chloride: hexane (1:3, v/v). The contents of each flask are then quantitatively transferred to a clean vial. The sample in the pear shaped flasks were evaporated using vacuum rotary evaporator until 1 mL. The samples were then dissolves with 1 mL methylene chloride and sonicated on ultrasonicator. The solvent in each vial are evaporated just the point of dryness under a gentle stream of purified nitrogen (N2).

4.3.3 Sulfur Removal by Activated Copper Column

The activated copper column used to remove the elemental sulfur (S8) from the total aliphatic fraction. The presence of sulfur in coal samples caused interference in aliphatic hydrocarbon analysis especially in the gravimetric determination of total aliphatic hydrocarbon (TAH) content in coal samples and gas chromatographic analysis of aliphatic
hydrocarbon in the F1 fraction. The composition of sulfur was caused by the acidity of peat and surface content of waters within the peat. The substances that have sulfur rich mainly from marine (brackish) peat and freshwater peats with marine roof rocks (Bechtel et al., 2004).

About 3 cm height of copper powder (40 mesh) was packed into a clean glass chromatographic column with a 1 cm plug of glass wool, a teflon stopcock and glass tip. The chromatographic column was washed by eluting with 25mL of acetone and 25mL distilled water. About 2mL of hydrochloric acid are added and the acid are eluted slowly through the column and washed the column with 50mL distilled water when the acid level reached the top of Cu until the pH of the eluant is neutral (pH 7). The column then are continued eluting with the 25mL of acetone and 25mL dichloromethane (DCM).

The F1 fraction was dissolved in the 1 mL of dichlromethane and transferred to the activated column by using a disposable glass pipette. The sample was allowed to elute slowly through the column with 25 mL dichloromethane and the eluant was collected into the clean 50 mL pear flask. The volumes of solvent in the flask are reduced by rotary evaporation until 1 mL. Dissolved the lipid extraction with 1 mL dichloromethane and sonicated it by ultrasonic sonicator and transferred it to the original vial. The solvent in the vial is evaporated under the gentle stream of purified nitrogen (N2). The total aliphatic hydrocarbon (TAH) is ready for gas chromatographic analysis.
4.3.4 Sephadex Chromatography

The PAH components in F2 fraction was enriched by chromatography on Sephadex LH-20. The F2 fraction consists of lot of non-PAH components that are polyunsaturated hydrocarbons such as heneicosahexaene and squalena.

1 g of Sephadex LH-20 was weighted into a clean 100 mL beaker. 30 mL of 1:1 mixtures benzene-methanol was added to the Sephadex LH-20 and poured into clean glass chromatographic column fitted with a plug of glass wool and a Teflon stopcock with glass tip. The solvent was then allowed to drain slowly through the column until reached level above the top of the packing support material.

The F2 fraction was dissolved in the 1 mL mixtures of benzene-methanol (1:1, v/v) and transferred to the top of Sephadex column by using pasteur pipette. The vial was rinsed twice with each 1 mL benzene:methanol (1:1, v/v) was transferred to the column. The first fraction collected was then eluant of 20 mL mixture of benzene:methanol (1:1, v/v) and second fraction subsequently the solid fraction collected by eluting with 30 mL mixture of benzene:methanol (1:1, v/v). Then, the aromatic fractions contained PAHs are further analyzed by gas chromatography and gas chromatography-mass spectrometry (Yang, 2000).