Ketones Biomarkers of Coal from Tarakan, Kalimantan Utara

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Abstract—Coal from Tarakan, Kalimantan Utara was formed during Pliocene analyzed to determine the character of the organic geochemistry. Coal was extracted using Soxhlet method with a mixture of dichloromethane:methanol (93:7) as a solvent. The extracts were fractionated into aliphatic, aromatic, ketones, and polar fractions using column chromatography. Ketone fraction was analyzed by gas chromatography-mass spectrometry (GC-MS). GC-MS analyzed shown presence of cyclohexyl ketones and methyl cyclohexyl ketones were distributed in the range C_{10}-C_{25}. These compounds were expected formed by fatty acids in the lipid membrane of bacteria. Besides, it was also found that tricyclic terpane ketones formed by oxidation of tricyclooctaprenol in bacterial membrane. Amyrenones were identified in the sample as a result of oxidation β-amyrin during diagenesis of terrestrial higher plants. The presence of these biomarker compounds indicate that coal of Tarakan, Kalimantan Utara derived from higher plants and bacteria input during burial, this coal is estimated to have passed the stage of diagenesis.

Key words: coal, biomarkers, ketones fraction, Pliocene, GC-MS

1. INTRODUCTION

Kalimantan Island is one of the coal producers in Indonesia. It has three depositional basins include the Barito basin (since 1938), Kutai (since 1897) dan Tarakan (since 1905) [1]. The coal from the Sajau Formation Tarakan Basin formed during Pliocene. Coal has different characteristics, depend on their origin, environment and time of burial. Characteristics of the coal can be described through biomarkers [2]. Biomarkers are a molecular fossil from the origin of its constituent compounds and derived from living organisms at the ancient time. During the process of coal formation a part of bio macromolecules from a dead organism would be coal, while the biomarker compounds still deposited with coal without decomposition or alteration of their structure [3]. One of the biomarker compounds is ketones which expected to be formed in the presence of oxygen at the stage of diagenesis.

Ketone compounds in geological samples generally found as derivatives of n-methyl ketone, such as in coal and carbonaceous samples from Dingxi Basin in Northwestern China. The presence of methyl ketone derivatives indicates that the samples formed from the microbial oxidation of higher plants [4]. Methyl ketone derivatives in the oil samples from the Guaymas Basin in the Gulf of California were formed under anoxic hydrothermal conditions of alkenes, alkanes or aliphatic-rich sedimentary organic matter [5]. The tricyclic terpane ketone series were found in Tasmanian tasmanite bitumen describe that the bitumen derived from bacteria [6]. Ketones hopane were found in sedimentary organic matter indicate the origin of the samples from oxidation microorganisms [7]. β-amyrone such as in sediment samples were taken from Lake Bera, Malaysia describe that organic matter in sediments derived from higher plants which preserved mainly under oxic condition and there is microbially-mediated alteration [8]. Tarakan coal formed during the Pliocene predicted including of low rank coals that not suitable for exploitation. This paper will discuss the rank of Tarakan coal, Kalimantan Utara based on ketones type of biomarkers.

2. EXPERIMENTAL

2.1 Materials

Coal sample was collected from outcrops of the Sajau Formation in the Tarakan Basin, Kalimantan Utara, Indonesia (Fig. 1). The sample have been crushed into fine powder.
2.2 Methods

2.2.1 Soxhlet Extraction

Bitumen extraction has been performed on approximately 200 g of the powdered samples using Soxhlet apparatus with an azeotropic mixture of dichloromethane (DCM) and methanol (CH$_3$OH) (93:7) for 96 h [10]. The extracts were concentrated with a rotary evaporator at 40 °C. The total hydrocarbon extract obtained was separated into different fraction by means of column chromatography.

2.2.2 Column Chromatography

The total extracts was separated using column chromatography over activated silica gel (50 g) and eluted sequentially into four fraction using n-hexane (fraction 1) for the saturated hydrocarbon fraction, n-hexane:DCM (9:1, fraction 2) for the aromatic hydrocarbon fraction, DCM (fraction 3) for the ketone fraction, and methanol (fraction 4) for the more polar compounds (NSO compounds) [11]. In this study, only the ketones fraction was further analyzed.

2.2.3 Gas Chromatography-Mass spectrometry (GC-MS) Analysis of Ketones Fraction

The ketones fraction was analysed by gas chromatography-mass spectrometry (GC-MS). GC-MS analysis was carried out on an Agilent coupled to an Agilent 122-5561 mass spectrometer. Separation of the compounds was achieved using GC capillary column coated with DB-5 MS (60m x 0,25mm ID x 0,10 μm film thickness). The oven temperature was programmed from 70 (1 min) to 150 °C at a rate of 10 °C/min, then from 150 to 290°C at a rate of 2 °C/min and 290-315°C at a rate of 5 °C/min, with a 6 min isothermal period at 315 °C. Helium was used as carrier gas. The mass spectrometer was operated in electron impact mode (EI) at 70 eV ionization energy. Mass spectra were obtained by scanning from m/z 50 to 550.

3. RESULTS AND DISCUSSIONS

3.1 Soxhlet Extraction and Column Chromatography

Soxhlet extraction of 200 g using solvent dichloromethane:methanol (93:7) resulting a mixture of extract (nonpolar, semi polar and polar). The total organic extract (TOE) of Tarakan coal is 57.3288 g (28.66 % weight) as a dark brown colored liquid. The organic extracts showed levels of bitumen (organic matter soluble in organic solvents) in the coal sample.
Ketone fraction from the coal extract can be separated from TOE using column chromatography with eluent dichloromethane produces brown colored solution were 0.1286 g (25.72 % weight) and will be analyzed further.

3.2 Composition of the Ketone Fraction in the Coal Extracts

Total ion current chromatogram (GC-MS) of biomarkers ketone fraction of Tarakan coal is shown in Fig. 2. In the chromatograms four groups of compounds are identified: derivatives of cyclohexyl ketones, methylcyclohexyl ketones, triyclic compound, and amyrrenones, respectively.

3.2.1 Cyclohexyl Ketones

Derivatives of cyclohexyl ketones in the ketones fraction is determined based on selected ion chromatogram of m/z 57 (Fig. 3). Cyclohexyl ketones identified in Tarakan coal consist of n-cyclohexyl ketones C_{10} to C_{22} and methylcyclohexyl ketones C_{11} to C_{25} with moderate odd-to-even C number predominance and C_{23} is the most abundant methylcyclohexyl ketones in the sample.

The ketones have been identified by interpretation of their mass spectra and consist of n-cyclohexyl ketones as 4-cyclohexylhexabutan-2-one (C_{10}), 8-cyclohexyl-octan-2-one (C_{11}), 11-cyclohexylundecan-2-one (C_{17}), 13-cyclohexyltridecan-2-one (C_{19}), 14-cyclohexyltetradecan-2-one (C_{20}), and 16-cyclohexylhexadecan-2-one (C_{22}). While the methylcyclohexyl ketone compounds was identified as the 4-(methylcyclohexyl)-butan-2-one (C_{11}), 14-(methylcyclohexyl)tetradecan-2-one (C_{21}), 16-(methylcyclohexyl)hexadecan-2-one (C_{23}), and C_{25}.

3.2.2 Methylcyclohexyl Ketones

The presence of n-alkyl cyclohexane and methyl-n-alkyl cyclohexane in the Guttenberg Oil Rock bitumen with the highest peak at C_{17} and C_{19} and also a strong odd carbon number predominance indicates that the sample could be derived from the cyclisation of algal fatty acids and thermoacidophilic bacterium, Bacillus acidocaldarius contribution [12]. If the sample contained n-C_{16} to n-C_{19} alkylcyclohexanes, the possible precursor is 11-cyclohexyl undecanoic acid and 13-cyclohexyl tridecanoic acid derived from acidophilic thermophilic bacteria, 11-cyclohexyl undecanoic acid and 13-cyclohexyl tridecanoic acid can lead diagenetic oxidation and reduction of the carboxyl functional groups in the alkyl chains that have been changed into alkanes such as alkylcyclohexanes [13].

The relationship between cyclohexyl-alkanoic acids and acidothermophilic bacterium Alicyclobacillus spp. in the oil samples have been investigated [14]. This research showed that alkyl cyclohexane and cyclohexyl-alkanoic acids derived from lipidic membranes of the bacteria Alicyclobacillus spp. The presence of derivatives cyclohexyl ketone and alkylcyclohexyl ketone in Tarakan coal indicates that there is acidothermophilic bacterium contribution in coal formation.

Methylcyclohexyl ketones have the same precursor with cyclohexyl ketones precursor which both of them derived from straight-chain alcohols or fatty acids in the bacteria by direct cyclization [13]. The cyclization reaction of straight-chain alcohols or fatty acids into
alkyl cyclohexane and methyl cyclohexane is shown in Fig. 4.

Fig. 4 Proposed mechanism for conversion of fatty acids and alcohols to alkylcyclohexanes [13]

A cyclohexyl ketones and methylcyclohexyl ketones was found in Tarakan coal. Ketones such as alkan-2-ones generally have similarities distribution with alkanes were identified in a sample. It is possible that ketones can be derived from microbially-mediated β-oxidation of corresponding alkane in the presence of bacteria [4]. n-alkan-2-ones can be derived also from β-oxidation of carboxylic acids to form the β-ketoacid and then formed ketone by decarboxylation process [5]. Saturated alkan-2-ones derived from the microbial oxidation of n-alkanes are commonly in nature. These compounds widely occur in soils and sediments. Mid-chain ketones are often found in higher plants, these compounds may be synthesized by means of elongation of the corresponding fatty acid precursors then lead decarboxylation [15].

3.2.2 Amyrenones

Amyrenones in the ketones fraction of Tarakan coal are determined based on selected ion chromatogram of m/z 204 in the form of compound 28-nor-β-amryrenone. This compound is a derivative of β-amyrins which undergoes oxidation at the alcohol functional group (-OH) in the presence of microbes into a ketone at the C3 position and loss of a methyl branch at the C28 position.

β-amyrins precursor are typical components in higher plants, it found in various plants and plant materials such as leaves, bark, wood, and resins [16]. β-amyrrenones also have been found in the wood of plant Lophanthera lactescens Ducke, Malpighiaceae, in the Brazilian Amazon region [17]. β-amyrins oxidizes to β-amryrenone by the presence of oxygen during burial at the stage of diagenesis. The presence of 28-nor-β-amrenones in the studied sample indicates that the coal-forming compound derived from higher plants buried under oxic conditions and alteration of microbial mediation.

3.2.3 Tricyclic Terpane Ketones

The tricyclic terpane ketones (m/z 191) in the extract of Tarakan coal consist of tricyclic terpane with molecular structure of C20 tricyclic terpane methyl ketones (2) (Fig.5). This compound is proposed to be derived from oxidation of double bonds in the side chain of tricyclocaprenol (1) (Fig.5). Tricyclic terpane can be formed from C20 tricyclohexaprenol contained in the bacterial membrane [18]. Tricyclic compounds in Tarakan coal indicate the contribution of bacteria during coal-forming.

Fig. 5 Proposed origin of tricyclic terpane ketones [8]

4. CONCLUSION

The presence of the biomarker compounds types of ketones in the Tarakan coal, Kalimantan Utara indicates that the burial of the coal occurs under oxidative conditions. Organic source of coal-forming derived from higher plants and bacteria input during burial. Amyrenones in the Pliocene coal that has passed the stage of diagenesis should have been loss of functional group into oleane. This indicates that the component of Tarakan coal bound with oxygen inhibit the process of coal maturation. So the coal that formed since Pliocene still at low rank.

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REFERENCES


