

EVALUATION OF SOURCE ROCK POTENTIAL OF TERTIARY COALS IN LABUAN,
MALAYSIA

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ABSTRACT

Potential of hydrocarbon generation of coals as an oil-generating source has been discussed by several researches and findings. Laboratory approach of kerogen thermal degradation is commonly performed to simulate the maturation of petroleum source rock compared to the longer geological period. This method requires high temperature to compensate for the shorter time observed in geological process. There is also laboratory simulation of thermal maturation of brown coal in both anhydrous and hydrous pyrolysis and reported that the pyrolysates expelled by hydrous pyrolysis was significantly closer to natural system of petroleum generation. Analysis of source rock potential by source rock analysis (SRA). This study focuses on comparison of source rock maturity before (free hydrocarbon) and after hydrous pyrolysis (trapped hydrocarbon) by biomarker parameter ratio. Tertiary coals from Labuan, Malaysia run in hydrous pyrolysis system using a PARR 4575 High Temperature High Pressure Reactor at temperature of 300°C, 320°C, 340°C and 360°C. Soxhlet extraction and liquid column chromatography separate saturated hydrocarbon fraction and analyze using Gas Chromatography – Mass Spectrometry (GC-MS) to produce biomarker parameters. Evaluation of source rock maturity using petroleum biomarkers ratios. Tertiary coals of Labuan, Malaysia will be showing as generative source rock potential based on SRA results. Hydrous pyrolysis will be increasing source rock maturity based on biomarker ratio.

ABSTRAK

Potensi penjanaan hidrokarbon batuan arang sebagai sumber penjanaan minyak telah dikaji oleh beberapa penyelidik dan dapatan. Degradasi berasaskan suhu kerogen menggunakan pendekatan makmal telah dipraktikkan secara meluas bagi simulasi pematangan batuan sumber petroleum untuk dibandingkan dengan tempoh geologi yang panjang. Pendekatan ini melibatkan suhu yang tinggi bagi mengimbangi penilaian singkatan masa di dalam proses alami geologi. Terdapat juga simulasi makmal pematangan suhu bagi batuan arang coklat yang melibatkan pirolisis anhidrat dan pirolisis hidrat. Hasil penyelidikan didapati bahawa penghasilan pirolat daripada pirolisis hidrat lebih hampir kepada penghasilan petroleum secara alami. Kajian ini memfokuskan kepada perbandingan pematangan batuan sumber sebelum dan selepas pirolisis hidrat menggunakan pendekatan nisbah parameter biomarker. Analisis potensi batuan sumber akan menggunakan Analisa Batuan Sumber (SRA). Batuan arang *Tertiary* daripada Labuan, Malaysia menjalani pirolisis hidrat pada suhu 300°C. Ekstraksi *Soxhlet* dan kromatografi cecair lajur digunakan untuk mengasingkan bahagian hidrokarbon tepu dan dianalisis menggunakan Kromatografi Gas – Spektometri Jisim (GC-MS) bagi penghasilan parameter biomarker. Akaun penghasilan S₂ adalah ber julat 131.11 -342.13mg HC/mg rock dan jumlah karbon organik adalah ber julat 40.10 – 70.94 %. Ini menunjukkan batuan sumber kajian mempunyai potensi penghasilan hidrokarbon. Tiga nisbah parameter biomarker telah digunakan. Didapati bahawa nisbah 22S/(22S+22R) dan Ts/(Ts+Tm) meningkat manakala nisbah moratene (C₂₉M)/hopane (C₂₉H) menurun selepas pirolisis hidrat. Perubahan nisbah ini menunjukkan bahawa tahap kematangan batuan sumber meningkat selepas proses pirolisis hidrat.

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LIST OF ABBREVIATIONS

HI	-	Hydrogen Index
TOC	-	Total Organic Content
SRA	-	Source Rock Analysis
S1	-	Free hydrocarbon release
S2	-	Hydrocarbon release during pyrolysis
S3	-	Carbon dioxide release during pyrolysis
Tmax	-	Maximum temperature of expelled hydrocarbon

CHAPTER 1

INTRODUCTION

1.1 Problem Background

Coals as defined by Schopf (1956) is one of source rock that contains organic matter. Amount of organic matter is more than 50% (by weight) and 70% (by volume). Coals is widely known as an important source of gas. Kohli et al (1994) stated that variables proportions of hydrogen-rich organic matter in the coal macerals contributing to potential of oil-generating for coals. Migration of hydrocarbon also favours in coals compares to shales. In addition, Snowdon (1991) suggested that coals that contains more than 10% of hydrogen-rich matter potentially can generate and expel oil.

Vast of studies to determine source rock potential of coals. Teerman and Hwang (1991) explains that potential of hydrocarbon generation of coals depends on composition of macerals. It is also affected quantity of expulsion and composition of products.

There are many types of laboratories experiments pyrolysis conducted to represent a simulation process of hydrocarbons generated and expulsions from the coals. There are several approaches to reproduce natural degradation by artificial thermal maturation. Systems employed to this laboratory work; open, closed and confined system. It proves that for hydrous pyrolysis in closed system closer to naturally occurring environment below critical temperature of water, 374 °C.

Rowland et al (1985) conducts research on compositions and segregation of aromatic hydrocarbon in expelled hydrocarbon. The sample for this research is dolomitic siltstones (Permian, Marl Slate). It also showed that the ratio of aromatic hydrocarbon to saturated hydrocarbon is 2:3.

Hydrous pyrolysis is conducted under five different temperatures; 280, 300, 320, 340 and 360 °C. At the lowest temperature (280 °C), component of pyrolysates is comparably similar to natural crudes which contains more minor components (e.g. alkylphenanthrenes, aromatic steroid). As the temperature increases, existences of non-natural components of crude oil such as methylanthracenes and Diels' hydrocarbon are proved. All these non-natural components are increased as the temperature increases.

Shale with organic-rich oil from Jurassic and Kimmeridge and no mineral asphaltic material produce similar result as stated above when it undergoes hydrous pyrolysis at 340 °C. It shows that higher proportions of organic sulphur detected in organic rich shale. It concludes that not only type of organic matter effected the formation of unusual compounds, it also a function of high temperature and high heating rate of reaction.

Temperatures that apply on hydrous pyrolysis experiments are higher compares to the natural petroleum genesis occurrence. Connan (1974) proves that to some extent, temperature can be substitution for time in laboratory oil generation studies. Difference of temperature between laboratory work and natural genesis occurrence allows shorter time for this artificial oil generation by hydrous pyrolysis.

Confining effects of water gives significant difference in the existence of alkenes in pyrolysates. Alkenes are absent in pyrolysates from hydrous pyrolysis (Monthieux et al, 1985). Free radicals are produced from the effect of water confining. These free radicals are closely contact with alkenes structure and promote saturated hydrocarbon forming. Major hydrocarbons of pyrolysates are produced by free radical pathways. Alkenes still exist in pyrolysates from anhydrous pyrolysis because of the lessened effects of water confining. If anhydrous pyrolysis is conducted in small-scaled vessels with minimum unfilled reactor, it will diminish the existence of alkenes.

Sediments that contain high organic matter (Marl State, Kimmeridge Oil Shale) are pyrolyzed at 280 °C to 360 °C produces hydrocarbon that have different characterization compared to natural crude oil. Proportions of aromatic-to-saturated hydrocarbons for hydrous pyrolysis are higher compared to natural crude oil. This difference is affected by organic matter type and temperature of pyrolysis. While for overall distribution of aromatic hydrocarbon are similar to the many natural crude oil. Besides that, there are number of aromatic that not abundant in natural also exist, which includes anthracene, methylanthracenes and Diels' hydrocarbon. This is caused by increases of phenanthrene that linearly to pyrolysis temperature.

Usage of water in hydrous pyrolysis implicates concern about the effects of water in kerogen. Kerogen is a three-dimensional cross-linked macro molecular system that does not dissolve in water. Theoretically, there are no contact between water and kerogen. This insolubility property of kerogen as a result of unfavourable entropy of molecules that makes kerogen is hydrophobic molecule. As water is heated, hydrogen bonds in water molecules disarranged and diminish the entropy driven hydrophobic effects. So that, water and kerogen can be swell together.

Lewan 1987, shows that more liquid petroleum yields in pyrolysates by hydrous pyrolysis than in absence of water. Early stage of reaction, less effect of water presence for decomposition of bitumen to rick-polar and higher molecular bitumen. It compared to decomposition of bitumen to oil that contain more hydrocarbon. It is because decomposition of bitumen to oil was cancelled by cross-linking reaction in the presence of water.

Li et al (2008) did study on hydrous pyrolysis experiments of Pennsylvanian coal in the Bohai Gulf Basin. It is proven that coals have a significant of oil generation. Not only that, it is also show that high expulsion of notable size of gas production. Liptinite content has significant effect in expelled oil as explain by Akande et al (2015).

Study on generation of biomarkers on matured Type II-S kerogen limestone and claystone with and without the presence of water. Instead of to assess the level of thermal maturity, biomarkers are also used to determine the degree of biodegradation and depositional environment of organic matter in geological samples. There are several ideas on the importance of water as in pyrolysis. Monthioux et. al. (1985) strongly agreed that water did not portray significant effect for pyrolysis. This contradict by Lewan (1987) which shows that amount of pyrolysates from hydrous pyrolysis at 350 °C of Woodford shale are twice of that generated by confined and unconfined anhydrous pyrolysis.

Biomarker generation during thermal maturation of kerogen is describes in two processes. Firstly, some of kerogen is decomposing to a high polarity bitumen. Boundary of moieties of kerogen and polar-rich bitumen is maintaining. As thermal increases, polar fraction releases the bound biomarker as free biomarker as the release of free hydrocarbon from decomposition of bitumen.

Anhydrous pyrolysis of claystone gives less of free biomarkers generation. This is because the clay minerals adsorbed the polar fraction, which contains abundant S-bound. Therefore, prevention of production of free hydrocarbon by cross-linking reaction happen.

Cross-linking reaction in this anhydrous pyrolysis become more dominant because of the existence of S-S bond in organic matters. For hydrous pyrolysis, S-bound biomarkers is not adsorbed by polar fraction due to the interlayer of minerals are filled by water and enhanced the free biomarker generation. These results explain the importance of water role in closed system laboratory experiments. This aim at simulating natural maturation of sedimentary organic matter, specifically in present of clay minerals.

1.2 Problem Statement

Laboratory approach of kerogen thermal degradation is commonly performed to simulate the maturation of petroleum source rock compared to the longer geological period. Anhydrous pyrolysis approach widely uses to simulate hydrocarbon potential. For this study, the best method that chosen is hydrous pyrolysis. It is because it is more closer to nature hydrocarbon generation.

Source rock maturity can be evaluated in several methods includes organic petrology, source rock evaluation and petroleum biomarkers ratios. This study will be focusing on biomarker ratios to determine hydrocarbon potential. The triterpanes ratios is used as biomarker parameter for determination of source rock maturity of the pyrolysates and will be compared to the non-hydrous pyrolysed samples.

1.3 Research Objectives

- 1) To analyze source rock potential
- 2) To compare source rock maturity before (free hydrocarbon) and after hydrous pyrolysis (trapped hydrocarbon) by biomarker parameter ratio

1.4 Scope of Study

- 1) Analysing source rock potential using parameters from Source Rock Analysis (SRA).
- 2) Performing hydrous pyrolysis on source rock at 300°C for 24 hours.
- 3) Separating compounds (saturated, aromatic, NSO fraction) using Soxhlet extraction, liquid chromatography.
- 4) Obtaining biomarker parameter using Gas Chromatography – Mass Spectrometry (GCMS).
- 5) Analysing source rock maturity referring to biomarker ratio.
- 6) Comparing source rock maturity before and after pyrolysis.

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