

Geochemical Characteristic and Correlation of Oil Seepage Boyolali, Center Java, Indonesia





GEOCHEMICAL CHARACTERISTIC AND CORRELATION OF OIL SEEPAGE BOYOLALI, CENTER JAVA, INDONESIA

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Abstract

Kendeng Zone is an interesting area for many explorationist because of it's hydrocarbon prospect, especially in Boyolali and surrounding areas. The hydrocarbon prospect is indicated by the existence of the production wells since colonialism and some oil seeps in this area that means petroleum system in this area is active. Oil seepages in this area can be generated from the same origin or different oil source rock. To know the origin of these oil seepages, this research are conducted. The aim of this research is to understand the characteristic of the oil seepages including biodegradation level, organic material origin, depositional environment and thermal maturity also determining the correlation of the oil seepages in this area.

Three oil seepages were collected by fieldwork activity in Gunungsari, Repaking and Kemusu area. These oil seepages are conducted by geochemical analysis including Liquid Chromatography, Gas Chromatography and Gas Chromatography-Mass Spectrometry analysis in LEMIGAS Laboratorium. The analysis result of Gunungsari oil seepage show high level of biodegradation while oil seepages from Repaking and Kemusu show minor biodegradation. The biomarkers interpretation of these oil seepages show the source input of all oil seepages derived from the higher plants materials that deposited in terrestrial environment with little contact with deltaic system. Thermal maturity of these oil seepages can be considered as thermally mature with Ts/(Ts+Tm) ratio ranging from 0.52-0,59 and $C_{29}20S/(20S+20R)$ ratio ranging from 0.42-0.48. The characteristics of Gunungsari, Repaking and Kemusu's oil seepages has same organic matter origin, depositional environment and thermal maturity which is show a positive correlation.

I. INTRODUCTION

The correlation of oil-to-oil provide valuable tools for helping the exploration geologist answer exploration questions (Hunt, 1996). The assumption that the organic material same and same depositional environment produce same oil genetically, make correlating oil family a crucial work. In this paper, oil-to-oil correlation is done by knowing oil characteristic (degree of biodegradation, organic material origin, depositional environment, and thermal maturity) and use biomarker fingerprinting of oils. Biomarkers are useful because they preserve most of the original carbon skeleton of the natural products (Peters et al., 2005).

Geologically, the study conducted in Kendeng Zone, especially at western part. The hydrocarbon prospect in this area is still questionable and need more detail identification. Oil seepages in Boyolali and surrounding areas proves that the petroleum system has been active which means there are mature source rocks that capable to generate hydrocarbons in this area.

The research is located in Wonosegoro sub-district, Boyolali Regency, Central Java (**Figure-1**). Three oil seepages found and sampled at Gunungsari, Repaking, and Kemusu village, Wonosegoro sub district. The distance between each oil seeps about ± 2 -11 km.

II. REGIONAL GEOLOGY

The study area is located in Kendeng Zone, the northern part of East Java Basin. Kendeng Zone is an anticlinorium that extend from west to east. This zone divided into three parts based on its anticlinorium slope, which are west, central, and east part (de Genevraye and Samuel, 1972). The study area is precisely located in the western part of Kendeng Zone.

Geological structures that occurred in Kendeng Zone are folds and faults. These structures are product of Plio-Pleistocene deformation. These folds have west-east trend, association with normal and thrust faults. Plio-Pleistocene deformation also provide north-south trend strike slip fault. Stratigraphy of Western Kendeng Zone is consisted of Tertiary-Quartenary sediments. Unit sediments that occurred in study area from the oldest to youngest, there are:

• Pelang Fm.

Pelang Fm. consisted of marl and clay-rich marl that deposited in open marine during Late Oligocene-Early Miocene (de Genevraye and Samuel, 1972). Pelang Fm. only exposed at Juwangi area, with 85 m thickness outcrop.

• Kerek Fm.

shale Kerek Fm. consisted of interbedded with pebby sandstone, limy sandstone and volcanic tuff (Ramadan et al, 2015). Kerek Fm. was deposited in shallow marine during Middle Miocene-Late Miocene. Oil seeps in study area were found in sandstone of Kerek Fm. Kerek sandstone is considered as possible reservoir rock in Kendeng stratigraphy (Ramadhan et al, 2015).

• Kalibeng Fm.

Kalibeng Fm. is consisted of marl and shale that deposited in shallow

marine during Pliocene. Shale of Kalibeng Fm can be considered as possible seal rocks in study area (Ramadhan et al, 2015).

Geological structure (fault and fold) in this area considered as migration pathway of hydrocarbon that indicated by hydrocarbon manifestation on surface (oil seeps). Explorations in Kendeng area categorized as high-risk project, particularly when discussing oil source rock generation (Ramadhan et al, 2015).

METHODS

Oil samples analyzed using a liquid chromatography prior to separate into saturated hydrocarbon and aromatic hydrocarbon by preparative column chromatography. The hydrocarbon fractions were carefully evaporated then transferred to sample vials. Isolation of cyclic fraction branched and from saturated hydrocarbons was done using a packed activated molecular sieve to trap n-alkane. The branched and cyclic fraction was introduced to a GCMS instrument. Figure-2 can represent the method used for completing this research. Three steps for this research are bellow.

Sample Collection

Three oil seepage samples have been collect by fieldwork activity. Oil seepages found in Repaking, Gunungsari and Kemusu Village, Wonosegoro District, Boyolali (Fig.1) that seep in shear zone of Kerek Formation. Each oil seepage sample collected by using glass bottle with volume of sample around 100ml.

Sample Preparation

Some preparation for the sample conducted before doing laboratory analysis (GC and GC-MS analysis). Three steps preparation for oil sample are: 1) oil separation from water or other contaminant using *dicloromethane*, 2) deasphaltene of oil sample to know amount of asphaltene that consisted in oil

and also to remove asphaltene from oil before sample are injected to GC-MS, 3) liquid chromatography of oil sample using column to separate saturated, aromatic, and NSO fraction. In this process, each fraction weighted to know the composition of oil sample.

Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GC-MS)

Oil samples were analyzed by Gas Chromatography (GC) with Agilent 6890N GC instrument coupled to a flame ionization detector (FID) with a 20m x 0.21mm i.d. DB-1 (J&W) fused-silica capillary column and Agilent 7673 auto sampler (split/splitless mode injector). Sample $(0.1\mu L)$ injected into the GC then through a column. In column, the temperature rises gradually. The oven temperature programmed from 35°C to 325°C. In this process, samples run into separation compounds (stationary phase and mobile phase) then evaporated and mixed with helium gas toward the detector (FID). The result was recorded in the computer. The GC analysis result is a fingerprint, which records the normal alkanes and isoprene. That result can be used for biomarker interpretation. GC schematic presented in Figure-2.

After fractionation, saturates and aromatic fraction from oils are performed GC-MS analysis. GC-MS system performs: 1) Compound separation by gas chromatography, 2) Transfer separated compound to the ionizing chamber of the mass spectrometer, 3) Ionization, 4) Mass analysis, 5) Detection of the ions by electron multiplier. Acquisition 6) processing and display of the data by computer (Peters and Moldowan, 1985). In this research, GC-MS analysis used an Agilent 6890 Gas Chromatograph (GC) coupled to an Agilent 5973 series Mass Selective Detector (MSD) - computer data system (Chemstation) with a 60m x 0.25mm i.d. DB-5 (J&W) fused-silica capillary column and Agilent 7673 auto

sampler (split/splitless mode injector). The result of this analysis is mass chromatogram (ex. m/z 217 for steranes and m/z 191 for terpanes) used for biomarker interpretation (**Figure-2**).

III. RESULT AND DISCUSSION

Biodegradation

Oil seepages from Gunungsari, Repaking, and Kemusu were conducted through geochemical analysis to know the oil characteristics. Based on the analysis results obtained by bulk data, GC data, and GC-MS data. The compounds were separated to saturated, aromatic, and NSO+asphaltene as the result of liquid chromatography process, the bulk data is weight calculation of each compound. Gunungsari oil seep consists of 33.9% saturated compounds, 45.8% aromatics, and 20.3% NSO+asphaltene, Repaking oil of 62.8% seep consists saturated compounds, 35.6% aromatics, and 1.6% NSO+asphaltene, while Kemusu oil seep consists of 60.3% saturated compounds, 31.4% aromatics. and 8.3% NSO+asphaltene (Table-1). Those percentage of compounds weight are plotted to the saturated. aromatic. NSO+asphaltene graphs (Tissot and Welte, 1984) showing the Gunungsari oil seep as a crude oil that has been biodegraded with higher level when compared to the other oil seepages (Figure-3).

Gunungsari oil seep shows major resolved compounds diminished, the chromatographic baseline hump becomes more prominent (Figure-5a). This hump is also called the unresolved complex mixture (UCM). Saturate and aromatic outside of the initial range as selective biodegradation removal because preferentially consume hydrocarbon, the residual oil become enriched in nitrogen, sulfur and oxygen causes a high content of NSO+asphaltene compounds. Repaking and Kemusu oil seeps are dominated by saturated compound that classify as normal crude oil based on weight percentages (Figure-3).

Reviewed from biomarker scale (Wenger et al., 2002), Repaking and Kemusu oil seeps are categorized as very slight biodegradation (Figure-4). The biodegradation process indicated by the higher abundance of isoprene (pristane) rather than normal alkane (Peters et al, 2005). Gunungsari oil seep classified as severe biodegradation by some biomarker indicators (Figure-4). From GC data, Gunungsari oil seep resembles a hump (Figure-5a), which there is no normal alkane and isoprene compounds that can be detected or have a very small abundances. From GC-MS data, saturated fraction shows the small abundance of C_{30} hopane (H) (Figure-7), and aromatic fractions also show naphthalene and phenanthrene compounds with very small abundances. These results support the interpretation that the normal alkane. isoprene. and several biomarkers compounds have been consumed by bacteria.

Organic material origin

Chromatogram results show the organic matters origin of three oil seepages. Parameters that determine the origin of oil-generating organic material one of which is the ratio of isoprene/normal alkane. Repaking oil seep has pr/C_{17} ratio 3.10 and ph/C_{18} ratio 1.07, if these values were plotted on the pr/C_{17} vs. ph/C_{18} diagram (Shanmugam, 1985) then would be known that the organic material which composes the source rock derived from terrestrial organic matter. Kemusu oil seep has pr/C_{17} ratio 2.36 and ph/C_{18} ratio 0.64; same as Repaking it shows the terrestrial organic matter as the source input (Figure-5b). Repaking and Kemusu oil seeps have values of pr/ph ratio 3.12 and 3.87; both values indicate oxidative environmental conditions. In Gunungsari oil seep cannot be interpreted the origin of organic input material based on

isoprene/n-alkane ratio, this is caused by biodegradation effect.

From the gas chromatography-mass spectrometry (GC-MS) analysis obtained chromatogram of each oil seepages. In saturated fraction (m/z 191) is known the tricyclic terpane $(C_{19}-C_{24})$ pattern (Figure-6a.), the pattern can show origin of organic material input which making up oil-generating source the rock. Gunungsari, Repaking, and Kemusu oil seeps show the same pattern of C_{19} - C_{24} tricyclic terpane (notations 1-6 m/z 191), which the pattern is formed by the domination of terrestrial organic matter (Price et al., 1987).

The saturated fraction (m/z 191) shows the abundance of oleanane (OL) which is very dominant on the three oil seepages. Oleanane is a biomarker produced by higher plant angiosperms that begin to exist at the end of Cretaceous (Grantham et al., 1983; ten Haven, 1988; Peters et al., 2005). In addition to oleanane (OL) on the three oil seeps, there are taraxtane (Tx) and bicadinane resins (notations W, T, T', and R) (**Figure-6b**.). Those biomarkers are produced by higher plants specifically *dipterocarpaceae* species (van Aarssen et al., 1992; Peters et al., 2005).

Depositional Environment

The source rock depositional environment which generate Gunungsari, Repaking, and Kemusu oil seeps are interpreted based on sterane C27, C28, and C29 percentages. The steranes biomarker obtained from GC-MS saturated fraction (m/z 217). Gunungsari oil seep has a percentage of 26% C₂₇ sterane, 29% C₂₈ sterane, and 45% C₂₉ sterane. Repaking oil seep has a percentage of 34% C₂₇ sterane, 34% C₂₈ sterane, and 32% C₂₉ sterane. Similar to Gunungsari and Repaking oil seeps, in Kemusu oil seep has a percentage of 20% C₂₇ sterane, 35% C₂₈ sterane, and 45% C₂₉ sterane. Those percentages indicating the hydrocarbon produced by organic material deposited in

terrestrial environment with a little contact with the deltaic system (Figure-8). The dominance of C₂₉ sterane shows the input material organic derived from of terrestrial plants. The depositional environment shows the influence of the deltaic system supported by the presence of bicadinane (T). The three oil seeps also show the presence of bicadinane resin (T) at m/z 217 (Fig. 7).

Thermal Maturity

Assessment of the thermal maturity of the three samples at the time of generation (and expulsion) has been evaluated based on n-alkane, saturated and aromatic maturity-specific biomarker parameters. Based on the result of gas chromatography (GC) analysis, carbon preference index (CPI) of Repaking and Kemusu oil seeps above one, which are 1.17 and 1.22 suggests oils are thermally mature source rock. Because of high biodegradation effect, CPI values for Gunungsari oil seep could not be count. The GC-MS results show the thermal maturity parameters from saturated and aromatics fraction. The thermal maturity based on saturated fraction is shown by several parameters, which Ts/(Ts+Tm), are $C_{29}20S/(20S+20R)$, and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$. Gunungsari, Repaking, and Kemusu oil seeps show Ts/(Ts+Tm) 0.57, 0.59, and 0.52, these values indicate the oils are thermally mature (Peters et al, 2005). Similar category, the value of $C_{29}20S/(20S+20R)$ for those three oils are 0.48, 0.42, and 0.44, while the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ values are 0.24, 0.41, and 0.37. Cross plot of Ts/(Ts+Tm) vs. $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ vs. C₂₉20S/(20S+20R) based on Peters et al classifications (2005) show the three oil seepages generated from thermally peak mature source rock (Figure-9).

Aromatics fraction from GC-MS analysis used to determine the thermal maturity. The parameter used is ratio of Triaromatic sterane I and Triaromatic sterane II [TA(I)/TA(I+II)]. The triaromatic sterane biomarkers are obtained at m/z 231 aromatic fraction. The ratio values generated for each oil seeps are 0.15, 0.26, and 0.15 for Gunungsari, Repaking, and Kemusu oil seeps. According to Peters et al. 2005, the values indicate that oils produced when the source rock is at peak mature level. Figure-10 shows the percentage of TA(I)/TA(I+II) in the logarithm scale derivative to the Ro thermal maturity parameter, where the three oil seeps are in the peak mature zone (value 0.65-0.90% Ro) (Peters and Cassa, 1994).

Oil-to-oil correlations

The oil seeps have slightly different characteristics, but generally all three have the relative same biomarker fingerprinting. The oil fingerprint can created a star diagram pattern by Hunt, 1996, in this paper the pattern formed by 10 biomarkers which each of them is represent the oil sample, they are homomoretane, resin bicadinana (W, T, T', R), C_{29} tricyclic terpane, trisnorneohopane, trisnorhopane, moretane, and gammacerane. Gunungsari, Repaking, and Kemusu oil generate the almost same pattern of star diagram (**Figure-11**). From that similarity, indicating the oil seeps are correlated and generated from the same source rock.

IV. CONCLUSION

The results of organic geochemical analyses of three oil seepages in Boyolali, can be concluded that:

- 1. Gunungsari oil seep shows highly biodegradation effect while Repaking and Kemusu oil seeps show very slight level of biodegradation.
- 2. The characteristics of three oil seepages (Gunungsari, Repaking, and Kemusu) are dominantly composed of terrestrial organic matter as the source rock material input, those material were deposited in terrestrial environment, and thermally mature oils.
- 3. The three oil seepages are correlate and generated from the same source rock.

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FIGURES AND TABLE

No					CODATA				GCMS DATA							
	o. Oil Sample ID	DULK DATA				GUI	JAIA		Triterpane Ratios		Sterane Ratios					Triaromatics Ratio
		Saturate (%)	Aromatics (%)	NSO + Aspaltene (%)	*	**	**	**	*	***	*	*	**	**	**	*
					СРІ	\mathbf{Pr}	Pr	$\mathbf{P}\mathbf{h}$	Ts	C35 Homohopanes	208	αββ C ₂₉	% Cor	% Coo	% Coo	TA (I)
						\mathbf{Ph}	nC17	nC18	(Ts+Tm)		(20S+ 20R)C29	(<i>ααα</i> + αββ) C ₂₉	Steranes	Steranes	Steranes	TA(I + II)
1	Gunungsari oil seep	33.90	45.76	20.34	-	-	-	-	0.57	0.05	0.48	0.24	26	29	45	0.15
2	Repaking oil seep	62.85	35.57	1.58	1.22	3.12	3.10	1.07	0.59	0.02	0.42	0.41	34	34	32	0.26
ŝ	Kemusu oil seep	60.29	31.39	8.32	1.17	3.87	2.36	0.64	0.52	0.02	0.44	0.37	20	35	45	0.15
* =	* = Maturity Indicator															
**	** = Source Depositional Environmental Indicators															

Table-1. The complete result analysis data.

*** = Source Rock Indicators



Figure-1. The study area, in Wonosegoro sub-district, Boyolali Regency, Central Java.



Figure-2. The method schematic procedure



Figure-3. The ternary diagram of weight percentage of oil seepages and bitumen extract (modified after Tissot and Welte, 1984).



Figure-4. Biodegradation parameter based on Biomarker scale, Wenger et al (2002); Peters et al (2005)



Figure-6. **a**. The GC-MS result of saturated fraction m/z 191, the C₁₉-C₂₄ tricyclic terpanes pattern (notation 1-6) showing the organic material origin, **b**. The GC-MS result of saturated fraction m/z 191 showing distributions of oleananes and bicadinane resins.



Figure-5. a) The GC chromatogram result of oil seepages, b) The pr/C_{17} vs. ph/C_{18} graph showing the origin of organic material (Shanmugam, 1985).



Figure-7. The GC-MS result of saturated fraction m/z 217 showing the distribution of steranes biomarker.



Figure-8. Steranes ternary diagram show the depositional environment of oil seepages (modified after Huang and Meinschen, 1979).



Figure-9. Ts/(Ts+Tm) vs. $C_{29}20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ vs. $C_{29}20S/(20S+20R)$ graph showing the thermal maturity (modified after Peters et al., 2005)



Figure-10. TA(I)/TA(I+II) ratio showing the thermal maturity of the samples (modified after Peters et al., 2005)



Figure-11. Star diagram



Figure 4 Well X-25 Stratigraphy