Geochemistry of Natural Gas Seepages in Boto Area, Bancak, Semarang, Central Java

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Abstract - Three seepage gas samples collected from Boto Area, Bancak, Semarang, Central Java, were studied to determine their chemical characteristics using GC and GC-IRMS methods. They are composed 53 - 85% of methane predominantly. However, gas seep Site 3 sample has the highest N₂ compound and the lesser extent to the samples Site 2 and Site 1 respectively. The two hydrocarbon gas seeps (Site 1, 2, and Site 3 samples) that are characterized by δ¹³C methane of -35.61‰ and -27.97‰, and values of δD methane of -112‰ and -109‰ respectively, are each isotopically distinct from all others suggesting, at least, they are derived from different maturity level. The Site 3 gas sample is suggested to be more mature than the others.

Keywords: isotope, gas seepage, methane, Boto, Bancak

INTRODUCTION

Background

Natural gas seepages found in Boto Area, Bancak, Semarang, Central Java (see Figure 1) have become a topic of studies related to the petroleum system in this area which have been done. Amijaya and Winardi (2006) examined the composition of seepage gases and concluded that the gas was composed of methane, ethane, carbon dioxide, and nitrogen. Pramono (2008) who studied about oil seep in this area concluded that the oil derived from mixed organic matter source rock. Wiloso (2008) and Wiloso et al. (2008) also showed mixed kerogen in Galeh oil seep analysis. However, the genetic of the gas is still unknown, whether it is of biogenic or thermogenic nature. Geochemical characterization of the gas, especially in this study which used stable isotope analysis, was conducted to find out the genetic type of the gas.

Natural gas is a gas phase of petroleum which generally contains 70 - 100% methane, 1 - 10% ethane, a lower percentage of wetter gases, and low up to high percentage of non-hydrocarbon gases (hydrogen sulfide, carbon dioxide, and nitrogen) (Hunt, 1996). Based on their formation, natural gas can be divided into two kinds: biogenic gas (a gas formed at low temperature as a result of decomposition of organic material by microorganism activity) and thermogenic gas (a gas formed by destruction of the source rock structure or oil at high pressure and temperature) (Rice, 1993).

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The composition and stable isotope of natural gas have an important role in the investigation of gas. Gas composition can indicate the genetic of natural gas. Biogenic gas typically contains less than 0.2% ethane (Schoell, 1983). Thermogenic gas may be either wet (C\textsubscript{2+} > 5%) or dry depending on the level of its thermal maturity. Dry thermogenic gases are associated with higher levels of thermal stress (Katz, 2002). However, it should be emphasized that the C\textsubscript{2+} content of a gas is sensitive to many secondary processes like the present-day temperature and pressure (Schoell, 1983; Katz, 2002).

Stable isotope concentration indicates the type and origin of natural gas (Schoell, 1983). The comparison of stable isotope \(^{13}\text{C}/^{12}\text{C}\) directly shows heavy concentration of this isotope, usually reported in one per mil (‰) relative to the standard.

\[
\delta = \frac{(R \text{ sample} - R \text{ standard})}{R \text{ standard}} \times 1000 \text{ (ppt)}
\]

Stable isotopes of carbon and hydrogen from methane are fractionated by biological processes, so it is possible to distinguish methane formed biologically from methane formed thermally during catagenesis. When bacteria form methane from carbon dioxide reduction, they tend to eat lighter carbon from \(^{12}\text{CO}_2\) than the heavier \(^{13}\text{CO}_2\) and make the value of comparison \(^{13}\text{C}/^{12}\text{C}\) becomes more negative. That is around -109‰ relative to Peedee belemnite (Hunt, 1996).

Carbon isotope values of thermal gases can also be distinguished. Carbon isotope values of thermal gases are thought to increase with increasing maturity of their precursors. The \(\delta^{13}\text{C}\) values of wet thermogenic methane range between -60‰ to -30‰, whereas dry thermogenic methane range
between -40‰ to -15‰ (Hunt, 1996). Berner and Faber (1996) also provided empirical relationships between the value of carbon isotopic of methane, ethane, propane, and vitrinite maturity level for different organic matter types. Methanogenic bacteria also utilize lighter hydrogen than the heavier (deuterium) one, so methane formed by the bacteria had isotope deuterium values (δD) more negative than -250‰, relative to standard mean ocean water (SMOW) (Hunt, 1996).

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**Geological Setting**

The stratigraphy and structural geology of the Kendeng Zone have been described by numerous authors (e.g. van Bemmelen, 1949; de Genevraye and Samuel, 1972; Sukardi and Budhitrisna, 1992; Smith *et al.*, 2005). The stratigraphy of the area is summarized below using a lithostratigraphy nomenclature.

**Stratigraphy**

The studied area is located in Kendeng Zone (van Bemmelen, 1949). Kendeng Zone is a west-east trending anticlinorium which extends from the Gunung Ungaran Volcano in the west to the Brantas River in the east. de Genevraye and Samuel (1972) distinguished Kendeng Zone into three parts. The studied area is included in the western part (Figure 2) which has a high content of volcanic material and major structural complications. The stratigraphy of the western part of Kendeng Zone according to de Genevraye and Samuel (1972) is:

**Late Oligocene to Early Miocene**

The Pelang Formation is the oldest sedimentary exposure in Kendeng Zone. It consists of marls and argillaceous marls. The Pelang Formation is very rich in planktonic foraminifera and was deposited in an open marine environment.

**Middle to Late Miocene**

The Kerek Formation consists of massive argillaceous and calcareous sequences where volcano-clastic material is very abundant. Seepages appear through this formation. In the westernmost part of the Kendeng Zone, the formation has been divided into two parts: Merawu Member and Penyatan Member. The Merawu Member, correlated with the Lower Kerek Formation, is a volcano-clastic sequence consisting of conglomeratic layers with pebbles of quartz, basalt, andesitic tuffs, and limestones. The Penyatan Member is essentially clastic and tuffaceous corresponded to the upper part of the Kerek Formation.

**Late Miocene to Middle Pliocene**

The Banyak Beds mainly consist of andesitic material deposited in a marine environment: tuffs, coarse tuff-sandstones, calcareous tuffaceous sandstones, and volcanic breccia alternating with marls bearing planktonic foraminifera.

**Late Pliocene**

The Damar Formation lies conformably on the argillaceous Kalibiuk Member. The Damar Formation consists of andesitic tuff-sandstones and conglomerates beds bearing the first vertebrate fossils. In the west and central Kendeng Zone, Pucangan Formation unconformably overlies the Upper Kalibeng carbonate and consists of continental coarse pyroclastic sediments, those are volcanic conglomerates and sandstones.

**Early Pleistocene**

The continental Notopuro Formation rests unconformably either on the Kabuh Formation or on the Pucangan Formation. The formation consists of coarse to very coarse volcanic conglomerates, tuffaceous sandstones, tuffs, and lahar deposits.

**Structural Geology**

In Kendeng Zone, there are many structural complications. The major structures are west-east trending folds, west-east trending reverse faults, and wrench faults which transversely cut the Kendeng Zone (de Genevraye and Samuel, 1972). The folds are tightly folded with steep, vertical, or reverse flanks. Faults are extremely frequent in this area. The intensity of folding and faulting appears to decrease from west to east of the Kendeng Zone.
Figure 2. Geological map and general stratigraphy of western Kendeng Zone (de Genevraye and Samuel, 1972). The gas in the studied area leaks through Kerek Formation.
Geochemistry of Natural Gas Seepages in Boto Area, Bancak, Semarang, Central Java (H. Amijaya and P.A. Pameco)

Beside the longitudinal reverse faults that spread along the anticlinorium, the latter is transversely cut by numerous wrench faults. Wrench faults between the Tuntang River and Salatiga, are structures which occur in the studied area (see Figure 2), and are believed to be deep-seated faults originating from the basement. The most conspicuous examples of the relative displacement transversely to the Kendeng Zone trending west-east, occur in its westernmost and easternmost parts. Westernmost block, which is the studied area, is situated between the Gunung Ungaran faulted area and the Tuntang River/Salatiga network of deep-seated faults. It has been displaced towards the north as shown by the northwards shift of the anticlinorium axis in this area.

Material and Methods

Geochemical analysis of a gas includes both molecular composition (relative abundance in the gas sample of $C_1$ to $C_3$ hydrocarbons and non-hydrocarbon gases such as $H_2$, $CO_2$, and $N_2$) and isotopic composition. The isotopic composition of a gas includes characteristics such as the stable carbon and hydrogen isotope ratios of the $C_1$-$C_5$ hydrocarbon gas species, stable isotope composition of non-hydrocarbon gases, radioactive carbon, and hydrogen isotopes of $C_1$. Data for molecular and isotopic characteristics of natural gas can be used to constrain the origin of a gas (bacterial and/or thermogenic) as well as the type and maturity of the organic matter that generated the thermogenic hydrocarbons in a sample. These data can also identify any secondary processes, such as gas oxidation, that may have affected a sample (Schoell, 1983; Whiticar and Faber, 1986; Jenden et al., 1993; Laughrey and Baldassare, 1998).

Locations of Seepage Samples

Three seepage gas samples were found in Boto Area (see Figure 3a). Table 1 shows the coordinates for the sample locations. Site 1 is located in Dusun Gunung and the others are located in Dusun Galeh, about 1.5 km to the southwest of the Site 1. The presence of seepages was known by the emergence of gas bubbles in the rice fields (see Figure 3b). One of the seepages, the Site 3 (see Figure 3d), had been cemented and the gas is streamed and utilized by local residents. Flame characteristics of gas when burned in daylight condition are partially reddish yellow colour and some are invisible (see Figures 3c and d for example).

Sampling and Analytical Methods

A field observation includes determination of location and visual observation of the seepage condition has been done. Samplings of gases were using some traditional equipments, such as vacuum pump, gas sampling bag, hose, and funnels.

In this study, the seepage gases were analyzed for molecular as well as $C_1$ and $C_2$ stable carbon isotope compositions. Samples were collected in sample bag following an in-house sampling protocol for seepage gas sample collection. The determination of the gas composition was conducted at the Laboratory of Gas Technology PPPTMGB LEMIGAS, using a Gas Chromatography instrument from Agilent Technologies 7890A series. Laboratory GHGeochem Ltd. analyzed the isotope compositions of methane using gas chromatography–isotope ratio mass spectrometry (GC-IRMS) systems with a precision of $\pm0.3\%$ - $0.4\%$ for $\delta^{13}C$ and $\pm5\%$ for $\delta^D$ values. Samples were prepared and analyzed according to internal standard procedures by the laboratory. After sample preparation, both the $^{13}C/^{12}C$ and $^2H/^{1}H$ analyses are performed on an Isoprime. Table 2 shows the results geochemical data for the $\delta^{13}C$ and $\delta^D$ isotopic methane and gas composition of gas seepage samples. The geochemical data were evaluated to constrain gas origin and thermal maturity.

Results and Discussion

Gas Composition

The major gas compositions and stable isotope data of the seepage gas samples collected are given in Table 2. GC results in the table show...
Table 2. $\delta^{13}$C and $\delta^D$ Isotopic Methane and Gas Composition of Gas Seepages in the Studied Area

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Isotopic Composition</th>
<th>Gas Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C CH4 $^a$</td>
<td>H2S</td>
</tr>
<tr>
<td>1.1</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>1.2</td>
<td>-35.61</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>-27.97</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: not analyzed, need another measurement technique

$^a$‰ relative to Peedee belemnite (PDB)

$^b$‰ relative to Standard Mean Ocean Water (SMOW)
that all the seepage gas samples are generally have the similar hydrocarbon compositions. Gases in the studied area are generally dominated by methane which normalized hydrocarbons to reach more than 99% (not shown in the table). Other than that, other hydrocarbon gases, i.e. ethane and propane, are found but in a small percentage. With exception to the N\textsubscript{2} for the seepage gas sample from the Site 3, in general, nonhydrocarbon gases found are relatively small percentage of CO\textsubscript{2}, N\textsubscript{2}, and O\textsubscript{2}. Relatively high O\textsubscript{2} compound in the samples are probably as atmospheric contaminant due to improperly samples collecting tool.

**Gas seepage composition of Site 1**

From several gas seepages in the Site 1 area, only two seepage gas samples have a good pressure capacity and suitable to be sampled, i.e. Seep 1.1 and Seep 1.2 gases. These gas samples are compositionally similar (see Table 2) consisting of ± 85% CH\textsubscript{4}, < 1% C\textsubscript{2}H\textsubscript{6}, < 1% CO\textsubscript{2}, ± 10% N\textsubscript{2}, and ± 5% O\textsubscript{2}. After normalization for the gas hydrocarbons only, the composition of gas seepage samples are almost identical with methane predominant to reach more than 99%. The presence of oxygen is probably atmospheric contamination.

**Gas seepage composition of Site 2**

The composition of the seepage gas sample in the Site 2 (see Table 2) has a different composition with that of in the Site 1, showing lower hydrocarbon composition ± 68.93% CH\textsubscript{4} only and relatively higher nonhydrocarbon gases in percentages of respective ± 0.08% CO\textsubscript{2}, ± 19.91% N\textsubscript{2}, and ± 11.08% O\textsubscript{2}. The smaller CH\textsubscript{4} composition is due to higher non-hydrocarbon content (see Table 2).

**Gas seepage composition of Site 3**

The composition of gas in the Site 3 (see Table 2) is dominated by hydrocarbon gas which comprises ± 53.74% methane. Other hydrocarbons found are ± 0.326% ethane and ± 0.11% propane. Non-hydrocarbon gases found are ± 0.17% carbon dioxide, ± 34.80% nitrogen, and ± 10.86% oxygen. It is interesting to note that N\textsubscript{2} content is very high compared to the other samples.

N\textsubscript{2} is sometimes a major constituent of natural gases, but the origin of this N\textsubscript{2} is still enigmatic. While atmospheric air contains some 78% N\textsubscript{2} and 21% O\textsubscript{2} by volume along with other components and rare gases. Unless otherwise N\textsubscript{2} in the gas seep samples come from the atmosphere during sample collection, relatively high N\textsubscript{2} fraction may be released from sedimentary organic matter during burial, several nonsedimentary sources of N\textsubscript{2} may also contribute to the natural gas.

**Isotopic Composition**

Sources of CH\textsubscript{4} include natural gas reservoirs, gas associated with oil and coal, landfills and the products of anaerobic degradation of organically contaminated groundwater. Although, there are many ways to characterize the methane source, a combination of C and H isotope analysis of natural gases is a powerful tool to discriminate different origins of gases. A plot of δ\textsuperscript{13}C vs. δD (see Figure 4a) not only reveals a distinction of biogenic and thermogenic gases from different environments, but it also allows delineating mixtures between the different types. For example, plots of the stable isotope ratios for C vs. H (e.g. Schoell, 1983) can be used to distinguish petroleum groups.

Identifying the gas origin may be very much more complicated if there is more than one source of methane exists, and where compositional evidence alone is used. It is important to have a well-defined database for the likely composition of possible source gases and to evaluate whether changes in composition have occurred during gas migration. Stable isotope ratios of carbon and hydrogen (i.e. \textsuperscript{13}C/\textsuperscript{12}C, \textsuperscript{2}H/\textsuperscript{1}H) potentially provide additional means by which methane can be characterized, but such data are scant for sources in Indonesia.

Different gases δ\textsuperscript{13}C values of given hydrocarbon generally increase with the increasing thermal maturity. Migrating methane could be enriched in \textsuperscript{13}C or \textsuperscript{15}N as 1 - 3‰ depending on the amount of organic matter on shales, the mechanism of
migration, and on the properties of the medium through which the gas is moving. There are two ways to determine maturation using isotopes that are isotopic composition of CH$_4$ and separation of carbon isotopes between hydrocarbon components.

Thermogenic (methane and wet gases), source, maturity, and chemical kinetics have the primary controls on the gas composition and the proportion of gaseous and liquid hydrocarbons (Rice, 1993). With maturity, the $\delta^{13}$C and $\delta$D values of thermogenic gases systematically increase from C$_1$ to C$_5$. Increasing temperatures modify the organic matter due to various chemical reactions such as cracking and H$_2$ disproportionation in kerogen. As these results in a $^{13}$C enrichment of the residue, more $^{13}$C - $^{12}$C bonds are broken with increasing temperatures which produce higher $\delta^{13}$C values.

Figure 4 shows plots of $\delta^{13}$C versus $\delta$D of CH$_4$ (Figure 4a) and $\delta^{13}$C methane versus gas wetness (Figure 4b) for samples in this study. The two hydrocarbon gas seeps (Site 1.2 and Site 3 samples) that are characterized by $\delta^{13}$C methane are -35.61‰ and -27.97‰, and the values of $\delta$D methane are -112‰ and -109‰ respectively which each are isotopically distinct from all others. The figures show that both samples indicate dry thermogenic gas within the range of -40‰ to -15‰ for $\delta^{13}$C$_1$ and -150‰ to -70‰ for $\delta$DC$_1$ suggesting, at least, they are derived from different maturity level. The Site 3 gas sample is prone to be more mature than the other.

All gas possibly derived from humic organic matter source rock based on the CD diagram (Whiticar, 1968; in Whiticar, 1999). Plotting carbon and deuterium isotope values can be seen in Figure 4a. Samples 1, 2, and 3 are plotted in the intersection zone between thermogenic non-associated gas from marine (sapropelic liptinitic) source rock and thermogenic non-associated gas from coal (humic) source rock. The amount of C$_2^+$, samples 1, 2, and 3 have been derived from mixed source (Figure 4b).

Pramono (2008) studied oil seep near gas seepages in the studied area. Its distance is around +2 km from gas seepage locations. He concluded that the oil was derived from mixed organic matter source rock. Wiloso (2008) and Wiloso et al. (2008) also showed mixed kerogen in Galeh oil seep analysis. Galeh oil seep located

![Figure 4. (a) Plotting of $\delta^{13}$C and $\delta$D methane values on the CD diagram (Whiticar, 1968; in Whiticar, 1999) showing sample 3 is derived from humic source, but samples 1.2 is not accurately plotted on humic. (b) Plotting of carbon stable isotopes and relative concentrations on Schoell’s Diagram (Schoell, 1983).](image-url)
in the Site 3 correlated with Ngimbang Formation rock sample from Rembang 1 well which is also mixed kerogen source rock (Wiloso, 2008; Wiloso et al., 2008).

There is a linkage between gas and oil in the studied area. However, it can not be known whether it is a result of oil thermal alteration process or source rock thermal cracking process. It requires an isotope analysis of ethane and propane (Katz, 2002) which are not found in the gas seepages.

**CONCLUSION AND FUTURE WORK**

Natural gases in the Boto area consist of methane predominant amounting 53 - 85% and more than 99% after hydrocarbon normalization. Those seepage gas samples that are dominated by thermogenic gas are each isotopically and compositionally distinct from all others. The exception to the Site 2 sample, the gas tends to indicate being derived from mixed organic matter source rocks. The Site 2 sample has not yet to determine its source rock due to lack of evidence in this study. Further work is needed especially in term of isotope study of gas in order to disclose the gas potential within the region.

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