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RESEARCH ARTICLE

# Natural Gas Geochemistry in Jambanan Area, Sidoharjo, Sragen, Central Java, Indonesia

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#### Abstract

Natural gas was encountered on PAMSIMAS well drilling in the Jambanan area. Geochemical studies are needed to determine gas genesis in this area. Geochemical studies were carried out using the GC gas composition method on gas samples located at three locations, namely SRG-01, SRG-02, and SRG-03. The three gas samples had a methane content of 47.61 - 87.97mol.%. All three have a low wettability level (0.03-0.05%) which indicates that the gas is very dry. GC-IRMS Method was also used on SRG-01 and SRG-02 gas sample. Those gas samples have  $\delta^{13}$ C Methane characteristics of -40.7‰ (SRG-01) and -45.6‰ (SRG-02) with  $\delta$ D methane values of -171‰ (SRG-01) and -178‰ (SRG-02). This shows that the gas at those are thermogenic gas and it comes from different levels of maturity, where the gas at SRG-01 is more mature than the gas at SRG-02.

Keywords: Natural Gas, Gas Composition, Jambanan, Sragen

#### 1. Introduction

In the Jambanan area, natural gas occurs in a well which was originally built for clean water fulfillment. The gas seeping out from the groundwater well is thought to be methane gas (Dinas ESDM Provinsi Jawa Tengah, 2023). Based on the geological map of the Salatiga (Sukardi & Budhitrisna, 1992), natural gas occurs in the alluvial deposits (SRG-01-JB) and Klitik Formation (SRG-02-GB and SRG-03-TN) which are include in Kendeng Zone.

Physiographically, the research area is included in the Solo zone which is stratigraphically close to Kendeng zone. Regionally, previous research was carried out by Satyana and Purwaningsih (2003) regarding genetic types of gas in the North East Java basin. Based on geochemical analysis, natural gas in East Java can be divided into 3 genetic gases, namely thermogenic gas, biogenic gas and a mixture of the two. Thermogenic gas has a similar source to oil. Meanwhile, biogenic gas probably comes from shale and coal of Neogene age.

Several previous studies stated that several seepage locations in the Kendeng zone, such as in Kedung Jati and Galeh, comes from the source rock which is the Ngimbang Formation (Wiloso et al, 2008). Pameco (2016) and Mardianza and Dianita (2018) also suspect that the source rock from several gas seep locations in the Kendeng zone is thermogenic gas which is correlated with rocks beneath the Pelang formation which is equivalent to the Ngimbang Formation.

Currently the source of methane gas at this location is not known and whether it is a thermogenic gas or a biogenic gas. To find out the origin of the gas, it is necessary to carry out geochemical characterization of the gas. Therefore, in this research geochemical analysis was carried out as a preliminary study to determine the genetics of hydrocarbons from the Jambanan area.

## 2. Regional Geology

#### 2.1. Stratigraphy

Based on de Genevraye and Samuel (1972) and Pringgoprawiro (1983), the stratigraphic sequence of the Kendang Zone from oldest to youngest are

#### 2.1.1 Pelang Formation

The Pelang Formation is the oldest formation in the Kendeng Zone. This formation is composed of lithology in the form of marl, clay marl with bioclastic calcarenite lenses. Pelang formation was deposited at Late Oligocene to Early Miocene.

#### 2.1.2 Kerek Formation

The Kerek Formation is characterized by lithology in the form of alternating layers of mudstone, marl, calcareous tuff sandstone and tuff sandstone. This formation is divided into 3 members: (1) The Banyuurip member is composed of lithology in the form of alternation between clay marl, clay with calcareous tuff sandstone and tuff sandstone. This member was deposited in N10 – N15 (upper middle Miocene). (2) The Sentul Member is almost the same as the Banyuurip member with the tuff layer being thicker. The Sentul Member is N16 (upper lower Miocene). (3) The kerek limestone member has a constituent lithology in the form of alternation between tuff limestone and layers of clay and tuff. This member has an age of N17 (middle upper Miocene).

## 2.1.3 Banyak Formations

The Banyak Formation is composed of lithology in the form of alternation between tuff, tuff sandstone, calcareous tuff breccia, volcanic breccia, and tuff marl. Pringgoprawiro gave an age of N17-N18 (Upper Miocene) based on the content of plankton foraminifera, with an outer neritic sedimentation environment.

#### 2.1.4 Kalibeng Formation

The Kalibeng Formation is divided into two parts, namely the lower part and the upper part: (1) The lower Kalibeng Formation is composed of yellowish white to bluish gray unlayered marl, rich in plangtonic foraminifera. (2) The upper Kalibeng Formation of this formation is sometimes also referred to as the Sonde Formation, with Pliocene in age (N19 – N21).

## 2.1.5 Pucangan Formation

The Pucangan Formation is composed of black clay facies and volcanic facies where the volcanic facies developed as lava deposits which were deposited conformably above of the Kalibeng Formation.

# 2.1.6 Kabuh Formation

The Kabuh Formation is composed of lithology in the form of sandstone with non-volcanic materials including quartz, a cross structure with conglomerate lenses, containing freshwater mollusks and vertebrate fossils.

## 2.1.7 Notopuro Formation

The lithology of Notopuro Formation is composed of tuff rock interbedded with tuff sandstone, lava breccia and volcanic conglomerate. The position of this formation is conformable above the Kabuh formation. The age of this formation is Late Pleistocene.

## 2.1.8 Bengawan Solo Undak Deposits

These deposits are composed of lithology in the form of polymic conglomerates with marl and andesite fragments in addition to sandstone deposits containing vertebrate fossils in the Brangkal and Sangiran areas.



Fig 1. Geological Map of Western Kendeng Zone (modified from de Genevraye and Samuel (1972) and Pringgoprawiro (1983))



Fig. 2. Locations of the three natural gas samples found in Jambanan Area and nearby location.

#### 2.2 Regional Petroleum Play

The Kendeng Zone is one of the hydrocarbon producing zones in Indonesia. Kendeng zone are active petroleum systems that generate type II to type III kerogen typical to the organic material (Septama et al, 2021). Pelang Formation consider as potential source rock in Kendeng Zone (Ramadhan, et al. 2015). In the middle Miocene, Kendeng depocenter were formed before Sundaland and East Java Micro-Continet collision in Middle Eocen (After Prasetyadi, 2007). Secondary migration of hydrocarbon may have taken place vertically along the faults after Pliocene uplifting to the North-, Northeast- and Northwest direction indicated by hydrocarbon manifestation on surface such as several oil seeps at Kerek, Kalibeng, and Lidah Beds around Kedungjati and Jatikuwung Nort of Djuwangi (Sukardi & Budhitrisna, 1992).

Miocene Kerek Sandstone which have thick sand body and good porosity is consider as possible reservoir rock in Kendeng Zone. Mio-Pliocene shales of Kalibeng Formation is possible to be a good seal with good lateral distribution and thickness (Ramadhan, et al 2015). The sedimentary trough that extends in an East-West direction along the island of Java is caused by overthrusting from long-standing geological elements in East Java. This pressure was still active until the Pliocene and was responsible for folds in the kendang zone (Lunt P., 2019). There are two trap mechanism observed in Kendeng Zone, structural and stratigraphic trap. Structural trap has been proven and widely known is in Lidah and Kuti.

## 3. Method

## 3.1. Location of gas sampling

Table 1. Coordinate of the sample location

N o	Location	Coordinate	Sample ID	
1	Jambanan	49S 497211	SRG-01	
-	Village	9180431	0110 01	
2	Gabus Village	49S 505958	SPC 02	
		9186664	3KG-02	
3	Tanggan Village	49S 500428	CDC 02	
		9186498	SKG-03	

In the Jambanan area, 3 gas samples were taken at each locations where natural gas occurred (Figure 2). Table 1 shows the coordinates of the sample locations. Location 1 is in Jambanan Village, location 2 is in Gabus Village, and location 3 is in Tanggan Village. Gas at location 1 occurred as a result of well drilling activities. The flame of the gas burned at this location is reddish in color. Gas at location 2 also occurred due to well drilling activities. The flame of the gas burned at this location is bluish in color and slightly invisible. The gas at location 3 is a from seepage that occurred in the river body and produced gas bubbles. The flame of the gas burned at this location is bluish in color and almost invisible.

#### 3.2. Sampling methods and analysis

Sampling is carried out funnels, hoses, gas bags and tape. Sampling of gas bags was carried out according to the in-house sampling protocol for collecting gas samples.

The Determination of the gas composition was conducted at the laboratory of Gas Technology PT Geoservices, using a Gas Chromatography Instrument from Agilent Technologies 190918-001 Series. Gas chromatography is carried out by separating the differences in distribution patterns between two components in the movement patterns of the mobile phase and the stationary phase so that there are differences in the average residence time of the compounds and differences in their movement speeds (Kendler, 2004). This method has high sensitivity and resolution, and allows accurate calculation of compounds in mixtures. They analyzed the isotopic composition of methane using gas chromatography - isotope ratio mass spectrometry (GC-IRMS) with precision values of  $\pm 0.2$ ppm for  $\delta^{13}$ C and  $\delta$ D. Samples were prepared and analyzed according to internal standard procedures established by the laboratory. After sample preparation, both <sup>13</sup>C/<sup>12</sup>C and <sup>2</sup>H/<sup>1</sup>H were analyzed using Isoprime. Table 2 shows the results of geochemical data for the composition of gas samples and Table 3 shows the results of geochemical data for the  $\delta 13C$  and  $\delta D$  isotopes of methane. The geochemical data is evaluated to determine the origin of the gas and thermal maturity. Table 2 shows the results of geochemical data on the composition of gas samples. Table 3 shows the results of geochemical data on the isotope composition of gas samples.



Fig. 3. Flame Test on well in Gabus village indicating high hydrocarbon content.

Table 2. Results of composition analysis of gas samples.

SAMPEL			mol.%	Non H	С		r	nol.%	HC	Total Gas	Norn	nalised	Perce	nt HC	% Gas	<u>C1</u>
ID	He	H2	02+Ar	H2S	CO2	N2	C1	C2	C3	(HC) mol.%	C1	C2	C3	C3H6	Wetness	(C2+C3)
SRG-01	nd	nd	2,3	nd	0,34	9,34	87,97	0,03	0,01	88,02	99,95	0,03	0,01	nd	0,05	2340
SRG-02	nd	0,17	10,25	nd	1,62	40,34	47,61	0,01	0	47,63	99,96	0,02	0,01	nd	0,03	3377
SRG-03	nd	nd	0,46	nd	5	15,36	79,17	0,01	0	79,18	99,99	0,01	0	nd	nd	nd

\*% Gas Wetness = (C5+/C1-C4)4

iC4 = Isobutane

nC4 = Normal Butane

nd = not displayed

#### 4. Result and Discussion

#### 4.1. Gas Composition

The overall gas composition can be seen in Table 2. In general, gas samples from the three locations have the same hydrocarbon content. This gas generally has a high hydrocarbon gas content in the form of methane (47.61 - 87.97mol.%) and a low non-hydrocarbon gas content ( $CO_2$ ,  $N_2$  and  $O_2$ ) with the exception of location 2 where quite high  $N_2$  was found. The relatively high  $O_2$  content is likely caused by air contamination.

#### 4.1.1 Gas composition at location 1

The gas at location 1 contains 88.02 mol.% of hydrocarbon gas (87.97 mol.% of C1, 0.03 mol.\% of C2, and 0.01 mol.\% of C3) and 11.98 mol.% (H<sub>2</sub> is 0 mol.% of non-hydrocarbon gas, 2.30 mol.% of O<sub>2</sub>+Ar, 0.34 mol.% of CO<sub>2</sub>, and 9.34 mol.% of N<sub>2</sub>). These gases contain low associated levels of gas wetness (0.05% %)

#### 4.1.2 Gas composition at location 2

The gas at location 2 contains 47.63 mol.% of hydrocarbon gas (47.61 mol.% of C1, 0.01 mol.% of C2, and 0 mol.% of C3) and 52.37 mol. % of non-hydrocarbon gas (0.17 mol.% of H<sub>2</sub>, 10.25 mol.% of O<sub>2</sub>+Ar is, 1.62 mol.% of CO<sub>2</sub>, and 40.34 mol.% of N<sub>2</sub>). The relatively high O<sub>2</sub> content may be caused by air contamination. These gases contain low associated levels of gas wetness (0.03% %).

#### 4.1.3 Gas Composition at location 3

The gas at location 3 contains 79.18 mol.% of hydrocarbon gas (79.17 mol.% of C1, 0.01 mol.% of C2, and 0 mol.% of C3) and 20.82 mol.% of non-hydrocarbon gas (0 mol.% of  $H_2$ , 0.46 mol.% of  $O_2$  is, 5.00 mol.% of  $CO_2$  is, and 15.36 mol.% of  $N_2$ ).

These gas samples contain a high proportion of hydrocarbon components (47.63-88.02 mol.%) which generally comprise predominantly methane (CH<sub>4</sub> 47.61-87.97 mol.%). The N<sub>2</sub> content in the gas sample from location 2 is higher than the others. N<sub>2</sub> can be found in atmospheric air, in natural gas which come from sedimentary organic material during burial, and several other non-sedimentary sources. These gases contain low associated levels of gas wetness (0.03-0.05% %) suggest that these gases may dry gases. Determining whether a gas is wet gases or dry gases is also carried out using plotting isotope values of  $\delta^{13}$ C Schoell diagram (1983).

## 4.2. Isotope Composotion

A combination of C and H isotope analysis of gases is used to distinguish different gas origins (biogenic or thermogenic). Plotting of  $\delta^{13}$ C and  $\delta$ D isotope values also can be used to determine the mixture between various other types, such as plotting the stable isotope ratio for C vs H (Schoell, 1983) can be used to differentiate petroleum groups.

A well-defined database of geochemical data is essential for determining the origin of gas with multiple methane sources and using only compositional data. In addition, compositional changes that occur during gas migration can also be evaluated. The stable isotope ratios of carbon and hydrogen (i.e.  $^{13}C/^{12}C$ ,  $^{2}H/^{1}H$ ) can be used to characterize them, but the data available in Indonesia is limited.

As maturity increases, it may results in different  $\delta^{13}C$  values. Enrichment at  $^{12}C$  and  $^{13}C$  from 1 to 3‰ occurs as

methane migrates, depending on the amount of organic material present in the shale, the migration mechanism, and the nature of the medium in which the gas migrates. The isotopic composition of  $CH_4$  and the separation of carbon isotopes into hydrocarbon components can be used to determine maturity.

Table 3. Result of Isotope analysis of Gas Samples

Sampel	δ13D (per	δ13C (per mille)*					
ID	mille)*	C1	C2	C3			
SRG-01	-171	-40,7					
SRG-02	-178	-45,6					
SRG-03	-	-					

\* Isotope values measured in parts per thousand relative to Peedee Belemnite (PDB) Standard. Results accurate to ± 0,2 ppt

The main controls on the composition and proportions of gases as well as the ratio of gas phase and liquid phase of hydrocarbons are heat generation (methane and wet gas), source, maturity level, and chemical kinetics (Rice, 1993). With increasing maturity level, the  $\delta^{13}$ C and  $\delta$ D values of thermogenic gases increase from C1 to C5. Increased temperature converts organic materials through various chemical reactions such as cracking and H<sub>2</sub> imbalance into kerogen. Due to <sup>13</sup>C-enriched residues, more <sup>13</sup>C-<sup>12</sup>C bonds are broken, resulting in higher  $\delta^{13}$ C values.



Fig. 4. plotting of isotope values of  $\delta^{13}$ C vs hydrocarbon generated (Bernard 1978 in Schoell, 1983)

Two hydrocarbon gases (SRG-01 and SRG-02) were characterized by methane  $\delta^{13}$ C -40.7% (SRG-01) and -45.6% (SRG-02) which is isotopically different from the other. Figure 4 show that SRG-01 gas samples is dry thermogenic gas and SRG-02 gas samples is wet thermogenic gases. SRG-02 They come from different maturity levels. The SRG-01 gas sample has a higher maturity level than SRG-02.



Fig. 5. Plotting of  $\delta$ 13C vs C2+ isotope values on the Schoell Diagram. (Schoell, 1983)

SRG-01 gas is a non-associated gas, while the SRG-02 gas is an associated gas that experienced compositional shift due to shallow migration (Figure 5). It is possible for this gas to be associated with oil but to date no oil has been found at the research location.



Fig. 6. Plotting of  $\delta^{13}$ C vs  $\delta^{2}$ H isotope values on the Schoell Diagram. (Schoell, 1983)

Basen on schoell's genetic classification, SRG-01 gas and SRG -02 gas possibly derived from sapropelic organic matter source rock (Schoell, 1983). Plotting carbon and deuterium isotope values can be seen in figure 6. Those gas are plotted in thermogenic sapropelic zone.

The gas formed in the research area may come from a different source than previous research. Based on those

maturity level (lower maturity level than previous study) and source of organic matter (sapropelic source), its possibly has a higher stratigraphic position than Ngimbang Formation which deposit at Late Eocene – Middle Oligocene. The lower level of maturity than previous research is probably due to the research area being on the southern of the Kendeng anticlinorium so that the buried material is thinner than the other. Ngimbang Formation is likely the source rock of the research area because it has a higher stratigraphic position and allows the deposition of kerogen which is rich in saporpelic organic material.

## 5. Conclusions

Natural gases in the Jambanan area contains methane predominant amounting (47.61 - 87.97mol. The gases are thermogenic origin of sapropelic source. This is indicated by high Bernard Ratios of 2340-3377,  $\delta$ 13C methane characteristics of -40.7‰ (SRG-01) and -45.6‰ (SRG-02) with  $\delta$ D methane values of -171‰ (SRG-01) and -178‰ (SRG-02). SRG-01 has higher maturity level than SRG-02. Further work is needed especially in term of isotope study of gas in order to verify genetic of gas and disclose the gas potential.

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