The effect of volcanism to the source rock maturity in Gunung Endut area: Insight for subvolcanic hydrocarbon exploration

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Abstract. Banten region is known to have subvolcanic hydrocarbon system but no proven play despite oil seeps and the potential source rock have been identified in this area. A Geochemical analysis of source rock have been done on Gunung Endut, Banten Province. There are four coaly shale sample from Genteng Formation and Bojongmanik Formation collected and analysed in this study. The purpose of this study is to understand the influence of volcanic environment towards the quality, quantity and maturity of source rock based on TOC, pyrolysis, and vitrinite reflectance analyses. The result obtained showed TOC value between 8–18 wt% which indicated excellent petroleum potential from the source rock. In addition, Pyrolysis data showed S1 value between 0.05–0.19, S2 value between 1.52–11.53, S3 value between 4.10–7.57 and Tmax 414.8–523.2 °C. From both analyses, TOC and Pyrolysis, the source rock is categorized as Type 3 Kerogen producing gas and Type 4. Based on its maturity, three sample are categorized as immature while one specimen is categorized as postmature. Furthermore, Vitrinite Reflectance analysis result shows Ro value between 0.27–0.63 that support the result of pyrolysis analysis. Maturity anomaly found in the sample is presumed to be caused by intrusion that have been identified by the geological mapping in the same region. The condition on the surface may also reflect the source rock in the subsurface. A number of source rock in Banten region may be matured due to intrusion that related to volcanic activities. Subsurface zone with abundance igneous bodies will have different maturity compare to other area. Hence, it is important for petroleum exploration activities in Banten region or other volcanic area to properly identify the distribution of subsurface igneous body due to its effect to the source rock maturity.

Keywords: Source rock, maturity, geochemical, pyrolysis, vitrinite reflectance

1. Introduction
Oil can be formed from the results of chemical processes from sedimentary rocks rich in organic content or known as source rock which has diagenesis process [1]. Factors that affect oil formation from source rock are temperature, pressure, time, and other minerals that can increase rate of reaction or inhibit reaction [2]. The source rock analysis can be done using geochemical methods that aim to determine the source rock maturity, abundance, composition, and distribution of chemical compounds in hydrocarbons in rock deposit [1]. Geochemical analysis parameters especially hydrocarbon maturity can be done by...
parameter analysis of total organic carbon, rock eval pyrolysis, gas analysis, organic petrography, thermal alteration index, and vitrinite reflectance [3]. Source rock evaluation is a geochemical exploration and the beginning for petroleum exploration to determine the quality of source rock [4]. The research was conducted at Gunung Endut area, Lebak Regency, Banten Province (figure 1). Lithology at research area generally consist of pyroclastic rock from volcanic eruption [5]. It is known that the Sandstone members of the Bojongmanik Formation at research area are deposited with rich organic rock like lignite [5].

This research focuses on the stage of rock maturity based on analysis of vitrinite reflectance, total organic carbon, and rock eval pyrolysis. The samples analyzed from rock that were exposed to the surface and then taken for macroscopic description and laboratory analysis.

2. Geological setting
The study area is in a quarter volcanic environment formed by the process of subduction between the Eurasia and Indo–Australia plates [6]. Source rock analyzed was found in three different rock formation, in the Genteng Formation, Sandstone Member of the Bojongmanik Formation, and Endut Volcanic Rock Formation.

Lithology of Genteng Formation consists of tuff, breccia, and marl. Sandstone Members of the Bojongmanik Formation consists of clay, napal, sand, tuff and lignite. Whereas in the Endut Volcanic Rock Formation composed by volcanic breccia, lava and tuff [5]. Volcanic eruption rocks have a temperature and precipitate over previous rocks which can affect characteristics of the underlying rock [7]. Temperature in the rock environment is a major factor in hydrocarbons derived from heated kerogens (pyrolysis) [2]. Volcanism activities at research area who produced lithology from eruption affects the maturity of the source rock deposited in the research area.

The research area is shown by figure 2. The lithology of research area composed by volcanic eruption rocks. Most of samples were found on the exposed surface in the East and West of research area. Figure 2 shows that the lithology and geological structure are formed by tectonic activity.

3. Materials and method
Rock samples were taken from four different locations (UI 17, UI 38, UI 73, UI 211.5) to know the physical characteristic and to know the characteristic of source rock who affected by volcanic activity with geochemical analysis.

Figure 1. Location of Gunung Endut research area.
3.1. Total organic carbon
Organic material contained in sedimentary rocks can be expressed as Total Organic Carbon [8]. This value shows the organic carbon content in the rock and in its measurement special treatment is needed to eliminate inorganic carbon content. The mashed sample weighed and added with Chloride Acid which aims to remove the CaCO$_3$ content and then burn using Leco Carbon Analyzer. The purpose of the TOC analysis is to determine the potential content of organic material (hydrocarbons) that can produce oil or gas [3]. In addition, TOC analysis is carried out to ascertain whether the rocks are included in the source rock based on the TOC value [3].

3.2. Pyrolysis
Pyrolysis is a geochemical method to determine the content of hydrocarbon and maturity in source rock by heating without oxygen [8]. During the heating of the source rock there are two type of hydrocarbons released from the source rock drawn from the values of S1 and S2 [8]. In addition to measuring hydrocarbons, carbon dioxide in kerogen is also released and measured. This carbon dioxide is measured by the detector and recorded as a S3 value after all hydrocarbon measurements have been completed. Pyrolysis method also measurement Tmax parameter. Tmax values are obtained from S2 peak temperature when reaching maximum. Pyrolysis temperature is used as an indicator of maturity because if kerogen maturity increases, rate temperature of pyrolysis also increases [8].

Table 1 shows the results of TOC measurements and pyrolysis of the source rock samples at Mount Endut [3]. These results can later be used for processing kerogen type data and products produced from source rock. Table 2 is a classification made by Peter et al. [3]. In the classification required data processing results from pyrolysis measurements. The pyrolysis data used are S2 and S3 which then obtained the type of product produced [3].

3.3. Vitrinite reflectance (Ro)
Vitrinite reflectance analysis is based on vitrinite reflected light capabilities [8]. The sample used is a block sample where rock is put into container and added with mixture of catalyst and resin. Samples that have been prepared are analyzed under a microscope and shootings are carried out in the vitrinite area. The vitrinite reflection analysis aims to determine the vitrinite reflectivity which can indicate the
maturity of the source rock [3]. Source rock which has a high reflecting value of vitrinite (Ro) is directly proportional to the temperature conditions in the deposited source rock [3].

Table 3 shows the classification of the level of maturity of the host rock made by Peters et al. [3]. Data needed to classify the level of maturity are the values of vitrinite reflectance, Tmax from the results of pyrolysis measurements and TAI [3].

### Table 1. Petroleum potential classification (quantity) based on total organic carbon and pyrolysis.

| Petroleum potential | TOC (wt %) | Organic matter | S1 | S2 |
|---------------------|------------|----------------|----|----|
| Poor                | 0–0.5      | 0–0.5          | 0–2.5 |
| Fair                | 0.5–1      | 0.5–1          | 2.5–5 |
| Good                | 1–2        | 1–2            | 5–10 |
| Very Good           | 2–4        | 2–4            | 10–20 |
| Excellent           | > 4        | > 4            | > 20 |

### Table 2. Kerogen type (quality) and main expelled product classification based on pyrolysis.

| Kerogen type | HI (mg HC/g TOC) | S2/S3 | Main expelled product |
|--------------|------------------|-------|-----------------------|
| I            | > 600            | > 15  | Oil                   |
| II           | 300–600          | 10–15 | Oil                   |
| II/IIIa      | 200–300          | 5–10  | Mixed oil and gas     |
| III          | 50–200           | 1–5   | Gas                   |
| IV           | < 50             | < 1   | None                  |

*Type II/III designates kerogens with compositions between type II and III pathways*

### Table 3. Thermal maturation classification based on vitrinite reflectance and pyrolysis.

| Stage of thermal maturity for oil | Maturation Ro (%) | Maturation Tmax (°C) | TAI |
|----------------------------------|-------------------|----------------------|-----|
| Immature                         | 0.2–0.6           | < 435                | 1.5–2.6 |
| Mature                           |                   |                      |     |
| Early                            | 0.6–0.65          | 435–445              | 2.6–2.7 |
| Peak                             | 0.65–0.9          | 445–450              | 2.7–2.9 |
| Late                             | 0.9–1.35          | 450–470              | 2.9–3.3 |
| Postmature                       | > 1.35            | > 470                | > 3.3 |

4. Results and discussion

Table 4 shows the values of TOC and pyrolysis measurements. From the data, it can be further processed to get the level of maturity and products produced from the source rock based on the classification of Peters et al. [3].
Formulas for pyrolysis calculation:

a. HI (Hydrogen Index) = (S2/TOC) x 100
   Hydrogen index is a value that shows the relative amount of hydrogen content in organic carbon contained in sample.

b. OI (Oxygen Index) = (S3/TOC) x 100
   Oxygen index shows the relative oxygen content in organic carbon contained in the sample.

c. PI (Production / Productivity Index) = S1/(S1 + S2)
   Production index shows the maturity of the source rock which is considered to be all homogeneous condition of the source rock.

d. PY (Potential Yield) = S1 + S2
   Potential yield shows that source rock that produce organic carbon or hydrocarbon.

e. MEP (Main Expelled Product) = S2/S3
   Main Expelled Product (S2 / S3) is a value that shows the hydrogen content in kerogen which shows the potential of the source rock to produce oil. High hydrogen content indicates the potential of source rock to produce oil.

Table 5 shows the results of the processing of pyrolysis data which will be used to calcify the quality of the host rock, the level of safety, and the type of product produced from the host rock. The data above is obtained using the calculation formula that has been attached.

Table 6 shows the quality of the new parent based on parameters S1, S2 and TOC. The data is obtained from the pyrolysis measurement using a source rock analyzer and TOC using a leco carbon analyzer.

Table 7 shows the level of maturity of the host rock based on the classification of Peter and Cassa [3]. The parameters used are Tmax from the results of pyrolysis measurements, Ro tie parameters measurement results of vitrinite reflectance, and PI (Production Index) parameters of pyrolysis data processing results.

Figure 3 shows that type of kerogen is determined by hydrogen index and oxygen index value. The value for hydrogen and oxygen index is obtained from pyrolysis data calculation and then plotted on a diagram that has been modified by Van Krevelen.

Table 4. Total organic carbon and pyrolysis result.

| No | Sample | TOC  | S1  | S2  | S3  | TMAX  |
|----|--------|------|-----|-----|-----|-------|
| 1  | UI 17  | 17.16| 0.11| 11.53| 4.48| 423.70|
| 2  | UI 38  | 8.02 | 0.05| 1.52 | 4.10| 416.80|
| 3  | UI 73  | 18.97| 0.19| 9.93 | 7.57| 414.80|
| 4  | UI 211.5| 13.57| 0.12| 1.92 | 5.55| 523.20|

Table 5. Calculation of pyrolysis data.

| No | Sample | HI    | OI   | PI   | PY   | MEP  |
|----|--------|-------|------|------|------|------|
| 1  | UI 17  | 61.552| 23.916| 0.009| 11.640| 2.573|
| 2  | UI 38  | 20.211| 54.516| 0.031| 1.570 | 0.370|
| 3  | UI 73  | 55.842| 42.571| 0.018| 10.120| 1.311|
| 4  | UI 211.5| 14.131| 40.847| 0.058| 2.040 | 0.345|
Table 6. Petroleum potential

| No | Sample | Petroleum Potential (S1) | Petroleum Potential (S2) | Petroleum Potential (Toc) |
|----|--------|--------------------------|--------------------------|--------------------------|
| 1  | UI 17  | 0.11 / Poor              | 11.53 / Very Good        | 17.159 / Excellent       |
| 2  | UI 38  | 0.05 / Poor              | 1.52 / Poor              | 8.024 / Excellent        |
| 3  | UI 73  | 0.19 / Poor              | 9.93 / Good              | 18.975 / Excellent       |
| 4  | UI 11.5| 0.12 / Poor              | 1.92 / Poor              | 13.571 / Excellent       |

Table 7. Stage thermal maturity

| No | Sample | Thermal Maturation (TMAX) | Thermal Maturation (Ro) | Thermal Maturation (PI) |
|----|--------|---------------------------|-------------------------|-------------------------|
| 1  | UI 17  | 423.7 Immature            | 0.289 Immature          | 0.009 Immature          |
| 2  | UI 38  | 416.8 Immature            | 0.297 Immature          | 0.031 Immature          |
| 3  | UI 73  | 414.8 Immature            | 0.278 Immature          | 0.018 Immature          |
| 4  | UI 211.5| 523.2 Postmature         | 0.632 Early Mature      | 0.058 Immature          |

Figure 3. Kerogen type modified Van Krevelen diagram based on oxygen index with hydrogen index.
Figure 4. Kerogen Type HI vs Tmax explain maturity stage of kerogen which is divided into immature, mature, and postmature. Tmax range 390–430 produces no hydrocarbon, 430–450 produces an oil window, 450–470 produces a wet gas, and > 470 produces a dry gas.

Hydrocarbon maturity can be determined by plotting hydrogen index value with maximum temperature (Tmax). Those data can be obtained from pyrolysis process. The different between figure 3 and 4 are in the parameter for determining kerogen type. Figure 3 used hydrogen index and oxygen index value, but figure 4 used hydrogen index and maximum temperature.

4.1. Petroleum potential
Based on the results of measurements of TOC obtained organic carbon content ranging from 8–18 wt%. If the samples are classified based on the TOC value, all samples categorized as excellent because the organic content is > 4 wt% [3]. However, based on the value of S1 from the measurement of pyrolysis, all samples are categorized as poor because the value is still in the range 0–0.5 and if based on S2 values, samples 1 and 4 are categorized as poor, sample 2 is categorized good, and sample 3 is categorized very good [3]. This shows that the quality of samples found in the volcanic environment has a large content of TOC because it has a value above > 4 wt% and is classified as excellent quality.

4.2. Kerogen type and character expelled product
Kerogen type classification can use two different methods, based on the Hydrogen index value and the S2/S3 value, but there processing data from the measurement result of pyrolysis [3]. Based on HI values, samples 1 and 4 are categorized as kerogen type IV and no product is produced because HI values are still relatively low and for samples 2 and 3 categorized as kerogen type III with products produced in the form of gases [3].

Based on the kerogen type, sample 1 which is included in the Endut Volcano Rock Formation and sample 4 which is included in the Genteng Formation is formed from the remaining organic matter after erosion. Before final deposition, this kerogen has weathering, combustion or biological oxidation in swamps or soil [3]. This type of kerogen has high carbon content and is poor in hydrogen [6]. Kerogen type IV does not have the potential to produce oil and gas [9]. Whereas sample 2 which is included in the Sandstone Member of the Bojongmanik Formation and sample 3 which is included in the Genteng
Formation is formed from land plants deposited in shallow seas to deep or on land [3]. This type of kerogen has lower hydrogen and higher oxygen than type I and type II. This type of kerogen will form dry gas [9].

Sample 4 and sample 3 which are both included in the Genteng Formation but have different kerogen types may occur because the deposited material is different. In addition, both of samples were found in locations far apart so that it might affect the deposited organic material and its kerogen type.

4.3. Stage thermal maturity

The maturity stage of rock can indicate whether the source rock has turned into a hydrocarbon or not [8]. There are several methods that can be used to classify maturity stage including based on Tmax, Ro, or PI values [3]. Based on the Tmax values of samples 1, 2 and 3 are classified as immature which indicate that the source rock has not changes to hydrocarbons. Whereas for sample 4 is classified as postmature or source rock has changes into hydrocarbons. Tmax values are obtained based on the results of pyrolysis measurements and can be used as a maturity indicator because if kerogen maturity increases the temperature that shows the maximum rate of pyrolysis also increases.

Based on the value of vitrinite reflectance (Ro), it was found that samples 1, 2 and 3 were included in the immature and this result was not different based Tmax value. But in sample 4 has early maturity stage. Early mature shows that the sample is not fully maturity.

4.4. Kerogen type and stage maturation

Kerogen types can also be determined based on the Van Krevelen diagram and based on the Hydrogen Index vs. Oxygen Index. After plotting, the results show that samples 1 and 4 are included in type IV kerogen which indicates that these two samples did not produce a product. While for samples 2 and 3 included in kerogen type III and shows that these two samples produce gas products.

Another method for determining kerogen types is by using the Hydrogen Index vs. Tmax diagram from the measurement results of pyrolysis. Using this diagram can be known kerogen type and maturity level in each sample. Each sample will be plotted based on HI and Tmax values so that samples 1, 2 and 3 are included in type III kerogen with immature maturity level and sample 4 is included in dry gas with postmature maturity level.

From the results of the maturity analysis, we know that north direction of the source rock has an increasingly large maturity parameter value. This can be seen based on maturity values on Tmax, Ro and PI. The maturity level of the source rock is influenced by the large temperature at which the source rock is deposited [10]. The results of the maturity level obtained can be caused by lithological factors compiled by the results of volcanic eruptions and intrusion activity. Erupting volcanoes will create hot materials and precipitate over previous lithology [11]. The results of the analysis show that at north research area the source rock more mature with the lithology dominated by volcanic eruption rocks with tertiary age.

5. Conclusion

Based on the results of the analysis it can be concluded that there is a correlation between the effects of volcanic activity on the maturity level of the host rock. Activities from volcanoes cause changes in the level of maturity in host rocks because of the influence of temperature due to the effect of volcanic activity.

Acknowledgments

We would like to extend our gratitude to PIT 9 Grant from Universitas Indonesia for funding the research with grant contract number NKB-0035/UN.R3.1/HKP.05.00/2009 and to Lemigas which provided the laboratory to conduct rock analysis.
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