Lithology Effect On Total Organic Content, Maturity Level And Depositional Environment Of Pemaluan Formation as a Shale Gas Bearing Formation, Kutai Basin, East Kalimantan

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Abstract. Organic material content (TOC) and maturity level is very important in the analysis of shale gas. The organic material is more easily preserved in fine grain sediment such as in shale or clay, so that shale or clay is commonly used to determine TOC value and maturity levels. The organic material will become an oil and gas through the complex transformation and migrated from the source rock to sandstone reservoir, so that the organic material content in sandstone reservoir preferably will represent TOC in shale, however the shale or claystone is commonly used to determine TOC value. This study aims to understand lithology effect on organic material content, maturity level and the depositional environment of sandstone and shale (claystone) of Pemaluan Formation in the Kutai Basin, East Kalimantan. Rock-eval pyrolysis, vitrinite reflectance and GC-GCMS performed on 90 outcrops shale samples and as comparison were one sandstone sample from Rasamala-1 well. Shale samples showed an average TOC value of 1.68 wt% (kerogen type III) and confirmed as a gas bearing formation, while sandstone samples had TOC values of 0.31 wt% which is lower than the shales samples. The maturity level on the shale sample varies from immature to mature, while the sandstone sample is in the mature phase. The organic material from both samples are generated from higher plant material which is strong by terrestrial influence and deposited in transitional environment such as estuarin or fluvio-deltaic setting.

1. Introduction
Shale gas is a non-conventional gas energy resources trapped in shale formation (clay) which is rich in organic content but has very low porosity and permeability [1], this shale gas is the source rock. in conventional reservoirs [2]. Shale gas was first discovered in 1821 in the Appalachian Basin [3] until 1976 only produced in the Appalachian Basin at the age of Devon and Misisipi, USA [4] Non-conventional oil and gas in Indonesia recently developed in 2008 by signing Sekayu Block shale gas contract and 6 contracts later until 2016. According to Geological Agency report in 2011, shale gas in Indonesia has potential reserves approximately 574.07 TCF.

Kutai Basin is the Tertiary Basin and second largest conventional oil and gas producing in Indonesia after the Central Sumatra Basin, with proven reserves of more than 11 BBOE (billion barrels of oil equivalent) [5]. Resource of gas in Mahakam Delta, Kutai Basin is derived from organic material concentrated in organic shale and coal associated with fluvial deltaic plain facies and shale from tidal delta plain and delta front [6]. One of the formations as the source rock and shale gas carrier in Kutai Basin is Pemaluan Formation [7]. Pemaluan Formation is deposited at Late Oligocene to
Early Miocene which consists of shales and sandstones and sandstone layer of Marah Formation [8]. Several wells have been explored, drilled and produced economically in the Kutai Basin, one of the exploratory wells located in the Kutai Basin is Rasamala-1 well [9].

2. Data And Method
The research was conducted in Kutai and surrounding areas, East Kalimantan during 2017. An outcrop shale sampling was conducted for one month in March 2017. Outcrop shale samples data were collected from 90 point locations and as comparison is one sandstone sample from Rasamala-1 well at depth of 3304 feet. All samples are fetched from the interval of Pemaluan Formation. Ninety samples of shale (claystone) and one sandstone sample were taken for rock-eval pyrolysis and three shale (claystone) samples for vitrinite reflectance analysis and GC-GCMS analysis.

2.1. Rock eval pyrolysis analysis
Rock-Eval Pyrolysis Analysis was carried out on ninety outcrop samples of shale (claystone) and one sandstone sample. Rock-Eval Pyrolysis analysis was performed to determine the value of TOC, kerogen type and environmental approach of sedimentation [10]. TOC is calculated to know the richness of organic material contained in the main rock. Rock-Eval Pyrolysis analysis was done by heating small samples (90-130 mg) at 300-600°C for 25 minutes per sample [10]. Rock-Eval Pyrolysis produces TOC, S1, S2, S3 and Tmaks values. S1 is a hydrocarbon were within the rock (bitumen). S2 is the hydrocarbon produced from the heating process in Rock-Eval pyrolysis. S3 is the carbon dioxide produced during the heating process.

Table 1. Classification of kerogen type and character of expelled products.

| Kerogen Type | HI (mg HC/g TOC) | S2/S3 | Atomic H/C at Peak Maturity | Main Expelled Product |
|--------------|------------------|-------|----------------------------|-----------------------|
| I            | >600             | >15   | >1.5                       | Oil                   |
| II           | 300-600          | 10-15 | 1.2-1.5                    | Oil                   |
| II/III       | 200-300          | 5-10  | 1.0-1.2                    | Mixed oil and gas     |
| III          | 50-200           | 1-5   | 0.7-1.0                    | Gas                   |
| IV           | <50              | <1    | <0.7                       | None                  |

(Peters and Cassa, 1994: page. 95).

Table 2. Kerogen type, organic material sources, and maceral.

| Maceral  | Kerogen Type | Original OM                                      |
|----------|--------------|-------------------------------------------------|
| Alginate | I            | Fresh-water algae                                |
| Exinite  | II           | Pollen, spores                                   |
| Cutinite | II           | Land-plant cuticle                                |
| Resinite | II           | Land-plant resins                                |
| Liptinite| II           | All land-plant lipids; marine algae              |
| Vitrinite| III          | Woody and cellulosic material from land plants   |
| Inertinite| IV         | Charcoal; highly oxidized or reworked material of any origin |

(Waples, 1985: page. 33).

Determination of kerogen type in this method using the value of hydrogen index (HI) and Tmaks [10] which explains that the lower value of hydrogen index (HI) and Tmaks, the main rock has kerogen type I, while the lower the HI value then the rock the parent has kerogen type III. Kerogen type based on [10] is influenced by hydrogen index, S2/S3 ratio, and comparison of hydrogen and carbon atoms. The ideal characteristics of shale gas based on [10] in Table 1 are having hydrogen index 50-200, S2 / S3 ratio 1-5, H / C ratio 0.7-1 and including kerogen type 3. After we get kerogen
type, we can know the origin of plant forming organic material and depositional environment, as well as its hydrocarbon potential in Table 2 [11][12][13].

2.2. Vitrinite reflectance analysis

Vitrinite reflectance analysis produced Ro value, from Ro value we can determine the maturity level of organic material. The maturity of organic material depends on temperature, time, and heat source. The maturity of organic matter can be determined by vitrinite reflectance analysis (Ro) and maximum temperature (Tmax). Maturity showed in Table 3.

Table 3. Level of thermal maturation.

| Stage of Thermal Maturity for Oil | Maturation Ro (%) | Tmax (°C) | TAI | Bitumen/TOCb | Bitumen PIc (mg/g rock) | [S1/(S1+S2)] |
|---------------------------------|------------------|----------|-----|--------------|------------------------|------------|
| Immature                        | 0.2-0.5          | <435     | 1.5-2.6 | <0.05 | <50 | <0.10 |
| Mature                          |                  |          |       |              |                        |            |
| Early                           | 0.6-0.65         | 435-445 | 2.6-2.7 | 0.05-0.10 | 50-100 | 0.10-0.15 |
| Peak                            | 0.65-0.9         | 445-450 | 2.7-2.9 | 0.15-0.25 | 150-250 | 0.25-0.40 |
| Late                            | 0.9-1.35         | 450-470 | 2.9-3.3 |            | -        | >0.40   |
| Postmature                      | >1.35            | >470     | >3.3  |            | -        | -       |

Ro = (0.018*Tmaks) -7.16

2.3. Analysis of Gas Chromatography (GC) and Gas Chromatography – Mass Spectrometric (GCMS)

GC and GC-MS analyzes were performed to determine biomarkers. Biomarkers are complex organic compositions consisting of carbon (C), hydrogen (H), and other elements [15]. Biomarkers consist of normal alkane biomarkers, isoprenoid, sterane, and triterpana biomarkers that are used for maturity indication, origin of organic material, and depositional environment. Before GC and GC-MS analysis, bitumen extraction is carried out first from the host rock (rock samples to be analyzed). Then bitumen was analyzed by column chromatography. Column chromatography analysis produces hydrocarbons which consist of saturated hydrocarbon fractions (saturate), unsaturated hydrocarbons (aromatic), and NSO (nitrogen, sulfur, and oxygen).

Geochemical analysis techniques to obtain biomarkers are GC and GC-MS based on biomarker standards [15]. GC is a gas chromatography analysis technique, while GC-MS is a combination of gas chromatography and mass spectrometry. In this study the samples used for GC and GCMS analysis were one sample of shale (clay) with a sample code of 17EH005D and a sandstone sample from Raslama-1 well. The results of GC analysis obtained normal alkane biomarker, isoprenoid, pr/ph ratio (Pristane phitane) from saturated hydrocarbon fraction (saturate), in GCMS analysis obtained sterane (m/z 217) between the C27-C30 complex and triterpana (m/z 191) of the saturated fraction and aromatic fraction.
In addition to using vitrinite reflectance, the level of maturity can be obtained from sterane biomarkers and triterpana saturate fraction with two methods as explained below: Two triterpana biomarkers are C30 moretan / C30 hopana. The range value of this ratio is 0.8 for immature samples up to 0.15 for very mature bitumen samples and 0.05 for oils samples. And Sterane biomarker are ratio of 22S / (22S + 22R), this ratio compares the compound at C-22 atom having the position of S and R formed by isomerization process. The sample with position S has a higher stability position compared to the R position sample, therefore if ratio this value shows a higher so value of maturity higher too. Based on Moldowan et al. (1985), the value of this ratio increased from 0 to 0.6 with the following maturity divisions; the value 0.50 - 0.54 represents the value of entering the oil window, 0.57 - 0.62 shows the top of the oil window [10,16–19].

3. Result And Discussion

3.1. Shales and sandstone characteristic of Pemaluan Formation

Based on observations in the field, the general characteristics of claystone and shale of Pemaluan Formation at stations 17EH004 and 17EH005 in Figure 1 consist of both claystone and shale which are inserted by both carbonan and coal materials, the common sedimentary structures found in these section are parallel lamination, wavy and cross lamination. Iron oxide nodules and limestone nodules are present in some parts of the outcrop. Whereas, sandstones on the Pemaluan Formation based on observations in the field are rich in quartz minerals and some have been oxidized, forming parallel and cross lamination intercalated with carbon material.

TOC (total organic content) from 90 surface samples of Pemaluan formation showed varied from 0.4 wt% to 15.63 wt% with average value of 1.68 wt% according to [10] classification TOC in those formation are well categorized, whereas based on Chinn (1991) TOC value more than 1% can be used as as one of shale characteristic parameter for commercial shale development. While sandstone samples from core samples (depth 3044 feet) has TOC values of 0.31 wt% classified as low category.

The Rock-Eval Pirolysis of ninety samples obtained the HI values has varied from 4.2 to 176 mgHC/g and Tmax 4110C - 4660C (average = 4300C). Hydrogen index (HI) vs Tmax crossplot in Figure 2 showed that the sample is counted as kerogen type III and gas bearing formation as well.

3.2. Maturity level

Vitrinite reflectance (Ro%), Tmax and PI (Rock-Eval analysis) are commonly used for maturity analysis of rocks.

The maturity level from vitrinite reflectance analysis 17EH003A, 17EH004D and 17EH008A showed Ro value ranged from 0.4 to 0.49% Ro, while from 87 samples with Jarvie equation obtained Ro value varied from 0.24-1.09% Ro (average = 2.71). Crossplot Ro vs Tmax in Fig. 3 showed that

Figure 1. An Outcrop of Pemaluan Formation in study area; A) closer look of fine clastic sediment of 17EH004 point location; B) interbedded sandstone and claystone of 17EH005D point location.

Figure 2. Hydrogen index vs Tmax crossplot.
the samples is categorized to be in immature phase (<0.6% Ro) to mature (0.6-1.35% Ro). In the 3304 feet sample of Rasamala-1 well Ro value obtained 0.65-0.80% Ro is categorized in the mature phase.

In addition to using vitrinite reflectance analysis, the maturity level can be determined by triterpana and sterana biomarkers of the saturate faction ratio as explained below: Triterpana biomarker of the sample moretan/hopana ratio of 17EH005D shows the maturity level entering the early maturity. And Sterana biomarker of the 22S / (22S + 22R) ratio gives a value of 0.59 indicating the value entering the oil tops zone.

3.3. Depositional Environment Identification

Peak identification was carried out so that the Phytane/nC18 and Pristane nC17 ratios were plotted in Figure 4, the Phytane/nC18 ratio obtained was 1.08 and the Pristane/nC17 ratio obtained was 5.82. The plot based on the development of research shows that the sample has an input of organic material consisting of type III, which means it has high oxidation (oxic) levels which tend to have terrigeneous environments.

![Figure 3. Plot vitrinite reflectance vs Tmaks.](image1)

![Figure 4. Plot Phytane/nC18 vs Pristane/nC17 of 17EH005D shale sample code (modified after [20]).](image2)

The carbon-saturated isotope in the sandstone depth sample of 3304 Rasamala-1 well has a value of -28.6, whereas the ratio of pr/ph is 5 which means pristane (pr) higher than phytane, indicating that the origin of organic material is in oxic environment. The pristane and phytane ratio can determine the depositional environment conditions [21,22]. Pristan (Pr) and phytane (Ph) are isoprenoids that can be used to determine the oxic condition of depositional environment (Powell and McKirdy, 1973). Pristan comes from phytol which is deposited in the oxic environment whereas phytane is derived from phytol deposited in anoxic environments. The higher pristane and phytane ratio the more oxic depositional environment conditions [23].

The result of the carbon isotope plot against the pr/ph ratio of the 3304 ft depth sample of Rasamala-1 well in Fig. 5 shows that the organic material of the Pemaluan Formation interval at Rasamala-1 well originated from strongly influenced terrestrial materials. This confirmed that the phytane/nC18 and pristane/nC17 ratio chart (Figure 4) of the 17EH005D shale sample code that the organic material source of the Pemaluan Formation comes from a terrestrial depositional environment.
Figure 5. Plot Pris/Phy vs carbon isotope (saturate) from sandstone sample at 3044 feet depth Rasamala-1 well (modified after [24]).

The configuration of triterpane chromatograms in the 17EH005D rock samples (Fig. 8) shows abundantly presence of 18αβ oleanana (OL) and oleanoid (*), as well as in the depth samples of 3044 feet Rasamala-1 well (Figure 7). Oleanana and oleanoids are lipid compounds produced by flowering plants of the angiosperm species and are common in Late Cretaceous. Triterpana fingerprint shows that the sample has input from high level plants from the land environment.

The depositional environment can be determined by C27, C28 and C29 sterane distribution triangle diagram [17,25]. Based on Peters and Moldowan (1993), C27 indicates that organic material originates from marine algae, C28 comes from lacustrine algae, and C29 comes from higher plants in terrestrial environments.

Figure 6. Modified after Huang and Meinchein (1979) for organic material originated determination based on sterane composition of shale sample (17EH005D) and sandstone sample (3044 feet).

The composition of C27-C28-C29 sterane shale sample of 17EH005D (Figure 6) shows the abundance of C29 (C29>C28>C27), which means that the organic material originated from the swamp environment and derived from higher plant of the terrestrial environment. Sandstone sample (3044 feet, Rasamala-1 well) in Figure 6 shows the quite abundant of C29 showing the transitional environment (estuarine/ shallow lacustrine).

Figure 7. Fragmentogram Triterpana (m/z 191) for extracted sandstone sample (3044 feet).
4. Conclusions
The results showed that Pemaluan Formation had a TOC value which was low-good category, kerogen type III as a gas bearing formation. The determination of lithology (rock type) tested has an effect on the organic content of the material (TOC), the TOC value on the shale has a greater value than the sandstone. The level of maturity gives results that are not too different because the two samples have reached the mature phase. The deposition environment of clay samples (shale) and sandstones showed that the organic material derived from relatively same environment in estuarin or fluvio-deltaic setting.

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