



Aliphatic Biomarker Signatures of Crude Oil from Tarakan Subbasin, Tarakan Basin, North Kalimantan, Indonesia

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Abstract - Organic geochemical studies of crude oil from Pamusian Field, Tarakan Subbasin, Tarakan Basin, North Kalimantan, have been done. Biomarker aliphatic hydrocarbon fractions were identified using a combined gas chromatography-mass spectrometer (GC - MS). Identified biomarkers consist of *n*-alkane groups, isoprenoids, bicyclic sesquiterpenoids, and pentacyclic triterpenoids. The most abundant aliphatic hydrocarbon biomarker is pristane followed by *n*-C₁₉. The existence of *n*-alkanes shows a homologous (*n*-C₁₆ - *n*-C₃₀) with a unimodal distribution type. The abundance of *n*-C₁₉ is higher than other *n*-alkanes, supported by LHCPI value of 2.03, as an indicator of organic matter derived from microbial organisms. The amount of long chain *n*-alkanes (*n*-C₂₅ - *n*-C₃₀) is almost the same as medium chain *n*-alkanes (*n*-C₁₉ - *n*-C₂₄) indicating the source of organic compounds is not only from microbial organisms, but also from terrestrial higher plants. The presence of 8β (H)-drimane compounds together with homodrimane shows the presence of bacterial input on the formation of oil from organic compounds. Ratio of Pr/Ph is 3.76, ratio of drimane/homodrimane is 1.058, ratio of Pr/*n*-C₁₇ is 34.41, and ratio of Ph/*n*-C₁₈ is 16.02 indicating the source of organic compounds came from terrestrial higher plants deposited in the oxic environment, and disposed to increase biodegradation. The CPI value is 0.95, and the highest amount of 17α (H), 21β (H)-hopane compounds suggest that Tarakan Subbasin oil was mature, and the source of organic compounds was derived from bacteria.

Keywords: Tarakan Basin, organic geochemistry, aliphatic hydrocarbon fraction, CPI

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INTRODUCTION

Background

The need of crude oil in Indonesia during 2016-2050 will increase with an average growth of 3.3% per year, and it will affect crude oil imports. Indonesia has the potential of oil reserves, spreading throughout the country which is significant to increase the crude oil and condensate production.

Several basins in Sumatra and Kalimantan have been proven as productive oil and gas sources (Doust and Noble, 2008; Yudiantono *et al.*, 2018). One of them is Tarakan Basin. Exploration of oil in Tarakan Basin has been carried out since 1899, and 14 oil and gas fields have been discovered. Today, 86% of oil production comes from two fields, namely Pamusian Field on Tarakan Island and Bunyu Field on Bunyu Island (Nawawi *et al.*, 1996).

Production of oil in Pamusian Field, Tarakan Subbasin, has entered the drainage stage (Nawawi *et al.*, 1996). Reactivation of oil wells is one of the methods to increase the crude oil production (Soeparyono and Lennox, 1990), but this method costs a lot of money, so feasibility data of wells were required before reactivation (Peters *et al.*, 2005). Optimization of petroleum exploration and production can be increased by studying its organic geochemical aspects. Organic geochemistry provides information about the relationship between petroleum and rock sources, the map of environmental conditions of oil deposition and rock sources, the estimated time of formation, and the migration and accumulation of oil (Peters and Fowler, 2002; Kvenvolden, 2008).

The presence of hydrocarbon information was needed for the reactivation of wells. The level of maturity and type of organic resources impacted the presence of hydrocarbon and productivity of rock sources (Peters and Fowler, 2002; Sutadiwiria *et al.*, 2018; Hu *et al.*, 2019). The studies of biomarker show that a good hydrocarbon source comes from higher plants. Some significant biomarkers of hydrocarbon from Guangdong Province, China, are long chain *n*-alkanes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁), isoprenoid C₁₉ and C₂₀, tricyclic terpane, and C₂₉ sterane (Hu *et al.*, 2019). The studies of organic geochemical of hydrocarbon aliphatic fraction had been reported to identify the source of organic matter, depositional environment, and thermal maturity of petroleum (Ahmed *et al.*, 2009; Al-Atta *et al.*, 2014; Xiao *et al.*, 2019). The biomarkers such as alkane, isoprenoid, terpane, and sterane are included in aliphatic hydrocarbon group on petroleum source (Peters *et al.*, 2005; El Nady *et al.*, 2014; Onojake *et al.*, 2015; Sutadiwiria *et al.*, 2018). The degree of biodegradation in the reservoir is detected through the loss of *n*-alkanes, isoprenoids, terpane, and sterane during the secondary process, and they determine the level of oil maturity (Peters *et al.*, 2005). The ratio of pristane and phytane and the distribution of *n*-alkanes can be used as environmental indicators of oil deposition (Al-Atta *et al.*, 2014; Hakimi *et al.*, 2016). Biomarker analysis had been applied to several

source rocks, including Sydney Basin sediments (Ahmed *et al.*, 2009), Niger Delta oil (Nytoft *et al.*, 2014), Sinamar Formation, Muara Bungo, Jambi (Zajuli and Panggabean, 2014), Ordos Basin oil (Ji *et al.*, 2016), North Arafura Shelf Papua (Sabra, 2021), and Eocene source rock in West Sulawesi (Sutadiwiria *et al.*, 2022). The Tarakan Basin, which has entered the exploitation of drainage, requires an in-depth study of organic geochemistry to determine the depositional environment, its maturity, and the source of its organic material. Aim of this paper, besides to discuss the aspects of organic geochemistry through the analysis of aliphatic hydrocarbon biomarkers in order to determine the potential of crude oil in the Tarakan Subbasin, North Kalimantan, it also focuses on depositional environment, origin of oil organic compounds, and thermal maturity.

Geological Setting of Tarakan Basin

The Tarakan Basin is located to the north eastern part of Kalimantan Island. To the northern part, the basin is bounded by Samporna Peninsula, to the west by Sekatak-Berau Ridge, to the south by Mangkalihat Peninsula, and to the east by deep water of Sulawesi Sea (Achmad and Samuel, 1984; Lentini and Darman, 1996).

The Tarakan Basin consists of four subbasins. They are Tarakan Subbasin in the centre offshore, Muara Subbasin in the southeast offshore, Berau Subbasin in the southwest onshore, and Tidung Subbasin in the northwest onshore (Figure 1). The Tarakan Basin occurred during Middle Miocene to Late Miocene, almost to Early Pleistocene (Prakash *et al.*, 2010).

Tectonically, several faults are responsible for isoclinal arch structures in the Tarakan Basin, named Tarakan Arch (100 km length) and Bunyu Arch (30 km length) (Lentini and Darman, 1996; Husein, 2017). The Tarakan and Bunyu arches produced 92% of all commercial hydrocarbon accumulations in the basin, and have been the most targetted of the offshore exploration activity (Wight *et al.*, 1993).

Tectonostratigraphy of the Tarakan Basin is divided into three phases, those are pre-rift, syn-

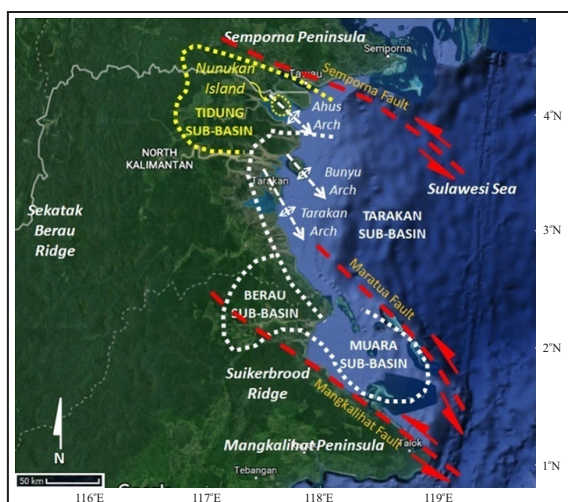


Figure 1. Regional setting of Tarakan Basin (image from Google Earth, Husein, 2017).

rift, and post-rift (Ellen *et al.*, 2008; Larasati *et al.*, 2016). Pre-rift phase comprises the basement of Danau Formation consisting of metamorphic rock. The initial stage of rifting basin evolution took place during the Early Eocene. In the Middle Eocene, the uplifting period to the western part of the basin caused the erosion at the Sekatak Ridge, and the deposition of sedimentation began (Biantoro *et al.*, 1996).

MATERIALS AND METHODS

Tarakan Basin Oil Samples

Crude oil samples were collected from the Pamusian Field, Tarakan Subbasin, Tarakan Basin, North Kalimantan. Bitumen and water content in crude oil samples were separated. Two grams of bitumen were separated from the molten layer in 50 mL *n*-hexane. The molten was further fractionated by silica gel GF₂₅₄ column chromatography. Then, it was eluted using *n*-hexane to obtain aliphatic hydrocarbon fraction, dichloromethane to obtain aromatic hydrocarbon fractions, and methanol to obtain polar fractions (Zetra *et al.*, 2018; Garcia *et al.*, 2019).

GC-MS Analysis

The aliphatic hydrocarbon fractions were analyzed by gas chromatography-mass spectrometry

(GC - MS). GC - MS was performed on Agilent (D5975C), mass spectrometer operated at 70 eV with a mass range of m/z 40 to 800, and a cycle time of 1.7 s. The gas chromatograph was equipped with a HP-5MS capillary column (30 m x 250 μ m x 0.2 μ m) and helium as carrier gas. The samples were injected at 70° C (isothermal for two minutes) with an oven programme of 10° C min⁻¹ to 100° C, 4° C min⁻¹ to 300° C, held for twenty min. Identification of biomarkers are based on published mass spectra (including the NIST98 spectral library) and interpretation of typical fragmentation patterns and references from previous published researchers.

RESULTS AND ANALYSIS

The structure of aliphatic hydrocarbon biomarkers of the Tarakan Subbasin oil was identified based on specific m/z fragmentograms, retention times, and mass spectra (including the NIST98 spectral library) and interpretation of observed fragmentation patterns (Seifert and Moldowan, 1978; Philp, 1985; Wang and Simoneit, 1991; Lu and Kaplan, 1992; Chattopadhyay and Dutta, 2014; Jiang and George, 2018; Li *et al.*, 2018). Identified aliphatic hydrocarbon biomarkers consist of *n*-alkane, isoprenoid, sesquiterpenoid bicyclic groups, and pentacyclic triterpenoids as seen in Total Ion Chromatogram (TIC) (Figure 2). Sterane compounds are not found in Tarakan Subbasin oil samples, and the most abundant aliphatic hydrocarbon biomarker is pristane.

n-Alkane and Isoprenoid Biomarkers

Identification of *n*-alkane and isoprenoid compounds for Tarakan oil was carried out based on fragmentogram m/z 57, retention time, and mass spectrum data compared with previous researches (Kim *et al.*, 2017; Li *et al.*, 2018). Fragmentogram of *n*-alkane and isoprenoid compounds as seen in Figure 3 shows the *n*-alkane homologous series which are distributed in the range of *n*-C₁₆ - *n*-C₃₀ with unimodal distribution type.

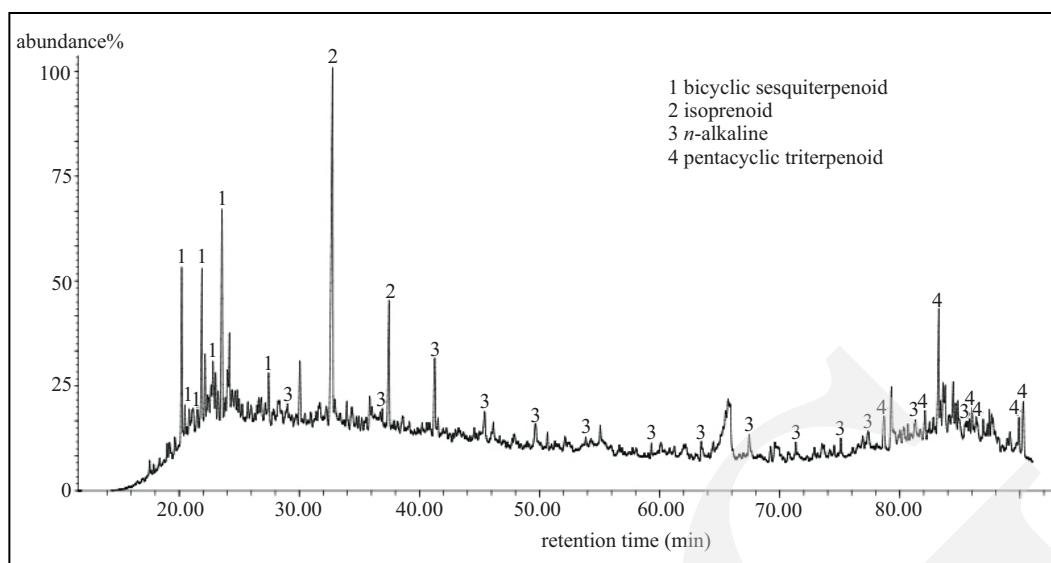


Figure 2. Total Ion Chromatogram (TIC) aliphatic hydrocarbon fraction of crude oil from Tarakan Subbasin. Condition: KG-SM temperature programme 70°C (2 min), 70°C -100°C (10°C/min), 100°C -300°C (4°C/min) isotherm temperature at 300°C.

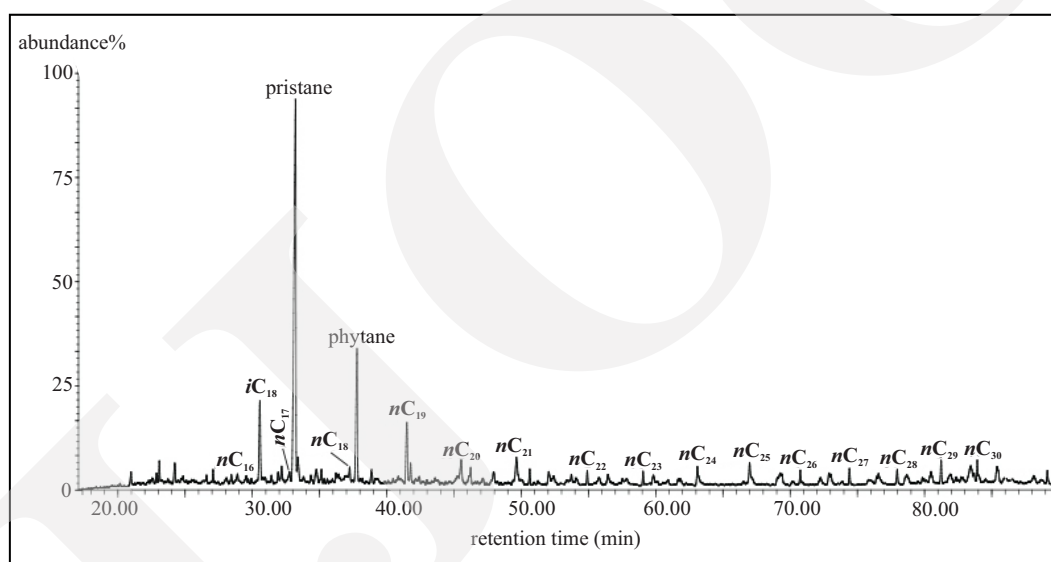


Figure 3. Fragmentogram m/z 57 that indicates n -alkane and isoprenoid.

Bicyclic Sesquiterpenoid Biomarkers

The presence of sesquiterpenoid compounds in Tarakan Subbasin oil samples was identified based on fragmentogram m/z 123. Identification of the structure of each compound was carried out based on fragmentation reactions, by comparing mass spectrum obtained, and the previous researches (Seifert and Moldowan, 1978; Philp, 1985; Lu and Kaplan, 1992; Stojanovic and Zivotic, 2013; Chattopadhyay and Dutta, 2014; Zdravkov *et al.*, 2020). The eight peaks in the

fragmentogram were identified as C_{14} bicyclic sesquiterpene; C_{15} bicyclic sesquiterpene; transcadinane; $4\beta(H)$ -eudesmane; $8\beta(H)$ -drimane; homocadinane; homodrimane, and C_{16} -bicyclic sesquiterpene (Figure 4).

Pentacyclic Triterpenoid Biomarkers

Identification of the structure of pentacyclic triterpane compounds in Tarakan oil samples was carried out based on fragmentogram m/z 191. Identification of biomarker structures was also

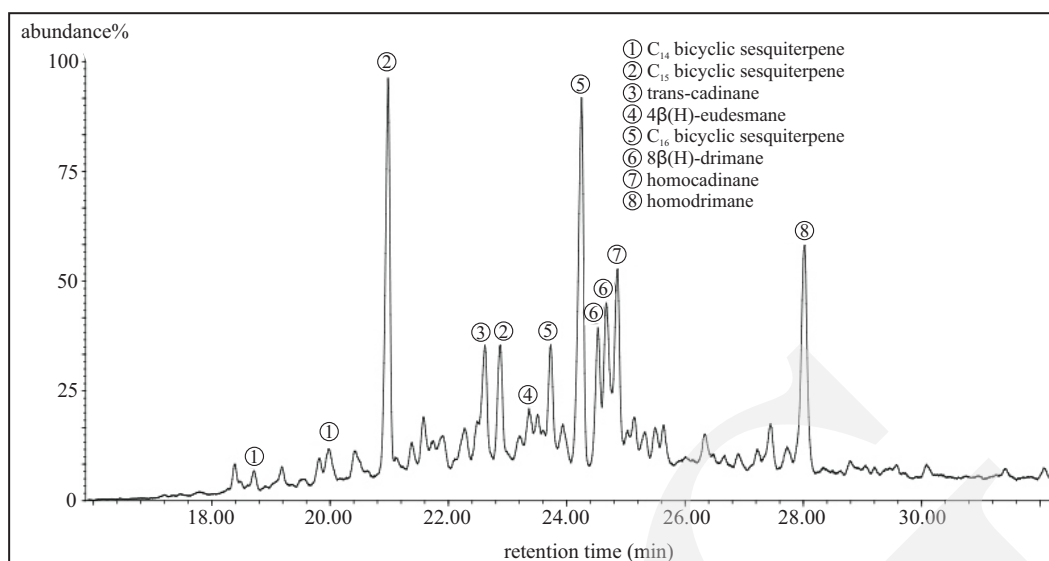


Figure 4. Fragmentogram m/z 123 that indicates bicyclic sesquiterpenoid.

done by comparing the mass spectrum obtained and the mass spectrum that has been published by previous researchers (Seifert and Maldowan, 1978; Philp, 1985; Wang and Simoneit, 1990; Lu and Kaplan, 1992; Chattopadhyay and Dutta, 2014; Jiang and George, 2018; Sutadiwiria *et al.*, 2018). The six peaks in the fragmentogram are identified as *cis-cis-trans-bicadinane*; *trans-trans-trans-bicadinane*; C_{30} triterpene; $17\alpha(H)-21\beta(H)$ -norhopane; $18\alpha(H)$ -oleanane and $17\alpha(H)-21\beta(H)$ -hopane with the most dominant compound is $17\alpha(H)-21\beta(H)$ -hopane (Figure 5).

DISCUSSION

The distribution of short-chain *n*-alkanes ($< n-C_{16}$) is extremely low, but pristane isoprenoids are at the highest amount (Table 1 and Figure 2). The low intensity of short chain *n*-alkanes indicates the very small role of algae in the formation of Tarakan oil organic compound. The existence of short chain *n*-alkanes ($< C_{17}$) proves that organic compounds are derived from algae, plankton, and marine bacteria (Peters *et al.*, 2005; Massone *et al.*, 2013). The identification of the

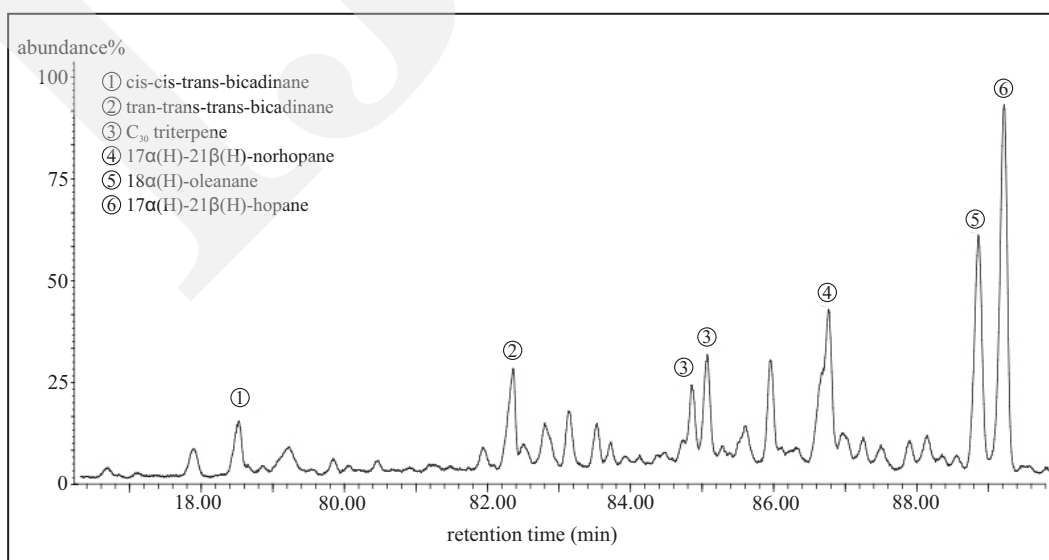


Figure 5. Fragmentogram m/z 191 that indicates pentacyclic triterpenoid.

Table 1. Percent Intensity of Each Peak *m/z* 57

Retention Time (minutes)	n-alkane	Intensity (%)
27.09	<i>n</i> -C ₁₆	2.01
32.77	<i>n</i> -C ₁₇	2.91
33.21	pristane	100.00
37.25	<i>n</i> -C ₁₈	1.66
37.79	phytane	26.57
41.49	<i>n</i> -C ₁₉	12.86
45.53	<i>n</i> -C ₂₀	6.75
49.63	<i>n</i> -C ₂₁	6.60
56.47	<i>n</i> -C ₂₂	2.06
59.07	<i>n</i> -C ₂₃	1.73
63.11	<i>n</i> -C ₂₄	5.27
66.99	<i>n</i> -C ₂₅	7.21
70.76	<i>n</i> -C ₂₆	2.98
74.42	<i>n</i> -C ₂₇	2.70
77.97	<i>n</i> -C ₂₈	2.72
81.24	<i>n</i> -C ₂₉	3.13
85.4	<i>n</i> -C ₃₀	5.87

medium chain *n*-alkane group (*n*-C₁₇ - *n*-C₂₄) suggests the presence of bacterial activity in the ancient depositional environment of Tarakan oil (Peters *et al.*, 2005; Fabiańska and Kurkiewicz, 2013). The maximum concentration for *n*-alkane medium chains (*n*-C₁₉ - *n*-C₂₄) is seen at *n*-C₁₉. The presence of *n*-C₁₉ was also previously detected with very high concentrations in green algae and anaerobic bacteria (Li *et al.*, 2018). The dominance of *n*-C₁₉ compared to other *n*-alkanes was also found in the study of El Nady *et al.* (2014) on Egyptian Gulf Suez oil which signify organic material derived from microbial organisms. The existence of long chain *n*-alkanes (*n*-C₂₅ - *n*-C₃₈) with almost the same amount as medium chain *n*-alkanes (except *n*-C₁₉) denotes the source of organic compounds derived from terrestrial higher plants (Xiaou *et al.*, 2019). The dominance of odd carbon to even carbon in long-chain *n*-alkanes (*n*-C₂₅ - *n*-C₃₀), especially in *n*-C₂₅, *n*-C₂₇ and *n*-C₂₉, shows the organic compound of Tarakan oil derived from the cuticular tissue of terrestrial higher plant wax (Massone *et al.*, 2013; Stojanović and Životić, 2013) was produced through decarboxylation reaction of fatty

acids (Killops and Killops, 2005). The dominance of odd carbon to even carbon is also indicated by the CPI (Carbon Preference Index) value of 0.95 as seen in Tables 1 and 2. The CPI value can be used to determine the level of sample maturity.

Table 2. Molecular Parameter of Tarakan Basin Oil

Parameter	CPI ^a	LHCPI ^b	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈
Value	0.95	2.03	3.76	34.41	16.02

$$a \text{ CPI} = \frac{1}{2} \left(\frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})} + \frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})} \right) \text{ (Kim, et al., 2017)}$$

$$b \text{ LHCPI} = \frac{C_{17}+C_{18}+C_{19}}{C_{27}+C_{28}+C_{29}} \text{ (Schwarzbauer, et al., 2013; Kim, et al., 2017)}$$

Dessort (2013) reported that a CPI value close to 1 indicated a mature sample, as well as in the research of Onojake *et al.* (2015) which had a CPI value between 0.72 and 1.09. Therefore, the CPI value of 0.95 obtained indicates a mature oil sample. The CPI value of 0.73 points out the level immature up to early mature, that is also shown by sedimentary rocks from the Sinamar Formation Muara Bungo, Jambi (Zajuli and Panggabean, 2013). The LHCPI value is 2.03, indicating the dominance of the medium chain over the long chain (Aldahik, 2010). This is due to the predominance of *n*-C₁₉. This LHCPI value denotes a high level of bacterial input (Commendatore *et al.*, 2012). High intensity *n*-C₁₉ indicates the presence of bacteria that survive the catagenesis stage. The specific bacteria for *n*-C₁₉ are photosynthetic bacteria (El Nemr *et al.*, 2016).

The identification carried out based on fragmentogram *m/z* 57 with molecular ion *m/z* 268, shows the presence of pristane (Ph) and *m/z* 282 (Figure 2) indicating the presence of phytane (Ph) with a Pr/Ph ratio of 3.76 in the analyzed oil sample (Table 2). This Pr/Ph ratio value can be used to determine the oil deposition environment. High ratio of Pr/Ph (> 3.0) indicates that the source of terrestrial organic compounds were from the oxidic environment, while a low ratio Pr/Ph (<0.8) denotes anoxic/hypersalin or carbonate depositional environments (Idris *et al.*, 2008). Therefore, a Pr/Ph ratio of 3.76 in the Tarakan Subbasin oil sample indicates oil samples was

formed in an oxidic environment with an input of terrestrial organic matter (Chattopadhyay and Dutta, 2014). Besides the Pr/Ph ratio, the organic geochemical aspects of the Tarakan Subbasin oil sample can also be determined based on the value of the isoprenoid ratio to *n*-alkanes. This value is used to determine the input source of organic matter, biodegradation, and maturity level. The Pr/*n*-C₁₇ ratio in the Tarakan Subbasin oil sample has a value of 34.41, while the Ph/*n*-C₁₈ value is 16.02 (Table 2). The two values were plotted into the graph as shown in Figure 6, and it was found that the source of organic material from the sample came from terrestrial higher plants, oxidic depositional environment, and the tendency of increasing biodegradation. This data is in accordance with the Pr/Ph ratio= 3.76 as an environmental indicator of the deposition of the Tarakan Subbasin oil which was analyzed, and the dominance of odd carbon to even carbon from the *n*-alkane homologous series.

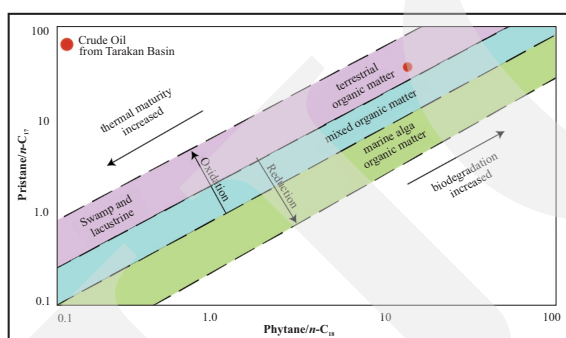


Figure 6. Graph plot of Pr/*n*-C₁₇ versus Ph/*n*-C₁₈ of crude oil from Tarakan Subbasin. Graph plotted based on Sefein *et al.* (2017) publication.

Therefore, this data confirmed with previous analysis stating that the source of organic material from Tarakan oil came from terrestrial higher plants deposited in an oxidic environment, tended to increase biodegradation.

The presence of dominant peaks in bicyclic sesquiterpenoid biomarkers is shown by the sesquiterpane C₁₅ and C₁₆-bicyclic (Figure 4). The dominance of bicyclic sesquiterpane C₁₅ compounds in oil samples analyzed indicated that organic material came from terrestrial plant resin and prokaryotic bacteria. This assumption is also

supported by the presence of C₁₄ bicyclic sesquiterpene compounds although in low intensity (Ji *et al.*, 2016; Zetra *et al.*, 2016). Cadinane originates from polycadinane precursors found in Angiosperms plant damar resins, especially the Dipterocarpaceae family that undergo depolymerization reactions. So, the presence of trans-cadinane compounds is considered an indicator of terrestrial higher plants of Angiosperms. This is supported by the existence of 4β(H)-eudesmane compounds in samples where these compounds can be found in plant tissue fossils. The structure of eudesmane compounds is related to the terpenoid carbon framework derived from terrestrial higher plants (Peters *et al.*, 2005; Zetra *et al.*, 2016; Jiang and George, 2018).

The presence of 8β(H)-drimane compounds together with homodrimane was also identified in the analyzed oil sample. Both of these compounds indicate the presence of bacterial input on the formation of oil organic compounds. This is shown by the relationship of the biomarker structure with the bacteriohopanepolyol precursors produced by Archaeobacteria, so that the existence of these two compounds can be related to bacterial input in the formation of oil organic material. The presence of drimane and homodrimane compounds as indicators of bacterial input has also been previously reported in low rank coal samples of Sangatta, East Kalimantan (Zetra *et al.*, 2016; 2018), Meghalaya coal samples, India (Rudra *et al.*, 2017), and samples of Gippsland Basin rocks, Australia (Jiang and George, 2018).

The ratio of drimane to homodrimane can be used to determine the depositional environment. The value of the ratio of drimane to homodrimane from the Tarakan Subbasin oil sample is 1.058. According to Yangming (2001), this value suggests that the sample was deposited in an oxidic environment. The rearrangement mechanism of the two compounds is similar to diasterane, which requires acidic clay minerals as a catalyst that is formed in an oxidic depositional environment (Yangming, 2001). The presence of homocadinane in the Tarakan Subbasin oil, is thought to originate from the same precursors as cadinane in the form of polycadinane as an abundant precursor in resin of higher plant Angiosperms. Therefore,

the identification of this homocadinane compound is potentially used as an indicator of terrestrial plants, Angiosperms. The same compound has also been reported in oil samples in the Yinggehai Basin, China (Zhu *et al.*, 2018). The presence of C_{16} bicyclic sesquiterpene compounds denotes the oil was formed in terrestrial environments, and is as an indicator of higher plants. This compound is thought to have formed through oleanoid degradation from the plant Angiosperms at the stage of diagenesis (Nytoft *et al.*, 2009; Zhu *et al.*, 2018).

The cis-cis-trans-bicadinane and trans-trans-bicadinane compounds (Figure 5) identified in the Tarakan Subbasin oil sample analyzed were dimeric cyclization products from cadinene. This compound was formed through the depolymerization reaction and ring closure of polycadinene macromolecules. Polycadinanes have been isolated from both fossil and damar resin extracts of the plant Angiosperms family Dipterocarpaceae whose vegetation was abundant in the Tertiary period. Therefore, the presence of this compound is also potential as an indicator of the plant Angiosperms family Dipterocarpaceae. The same result was reported in the sediments of Northeast India (Chattopadhyay and Dutta, 2014) and some oil seeps from West Sulawesi, Indonesia (Sutadiwiria *et al.*, 2018). Besides that, triterpane compounds, generally C_{30} is also mostly derived from bacteria. Since the synthesis of triterpenoids in sediments is carried out by bacteria, these compounds are also used as important indicators to determine the presence of bacterial inputs in the formation of oil organic compounds (Zhu *et al.*, 2018). The presence of bicadinane compounds identified based on the m/z 191 fragmentogram (Figure 5) in the analyzed sample is closely related to one of the sesquiterpane bicyclic compounds; namely: cadinane. This is due to these two compounds derived from the same precursors; namely: polycadinane (Peters *et al.*, 2005). Thus, the occurrence of these two compounds confirmed the idea that the Tarakan Basin oil sample comes from the plant of Angiosperms family Dipterocarpaceae.

The oleanane compound identified in the analyzed oil sample is a triterpenoid pentacyclic compound derived from β -amyrin as a precursor

(Taylor *et al.*, 2006; Jiang and George, 2018). Oleanane compounds have two isomers; namely: $18\alpha(H)$ -oleanane and $18\beta(H)$ -oleanane, where the more stable configuration is $-\alpha$ (Alberdi and Lopez, 2000). Therefore, the presence of $18\alpha(H)$ -oleanane compounds in the oil samples analyzed indicates that the Tarakan Subbasin oil is derived from higher plants Angiosperms. The presence of this oleanane compound has also been previously reported in rock samples in the Gippsland Basin, Australia (Jiang and George, 2018).

Hopane compounds with configurations of $17\alpha(H)$, $21\beta(H)$ -hopane based on fragmentogram m/z 191 were also identified in the oil sample analyzed. The presence of hopane compounds can be used to determine the maturity of the sample. Hopane biomarkers have several isomer configurations; namely: $17\beta(H)$, $21\beta(H)$; $17\beta(H)$, $21\alpha(H)$, and $17\alpha(H)$, $21\beta(H)$ which are the isomers with the highest stability. High intensity of isomers which have high structural stability indicates mature sediment samples (Burhan *et al.*, 2002; Han *et al.*, 2019). Hence, the $17\alpha(H)$, $21\beta(H)$ -hopane compounds with the highest amount were identified, but no other hopane isomers found in the form of $17\beta(H)$, $21\beta(H)$; $17\beta(H)$, $21\alpha(H)$ is a very strong indication that the Tarakan Subbasin oil is mature. The presence of $17\alpha(H)$, $21\beta(H)$ -hopane compounds has also been reported previously in the Brown Shale sample of the Central Sumatra Basin (Sefein *et al.*, 2017), samples of the Central Sichuan Basin, China (Cheng *et al.*, 2018), and oil seeps from West Sulawesi, Indonesia (Sutadiwiria *et al.*, 2018).

The presence of several hopanoid compounds in the analyzed oil sample also shows the presence of bacterial input in the oil formation environment, because the hopanoid compound is produced by the bacteriohopanepolyol precursors produced by aerobic bacteria (Killops and Killops, 2005; Han *et al.*, 2019). The presence of bacterial activity that plays a role in the ancient environment of Tarakan Subbasin oil formation, has also been proven by the presence of other biomarkers in the analyzed samples, such as the high amount of n - C_{19} medium chains, C_{15} -bicyclic sesquiterpane, drimane and homodrimane. The

dominance of n -C₁₉ indicates the role of photosynthetic bacteria in the formation of the analyzed Tarakan Basin oil (El Nemr *et al.*, 2016).

CONCLUSION

The study of organic geochemistry through the analysis of biomarkers of the Tarakan Subbasin oil, North Kalimantan, provides information on the composition of organic matter, the depositional environment, and the maturity of sources. The existence of long chain n -alkanes, cadinane; 4 β (H)-eudesmane; 18 α (H)-oleanane derived compounds indicate the source of organic material that comes from the damar resin of the plant Angiosperms. It is also reported that drimane compounds, homodrimane, and hopane are indicators of bacterial input in the formation of oil from organic compounds. A value of LHCPI is 2.03 and high amount of n -C₂₂ also indicate the presence of photosynthetic bacterial input. CPI value of 0.95 indicates that the samples are mature. The obtained Pr/Ph ratio of 3.76 and drimane/homodrimane ratio of 1.058 indicate the oxidic depositional environment of oil samples in the Tarakan Subbasin.

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REFERENCES

- Ahmad, Z. and Samuel, L., 1984. Stratigraphy and depositional cycles in the N.E. Kalimantan Basin. *Proceedings of Indonesian Petroleum Association 13th Annual Convention*, p.109 - 120.
- Ahmed, M., Volk, H., George, S.C., Faiz, M., and Stalker, L., 2009. Generation and expulsion of oils from Permian coals of the Sydney Basin, Australia. *Organic Geochemistry*, 40, p.810-831. DOI : 10.1016/j.orggeochem.2009.04.003.
- Al-Atta, M.A., Issa, G.I., Ahmed, M.A., and Afife, M.M., 2014. Source Rock Evaluation and Organic Geochemistry of Belayim Marine Oil Field, Gulf of Suez, Egypt. *Egyptian Journal of Petroleum*, 23, p.285-302. DOI : 10.1016/j.ejpe.2014.08.005.
- Alberdi, M. and Lopez, L., 2000. Biomarker 18 α (H)-oleanane: a geochemical tool to assess Venezuelan petroleum systems. *Journal of South American Earth Science*, 13, p.751-759. DOI : 10.1016/S0895-9811(00)00055-9.
- Aldahik, A., 2010. *Crude Oil Families in the Euphrates Graben Petroleum System*. Ph.D. Thesis, Berlin Institute of Technology (TU Berlin), Berlin, 237pp.
- Biantoro, E., Kusuma, M.I., and Rotinsulu, L.F., 1996. Tarakan sub-basin growth faults, North-East Kalimantan: Their roles hydrocarbon entrapment. *Proceedings of Indonesian Petroleum Association, 25th Annual Convention*, Jakarta. DOI: 10.29118/ipa.2496.175.189
- Burhan, R.Y.P., Trendel, J.M., Adam, P., Wehrung, P., Albrecht, P., and Nissenbaum, A., 2002. Fossil bacterial ecosystem a methane seeps: Origin of organic matter from Be'eri sulfur deposit, Israel. *Geochimica et Cosmochimica Acta*, 66, p.4085-4101. DOI : 10.1016/S0016-7037(02)00979-1.
- Chattopadhyay, A. and Dutta, S., 2014. Higher plant biomarker signatures of Early Eocene sediments of North Eastern India. *Marine and Petroleum Geology*, 57, p.51-67. DOI : 10.1016/j.marpetgeo.2014.04.004.
- Cheng, B., Chen, Z., Chen, T., Yang, C., and Wang, T.G., 2018. Biomarker signatures of the Ediacaran–Early Cambrian origin petroleum from the central Sichuan Basin, South China: Implications for source rock characteristics. *Marine and Petroleum Geology*, 96, p.577-590. DOI : 10.1016/j.marpetgeo.2018.05.012.
- Commendatore, M.G., Nievas, M.L., Amin, O., and Esteves, J.L., 2012. Sources and distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina). *Marine Environment*, 74, p.20-31. DOI : 10.1016/j.marenvres.2011.11.010.

- Dessort, D., 2013. Short Course Mineral and Organic Geochemistry. In: *TPA Integrated Week*, (June 17-21,2013), Surabaya, 2013.
- Doust, H. and Noble, R.A., 2008. Petroleum systems of Indonesia. *Marine and Petroleum Geology*, 25, p.103-129. DOI : 10.1016/j.marpetgeo.2007.05.007.
- El Nady, M.M., Harb, F.M., and Mohamed, N.S., 2014. Biomarker characteristics of crude oils from ashrafi and GH oilfields in the Gulf of Suez, Egypt: an Implication to Source Input an Paleoenvironmental Assesments. *Egyptian Journal of Petroleum*, 23, p.445-459. DOI: 10.1016/j.ejpe.2014.11.002.
- El Nemr, A., Moneer, A.A., Ragab, S., and El Sikaily, A., 2016. Distribution and sources of n-alkanes and polycyclic aromatic hydrocarbons in shellfish of the Egyptian Red Sea coast. *Egyptian Journal of Aquatic Research*, 42, p.121-131. DOI : 10.1016/j.ejar.2016.05.003.
- Ellen, H., Husni, M.N., Sukanta, U., Abimanyu, R., Feriyanto, and Herdiyan, T., 2008. Middle Miocene Meliat Formation in the Tarakan Island, regional implications for deep exploration opportunity. *Proceedings of Indonesian Petroleum Association, 32nd Annual Convention*, Jakarta, 1. DOI: 10.29118/ipa.498.08.g.048
- Fabiańska, M.J. and Kurkiewicz, S., 2013. Biomarkers, Aromatic Hydrocarbons and Polar Compounds in the Neogene Lignites and Gangu Sediments of The Konin and Turossów Brown Coal Basins (Poland). *International Journal of Coal Geology*, 107, p.24- 44. DOI : 10.1016/j.coal.2012.11.008.
- Garcia, M.R., Cattani, A.P., Lana, P.C., Figueira, R.C.S., and Martins, C.C., 2019. Petroleum biomarkers as tracers of low-level chronic oil contamination of coastal environments: A systematic approach in a subtropical mangrove. *Environmental Pollution*, 249, p.1060-1070. DOI : 10.1016/j.envpol.2019.03.006.
- Hakimi, M.H., Ahmed, A.F., and Abdullah, W.H., 2016. Organic Geochemical and Petrographic Characteristics of The Miocene Salif Organic-Rich Shales in The Tihama Basin, Red Sea of Yemen: Implications for Paleoenvieromantal Conditions and Oil-Generation Potential. *International Journal of Coal Geology*, 154-155, p.193-204. DOI : 10.1016/j.coal.2016.01.004.
- Han, Y., John, G.F., and Clement, T.P., 2019. Understanding the thermal degradation patterns of hopane biomarker compounds present in crude oil. *Science of the Total Environment*, 667, p.792-798. DOI : 10.1016/j.scitotenv.2019.02.445.
- Husein, S., 2017. Lithostratigraphy of Tabul Formation and Onshore Geology of Nunukan Island, North Kalimantan. *Journal of Applied Geology*, 2 (1), p.25-35. DOI: 10.22146/jag.30255.
- Hu, G., Yang, R., Wang, L., Hu, W., and Cao, J., 2019. Hydrocarbon potential and depositional environment of the Lower Cretaceous black mudstones and shales in the coastal Guangdong Province, China. *Marine and Petroleum Geology*, 99, p.92-106. DOI : 10.1016/j.marpetgeo.2018.10.008.
- Idris, H.K.A., Salihu, I., Abdulkadir, M.N., and Almustapha, 2008. Application of geochemical parameters for characterization of oil samples using GCMS technique. *International Journal of Physical Sciences*, 3, p.152-155.
- Ji, L., He, C., Zhang, M., Wu, Y., and Li, X., 2016. Bicyclic alkanes in source rocks of the Triassic Yanchang Formation in the Ordos Basin and their inconsistency in oil-source correlation. *Marine and Petroleum Geology*, 72, p.359-373. DOI : 10.1016/j.marpetgeo.2016.02.021.
- Jiang, L. and George, S.C., 2018. Biomarker signatures of Upper Cretaceous Latrobe Group hydrocarbonsource rocks, Gippsland Basin, Australia: Distribution and palaeoenvironment significance of aliphatic hydrocarbons. *International Journal of Coal Geology*, 196, p.29-42. DOI : 10.1016/j.coal.2018.06.025.
- Killops, S. and Killops, V., 2005. *Introduction to organic geochemistry* (2nd ed.). Blackwell Publishing, United Kingdom, 393pp. DOI: 10.1002/9781118697214
- Kim, J.H., Lee, D.H., Yoon, S.H., Jeong, K.S., Choi, B., and Shin, K.H., 2017. Contribution of petroleum-derived organic carbon to sedimentary organic carbon pool in the eastern Yellow Sea (the northwestern Pacific). *Chemo-*

- sphere*, 168, p.1389-1399. DOI: 10.1016/0016-7037(61)90069-2.
- Kvenvolden, K.A., 2008. Origins of Organic Geochemistry. *Organic Geochemistry*, 39, p.905-909. DOI: 10.1016/j.orggeochem.2008.02.017.
- Larasati, D., Suprayogi, K., and Akbar, A., 2016. Crude Oil Characterization of Tarakan Basin: Application of Biomarkers. *The 9th International Conference on Petroleum Geochemistry in the Africa-Asia Region*. Bandung.
- Lentini, M.R. and Darman, H., 1996. Aspects of the Neogene tectonic history and hydrocarbon geology of the Tarakan Basin. *Proceedings of Indonesian Petroleum Association 25th Silver Anniversary Convention*, p.241-251.
- Li, G., Li, L., Tarozo, R., Longo, W.M., Wang, K.J., Dong, H., and Huang, Y., 2018. Microbial production of long-chain n-alkanes: Implication for interpreting sedimentary leaf wax signals. *Organic Geochemistry*, 298, p.24-31. DOI: 10.1016/j.orggeochem.2017.10.005.
- Lu, S.T., and Kaplan, I.R., 1992. Diterpanes, triterpanes, steranes, and aromatic hydrocarbons in natural bitumens and pyrolysates from different humic coals. *Geochimica et Cosmochimica Acta*, 56, p.2761-2788.
- Massone, C.G., Wagener, A.D.L.R., Abreu, H.M., and de Veiga, Á., 2013. Revisiting hydrocarbons source appraisal in sediments exposed to multiple inputs. *Marine Pollution Bulletin*, 73, p.345-354. DOI: 10.1016/j.marpolbul.2013.05.043.
- Nawawi, A., Suseno, A., and Heriyanto, N., 1996. *Petroleum Geology of Indonesian Basins Volume V Tarakan Basin, Northeast Kalimantan*. Pertamina, Jakarta.
- Nytoft, H.P., Andersen, G.K., Knudsen, T.S., Stojanovic, K., and Rise, F., 2014. Compound "J" in Late Cretaceous/Tertiary terrigenous oils revisited: Structure elucidation of a rearranged oleanane coeluting on GC with 18 β (H)-oleanane. *Organic Geochemistry*, 77, p.89-95. DOI: 10.1016/j.orggeochem.2014.09.010.
- Nytoft, H.P., Samuel, O.J., Kildahl-Andersen, G., Johansen, J.E., and Jones, M., 2009. Novel C15 sesquiterpanes in Niger Delta oils: structural identification and potential application as a new markers of angiosperms input in light oils. *Organic Geochemistry*, 40, p.595-603. DOI: 10.1016/j.orggeochem.2009.02.003.
- Onojake, M.C., Osuji, L.C., and Abrakasa, S., 2015. Source, depositional environment and maturity levels of some crude oils in southwest Niger Delta, Nigeria. *Chinese Journal of Geochemistry*, 34, p.224-232. DOI: 10.1007/s11631-015-0035-9.
- Peters, K.E. and Fowler, M.G., 2002. Application of petroleum geochemistry to exploration and reservoir management. *Organic Geochemistry*, 33, p.5-36. DOI: 10.1016/S0146-6380(01)00125-5.
- Peters, K.E., Walters, C.C., and Moldowan, J.M., 2005. *The Biomarker Guide: I. Biomarkers and Isotopes in the Environment and Human History*. Cambridge University Press, USA.
- Philp, 1985. Biological markers in fossil fuel production. *Mass Spectrometry Review*, 4, p.1-54.
- Prakash, K.S., Singh, M.P., Alok, K.S., and Arora, M., 2010. Petrographic characteristics of coal from the Lati Formation, Tarakan basin, East Kalimantan, Indonesia. *International Journal of Coal Geology*, 81, p.109-116. DOI: 10.1016/j.coal.2009.11.006.
- Rudra, A., Dutta, S., and Raju, S.V., 2017. The Paleogene vegetation and petroleum system in the tropics: A biomarker approach. *Marine and Petroleum Geology*, 86, p.38-51. DOI: 10.1016/j.marpetgeo.2017.05.008.
- Sabra, E., 2021. Evaluation of Hydrocarbon Source Rock Potential and Organic Geochemistry in North Arafura Shelf, Papua (Indonesia). *Indonesian Journal on Geoscience*, 8 (3), p.401-418. DOI: 10.17014/ijog.8.3.401-416.
- Sefein, K.J., Nguyen, T.X., and Philp, R.P., 2017. Organic geochemical and paleoenvironmental characterization of the Brown Shale Formation, Kiliran sub-basin, Central Sumatra Basin, Indonesia. *Organic Geochemistry*, 112, p.137-157. DOI: 10.1016/j.orggeochem.2017.06.017.
- Schwarzbauer, J., Littke, R., and Strauss, H., 2013. Stable carbon isotope ratios of aliphatic biomarkers in Late Palaeozoic coals. *International Journal of Coal Geology*, 107, p.127-140. DOI: 10.1016/j.coal.2012.10.001

- Seifert W.K. and Moldowan, J.M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. *Geochimica et Cosmochimica Acta*, p.116-126.
- Soeparyono, N. and Lennox, P., 1990. Structural development of hydrocarbon traps in the Cepu oil fields, northeast Java, Indonesia. *Journal of Southeast Asian Earth Sciences*, 4, p.281-291. DOI: 10.1016/0743-9547(90)90003-V.
- Stojanović, K. and Životić, D., 2013. Comparative study of Serbian Miocene coals - Insights from biomarker composition. *International Journal of Coal Geology*, 107, p.3-23. DOI: 10.1016/j.coal.2012.09.009.
- Sutadiwiria, Y., Hamdani, A.H., Sendjaja, Y.A., Haryanto, I., and Yeftamikha., 2018. Biomarker Composition of Some Oil Seeps from West Sulawesi, Indonesia. *Indonesian Journal on Geoscience*, 5 (3), p.211-220. DOI:10.17014/ijog.5.3.211-220.
- Sutadiwiria, Y., Burhannudinnur, M., Jambak, M.A., Riyandhani, C.P., and Yeftamikha, 2022. Geochemical Characterization of Coal, Carbonaceous Shale, and Marine Shale As Source Rock in West Sulawesi, Indonesia. *Indonesian Journal on Geoscience*, 9 (3), p.303-314. DOI: 10.17014/ijog.9.3.303-314
- Taylor, D.W., Li, H., Dahl, J., Fago, F.J., Zinniker, D., and Moldowan, J.M., 2006. Biogeochemical evidence for the presence of the angiosperm molecular fossil oleanane in Paleozoic and Mesozoic non-angiospermous fossils. *Paleobiology*, 32, p.179-190. DOI:10.1666/0094-8373(2006)32[179:BEFTPO]2.0.CO;2.
- Wang, T.G. and Simoneit, B.R.T., 1991. Organic geochemistry and coal petrology of Tertiary brown coal in the Zhoujing mine, Baise Basin, South China: 3. Characteristics of polycyclic aromatic hydrocarbons. *Fuel*, 70, p.819-829. DOI:10.1016/0016-2361(91)90188-G.
- Wight, A.W.R., Hare, L.H., and Reynolds, J.R., 1993. Tarakan Basin, NE Kalimantan, Indonesia: a century of exploration and future potential. *Geology Society Malaysia, Bulletin*, 33, p.263-288. DOI: 10.7186/bgsm33199319.
- Xiao, H., Li, M., Liu, J., Mao, F., Cheng, D., and Yang, Z., 2019. Oil-oil and oil-source rock correlations in the Muglad Basin, Sudan and South Sudan: New insights from molecular markers analyses. *Marine and Petroleum Geology*, 103, p.351-365. DOI: 10.1016/j.marpetgeo.2019.03.004.
- Yangming, Z., 2001. Geochemical Characteristics of Different Kinds of Crude Oils in the Tarim Basin, Northwest China. *Chinese Journal of Geochemistry*, 20, p.73-87. DOI: 10.1177/0144598717742969.
- Yudiartono, Anindhita, Sugiyono, A., Wahid, L.M.A., and Adiarso, 2018. Outlook Energi Indonesia 2018: Energi Berkelanjutan untuk Transportasi Darat. Pusat Pengkajian Industri Proses dan Energi, Tangerang. DOI: 10.14710/jebt.2022.14264
- Zajuli, M.H.H. and Panggabean, H., 2014. Hydrocarbon Source Rock Potential of Sinamar Formation, Muara Bungo, Jambi. *Indonesian Journal on Geoscience*, 1 (1), p.53-64. DOI: 10.17014/ijog.v1i1.175.
- Zetra, Y., Sosrowidjojo, I.B., and Burhan, R.Y.P., 2016. Paleoenvironment of Brown Coal From Sangatta Coal Mines, East Borneo, Indonesia. *Jurnal Teknologi*, 78 (7), p.121-129. DOI: 10.11113/jt.v78.9166.
- Zetra, Y., Kusuma, H.S., Riandra, F., Sosrowidjojo, I.B., and Burhan, R.Y.P., 2018. The Oxygenated Biomarker as an Indicator of Origin and Maturity of Miocene Brown Coal, Sangatta Coal Mines, East Kalimantan. *Indonesian Journal on Geoscience* 5 (2), p.107 -116. DOI:10.17014/ijog.5.2.107-116.
- Zhu, Y., Sun, L., Hao, P., and Tuo, L., 2018. Geochemical composition and origin of Tertiary oils in the Yinggehai and Qiongdongnan Basins, offshore South China Sea. *Marine and Petroleum Geology*, p.139-153. DOI: 10.1016/j.marpetgeo.2018.05.029.
- Zdravkov, A., Stefanov, M., Worobi, E., Bechtel, A., Marinov, S., and Kortenski, J., 2020. Implications for peat formation in Maritsa-West Basin, SE Bulgaria : Insights from organic petrology, palynology and biomarker assemblage. *International Journal of Coal Geology*, 222, p.103-447. DOI: 10.1016/j.coal.2020.103447.