Organic Geochemistry Characteristics of Aliphatic Hydrocarbon Fraction of Crude Oil from Tarakan Basin, North Borneo, Indonesia

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***Abstract*— The study of organic geochemistry of crude oil from Pamusian field, Tarakan Basin, North Borneo has been done. The oil is fractionated by column chromatography and identified using gas chromatography-mass spectrometer (GC-MS). The presence of long chain *n*-alkanes, cadinane, 4β(H)-eudesmane, and 18α (H)-oleanane indicates organic matter derived from resin dammar Angiospermae family Dipterocarpaeae. It is also reported that there are drimane together with homodrimane and hopane as an indicator of bacterial input. The LHCPI value of 2.03 also indicates a high input of photosynthetic bacteria. Pr/Ph ratio of 3.76 and a drimane/homodrimane ratio of 1.058 indicating the oxic depositional environment of the sample. Isomer analysis of 18α(H)-oleanane and 17α(H),21β(H)-hopane provides information that the crude oil from Tarakan Basin is mature.**

***Keywords*—Tarakan Basin Crude Oil, Organic Geochemistry, Aliphatic Hydrocarbon Biomarkaer, GC-MS**

I. INTRODUCTION

CRUDE oil needs by Outlook Energy Indonesia (2018) is expected to increase more than 3 times in the period 2016-2050 with an average growth of 3.3% per year [1]. This condition causes the possibility to import crude oil even higher. However Indonesia still has the potential to increase the production of crude oil and condensate, where there are still many basins that have the potential of oil reserves scattered throughout Indonesia. More than 60 sedimenter basin in Indonesia, some of which have been proven to be productive as oil and gas producers. The basin is largely located on the island of Sumatra and Borneo. One of the still-productive basins is the Tarakan basin [2].

The Tarakan Basin is located in the east part of Borneo and is divided into 4 sub-basin namely Tidung sub-basin, Tarakan sub-basin, Berau sub-basin, Muara sub-basin [3]. It is bounded by the Sekatak Berau Ridge on the west, the Suikerbrood Ridge and the Mangkalihat Peninsula to the south, the Sempurna ridge in the north, and the Sulawesi Sea in the East [3]. Oil exploration in the Tarakan Basin was conducted since 1899 and has been found 14 oil and gas fields. Up to now 86% of oil production comes from two fields, namely Pamusian field in Tarakan Island and Bunyu field on Bunyu Island [4].

Oil production of Pamusian field in Tarakan sub-basin has entered the drain stage [4]. The reactivation of abandoned oil wells is one of the attempts to increase crude oil production [5]. But this effort requires a large fee so that the feasibility data is required for well before reactivation [6]. The exploration and production of petroleum can be improved, one of them through the application of organic geochemical sciences [7] as a complement to geological data [8]. Geochemical characteristics can be used to determine the relationship between petroleum and source rocks, mapping the geographical conditions of the petroleum system and rock source, as well as assess the timing, migration, and accumulation of oil [7].

To reactivation the well, it is necessary to know the hydrocarbon potential of the well. The maturity and source of the main organic material has a significant effect on the potential of hydrocarbons and the productivity of a source rock [9,10,11]. The source of the dominant organic material that provides good hydrocarbon potential is the source of organic material type 3 or derived from higher plants [11]. Hu et al. (2019) has used biomarkers to determine the hydrocarbon potential of Guangdong province, China. Some of the essential biomarker as indicators are long chain n-alkanes (*n*-C_{27}, *n*-C_{29}, *n*-C_{31}), isoprenoid C_{19} and C_{20}, tricyclic terpane and C_{29} Sterane.

The study of organic geochemistry through biomarker analysis has been conducted by researchers on sedimenter, such as petroleum and coal [12,13,14]. Some research through biomarker analysis of the alifatic hydrocarbon fraction has been reported to identify the source of organic matter, the depositional environment, and the thermal maturity of petroleum [12,13,14]. Biomarker such as alkanes, isoprenoid, terpene, and sterane are groups of aliphatic hydrocarbon compounds found in petroleum [6,15,16]. The loss of *n*-alkane, isoprenoid, terpane, and sterane during the secondary process can be used to determine the degree of biodegradation in the reservoir[6] and determine the level of oil maturity[17]. The comparison of pristane to phytane and the distribution of *n*-alkane can be used as an indicator of depositional environment [13,18]. Some biomarker analyses have also been performed by earlier researchers on some source rocks, including the sediment of the Sydney basin [12], the Niger Delta oil [19], and the Ordos Basin oil [20]. But until now there is no organic geochemistry study of the crude oil from Tarakan Basin to determine the depositional environment, maturity and the source of its organic matters. This paper will analyze the aspect of organic geochemistry through the analysis of the aliphatic hydrocarbon biomarker to determine the potency of crude oil from the Tarakan Basin, North Borneo before reactivation.

II. METHOD

Bitumen and water content in oil sample was separated. 2

grams bitumen is separated from the Malten layer in 50 mL n-hexane. Malten is fractionated by chromatography column of silica gel GF_{254} based on solvent gradient system. Elution has done with n-hexane to obtain an alifatic hydrocarbon fraction, dichloromethane for obtaining aromatic hydrocarbon fractions, and methanol to obtain a polar fraction [21,22,23]. This Paper only reports aliphatic hydrocarbon fractions. Analysis of the aliphatic hydrocarbon fraction is carried out with the Gas Chromatography-Mass Spectrometer (KG-SM) Agilent GCMS D5975C, a column type HP-5MS (30 m x 250 µm x 0.2 µm) with 5% phenyl methyl Silox and helium (He) as the carrier gas. The temperature setting of the column is 70^oC (isothermal for 2 minutes) and then increased temperature up to 100^oC at a rate of 10^oC/min and increased back to 300^oC, with a flow rate of 4^oC/min and isothermal for 20 minutes. Biomarker of aliphatic hydrocarbon fraction is identified based on specific m/z fragmentation, retention time, mass spectrum, and the comparison of previous research results that have been published in the literature.

III. RESULTS AND DISCUSSION

The structure of the aliphatic hydrocarbon biomarker of the Tarakan Basin crude oil is identified based on the specific m/z Fragmentogram, retention time and through the comparison of the masse spectrum obtained with the mass spectrum data that has been published by earlier researchers (e.g. Bray and Evan (1961), Eglinton and Hamilton (1967), Seifert and Moldowan (1978), Philp (1985), Lu and Kaplan (1992), Wang et al. (1994), Chattopadhyay and Dutta (2014), Li et al. (2018), Jiang and George (2018)). The identified aliphatic hydrocarbon biomarker consist of a group of n-alkanes, isoprenoids, bicyclic sesquiterpenoids, and pentacyclic triterpenoids as seen in Total Ion Chromatogram (TIC) Figure 1 and further spelled out in table 1. The sterane compound is not found in the Tarakan Basin oil samples. The most abundant aliphatic hydrocarbon biomarker is pristane.

A. n-Alkane and isoprenoid

The identification of *n*-alkane and isoprenoid compounds against Tarakan oil is conducted based on Fragmentogram m/z 57, retention time data and mass spectrum data compared to data that has been reported by past researchers (e.g. Bray and Evan (1961), Eglinton and Hamilton (1967), and Li et al. (2018)). Fragmentogram *n*-alkane and isoprenoid compounds as seen in Figure 2 show homologous *n*-alkane distributed in n-C_{16} – n-C_{30} range with the unimodal distribution type. The short-chain *n*-alkane distribution (under n-C_{16}) looks very small, but the isoprenoid Pristane delivers the highest abundance in the oil compound group analyzed in this study. The low intensity of the short-chain *n*-alkane indicates the absence of (very small) algae role in the formation of the Tarakan oil organic compounds. The short-chain *n*-alkane existence ($<C_{15}$) indicates that organic compounds are derived from phytoplankton, zooplankton, sea bacteria, and algae [6,24]. The identification of the medium chain *n*-alkane group (n-C_{19}-n-C_{25}) indicates the existence of bacterial activity in the paleoenvironmental of Tarakan oil [25,9,6,26].

The maximum concentration for the medium chain *n*-alkane (n-C_{19} – n-C_{25}) is n-C_{19}. Previous n-C_{19}existence was also detected with very high concentrations in green algae and anaerobic bacteria [27,28]. The predominance of n-C_{19} was also found in the study of El Nady et al. (2014) on Egyptian Gulf of Suez Oil and Liu et al. (2019) on the coal samples of the Slovenia basin and indicating that organic matter derived from microbial organisms. The existence of long-chain *n*-alkane (n-C_{26}-n-C_{30}) with abundance almost equal to medium-chain *n*-alkane (except n-C_{19}) indicates the source of organic matter derived from the wax layer of higher terrestrial plants [9]. The same was found in the research of Bakar et al. (2011) with a long chain of *n*-alkane in the n-C_{25} – n-C_{37} range and in the research of Xiaou et al. (2019) with a long chain of *n*-alkane in the n-C_{25} – n-C_{38} range. Both indicate the input of organic matter derived from higher terrestrial plants [9,29].

Odd carbon predominance against even carbon on long-chain *n*-alkane (n-C_{25}-n-C_{30}) especially on n-C_{25}, n-C_{27} and n-C_{29} showed that the organic matter of Tarakan oil were derived from higher terrestrial plants wax layer [9,24,30] that produced through fatty acid decarboxylation [31]. Odd carbon domination of even carbon is also demonstrated by the CPI value of 0.95 as seen in table 3. The value of CPI (Carbon Perference Index) can be used to determine the maturity level of a sample. Dessort (2013) reported CPI value of close to 1 indicated a mature sample, as well as the Onojake et al (2015) study which has CPI value between 0.72 – 1.09. Therefore the value of CPI 0.95 indicates a mature sample of Tarakan oil.

The LHCPI value of 2.03 indicates the relative dominance of the medium chain to the long chain [32]. This is due to the predominance of n-C_{19}. This LHCPI value indicates a sufficiently high input from the bacteria [33]. The high n-C_{19} intensity indicates the presence of bacteria that persist in catagenesis stge. The specific bacteria for n-C_{19} are photosynthetic bacteria [34].

The identification based on fragmentogram m/z 57 with molecular ion m/z 268 indicating the presence of Pristane (Ph) and molecular ion m/z 282 indicates the presence of Phytane (Ph) with a ratio of Pr/Ph 3.76 in an analysed oil sample. The value of this Pr/Ph ratio can be used to determine the oil depositional environment. The high-ratio of Pristane/Phytane (Pr/Ph) (>3.0) indicates the input of terrestrial organic matter in oxic conditions whereas the low Pr/Ph (<0.8) indicates an anoxic/hypersaline or carbonated depositional environment [35,36,37]. Therefore, the ratio of Pr/Ph of 3.76 in the sample crude oil from Tarakan Basin indicating that the oil samples were formed in a oxic environment with terrestrial organic input [38].

Besides the ratio of Pr/Ph, organic geochemical aspect of the analyzed Tarakan Basin oil can also be determined based on isoprenoid against *n*-alkanes ratio to know the source of input of organic matter, biodegradation, and maturity level. The Pr/n-C_{17} ratio of the Tarakan Basin oil sample has a value of 34.41 while the Ph/n-C_{18} value is 16.02. When plotted into the chart as shown in Figure 3, it is obtained that the source of organic matter from the sample comes from a higher terrestrial plant with an oxic depositional environment. This data is in accordance with the ratio of Pr/Ph = 3.76 as an indicator of oxic environment of the Tarakan basin which is analyzed and the dominance of odd carbon to even carbon from the homologous series *n*-alkanes. Therefore, this data reinforces the previous analysis of the suspicion that the source of the organic matter of crude oil from Tarakan Basin comes from higher terrestrial plants in oxic depositional environment.

B. Bicyclic sesquiterpenoid

The presence of sesquiterpenoid compounds in Tarakan Basin oil samples was identified based on 123 m/z fragmentogram. Identification of the structure of each compound was based on fragmentation reactions and by comparing the mass spectrum obtained with the published mass spectrum [39,40,41,42,]. The eight peaks in the fragmentogram were identified as C_{14} bicyclic sesquiterpane, C_{15} bicyclic sesquiterpene, trans-cadinane, 4β(H)-eudesmane, 8β(H)-drimane, homocadinane, homodrimane, and C_{16} bicyclic sesquiterpene, where the dominant peaks are C_{15} and C_{16}- bicyclic sesquiterpane.

The dominance of C_{15} bicyclic sesquiterpane in the oil samples analyzed indicated that organic matter was derived from higher terresrial plants resins and prokaryotic bacteria. This assumption is also supported by the presence of C_{14} sesquiterpane compounds in low intensity[20,43,44,45]. Cadinana is derived from polycadinene precursors found in dammar resin of Angiospermae plants, especially the family of Dipterocarpaeae which undergoes a depolymerization reaction[46], so that the presence of trans-cadinane compounds is considered an indicator of higher Angiospermae plants. In samples there also found 4β(H)-eudesmane where these compounds can be found in fossil plant tissue. The structure of the eudesmana compound is related to the order of terpenoid carbon originating from higher terrestrial plants [6,41,45,47,48]

The presence of 8β(H)-drimane compound together with homodrimane was also identified in the analyzed oil sample. These two compounds identified indicate bacterial input to the formation of organic oil compounds [47]. This is due to the relationship between the structure of the biomarker and the bacteriophopanepoliol precursor produced by Archaebacteria[47], so that the presence of these two compounds can also be associated with bacterial input on the formation of organic matter. The presence of drimane and homodrimane compounds as indicators of bacterial input has also been reported previously in low rank coal samples, Sanggata, East Kalimantan[45], Meghalaya coal samples, India[49] and rock samples in the Gippsland Basin, Australia[48].

The ratio of drimane agains homodrimane (as calculated based on Table 1) can be used to determine the depositional environment. The ratio of drimane agains homodrimane value of the Tarakan Basin Oil sample is 1.058. According to Weston et al. (1989) and Yangming (2001), this value indicates that the sample is deposited in an oxic environment. The rearrangement mechanism of these two compounds is similar to diasterana[47], which requires acidic clay minerals as catalysts formed in the oxidic depositional environment [50].

The presence of homocadinane in the Tarakan Basin oil, ascribed to the same precursor as cadinana, is in the form of polycadinane as an abundant precursor in high-resin Angiospermae[51]. Therefore, the identification of this compound, potentially used as an indicator of high terrestrial plants, Angiosperms. Similar compounds have also been reported in the oil samples of the Surma Basin, Bangladesh [52] and in the oil samples of the Yinggehai Basin, China[53]. The presence of C_{16} bicyclic sesquiterpene compounds indicates that oil is formed in the terrestrial environment and the organic matter derived from higher terrestrial plants[41]. This compound is thought to be formed by the degradation of oleanoids from Angiospermae at diagenesis stage [53,54].

C. Pentacyclic Triterpenoid

Identification structure of triterpane pentacyclic compounds in Tarakan oil samples was studied based on m/z 191 fragmentogram and its retention time. Identification of biomarker structures is also done by comparing the mass spectrum obtained with the mass spectrum that has been published by previous researchers (eg Seifert and Maldowan (1978), Philp (1985), Wang et al. (1994), Jiang and George (2018)) . The six peaks in the fragmentogram were identified as cis-cis-trans-bicadinane, trans-trans-bicadinane, C30 triterpane, 17α(H),21β(H)-norhopane, 18α(H)-oleanane, and 17α(H),21β(H)-hopane with the most dominant compound is 17α(H),21β(H)–hopane.

The cis-cis-trans-bicadinane and trans-trans-trans-bicadinane compounds identified in the Tarakan Basin oil sample analyzed were cyclization products of cadinene dimeric formed from polycadinene macromolecules through depolymerization and ring closure reactions. Polycadinene has been isolated from both fossils and extracts of the dammar resin of the Angiospermae family of the Dipterocarpaceae family, whose vegetation is abundant in the Tertiary period [46,52,55]. Therefore, the existence of this compound is also potential as an indicator of the Angiospermae family Dipterocarpaceae. The same was reported in the Surma Basin oil sample, Bangladesh[52] and in Northeast Indian sediment samples [39]. In addition, triterpane compounds, generally C30, are also mostly from bacteria. Because the synthesis of triterpenoids in sediments is carried out by microbial, this compound is also used as an important indicator to determine the presence of bacterial input on the formation of organic cmatter in crude oil[56]. The same was reported by Zhu et al. (2018) in crude oil from the Yinggehai basin and the Qiongdongnan basin, China

The presence of bicyclic compounds identified based on the m z 191 fragmentogram in the analyzed sample is closely related to one of the biscyclic sesquiterpana compounds namely cadinane. This is because these two compounds come from the same precursor, namely polycadinene [6]. Therefore, the discovery of these two compounds simultaneously confirmed the assumption that the Tarakan Basin oil sample originated from the Angiospermae family Dipterocarpaceae.

The oleanane compound identified in the oil sample analyzed was a triterpenoid pentacyclic compound derived from β-amyrin as a precursor [48,57]. This β-amyrin compound is produced in terrestrial plants Angiosperms whose vegetation is abundant in the Tertiary era [58]. The oleanane compound has 2 isomers namely 18α(H)-oleanana and 18β(H)-oleanana, where the alpha (α) configuration is more stable [59]. Therefore, the presence of 18α(H)-oleanana compound in the oil sample analyzed indicated that the Tarakan Basin oil originated from higher Angiosperm plants and was a mature oil. The existence of this oleanane compound has also been previously reported in rock samples from the Gippsland Basin, Australia [39].

Hopane compounds with configuration of 17α(H), 21β(H)-hopane based on m / z 191 fragmentogram were also identified in the analyzed oil samples. The presence of hopane compounds can be used to determine the maturity of the sample. Biomarka hopane has several isomeric configurations namely 17β(H),21β(H); 17β(H), 21α(H) and 17α(H),21β(H) which are the most stabil isomers. The high intensity of the isomers that have high structural stability indicates mature sediment samples. [60,61,62,63].

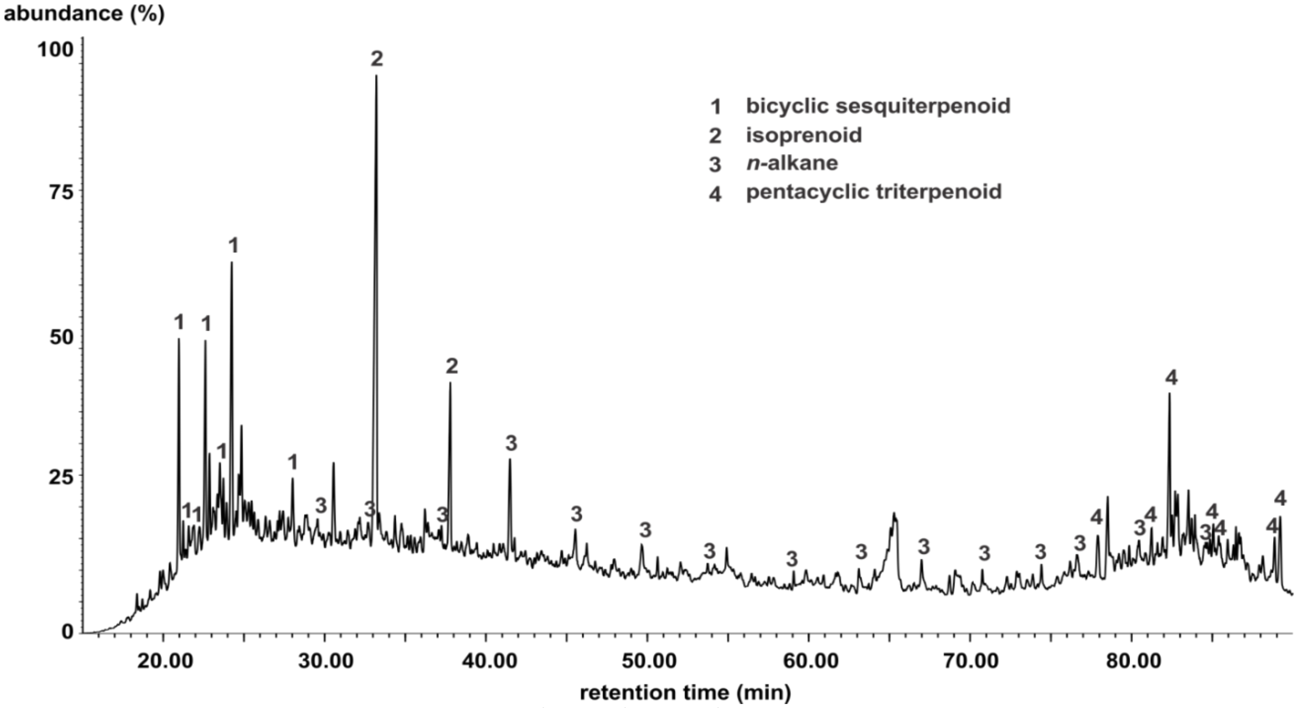

Figure 1. Total Ion Chromatogram (TIC) aliphatic hydrocarbon fraction of crude oil from Tarakan Basin. Condition: KG-SM temperature program 70ºC (2 min), 70ºC-100ºC (10ºC/min), 100ºC -300ºC (4ºC/min) isotherm temperature at 300ºC.

Table 1.
Percent Intensity Of Each Peak Of The Aliphatic Hydrocarbon Fraction Of Basin Oil

Group	Retention time	Compound	% intensity
n-alkana	27.09	*n*-C_{16}	2.008
	32.77	*n*-C_{17}	2.906
	37.25	*n*-C_{18}	1.658
	41.49	*n*-C_{19}	12.856
	45.53	*n*-C_{20}	6.747
	49.63	*n*-C_{21}	6.602
	56.47	*n*-C_{22}	2.062
	59.07	*n*-C_{23}	1.733
	63.11	*n*-C_{24}	5.267
	66.99	*n*-C_{25}	7.205
	70.76	*n*-C_{26}	2.982
	74.42	*n*-C_{27}	2.705
	77.97	*n*-C_{28}	2.725
	81.24	*n*-C_{29}	3.127
	85.4	*n*-C_{30}	5.867
isoprenoid	33.21	Pristane	100.000
	37.79	Phytane	26.571
Bicyclic sesquiterpenoid	18.72 , 19.98	C_{14} bicyclic sesquiterpane	11.589
	20.98 , 22.88	C_{15} bicyclic sesquiterpane	12.533
	22.62	Trans-cadinane	3.651
	23.37	4β(H)-eudesmane	1.720
	23.73 , 24.25	C_{16} bicyclic sesquiterpane	13.280
	24.53, 24.67	8β(H)-drimane	7.713
	24.86	Homocadinane	4.464
	28.02	Homodrimane	7.287
Pentacyclic triterpenoid	78.53	cis-cis-trans-bicadinane	1.061
	82.36	trans-trans-trans-bicadinane	1.762
	84.86, 85.08, 85.96	C30 triterpane	4.470
	86.77	17α(H)-21β(H)-norhopane	3.977
	88.87	18α(H)-oleanane	4.259
	89.22	17α(H)-21β(H)-hopane	6.392

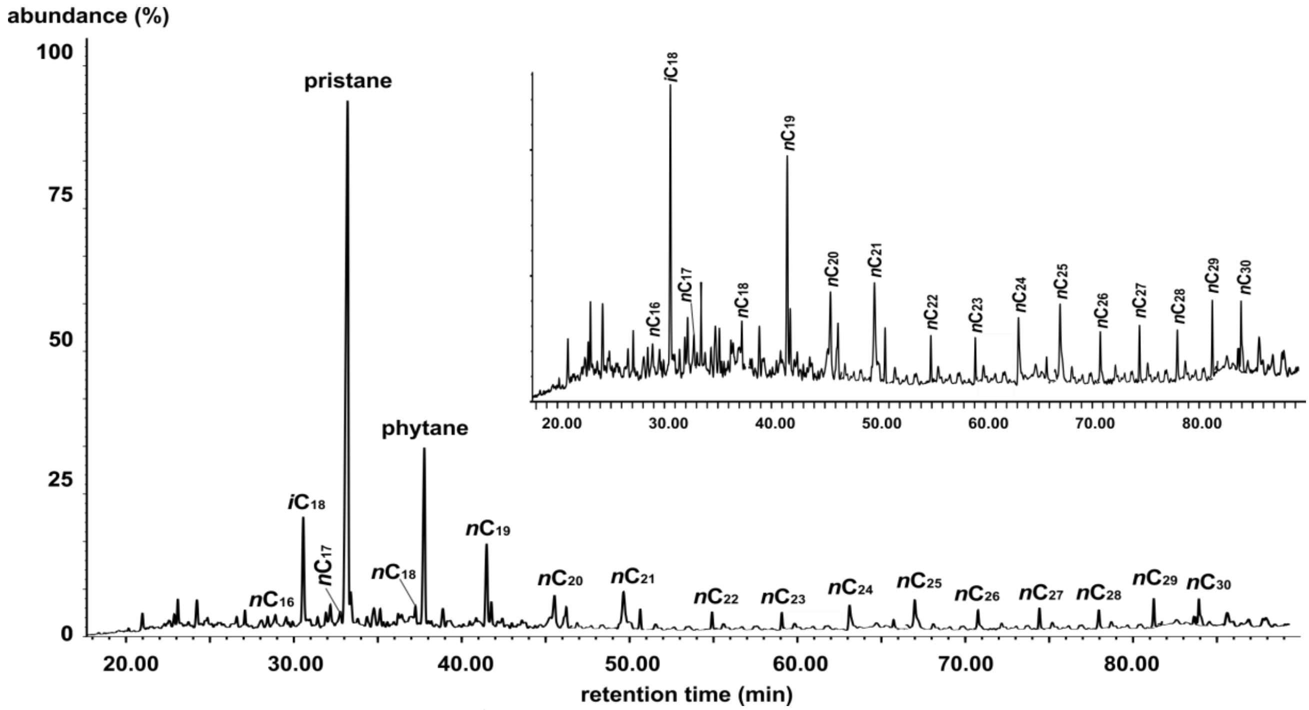

Figure 2. Fragmentogram m/z 57 aliphatic hydrocarbon fraction that indicates *n*-alkanes and isoprenoids

Table 2.
Molecular Parameter For Crude Oil From Tarakan Basin

Parameter	Value
CPI[a]	0.95
LHCPI[b]	2.03
LHCPI[b]	3.76
Pr/*n*-C_{17}	34.41
Ph/*n*-C_{18}	16.02

[a] CPI [61] = $\frac{1}{2}\left(\frac{(C25+C27+C29+C31+C33)}{(C24+C26+C28+C30+C32)}+\frac{(C25+C27+C29+C31+C33)}{(C26+C28+C30+C32+C34)}\right)$

[b] LHCPI = $\frac{C17+C18+C19}{C27+C28+C29}$

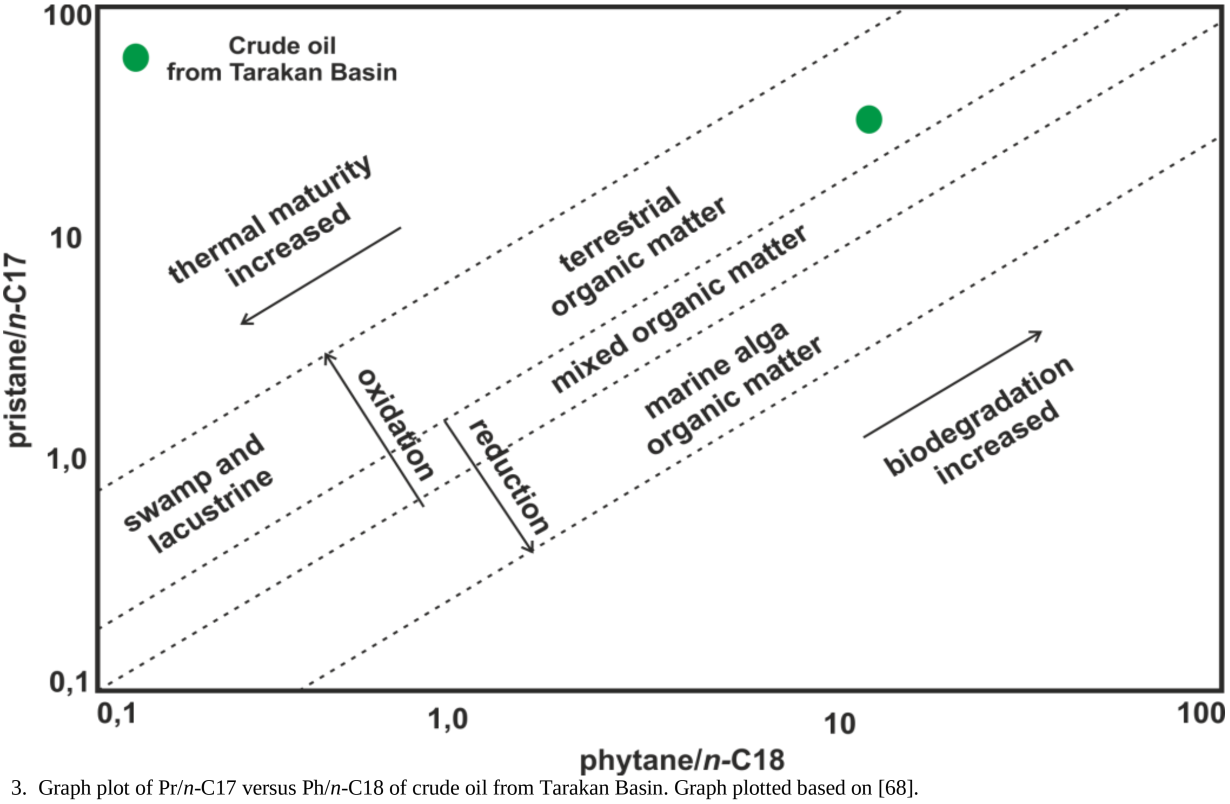

Figure 3. Graph plot of Pr/*n*-C17 versus Ph/*n*-C18 of crude oil from Tarakan Basin. Graph plotted based on [68].

Therefore, the identification of compound 17α(H),21β(H)-hopane with the highest abundance, but no other hopone isomers are found in the form of 17β(H),21β(H); 17β(H),21α(H) is very strong evidence that the Tarakan Basin oil is mature.The presence of this compound 17α(H),21β(H)-hopane has also been reported previously in the sample Brown Shale Central Sumatra Basin[64] and samples of the Central Sichuan Basin, China[65]. The presence of several hopanoid compounds in the analyzed oil samples also shows the presence of bacterial input in the oil formation environment, because hopanoid compounds are produced by bacteriophopanepoliol precursors produced by aerobic bacteria [40,31,62]. The presence of bacterial activity that plays a role in the ancient environment of oil formation in the Tarakan Basin, has also been proven by the presence of other biomarkers in the analyzed samples, such as low-intensity of short chain *n*-alkanes, high intensity of *n*-C_{19}, C_{14}-bicyclic sesquiterpane, drimane and homodrimane. High intensity of *n*-C_{19} indicates that the bacteria that play a role in Tarakan Basin's paleoenvironmental are photosynthetic bacteria [34].

IV. CONCLUSION

Organic geochemical studies through biomarker analysis of aliphatic hydrocarbon fraction of crude oil from Tarakan Basin, North Borneo provide information of organic matter, depositional environment, and level maturity of the sample. Four groups of identified aliphatic compounds, namely *n*-alkane, isoprenoid, bicyclic sesquiterpenoid and pentacyclic triterpenoid. The presence of long chain *n*-alkanes, trans-cadinanae, homocadinane, 4β(H)-eudesmane, bicadinana, and 18α (H)-oleanane indicates organic matter derived from resin dammar Angiospermae family Dipterocarpaeae. It is also reported that there are drimane together with homodrimane and hopane as an indicator of bacterial input. The LHCPI value of 2.03 also indicates a high input of photosynthetic bacteria. The CPI value of 0.95 indicates a mature sample. Pr/Ph ratio of 3.76 and a drimane/homodrimane ratio of 1.058 indicating the oxic depositional environment of the sample. Isomer analysis of 18α(H)-oleanane and 17α(H),21β(H)-hopane provides information that the crude oil from Tarakan Basin is mature.

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