Biomarking Study of Aromatic Hydrocarbon Fraction Crude Oil Tarakan, North Kalimantan

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***Abstract*— The study of the aromatics of aromatic hydrocarbons from Tarakan crude oil, North Kalimantan, has been carried out through the analysis of Gas Chromatography-Mass Spectroscopy (GC-MS) analysis. The biomarkers identified showed the presence of naphthalene groups, phenanthrene and pentacyclic triterpenoids where the pentacyclic triterpenoid showed the highest abundance. The presence of 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene biomarkers; 1,2,9-trimethyl-1,2,3,4-tetrahydropicene; 2,7-dimethyl-1,2- (isopropylpenteno) -1,2,3,4-tetrahydrochrysene and dinorursa-1,3,5 (10), 13 (18) -tetraene as indicators of plants Angiosperms and chrysene indicate input bacteria. The existence of 1,3,7 + 2,6,9 + 2,7,9-TMP biomarkers; 3-MC and 2-MC indicate mature oil samples. The presence of DMP, TMP and chrysene biomarkers indicates terrestrial and marine depositional environments.**

***Keywords*— Tarakan Oil, Aromatic Fraction, Terrestrial, Marine, Oxic**

I. INTRODUCTION

THE need for hydrocarbon products is still the main energy used by many countries. Including Indonesia, which still uses fossil energy as the main energy, especially petroleum, in fulfilling the country's consumption needs in 2016 it is still dominated by fuel oil by 47% [1]. The average GDP growth rate is 6.04% per year and population growth is 0.71% per year during 2016-2050 resulting in a growth rate of final energy requirements of 5.3% per year. Thus, energy demand is predicted to increase from 795 million in 2016 to 4,569 million in 2050 [1].

In order to meet the increasing oil consumption needs by maximizing oil production. The Tarakan Basin is in the northeastern part of Kalimantan and is divided into 4 sub-basins namely the Tidung Basin, the Tarakan Basin, the Berau Basin, and the Muara Basin [2]. However, currently the Tarakan Basin oil production has entered its final stage. The possibility of optimizing petroleum exploration and production can be known through the application of geochemistry [2] as a complement to geological data [3].

Organic geochemical studies are carried out through biomarker analysis on a particular sedimenter. Biomarker (biological marker) or commonly called a biological marker compound is a molecular fossil in sediments, rocks and petroleum which has shown a slight change in the structure of the compounds from living organisms based on the geology that occurs. This biological marker compound was identified through analysis with the Gas Chromatography - Mass Spectrometry (GC-MS) instrument after separation [4]. The distribution and abundance of aromatic hydrocarbon biomass are used as identification of sources of depositional organic matter, thermal maturity and depositional environment [5]. Naphthalene, phenanthrene and alkylated benzene are a number of groups of aromatic compounds that are commonly found in petroleum [2]. The methylphenantrene index is identified based on the 178 m/z fragmentogram as an indicator of the maturity level of petroleum [2]–[5]. Several groups of alkylnaphthalene, such as 1,6-dimethylnaphthalene (1,6-DMN), 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1,7-dimethylnaftalene (1,7-DMN), and cadalene can also be used as an indicator of the source of organic material for terrestrial plants [4]–[7]. Groups of heterocyclic aromatics such as dibenzothiophene, dibenzofuran and fluorene are found in terrestrial and marine oil from the Early Miocene to the Late Miocene as indicators of depositional environments [5]–[7].

This paper will report the presence of aromatic hydrocarbon biomass in Tarakan oil samples and their organic geochemical aspects, including sources of origin of organic matter, depositional environment and maturity so that the potential of the Tarakan oil well to be reactivated can be known.

II. METHOD

As much as 2 grams of bitumen were extracted with 50 mL of n-hexane to obtain maltene. Maltene is then fractionated by column chromatography based on the solvent gradient system. Elution with n-hexane solvent to obtain aliphatic hydrocarbon fractions, dichloromethane solvents to obtain aromatic hydrocarbon fractions, and methanol for the separation of polar fractions [3], [5], [6]. This paper only reports biomarkers contained in romatic hydrocarbon fractions. The analysis was carried out by Agilent GCMSD5975C Gas Chromatography-Mass Spectrometer (GC-MS), HP-5MS column type (30 m x 250 µm x 0.2 µm) with 5% phenyl methyl silox and helium (He) gas as carrier gas. The column temperature setting is 70ºC (isothermal for 2 minutes) then the temperature is raised to 100ºC at a rate of 10ºC/minute and raised again to 300ºC, the rate of 4ºC/minute, for 20 minutes. Biomarker of aromatic hydrocarbon fractions were identified based on specific m/z fragmentation, retention time, mass spectrum, and compared the results of previous studies published by previous researchers as references

III. RESULTS AND DISCUSSION

A. Identification of Aromatic Hydrocarbon Biomarker Compounds

Gas chromatography-mass spectrometer (GC-MS) analysis of the aromatic hydrocarbon fraction of Tarakan

crude oil samples, North Kalimantan can be seen in the Total Ion Chromatogram (TIC) Figure 1. Identification of structures based on specific m/z fragmentogram, retention time and through comparison between spectra mass obtained with the mass spectrum that has been published in previous studies [7]–[15]. The results of the identification showed three (3) groups of compounds namely: naphthalene and derivatives; phenanthrene and its derivatives and the aromatic pentacyclic triterpenoid group.

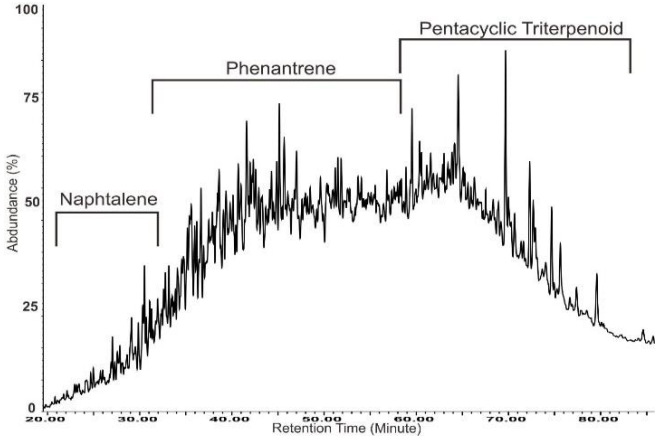

Figure 1. The total ion chromatogram (TIC) aromatic hydrocarbon fraction which shows the distribution of aromatic hydrocarbons. Condition: Agilent KG-SM GCMSD5975C. Program temperature: 70ºC isothermal for 2 minutes, temperature rise to 100ºC is programmed at a rate of 10ºC / minute, from 100ºC-300ºC at a rate of 4ºC / minute, and isothermal temperature at 300ºC for 20 minutes.

B. Biomarker of the Naphtalene Group

Naphthalene derivatives in Tarakan oil samples were identified based on 128/142, 156, 170 and 184 fragmentogram m, as well as comparison of mass spectrum data obtained with mass spectrum data that had been published by previous researchers [8]–[15]. The presence of naphthalene and its derivatives is identified as naphthalene (m / z 128), methylnaphthalene (MN, m / z 142), dimethylnaphthalene (DMN, m / z 156), trimethylnaphthalene (TMN, m / z 170), and tetramethylnaftalene (TeMN, m / z 184). The presence of naphthalene compounds and their derivatives can provide information about the source of organic matter [8]–[15], level of thermal maturity [8]–[11], and depositional environments [12]–[15].

Methylnaphthalene (MN) compounds identified by m / z 142 fragmentogram, show 2-MN and 1-MN isomers [8]–[15]. The abundance of 2-MN compounds is slightly lower than 1-MN as shown in Figure 2 and Table 1 below. 2-MN substituted by the methyl group at position β has a higher stability than 1-MN substituted by the methyl group at position α [8]–[15]. An almost equal abundance between 2-MN and 1-MN indicates oil that is near thermal maturity [8]–[15]. However, the indication of Tarakan oil maturity was not only reviewed based on the presence of methylnaphtalene compounds, but also the presence of other biomarkers in the samples analyzed.

Table 1.
Intensity of MN group

Compound	Rt (Minute)	Intensity (%)
2-MN	18.89	98,7
1-MN	19.34	100

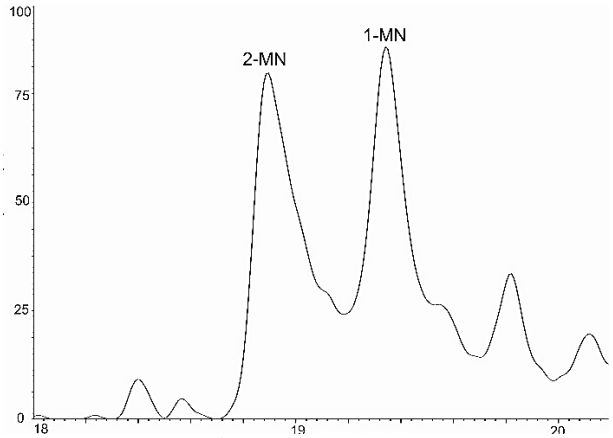

Figure 2. Fragmentogram of MN

Dimethylnaphthalene (DMN) compounds identified based on m / z 156 fragmentogram showed the presence of structural isomers 2.6 + 2.7, 1.3 + 1.7 and 1.6-DMN [8]–[15]. Distribution of DMN compounds in Tarakan crude oil samples showed the highest intensity was 1.6 DMN, while the lowest intensity was 1.3 + 1.7-DMN (Figure 3 and Table 2). High stability isomers at 2.6 + 2.7-DMN are also lower than 1.6-DMN isomers. The high abundance of 1.6-DMN is caused by the abundant source of input of organic matter. 1.6-DMN originates from the aromatization of polycadene resin in the catagenesis stage which produces a 1.6-DMN compound [8]–[15]. The discovery of the 1.6-DMN compound with the highest abundance in the Tarakan oil sample showed oil produced from terrestrial plants [11].

Table 2.
Intensity of DMN group

Compound	Rt (Minute)	Intensity (%)
2,6+2,7-DMN	21.45	64,4
1,3+1,7-DMN	21.77	53,4
1,6-DMN	23.93	100

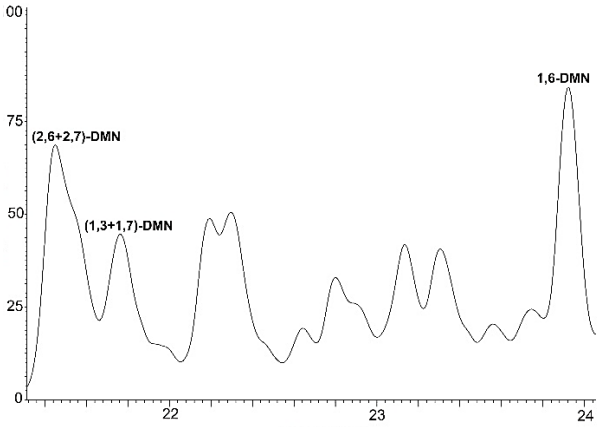

Figure 3. Fragmentogram of DMN

Trimethylnaphthalene (TMN) compounds identified based on fragmentogram m / z 170 in Tarakan oil samples showed 1,3,7-TMN isomers, 1,3,6-TMN, 1,4,5 + 1,3,5-TMN, 2 , 3,6-TMN, 1,2,7-TMN, 1,6,7-TMN as seen in Figure 4 [8]–[15]. TMN compounds can be used as indicators of sources of organic matter and depositional environments [8]–[15]. The presence of 1,2,7-TMN isomers was found with the highest intensity and followed by an abundance of 1,6,7-TMN and 1,4,5 + 1,3,5-TMN in Tarakan oil samples (Table 3, Figure 4) is an indicator of the input of sources of organic matter from the degradation of oleanene-type triterpenoid compounds in high plants, especially Angiosperms [8], [9],

[12]. Besides that, the existence of these biomarkers also indicates the oxidation depositional environment, so that it can be said that the formation of Tarakan oil is deposited in the oxic environment [13].

Table 3.
Intensity of TMN group

Compound	Rt (Minute)	Intensity (%)
1,3,7-TMN	23,14	13,8
1,3,6-TMN	24,09	28,1
1,4,5+1,3,5-TMN	25,25	41,3
2,3,6-TMN	25,42	19,7
1,2,7-TMN	25,73	100
1,6,7-TMN	25,95	66,8

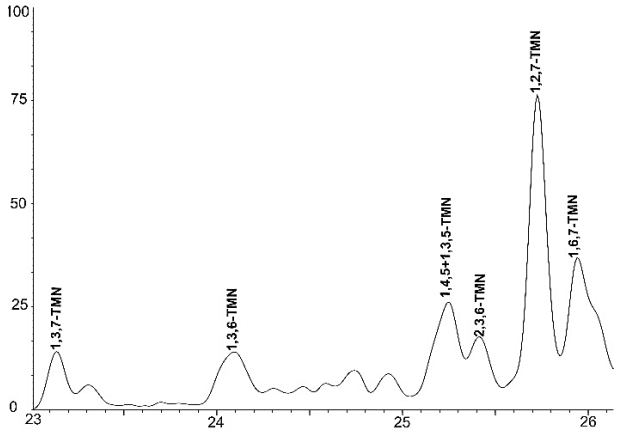

Figure 4. Fragmentogram of TMN

Tetramethylnaphtalene (TeMN) compounds identified based on the m / z 184 fragmentogram in the Tarakan Basin oil sample showed a 1,3,5,7-TeMN isomer, 1,3,6,7-TeMN, 1,2,4,6 + 1 , 2,4,7 + 1,4,6,7-TeMN, 1,2,5,7-TeMN, 2,3,6,7-TeMN, 1,2,6,7 + 1,2,3 , 7-TeMN, 1,2,3,6-TeMN and 1,2,5,6 + 1,2,3,5-TeMN [8]–[15]. 2,3,6,7-TeMN isomers showed the highest intensity followed by 1,2,5,7-TeMN, 1,3,6,7-TeMN, (1,2,6,7 + 1,2,3, 7) -TeMN (Figure 5, Table 4). 1,2,5,6-TeMN isomers are α-substitution isomers, whereas 1,3,6,7-TeMN is β-substitution isomer. The methyl group at position β is more stable at high temperatures than the position until so that the peak intensity of 1,3,6,7-TeMN higher than 1,2,5,6-TeMN indicates that the oil is ripe. Strachan et al., 1988 said that 2,3,6,7-TeMN and 1,2,5,6-TeMN isomers were obtained from the aromatication process of β-amyrin in high-level Angiosperm plants. In addition, this 1,2,5,6-TeMN compound is also produced from hopanoid precursors produced by bacteria, so the presence of this compound indicates the presence of bacterial input on the formation of Tarakan oil organic compounds analyzed [15].

Table 4.
Intensity of TeMN group

Compound	Rt (Minute)	Intensity (%)
1,3,5,7-TeMN	27.48	44
1,3,6,7-TeMN	29.1	73
1,2,4,6+1,2,4,7+1,4,6,7-TeMN	29.45	17
1,2,5,7-TeMN	30.36	92
2,3,6,7-TeMN	30.46	100
1,2,6,7+1,2,3,7-TeMN	30.48	62
1,2,3,6-TeMN	31.41	20
1,2,5,6+1,2,3,5-TeMN	31.97	26

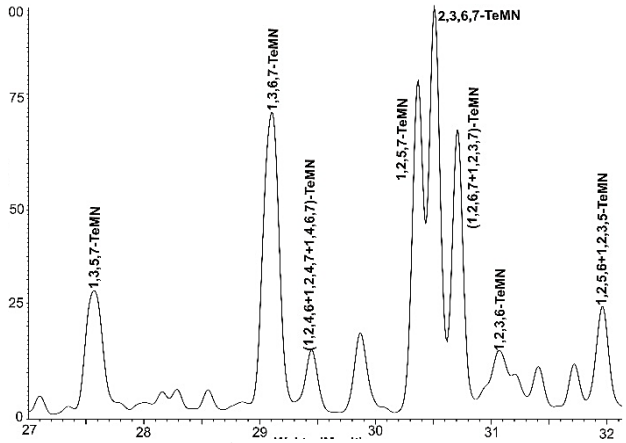

Figure 5. Fragmentogram of TeMN

C. Biomarker of the Phenantrene Group

Phenantrene and derivatives in Tarakan oil samples were identified based on m/z fragmentogram 178, 206, 220. Structure identification was carried out by comparing retention times and mass spectrum data obtained with mass spectrum data that had been published by previous researchers [7]–[11]. Phenantrene and its derivatives were identified as dimethylphenanthrene (DMP, m/z 206) and trimethylphenanthrene (TMP, m/z 220). The dimethylphenantrene (DMP) compound identified based on the m/z 206 fragmentogram showed a isomer of 3,6-DMP, 2,7-DMP, (1,6 + 2,9) -DMP, 2,6-DMP, 1,3+ 2,10 + 3,9 + 3,10-DMP, 1,7-DMP and 2,3-DMP [7]–[12]. 3,6-DMP isomer (Table 5, Figure 6) shows high intensity and low 1.7-DMP isomer. DMP isomers substituted with the methyl group at C9 and C10 1.3 + 2.10 + 3.9 + 3.10-DMP indicate the marine environment as also previously reported by other researchers [9]–[11], [14]. The abundance of the 1.7-DMP isomer (pimantrene), is considered to have a relationship with the natural precursors of pimaric acid in terrestrial plant resins [9]. Therefore, the presence of DMP isomers in the oil samples of the Tarakan Basin analyzed this shows the sources of the origin of organic compounds from terrestrial and marine environments.

Table 5.
Intensity of dimethylphenanthrene (DMP) group

Compound	Rt (Minute)	Intensity (%)
3,6-DMP	41.59	100
2,6-DMP	41.80	34
2,7-DMP	42.01	50
1,3+2,10+3,9+3,10-DMP	42.18	28
1,6+2,9-DMP	42.34	39
1,7-DMP	42.78	12
2,3-DMP	43.27	11

Trimethylphenanthrene (TMP) compounds in Tarakan Basin oil identified by m/z 220 fragmentogram, show isomeric distribution (1,3,6 + 1,3,10 + 2,6,10) -TMP; (1,3,7 + 2,6,9 + 2,7,9) -TMP; (1,3,9 + 2,3,6) -TMP; (1,6,9 + 1,7,9 + 2,3,7) -TMP; 1,3,8-TMP; 2,3,10-TMP; 1,6,7-TMP and 1,2,6-TMP [15]–[18]. Isomer (1,3,7 + 2,6,9 + 2,7,9) -TMP has a high intensity as seen in Table 6 and Figure 7. TMP compounds are used as information on indicators of sources of origin of organic compounds and thermal maturity [15]–[19]. The stability of TMP will be high if the methyl group is substituted in the position of βββ such as 2,3,6-TMP and the position of αββ such as 2,6,9-TMP; 2,6,10-TMP; 2,7,9-TMP; 1,3,6-TMP and 1,3,7-TMP [17], [18]. Therefore, the

dominance of 1,3,7 + 2,6,9 + 2,7,9-TMP isomers with αββ substituents compared to other isomers indicates that the Tarakan oil samples are ripe. In addition, the presence of αββ-substituted isomers provides information on sources of input for terrestrial organic matter [18], [19].

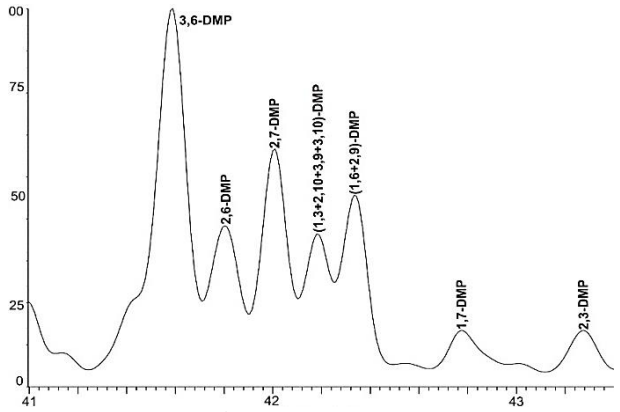

Figure 6. Fragmentogram of DMP

While other TMP isomers such as 1,6,9-TMP; 1,7,9-TMP and 1,3,8-TMP are indicators of marine environmental sources [17]–[19]. Therefore, the presence of TMP isomers in the Tarakan oil sample indicates oil that is ripe and deposited in terrestrial and marine environments.

Table 6.
Intensity of trimethylphenantrene (TMP) group

Compound	Rt (Minute)	Intensity (%)
(1,3,6+1,3,10+2,6,10)-TMP	44.86	76
(1,3,7+2,6,9+2,7,9)-TMP	45.15	100
(1,3,9+2,3,6)-TMP	45.45	20
(1,6,9+1,7,9+2,3,7)-TMP	45.65	58
1,3,8-TMP	46.03	17
2,3,10-TMP	46.32	9
1,6,7-TMP	46.54	17
1,2,6-TMP	46.79	12

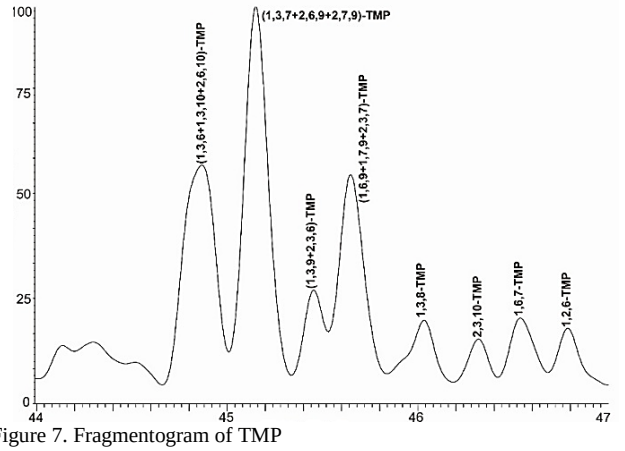

Figure 7. Fragmentogram of TMP

Besides trimethylphenanthrene, retene compound were also identified based on 234 m/z fragmentogram [19], [20]. Retene compound are produced from precursors of abietic acid which are found abundantly in conifer plants Gymnosperms [14]. Abietic acid gradually undergoes aromatization with an increase in high thermal temperatures resulting in perfectly dehydroabiethane, simonellite and retene [19], [20]. This data shows that the presence of low intensity retene in Tarakan oil samples analyzed is potentially used as a mature oil indicator. Besides that, the retinal presence in Tarakan oil samples also indicates the presence of small amounts of Gymnosperme plant input, in addition to the input of Angiospermae plants [19], [20].

Cadalene and isocadalene compounds were identified in Tarakan oil samples based on 183 m / z fragmentogram [8], [19]–[21]. Cadalene compounds showed higher intensity than isocadalene (Table 7, Figure 8). Isocadalene isomer is a more stable isomer than Cadalene. Therefore, the discovery of isocadalene with a fairly high intensity (42.9%) compared to Cadalene (100%) indicates that the oil is ripe, but has not reached maximum maturity [21]. The higher the maturity of an oil, the more isocadalene intensity will be higher than cadalene [20], [21].

Table 7.
Intensity of cadalene and isocadalene

Compound	Rt (Minute)	Intensity (%)
Cadalene	32.79	100
Isocadalene	33.17	42,9

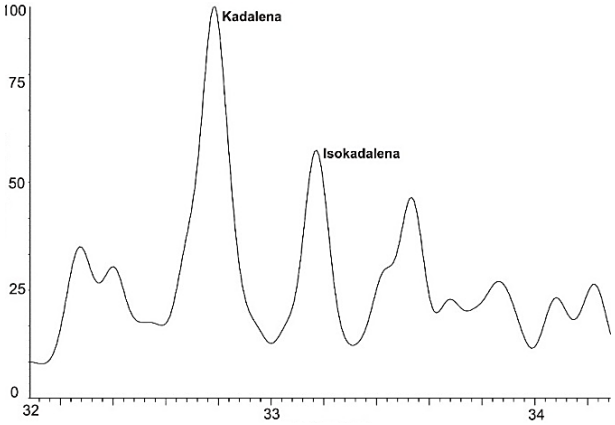

Figure 8. Fragmentogram of cadalene and isocadalene

Ionene compound in Tarakan oil samples were identified based on m/z 159 fragmentogram as the base peak and m/z 174 as molecular ion peaks [7], [8], [21]–[23]. Ionena is the result of sporopollenine degradation originating from high-spore spores plants [22]–[24]. However ionene is also obtained through degradation of labdene diterpenoids which are a major component of conifer resin in an oxidative environment [21], [22]. Therefore, ionene compounds are not specific biomarkers used in geochemical analysis, because their structure has undergone degradation and oxidation at the diagenetic stage [21]–[24].

Compound 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene identified based on m/z 274 fragmentogram [23]–[25] have the potential to be used as indicators of Angiosperm plants. This is because 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene is produced from β-amyrin precursors which undergo biodegradation or geodegradation during the initial stages of diagenesis [23]–[25].

Methylchrysene (MC) in Tarakan oil samples was identified based on m/z 243 fragmentogram with the distribution of 3-MC, 2-MC, 6-MC and 1-MC isomers, as seen in Table 8 and Figure 9 [26]–[29]. 3-MC and 2-MC isomers have the highest stability compared to other isomers. Therefore, the dominance of this isomer compared to others, indicates a mature oil sample. In addition to methylchrysene (MC), chrysene compounds were also identified based on fragmentogram m/z 228 [26]–[29]. Chrysene is a derivative of α- and β-amyrin pentacyclic triterpene precursors which are found abundantly in high terrestrial epicuticular wax [28]. In addition, chrysene is also a hopper degradation product at the diagenesis stage, followed by aromatic reactions [28], [29]. This shows that the presence of chrysene is an indicator

of ripe oil and the organic matter of the sample comes from terrestrial plants and the bacterial input to the oil formation is analyzed.

Table 8.
Intensity of the methylcrisene group (MC)

Compound	Rt (Minute)	Intensity (%)
3-MC	57.32	100
2-MC	57.48	66
6-MC	57.79	52
1-MC	58.03	48

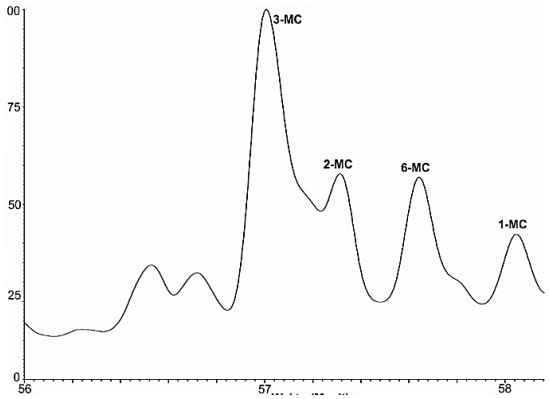

Figure 9. Fragmentogram of MC

D. Biomarker Pentacyclic Triterpenoid Group

The pentacyclic triterpenoid group in the Tarakan oil sample was identified based on fragmentogram m/z 231, 342, 324 and 376. Identification was done by comparing the pattern of retention time and compound mass spectrum data with results published by previous researchers [7], [8], [30]–[33]. The presence of pentacyclic triterpenoids and their derivatives is identified as sterane triaromatic (m/z 231), aromatic pentacyclic (m/z 342), pentacyclic tetraaromatic (m/z 324) and pentacyclic triaromatic (m/z 376).

Sterane triaromatic compounds are identified based on m/z 231 fragmentogram [7], [8], [30], [33]. Sterane or C20 triaromatic sterane compounds are produced from sterol derivative compounds formed during the process of diagenesis, catagenesis, and maturation. Aromatic steroids can only be found at high levels of biodegradation [30]. The precursors of aromatic steroids commonly found in sediments are stenol and stanol [10]. This compound undergoes transformation at the diagenesis and catagenesis stages to produce aromatic steroids [10]. Perfect aromatization of three steroid rings indicates a high level of thermal maturity [30]–[33]. However, the low C20-triaromatic sterane intensity in Tarakan oil samples shows that the oil is ripe, but has not reached very high thermal maturity.

Triaromatic pentacyclic compounds and their abundance identified by m/z 342 fragmentogram show distribution 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene, 2,7-dimethyl-1,2-(isopropylpenteno)-1,2,3,4-tetrahydrochrysene and 2,3,4a,9-tetramethyl-l,la,2,3,4,4a,5,6-octahydropicene (triaromatic ursane) as seen in Table 9 and Figure 10 [31]–[34]. Compounds 2,7-dimethyl-1,2-(isopropylpenteno)-1,2,3,4-tetrahydrochrysene which are relatively more stable than others are found with more dominant intensity. This indicates a mature oil sample. In addition, these triaromatic pentacyclic compounds are produced from β-amyrin and α-amyrin precursors which are produced abundantly in Angiospermae plants [31]–[34]. Therefore, the presence of triaromatic pentacyclic biomarkers in Tarakan oil samples analyzed showed samples that were ripe and produced from the vegetation of the Angiospermae plant which was very abundant.

Table 9.
Intensity of the triaromatic pentacyclic group

Compound	Rt (Minute)	Intensity (%)
2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene	71.63	14
2,7-dimetil-1,2-(isopropilpenteno)-1,2,3,4-tetrahydrochrysene	72.30	100
2,3,4a,9-tetramethyl-l,la,2,3,4,4a,5,6-octahydropicene	72.68	43

The presence of pentacyclic tetraaromatic compounds (Table 10, Figure 11) has been identified based on the m/z fragmentogram 324. Three identified peaks are shown as 2,2,9-trimethyl-1,2,3,4-tetrahydropicene; 1,2-(1'-isopropylpropano)-7-methylchrysene and 1,2,9-trimethyl-1,2,3,4-tetrahydropicene [7], [8], [32]–[35]. The abundance of the 1,2,9-trimethyl-1,2,3,4-tetrahydropicene compound looks more dominant in this fragmentogram. The discovery of this compound in the Tarakan oil sample analyzed indicated that there was an abundant input of Angiospermae vegetation in the formation of Tarakan oil.

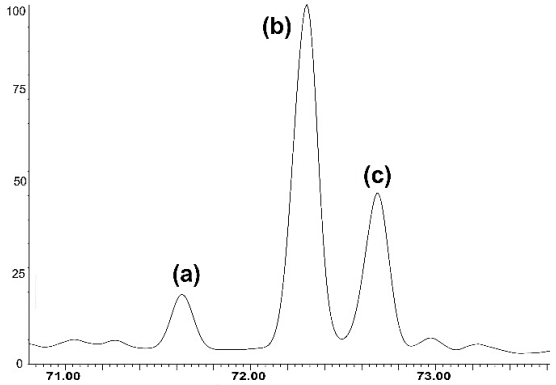

Figure 10. Fragmentogram of (a) 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene; (b) 2,7-dimetil-1,2-(isopropilpenteno)-1,2,3,4-tetrahydrochrysene; (c) 2,3,4a,9-tetramethyl-l,la,2,3,4,4a,5,6-octahydropicene

Table 10.
Intensity of the pentacyclic tetraaromatic group

Compound	Rt (Minute)	Intensity (%)
1,2-(1'-isopropylpropano)-7-metilchrysene	71.63	7
1,2,9-trimetil-1,2,3,4-tetrahydropicene	72.30	100
2,2,9-trimetil-1,2,3,4-tetrahydropicene	72.68	5

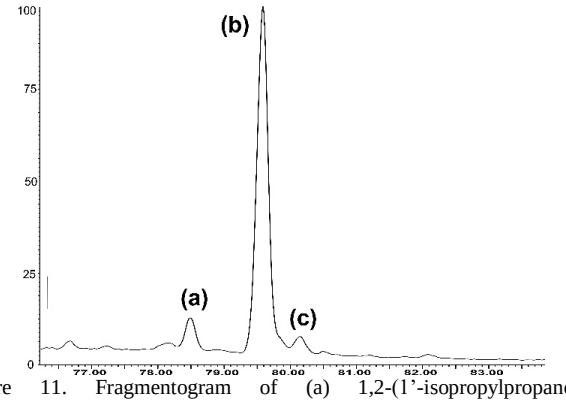

Figure 11. Fragmentogram of (a) 1,2-(1'-isopropylpropano)-7-metilchrysene; (b) 1,2,9-trimetil-1,2,3,4-tetrahydropicene; (c) 2,2,9-trimetil-1,2,3,4-tetrahydropicene

Pentacyclic triaromatic compounds (Table 11, Figure 12) identified based on m/z 376 fragmentogram showed two compounds, namely dinoroleana-1,3,5 (10), 13 (18) -tetraene and dinorursa-1,3,5 (10), 13 (18) -tetraene [7]–[9], [36]–[39]. Both compounds that have oleanane and ursane skeletons are produced by β-amyrin precursors in Angiosperm plants and only a small portion of Gymnosperm plants can produce this compound [37]–[39]. Therefore, the presence of pentacyclic triaromatic compounds in Tarakan oil samples analyzed was potentially used as an indicator of the Angiosperm plants.

Table 11.
Intensity of the pentacyclic triaromatic group

Compound	Rt (Minute)	Intensity (%)
Dinoroleana-1,3,5(10),13(18)-tetraene	71,63	63
Dinorursa-1,3,5(10),13(18)-tetraene	72,30	100

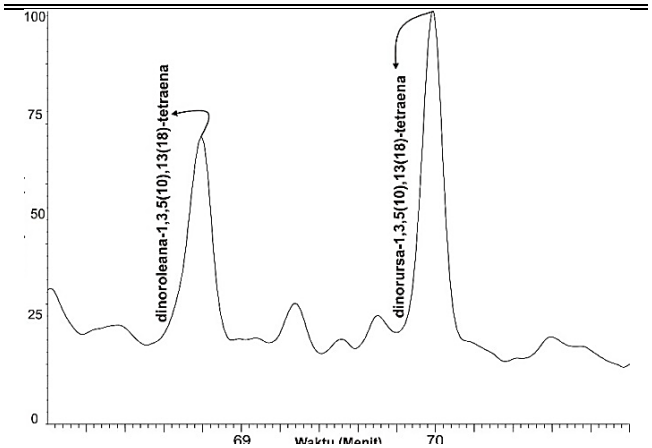

Figure 12. Fragmentogram of pentacyclic triaromatic group

IV. CONCLUSION

The geochemical aspects of the Tarakan Basin crude oil to assess ancient depositional environments have been carried out through biomarker analysis. Some identified biomarkers are used as indicators of the source of origin of sample organic matter, depositional environment and thermal maturity of oil samples. Some of these biomarkers are:

- Compounds 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene; 1,2,9-trimethyl-1,2,3,4tetrahydropicene; 2,7-dimethyl-1,2-(isopropylpenteno)-1,2,3,4-tetrahydrochrysene and dinorursa-1,3,5 (10), 13 (18) -tetraene potential as an indicator of the source of organic material from the Angiosperm plant . Besides that, it is also found biomarker chrysene as an indicator of bacterial input on the formation of organic compounds in oil samples.
- Biomarker 1,3,7 + 2,6,9 + 2,7,9-TMP, 3-MC and 2-MC as mature indicators of the Tarakan Basin oil, making it possible to optimize oil production.
- The presence of DMP, TMP and chrysene biomarkers indicates terrestrial and marine depositional environments.

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REFERENCES

[1] Yudiartono, A. Anindhita, Sugiyon, Wahid, and Adiarso, *Outlook Energi Indonesia 2018*. Jakarta: BPPT, 2018.
[2] C. Stanford, *The Coal Handbook: Towards Cleaner Production*. Queensland: Woodhead Publishing Limited, 2013.
[3] D. Ewart and R. Vaughn, *The Indonesian thermal coal industry*. 2009.
[4] M. C. Friederich, R. P. Langford, and T. A. Moore, "The geological setting of Indonesian coal deposits," *AusIMM Proc.*, vol. 304, pp. 23–29, 1999.
[5] H. E. Belkin, J. T. Susan, C. H. James, J. D. Stucker, and J. M. K. O'Keefe, "Geochemistry and petrology of selected coal samples from Sumatra, Kalimantan, Sulawesi, and Papua, Indonesia," *Int. J. Coal Geol.*, vol. 77, pp. 260–268, 2009.
[6] Y. Zetra, "The Role of Brown Coal's Organic Geochemistry Characteristic in Coal Liquefaction," Sepuluh Nopember Institute of Technology, 2016.
[7] Y. Zetra, I. B. Sosrowidjojo, and R. Y. P. Burhan, "Aromatic biomarker from brown coal, Sangatta Coalfield, East Borneo of Middle Miocene to Late Miocene age," *J. Teknol.*, vol. 78, no. 6, pp. 229–238, 2016.
[8] Y. Zetra, I. B. Sosrowidjojo, and R. Y. P. Burhan, "Paleoenvironment of Brown Coal from Sangatta Coal mines, East Borneo, Indonesia," *J. Teknol.*, vol. 78, no. 7, pp. 121–129, 2016.
[9] Y. Zetra, H. S. Kusuma, F. Riandra, and I. B. Sosrowidjojo, "The oxygenated biomarker as an indicator of origin and maturity of Miocene Brown Coal Sangatta Coal mines, East Kalimantan," *Indones. J. Geosci.*, vol. 5, no. 2, pp. 105–116, 2018.
[10] H. Amijaya and R. Littke, "Properties of thermally metamorphosed coal from Tanjung Enim Area, South Sumatra Basin, Indonesia with special reference to the coalification path of macerals," *Int. J. Coal Geol.*, vol. 61, pp. 195–221, 2005.
[11] H. Amijaya, J. Schwarzbauer, and R. Littke, "Organic geochemistry of the Lower Suban coal seam, South Sumatra Basin, Indonesia: palaeoecological and thermal metamorphism implications," *Org. Geochem.*, vol. 37, pp. 261–279, 2006.
[12] S. Widodo, A. Bechtel, K. Anggayana, and W. Püttmann, "Reconstruction of floral changes during deposition of the Miocene Embalut coal from Kutai Basin, Mahakam Delta, East Kalimantan, Indonesia by use of aromatic hydrocarbon composition and stable carbon isotope ratios of organic matter," *Org. Geochem.*, vol. 40, pp. 206–218, 2009.
[13] W. Püttmann and H. Villar, "Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene," *Geochim. Cosmochim. Acta*, vol. 51, no. 11, pp. 3023–3029, 1987.
[14] M. F. Romero-Sarmiento, A. Riboulleau, M. Vecoli, and G. Versteegh, "Aliphatic and aromatic biomarkers from Gondwanan sediments of Late Ordovician to Early Devonian age: An early terrestrialization approach," *Org. Geochem.*, vol. 42, no. 6, pp. 605–617, 2011.
[15] M. Radke and H. Willsch, "Extractable alkyldibenzothiophenes in Posidonia Shale (Toarcian) source rocks: Relationship of yields to petroleum formation and expulsion," *Geochim. Cosmochim. Acta*, vol. 58, no. 23, pp. 5223–5244, 1994.
[16] J. Schwarzbauer, R. Littke, and V. Weigelt, "Identification of specific organic contaminants for estimating the contribution of the Elbe River to the pollution of the German Bight," *Org. Geochem.*, vol. 31, no. 12, pp. 1713–1731, 2000.
[17] W. Orem and R. Finkelman, *Coal Formation and Geochemistry. In: K. Turekian, H. Holland, Treatise on Geochemistry*, 2nd ed. Amsterdam: Elsevier Ltd, 2013.
[18] J. Smith, S. George, and B. Batts, "The geosynthesis of alkylaromatics," *Org. Geochem.*, vol. 23, no. 1, pp. 71–80, 1995.
[19] K. Stojanović, B. Jovančićević, G. Pevneva, J. Golovko, A. Golovko, and P. Pfendt, "Maturity assessment of oils from the Sakhalin oil fields in Russia: Phenanthrene content as a tool," *Org. Geochem.*, vol. 32, no. 5, pp. 721–731, 2001.
[20] J. Tuo and R. Philp, "Saturated and aromatic diterpenoids and triterpenoids in Eocene coals and mudstones from China," *Appl. Geochemistry*, vol. 20, no. 2, pp. 367–381, 2005.
[21] A. Armstroff, H. Wilkes, J. Schwarzbauer, R. Littke, and B. Horsfield, "Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age," *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, vol. 240, pp. 253–274, 2006.
[22] O. Sonibaire, T. Hoffmann, and S. Foley, "Molecular composition and chemotaxonomic aspects of Eocene amber from the Ameki Formation, Nigeria," *Org. Geochem.*, vol. 51, pp. 55–62, 2012.

[23] M. Fabiańska and S. Kurkiewicz, "Biomarkers, aromatic hydrocarbons and polar compounds in the Neogene lignites and gangue sediments of the Konin and Turoszow Brown Coal Basins (Poland)," *Int. J. Coal Geol.*, vol. 107, pp. 24–44, 2013.
[24] K. Anggayana, "Mikroskopische und organisch-geochemische Untersuchungen an Kohlen aus Indonesien, ein Beitrag zur Genese und Fazies verschiedener Kohlenbecken," RWTH Aachen University.
[25] S. Lu and I. Kaplan, "Diterpanes, triterpanes, steranes and aromatic hydrocarbons in natural bitumens and pyrolysates from different mimic coals," *Geochim. Cosmochim. Acta*, vol. 56, no. 7, pp. 2761–2788, 1992.
[26] A. Borrego, C. Blanco, and W. Puttmann, "Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain," *Org. Geochem.*, vol. 26, pp. 219–228, 1997.
[27] S. Killops and V. Killops, *Introduction to Organic Geochemistry*, 2nd ed. Carlton: Blackwell Publishing, 2005.
[28] R. Alexander, R. Kagi, R. Singh, and I. B. Sosrowidjojo, "The Effect Of Maturity On The Relative Abundances Of Cadalene And Isocadalene In Sediments From The Gippsland-Basin, Australia," *Org. Geochem.*, vol. 21, no. 2, pp. 115–120, 1994.
[29] M. Strachan, R. Alexander, and R. Kagi, "Trimethylnaphthalenes in crude oils and sediments: Effects of source and maturity," *Geochim. Cosmochim. Acta*, vol. 52, no. 5, pp. 1255–1264, 1988.
[30] J. Anderson and J. Müller, "Palynological study of a Holocene peat and a Miocene coal deposit from NW Borneo," *Rev. Palaeobot. Palynol.*, vol. 19, no. 4, pp. 291–351, 1975.
[31] R. Alexander, T. Bastow, R. Kagi, and R. Singh, "Identification of 1,2,2,5-Tetramethyltetralin and 1,2,2,3,4-Pentamethyltetralin as Racemates in Petroleum," *J. Chem. Soc. Chem. Commun.*, vol. 1906, pp. 1712–1714, 1992.
[32] B. Van Aarssen, J. Hessels, O. Abbink, and J. de Leeuw, "The occurrence of polycyclic sesqui-, IS-, and oligoterpenoids derived from a resinous polymeric cadinene in crude oils from southeast Asia," *Geochim. Cosmochim. Acta*, vol. 56, pp. 1231–1246, 1992.
[33] T. Bastow, R. Alexander, and I. B. Sosrowidjojo, "Pentamethylnaphthalenes and related compounds in sedimentary organic matter," *Org. Geochem.*, vol. 28, pp. 585–595, 1998.
[34] R. Hayatsu, R. Winans, R. Scott, L. Moore, and M. Studier, "Trapped Organic Compounds and Aromatic in Coals," *Fuel*, vol. 57, no. 9, pp. 541–548, 1978.
[35] P. Garrigues, R. de Sury, M. Angelin, J. Bellocq, J. Oudin, and M. Ewald, "Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta," *Geochim. Cosmochim. Acta*, vol. 52, no. 2, pp. 375–384, 1988.
[36] M. Escobar, G. Marquez, I. Suarez-Ruis, T. Juliao, and G. Carruyo, "Source-rock potential of the lowest coal seams of the Marcelina Formation at the Paso Diablo mine in the Venezuelan Guasare Basin: Evidence for the correlation of Amana oils with these Paleocene coals," *Int. J. Coal Geol.*, vol. 163, pp. 149–165, 2016.
[37] H. Budzinski, P. Garrigues, M. Radke, J. Connan, and J. L. Oudin, "Thermodynamic calculations on alkylated phenanthrenes: geochemical applications to maturity and origin of hydrocarbons," *H. Budzinski, P. Garrigues, M. Radke, J. Connan, J.L. Oudin*, vol. 20, no. 7, pp. 917–926, 1993.
[38] A. Chaffee and C. Fookes, "Polycyclic aromatic hydrocarbons in Australian coals—III. Structural elucidation by proton nuclear magnetic resonance spectroscopy," *Org. Geochem.*, vol. 12, pp. 261–271, 1988.
[39] H. Villar, W. Puttmann, and M. Wolf, "Organic geochemistry and petrography of Tertiary coals and carbonaceous shales from Argentina," *Org. Geochem.*, vol. 13, pp. 1011–1021, 1987.