PALEOENVIRONMENTAL AND MATURITY INDICATOR OF CEPU BLOCK OIL, WONOCOLO FORMATION, EAST JAVA-INDONESIA
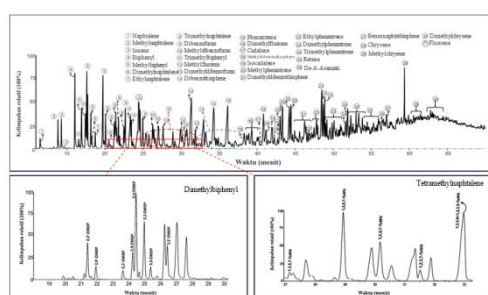
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Graphical abstract

Abstract

Biomarkers identification of aromatic hydrocarbon fraction of Cepu oil samples was carried out to determine the ancient depositional environment, the source of origin and indicators of the maturity of the old well of the Cepu Block oil, Wonocolo Formation, East Java Indonesia. Biomarkers were identified through the Gas Chromatography-Mass Spectroscopy (GC-MS) method. The distribution of aromatic hydrocarbon biomarkers indicates the presence of naphthalene compounds and their derivatives, sesquiterpenoids, diterpenoids and heterocyclic aromatic groups. The presence of identified biomarkers indicates the source of the oil organic compound coming from higher plants Angiosperms. The presence of methyl phenanthrene and aromatic heterocyclic biomarkers such as dibenzothiophene and dibenzofuran, as well as fluorene shows that Cepu Block oil was deposited not only in the terrestrial environment, but also lacustrine and marin under oxidic precipitation conditions. The presence of methyl phenanthrene with MPI value of 0.86 and isocadalene abundance higher than cadalene indicates moderate to high maturity of the Cepu Block oil analyzed.

Keywords: Cepu Block oil, aromatic hydrocarbon, biomarker, paleoenvironment, GC-MS analysis

1.0 INTRODUCTION

The Cepu Block is a major oil-producing region located in Rembang zone, northern East Java-Indonesia Basin [1]. The Rembang zone is represented by hills with anticline domination and hydrocarbon trap structures [2]. These structures were formed due to tectonic activity and changes in the slope configuration of rock layers during the Late Oligocene to Early Miocene period [1]. Hydrocarbons migrated and were trapped until they accumulated at the base of the anticline during the Pliocene-Pleistocene period. The Rembang Zone were composed of ten formations; namely: the Ngimbang, Kujung, Prupuh, Tuban, Ngrayong, Bulu, Wonocolo, Ledok, Mundu, and Lidah formation [1, 2]. The Cepu Block exploration area is divided into five oil fields or wells; namely: Kawengan, Ledok, Nglobo, Semanggi, Wonocolo and one gas field Balun [3].

The Wonocolo oil well is found in the Wonocolo formation which is a well known formation and has

been investigated a lot because of its considerable role in contributing oil products in the northern East Java Basin since the 1940s [4]. However, at present, many old oil wells in Wonocolo field have been abandoned because they are considered to be no longer potential [2, 4]. Even though it is considered to be no longer potential, Wonocolo villagers still continue to conduct oil mining traditionally [2]. Most of the Wonocolo villagers use traditional oil mining as their daily source of income [4]. The increasing need for oil in Indonesia and the limited number of oil wells are urging the government to look for more new oil sources, including reactivation of existing old wells [3]. The Wonocolo oil field is one of the old wells that can possibly be reactivated [5].

This project needs information relating to the quality of oil from the well to see its potential. Organic geochemical data obtained through biomarker analysis provides information of the quality and potential of Wonocolo formation oil. Biomarker analysis provides information on

depositional environments, the origin of organic matter, and the maturity of oil samples [6].

Some studies suggest that Wonocolo formation formed in the Early Miocene - Late Miocene period relates to marine depositional environment [7, 8]. This is proved by an abundance of massive carbonates rich in fossils of benthic foraminifera (especially *Cycloclypeus annulatus*), small corals, red algae, and sandy carbonates [2]. Benthic foraminifera included in phylum protozoa associates with marine environmental conditions in which their amount was abundant during the Middle Miocene - Late Miocene [7]. The presence of marine biota fossils in the Wonocolo formation may relate to a shift in the Eurasian, Indian and Australian plates during Cenozoic period [9]. This shift caused tectonic movements which led to the formation of longitudinal slits in the East Java Basin. In the Eocene to Early Oligocene period, there was a movement of sea water [10] and flooded the land surface in the Cepu area. Many marine carbonates were dominated by corals, algae and other marine biota accumulated in the East Java Basin since the occurrence [7].

However, there are also several studies linking the Wonocolo formation with the previous Ngimbang formation formed since the Late Eocene. The Ngimbang formation is predicted to be an important hydrocarbon source in the East Java Basin regional stratigraphy. This formation supports the input of organic matter deposited on lacustrine and delta environments [1, 11]. Other predictions have been published regarding the well known organic matter in Miocene period. The Miocene period was dominated by Angiosperm plants and few conifers [12, 13, 14]. This is proven by several previous studies which found aromatic hydrocarbons such as retene, tetrahydroretene, simonellite, and some tricyclic diterpenoids in oil and coal as coniferous organic material indication [13, 15]. Naphthalene derivatives and sesquiterpenoid group such as cadalene were also found abundantly in some Miocene period oil and condensate samples. These biomarkers were used as indicators of high level terrestrial organic matter, especially Angiosperms [12, 14, 15, 16]. Heterocyclic aromatic compounds such as dibenzothiophene, dibenzofuran and fluorene have been applied as indicators of terrestrial and marin depositional environments and the level of maturity deposited in the Early Miocene - Late Miocene period [17, 18].

This paper discusses aspects of the organic geochemistry of Cepu Block oil including the origin of organic matter, the depositional environment and its maturity so that the potential of Cepu block old oil wells could be known.

2.0 METHODOLOGY

Oil samples were taken from the location of the old Cepu block oil well in the Wonocolo-East Java-Indonesia formation. Oil is separated from water by a centrifuge. Then the oil is separated from malten and asphalten using excess n-hexane solvent [19].

Malten obtained was fractionated by a silica gel column chromatography GF$_{254}$ with a solvent gradient method to separate the aliphatic, aromatic and polar hydrocarbon fractions. The aliphatic hydrocarbon fraction was obtained with n-hexane solvent, aromatic hydrocarbon fraction with dichloromethane and polar fraction with methanol [20, 21, 22]. The aromatic hydrocarbon fraction is desulfurized using Cu powder, then it is identified by the gas chromatography - mass spectroscopy (GC-MS) method. This paper only discusses the aromatic hydrocarbon fraction existing in the analyzed Cepu oil samples.

The GC-MS used in this research is Agilent GCMSD 5975C GCMS with HP-5MS column type (60 μm x 250 μm x 0.33 μm). The carrier gas is helium (He) with a flow velocity of 1 mL/min. An aromatic fraction sample of 1μL was injected into the GCMS instrument. Column temperature was 70 °C at first (held for 1 minute), raised to 100 °C (rate of increase was 10 °C/minute), then raised again to 180 °C (rate of increase was 1 °C/minute). Final raised temperature was 300 °C approximately (rate of increase for 30 minutes [22].

3.0 RESULTS AND DISCUSSION

Identification of the aromatic hydrocarbons in Cepu oil sample is based on specific fragmentograms through fragmentation reactions and comparison of mass spectra obtained with previously published data [23-27]. The results obtained in TIC (Total Ion Chromatogram) with groups of compounds can be seen in Figure 1. Based on the obtained TIC, Cepu oil sample from Wonocolo formation consists of naphthalene derivatives (naphthalene, methyl naphthalene, dimethyl naphthalene, trimethyl naphthalene, and tetramethyl naphthalene), sesquiterpenoid groups (ionene, cadalene, and isocadalene), diterpenoid groups (retene, phenanthrene, methyl phenanthrene, dimethyl phenanthrene, and trimethyl phenantrene), heterocyclic aromatic groups (dibenzothiophene and dibenzofuran), fluorene, biphenyl, and chrysene. Based on the total ion chromatogram (TIC) as shown in Figure 1, it can be seen that the dimethyl naphthalene compound is the highest amount, while the lowest amount is represented by the ionene compounds.

3.1 Naphthalene Derivatives

The naphthalene derivatives in Cepu oil from Wonocolo formation were identified based on *m/z* 128, 142, 156, 170 and 184 fragmentogram, as well as comparison of mass spectrum data obtained with mass spectrum data published previously [28-36]. The presence of naphthalene and its derivatives are identified as naphthalene, methyl naphthalene (MN), dimethyl naphthalene (DMN), trimethyl naphthalene (TMN), and tetramethyl naphthalene (TeMN). The presence of naphthalene compounds and their derivatives provides information relating to the source of organic matter [6, 36], the level of thermal maturity [30, 32] and the

depositional environment [32, 33] of petroleum samples. Naphthalene and its derivatives originate from the β-amirin precursors found abundantly in higher plants, especially Angiosperms [6, 29, 32, 36]. Methyl naphthalene (MN) were identified based on *m/z* 142 fragmentogram, showing the presence of 2-MN and 1-MN [27, 32] in which the amount of 2-MN is higher than 1-MN. The 2-MN which is substituted for methyl group in β-position has a higher level of stability than 1-MN substituted for methyl group in the α-position [30, 37].

Therefore, the high amount of 2-MN relative to 1-MN in Cepu oil sample, indicates oil maturity [32]. However, this indication of Cepu oil maturity cannot be reviewed based only on 2-MN and 1-MN only, but it is necessary to discuss the presence of other biomarkers in the analyzed sample. Dimethyl naphthalene (DMN) and ethyl naphthalene (EN) were identified based on *m/z* 156 fragmentogram. DMN were identified as 2,6-DMN; (1,3 + 1,7)-DMN; 1,6-DMN; (2,3 + 1,4)-DMN and 1,5-DMN. Whereas EN was identified as 2-EN with very low intensity [30, 35]. The 1,6-DMN distribution seems to dominate compared to the others. High-stability isomers such as 2,6-DMN [32] have lower amount than 1,6-DMN. Whereas isomers with low stability such as 1,5-DMN have the least abundance compared to other DMN isomers. The high amount of 1,6-DMN is caused by abundance of organic material input. 1,6-DMN originates from aromatization of polycadinene resins at the catagenesis stage together with cadalene [6]. Thus, high amount of 1,6-DMN compounds may associate with high amount of cadalene. However, the presence of cadalene in Cepu oil sample identified through a fragmentogram *m/z* 183 was very low. The low amount of cadalene due to isomerization results in isocadalene with a more stable structure. The high amount of isocadalene from cadalene indicates the high maturity of the analyzed Cepu oil [32]. The low intensity of cadalene is due to cracking at high temperatures releasing isopropyl group from cadalene structure then forming 1,6-DMN with high intensity. As a result, the amount of cadalene decreases meanwhile the amount of 1,6-DMN became higher [37]. Polycadinene resins which become precursors for 1,6-DMN and cadalene are found in higher plant resin so this indicates the source of terrestrial organic input [39, 49].

Trimethyl naphthalene (TMN) was identified based on *m/z* 170 fragmentogram and showed the presence of 1,3,7-TMN compounds; 1,3,6-TMN; (1,4,5 + 1,3,5)-TMN; 2,3,6-TMN; 1,2,7-TMN; 1,6,7-TMN; 1,2,6-TMN; and 1,2,5-TMN [33,35]. The presence of TMN determines the organic source matter and depositional environment condition [6, 29]. From the all TMN isomers, 1,2,7-TMN has the highest amount followed by 1,6,7-TMN and 1,2,5-TMN. The presence of 1,2,5-TMN and 1,2,7-TMN in oil sample is an indicator of organic material input coming from the degradation of oleanane-type triterpenoid in higher plants, especially Angiosperms [29, 35]. Both of these compounds also show that oil deposition environment took place under oxidic conditions [33].
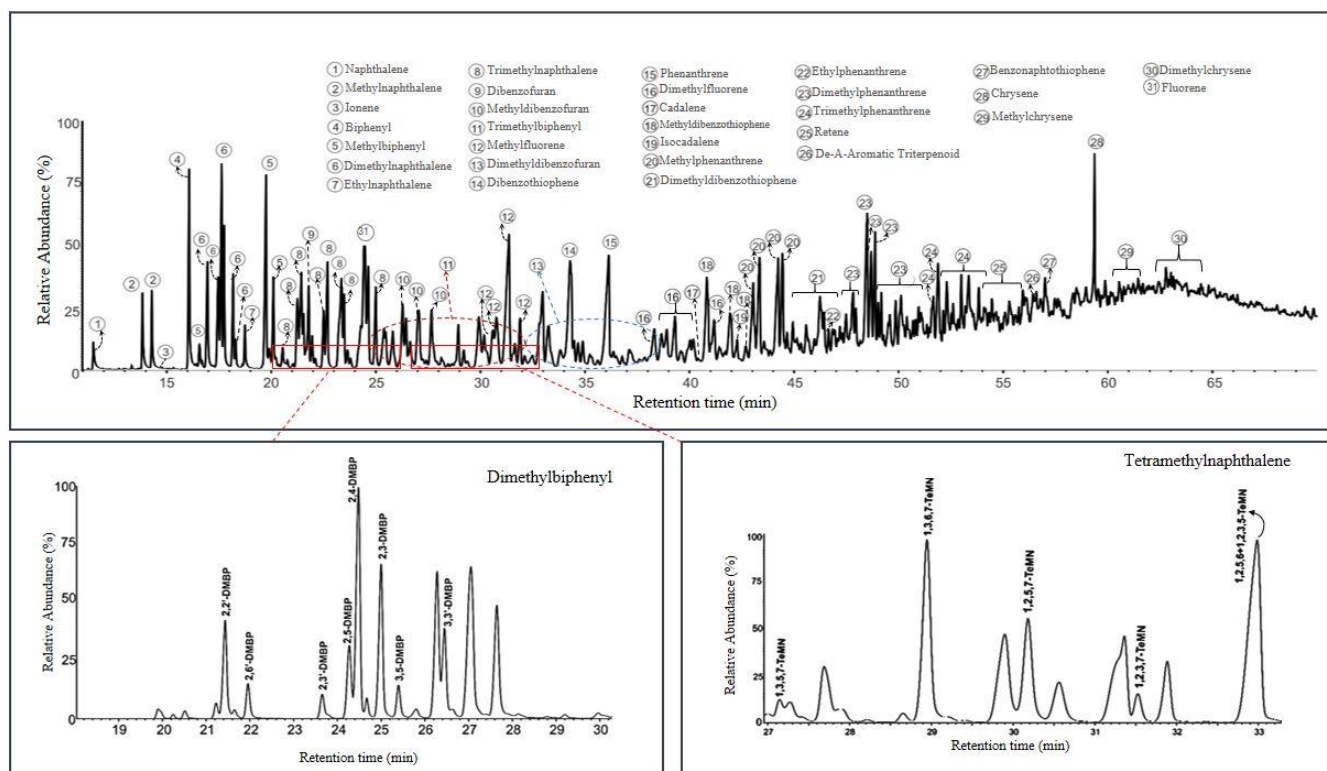
Figure 1 Total ion chromatogram (TIC) of aromatic hydrocarbon fraction showing the distribution of aromatic hydrocarbon compounds. Condition: GCMS Agilent 5975C. Program setting: isothermal temperature of 70°C for 1 minute, increase the temperature up to 100°C at a rate of 10°C/minute, 100°C -180 °C at a rate of 1°C/minute, and the temperature was raised again to 300 °C at a rate of 5 °C/minute, held isothermal for 20 minutes

The intensity of tetramethyl naphthalene (TeMN) in Cepu oil sample is lower than other naphthalene derivatives. The TeMN was identified based on the m/z 184 fragmentogram, showing the presence of 1,3,5,7-TeMN; 1,3,6,7-TeMN; 1,2,5,7-TeMN; 1,2,3,7-TeMN and (1,2,5,6 + 1,2,3,5)-TeMN [43]-[46]. The presence of 1,2,5,6-TeMN biomarker has the highest amount followed by 1,3,6,7-TeMN in very small intensity differences. The 1,2,5,6-TeMN biomarker is an α-substitution isomer, while 1,3,6,7-TeMN is an β-substitution isomer. Methyl group at β-position is more stable at high temperatures than α-position so the presence of 1,3,5,7-TeMN which is slightly lower than 1,2,5,6-TeMN indicates oil maturity. It is suggested that 1,2,5,6-TeMN was formed from aromatization process of β-amirin compounds coming from Angiosperms and bacterial input [38]. Other naphthalene derivatives were identified based on the m/z 183 fragmentogram showing the presence of cadalene and isocadalene. Both of these compounds are commonly found in petroleum and coal samples as an indicator of organic material sources and thermal maturity [13, 36, 38, 39].

Cadalene together with 1,6-DMN are the two compounds formed from polycadinene polymerization which is found abundantly in resin from Dipterocarpaceae plants of Angiosperms [13, 38]. The cadalene shows lower intensity than isocadalene. Isocadalene is produced through isomerization of cadalene at high temperatures [38]. The experiments in laboratory prove that cadalene found abundantly in petroleum samples can be converted to isocadalene by heating oil in aluminum at a certain temperature. This process results in the abudance of isocadalene which is higher than cadalene. This experiment proves that the structure of isocadalene which is more stable than cadalene may only be found abundantly in the mature oil samples [29]. Therefore, the high intensity of isocadalene compared to cadalene shows a high maturity of Cepu oil sample.

The other naphthalene derivatives was identified as ionene based on m/z 159 fragmentogram [15, 36, 40]. The existence of this compound is not specific, because it could be formed through carotenoid [41] and labdane degradation which are the main components of conifers resin in the oxidative environment [42, 43]. Therefore, the presence of ionene can not be used as a geochemical indicator because its basic structure has undergone a change during the oxidation reaction at the diagenesis stage [44].

3.2 Phenanthrene Derivatives

The phenanthrene derivatives were identified based on m/z 178 fragmentogram, m/z 192 as methyl phenanthrene, m/z 206 as dimethyl phenanthrene and m/z 220 as trimethyl phenanthrene. These compounds were identified by comparing fragmentation and mass spectrum data to data that has been published by previous researchers [31, 36, 37, 41, 44]. Phenanthrene and alkyl phenanthrene belong to diterpenoid triaromatic group [12]. Diterpenoids compounds are commonly found in higher plant resins, especially Gymnosperms [12, 24]. However, this compound can also be found in Angiosperms, such as Burseraceae [41].

Methyl phenanthrene (MP) was identified based on m/z 192 fragmentogram showing the presence of 3-MP; 2-MP; 9-MP and 1-MP in sequence with four typical peaks. The presence of methyl phenanthrene (MP) together with phenanthrene is commonly used as an indicator of the maturity of oil and coal samples through the β/α ratio [6]. Methyl group in the β-position is more stable than the α-position [37]. So an increase in the β/α ratio can be an indication of oil or coal maturity [45, 46]. The 9-MP and 1-MP are isomers with methyl groups in the α-position while 2-MP and 3-MP are isomers to methyl groups in the β-position [32]. The abundance of 9-MP and 1-MP is not too significant compared to 2-MP, so the presence of 9-MP; 1-MP; 2-MP and 3-MP compounds do not specifically describe the maturity level of Cepu oil sample.

Besides using the β/α ratio, the methyl phenanthrene index (MPI) can also be used to determine the level of maturity of the analyzed sample. MPI serves as a more accurate complementary data for determining the maturity level of petroleum samples [47, 48]. There are three parameters of maturity according to MPI analysis, namely $MPI_1 = [1.5 \times (2\text{-}MP + 3\text{-}MP) / (P + 1\text{-}MP + 9\text{-}MP)]$ [46,48]; $MPI_2 = [3 \times (2\text{-}MP)] / [(P) + (1\text{-}MP) + (9\text{-}MP)]$ [35]; and $MPI_3 = [(2\text{-}MP + 3\text{-}MP) / (1\text{-}MP + 9\text{-}MP)]$ [47]. The MPI calculations focus on the peak chromatogram area of each phenanthrene and four homologous methyl phenanthrene [48, 49]. Based on the value of MPI_3, the maturity level of the sample can be determined directly, as the calculation of MPI_3 is more easily applied. Based on the MPI_3 calculations on Cepu oil samples, a value of 0.86 is obtained indicating oil with moderate to high maturity.

The presence of MP provides information on the depositional environment. In Cepu oil sample, it was found that 9-MP has the higher amount than 1-MP followed by 2-MP. These three MP isomers provide a contrasting depositional environment implication. The 9-MP is a typical biomarker of marine environment. Whereas 1-MP and 2-MP are typical of lacustrine and terrestrial environment [45, 50]. Therefore, the discovery of 3-MP; 2-MP; 9-MP and 1-MP can be seen on the chromatogram in Figure 2 with almost similar intensity, showing possibility of marine, lacustrine and terrestrial depositional environment. This is the uniqueness of Cepu Block oil deposition environment [1, 7].

Dimethyl phenanthrene (DMP) in Cepu oil sample was identified based on m/z 206 fragmentogram. Identification of molecular structure was conducted by comparing fragmentogram data and mass spectrum to data that had been published by previous researchers [36, 45, 51]. The distribution of DMP shows the presence of 3,6-DMP; 2,6-DMP; 2,7-DMP; (1,3 + 2,10 + 3,9 + 3,10)-DMP; (1,6 + 2,9)-DMP; 1,7-DMP; 2,3-DMP; (1,9 + 1,4)-DMP; 1,8-DMP and 4,5-DMP as seen in the chromatogram Figure 3. In addition, ethyl phenanthrene compounds are also seen (EP) with

very low intensity. The DMP methyl groups substituted in C9 and C10 which is (1,3 + 2,10 + 3,9 + 3,10)-DMP shows the highest amount in Cepu oil sample, as reported by researchers before [45,52]. Methyl-substituted DMP at position C9 and C10 are an indicator of marine environment, similar to the case of 9-MP [45]. The low amount of 1,7-DMP (pimanthrene) produced through pimaric acid precursors in terrestrial plant resins compared to (1.3 + 2.10 + 3.9 + 3.10)-DMP, indicates the source of organic compounds originating from the environment marine and terrestrial environment. This data supports the assumption that Cepu oil organic compounds are deposited in terrestrial and marine environment.

Trimethyl phenanthrene (TMP) was identified based on *m/z* 220 fragmentogram showing the presence of (1,3,6 + 2,6,10 + 1,3,10-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; (1,2,7 + 1,2,9)-TMP and 1,2,8-TMP. These can be seen on the chromatogram in Figure 4 [37,45,53]. The presence of TMP is an indicator of organic source matter and maturity [45, 54]. The TMP isomer will be stable if the methyl group is substituted in the βββ-position such as 2,3,6-TMP and the αββ-position like 2,6,9-; 2,6,10-; 2,7,9-; 1,3,6- and 1,3,7-TMP [45]. Stable subsituents are found abundantly in terrestrial environment oil [33, 37, 53]. The TMP isomer with αββ-subsituents such as (1,3,7 + 2,6,9 + 2,7,9)-TMP seems having a higher intensity compared to other isomers. While TMP isomers with low stability such as 1,6,9-TMP; 1,7,9-TMP and 1,3,8-TMP indicating marine environment show a slightly lower abundance compared to 1,3,7 + 2,6,9 + 2,7,9-TMP. This shows that not only terrestrial environment, but also the marine environment can affect the Cepu Block oil deposition environment [33].
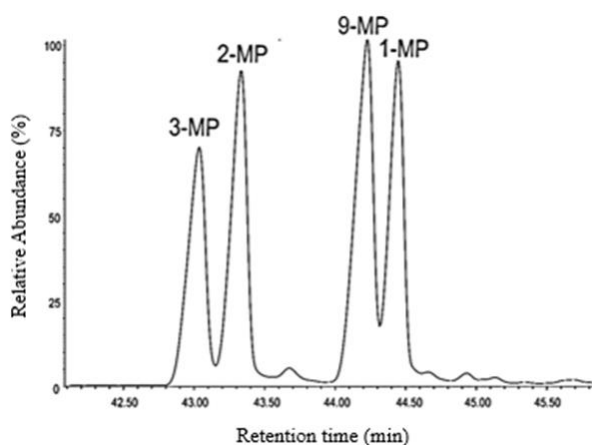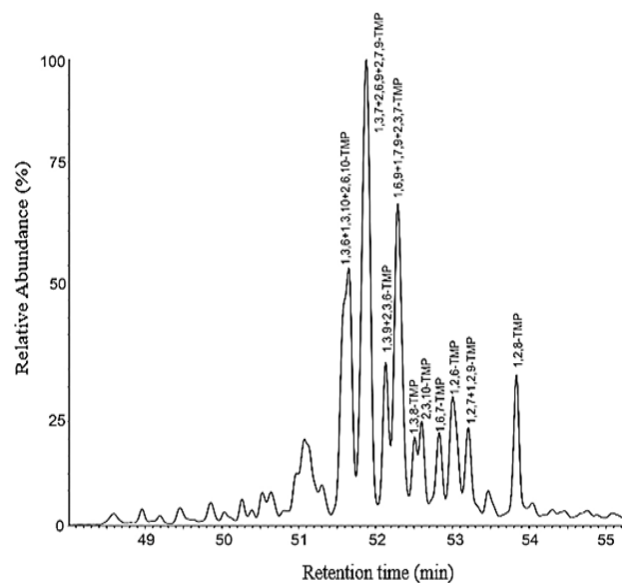

Figure 2 Fragmentogram at *m/z* 192 showing the distribution of MP

Another phenanthrene derivative was identified in Cepu oil as retene with low amount. Retene was identified based on the *m/z* 234 fragmentogram deriving from abietic acid found abundantly in Gymnosperms coniferous plants [36]. Abetic acid gradually aromatizes in line with temperature increase, resulting in dehydroabietane, simonellite

and retene [32, 36]. Therefore the low amount of retene in mature Cepu oil samples, indicates a little input of Gymnosperms in the formation of organic compounds in analyzed oil samples [28, 31, 32, 55].
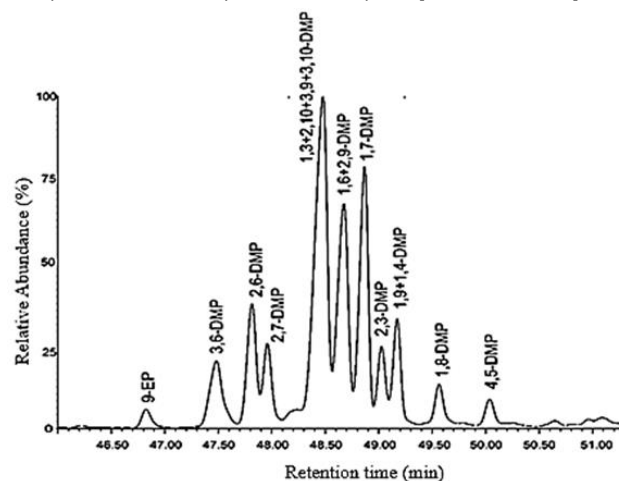
Figure 3 Fragmentogram at *m/z* 206 showing the distribution of EP dan DMP

Figure 4 Fragmentogram at *m/z* 220 showing the distribution of TMP

3.3 Heterocyclic Aromatics

Fluorene (FL), dibenzofuran (DBF) and dibenzothiophene (DBT) are important aromatic heterocyclic compounds in petroleum and organic sediment sample because their presence in significant quantities provides geochemical information [18]. These three compounds exhibit a similar structural framework related to the depositional environment of oil and sediments [39]. The depositional environment of organic compounds in oil formation can be determined through a ternary diagram representing a concentrations comparison among fluorene, DBF and DBT [45]. Fluorene, DBT, and DBF may originate from biphenyl precursor, but were formed in different environment [56, 57]. Fluorene is a typical indicator of the organic sources deposition in

deltaic, estuary or river estuaries, fresh water lacustrine, and brackish lacustrine [39, 58], whereas dibenzothiophene (DBT) in oil is originating from marine and saline lacustrine environment [18]. Oil derived from the paludal facies and coal deposit environment is characterized by the dominance of DBF [59].

The amount of DBT and DBF provides another geochemical information, such as an organic source matter and a maturity level [18]. The existence of DBF and its homologues relate to the organic material input from mosses. This is due to mosses as the only organism that produces dibenzofuran compounds through secondary metabolism, likewise, the presence of dibenzothiophene as an indicator of the level of thermal maturity through the substitution of methyl groups such as methyl dibenzothiophene (MDBT) and dimethyl dibenzothiophene (DMDBT) [37].

Subsequent identification of Cepu oil sample showing the presence of fluorene and its derivatives such as methyl fluorene (MF) and dimethyl fluorene (DMF) were identified based on *m/z* 166, 180, and 194 fragmentogram [18, 57]. Dibenzothiophene (DBT). Methyl dibenzothiophene (MDBT) and dimethyl dibenzothiophene (DMDBT) compounds were identified based on fragmentogram *m/z* 184, 198 and 212. Whereas dibenzofuran (DBF), methyl dibenzofuran (MDBF) and dimethyl dibenzofuran (DMDBF) were identified based on *m/z* 168, 182, and 196 fragmentogram [58].

Fluorene was found together with four methyl fluorene (MF) and eight dimethyl fluorene (DMF) biomarkers. MF distribution showed the presence of 3-MF, 2-MF, 1-MF, and 4-MF as seen in the chromatogram in Figure 5 [18, 58] where 1-MF showed the highest amount compared to other isomers. It is suggested that 1-MF was obtained from the cyclization reaction of 2,3-dimethyl biphenyl (2,3-DMBP) and its presence will be more abundant as increasing sample maturity [38]. Thus, the presence of 1-MF which is far more abundant than other MF isomers is an indication of mature Cepu oil. In DMF group, only 1,7-DMF isomers were identified [57]. The presence of fluorene and their homologues indicate the aquatic environment, such as delta, estuary, fresh water lacustrine, and brackish lacustrine depositional environment [58, 60]. The dibenzofuran compound (DBF) is found together with methyl dibenzofuran (MDBF) and dimethyl dibenzofuran (DMDBF). MDBF biomarkers are found as 4-MDBF; (3 + 2) –MDBF and 1-MDBF, while the presence of nine DMDBF isomers has not been identified in Cepu oil samples [18]. The high amount of 4-MDBF and (3 +2)-MDBF compared to other isomers, show an indicator of organic input from terrestrial environment [61]. In addition, DBF, MDBF and DMDBF also indicate mosses organic input [18, 61].

Dibenzothiophene (DBT) was identified based on *m/z* 184 fragmentogram. The presence of DBT was quite abundant in Cepu oil sample as seen in Total Ion Chromatogram (Figure 1). The high abundance of DBT indicates saline water lacustrine and marine depositional environment [18]. In addition, methyl dibenzothiophene (MDBT), ethyl dibenzothiophene (EDBT) and dimethyl dibenzothiophene (DMDBT) were also successfully identified as 4-MDBT; (2 + 3)-MDBT; 1-MDBT based on *m/z* 198 fragmentogram and 4-EDBT; 4,6-DMDBT; 2,4-DMDBT; 2,6-DMDBT; 3,6-DMDBT; 2,8-DMDBT; (2,3 + 3,7)-DMDBT; (1,6 + 1,4)-DMDBT based on *m/z* 212 fragmentogram [18]. The distribution of methyl dibenzothiophene shows that 4-MDBT which is structurally more stable than other isomers is also in the highest amount. The predominance of 4-MDBT is relative to the others, indicating oil maturity. The high intensity of 4,6-DMDBT whose structure is relatively more stable compared to (1,6 + 1,4)-DMDBT as seen in the chromatogram in Figure 6 supports the high maturity of Cepu oil [37].
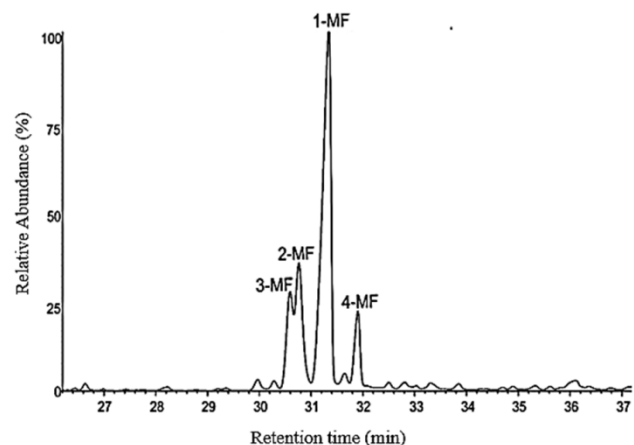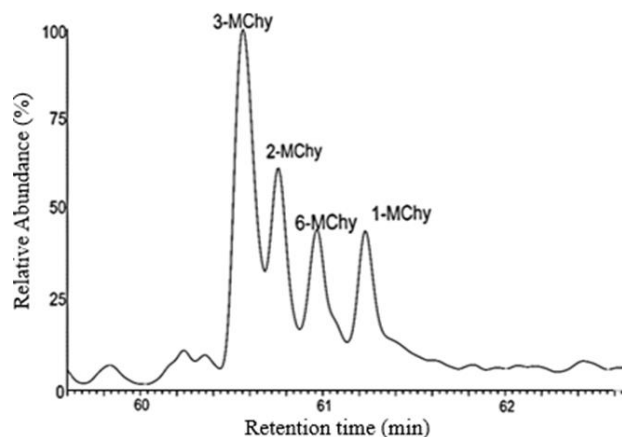

Figure 5 Fragmentogram at *m/z* 180 showing the distribution of MF
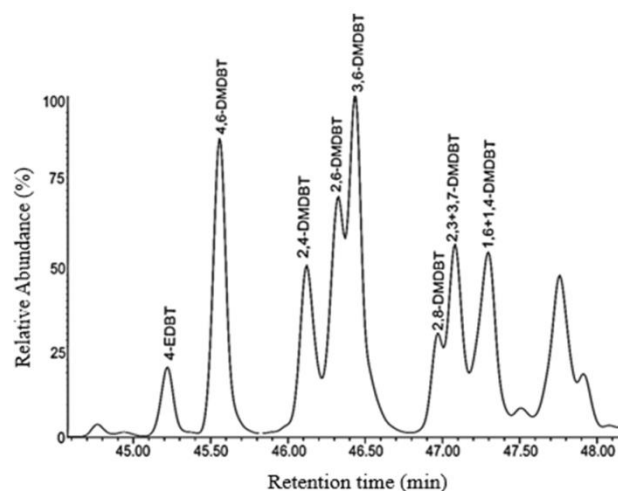
Figure 6 Fragmentogram at *m/z* 212 showing the distribution of EDBT and DMDBT

Other aromatic polycyclic and heterocyclic whose existence was identified in Cepu oil were chrysene and biphenyl. A structure identification was based on a typical *m/z* fragmentogram and mass spectra that have been published by previous researchers [26, 62]. Chrysene (Chy) was identified based on *m/z* 228; methyl chrysene (MChy) based on *m/z* 242 and dimethyl chrysene (DMChy) based on *m/z* 256 fragmentogram. The

identified methyl chrysene was 3-MChy, 2-MChy, 6-MChy, and 1-MChy [62] as seen in Figure 7.

Figure 7 Fragmentogram at m/z 242 showing the distribution of Mchy

Based on the methyl chrysene isomers obtained, 2-MChy and 3-MChy have the highest level of stability and show the highest dominance over other isomers. The dominance of 3-MChy relative to other isomers indicates the high maturity of Cepu oil. In addition, it also detects the presence of five DMChy isomers whose structure has not been identified in this study [62].

Chrysene, derived from pentacyclic triterpene precursors such as α- and β-amyrin, is abundant in the epicuticular wax of terrestrial higher plant through microbial degradation reaction [46]. In addition, alkylated chrysene is a degradation product of hopane through an aromatization reaction at diagenetic stage [63, 64]. Therefore, the presence of chrysene and its alkyl derivatives indicate the organic input from terrestrial higher plant and bacteria. Biphenyl and their alkyl derivatives found as methyl biphenyl (MBP) were identified based on m/z 168 fragmentogram, ethyl biphenyl (EBP) and dimethyl biphenyl (DMBP) based on m/z 182 fragmentogram and trimethyl biphenyl (TMBP) based on m/z 196 fragmentogram. The identification of this compound was done by comparing mass spectrum fragmentation data that have been reported by previous researchers [39, 57]. It is suggested that the abundance of biphenyl compounds relates to the abundance of dibenzothiophene as biphenyl is dibenzothiophene's precursor in nature [57]. Alkyl biphenyl found abundantly in petroleum is derived from lacustrine and marine environment. The presence of alkyl biphenyl provides an indication of Cepu oil high maturity based on stability isomer in terms of substituted methyl group position in biphenyl ring [26].

Another biomarker analysis in Cepu oil shows the presence of methyl biphenyl (MBP) identified as 2-MBP, 3-MBP and 4-MBP based on m/z 168 fragmentogram. This 3-MBP shows the highest intensity compared to other isomers as seen in Figure 8. The 3-MBP with β-position methyl-substituted shows the most stable structure compared to other isomers, so the presence of this compound indicates a high level of oil maturity.
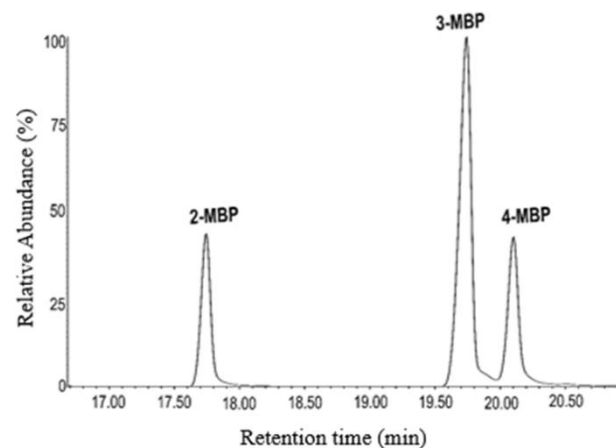
Figure 8 Fragmentogram at m/z 168 showing the distribution of MBP

Whereas, dimethyl biphenyl (DMBP) is identified as 2,2'-DMBP; 2,6'-DMBP; 2,3'-DMBP; 2,5-DMBP; 2,4-DMBP; 2,3-DMBP; 3,5-DMBP; 3,3'-DMBP based on m/z 182 fragmentogram as seen in the Total Ion Chromatogram (TIC) in Figure 1. The presence of 2,4-DMBP in a higher intensity and more stable than the other isomers indicates oil maturity. Likewise, the trimethyl biphenyl compound (TMBP) was identified as 2,4,2'-TMBP; 2,6,3'-TMBP; 2,4,6-TMBP; 2,3,2'-TMBP; (2,5,3'+ 2,5,2')-TMBP; 2,4,3'-TMBP; 3,5,3'-TMBP and 3,4,3'-TMBP based on m/z 196 fragmentogram [26, 39] as seen in Figure 9.
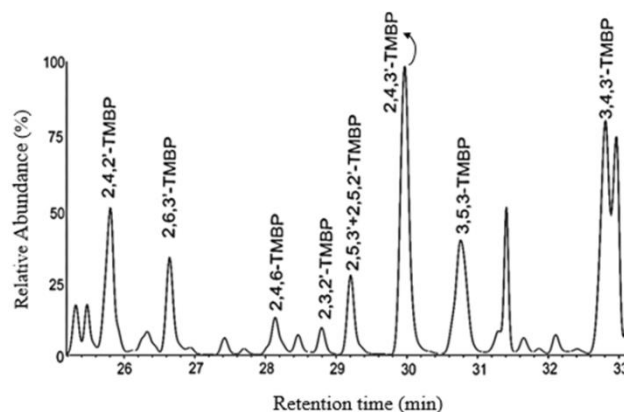
Figure 9 Fragmentogram at m/z 196 showing the distribution of TMBP

The 2,4,3'-TMBP which is more stable and showing the highest amount compared to other isomers also indicates the high level of Cepu oil maturity.

Other compounds identified in Cepu oil were benzonaphtothiophene based on the m/z 234 fragmentogram and de-A-aromatic triterpenoid based on the m/z 306 fragmentogram [15, 41, 59]. One of the identified benzonaphtothiophene isomer is benzo(b)naphto(2,1-d)thiophene with a low intensity. This compound is commonly used as an indicator of oil migration by comparing it to other isomers such as benzo(b)naphto(1,2-d)thiophene or benzo(b)naphto(2,3-d)thiophene [59]. As the presence of these isomers was not identified in the oil sample, the presence of

benzo(b)naphto(2,1-d)thiophene was unable to provide the expected information. However, the presence of triterpenoid de-A-aromatic biomarker identified in Cepu oil indicates organic input derived from higher plant especially Angiosperms [58].

4.0 CONCLUSION

Different types of biomarkers found in Cepu oil provide varied information. Some biomarkers that show organic source input from terrestrial plants, especially Angiosperms are distributed in large quantities. However, some low amount of biomarkers that indicate sources of organic compounds from Gymnosperms and bacteria are also identified in the formation of Cepu oil. The existence of naphthalene (MN, DMN, TMN, TeMN), biphenyl homologous derivatives, and methyl chrysene (MChy) proves the origin source of Angiosperm. The discovery of retene, ionene in low intensity provides information on the presence of a small amount of Gymnosperm plant input in the Cepu oil. In addition, an identification of several biomarkers, such as methyl phenanthrene, dibenzothiophene, dibenzofuran and fluorene shows that the organic compounds of Cepu oil were deposited not only in terrestrial environment, but also in lacustrine and marine environment with oxic conditions. The identification of these biomarkers shows the evidence of the depositional environment uniqueness in Cepu oil formation. Based on biomarkers distribution and supported by the MPI values given, it can be concluded that the Cepu oil taken from Wonocolo formation is mature therefore it still has the potential to be further explored and rejuvenated.

Acknowledgement

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