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Paleoenvironmental and Maturity Indicator of Sawahlunto Coal, Ombilin Basin

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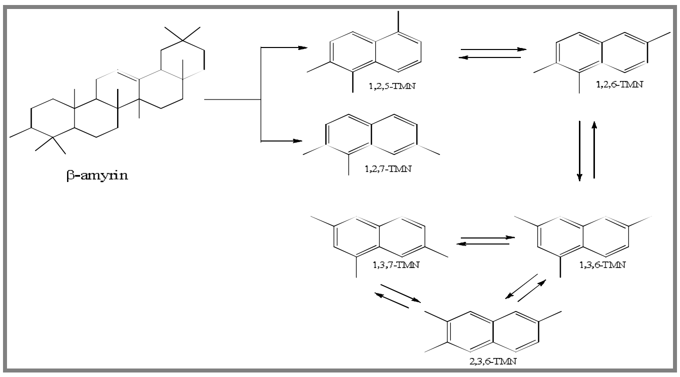
ABSTRACT

Coal geochemical studies of the Eocene Ombilin Basin were conducted through a biomarker analysis. The coal studied came from the Sawahlunto coal, West Sumatra. The coal extract was fractionated by column chromatography and biomarkers of aromatic hydrocarbon groups were identified using gas chromatography-mass spectrometry. The results showed the distribution of naphthalene compounds with sesquiterpenoid skeleton, phenanthrene compounds with diterpenoid skeletons, and aromatic pentacyclic triterpenoid compounds. The presence of sesquiterpenoid and triterpenoid compounds indicates that the organic compounds of coal are derived from the α-/β-amyrin precursors which are abundant in angiosperms and there is a contribution from bacteria. In addition, gymnosperms plants also provide little contribution on the availability of organic material which is indicated by the presence of a little amount of diterpenoid compound. Organic geochemical studies through biomarker analysis indicate that coal is mature and classified as sub-bituminous coal.

Graphical Abstract



Schematic reaction of trimethyl naphthalene isomerization

Keywords: Sawahlunto coal, Organic geochemistry, Aromatic hydrocarbon, GCMS.

INTRODUCTION

Indonesia has more than 60 sedimentary basins with coal deposits scattered on six islands. Most of the sources and reserves are located on the islands of Sumatra and Kalimantan. Indonesia has around 126 billion tons of coal resources with reserves of around 32 billion tons. More than 80% of Indonesian coal is categorized as coal with a low level of maturity (lignite and sub-bituminous) which has very low ash and sulfur levels. Indonesian coal is generally formed during the Early Eocene, including the one deposited in the Ombilin (West Sumatra) and several small basins in Java and South Sulawesi [1-3].

The Ombilin Basin, a small (20 × 60-km) Paleogene onshore basin, is located just west of the much larger Central Sumatra Basin. It contains thick Eocene to Miocene marine and terrestrial sediments that share a similar tectonic and stratigraphic history which is similar to all of the rift basins on Sumatra. The economic coal occurs within the Eocene Sawahlunto formation which is composed of gray mudstone and siltstone and coal seams with minor quartz-rich sandstone. Three coal seams, locally up to 8-m thick, occur in the upper part of the Sawahlunto formation and are the main units mined [4].

The Ombilin or Sawahlunto coal mine, located 57-km northeast of Padang, West Sumatra, is owned by PT Tambang Batubara Bukit Asam (PTBA), and includes both mining and Eocene age coal underground and surface operations. The underground mine uses a longwall retreating system, with semi-mechanized equipment, operated manually, and fully mechanized longwall equipment, hydraulically operated [5].

The Sawahlunto coal mine was first exploited in 1891 with an underground mining system and mining activities have been formally closed since February 2016 because they are considered uneconomical. But in reality, the coal mines that have been closed, are still producing because the Sawahlunto coal generally has a high heat rating. This mining is done traditionally by the people around the mine. The high interest of the community in mining activities is certainly a special attraction for the study of organic geochemistry through biomarker analysis of Sawahlunto coal. Organic geochemical studies include paleo environment of coal, the source of the origin of coal organic compounds and the maturity of coal.

Rresearch in organic geochemistry have carried out biomarker analysis of aliphatic, aromatic, ketone, alcohol, acid and other polar fraction of several coals with different heat ratings and different mine locations in Indonesia. Among them, the Inul coal of Sangatta coal mines, East Borneo, the Balikpapan formation, aged as old as Middle Miocene to Late Miocene [6-9], Coal Tertiary, Tanjung Enim, South Sumatra Basin [10], Lower Suban, coal seam, South Sumatra Basin [11], and the Miocene Embalut coal from Kutai Basin, Mahakam Delta, East Kalimantan [12]. Aromatic hydrocarbon biomarkers are compounds that are abundant in the sediment as the thermal maturity process increases. Some aromatic biomarkers in sedimentary samples of the Late Ordovician Period-Early Devonian are known to be formed from terrestrial and marine environmental precursors. The terrestrial environmental biomarkers are shown by methyl phenanthrene (MP), dimethyl phenanthrene (DMP), cadalene, retene, simonelitte, and tetrahydroretene compounds [13, 14]. The anoxic environment of sediment formation is indicated by the presence of alkylibenzothiopene [15]. The level of coal maturity is shown by the abundance of naphthalene, phenanthrene and picene derivatives [12]. Through petrography analysis, it shows that Sawahlunto coal is mature and belongs to the high volatile bituminous group [5]. But there has been no organic geochemical study of the Sawahlunto coal to determine the depositional environment and source of origin of coal-forming organic compounds. This paper will examine the aspects of organic geochemistry through biomarker analysis of aromatic hydrocarbon fractions to determine the coal potential of Sawahlunto, Ombilin Basin.

MATERIALS AND METHODS

A total of 50 g of fine Sawahlunto coal samples were extracted for 10 days using Sohxlet equipment with a mixture of acetone, methanol, and chloroform (47/23/30) [11] The concentrated extract of coal obtained was fractionated using silica gel column chromatography based on the method of Schwarzbauer *et al.*[16], to obtain 4 fractions. Fraction 1 eluted with *n*-hexane, fraction 2 with *n*-hexane/dichloromethane (95/5), fraction 3 with *n*-hexane/ dichloromethane (90/10), and fraction 4 with n-hexane/dichloromethane (40/60). This paper only reports the results of fraction 1 biomarker analysis.

Biomarker identification used Hewlett Packard 5890 Series II gas chromatography-mass spectroscopy (GC-MS) equipped with a combination of silica and HP-5 films 30 m x 0.25 mm x 0.25 µm. Gas carried Helium with a flow rate of 1.2 mL min^{-1}. The temperature was programmed at 70°C (1 min), 70°C- 150°C at a rate of 10°C min^{-1}, 150°C-180°C at a rate of 1°C min^{-1}, 180°C-300°C at a rate 5°C min^{-1}, isothermal temperature at 300°C for 7 min.

The mass spectrometer was operated with Hewlett Packard 5972 Series Mass Selective Detector with 70 eV electron energy.

RESULTS AND DISCUSSION

Classification of Sawahlunto Coal: The calorific value test using the calorimeter bomb against the Sawahlunto coal sample showed a calorific value of 7472 calories g^{-1} means that the coal is classified as sub-bituminous rank [17], in which the coal goes to mature process (medium).

Identification of Aromatic Biomarkers: Biomarker of aromatic hydrocarbon fraction of Sawahlunto coal was identified based on specific fragmentograms, (example: Widodo *et al.*[12], Romero-Sarmiento *et al.* [14], Smith *et al.*[18], Stojanovic *et al.*[19], Tuo and Philp [20], Armstroff *et al.*[21], Sonibaire *et al.*[22], Fabianska and Kurkiewicz [23]). Identified aromatic compounds consisted of naphthalene groups with sesquiterpenoid skeletons, phenantrene with diterpenoid skeletons and pentacyclic triterpenoid compounds, as seen in figure 1. Steroid compounds were not found in Sawahlunto coal samples. The absence of aromatic steroid compounds was also in accordance with Amijaya *et al.* [11] Anggayana [24] and on several coal Tertiary Periods in Indonesia. Steroid compounds which are not found in coal are caused by the unchanging organic compound precursors into sterane and sterene [25].

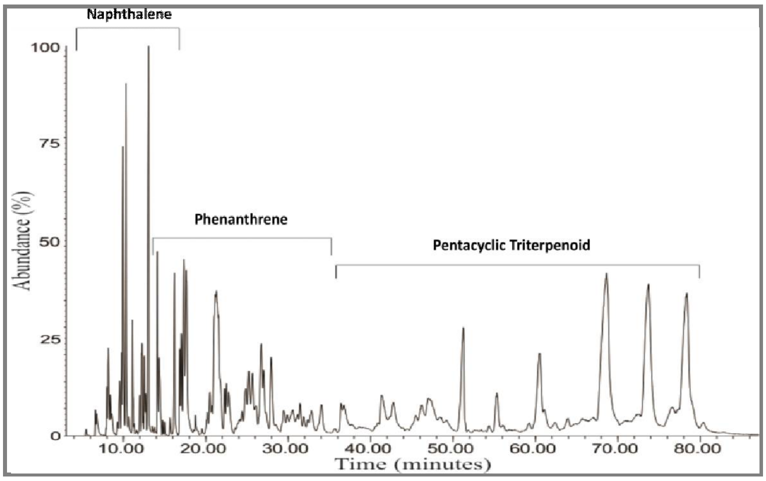


Figure 1. The gas chromatography-mass spectrometry (GC-MS) of the total ion chromatograms (TIC) of the aromatic hydrocarbon fractions which shows the distribution of aromatic hydrocarbon compounds.

Biomarker of Naphthalene Group: The presence of naphthalene compounds was identified based on specific fragmentograms at *m/z* 128, methylnaphthalene, MN (*m/z* 142), dimethyl naphthalene, DMN (*m/z* 156), trimethyl naphthalene, TMN (*m/z* 170), tetramethyl naphthalene, TeMN (*m/z* 184), and pentamethyl naphthalene, PMN (*m/z* 198). Chromatogram analysis of methylnaphthalene peak (*m/z* 142), indicates the presence of 1-methylnaphthalene (1-MN) and 2- methylnaphthalene (2-MN) compounds. The peak intensity of 2-MN is higher than that of 1-MN which shows coal with medium maturity. 2-MN intensity higher than 1-MN (Figure 2) is also found in the coal samples studied by Armstroff *et al.* [21] and Borrego *et al.* [26]. The maturity of a coal can be shown by the high intensity of an isomer against another isomer. The higher the intensity of the isomer structure, which is more stable than the less stable one, the higher the maturity of the coal will be. Compound 2-MN where the methyl group is substituted at the β-position is more stable than 1-MN substituted at the α-position of the naphthalene ring [27].

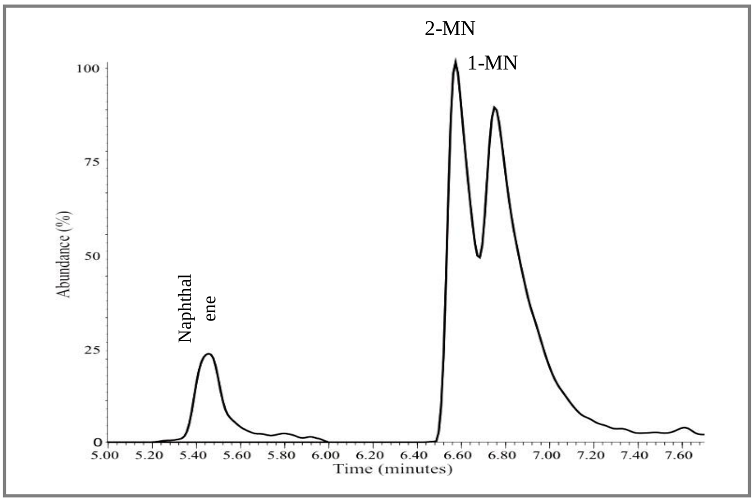


Figure 2. Distribution of naphthalene (*m/z* 128) and methylnaphthalene (*m/z* 142)

Coal maturity can also be shown by the presence of dimethyl naphthalene (DMN) compounds identified based on fragmentograms *m/z* 156 (Figure 3). The high intensity of the peak 1,6-DMN compared to 2,6+2,7-DMN and 1,3+1,7-DMN indicates the maturity of the coal medium. Characteristics of coal with medium maturity are also reported by Alexander *et.al.* [28] where the abundance of 1,6-DMN isomers which are less stable is higher than that of 1,3- and 1,7-DMN which are more stable. This shows that coal does not have high maturity.

The presence of the 1,2,7-TMN compound identified based on the *m/z* 170 fragmentograms (Figure 4) shows the source of the coal organic compound derived from the abundant β-amyrin precursor in the angiosperm plant. Pentacyclic triterpenoid compounds with oleane skeleton (β-amyrin) degraded to produce 1,2,5-TMN and 1,2,7-TMN as reported by Strachan *et al.* [29]. Besides that, 1,2,5-TMN compounds can also be derived from diterpenoids such as agatic acid in conifer plants through aromatization reactions [21]. The vegetation of several coniferous plant genera such as *Dacrydium*, *Podocarpus*, and Burseraceae families in gymnospermae plants is also found in the southwestern peat deposition environment of Kalimantan [30].

The *Dacrydium* genus is also a prominent peat swamp forest in Sumatra, so the presence of 1,2,5-TMN compounds also shows the contribution of gymnospermae plants to the formation of Sawahlunto coal [11]. The peak intensity of 2,3,6-TMN compounds is higher than 1,3,7-TMN and 1,3,6-TMN and the high intensity of 1,2,5-TMN shows the maturity of coal medium.

Coal with medium-high maturity will have a distribution of TMN isomers with methyl groups substituted at the β-position. Isomerization reaction as seen in figure 5 below shows a 1,2,5-TMN compound having a methyl group at a less stable α-position to a more stable 2,3,6-TMN isomer [29].

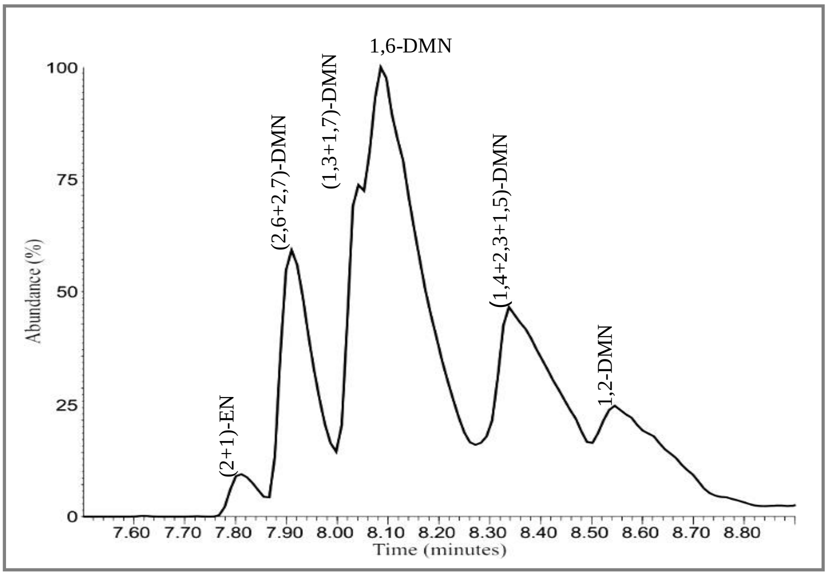


Figure 3. Distribution of dimethylnaphthalene (DMN) based on fragmentograms *m/z* 156.

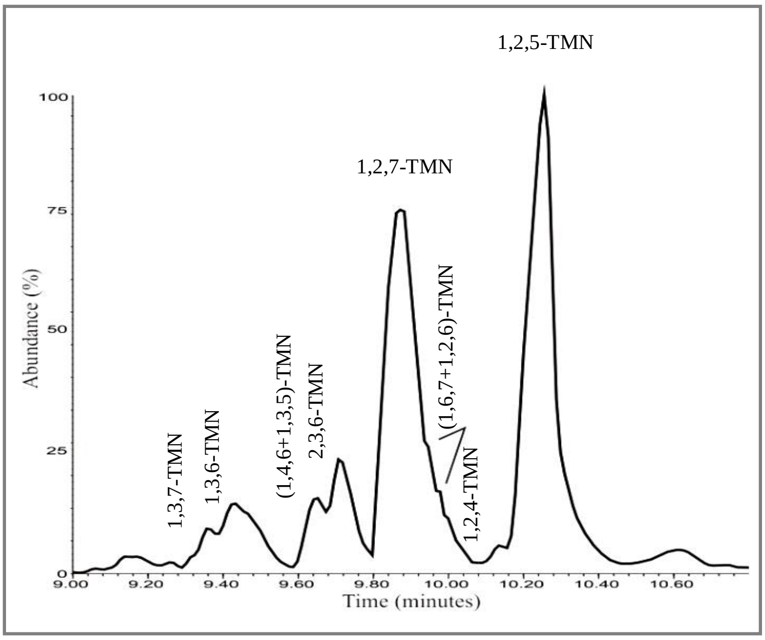


Figure 4. Distribution of trimethylnaphthalene (TMN) based on fragmentograms *m/z* 170.

The 1,2,5,6-TeMN compound identified based on fragmentograms *m/z* 184 in the Sawahlunto coal sample as seen in figure 6 can be produced from the β-amyrin precursor which has been degraded to form the 8,14-secotriterpenoid compound (Figure 6). Beside β-amyrin, secohopane monoaromatic is a precursor for the formation of 1,2,5-TMN and 1,2,5,6-TeMN compounds [13]. The compounds 1,2,6-TMN; 1,2,5,7-TeMN and 1,2,3,5-TeMN identified in the sample, can be formed from 1,2,2,5-tetramethyltetraline and 1,2, 2,5,6-pentamethyltetraline derived from hopanoid precursors [31].

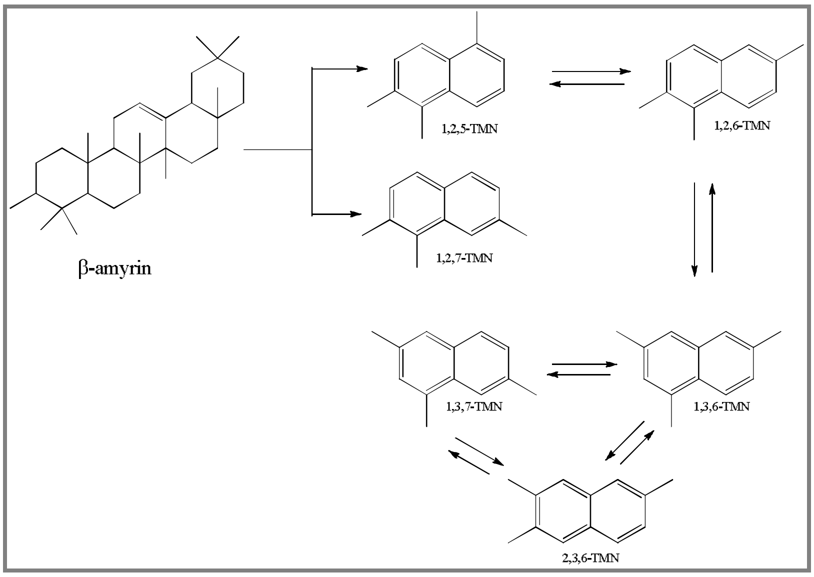


Figure 5. Schematic reaction of trimethylnaphthalene isomerization [**29**].

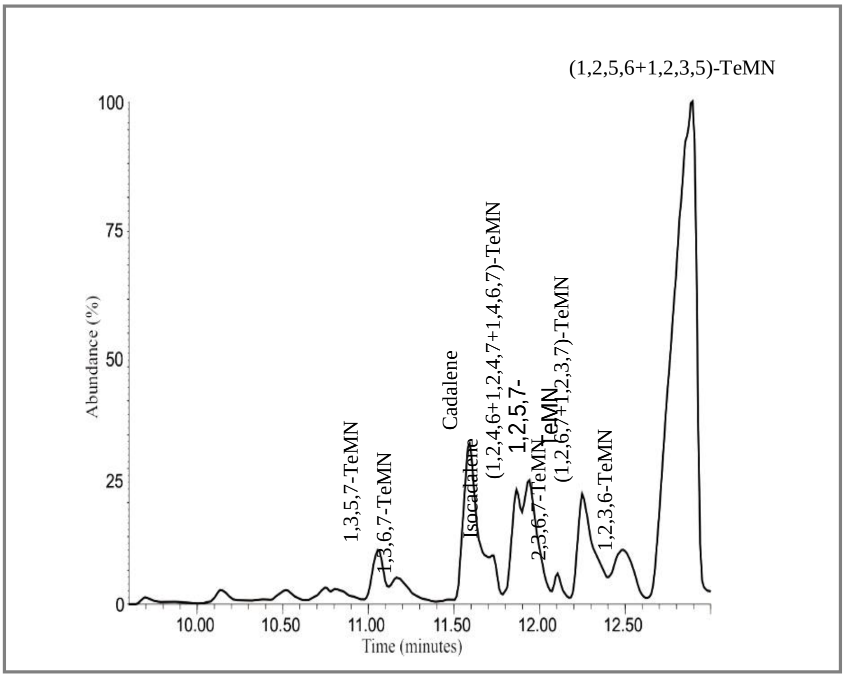


Figure 6. Distribution of tetramethylnaphthalene (TeMN) based on fragmentograms *m/z* 184.

Heating at high temperatures 1,2,2,5-tetramethyltetralin compounds will produce 1,2,5-TMN and 1,2,3,5-TeMN. The compounds 1,2,2,5,6-pentamethyltetralin in the same condition also produce 1,2,5,7-TeMN and 1,2,6-TMN as the main products. The presence of these compounds is likely to be formed due to alteration by bacteria at the time of the formation of Sawahlunto coal organic compounds. The high abundance of 1,2,5-TMN and 1,2,5,6-TeMN compounds compared to their respective isomers in the sample indicates the medium rank of coal maturity as reported by Armstroff *et al*. [**21**].

The presence of cadalene compounds in Sawahlunto coal samples identified based on fragmentograms *m/z* 183 can be derived from cadinene and cadinol which are abundant in high-grade resin as precursors [7, 10, 32]. Dipterocarpaceae is the most common resin family found in Southeast Asia. One of its genera, *Shorea*, is a plant found in modern tropical (ombrogenous) lowland peat swamps, especially in Sumatra and Kalimantan [11]. Indicators of coal maturity can be shown by the presence of cadalene and isocadalene. The high abundance of cadalene compared to isocadalene, indicates coal with medium maturity. Coal with high maturity will produce isocadalene which is more abundant than cadalene. The increasing amount of isocadalene in coal samples can be caused by heating and the presence of catalytic clay or acid components in the sediment [31].

Pentamethyl naphthalene compound (PMN) as 1,2,3,5,6-and 1,2,4,6,7-PMN. PMN in coal samples analyzed indicate the source of organic compounds produced by precursor drimenol in higher plants. The presence of this PMN compound also indicates the role of microbes in the formation of coal organic compounds. The high abundance of compounds 1,2,3,5,6-PMN, compared to 1,2,4,6,7-PMN as seen in figure 7, is indicating that coal is immaturity. The same thing was also reported by Bastow *et al.* [33], who found an abundance of 1,2,3,5,6-PMN compared to 1,2,4,6,7-PMN as an indicator of coal that did not have high maturity. Compounds with saturated drimanoid structure formed 1,2,2,5,6-pentamethyltetralin, then experienced methyl group rearrangement accompanied by aromatization to form 1,2,3,5,6-PMN. Mature organic material is characterized by 1,2,4,6,7-PMN abundance in the isomer distribution, whereas abundance 1,2,3,5,6-PMN which is relatively high indicates immature organic matter. High abundance of 1,2,3,5,6-PMN compounds in the sample can also be produced through 1,2,5,6-TeMN methylation as an indicator of coal leading to the thermal maturation process [33].

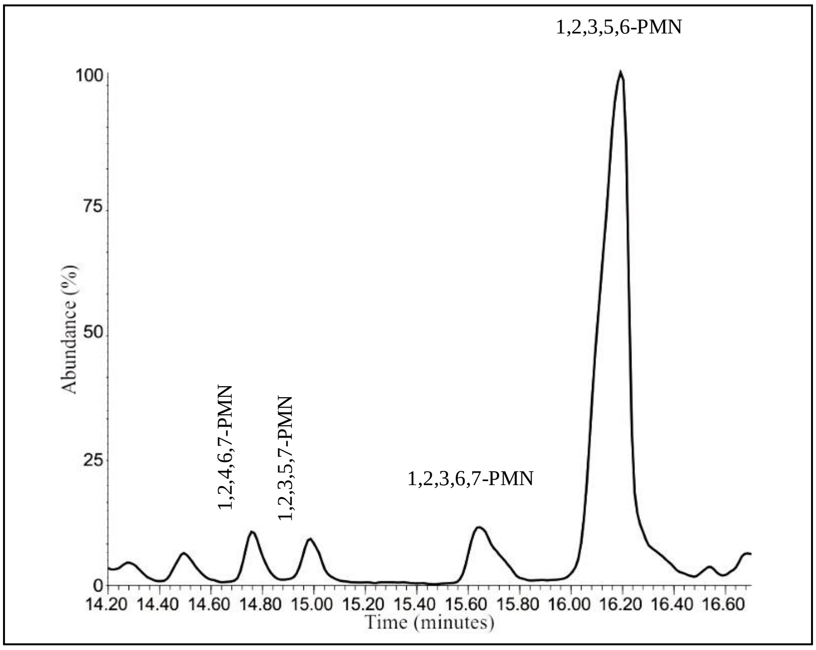


Figure 7. Distribution of pentamethylnaphthalene (PMN) based on fragmentograms *m/z* 198.

Biomarker of phenanthrene group: The presence of phenanthrene (P) compounds in coal samples is generally derived from the diterpenoid found in higher plant gymnosperms resins and is used as an indicator of organic compounds from higher plants [12]. Increased coal maturity is indicated by isomerization of alkyl phenanthrene (α-isomer to β-isomer) and dealkylation of alkyl phenanthrene (α-/β- isomer to phenanthrene) in its compound distribution [19]. The high abundance of phenanthrene compared to alkyl phenanthrene indicates the maturity of coal [34].

The presence of methylcholanthrene (MP) identified based on fragmentograms *m/z* 192 in mature coal samples is indicated by an increase in 2-MP and 3-MP abundance against 9-MP and 1-MP [19]. Samples with an abundance of 9-MP and 1-MP were more dominant than 3-MP and 2-MP, indicating the continued process of coal formation in coal. In addition, the presence of 1-MP compounds is also associated with the precursors of isopimaroid, rimuoid, beyeroid, kauroid, phyllocladoid, or podocarpic acid, as indicators of higher plant gymnosperms [27]. The 1-MP and 1,7-DMP compounds, usually formed together with retene, are produced from the precursors of abietane types, such as abietic acid which is abundant in gymnosperms. This shows the slight contribution of gymnosperms plants to the formation of coal organic compounds [14].

Identification of peaks based on fragmentograms *m/z* 178 and 192 also showed the presence of anthracene (A) and methyl anthracene, (MA) compounds. The 2-MA abundance of the other isomers indicates mature coal and the duration of the soaking process [35]. In addition, the presence of A (peak 2) and MA (peak 4) in the sample, as seen in figure 8 and table 1, also indicates the occurrence of combustion of terrestrial plant material [36].

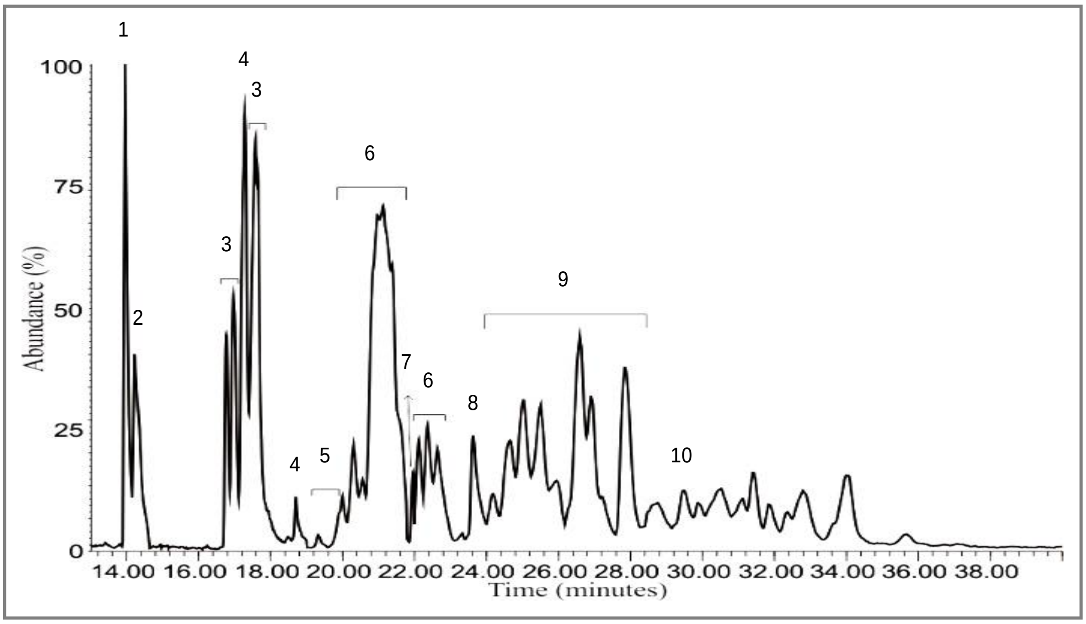


Figure 8. Distribution of phenanthrene group

Table 1. Distribution of phenanthrene on the sample

Peak Number	Base peak (*m/z*)	Compound
1	178	phenantrene (P)
2	178	anthrachene (A)
3	192	methylphenanthrene (MP)
4	192	methylanthracene (MA)
5	206	ethylphenanthrene (EP)
6	206	dimethylphenantrene (DMP)
7	202	fluoroanthene
8	202	pyrene
9	220	trimehylphenantrene (TMP)
10	219	retene

The increase in thermal maturity of coal is also based on the distribution of DMP isomers. More stable DMP isomers such as: 2.6-; 2,7-; 3,6-; 2,3-; 2,10- and 2,9-DMP have increased abundantly along with the increasing maturity [37]. The high abundance of DMP isomers that are less stable than the more stable isomers in the analyzed samples indicates that coal continues to mature.

The presence of trimethyl phenanthrene (TMP) compounds such as: 2,3,6- and 2,3,7-TMP identified based on fragmentograms *m/z* 220 as seen in figure 9 is also used as an indicator of coal maturity because the isomer structure is relatively stable. This compound is stored in coal that is mature [**37**].

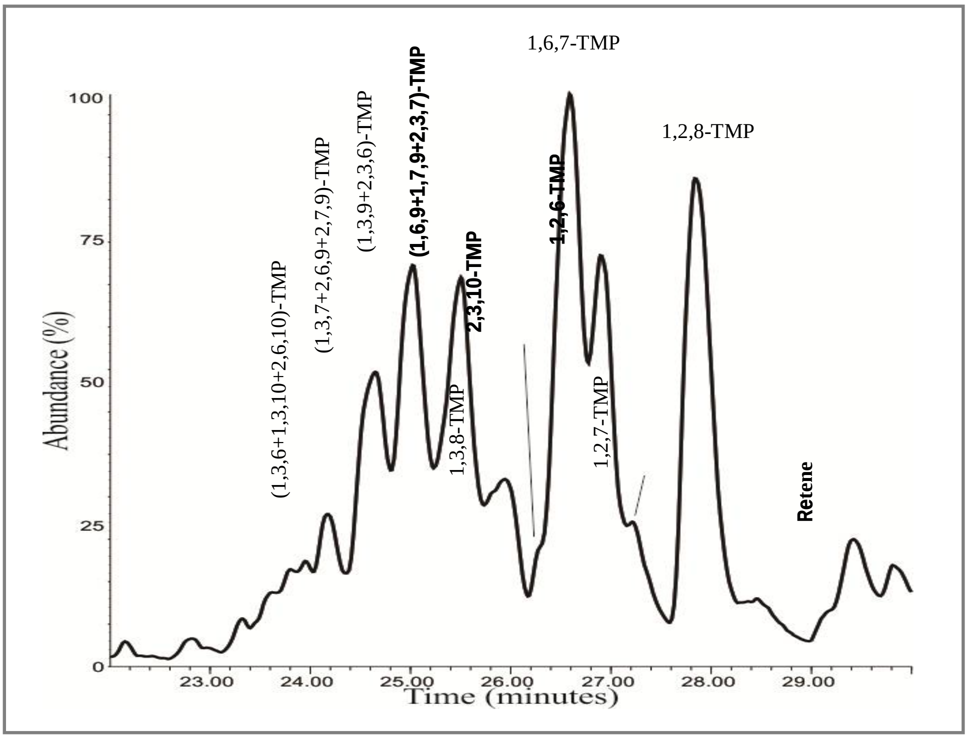


Figure 9. Distribution of trimethyl phenanthrene group based on fragmentograms *m/z* 220.

The high abundance of unstable TMP such as 1,2,8-TMP in the analyzed sample indicates that coal has not shown a high maturity level (medium). Increased maturity will lead to a shift in the methyl group in the less stable C-1,2,8 position towards the more stable position of C-1,2,6 and C-1,2,7. This methyl group shift is identical to the isomerization reaction of 1,2,5-TMN compounds as shown in figure 5. Therefore, the high abundance of 1,2,8-TMP compared to 1,2,6-TMP and 1,2,7-TMP shows that coal will continue to lead to a higher maturation process. The existence of 1,2,8-TMP is also linked to terrestrial plant precursors, because these compounds are produced through pentacyclic triterpenoid dehydrogenation reactions, such as β-amyrin and lupeol [**37**].

Biomarker of triterpenoid pentacyclic aromatic group: The group distribution of pentacyclic aromatic triterpenoid compounds is shown in figure 10 and table 2. The presence of picene derivatives (peak 7,8,9) which is dominant in Sawahlunto coal indicates the precursors of the angiospermae plants (β-amyrin). The formation of picene derivatives in sediment and peat is estimated through the aromatization reaction of β-amyrin mediated by microbial activity or catalytic clay processes that take place during the initial diagenesis [**12**].

The identification of compounds based on fragmentograms *m/z* 342 showed the presence of pentacyclic triaromatic compounds (peak 6) with the oleanoid skeleton of β-amyrin, ursanoids of α-amyrin, and lupanoids of lupeol. The availability of pentacyclic aromatic triterpenoid compounds derived from triterpenoids with the oleane, ursane, and lupane skeletons in Sawahlunto coal is used as an indicator of higher terrestrial plants.

The identification of peaks based on fragmentograms *m/z* 169 showed the presence of a C_{27}-triaromatic-8,14-secotriterpenoid compound with an oleanoid skeleton. The C_{27} triaromatic-8,14-

secotriterpenoid compound (peak 4) is formed by the breaking of the ring C from the pentacyclic triterpenoid skeleton and is considered as an intermediate to the formation of trimethyl naphthalene

Table 2. Triterpenoid pentacyclic aromatic compound

Peak Number	Base peak (*m/z*)	Compound
1	228	chrysene
2	242	methylchrysene
3	256	dimethylchrysene
4	169	C_{27} triaromatic-8,14-secotriterpenoid
5	183	C_{28} triaromatic-8,14-secotriterpenoid
6	342	pentacyclic triaromatic
7	324	2,2,9-trimethyl-1,2,3,4-tetrahydropicene
8	306	2,9-dimethylpicene
9	320	1,2,9-trimethylpicene

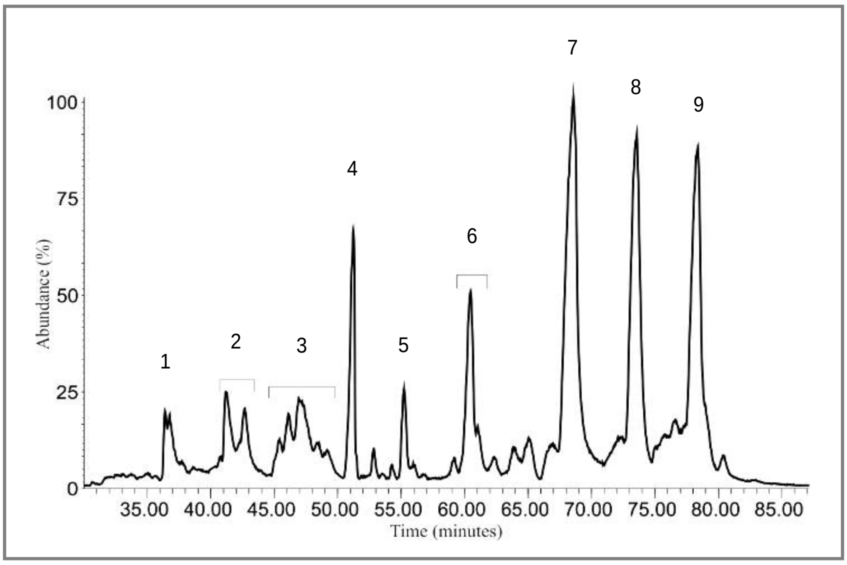


Figure 10. Distribution of triterpenoid pentacyclic aromatic group.

(TMN) from β-amyrin [20]. The dominance of β-amyrin as a precursor of Sawahlunto coal organic material is also supported by the presence of 3,3,7- trimethyl -1,2,3,4-tetrahydrochrysene and 2,2,9-trimethyl-1,2,3,4-tetrahydropicene (peak 7). The presence of biomarker 3,3,7-trimethyl-1,2,3,4-tetrahydrocrysene was identified based on fragmentograms *m/z* 218, while the compound 2,2,9-trimethyl-1,2,3,4-tetrahydropicene was identified based on fragmentograms *m/z* 324 [38] as shown in figure 10. Biomarker 3,3,7-trimethyl- 1,2,3,4- tetrahydrocrysene is obtained from ring A degradation of the β-amyrin structure accompanied by aromatization of B, C, D rings in a pentacyclic triterpenoid skeleton.

The effect of increasing aromatization and isomerization reactions on triterpenoid derivatives along with the availability of a large number of naphthalene, phenanthrene and chrysene compounds indicates the occurrence of an increase in coal maturity. Therefore, with the discovery of compounds 1,2,5-TMN, 1,2,7-TMN and 1,2,5,6-TeMN together with picene derivatives in the Sawahlunto coal sample indicated that the sample of coal was mature, but had not shown high maturity of coal.

The identification of fragmentograms based on *m/z* 183 in the sample showed the presence of a C_{14} triaromatic-8,14-secotriterpenoid compound. C_{28} triaromatic-8,14- secotriterpenoid compound (peak 5) is an intermediate compound of 1,2,5,6-TeMN formation from β-amyrin precursors. This reinforces the indication that the sample is dominated by the precursor of the angiospermae plant. The high abundance of 1,2,5,6-TeMN against the C_{28} triaromatic-8,14-secotriterpenoid in the sample also indicated that the Sawahlunto coal was mature.

Full aromatization reaction of triterpenoid derivatives shown by the presence of 2,9-dimethylpicene (peak 8) with relatively high abundance of 1,2,9-trimethylpicene (peak 9). 2,9-dimethyl picene and 1,2,9-trimethylpicene compounds in the sample were identified based on fragmentograms *m/z* 306 and *m/z* 320 as seen in figure 10 and table 2 [**39**]. The higher abundance of 2,9-dimethylpicene compounds compared to 1,2,9-trimethylpicene indicates that the process of combustion in the process of coal formation is still continues. In addition, compounds 2,9-dimethylpicene and 1,2,9-trimethylpicene can also be used as an indicator of angiospermae plants. The full aromatization reaction of β-amyrin will produce 2,9-dimethylpicene compounds, while 1,2,9-trimethylpicene is produced through full aromatization of α-amyrin [**27**].

APPLICATION

This study is useful to know the type of coal, the maturity of coal and strengthened calorific value.

CONCLUSION

Biomarker analysis of aromatic hydrocarbon fraction of Sawahlunto coal samples, Ombilin Basin provides information on the composition of organic compounds contained in it. Three groups of aromatic compounds are: naphthalene with sesquiterpenoid skeleton, phenanthrene group with diterpenoid skeleton, and pentacyclic aromatic triterpenoid group. Biomarker analysis shows that coal organic compounds are from terrestrial plants, especially angiosperms and little input from bacteria. The existence of the analyzed biomarkers also showed that Sawahlunto coal samples analyzed were mature, but had not yet entered the catagenesis stage. This is also strengthened by the coal calorific value of 7472 cal g^{-1} and classified as sub-bituminous coal.

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REFERENCES

[1]. A. Sugiyono, A. Anindhita, M.S. Boedoyo, A. Adiarso, Outlook Energy Indonesia, Center for Energy Resources Development Technology (BPPT), Jakarta, **2017**, p. 119.
[2]. C. Stanford, In. D. Osborne (Ed.), *The Coal Handbook: Towards Cleaner Production* (Woodhead Publishing Limited, Queensland, **2013**), 200-219.
[3]. D.L. Ewart, Jr., R. Vaughn, Review the Indonesian thermal coal Industry. World Coal Asia Special, December 2, 2011, 16-18.
[4]. M.C. Friederich, R.P. Langford, T.A. Moore, The geological setting of Indonesian coal deposits. In: The AusIMM Proceedings 304, **1999**, 23–29.
[5]. H.E. Belkin, J.T. Susan, C.H. James, J.D. Stucker, J.M.K. O'Keefe, Geochemistry and petrology of selected coal samples from Sumatra, Kalimantan, Sulawesi, and Papua, Indonesia, *International J. of Coal Geol*., **2009**, 77, 260–268.
[6]. Y. Zetra, PhD Thesis, The Role of Brown Coal's Organic Geochemistry Characteristic in Coal Liquefaction, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia, **2016**.
[7]. Y. Zetra, I.B. Sosrowidjojo, R.Y.P. Burhan, Aromatic biomarker from brown coal, Sangatta Coalfield, East Borneo of Middle Miocene to Late Miocene age, *Jurnal Teknologi*, **2016**, 78(6), 229–238.

[8]. Y. Zetra, I.B. Sosrowidjojo, R.Y.P. Burhan, Paleoenvironment of Brown Coal from Sangatta Coal mines, East Borneo, Indonesia, *Jurnal Teknologi*, **2016**, 78(7), 121-129.
[9]. Y. Zetra, H.S. Kusuma, F. Riandra, I.B. Sosrowidjojo, R.Y.P. Burhan, The oxygenated biomarker as an indicator of origin and maturity of Miocene Brown Coal Sangatta Coal mines, East Kalimantan, *Indonesian Journal On Geoscience*, **2018**, 5(2), 105-116 (2018).
[10]. H. Amijaya, R. Littke, Microfacies and depositional environment of Tertiary Tanjung Enim low rank coal, South Sumatra Basin, Indonesia. *International J. of Coal Geol*., **2005**, 61, 197– 221.
[11]. H. Amijaya, J. Schwarzbauer, R. Littke, Organic geochemistry of the Lower Suban coal seam, South Sumatra Basin, Indonesia: Palaeoecological and thermal metamorphism implications, *Organic Geochem*., **2006**, 37, 261–279.
[12]. S. Widodo, A. Bechtel, K. Anggayana, 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, *Organic Geochem*., **2009**, 40, 206-218.
[13]. W. Püttmann, H. Villar, Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene, *Geochim. et Cosmochimim. Acta*, **1987**, 51, 3023-3029.
[14]. M.F. Romero-Sarmiento, A. Riboulleau, M. Vecoli, G. Versteegh, Aliphatic and aromatic biomarkers from Gondwanan sediments of Late Ordovician to Early Devonian age: An early terrestrialization approach, *Organic Geochem*., **2011**, 42, 605-617.
[15]. M. Radke, H. Willsch, Extractable alkyldibenzothiophenes in Posidonia shale (Toarcian) source rocks: relationship of yields to petroleum formation and expulsion, *Geochim. et Cosmochim. Acta*, **1994**, 58, 5223-5244.
[16]. J. Schwarzbauer, R. Littke, V. Weigelt, Identification of spesific organic contaminants for estimating the contribution of the Elbe river to the polution of the German Bight, *Organic Geochem*., **2000**, 31, 1713-1731.
[17]. W. Orem, R. Finkelman, In: K. Turekian, H. Holland (Eds.), Treatise on Geochemistry 2nd ed., *Elsevier Ltd., Amsterdam,* **2013**, 207-232.
[18]. J. Smith, S. George, B. Batts, The geosynthesis of alkylaromatics, *Organic Geochem*., **1995**, 23, 71-80.
[19]. K. Stojanović, B. Jovančićević, G. Pevneva, J. Golovko, A. Golovko, P. Pfendt, Maturity assessment of oils from the Sakhalin oil fields in Russia: phenanthrene content as a tool, *Organic Geochem*., **2001**, 32, 721-731.
[20]. J. Tuo, R. Philp, Saturated and aromatic diterpenoids and triterpenoids in Eocene coals and mudstones from China, *Applied Geochem*., **2005**, 20, 367-381.
[21]. A. Armstroff, H. Wilkes, J. Schwarzbauer, R. Littke, B. Horsfield, Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age, *Palaeogeography, Palaeoclimatology, Palaeoecology*, **2006**, 240, 253-274.
[22]. O. Sonibaire, T. Hoffmann, S. Foley, Molecular composition and chemotaxonomic aspects of Eocene amber from the Ameki Formation, Nigeria, *Organic Geochem*., **2012**, 51, 55-62.
[23]. M. Fabiańska, S. Kurkiewicz, Biomarkers, aromatic hydrocarbons and polar compounds in the Neogene lignites and gangue sediments of the Konin and Turoszów Brown Coal Basins (Poland), *International J. of Coal Geol*., **2013**, 107, 24-44.
[24]. K. Anggayana, PhD. Dissertation, Mikroskopische und organisch-geochemische Untersuchungen an Kohlen aus Indonesien, ein Beitrag zur Genese und Fazies verschiedener Kohlenbecken, RWTH Aachen, Germany, **1996**.
[25]. S. Lu, I. Kaplan, Diterpanes, triterpanes, steranes, and aromatic hydrocarbons in natural bitumens and pyrolysates from different humic coals, *Geochim. et Cosmochim. Acta*, **1992**, 56, 2761-2788.
[26]. A. Borrego, C. Blanco, W. Puttmann, Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain, *Organic Geochem*., **1997**, 26, 219-228.
[27]. S. Killops, V. Killops, Introduction to Organic Geochemistry, Blackwell Publishing, Carlton, **2005**, 2nd ed.

[28]. R. Alexander, R. Kagi, R. Singh, I.B. Sosrowidjojo, The effect of maturity on the relative abundances of cadalene and isocadalene in sediments from the Gippsland Basin, Australia, *Organic Geochem*., **1994**, 21, 115-120.
[29]. M. Strachan, R. Alexander, R. Kagi, Trimethylnaphthalenes in crude oils and sediments: effects of source and maturity, *Geochim. et Cosmochim. Acta*, **1988**, 52, 1255-1264.
[30]. J. Anderson, J. Müller, Palynological study of a Holocene peat and a Miocene coal deposit from NW Borneo, *Rev. of Palaeobotany and Palynology*, **1975**, 19, 291-351.
[31]. R. Alexander, T. Bastow, R. Kagi, R. Singh, Identification of 1,2,2,5-tetramethyltetralin and 1,2,2,3,4-pentamethyltetralin as racemates in petroleum, *J. Chem. Soc.; Chem. Comm*., **1992**, 1906, 1712-1714.
[32]. B. van Aarssen, J. Hessels, O. Abbink, J. de Leeuw, The occurrence of polycyclic sesqui-, tri-, and oligoterpenoids derived from a resinous polymeric cadinene in crude oils from southeast Asia, *Geochim. et Cosmochim. Acta*, **1992**, 56, 1231-1246.
[33]. T. Bastow, R. Alexander, I.B. Sosrowidjojo, Pentamethylnaphthalenes and related compounds in sedimentary organic matter, *Organic Geochem*., **1998**, 28, 585-595.
[34]. R. Hayatsu, R. Winans, R. Scott, L. Moore, M. Studier, Trapped organic compounds and aromatic units in coals, *Fuel*, **1978,** 57, 541-548.
[35]. P. Garrigues, R. de Sury, M. Angelin, J. Bellocq, J., Oudin, M. Ewald, Relation of the methylated aromatic hydrocarbonn distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta, *Geochim. et Cosmochim. Acta*, **1988**, 52, 375-384.
[36]. M. Escobar, G. Marquez, I. Suarez-Ruis, T. Juliao, 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 coal, *International J. Coal Geol*., **2016**, 163, 149-165.
[37]. H. Budzinski, P. Garrigues, M. Radke, J. Connan, J.L. Oudin, Thermodynamic calculations on alkylated phenanthrenes: Geochemical applications to maturity and origin of hydrocarbons, *Organic Geochem*., **1993**, 20, 917-926
[38]. A. Chaffee, C. Fookes, Polycyclic aromatic hydrocarbons in Australian coals--Ill. Structural elucidation by proton nuclear magnetic resonance spectroscopy, *Organic Geochem.*, **1988**, 12, 261-271.
[39]. H. Villar, W. Puttmann, M. Wolf, Organic geochemistry and petrography of Tertiary coals and carbonaceous shales from Argentina, *Organic Geochem.,* **1987**, 13, 1011-1021.