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Aromatic Biomarkers as a Tool to Identification a Source and Palaeodepositional of Sajau Coal, Berau Basin, Indonesia

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***Abstract*—** *The distributions and concentrations of plant-derived aromatic biomarkers were investigated in the Pliocene coal seam from Pliocene Sajau Formation in Berau Basin, Indonesia. The study aims to identify vegetational sources and ancient depositional of these coals. The distribution of aromatic hydrocarbons were detected, including 1,2,7-Trimethylnaphthalene (TMN), 1,6,7-TMN, and 1,2,5-TMN, cadalene, retene,1-methylphenanthrene (MP), 3-MP, 9-MP, 1, 2,-dimethylphenanthrene (DMP), 2,6-DMP, 2, 7-DMP, 1.3. 8 Trimethyl Phenanthrene (TMP) and polycyclic aromatic hydrocarbons (PAHs). The distribution of aromatic biomarkers indicated that in the Lower part of Sajau Coal were relatively dominated gymnosperms, while in the middle and upper part of Sajau Coal, an angiosperm dominated higher plant and conifers. The coals showed mainly charred indicated by abundances of combustion-derived PAHs such as Benzo[a] anthracene, fluoranthene, and benzofluoranthene in coals indicated the coals. The deltaic depositional environment is the place for forming Sajau Formation coal.*

***Keywords*—** *Aromatics, biomarker, Sajau coal, palaeodepositional, Berau Basin.*

I. INTRODUCTION

Coal is a sedimentary rock that is essential to Indonesia's energy sector. The coal of the Sajau Formation in the Berau basin, North Kalimantan, is classified as lignite to sub-bituminous coal. Several studies have been related to coal quality, palynology, and organic petrography [1, 2], but organic geochemical research is still limited, especially the distribution application of aromatic biomarkers. Biomarkers are often referred to as "fossil chemical markers" believed to originate from living organisms [3]. Defined as a typical compound found in rock, sediment, or oil; with a relatively stable molecular structure during the process of geological evolution and provides a remarkable record of molecular structure information from the original biomarker biological parent material. Various geological information, such as the depositional environment, the maturity level of a rock, and the correlation of petroleum with its parent rock; and the biodegradation level by identifying sediments and oil biomarkers [4-6]. To better understand the distribution of the Sajau coal Berau Basin, it is necessary to identify the depositional environment and coal sources.

The study aimed to identify the distribution of aromatic biomarkers in Sajau coal samples in the Berau Basin to determine the organic matter's origin and depositional environment.

II. METHODS

A. Samples, Materials, and Reagents

This study collected seven coal samples from the Kasai Village, Berau Regency coal field. The coal samples consist of A-B coal seams, coal seams C-E, and coal seams K-L. The materials used in this research were hexane, acetone and dichloromethane, sodium sulfate (AR grade), and acetonitrile procured from Fisher Scientific and Merck.

B. Preparation of Samples and Extraction

The EPA 3540C protocol used the Soxhlet Extraction Method to extract coal samples. We are mixing 1.0 grams of coal with DCM solvent in a conical flask with a volume size of 50 cm^3 [7-9]. The extraction uses an ultrasonic field with a working frequency of 35 kHz and a 200 W—ultrasonic treatment power for 20 minutes at 25–30°C.

The extraction filtering process was carried out using a white ribbon filter with a 2.0–2.5 cm thickness and a sodium sulfate drying agent (Na_2SO_4). Purification of the extraction results used a chromatographic column containing aluminum oxide (Al_2O_3); the extraction was washed and cleaned using DCM. For HPLC investigations, the sample evaporated, and replaced with acetonitrile; while for GC-MS measurement used, hexane solvent; until it reaches a final volume of 1 cm^3. Extraction experiments were replicated three times to ensure the reproducibility of results.

C. Gas Chromatography- Mass Spectrometry (GC-MS)

The combination of the Shimadzu GCMS-QP2010 with the Shimadzu GC-2010 instrument was used to identify quantitatively and qualitatively the aromatic composition of biomarkers. At a rate of 1 cm^3/min, helium gas is injected. At the start of this device's operation, the capillary column's initial temperature is set at 50°C for 2 minutes. Furthermore, the temperature is adjusted dynamically to 60-200ºC at 5ºC/minute, increased to 200-250ºC at 2ºC/minute, 250-290ºC at 20ºC/minute, and maintained at 290ºC for 20 minutes. The spectrum resulting from each peak read on the chromatogram was then identified using the GCMS Postrum Analysis software with several libraries, including BENZODIAZEPINE, PESTEI_3, NIST 08, and WILEY.

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Quantification was made in the instrument's Selected Ion Monitoring (SIM) mode. The peak area responses of the calibration standards were used to determine the aromatic biomarker.

III. GEOLOGY

The research area is part of the Berau Basin (some researchers say it is a sub-Berau Basin), which is a stable block part of the Greater Tarakan Basin [10, 11], located in the northeastern part of the island of Borneo. The basin is bounded in the south-southeast by the Suikerbrood Ridge, the Mangkalihat High / Peninsula, and along the Berau River, as well as the left horizontal fault in the NW-SE (Mangkalihat Fault) direction, which is an extension of the Palu Koro fault which separates it from the Kutai Basin and Estuary Basin; towards the west the Berau Basin is bounded by the Sekatak - Berau Heights which are composed of Pre-Tertiary rocks; meanwhile, to the north it is bounded by a horizontal fault to the left of the Maratua Fault and to the north by Latong High which separates it from the Tidung Basin. This basin opens in an arc to the west bordering the Tarakan Basin.

The surface geological map compiled by Situmorang and Burhan [12] on the Tanjung Redeb Sheet shows NW-SE and NNW-SSE anticlines and synclines, respectively. A NNW - SSE. Normal faults were identified. The stratigraphic order deposited from the Early Eocene to the Pleistocene (Figure 1).

One of the coal-bearing rock formations in the Berau Basin is the Pliocene to Pleistocene Sajau Formation which is exposed in the eastern part of the basin. The Sajau Formation was deposited in a fluvial environment up to the delta, with rock formations dominated by alternating sandstones, claystone, and shale with coal and conglomerate inserts. A total of 13 coal seams can be identified in the study area.

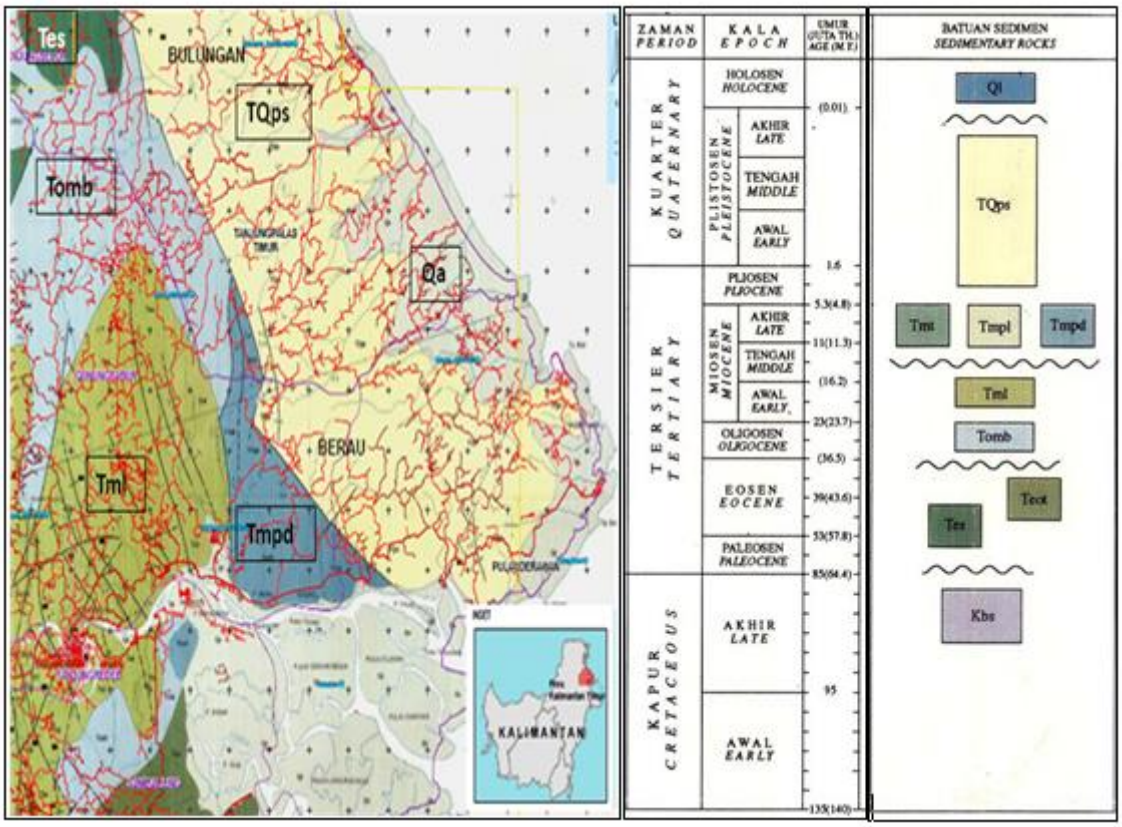

Fig. 1. Part of the geological map of the Tanjung Redeb Sheet and stratigraphic sequences that are part of the Berau Basin (Geological Map of the Tanjung Redeb Sheet, Situmorang and Burhan, 1992).

IV. RESULT AND DISCUSSION

To identify the distribution of the aromatic biomarker fraction, Gas Chromatography-Mass Spectrometry (GC-MS) uses several MIC chromatograms with different ions, consisting of ions m/z 156, m/z 170, m/z 178, m/z 192, m/ z 231, m/z 220 and m/z 253. The methyl phenanthrene (MN), dimethyl naphthalenes (DMP) and trimethyl naphthalenes (TMN), trimethyl Phenanthrene (TMP), and other polycyclic aromatic hydrocarbons (PAHs), as well as retene, and cadalene; were identified in coal samples. And small amounts of bicadinane. Table I and Figure 3 present concentrations of biomarkers.

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TABLE I. Distribution of aromatic biomarker of Sajau coal in Berau Basin.

No/Seam	MP (m/z 178; 192)				DMN; m/z 156		TMN; m/z 170		TMP	Rt 9-MP	Cd
	P	1-MP	9-MP	3-MP	1,7-DMP	1.2-DMP	1,2,5 TMN	1,2,7-TMN	1,3,8-TMP		
SG-19/A	19.81	25.4	1.09	8.16	6.94	14.63	8.39	7.69	0.08	0.12	0.08
S003/B	11.22	19.21	0.99	7.14	6.48	12.26	8.01	7.12	0.11	0.12	0.06
S3/C	16.36	15.10	1.14	8.12	7.47	11.51	8.14	7.24	0.12	0.21	0.08
SG-1/D	13.46	15.26	1.61	8.14	8.49	11.70	9.01	6.11	0.17	0.18	0.05
SJ-12/E	9.16	14.24	1.72	7.85	7.47	9.28	5.24	5.23	0.18	0.20	0.05
S7/K	10.80	8.22	1.70	6.18	5.45	10.31	4.12	5.11	0.12	0.21	0.05
S8/L	9.86	9.08	1.84	7.28	6.02	9.25	5.24	5.02	0.14	0.23	0.05

MP : Methyl Phenanthrene TMP : Trimethyl Phenanthrene Rt : Retene
TMN : Trimethyl Naphthalene DMN : Dimethyl Naphthalene Cd : Cadalene

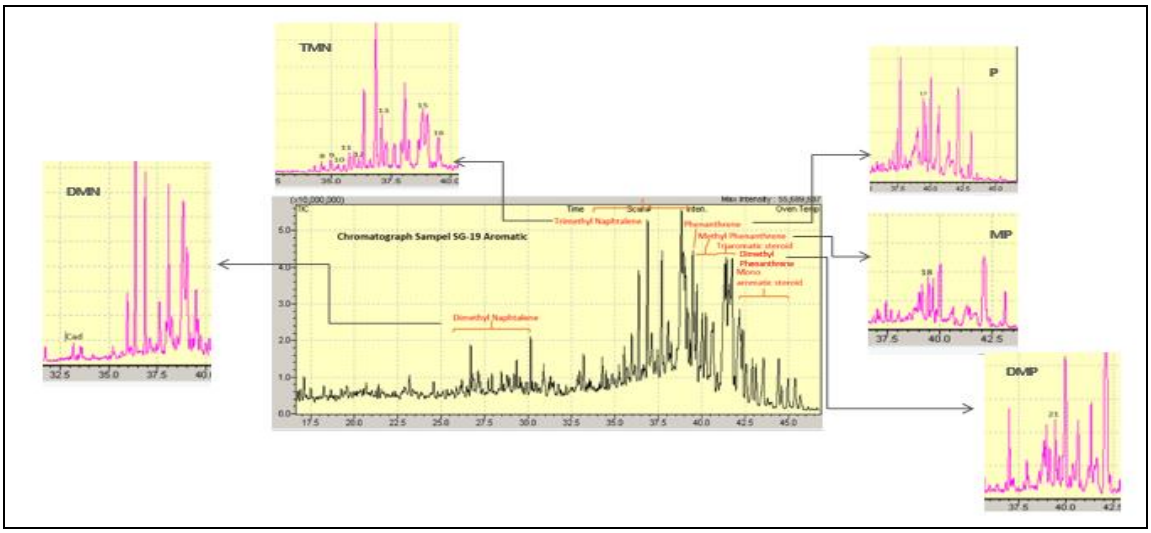

Fig. 2. Compounds concentrations of 1,2.5-TMN, 1,2,7-TMN, 1-MP, and 1,7-DMP, in coal of Berau Basin

Concentrations of compounds 1,2.5-TMN, 1,2,7-TMN, 1-MP, and 1,7-DMP, in coal in the lower- middle Sajau Formation (coal seam A-E) are relatively higher than the coal in the upper part of this formation (coal seam K-L). Likewise, concentrations of retene and cadalene are higher in the lower-middle part of the Sajau Formation.

Likewise, Phenanthrene concentrations were identified in large quantities in seams A - D, compared to coal seams K and L.

In contrast to the concentration of 1,4,8-Trimethylphenanthrene, the concentration is a minor in A-D seam coal; when compared to coal seam K-L

Table 2 presents the concentrations values and weight percentage (wt.%) of PAH compounds in Sajau coals from the.GC-MS analysis

TABLE II. Concentration and weight % of PAH in Sajau coal

Peak No.	PAHs Compound	Retention Time	No. of Rings	Relative amount (wt. %)
1	Naphthhalene	2.44	2	0.8
2	Acenaphthylene	3.11	3	21.1
3	Acenaphthene	3.81	3	2.1
4	Fluorene	4.01	3	1.2
5	Phenanthrene	5.16	3	1.1
6	Anthracene	6.72	3	0.9
7	Fluoranthene	7.48	4	0.7
8	Pyrene	8.76	4	69.9
9	Benzo[a]anthracene	13.52	4	0.3
10	Chrysene	14.06	4	0.4
11	Benzo[b]fluoranthene	17.93	5	0.3
12	Benzo[k]fluoranthene	18.26	5	0.4
13	Benzo[a]pyrene	19.14	5	0.2
14	Indeno[1,2,3-cd] pyrene	23.08	6	0.1
15	Dibenzo [a, h] anthracene	23.14	6	0.2
16	Benzo [g, h] perylene	23.86	6	0.3
	Total PAHs			100

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Discussion

The higher concentrations of 1,2,5- and 1,2,7-TMN compared to other aromatic compounds indicate the possibility of formation from the aromatization products of angiosperms, as indicated by Chaffe [13]; but do not rule out the possibility also comes from the contribution of gymnosperms [14]. The detection of 1-MP, 1,7-DMP, indicated the presence of retene decomposition, but it could also be from abietane-type diterpenoids in conifers [15]. Simoneit [16] stated that retene showed a relationship with abietane-type diterpenoids, which occur everywhere in conifers. However, it is different; from the opinion of another scholar [17], who said that retene could come from algae. Cadalene and bicadinane are available from vascular plants [18].

The high aromatic ratio of (1-MP/9-MP), (and (retene/9-MP) C-D-E and K-L coal seams indicated conifers are a source of coals (Figure 3).

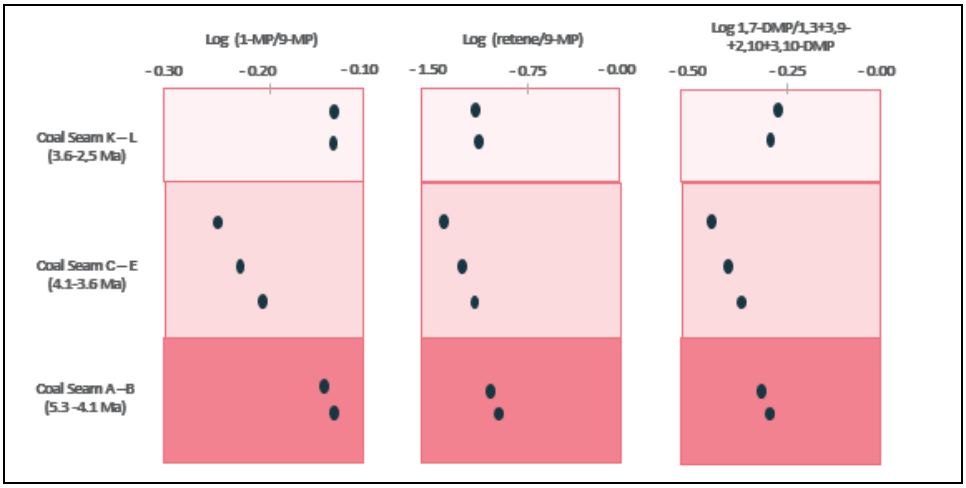

Fig. 3. Distribution of aromatic biomarker ratio from Coal A to coal seam L

Figure 3 indicates a much higher plant-dominated intake by angiosperms during the formation of seam A-E coal in the lower middle to middle Sajau Formation. Environmental factors indicate a warm and humid climate during coal formation caused by the falling heavy rain. Different in the time of coal formation of coal seams K and L in high and hot climatic peak conditions.

The proportions of angiosperms and ferns decreased during coal seam formation from the middle part (Coal seam C-E) to the upper part of the Sajau Formation (coal seam K - L), followed by a higher relative abundance of conifers, compared to the abundance of vegetation during the formation of coal in the lower part (coal seam A-B)' indicates a cold climate and more humid conditions at the bottom of the Sajau Formation. The changes in vegetational patterns indicate a change in climate patterns in the Berau Basin from the Upper Miocene to the Pliocene. It is consistent with the pollen and spore study conducted by Vera [2], which found that in the Lower Sajau Formation (Seam A-B), there was a decrease in Angiosperm content, followed by an increase in Pteridophyte (Seam C - E); while the Gymnosperm content is relatively stable. During the sedimentation of the C-E coal seam (middle part of the Sajau Formation), the Gymnosperm and Pteridophyte were more dominant than the Angiosperm. The K-L coal seam, Gymnosperm, and Pteridophytes still dominate.

The distribution of PAH in Sajau's coal indicates that the depositional environment is deltaic; this is indicated by the low ratio of phenanthrene to anthracene (Ph/An: 1.22); fluoranthene to pyrene (Flu/Pyr: 0.009), and low molecular weight to high molecular weight (LMW/HMW: 0.39) [19, 20]. Incomplete coal, oil, and wood combustion will produce high pyrene (Joseph, 2015)). The mixing of terrestrial and marine materials indicates that the environment for the deposition of Coal Formation alone is a delta system. There is a link between the natural precursor of pimaric acid in terrestrial plant resins and the presence of Dimethyl Phenanthrene (DMP) compounds, together with Trimethylphenanthrene (TMP) in the form of a 1,3,8-TMP, reflected marine environment. The depositional environment for the Sajau Coals formation is a delta system, indicated by a mixture of material from land and marine origin,

V. CONCLUSION

An analysis of aromatic biomarkers in coal to study the sources and palaeodepositional of coal in the research area. Research has identified several aromatic biomarker compounds; as follows:

1) The high content of 1-Methylphenanthrene, 1,7-Dimethylphenanthrene, and 1,2,5-Trimethylnaphthalene in coal indicates that the Gymnospermae plants are a source coal seam A-B.
2) The high aromatic ratios of (1-Methylphenanthrene/9-MP) and (retene/9-Methylphenanthrene) in the middle and upper coal of Sajau Coal indicated that they originate from the dominant intake of higher coniferous plants.

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3) The evenly detected biomarkers compound of 1, 3, 8 Trimethylphenanthrene indicates the presence of marine material intake in the coal of the Sajau Formation.

Mixing the biomarker compound Dimethylphenanthrene and Trimethylphenanthrene, PAH indicates that the ancient depositional environment was delta.

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