Geochemical characterization of Kutai Basin coals using proximate and ultimate analysis

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Abstract. This study aims to determine the characteristic of Kutai Basin coals on chemical composition parameter through proximate and ultimate analysis. Coal samples are taken from the Kutai Basin, where in this basin there are two formations containing coal, namely Pulaubalang and Balikpapan Formation. The methods used proximate and ultimate analysis. The statistical analysis of the results show the average concentration of moisture as 13.4 %, ash content as 5.8 %, volatile matter as 40.6 %, and fixed carbon as 40.2 % on Pulaubalang Formation and the average concentration of moisture as 14.0 %, ash content as 4.5 %, volatile matter as 40.8 %, and fixed carbon as 40.6 % on Balikpapan Formation. The increased volatile contents are characteristic of lower-rank coals, while the decreased values are indicative of higher-rank coals. The statistical analysis of the results show the average concentration of carbon as 63.21 %, hydrogen 6.10 %, nitrogen as 1.30 %, sulphur as 0.67 %, and oxygen as 22.96 % on Pulaubalang Formation and the average concentration of carbon as 59.24 %, hydrogen 5.92 %, nitrogen as 1.34 %, sulphur as 1.23 %, and oxygen as 27.75 % on Balikpapan Formation. The analytical results suggest the existing coal on Pulaubalang and Balikpapan Formation are of sub-bituminous A coal rank. Moreover proximate and ultimate analyses when interpreted in detail may form an effective tool to characterize the coals of any area.

Keywords: Proximate, Ultimate, Kutai Basin coal, Geochemical characterization

1. Introduction

Coal is an organic sedimentary rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace amounts of other elements, including mineral matter [1].

Proximate and ultimate analysis were chosen to analyse the coal quality chemically [1]. Proximate analysis is used to determine the rank of coal, a geochemical analysis of coal to determine the moisture content (water in the coal), ash (residual of the inorganic elements of combustion), volatile matter (gas and vapour exiting during pyrolysis), and fixed carbon (coal non-volatile fraction). While the ultimate analysis is a simple analysis used to determine the constituent of coal-forming with only attention to the important chemical content (carbon, hydrogen, sulphur, nitrogen, oxygen and ash) and ignore the existence of complex compounds that exist in coal [2]. The organic material in coal contains elements such as carbon (C), hydrogen (H), oxygen (O), sulphur (S) and nitrogen (N) in the form of chemical bonds [3]. The composition of these elements will change with increasing rank of coal. The carbon element on lignite about 55 wt% will be about 92 wt% at anthracite, hydrogen about 10 wt% will drop to 3 wt% and oxygen from about 35 wt% to 2 wt%. Sulphur and nitrogen are only a few percent and the changes are not very significant. The purpose of this study is to determine the quality of low rank coal especially in Formation Pulaubalang and Balikpapan in Kutai Basin.

2. Geological Background

The study area is located in the Kutai Basin (Figure 1), where this basin is one of the largest Tertiary basins in Indonesia, covering an area of 165,000 km^2 and a depth of approximately 14,000 m. The Kutai Basin is located at the northern part by area of the bedrock that occurs in the Oligocene, namely Mangkalihat High and Sangkulirang Fault which separates it with the Tarakan Basin. In the eastern part of this basin area, there is the Mahakam Delta which opens to the Makassar Strait. In the western part, the basin is bounded by the Cretaceous Kuching Orogenic Complex (Central Kalimantan Ranges). In the southeastern part of this basin, there are a cluster of Meratus Mountains and Adang Fault [4-6].

The Kutai Basin may divided into two (sub-) basins; a western Inner or Upper Kutai (sub-) Basin, and an eastern Outer or Lower Kutai (sub-) Basin. Today the Upper Kutai Basin is an area of major tectonic uplift as a result of Lower Miocene inversion of Paleogene depocentres and the effects of subsequent erosion, while the Lower Kutai Basin as we know it today was defined only during the Neogene, and overlies and encompasses many of the Palaeogene depocentres of the Upper Kutai Basin. The boundaries of the present day Kutai Basin, or its Neogene equivalent, do not correspond to the margins of any single Palaeogene depocentres. Many of the Palaeogene rifts were inverted and deeply eroded in the Neogene, further masking their true extent [4].

The Tertiary sediments of the Kutai Basin contain open folds with a general NE-SW trend, except near to the northern margin the basin where the trend is N-NNE. Immediately to the north of the Meratus Mountains, folds within the Tertiary are oriented ENE-WSW. Within the central region of the Lower Kutai Basin, referred to as the Samarinda anticlinorium (Figure 1), folds trend NNE-SSW and form continuous anticlinal ridges for over 100 km [4].

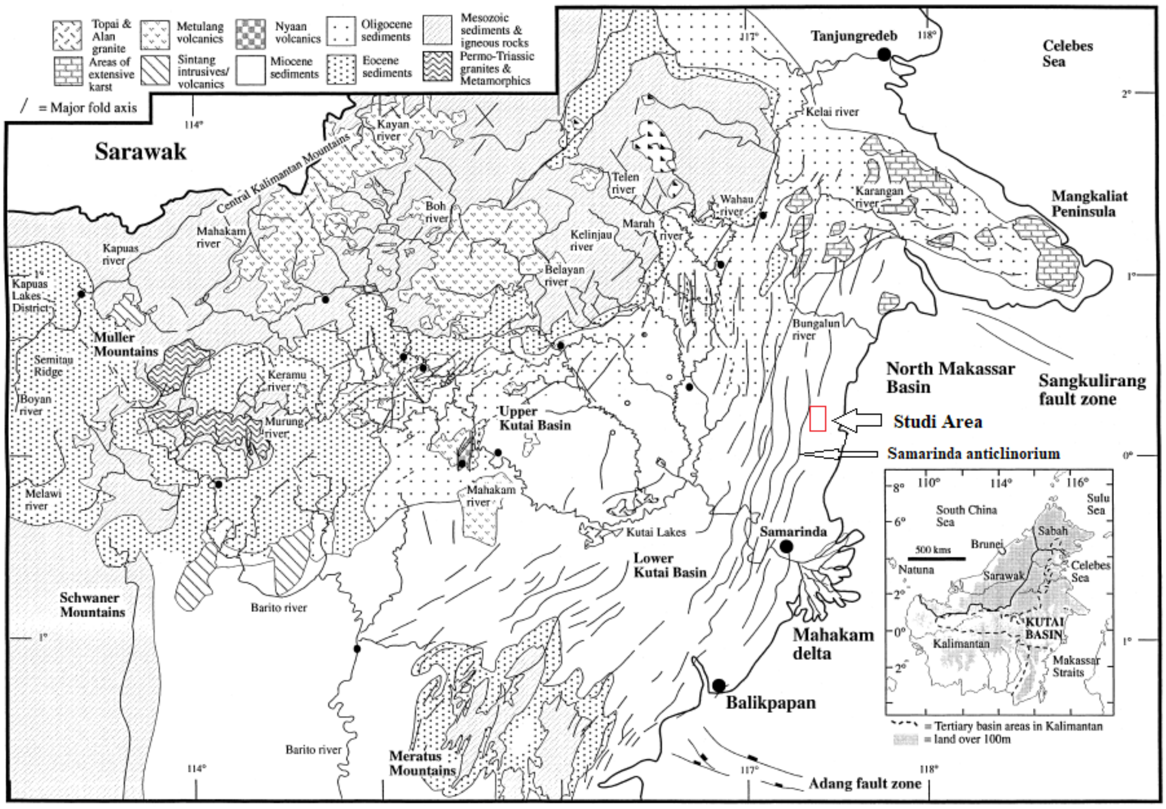

Figure 1. Geological map of Kutai Basin and East Kalimantan. The approximate basement-Tertiary contact, Eocene, Oligocene, and Miocene positions are shown (modified from [4]).

The major coal seam formations in the Kutai Basin are the Early Miocene Pulaubalang Formation, the Late Miocene Balikpapan Formation and the Kampungbaru Pliocene Formation (Figure 2). The coal quality of Pulaubalang Formation is relatively moderate with the rank of lignite-bituminous [7], due to relatively young rock formations (Middle Miocene) and the sedimentary environment influenced by fluvial and tidal systems, so surely the influx of sediment deposit is still dominant. The rank of the Balikpapan Coal formation includes a lignite-subbituminous [8,9]. The coal produced is dominated by ombrotrophic and autochthonous, indicating that the coal is formed in peat bogs during Middle Miocene [7,9]. The rank of coal in this area is brown coal, with a delta front-delta plain deposition environment.

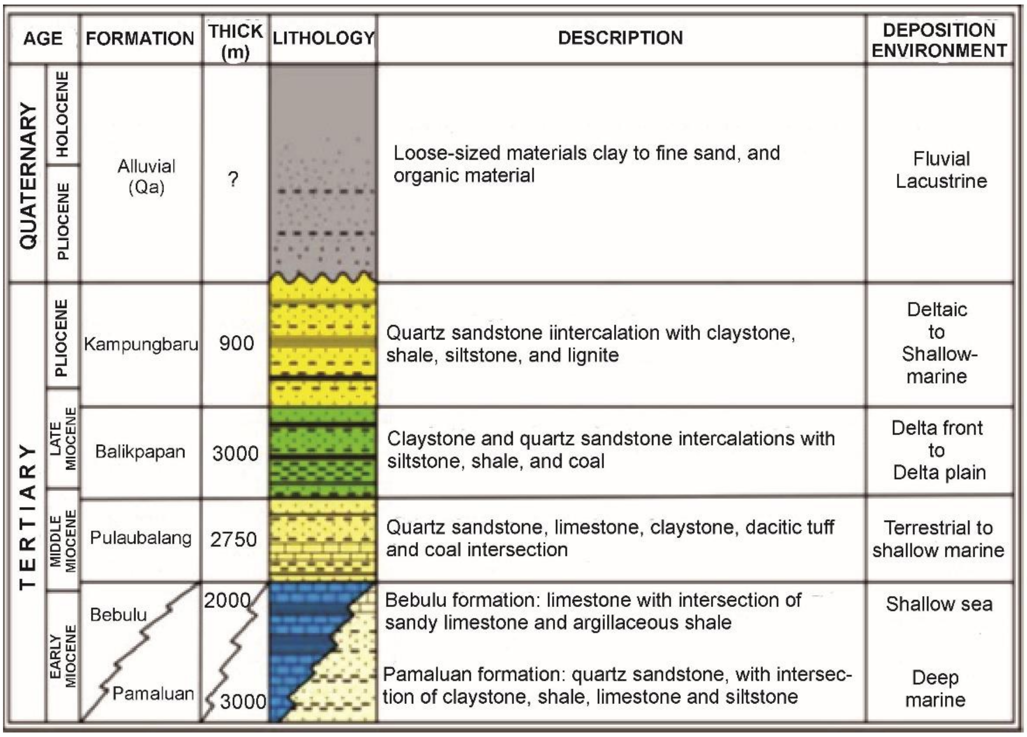

Figure 2. Stratigraphy of the Lower Kutai Basin (modified from [10]).

3. Research Methods

3.1. Samples

The coal samples used in this study were taken from the Lower Kutai Basin which have potential of coal spesifically in Pulaubalang Formation (Tmpb) and Balikpapan Formation (Tmbp). Channel sampling method was proposed for the coal sampling, which involves the process of collecting sample by channel ply sampling / ply by ply. The method of channel ply sampling / ply by ply is the best method for sampling in coal seams because the coarse coal layer is homogenous throughout its thickness [11,12]. Sampling method by channel ply sampling / ply by ply is done from the roof to the floor by dividing the layer into several sub-sections (Figure 3). The minimum distance of samples taken is 0.25 m from the roof and 0.25 m from the coal floor with a thickness of each ply of at least 0.1 m and a maximum of 1.0 m, if there is a layer other than coal (parting) with a thickness> 0.25 m then the layer is not taken. Each weight of this ply is at least 2.0 kg.

3.2. Laboratory analysis

Coal proximate and ultimate analyses were conducted on coal samples aimed at finding out the parameters of coal quality [2].

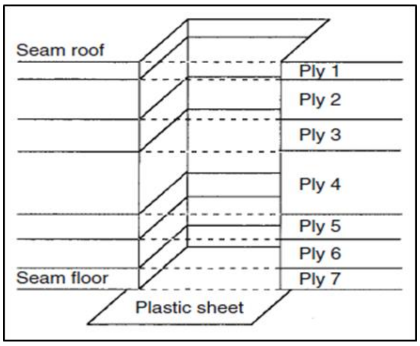

Figure 3. Channel sampling procedure with channel ply sampling / ply by ply [12].

3.2.1. Proximate analysis.
Coal proximate analysis includes moisture content (ISO 11722: 2013), ash content (ISO 1171: 2010), volatile matter (ISO 562: 2010), and fixed carbon (17246: 2010).

- Moisture content analysis
  Water moisture content from coal after reaching equilibrium with laboratory atmosphere and then done by heating 1 gram of coal samples size -212 μm in nitrogen flow at 105°C ± 5°C and dried to constant weight. The weight of moist water is obtained from heavy loss during heating (ISO 11722: 2013).
- Ash content analysis
  Determination of ash content is done by weighing the residual result of perfect combustion of coal. The analysis was done by weighing 1 gram of coal size -212 μm and then heated in a furnace with a temperature of 500°C for the first hour. The sample was then heated to 815°C ± 10°C for 1 hour. When the incineration period is over, the sample is allowed to cool and then weighed (ISO 1171: 2010).
- Volatile matter analysis
  Determination of volatile matter is a loss of mass when coal is heated in an atmosphere isolated with air under standard conditions. The analysis was carried out by heating coal samples of -212 μm size with a weight of 1 gram without oxidation with silica crucible at 950°C ± 5°C for 7 minutes in a horizontal furnace. Estimates were made by calculating the weight lost after heating was corrected moisture content (ISO 562: 2010).
- Determination of fixed carbon
  The calculated fixed carbon is not obtained by analysis, but is obtained from the calculation of 100% -% (moisture + ash + volatile matter) (ISO 17246: 2010).

3.2.2. Ultimate analysis.
The ultimate analysis includes elements in coal such as carbon, hydrogen, and nitrogen (ASTM D.5373-13: 2013); sulfur (ASTM D.4329: 2012); and oxygen (ASTM D.3176: 1990).

- Determination of carbon, hydrogen and nitrogen
  The analysis was done by preparing a sieve -60 mesh-size coal with a weight of 1 g. Carbon, hydrogen and nitrogen in coal are sought simultaneously in an instrumental procedure using furnaces operating at temperatures in the range of 900°C - 1050°C. Conversion of carbon, hydrogen and nitrogen values into the corresponding gases (CO_2, H_2O, and NOx) occurs during sample combustion at high temperatures in the presence of oxygen gas. Combustion results that may interfere with gas analyses are subsequently discarded. The nitrogen oxide (NOx) is converted to N_2 before it is analysed. Carbon dioxide, moisture and nitrogen elements in the gas stream are determined by appropriate analytical procedures. Record total carbon, hydrogen and nitrogen deposited as a percentage of mass. Report the results on the dry base (adb) to the nearest 0.1% for carbon, 0.01% for hydrogen and close to 0.01% for nitrogen (ASTM D.5373-13: 2013).

- Determination of sulphur
  The analysis was done by preparing a sieve -60 mesh-size coal with a weight of 1 g. Weighed samples were burned in a tube furnace at a minimum operating temperature of 1350°C in the oxygen stream. During combustion, all sulphur contained in the sample is oxidized to sulphur oxide gas (sulphur dioxide / SO_2 and sulphur trioxide / SO_3) and chlorine in the sample is released as Cl_2. The product is then absorbed into a solution of hydrogen peroxide (H_2O_2) and dissolved into a sulphuric acid solution (H_2SO_4) and dilute hydrochloric acid (HCl). The amount of both directly produced acids depends on the amount of sulphur and chlorine present in the coal (ASTM D.4329: 2012).
- Determination of oxygen
  Determination of oxygen content is not done directly, but determined based on the difference of carbon, hydrogen, nitrogen, sulphur, and ash content. The percentage of oxygen content is obtained from the calculation of 100% – (% C + % H + % S + % N + % *ash*) (ASTM D.3176).

4. Result and Discussion

4.1. Proximate analysis
The results of proximate analysis for moisture content, ash content, volatile matter, and fixed carbon are given in Table 1.

Table 1. Descriptive statistics of proximate analysis of coal samples

	Moisture	Ash	Volatile matter	Fixed carbon
		%, adb		
Pulaubalang Formation				
Maximum	15,3	7,5	43,5	42,5
Minimum	11,4	3,7	37,9	37,0
Median	13,5	5,9	40,7	40,4
Standard Deviation (DV)	1,6	1,5	2,1	2,0
Average	13,4	5,8	40,6	40,2
Balikpapan Formation				
Maximum	14,4	5,8	41,3	41,7
Minimum	13,7	2,6	39,6	40,2
Median	13,8	4,7	41,1	40,3
Standard Deviation (DV)	0,3	1,2	0,7	0,7
Average	14,0	4,5	40,8	40,6

4.1.1. Moisture content.
There are several sources of the water found in coal. The vegetation from which coal was formed had a high percentage of water that was both physically and chemically bound, and varying amounts of this water were still present at various stages of the coalification process. But the overall result of the continuation of the coalification process was to eliminate much of the water, particularly in the later stages of the process. The total moisture in coal is determined by moisture (in all forms except water of crystallization of the mineral matter) that resides within the coal matrix. In fact, moisture (or water) is the most elusive constituent of coal to be measured in the laboratory [2]. Generally, the moisture content of coals ranges from 5% to nearly 70% which is an undesirable constituent as it reduces the heating value and adds weight to the transportation cost. The increased contents of this physically and chemically adsorbed water are characteristic of lower-rank coals, while the decreased values of this parameter are typical of higher-rank coals [13]. In the present study the moisture content coal samples ranges between 11.4 to 15.3 wt% and arithmetic mean of 13.4 wt% on Pulaubalang Formation and on Balikpapan

Formation between 13.7 to 14.4 wt% and arithmetic mean of 14.0 wt%. From the arithmetic mean in both this formations indicate that the coal is sub-bituminous.

4.1.2. Ash content.

The ash of a coal is that inorganic residue that remains after combustion. It should be remembered that the determined ash content is not equivalent to the mineral matter content of the coal. It does, however, represent the bulk of the mineral matter in the coal after losing the volatile components such as CO_2, SO_2 and H_2O, which have been driven off from mineral compounds such as carbonates, sulfides and clays [2]. The high ash yield is normally a marked by the relatively abundant supply of detrital materials in swamp, wherein; the authigenic minerals dominate mostly with low-ash (8-10%) coals, whereas the proportion of detrital minerals increases [14] and the concentration of organically bound elements decreases [15] with increased ash yield. The ash content of samples between 3.7 to 7.5 wt% and arithmetic mean of 5.8 wt% on Pulaubalang Formation and on Balikpapan Formation between 2.6 to 5.8 wt% and arithmetic mean of 4.5 wt%.

4.1.3. Volatile matter.

Volatile matter represents that component of the coal, except for moisture, that is liberated at high temperature in the absence of air. This material is derived chiefly from the organic fraction of the coal, but minor amounts may also be from the mineral matter present. Correction for the volatile matter derived from the latter may be made in technical works, but is not usually necessary in commercial practice [2]. The increased VM content is more characteristic of low-rank coals, while the decreased value is more typical of higher-rank coals [13]. The volatile carbon content in the samples of the study area ranges between 37.9 to 43.5 wt% and arithmetic mean of 40.7 wt% on Pulaubalang Formation and on Balikpapan Formation between 39.6 to 41.3 wt% and arithmetic mean of 40.8 wt%.

4.1.4. Fixed carbon.

Fixed carbon is the material remaining after the determination of moisture, volatile matter, and ash. It is, in fact, measurement of the solid combustible material in coal after the expulsion of volatile matter. The fixed-carbon value is one of the values used in determining the efficiency of coal-burning equipment. It is a measure of the solid combustible material that remains after the volatile matter in coal has been removed [2]. The fixed carbon content of coals, not including the moisture and ash, ranges from 50% to about 98%. It is well known that the FC content increases with coal rank advance [16]. The fixed carbon content the samples of the study area ranges between 37.0 to 42.5 wt% and arithmetic mean of 40.2 wt% on Pulaubalang Formation and on Balikpapan Formation between 40.2 to 41.7 wt% and arithmetic mean of 40.6 wt%.

4.2. Ultimate analysis

The results of ultimate analysis for carbon, hydrogen, nitrogen, sulphur and oxygen are given in Table 2.

4.2.1. Carbon.

The high concentrations of Carbon are normally characteristic of vitrinite macerals. It is also well known that the C content in coal increases steadily with increasing coal rank. The measurement of Carbon concentration in coal is still the leading and most accurate parameter among other chemical characteristics for evaluation of coal rank despite some limitations [13]. The Carbon in the samples ranges between 59.02 to 66.13 wt% and arithmetic mean of 63.21 wt% on Pulaubalang Formation and on Balikpapan Formation between 58.67 to 59.73 wt% and arithmetic mean of 59.24 wt%.

4.2.2. Hydrogen.

The increased content of Hydrogen is normally more characteristic of low rank coals, while the decreased values are commonly more typical of higher-rank coals [3]. The Hydrogen in the samples ranges between 5.80 to 6.46 wt% and arithmetic mean of 6.10 wt% on Pulaubalang Formation and on Balikpapan Formation between 5.62 to 6.11 wt% and arithmetic mean of 5.92 wt%.

4.2.3. Nitrogen.
Nitrogen occurs almost exclusively in the organic matter of coal. Very little information is available concerning the nitrogen-containing compounds present in coal, but they do appear to be stable and are thought to be primarily heterocyclic [2]. The increased contents of Nitrogen are normally more characteristic of higher-rank coals, while the decreased values of this element are commonly more typical of lignites. The Nitrogen in the samples ranges between 1.19 to 1.43 wt% and arithmetic mean of 1.30 wt% on Pulaubalang Formation and on Balikpapan Formation between 1.30 to 1.38 wt% and arithmetic mean of 1.34 wt%.

4.2.4. Sulphur.
The Sulphur is an important consideration in coal utilization, and hence, there is a considerable amount of published work relating to the development of methods to improve the efficiency of the techniques as well as improve the accuracy and precision of the sulfur determination. Total sulphur data are necessary for the effective control of the emissions of oxides of sulphur whenever coal is used as a fuel. The emission of sulphur oxides leads to the corrosion of equipment and slagging of combustion or boiler equipment, as well as contributing to atmospheric pollution and environmental damage. Sulfur data are therefore necessary for the evaluation of coals to be used for combustion purposes. The Sulphur in the samples ranges between 0.15 to 2.51 wt% and arithmetic mean of 0.67 wt% on Pulaubalang Formation and on Balikpapan Formation between 0.18 to 2.28 wt% and arithmetic mean of 1.23 wt%. Deposition environments affected by marine sediments will produce high sulfur coals [17].

4.2.5. Oxygen.
The increased content of Oxygen is characteristic of low rank coals, while the decreased concentration is typical of higher-rank coals. The increased Oxygen concentration is in accordance with greater contents of moisture and hydrated minerals or as a result of advanced coal weathering [3,13]. The Oxygen in the samples ranges between 20.63 to 27.60 wt% and arithmetic mean of 22.96 wt% on Pulaubalang Formation and on Balikpapan Formation between 26.54 to 31.22 wt% and arithmetic mean of 27.75 wt%.

Table 2. Descriptive statistics of ultimate analysis of coal samples

	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
			%, adb		
Pulaubalang Formation					
Maximum	66,13	6,46	1,43	2,51	27,60
Minimum	59,02	5,80	1,19	0,15	20,63
Median	64,00	6,06	1,28	0,22	22,21
Standard Deviation (DV)	2,65	0,31	0,10	1,03	2,78
Average	63,21	6,10	1,30	0,67	22,96
Balikpapan Formation					
Maximum	59,73	6,11	1,38	2,28	31,22
Minimum	58,67	5,62	1,30	0,18	26,54
Median	59,39	5,96	1,34	1,34	27,02
Standard Deviation (DV)	0,47	0,18	0,03	0,92	1,95

5. Conclusions
The present study aimed to characterize the coal at Kutai Basin (Pulaubalang and Balikpapan Formation) through chemical composition utilizing the parameters through proximate and ultimate analyses. The proximate analysis results show that the moisture content is 13.4 %, volatile matter is 40.6 %, and fixed

carbon is 40.2 % on Pulaubalang Formation and the moisture is 14.0 %, volatile matter is 40.8 %, and fixed carbon is 40.6 % on Balikpapan Formation. The ultimate analysis results show that the carbon is 63.21 %, hydrogen is 6.10 %, and oxygen is 22.96 % on Pulaubalang Formation and the carbon is 59.24 %, hydrogen is 5.92 %, and oxygen is 27.75 % on Balikpapan Formation. The proximate and ultimate analyses of coals show the typical characteristics properties of sub-bituminous coal.

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References
[1] Van Krevelen, D.W. *Coal, Typology-Physics-Chemistry-Constitution,* 3rd ed.; Elsevier: Amsterdam. 1993.
[2] Speight, J. G. *Handbook of Coal Analysis,* Published by John Wiley & Sons, Inc. Hoboken, New Jersey. 2005.
[3] Haenel, M.W. *Recent Progress in Coal Structure Research*, Fuel, Vol. 71, November, p. 1211-1223. 1992.
[4] Moss, S.J. dan Chambers, J.L.C. *Depositional Modelling and Facies Architecture of Rift and Inversion in The Kutai Basin, Kalimantan, Indonesia*, Indonesian Petroleum Association, Proceedings 27th Annual Convention. Jakarta, (1999) 459-486.
[5] Satyana, A.H., Nugroho, D., Surantoko, I. (1999). *Tectonic Controls on The Hydrocarbon Habitats of The Barito, Kutai and Tarakan Basin, Eastern Kalimantan, Indonesia; Major Dissimilarities,* Journal of Asian Earth Sciences Special Issue, 17(1-2) (1999) 99-120, Elsevier Science, Oxford.
[6] Bachtiar, A. *Kerangka Stratigrafi Sekuen dan Karakter Batuan Induk Miosen Awal di Cekungan Kutai Hilir, Kalimantan Timur.* Disertasi, Program Doktor, Institut Teknologi Bandung. 2004.
[7] Widodo, S., Bechtel, A., Anggayana, A., Püttmanna, W. *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 Geochemistry, 40 (2009) 206–218.
[8] Ulfaniyah, N.I., Burhan, R.Y.P. *Karakterisasi Geokimia Organik Batubara Samarinda*, Sains dan Terapan Kimia, Vol. 8. No. 2 (Juli 2014), (2014) 57-68.
[9] Win, C.T. *Sedimentology and Organic Petrology of Coal and Coal-Bearing Sequences in The Samarinda Area, Lower Kutai Basin, Indonesia,* Disertation, The Post Graduate Program of Geological Engineering Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia. 2015.
[10] Sukardi, Sikumbang, N., Umar, I., Sunaryo, R. *Peta Geologi Lembar Sangatta, Kalimantan,* Pusat Penelitian dan Pengembangan Geologi, Bandung, Indonesia. 1995.
[11] Speight, J.G. *The Chemistry and Technology of Coal*. 3rd ed.; CRC Press Taylor & Francis Group, Broken Sound Parkway NW, Florida. 2013.
[12] Thomas, L. *Coal Geology*. 2nd ed.; Wiley-Blackwell, John Wiley & Sons, Ltd. England, 2013.
[13] Stach, E., Mackowsky, M., Teichmuller, M., Taylor, G., Chandra, D., Teichmuller, R. *Stach's Textbook of Coal Petrology*. Gebruder Borntraeger, Berlin, 535 pp. 1982.
[14] Finkelman, R. *The inorganic geochemistry of coal: a scanning electron microscopy view*. Scanning Microscopy 2, 97–105. 1988.
[15] Nicholls, G.D. *The geochemistry of coal-bearing strata.* In: Murchison, D., Westall, T. (Eds.), Coal and Coal bearing Strata. Oliver & Boyd, 269–307. 1968.

[16] Sahni, A., Saraswati, P.K., Rana, R.S., Kumar, K., Singh, H., Alimohammadian, H., Sahni, N., Rose, Kd, Singh, L. And Smith, T. Temporal constraints and depositional palaeoenvironments of the Vastan lignite sequence, Gujarat: Analogy for the Cambay Shale hydrocarbon source rock. Indian Jour. Petrol. Geol., v.15, pp.1-20. 2006.
[17] Casagrande, D.J. *Sulphur in Peat and Coal,* in Scott, A.C. (ed.), Coal and Coal-Baering Strata. Recent Advances, Geol. Soc. Spec. Publ. 32 (1987) 87-105.