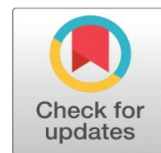# COAL STRUCTURAL CHARACTERISTICS OF BAYAH FORMATION BASED ON X-RAY DIFFRACTION ANALYSIS

Ahmad Helman Hamdani [1] ✉ iD, Agus Didit Haryanto [1] iD, Muhamad Iqbal [1] iD

[1] Department of Geology, University of Padjadjaran, Indonesia

ABSTRACT

The coal of Bayah Formation in Lebak Regency, Indonesia have been subjected to attenuated to X-ray diffraction (XRD), to study their chemical and structural characteristics. X-Ray Diffraction (XRD) has been widely used throughout the world and has high accuracy in identifying the molecular structure of coal. Curve-fitting analysis was employed to characterize coal structural. Based on ASTM, the coal rank from this area is high-volatile bituminous B. The research results show all coals have the similar coal structural crystallite characteristics. The value of d_{002} is in the range of 3.87 to 3.96, reflecting the coals have a low content of crystalline structure. The crystallite height (Lc) and diameter (La) were increase, while d_{002} decrease in relation of more mature coals. Due to structural parameters (d_{002}, Lc and La) the coals of Bayah Formation dominantly by disordered amorphous structure, with small amount crystallite structure.

Keywords: Coal, Structural, XRD, Curve Fitting, Bayah Formation

1. INTRODUCTION

During coalification process, various kinds of inorganic, organic and water materials are involved together, so coal is heterogeneous; and provides diverse physical and chemical characteristics which are reflected in the values of the heterogeneous crystalline structural parameters in coal. Therefore, study on the crystal coal structure is important; with knowledge of molecular structure of coals; physicochemical reactions during the coal combustion, gasification, and pyrolysis can be controlled. Singh et al. (2015), Sonibare et al. (2010), Saikia et al. (2007).

XRD is a non-damage method that is often used to study the crystallite structural of materials containing carbon, such as coal Haenel (1992), Lu et al. (2001), Vivek et al. (2016). Several indicators of crystal structure in coal measured by XRD are stacking height of crystallite (Lc), average lateral sizes (La), interlayer spacing of the crystalline structure (d002), aromaticity (fa). The coal rank was controlled the development of coal crystal structure parameter. An increase in coal maturation will be followed by a decrease in the value of d002, and an increase in the value of La and Lc, but the value of Lc gradually decreasing. In the throughout the coalification process, an increase crystal structure of coal and a decrease in the amorphous structure Jiang et al. (2019). Hirsch (1979), Watanabe et al. (2002). Qualitatively, the structure in coal generally consists of crystalline carbon and amorphous carbon Lu et al (2015). In Banten Province the

occurrence of coal is reported found within Bayah Formation of Eocene strata Sujatmiko and Santosa (1992) Investigation of the Bayah Formation coal was limited to the analysis of proximate, ultimate and maceral compositions. However, research on the structure of coal has not been investigated. The aim of this research is the use of XRD technique to study the structural characteristics of the Bayah Formation coal.

2. MATERIALS AND METHODS
2.1. SAMPLE AND SAMPLE PREPARATION

Five bituminous coals from Bayah Formation, Banten Province were selected for this investigation. Several analyses were carried out to obtain the chemical molecular structure characteristics of bituminous coal, such as proximate, ultimate, XRD analysis.

2.2. EXPERIMENTAL METHODS

Proximate, Ultimate Analysis. The series measurement of moisture, ash, fixed carbon, and volatile matter in coal which is grouped in Proximate Analysis. The ASTM Standard of moisture, ash, fixed carbon, volatile matter was used, such as D-3173, D-3174, D-388, D-3175, respectively. The ultimate analysis was measured carbon and hydrogen, nitrogen, sulphur, and oxygen based on ASTM Standard of ASTM D-3178, ASTM D-3179, ASTM D-3177, and ASTM D-3176, respectively. The result of all analysis was presented in Table 1.

XRD. An X-ray diffractometer device (BrukerAXSD8) was used to obtain the spectral characteristics of the XRD. The operational conditions used are as follows: CuKa radiation (40Kv, 40mA) in the angular range of 100 –800 (2θ) with 0.020 step interval and a scanning rate of increments from 50 to 900 (2θ) at intervals of 0.02 and counted for 0.5 sec per step. The Bragg's and Scherrer equations were used calculated the structural parameters Equation 1, Equation 2, Equation 3, Equation 4 Equation 5, Iwashita et al. (2004), Okolo et al (2010), Robert et al. (2015), Baysal et al. (2016), Li et al. (2013), Li and Zhu (2014)

$$\int a = C_{ar} / (C_{ar} + C_{al}) = A_{002} / (A_{002} + A\gamma) \qquad \textbf{Equation 1}$$

$$d002 = \frac{\lambda}{2 sin\theta 002} \qquad \textbf{Equation 2}$$

$$La = 1.84\lambda / (\beta_{002} cos\theta_{002}) \qquad \textbf{Equation 3}$$

$$Lc = 0.89\lambda / (\beta_{100} cos\theta_{100}) \qquad \textbf{Equation 4}$$

$$N = \frac{Lc}{d002} \qquad \textbf{Equation 5}$$

Where *Car* is the sum of the aromatic carbons, and the value of *Cal* is the sum of the aliphatic carbons. A_{002} and A_{γ} are areas of peak 002 and peak γ which are around the 26° and 20° x coordinates respectively on the XRD graph. λ =1.54056 for copper Ka radiation; λ is the wavelength of the radiation used. θ_{002} and θ_{100} are the diffraction angles from peak 002 and peak 100. β_{002} and β_{100} are full width half at maximum values (FWHM) of peak 002 and peak 100.

To determine coal rank from XRD from the formula Equation 6, Yoshizawa et al. (2002)

$$Coal\ rank = (I_{26}/I_{20})$$ **Equation 6**

3. RESULTS AND DISCUSSIONS
3.1. PROXIMATE AND ULTIMATE ANALYSIS

Result of analysis of Bituminous coals from Bayah Formation, Banten Province was shown in Table 1. The average atomic ratios of H/C, O/C, were calculated to be 0.86, 0.08, respectively. The moisture is low in all coals (1.8–2.4wt%), and low ash yield (, 5% wt.%). The coals have a high volatile matter, and fixed carbon, i.e., 45.7% to 46.1%, 47.5% to 51.1%., respectively. The sulfur in samples is low (0.76–n1.21 wt.%). Measurement of C-H-O elements in coals showed that the carbon content was very high, which was followed by oxygen and hydrogen as presented in Table 1.

Table 1 Result of proximate and ultimate measurement of coal samples						
	Parameters	**ST-11.2**	**ST-14**	**ST-17**	**ST-21**	**ST-24**
Proximate (ad)	Moisture	4,13	4.21	4.73	3.92	4.28
	Ash	5.81	4.21	3.78	2.61	2.17
	Volatile Matter	39.31	40.12	41.42	42.18	42.51
	Fixed Carbon	50.75	51.46	50.07	51.29	51.03
Ultimate (daf)	Carbon	79.64	78.49	80.05	78.43	78.34
	Hydrogen	3.35	4.19	4.2	4.54	5.23
	Oxygen (by diff)	15.31	14.82	14.4	16.18	15.44
H/C		0.5	0.64	0.62	0.69	0.8
O/C		0.14	0.14	0.13	0.15	0.15

3.2. XRD

In the XRD graph Figure 1, it is clear that the peaks of XRD spectral intensity of 002, 10, and 100 are identified. These three peaks are at diffraction degrees of 2ө at 26°, 42° and 47°, respectively. In addition, to the left of peak γ is identified peak, both of which are Gaussian peaks.
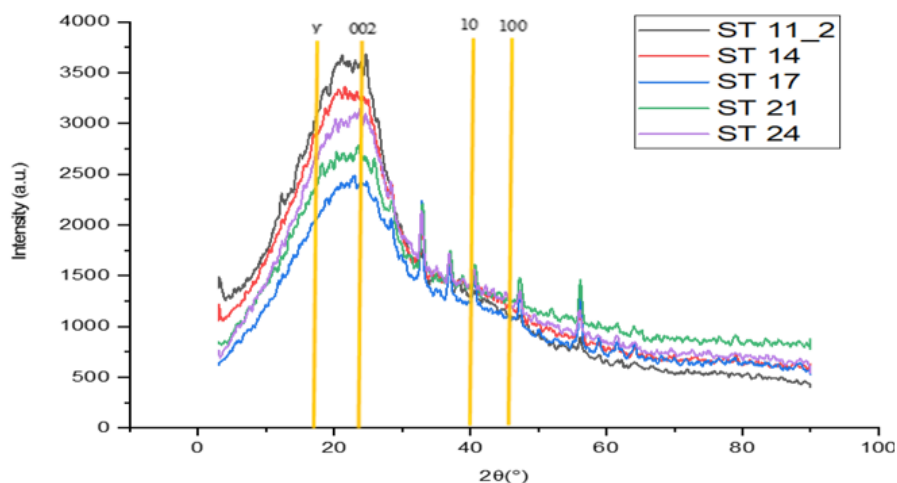

Figure 1 XRD spectra of Bayah coal samples

To get the peak area, diffraction angle 2θ, intensity value and FWHM (Full Width Half Maximum) value; Curve fitting analysis (Gaussian method) was performed on all coal samples. Figure 2 shows the results of the Curve fitting sample no. ST. 17, and ST. 21, which represents all coal samples. Table 2 tabulated the results of the calculation of the structural parameters of coal with the XRD method of Bayah Formation coal
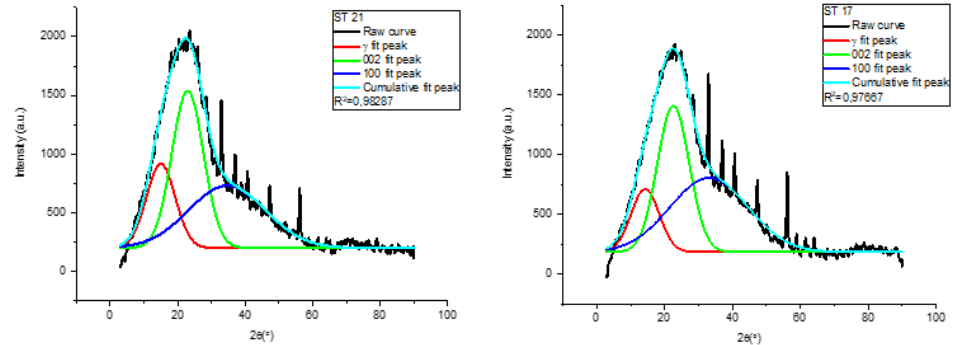

Figure 2 Gaussian's curve fitting XRD Spectral from coal samples of Bayah Formation

Table 2 Structural parameters of coal by XRD

Sample	d_{002} (Å)	La (Å)	Lc (Å)	ʃa	N	n2	I_{26}/I_{20}	Ro (%)
ST 11_2	3.96	15.3	7.3	0.76	2.85	2.61	2.61	0.72
ST 14	3.94	13.16	5.81	0.64	2.49	1.98	2.01	0.71
ST 17	3.94	14.9	3.01	0.73	1.76	1	1.98	0.68
ST 21	3.86	15	3.12	0.67	1.79	1.03	1.69	0.74
ST 24	3.91	14.1	3.31	0.68	1.84	1.09	1.93	0.65

Where:

D002: Interlayer spacing   fa: aromaticity

Lc: Crystallite height   N: Average Number of aromatic layers

La: Crystallite diameter   n: average total carbon atoms in the aromatic layer

I26/I20: Coal rank

From the results of measurement of coal structural parameters by XRD analysis Table 2, it can be seen that the value of the interlayer distance (d_{002}) is in the range of 3.86 to 3.96 Å, the average diameter of crystallite (La) is in the diameter of 13.16 to 15.30 Å, the average size of crystallite height is (Lc) in the range 3.01 to 7.30 Å, carbon aromaticity (ʃa) in the range 0.64 to 0.76, coal rank (I_{26}/I_{20}) in the range 1.69 to 2.61, and carbon layer (N) in the range of 1.76 to 2.85, and the value of n is between 1.00 - 2.61.

4. DISCUSSION

Based on the analysis of proximate and ultimate analysis; ratio of H/C and O/C indicated that all coals were classified as the High Volatile Bituminous-B coal.

The results of the observation of coal XRD spectral peaks show that peak 002 is higher compared to peak 10 or 100; apart from structured; it was clearly found at 26°, 42° and 47°, respectively. Generally, in coals the XRD spectral consists of 002 and 100 peaks, which peak 002 has the position in areas between 15–30°: and peak

100 in the range of 40–50°. Smędowski et al. (2011), Baysal et al. (2016). This reflects that the coal studied have a structure like graphite (crystallite carbon). However, with the high detected background, the coal also contains an amorphous material structure (highly disordered materials). Therefore, based on the appearance of the peak of the spectral XRD; Therefore, Bayah coal is composed of amorphous and crystalline material Lu et al. (2001), Okolo et al. (2015).

The values of coal crystallite structures such as d_{002}, La, and has a relation with coal maturity (%Ro). For all the coal samples were shown that with an increase of %R_o, the variation of L_a increase slightly for coal from 13.16 – 15.30 Å; d_{002} decrease slightly of 3.86-3.96 Å, while Lc decreasing from 3.91 – 3.86 Å. In high rank coal, graphite structure is more likely to form compared than in low rank coal. The interlayer distance (d_{002}) in all samples showed a higher range (3.86 to 3.96 Å) than d_{002} pure graphite (d_{002}= 3.36-3.37Å), reflecting the low degree of crystal regularity in coals. Bhupati et al (2017).

The interlayer spacing (d_{002}) in the high mature bituminous coal (Ro =0.74%) of the Bayah Formation was small (3.86 Å); associated with a lower carbon element content value (79 - 80%) compared to that contained by pure graphite Singh et al. (2015), Singh et al (2017). Besides that, it is also related to the aromatic ring in the coal continues to solidify as the coal matures.

Overall, the findings in this study indicate that the more mature (high %Ro), the smaller the amorphous structure, which is followed by an increase in crystallite height and diameter; but the interlayer spacing is getting smaller. The same finding was also conveyed by other researchers. Shike et al. (2021), Takagi et al. (2004)

5. CONCLUSIONS AND RECOMMENDATION

A total of 5 coal sample from Bayah Formation, Indonesia have been identified the structural characteristic based on XRD measurement. Following conclusion are drawn:

1) The coals are classified as the High Volatile Bituminous B
2) The XRD investigations show the highly disordered amorphous and crystallite structure were identified in coals.
3) The crystalline carbon in coals having the sizes of La, (Lc), and d_{002} ranging from 13.16-15.30 Å, 3.01 to 7.30 Å, and 3.86 to 3.96Å, respectively.

We, recommend XRD study to be used to indicate coal maturity level

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