RELATIONSHIP BETWEEN MOLECULE STRUCTURE AND COAL MATURITY OF BAYAH FORMATION BASED ON X-RAY DIFFRACTION ANALYSIS

Muhammad Iqbal Ardiansyah[1], Ahmad Helman Hamdani[2], Agus Didit Haryanto[2]
[1]Faculty of Geological Engineering, Universitas Padjadjaran
[2]Department of Geological Science, Universitas Padjadjaran

Corresponding author: iqbal17023@mail.unpad.ac.id

ABSTRACT

Coal is the richest source of energy used worldwide. Characterization of the structure of coal is one of the important things in studying the use of coal. X-Ray Diffraction (XRD) has been successfully used as a tool to study the molecular structure characteristics of coal with various coal ranks. There are five coal samples to be examined from the Bayah Formation in Lebak Regency, Banten. This study aims to measure the crystal structure parameters in coal and use them to predict coal maturity level. The results of XRD analysis showed that the five coal samples had the same crystal structure characteristics. The value of d002 is in the range of 3.87 to 3.96 Å, indicating that the studied sample has a low content of microcrystalline units. The measurement of carbon aromaticity (fa) values in the study area ranged from 0.67 to 0.76. There is a strong correlation between the value of coal maturity as measured by vitrinite reflectance (Ro) and the value of aromaticity; which is characterized by a correlation value of r of 0.88. Thus, the aromaticity (fa) value of XRD can be used to predict the maturity level of coal.

Keyword: Molecular Structure, Coal Maturity, Carbon Aromaticity, Bayah Formation

INTRODUCTION

Coal is natural carbon with physicochemical properties that vary according to the location of origin of the coal. Coal formed by various kinds of organic and organic materials making coal very heterogeneous, both physically and chemically. In studying the use of coal, structural characterization of coal is the most important activity to do.

One of the most frequently measured molecular structure parameters in coal is carbon aromaticity (ƒa). Van Krevelen is the first man to determine the value of ƒa using a graphical density approach (Van Krevelen, 1967). The main finding of all researchers regardless of which method they use to determine the value of ƒa is that the value ƒof a increases as a coal matures (Davidson 1986; Axelson, 1985). Although many researchers use chemical parameters (such as H/C ratio) as an indicator of coal rank, several other researchers have used vitrinite reflectance (Ro) (Axelson, 1987).

XRD is often used to study the characteristics of the crystal structure of materials containing carbon (Haenel, 1992, Lu et. al., 2001), one of things that studied is coal. Several indicators of crystal structure in coal as measured by XRD are average lateral sizes (La), stacking height of crystallite (Lc), interlayer spacing of the crystalline structure (d002), aromaticity (fa). The crystal structure parameter in coal is controlled by coal rank. An increase in coal rank 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 decreases. Jiang (2018), stated that during the coalification process, there will be an increase in the crystal structure of coal and a decrease in the amorphous structure.

Research on the molecular structure of coal in Nigeria is an example of the use of XRD as a research tool for the molecular structure of coal. The results showed that there was a linear relationship between the crystal structure parameters in coal such as fa, d002 and Lc with carbon content and volatile matter. This illustrates that the composition of coal affects the molecular structure of coal.

The study area is located in the Bayah Formation in Lebak Regency, Banten. Based on the Geological Map of the Leuwidamar Sheet (Sudjatmiko and Santosa, 1992), coal was found in the Conglomerate Member (Teb). At this time there has been no research on the relationship between the molecular structure and coal maturity of the Bayah Formation, so this research is important to be carried out to be able to determine the potential for optimal utilization of coal for the Bayah Formation. This study aims to measure the crystal structure parameters in coal and use them to predict coal maturity level.

REGIONAL GEOLOGY

West Java and Banten has four structure patterns, there are Meratus pattern, Sunda

E-ISSN : 2579 – 3136

pattern, Sumatran pattern, and Java pattern. Van Bemmelen (1949) mentions that Bayah undergoes three phases of orogenesis. Orogeny I occurs in Early Oligocene-Early Miocene in the form normal fault, slip fault with E-W and NE-SW direction. Orogeny II occurs in Early Miocene- Middle Miocene in the form normal fault and slip fault with NE-SW and EW direction. Orogeny III occurs in Middle Miocene-Pliocene in the form normal fault, slip fault with N-S, NE-SW, and NW-SE direction and fold with N-W and NE-SW direction. This orogeny is caused by Indo- Australia and Eurasia plate collisions. Meratus pattern occurs in Early Cretaceous-Early Eosen with NE-SW direction, Sunda pattern occurs in Early Eosen-Early Oligocene, Java pattern occurs in Oligocene-Holocene with E-W direction, Sumatran pattern occurs in Pra Tersier-Early Tersier with N-S and NW-SE direction.

Stratigraphically, the oldest rock unit exposed in Leuwidamar sheet are known as Bayah Formation with Eosen age. Bayah Formation consists of three members, there are Conglomerate member (Teb) consists of conglomerate, coal, quartz sandstone, tuff, and mudstone with Eosen age. Mudstone member (Tebm) consists of marly claystone, black claystone, shale, and sandstone with Eosen age. And then the third Limestone Member (Tebl) consists of limestone and marl.

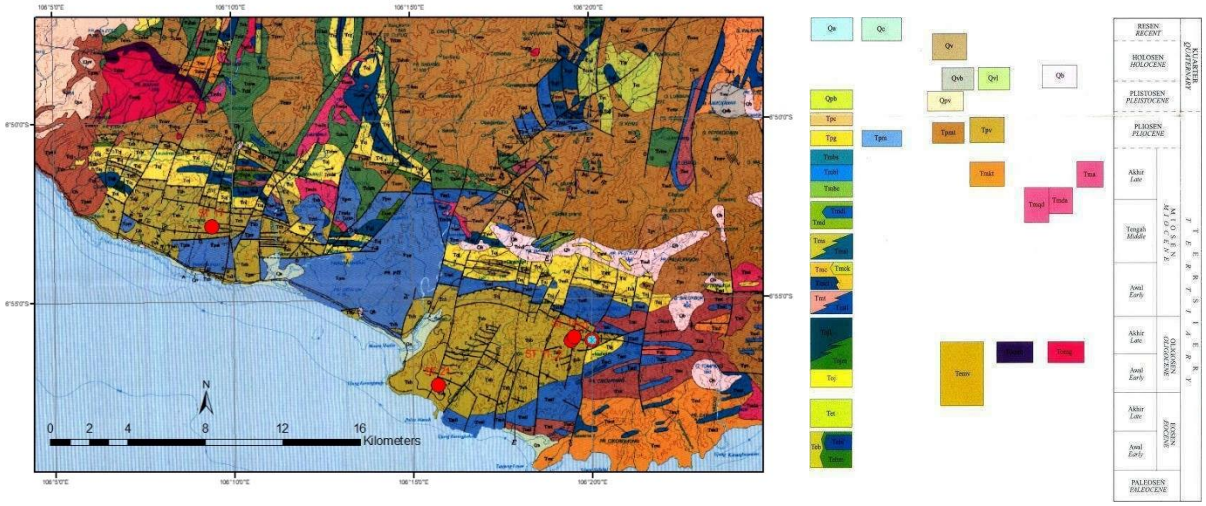

Figure 1. Regional Geological Map of the research area (modification from Sujatmiko and Santosa, 1992)

RESEARCH METHOD

There are five samples analysed from Bayah Formation, BYH 11.2, BYH 14, BYH 21, BYH 24, and BYH 17. Each sample was air dried and crushed until it is fine enough to pass trough a 200-mesh sieve. It was then divided into representative amounts for chemical analysis by G Labs, Bandung, Indonesia.

Proximate and Ultimate Analysis

Proximate and ultimate analysis is used to determine the value 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.

X-Ray Diffraction Analysis

Tto determine the structural parameters of carbon-based materials the XRD was used. Through XRD analysis, it can be seen the value of carbon aromaticity (f_a), inter-layer spacing (d_{002}), the average diameter of coal crystallite (La), the average height of coal crystallite (Lc) , coal rank (I_{26}/I_{20}) , the number of aromatic carbon layers (N), and the average total aromatic layer carbon atoms (n).

The value of the structural parameters that have been mentioned can be calculated through the following equation:

$f_a = Car/(Car + Cal) = A002/(A002 + A_Y)$ (Yen, 1961) (1)

E-ISSN : 2579 – 3136

The value of 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.

Coal rank = I_{26}/I_{20} (Yoshizawa, 2001) (2)

$$d002 = \frac{\lambda}{2sin\theta 002} \quad (3)$$

La = 1.84λ/(β002cosθ002) (4)

Lc = 0.89λ/(β100cosθ100) (Hirsch, 1955) (5)

$$N = \frac{Lc}{d002} \quad (6)$$

$n = 0{,}32N^2$ (7)

The value of the parameters above is based on the formula according to Braggs and Scherrer. The wavelength of X-ray (γ = 0.15405nm), θ002 and θ100 are the diffraction angles from peak 002 and peak 100. β002 and β100 are FWHM values (full width half at maximum) of peak 002 and peak 100.

Data Analysis

To measure the strength of the relationship between two variables used correlation analysis. Positive correlation if the relationship between the two variables is unidirectional; on the other hand, if it is not in the same direction, it is stated as a negative correlation. Sarwono (2006) provides correlation (r) criteria between two variables; as follows

r value	Interpretation
1.0	Perfect correlation
0.75-0.99	Very strong correlation
0.50-0.75	Strongly correlation
0.25-0.50	Moderately correlation
0.0-0.25	Very weak correaltion
0	No correlation

RESULT AND DISCUSSION

The chemical properties of coal

Table 1 shown lists of these analysis results of Bituminous coals from Bayah Formation, Banten Province. The average atomic ratios of H/C, O/C, were calculated to be 0.65, 0.14, 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 are low (0.76–n1.21 wt.%). Measurement of C-H-N-S-O elements in coals showed that the carbon content was very high, which was followed by oxygen and hydrogen as shown in Table 1 Based on ratio H/C vs O/C (Figure 2), and the heating value between 13,329.08 to 13,629.44 Btu/Lb., these coals are highly volatile bituminous-B in rank (ASTM Coal Classification).

Table 1. Proximate and ultimate analysis calculation results

Sample	Proximate Analysis (adb)					Ultimate Analysis (daf)			Atomic Ratio	
	M	A	VM	FC	Btu/lb	C	H	O	H/C	O/C
ST 11_2	4.13	5.81	39.31	50.75	13329.08	79.64	3.35	15.31	0.5	0.14
ST 14	4.21	4.21	40.12	51.46	13692.44	78.49	4.19	14.82	0.64	0.14
ST 17	4.73	3.78	41.42	50.07	13541.34	80.05	4.2	14.4	0.62	0.13
ST 21	3.92	2.61	42.18	51.29	13386.64	78.43	4.54	16.18	0.69	0.15
ST 24	4.28	2.17	42.52	51.03	13534.14	78.34	5.23	15.44	0.8	0.15

X-Ray Diffraction Analysis

Generally, coal has two types of carbon structures, namely crystalline carbon and amorphous carbon. Crystalline carbon refers to a turbostrate structure, while amorphous carbon refers to non-aromatic carbon. (Lu, 2001). Crystallites in coal samples have an intermediate between a turbostrate structure and a non-aromatic structure. On the XRD graph, it is clear that the peaks are 002 and 100. These two peaks are at diffraction degrees of 26° and 47°. Peak 002 indicates the arrangement of the aromatic ring which is a turbostrate structure, and corresponds to

E-ISSN : 2579 – 3136

the microcrystals encapsulated in the aromatic ring. To the left of peak 002 is the peak, which is formed by branched chains of aliphatic hydrocarbons, various types of branched alicyclic hydrocarbons and connected by aromatic rings. Each coal sample has the same crystallite characteristics, this can be seen from peak 002 and peak 100 which show high intensity.

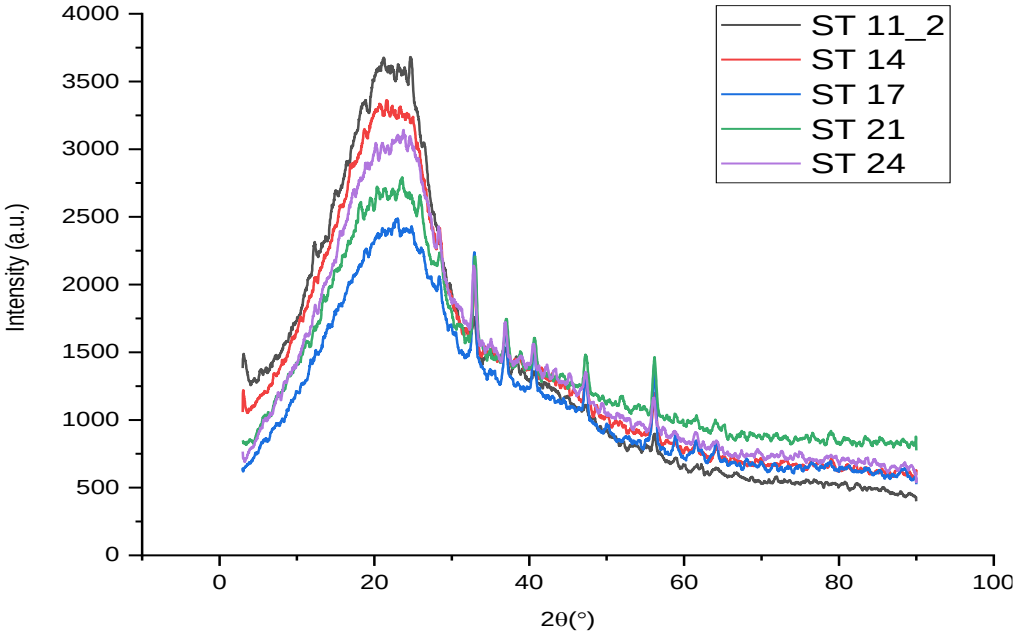

Figure 2. XRD chart of the five samples

Table 2. XRD analysis calculation result

Sample	d002 (Å)	La (Å)	Lc (Å)	ƒa	N	n	I26/I20	Ro (%)
ST 11_2	3.96	15.30	7.30	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	14.90	3.01	0.73	1.76	1.00	1.98	0.68
ST 21	3.86	15.00	3.12	0.67	1.79	1.03	1.69	0.74
ST 24	3.91	14.10	3.31	0.68	1.84	1.09	1.93	0.65

The calculation results of parameters d_{002}, La, Lc, ƒa, I_{26}/I_{20}, N, and n are shown in Table 2. Their ranges are d002: 3.87–3.96 Å, La: 13.16–15.30 Å, Lc: 3.01-7.30 Å, fa: 0.64-0.76, N: 1.76-2.85, n: 1.76-2.85, and I_{26}/I_{20}: 1.69–2.61, respectively. The relationships between the above parameters and Ro are shown in Figure 3.

The results of XRD analysis show that the value of d_{002} decreases with increasing the value of Ro, indicates that the aromatic ring in the coal continues to solidify as the coal matures. But it shows a very weak correlation with r value <0.25. The values of Lc and La also continue to increase, reflecting that the crystallite size in coal continues to increase in line with the maturity level of the coal. However, the two parameters show a moderate correlation because they all have a r value lies between 0.25-0.5 . Most likely, because the five samples have the same rank on High Volatile Bituminous-B. The value of ƒa shows very weak correlation with a value of Ro, indicated by value of r = 0.052.

The value of number of aromatic carbon layers (N) and the average total carbon atoms in the aromatic layer (n) showed a moderate correlation with r value lies between 0.25-0.5 . It can be seen from the graph that it increases, the more mature a coal, the more aromatic carbon layers and the total carbon atoms in that layer will be.

For the last parameter, namely coal rank, it can be seen in Figure 3 that this parameter

E-ISSN : 2579 – 3136

has a moderate correlation (near strong) with the value of r = 0.48. It can be seen from the graph that the maturity level is getting higher according to its rank.

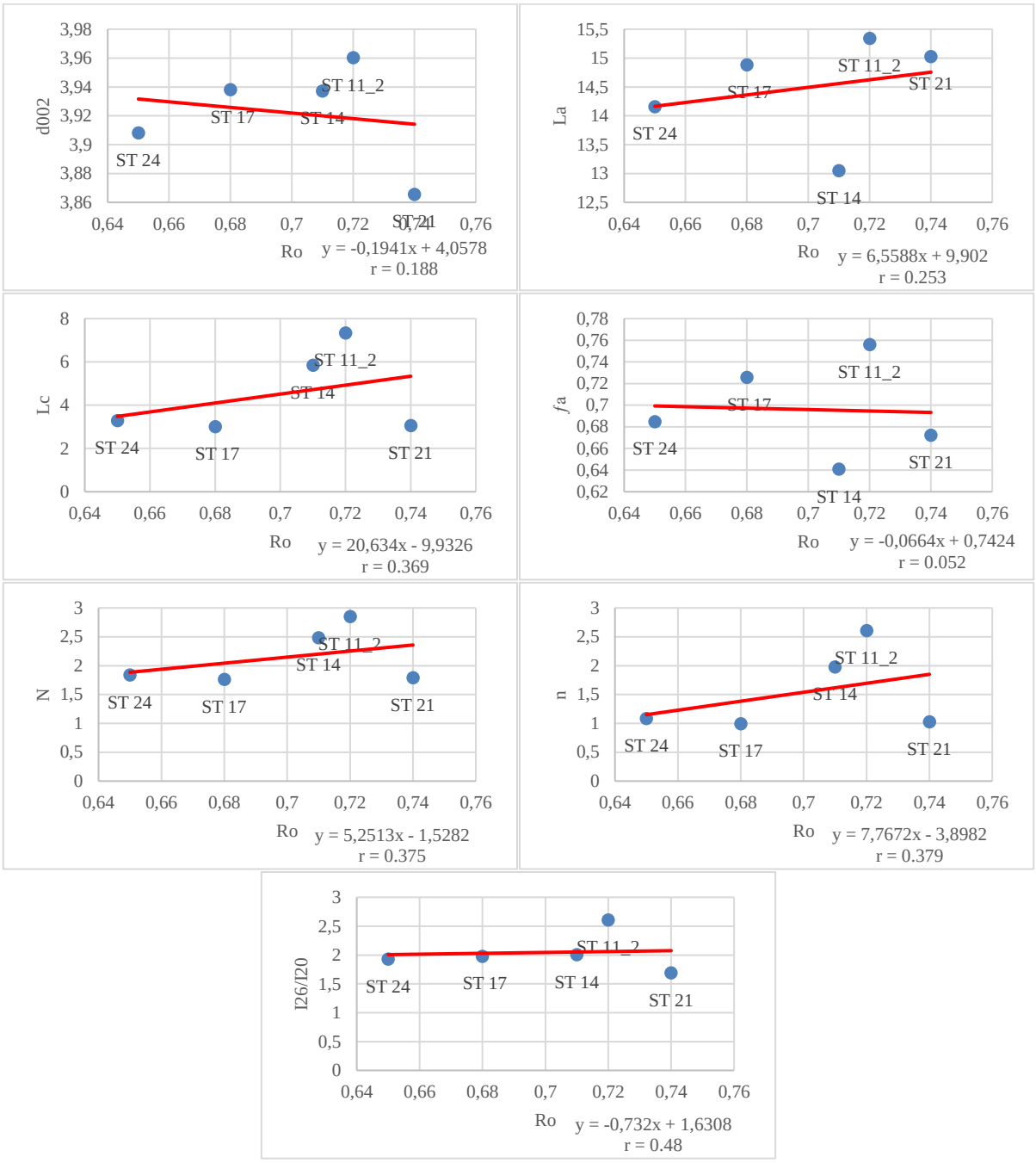

Figure 3. XRD analysis results of each molecular structure parameter

Relationship ƒa with Ro

Table 3 shown the value of fa from the various coal rank. Samples were taken from Huaibei, Tiefa, Qinshui and Yangquan areas in China with sample codes SL, SJZ, and WLH. (Jiang, 2018) Bayah Formation. By paying attention to Figure 4 and Table 3, it shows that the value of aromaticity (fa) using the XRD method has a very strong correlation with Ro (measured by the vitrinite reflectance measurement method) of various coal ranks, which is indicated by the correlation value (r) = 0.88.

E-ISSN : 2579 – 3136

Table 3. The value of ƒa resulting from both analyzes

Sample	Rank	ƒa (XRD)	H/C	Ro(%)
ST 11_2	High Volatile Bituminous	0.76	0.5	0.72
ST 14	High Volatile Bituminous	0.64	0.64	0.71
ST 17	High Volatile Bituminous	0.73	0.62	0.68
ST 21	High Volatile Bituminous	0.67	0.69	0.74
ST 24	High Volatile Bituminous	0.68	0.8	0.65
SL	Low Volatile Bituminous	0.86	0.81	1.21
SJZ	Semi Anthracite	0.93	0.49	2.63
WLH	Semi Anthracite	0.93	0.32	3.18

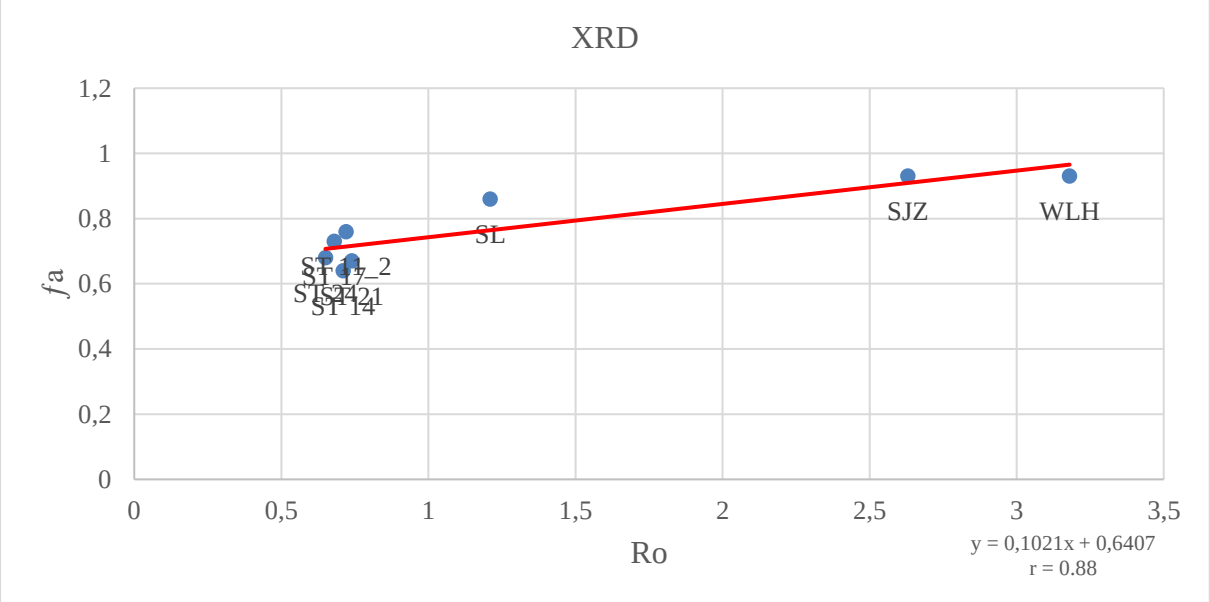

Figure 4. The value of ƒa resulting from both analyzes

When compared with other parameters in assessing coal maturity, namely the H/C ratio (Fig.5), it shows different results. The value of r = 0.533 shows a strong correlation but not as much as that the Ro measurement method.

It shows that Ro more accurate to assessing coal maturity relationship with ƒa instead of H/C ratio.

E-ISSN : 2579 – 3136

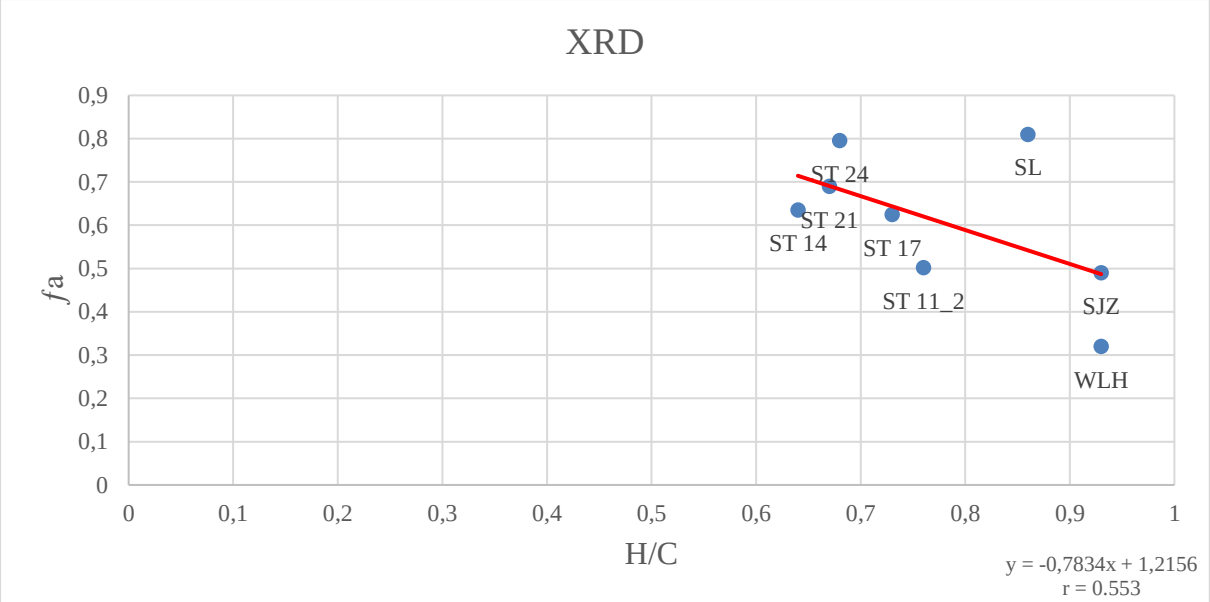

Figure 5. The relationship between ƒa and the H/C ratio in both analytical methods

CONCLUSION

The results of XRD analysis can be seen that the five coal samples of the Bayah Formation have the same crystal characteristics with the value of each parameter in a range that is not much different. The value of d002 is in the range of 3.87 to 3.96 Å, indicating that the studied sample has a low content of microcrystalline units.
Measurement of the fa value using the XRD method shows that there is a strong relationship between the fa value and the Ro value of various coal ranks. Thus the XRD method can be used to predict the maturity level of coal through the fa value.

ACKNOWLEDGEMENT

The authors would like to thank all those who have helped in the preparation of this journal. An expression of gratitude was conveyed to the Chancellor of the University of Padjajaran who has funded this research through the 2021 ALG scheme.

REFERENCES

Brown, J. K., & Hirsch, P. B. (1955). Recent Infra-red and X-ray Studies of Coal. In Nature (pp. 229-233). Cambridge: Nature Publishing Group.

Davidson, R. M. (1982). Molecular Structure of Coal. In M. L. Gorbaty, J. W. Larsen, & I. Wender, Coal Science Volume 1 (pp. 83-155). London: IEA Coal Research.

Haenel, M. W. (1992). Recent progress in coal structure research. Fuel, Vol 71, 1211-1223.

Hirsch, P. (1954). X-ray scattering from coals. Proceedings of The Royal Society, 143-169.

Jiang, J., Yang, W., Cheng, Y., Liu, Z., & Zhang, Q. (2019). Molecular structure characterization of middle-high rank coal via XRD, Raman and FTIR spectroscopy: Implications for coalification. Fuel 239, 559-572.

Lu, L., Sahajwalla, V., Kong, C., & Harris, D. (2001). Quantitative X-ray diffraction analysis and its application to various coals. Carbon, 1821-1833.

Yen, T. F., Erdman, J. G., & Pollack, S. S. (1961). Investigation of the Structure of Petroleum Asphaltenes by X-Ray Diffraction. Analytical Chemistry Vol.33, 1587-1594.

Yoshizawa, N., Maruyama, K., Yamada, Y., Ishikawa, E., Kobayashi, M., Toda, Y., & Shiraishi, M. (2002). XRD evaluation of KOH activation process and influence of coal rank. Fuel 81, 1717-1722.

E-ISSN : 2579 – 3136