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The Characterization of Molecular Structural of Coals from Papua Barat

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Abstract
The molecular structural of Steenkool Bituminous coal was analyzed by proximate, ultimate analysis, and X-ray diffraction spectroscopy. The structural molecule parameters, measured by XRD such as Lc (crystallite height), La (crystallite diameter), d_{002} (interlayer spacing), N (number of aromatic layers), fa (coal aromaticity), and I_{26}/I_{20} (coal rank). A polynomial relationship has been detected between coal structural parameter with %Ro; all these parameters were increase with the increasing the %Ro; except d_{002} was decrease. The bituminous coals consist a turbostratic structure with low amorphous structure.

Keywords: coal, structural molecule, Steenkool, XRD, West Papua.

1. Introduction
In the Bintuni Basin, West Papua; as the coal-bearing formation is the Steenkool formation, Coal is composed of organic and mineral materials; form complex of molecular structures, and heterogeneous compositions. The complexity of the coal structure will affect the utilization of coal. Therefore, to understanding coal structure is very important and becomes a challenge for geochemists[1-2]. XRD measurement is a method that has been widely used by a number of researchers in the world to analyze the molecular structure of the carbon material in coal[3-5]. The structural parameters in coal as measured by the XRD method, consist of interlayer spacing of the crystalline structure (d002), aromaticity (fa), stacking height of crystallite (Lc), average lateral sizes (La), number of aromatic layers[6-8].
Indonesia, is the one of that have a huge coal resource in the world. Indonesia, apart from being a coal producer; as well as a large user and exporter. Data as of June 2021 shows that coal resources are recorded at 149.7 billion tons; with coal reserves reaching 38.84 billion tons[9]. Most of the coal in Indonesia is used for domestic energy sources in the form of steam power plants (PLTU) and is exported to various countries such as China, Japan, India and South Korea. However, with the development of environmental issues in the form of reducing CO2 emissions due to coal combustion. Therefore, several technologies and the use of friendly coal have become a priority for the Indonesian government. However, study on the coal structure is scarce today.
In the Bintuni basin; as the coal-bearing formation is the Steenkool Formation deposited in the NE Bintuni Basin, while in the SE of the basin the sediment was deposited in Early Low Stand Wedge to Late Low Stand Wedge Submarine Fan[10-12].
West Papua, is one of the large coal-producing areas in Indonesia, and not much research has been done on coal, it becomes interesting for further research; so that optimal utilization of coal can be carried out.
The purpose of this research is to characterize the molecular structure of bituminous coal from Steenkool Formation in Bintuni Basin, West Papua.

2. Materials and methods
2.1. Preparation of coal samples
Five coal samples taken from the Tisihu coal field, Bintuni Basin, West Papua. For proximate and ultimate analysis; these samples were grounding into powder size. The result

was presented in Table 1.
For to get an accurate XRD measurements; these prepared samples were demineralized by adding the mixed of HCl (40%) and HF acid (40%) in 50 ml solution. Distillated water was used to filtered the coals, and dried in the oven at the ambient temperature.

2.2. X-Ray Diffraction Analysis

A Bruker AXSD8-X -ray diffractometer device was applied to obtain the characteristics of the XRD spectral. X-ray tube were U = 40 kV and I = 30 mA, and the XRD scans were conducted on a Cu target diffractometer using K radiation with scanning rate 30 per minute. The calculated the structural lattice parameters, the Bragg's and Scherrer equations was applied (Equation (1) to (5)[13-17]. The structural lattice parameters which measured by XRD; as follows:

$$fa = Car/ (Car + Cal) = A_{002}/ (A_{002} + A\gamma) \quad (1)$$

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

$$La = 1.84\lambda/(\beta_{002}cos\Theta_{002}) \quad (3)$$

$$Lc = 0.89\lambda/(\beta_{100}cos\Theta_{100}) \quad (4)$$

$$N = \frac{Lc}{d002} \quad (5)$$

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 FWHM values (full width half at maximum) of peak 002 and peak 100.
The coal can be determined from XRD which the equation formula (6)[18]

$$\text{Coal rank} = (I_{26}/I_{20}) \quad (6)$$

The curve fitting (Gaussian) was applied on all coals, to determine the diffraction angle 2Θ, peak area, intensity value and FWHM (Full Width Half Maximum) value.
The result of structural parameter calculation was presented in Table 2.

3. Results & Discussion

3.1. Proximate and Ultimate analysis

The five bituminous coals from Bintuni Basin, West Papua; were analyzed of proximate (measure the moisture, ash, volatile matter and fixed carbon); while the ultimate analyses were measure the C, H, N, S and O. Table 1 presented the result of proximate and ultimate measurement of coal samples.

Table 1: Result of proximate and ultimate measurement of coal samples

Type of Analysis	Parameters	N-104	N-108	N-112	STN-12	STN-14
Proximate (ad)	Moisture	2,4	2,1	1,9	2,3	1,8
	Ash	4.2	3.8	4.1	1.8	1,8
	Volatile Matter	45.8	45.7	45.2	46.1	45.8
	Fixed Carbon	47.6	48.4	47.9	51.1	50.6
Ultimate (daf)	Carbon	81.1	81.6	81.42	82.5	81.8
	Hydrogen	5.9	5.6	6.08	5.91	5.65
	Nitrogen	2.08	2.14	2.16	2.2	2.24
	Sulfur	1.15	1.21	0.86	0.76	0.77
	Oxygen (by diff)	9.77	9.45	9.48	8.63	9.54
	H/C	0.87	0.87	0.82	0.90	0.86
	O/C	0.09	0.09	0.09	0.09	0.08

From this table; these coals have a low moisture content ((1.8–2.4wt%), and low ash yield (1.8- 4.2% wt.%). The concentration volatile matter, and fixed carbon were high in coals, as 45.7% to 46.1%; 45.7- 46.1%, respectively. The carbon was a highest element compared to other elements within coal sample. The average atomic ratios of H/C, O/C, were calculated to be 0.86, 0.08, respectively, and the heating value between 14,2747 to 14,277 Btu/Lb[19]. Therefore, these coals are classified as a highly volatile bituminous-A in rank (ASTM Coal Classification).

3.2. X-ray Diffraction Analysis

A number of spectral peaks have been identified such as the 002, 10, 100, and γ peaks in the coal samples (Figure 1). These peaks are at diffraction degrees (2θ) at 25°, 43° and 47°, 18^0 respectively. Several studies have shown the same results in coal samples in various places; in which the 002 peak is closely related to the aromatic layer stacking at approximately 15−30°; while 100 peak in the range of 40−50°.[19-21]; while the 100 peak relates to the condensation degree of aromatic rings and the size of the aromatic carbon network layer.[22-23]. The γ band is related to the presence of aliphatic structures; attached to the aromatic nucleous[24].

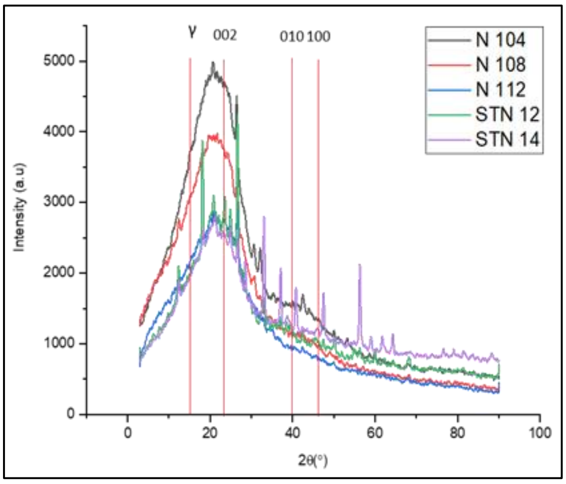

Fig. 1: XRD spectral of bituminous coal from West Papua.

Intensity value and FWHM (Full Width Half Maximum) value, peak area, diffraction angle 2Θ; has been determined using curve fitting (Gaussian method) to all coal samples (Figure 2).

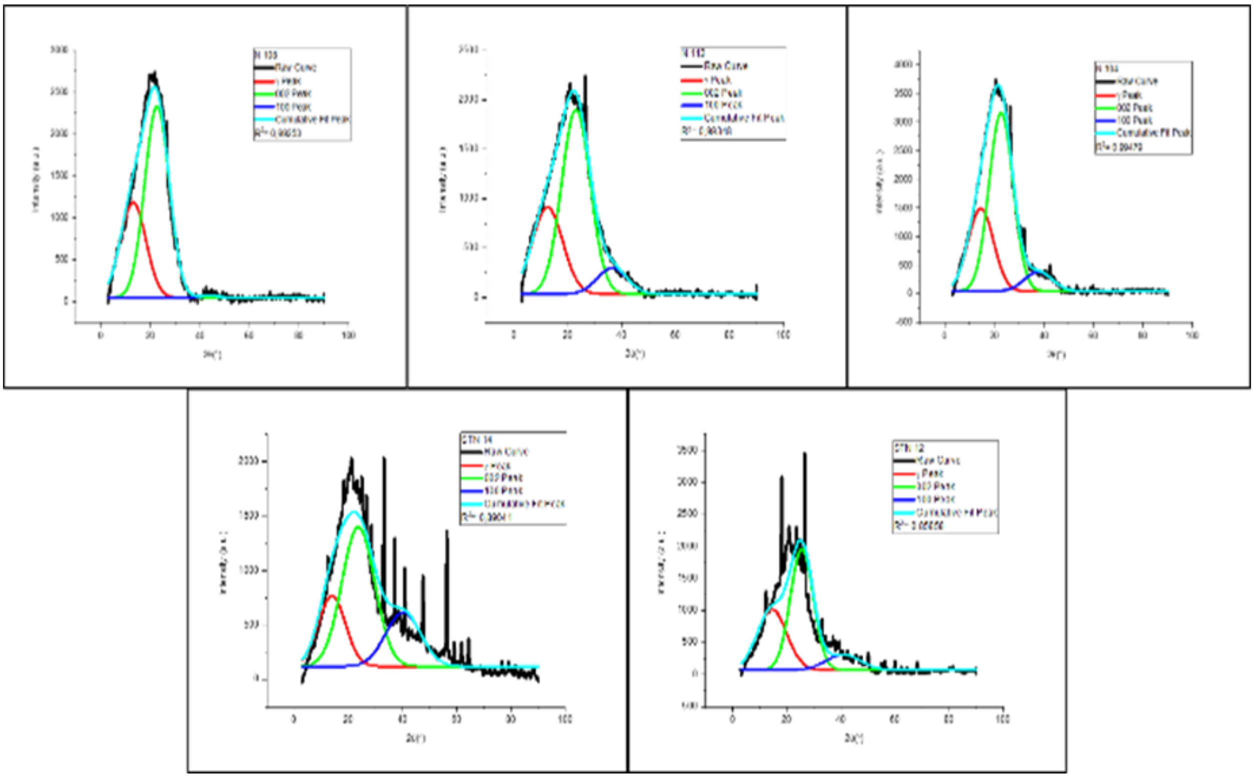

Fig.2: Curve fitting of XRD spectral from all bituminous coal from West Papua.

Table 2 tabulated the results of the calculation of the structural parameters of coal with the XRD method of Bayah Formation coal

Table 2: Molecular structural parameters of bituminous coal in West Papua.

Sample No.	d002 (Å)	La (Å)	Lc (Å)	*fa*	N	n	I_{26}/I_{20}	Ro (%)
N 104	3.92	14.08	6.26	0.67	2.60	2.16	2.12	0.64
N 108	3.93	13.86	5.68	0.66	3.46	3.84	1.97	0.63
N 112	3.86	14.70	6.56	0.67	2.65	2.24	2.07	0.66
STN 12	3.49	16.78	8.66	0.61	2.62	2.20	1.92	0.67
STN 14	3.76	14.82	6.89	0.71	2.46	1.94	1.82	0.66

Where:

d_{002} :	: Interlayer spacing	fa	: aromaticity
Lc :	Crystallite height	Nave	: Average number of aromatic layers
La :	Crystallite diameter	n	: average total carbon atoms in the aromatic layer
I_{26}/I_{20}	Coal rank	Ro	: vitrinite reflectance

Table 2 was shown the structural parameters from bituminous coal. The value of interlayer distance (d_{002}) is in the range of 3.49 to 3.92 Å, the average diameter of crystallite (La) is in the diameter of 13.86 to 16.78 Å, the average size of crystallite height is (Lc) in the range 5.68 to 8.66 Å, carbon aromaticity (*fa*) in the range 0.61 to 0.71, coal rank (I_{26}/I_{20}) in the range 1.82 to 2.12, and carbon layer (N) in the range of 2.46 to 3.46, and the value of n is between 1.94 – 3.84.

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-A coal.

From figure 2 which shows the XRD spectral graph; it is very clear that the coal of the Steenkool Formation has a structure similar to graphite (turbostratic structure), as other researchers have found[19-20, 25-26]. This is indicated by clearly identifying peak 002 and peak 100, and the peak values appear around 2theta :25^{0}, and 44^{0}, respectively. However, with the high detected background, the coal also contains an amorphous material structure (highly disordered materials). The coals have two type crystallite lattice structure; a turbostratic structure and amorphous structure. The interlayer distance (d_{002}) in all samples showed a higher range (3.49 to 3.93 Å) than d_{002} pure graphite (d_{002}= 3.36-3.37Å), reflecting the low degree of crystal regularity in the coals[27].

The values of coal crystallite structures such as d_{002}, La, and has a relation with coalification which reflected in the value of %Ro (coal maturity. For all the coal samples were shown that, L_a increase slightly for coal from 13.86 – 16.78 Å; while Lc increase from 5.681 – 6.89 Å; and the variations reflecting that the crystallite size were influences by degree of coalification (Figure 3). Other crystallite parameters such d_{002}, varying from 5.53 to 8.09 Å; which increasing coal rank (% Ro) as shown in figure 3(C). The curve of Nave against %Ro showing the similar trend with Lc and La (Figure 4D).

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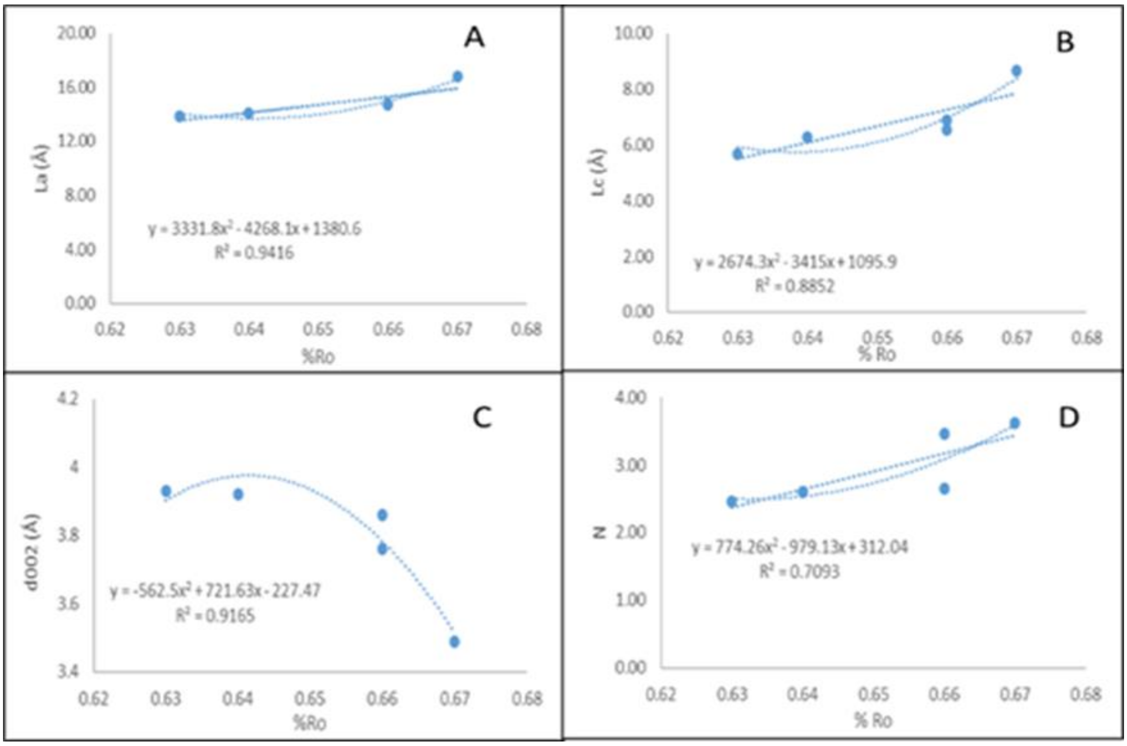

Fig. 3: Graph of structural parameters against the coal rank (% Ro): (A) La, (B) Lc, (C) d_{002}, and (D) N_{ave}

Coalification degree which measured by XRD are fa and I_{26}/I_{20}; showing the increasing with degree of coalification was increased (Figure 4)

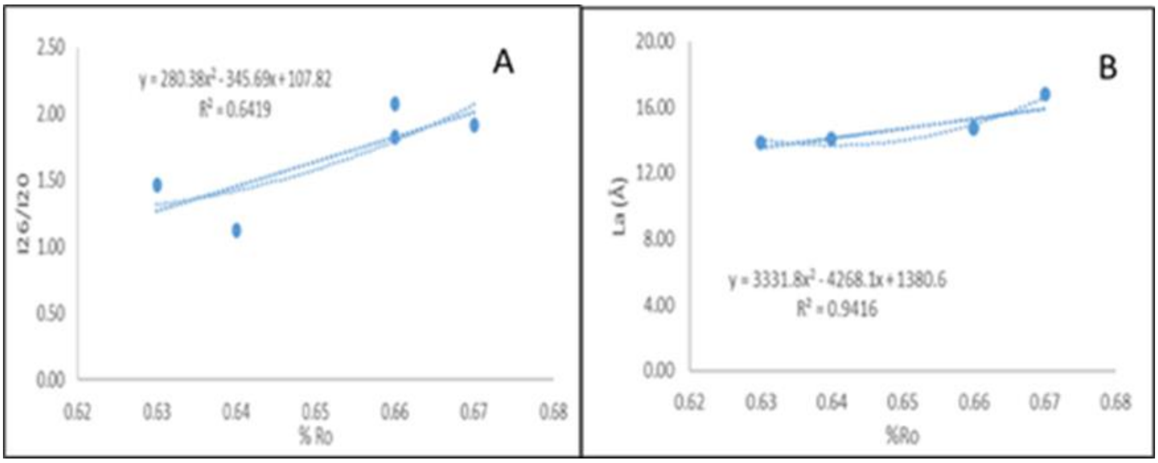

Fig.3: Graph of structural parameters against the coal rank (% Ro): (A) I_{26}/I_{20}, (B) fa

The research findings in 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[4, 28-29].

5. Conclusion

Total five bituminous coal from Steenkool Formation have been determined the structural lattice crystallite by X-ray Diffraction. The influence of coalification degree evolution on the crystallite structural evolution was analyzed and discussed, and the following conclusions are obtained:

1. With the more matured coals (increase %Ro); all the structural lattice parameter i.e., La, Lc, Nave, $I_{26}/I_{2o,}$ fa was increase, except the $d_{002.}$ was decreased.
2. The variations of crystallite lattice parameters reflect evolution during coalification.
3. All bituminous coal consists of turbostratic structure and amorphous structure.

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