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THE FTIR INVESTIGATION TO CHARACTERIZE OF FUNCTIONAL GROUPS IN BITUMINOUS COAL

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ABSTRACT
The study of chemical functional groups in coal using the methods of an FTIR investigation has been carried out on five samples of bituminous coal from Bintuni Basin in West Papua, Indonesia. The FTIR spectra fitting results reveal that the aromatic chains of Steenkool Coals (SC) were dominated compared to aliphatic and oxygen-bearing. The aromatic SC's molecular structures are mainly C=C and C-H followed by -CH. The oxygen-bearing SCs are mainly -C-O-C; and contain a small amount of C=O. The -CH_2- is mainly in aliphatic SC. The apparent aromaticity (fa), Hal/Ha, (R/Cu), and other semi-quantitative parameters from the compared FTIR data indicated that the aromatic is increased with a decrease in aliphatic and oxygen-containing groups. The potential for spontaneous combustion resulting from the bituminous coal of the SC is relatively small, as more aromatic and aliphatic functional groups are detected than the oxygen-bearing functional groups.
Keywords: Coal, FTIR, Steenkool Formation, Aromaticity, Coal Rank.
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INTRODUCTION

From several centuries to the present, coal has greatly influenced human civilization as a key source of energy. Moreover, coal has many uses; such as coke material for burning steel, anode material for lithium (LiB)[1,2] or sodium (PiB)[3] batteries, etc. Through various processes, coal and its by-products can also produce various new products such as ethanol, methanol, and dimethyl ether (DME). Coal is generally a heterogeneous material and has a complex chemical structure[4]. Coal provides humans with great benefits; however, it also has the potential to cause problems for environmental sustainability. For example, acid mine drainage, spontaneous coal combustion, and more. The spontaneous burning process can result in large fires that endanger both miners and other habitats around the mine. Therefore, it is important to study the functional groups in coal to obtain accurate information on the use of coal for various applications. It will also help understand the potency of hazards related to coal, like spontaneous combustion. The Fourier Transform Infrared (FTIR) tool has been widely applied for the identification of functional groups in various natural materials, such as minerals in silicate soils[5], organic materials[6], health materials[7], and minerals.[8-9] Several organic geochemists agree that the FTIR method is one of the most important methods for identifying functional groups in coal.[10-15] In FTIR spectroscopy, a molecule absorbs or transmits a certain frequency which is the characteristic of the molecular structure. For coal, the wave number range studied is generally in the middle infrared zone, around 400–4000 cm^{-1}. Infrared spectroscopy can be used to obtain information on the rotational vibrational modes of the motion of molecules. Therefore, it is highly essential for the detected functional groups. Unique fingerprints which are easily distinguishable from the transmission pattern of all organic compounds can be recognized from infrared spectra.[16-17] The FTIR method is a non-destructive method for characterizing qualitative and semi-quantitative studies of functional groups in coal, and can also be used for the characterization of insoluble organic compounds in coal. Thus it is a means of estimating the comprehensive absorbance of organic components based on the main functional groups (such as alkyl CH, CH_2, and CH_3, aromatics C=C and C-H, carbonyl/carboxylic acids C=O, hydroxyl-OH).[18-19] The purpose of the study is to develop a comprehensive understanding of the chemical functional group within bituminous coal using FTIR analysis.

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EXPERIMENTAL

Material and Methods

Five bituminous coals from Bintuni Basin, West Papua have been used in this research. To identify the characterization of the functional groups of bituminous coal, proximate, ultimate, and FTIR analyses were carried out.

Proximate, and Ultimate Measurements

The proximate analysis measured moisture, ash, fixed carbon, and volatile matter of coals. The ASTM Standard of D-3173, D-3174, D-388, and D-3175; was used as a reference for moisture, ash, fixed carbon, and volatile matter, respectively. The Standard reference used in identifying elements in coal through ultimate analysis is as follows ASTM D-3178 for carbon and hydrogen, ASTM D-3179 for nitrogen, ASTM D-3177 for sulphur, and oxygen (%) by difference: 100 - (%C + %H + %N + %S $_{organic}$). Table-1 shows the results of proximate and ultimate measurements.

FTIR Spectroscopy

Preparation Sample for FTIR Measurement

In the pre-treatment of FTIR investigation, coals were treated with acid to remove the impurities within these samples. In the acid treatment experiment, coal was crushed to powder size (200 mesh), as much as 50 grams. It was then kept in 300 ml of an acid mixture consisting of 120 ml of hydrochloric acid and 180 ml of hydrofluoric acid for 1 day at a temperature of 60^0 C. Furthermore, to ensure that the coal sample remains in a neutral state, the sample was washed with deionized water and filtered. In this study, the potassium bromide pellet (KBr pellet) technique has been used in the FTIR measurement. Scans were carried out with a 4 cm^{-1} resolution scanning of 4000-400 cm^{-1} from 32 scans per spectrum FTIR interferogram. Bruker FT Infrared spectrometer was used for this process.

Spectrum Deconvolution

The FTIR spectrum must be deconvoluted to get the correct position, bandwidths, and relative intensity. The semi-quantitative distribution of the functional groups in coal was obtained using the Curve fitting method of FTIR spectra; where each peak area represents each functional group. In this study, the spectral ranges of 700-900 cm^{-1} and 2800-3000 cm^{-1} were chosen as the baseline for curve fitting. Using Origin 8.0 software as a basis, Gaussian-Lorentzian function, Fourier deconvolution data, and the second derivative spectra were applied to identify the functional groups. Fig.-1 showed the example of curve-fitting of FTIR spectra of a selected coal samples.

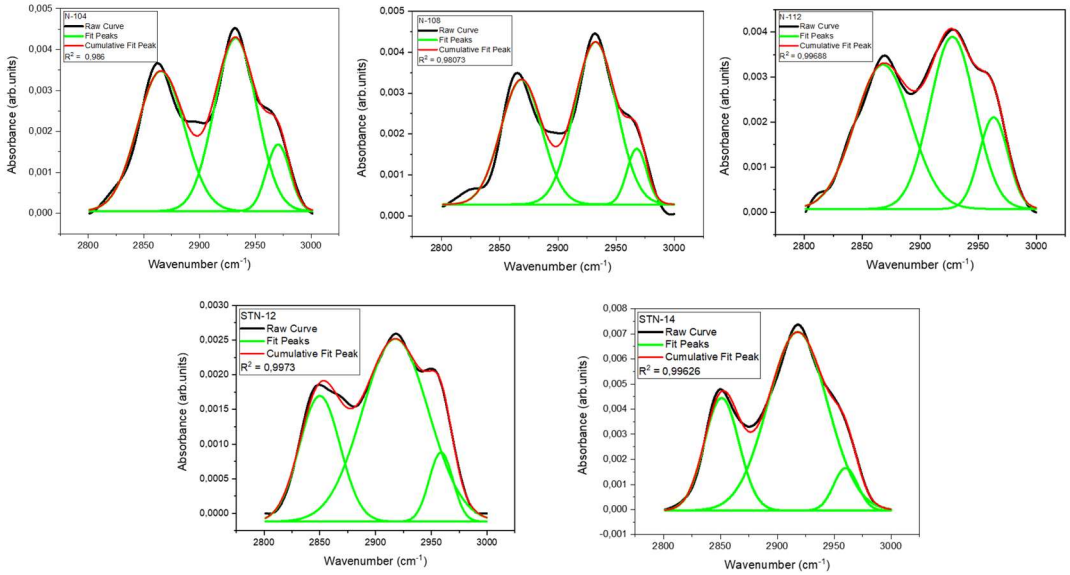

Fig.-1: Curve Fitting of FTIR Spectra in Coals of N-104/E, N-108/E, N-112/E, STN-12/A, and STN-14/G

FTIR Parameters

To calculate the apparent aromaticity (fa); the following formula was applied:

$$fa(FTIR) = 1 - \frac{Cal}{C} \quad (1)$$

$$\frac{Cal}{C} = \left(\frac{Hal}{H} x \frac{H}{C}\right) / \frac{Hal}{Cal} \quad (2)$$

Hal/H : Concentration ratio of aliphatic (H_{al}) and total hydrogen atoms (H)
H/C : The ratio of the hydrogen atoms to carbon atoms
Hal/Cal : The ratio of hydrogen and carbon in aliphatic groups (for coals = 1.8)
Cal/C : The ratio of the aliphatic carbon to carbon atoms.

The ratio of CH_2/CH_3 (Eq.-3) parameter was used to identify the degree and length of branching of aliphatic chains, by deconvolution of accredited to asymmetric $-CH_2$ stretching (wave number at 2,922 cm^{-1}, and asymmetric $-CH_3$ stretching (wave number at 2,9520 cm^{-1}).

$$\frac{CH2}{CH3} = \frac{A2922\ cm^{-1}}{A295\ \ cm^{-1}} \quad (3)$$

$$\left(\frac{R}{C}\right)u = 1 - \frac{fa\ (FTIR)}{2} - \frac{\left(\frac{H}{C}\right)}{2} \quad (4)$$

$$\frac{Aar}{Aal} = \frac{A900-700\ cm^{-1}}{A3000-2800\ cm^{-1}} \quad (5)$$

$$DOC = \frac{A700-900}{A160} \quad (6)$$

RESULT AND DISCUSSION

Proximate and Ultimate Measurements

Table-1 shows the results of the analyses of Bituminous coals from Bintuni Basin, West Papua. The arithmetic mean of H/C = 0.86, and O/C = 0.08. All the coals show low moisture, and yield; 1.8–2.4wt. % and 5% wt. %, respectively. The coals have high volatile matter (45.7% to 46.1%) and fixed carbon (47.5% to 51.1%). The samples have low sulfur (0.76–1.21 wt. %). The measurement of C-H-N-S-O elements in coals indicated that shows the carbon element is the highest, compared to other elements. Next followed by oxygen, hydrogen; while elemental sulfur is the smallest element identified (Table-1). Based on the ratio H/C vs O/C (Fig.-2) and heating value of 14,2747-14,277 Btu/Lb., these coals are highly volatile bituminous-A in rank (ASTM Coal Classification).

Table-1: Proximate and Ultimate Measurement of Coal Samples

	Parameters	N-104/E	N-108/E	N-112/E	STN-12/A	STN-14/G
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

FTIR Measurement from Coals

Figure-3 shows the absorption peaks of functional groups of coals, and Table-2 shows the FTIR spectral analyses. The percentage distribution of functional groups in coals was presented in Table-3. The FTIR parameters of Steenkool coals were tabulated in Table- 4.

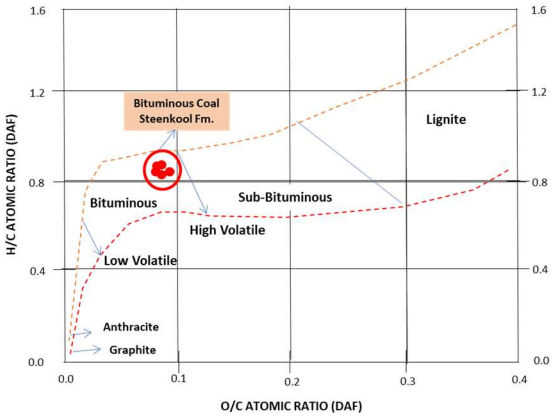

Fig.-2: Van Krevelen Diagram of Ratio H/C against O/C from Coals

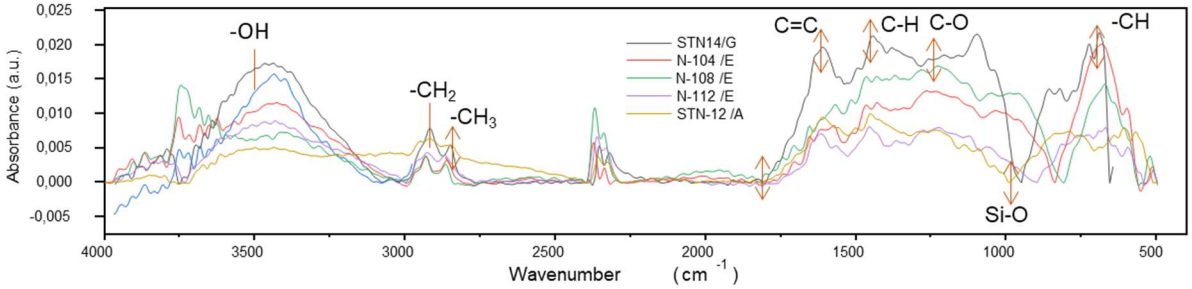

Fig.-3: The FTIR Spectra from Coals IN Bintuni Basin, West Papua, Indonesia

FTIR measurements have identified three functional groups consisting of aromatic hydrocarbons, aliphatic hydrocarbons, and oxygen-containing groups. The distribution of the functional group absorption bands was found to be relatively similar among the five coal samples. Attributing to the bands, a standard pattern of absorption from many scholars was used.[20, 21, 22] From the coal under study, it is known that the aliphatic functional groups are found as $-CH_3$ and $-CH_2-$, while the aromatic functional groups are present as the stretching vibrations of C=C, C-H, and C=O or C-N. The oxygen-bearing functional groups are present as -C-O– C, -OH, and C=O. A strong absorption band was detected in coals in the wavenumber of 3358−3250 cm^{-1}; it was assigned to N-H and O-H groups. In raw coals, the peak of the –OH stretching vibration group indicated that coals contained clay minerals (kaolinite, montmorillonite, and illite). Aliphatic side chains, assigned to C-H stretching of spectral peaks, were seen in the region of 2930–2861cm^{-1}.

Table-2: Band of Spectral and Motion of Functional Group and Wave Number

Band of spectral and motion of the functional group	Wave Number (Cm^{-1})
N-O-H stretching inter molecular vibration	3792 – 3358
Aliphatic asymmetric stretching vibration of CH_3	2930 - 2861
Aliphatic asymmetric stretching vibration of CH_2	2925 - 2919
Aromatic (carbonyl/carboxyl groups) (C=O)	1700 - 1650
C=C stretching cyclic alkene	1612 - 1570
C-H Bending Alkene	1467 - 1446
C=O stretching (aromatic ester) or C-N stretching (aromatic amine)	1126-1036
Si–O–Si stretching vibration	1031-1008
Aromatic bonds (C-H) (Out - of Plane Deformation)	900 - 700

The presence of a long aliphatic CH_2 chain and no identification of CH_2 symmetric stretching vibrations indicated strength absorption in 2930-2919 cm^{-1} the wavenumber of the CH_2 functional group asymmetric stretching vibrations. In addition, the different peak at 2920-2861 cm^{-1} is due to CH_3 asymmetric vibrations. The presence of aldehydes, acids, and ketones at 1700-1650 cm^{-1} is related to the aliphatic -C-O– C and =O stretching vibrations in this region. The aromatic structure vibration of aromatic rings was related to spectral peaks aromatic C=C vibration identified at 1612 - 1570 cm^{-1}. This aromatic structure was also an influence of the C=O stretching vibration of carbonyl groups (1700 – 1650 cm^{-1}). The deformation asymmetric bands

of the CH_2 and CH_3 symmetric bending groups were identified in the band of 1446 cm^{-1} and 1467 cm^{-1}, respectively. The 1126-1036 cm^{-1} band is a stretching (aromatic ester) or C-N stretching (aromatic amine) band. Quartz and clay minerals were found in the spectra of 1100 and 400 cm^{-1}. Absorption at 1031 and 1008 cm^{-1} was identified as Si–O–Si stretching vibration. In the 700-900 cm^{-1} region, high-intensity aromatic -CH bands were identified in all coals. The bending vibrations of aromatic rings that appeared in the 700-900 cm^{-1} range were believed to be an aromatic C-H out-of-plane bending vibrations. Table-3 shows the above-mentioned three functional groups consisting of aromatic hydrocarbons, aliphatic hydrocarbons, and oxygen-containing groups accounted for certain percentages of their distribution in coals. Among the three types of functional groups, the content of aromatic functional groups showed the largest number (more than 50%), followed by oxygen-bearing functional groups; the aliphatic functional group showed the lowest number. The above findings are consistent with the findings of several researchers. The highly volatile bituminous coal that has undergone increased coalification is found to be characterized by an increase in aromatic functional groups followed by a decrease in aliphatic hydrocarbons.[17,23] The dominance of aromatic hydrocarbon in all coals indicated that these coals have a high tendency for spontaneous combustion during mining. Some spontaneous combustion events were more related to the high content of oxygen carriers such as the compound -C-O-O−, an unstable element that is reactive to spontaneous combustion.[24] As an advantage, with the excess of aromatic functional groups, coal can be used for combustion as metallurgy coal. The aromatic structure will remain unchanged and the graphitization process will continue to increase during the combustion process. The temperature of 350 – 550^0 C which is a thermoplastic temperature will affect the plasticity of cooking coal.

Table-3: Percentage of Functional Group Composition

Functional Group	Sample No.				
	STN-12/A	N-104/E	N-108/E	N-112/E	STN-14/G
Oxygen-bearing (%)					
- OH	8.000	15.873	11.594	16.327	14.815
C=O	2.000	1.587	2.899	2.041	0.926
- C- O – C	18.000	15.873	20.290	14.286	14.815
Sub Total	26.000	33.333	34.783	32.653	30.555
Aliphatic Hydrocarbon (%)					
- CH_2 -	14.000	6.349	5.797	10.204	7.407
- CH_3	10.000	7.937	4.348	8.163	6.481
Sub Total	24.000	14.286	10.14	18.367	13.889
Aromatic Hydrocarbon (%)					
C=C	18.000	15.873	17.391	18.367	21.296
C-H	18.000	11.111	17.391	14.286	19.444
- CH	14.000	25.397	20.290	16.327	14.815
Sub Total	50.000	52.381	55.072	48.980	55.556

The FTIR semi-quantitative was presented in Table-4. The *(*CH_2)/(CH_3) parameter is used to measure the length of aliphatic chains. As shown in this table, all coals have a high value (CH_2)/(CH_3), reflecting that the aromatic ring binds to the longer aliphatic chain, and less space between aromatic clusters. Most of the higher coal ranks like bituminous to anthracite have a methylene group (CH_2) compared to CH_3 (methyl group). This is related to the formation of an aromatic ring or branched aliphatic structure from the conversion of hydro-aromatic methyl compounds and the loss of alkyl chains during coalification.[18,19] The high volatile matter (Table-1), as seen in the 46.1 (STN-12/A) and 45.8 (STN-14/G), have a higher ratio of *A(CH_2) / A(CH_3);* 2.36 (STN-12/A) and 2.71 (STN-14/G).

Table-3: FTIR Semi-Quantitative Analysis of Coals

FTIR Parameters	STN-12 /E	N-104 /E	N-108/E	N-112 /E	STN-14/G
Hal / H	0.76	0.7	0.79	0.73	0.79
Cal / C	0.21	0.40	0.38	0.30	0.24
*f*a	0.79	0.60	0.62	0.70	0.76
(CH_2) / (CH_3)	2.36	1.62	1.34	0.96	2.71
Factor 'C'	0.04	0.13	0.16	0.08	0.03

(R/C)u	0.25	0.24	0.27	0.23	0.26
DOC	0.46	0.13	0.20	2.12	0.39

The relationship trend of three FTIR parameters (Table-3) as Hal/Ha, fa, and (R/C)u, with the ratio H/C (derived from ultimate analysis) is shown in Fig.-3. It indicates that the coalification process takes place during the coal formation process. The bad linear relationship is shown by *fa* with the H/C atomic ratio (Fig.-3A). In contrast, parameters *(R/C)u* and *Hal/H* show a very good linear relationship; as shown in Fig.-3B and 3C. Thus, these parameters better describe the coalification process; where coal with an increasing trend of content in the H/C ratio (as shown in the coal studied, Table-1) will be followed by a decrease in the *(R/C)u* and *Hal/H* ratio.[10,17] During the thermal evolution of coal coalification, the aromatic functional group increase with the loss of the aliphatic and oxygen-bearing functional group; which is reflected in the value of CH_2/CH_3 *fa, Hal/Har*, and *(R/C)u*.

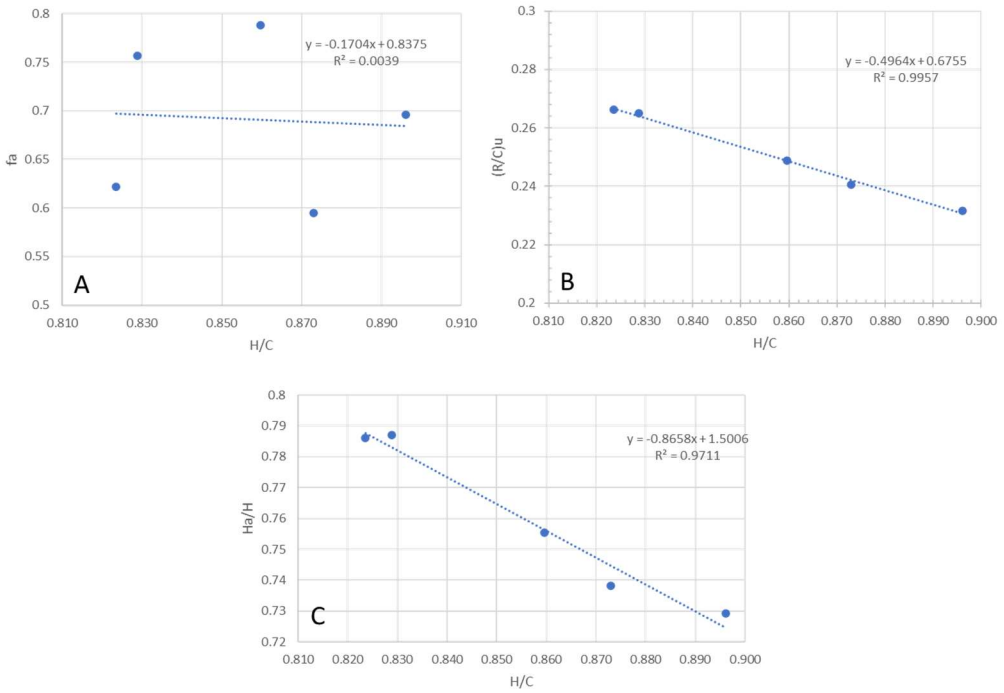

Fig.-3: The Trend Relationship of H/C of Coals with FTIR Parameters: (A) H/C against fa (Apparent Aromaticity); (B) H/C against (R/C)u; and (C) H/C against Hal/H

CONCLUSION

This study investigated and discussed diagnostic FTIR bands from five coal samples of the Steenkool Formation in Bintuni Basin, West Papua. The following conclusions have been drawn:

(1) The Steenkool coals from the Bintuni Basin of West Papua are highly volatile bituminous A in rank, as identified based on the ratio of H/C and O/C.

(2) Three functional groups have been determined from the FTIR analysis, which are aliphatic (–CH2 and–CH_3 group), aromatic (C=C, C-H, and C=O or C-N), and oxygen-bearing (-C-O– C, OH, and C=O) functional groups.

(3) The low content of oxygen-bearing functional groups indicated these coals are not prone to spontaneous combustion.

(4) The FTIR semi-quantitative methods indicated that the aromatic functional groups in coals increase with a decrease in aliphatic and oxygen-containing groups. The aromatic ring is more stable than the aliphatic group.

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