EXPLORING THE RELATIONSHIP BETWEEN HYDROCARBONS WITH TOTAL CARBON AND ORGANIC CARBON IN BLACK SHALE FROM PERAK, MALAYSIA

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Abstract
Representative samples of Paleozoic black shale from Carboniferous Batu Gajah (BG) Formation are subjected to detailed organic geochemical investigations during this study to provide an opportunity to explore the organic and total carbon quantity, type of hydrocarbons and type of humic substance present in these black shale. Furthermore relationship of total organic carbon, total carbon with aromatic hydrocarbons and aliphatic hydrocarbons is also determined. Total organic carbon contents (TOC) of the BG black shale range from 0.54 to 2.86 wt. %. Ultraviolet–visible spectroscopy (UV-Vis) has been used to identify the type of humic substance present in these black shale. Spectroscopic UV-visible ratio (E4/E6) indicates the presence of humic acid in black shales. Aromatic and aliphatic hydrocarbons functional groups were measured by attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR). Aromatic out of plane CH stretching (Aromatic OPCH) hydro-carbon and alkyne =C–H bending aliphatic (Alkyne APCH) hydrocarbon functional groups are found. The absorbance of Aromatic OPCH hydrocarbons and Alkyne APCH hydrocarbon from ATR-FTIR was calculated and both are plotted against TOC and TC. However, TOC and TC in BG black shale samples was found to be significantly and positively correlated with aromatic OPCH hydrocarbons (r2=0.852 for TOC and r2=0.712 for TC) and alkyne APCH hydrocarbon (r2=0.739 for TOC and r2=0.753 for TC) concentrations. This positive correlation indicates that the TOC and TC plays a significant role in controlling the aromatic and aliphatic hydrocarbon level in the black shale. Presence of more infrared bands of aromatic hydrocarbons and presence of humic acid by spectroscopic UV-visible ratio (E4/E6) in BG formation indicates that black shale from this formations belongs to terrestrial higher plants origin.

Keywords: Black shale; Hydrocarbons; Humic Acid; Organic carbon; Spectroscopy.

1. Introduction
Hydrocarbons can be classified into saturated, unsaturated and aromatic hydrocarbons and extensively distributed in crude oils and source rocks [1], which are capable to deliver information on migration, sedimentary environments, thermal maturity, source input and oil-source rock correlation [2-6]. Aromatic hydrocarbons are large group of organic compounds possess two or more aromatic carbon rings [7-8]. They produced usually from incomplete combustion of organic matter and fossil fuels and are ubiquitous throughout the environment [9-11].

Black shales are dark carbonaceous shales rich in organic matter, containing 0.5 to more than 10% organic carbon [12]. Paleozoic black shale outcrops are widely distributed in Western belt of Malaysia. Paleozoic black shale reported in Perak state belonging to the Carboniferous Batu Gajah Formation. This formation has been studied widely for their geology, stratigraphy, occurrence, mineralogy and trace and rare earth element geochemistry [13-16]. However, nothing has been published in detailed regarding their distribution of hydrocarbons and existing type of humic substance in the organic matter of black shale. Several studies have demonstrated that TOC is a key property influencing aromatic hydrocarbon concentration in sediments [11, 17] and have shown a positive correlation between aromatic hydrocarbons and total organic carbon (TOC) in sediments [18]. In those studies presence of aromatic hydrocar-
bons and aliphatic hydrocarbon in sediments or black shale has been measured from gas chromatography and mass spectrometry. Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) also capable to calculate Aromatic and aliphatic hydrocarbons presence in Black shale. Moreover, there is also no available literature in which the relationship of aromatic OPCH and alkyne APCH from (ATR-FTIR) with total carbon and total organic carbon has established. Therefore, the aim of this study is to evaluate the hydrocarbon functional groups, type of humic substance and quantity of total organic carbon in the black shale of BG formation and interpret their origin based on spectroscopic method such as UV-Vis and ATR-FTIR and potential of source rock in term of TOC. Furthermore, absorbance of aromatic OPCH and aliphatic APCH hydrocarbons measured from (ATR-FTIR) plotted against total carbon and total organic carbon to find their relationship.

2. Study area

Kinta limestone has subdivided into the H.S. Lee beds, Nam Loong beds, Kim Loong No. 3 beds, Kuan On beds, Thye On beds and Kim Loong No. 1 beds from youngest of oldest [19-20]. Batu Gajah formation is a part of Kim Loong No. 3 beds of kinta limestone comprises Upper Carboniferous black shale (Figure 1). The origin of name is taken after Kim Loong No. 3 Mine, Kinta District, Perak. This study focus on two outcrop of black shale from Batu gajah formation, 4°28’31.2”N 101°04’13.8”E and 4°28’31.6”N 101°04’13.0”E respectively (Figure 1). Batu gajah formation composed of pyritiferous Grey to black flaggy shales and argillaceous sandstone.

![Figure 1. Map and stratigraphy log of study area (after Lee chai peng, 2009)](image-url)
3. Experimental

3.1. Chemical reagents and samples

All chemical reagents and solvents had a high degree of purity and were used without prior purification. Distilled and deionized water was used to wash samples after acid digestion. For identifying the type of humic substance dichloromethane and dichloromethane: methanol (Aldrich) was used as a solvent, and Hydrochloric acid was used to prepare samples for TOC analysis.

Thirty outcrop samples were collected from the BG formation. All the samples were handpicked from non-weathered surface, and stored in closed bags. The collected samples were also thoroughly cleaned in the lab prior to geochemical analyses. Geochemical analyses for the studied black shale samples were carried out at the Geochemistry Laboratories located in the Department of Petroleum Geoscience, University Teknologi PETRONAS, Seri Iskandar Malaysia.

3.2. Analysis

3.2.1. Acid digestion for inorganic carbon removal

The whole rock samples were crushed to powder and treated with 50 mL of 37% hydrochloric acid over a hot plate at 60–65°C. They were then rinsed with deionized water three times and dried overnight at approximately 60°C in a drying oven to remove carbonates before being analyzed. Hydrochloric acid dissolves most carbonates (e.g., CaCO$_3$ + 2H$^+ \rightarrow$Ca$^{2+}$ + H$_2$O + CO$_2$), sulphides (e.g., ZnS + 2H$^+ \rightarrow$Zn$^{2+}$ + H$_2$S), and basic or amphoteric oxides and hydroxides. Following inorganic removal analysis, the samples were selected for further organic geochemical analyses.

3.2.2. Identifying the type of humic substance in shale with dichloromethane and dichloromethane: methanol

In this study type of humic substance has been investigated on the powdered samples using methanol and Dichloromethanol. For humic substance type the U.S. EPA method 3550 was optimized using ultrasonic extraction with dichloromethane and dichloromethane: methanol as solvent. In a glass flask with cap, 2 g was weighed of each shale from Batu Gajah Formation. The samples were then submitted to three consecutive extractions with 8mL of dichloromethanol and methanol each time, by 3 minutes of ultrasonic stirring and 5 minutes of centrifugation at 2500 rpm.

3.2.3 Fourier transform infrared spectroscopy

Infrared measurements were made using a Cary 660 Series FTIR Spectrometer equipped with PIKE MIRACLE diamond attenuated total reflectance spectroscopy (ATR). Data collection was done using the Resolutions Pro software package which was also used for background and automatic baseline correction of all spectra. Spectra were acquired and converted to absorbance mode from 16 coded scans between 4000 and 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$, then area normalized prior to further analysis. The limit of detection of the instrument is 0.08%. Background scans were collected using the same settings as the sample analyses. Replicate spectra collected on selected samples showed consistent peak positions and absorbance intensities. The area percentage of hydrocarbon functional groups was calculated by summing the absorbance intensities between the respected wavelength.$^{[21]}$

3.2.4. TC, TOC and TIC Analyses

Multi N/C 3100 with combination of catalytic high-temperature combustion, VITA, the Focus Radiation NDIR Detector. Catalyst promoted was set to high temperature combustion up to 1200°C was used to measure total carbon (TC). Total organic carbon (TOC) was measured using the same instrument on samples pre-treated with concentrated HCl. Total inorganic carbon (TIC) contents were calculated as the weight loss of inorganic carbon after acid treatment.
3.2.5. Ultraviolet–visible spectroscopy (UV–VIS)

The UV–VIS technique analysis of the dichloromethane and dichloromethane: methanol extract solution was performed using a Shimadzu UV-3150 UV Vis Spectrophotometer with the liquid samples placed in quartz cells. The scanning wavelength range was 200–800 nm.

4. Results

4.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was conducted to characterize the functional groups in the black shale. The FTIR spectra of BG black shale exhibited similar absorption bands and characteristic absorption peaks (Figure 2). The FTIR spectra of the black shale samples can be divided into four zones, -OH groups stretching vibration, Alkyne C-H bending bands in Aliphatic hydrocarbons, absorption spectrum of oxygen-containing functional groups and Aromatic In-plane C–H bending and Aromatic out of plane C–H bending.

![Figure 2. FTIR spectra of some Batu Gajah shale samples](image)

Aliphatic hydrocarbons may be alkanes, alkenes or alkynes. Shale from Batu gajah contains only Alkyne APCH bending bands. The critical region of the infrared spectrum for assessing alkyne C-H bending bands in aliphatic hydrocarbon is 600–700 nm. The Aromatic In-plane C–H bending and Aromatic out of plane C–H bending appear in the regions 1275–1000 cm⁻¹ and 900–690 cm⁻¹. Aromatic C=C stretching can be observed in 600-700 cm⁻¹. Strong intensity peak of free OH-compounds are detected in the region of 3700–3200 cm⁻¹ [22-23]. Most samples of black shale from Batu Gajah formations contains only Aromatic out of plane C–H bending and Alkyne APCH bending band. Therefore in this study absorbance of Alkyne APCH and Aromatic out of plane C–H bending bands was calculated by summing the absorbance intensities between 900–670 cm⁻¹, and 700-600 cm⁻¹ [21] (Table 1).

There are three infrared bands of aromatic hydrocarbons in the Batu Gajah formation has been observed: an infrared band of Aromatic C=C stretching, an infrared bands of Aromatic out of plane C–H bending and an Infrared bands of Aromatic In-plane C–H bending. All samples of Batu Gajah formation contains Aromatic out of plane C–H bending. Aromatic C=C stretching and Aromatic In-plane C–H bending are only observed in few samples. For Aliphatic hydrocarbon Batu Gajah formation comprises only Alkyne =C–H bending band. Most of the samples of Batu Gajah formation contain Alkyne =C–H bending. While this bands is not present in only BG-10, 11, 13, 17, 19 and BG-28 samples (Table 1).
Table 1. Functional groups identified through FTIR spectra (600-900 cm⁻¹) in the BG shale samples

<table>
<thead>
<tr>
<th>SN.</th>
<th>Alkyne APH 700–600 cm⁻¹ =C–H bending</th>
<th>Aromatic bending 900–690 cm⁻¹ Out-of-plane C–H bending Absorbance</th>
<th>SN.</th>
<th>Alkyne APH 700–600 cm⁻¹ =C–H bending</th>
<th>Aromatic bending 900–690 cm⁻¹ Out-of-plane C–H bending Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG-1</td>
<td>0.2</td>
<td>0.21</td>
<td>BG-16</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>BG-2</td>
<td>0.1</td>
<td>0.15</td>
<td>BG-17</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>BG-3</td>
<td>0.14</td>
<td>0.12</td>
<td>BG-18</td>
<td>0.04</td>
<td>0.1</td>
</tr>
<tr>
<td>BG-4</td>
<td>0.15</td>
<td>0.16</td>
<td>BG-19</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>BG-5</td>
<td>0.11</td>
<td>0.13</td>
<td>BG-20</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>BG-6</td>
<td>0.1</td>
<td>0.14</td>
<td>BG-21</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>BG-7</td>
<td>0.11</td>
<td>0.15</td>
<td>BG-22</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>BG-8</td>
<td>0.16</td>
<td>0.18</td>
<td>BG-23</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>BG-9</td>
<td>0.14</td>
<td>0.17</td>
<td>BG-24</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>BG-10</td>
<td>0.09</td>
<td>0.07</td>
<td>BG-25</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>BG-11</td>
<td>0.07</td>
<td>0.07</td>
<td>BG-26</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>BG-12</td>
<td>0.08</td>
<td>0.08</td>
<td>BG-27</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>BG-13</td>
<td>0.09</td>
<td>0.09</td>
<td>BG-28</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>BG-14</td>
<td>0.04</td>
<td>0.13</td>
<td>BG-29</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>BG-15</td>
<td>0.03</td>
<td>0.07</td>
<td>BG-30</td>
<td>0.08</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4.2. Ultraviolet–visible spectroscopy (UV-Vis)

The spectra in the UV-VISs were obtained according to procedures described in [24] in a 200 to 800 nm wave length. The UV-Vis analysis of this study is interested primarily on the E4/E6 ratio. The ratio of optical densities or absorbance of dilute aqueous Humic acid and Fulvic acid solution using the UV-Vis techniques at 465 nm 665 nm is widely used by soil scientist for the characterization of organic matter. E4 was determined at an absorption frequency of 465 nm, and E6 at 665 nm has been reported to be independent of concentration of humic material extracted from different soil types. It has also been stated that the UV-Vis adsorption spectroscopy for evaluation of petroleum have been strongly underestimated as E4/E6 ratio from the UV-Vis, has been used widely as a measured of aromacity or humification [25].

Spectroscopic UV-visible ratio (E4/E6) results of BG shale samples which were treated with dichloromethane and dichloromethane: methanol, shows dominance of aromatic component within the samples (Table 2). Almost equal values of E4 and E6 also indicate the presence of aromatics in Batu gajah shale. Less aliphatic component in the results also show that migration of aliphatics might have occur. Only samples (BG-2,BG-3, BG-4 and BG-6) from Batu gajah formations was treated with dichloromethane and sample BG-1 which has been treated with dichloromethane: methanol shows aliphatic component (Table 2).

Table 2. UV-Vis results of Batu Gajah Shale samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance At (DCM) λ = 465 nm (E4)</th>
<th>Absorbance At (Methanol) λ = 465 nm (E4)</th>
<th>E4/E6</th>
<th>Absorbance At (DCM) λ = 665 nm (E6)</th>
<th>Absorbance At (Methanol) λ = 665 nm (E6)</th>
<th>E4/E6</th>
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</thead>
<tbody>
<tr>
<td>BG-1</td>
<td>0.14</td>
<td>0.14</td>
<td>1</td>
<td>0.8</td>
<td>0.84</td>
<td>0.95</td>
</tr>
<tr>
<td>BG-2</td>
<td>0.19</td>
<td>0.19</td>
<td>0.97</td>
<td>0.59</td>
<td>0.54</td>
<td>1.1</td>
</tr>
<tr>
<td>BG-3</td>
<td>0.2</td>
<td>0.22</td>
<td>0.97</td>
<td>1.28</td>
<td>1.29</td>
<td>0.99</td>
</tr>
<tr>
<td>BG-4</td>
<td>0.34</td>
<td>0.37</td>
<td>0.91</td>
<td>0.15</td>
<td>0.13</td>
<td>1.13</td>
</tr>
<tr>
<td>BG-5</td>
<td>0.13</td>
<td>0.12</td>
<td>1.07</td>
<td>0.09</td>
<td>0.08</td>
<td>1.09</td>
</tr>
<tr>
<td>BG-6</td>
<td>0.04</td>
<td>0.04</td>
<td>0.98</td>
<td>0.8</td>
<td>0.77</td>
<td>1.04</td>
</tr>
<tr>
<td>BG-7</td>
<td>0.01</td>
<td>0.01</td>
<td>1.16</td>
<td>0.03</td>
<td>0.03</td>
<td>1.13</td>
</tr>
<tr>
<td>BG-8</td>
<td>0.04</td>
<td>0.03</td>
<td>1.05</td>
<td>0.04</td>
<td>0.02</td>
<td>1.76</td>
</tr>
<tr>
<td>BG-9</td>
<td>0.08</td>
<td>0.08</td>
<td>1.03</td>
<td>0.13</td>
<td>0.12</td>
<td>1.06</td>
</tr>
<tr>
<td>BG-10</td>
<td>0.04</td>
<td>0.03</td>
<td>1.44</td>
<td>0.38</td>
<td>0.34</td>
<td>1.09</td>
</tr>
</tbody>
</table>
4.3. TC, TOC and TIC

In general, two types of carbon are present: organic carbon and inorganic carbon. Organic carbon bonds with hydrogen or oxygen to form organic compounds. Inorganic carbon is the structural basis for inorganic compounds such as gas carbonates and carbonate ions. Collectively, these two forms of carbon are referred to as total carbon (TC). The result of BG black shale samples of TOC, TC and IC measurement is shown in Table 3. Shale from Batu gajah characterized by low to medium weight percent of TOC (from 2.86 to 0.52%). BG-1 gave the highest TOC value of 2.86%.

Table 3. TOC and TC results of Batu Gajah Shale

<table>
<thead>
<tr>
<th>Samples</th>
<th>TOC</th>
<th>TC</th>
<th>IC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Error</td>
<td>A</td>
</tr>
<tr>
<td>BG-1</td>
<td>2.86</td>
<td>2.73</td>
<td>2.80</td>
</tr>
<tr>
<td>BG-2</td>
<td>1.64</td>
<td>1.62</td>
<td>1.63</td>
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<td>BG-3</td>
<td>1.72</td>
<td>1.65</td>
<td>1.69</td>
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<td>BG-4</td>
<td>2.02</td>
<td>1.99</td>
<td>2.01</td>
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<td>BG-7</td>
<td>1.84</td>
<td>1.73</td>
<td>1.79</td>
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<tr>
<td>BG-8</td>
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<td>1.90</td>
<td>1.95</td>
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<td>BG-9</td>
<td>2.07</td>
<td>2.06</td>
<td>2.07</td>
</tr>
<tr>
<td>BG-10</td>
<td>0.75</td>
<td>0.72</td>
<td>0.74</td>
</tr>
<tr>
<td>BG-11</td>
<td>0.75</td>
<td>0.72</td>
<td>0.73</td>
</tr>
<tr>
<td>BG-12</td>
<td>0.58</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>BG-13</td>
<td>0.99</td>
<td>0.94</td>
<td>0.96</td>
</tr>
<tr>
<td>BG-14</td>
<td>1.21</td>
<td>1.18</td>
<td>1.20</td>
</tr>
<tr>
<td>BG-15</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
</tr>
<tr>
<td>BG-16</td>
<td>1.35</td>
<td>1.29</td>
<td>1.32</td>
</tr>
<tr>
<td>BG-17</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>BG-18</td>
<td>0.95</td>
<td>0.90</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Samples | TOC | TC | IC
---|---|---|---
BG-19 | A | 0.70 | 0.69 | 0.69 | 0.14 | 0.58 | 1.00 | 0.99 | 0.02 | 0.14 | 0.58 | 1.00 | 0.99 | 0.02
BG-20 | B | 0.55 | 0.52 | 0.54 | 2.80 | 0.41 | 1.18 | 1.19 | 0.84 | 0.15 | 0.41 | 1.18 | 1.19 | 0.84 | 0.15
BG-21 | Average | 0.70 | 0.58 | 1.29 | 1.31 | 1.53 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-22 | Error | 0.68 | 0.57 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-23 | Average | 0.70 | 0.58 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-24 | Error | 0.68 | 0.57 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-25 | Average | 0.70 | 0.58 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-26 | Error | 0.68 | 0.57 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-27 | Average | 0.70 | 0.58 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-28 | Error | 0.68 | 0.57 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-29 | Average | 0.70 | 0.58 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02
BG-30 | Error | 0.68 | 0.57 | 1.17 | 0.84 | 0.15 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02 | 0.32 | 0.54 | 1.00 | 1.01 | 0.99 | 0.02

5. Discussions

5.1. Organic carbon distribution

Almost all of the organic carbon deposited on the seafloor originates from biological photosynthetic activity in the terrestrial or marine biosphere. The photosynthetic production of this organic matter is represented by:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{light}) \text{“CH}_2\text{O”} + \text{O}_2 \]

In this greatly simplified reaction, “CH2O” is an idealized chemical formula representing the multitude of different types of organic compounds produced in variable proportions by photosynthetic organisms \[^{[26]}\]. Total organic carbon content of BG formation shows extreme variation in organic carbon concentration. Reason of this variation in organic carbon concentration associated with the degradation, preservation or burial of organic matter in marine sediments. Field data reveals that the degradation efficiency is not constant \[^{[27]}\] and that organic carbon burial rates vary significantly in space \[^{[28]}\] and time. Spectroscopic studies in this research already indicates terrestrial organic matter has found in studied shale samples. Terrestrial organic matter export from land and has undergone with variable controls on residence times in soils, followed by widely varying degrees of alteration during transport through the riverine/estuarine/deltaic system and across the continental shelf \[^{[26]}\]. As BG shale samples has deposited in shallow marine, variation on organic carbon might be caused by the degrees of alteration during transport.

5.2. Degree of aromacity

The E4/E6 ratio is considered to be inversely related to the degree of condensation and aromacity of the humic substances and to their degree of humification \[^{[24]}\]. It is suggested that values of the relationship E4/E6 for humic acid is smaller than 5.0 and between 6.0 and 8.0 for fulvic acids \[^{[24]}\]. Higher degree of aromacity of humic acid in shale was evidenced by lower E4/E6 ratio value (0.95-1.36) in Batu Gajah formation extracted by methanol and (0.91-1.44) extracted by DCM.

Higher degree of aromacity in BG shale samples are also due to the reason that these shales was deposited in upper carboniferous period and this period was marked by an abrupt change in the nature of organic matter, and organic carbon. This change corresponds to a major step in the history of life, that is, the appearance of dense plant cover on the continents. The climate conditions during this period were humid and favorable for the growth of terrestrial vegetation. Consequently large amount of biomass of humic type were formed during this period. The emergence of land plants played an important role in the nature and amount of organic matter preserved in rocks of this age. Therefore higher degree of aromacity in BG shale indicates the source of organic matter in Batu gajah shale belongs to terrestrial environment.
5.3. TOC, TC relationship with FTIR functional groups

The processes controlling the level of aromatic and aliphatic hydrocarbon in the shale are complex. Among important factors are chemical properties of the compounds (especially their water solubility), the composition of sediment such as TOC and clay content, and sedimentary depositional patterns. In this work, the effect of TOC and TC on the aromatic and aliphatic hydrocarbon was investigated. The total organic carbon values in the black shale of BG formation are given in Table 3. Most samples of black shale from Batu Gajah contain only Aromatic out of plane C-H bending and Alkyne APCH bending band (Figure 3). Therefore in this study absorbance of Alkyne APCH and Aromatic out of plane C-H bending bands was plotted against TOC and TC to find any relationship if exist.

5.3.1. TOC, TC and aromatic OPCH relationship

Aromatic hydrocarbons are large group of organic compounds possess two or more aromatic carbon rings. They produced usually from incomplete combustion of organic matter and fossil fuels and are ubiquitous throughout the environment. The phenomenon of increasing absorbance as result of an increase of total organic carbon in the structure of humic substances is known. The performed investigations allowed the formulation of the linear relationship between the values of aromatic OPCH with total carbon and total organic carbon concentration. For BG, the correlation coefficient calculated for these linear relationship are equal to r²=0.852 for TOC and r²=0.712 for TC (Figure 4). The evaluation of the regression line shows directly proportional correlation between total carbon total organic carbons with aromatic OPCH in BG formation, which suggested that if black shale enriched in organic matters had the more powerful absorption of aromatic hydrocarbons.

5.3.2. TOC, TC and alkyne APH relationship

The relationship between TOC and TC with Alkyne APH has first time established in this study. Positive correlations of TOC and TC with Alkyne APH have been observed in this study. For BG, the correlation coefficient calculated for these linear relationship are equal to r²=0.739 for TOC and r²=0.753 for TC (Figure 4).
5.4. Functional group distribution

Infrared spectroscopy has great potential as an inexpensive and rapid screening tool for field surveys of wellsite geochemical analysis of cuttings and outcrop rocks [21]. There are several studies which reveal the utility of spectroscopic methods that need no or little sample alteration to evaluate sample properties like presence of hydrocarbon [30-35].

Abundance of Aromatic compounds has been seen in ATR-FTIR spectra of Batu Gajah black shale samples. The broad absorption band at 3700–3000 \text{cm}^{-1} appeared to be -OH groups stretching vibration. The strong absorption peaks situated at 3623, 3696 and 3619 \text{cm}^{-1} were assigned to free -OH groups stretching vibration of crystal water [36]. The strong absorption peak at 1013 \text{cm}^{-1} was caused by Si-O-Si symmetric stretching vibration. The 900–700 \text{cm}^{-1} zone was induced by absorption spectrum of various aromatic C-H groups out-of-plane bending vibration [37]. Peaks at 752, 775, 795 and 827 \text{cm}^{-1} in Batu gajah black shale was caused by the deformation vibration of benzene ring four adjacent H. Presence of these bands shows medium to strong absorption of C-H out of plane bending on an aromatic ring. Peaks at 752 and 827 in Batu gajah black shales are indicative of ortho and para substitution of the aromatic ring (fig. 3) [38]. The peak at 913 \text{cm}^{-1} was due to carboxylic acid OH out-of-plane bending vibration. The peak at 669 and 695 \text{cm}^{-1} was assigned to alkane =C-H bending.
6. Conclusions

ATR-FTIR is shown to be a promising method for rapid assessment of geochemical properties related to distribution of hydrocarbon functional groups. Previous studies have already proven the positive correlation of aromatic hydrocarbons from GC-MS with TOC and TC, but in this study aromatic hydrocarbons calculated from ATR-FTIR has also shown positive correlation with TOC and TC. TOC and TC of black shale shows positive correlation with aromatic OPCH and alkyne APCH. BG formation correlation coefficient values are equal to r2=0.852 for TOC and r2=0.712 for TC. Therefore, present study indicates that the TOC and TC play an important role in controlling the aromatic and aliphatic hydrocarbon level in the Black shale. The obtained values of TOC in BG black shale shows very low values indicating the oxidation of organic matter in outcrop. The FTIR spectra of the black shale samples from BG comprises 4 zones of functional groups, -OH groups stretching vibration, Alkyne C-H bending oxidation of organic matter in outcrop. The FTIR spectra of the black shale samples from BG comprises 4 zones of functional groups, -OH groups stretching vibration, Alkyne C-H bending and Aromatic in-plane C=C stretching bands. More functional groups of aromatic hydrocarbons and lowest humic spectroscopic UV-visible ratio (E4/E6) was observed in BG formations indicates that the origin of formation is terrestrial higher plants.

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