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## THE EFFECT OF PEROXYACETIC ACID TREATMENT AT ELEVATED TEMPERATURE ONTO THE INDONESIAN COAL MICROSTRUCTURE

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### ABSTRACT

*A sub-bituminous high sulphur Indonesian coal, namely Banjarmasin Hj. Ali-Aliansar (BMHA) has been treated with peroxyacetic acid, a mild oxidising agent at temperature of 70°C and at atmospheric pressure. Initial findings have shown that this reagent is capable of removing up to 60 % of the total sulphur in the coal. Almost all pyrite together with ~18 % of simple organic sulphur are being removed from the coal without severely affecting the coal microstructures. Scanning electron microscope with energy dispersive x-ray (SEM-EDX) analysis was used to observe the molecular structure changes within the coal matrix.*

*Keywords: peroxyacetic acid, organic sulphur, pyrite, SEM-EDX*

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### 1. INTRODUCTION

Utilisation of high ash and high sulphur coals are unsuitable for efficient use due to its detrimental effect to the environment. Combustion of this coal will emit notorious gases such as sulphur dioxide and sulphur trioxide<sup>1</sup>, which could lead to serious environmental effect such as the acid rain phenomena. Hence, desulphurisation of coal prior to combustion is important

for the effective utilization of these vital energy resources without polluting the environment.

Presently, control of sulphur oxide emissions is achieved mainly by stack gas scrubbing or physical coal cleaning techniques<sup>2</sup>. The former process is both expensive and energy intensive. The latter, although relatively inexpensive and simple to operate, is less effective. Various chemical processes employing

either oxidizing agents such as ferric chloride<sup>3</sup>, treatments with hydrogen peroxide<sup>4,5</sup>, air oxidation procedures<sup>6</sup>, oxygen dissolved in solvent<sup>7</sup> etc., reducing agents such as single electron transfer techniques<sup>8,9</sup> etc., or mineral acids such as nitric acid<sup>10</sup> have been suggested to reduce the sulphur and ash in coal.

Previously, we have reported the use of peroxyacetic acid (PAA, i.e. mixtures of acetic acid and 6% hydrogen peroxide) treated at 28 and 50 °C, for the chemical desulphurisation of sub-bituminous high sulphur Indonesian coals<sup>11</sup>. The results showed that about 60% of the total sulphur was removed from the coal at reaction temperature of 50 °C with moderate coal dissolution, and without severely affecting the coal microstructure as revealed by the Scanning Electron Microscope (SEM) photomicrographs.

Thus, the aim of this paper is to report the effect of PAA treatment at a reaction temperature of 70 °C on the coal microstructures using Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX).

## 2. MATERIALS AND METHODS

The procedure for the ultimate and proximate analyses on the coal samples have been reported earlier<sup>11</sup>.

### 2.1 PAA treatment on coal

The detail on PAA coal desulphurisation procedure has been described previously<sup>11</sup>. The reagent mixture of acetic acid to peroxide volume ratio was 70:30 with 6% hydrogen peroxide concentration. The reactions were carried out at 70 °C with reaction time duration of 72 hours.

### 2.2 SEM-EDX analyses

The SEM-EDX analyses were conducted using a Leica Cambridge S360 with Camscan Editor ED4 Energy Dispersive Spectroscopy system at the Electron Microscopy Unit, School of Biological Sciences, Universiti Sains Malaysia, Penang. The powdered coal sample (particle size < 75 µm) was sprinkled on the carbon adhesive disc attached on aluminium stub. The analyses were carried out with an accelerating voltage of 10 eV using the spot mode with approximate beam diameter of 200 nm. Collection of X-ray signals was set for about 50 live s. at a minimum of 1000 cps.

## 3. RESULTS AND DISCUSSION

The coal sample used in this study is a sub-bituminous high sulphur Indonesian coal, namely Banjarmasin Hj. Ali-Aliansar (BMHA), originating from Kalimantan, Indonesia. Table 1 represents the ultimate and proximate analyses of the fresh untreated BMHA coal and Table 2 is details of the oxidised BMHA coal with PAA at 70 °C.

### 3.1 Coal desulphurisation

The enhancement of desulphurisation should be interpreted carefully since the addition of oxygen upon oxidation dilutes the remaining sulphur and would result in lower sulphur contents in the coal. Hence, one way to determine the effect of desulphurisation is to compare the S/C atomic ratio of the desulphurised coal with the untreated fresh coal.

The treatment of BMHA coal with PAA at 70 °C was carried out and the results are shown in Table 2. It seems that the PAA was able to reduce the total sulphur from 3.46 to 1.39 % by weight, corresponding to ~60% of the total sulphur removal from the coal. The distribution of sulphur forms as displayed in Table 1 shows that pyritic sulphur content of the coal is ~1.74% by weight.

**Table 1.** Characterisation of fresh untreated Banjarmasin Hj. Ali-Aliansar (BMHA) coal sample.

<i>Ultimate analysis</i>	<i>(wt % db)</i>	<i>Sulphur forms</i>	<i>(wt %)</i>
Carbon	68.00	Pyritic	1.74
Hydrogen	6.55	Sulphate	0.10
Nitrogen	1.37	Organic	1.62
Sulphur	3.46		
Oxygen (by difference)	20.62		
S/C ratio ( $10^{-4}$ )	191		

<i>Proximate analysis</i>	<i>(wt %)</i>
Moisture	3.41
Ash	6.16
Volatiles matter	48.45
Fixed carbon	41.98

**Table 2.** Characterisation of PAA treated at 70 °C of Banjarmasin Hj. Ali-Aliansar (BMHA) coal sample.

<i>Ultimate analysis</i>	<i>(wt % db)</i>	<i>Proximate analysis</i>	<i>(wt %)</i>
Carbon	69.18	Moisture	4.95
Hydrogen	5.44	Ash	6.10
Nitrogen	1.56	Volatiles matter	48.02
Sulphur	1.39	Fixed carbon	40.24
Oxygen (by difference)	22.43		
S/C ratio ( $10^{-4}$ )	75.3		
Sulphur total removed (%)	61		

Our previous study with acidic chromous chloride treatment of BMHA coal<sup>12</sup> has shown that mainly pyritic sulphur (~52%) is being removed by this treatment, which suggests that ~48 % of the sulphur that still remain in the coal is mostly organic sulphur. Hence, the results of desulphurisation using PAA in this study reveal that almost all pyrite together with some organic sulphur forms (i.e. ~8%) are being removed from the coal. Thus, this additional 8% account to about ~18 % of total organic sulphur removal from the coal.

### 3.2 Microstructure changes in coal with SEM-EDX

The effect of PAA treatments on the microstructure of the BMHA coal are displayed in Figures 1 to 4, allowing comparison between the structures of the fresh and treated samples.

Surprisingly, the PAA treatment at 70 °C does not has an adverse effect on the morphology of coal surfaces with comparison to the PAA treatment at 50 °C as reported earlier<sup>11</sup>. The SEM photomicrographs of the treated samples (see Figure 3 and 4) show the presence of porosity with slight formation of depressions and micro-fissures on the coal surfaces.

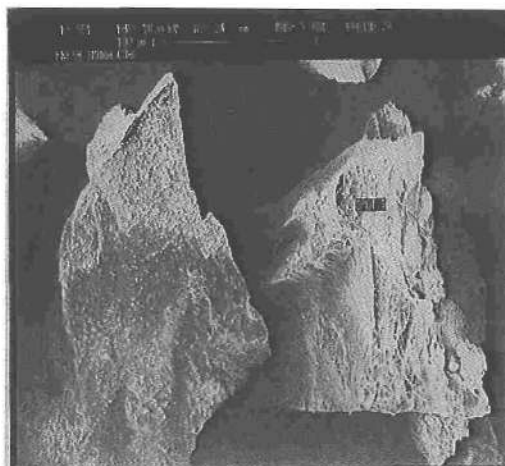
These observations are not yet fully understood, but it is believed that the high temperature regime might have

caused the hydrogen peroxide to dissociate rapidly before further reaction forming the peroxy acid<sup>13</sup>, and thus, reduces the oxidising effect on the coal. However, the effect of increasing heat, in fact, induced further fragmentation to the coal particles (see Figures 1 and 3 for comparison). Further, an appreciable amount of coal desulphurisation (~60%) might suggest that the reduction in the coal particle size is an important factor for the reagent to access through the coal structure and finally the organic matrix. Furthermore, since the morphological structure of the coal is not that affected by this treatment in comparison to the PAA treatments at 50 °C as reported earlier<sup>14</sup>, it is anticipated that the mild oxidizing treatment at 70 °C would not have any significant effect on the coal calorific value and, hence, on the efficiency of coal as fuel.

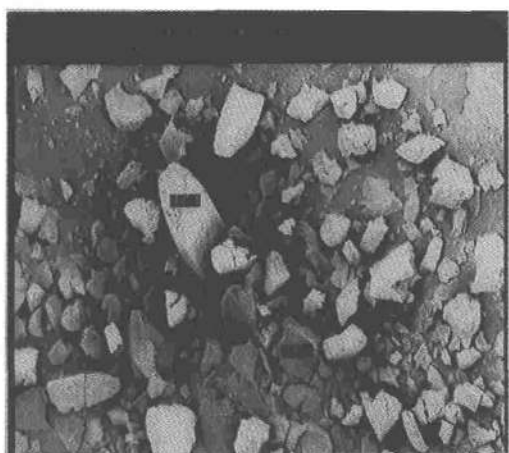
Figures 5 and 6 represent the EDX spectra for the fresh and PAA treated coal samples at 70 °C. A comparison of the two spectra reveals generally reduced levels of elements mainly silica (Si), aluminium (Al) and sulphur (S) after the PAA treatment. The sulphur  $K_{\alpha 1}$  and  $K_{\beta 1}$  line peaks which were obtained with 10 kV with 200 nm beam diameter and 50 live/s exposure indicate an appreciable reduction in the sulphur peaks (i.e. ~60% reduction) after the PAA treatment, and is consistent with the result shown in Table 2.



**Figure 1:** SEM photomicrograph of overall spot of fresh untreated BMHA coal sample.



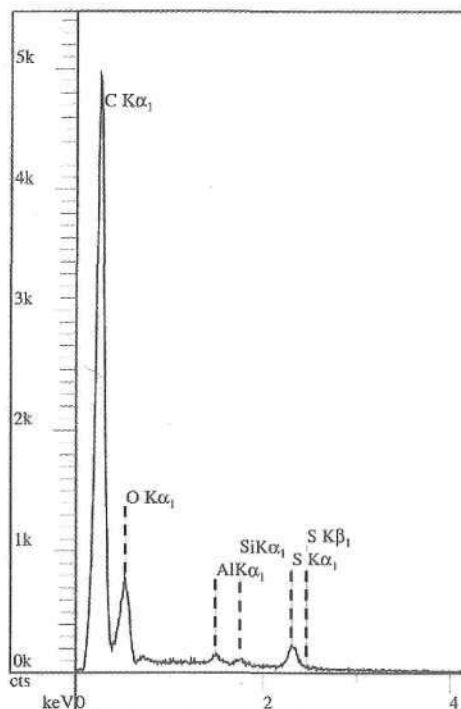
**Figure 2:** SEM photomicrograph of magnified spot of fresh untreated BMHA coal sample.



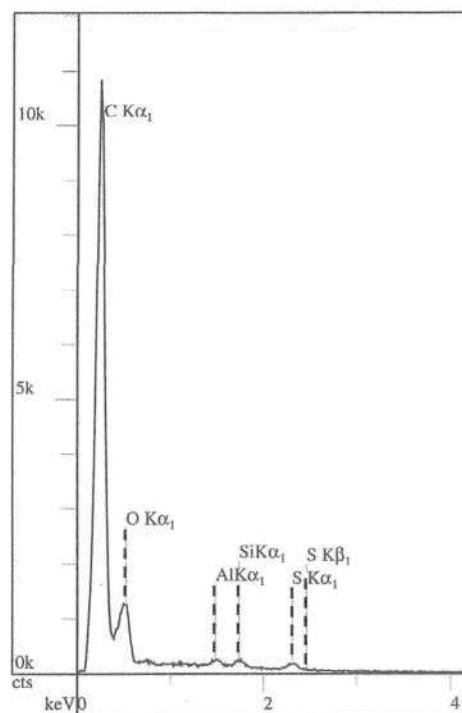
**Figure 3:** SEM photomicrograph of overall spot of treated BMHA coal with PAA at 70 °C for 72 hours.



**Figure 4:** SEM photomicrograph of magnified spot of treated BMHA coal with PAA at 70 °C for 72 hours.



**Figure 5:** EDX spectrum of fresh untreated BMHA coal sample.



**Figure 6:** EDX spectrum of treated BMHA coal with PAA at 70 °C for 72 hours.

#### 4. CONCLUSIONS

The PAA mild oxidation leads to an appreciable amount of coal desulphurisation, i.e. ~60% of total sulphur removal after 72 hours reaction at reaction temperature of 70 °C. The SEM results demonstrate a clear effect of the reagent on the coal particle size whereby fragmentation of the coal particles being observed as a result of PAA treatment. Further, the EDX analyses indicate that the concentration of pyrite and some other minerals mainly aluminium and silica are substantially reduced from the coal.

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