

Indonesian low rank coal oxidation : The effect of H₂O₂ concentration and oxidation temperature

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Abstract. Extraction of Indonesian low rank coals by alkaline solution has been performed to isolate the humic substances. Pretreatments of the coals by oxidation using H₂O₂ prior to extraction are required to have higher yield of humic substances. In the previous research, only the extraction process was considered. Therefore, the effects of reaction temperature and residence time on coal oxidation and composition of extract residues are also investigated in this research. The oxidation temperatures studied were 40°C, 50°C, and 70°C and the H₂O₂ concentrations studied were 5%, 15%, 20 %, and 30 %. All the oxidation variables were studied for 90 minutes. The results show that the higher the concentration of H₂O₂ used, the less oxidized coal produced. The same trend was obtained by using higher oxidation temperature. The effect of H₂O₂ concentration, oxidation temperature and reaction time to the yield of humic substances extraction have positive trends.

1. Introduction

Coal is an important fossil energy source for electricity. This material consists of a wide range of organic structures in its complex macromolecular, primarily composed by carbon, hydrogen, oxygen, nitrogen, and sulfur. The molecular structure depends on its rank and the environmental conditions during coalification of plant matter. The rank classification is usually based on the contents of volatile matters, moisture, calorific value, and ash. Indonesian low rank coals, have calorific value: 4300 – 5000 kcal/kg are abundant resources and commonly have been utilized for electric power generation [1]. Others application of this low rank coal is limited due to the difficulty (auto ignition) for handling or transportation and storage.

Coal also regarded as the source of humic acids, organic acids are commonly used as a soil supplement in agriculture, and sometimes as a human nutritional supplement [2]. The non energy utilization of the coal, especially for humic acid, is still unpopular. Hence, it is important to study the methods for utilizing it efficiently.

From the published structural model, humic acid is a complex of many different acids, mainly composed of hydrophilic functional groups, such as carboxyl –COOH and hydroxyl – OH groups [3]. Humic acid is a principal component (the most chemically active component) of humic substances (humus), the major organic constituents of soil, which usually also present in sediments and coals. Humic substances can be divided into three main fractions: humic acids, fulvic acids, and humin. Humic and fulvic acids are highly soluble in alkaline, while humin is insoluble in alkaline [2]. Hence, humic and fulvic acids extracted from the sources into an alkaline solution (NaOH or KOH). Humic acids precipitated from the solution by adjusting the pH to 1 with HCl, leaving the fulvic acids in solution.

Humic substances are obtained from decomposition or biodegradation of plant or dead organic matter which happen during coalification process. Progressively the humic substances are converted to peat, lignite, subbituminous coal, bituminous coal and finally into anthracite. Consequently, the amounts of extractable humic acids depend on the degree of coalification. Peat and lignite are coal



with lower degree of coalification having higher humic substances contents than bituminous. So, sufficient extraction of humic acids depends on the chemical composition of the source, and the method of extraction.

To increase the extraction yield, pretreatment process prior to extraction the low rank coals are performed. Oxidizing is pretreatment for the low rank coal which result higher content of extractable humic substances [4]. Oxidation with nitric acid indicate a substantial improvement in the yield of the coal to humic acids from 20% to 85%. In addition to nitric acid, the oxidators might be used are KMnO_4 and H_2O_2 . By oxidating the coal with hydrogen peroxide in liquid phase at 60 °C for 2 h, some weak covalent bonds are broken and oxygen functional groups are introduced [3]. A comparative evaluation of the oxidators indicated that weight losses upon HNO_3 oxidation is relatively lower than H_2O_2 oxidation, while KMnO_4 was not recommended for coal oxidation, as a substantial amount of inorganic compounds was introduced to the products and the essential yield generated was low [4]. Even though, the weight losses involved in nitric acid oxidation was acceptable, but this reaction generates nitro humic acid and produces a large amount of waste water which causing serious environmental problems. Therefore H_2O_2 is chosen as oxidator for extraction of humic acids. In addition, H_2O_2 is an effective oxidator to convert Low Rank Coal into useful product[5]. The objective of this research is to study effect of oxidation parameters (H_2O_2 concentrations, temperatures, and reaction times) on the yield of humic acids.

2. Materials and Experimental Procedure

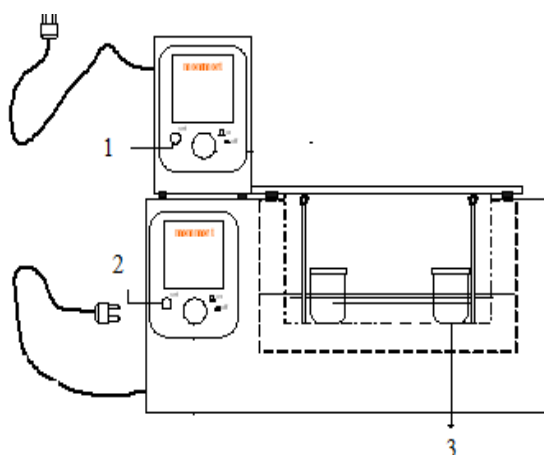
2.1. Materials

Low rank coal used for this study came from East Kalimantan. It has calorific value 4828.51 cal/g. Before use, the coal was ground into smaller size, screened into -70 +80 mesh, and dried at 60°C for 48 hours. The proximates analysis (% adb): moisture 12.73, ash content 14.53, volatile matter 45.75, and fixed carbon 26.99.

2.2. Experimental Procedure

2.2.1. Oxidation of coal

Oxidation of the coal was performed as follows: 6 times 2.5 g of dried coal were weighed accurately. Each portion ($= m_c$) was for oxidation of 15, 30, 45, 60, 75, and 90 minutes, respectively. Each portion of dried coal was mixed individually into 25 mL of certain concentration (varied from 5%, to 20%) of H_2O_2 in a 250 mL beaker glass. Mixing speed was 80 shakes/ min in a water bath (Figure 1).



Notes :

1. Shaker speed controller
2. Temperature controller
3. Beaker glass

Figure 1. Experimental set up

The water bath was operated at a constant temperature (e.g. 60°C) during the time of oxidation (15, 30, 45, 60, 75, and 90 minutes). When the certain time of extraction has completed, the beaker glass was taken off individually from the bath, then filtered immediately through 42 Whatman's paper (the weight of the paper is known before used), then washed with distilled water to remove the water soluble matters. The filtrate was collected, while the solid residue (oxidized coal) was dried at 105°C until constant weight. The nett weight of oxidized coal was noted ($= m_{OC}$). To examine the effect of the temperature, the oxidation was also performed at various temperature (40°C, 50°C, and 70°C). The weight ratio of the coal after and before oxidation is:

$$Y_o = \frac{m_{OC}}{m_c} \quad (1)$$

2.2.2. Oxidized coal extraction

In order to analyze the effect of oxidation process parameter on the yield of extractable humic acid, every sample of oxidized coal was extracted at certain condition, i.e : 0.1 g oxidized coal sample, 50 mL 0.1 N standard solution of KOH as solvent. Extractions were performed for 7 samples, in 7 beaker glasses which placed in a water bath operated at 60°C. Five milliliter of extract sample was taken off after 60 minutes extraction, diluted to 100 mL in a volumetric flask. The diluted samples were titrated using 0.001 N HCl to find the remaining KOH. By assuming that the humic acid completely reacted, then its amount was equivalent to the amount of KOH reacted ($= C_{HA}$). If all the humic acid in the oxidized coal was assumed to be completely extracted, then the yield

$$Y_E = \frac{m_{OC} C_{HA}}{m_c} \times 100\% \quad (2)$$

3. Results and Discussions

3.1. Oxidation

In a solid-liquid system, H_2O_2 will be adsorbed into the coal surface and oxidation happened, which resulted, long chains of humic substances cracked into short. Table I summarized the weight ratio of coal after and before oxidation (Y_o) at various process conditions.

Tabel I. Weigh Ratio of Coal, After to Before Oxidation

Oxidation time, min	Yield of oxidation					
	40°C & 10% H_2O_2	50°C & 10% H_2O_2	70°C & 10% H_2O_2	60°C & 5% H_2O_2	60°C & 15% H_2O_2	60°C at 20% H_2O_2
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
15	0.9078	0.8725	0.6761	0.8561	0.7199	0.6770
30	0.9044	0.8644	0.6599	0.8532	0.7185	0.6561
45	0.8884	0.8558	0.6356	0.8532	0.7189	0.6432
60	0.8169	0.8066	0.5815	0.8501	0.7141	0.6136
75	0.8041	0.7842	0.5652	0.8491	0.7072	0.6463
90	0.8029	0.7912	0.5495	0.8558	0.7110	0.6233

Table 1 shows that there are weight losses of the coal during oxidation using H_2O_2 . The weight lost due to solubilization of various products of oxidation. Due to H_2O_2 is acidic, so the humic acids are not dissolved out of coal while fulvic acid and other water-soluble organics dissolved and diffuses into the solvent of H_2O_2 . The lost is quite significant (45.05%) when oxidation conducted for 90 min using 10 % H_2O_2 at 70°C. Eventhough, this value is comparable to the oxidation of low rank

coal of Mukah. At the same H_2O_2 concentration and oxidation temperature, Fong et.al [4] reported that for 120 min oxidation the weight lost was 50.33 %. At another condition (5 % H_2O_2 , 70°C, and 120 min) Fong, et.al [4] reported the loss was 32.23 %, while this research (5 % H_2O_2 , 60°C, 90 min) only 14.42%. The higher the temperature of oxidation or the H_2O_2 concentration, the more the weight lost.

3.2. Extraction

The humic acid contained in oxidized coal which prepared under various conditions extracted using 0.1 N KOH solution at 60°C. The extractions were conducted for 60 minutes. The yields of humic acid on the extraction of oxidized coal summarized at Figure 3 for yield of humic acid based on oxidized coal weight (Y'_E) while Figure 4. Yield of humic acid based on original coal weight (Y_E). Compared to the original coal (non - oxidized), the yield of humic acids prepared with oxidation using 20% H_2O_2 at 60°C for 90 min, increased from 8.37 mgeq KOH to 19.65 mgeq KOH/gram of coal oxidized for coal or from 46.95% to 68.57 %. This value was comparable with from 46 to 63 % [5]. Although appeared to be promising, the considerable weight losses of coal upon oxidation as much as 45.05% render it incomparable. The losses were also observed to correspond to the concentration possibly due to prominent occurrence of desulfurization and demineralization. These processes were commonly reported for oxidation with H_2O_2 [4].

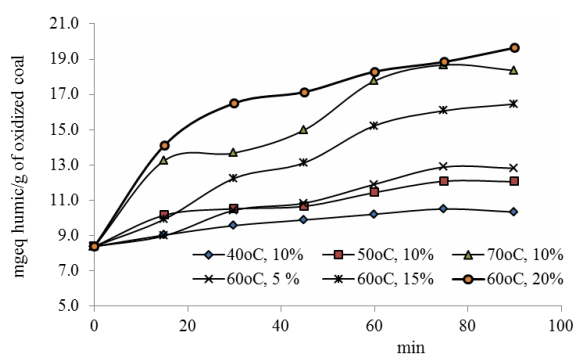


Figure 2. Yield of oxidized coal to humic acid

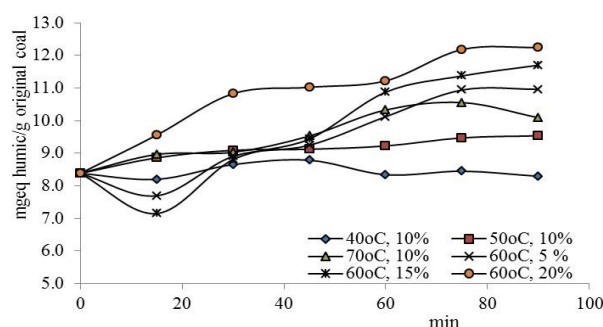


Figure 3. Yield of original coal to humic acid

The increasing yield of humic acid proved that the low rank coal have lots of hydrophilic functional groups such as $-\text{COOH}$ and $-\text{OH}$. The increasing yield as the oxidation resulted more acidic groups in the coal, and as the coal is extracted with a base, the more acidic groups are reacted and dissolved in the solvent. More carboxylic functional groups, more water solubles usually obtained, so that the humic acid produced will increase. Figure 4 -7 present the FTIR for analyze the absorbance of the carboxylate (1700 $1/\text{cm}$) and phenolate (3300 $1/\text{cm}$).

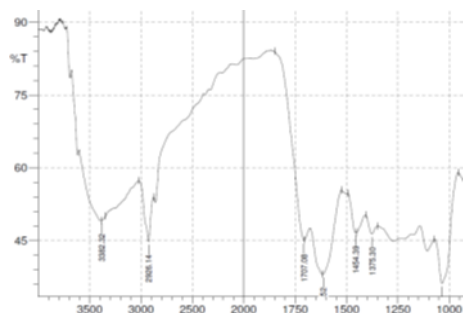


Figure 4. FTIR spectra for non oxidized coal



Figure 5. FTIR spectra oxidized coal (5%, 60°C, 60 min)

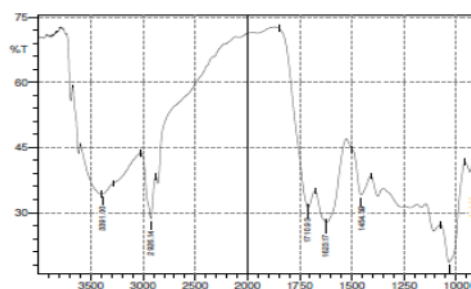


Figure 6. FTIR spectra oxidized coal (10%, 50°C, 60min)

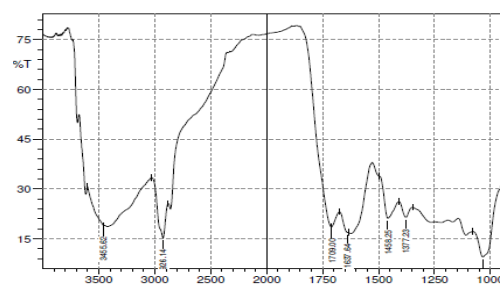


Figure 7. FTIR spectra oxidized coal (10 %,60°C, 90 min)

4. Conclusions

The effect of variation of H_2O_2 concentration, oxidation temperature, and time of oxidation to the weight loss of original coal have positive trends. The same trends to the yield of humic acids. Eventhough the trends are not too significant especially for lower temperature or lower concentration. Liquid phase oxidation of Indonesian low rank coal using H_2O_2 increases the yield of humic acid from 46.95% to 68.57 % of the original coal. Oxidation using H_2O_2 resulted more water soluble materials, but less overall yield of humic acids.

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