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GRANULAR-ACTIVATED CARBON FROM MUKAH COAL USING CARBON DIOXIDE ACTIVATION

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Graphical abstract

Abstract

A study was conducted on Mukah coal using fixed bed reactor and one step activation with varying resident time and temperatures. CO_2 gas was used for the activation process. The one-step continuous process comprised of carbonization and activation processes. The burn off analysis for 80 grams of Mukah coal was done to obtain volatiles removal at various carbonization temperatures. The results obtained showed that at 900°C, the percentages of burn off and the remaining weight were 42.2% and 57.8% respectively. Micrometrics ASAP2010 was used to analyze Mukah coal activated carbon in obtaining the BET surface area, the micropore area, and the average pore diameter. The results obtained indicated that activation at 900°C gave the highest BET surface area with 675m^2/g, while the highest micropore area with 427 m^2/g was obtained at 800°C. In addition, the average pore diameter range was within 18.5 to 26.4 A.

Keywords: Mukah coal; one-step activation; burn off analysis; BET surface area; micropore area; average pore diameter

Abstrak

Satu kajian telah dijalankan ke atas arang batu Mukah dengan menggunakan satu reaktor tetap dan satu langkah pengaktifan dengan pelbagai masa dan suhu yang berbeza. Gas CO_2 digunakan untuk proses pengaktifan. Langkah proses yang berterusan merangkumi pengkarbonan dan proses pengaktifan. Analisis pembakaran bagi 80 gram arang batu Mukah telah dijalankan bagi menyingkirkan bahan meruap pada pelbagai suhu pengkarbonan. Keputusan yang diperolehi menunjukkan bahawa pada 900°C, peratusan pembakaran dan berat yang tinggal adalah 42.2 % dan 57.8 % masing-masing. Micrometrics ASAP2010 digunakan untuk menganalisis arang batu Mukah karbon yang telah diaktifkan bagi mendapatkan nilai luas permukaan BET, luas kawasan liang mikro, dan purata diameter liang. Keputusan yang diperolehi menunjukkan bahawa pengaktifan pada 900°C memberi luas permukaan BET tertinggi dengan 675m^2/g dan pada 800°C, luas kawasan liang mikro tertinggi adalah 427 m^2/g. Di samping itu, purata julat diameter liang adalah di antara 18.5 sehingga 26.4 A.

Kata Kunci: Arang batu Mukah; satu langkah pengaktifan; analisis pembakaran; BET kawasan permukaan; kawasan liang mikro; purata diameter liang

1.0 INTRODUCTION

Activated carbon is a porous material, which can be used as a good adsorbent if it possesses high amount of total surface area. Some manufacturers have considered other criteria, such as micropore area and pore size diameter, depending on the application. Activated carbon sources, which can be either biomass waste [1-5] or coal [6-9], have been discussed and

studied in many journals and publications. For example, biomass activated carbon was made from various nutshells, such as almond shell (AM), coconut shell (CN), oil palm shell (OP), pistachio shell (PT), and walnut shell (WN). They identified that with the activation process using chemical activation at 1073 K; all the nutshells had maximum specific surface areas [1]. Referring to Ahmad pour and Do (1996), a series of activated carbons was prepared from bituminous coal; 1) via chemical activation with potassium hydroxide and zinc chloride, and 2) via physical activation with carbon dioxide. The effect of process variables, such as carbonization time, temperature, particle size, chemical agents, as well as method of mixing and impregnation ratio in the chemical activation process had been studied in order to optimize those preparation parameters [6].

Commercial coal activated carbon DX-30 with specific surface area > 1000 m^2/g was used to adsorb radioactive iodine and stable iodine [7]. The experiment proved the effectiveness of using coal-activated carbon for iodine removal. Nevertheless, how the activated carbon coal was prepared was not discussed in the journal. According to Hwang et al., [10], carbonization could remove a considerable amount of organic matter from waste. From their results, carbonization could be considered as a pre-treatment method for waste before landfilling, as well as for fuel recovery.

On the other hand, Turkan and Atakan prepared coal-activated carbon from Zonguldak region coals via physical and chemical activations for hydrogen sorption, which were collected from two mines (Kilimli and Armutcuk)[11]. The BET surface area of the Kilimli coal samples, which initially had a value of 1.20 m^2/g, increased to 52.62 m^2/g after pyrolytic heat treatment at 800◦C and increased to a value of 830.5m2/g by treating the coals with KOH + NH_4Cl mixture at 750°C, and followed by oxidation of the samples mixed with $ZnCl_2$.

Meanwhile, oil palm shell is one of the biomass residues used to produce activated carbon. Low cost and availability are the factors of the selection for this material. Besides, good surface area and porosity characterization are added values for oil palm shell. Ku Hamid and Abdul Rahman [12] investigated the effects of activating agents on the yield and the porosity of chemically-produced activated carbon from oil palm shell. $ZnCl_2$, H_3PO_4, and KOH were used as activants in the production of activated carbon. The results revealed that H_3PO_4 was the most suitable activant. Wan Mohd Ashri Wan Daud et al., [13] also studied oil palm shell for the development of activated carbon with various carbonization temperatures. The activation agent for the experiment was steam. He found that carbonization temperature strongly affected the properties of activated carbon to be manufactured. Meanwhile, preparation of activated carbon from oil-palm-stone chars by microwave-induced carbon dioxide activation was done by Jia Guo and Aik Chong Lua [14]. The experimental results showed that it was feasible to prepare activated carbons with high density and predominant microporosity from oil-palm-stone chars via microwave heating. These activated carbons were used as gas-phase adsorbents or carbon molecular sieves after further modification of carbon deposition. CO_2 gas flow rate, input microwave power, and exposure time were found to be the important processing parameters that significantly affected the quality of the final products. Besides, adding CuO receptors to the char samples increased the surface temperature and significantly reduced the processing time. However, these receptors caused an external heating that resulted in heterogeneous pore structures, as shown in the scanning electron microscope (SEM) micrographs.

On the other hand, a three-step process activation of Illinois Basin Coal (IBC-106), which were oxidation of the coal in air at 150-250°C for 2-40 hours, devolatilization of these oxidized coals in nitrogen at 500-730°C for 1 hour, as well as activation (gasification) of the chars in 45% steam, and 4% oxygen in nitrogen at 730-880°C for 3.5-96 hours had been done by Jian Sun et al., [15]. It was confirmed that the application of oxidation pretreatment eliminated the caking of IBC-106, preserved the microstructure of the coal, and led to high carbon surface areas. In comparison with Darco coconut charcoal, a commercially-activated carbon (Fisher Scientific), whose surface area was 547 m^2g^{-1}(dry), the largest toluene adsorption capacity of activated carbons was 1.57 g g^{-1}, four times more than that of Darco. Meanwhile, the research on the influence of the carbonization-heating rate on the physical properties of activated carbon from a sub-bituminous coal was done by Marcilla et al., [16]. They discovered that chars from carbonization experiments at high heating rates showed higher reactivity than those subjected to slow heating rates and yielded a slightly increased surface area of activated carbons.

Producing activated carbon from lignin coal via chemical activation was attempted by Jun'ichi Hayashi et al., [17]. The influence of carbonization and activating reagent on the pore structure of the activated carbon was investigated. Activated carbons were prepared from lignin via chemical activation with $ZnCl_2$, H_3PO_4, and some alkali metal compounds. It was found that the maximum surface areas obtained at the carbonization temperature of 600°C in both $ZnCl_2$ and H_3PO_4 activation, and the surface areas were as large as those of the commercially-activated carbons. On the other hand, in alkali metal activation, it was found that the maximum surface areas were obtained at the carbonization temperature of 800°C, except for Na_2CO_3 maximum surface areas, which were larger than those of the commercially-activated carbons. The activated carbon prepared with K_2CO_3 activation showed a surface area of nearly 2000 m^2 / g. It was shown that $ZnCl_2$ worked effectively as a dehydration reagent below 600°C. On the other hand, K_2CO_3 worked effectively in two temperature ranges, below 500°C and above 600°C. When below 500°C, the carbonization behavior was modified with the impregnation of K_2CO_3, but the pore structure changed a little. Meanwhile, above 600°C, carbon was

consumed by K_2CO_3 reduction, and then, the surface area increased.

In comparison, a research done by Teng et al., [18] prepared activated carbon from three Australian bituminous coals. The activation was done with CO_2 gas. In the coal analysis, the coals had higher carbon content at 83.2 %(wt%). The experiment succeeded in producing activated carbon with high BET surface area.

Among the coal-based activated carbon, bituminous products are in greater demand since they have greater density, hardness and abrasion resistance, as well as more durable. Besides, previous researches have shown good result on activated carbon properties for non-coal based. It had been proven that the performance of activated carbon depended on carbonization and activation processes regardless of the sources of the raw material. In this study, the effects of one-step activation at 900°C for carbonization and various activation temperatures from 600°C to 900°C using Mukah coal, had been observed. The results focused on BET surface area, micropore area, and average pore diameter.

2.0 EXPERIMENTAL SETUP

2.1 Preparation of Raw Material

The experiment was conducted at Thermodynamic Laboratory, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM). Mukah coal was obtained from Global Minerals (S) Sdn Bhd, one of the main coal mining companies in Sarawak. Mukah coal was dried at 90°C for 24 hours and then sieved to 1.2mm<size<4mm.

2.2 Carbonization and Activation Processes

80 grams of raw material was prepared and then placed into a fixed bed reactor. N_2 gas with a flow rate of 1.5 L/min was used for carbonization.

Then, the sample was activated by using CO_2 (99.98% of purity) with a flow rate of 1.0 L/min. Figure 1 illustrates the experimental setup for this process. A photograph for the test rig is shown in Figure 2. The setup of the rig included a vertical tube furnace with a programmable heating controller (Carbonite VST 12/25/400), a fixed bed reactor, gas cylinders with gas regulators, manual switching valves, flow meters, a blower, and piping system.

Besides, carbonization was done at 900° C for 0.5 hour holding time at 15° C/minute of heating rate for each sample, then, it was activated at 600° C–900° C for 1 hour at 15° C/minute of heating rate. After the activation process was accomplished, the sample was cooled down to room temperature. All the processes were repeated to obtain the weight of the samples.

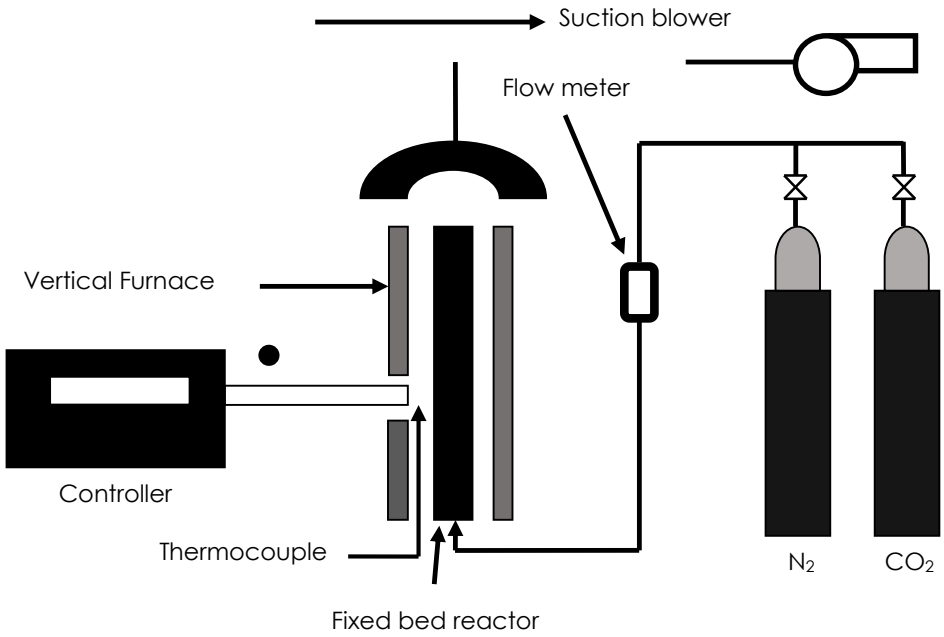

Fig 1 Experimental setup for activated carbon production

Fig 2 Photograph of experimental setup for activated carbon production

3.0 RESULTS AND DISCUSSION

3.1 Burn Off Analysis

Figure 3 shows that at 700° C, volatile matter started to be removed totally because there was no significant change of burn off percentage within 700° C to 900° C. Therefore, 700° C, 800° C, or 900° C were selected and used for carbonization process. When more sample was exposed to high temperature, higher porosity was obtained, and therefore, 900° C was chosen as the temperature for carbonization.

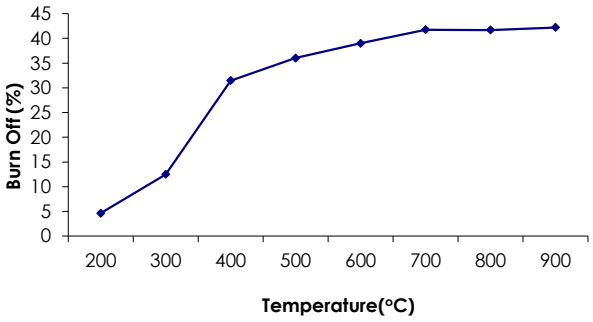

Fig 3 Burn off Mukah coal against temperature

3.2 BET Surface and Micropore Area Analyses

All the characterization experiments in this study were carried out by using a unit of Micromeritics ASAP2010 from Micromeritics, Inc. Norcross, GA, USA.
The method used was static volumetric method and the adsorption was measured by using mass balance equations, appropriate gas equations of state, and measured pressures to obtain all the adsorption isotherms of the activated carbon.

Table 1 Results of BET and Micropore Area analyses

Carbonization temperature, °C	Activation temperature, °C	BET Surface area (m^2/g)	Micropore Area (m^2/g)	Average Pore Diameter (A)
900	Not activate	22.74	12.54	25.22
900	600	25.37	19.47	18.51
900	700	220.81	174.74	22.64
900	800	564.07	426.67	20.85
900	900	674.81	317.93	26.44

Without any activation process, the total BET surface area and the micropore area showed small development in the total surface area. The result was approximately the same for the activation at 600 ° C. It showed that at 600° C–700° C, the development of pore structure was less. Besides, the change in the total BET and micropore areas had been obvious for the increasing activation temperature starting from 700° C to 900° C. The maximum total BET surface area was obtained at 900° C with 674.81m^2/g, whereas the maximum total micropore area was obtained at 800°C with 426.67m^2/g. Besides, the total micropore area drop at 900° C due to high temperature, while the pore size structure changed from micropore to mesopore although it showed a high value for BET surface area.

4.0 CONCLUSION

This experiment depicted that in order to obtain more surface area in Mukah coal activation, high activation temperature had been needed to produce more pore structures. Mukah Coal endurance and hardness characters were the factors for it to be carbonized at a high temperature. Nevertheless, at 900°C for activation, the structure of the Mukah coal started to change from micropore to mesopore, resulting in less micropore area building, as well as the increment in pore size diameter.

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