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Comparative Study of Hydrogen Sulfide Adsorption by using Alkaline Impregnated Activated Carbons for Hot Fuel Gas Purification

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Abstract

Biogas, natural gas, and synthesis gas from coal gasification contain hydrogen sulfide (H₂S) that is highly toxic for human and corrosive for machine. H₂S must be removed from fuel gases prior utilization. The objective of this research was to compare the adsorption of H₂S by using commercial and alkaline impregnated activated carbons. The commercial and alkaline impregnated activated carbons were tested by the temperature program adsorption of H₂S at 30 °C and 550 °C. At high temperature of adsorption, alkaline activated carbons adsorbed H₂S significantly higher than commercial activated carbon (in the range of 3-29 times higher depending on modification method). Furthermore, the concentration of H₂S came out at the outlet gas after treated by the KOH and Na₂CO₃ impregnated activated carbons was less than 30 ppmv, which was safe for utilizing in mechanical and power engine.

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1. Introduction

Biogas that produced from anaerobic digestion of biodegradable materials can be utilized for generation of electrical power and heat production. Generally, biogas (as well as natural gas and synthesis gas from coal gasification) contained hydrogen sulfide (H_2S) that was highly toxic for human body and corrosive for machine. The content of H_2S in biogas was about 0-1% and H_2S must be removed from fuel gases prior utilization [1].

Activated carbon that is a highly porous material was used for removal of impurities from gases and liquids including gas separation and purification, vehicle exhaust emission control, and environmental technology [2]. For low concentration H_2S removal, the adsorption by activated carbon was known as an efficient process [3-4]. Moreover, activated carbon has a high activity and long-lasting. In Thailand, it is inexpensive adsorbent as compared to inorganic adsorbents such as alumina, zeolite and metal oxide. It was produced from agricultural waste such as coconut shell, palm shell, and corncob.

The adsorption capacity of activated carbons was determined by their physical or surface property, but also influenced by their chemical property. Typically, the surface properties of activated carbon such as surface area, pore volume, and pore size affect on the adsorption capacity.

Activated carbon that was impregnated with alkaline material such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) was used for the H_2S removal at ambient temperature [5-6]. At surface of the impregnated activated carbon, acid-base reaction occurs. The advantages of impregnated activated carbon in the removal of H_2S are high efficiency and fast kinetically reaction. However, the adsorption of H_2S on alkaline impregnated activated carbon under the adsorption temperature program has not been investigated. Therefore, this research focuses on the effect of temperature toward H_2S adsorption characteristic and capacity. Commercial and four types of alkaline impregnated activated carbons were studied. In addition, the reaction of H_2S on the commercial and alkaline impregnated activated carbon at room and high temperature were proposed.

2. Experimental

2.1. Materials

Materials in this experiment were commercial and modified activated carbons. The granular commercial activated carbon (A) made from coconut shell. The parameters of surface properties for commercial activated carbon are shown in Table 1.

The commercial activated carbon was impregnated with alkaline compound such as KOH, NaOH, sodium carbonate (Na_2CO_3), and potassium iodide (KI) according to the following procedure. First, the A was soaked with this alkaline solution (10% w/v) for 30 minutes. Then, the sample was heated at 100 °C to evaporate water. Finally, the sample was dried at 110 °C for 24 h. Activated carbon which was impregnated with KOH, NaOH, Na_2CO_3 , and KI was referred to A_100-KOH, A_100-NaOH, A_100- Na_2CO_3 , and A_100-KI, respectively.

Table 1. Surface properties of the commercial activated carbon.

Parameters	Value
Surface area (m ² /g)	1343
Pore volume (m ³ /g)	0.45
Pore size (nm)	0.67

2.2. Adsorption test apparatus

Schematic diagram of adsorption system as shown in Figure 1 consisted of gas supply unit, a fixed-bed reactor in the horizontal furnace, and gas monitor system. The mixture of He and H₂S gas that was controlled by mass flow controllers was pass through the fixed-bed reactor. The reactor (12.0 mm of internal diameter and 70 cm of length) was filled with adsorbent bed. The amount of activated carbon in the reactor was 1.0 g. The H₂S continuous monitor system used QRAE model PGM-50Q to measure concentration of H₂S from the outlet of reactor.

2.3. Temperature program adsorption of hydrogen sulfide

In Figure 1, the condition of H₂S adsorption was H₂S inlet concentration as 3000 part per million by volume (ppmv). The flow rate of inlet gas was 100 ml/min. The A, A_100-KOH, A_100-NaOH, A_100-Na₂CO₃, and A_100-KI were tested by the H₂S adsorption temperature program. The temperature program had 2 parts. The first part was processed at 30 °C that H₂S gas was fed into the reactor and the concentration of H₂S was recorded until the concentration at the outlet reached to 3000 ppmv. The condition of the second part was the same as the first, but the temperature was programmed to increase from 30 to 550 °C at a rate of 10 °C/min. Then reactor temperature was held constant at 550 °C. When the H₂S outlet concentration was 300 and 3000 ppmv, the breakthrough time and total adsorption time were recorded. The adsorption capacity of activated carbon was calculated using the integrated area above the adsorption curve; the difference between the inlet concentration and the outlet concentration curves, the flow rate, and the mass of activated carbon.

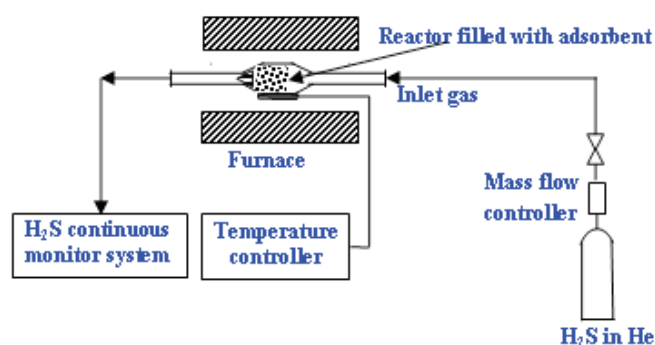


Fig. 1. Schematic diagram of adsorption system.

2.4. Sulfur analysis

The content of sulfur in fresh and exhausted activated carbons was analyzed with sulfur analyzer (TruSpec CHNSO, LECO). Samples were analyzed in triplicate.

3. Results and discussion

3.1. H₂S adsorption test at 30 °C

Performances of the commercial and alkaline impregnated activated carbons in H₂S adsorption process at 30 °C were shown in Table 2. Adsorption curve of H₂S by NaOH impregnated activated carbon at 30 °C was shown in Figure 2. At an initial time of adsorption, the concentration of outlet H₂S decreased suddenly from 3000 ppmv to about 10 ppmv. Then the concentration of H₂S increased continuously when the time was increased until the concentration at the outlet reached to 300 ppmv. At this point, the ratio of concentration of outlet H₂S per concentration of inlet H₂S was 0.1 so that this point indicates the breakthrough time. The breakthrough time of A_100-NaOH was 4 minutes. After that, the concentration of H₂S at the outlet increased continuously until the concentration of H₂S reached to 3000 ppmv. At this point, the outlet concentration is equal to the inlet concentration so that this point indicates the total adsorption time. The total adsorption time was 24 minutes (Table 2). The adsorption capacity of A_100-NaOH was 0.4 mg of H₂S per one gram of activated carbon.

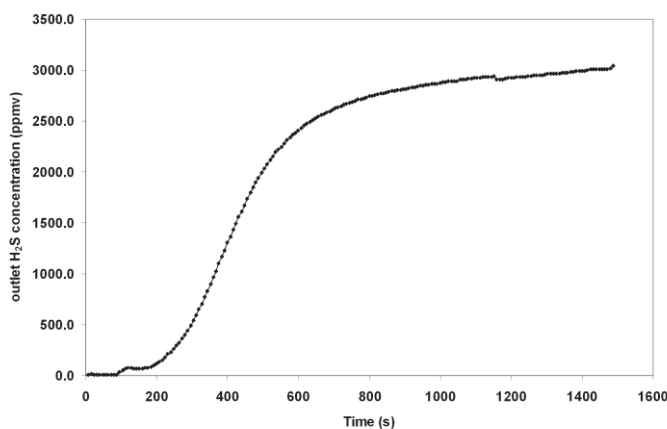


Fig. 2. Adsorption curve of H₂S at 30 °C by NaOH impregnated activated carbon.

For the adsorption of H₂S by the commercial activated carbon, the concentration of H₂S came out at the outlet gas was almost 0 ppmv for 4 minutes. Then the concentration of H₂S increased continuously when the time was increased until the concentration at the outlet reached to 3000 ppmv. The breakthrough time and total adsorption time were 15 and 67 minutes, respectively. Adsorption capacity of the A was higher than that of the A_100-NaOH (4 times higher). From the result, NaOH might occupy a portion of the carbon pore volume and surface area, so physical adsorption of H₂S was limited.

The reactions of H₂S on the commercial and alkaline impregnated activated carbon at room temperature could be proposed as physical adsorption. For physical adsorption, a conceptual reaction of

H₂S adsorption was proposed. First, the H₂S transferred from the bulk stream into the pore or surface of the activated carbon. Then H₂S adsorbed on activated carbon (equation 1).



H₂S (g) and H₂S (ads) correspond to H₂S in gas and adsorbed phases.

Table 2. Adsorption time and adsorption capacities of activated carbons at 30 °C.

Sample	Adsorption time (min)	Adsorption capacity (mg of H ₂ S/ g of activated carbon)
A	67	1.67
A_100-NaOH	24	0.4
A_100-KOH	151	1.58
A_100-KI	145	1.56
A_100-Na ₂ CO ₃	109	1.58

For the adsorption of H₂S by the A_100-Na₂CO₃, A_100-KOH, and A_100-KI, the concentration of H₂S came out at the outlet gas after treatment was less than 10 ppmv for 1-3 minutes. The breakthrough times of alkaline impregnated activated carbons were less than that of the commercial one. In detail, the breakthrough time of A_100-Na₂CO₃, A_100-KOH, and A_100-KI were 10, 2, and 2 minutes, respectively. However, the total adsorption times of alkaline impregnated activated carbons were significantly higher than that of the commercial one (2 times higher). Therefore, the adsorption capacities of alkaline impregnated activated carbons were slightly less than that of the commercial one (Table 2).

3.2. H₂S adsorption test at high temperature

Performances of commercial and alkaline impregnated activated carbons in H₂S adsorption process at high temperature are shown in Tab. 3 and Figures 3-5.

Table 3. Adsorption time and adsorption capacities of activated carbons at high temperature.

Sample	Adsorption time (min)	Adsorption capacity (mg of H ₂ S/ g of activated carbon)
A	472	1.41
A_100-NaOH	475	10.02
A_100-KOH	1530	40.46
A_100-KI	1174	4.45
A_100-Na ₂ CO ₃	2554	29.5

Figure 3 shows adsorption curve of H₂S under temperature program by using the commercial activated carbon as an adsorbent. The temperature increased from 30 to 550 °C at a rate of 10 °C per minute. At temperature in the range of 30 - 150 °C, the concentration of H₂S came out at the outlet gas was increased from 3000 to about 6610 ppmv, this result indicated that adsorbed H₂S on activated carbon was desorbed. At temperature between 150 - 550 °C, the outlet concentration of H₂S was decreased from 6610 to about

187 ppmv. This phenomenon showed that H_2S was adsorbed on activated carbon. The adsorption capacity of the A was 1.41 mg of H_2S per gram of activated carbon.

For the A_100-NaOH, the concentration of H_2S came out at the outlet gas was decreased from 3000 to about 40 ppmv in the heating step (Figure 4). At 550 °C, the outlet concentration of H_2S was about 10 ppmv for 170 minute. The breakthrough time and total adsorption time were 252 and 475 minutes, respectively. The adsorption capacity of activated carbon was increased more than seven times after impregnation with 100% weight of NaOH.

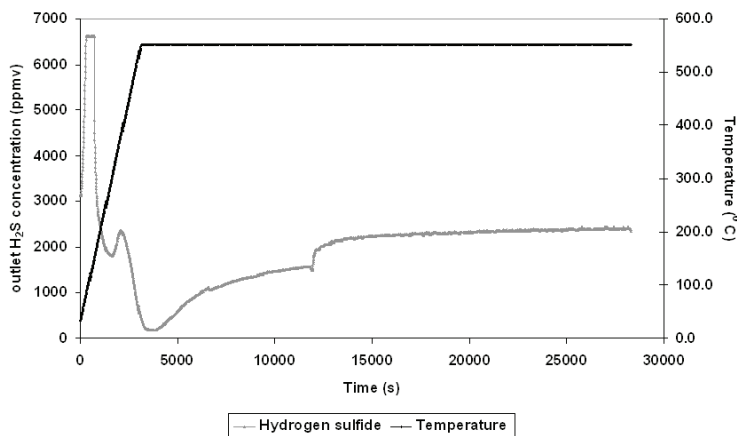


Fig. 3. Adsorption curve of H_2S at high temperature by commercial activated carbon.

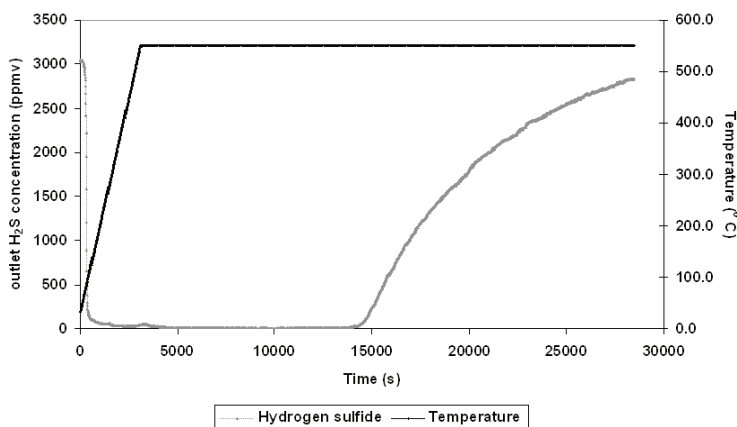


Fig. 4. Adsorption curve of H_2S at high temperature by NaOH impregnated activated carbon.

For the A_100-KOH, A_100- Na_2CO_3 , and A_100-KI, the adsorbed H_2S on activated carbon was desorbed at temperature in the range of 30 - 140 °C. After that, the outlet concentration of H_2S was decreased that indicated that H_2S was adsorbed on activated carbon (Figure 5-7). Chemical adsorption of H_2S on activated carbon was mainly occurred but physical adsorption was partly.

The breakthrough time of A_100-KOH, A_100- Na_2CO_3 , and A_100-KI were 617, 182, and 71 minutes, respectively. The adsorption capacity of A_100-KOH and A_100- Na_2CO_3 was greater than the

A. The adsorption capacity increased more than 29 and 21 times after impregnation with 100% weight of KOH and Na₂CO₃, respectively (Table 3). The adsorption capacity of activated carbon was increased more than three times after impregnation with 100% weight of KI. The results clearly indicated that the breakthrough was delayed by alkaline impregnation.

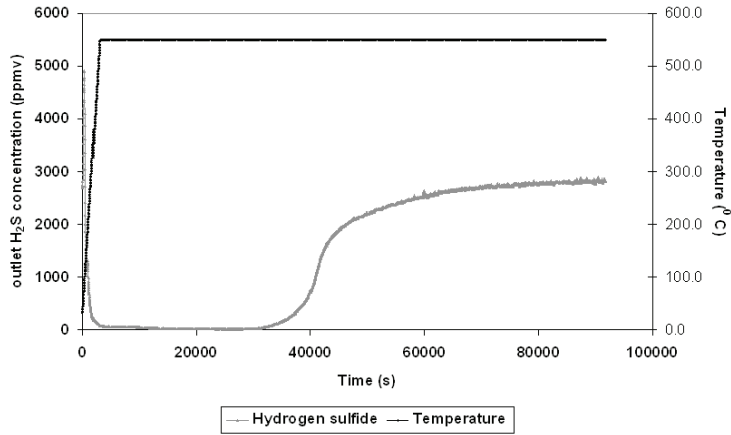


Fig. 5. Adsorption curves of H₂S at high temperature by KOH impregnated activated carbon.

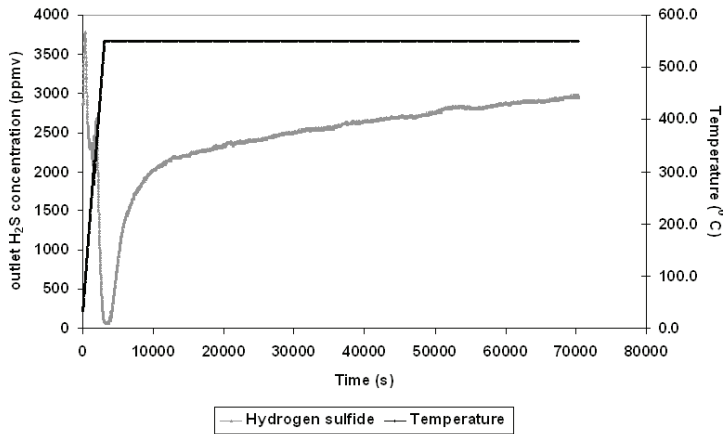


Fig. 6. Adsorption curves of H₂S at high temperature by KI impregnated activated carbon.

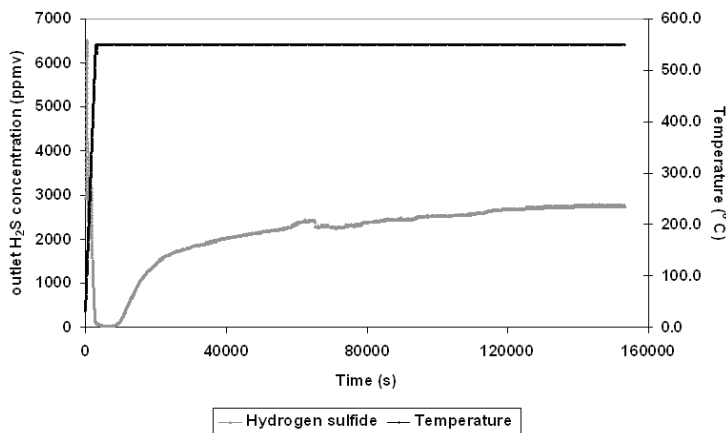


Fig. 7. Adsorption curves of H₂S at high temperature by Na₂CO₃ impregnated activated carbon.

The reactions of H₂S on alkaline impregnated activated carbon at high temperature could be chemical adsorption as the main reaction and physical adsorption. For chemical adsorption, H₂S reacts with alkali at carbon surface. The reactions of H₂S and four kinds of alkaline are as follows:

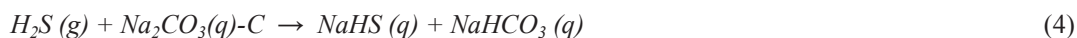
1. KOH or NaOH



A was indicated as K or Na

AOH(q)-C is the KOH or NaOH impregnated on the activated carbon covered by the water film which was generated by the produced water from equation 2 and 3.

2. Na₂CO₃



Na₂CO₃(q)-C is the Na₂CO₃ impregnated on the activated carbon.

3. KI



KI(q)-C is the KI impregnated on the activated carbon. The chemical adsorption was the endothermic reaction. Therefore, the chemical adsorption effected to increase adsorption capacity with increasing temperature in the reactor into high temperature.

Furthermore, the outlet concentration of H₂S after treated by the KOH and Na₂CO₃ impregnated activated carbons at temperature as 550 °C was less than 30 ppmv, which is safe for utilizing in mechanical and power engine. The outlet concentration of H₂S after treated by the KI impregnated activated carbons at temperature as 550 °C was less than 90 ppmv. Therefore, the KOH and Na₂CO₃ impregnated activated carbons are applicable for hot fuel gas purification.

3.3. Sulfur analysis

The contents of sulfur in the commercial and alkaline impregnated activated carbons before and after H₂S adsorption test were measured with a sulfur analyzer. The results were shown in Table 4. The contents of sulfur in fresh activated carbons were in the range of 0.30 - 0.60 %. After H₂S adsorption test, the content of sulfur in commercial activated carbon was increased to 3.80 %. The contents of sulfur in exhausted KOH and Na₂CO₃ impregnated activated carbons are significantly higher than that of the exhaust commercial activated carbon (2-6 times higher). The content of sulfur could be originate from H₂S that was adsorbed on surface of activated carbon and sulfur compound that was produced from chemical adsorption such as KHS, K₂S, NaHS, and Na₂S. This result was consistent with the adsorption capacities of KOH and Na₂CO₃ impregnated activated carbons that are high performance when using for H₂S removal at high temperature. It is indicated that chemical reaction between H₂S and KOH or Na₂CO₃ was mainly occurred at high temperature.

Table 4. Content of sulfur in fresh and exhausted activated carbons.

Sample	Sulfur in fresh sample (%)	Sulfur in exhausted sample (%)
A	0.60	3.80
A_100-NaOH	0.32	6.04
A_100-KOH	0.39	9.31
A_100-KI	0.30	20.97
A_100-Na ₂ CO ₃	0.34	2.15

4. Conclusion

The commercial and alkaline impregnated activated carbons were tested by the temperature program adsorption of H₂S at 30 °C and 550 °C. At 30 °C, the adsorption capacities of alkaline impregnated activated carbons were slightly less than the commercial one. Alkaline solid might occupy a portion of the carbon pore volume and surface area, so physical adsorption of H₂S was limited. The reactions of H₂S on the commercial and alkaline impregnated activated carbon at room temperature could be proposed as physical adsorption.

At high temperature of adsorption, alkaline activated carbons adsorbed H₂S significantly higher than commercial activated carbon (in the range of 3-29 times higher depend on modification method). In detail, 1 gram of activated carbon that was modified by KOH, Na₂CO₃, NaOH, and KI impregnation can

adsorb H₂S as 40.46, 29.50, 10.02, and 4.45 mg, respectively. The results clearly indicated that the breakthrough was delayed by alkaline impregnation.

The reactions of H₂S on the alkaline impregnated activated carbon at high temperature could be proposed as chemical adsorption that was the main reaction and physical adsorption that partly occurred. The chemical adsorption effected to increase adsorption capacity with increasing temperature in the reactor into high temperature. Furthermore, the concentration of H₂S came out at the outlet gas after treated by the KOH and Na₂CO₃ impregnated activated carbons was less than 30 ppmv, which was safe for utilizing in mechanical and power engine. Therefore, the KOH and Na₂CO₃ impregnated activated carbons were applied for hot fuel gas purification.

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