The influence of K$_2$CO$_3$ to rice husk ratio for CO$_2$ adsorption in fixed bed column

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Abstract. Carbon dioxide emissions contributed by fossil fuel, have become a severe concern in relation to global warming and health issues. High content of CO$_2$ will caused low content of heat value. This study is to reduce the concentration of CO$_2$ gas by adsorption using K$_2$CO$_3$ rice husk. The method used is adsorption using a laboratory scale fixed bed column equipment at atmospheric condition and room temperature. The adsorption column was filled with K$_2$CO$_3$ and rice husk which composition (50: 8; 75: 8; 100: 8; 125: 8) grams, CO$_2$ gas flowed from the bottom of the column which flow rate 9 liter per minutes (LPM). Then the sample was taken at the top of the column every 5 minutes. It showed that the highest adsorption capacity is 7.54 percent CO$_2$ removal/gr adsorbent which amount of K$_2$CO$_3$ adsorbent 50 gr at 9 LPM CO$_2$ inlet flow rate. It showed that most adsorbents have the most active sites to adsorb CO$_2$. It also showed that K$_2$CO$_3$50 gr have the longest breakthrough time than others amount of K$_2$CO$_3$.

1. Introduction
Carbon dioxide emissions contributed by fossil fuel combustion, get severe concern to global warming and health issues. Gas emissions removal appear as a key way in constructing a better atmosphere for the living society. A lot of methods have been devoted to build technologies for CO$_2$ removal such as cryogenic separation, chemical separation, membrane separation and adsorption method [1]. Adsorption is one of the promising methods that useable for separating CO$_2$ from gas mixtures [2]. On the other hand, adsorption is a one of technology which can operate to separate CO$_2$ at high temperature [3]. Nowadays, CO$_2$ adsorption has found application in adsorption reaction where CO$_2$ is by product. The principle of adsorption reactor enables natural separation of CO$_2$ from the product mixture. It is enhancing yield and selectivity of the urge product, primary to process intensification [4]. A lot of study has been devoted to improve CO$_2$ adsorption and selectivity by chemical alteration on the surface of solid material. The basic organic group and inorganic metal oxide (alkali or alkal earth metal) are of specific concern. The interaction between the acidic CO$_2$ molecules and altered basic active sites on the surface areas CO$_2$ adsorption through the formation of covalent bonding [5].

Several prominent criteria of the sorbent materials must fulfil to become economical and operational for CO$_2$ capture from flue gas [6]. Chemical adsorption of CO$_2$ by a dry regenerated alkali metal-based solid sorbent became robust choice for CO$_2$ adsorption which giving benefit to existing power generation plants. The reaction is shown below.

\[ \text{M}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \leftrightarrow 2 \text{MHCO}_3(\text{s}) \]
Water is very important for making potassium hydrogen carbonate in adsorption reaction [7]. Furthermore, MHCO\textsubscript{3} is used for CO\textsubscript{2} removal reaction or carbonation. On contrary, adsorbent regeneration is a reverse reaction [8], Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} are considered to be appropriate for adsorption operation under post combustion conditions, but it is not identified if the carbonation and regeneration reaction capacities are proper [9]. The objective of this paper is investigated the influence of K\textsubscript{2}CO\textsubscript{3} to rice husk ratio as a solid adsorbent for CO\textsubscript{2} adsorption in fixed bed column.

2. Experimental

2.1. Material
Carbon dioxide was purchased from local product. A commercial material K\textsubscript{2}CO\textsubscript{3} purchased from Brataco Chemical is used as an adsorbent. Particle size of K\textsubscript{2}CO\textsubscript{3} characterized with size ≤150µm. Rice husk from local farmer is used as K\textsubscript{2}CO\textsubscript{3} support. CO\textsubscript{2} concentration were analysed by acid-based titration. Chemicals used for titration were HCl, NaOH, methyl orange and phenolphthalein. HCl is a pro analysis grade which purchased from Merck. NaOH product name is Bintang Kimia. Methyl orange and phenolphthalein were supplied by Merck.

2.2. Preparation of adsorption
A gas-solid adsorption column was used for all experiments CO\textsubscript{2} adsorption. The apparatus using for CO2 adsorption presented in Figure 1. Adsorption column made by pipe with length 30 cm and diameter 1 inch (2.54 cm). K\textsubscript{2}CO\textsubscript{3} and rice husk were put into adsorption column and used to CO\textsubscript{2} adsorption. There are several mass variations of K\textsubscript{2}CO\textsubscript{3} and CO\textsubscript{2} flow rate. K\textsubscript{2}CO\textsubscript{3} mass variation are 50, 75, 100 and 125 gr. CO\textsubscript{2} flow rate is 9 liter per minutes (LPM). Breakthrough curves of each experiment at 9 LPM flow rate were measured. Adsorption occurred at atmospheric pressure and room temperature.

![Figure 1. Experimental set up for CO\textsubscript{2} adsorption.](image)

2.3. Carbon dioxide adsorption measurement
Carbon dioxide gas flowed from the bottom of the column which flow rate. CO\textsubscript{2} was captured by solid sorbents in the column. The adsorption performance of the adsorbent was measured by calculating the
concentration of CO$_2$ which adsorb by adsorbent. In this study, the CO$_2$ inlet and outlet were measured by acid-based titration. Gas CO$_2$ outlet were analysis every 5 minutes operation.

3. Results and discussion
The CO$_2$ capture by dry adsorbent characteristics in the fixed bed reactor were analysed. CO$_2$ gas is captured by K$_2$CO$_3$ with rice husk adsorbent in various amount of adsorbent. The data showed at Table 1.

Table 1. CO$_2$ Adsorption by K$_2$CO$_3$/rice husk with CO$_2$ inlet flow rate 9 liter per minute (LPM).

| No. | K$_2$CO$_3$ Amount (gram) | K$_2$CO$_3$ to rice husk ratio | CO$_2$ removal percentage (%) | Adsorption capacity (% CO$_2$ removal/gr adsorbent) |
|-----|----------------------------|-------------------------------|-------------------------------|-----------------------------------------------|
| 1   | 50                         | 6.25                          | 47.11                         | 7.54                                          |
| 2   | 75                         | 9.375                         | 58.57                         | 6.25                                          |
| 3   | 100                        | 12.5                          | 64.15                         | 5.13                                          |
| 4   | 125                        | 15.625                        | 70.03                         | 4.48                                          |

The effect of K$_2$CO$_3$ to rice husk ratio is directly proportional to CO$_2$ removal percentage. It can be seen from the greater K$_2$CO$_3$ to rice husk ratio, the greater percentage of CO$_2$ removal.

Figure 2 shows that the adsorption capacity decreased as the amount of adsorbent increased (indicated by the ratio of K$_2$CO$_3$ to rice husk). The addition of adsorbents did not increase the capacity of adsorption. The highest adsorption capacity was detected in ratio K$_2$CO$_3$ 50 gr because CO$_2$ flow rate was appropriate for binding/adsorb CO$_2$ molecules with all of K$_2$CO$_3$/rice husk. Meanwhile, at other K$_2$CO$_3$/rice husk ratio, CO$_2$ molecules did not bind all K$_2$CO$_3$ active site. The adsorption experiment was continued by making a breakthrough curve for each variation of the amount of adsorbent.
Figure 3. Breakthrough Curve at gas flow rate 9 LPM with various variations of K$_2$CO$_3$.

Y axis at figure 3 showed C/Ce. C defined as inlet CO$_2$ gas concentration while Ce as outlet CO$_2$ gas concentration. There are two main differences condition of each curve in Figure 3. The first is the difference in initial C/Ce values of the operation. At the beginning of the operation, the C/Ce value is different for each breakthrough curve. The breakthrough curve with K$_2$CO$_3$ 50 gr, 75 gr, 100 gr, and 125 gr initial values of C/Ce are 0.53, 0.41, 0.36, and 0.3 respectively. This is due to the fact that the greater amount of adsorbent has the greater amount of active sites capacity to adsorb CO$_2$. The greater amount of adsorbent will also provide an opportunity for greater interaction with the adsorbate.

Second, the breakthrough curve showed that the greater amount of adsorbent, the faster the saturation time of adsorbent. This can be seen from the breakthrough curve with K$_2$CO$_3$ 50 gr, which are breakpoint at 45 minutes (2700 s), balance point at 185 minutes and saturation point at 195 minutes. Meanwhile the breakthrough curve with K$_2$CO$_3$ 125 gr, breakpoint at 20 minutes (1800 s), balance point at 145 minutes and saturation point at 160 minutes. The results obtained that K$_2$CO$_3$ 50 gr was characterized by longest breakthrough time than others K$_2$CO$_3$. It happened because the amount of CO$_2$ absorbed is less than other adsorbent at the same flow rate (9 LPM). It means that amount of 50 gr K$_2$CO$_3$ works more effectively than other amount of CO$_2$ (at CO$_2$ flow rate 9 LPM).

Zulkurnai et al. investigated adsorption by activated carbon which functionalized with deep eutectic solvent (DES). The breakthrough time from adsorbent K$_2$CO$_3$ 50 gr (2700 s) in this study was greater than from activated carbon CO$_2$ functionalized with DES adsorbent [10]. It means the performance of K$_2$CO$_3$/rice adsorbent deserves for further investigating.
Figure 4 shows that higher amount of K$_2$CO$_3$ in the adsorption, then higher CO$_2$ removal percentage will be made but K$_2$CO$_3$ adsorbent becomes saturated faster.

4. Conclusions
Solid adsorbent for CO$_2$ captured was investigated in fix bed column. It shows that the highest adsorption capacity is 7.54 % CO$_2$ removal/gr adsorbent which amount of K$_2$CO$_3$ adsorbent 50 gr at 9 LPM CO$_2$ inlet flow rate. Breakthrough curve shows that higher number of adsorbents will have higher active sites to adsorb CO$_2$. It also shows that K$_2$CO$_3$ 50 gr has the longest breakthrough time than others amount of K$_2$CO$_3$. This study identified that increasing flow rate causes decreasing saturation time and CO$_2$ removal percentage.

5. References
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