Breakthrough curve investigation for analysing effectiveness of CO\textsubscript{2} adsorption using K\textsubscript{2}CO\textsubscript{3} in fixed bed column

L Elizabeth, H Heriyanto*, H Immah and K Aqshanrilyan
Chemical Engineering Department, Politeknik Negeri Bandung, Gegerkalong Hilir Street, Bandung 40559, West Java, Indonesia

*heriyanto@polban.ac.id

Abstract. Carbon dioxide contributed great amount of Green House Gas (GHG) emission. Solid adsorption is one of the way to ease or lower carbon dioxide emission. The objective of this study is investigating breakthrough curve of CO\textsubscript{2} adsorption using K\textsubscript{2}CO\textsubscript{3} solid in fixed bed column. Adsorption experiment is used to analysed adsorption capacity, breakpoint time and length of effective bed height. K\textsubscript{2}CO\textsubscript{3} used as adsorbent and rice husk as support. The K\textsubscript{2}CO\textsubscript{3} adsorption occurred under mild condition. The CO\textsubscript{2} inlet and outlet concentration were analysed by acid-base titration. The highest adsorption capacity by K\textsubscript{2}CO\textsubscript{3}/rice husk is 0.2 mmol/g adsorbent at CO\textsubscript{2} inlet flow rate 28 LPM (litre per minutes) by 50 gr K\textsubscript{2}CO\textsubscript{3} adsorbent. it is necessary to vary other parameter because CO\textsubscript{2} flow rate (15.9 and 28 LPM) and adsorbent amount (50-125 gr) do not affect adsorption capacity significantly.

1. Introduction
One of the global issue whose handling being development abundantly is CO\textsubscript{2} emission. Carbon dioxide contributed about 78% to the Green House Gas (GHG) emissions increase from 1970 to 2010. In 2010, CO\textsubscript{2} contributed great amount of GHG emission which is up to 76%. The other consisting of 16% from methane (CH\textsubscript{4}), 6.2 % from nitrous oxide (N\textsubscript{2}O) and 2% from fluorinated gases [1]. It means capturing CO\textsubscript{2} is a serious handling to develop. There are plentiful method of to decrease carbon dioxide. Commonly, it divided into three type such as pre-combustion, oxy-fuel combustion and post-combustion. Post-combustion capture can be divided into several methods such as chemical absorption, microbial and adsorption [2].

There are two types of CO\textsubscript{2} adsorption consisting of physical and chemical adsorption. Physical adsorbent are consisting of carbonaceous adsorbent likes activated carbon. Activated carbon can be utilized in the PSA process for recovery of CO\textsubscript{2} [3]. Activated carbon give important advantages likes hydrophobicity, lower cost and energy [4]. Another carbonaceous adsorbent such as CNTs (carbon nanotubes) fabricated by catalytic chemical [5]; zeolite based adsorbents [6]; ordered mesoporous silica (OMS) [7] and metal-organic frameworks (MOFs) [8,9]. Chemical adsorbent consisting of amine from basic organic such as polyethyleneimine (PEI), dendrimers, hyperbranched aminosilica [10] and alkali or alkali earth metal from inorganic compound such as CaO-modified sorbents [11].

A lot of of CO\textsubscript{2} adsorption processes are mixed of physical and chemical force. Physical adsorption occurs according to van der Waals forces between adsorbate and adsorbents molecules whereas chemical adsorption occurs according to chemical interactions between adsorbate and surface functional groups of adsorbents [5]. Solid adsorption process has various advantages compared to chemical
absorption such as low price raw material, low heat energy consumption, stabilities of chemical and thermal and high CO$_2$ adsorption capacity [12,13]. One of the CO$_2$ adsorbent that can be used is K$_2$CO$_3$. K$_2$CO$_3$ is selected as CO$_2$ adsorbent according to its low volatility, low toxicity and non-degradation.

The objective of this study is investigating breakthrough curve of CO$_2$ adsorption using K$_2$CO$_3$ in fixed bed column.

2. Experimental

2.1. Experimental material

Potassium carbonate (K$_2$CO$_3$) adsorbent were purchased from local brand. Particle size of K$_2$CO$_3$ characterized with size ≤150µm. Rice husk as adsorbent support obtained from local rice fields. Hydrochloric acid purchased from Merck. Sodium Hydroxide purchased from local brand. Carbon dioxide were supplied from PT. Limas Raga Inti. Fixed bed column were used for CO$_2$ adsorption.

2.2. Experimental method

The adsorption started by flowing the mixed of CO$_2$ and air from bottom of the fixed bed column. The inlet concentration of CO$_2$ are 56% and 78% (v/v). Adsorption column made by glass pipe with diameter 1 inch and length 30 cm filled with mixed of K$_2$CO$_3$ adsorbent (50,75,100 and 125 gr) and fixed amount of rice husk (8 grams). CO$_2$ flow rate are 15,9 and 28 litres per minutes (LPM). Adsorption carried out at mild condition (atmospheric pressure). Carbon dioxide outlet concentration were measured periodically in adsorption process until CO$_2$ outlet concentration getting constant. Sample of CO$_2$ outlet was taken from top of the fixed bed column. It taken by syringe which filled with 15 ml of sodium hydroxide solution. The solution of CO$_2$ and sodium hydroxide were analysed by acid basic titration to determine the outlet concentration of CO$_2$.

3. Results and discussion

The experiment was carried out with two variation of CO$_2$ flow rate consisting of 15,9 LPM and 28 LPM. The amount of rice husk is fixed for each experiment. Table 1 and Table 2 showed state of the art adsorption capacity by various adsorbent. Table 3 showed adsorption capacity in each experiment which the difference is insignificant.

| Table 1 | Adsorption Capacity from various adsorbent type [14]. |
|---------|------------------------------------------------------|
| No | Adsorbent | Adsorption capacity (mmol/g adsorbent) |
| 1 | Carbon based | ≤ 8 |
| 2 | zeolite based | ≤ 5.4 |
| 3 | MOF based | ≤ 48.7 |
| 4 | Amine based | ≤ 5.9 |
| 5 | calcium based | ≤ 11.6 |
| 6 | alkali ceramic base | ≤ 6.5 |

| Table 2 | Adsorption Capacity from K$_2$CO$_3$ as active phase with various catalyst support [2]. |
|---------|------------------------------------------------------|
| No | Active phase | Catalyst support | Temperature (°C) | Adsorption capacity (mmol/g adsorbent) |
| 1 | K$_2$CO$_3$ | ZrO$_2$ | 50–100 | 2.08 |
| 2 | K$_2$CO$_3$ | MgO | 50–100 | 4.06-4.49 |
| 3 | K$_2$CO$_3$ | Al$_2$O$_3$ | 70–90 | 2.9 |
| 4 | K$_2$CO$_3$ | AC, silica gel | 60 | 0.34-1.7 |
| 5 | K$_2$CO$_3$ | Activated coke and silica | 100 | 2.1 |
| 6 | K$_2$CO$_3$ | TiO$_2$, SiO$_2$, CaO and zeolites | 60–100 | 1.1-2.7 |
Table 3. Adsorption Capacity of K₂CO₃/rice husk.

| No | CO₂ inlet flow rate (LPM) | Adsorbent [K₂CO₃] (gram) | Adsorption capacity (mmol/g adsorbent) |
|----|--------------------------|--------------------------|--------------------------------------|
| 1  | 15.9                     | 50                       | 0.13                                 |
|    |                          | 75                       | 0.10                                 |
|    |                          | 100                      | 0.08                                 |
|    |                          | 125                      | 0.07                                 |
| 2  | 28                       | 50                       | 0.20                                 |
|    |                          | 75                       | 0.15                                 |
|    |                          | 100                      | 0.13                                 |
|    |                          | 125                      | 0.10                                 |

It can be seen from Table 3 and prior experiment and from Table 1 and Table 2 that adsorption capacity in this experiment lower than prior experiment [2,14]. The highest adsorption capacity in this research is 0.2 mmol/g adsorbent at CO₂ inlet flow rate 28 LPM with 50 gr K₂CO₃. The reaction occur during adsorption: K₂CO₃(s) + H₂O(g) + CO₂(g) ↔ 2 KHCO₃(s).

KHCO₃ are in solid shape at room temperature but it becomes soluble at high temperature (140-200°C) [15]. The increasing amount of adsorbent lead to formation of KHCO₃ solid faster and greater. Therefore, it makes the greater possibility of solid KHCO₃ inhibits adsorption. It decrease the adsorption capacity. Experiment continued by making breakthrough curve of each experiment. From breakthrough curve, breakpoint time calculated which used to estimate HB (length of effective bed height) and HUNB (length of unused bed). The effectiveness of CO₂ adsorption by solid K₂CO₃/rice husk in fixed bed column by evaluated breakpoint time, length of effective bed height/HB and length of unused bed/HUNB were investigated. Breakthrough curve of CO₂ adsorption by K₂CO₃/rice husk in fixed bed column presented at Figure 1 and Figure 2.

Figure 1. Breakthrough Curve for CO₂ flow rate 15.9 LPM.

C/Cₑ at Figure 1 and Figure 2 defined as CO₂ inlet concentration per CO₂ outlet concentration. Figure 1 showed that the addition of adsorbent will lead to enhance CO₂ adsorbed at the beginning of
experiment. On the other hand, the time required to reach saturation is faster along with addition of adsorbent amount. This is due to amount of CO$_2$ adsorp increasing along with the increasing amount of adsorbent. The CO$_2$ adsorption to the K$_2$CO$_3$ forms KHCO$_3$ solid which inhibits the pore of K$_2$CO$_3$/rice husk. Therefore, the enhancement of KHCO$_3$ formed lead to saturation of adsorbent.

The breakthrough curve of 125 gr K$_2$CO$_3$ adsorbent is a steep curve compared to other breakthrough curve in Figure 1. It showed not only the fastest mass transfer zone but also breakpoint time. This indicate that although it was a short mass transfer zone, it is not effectively used at a flow rate of 15,9 LPM due to its small adsorption capacity. Adsorbent of 50 gr is the most effective CO$_2$ adsorption at 15,9 LPM flow rate, because it has longest breakpoint time.

![Breakthrough Curves for CO$_2$ flow rate 28 LPM](image1)

**Figure 2.** Breakthrough Curve for CO$_2$ flow rate 28 LPM.

Figure 2 showed that the C/Ce value is quite constant in the range of breakpoint time. It can be seen from Figure 2 that the addition of adsorbent will lead to enhance CO$_2$ adsorbed at the beginning of experiment. The initial C/Ce value on 28 LPM breakthrough curve is higher than the 15,9 LPM breakthrough curve. This is owing to the increasing of CO$_2$ flow rate triggers contact time between CO$_2$ and K$_2$CO$_3$ shorter.

It can be seen that Figure 2 and Figure 1 showed the same pattern saturation of adsorbent that the time required to reach saturation is faster along with addition of adsorbent amount. The time required to reach saturation at CO$_2$ flow rate 28 LPM shorter than (95-125 minutes) CO$_2$ flow rate 15,9 LPM (115-160 minutes).

In Figure 2, the breakthrough curve of 50 gr and 75 gr adsorbents is sloping compared to the breakthrough curves with adsorbents of 100 gr and 125 gr. Furthermore, the breakpoint time is also quite longer compared to 100 gr and 125 gr adsorbents. This indicate that CO$_2$ adsorption using 50 gr K$_2$CO$_3$ adsorbents with flow rate 28 LPM is most effective.

Breakthrough curve were analysed to evaluate the effectiveness of fixed bed column for CO2 adsorption using K$_2$CO$_3$. The results are presented in Table 4, Figure 3 and Figure 4.
Table 4. HB dan HUNB at CO₂ flow rate 15.9 LPM.

| No | CO₂ flow rate (LPM) | adsorbent K₂CO₃ (gr) | breakpoint time (second) | HB (cm) | HUNB (cm) | HB/total length column (%) |
|----|----------------------|-----------------------|--------------------------|---------|-----------|-----------------------------|
| 1  | 15.9                 | 50                    | 685.5                    | 13.22   | 16.78     | 44.07                       |
| 2  |                      | 75                    | 240                      | 15.53   | 25.28     | 15.75                       |
| 3  |                      | 100                   | 361.5                    | 20.08   | 24.23     | 19.25                       |
| 4  |                      | 125                   | 174                      | 13.76   | 27.10     | 9.66                        |
| 5  |                      | 50                    | 310.5                    | 15.04   | 14.96     | 50.12                       |
| 6  |                      | 75                    | 385.5                    | 15.21   | 14.79     | 50.69                       |
| 7  |                      | 100                   | 409.5                    | 11.80   | 18.20     | 39.34                       |
| 8  |                      | 125                   | 217.5                    | 7.39    | 22.61     | 24.62                       |

Table 4 showed that the highest breakpoint time is 685.5 second which at CO₂ flow rate 15.9 LPM and K₂CO₃ adsorbent 50 gr. It indicates that lowering CO₂ flow rate and amount of adsorbent makes breakpoint time longer. Furthermore, it can be seen that the longer breakpoint time gaining HB more effective. Hence, designing fixed bed column of CO₂ adsorption very affected by breakpoint time.

**Figure 3.** Breakpoint time of adsorption CO₂ by K₂CO₃ with fixed bed column.

Figure 3 indicates that at adsorbent amount of 100 gr dan 125 gr, the flow rate of CO₂ do not influence breakpoint time. Whereas, at adsorbent amount of 50 gr dan 75 gr, the flow rate of CO₂ influence breakpoint time significantly.

**Figure 4.** Length of effective bed height/HB of adsorption CO₂ by K₂CO₃ with fixed bed column.

It can be seen from Figure 4 that the highest HB at both flow rate of CO₂ were at 50 gr K₂CO₃. That indicate that lowering amount of K₂CO₃ will fixed bed column more effective.

4. **Conclusion**

The results obtained in this work consisting of several things. The highest adsorption capacity by K₂CO₃/rice husk is 0.2 mmol/g adsorbent at CO₂ inlet flow rate 28 LPM with 50 gr K₂CO₃. Meanwhile, the highest breakpoint time is 685.5 second which at CO₂ flow rate 15.9 LPM and K₂CO₃ adsorbent 50 gr.
gr. Perhaps, CO$_2$ flow rate consist of 15,9 and 28 LPM and amount of adsorbent (50-125 gr) do not affect CO$_2$ adsorption capacity significantly. Therefore, it is necessary to vary other parameter. For example mechanical treatment the adsorbent such as size reduction or varying operation condition such as adsorption temperature.

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