Development of New Potassium Carbonate Sorbent for CO_2 Capture under Real Flue Gas Conditions

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Abstract

In this paper, the development of a new potassium carbonateon alumina support sorbent prepared by impregnating K_2CO_3 with an industrial grade of Al_2O_3 support was investigated. The CO_2 capture capacity was measured using real flue gas with 8% CO_2 and 12% H_2O in a fixed-bed reactor at a temperature of 65 °C using breakthrough curves. The developed sorbent showed an adsorption capacity of 66.2 $mgCO_2$/(gr sorbent). The stability of sorbent capture capacity was higher than the reference sorbent. The SO_2 impurity decreased sorbent capacity about 10%. The free carbon had a small effect on sorbent capacity after 5 cycles. After 5 cycles of adsorption and regeneration, the changes in the pore volume and surface area were 0.020 cm^3/gr and 5.5 m^2/gr respectively. Small changes occurred in the pore size distribution and surface area of sorbent after 5 cycles.

Keywords: Flue Gas, CO_2 Capture, K_2CO_3/Al_2O_3, Solid Sorbent

1. Introduction

Growing environmental concerns for global warming and climate change in recent years have motivated research activities toward developing more efficient and improved processes for carbon dioxide (CO_2) capture from large point sources of CO_2. The Intergovernmental Panel on Climate Change (IPCC)'s fourth assessment report (Rogner et al., 2007) states that, as a result of anthropogenic CO_2 emission, global atmospheric concentration has increased from a preindustrial value of ∼280 ppmv to 379 ppmv in 2005 and to ∼390 ppmv in 2011. Global annual CO_2 emissions due to fossil-fuel use have grown by∼80%, from ∼21 Gt in 1970 to ∼38 Gt in 2004 (Pachauri et al., 2007). This represented 77% of total anthropogenic greenhouse gas (GHG) emissions in 2004 and was attributed to stationary emission sources such as power plants, gas processing industries, refineries, chemical and petrochemical industries, iron and steel industries, and cement industries. Without the prompt introduction of supportive and effective policy actions by governments, energy-related GHG emissions, mainly from fossil fuel combustion, are projected to raise by over 50%, from 26 Gt CO_2 in 2004 to ∼37-40 Gt CO_2 by 2030, and possibly even higher (Samanta, 2012). Therefore, mitigation has become even more challenging. The global concern for this situation is well-reflected in the deep global engagements that continue from the Rio Earth Summit in 1992 through the 1997 Kyoto Protocol of United Nations Framework Convention on Climate Change (UNFCCC) to the recently concluded UN Climate Change Conference in Cancun, Mexico in December 2010. Capture of CO_2 from large point sources such as coal-based power plants, natural and synthesis gas processing

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plants, cement plants, and its sequestration (carbon capture and sequestration (CCS)) is identified as a major option to address the problem of global warming and climate change. However, the main focus of CCS today is coal-based power plants. CCS includes four primary steps: CO_2 capture, compression, transport, and storage. To economically sequester CO_2, it is important to have cost-effective capture in a relatively concentrated stream and then compressing the CO_2 to high pressures (Siriwardane et al., 2001).

Thus, the cost-effective processes for CO_2 capture from the flue gas streams of power plants are essential today in order to mitigate the global warming problems. Among the many process technology options used for CO_2 capture from flue gases, there is a growing interest in using adsorption processes as a promising alternative separation technique. Adsorption processes using novel solid sorbents capable of reversibly capturing CO_2 from flue gas streams have many potential advantages compared to other separation techniques for CO_2 capture. These advantages included reduced energy for regeneration, greater capacity, selectivity, ease of handling, etc. Adsorption on porous solid media using pressure and/or temperature swing approaches is an emerging alternative that seeks to reduce the costs associated with the capture step. The regeneration energy requirement for CO_2 capture using dry solid sorbent is significantly reduced more than that of the aqueous amine-based process, because of the absence of large amounts of water. Moreover, the heat capacity of solid sorbent is comparatively lower than that of an aqueous amine solvent. The success of such an approach is also dependent on the development of new materials with high adsorption capacity, high CO_2 selectivity, durability, and relatively fast kinetics of sorption and desorption (Yang et al., 2002; Yong et al., 2003; Zheng et al., 2007; Sayari et al., 2011).

Sorbents containing alkali and alkaline-earth metals like potassium carbonate and calcium oxide are investigated for commercial applications (Hoffman and Pennline, 2001). Alkaline-earth-based sorbents such as MgO and CaO are applicable at much higher adsorption and regeneration temperatures (Lee et al., 2006). Alkali metal-based sorbents were employed in CO_2 adsorption at low temperatures (50-70 °C) with thermal regeneration easily occurring at low temperatures (<200 °C). CO_2 capture using a dry sodium-based sorbent was also reported (Liang et al., 2004; Seo et al., 2007). However, when CO_2 reacted with Na_2CO_3, the global carbonation reaction rate was rather slow (Zhao et al., 2009). The CO_2 adsorption and regeneration of potassium-based sorbents with several supports such as activated carbon (Hirano et al., 1995; Hayashi et al., 1998; Shigemoto et al., 2006), TiO_2, SiO_2, MgO, ZrO_2, CaO, and Al_2O_3 were studied (Okunev et al., 2000; Okunev et al., 2003; Lee et al., 2004). Al_2O_3 is one of the most proper materials used as sorbent support. An ideal dry sorbent must have a high CO_2 capture capacity, high adsorption rate, excellent regeneration property, and high attrition resistance to remove CO_2 from the flue gas.

In all of the previous works, initial materials used were from high pure materials that had low impurities and high costs. The objective of this work is to develop a high capacity CO_2 sorbent and to demonstrate its technical and economical potentials for post-combustion CO_2 capture using real flue gas feed. For the synthesis of sorbent an industrial grade of alumina, which has the highest cost in sorbent preparation, was used and some of the important specifications of the prepared sorbent such as capture capacity at single and multiple cycles, surface area, and structural properties were obtained in this work. Moreover, the effect of the impurities present in flue gas such as free carbon, oxygen, and sulfur oxides has been studied.

2. Experiments

2.1. Preparation of sorbents

The potassium-based sorbents used in this study were prepared by impregnating K_2CO_3 on alumina of industrial grades as the support. Twenty grams of Al_2O_3 was added to 200 ml of an aqueous solution of anhydrous potassium carbonate with a concentration of 30 wt.% in deionized water. Then, it was mixed with a magnetic stirrer at room temperature for 14 hours. After that, the mixture was dried in a rotary vacuum evaporator at 60 °C. The dried samples were calcined in a furnace under the N_2 flow (100 cc/min) for 4.5 hours at 350 °C. The amount of K_2CO_3 loaded was 33.1% and the sorbent had an apparent density of 2.26 g/cm^3.

2.2. Apparatus and procedures

A fixed bed stainless steel reactor (with a diameter of 15 mm) which was placed in an electric furnace under atmospheric pressure was used for the adsorption process. Two (2.0) grams of the sorbent was packed into the reactor. In order to prevent the condensation of water vapor injected into the reactor and the gas chromatography (GC) column, the temperatures of the inlet and outlet lines of the reactor were maintained above 100 °C. The column used in this analysis was a 1/8 inch stainless tube packed with Porapak Q. When the CO_2 concentration of the outlet gas reached the same level as that of the inlet gas in the CO_2 adsorption process, process was stopped. The outlet gas from the reactor was automatically analyzed every 5 min by a thermal conductivity detector (TCD), which was equipped with an auto sampler (Valco online valve). A schematic diagram of the fixed bed reactor is shown in Figure 1. The feed stream conditions and components are shows in Table 1.
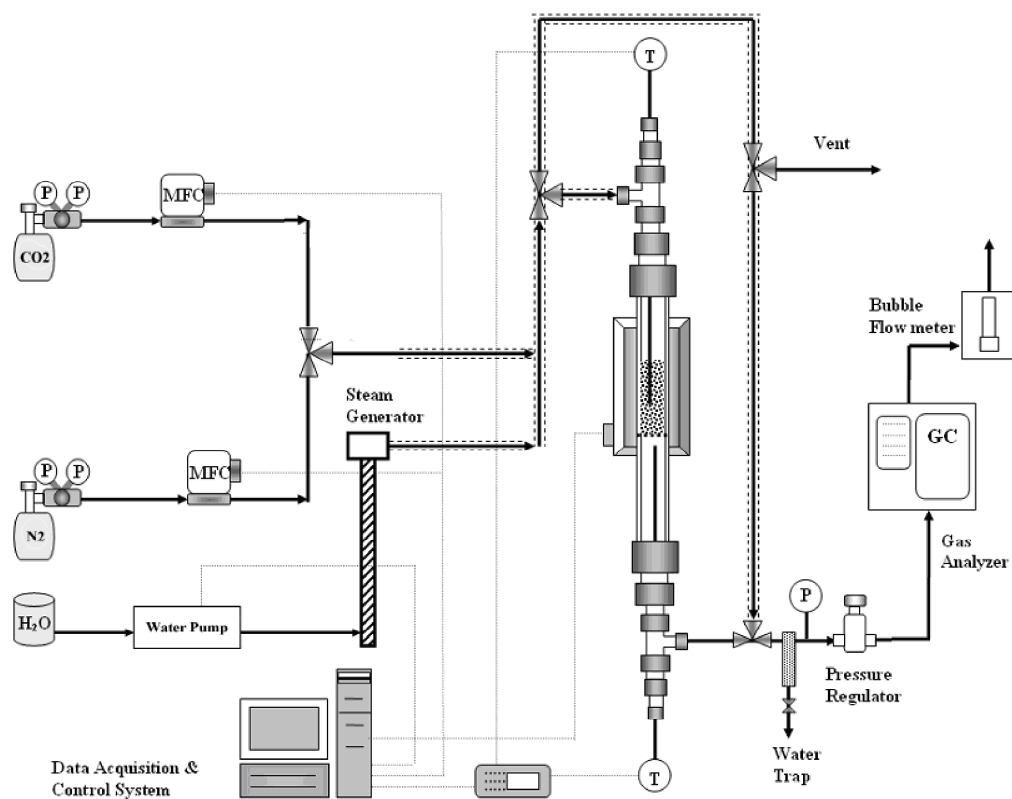

Figure 1
A schematic diagram of the fixed-bed reactor.

Table 1
The feed stream conditions/components.

Conditions/Components	Value	Units
Pressure	1	atm
Temperature	65	°C
Flow	450	cc/min
CO_2	8.0	Vol.%
SO_2	0.1	Vol.%
O_2	6.8	Vol.%
N_2	73.1	Vol.%
H_2O	12.0	Vol.%

In this study, the CO_2 capture capacity of sorbent was calculated from its breakthrough curve during CO_2 adsorption. The CO_2 capture capacity describes the amount of CO_2 absorbed until the output concentration of CO_2 reached the same value as that of the inlet. The regeneration process was carried out at 200 °C.

3. Results and discussion

Figure 2 shows the CO_2 breakthrough curve (CO_2 concentration changes during adsorption step at the bed outlet) for the new, developed sorbent. The CO_2 concentration was nearly zero during the first 8 minutes, indicating that CO_2 was completely adsorbed. The CO_2 concentration then slowly increased to 8% after 170 minutes indicating the complete conversion of available K_2CO_3 in sorbent at this time.
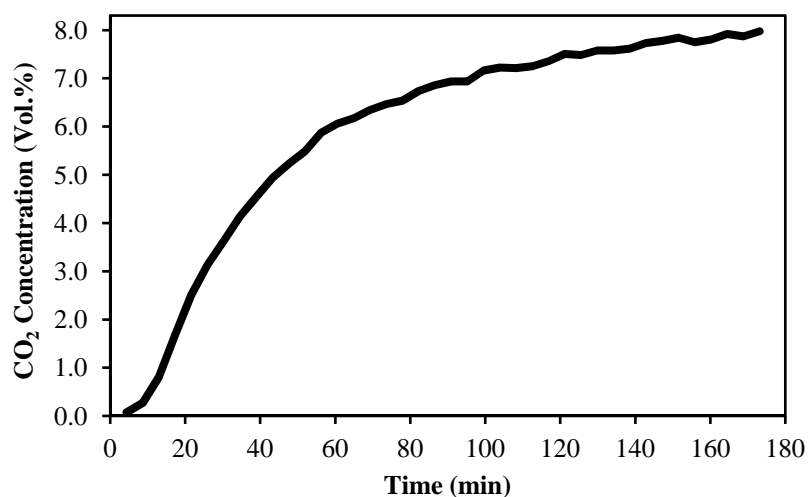

Figure 2
Change of the CO_2 concentration during the adsorption.

Figure 3 shows the total CO_2 capture capacities of the new, low-cost sorbent as well as those obtained from literature (Lee et al., 2006) as a function of cycle number. In this Figure, both adsorption and regeneration are considered as a one-cycle process. As shown in Figure 3, the total capture capacity of the new, low-cost sorbent was about 66.2 mg CO_2/gr sorbent at the first cycle. This amount is lower than the value of the sorbent developed by Lee et al. (2006) at the first cycle; but the stability of capture capacity is higher because, after 5 cycles, capture capacity decreases only by 35% which is

lower than the reference sorbent. These results show that the new, low-cost sorbent developed in this study is more suitable for multiple cycle operations usually required for industrial applications.
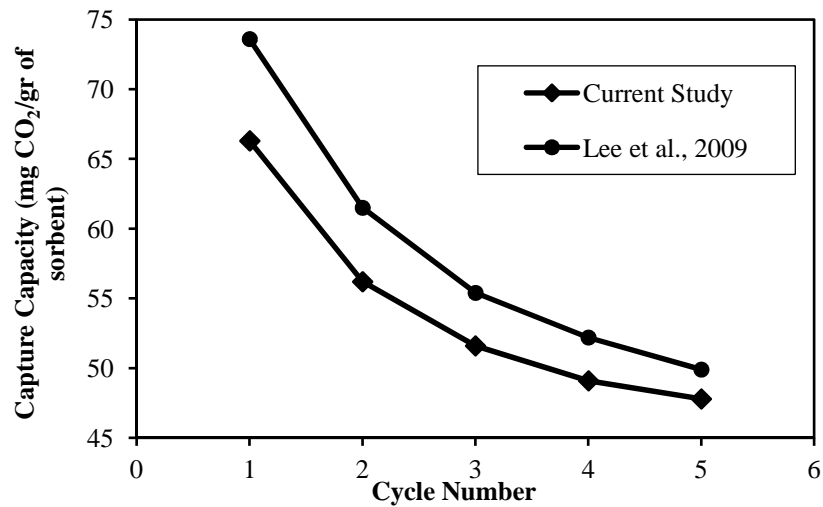
Figure 3

The CO_2 capture capacity of the sorbents as a function of cycle number.

The SO_2 impurity present in flue gas is the results of sulfur components in fuel. The SO_2 in the presence of water reacts with K_2CO_3 and decreases the sorbent capacity. The adsorption test for fresh sorbent with a feed free of sulfur shows a capacity of 73.4 mg/gr. Therefore, about 10% of sorbent capacity is used by SO_2. Due to the low concentration of SO_2 in the feed, SO_2 adsorption compared to the CO_2 has an obvious priority.

For studying changes in the sorbent structure during the adsorption and regeneration processes, three samples (0.5 gr) were taken out of the fixed-bed reactor after the first, third, and fifth cycles. The surface area and pore volume of the samples were measured using the N_2 adsorption method and are shown in Figure 4 and Figure 5 respectively. The surface area and pore volume of the sorbent decrease as the number of cycles increases, because the physical structure of the porous sorbent is destroyed as reported in previous studies (Lee et al., 2006).
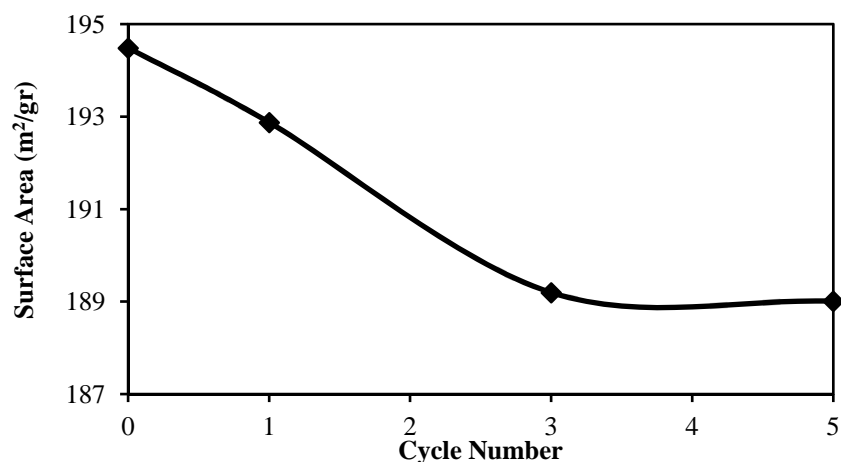
Figure 4

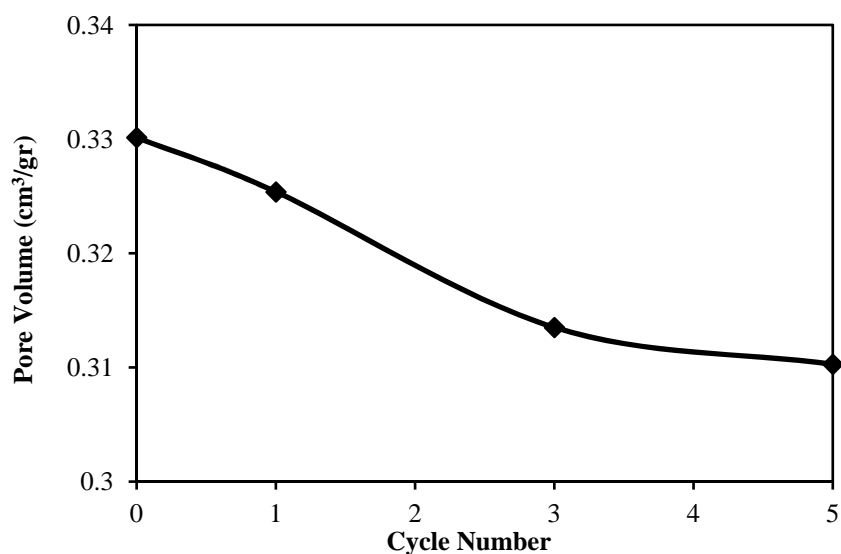Changes in the sorbent surface area with the cycle number.

Figure 5
Changes in the sorbent pore volume with the cycle number.

As shown in Figure 6, for 80% of the pores of the fresh sorbent, the pore size distribution ranges from 1.8 to 20.0 nm. The maximum value of the pore volume appears at 5.4 nm. There is little change in pore-size distribution after five cycles, which shows the changes in the structure occur in the all of pore sizes, thereby making this sorbet proper for long term adsorption cycles.
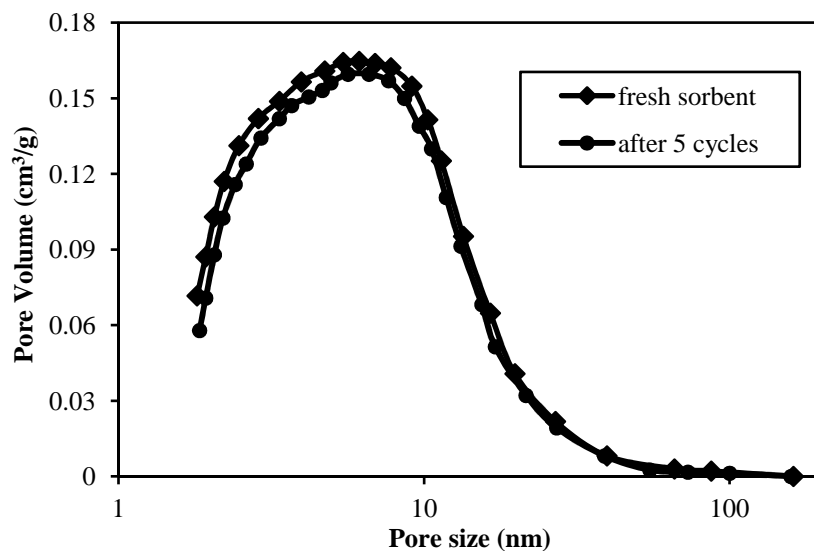

Figure 6
Pore size distribution of the sorbent for fresh sorbent and the sorbent after 5 cycles.

4. Conclusions

The low-cost sorbent developed in this study showed an adsorption capacity of 66.2 $mgCO_2$/(gr sorbent) in the present of 8.0% CO_2 and 12.0% H_2O at 65 °C. The capture capacity of the sorbent as a function of cycle number was investigated in a fixed-bed reactor. The stability of the sorbent capture capacity was higher than the reference sorbent. The changes in the pore volume and surface area were

0.020 cm^3/gr and 5.5 m^2/gr respectively. Small changes occurred in the pore size distribution and surface area of the prepared sorbent. This sorbent could be used for an industrial CO_2 capture processes with fixed-bed reactors. To investigate this purpose, a dual fixed-bed reactor was needed to operate under real, cyclic, steady-state, conditions.

Nomenclature

CCS	: Carbon capture and sequestration
GHG	: Greenhouse gas
Gt	: Giga-tone
TCT	: Thermal conductivity detector

References

Hayashi, H., Taniuchi, J., Furuyashiki, N., Sugiyama, S., Hirano, S., Shigemoto, N., and Nonaka, T., Efficient Recovery of Carbon Dioxide from Flue Gases of Coal-fired Power Plants by Cyclic Fixed-bed Operations over K_2CO_3-on-carbon, Industrial and Engineering Chemistry Research, Vol. 37, p. 185–191, 1998.

Hirano, S., Shigemoto, N., Yamaha, S., and Hayashi, H., Cyclic Fixed-bed Operations over K_2CO_3-on-Carbon for the Recovery of Carbon Dioxide under Moist Conditions, Bulletin of Chemical Society of Japan, Vol. 68, p. 1030-1035, 1995.

Hoffman, J. S. and Pennline, H. W., A Study of Regenerable Sorbents for CO_2 Capture, First National Conference on Carbon Sequestration, Washington, 2001.

Lee, S. C., Choi, B. Y., Lee, S. J., Jung, S. Y., Ryu, C. K., and Kim, J. C., CO_2 Absorption and Regeneration using Na- and K-based Sorbents, Studies in Surface Science and Catalysis, Vol. 153, p. 527–530, 2004.

Lee, S. C., Choi, B. Y., Lee, T. J., Ryu, C. K., Ahn, Y. S., and Kim, J. C., CO_2 Absorption and Regeneration of Alkali Metal-based Solid Sorbents, Catalysis Today, Vol. 111, p. 385-390, 2006.

Liang, Y., Harrison, D. P., Gupta, R. P., Green, D. A., and McMichael, W. J., Carbon Dioxide Capture Using Dry Sodium-based Sorbents, Energy Fuels, Vol. 18, p. 569-575, 2004.

Okunev, A. G., Sharonov, V. E., Aistov, Y. I., and Parmon, V. N., Sorption of Carbon Dioxide from Wet Gases by K_2CO_3-in-prous Matrix: Influence of the Matrix Nature, Reaction Kinetics and Catalysis Letters, Vol. 71, No. 2, p. 355-362, 2000.

Okunev, A. G., Sharonov, V. E., Gubar, A. V., Danilova, I. G., Paukshtis, E. A., Moroz, E. M., Kriger, T. A., Malakhov, V. V., and Aistov, Y. I., Sorption of Carbon Dioxide by the Composite Sorbent: Potassium Carbonate in Porous Matrix, Russian Chemical Bulletin, Vol. 52, No. 2, p. 359-363, 2003.

Pachauri, R. K. and Reisinger, A., Eds., Climate Change: Synthesis Report, Core Writing Team; IPCC, Geneva, Switzerland, 2007.

Rogner, H. H., Zhou, D., Bradley, R., Crabbe, P., Edenhofer, O., Hare, B., Kuijpers, L., and Yamaguchi, M., Introduction, In Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change; Metz, B., Davidson, O.R., Bosch, P. R., Dave, R., Meyer, L. A., Eds., Cambridge University Press, Cambridge, U.K. and New York, 2007.

Samanta, A., Post-combustion CO_2 Capture Using Solid Sorbents: A Review, Industrial and Engineering Chemistry Research, Vol. 51, p. 1438-1463, 2012.

Sayari, A., Belmabkhout, Y., and Serna-Guerrero, R., Flue Gas Treatment via CO_2 Adsorption, Chemical Engineering Journal, Vol. 171, p. 760-774, 2011.

Seo, Y. W., Jo, S. H., Ryu, C. K., and Yi, C. K., Effects of Water Vapor Pretreatment Time and Reaction Temperature on CO_2 Capture Characteristics of a Sodium-based Solid Sorbent in a Bubbling Fluidized-bed Reactor, Chemosphere, Vol. 69, p. 712-718, 2007.

Shigemoto, N., Yanagihara, T., Sugiyama, S., and Hayashi, H., Material Balance and Energy Consumption for CO_2 Recovery from Moist Flue Gas Employing K_2CO_3-on-activated Carbon and its Evaluation for Practical Adaptation, Energy Fuels, Vol. 20, No. 2, p. 721-726, 2006.

Siriwardane, R. V., Shen, M. S., Fisher, E. P., and Poston, J. A., Adsorption of CO_2 on Molecular Sieves and Activated Carbon, Energy Fuels, Vol. 15, p. 279-284, 2001.

Yang, R. T., Adsorbents: Fundamentals and Applications, Wiley Interscience, NJ, 2003.

Yong, Z., Mata, V., and Rodrigues, A. E., Adsorption of Carbon Dioxide at High Temperature: A Review, Separation and Purification Technology, Vol. 26, p. 195-205, 2002.

Zhao, Chu., Chen, X., and Zhao, Cha., CO_2 Absorption Using Dry Potassium-based Sorbents with Different Supports, Energy Fuels, Vol. 23, p. 4683-4687, 2009.

Zheng, F., Addleman, R. S., Aardahl, C. L., Fryxell, G. E., Brown, D. R., and Zemanian, T. S., Amine Functionalized Nanoporous Materials for Carbon Dioxide (CO_2) Capture, Environmental Applications of Nanomaterials: Synthesis, Sorbents and Sensors, Fryxell, G. E., Cao, G., Eds., Imperial College Press, Singapore, p. 285-311, 2007.