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CO_2 Separation Process Using Circulating Fluidized Bed Based on Exergy Recuperation

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In this paper, an innovative energy saving CO_2 separation process using chemical absorption was proposed from an energy saving point of view. In this process, metal oxide particles were selected as absorbents, which do not require separation energy of liquid/gas. These particles were fluidized by feed gas mixture for increasing segregation effect in the bed and heat transfer rate from chemical reaction to a heat pump system. Heat of absorption was recuperated and supplied as heat of thermal decomposition through a heat pump system based on the principle of exergy recuperation. In addition, some of the heat was circulated with the absorbents. The energy saving performance of the proposed process was evaluated by simulations.

1. Introduction

From fossil fuel combustion, large amounts of greenhouse gases (GHGs) are generated and emitted into the atmosphere. The reduction of CO_2 emission has become a major target in efforts to suppress global warming (White et al., 2005). Carbon emission capture and storage (CCS) has attracted attention in the past decades to reduce GHG emissions (Figueroa et al., 2008). CO_2 separation from gas mixtures requires huge amounts of energy. In fact, CO_2 separation from gas mixtures is one of the most energy intensive processes in CCS. Therefore, it is necessary to reduce the energy consumption of CO_2 separation for propagation of CCS.

Among different CO_2 separation methods, the most widely used method is chemical absorption using amine based solutions (Arias et al., 2016) such as monoethanolamine (MEA) (Harbou et al., 2014) and diethanolamine (DEA) (Dinca, 2016). In the conventional CO_2 separation by absorption using amine based solutions, thermal energy is supplied from the bottom of a regenerator which utilizes reaction heat for regeneration of the solutions and heat of vaporization for stripping. To reduce the supply of the thermal energy, many researchers have developed new amine based solutions.

Meanwhile, authors have developed CO_2 gas separation processes based on self-heat recuperation for power generation systems by post-combustion (Kishimoto et al., 2011) and pre-combustion (Kishimoto et al. 2012) from heat integration and process design points of view. By applying self-heat recuperation to thermal processes, not only the latent heat but also the sensible heat of the process stream can be circulated into the processes without any heat addition (Kansha et al., 2009), which leads to minimum exergy destruction of heat transfer and reduction of the process energy consumption (Kansha et al. 2013). In fact, by applying self-heat recuperation to CO_2 gas separation processes with a heat transformer, exothermic heat of absorption was successively utilized and supplied to the endothermic desorption reaction, thus leading to a large saving in the process energy.

The absorption using solutions requires additional energy for physical and chemical separation of liquid/gas, vaporization for stripping. This additional amount of energy is considerably large compared with the reaction heat for regeneration of the solutions (Kishimoto et al., 2011). To reduce the additional energy for the vaporization, some researchers have investigated solid absorbents such as lithium-based sorbents (Li_4SiO_4) (Puccini et al., 2013) and metal oxides (Bhatta et al., 2015) such as zinc oxide (Lavalley et al., 1982) and calcium oxide with iron oxide (Fernández et al., 2016). Although processes using these absorbents do not

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require the stripping heat, the reaction temperatures are normally high for increasing gas-solid reaction rate for CO_2 separation (Kato et al., 2002).

In this paper, an innovative energy saving CO_2 separation process using chemical absorption was proposed and the energy saving performance of the proposed process was evaluated by simulations. In this process, metal oxide particles were selected as absorbents, which do not require separation energy of liquid/gas. These particles were fluidized by feed gas mixture for increasing segregation effect in the bed and heat transfer rate from chemical reaction to a heat pump system. Heat of absorption was recuperated and supplied as the heat of desorption, i.e. thermal decomposition, through the heat pump based on the principle of exergy recuperation. In addition, some of the heat was circulated with absorbents through a circulating fluidized bed.

2. Conceptual design of the proposed process

2.1 Design of the proposed process

Figure 1 shows a conceptual design of the proposed process. In this process, the feed mixture containing CO_2 and other gases is fed as stream 1 and supplied to an absorber through a blower. This absorber is a fluidized bed. In the absorber, there are metal oxide particles which are fluidized by the feed mixture gas itself. CO_2 gas reacts with metal oxide particles and reacted particles are transformed to metal carbonate particles with exothermic heat. The unreacted gases are exhausted from absorber as stream 3. Most of the metal carbonate particles are separated from the metal oxide particles by the segregation effect in the fluidized bed. The metal carbonate particles from the absorber are fed to a heat exchanger with carrier gas (stream 4). In the heat exchanger, the stream 4 is heated by exchanging heat with an effluent stream from regenerator (stream 10). The heated metal carbonate particles (stream 5) are fed to the regenerator. This regenerator is also a fluidized bed. In the regenerator, the reverse reaction, i.e. thermal decomposition takes place. The metal carbonate particles are decomposed into CO_2 and metal oxide particles. The CO_2 gas is automatically separated from the particles (stream 6→ stream 7). Stream 7 is a separated CO_2 gas. A part of produced CO_2 gas is supplied to the regenerator as a fluidizing gas through a blower (stream 8 → stream 9).

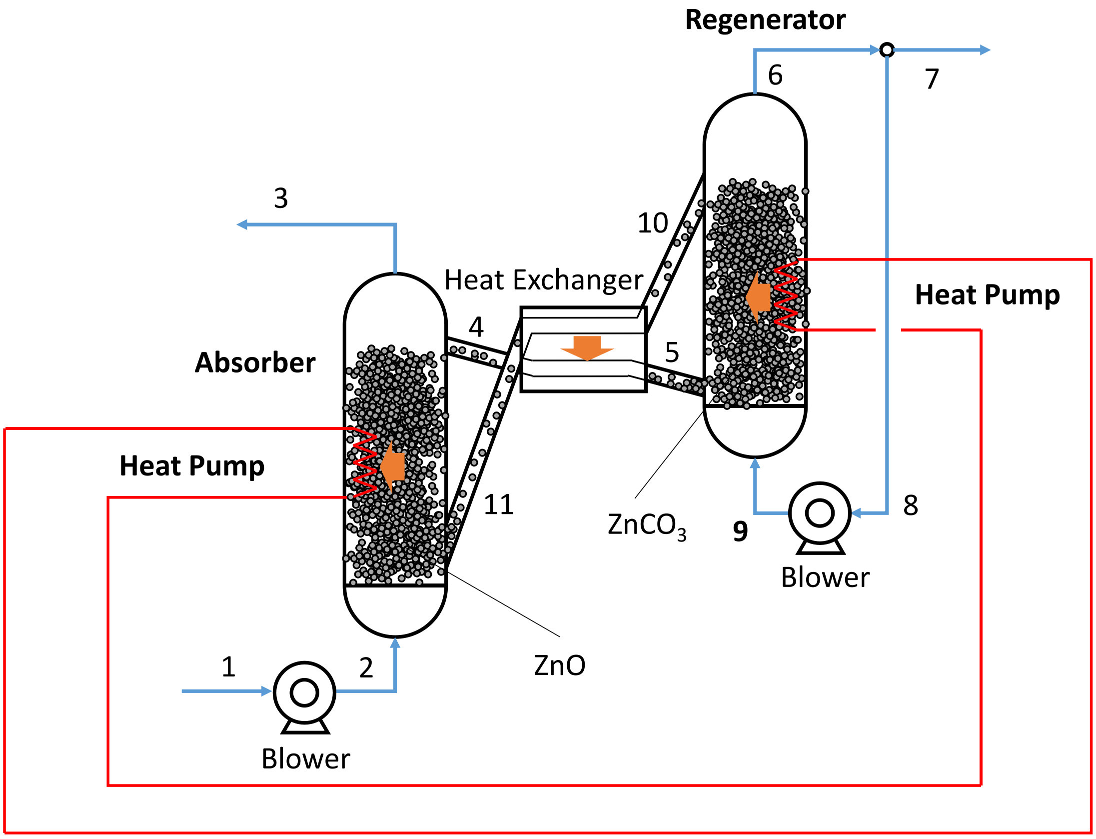

Figure 1: Conceptual design of the proposed CO_2 separation process

The decomposed particles with carrier gases from the regenerator are supplied to the absorber through the heat exchanger (stream 10 → stream 11). At the same time, the exothermic heat produced during absorption in the absorber is pumped by a heat pump system and supplied to the regenerator for the endothermic reaction using exergy recuperation concept for saving regeneration energy.

2.2 Reaction

In this process, metal oxides were selected as absorbents. Metal oxides react with CO_2 and metal carbonates are produced. Simultaneously, metal carbonates are thermally decomposed to metal oxides and CO_2. Thus, these reactions are reversible. One of the most common metal oxides for this reaction is calcium oxide (CaO). However, temperature for the reaction from calcium carbonates ($CaCO_3$) is too high to apply the heat pump system as shown in Figure 1. Considering the reaction temperatures, zinc oxide (ZnO) was selected. The reaction is represented as:

$$\mathrm{ZnO} + \mathrm{CO_2} \rightarrow \mathrm{ZnCO_3} \qquad \Delta H_{298} = -71.0\,\mathrm{kJ/mol} \tag{1}$$

where ΔH_{298} is the reaction heat at 298 K and 101.3 kPa.

The lowest temperature for the thermal decomposition of zinc carbonates ($ZnCO_3$) is about 325 K. Therefore, a heat pump system is commercially available to transfer heat from the absorption reaction in the absorber to the thermal decomposition reaction in the regenerator.

2.3 Fluidized bed

The contact of solid particles (ZnO) with feed mixture gas including CO_2 is enhanced as compared with packed beds owing to the fluidized bed properties. Thus, the reaction rate of the solid-gas reaction is expected to be enhanced. At the same time, it is well known that heat transfer inside the bed is enhanced and the bed temperature becomes uniform, leading to good heat transfer from reaction in the absorber to the heat pump system. Furthermore, segregation phenomena can be observed in the bed due to difference in densities of the particles. It is notable that fluidized particles continuously circulate in the reactor and these particles have a role of heat carrier when a circulating fluidized bed is used. From these reasons, we selected circulating fluidized beds for application in the proposed CO_2 separation process.

3. Simulation results

A simulation was conducted using PRO/II Ver. 9.1 (Invensys, SimSci) combined with Materials-oriented Little Thermodynamic Database for PC (MALT, Kagaku Gijutsu-Sha) to examine the energy saving performance of the proposed process at steady-state conditions. In this simulation, the Soave-Redlich-Kwong equation was selected for the thermodynamic~~s~~ data and an adiabatic efficiency of 100 % was assumed for the compressor in the heat pump system. Water was selected as a representative working fluid in the heat pump system. The Gibbs free energy and the reaction heat changes with respect to reaction temperature, as obtained from MALT, are shown in Figure 2.

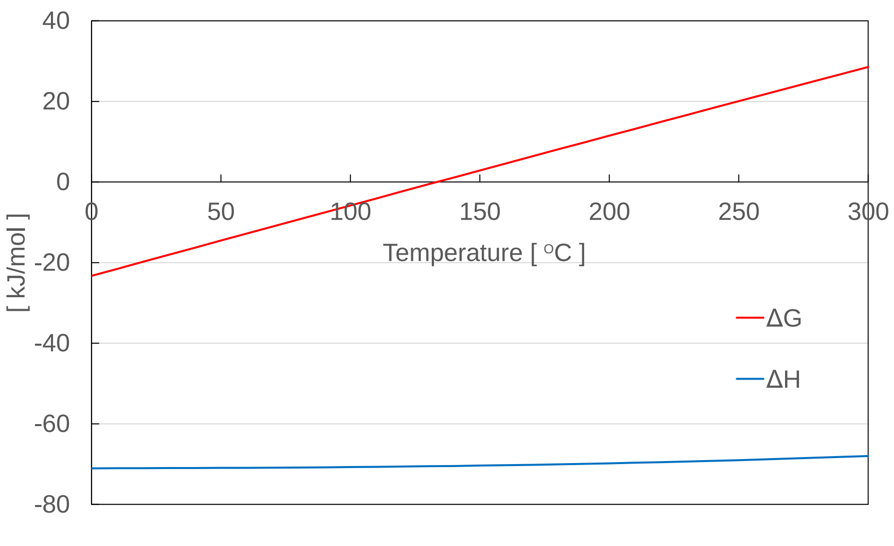

Figure 2: Gibbs free energy and reaction heat changes with respect to reaction temperature

At the steady-state condition, particle circulation cannot take part in the simulation. Therefore, the following simple process flow diagram as shown in Figure 3 was considered to examine the energy saving performance of the proposed process.

In this process, absorber and regenerator were isolated and sensible heat amounts were assumed to be negligible as compared with reaction and latent heat amounts. Absorption in the absorber and thermal decomposition in the regenerator were assumed to be isothermal reactions. Reaction data were acquired from MALT and fed to PRO/II to examine the energy required for the proposed process. At the same time, all of reaction heat of absorption was assumed to be pumped by the heat pump system and supplied to the regenerator. According to Figure 2, absorption reaction takes place below 140 °C from the reaction equilibrium point of view.

Therefore, we assumed that the reaction temperature at the absorber was 100 °C and that the temperature of the thermal decomposition in regenerator was 180 °C. In addition, the bed temperature was assumed to be uniform in the bed due to fluidized bed properties. Therefore, we assumed that the heat pump system successfully received the reaction heat of adsorption at the bed temperature in the absorber and provided the reaction heat to the thermal decomposition at the bed temperature in regenerator. From these assumptions, we evaluated the energy required for several reaction temperatures in the simulation. The results are summarized in Table 1. To see the effect of the adiabatic efficiency of the compressor used in the heat pump system, the same simulation with 80 % adiabatic efficiency of the compressor was conducted. The energy required for the process at each temperature with 80 % adiabatic efficiency is summarized in Table 2.

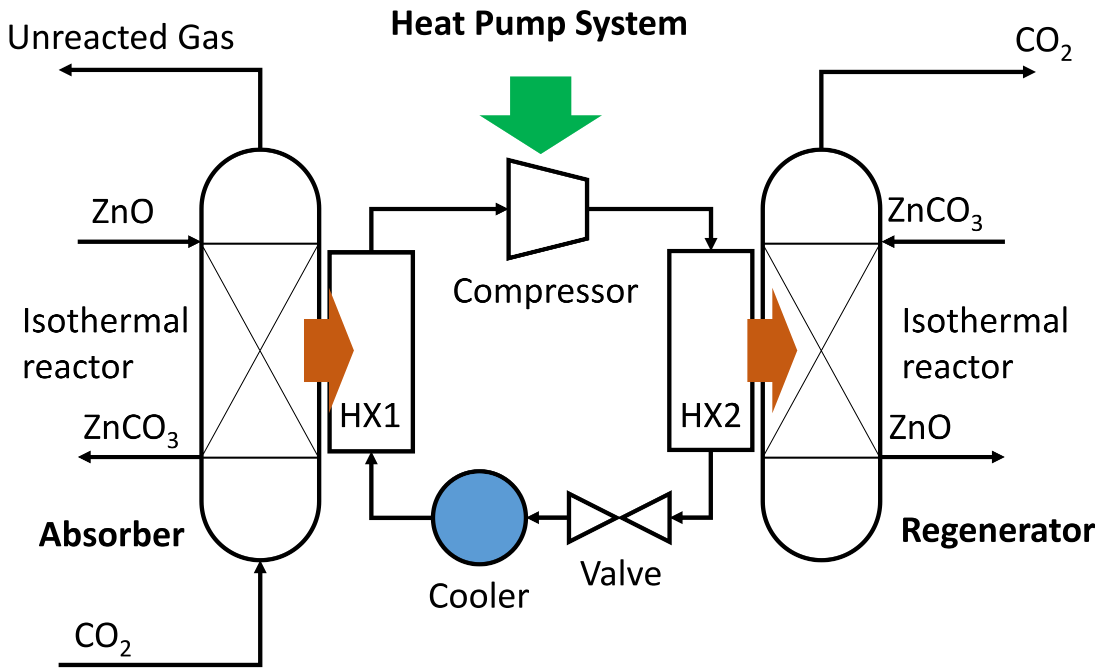

Figure 3: Simplified process flow for examining energy saving performance

Table 1: Energy required (adiabatic efficiency of compressor: 100 %)

Temperature at Absorber [°C]	100	85	100	85
Temperature at Regenerator [°C]	180	180	195	195
Work for heat pump [MJ/kg-CO_2]	0.34	0.47	0.44	0.54

Table 2: Energy required (adiabatic efficiency of compressor: 80 %)

Temperature at Absorber [°C]	100	85	100	85
Temperature at Regenerator [°C]	180	180	195	195
Work for heat pump [MJ/kg-CO_2]	0.43	0.59	0.55	0.68

4. Discussion

In this simulation, we examined the energy required for the proposed CO_2 separation process. From the simulation results, the energy required for the proposed process was about 0.5 MJ/kg-CO_2 with 100 % adiabatic efficiency of the compressor at the steady-state condition. When we changed the adiabatic efficiency to 80 %, the energy required for the proposed process was less than 0.7 MJ/kg-CO_2 at the steady-state condition. These values are almost 1/8-1/6 of those for the conventional CO_2 gas separation processes using amine based absorption (4.1 MJ/kg-CO_2). At the same time, these values are almost identical to those of regeneration energy of exergy recuperative CO_2 gas separation processes using amine based absorption (Kishimoto et al., 2011). However, their processes require additional stripping energy. The amount of stripping energy is almost same as the amount of regeneration energy, although they applied self-heat recuperation to the stripping section. Therefore, it can be said that the proposed process has a potential for reducing energy to the half of their processes. In fact, the energy required for the proposed process calculated from this simulation is small as compared with conventional adsorption process (Yu et al., 2012) and that applying self-heat recuperation (Song et al., 2015).

To realize the proposed process, it is necessary to examine the reaction rates of absorption and thermal decomposition at several temperatures by experiment. Simultaneously, the blower work for fluidizing gas has to be examined. These values are strongly related to the energy required for the proposed process, the surface area of the heat pump and reactor, and reactor size. Furthermore, segregation and agglomeration phenomena in the fluidized bed should be observed.

The proposed process could have further energy saving potential owing to particle circulation in the circulating fluidized beds. The reaction heat from adsorption in the absorber is transferred to the regenerator through the circulating particles. If this circulating heat amount is large, pumped heat amount by the heat pump system will decrease and work amount for the compressor in the heat pump system will decrease proportionally. Thus, we must examine the relationship between particle circulation and fluidizing gas rates. In addition, we should select a suitable working fluid for this process considering temperatures of the absorber and the regenerator.

5. Conclusions

In this paper, an innovative energy saving CO_2 separation process using chemical absorption was proposed and the energy saving performance of the proposed process was evaluated by steady-state simulations. Although further investigations are required for realizing the proposed process for practical application in industry, the proposed process using a circulating fluidized bed and a heat pump showed a large energy saving potential for CO_2 separation as compared with conventional counterparts.

Acknowledgments

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