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Economic process design for separation of CO_2 from the off-gas in ironmaking and steelmaking plants

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ABSTRACT

We develop an economic process design for separation of CO_2 from the off-gas in ISMPs (iron and steel making plants). Based on the characteristics of the off-gas from which CO_2 must be separated, we design two process configurations: PSA (pressure-swing adsorption) and MEA (monoethanolamine)-based chemical absorption. We also develop a simulation model of each process, and perform an economic evaluation of the configurations. Our technical performance analyses show that the CO_2 recovery and purity are >90% in the both processes and that highly-concentrated combustible gas (CO and H_2) can be obtained as a byproduct. Our economic performance analyses show that the designed processes lead to cost-effective and competitive options ($62/t CO_2 separated), compared to the CO_2 separation processes used in power plants. Using the combustible gas as a fuel for the boiler of power cycle greatly reduces the cost of CO_2 separation in ISMPs.

1. Introduction

Many countries have agreed to reduce their emissions of CO_2, which is a major greenhouse gas that contributes to global warming [1], and signed the Kyoto Protocol in 1997 [2,3]. CO_2 is emitted mainly by burning fossil fuels to generate energy in power plants and for production of cement, iron and steel in industrial processes [4]. CO_2 separation technologies have been a promising solution for removing CO_2 from gas streams emitted by power plants and industrial processes [1,5,6]. Four major separation technologies are used to separate CO_2 from exhaust gases: absorption, adsorption, membranes and cryogenics [5,7]. A chemical absorption process using a solvent based on MEA (monoethanolamine) is well known as the most suitable technology for use in conventional power plants, because it is effective for dilute CO_2 streams (about 3.5–13.5 mol% in mostly N_2) emitted from the plants [7–11], but requires a very high heating energy to regenerate the MEA solvent [12,13]. The PSA (pressure-swing adsorption) process can be also commercially viable for CO_2 separation [14,15], but has some drawbacks such as low capacity and low CO_2 selectivity of available adsorbents [16–18].

However, despite the large number of techno-economic evaluations of the CO_2 separation processes in power plants [6,7,12,13,19–34], few studies have been conducted in other industrial processes, especially ISMPs (iron- and steel-making plants). Iron (or steel) can be produced by indirect reduction of iron oxides (Equations (1)–(3)) by a reducing gas (CO) produced from burning coke (Eq. (4)); the reaction pathway emits a huge amount of CO_2 [35]:

$$\text{Reduction of Hematic}: \ 3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{1}$$

$$\text{Reduction of Magnetic}: \ Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \tag{2}$$

$$\text{Reduction of Wustite}: \ 2\text{FeO} + CO \rightarrow 2FeO_{0.5} + CO_2 \tag{3}$$

$$\text{Combustion of cokes}: \ C + 0.5O_2 \rightarrow CO + 111\text{kJ mol}^{-1}. \tag{4}$$

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Especially, the steel industry in Korea emits 14% of the county's total CO_2 emissions, which is second only to power plants (30%) [35]. CO_2 separation processes have been demonstrated in power plants [7–11,16], but the off-gas emitted by ISMPs differs from the flue gas emitted by power plants, so designing a suitable process for CO_2 separation from off-gases requires understanding of their characteristics.

Our goal is to develop an optimal design for CO_2 separation processes in ISMPs. We present a broad overview of the technologies to develop the design of CO_2 separation processes in Section 2. We then design two process configurations and develop each process simulation model in Section 3. Last, we perform an economic evaluation of the configurations in Section 4. Thus, we can suggest the best design of CO_2 separation process in IMSPs in Section 5.

2. Technology overview

ISMPs typically emit three types of off-gas: BFG (blast furnace gas), oxygen furnace gas (LDG) and COG (coke oven gas). They all contain large amounts of CO and CO_2, moderate amounts of H_2 and N_2, and small amounts of CH_4. But they also have unique features. Compared to the other gases, BFG has a higher concentration of N_2 [36], LDG has a higher concentrations of CO [37]and COG has a higher concentration of H_2 [38]. Thus, this paper considers the gas composition and a certain value of gas flow rate as an input gas condition of the CO_2 separation process (Table 1). The gas flow rates are real data, which were obtained directly from a conventional ISMP in Korea.

Four technologies are available for separation of CO_2 from the off-gas: chemical absorption, pressure swing adsorption, cryogenic, and membrane (Table 2). Although these technologies have been demonstrated in power plants [7], the technologies are not suitable for application in existing ISMPs for two reasons. The first is that the off-gas emitted from ISMPs contain higher concentrations of CO_2 (30–40 mol%) and lower concentrations of N_2 (10–20 mol%) than gases emitted from power plants [36–38]. Higher purity of CO_2 (90–99 mol%) can be obtained using PSA in ISMPs than in power plants (48 mol%) because CO_2 purity in the recovered (separated) stream depends on the composition CO_2 in the off-gas that enters the PSA process [39]. PSA can then be a cost-effective and competitive option to commercial MEA-based CO_2 absorption process. The other difference is that the off-gas contains combustible species, which can be burned to produce heat and electricity; this process can decrease the operating cost of separating the gases.

The cryogenic and membrane processes are not suitable [7] for separating off-gases. The cryogenic process requires a very large amount of energy for refrigeration. The membrane process requires high operating pressures and needs multiple stages and recycling to separate CO_2 from the off-gas. Thus, CO_2 separation using PSA or MEA-based chemical absorption is considered in this paper.

Table 1
Input gas information.

Descriptions	Values	Units
Flowrate	7000–8000	kmol/h
Temperature	25–45	°C
Pressure	1–3	Bar
Composition		
H_2	10–20	mol %
CH_4	0–10	mol %
CO	30–40	mol %
CO_2	30–40	mol %
N_2	10–20	mol %

3. Process development

3.1. PSA modeling

The design of PSA process (Fig. 1; Table 2) is modified from Ref. [39] that includes a pre-treatment system and a dehydrator, because off-gases do not include water and impurities (i.e., NO_x and SO_x). In principle, an off-gas is pressurized by a compressor and then sent to PSA vessel to separate CO_2. Adsorbents (e.g., zeolites) are used to adsorb CO_2 from the off-gas at high pressure and the process then swings to low pressure to desorb the adsorbed material. After desorption, a product gas containing a high concentration of CO_2 is pressurized for transport to a CO_2 storage site. Thus, the operation of PSA process is assumed to be a Skarstrom cycle [39,40], which is composed of four steps: pressurization, adsorption, depressurization, and purging.

Detailed process flowsheet of PSA was developed using short-cut modeling [39,40] and simulated using gPROMS [41]. This modeling categorizes four steps of the Skarstrom cycle into two groups: “adsorption”, which consists of pressurization and adsorption; and “desorption”, which consists of depressurization and purging. This modeling provides an approximate result is fast and simple. The assumptions of the modeling are [39,40]:

1. All steps are assumed to be batch processes.
2. The batch process occurs in a vessel with a fixed volume.
3. The bulk gas and adsorbed gas are in equilibrium with each other.
4. After desorption, the bed does not contain residual gases.
5. Adsorption is adiabatic.
6. All gas components can be adsorbed, assuming a multicomponent system compared to the bicomponent system of [39,40].

Modeling Equations (5)–(10) (notation definitions: Appendix I; input parameters: Supplementary Information) are the developed material balances based on the Langmuir isotherm using zeolite 13X [39,42–44]. Equations (5) and (6) are overall material balances of each component in the adsorption and desorption processing steps, respectively. Equations (7) and (8) are total flow rates of each component in exhaust and product streams separated from the processing steps, respectively, and are determined by the efficiency at which each component is removed in each processing step (Equations (9) and (10)).

$$f_{in,n}^{vessel} = m_n + q_n + s_n \tag{5}$$

$$m_n + q_n = n_n + r_n + t_n \tag{6}$$

$$f_{Exhaust,n}^{vessel} = s_n + t_n \tag{7}$$

$$f_{Product,n}^{vessel} = n_n + r_n \tag{8}$$

$$q_n = \frac{a_n b_n P_n^{hp} W_{ads}^{vessel}}{1 + \sum_n b_n P_n^{hp}} \tag{9}$$

$$r_n = \frac{a_n b_n P_n^{lp} W_{ads}^{vessel}}{1 + \sum_n b_n P_n^{lp}} \tag{10}$$

Equations (11) and (12) calculate electricity requirements of compressors and vacuum pumps in the process [45].