Cleaning and Poly-generation of Coal-fired Flue Gas Integrated with a LNG Station

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Abstract. In the present work, a simultaneous SO_2 and CO_2 capture method was proposed for coal-fired flue gas based on the desublimation phenomena of SO_2 and CO_2 under cryogenic conditions. The fundamentals of the method were introduced, and a separation and poly-generation scheme was presented, which can capture nearly 100% SO_2 and > 95% CO_2 of the flue gas, and can produce clean and concentrated nitrogen (>95 v% N_2), natural gas, H_2SO_4, and high purity CO_2 (>99.9 mol%). The scheme does not introduce any separation agent in the flue gas and uses only the cold energy of LNG for the separation. The operational cost is also investigated and compared with that of other carbon capture methods. The results indicate that the present method has lower energy consumption, and its advantage is more profound considering the offered economic products.

1. Introduction

Coal has been serving the world energy demand for more than a century as those found in coal-fired heat or power plants. As the trend of global warming changes more appreciably and environmental regulations become more stringent, more and more institutes and researchers have paid attention to reducing CO_2 or pollutant emissions caused by coal combustion[1]. While more clean energy resources, such as natural gas, nuclear energy, biomass, solar energy, and wind energy, can be used for power or heat generation, coal will still play a significant role in the present and foreseeable future[2], especially for those countries with abundant coal but short of other clean fuels like China[3]. Therefore, one possible trade-off solution is to develop an efficient cleaning technology for coal combustion before a more clean and economic fuel can completely substitute coal in heat or power generation. Most present coal-fired boilers are operated under excessive air and near-ambient pressure conditions, and its moisture-free flue gas contains N_2, O_2, and CO_2 three major species plus small amount of Ar, and trace contaminants like SO_2, NOx, particulate matters (PM), and Hg (elemental mercury (Hg^0), oxidized mergucy (Hg^{2+}), or particle bound Hg (Hg_p)) etc. Among these pollutants, SO_2 is a major concern for both human health and environment and is typically captured either by a dry or wet flue gas desulfurization method[4], which is expensive and consumes a large amount of desulfurizer like lime. The CO_2 emission is the biggest contributor of the greenhouse effect, and the main proposed CO_2 separation technologies are amine washing (MEA, etc.) [5], PSA[6, 7], membrane separation[8, 9], etc. However, these CO_2 separation processes are either economically expensive or technically not yet matured for industrial usage. Recently, a CO_2 separation technology based on CO_2 desublimation has been proposed and attracted more interests of researchers. Baxter et al.[10-12] presented a cryogenic carbon capture (CCC) process for typical coal-fired flue gas based on CO_2 desublimation, and reported that the overall energy consumption of CCC is lower than that of typical MEA methods. In addition, Baxter et al. pointed out that gaseous pollutants like Hg^0 and SO_2 can also

be separated using the desublimation method. However, the CO_2 desublimation-based technology is typically operated at temperatures low to -150°C, and thus, large high-level cold energy is needed to decrease the flue gas temperature to the desired conditions.

One possible candidate with high-level cold energy is liquefied natural gas (LNG) [13]. LNG has become a popular fossil fuel in the world energy market due to its high energy density, low carbon emission, transport convenience, and low infrastructure construction cost compared with long-distance natural gas (NG) pipelines[14]. It is typically stored at temperature around -162°C and has to be regasified in a vaporizer before it is transported to end-uses, which offers an ideal cheap or free high-level cold energy source. Antonio et al.[15] pointed out that the cold energy of LNG can be recovered and used efficiently in many other industrial applications by appropriate cascade cold energy utilization schemes. In the present work, we investigated the CO_2 and SO_2 desublimation conditions. A cleaning and poly-generation scheme was then presented for a coal-fired flue gas example to separate SO_2 and CO_2 by integrating with a LNG regasification process. A cost comparison was made for the present work with other technologies.

2. Gas-solid phase equilibrium of flue gas under cryogenic conditions

To utilize the desublimation method in flue gas separation, phase equilibrium properties are needed for the gaseous flue gas species and solid species of SO_2 ($SO_2(s)$) and dry ice ($CO_2(s)$). The gaseous properties and the heat capacities of $SO_2(s)$ and $CO_2(s)$ can be obtained using the DIPPR database[16]. For a given reference temperature (T_{ref}), the reference enthalpy (H_{ref},s) and entropy (S_{ref},s) of the two solid species can be obtained using solid vapor pressure data. In the present work, the H_{ref},s and S_{ref},s values of $SO_2(s)$ and $CO_2(s)$ are regressed according to the solid-gas equilibria in Aspen Plus using the reported solid vapor pressure data of $SO_2(s)$[17, 18] and $CO_2(s)$[17-22], respectively. The regressed H_{ref},s and S_{ref},s values are shown in Table 1.

Table 1. Regressed data for $CO_2(s)$ and $SO_2(s)$

Species	T_{ref} (K)	S_{ref},s (J/molK)	$H_{ref,s}$ (kJ/mol)
$CO_2(s)$	216.58	-136.25	-421.28
$SO_2(s)$	197.67	-155.7	-337.36

Fig. 1 shows the comparisons of the reported solid vapor pressures of SO_2 and CO_2 with those calculated using the regressed H_{ref},s and $S_{ref,s}$ values and the PR model (for gas phase) in Aspen Plus. The excellent data agreement implies that the PR alpha function defined in Aspen Plus can be safely used for the gaseous properties. It can be found that relative solid vapor pressure ratio of CO_2 to SO_2 (R_{CS}) increases dramatically as temperature decreases. For example, R_{CS} increases from 62 to 4850 as temperature decreases from 205 K to 130 K, which implies a possible approach to sequentially separate SO_2 and CO_2 from flue gas using the desublimation method.
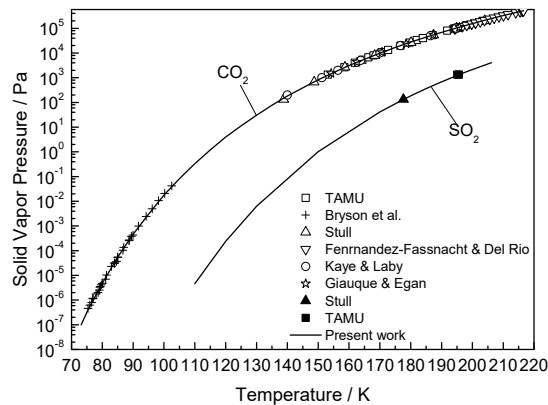
Fig. 1. Solid vapor pressure of SO_2 and CO_2 as a function of temperature. □ & ■: [18]; +: [19]; △ and ▲: [17]; ▽: [20]; ○: [21]; ☆: [22].

To analyze the SO_2 and CO_2 separation effect of the desublimation method, a flue gas sample is defined which contains N_2, O_2, CO_2, SO_2, and Ar five gaseous species. Other substances, such as PM, moisture, NOx, and Hg, are assumed to have been removed from the flue gas before entering the SO_2 and CO_2 separation units. The CO_2 content is typically less than 15 v% in coal-fired flue gas [12]. The SO_2 concentration varies according to the coal characteristics and available desulfurizing agent in the feedstocks. For an average, a concentration of ~2300 ppmv is assumed[4] for SO_2 in the present work. The oxygen content in flue gas is typically around 2~4 v% due to the excessive air supply in coal combustion. The Ar content can be estimated according to the Ar/N_2 molar ratio in the air (e.g., 0.94 v% Ar, and 78 v% N_2 in the air). Therefore, a flue gas example containing 13.79% CO_2, 3% O_2, 82% N_2, 0.98% Ar, and 2300 ppmv SO_2 is used in the present work for desublimation separation analysis. The PR model is selected in this investigation to calculate the gaseous properties because its application has been widely accepted in modeling the cryogenic air separation processes. In addition, most necessary binary interaction parameters (k_{ij}) in the PR model have been pre-defined in Aspen Plus based on available thermodynamic data.

Fig. 2 depicts the calculated desublimation fraction of SO_2 and CO_2 for the given flue gas example. No liquid has been predicted at the given temperatures and pressures. The curves indicate that both SO_2 and CO_2 can be separated using the desublimation method. As pressure increases, more SO_2 and CO_2 will change into solids at a given temperature. As temperature decreases, $SO_2(s)$ will precipitate from the flue gas first until the temperature is low enough for the CO_2 desublimation. At a given pressure, there is a temperature region (>10K) where only SO_2 desublimation occurs and no $CO_2(s)$ is formed. For example, at 1 atm, around 88% SO_2 in the flue gas changes into solid as temperature decreases from -85.2°C to -99.8°C where CO_2 has not begun to freeze; when temperature decreases further, CO_2 begin to desublimate with SO_2, and the solid becomes a mixture of $CO_2(s)$ and $SO_2(s)$ where $CO_2(s)$ dominates. As temperature approaches ~ -130°C, nearly all SO_2 and over 95% CO_2 change into solid for the three pressure cases. Fig. 2 implies a possible high efficient SO_2 and CO_2 capture scheme if a suitable cold energy source (< -130°C) is available: most SO_2 (e.g., >80%) can be captured in one cold unit separately, and a high purity (>99.5 mol%) $CO_2(s)$ can be obtained in another unit using the desublimation method. The main contaminant in the $CO_2(s)$ solid is $SO_2(s)$ which can be easily separated or treated in the concentrated fluid phase after melting (e.g., by fractionation or chemical absorption). For an individual SO_2 capture scheme, the flue gas can be cooled to a condition (e.g., 1atm, -113°C) where over 99% SO_2 can be captured in a solid mixture of $CO_2(s)$ and $SO_2(s)$.
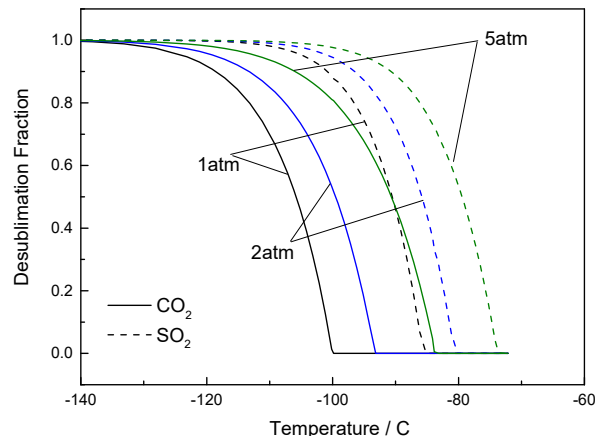
Fig. 2. SO_2 and CO_2 desublimation as a function of temperature and pressure for the flue gas example.

3. Cleaning and poly-generation scheme example

Fig. 3 illustrates an example for the flue gas cleaning and poly-generation unit integrated with a LNG station. The separations of SO_2 and CO_2 are conducted in a SO_2 absorber and CO_2 absorber, respectively. The absorber can be taken as a heat exchanger or a heat exchanging system that offers the cooling and freezing environment for SO_2 or CO_2 desublimation. The pressure of the natural gas after a vaporizer is typically 3~5 bar, which corresponds to a bubble temperature of -146 ~ -137°C. Therefore, the CO_2 absorber must be operated at a temperature no less than -140~-130°C (i.e., above 5~10°C of the LNG bubble temperature) for effective heat transfer between the LNG and the flue gas. The corresponding CO_2 capture efficiency is set to >95~99.99% at the given operating temperature. The process in Fig. 3 is described in the following. The flue gas after PM, Hg, and NOx removal is firstly cooled to ~60°C in a cooler, and then compressed to a pressure around ~1.2 bar to compensate the pressure drop of the downstream units. After compression, the flue gas enters a cold box where it is further cooled to a temperature ~5°C above the SO_2 desublimation point (~ -90°C in the present case) to avoid possible frost formation in the cold box, and then enters the SO_2 absorber where up to ~85% pure SO_2(s) is frozen into solid at the operating temperature of ~ -99°C. The SO_2-lean flue gas then enters the CO_2 absorber where all the remaining SO_2 and > 95% CO_2 are desublimated at the temperature around -130°C. The flue gas after SO_2 and CO_2 removal can either enter the air separation unit (ASU) to make high-purity nitrogen, or enter the cold box again to recover its cold energy and be used as a N_2-rich (>95 v%) gas. Similarly, The LNG from the SO_2 absorber (~ -101°C) can be used for other cryogenic applications directly, or can be heated to around the ambient temperature for pipeline transport after its cold energy is recovered in the cold box. The collected SO_2(s) can be heated and reacted into sulfur acid or used for other applications. The CO_2(s) can be melted using the recycled CO_2 fluid and further purified in a fractionator to get high-purity (>99.9 mol%) CO_2 fluid for other applications (e.g., food industry, CO_2 flooding etc.), or sold as the final product.
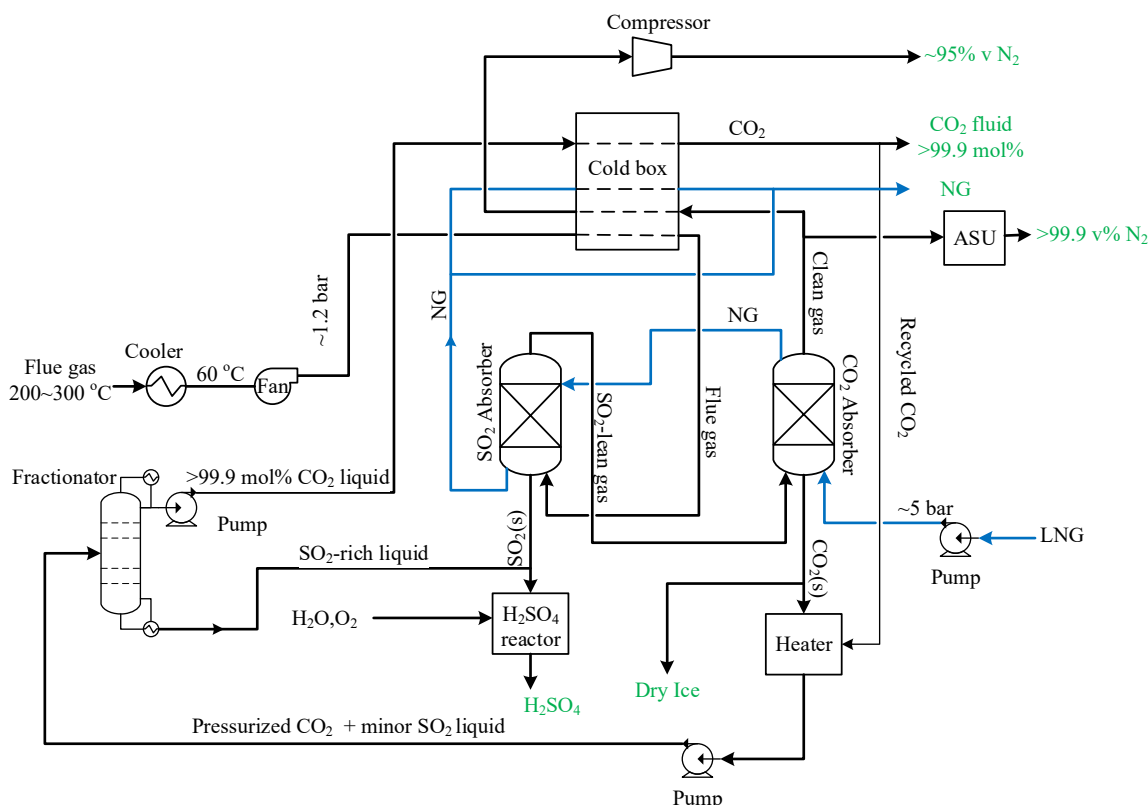
Fig. 3. Flue gas cleaning and poly-generation scheme.

Based on the case shown in Fig. 3, 504 Nm^3 LNG is needed to capture all the SO_2 and >95% CO_2 for every 1000 Nm^3 flue gas example. Therefore, the cleaning and poly-generation scheme for the coal-fired flue gas is suitable only when a LNG station is available and can be integrated into the heat or power plant. A rough operational cost of the present method is estimated in Fig. 4 by assuming ~0.05$/kWh energy cost for the given flue gas separation. The operational cost is mainly caused by pumping liquids, compressing gases, and rectifying SO_2-CO_2 in a fractionator involved in the scheme, and the solid treatment is temporarily assumed to be ~20% of the total operational cost due to unavailable reported data. The operational cost is much cheaper than that of the compared CO_2 capture technologies[10, 23] since the cold energy in LNG is free and no extra separation agent is introduced into or separated from the system. It should be pointed out that the operational cost in Fig. 4 includes the SO_2 separation. Therefore, the total cleaning cost becomes even more competitive than other SO_2+CO_2 separation technologies. In addition, the products offered by the present scheme enhance its economic advantage over other technologies.
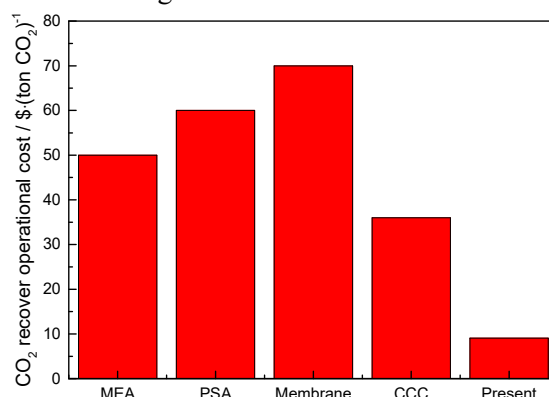

Fig. 4. Operational cost comparison for CO_2 capture.

4. Conclusion

In the present work, the desublimation method is introduced to separate SO_2 and CO_2 simultaneously from coal-fired flue gas. Fundamentals of the SO_2 and CO_2 desublimation are analyzed, and a typical flue gas is used as an example to investigate the effects of operating conditions on the capture efficiency. It is found that temperature is the most significant factor for the desublimation of SO_2 and CO_2. The capture efficiency increases with increasing pressure. Most SO_2 can be captured separately without $CO_2(s)$ formation within a temperature region. A cleaning scheme is then presented that can separate SO_2 and CO_2 using the desublimation method by integrating with a LNG regasification process. The scheme can capture >95% CO_2 and nearly all SO_2 from the flue gas, and can produce concentrated nitrogen, NG, high–purity CO_2, and H_2SO_4 products. The operational cost is lower than that of many other available schemes, and the economics becomes even more appreciable when the poly-generated products are considered.

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