14th International Conference on Greenhouse Gas Control Technologies, GHGT-14

21st -25th October 2018, Melbourne, Australia

Evaluation of Cryogenic Systems for Post Combustion CO_2 Capture

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Abstract

Cryogenic capture of carbon dioxide from flue gas streams is one potential pathway to reduce the CO_2 emissions from power plants and industrial sources. In this paper, a minimum energy analysis of idealized cryogenic carbon capture processes is performed. Parametric studies on this idealized process are quantified to study the effect of minimum capture temperature and simulated heat exchange approach temperatures. The theoretical and practical difficulties in approaching this ideal process are described and discussed. Finally, the Sustainable Energy Solutions External Cooling Loop Cryogenic Carbon Capture™ process is evaluated and compared to the idealized carbon-capture process.

Keywords: Cryogenic Separations, CO_2 Capture, CCS, Thermodynamic Evaluation, Sustainable Energy Solutions

1. Introduction

Phase change can be used to separate components from a gas stream. This is typically accomplished by cooling the gas stream until one or more of the components changes phase to a dense liquid or a solid that can be physically separated from the non-condensing species. CO_2 capture through phase change has been proposed and developed as a means of removing CO_2 from power plant flue gas streams. Major advantages of cryogenic carbon capture over amine capture systems include eliminating issues of reaction rates and degradation, no impact on the steam cycle of the associated power plant, pumping CO_2 to pressure as a liquid to minimize compression energy, and an overall low energy consumption per ton of CO_2 captured. Drawbacks include difficulties associated with two-phase flow, solids handling, and large heat exchangers with small temperature approaches.

Carbon dioxide forms a solid when condensed below its triple point pressure of 517 kPa. When it does so, it deposits on the lowest temperature surface, forming a barrier to heat transfer and plugging the gas flow within typical heat exchangers. The difficulty of removing a solid through deposition in a continuous process is best illustrated by moisture removal from a gas stream. Dehydrating gas streams to dew points above 0°C can be accomplished through cooling, moisture condensation, and liquid collection. However, for lower levels of moisture levels, temperatures below 0°C are required, but water forms solid ice under these conditions that would coat heat transfer surfaces and

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plug the flow within typical heat exchangers. As a result, a range of dehydration options exist for low dew-point applications that includes liquid desiccants such as glycols and solid desiccants such as silicas and zeolites. These options tend to be more complex, expensive, and energy intensive compared to liquid water removal through condensation.

Cryogenic technologies are used for large-scale air separation. The inlet air is dehydrated, scrubbed of CO_2, then chilled, liquefied and distilled to separate air into its individual components of oxygen, nitrogen, and other gases. Water and CO_2 are removed in the pre-treatment steps so that they do not form a solid in the air separation unit. Likewise, for cryogenic CO_2 capture from flue gas, moisture needs to be removed which presents a similar challenge. One option is to cool the flue gas stream to approximately -100°C (<0.1 ppm moisture) to avoid moisture condensation on heat transfer surfaces or cool the gas in a way that does not involve heat transfer through fixed surfaces. SES has patented and is developing such processes.

For all cryogenic systems, thermal integration and temperature management are typically required to minimize the energy consumption of the process which also minimizes the separation work. In this paper we describe and analyze an idealized cryogenic carbon capture process in which there is no lost work from heat transfer or heat loss. We can then compare existing processes to the idealized process to benchmark the performance and understand potential improvements.

2. Methods

2.1. Minimum Energy of Separation and Compression

For an ideal gas, the minimum energy input required to separate a gas stream into its pure components is the difference in Gibbs Energy between the mixed and separated streams. This can be calculated for a gaseous stream through equation 1:

$$E_{\min} = \Delta G_{mix} = T\Delta S_{mix} = -RT\sum_i x_i \ln(x_i) \tag{1}$$

where $E_{\min}$ is the minimum energy of separation, ΔG_{mix} is the Gibbs energy of mixing, T is the ambient temperature, ΔS_{mix} is the entropy of mixing, R the universal gas constant, and x_i is the mole fraction of species *i*. For flue gas separation with a CO_2 capture percentage of η and treating the gas as a binary mixture of CO_2 and "non-CO_2" species, Eq (1) becomes[1]:min

$$E_{\min} = -\frac{RT}{\eta x_{CO2}}\left\{\left[x_{CO2}\ln x_{CO2} + (1-x_{CO2})\ln(1-x_{CO2})\right] - \left[1-\eta x_{CO2}\right]\left[(1-\eta)x_{CO2}\ln\left\{(1-\eta)x_{CO2}\right\} + \left\{1-(1-\eta)x_{CO2}\right\}\ln\left\{1-(1-\eta)x_{CO2}\right\}\right]\right\} \tag{2}$$

Of note with this minimum energy is that the lower the concentration of CO_2 the lower the overall minimum energy for separation per mole of inlet gas. However, when considered on a basis normalized to moles of CO_2 captured, lower CO_2 concentrations result in higher minimum energy costs per quantity of CO_2. Note that a lower ambient temperature results in a lower minimum energy of separation.

For CO_2 capture applications, we are often interested in a final product of pure CO_2 compressed to 150 bar for pipeline transportation. The minimum energy of compression is 209.3 kJ/kg CO_2 to compress pure CO_2 from 1.01325 bar to 150 bar at an isothermal temperature of 289.6 °K. This was calculated through comparing the Gibbs energy at the compressed and non-compressed states using rigorous property data for CO_2 from NIST REFPROP[2].

2.2. Minimum Energy of Cryogenic Separation

Cryogenic CO_2 capture processes must cool the flue gas to desublimate CO_2. In an ideal process, the entire flue gas cools uniformly to the temperature at which 90% of the CO_2 changes phase. At this point, the solid CO_2 separates from the gas phase, is pressurized, and each stream returns to ambient temperature. The CO_2 produced is in a dense phase, it is possible to compress CO_2 while it is a solid or a liquid minimizing the energy of compression.

The minimum energy of compression is the least amount of work that has to be performed on an object to change its pressure. This can be expressed as:

$$W_{comp,\min} = -\int_{v_1}^{v_2} P dv \tag{3}$$

Where $W_{comp,\min}$ is the minimum compression work, P is pressure and v volume of the material being compressed from state 1 to state 2. For a gas with large volume and large volume changes, the compression energy is significant. For near-isochoric solids and liquids, this work becomes almost negligible as it is less than 1 kJ/kg CO_2 which is <0.5% of the gaseous compression work requirement as calculated from state-point ΔG calculations using Refprop[2].

The minimum energy to cool the flue gas and condense the CO_2 can be calculated by considering the total cooling requirement at each temperature and multiplying by the Carnot efficiency of providing cooling at those temperatures. The Carnot efficiency is the maximum amount of work that can be extracted via a heat engine per unit of thermal energy input. This efficiency is expressed as equation 4. This efficiency can be used to calculate the reversible work supplied or consumed via a heat engine according to equation 5.

$$\eta_{carnot} = (1 - {T_0}/{T}) \tag{4}$$

$$W_{rev} = Q * \eta_{carnot} \tag{5}$$

where W_{rev} is the reversible work that can be extracted, Q is the thermal input at temperature T, and T_0 is the temperature of ambient heat transfer. Note that at temperatures $T<T_0$, heat addition Q yields a negative W_{rev} reflecting that work can be extracted by heating a sub-ambient stream while cooling a sub-ambient stream requires work input.

For a given temperature and enthalpy profile, we can then use this efficiency measure to calculate the total amount of reversible work that could be generated or needs to be provided. This is also the amount of work that would be required to recreate the temperature and thermal flux profile from an environment at the ambient temperature. By summing the amount of cooling work required to cool the flue gas and the amount of work that can be extracted from the cold CO_2 and flue gas streams as they are heated up to ambient temperature, a minimum work of cryogenic capture processes can be calculated.

The temperature–enthalpy profile can be described by cooling a representative flue gas from the ambient temperature to the temperature at which the desired percentage of CO_2 has formed a solid. Initially, the cooling requirement for each step in temperature is determined by the specific heat of the gas stream and heat of phase change for water vapor forming liquid water. Below 0°C, the thermal requirement is determined by the specific heat of the gas stream and the heat of phase change for water vapor forming ice. From the CO_2 frost point of approximately 172 K (-101 °C) until the final temperature, the thermal requirement is determined by the energy of phase change for gaseous CO_2 forming a solid and the specific heat of the remaining gas stream.

Once the streams are separated into a solid CO_2 stream and the remaining gases at the minimum temperature achieved, a temperature-enthalpy profile for each stream can be created while they are warmed back up incrementally. There is no phase transition in the light-gas stream so only sensible energy needs to be considered. For the solid CO_2 stream, any excursion into the vapor-phase is to be avoided due to large compression costs. Instead, compression to just above the triple point pressure as a solid yields the lowest melting point temperature and the largest energetic benefit of melting. The maximum work that can be extracted from the liquid CO_2 via an ideal heat engine occurs when the CO_2 is compressed to its final pressure and then warmed to ambient temperature.

2.3. Deviations from Minimum Energy Cryogenic Systems

Real cryogenic carbon capture systems cannot perform as well as the idealized process. The idealized calculations assume that there is no heat transfer resistance and that all heat exchange is isothermal. Similarly, the assumption that all heat at any temperature can be converted reversibly to work at the Carnot efficiency is invalid and even approaching that ideal would be prohibitively expensive. Instead, due to similar thermal fluxes at similar temperatures for streams that need to be cooled and streams that need to be warmed, thermal recuperators and heat exchangers can be employed. The temperature difference throughout the thermal recuperators is of prime importance in determining the amount of exergy lost in the heat transfer.

Further differences between the available cooling and the required cooling occur due to mismatches in the temperature at which phase change occurs. During CO_2 deposition, the equilibrium CO_2 partial pressure drops as the temperature decreases. This leads to a gradual phase change over a range of temperatures. However, the CO_2 melting occurs over a very narrow range of temperatures as the purity of the solid and then liquid CO_2 is high and pure components have a single melting temperature at a given pressure. The melting temperature also occurs at a higher temperature than the deposition temperature, which requires additional process steps to make use of the phase change enthalpy.

Other non-idealities in a real system include pressure drop through the system for both the refrigerant and the flue gas, non-isentropic rotating machinery, non-isothermal compression and expansion, and additional process steps including dehydration and additional or non-ideal mixing and purification steps.

3. Results

3.1. Idealized Cryogenic CO_2 Separations

A study of idealized cryogenic carbon capture systems was performed as described in section *2.2*. The proportion of CO_2 captured is determined by the CO_2 vapor pressure at the coldest temperature achieved by the flue gas. For the flue gas described in the NETL Bituminous baseline Rev. 3 case B12B[3], with 15.02 mole % CO_2 on a dry basis, 90% capture occurs at a temperature of 155K and 99% capture at 140K. The enthalpy-temperature profile for this cooling is shown in the dashed lines of figure 1.

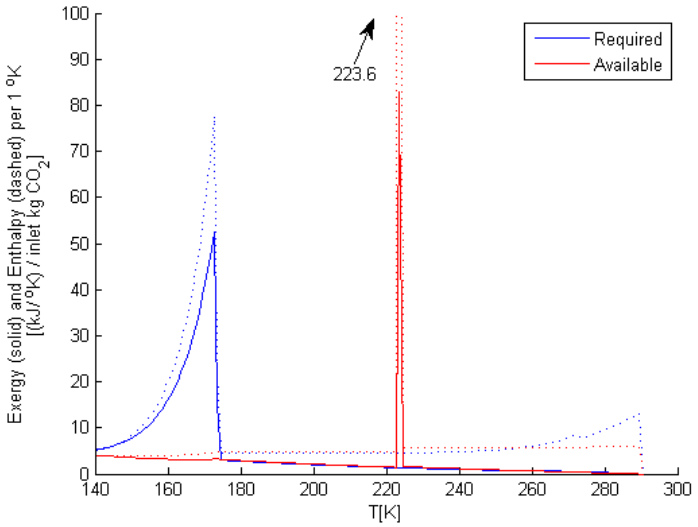

Fig. 1. Chilling enthalpy (dotted lines) and exergy (solid lines) available and required per degree of cooling for an ideal cryogenic capture process. The peak of the available cooling line extends beyond the scale of the graph to a maximum value of 223.6 kJ/K kg CO_2 inlet.

while the exergy-temperature profile is illustrated with solid lines. The required chilling enthalpy has two major excursions from the flat line that would indicate a constant Cp cooling. These are the moisture removal that peaks at the highest temperatures and the CO_2 removal that peaks at the CO_2 frost point of 172 K. The chilling enthalpy available is flat other than the excursion at the melting point of solid CO_2 above the triple point. At temperatures close to the ambient temperature, the exergetic impact of the enthalpy transfer is small. As the temperature drops, the absolute value of the Carnot efficiency $\eta_{carnot} = (1 - T_0/T)$ increases, which increases the exergetic impact. The ambient temperature is taken to be the cooling water temperature of 289.6 °C from the NETL baseline report[3]. The minimum work is calculated by taking the difference in areas between the required chilling exergy and the supplied chilling exergy. In the ideal case the separation work must be supplied as cooling to overcome the heat of phase change released by CO_2 undergoing deposition. This is because the cooling and warming streams have well matched specific heats and only the additional energy associated with phase change needs to be supplied.

Parametric studies of this ideal system were studied to understand the performance of cryogenic systems. The CO_2 capture fraction is determined by the vapor pressure of CO_2 at the lowest temperature of the flue gas in the process. 90% capture is achieved at 155 K, 95% at 150 K and 99% at 140 K. For cryogenic systems, the additional incremental work required for capture increases in proportion to the Carnot efficiency as the temperature decreases. However, because the majority of the chilling work has already been performed and the quantity captured at the low temperatures is relatively small, the impact on the overall minimum capture work is small as seen in figure 2.

The assumption for our ideal case that heat transfer is isentropic and reversible can also be modified by comparing the effect of minimum heat transfer approach temperatures. This can be implemented through assuming that the streams requiring cooling have to be cooled by a stream at temperature T-ΔT, and the streams providing cooling can do so at a minimum temperature of T+ΔT. The substantial effect of ΔT can be seen in figure 2.

The minimum ideal chilling work required for capturing and compressing 90% of the CO_2 is calculated to be 375.1 kJ/kg CO_2 at 90% from an ambient temperature of 289.6 K. This value is 4.5% higher than the calculated minimum work of separation of 359.1 kJ/kg CO_2 which is comprised of 149.8 kJ/kg CO_2 for 90% capture plus 209.3 kJ/kg CO_2 for CO_2 compression to 150 bar. The discrepancy between these minimum values can be explained in large part due to the moisture removal from the flue gas stream and the additional cooling required to overcome the latent heat of vaporization and sublimation of the condensing moisture.

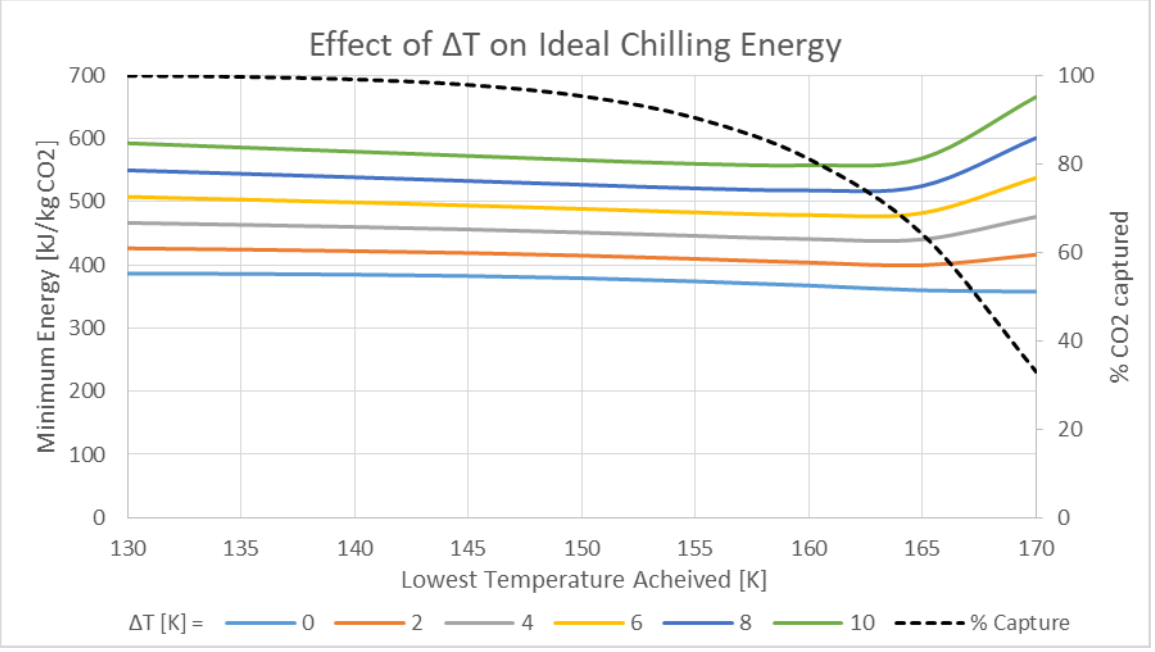

Fig. 2. Effect of ΔT on ideal cryogenic CO_2 capture processes.

3.2. Sustainable Energy Solutions

Sustainable Energy Solutions LLC (SES) has developed and field tested their Cryogenic Carbon Capture™ (CCC) process for capturing CO_2 through deposition at low temperatures. This process is designed to operate on either scrubbed or raw flue gas from a natural-gas-, biomass-, coal-, or waste-fired combustor or power plant. SES has developed and operated a skid-scale version of the process on fuels that include biomass, natural gas, bituminous and subbituminous coal, shredded tires, and municipal waste and at host sites that include several utility boilers, two cement plants, heating plants, and pilot-scale reactors. The CCC process dries and cools flue gas from existing systems, compresses it to overcome the system pressure drop, cools it to a temperature slightly above the CO_2 frost point, condenses CO_2 in a patented desublimating heat exchanger, precipitating an amount of CO_2 as a solid that depends on the final temperature, pressurizes the CO_2, and reheats the CO_2 and the remaining flue gas by cooling the incoming gases. The final product is the CO_2 in a liquid phase and a cleaned flue gas stream that is primarily nitrogen at near ambient temperature. A simplified process flow diagram of this process is shown in figure 3.

EPRI has performed an independent analysis of the CCC process as part of NETL award FE-0028697. While the process and configuration are undergoing continued development, evolution, and optimization, the results of this analysis can serve as a benchmark and to guide development of cryogenic capture systems.

While the CCC process looks broadly like the idealized capture system described above, several concessions to physics are necessary to implement the process. Flue gas dehydration to -100 °C dewpoint (sub 0.1 PPM moisture) requires significant contacting area and a material with strong affinity for moisture that then must be regenerated. A packed bed of zeolites regenerated with warmed dry, CO_2-free flue gas stream was considered for this evaluation. While the energy impact of regenerating the bed is minimal, the pressure drop for the flue gas to flow through the packed bed twice – once for dehydration, once for bed regeneration – has a significant impact. SES has developed an alternative cooling and drying process to minimize these issues.

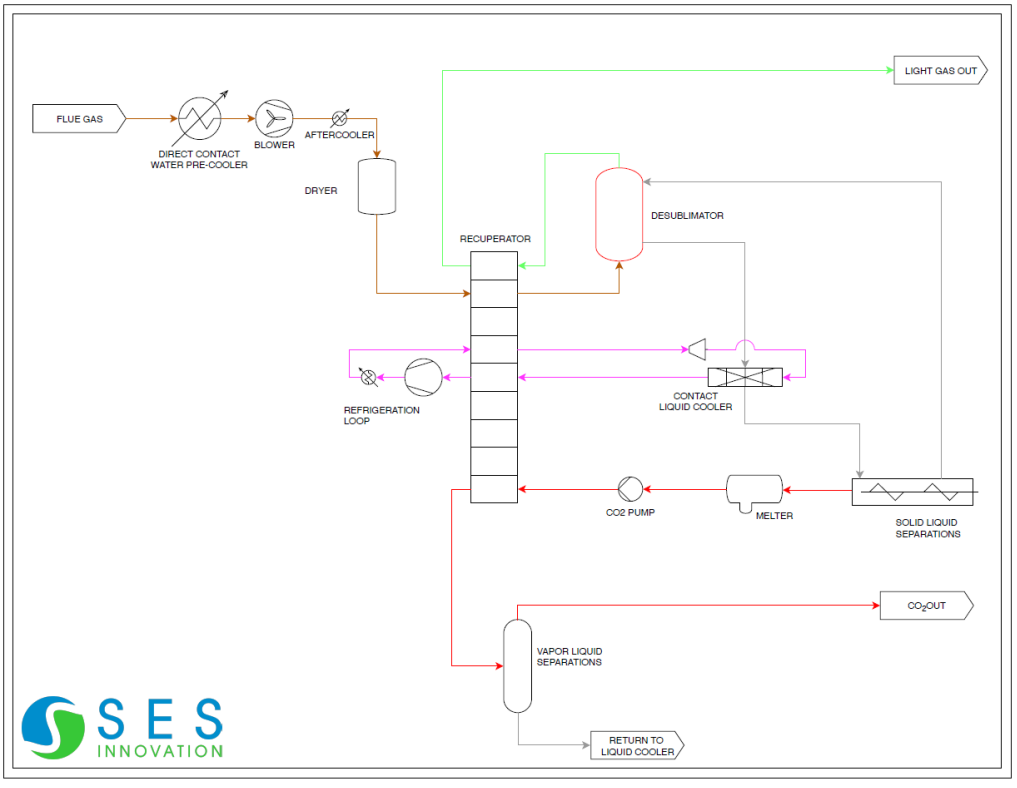

Fig. 3. Simplified flow diagram of SES CCC process.

The majority of the thermal integration of the system occurs in the large recuperating heat exchanger. This entails the flue gas cooling, clean flue gas warming, and product stream warming, refrigerant warming and cooling, and heat exchange involved in product purification. For a heat exchanger with this many streams, full system integration and selection of refrigerants and refrigerant mixtures and loops is vital to minimize lost work due to heat transfer.

The solid CO_2 deposits in a desublimating heat exchanger onto a contact fluid. CO_2 forming a solid on a solid heat transfer surface can lead to plugging heat exchangers and does not allow for easy collection of CO_2. The CCC process uses a cold contacting liquid to cool the flue gas beyond the CO_2 frost point and cause CO_2 deposition onto the droplets of the contacting liquid. The solid CO_2 and contacting liquid slurry flows through the system without plugging. However, an additional step is then required to separate the CO_2 from the contacting liquid. This entails a physical solid-liquid separator in the form of a screw-driven filter-press for bulk separation which also serves to increase the pressure of the slurry to above the triple point of CO_2. After the product CO_2 with trace contacting liquid melts to form a liquid, an additional purification step increases the product purity and recovers the contacting liquid.

The evaluation of the process included rigorous modeling of all process operations and integration in Aspen Plus. Where solids formation and handling was required, separate modules developed in Matlab were implemented and integrated. The basis of evaluation is the NETL Cost and Performance Cost and Performance Baseline for Fossil Energy Plants, revision 3 case B12B[3], which is an aspirational target with better performance than existing technologies. Results from the evaluation are shown in table 1.

Table 1. Performance results for Sustainable Energy Solutions External Cooling Loop CCC process.

	Work required for CCC [KJ/kg CO_2]	Percent of TMCW
Theoretical minimum chilling work (TMCW)	375.1	--
Losses from heat exchangers	101.7	27.12%
Pumping work (solids + liquids)	32.2	8.59%
Process losses (purification, refrigerant dP)	83.6	20.54%
Total thermodynamic work (TTW)	586.1	156.25%
Thermodynamic losses	85.6	22.83%
Overcoming gas pressure drop	256.8	68.47%
Total energy consumption	928.6	247.55%

The total energy consumption translates to an 18.85% reduction in total power plant output due to the CCC process compared to the same unit with no CO_2 capture. This uses 6.8% less energy than the equivalent 3 B12B from capture unit with 20.23% lost electricity. The net HHV efficiency of the plant with CO_2 capture of 33.06% compares favorably to HHV net efficiency of 32.5% in case B12B.

4. Discussion

Overall, the SES CCC process shows the potential for reduction in lost electrical output compared to NETL amine scrubbing base case. The major areas of irreversible work loss in the SES CCC system are the heat exchanger losses, the process losses, the thermodynamic losses, and the losses due to pressure drop.

The parametric studies on the impact of increasing the heat transfer approach temperature indicate an approximately 4.8% loss compared to the theoretical minimum chilling work per °C increase in ΔT. Using that result, the heat exchanger losses of 27% of the theoretical minimum chilling work calculated in the SES performance results would indicate a ΔT of 5.6 °C. However, there are more heat transfer streams in the real process compared to the idealized process. These include additional heat transfer to and from the direct contacting liquid, recuperator heat loss from refrigerant streams, and heat streams associated with purification. Minimizing the heat loss from heat transfer can be accomplished by minimizing the approach temperatures in heat exchangers, especially at low temperatures and decreasing the number of streams that need to be heated and cooled. However, lower approach temperatures require larger surface area equipment with higher capital cost and higher pressure drop through the system. We note that the

heat transfer losses calculated for this paper may be further reduced as the losses were calculated using a different set of properties data than the original optimization.

The thermodynamic losses in the process incorporates the added work due to the inefficiencies in spinning machinery including pumps, compressors, and turbines. Increasing the efficiency of the compressors, especially the main refrigerant compressors for the vapor compression cycle is the main approach to minimizing these losses.

One of the largest components of lost work is described as process losses. This is the difference between the thermodynamic work performed in the system and the theoretical minimum work that would have to be performed plus all measured losses. This includes the direct effects of additional process steps, such as separation of CO_2 from the contacting liquid, dehydration, and pressure loss within refrigerant and internal loops, but does not capture the additional heat-transfer losses due to additional flow paths.

The single largest driver of the total energy consumption is in compression to overcome the flue gas pressure drop. The flue gas flow path includes direct contact cooling, compression, aftercooling, dehydration in a packed bed, heat exchange at low ΔT approach for over 100 °C, direct contact cooling and CO_2 removal in the desublimating heat exchanger, warming back to ambient temperature with low ΔT approach for over 100 °C, and passing through the dehydration packed bed to regenerate the sorbent. In addition, at the flow rates representative of power plant flue gas, rapid flow is desired through these unit operations to minimize the total size of the system resulting in an overall pressure drop of 50 kPa. This pressure drop can be reduced through reducing the flow velocity through each unit, though that results in larger equipment, or in using more open geometries in the direct contacting systems and heat exchangers. The largest reduction could be through redesigning the dehydration process to eliminate the packed bed and use a low-pressure drop dehydration that does not require a double-pass to regenerate, as is already being developed by SES.

5. Conclusions

The idealized minimum energy of CO_2 capture via phase change and pumping CO_2 to pipeline pressure has been calculated to be substantially the same as the theoretical minimum energy of separation. However, there are difficulties associated with realizing the idealized cryogenic minimum energy configuration. These difficulties are primarily complications stemming from the CO_2 deposition to form a solid below the triple point pressure of 517 kPa. The SES CCC system provides a real-world example of a process that addresses many of the challenges of cryogenic carbon capture and independent analysis and process simulation show an improvement over the NETL baseline advanced amine energetic performance. Further improvements to the SES CCC process are possible and show cryogenic carbon capture as a promising route to lowering the energetic cost of CO_2 capture from post-combustion flue gas streams.

Acknowledgements

This material is based upon work supported by the Department of Energy under Award Number DE-FE0028697

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