

Cryogenic CO₂ Capture to Control Climate Change Emissions

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Abstract

An innovative CO₂ capture technology called the cryogenic CO₂ capture (CCC) process has significant energy and cost advantages compared to alternatives. The process is a post-combustion technology that cools CO₂-laden flue gas to desublimation temperatures (-100 to -135 °C), separates solid CO₂ that forms from the flue gas from the light gases, uses the cold products to cool incoming gases in a recuperative heat exchanger, compresses the solid/liquid CO₂ to final pressures (100-200 atm), and delivers a compressed CO₂ stream separated from an atmospheric pressure light-gas stream. The overall energy and economic costs appear to be at least 30% lower than most competing processes that involve air separation units (ASUs), solvents, or similar technologies. In addition, the CCC process enjoys several ancillary benefits, including (a) it is a minimally invasive bolt-on technology, (b) it provides highly efficient removal of most pollutants (Hg, SO_x, NO₂, HCl, etc.), (c) possible energy storage capacity, and (d) potential water savings. This paper outlines the process details and economic and energy comparisons relative to other well-documented alternatives.

Introduction

Energy and related environmental issues span national and regional boundaries and influence many generations. Their solutions require comparable scope and duration. Many people envision a future dominated by non-fossil energy generation, a dramatic departure from the current infrastructure. However, solutions to the most daunting energy issues cannot wait for a fossil-free energy future. There is a critical need for an energy supply and utilization infrastructure based on currently available processes that provides for current needs while greatly reducing the environmental consequences to future generations [1]. The global and multi-generational environmental concerns include traditional and climate-change pollutant emission, energy-driven water demand, resource depletion, and economics, all of which this center addresses. The program addresses several aspects of energy generation, as it is clear that no one topic will solve all of the problems [2].

Fossil fuels provide about 85% of US and global energy, making it unrealistic to imagine a near-term, fossil-free infrastructure. Fossil fuels also dominantly contribute to global climate change. Therefore, carbon capture and storage (CCS) looms large in any transitional energy infrastructure. A recently patented process for CO₂ removal from flue gas [3-5] portends a substantial decrease in both cost and energy consumption compared to solvent- and oxygen-based systems. Some of the detailed issues associated with this technology include (a) characterization (size distribution, morphology) of desublimated CO₂ particles, (b) particle separation from gases and subsequent pressurization of the

condensed phase at cryogenic temperatures, (c) process and scientific models of CO₂ removal as a function of operating conditions (temperature, pressure, composition) addressing CO₂ and trace gases (SO₂, NO, Hg, etc.), (d) standardized comparisons of CO₂ removal processes [6-8], and (e) providing laboratory-scale verification and validation of the predicted performance [6, 7, 9]. In these ways it is similar to the most thoroughly analyzed alternatives and some of their primary challenges, namely oxyfuel firing (burnout, deposit formation, heat transfer patterns) and combustor, gasifier, and pyrolyzer cofiring with biomass, including methods of increasing gasification and combustion efficiency and reliability [10-21].

Process Description

The cryogenic CO₂ capture (CCC) process (Figure 1) dries and cools flue gas from existing systems, modestly compresses it, cools it to a temperature slightly above the point where CO₂ forms a solid, expands the gas to further cool it, precipitating an amount of CO₂ as a solid that depends on the final temperature, pressurizes the CO₂, and reheats the CO₂ and the remaining flue gas by cooling the incoming gases. The final result is the CO₂ in a liquid phase and a gaseous nitrogen stream. CO₂ capture efficiency depends primarily on the pressure and temperature at the end of the expansion process. At 1 atm, the process captures 99% of the CO₂ at -211 °F (-135 °C) and 90% at -184 °F (-120 °C). These are relatively mild conditions as compared to competing processes, as is discussed next. Most alternative processes are not reasonably capable of achieving 99% CO₂ capture. Furthermore, the captured CO₂ has virtually no impurity in it. A thermodynamic feature of CO₂ in flue gases (< 15% CO₂ on a dry basis) is that the CO₂ will not form a liquid phase at any temperature or pressure. Rather, the CO₂ desublimates, forming an essentially pure solid phase rather than a liquid solution that must be distilled.

This process shares some similar unit operations with oxygen-fired combustion followed by CO₂ compression, often called oxyfiring and a competing CO₂ separation process. A comparison of the two illustrates the cost and energy efficiency advantages of CCC (Figure 2). A typical oxyfiring process (1) separates oxygen from nitrogen in an air separation unit (ASU) that includes compressors, expanders, heat exchangers and distillation columns; (2) fires the combustion process with nearly pure oxygen, producing a gaseous CO₂ and H₂O product (plus impurities); (3) recirculates a fraction of the CO₂ to manage the temperatures and heat loads in the boiler; (4) condenses the water in the exit gas to produce a nearly pure CO₂ product; and (5) compresses the resulting CO₂ stream to nominally 100 bar. The steps that consume the greatest energy appear in the top of Figure 2. By comparison, the CCC process deals with a slightly lower volumetric flow rate of gases leaving the combustor on a dry basis compared to the dry volumetric flow rate of air entering the combustor with which the oxyfiring system deals. More significantly, the lowest temperatures in the CCC process range from -211 °F (-135 °C) to -184 °F (-120 °C), depending on desired capture efficiency. By comparison, the lowest temperatures in the ASU are about -328 °F (-200 °C), leading to higher losses in the cooling cycles, requiring more energy for cooling, and constraining quite severely suitable materials of construction. More significantly still, the CCC process compresses a solid/liquid CO₂ stream whereas the oxyfiring process compresses a gaseous CO₂ stream, both from nominally atmospheric pressure to about 100 atm. Solids and liquid compression requires a very small fraction of the energy required for gaseous compression. Finally and most significantly, the CCC separates solid CO₂ from nitrogen, a far less capital and energy intensive task

than separating oxygen from nitrogen. The distillation stages in an air separation unit and the associated gas compression and cooling represent the most energy intensive portion of an ASU.

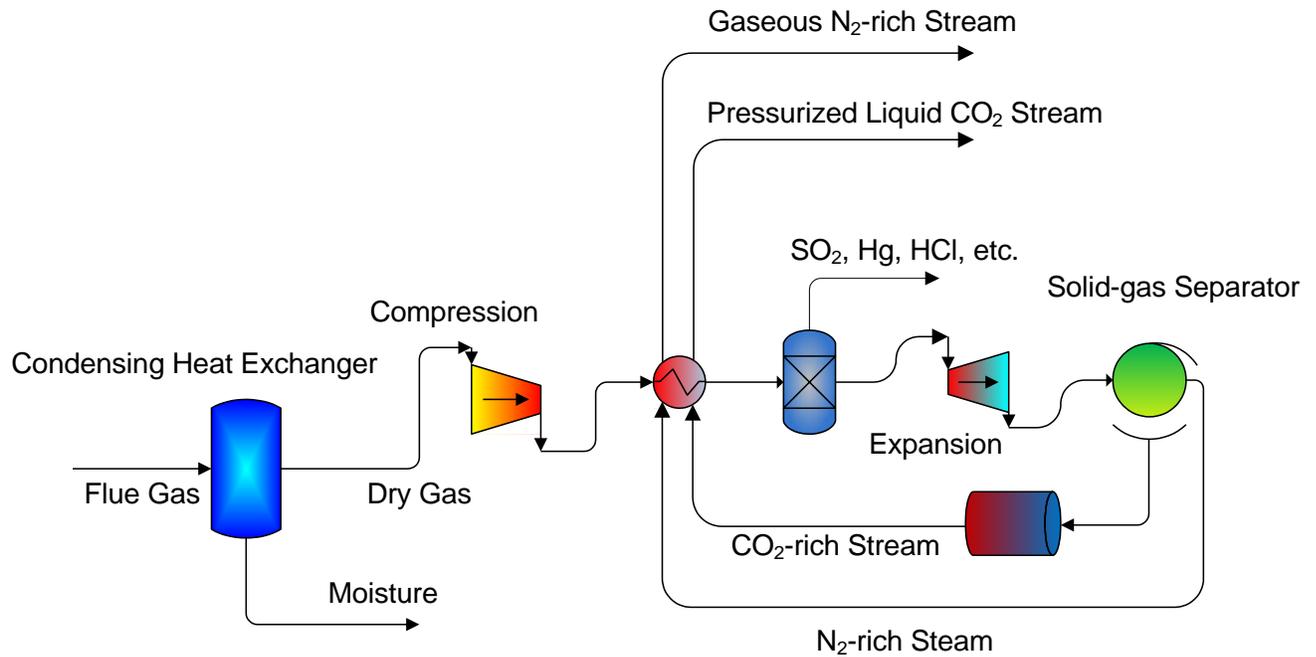


Figure 1 Simple schematic diagram of the cryogenic carbon capture (CCC) process.

As indicated later, the oxyfiring process has about the same energy and cost performance as the alternative (mostly solvent-based) processes. The solvent-based systems differ in more significant ways from the CCC process and the systems do lend themselves to step-by-step comparisons. However, the CCC process also handily outperforms the solvent-based systems, primarily because the solvent-based systems require a large mass of solvent to be cyclically heated and cooled (or in some cases pressurized and depressurized) to produce a comparatively small amount of CO₂. The energy invested in the cyclical heating and cooling represents a major entropy source and hence energy sink in the process. Such cyclical and energy-intensive steps that involve the same materials generally represent the largest energy sinks in all of these processes. The analog in oxyfiring is the reflux in the distillation columns. By comparison, there are no materials in the CCC process that cyclically change temperature, pressure or phase. The flue gas heating and cooling always involves new flue gas. In this sense, aside from losses in compression, expansion, and heat exchange, this process consumes no energy other than that required for the phase change and separation. That is, the CCC process has no embedded cycles that primarily produce energy.

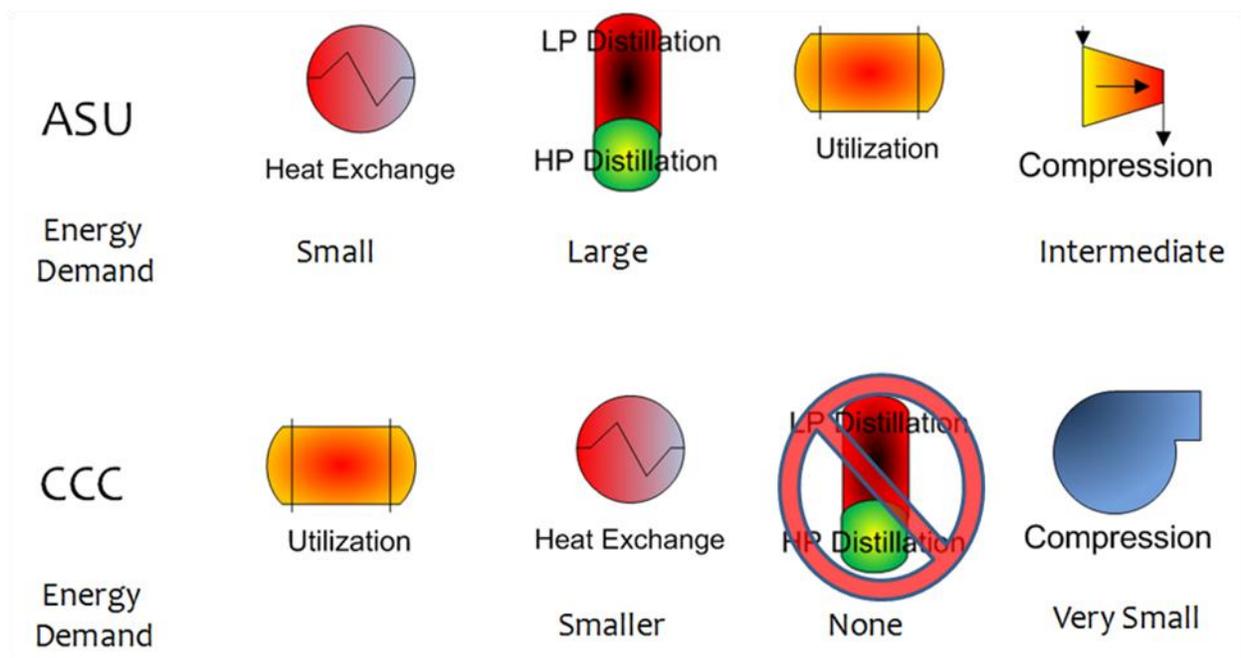


Figure 2 Comparison of the primary energy demands in an air-separation-based unit and in the cryogenic carbon capture process.

Ancillary Advantages

In addition to the cost and energy efficiency advantages, the CCC process enjoys several ancillary benefits, including leveraging of existing capital investments, pollutant control, water savings, and potential energy storage. Each of these are discussed below, followed by some quantitative estimates of the costs of the CCC process.

Retrofit Technology

This CCC process can be installed either as a bolt-on retrofit technology or as an integrated technology. The bolt-on option makes this technology highly attractive for existing assets and for permitting new assets. In this configuration, essentially no changes to the existing facility are required. The flue gas is intercepted prior to the stack and flows through this process without modification of upstream systems. The only major requirement is that enough footprint is available for the new equipment (compressors and turbines).

Retrofitting existing plants leverages existing capital investments, improving project economics markedly. The economics of carbon capture processes that require new plant construction or significant alteration of existing plants often are dominated by the levelized plant capital costs, that is, the levelized capital expenses for the new/modified plant exceed all other costs. If permitting costs and construction costs and delays are also incurred, the new/modified plant becomes by far the largest cost element in the project. A retrofit technology such as CCC mitigates most of the problems and substantially reduces cost.

Pollutant Control

There are several compelling benefits to a fully integrated installation. The cooled, compressed gases make it possible to extract SO₂, NO₂, HCl, and Hg (among other things) in condensed-phase forms with efficiencies that exceed current best available control technologies. NO does not condense as readily as the previous gases and will need alternative treatment, but pressure and temperature regimes of this process offer alternative means of removing NO that may reduce costs as well. Therefore, a green-field, fully integrated plant can redirect the capital, operating cost, and footprint resources currently dedicated to SO_x, NO_x, and Hg control and redirect these toward the carbon capture system.

Reduced Water Use

The substantial energy savings of this process directly lead to significant cooling water decreases relative to other carbon capture processes. Additionally, a fully integrated installation can heat the pressurized, nitrogen-rich stream with the boiler to drive a light-gas turbine cycle which requires no cooling water. A pressurized nitrogen stream heated to the same temperature as typical steam turbine inlet temperatures (nominally 600 °C) generates power with approximately three times the efficiency as steam under similar conditions if the gas need not be recompressed. On a once-through basis, the steam is far more efficient than steam/water and avoids the cooling water load associated with water. This further reduces water demand by between 25-30%.

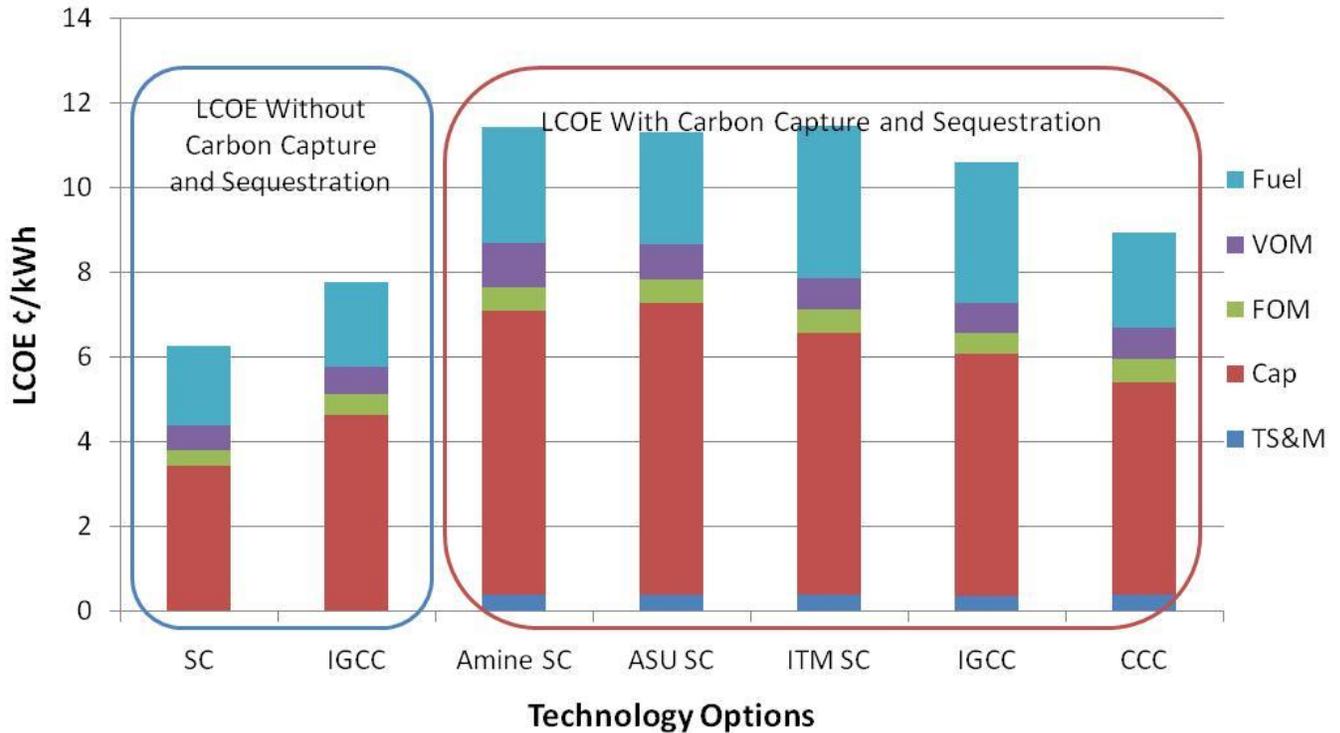
Energy Storage

Depending on the temperature and pressure of operation, the processes can produce a pressurized gaseous stream useful for energy storage. The CCC process is most energy efficient when the exiting light-gas stream is at atmospheric pressure. However, if the end-point pressure is above atmospheric, the gases do not need to be cooled as far for a given capture efficiency or the capture efficiency increases at a given temperature, improving the process performance. These performance increases couple with the energy storage potential of the compressed gas to provide a solution, or at least a partial solution, to what the authors believe one of the largest issues in CO₂ capture and storage – the impact on peak load generating capacity. The compressed gas could be released through a turbine or, better still, heated to higher temperatures and released through a turbine at peak load times to compensate for the capacity losses associated with carbon capture. The process would need to store enough compressed gas to last through the peaking period and would recompress gas at off-load times.

Performance Comparisons

Figure 3 illustrates estimated levelized costs for electricity for the proposed process (CCC) and several alternatives, including the fuel, fixed operating and maintenance (FOM), variable operating and maintenance (VOM), capital (Cap), and transportation, storage and monitoring (TS&M) costs associated with CO₂ management. Systems include supercritical pc combustion (SC), ultra-supercritical pc combustion (USC), integrated gasification combined cycle (IGCC), and CO₂ capture technologies based on amine scrubbing (Amine), air separation units (ASU), and ion-transport membranes (ITM). Aside from CCC, the costs come from US Department of Energy NETL-based analyses [8, 22, 23], with methods

and assumptions as similar as possible between the NETL-based systems and the CCC system. However, the extensive documentation of the NETL-based systems does not include many critical parameters, including such basic things as turbine and compressor efficiencies and costs associated with SO_x and NO_x control. NETL personnel indicate their commercial partners who helped develop the report asked that these numbers not be published and that the process simulations not be shared publicly.



which when coupled with the other advantages suggests it would be the process of choice among those reviewed here.

The cost savings stem primarily from two areas. First, the substantially lower energy demand discussed earlier also decreases the cost of the system. Second, the equipment available for this process is relatively simple and inexpensive. While the process operates at low temperatures, they are not so low as to require special materials. Essentially all equipment are essentially commodity items produced in large numbers by existing industry, albeit the size of the equipment required for a large coal-fired power plant would meet or somewhat exceed the largest sizes routinely produced by industry. Costs of this nature are always difficult to quantify and generally can be challenged on several fronts. However, the costing estimates done here have been done conservatively and as consistently as possible with those documented for the other processes. The relative costs are perhaps more reliable than the absolute costs.

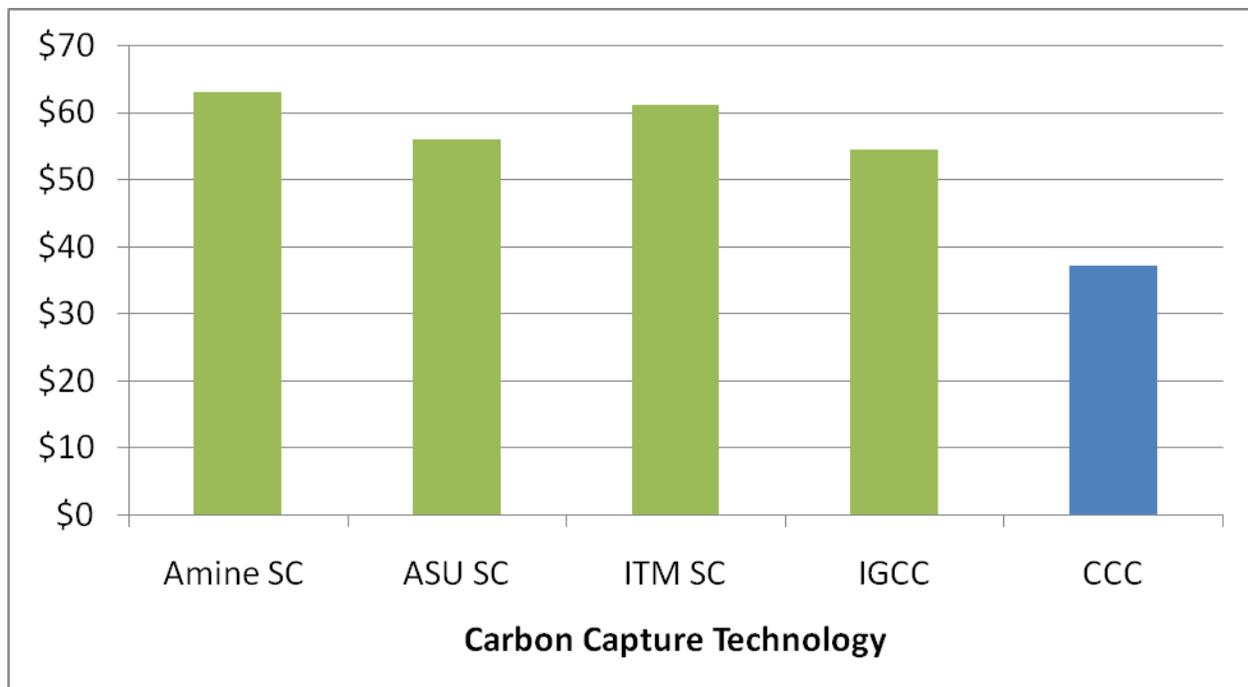


Figure 4 Estimated cost per avoided ton of CO₂ for a variety of processes and perturbations of these processes compared with the CCC process. Non-CCC data come from DOE reports [8, 22, 23].

Technical Details

Process models and detailed transport/thermodynamic analyses form the basis of the quantitative analysis presented here. The system thermodynamic performance plays a central role in this analysis and is discussed first. Following this discussion are more detailed process flow diagrams, analyses of energy storage, water conservation, criteria pollutant reduction.

Thermodynamics

The cool temperatures and high pressures encountered in much of this process lead to highly non-ideal thermochemical behavior, in particular as CO₂ and several pollutants, especially SO₂, are concerned. In the ideal approximation, CO₂ mole fractions times total pressure (partial pressures) provides the same behavior as CO₂ vapor pressures. That is, in ideal systems CO₂ forms two phases through condensation or freezing whenever its partial pressure exceeds the vapor pressure of CO₂ at the same pressure.

Figure 5 illustrates the CO₂ phase diagram over a broad range of temperature (linear scale) and pressure (logarithmic scale). The solid lines separate regions of solid, liquid, and vapor, with the triple point and critical point indicated. Assuming a typical coal combustion flue gas with approximately 14% CO₂ in light gas, the various lines that are not solid indicate the combination of pressure and temperature at which CO₂ first condenses as either a liquid (dewpoint) or solid (frost point), and the conditions at which 90%, 95%, and 99% of the CO₂ is in the condensed phase. As indicated, higher amounts of capture require increasingly extreme conditions of higher pressure and lower temperature.

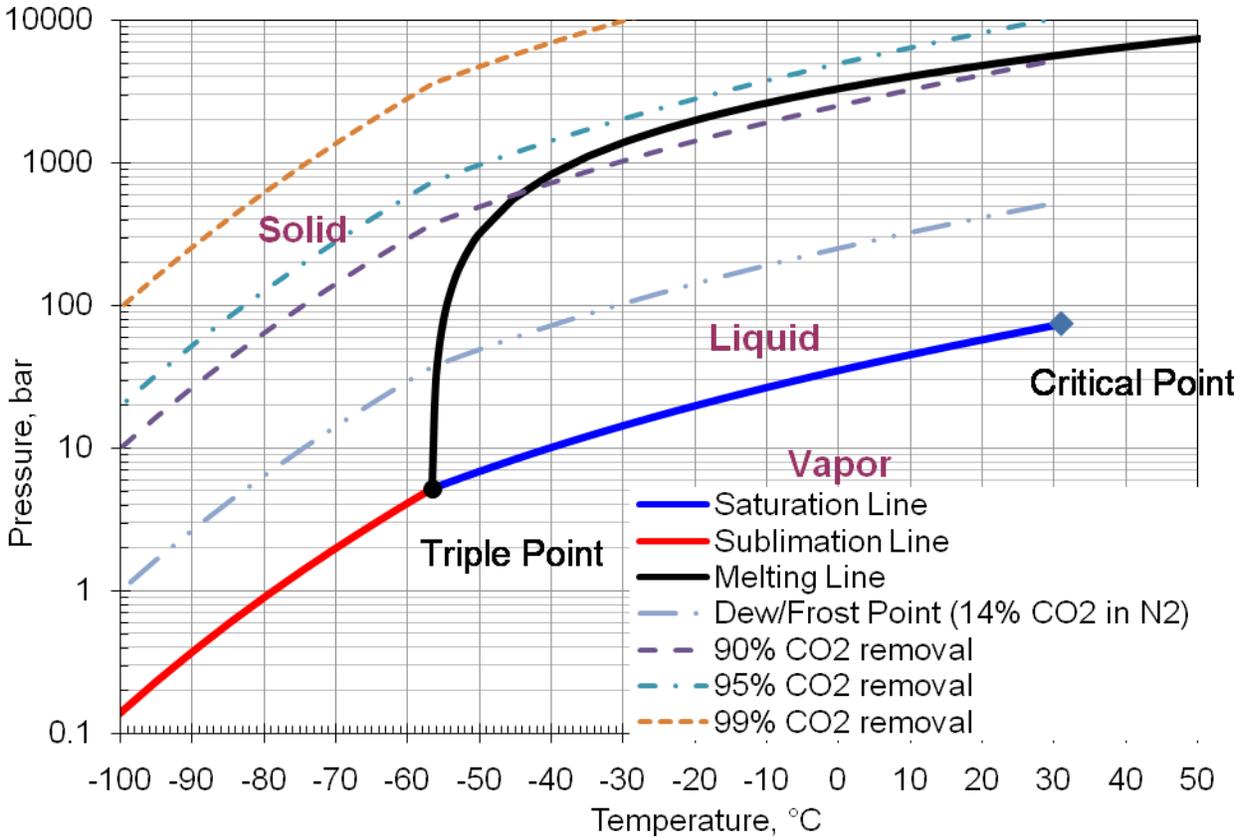


Figure 5 CO₂ phase diagram. The three solid lines separating the solid, liquid, and vapor regions are accurate. The dew/frost point line and the removal lines assume ideal behavior and 14% CO₂ in light gas and are conceptually instructive but not quantitatively, and in some cases not even qualitatively, accurate (see following plots).

The dewpoint and other lines are not quantitatively or even qualitatively accurate over the entire range of temperatures and pressures. That is, CO₂ in light gases does not form an ideal system under these conditions. In the liquid region, the liquid that forms is a mixture of CO₂ and light gases. More significantly, with 14% CO₂ in nitrogen, no liquid forms under any conditions of temperature or pressure. Nonideal thermodynamics of the binary CO₂-N₂ system appear with measured data [24] in Figure 6 at three temperatures ranging from 0 °C to -55 °C, near the CO₂ triple point. The data on the vapor and liquid branches of each curve represent corresponding endpoints of equilibrium tie lines in the two phases. No tielines appear to avoid clutter.

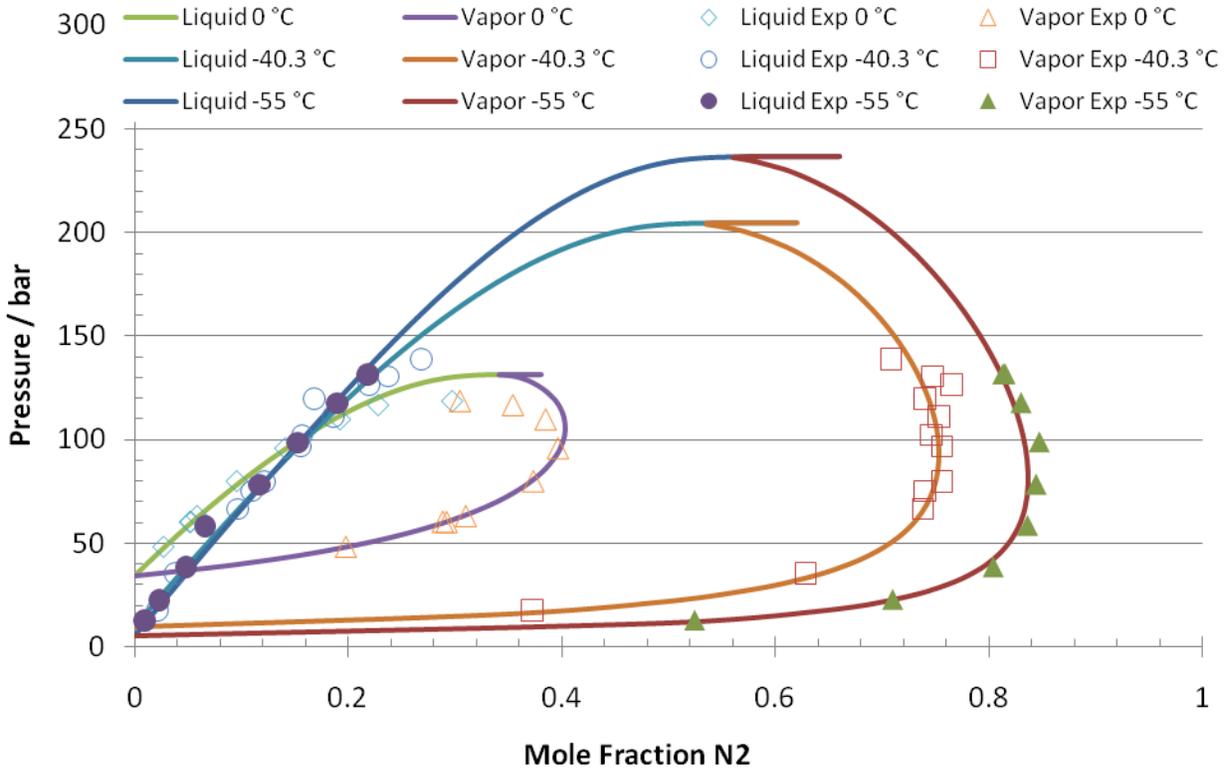


Figure 6 Binary CO₂-N₂ thermodynamic data and non-ideal predictions. Data are from [24]

The data and predictions agree reasonably well over most of the region and represent a substantial improvement compared with the ideal predictions. As temperature decreases, the size of the two phase region increases. However, decreasing the temperature further forms solid rather than liquid CO₂. At a nominal 14% CO₂ in nitrogen (typical flue gas), no liquid forms at any temperature or pressure, in stark contrast to ideal behavior shown in Figure 5. That is, the frost/dew point line for typical flue gases (14% CO₂) never enters the liquid-vapor region, unlike the Raoult's law estimates in the figure. This behavior presents some operational difficulties in that it requires solids handling. However, the formation of a solid represents a substantial thermodynamic and energy advantage since the solid that forms contains essentially no nitrogen or oxygen impurities and does not have to go through a subsequent distillation process. Liquid distillation in air separation units represents the largest energy demand, mostly associated with cooling for the condenser. The operational challenges associated with solids handling are discussed later.

The compressed gases contain small amounts of oxygen in addition to carbon dioxide and nitrogen. The oxygen contents change (generally decrease) the size of the two-phase region shown in Figure 6. Typical three-component data appear in Figure 7, for conditions of an average 129 atm and -55 °C. The left side of this diagram represents 0% O₂ and corresponds to the conditions in Figure 6 at 129 atm, as can be verified by checking the data. Increasing O₂ concentrations decrease the composition range over which two phases form. However, the changes are not overly complex. That is, the O₂, under these conditions, behaves much the same as an equivalent amount of extra nitrogen would behave. We have additional data at other pressures and temperatures. We are highly confident that we can provide thermodynamic

models capable of predicting the two-phase regions for the three-component $\text{N}_2\text{-CO}_2\text{-O}_2$ system, and the model predictions demonstrated above reasonably predict the two-phase region for the $\text{N}_2\text{-CO}_2$ system. However, we have not yet taken the time to regress the coefficients in the three- and higher-component models.

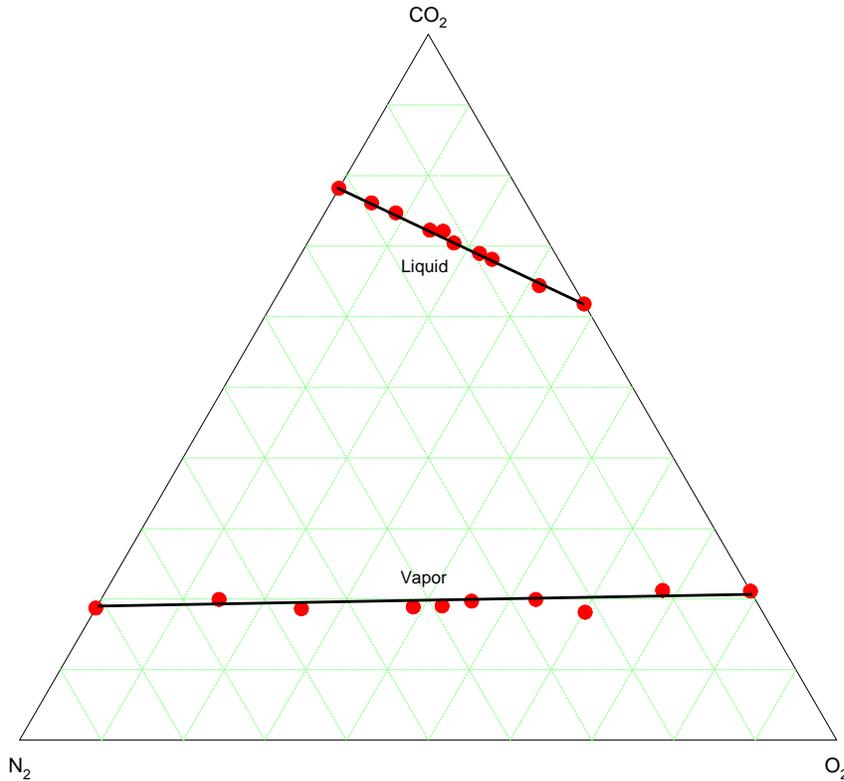


Figure 7 Three-phase $\text{N}_2\text{-O}_2\text{-CO}_2$ at $-55\text{ }^\circ\text{C}$ and an average 129 atm. Data from [24]

Thermodynamic data for typical flue gases including nitrogen- and sulfur-containing impurities at conditions of temperature and pressure of importance to this analysis do not exist. However, similar thermodynamic models used to predict the data above can be used to generate such data. A useful summary of such data relevant to this process appears in Figure 8, where the frost points (dry ice formation) for a typical dry flue gas containing 14% CO_2 , 3% O_2 , and trace amounts (100 ppm) of HCl , NO , and SO_2 . Corresponding conditions for 90%, 95%, and 99% of the CO_2 removed from the gas phase also appear. The labeled points correspond to the peak temperatures on each curve. To achieve any of the indicated performance points (frost formation, 95% CO_2 removal from the gas phase, etc.), conditions in the process at the point of separation must lie somewhere on the line.

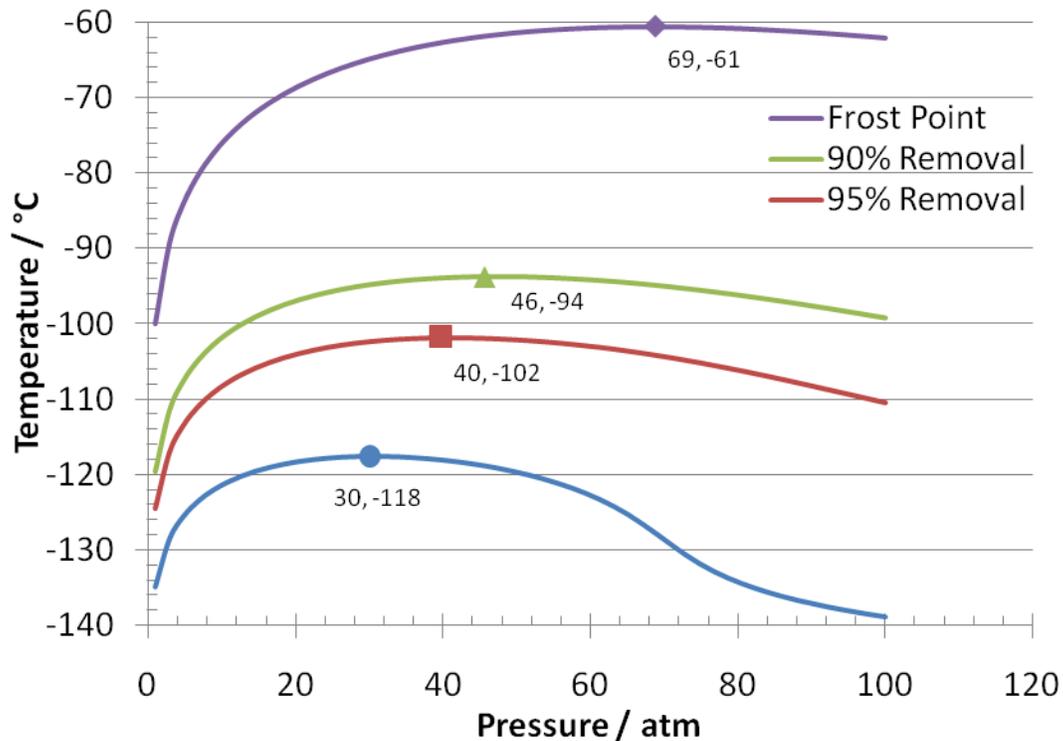


Figure 8 Frost/freezing points (dry ice formation) for a typical dry flue gas containing 14% (molar) CO₂, 3% O₂, and trace amounts of HCl, NO, and SO₂. Corresponding conditions for 90%, 95%, and 99% of the CO₂ removed from the gas phase appear as a function of temperature and pressure. The labeled points represent approximate peak temperatures on each curve.

As indicated, either high pressures or low temperatures, and in general both, must be achieved to remove the CO₂ by condensation/desublimation. The labeled points of the curve represent the highest pressures that would make sense in this section. That is, beyond these point, higher pressures and lower temperatures are required, both of which would require more energy. The portion of each curve up to this point is the functionally interesting option for this process.

Gas compression, cooling, and expansion generally provides the low temperatures indicated in Figure 8. This can involve either a closed-loop, typically nitrogen-based refrigeration system or can involve direct compression and expansion of the flue gas without a separate refrigeration cycle. The latter has the advantage that no additional temperature difference needs to be developed to drive heat transfer in a heat exchanger but has the disadvantage of a lower quality working fluid. Either process works, but this discussion assumes direct compression/expansion of the flue gas. The overall scheme is to compress and cool the gas to a sufficient pressure that its subsequent expansion through a turbine brings the gas near the frost point. The gas then further expands, typically through an expansion valve (turbines generally have low tolerance for condensation), until it reaches a temperature and pressure shown for a given fractional capture in Figure 8. In an externally cooled implementation, the second stage is accomplished in a heat exchanger rather than by expansion. A critical design parameter is the maximum pressure required to reach a condition along the curve representing the desired removal efficiency starting from a near room temperature initial condition.

Figure 8 provides some indication of the advantages of this process over air separation and oxyfiring. Traditional air separation units require much more cooling, for example to temperatures between -196 °C and -183 °C at 1 atm (50 to 60 °C cooler than the proposed process). Additionally, a series of two or three distillation columns revaporize and recondense the gases several times each, and the product CO₂ must be recompressed as a gas. All three of these considerations greatly increase the energy requirements for the system.

Conclusion

Cryogenic separation of CO₂ from flue gases represents a cost effective and energy efficient alternative to providing a pure and highly efficient separation of CO₂ from flue gas. The process advantages stem from (in approximate order of importance) (a) elimination of energy- and entropy-intensive cyclic separation processes such as distillation and absorption, (b) compressing a condensed phase rather than a gas, (c) somewhat smaller dry volumetric flow rates, and (d) several ancillary process advantages (bolt-on technology, energy and water savings, simultaneous treatment of pollutants).

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