Distillation Based CO2 Removal from Natural Gas for Small and Medium Sized Plant

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Abstract. The removal of excess CO2 from natural gas to levels as low as 50 ppm is essential for the safe and reliable operation of liquefied natural gas (LNG) transport and delivery systems. Current chemical purification techniques, which are suitable for large processing plants, might not be suitable for small or mid-size plants which are expected to operate in future LNG delivery networks. The feasibility of purification of natural gas (NG) from CO2 down to a concentration of 50 ppm by multi-stage distillation is studied. A three-column distillation system is proposed that can purify NG to lower than 50 ppm concentration of CO2, while avoiding CO2 freezeout. The columns include a 30-stage demethanizer, in which high purity methane is obtained in the distillate by separating the impurities from natural gas including CO2; a 50-stage extractive column where the azeotrope between CO2 and ethane is broken; and a 50-stage solvent recovery column that recovers a mixture of heavy hydrocarbons suitable for recycling as a solvent back into the extractive column. The proposed system avoids CO2 freezeout by utilizing a multi component feed of some heavier hydrocarbons added to natural gas; propane, butane and pentane additives are injected into stage 20 of the demthanizer column alongside the raw feed. Furthermore, arrangements are made to break the CO2-ethane azeotrope, which may occur in the bottoms stream of the demthanizer by administering a solvent stream in the extractive column. The proposed system can operate in a closed loop arrangement where the bottoms stream that leaves the recovery column can be recycled and injected into the extractive column for azeotrope prevention.

1. Introduction

The removal of CO2 from natural gas (NG) can be a challenging and expensive process. CO2 is naturally present in natural gas in amounts usually varying from 0.1 to 15% volume range [1, 2]. The current global energy demands dictate that we tap into new natural gas reservoirs with higher levels of contamination to meet our needs which were previously ignored owing to high extraction costs. This has led to the re-evaluation of extraction technologies aimed at developing better contamination removal methods and technology. Natural gas can be obtained from different sources and in this particular work we are using pipeline natural gas for our simulations. Our aim is to reduce the CO2 to commercially acceptable level of 50 ppm.

CO2 needs to be removed from NG for various reasons. CO2 provides no heating value and its removal improves the heating value of NG. The most important reason for CO2 removal from NG, however, is the prevention of solidification of CO2 during the transport and delivery of liquefied natural gas (LNG). CO2 freeze out in LNG transport and delivery operations can lead to plugged equipment and
other operational problems. Furthermore, CO$_2$ and other acid gases, including H$_2$S and SO$_2$, in the presence of water can corrode the pipelines as well as any equipment they may contact. One of the most common industrial processes is absorption which uses chemical or physical solvents. Currently the most widely used technique for CO$_2$ removal from natural gas is by chemical absorption using amines. The literature dealing with amine processes in great detail is extensive and includes [3-8].

While the aforementioned techniques of absorption work well for very large plants, for small and medium sized plants (10,000 gallon/day of LNG, equivalent to 37.85 m$^3$/s) they may not be economically viable. A promising alternative method that may be economic for mid-size plants is multi-stage fractional distillation, which utilizes the difference in volatiles of mixture components for separation. Species in the feed mixture undergo partial condensation or partial vaporization, and higher volatility species are preferentially boiled out. If the volatility differences are not large they cannot be separated in a single contact stage, and multiple vapor-liquid contact stages are required for adequate separation, and this is the basis for multistage distillation.

There are two technical challenges in the distillation-based removal of CO$_2$ from natural gas. The first problem is that the CO$_2$ freezes out in the demethanizer distillation column. CO$_2$ exists primarily as vapor-solid phase at typical demethanizer conditions. Significant research has been done on the CO$_2$-CH$_4$ phase equilibrium [9-12]. The phase diagram of CO$_2$-CH$_4$ shows why CO$_2$ freeze out poses a problem. The right side boundary in the phase diagram shown in Figure 1 [13] is the CO$_2$ vapor-liquid equilibrium while the left boundary is methane vapor-liquid equilibrium line. The unshaded region in between these lines represents the co-existence of equilibrium vapor-liquid phases of CO$_2$-CH$_4$. The shaded inner corner is the region of vapor-solid CO$_2$ equilibrium. To avoid freeze out we must steer clear of this shaded region. The critical pressure of CH$_4$ is 4.64 MPa (673 psia) [10], and is thus lower than the peak pressure of the solid region of CO$_2$, thereby making it impossible to get pure methane at a constant pressure without CO$_2$ freezeout as we will have to pass the solid region of CO$_2$, if substantial CO$_2$ is present in the mixture. Ryan and Holmes [13] altered the solubility characteristics of the CO$_2$-methane system by adding C$_3$+ hydrocarbons to the distillation column thereby circumventing the freeze out problem.

![Figure 1. Phase diagram of CO2-CH4 (after [13]).](image)

The other major problem associated with distillation-based removal of CO$_2$ from NG is that CO$_2$ and ethane, the second largest constituents of NG after methane, form an azeotrope in the bottom streams of distillation system, as will be discussed shortly. The ease of separation by distillation is closely related to relative volatility, which is a measure of the effective vapor pressure ratio of the key components that need to be separated. The ratio of vapor pressures cannot be changed appreciably by altering operating conditions. When the mixture consists of species where relative volatilities are at or near unity separation cannot occur by fractional distillation. Extractive distillation and azeotropic distillation methods are then used where a component called solvent or entrainer is used to alter the relative volatilities of the key components.
A recent study by Pellegrini [14, 15] shows an innovative new approach for CO₂ removal process that is based on dual pressure distillation. De Guiodo et al. [16] studied the effect of hydrocarbons heavier than methane on the dual pressure low temperature distillation process. An energy and exergy analysis by M. Baccanelli et al. [17] examined the differences in low temperature distillation, anti-sublimation and hybrid configuration purification techniques.

The objective of this investigation is to examine the feasibility of designing a multi-stage distillation based CO₂ removal system for LNG, where freeezeout of CO₂ and azeotropes are avoided, and to develop and theoretically demonstrate a self-sustaining, multi-tower pseudo-closed loop distillation system with solvent recovery which can be recycled back into the system. This is a more traditional approach which involves fewer distillation towers but at the same time, faces azeotrope formation challenges. Furthermore, operating pressures in this investigation are lower than most pressures found in the literature, and are consistent with current industry needs.

2. Method
Aspen Plus Version 9 [18] is used as the primary design and analysis tool. Aspen Plus is a process modeling tool for the design, optimization and performance monitoring in various applications including physical chemistry, mass-energy balance, thermodynamics, heat transfer, fluid mechanics, process design and control. It has been used in similar distillation studies extensively [19-22]. Aspen Plus simulation in steady state with Peng-Robinson physical properties is used in the current work.

2.1. Column I: Demethanizer column, D
To obtain industrial quality natural gas with less than 50 ppm of CO₂, a three-column system is used, as shown schematically in Figure. 2. We start by designing the first column which produces a stream of pure industrial grade methane (the demethanizer column).

The freeze out problem is particularly challenging because the demethanizer column is highly susceptible to CO₂ freezeout at the operating conditions at which distillation of methane and CO₂ is usually carried out. Comprehensive freeze-out analysis simulations were conducted in a different setup under identical conditions of temperature and pressure. It was found that, with the composition of the mixture kept constant, as pressure increases the freezeout temperature or the tendency of CO₂ to freeze out also increases. At constant pressure, as the concentration of CO₂ increases, the freezeout temperature also increases. Moving down the column stages, the operating temperatures increase giving the illusion that freeze out would occur at the top or the coldest regions of the column. However, the concentration of CO₂ also increases as we go down the column. This makes it necessary to perform freezeout analysis at every stage in the column. We adopted the concept of pseudo streams at each stage and performed freezeout analysis to ensure that no freezeout takes places anywhere in the system. A pseudo stream is a representative side product stream having zero velocity. Pseudo streams duplicate column internal streams and pump around as external streams without drawing material from the column. To ascertain the reliability of the freezeout utility function in Aspen, the utility function was tested separately and compared to the work of [23] which deals with similar mixture components. The freezeout utility function performed well and was able to match the results of [23].

2.2. Column II: Extractive column, E
The bottoms product of the demethanizer column comprises of CO₂, ethane, propane, butane and pentane, i.e. all the components of the feed natural gas minus the methane that has been extracted in the distillate of the demethanizer column. An azeotrope between CO₂ and ethane forms in this mixture. A second distillation column is therefore added to perform extractive distillation and break the azeotrope between CO₂ and ethane. A solvent stream consisting of heavier hydrocarbons inspired by [13, 19, 20, 24] is used in this extractive column. The solvent stream must be injected near the top of the column for best results. This approach works well, the azeotrope is broken and a very high percentage of CO₂ is extracted in the distillate. The bottoms product of the extractive column consists of ethane, propane, butane and pentane.
2.3. Column III: Solvent Recovery column, R
A self-sustainable system where bye-products of distillation can be recycled back into the system as solvent to the extractive column is aspired. Further analysis shows that a third column, referred to as the solvent recovery column, can be added to obtain a mixture of heavier hydrocarbons that works well as a solvent for breaking the CO\textsubscript{2} ethane azeotrope. Ethane is obtained as a distillate or light key component of distillation in this column.

The final step is solvent recycle implementation using the heavy component of the solvent recovery column. A stream splitter is fitted to the bottoms product of the solvent recovery column to control the fluid flow rate back into the extractive column, because more solvent is produced in the extractive column than is needed.

3. Results and Discussion

3.1. Feed and System Conditions

Figure 2. Schematic of a three column distillation system used in this work.

Figure 2 displays the schematic of the three column system that meets the aforementioned objectives of this investigation. The first column denoted by D represents the demethanizer column. The feed (natural gas) comprises of a multicomponent mixture of hydrocarbons like C\textsubscript{3}, iC\textsubscript{4}, nC\textsubscript{4}, iC\textsubscript{5} and nC\textsubscript{5}, as shown in Table 1. The feed natural gas is 85\% methane and contains other hydrocarbons and carbon dioxide occurring naturally in most reserves. The feed is preconditioned to -80°C temperature and 40 bars pressure. The feed flow rate, typical LNG demand of a small-sized plant, is 10,000 kmol/hr. The total number of stages in D is 30 and the feed is introduced at stage 20. As discussed earlier freezeout analysis is done at every stage to ensure smooth operation and thus 28 pseudo streams in between the top and bottom “real” streams are employed.

| Feed composition to demethanizer | CH\textsubscript{4} | CO\textsubscript{2} | C\textsubscript{2}H\textsubscript{6} | C\textsubscript{3}H\textsubscript{8} | n-C\textsubscript{4}H\textsubscript{10} | i-C\textsubscript{4}H\textsubscript{10} | n-C\textsubscript{5}H\textsubscript{12} | i-C\textsubscript{5}H\textsubscript{12} |
|----------------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Component                       | Mole fraction     | Mole fraction   | Mole fraction   | Mole fraction   | Mole fraction   | Mole fraction   | Mole fraction   | Mole fraction   |
| CH\textsubscript{4}             | 0.85              | 0.03            | 0.04            | 0.02            | 0.02            | 0.01            | 0.02            | 0.01            |
The second column denoted by E in Fig. 2 is the extractive column. The bottoms azeotropic mixture from D is injected at location T and the solvent is injected at location V. The feed composition to E (heavy stream distillation obtained from column D) is shown in Table 3. The total number of stages is 50, feed is injected at stage 26 and solvent at stage 3. In this case solvent injected at the top of the column is more effective in breaking the CO₂ – C₂H₆ azeotrope. Column E can be operated at a considerably lower pressure than D since all the methane has been separated from CO₂ and there is no risk of CO₂ freezeout. The recovery column is denoted by R and has a total of 50 stages, and operates at 24 bars. Some important parameters of columns D, E and R are summarized in Table 2.

| Column specifics | D  | E  | R  |
|------------------|----|----|----|
| Total stages     | 30 | 50 | 50 |
| Feed stage       | 20 | 26 | 15 |
| Solvent stage    | -  | 3  | -  |
| Pseudo streams   | 28 | 0  | 0  |
| Reflux ratio     | 2  | 3.3| 6  |
| Distillate to Feed ratio | 0.85 | 0.12 | 0.13 |
| Pressure (bar)   | 35 | 24 | 24 |

The simulations are sensitive to a number of parameters including the total number of stages, feed stage, solvent inlet stage, reflux ratio, operating pressures and solvent stream composition. Furthermore, since columns E and R are coupled, the solvent stream composition affects the distillation process in both columns to a great extent. The coupling of the latter two columns adds to the complexity of the simulations and causes sensitivity to a number of parameters.

3.2. Case Studies

Results are shown for three cases. Case I refers to using a solvent stream which has composition based on Hong and Kobayashi [26], and is an equal mixture of n-pentane and iso-pentane. Case II refers to a solvent stream which has a composition similar to the stream composition that is to be recycled from the solvent recovery column. The purpose of this case is to study how recycling can be implemented and how it can affect the overall system. It is also used to study how the coupling among the three columns can affect the system’s performance. Case III utilizes a flow controller (FC) or stream splitter to control solvent flow rate. For Cases I and II the solvent stream needs to be preconditioned. For these simulations they were preconditioned to -10°C temperature and 30 bars pressure. For Case III the solvent stream has the physical properties and composition of the recycle stream from the flow controller or stream splitter. The ratio of the flow being recycled to that being stored away for other industrial applications is 1:2.6. Table 3 shows the solvent stream composition for Cases I and II.

| Table 3. Solvent stream compositions used in Case I and II. |
|------------------|------------------|
| **Case 1: Arbitrary solvent composition to extractive column** | **Mole fraction** |
| n-C₅H₁₂           | 0.5              |
| i-C₅H₁₂           | 0.5              |
| **Case 2: Solvent stream composition similar to recycle stream** | **Mole fraction** |
| CH₄               | 0                |
| CO₂               | 0                |
| C₂H₆              | 0                |
Table 3. Case 2: Solvent stream composition similar to recycle stream (continued)

| Component | Mole fraction Case I | Mole fraction Case II | Mole fraction Case III |
|-----------|----------------------|-----------------------|------------------------|
| C\textsubscript{3}H\textsubscript{8} | 0.11 | 0.11 | 0.11 |
| n-C\textsubscript{4}H\textsubscript{10} | 0.11 | 0.11 | 0.11 |
| i-C\textsubscript{4}H\textsubscript{10} | 0.06 | 0.06 | 0.06 |
| n-C\textsubscript{5}H\textsubscript{12} | 0.388 | 0.388 | 0.388 |
| i-C\textsubscript{5}H\textsubscript{12} | 0.332 | 0.332 | 0.332 |

The distillation results for column D are shown in Table 4. As expected, the distillation results of column D are identical for all three cases. The final product as distillate in the demethanizer column is methane that has a CO\textsubscript{2} purity of greater than 99.99%. CO\textsubscript{2} is present in trace amounts in the distillate but is significantly below the acceptable limit of 50 ppm.

Fig 3(a) shows the temperature profile in column D from stage 1 to 30, and the freezeout temperatures in the corresponding stages. At all points in the D column the freezeout temperature of CO\textsubscript{2} is below the operating temperature, as desired. Stages 28 and 29 are the “pinch points” and represent the locations in the system where the difference in the actual temperature and the CO\textsubscript{2} freezeout temperature is the lowest. These are the stages that are most susceptible to freeze out. To a large extent the freezeout profile in Fig 3(a) can be explained by the concentration of CO\textsubscript{2} increasing in the lower stages (22 to 29) as can be seen in Fig 3(b). The composition of bottoms product of D, which acts as a feed to E, is listed in Table 5.

Table 4. distillation results of demethanizer column, D and extractive column, E.

| Component    | Demethanizer light stream | Extractive column light stream | Extractive column heavy stream |
|--------------|---------------------------|-------------------------------|--------------------------------|
|              | Mole fraction Case I      | Mole fraction Case II         | Mole fraction Case III         |
| CO\textsubscript{2} | 4.527 ppm                 | 4.527 ppm                     | 4.527 ppm                     |
| CH\textsubscript{4} | 0.9999                    | 0.9999                        | 0.9999                         |
| CO\textsubscript{2} | 0.99714                   | 0.98134                       | 0.93719                       |
| C\textsubscript{2}H\textsubscript{6} | 6.522e-04                 | 6.643e-4                      | 0.0212                         |
| CO\textsubscript{2} | 0.000371                  | 0.002545                      | 1.9e-05                       |
| C\textsubscript{2}H\textsubscript{6} | 0.181729                  | 0.181727                      | 0.1388                         |

Figure 3(a). Temperature profile of demethanizer column from stage 1 to 30 and the freezeout temperature at the corresponding stages
Figure 3(b). Mole fraction of methane and carbon dioxide in the demethanizer column from stage 1 to 30.

Table 5. Bottoms product of demethanizer column acts as feed to extractive column.

| Component     | Mole fraction |
|---------------|--------------|
| CH₄           | 2.564e-05    |
| CO₂           | 0.1999       |
| C₂H₆          | 0.2667       |
| C₃H₆          | 0.1333       |
| n-C₄H₁₀       | 0.1333       |
| i-C₄H₁₀       | 0.0667       |
| n-C₅H₁₂       | 0.1333       |
| i-C₅H₁₂       | 0.0667       |
| Total flow rate (kmol/hr) | 1500 |

The simulation results for the extractive column E are summarized in Table 4. Case I shows the best results by breaking the azeotrope to give 99.7% CO₂ in the distillate. The solvent used in case I is very close to an ideal solvent for this azeotrope. Case II and Case III give 98.13 % and 93.72 % pure CO₂, respectively, in the distillate. This is an instance that demonstrates how a very similar solvent composition can have a considerably different effect on the azeotrope as a result of coupling in Case III. The distillate obtained in R is 99.99% ethane. The results for column R can be seen in Table 3, as solvent composition of Case II is a reflection of the distillation process in R and represents the heavy stream composition which is recycled. Depending on the number of species that need to be separated additional distillation columns can be added and the relatively lighter hydrocarbon can be purified in the distillate products.

The aforementioned results confirm that in theory a distillation based CO₂ removal system for LNG is feasible. Evidently however, further study is needed in order to examine the energetic and economic aspects of such a system, in particular for commercial plant scales.

4. Conclusion

A methodology for the design of a multi-tower distillation system for the removal of carbon dioxide from natural gas was proposed and demonstrated by simulation. A three tower distillation system has been designed that can purify natural gas initially having 3% carbon dioxide to as low as 5 ppm of CO₂, and therefore render natural gas suitable for industrial applications with the carbon dioxide levels below 50 ppm. The system avoids CO₂ freezeout at all points, and ensures that CO₂ – C₂H₆ azeotropes are broken.
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