Distillation Based CO_2 Removal from Natural Gas for Small and Medium Sized Plants

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Introduction

- Removal of excess CO2 from natural gas to ~ 50 ppm is essential for the safe and reliable operation of liquefied natural gas (LNG) transport and delivery systems.
- 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 including:
- 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
- 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 can operate in a closed loop where the bottoms stream that leaves the recovery column can be recycled and injected into the extractive column for azeotrope prevention.

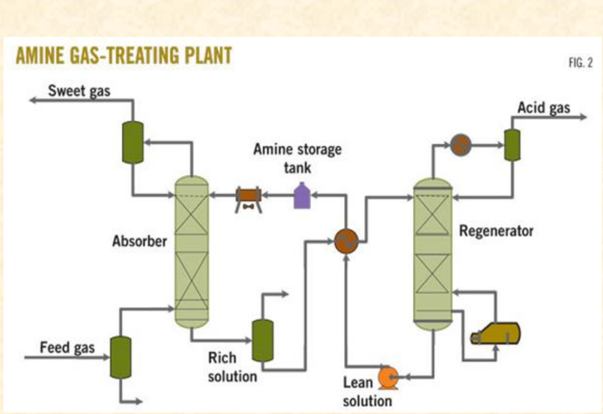
Why do we need to remove CO_2 ?

- Current global energy demands dictate we tap into new NG reservoirs with high levels of contamination
- Previously ignored owing to high extraction costs
- Climate change and global warming → companies leading towards greener practices and cleaner emissions
- CO2 provides no heating value
- Difficult to use in cryogenic applications:
  Freezing leads to plugged equipment
  Massive replacement cost, operating problems, plant shutdown
- CO2 (and other acid gases like H2S) corrode pipes and equipment in the presence of water

Separation Principles

Separation is based on:

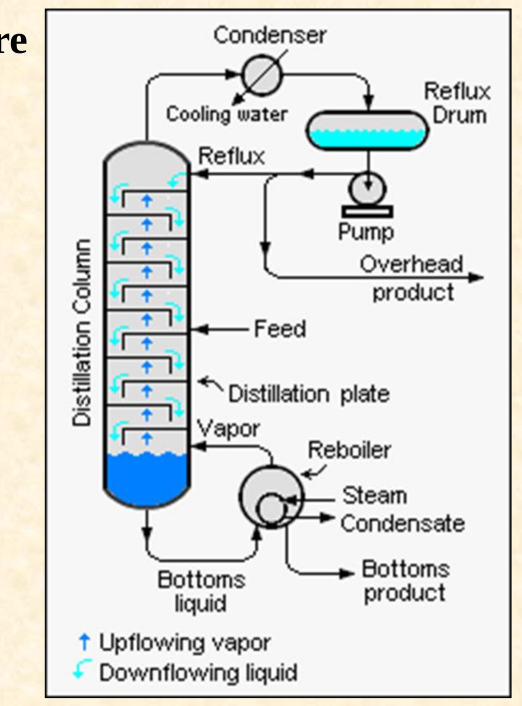
- **Molecular properties**
  -- Kinetic diameter, polarizability, molecule moments
- **Thermodynamic and transport properties**
  -- Vapor pressure, boiling points, solubility, absorption



- Most common industrial process is absorption using physical or chemical solvents
  -- Chemical absorption using amines → exothermic reaction follows and amines act as a solvent to remove the acid gases
  Commercially feasible at large industrial scales

Separation Principle: Distillation

- Distillation separation principles are based on differences in in relative volatilities of mixture components
- Mixtures create liquid and vapor phases that have different species concentrations
- Higher volatility species are preferentially boiled out
- Usually need multiple vapor-liquid contact stages for adequate separation
- For mall and medium scale plants absorption techniques are not economically viable

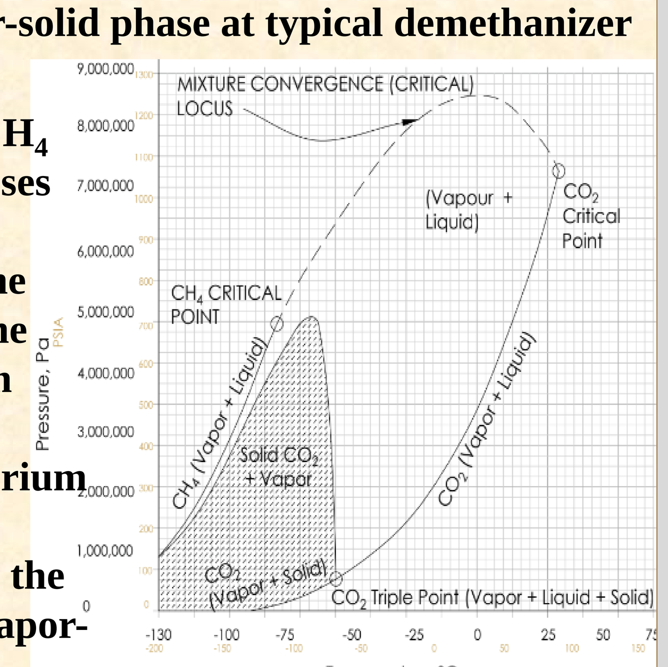


Technical Challenges

There are two technical challenges associated with removal of CO_2 using distillation techniques:

1. CO_2 Freeze out

- CO_2 exists primarily as vapor-solid phase at typical demethanizer conditions
- The phase diagram of CO_2-CH_4 shows why CO_2 freeze out poses as a problem.
- The right side boundary in the CO_2-CH_4 phase diagram is the CO_2 vapor-liquid equilibrium while the left boundary is methane vapor-liquid equilibrium line. The unshaded region in between these lines represent 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.



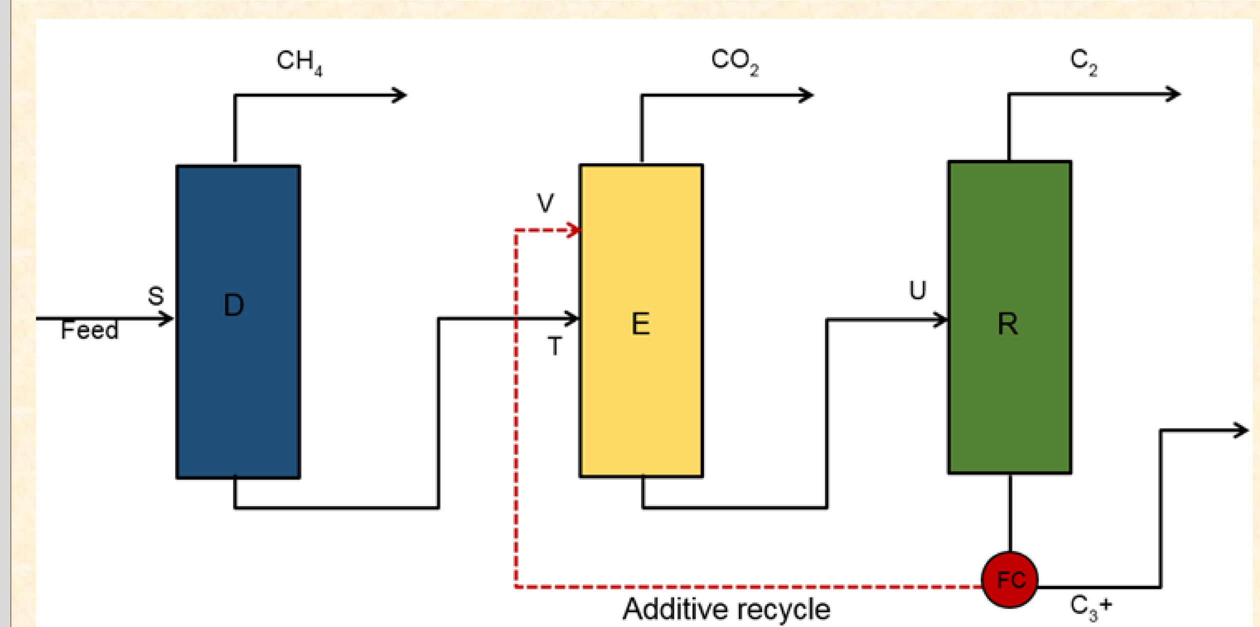
- In order to avoid freeze out we must steer clear of this shaded region. The critical pressure of CH_4 as shown is 673 psia, is at a lower pressure than the peak of the solid region of CO_2, thereby making it impossible to get pure methane at a constant pressure as we will have to pass the solid region of CO_2 if substantial CO_2 is present in the system.

2. Formation of azeotrope

An azeotrope or a constant boiling point mixture is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation. This happens because when an azeotrope is boiled, the vapor has the same proportions of constituents as the unboiled mixture.

- 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.
- CO_2 – C_2H_6 form an azeotrope in the heavier component stream in the demethanizer
- The approximate composition of this azeotrope is 67% CO_2 and 33% C_2H_6
- To effect separation single-additive/additives must be added to change the liquid vapor phase equilibria

Methodology



Column D: Demethanizer
Column R: Recovery or solvent recovery
Multicomponent solvent:
C3, iC4, nC4, iC5, nC5

Column E: Extractive or azeotropic coloumn
Total number of components in the system = 8

Aspen Plus Version 9 [20] is used as the primary design and analysis tool.

Column I: Demethanizer column, D

- Produces a stream of pure industrial grade methane
- Lighter component → methane is the distillate product
- Heavier components → including CO2 constitute the bottoms product
- Feed comprising of heavier hydrocarbons is used for altering the phase characteristics of the mixture and preventing freezeout.

Freeze Out:

- Demethanizer column is susceptible to CO2 freezeout at the operating conditions at distillation conditions of methane and CO2
- At constant composition of the mixture, as pressure increases the freezeout temperature increases
- At constant pressure, as the concentration of CO2 increases, the freezeout temperature increases.
- Moving down the column, 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.
- Pseudo streams at each stage and performed freezeout analysis to ensure that no freezeout takes places anywhere in the system.

Column II: Extractive column, E

- Performs extractive distillation and breaks the azeotrope between CO2 and ethane that forms in the bottoms of Column I
- Solvent stream comprising of heavy hydrocarbons injected near the top of the column

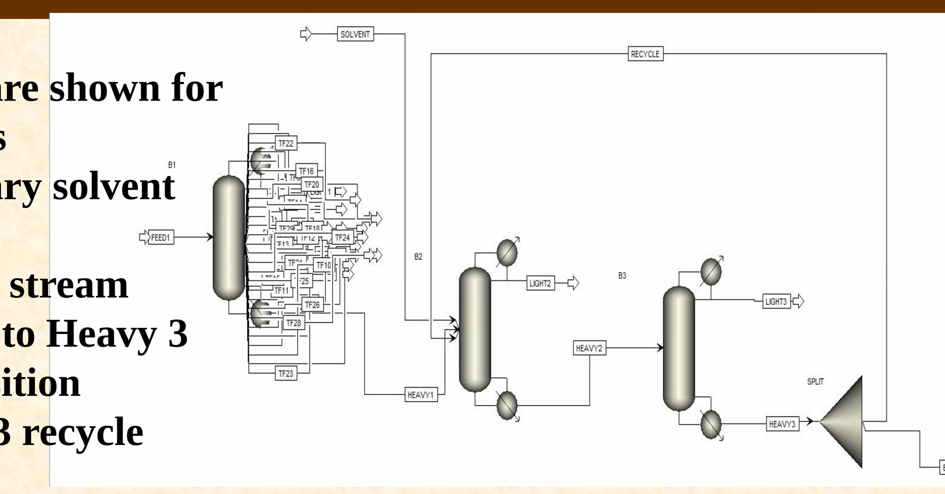
Column III: Solvent Recovery column, R

- A self-sustainable system where bye-products of distillation can be recycled back into the system as solvent to the extractive column is aspired.
- Third column (solvent recovery column), can be added to obtain a mixture of heavier hydrocarbons that works well as a solvent for breaking the CO2 ethane azeotrope
- The final step is solvent recycle implementation using the heavy component of the solvent recovery column.

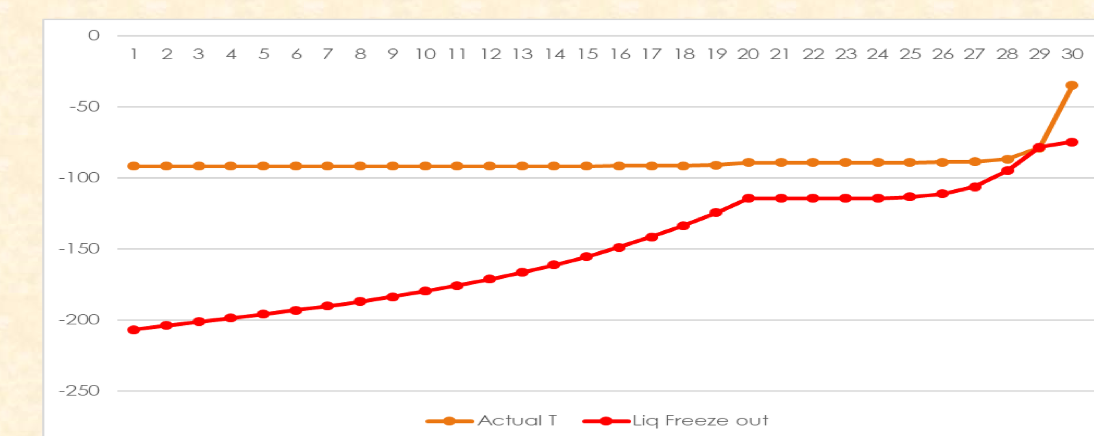
Simulation and Results

Results are shown for three cases

1. Arbitrary solvent stream
2. Solvent stream similar to Heavy 3 composition
3. Heavy 3 recycle



Freeze out results and column results are shown below:



Demethanizer column light stream

Component	Mole fraction arbitrary (Case I)	Mole fraction solvent (Case II)	Mole fraction recycle (Case III)
CO_2	4.527 ppm	4.527 ppm	4.527 ppm
CH_4	0.9999	0.9999	0.9999

Extractive column light stream

Component	Mole fraction arbitrary (Case I)	Mole fraction solvent (Case II)	Mole fraction recycle (Case III)
CO_2	0.99714	0.98134	0.93719
C_2H_6	6.522e-04	6.643e-4	0.0212

Extractive column heavy stream

CO_2	0.000371	0.002545	1.9e-05
C_2H_6	0.181729	0.181727	0.1388

Case 1 performs the best → ideal conditions
Interesting to note the results of Case 2 and Case 3 even though the solvent streams are "identical"

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 CO_2, and therefore render natural gas suitable for industrial applications with the carbon dioxide levels below 50 ppm. The system avoids CO_2 freezeout at all points, and ensures that CO_2 – C_2H_6 azeotropes are broken

Acknowledgment

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