LOW TEMPERATURE CARBON DIOXIDE REMOVAL FROM NATURAL GAS

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Introduction

This paper is aimed at providing a scoping analysis of the removal of carbon dioxide from natural gas at low temperatures by the method of distillation and overcome some of the common problems associated with it. Conventional and developing gas processing technologies for CO_2 removal from natural gas include absorption, distillation, adsorption, membrane separation and hydrates. The process of distillation is often considered to be suitable and commercially viable at large industrial scales. The aim of this work is to purify the natural gas from CO_2 and other heavier hydrocarbons and also to efficiently separate the individual components for reuse and recycle.

Distillation is a technique based on the principles of relative volatilities. The relative volatility is the ease of separation or the ratio between the tendency to vaporize of the two components. Thus distillation is a process of physically separating a mixture into two or more products that have different boiling points, the vapor of a boiling mixture will be richer in the components that have lower boiling points. When this vapor is cooled and condensed, the condensate will contain more volatile components. At the same time, the original mixture will contain more of the less volatile material.

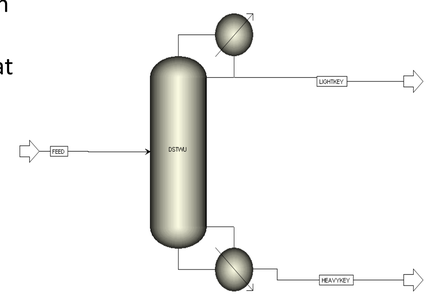
LNG production commercially requires the CO_2 amount to be 50 ppm. This works aims at achieving 50 ppm of CO_2 in natural by low temperature high pressure extractive distillation.

Simulation specifications and preliminary results

All simulations and post processing has been performed on Aspen Plus, which is a process modeling tool for conceptual design, optimization and performance monitoring. RadFrac column distillation has been performed which is a rigorous fractionation process capable of simulating multi stage, three phase flow, multi-component systems. Peng Robinson equation of state has been used and no shortcut empirical calculations have been performed. The feed gas is normally pre-conditioned to be at -10° C. Methane is the light key component and CO_2 and C_2 + are the heavy key component. Results shown below are for the following conditions:

Simulation parameters:
Calculation type: Equilibrium
Number of stages: 30; Feed stage: 8
Condenser pressure: 30bar
R = 4 ; D/F = 0.95

The desired 50 ppm or less concentration of CO_2 has been achieved using this method in the light key component of LNG. CO_2 ppm as low as 23 ppm has been achieved at high energy operating costs.



Stream properties

Property	Feed	Top	Bottom
CO_2 flow rate (kmol/hr)	3	0.004765	2.9952
C_2H_6 flow rate (kmol/hr)	2	2.772E-05	1.999972
CH_4 flow rate	95	94.99521	0.004793
Total flow rate (kmol/hr)	100	95	5
Temperature (C)	-10	-96.176	-10.898
Pressure	40	30	30
Enthalpy (cal/mol)	-20658.86	-20198.81	-67307.51
Entropy (cal/mol-K)	-27.60663	-37.50096	-32.3042
Density (gm/cc)	0.0363386	0.2885114	0.6963723
Average MW	17.1623	16.0442	34.407

Condenser/ Top stage performance

Temperature (C)	-96.172
Heat duty (cal/sec)	-131684.55
Distillate rate (kmol/hr)	95
Reflux rate (kmol/hr)	380

Reboiler/ Bottom stage performance

Temperature (C)	-10.898
Heat duty (cal/sec)	79034.93
Bottoms rate (kmol/hr)	5
Boilup rate (kmol/hr)	133.625493
Bottoms to feed ratio	0.05

Technical challenges

There are two significant technical challenges in applying distillation techniques to low temperature natural gas purification processes:

1. The formation of solid CO_2 during separation of methane in the demethanizer column
2. The existence of an azeotrope in the CO_2 recovery column between CO_2 and ethane

To circumvent this problem we add butane and other heavier hydrocarbons. This alter the vapour-liquid-solid phase equilibrium and changes the freezing point of CO_2

Operating conditions above the freeze out temperature of CO_2 in the demethanizer column and lowest possible pressure is desired. Across the height of the distillation tower the freeze out temperature varies significantly since it it is pressure and composition dependent. Thus arises the need for a utility function to calculate the freeze out temperature at every stage of the tower: TFREEZE utility function.

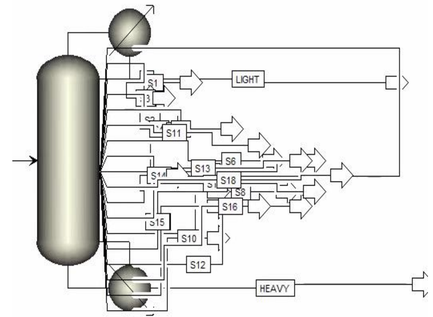
Even though the temperature is lowest at stage 1, freeze out may occur in lower stages at higher temperatures since CO2 concentration exhibits large variations across column.

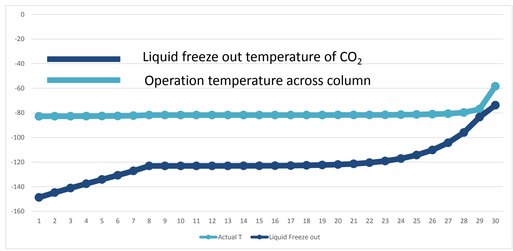
Azeotrope is a constant boiling mixture of two or more liquids whose proportions cannot be altered by simple distillation. This happens because, when an azeotrope is boiled, the vapor has the same proportions of constituents as the liquid mixture. The relative volatility is 1 or close to 1.

Addition of heavier hydrocarbons also help in breaking the azeotrope between CO_2 and C_2H_6 at these low temperatures.

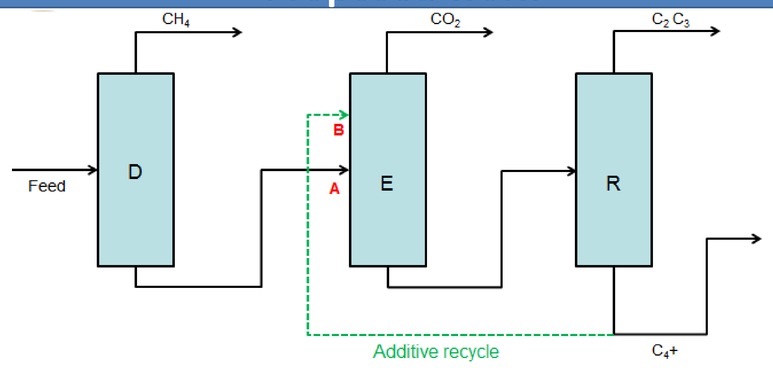
Freeze out

Even though the temperature is lowest at stage 1, freeze out may occur in lower stages at higher temperatures since CO2 concentration exhibits large variations across column. Freeze out analysis property set can analyze only material streams . The concept of "pseudo streams" is explored. Pseudo-streams duplicate column internal streams and pumparounds as external streams, without actually drawing material as with a side product. Pseudo stream specifications do not affect the distillation column calculations. Freeze out results were matched manually using TFREEZE utility function and analysis toolbox. Results are shown below for freeze out curves using butane as a single component solvent additive at 40 bar .





Proposed work



A three column simulation is proposed. Column D is the demethanizer column for purification of LNG with the desired concentration of CO_2 at 50 ppm. This has already been achieved as mentioned earlier. Column E is the extractive distillation column or azeotropic column. The light key component is CO_2 and the heavy key component is C_2 + . Column R is the recovery column or solvent recovery. The recovery column supplies an additive stream for additive or solvent recycle. Multicomponent solvent is used consisting of:
C3, nC4, iC4, nC4, iC5, nC5 thereby making the total number of components in the system = 9
The following parameters will be studied for separation and cost efficiencies:

- S/F ratio
- Position of A
- Position of B
- Solvent composition
- RR