Alternative Extractive Distillation System for CO₂-Ethane Azeotrope Separation in Enhanced Oil Recovery Processes

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Abstract

CO₂ is a common constituent of natural gas. Standards for its maximum concentration differ from about 2% for pipeline to 50 ppm for liquefaction. All natural gas constituents absorb CO₂ to some degree when in the liquid phase, requiring multi-step natural gas treatment processes. The existence of a minimum-boiling temperature azeotrope between ethane and carbon dioxide particularly complicates CO₂ separation. Extractive distillation with higher molecular weight hydrocarbons as the solvent represents the most competitive means for the separating CO₂ from ethane. The conventional separation method involves two distillation columns in series and rather high amount of energy.

This investigation proposes an efficient method for CO₂-ethane separation that produces all products at high purity with less capital and operating costs in comparison with the conventional system. The new operating flowsheet includes three columns: a CO₂ recovery column, a solvent recovery column, and a concentrator column. The proposed system requires 10 % less total annual cost (TAC) and 16% less energy compared to the conventional system at the same purification. Additionally, unlike the conventional system, the proposed design separates CO₂ in the form of a liquid product, which avoids the high amount of energy required for the liquefaction. Thus, this technology provides a useful alternative towards the less expensive CO₂-ethane separation process.

Keywords: Extractive distillation, CO₂-ethane azeotrope, Simulation, Optimization, Aspen Plus, Costs.

1. Introduction

US domestic natural gas demand increased 3% in 2014 – a greater increase than any other fossil fuel. Some estimates indicate that natural gas primary energy supply will outstrip that of both crude oil and coal, moving it into second place, ahead of coal, by 2035 in the overall domestic energy supply. Natural gas treatment processes play important current and future roles in this energy source [1].

The practice of natural gas treatment involves four steps: acid gas removal (sweetening), water removal (dehydration), oil and condensate removal, and separation of natural gas liquids (liquefaction) [2]. The sweetening process removes acid gases (CO₂ and H₂S). The separation of these gases is crucial for preventing CO₂ solidification during the cryogenic steps [3-6].

Methods for natural gas sweetening include chemical absorption with amines, physical absorption, membrane permeation, and low-temperature distillation. Of these practices, absorption using alkanolamines is the most widely used. However, this process requires a significant amount of solvent for high CO₂ concentration feedstock and presents significant safety and operational issues. Furthermore, this process generates a low-pressure gaseous CO₂ product that must be either compressed or liquefied for possible geological sequestration. Similarly, the membrane CO₂ removal system generates a low-pressure CO₂ product and also suffers from high pressure drop.

The low-temperature extractive distillation process, which separates CO₂ from hydrocarbons in a conventional direct sequence of two distillation columns, has the potential to overcome some of the aforementioned disadvantages [7]. This process presents two significant challenges: (1) CO₂ sublimation in the demethanizer, and (2) a minimum-boiling azeotrope between CO₂ and ethane (C₂). Recycling some of the natural gas liquids (NGL) product from the solvent recovery column as a solvent overcomes some of these challenges. The solvent is a mixture of the C₃ and heavier components from the original gas feed and entrains some of the CO₂ down the column, thereby reducing the CO₂ freezing temperature and preventing

1 formation of solid CO₂. It also aids in breaking the CO₂-ethane azeotrope in the extractive distillation
2 process. Compared to the amine process, this alternative has several advantages:

- 3 • The system is efficient for high CO₂ feed content;
- 4 • The solvent is the by-product of the natural gas supply, which avoids using an external solvent for
5 the process;
- 6 • The non-corrosive behavior of the solvent avoids using stainless steel sieves in the column;
- 7 • The anhydrous behavior of the solvent avoids the need for a dehydration unit in the process.

8 Distillation is one of the most common thermal separation technologies. In spite of its widespread industrial
9 use and major benefits, its high energy demand commonly represents over 50% of the plant operating costs
10 [8, 9]. Separation with lower energy demand can be achieved if the various components have a higher
11 relative volatility. The last decades have led to several energy efficient distillation solutions based on
12 process integration and intensification techniques, such as: cyclic distillation, a heat-integrated distillation
13 column, reactive distillation, and thermally coupled columns [10-13].

14 Hong and Kobayashi [14] provide vapor-liquid equilibrium data for CO₂-ethane separation using n- pentane
15 as a heavy entrainer in an extractive distillation system. Torres-Ortega [15] investigate an alternative
16 thermally coupled sequence (CEDSR) configuration based on a low-temperature extractive distillation
17 column to increase the carbon dioxide removal with lower total annual cost (TAC). They also investigate
18 the effect of different liquefied hydrocarbon fractions as an entrainer, the theoretical control properties, the
19 thermodynamic efficiency and the greenhouse gas generation of the proposed system, and conclude that
20 the proposed alternative has better generalized performances than the conventional chemical absorption
21 system. Lastari et al. [16] studied the effects of solvent composition, solvent-to-feed ratio, and feed tray
22 locations on the energy requirement of the extractive distillation for a CO₂-ethane azeotrope separation.

23 Tavan et al. [17] discuss extractive distillation for the azeotropic separation of CO₂ and ethane and the effect
24 of feed splitting on energy demand of the extractive distillation of this process and observed that their
25 proposed scheme has superior performance in terms of total energy demand and environmental issues
26 compared with the conventional process. Tavan et al. [18] explore the application of the dividing-wall

column (DWC) technology for the azeotropic separation of CO₂ and ethane at cryogenic temperatures and compare the economic and environmental aspects of the DWC process with the conventional system. Tavan et al. [19, 20] investigate the application of reactive absorption (RA) to break the CO₂-ethane azeotrope with low energy requirement and compared their results with the conventional extractive distillation process. They optimize diethanolamine (DEA) flow rate, DEA inlet temperature, and feed inlet location with respect to process energy demand. In another investigation [21], Tavan et al. explore CO₂-ethane azeotropic mixture as the feed of a reforming process to convert CO₂ and ethane to syngas (H₂ and CO). They suggest a Mg-type catalyst and a minimum steam/HC ratio of 1.5 to avoid coke formation during reforming.

These methods, however, have high energy requirements and/or equipment costs as well as long payback periods [22]. To reduce these costs, this work proposes a novel extractive distillation system for CO₂-ethane separation based on a three-column configuration and the model results are compared with the conventional two-column extractive system. This new unit meets the desired purification with less capital investment and energy requirement. Unlike the conventional two-column process, this configuration produces CO₂ in the form of a liquid product. Additionally, the described process can be retrofitted to an existing plant by adding a concentrator column sequentially to the extractive and solvent recovery columns. Aspen Plus simulates and optimizes the process. To establish a fair comparison, all designs analyzed here use the sequential quadratic programming (SQP) optimization method.

2. Simulation

2.1. Thermodynamic analysis

There are several methods to separate binary azeotropes:

1. *Pressure-swing distillation*: Two columns operating at two different pressures can achieve separation if changes in pressure significantly shifts the azeotropic composition.
2. *Azeotropic distillation*: A light entrainer component modifies the relative volatilities, or breaks the azeotrope, with at least two components collected as distillate. Frequently, these components are

immiscible in the liquid phase and a decanter separates them. One phase, commonly organic, refluxes the first column, whereas the second phase, commonly aqueous plus the solvent, feeds another column to regenerate the solvent, which recycles to the first column.

3. *Extractive distillation*: A third, typically heavy, component enters near the top of the first extraction column to break the azeotrope and preferentially carry one of the light feed components out the bottom of the column. The other light component forms a high-purity distillate stream. The bottoms stream feeds a second column to produce a solvent bottoms product and a high-purity light distillate product. The regenerated solvent is recycled back to the first column. [23].

Thermodynamic and process analyses indicate the preferred separation method. The separation method considered in this analysis includes a ternary mixture of ethane, carbon dioxide, and n-butane. Carbon dioxide and ethane have normal boiling points of 194.5 and 184.5 K, and molecular weights of 44 and 30 kg/kmol, respectively. Carbon dioxide and ethane form a minimum-boiling homogenous binary azeotrope as shown in Figure 1(a) with the azeotrope at about 67% CO₂ on a molar basis. Figure 1(b) shows that pressure changes do not shift the relative volatility of the CO₂-ethane mixture appreciably, indicating that the pressure swing distillation is not an appropriate method for the present investigation. However, Figure 1(c) clearly shows that the addition of n-butane considerably changes the phase envelope of the system. Moreover, addition of n-butane decreases the CO₂ freezing point to -71.6 °C, avoiding solid formation in the column at cryogenic temperatures. CO₂ and ethane behave similarly with most heavier alkane hydrocarbons.

The residue curve map and ternary diagram clarify the distillation process. Figure 2(a) shows the single binary azeotrope at -18.64 °C at 67 mol % CO₂, without any liquid phase splitting. Figure 2(b) presents the residue curve lines emanating from the minimum boiling azeotrope to the highest boiling component.

The isovolatility curve guides selection of an appropriate entrainer and determines the desired product in the distillate stream of the extractive distillation column. The isovolatility curve traces the conditions that

produce a relative volatility of unity in a binary mixture by adding another component to the system. Figure 2(c) plots the isovolatility curve of the ternary mixture of CO₂, ethane, and n-butane system. The relative volatility of ethane and CO₂ is unity at the azeotrope, which is marked on the ordinate of Figure 2(c). As n-butane is added, the isovolatility line moves towards the adjacent side, where the concentration of ethane goes to zero. n-butane is an effective solvent because of the point of intersection with the CO₂-nC₄ edge of the triangle. Generally, systems require less entrainer as the intersection point moves closer to the light key component corner, which leads to decreased operating and capital costs. As shown in Figure 2(c), this location is at $x_s = 0.21$ (21 mol % n-butane).

The isovolatility curve also indicates the identity of the distillate product from the extractive distillation column. The relative volatility between ethane and CO₂ exceeds one in the region above (to the right of) the isovolatility curve. Since the isovolatility curve in Figure 2(c) intercepts the CO₂-nC₄ edge of the triangle, CO₂ is the distillate product since the addition of n-butane into the system shifts the relative volatility to greater than one, causing CO₂ to go overhead. These results indicate that extractive distillation can be used in the presence of a miscible mixture and a homogeneous azeotrope. Moreover, this azeotrope reveals the attainable separation in a single column.

2.2. Process studied

A typical feed to the CO₂ recovery column is the methane-free product of the demethanizer column, which contains CO₂, ethane, and higher molecular weight hydrocarbons. This analysis considers the separation of a typical multi-component mixture [19, 24]. For the base case (two-column sequence) and the new alternative (three-column scheme), the feed basis is 4 kmol/s with a composition of 32.25 mol % CO₂ and 46.23 mol % C₂. The remainder consists of hydrocarbons ranging from propane (C₃) to n-pentane (nC₅). The desired product purities are 95.6 mol % CO₂ and 99.7 mol % ethane in the extractive and recovery columns, respectively. Aspen Plus with the Peng-Robinson equation of state provides predicted thermodynamic data.

2.3. Conventional direct sequence

Figure 3 illustrates a direct sequence of extractive distillation columns (conventional scheme) used to separate CO₂ from ethane, and is based on the information provided by Luyben and Tavan et al. [19, 24]. Figure 4 displays the temperature and liquid composition profiles for this base case. CO₂ collects as the top distillate from the first distillation column (extraction column), while the bottom product – consisting of ethane and heavier hydrocarbons (C₃+) – feeds the second distillation column (solvent recovery column). High purity ethane is obtained as the distillate product, and heavier hydrocarbons (NGL) as the bottom product of the solvent recovery column. The recovered NGL is divided into two parts, one of which is pumped back into the first column for breaking the azeotrope, and the second part goes to a sequence of distillation column for separation into C₃, iC₄, nC₄, iC₅, and nC₅ product streams.

2.4. Alternative process

Figure 5 exhibits the new flow sheet for a proposed alternative distillation sequence, which involves three columns: the CO₂ recovery or extraction column, the solvent recovery column, and the concentrator column. In this process, not all the CO₂ exits the top of the extraction column. The bottom product of the extraction column contains 10 mol % CO₂ along with ethane and heavier hydrocarbons. The second column recovers high-purity solvent. The recovery column distillate feeds a third or concentrator column, which produces ethane as a product and an azeotropic mixture recycle stream.

To establish a fair comparison, the sequential quadratic programming (SQP) method optimized all designs. The SQP method has become one of the most successful methods for solving nonlinearly constrained optimization problems [25-31]. SQP techniques have evolved from the initial approaches introduced in the early 1960s to the more state-of-the-art techniques, which are based on multiple shooting techniques. These SQP approaches have already proven useful in model predictive control and dynamic optimization, among others [32-40].

2.4.1. Extraction column

The SQP optimization method coupled with the efficient sensitivity analysis tool from Aspen Plus minimized the total energy requirement for the extractive column, as follows:

$$\begin{aligned} \text{Min}(Q) &= f\left(N_T, N_F, N_S, RR, V, \frac{S}{F}\right) \\ \text{subject to } \vec{y}_m &\geq \vec{x}_m \end{aligned} \quad (1)$$

where the optimization parameters used here are: the total number of stages (N_T), feed location (N_F), solvent location (N_S), reflux ratio (RR), boilup rate (V), and solvent to feed flow rate ratio ($\frac{S}{F}$), while y_m and x_m are the vectors of the obtained and desired purities for the m products, respectively. An additional objective function determines the optimal energy cost vs. the number of stages [41-43].

The optimum converged extractive column has 39 stages and operates at 24 atm. The optimization time is 2.3 seconds. The feed gas enters on tray 36 and the solvent with the flow rate of 2.4 kmol/s ($S/F = 0.6$) enters on tray 5 near the top. Figure 6(a) and (b) plot the temperature and liquid composition profiles in the extractive column, respectively. The solvent in the extractive distillation column alters the relative volatility between CO_2 and ethane, driving CO_2 to the top of the column and ethane to the bottom. The upper section of the column (above the entrainer feed location) separates the CO_2 and the entrainer. Figure 6(b) indicates that the CO_2 concentration increases at the entrainer entry point (stage 5). The middle of the column, between the entrainer feed stage and the fresh feed stage, prevents ethane from going up the column. Figure 6(b) clearly shows that the concentration of ethane increases from stages 5 to 36, where the entrainer and the feed enter, respectively. The bottom of the column, below the fresh feed location, prevents CO_2 from going down the column.

The extractive column produces a CO_2 -rich distillate (95.6 mol %). Figure 7 illustrates the effects of changing the solvent flow rate (S) and/or reflux ratio (RR). Increasing the reflux ratio decreases the impurity of solvent in the distillate, while increasing solvent flow rate improves the distillate CO_2 purity. However, the same is not true for the CO_2 -ethane system when using the NGL solvent. The effect of higher solvent

flow rates depends on the reflux ratio; in the higher RR range, increasing solvent flow rate also increases the distillate CO₂ purity (Figure 7(a)). However, in the lower RR range, the opposite occurs.

Additionally, Figures 7 (b) and (c) reveal nonmonotonic relationships between RR and both of the distillate impurities (C₂ and C₃), but they are opposite in shape. The C₂ curve (the HK component) reaches a minimum and the C₃ curve (the lightest of the components in the NGL solvent) reaches a maximum. The same relationships are also true of the solvent flow rate: more solvent decreases C₂ impurity, but increases C₃ impurity.

These interesting phenomena occur because the solvent is chemically similar to the LK component being separated from the CO₂. While operating at the lower of the two possible reflux ratios, the minimum solvent flow rate is found which meets the two specifications for the extractive column. As shown in Figure 5, the solvent flow rate is 2.4 kmol/s and the reflux ratio is 4.61. The resulting heat exchanger duties are 87.86 MW in the condenser and 15.12 MW in the reboiler. The heating utility used for all the reboilers in this study is steam at 100 psi and it is believed that it comes from an already existing steam generation unit in the plant. The distillate flow rate is 1.347 kmol/s of mostly CO₂ (95.6 mol %) with impurities of 2.9 mol % ethane and 1.4 mol % propane. The bottoms flow rate of the column is 6.4 kmol/s and carries most of the ethane, some of the CO₂ in the fresh feed, and heavier hydrocarbons to the solvent recovery column.

The distillate of the extractive column in this design remains liquid. However, the distillate of the conventional design cools the recycled NGL, which converts it to a vapor stream. There are several potential heat integration steps for this liquid stream, depending on the potential use of the CO₂. For example, a simple pump could pressurized the stream to above its vapor pressure at ambient conditions. The stream could then warm to ambient temperature by heat integration with any one or several of the condensers, further decreasing the process energy demand. The final liquid stream would then be suitable for enhanced oil recovery or other pipeline-based, large-scale CO₂ applications. Alternatively, if the CO₂ is to be locally

vented, the stream could reduce the overall process energy demand significantly by heat integration with one or more of the condenser circuits. Future work is exploring these and other potential applications.

2.4.2. Solvent recovery column

The solvent recovery column has 37 stages and the bottom stream of the extractive column is fed on tray 15. Unlike the conventional design that uses a total condenser, this column in the proposed design has a partial condenser. The design specifications of this column are 0.3 mol % propane in the distillate and 0.05 mol % ethane in the bottoms. A reflux ratio of 1.08 achieves these specifications.

Figure 6(a) and Figure 6 (c) exhibit the temperature and liquid composition profiles in the solvent recovery column, respectively. The ethane and CO₂ concentrations functionally monotonically decrease from the distillate to the bottoms but the C₃ profile has two local maxima, one each between the feed and the distillate and the feed and the bottoms, with overall increasing concentration from the distillate to the bottoms.

The condenser duty is 37.1 MW, and the reboiler duty is 20.9 MW. The heavy hydrocarbons exit with the bottom product and split into the NGL product (0.834 kmol/s) and the solvent, which recycles back to the extractive column. The NGL stream passes through a sequence of traditional distillation columns for propane, butane and pentane recoveries, which are not included in any of these simulations. The distillate of the solvent recovery column is a mixture of CO₂ (20 mol %) and ethane (80 mol %) that needs to be concentrated before recycling to the initial feed.

2.4.3. Concentrator column

The concentrator column has 43 stages and the distillate of the recovery column is fed on tray 10. This column also has a partial condenser. High-purity ethane with high purity (99.7 mol %) forms the bottoms product (1.82 kmol/s) after heat recovery. The mixture of CO₂-ethane goes overhead with molar flow rate of 1.35 kmol/s with the CO₂ concentrated up to 46 mol %. After heat recovery, this is recycled back to the extraction column as part of the feed.

3. Process comparison

To perform a fair economic comparison of the two process alternatives, the total capital costs, total operating costs, and total annual costs (TAC) are calculated. TAC is calculated as,

$$TAC = \text{operating cost} + \frac{\text{capital cost}}{\text{life of the plant}} \quad (2)$$

where a plant life of 30 years is considered in this investigation. This somewhat exceeds many natural gas process plant lifetimes but also allows for equipment reuse. As will be shown, most of the savings in the alternative process are in operating costs, so the economics are relatively insensitive to the plant cost. The Aspen Process Economic Analyzer provides relative costs, taking into account capital and operating costs together with technical and process parameters. Table 1 compares the key economic performance indicators of the two processes. The introduction of the third column causes a noticeable decrease in the reflux ratios of the extractive and recovery column, which is 4.61 and 1.08, respectively, compared with 6.04 and 2.18 in the conventional system. The capital costs of the columns are significantly altered by the reflux ratios, recycle flow rates, and entrainer usage in the distillation cases. More importantly, these parameters determine the process heat duties and product quality. As a result, the new alternative leads to 10 % lower TAC, with 14% reduction in specific energy demand and CO₂ emissions. All costs indicated here decrease. Total capital costs and most operating costs decrease by about 5%, with a 10% reduction in steam costs, consistent with the sum of the reboiler thermal loads being the biggest change.

The energy requirements closely correlate with CO₂ emissions when no heat integration is considered. When part of the process heat is reused instead of primary energy, then the CO₂ emissions are lower as compared to the figure expected from the energy data [17, 22]. Fuel combustion calculations assume that air is in excess, which ensures complete combustion and prevents formation of carbon monoxide. The amount of CO₂ emitted is related to the amount of fuel burned in the heating device, and is calculated according to the method described by Gadalla et al and Kiss et al. [44, 45]:

$$(CO_2)_{emissions} = \left(\frac{Q_{fuel}}{NHV} \right) \left(\frac{C\%}{100} \right) \alpha \quad (3)$$

where $\alpha = 3.67$ is the ratio of molar masses of CO_2 and C, NHV is the net (lower) heating value of natural gas with a carbon mass fraction of 0.41. Hence the quantity of fuel used can be calculated as follows:

$$Q_{fuel} = \frac{Q_{proc}}{\lambda_{proc}} (h_{proc} - 419) \frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \quad (4)$$

where λ_{proc} (kJ/kg) and h_{proc} (kJ/kg) are the latent heat and enthalpy of the steam, and T_{FTB} (K) and T_0 (K) are the flame and stack temperature, respectively. This equation represents a steam balance around the boiler and relates the quantity of fuel necessary to provide a heat duty of Q_{proc} [46-48]. The hourly rate of CO_2 emissions for the conventional and the new alternatives also appear in Table 1. This indicates that the new system decreases the carbon footprint.

4. Conclusions

This document proposes a new extractive distillation strategy for the CO_2 -ethane azeotrope with three columns. This strategy shows an approximately 14% reduction in total energy demand, most of which is for steam. Aspen Plus process economics analyses indicate about a 5% reduction in capital and 10% reduction in operating costs when comparing optimized versions of conventional and the new process. The new process reduces the total annual costs (TAC) by 10 %, without compromising the desired purification. The new process is also easier to operate because it is unnecessary to withdraw CO_2 completely in the extractive column. The novel separation scheme represents a retrofit option for existing units. Additionally, the new operation strategy produces CO_2 as a liquid product, which avoids the significant amount of energy required for liquefaction.

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Figure 1. $T - xy$ diagram (a) xy diagram (b) and phase envelope (c) of the azeotrope mixture of CO₂-ethane generated by Aspen Plus software over a range of pressures and compositions.

Figure 2. Ternary diagram (a), residue curve map (b) and isovolatility curve map (c) of the mixture of CO₂, ethane and nC₄ at 24 atm generated by Aspen Plus software.

Figure 3. CO₂-ethane separation with C₃+ solvent in the conventional extractive distillation system.

Figure 4. Temperature (a) and composition profiles in the extractive (b) and recovery (c) columns of the conventional system.

Figure 5. The flowsheet for the proposed CO₂-ethane azeotrope separation.

Figure 6. Temperature (a) and composition profiles in the extraction (b) and solvent recovery (c) columns of the proposed process.

(a)

Figure 7. Effect of solvent and reflux ratio on CO₂ purity: (a) and CO₂ impurities in the extractive column distillate (b) and (c).

Table 1. Comparison of the conventional and the proposed process economic and energy figures of merit.

Key performance indicators	Conventional process		Proposed alternative		
Capital Costs					
	Extractive column	Recovery column	Extractive column	Recovery column	Concentrator column
Tower (USD)	8,164,700	10,589,600	4,556,700	10,939,100	2,502,700
Reboiler (USD)	301,400	549,600	62,100	693,100	69,600
Condenser (USD)	2,928,600	1,125,500	2,217,800	805,400	1,026,900
Reflux pump (USD)	125,300	68,300	104,500	46,300	46,200
Heat exchanger (USD)	988,000		599,700		
External Cooler (USD)	56,300		-		
Total capital costs (USD)	24,897,300		23,670,100		
Operating Costs					
Electricity (USD/year)	516,657		491,334		
Refrigerant (USD/year)	5,986,169		5,632,501		
Steam (USD/year)	39,436,732		35,236,607		
Cooling Water (external cooler) (USD/year)	55,191		-		
Total operating costs (USD /year)	45,994,747		41,360,441		
Annualized Cost					
Total Annual Cost (USD/year)	46,824,657		42,149,445		
Specific energy requirement (kW h/kg CO ₂)	1.627		1.401		
CO ₂ emissions (kg CO ₂ /s)	7.16		6.15		