Strategies to Maximize Ethane Recovery with High-CO_2 Feeds

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Abstract

Elevated feed-CO_2 levels decrease the maximum ethane recovery in GSP and similar demethanizer configurations. This can be attributed to two causes. First, as CO_2 displaces methane in the feed, the feed tends to behave more like a richer gas, which tend to have decreased ethane recoveries. Secondly, the choice of column operating conditions is complicated by the tendency of high-CO_2 feeds to form dry ice in the upper sections of the column, or in the feed or residue lines. This often requires a sacrifice of ethane recovery to avoid dry ice formation. However, by manipulating column operating parameters, namely the vapor and liquid split to the subcooler, the column operating pressure, and the inlet split to the reboiler, the CO_2 concentration profile in the column can be tailored to avoid dry ice formation, while still maximizing ethane recovery. This paper explores the effects of adjusting these operating parameters with both lean and rich feeds.

Background

Enbridge operates a gas processing facility in Longview, TX that includes a demethanizer followed by amine treatment of the NGL (liquid product) stream from the demethanizer. The feed to the facility is a fairly lean gas (~90% methane) with a CO_2 content that varies between 1.6% and 1.8% on a molar basis. The facility has repeatedly experienced operational stability problems in the demethanizer when attempts are made to increase ethane recovery. Some of the problems are: increased column pressure drop, carryover of liquid in the overhead line, and unsteady liquid production from the tower.

ProMax® [1] simulations of the demethanizer under conditions that correspond with the carryover mentioned above do show that dry ice formation is likely near the top of the tower. If dry ice were to form in the top section of the tower, it could accumulate in the packing. This would reduce cross-sectional area available for flow, which would lead to increased vapor and liquid velocity and possibly column flooding. Symptoms of flooding at the top of the tower would be increased column pressure drop, carryover of liquid into the overhead line, and unsteady liquid production from the tower, exactly the problems that Enbridge has experienced.

A study by Enbridge, Bryan Research & Engineering, and Koch identified other column hardware issues that appeared to be contributing to column flooding, but it is likely that resolving these other issues will not prevent dry ice formation. ProMax models showed that dry ice had the potential to form in the top section of the tower. Since the plant was running so poorly to begin with, due to the lack of heat from a clogged side reboiler, it was very difficult to determine if dry ice was forming. Previous inspections of the demethanizer clearly indicated that CO_2 freezing had occurred at some point(s) in the past as the mist eliminator had been "relocated" and lodged in the outlet piping, and the flow distribution trough above the top bed had been thoroughly mangled. This makes an interesting basis for a case study on how to deal with elevated CO_2 feed in a demethanizer.

Introduction

This paper will focus on a GSP (Gas Subcooled Process) facility as shown in Fig. 1, but many of the lessons learned can be applied to other demethanizer configurations. In ethane recovery mode, methane is separated from ethane and heavier components in the tower with methane concentrated into the residue gas, and the ethane and heavier components recovered in the NGL. In ethane rejection, ethane is directed to the residue gas. This paper will focus on ethane recovery mode. CO_2 volatility is between that of methane and ethane. CO_2 recovery will be lower than ethane recovery, but will typically increase as ethane recovery increases.

Stepping through the GSP plant,

- The inlet flow is split and follows two possible cooling paths before recombining at the inlet of the Low Temperature Separator (LTS).
    - In the top path the gas is cooled by the exiting residue gas.
    - In the bottom path the gas is used as a heat source for the bottom and side reboiler of the tower.
    - A bypass path is typically included as a way to moderate cooling before the LTS.
- The vapor leaving the LTS is split, with approximately 70% directed to the expander and the remaining 30% [2] sent to the subcooler.
    - The subcooler condenses and subcools the gas by heat exchange with the residue gas exiting the top of the tower. The subcooled liquid is then flashed down to column pressure, which provides additional cooling before entering the column.

  - The expander extracts energy from the gas to cool it before it enters the column below the subcooled liquid. The expander is typically combined with the booster compressor to harness the extracted energy. By lowering the column pressure, more energy can be extracted, thus lowering the temperature and increasing ethane recovery.
  - The fraction split to the subcooler is typically adjusted to maximize ethane recovery when in recovery mode.
- The liquid leaving the LTS can also be split, with some flashed across a JT valve before entering the column below the expander outlet connection. A portion of the liquid can also combine with the LTS vapor entering the subcooler to provide a richer feed mixture at the top of the column.
- Residue gas leaves the top of the tower. Typically it must be compressed to pipeline pressure. The energy recovered from the expander provides a modest pressure increase in the booster compressor, but in most cases, not enough to reach pipeline pressure. This leaves the residue compressor to provide the bulk of the recompression energy. When the tower pressure is lowered to increase recovery, residue compression power increases. Thus, there is a tradeoff between increased revenue from higher recovery versus higher residue compression costs.
- NGL leaves the bottom of the tower as a liquid and can be pumped at a relatively low cost compared to residue gas compression.

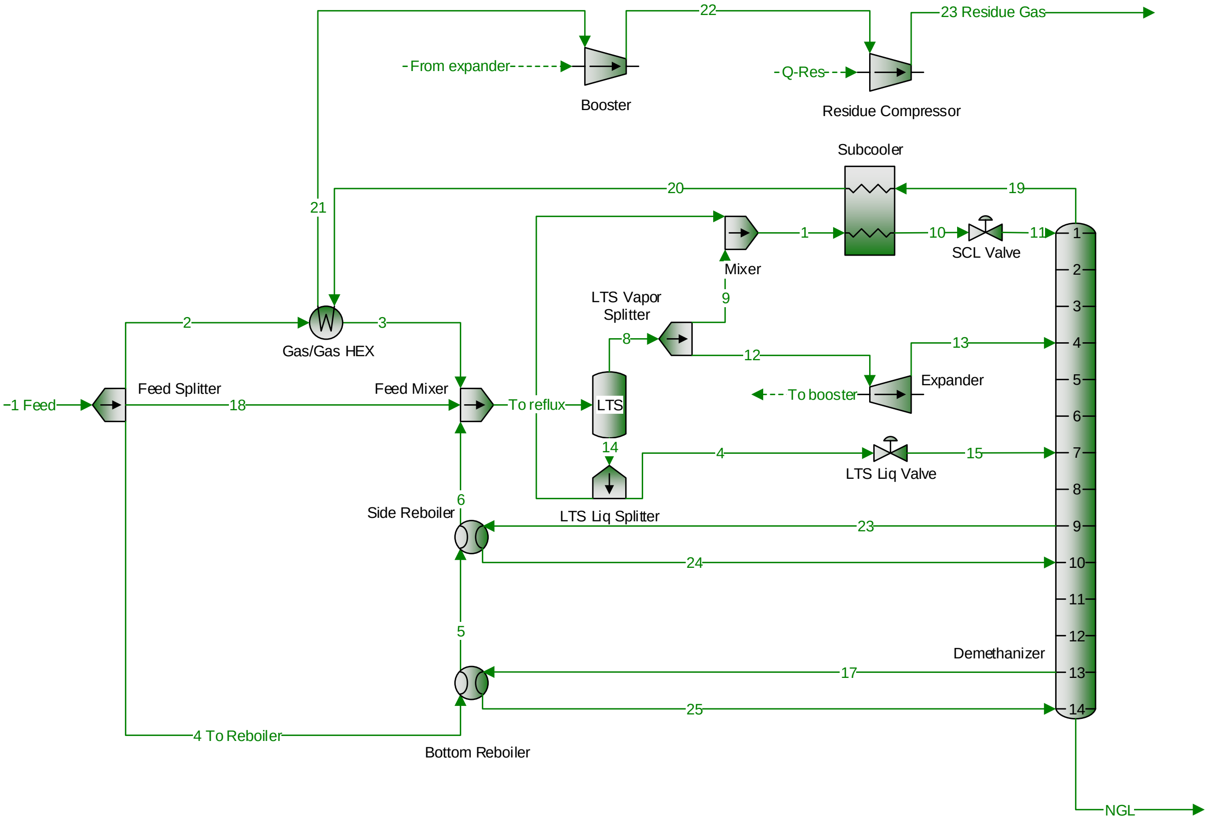

Figure 1. GSP layout

For this paper, the fractions of the LTS vapor and liquid sent to the subcooler will hereafter be called the Vapor Split and the Liquid Split. The fraction of the inlet sent through the reboiler will be called the Reboiler Inlet Split. This is shown in Figure 2.

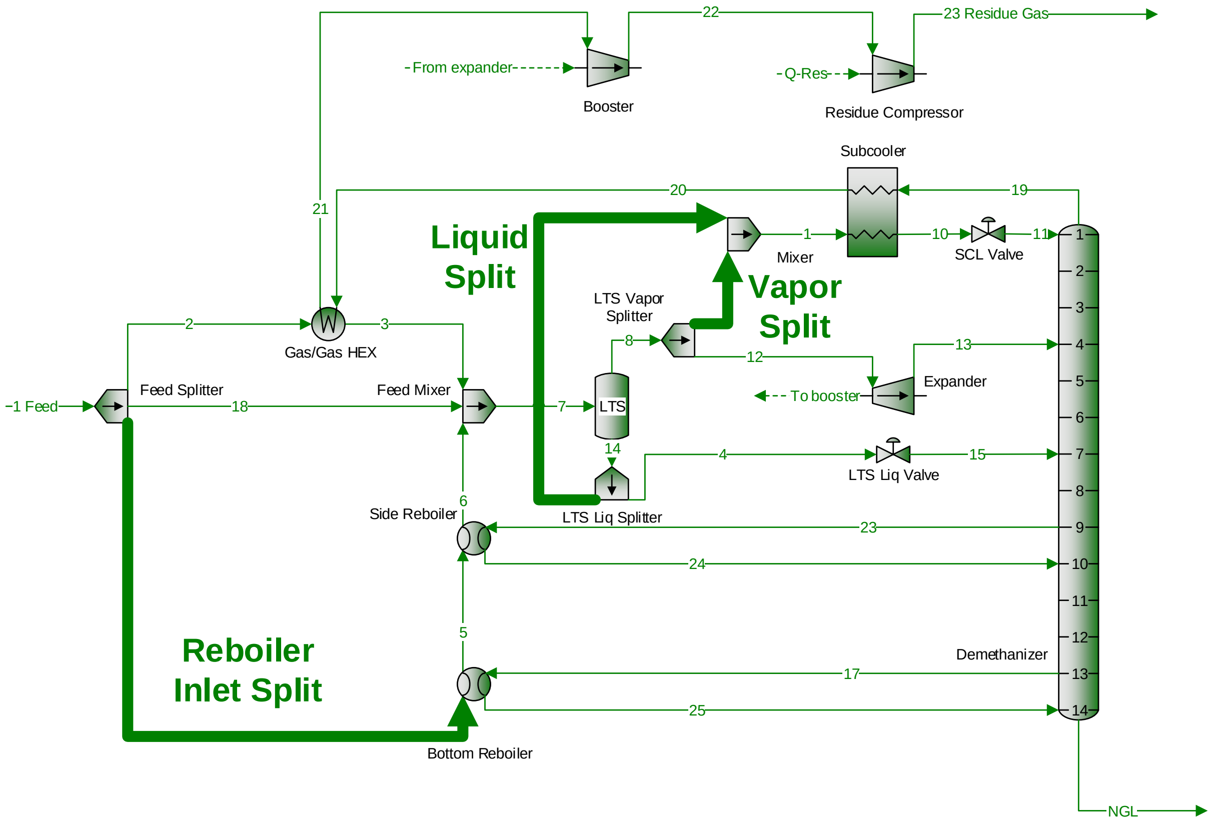

Figure 2. Reboiler Inlet Split, Liquid Split and Vapor Split Definitions

There are many demethanizer plants where CO_2 removal occurs after methane removal, typically in the NGL stream. There are some benefits to this type of operation. CO_2 removal from the NGL is more efficient since the CO_2 concentration will be higher in the NGL than in the feed gas. Oftentimes, the CO_2 in the residue gas can bypass the removal steps altogether since the residue gas specifications typically allow for some CO_2 [3].

The drawback to removing CO_2 downstream of the demethanizer, as opposed to upstream, is that CO_2 is known [3] to decrease the maximum ethane recovery. There are a few reasons for this. First, as the CO_2 content in the feed rises, the gas behaves as a richer gas. But, heat integration in a demethanizer plant is poorer with a richer gas [4]. This leads to warmer temperatures at the top of the demethanizer, which allows more ethane to escape into the residue gas.

Furthermore, as the CO_2 content of the feed gas rises, the minimum allowable temperature near the top of the tower increases (becomes less negative) due to the need to avoid dry ice formation. A typical method to achieve higher recoveries is to increase the cooling across the turboexpander and JT valves by lowering the column pressure. The tradeoff is increased residue compressor power. Many times this tradeoff is justified and an economic optimum can be found that balances increased recovery versus compression power. However, with high-CO_2 feed concentrations it may not be possible to operate at the optimal tower pressure due to the need to avoid low temperatures and dry ice formation in the top of the tower or in associated feed and product piping.

Dry ice formation

Dry ice forms as an essentially pure, solid CO_2 phase in natural gas. At a given temperature and pressure, CO_2 can form a stable, solid phase in a vapor (V), liquid (L) or vapor/liquid (VL) mixture when the chemical potential of pure solid CO_2, $\mu_{CO_2}^S$, is lower than or equal to the chemical potential of CO_2 in the other phase(s), $\mu_{CO_2}^V$ and/or $\mu_{CO_2}^L$ [5]. (If both a liquid and vapor are present, then $\mu_{CO_2}^V = \mu_{CO_2}^L$ at equilibrium.)

This can be understood by first reviewing the phase envelope for pure CO_2 shown in Fig. 3. If we start at a point A (290 psig, 60 °F), CO_2 exists solely as a vapor because $\mu_{CO_2}^S > \mu_{CO_2}^V$.

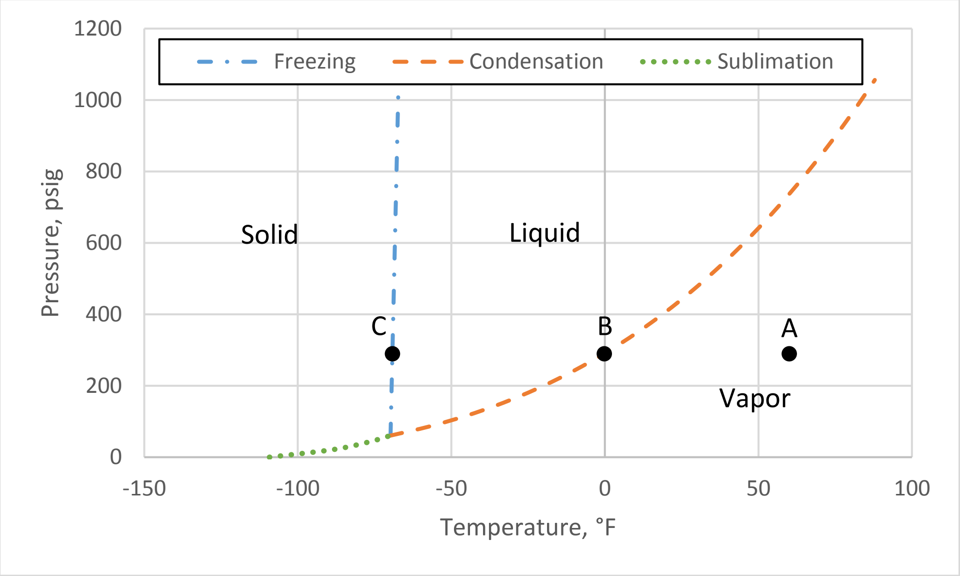

Figure 3. Pure CO_2 **phase diagram**

If the CO_2 is then chilled from A at constant pressure, it will remain a vapor until the temperature reaches 0 °F (Point B). At this point, $\mu_{CO_2}^V = \mu_{CO_2}^L < \mu_{CO_2}^S$. If heat is further removed, CO_2 will condense at constant temperature (since it is a pure substance) until all the vapor has condensed. With continued heat removal, the temperature will decrease and the CO_2 will remain as a liquid until -69 °F (Point C). At this temperature, $\mu_{CO_2}^L = \mu_{CO_2}^S$ and continued heat removal will isothermally transform liquid CO_2 into solid CO_2. After all CO_2 solidifies, the temperature will decrease with continued heat removal. Below the freezing temperature, $\mu_{CO_2}^S < \mu_{CO_2}^L$.

Transitioning from pure CO_2 to CO_2-containing mixtures, there are some interesting behaviors that appear. Dry ice will form in natural gas mixtures as essentially pure CO_2 whenever $\mu_{CO_2}^S \leq \mu_{CO_2}^V$ and/or $\mu_{CO_2}^L$. However, in a mixture, $\mu_{CO_2}^V$ and $\mu_{CO_2}^L$ decrease as the CO_2 mole fraction decreases, which means that the dry ice formation temperature will decrease as the CO_2 mole fraction decreases. Fig. 4 below shows the phase envelope and dry ice formation curve for the 2nd-stage composition of a typical demethanizer. Comparing Fig. 4 to Fig. 3, not only is the shape of the dry ice curve different, but it is also shifted to colder temperatures in the mixture versus pure CO_2.

Starting in the vapor phase at Point A in Fig. 4, once again $\mu_{CO_2}^V < \mu_{CO_2}^S$. With isobaric cooling, the mixture will remain a vapor until Point B, the dewpoint, where $\mu_{CO_2}^V = \mu_{CO_2}^L < \mu_{CO_2}^S$. With additional heat removal, the overall liquid fraction will increase and the temperature will decrease (as opposed to the isothermal phase change of pure CO_2) until the mixture arrives at Point C, which lies on the dry ice curve. At Point C, dry ice can begin to form since $\mu_{CO_2}^{V} = \mu_{CO_2}^{L} = \mu_{CO_2}^{S}$.

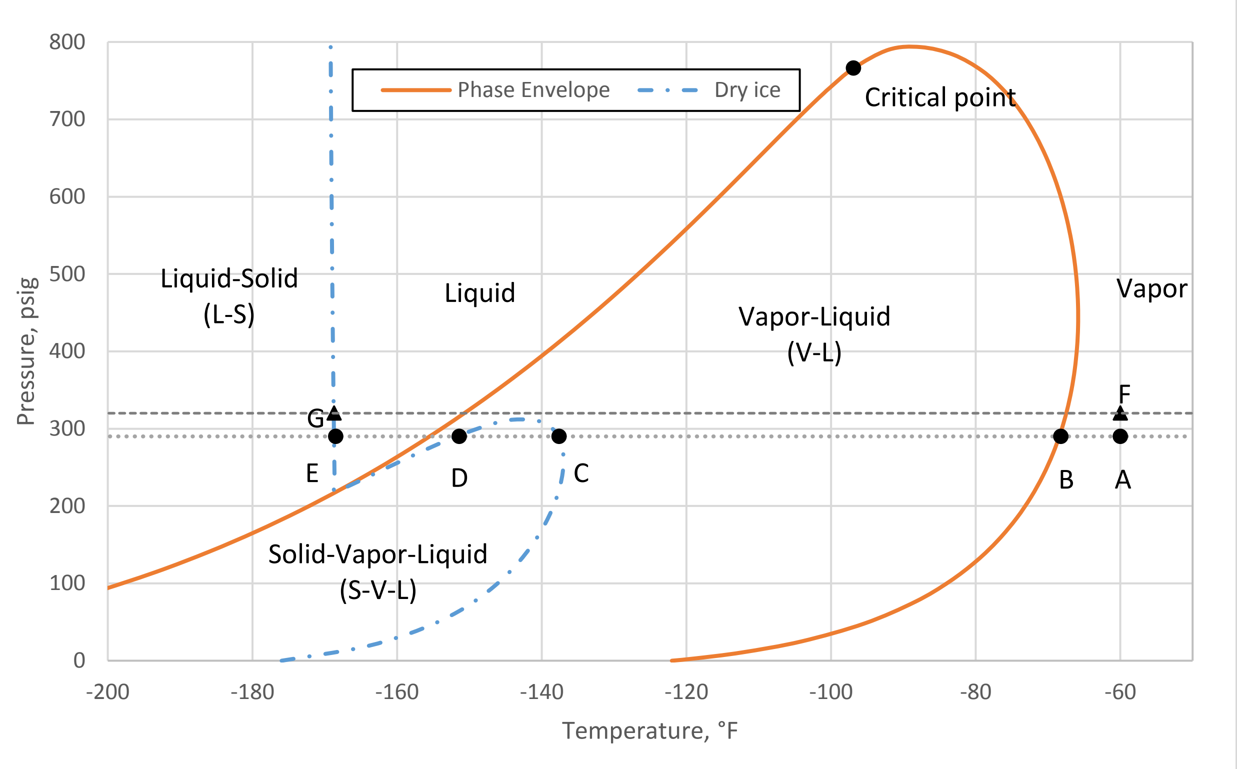

Figure 4. Phase diagram of typical Stage 2 composition

With further cooling, additional vapor will condense and the solid fraction will increase to a maximum. Then, counterintuitively, the dry ice will begin to “melt” and completely disappear when the mixture is cooled to Point D. This melting behavior can be explained by the fact that CO_2 is more stable in the liquid phase than in the vapor phase at these conditions. Under the right conditions (such as between points C and D), when a portion of vapor condenses, it can hold more CO_2 without forming dry ice than it previously could as a vapor. Therefore, as more liquid forms it absorbs CO_2 from the solid phase, thereby dissolving the dry ice. This can be mathematically expressed as follows. At the conditions on Stage 2, $K_{CO_2} < 1$, where

$$K_{CO_2} = {}^{y_{CO_2}}/_{x_{CO_2}}$$

y_{CO_2}, x_{CO_2} = vapor- and liquid-phase CO_2 mole fractions

When vapor condenses with $K_{CO_2} < 1$, y_{CO_2} must decrease to maintain vapor-liquid equilibrium. As y_{CO_2} decreases, $\mu_{CO_2}^{V}$ can become lower than $\mu_{CO_2}^{S}$. If $\mu_{CO_2}^{V} = \mu_{CO_2}^{L} < \mu_{CO_2}^{S}$, CO_2 will move back from the solid phase into the vapor and liquid phases to reestablish equilibrium.

Between Points D and E, the mixture will transform from a VL mixture to a single liquid phase. At point E, $\mu_{CO_2}^{L} = \mu_{CO_2}^{S}$, and dry ice will start to form in the liquid mixture. With further heat removal, the temperature will decrease and more CO_2 will transfer from the liquid phase into the pure CO_2 solid phase.

There are two interesting corollaries to this behavior. First, by shifting the pressure higher from Point A to Point F of Fig. 4, the S-V-L region can be avoided and a significant decrease in the dry ice formation temperature can be achieved. For instance, when isobarically cooling from Point F, dry ice will not form until Point G, which is roughly 30 °F colder than the dry ice formation temperature when starting at Point A. This can be explained by the fact that for a fixed composition and temperature with a pressure below the critical pressure, the overall liquid fraction will increase as the pressure is increased. By shifting to a higher pressure, which increases the amount of liquid available to absorb CO_2 from the vapor, $\mu_{CO_2}^{V}$ remains below $\mu_{CO_2}^{S}$ and dry ice does not form in the 2-phase region.

Secondly, if a rich and lean gas both have the same overall CO_2 mole fraction, z_{CO_2}, the S-V-L region will shift to lower temperatures and pressures for the richer gas. To illustrate this, Figure 5 shows dry ice formation curves for four gas compositions, all containing 1.8% CO_2. The compositions are defined in Table 1. Observe that a richer gas composition has a dry ice curve that is shifted to colder temperatures and lower pressures.

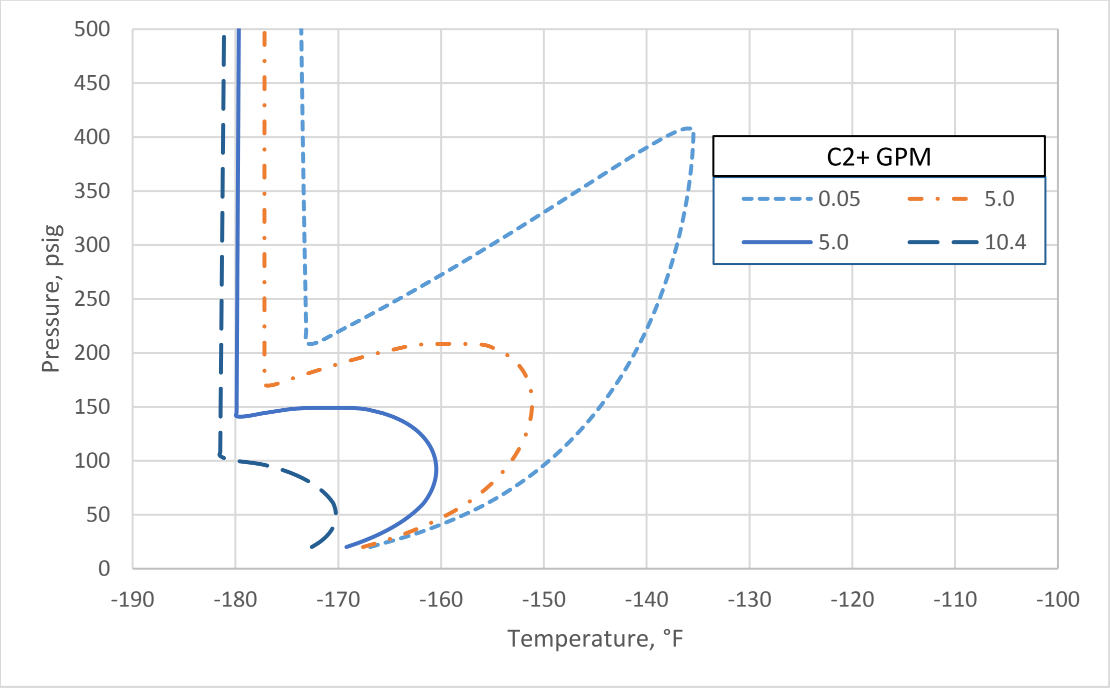

Figure 5. Impact of methane content on dry ice curve with constant (1.8%) CO_2 mole fraction

Finally, CO_2 content has a noticeable effect on the location of the dry ice curve. Fig. 6 compares the dry ice formation curve at 1.5%, 1.8%, and 2.1% CO_2 with a constant C_2+ GPM = 2.3 gal/MSCF.

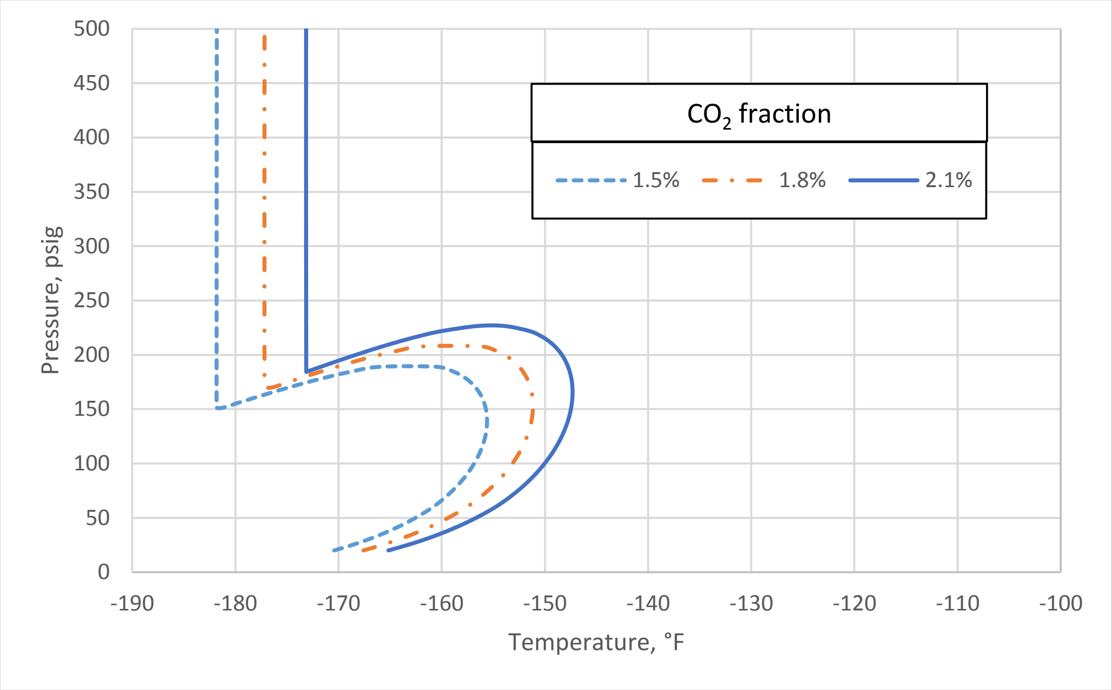

Figure 6. Effect of CO_2 content on dry ice curve.

Implications for operating GSP demethanizer with high-CO_2 feeds

As mentioned previously, high-CO_2 feeds can prevent operation at what would be considered economically optimum ethane recoveries due to the need to avoid dry ice formation. As every plant offers a different combination of feed conditions and compositions, there is not a single solution to maximize profit while avoiding freezing in the column. What is offered here are levers that can be pulled to move the demethanizer operating envelope out of the region where dry ice can form.

These levers are,

- Column pressure
- Reboiler Inlet Split
- Liquid Split
- Vapor Split

In this study it will be helpful to refer to a few different feed gas compositions for comparison purposes. These are listed below in Table 1. All simulations were performed in ProMax with the GSP layout shown in Fig. 1. The feed flowrate, temperature and pressure were 50 MMSCFD, 100 °F, and 800 psig for all cases. Constant UA values were maintained in the bottom reboiler, side reboiler, subcooler, and gas/gas exchanger, as 55,000, 120,000, 480,000 and 760,000 BTU/(hr·°F), respectively. Unless otherwise indicated, the NGL C_1/C_2 liquid volume ratio was controlled at 0.015, and the tower was modeled with 14 ideal stages, to correspond with 28 real trays [6]. The turboexpander isentropic efficiency was 85%.

Table 1. Gas compositions used in study

	Gas compositions (mole %)						
Component	A	B	C	D	E	F	G
CO_2	1.8	1.5	2.1	1.8	1.8	3.8	1.8
Methane	90	90.3	89.7	98	80	78	60
Ethane	5	5	5	0.15	10	10	25
Propane	1.2	1.2	1.2	0.05	6.2	6.2	11.2
i-Butane	0.4	0.4	0.4	0	0.4	0.4	0.4
n-Butane	1	1	1	0	1	1	1
i-Pentane	0.2	0.2	0.2	0	0.2	0.2	0.2
n-Pentane	0.4	0.4	0.4	0	0.4	0.4	0.4
Richness, C_2+ GPM	2.3	2.3	2.3	0.05	5.0	5.0	10.4

Column Pressure

In some cases one might be able to select a column pressure above the S-V-L region to significantly decrease the dry ice formation temperature. All else being equal, increasing the column pressure will lower ethane recovery by decreasing the cooling through the expander and J-T valves. However, the required pressure increase could be small, such that it doesn't significantly decrease ethane recovery.

Dry ice can form in a number of places in and around the top section of the tower. It is possible for dry ice to form in the feed, overhead product, or in the top section of the tower above the expander outlet. Although the temperature rises moving down the column, the CO_2 can concentrate below the top of the tower under certain conditions [7] as it is carried up by the methane leaving the expander and then recondensed by the colder temperatures at the top of the tower. The increased CO_2 concentration will expand the S-V-L region, which can lead to dry ice formation on stages below the top of the tower even though the temperature increases. An example of this is shown in Table 2.

Table 2. Top of the tower conditions for Feed A (0% LTS liquid and 27% LTS vapor to top). Highlighted cells show potential dry ice formation.

Top Stage Pressure, psig	Stage	Vapor CO_2, mol%	Liquid CO_2, mol%	Temperature, °F	Dry Ice Formation Temperature, °F
315	1	1.07	5.00	-144.9	-174.4
	2	1.81	8.10	-137.2	-134.9
	3	2.28	8.74	-128.3	-159.8
	4	2.13	6.61	-118.6	-164.7
325	1	1.16	5.21	-142.4	-173.2
	2	1.93	8.13	-133.9	-161.9
	3	2.33	8.36	-124.7	-160.3
	4	2.12	6.24	-115.5	-165.6

By increasing the pressure by 10 psi, the column is able to operate in a region that avoids dry ice formation. Fig. 7 compares the operating point for Stage 2 in the column at the two pressures with the ProMax-generated phase envelope overlaid with the dry ice formation curve. This shows the operating point for this tray to be within the S-V-L region at the lower pressure while, with a 10-psi pressure increase, the operating conditions in the tower avoid the dry ice region. Higher pressure operation did two things to move into the dry ice-free region. First, higher pressure increased the temperature and pressure on the tray, moving the operating point up and to the right. Secondly, higher pressure increased the liquid content, moving the S-V-L region down and to the left. By moving to a higher-pressure, the ethane recovery decreased from 86.9% to 84.8%, while the residue compressor power decreased from 2,288 hp to 2,191 hp. So, this is the first tradeoff. Raising the pressure allows one to avoid the S-V-L region and lowers the residue compression power requirement at the expense of reduced ethane recovery.

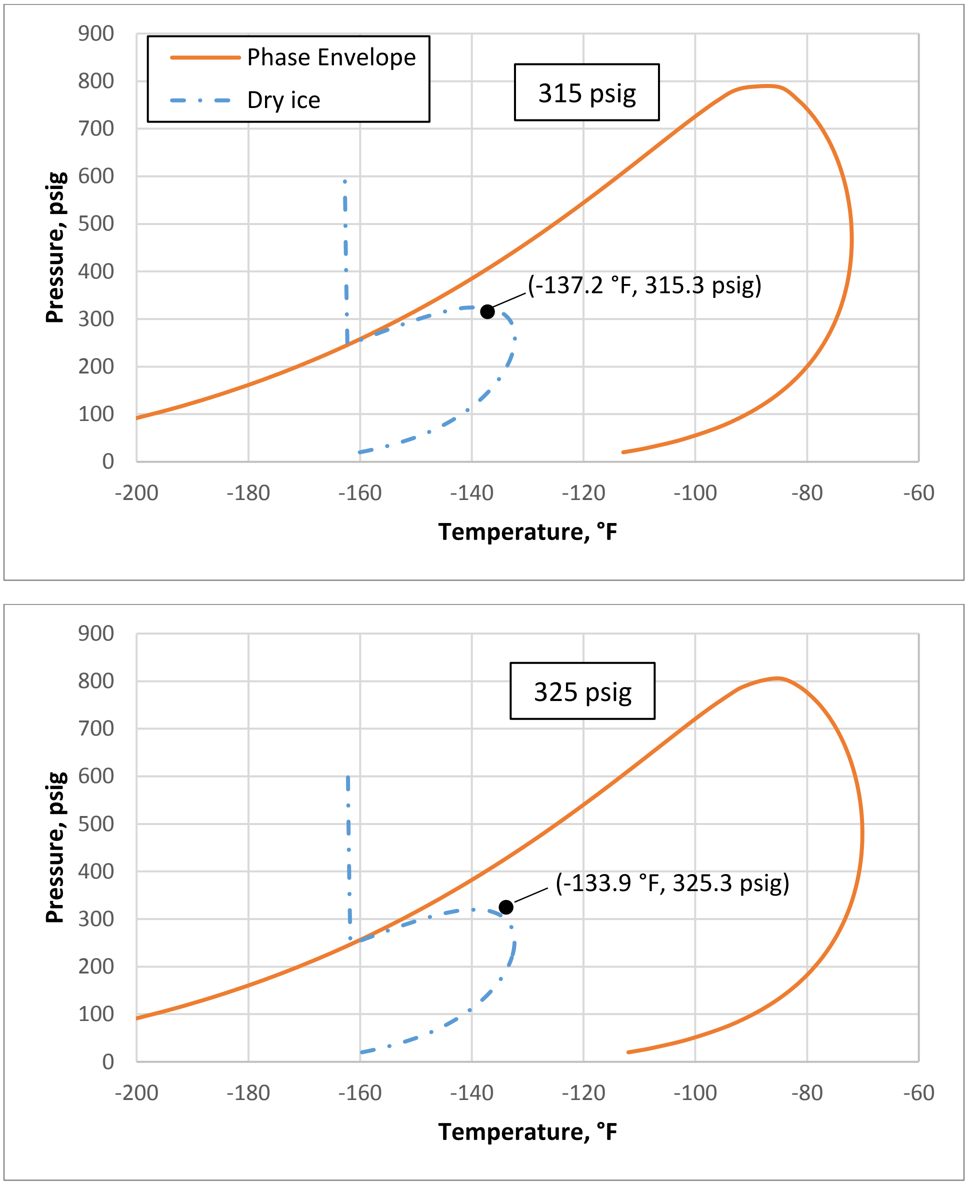

Figure 7. Stage 2 operating point at 315 and 325 psig (Feed A)

Reboiler Inlet Split

A typical GSP plant has the ability to change the bottom and side reboiler duty by adjusting the fraction (Reboiler Inlet Split) of the warm inlet gas that passes through these exchangers. A common method for decreasing the methane fraction in the NGL product is to increase the bottoms temperature by increasing the Reboiler Inlet Split. This will also decrease the amount of CO_2 in the NGL, boiling the CO_2 back up the column. Conversely, lowering the Reboiler Inlet Split will increase the CH_4 and CO_2 fractions in the NGL product, allowing the CO_2 to leave in the column bottoms.

As the column bottoms temperature is lowered, the CO_2 concentrations at the top of the tower will decrease as shown in Figure 8. This shifts the dry ice formation curve to lower pressures and colder temperatures, as detailed in Figure 6. Therefore, if one is trying to avoid dry ice formation then operate the column bottom as cold as NGL specifications will allow. Typically, the NGL specifications will limit the amount of CH_4 and/or CO_2 in the NGL. These limits effectively set a lower bound on the bottoms temperature.

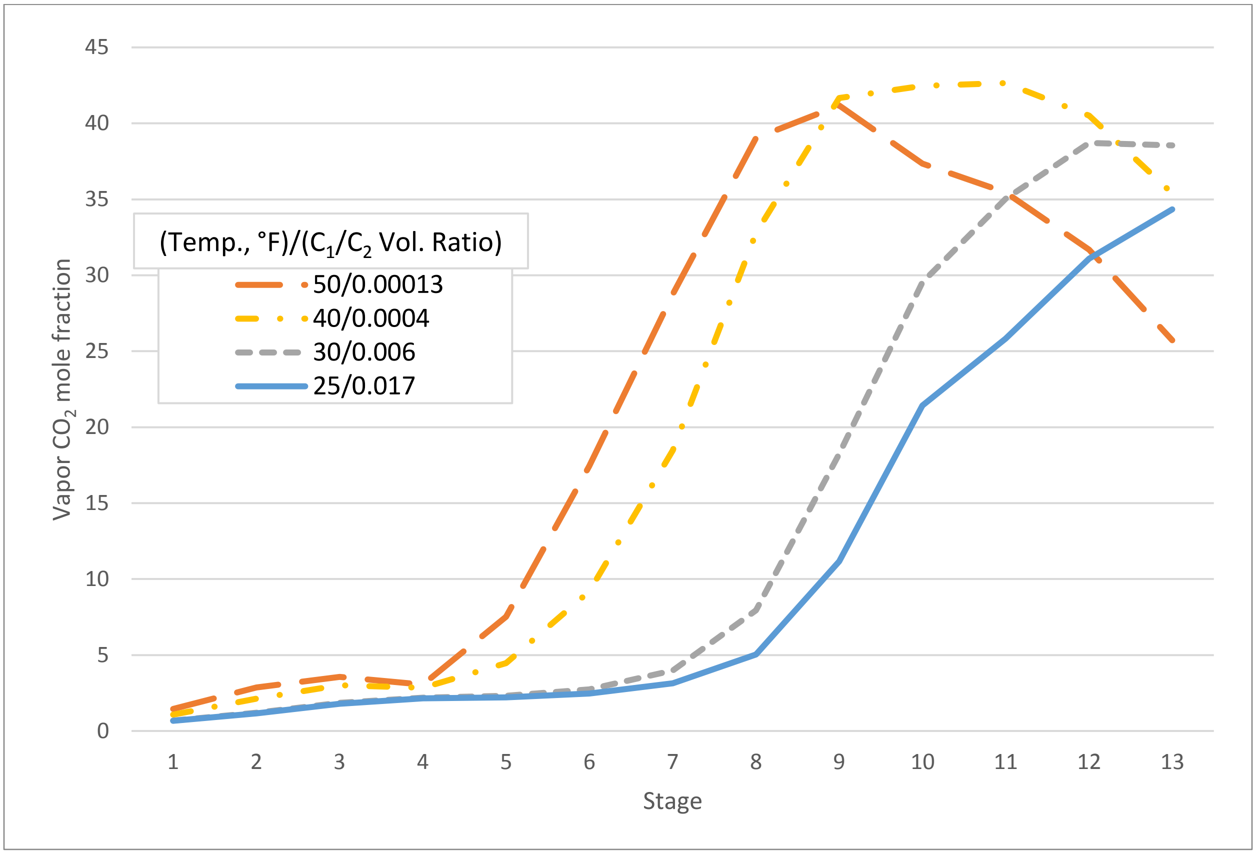

Figure 8. Effect of NGL temperature on CO_2 concentrations in the tower

Liquid Split and Vapor Split

In the discussion about tower pressure, the dry ice region could be avoided with just a small change in the operating pressure. In some cases, the pressure change needed to get above the S-V-L region might be so large that it causes an unacceptable drop in ethane recovery. Another alternative is to increase the fraction of heavy components in the top of the tower, which, as shown in Figure 5, will move the dry ice formation curve to lower pressures and colder temperatures. This can be done by *increasing* the LTS liquid split to overhead (Liquid Split). The effect can be magnified by simultaneously *decreasing* the LTS vapor split to overhead (Vapor Split). Fig. 9 shows how the vapor CO_2 concentration in the top of the tower decreases when increasing Liquid Split and decreasing Vapor Split. This occurs even though the LTS liquid has a higher CO_2 concentration than the LTS vapor.

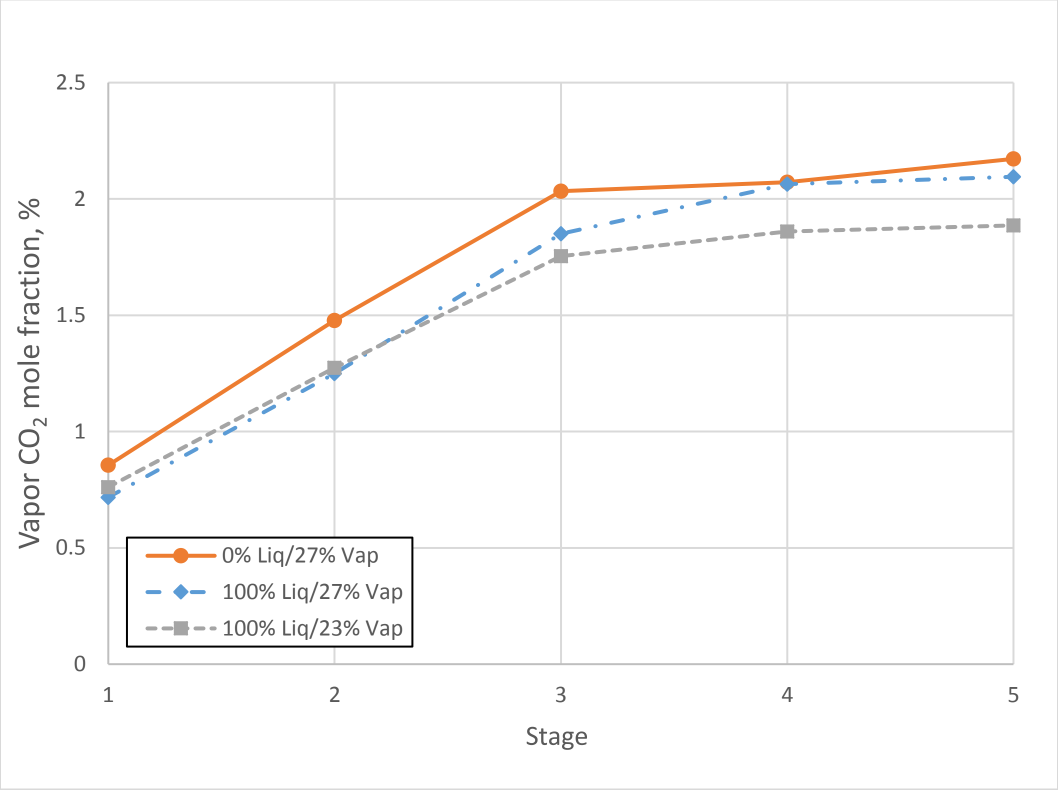

Figure 9. Effect of Liquid Split and Vapor Split on CO_2 concentrations near top of tower

For the set of conditions used in this example, dry ice formation is expected on stages 2 and 3 with 0% Liquid Split. Fig. 10 compares the dry ice formation curve on Stage 2 for 0% versus 100% Liquid Split. Other parameters are the same in these scenarios (290-psig tower pressure, 27% Vapor Split). As can be seen, the additional liquid to the top moves the dry ice curve to lower pressures and colder temperatures, giving a larger dry-ice free operating envelope, which allows the operating point for the 100% Liquid Split to lie outside of the S-V-L region

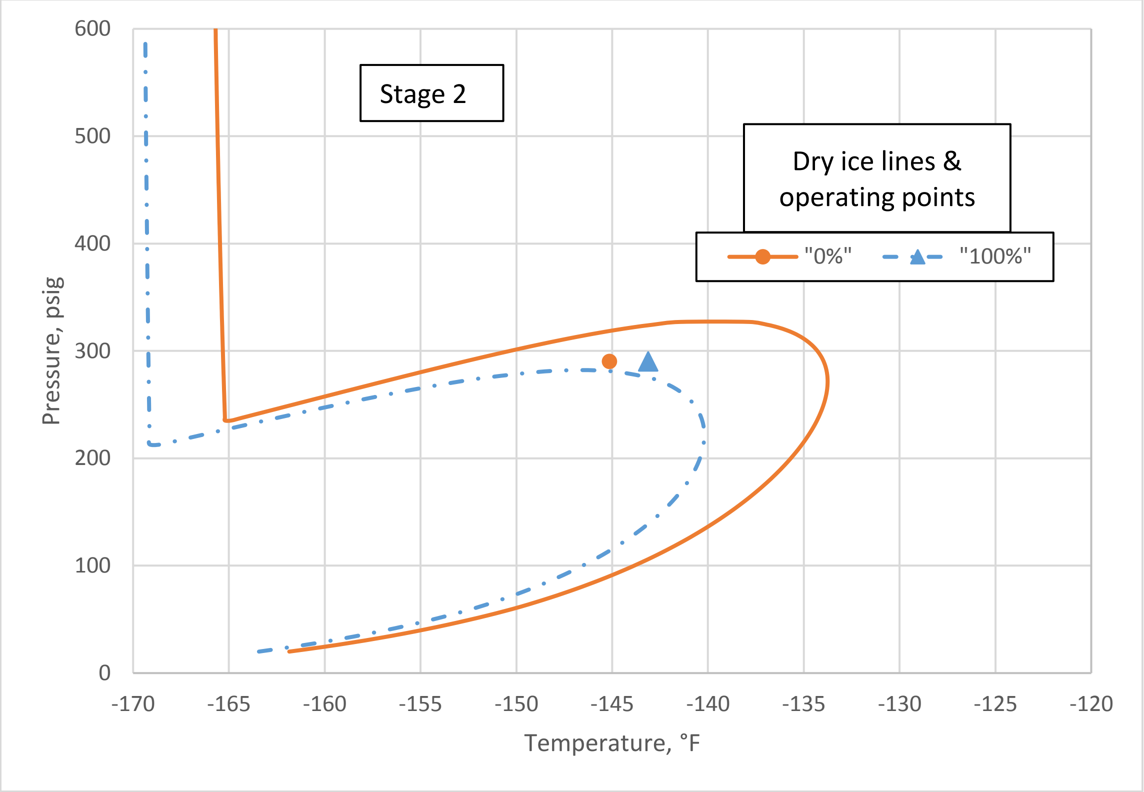

Figure 10. Comparison of Stage 2 operating point and dry ice curve for 0% and 100% Liquid Split (Feed A, Pressure = 290 psig, 27% Vapor Split)

Intuition would lead one to think that sending a richer composition to the top of the tower would decrease ethane and propane recovery. Table 3 shows the maximum ethane and propane recoveries for for 0% versus 100% Liquid Split (if one neglects the potential to form dry ice). The maximum ethane and propane recovery is found by varying the Vapor Split with a fixed Liquid Split. The results are shown for a top-stage pressure of 290 psig, but similar results are found at other pressures. The results confirm our intuition that sending richer liquid to the top of the tower results in loss of the richer components into the residue gas. However, simulation models can predict dry ice formation and then ignore dry ice accumulation in the column calculations. In real equipment dry ice accumulation can lead to flooding, poor separation, or complete flow blockage. Therefore, simulation results that indicate dry ice formation should be treated with caution. In the present case of Table 3, the 100% Liquid Split is the only viable option of the two.

Table 3. Effect of Liquid Split on Maximum Ethane & Propane Recovery (Feed composition A, Pressure = 290 psig)

Liquid Split, %	Vapor Split, %	C_2 Recovery, %	C_3 Recovery, %
0*	29	91.0	99.2
100	27	90.9	98.7

*Dry ice formation predicted at this condition

Also of note is that the Vapor Split that yields the maximum ethane recovery, and coldest overhead product temperature, is lower when the Liquid Split increases. This is a trend that will continue to appear later in this paper. Therefore, if the Liquid Split increases, reduce Vapor Split to maximize recovery.

Optimization

The operational levers mentioned above are not exclusive of each other. As is often the case, a combination of lever adjustments will yield optimal performance. The definition of optimal is not fixed. The relative value of increased ethane recovery versus increased residue compressor power must be determined for each facility regardless of whether dry ice formation is an issue. The possibility of dry ice formation simply complicates the analysis by constraining the available process setpoints.

Presented below is a comparison of the operating points that yield the maximum dry ice-free ethane recovery for 0%, 50%, and 100% Liquid Split at pressures from 270 to 320 psig. (Dry ice-free operation is defined as not having a predicted dry ice formation temperation within 5 °F of the operating temperature.) For each pressure and Liquid Split combination, the Vapor Split is adjusted to find the maximum dry ice-free ethane recovery for that combination. Tables 4, 5 and 6 present the results for feed composition A (1.5% CO_2), B (1.8% CO_2), and C (2.1% CO_2). Moving from A to C, CO_2 replaces methane, while the rest of the gas composition is fixed to give a C_2+ GPM of 2.3 gal/MSCF.

Table 4 shows that with 1.5% CO_2 in the mixture, dry ice formation cannot be avoided at or below 290 psig with 0% Liquid Split. At 300 psig, the column is able to avoid dry ice formation if the Vapor Split is reduced to 23%. This is lower than the typical GSP Vapor Split of 30% [4]. By operating at a reduced Vapor Split, the heat integration is suboptimal. The resultant warmer tower allows more CO_2 to escape in the residue gas, reduces the concentration in the tower, and shrinks the dry ice-formation region of the operating envelope. By shifting the pressure 10 psi higher, the Vapor Split can move to 30% without dry ice formation, achieve better heat integration, and actually *increase* ethane recovery. (This is opposite of the typical recovery *decrease* with higher column pressure.) For 50% and 100% Liquid Split, the tower is able to operate with a Vapor Split that yields maximum heat integration. The recoveries and residue compressor power go down as the pressure is increased, except as noted above for the suboptimal case. Propane recovery seems to decrease more with increased Liquid Split than does ethane recovery.

In Table 5 with higher CO_2 feed concentration (1.8%) there are fewer options for dry ice-free operation. Below 300 psig, the 100% Liquid Split is the only one that avoids dry ice. Below 290 psig, even with 100% Liquid Split, the Vapor Split has to be set lower than what achieves the lowest residue gas temperature. Due to this, as the tower pressure is changed from 270 to 290 psig the achievable ethane recovery only decreased 0.3%, while the residue power decreased by 9%. At 300 psig, 50% Liquid Split becomes an option but requires a reduced Vapor Split, making the ethane recovery lower than at 100% Liquid Split. The same trend holds that propane recovery decreases more than ethane recovery with higher Liquid Split.

Table 4. Recoveries and residue compression power at conditions producing maximum ethane recovery. (Feed composition A, 1.5% CO_2)

			Recovery, %		
Top-stage pressure, psig	Liquid Split, %	Vapor Split,%	C_2	C_3	Res. Comp Power, hp
270	0	*	--	--	--
	50	28	93.1	99.1	2778
	100	27	92.7	98.9	2771
280	0	*	--	--	--
	50	28	92.5	99.0	2655
	100	27	92.1	98.8	2648
290	0	*	--	--	--
	50	29	91.7	99.0	2541
	100	27	91.4	98.7	2530
300	0	23	88.8	99.2	2463
	50	28	90.8	98.9	2431
	100	28	90.5	98.6	2425
310	0	30	89.4	99.0	2345
	50	29	89.6	98.7	2332
	100	27	89.4	98.4	2318
320	0	29	87.6	98.9	2242
	50	29	87.9	98.6	2229
	100	27	87.9	98.3	2215

*At these conditions, no Vapor Split was found that maintained a 5 °F buffer above dry ice formation temperature.

Table 5. Recoveries and residue compression power at conditions producing maximum ethane recovery. (Feed composition B, 1.8% CO_2)

			Recovery, %		
Top-stage pressure, psig	Liquid Split, %	Vapor Split,%	C_2	C_3	Res. Comp Power, hp
270	0	*	--	--	--
	50	*			
	100	21	91.2	98.6	2761
280	0	*	--	--	--
	50	*	--	--	--
	100	24	91.1	98.7	2632
290	0	*	--	--	--
	50	*	--	--	--
	100	27	90.9	98.7	2516
300	0	*	--	--	--
	50	23	88.3	98.6	2433
	100	28	89.8	98.6	2415
310	0	*	--	--	--
	50	28	88.7	98.7	2321
	100	28	88.5	98.4	2313
320	0	29	86.7	98.9	2238
	50	29	87.1	98.5	2227
	100	28	87.1	98.2	2220

With 2.1% CO_2, Table 6 shows a more limited range of dry ice-free conditions. Even with 100% Liquid Split the column must be operated with a suboptimal Vapor Split.

Table 6. Recoveries and residue compression power at conditions producing maximum ethane recovery. (Feed composition C, 2.1% CO_2)

			Recovery, %		
Top-stage pressure, psig	Liquid Split, %	Vapor Split,%	C_2	C_3	Res. Comp Power, hp
310	0	*	--	--	--
	50	*	--	--	--
	100	25	87.2	98.2	2301
320	0	*	--	--	--
	50	*	--	--	--
	100	27	86.1	98.2	2206

*At these conditions, no Vapor Split was found that maintained a 5 °F buffer above dry ice formation temperature.

Tables 4-6 compare the effect of CO_2 concentration with a relatively lean gas (2.3 C_2+ GPM). Table 7 shows how a richer gas (Composition E, 5.0 C_2+ GPM) behaves. GSP processes with rich gas feeds typically need external mechanical refrigeration [5]. In this case mechanical refrigeration is used to cool the low-temperature separator to -30 °F. (The refrigeration power listed in Table 7 assumes a power to duty ratio of 250 hp/MMBtu.)

It can be seen in Table 7 that ethane recoveries are lower than with the leaner gas. As ethane recovery decreases, so do CO_2 recovery and concentrations in the tower. This, along with more liquids in the column, moves the dry ice formation region farther from the operating envelope. Consequently, except for the 0% Liquid Split at 270 psig, the need to avoid dry ice formation does not affect the maximum recovery Vapor Split in Table 7. The richer feed gas tends to suppress dry ice formation.

Some interesting observations can be made about Table 7. Some important parameters move inversely with Liquid Split. As Liquid Split increases these items decrease,

- propane recovery (more so than with leaner feed gas)
- residue compression power (more so than with leaner feed gas)
- refrigeration power

However, there appears to be a maximum ethane recovery between 0% and 100% Liquid Split.

Table 7. Recoveries and residue compression power at conditions producing maximum ethane recovery. (Feed composition E, 1.8% CO_2, 5.0 C_2+ GPM)

			Recovery, %		Power, hp	
Top-stage pressure, psig	Liquid Split, %	Vapor Split, %	C_2	C_3	Residue	Refrigeration
270	0	28	84.1	99.4	2518	616
	50	25	88.4	98.7	2472	666
	100	18	85.4	97.9	2418	613
280	0	35	87.0	99.4	2446	709
	50	25	87.3	98.6	2358	683
	100	18	84.5	97.7	2304	634
290	0	36	85.3	99.3	2333	744
	50	25	86.2	98.4	2241	713
	100	18	83.5	97.5	2185	673
300	0	37	83.7	99.2	2210	808
	50	25	85.1	98.2	2120	763
	100	18	82.6	97.2	2064	728
310	0	38	81.9	99	2060	933
	50	25	83.9	98.1	1981	855
	100	18	81.6	97.0	1925	828
320	0	38	80.0	98.9	1824	1216
	50	25	82.6	97.9	1797	1053
	100	18	80.5	96.7	1741	1030

If the feed gas CO_2 content rises, most of the trends seen in Tables 4-7 continue. This is shown in Table 8, where the feed CO_2 content increases to 3.8%, while maintaining the same richness (5.0 C_2+ GPM) as in the previous example. At the higher CO_2 content, a higher Liquid Split and/or lower Vapor Split is necessary to avoid dry ice formation at lower pressures, similar to the leaner gas. Also, with the richer gas, more pronounced difference in recoveries, compression power, and refrigeration power versus Liquid Split are still present.

Table 8. Recoveries and residue compression power at conditions producing maximum ethane recovery. (Feed composition F, 3.8% CO_2, 5.0 C_2+ GPM)

			Recovery, %		Power, hp	
Top-stage pressure, psig	Liquid Split, %	Vapor Split,%	C_2	C_3	Residue	Refrigeration
270	0	*	--	--	--	--
	50	*	--	--	--	--
	100	16	83.3	97.5	2403	678
280	0	*	--	--	--	--
	50	20	82.6	98.0	2341	672
	100	16	82.4	97.3	2301	680
290	0	*	--	--	--	--
	50	25	84.1	98.1	2266	742
	100	16	81.6	97.1	2200	688
300	0	*	--	--	--	--
	50	25	83	97.9	2163	755
	100	16	80.7	96.8	2098	705
310	0	*	--	--	--	--
	50	25	82	97.7	2060	778
	100	16	79.8	96.6	1994	738
320	0	*	--	--	--	--
	50	25	80.9	97.5	1953	819
	100	16	78.9	96.3	1889	778

*At these conditions, no Vapor Split was found that maintained a 5 °F buffer above dry ice formation temperature.

Conclusion

Dry ice formation in a demethanizer tower is a problem that must be managed as feed CO_2 levels increase. There are multiple operational levers in a GSP facility that can be adjusted to avoid dry ice, including tower pressure, Inlet Reboiler Split, Vapor Split and Liquid Split. The effect of these levers is summarized below.

- Tower pressure—Higher tower pressures may allow operation above the S-V-L region of the phase envelope. All else being equal, higher pressure will warm the tower and decrease recoveries.
- Inlet Reboiler Split—Increased flow to the bottom reboiler will increase the bottom temperature, which will force CO_2 back up the column and lead to higher CO_2 concentration in the top of the tower. This could cause dry ice formation. Decreased flow to the reboiler will lower the bottom temperature, which will increase NGL CO_2 and CH_4 concentrations.
- Vapor Split—There is a vapor split that will produce the coldest overhead product temperature, which typically corresponds to maximum ethane and propane recovery. To avoid dry ice formation, it may be necessary to adjust the vapor split to warm the column.
- Liquid Split—Increasing the Liquid Split tends to suppress dry ice formation, but does have an adverse effect on propane recovery for both rich and lean feed gas, and ethane recovery for lean gas. With richer gas, there appears to be an optimal Liquid Split between 0% and 100% that maximizes ethane recovery.

This summary is captured in Table 9.

Table 9. Effect of operating levers on plant performance.
Lever direction set to reduce likelihood of dry ice formation.

Lever	Direction to move	Likelihood of Dry Ice	C2 Recovery/ NGL production	Compressor Power/Fuel Usage	Bottoms Temp
Column Pressure	⬆	⬇	⬇	⬇	⬌
Reboiler Inlet Split	⬇	⬇	⬆	⬌	⬇
Liquid Split	⬆	⬇	* ⬇	⬌	⬌
Vapor Split	⬇	⬇	** ⬌	⬌	⬌

* For richer gases, there appears to be a Liquid Split between 0% and 100% that maximizes C_2 recovery.
** There is a vapor split that maximizes recovery and NGL production.

Equipment limitations and process economics will dictate the available range of adjustment for these levers. A thorough analysis can help find the optimal combination.

The steps below are suggested as a methodology to determine the right set of conditions for a facility to maximize profitability while avoiding dry ice formation.

1. Work with the Operations team to determine the operating limits of the existing equipment, and the product specifications that must be maintained when changing process settings. For instance, at the Enbridge Longview facility the column pressure is controlled by the speed of the residue compressors. Lower compressor speed causes the column pressure to increase. However, the residue compressors have a minimum flow limit. This flow limit can prevent higher tower pressures when the feed flowrate to the demethanizer is low.
2. Develop a working simulation model that can reproduce plant operating data. Keep in mind that the plant might not be in “as new” condition, which might make it more difficult to match operating data. As an example,
    a. In the Longview plant, the Operations group was deeply concerned as to the actual flow through the side reboiler. All passes of the gas-gas heat exchanger had been previously cleaned and hydrostatically tested with no indications of any leaks and/or excessive fouling. Tests indicated that the side reboiler flow was essentially zero (based on temperature profiles around the reboiler as the plant was manipulated). Radiography of the reboiler piping revealed no obvious metallic obstructions. The plant was shutdown and the piping was probed with remote video cameras where it was discovered that the inlet piping to the reboiler, from the tower, was completely plugged with packing. This led to a longer duration shutdown where the tower was unpacked, copious amounts of

    packing removed from in between the flow distributors between the packing beds, and the tower was repacked. Further investigation of the flow distributors revealed that they had not been manufactured in accordance with the manufacturer's drawings. When pressure surges had occurred over time, packing had worked its way through the flow distributors and ultimately in between the packing beds and into the reboiler side draw piping.
    b. The first iteration of the simulation model assumed that the reboiler feed was a total draw from the middle of the column. To fit the data better, this had to be modeled as a partial draw instead.
3. Obtain management support to manipulate the plant and encourage the operators to move away from the thinking of "that is not the way we do it".
4. With a validated model in hand, work with Operations to develop an overall test plan. The model can be used to produce expected results for a set of operating setpoints for the tower pressure, Inlet Reboiler Split, Vapor Split and Liquid Split. Confirm with Operations the desirability of these results. For instance, setpoints to maximize recovery may cause excessive C_1/C_2 ratios or unacceptable NGL CO_2 concentration.
    a. Establish a series of scenarios to test how well the plant responds in accordance with the predictions made by the process model. For example, at the Longview plant, several scenarios were developed to test the plant response to raising the tower pressure in 10 psi increments. The first goal of the test was to determine the adverse effects of operating the plant at higher tower pressures. In this case, due to customer requirements, the tower pressure could not be raised by more than about 35 psig over normal operating conditions. This constraint was then carried forward into the development of other scenarios.
    b. Include in the plan a pathway for moving from current setpoints to new setpoints. The simulation model can be used to determine if intermediate steps between current and desired setpoints might be susceptible to dry ice formation.
    c. Expect the unexpected, since the simulation model might not have captured everything. Think in terms of a long-distance race, not a short-distance sprint. Make changes slowly and maintain the rigor and discipline to not initiate a new change until all of the observations from the existing change have been completed and the resulting behavior understood.
    d. If unexpected behavior does occur, determine whether the model should be refined to incorporate this behavior while still maintaining fidelity to previous operating data. If necessary, revise the test plan before moving forward.

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