



Advancing Export Terminal Technology: An Optimized Process for the Refrigeration of Cryogenic Hydrocarbons

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ABSTRACT

As a result of the “shale revolution” in the United States, the availability of competitively priced chemical pre-cursor feedstocks, primarily ethane and propane, has resulted in increased grassroots construction and/or expansion of various petrochemical complexes along the gulf coast. Thanks to this build-out, domestic production of petrochemical commodities, like ethylene and propylene, is expected to greatly outpace domestic consumption. Excess US domestic production and the resulting lower prices will lead to escalating international demand for these commodities overseas; domestic petrochemical producers are looking at large consumers in China, India, and Europe to take up the slack and import this excess production. In order to export these feedstocks, refrigeration units are required to chill the hydrocarbons to cryogenic temperatures. Installation of the most efficient refrigeration process at the export terminal is vital for the terminal owner to maximize their investment potential.

This paper presents the technical design for an ethylene export terminal utilizing two (2) different refrigeration processes: the traditional open cycle (OC) and a more advanced single mixed refrigerant (SMR) scheme. The two processes were modelled in-house at Chiyoda using the generic concepts of refrigeration cycles and UNISIM Design suite 450 simulation software. Each process is optimized through adjusting the available process variables to achieve an overall efficient refrigeration process for an ethylene production rate of 100 metric tonnes per hour (mt/hr). The technical design is concluded by defining major equipment sizes, layout, and a relative cost for the units. While the technical paper will focus on ethylene, similar results can be obtained for other hydrocarbons including ethane and propylene.

As this sustainable production of ethane continued, the depressed ethane commodity price led to a rapid build-out and expansion of ethylene production in North America, primarily along the Gulf Coast region. A map of the existing US ethylene cracker plant and HGL pipelines is shown in Figure 3. As evident on the map, the bulk of the existing ethylene cracker plants are located along the Gulf Coast. Ethylene is arguably the most vital petrochemical in the world and is widely used in the production of everything from plastics to textiles.

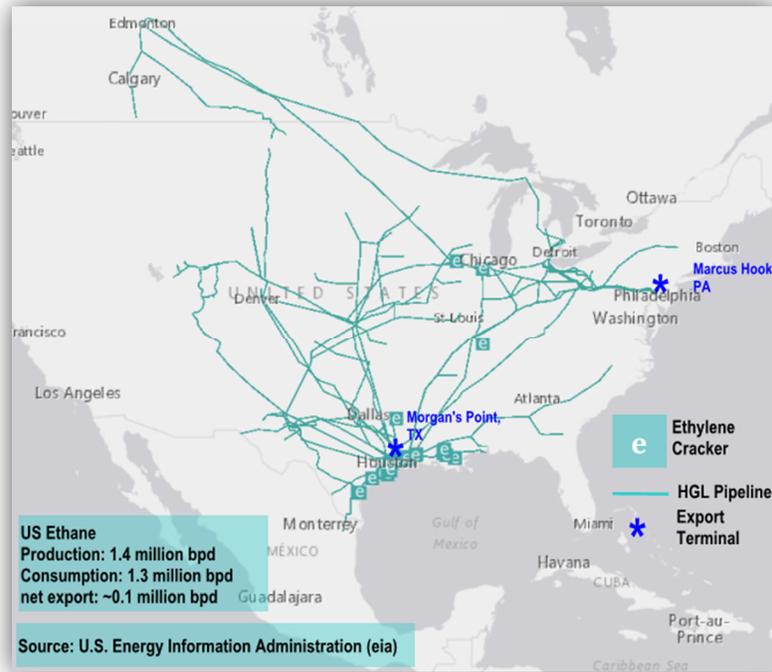


Figure 3 – Existing US Ethylene Cracker, Export Terminal and HGL Pipeline

The first wave of ethylene expansion is expected to add a total of 10 million to 12 million metric tonnes per year to the current market; this expansion has been ongoing since 2014 and is expected to crest in 2019. Table 1 provides a list of the current on-going ethylene expansions in North America.

Table 1- Ongoing North America Ethylene Projects

| Company | Location | Size (tonnes) | Status |
|-------------------------------|-------------------------|---------------|---------------------------------|
| OxyChem / Mexichem | Ingleside, Texas | 550,000 | Start-Up in Q1 2017 |
| Dow Chemical | Freeport, Texas | 1,500,000 | Start-Up Q2 2017 |
| ExxonMobil Chemical | Baytown, Texas | 1,500,000 | Under Construction |
| Chevron Phillips Chemical | Cedar Bayou, Texas | 1,500,000 | Under Construction – Q4 2017 |
| Formosa Plastics | Point Comfort, Texas | 1,590,000 | H2- 2018 |
| Sasol | Lake Charles, Louisiana | 1,500,000 | Under Construction – 2018 |
| Axiall / Lotte Chemical | Lake Charles, Louisiana | 1,000,000 | Under Construction - 2019 |
| Shintech | Plaquemine, Louisiana | 500,000 | Under Construction – Q2 2018 |
| Shell | Monaca, Pennsylvania | 1,500,000 | Starting Construction – Q1 2020 |
| Dow Chemical | Plaquemine, Louisiana | 250,000 | Expansion– Startup Q4 2016 |
| LyondellBasell | Corpus Christi, Texas | 363,000 | Start-Up - Q3 2017 |
| Westlake Chemical Corporation | Calvert City, Kentucky | 32,000 | H1 - 2017 |
| Indorama | Carlyss, Louisiana | 370,000 | Start-Up - Q4 2017 |

In addition to the current projects under construction, there is a second wave of ethylene projects being considered at various stages of development. With this expansion, North America's ethylene production is expected to climb from approximately 32.2 metric tonnes to nearly 44.6 metric tonnes by 2026 [1].

This build-out of ethylene capacity has had a measurable impact on the petrochemical market in North America: ethane prices are slowly rising due to higher consumption rates (whether used internally or exported) and ethylene prices are falling due to higher production rates amid weaker domestic demand. This bear market dynamic has resulted in some petrochemical companies looking to export ethylene from the United States to overseas markets. In order to export ethylene, the gas must be refrigerated (liquefied) to cryogenic temperatures and placed on special gas carriers for transit. This mode of transport is similar to liquefied natural gas (LNG) carriers albeit on a much smaller scale; a typically ethylene carrier will range from 10,000 to 25,000 m³ while an LNG carrier will range from 140,000 to 250,000 m³.

Currently, the majority of ethylene export terminals around the world utilize an open cycle system. These systems typically include a pre-cool refrigeration system, using propane or propylene as the refrigerant, followed by a series of flash stages, with recompression and recirculation of the flash vapors back to the front end of the unit. Chiyoda, with its pedigree in LNG, has developed a unique application of single mixed refrigerant technology as a competing refrigeration technology option. This paper provides a comprehensive comparison between these two technologies with emphasis on process efficiency, layout, capital expenditures, and operating cost.

OPEN CYCLE REFRIGERATION TECHNOLOGY

Open cycle refrigeration is a common technology utilized throughout the hydrocarbon industry for refrigeration of multiple fluids (propane, propylene, ethane, ethylene, etc.). While many different configurations are possible, there are two broad categories of design which are based on one simple design criteria: operational decision on whether to utilize cryogenic or non-cryogenic compressors. Using cryogenic compressors with a lower inlet temperature results in a lower overall horsepower due to the higher mass volumes entering the machines (higher actual cubic feet per minute – ACFMs). Non-cryogenic compressors are frequently utilized in the refrigeration industry but typically involve more equipment, particularly economizer heat exchangers, to warm the flash gas to non-cryogenic temperatures prior to re-compression. These machines tend to cost less due to simplicity and metallurgy factors although size limitations will sometimes require multiple parallel compressors. This paper will focus on the use of cryogenic compressors for the open cycle as the inclusion of non-cryogenic machines will result in additional equipment and higher horsepower.

Using cryogenic compressors, Figure 4 shows a schematic of a typical open cycle refrigeration unit which including three stage propylene compression for ethylene precooling and three stage ethylene flash gas compression and cooling. Each stage of flash requires a flash drum vessel which also serves at a suction drum for the flash gas compressor. For simplicity, the flash drums are not shown on the process diagram.

Ethylene is chilled in a consecutive series of three (3) kettle type heat exchangers. The kettle type heat exchangers have one refrigeration source, propylene, but contain two separate tube sheets in order to conserve the overall equipment count. Ethylene flash vapors are recompressed up to nominally 500 psia and recycled back to the kettle type heat exchangers albeit in a separate pass due to the lower operating

Table 2- Equipment List for Open Cycle Refrigeration Unit

| Equipment Type | Item Number | Equipment Call-Out | Comments |
|--------------------------|-------------|--|------------------------------------|
| Exchanger(s) | 02-E-01 | 1 st Stage Ethylene Chiller | Kettle type, two sided tube sheets |
| | 02-E-02 | 2 nd Stage Ethylene Chiller | Kettle type, two sided tube sheets |
| | 02-E-03 | 3 rd Stage Ethylene Chiller | Kettle type, two sided tube sheets |
| Vessel(s) | 02-V-01 | HP Ethylene Flash Drum | Horizontal vessel, 304SS |
| | 02-V-02 | MP Ethylene Flash Drum | Horizontal vessel, 304SS |
| | 02-V-03 | Ethylene Product Receiver Drum | Horizontal vessel, 304SS |
| | 03-V-01 | LP Propylene Comp. Suction Drum | Horizontal vessel, 304SS |
| | 03-V-02 | MP Propylene Comp. Suction Drum | Horizontal vessel, LT CS |
| | 03-V-03 | HP Propylene Comp. Suction Drum | Horizontal vessel, LT CS |
| | 03-V-04 | Propylene Refrigerant Accumulator | Horizontal vessel, CS |
| Pump(s) | None | | |
| Compressor(s) | 02-K-01 | LP Ethylene Recycle Compressor | Cryogenic, Variable Speed |
| | 02-K-02 | MP Ethylene Recycle Compressor | Cryogenic, Variable Speed |
| | 02-K-03 | HP Ethylene Recycle Compressor | Cryogenic, Variable Speed |
| | 03-K-01 | LP Propylene Refrigerant Compressor | Non-Cryogenic, Variable Speed |
| | 03-K-02 | MR Propylene Refrigerant Compressor | Non-Cryogenic, Variable Speed |
| | 03-K-03 | HP Propylene Refrigerant Compressor | Non-Cryogenic, Variable Speed |
| Process Cooler(s) | 03-E-01 | HP Propylene Refrig Comp Aftercooler | Air Coolers [1] |
| | 02-E-04 | HP Ethylene Recycle Comp Aftercooler | Air Coolers [1] |

Notes:

1. Compressor Aftercoolers can be cooled with cooling water, air coolers, or wetted surface air coolers. For the purpose of this comparison, air coolers are selected.
2. Common abbreviations: carbon steel is "CS", low temperature carbon steel is "LT CS", and 304 stainless steel is "304SS".

An open cycle refrigeration unit can be pre-fabricated on multiple skids and "re-assembled" on-site to minimize field construction mobilization. As a result, the vessels in this open cycle refrigeration unit are to be installed horizontally to reduce the potential impact of shipping to site (complications of fabricating in a vertical position and trying to ship to site or field erecting at site).

Metallurgy of the equipment will be varied but in general all equipment after the 3rd Stage Ethylene Chiller will be low temperature carbon steel or 304 stainless steel due to the colder process temperatures. All the equipment and piping in these sections will be insulated to minimize heat leak into the process (and retention of cold temperatures).

A major disadvantage of the open cycle system is the effect impurities in the process stream have on the overall performance of the unit. While ethylene is relatively clean (in most cases greater than 99.7% pure), the small amount of methane impurities will flash in the flash drums and result in an artificially high recycle until equilibrium is reached and the methane is dispensed with the ethylene product. This artificial recycle will increase the compression horsepower and result in a less efficient process. Heavy impurities in the propylene pre-cool refrigeration will have the opposite effect in that components heavier than propylene will accumulate in the 3rd Stage Ethylene Chiller and could potentially warm the refrigerant up slightly, reducing the ability to transfer refrigeration to the process. For that purpose, a heavy hydrocarbon "drag line" is typically required to circulate accumulated liquids from the last flash stage.

SMR REFRIGERATION CYCLE

SMR is a proven refrigeration technology which uses a closed loop, single cycle, mixed refrigerant. The technology is heavily utilized in the production of liquefied natural gas (LNG) including baseload facilities, mid-scale and peak shaver units, and the cryogenic cold sections of the ethylene fractionation overheads used in the production of ethylene. The fundamentals of the process are rooted in a simplistic design which inherently leads to less piping, fewer controls, and a lower equipment count while providing an efficient refrigeration process.

The schematic for SMR Refrigeration cycle is shown in Figure 5 for the refrigeration of ethylene. The mixed refrigerant, a blend of methane, ethylene, propylene, and normal butane components, is circulated in a closed loop system with recompression provided by a two (2) stage, centrifugal, non-cryogenic compressor. Hydrocarbon impurities in the refrigerant components such as butanes or pentanes have no significant effect on the operations at the concentrations normally encountered. Water and other components (primarily CO₂) that can freeze at cryogenic temperatures must be removed from make-up refrigerant prior to loading into the mixed refrigerant cycle. Similar to the open cycle, the compressor is driven by an electric motor with a variable speed drive to maximize turndown and limit electrical current in-rush during start-up.

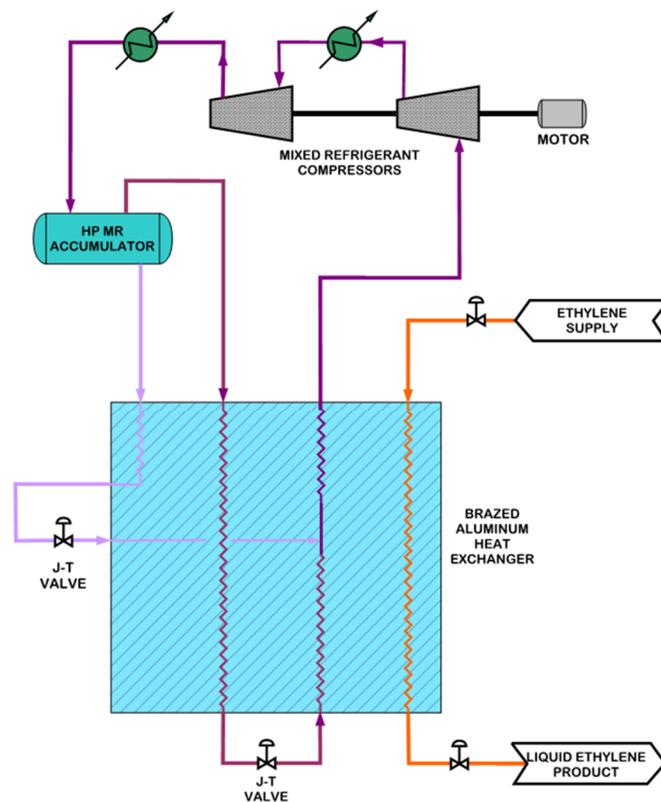


Figure 5 - Simplified Schematic of SMR Refrigeration Unit

From the discharge of the HP MR Compressor, 03-K-02, the refrigerant is cooled and split into a liquid and vapor refrigerant in the HP MR Accumulator, 03-V-03. The liquid and vapor refrigerants are chilled in separate paths within the Brazed Aluminum Heat Exchanger (BAHE) prior to routing through separate

Joule-Thompson valves (J-T) which drops the pressure to nominally 70 psig prior to re-entry into the BAHE. The BAHE is installed vertically, with the feed gas entering at the top and flowing downward to the cold end at the bottom. Cryogenic liquid produce and exits only from the bottom end of the BAHE. During a shutdown, these liquids are isolated at the bottom of the BAHE by gravity and cannot migrate to areas of the process not designed for low temperature. To enhance the design of the BAHE, the vapor and liquid refrigerant are recombined at an intermediate point in the exchanger to maximize thermal efficiency. Upon exiting the BAHE, the LP refrigerant is then recompressed in the LP MR Compressor, 03-K-01, cooled, and returned to the HP MR Compressor as previously identified.

Ambient ethylene, at pipeline pressure, is cooled in a single pass of the BAHE to the desired product temperature and flashed down to the required storage (on-site and/or carrier) pressure using a JT-valve. The desired product temperature is selected in order to sub-cool the ethylene product and minimize Boil off Gas (BOG) flash vapors at the product pressure. A key advantage of the SMR Refrigeration Cycle is the ability to adjust the refrigerant composition mixture to achieve a wide range of process temperatures using the available compression power. Table 3 provides a list of the necessary equipment for a SMR refrigeration cycle.

Table 3 - Equipment List for SMR Refrigeration Unit

| Equipment Type | Item Number | Equipment Call-Out | Comments |
|--------------------------|-------------|---------------------------------------|-------------------------------------|
| Exchanger(s) | 02-E-01 | Brazed Aluminum Heat Exchanger (BAHE) | Mounted on saddles; field insulated |
| Vessel(s) | 03-V-01 | LP MR Compressor Suction Drum | Horizontal vessel, CS |
| | 03-V-02 | HP MR Compressor Suction Drum | Horizontal vessel, CS |
| | 03-V-03 | HP MR Accumulator | Horizontal vessel, CS |
| Pump(s) | 03-P-01 A/B | LP MR Pumps | Horizontal, In-line Pump |
| | 03-P-02 A/B | HP MR Pumps | Horizontal, In-line Pump |
| Compressor(s) | 03-K-01 | LP MR Compressor | Non-Cryogenic, Variable Speed |
| | 03-K-02 | HP MR Compressor | Non-Cryogenic, Variable Speed |
| Process Cooler(s) | 03-E-01 | LP MR Compressor Aftercooler | Air Coolers [1] |
| | 03-E-02 | HP MR Compressor Aftercooler | Air Coolers [1] |

Notes:

1. Compressor Aftercoolers can be cooled with cooling water, air coolers, or wetted surface air coolers. For the purpose of this comparison, air cooler are selected.
2. Carbon steel is abbreviated "CS".

As with the open cycle, the SMR refrigeration unit can be pre-fabricated on multiple skids and "re-assembled" on-site to minimize field construction mobilization. The BAHE and JT-Valve loops are insulated along with the ethylene product outlet piping; all other process piping is un-insulated. Metallurgy of the SMR is carbon steel piping with the exception of the ethylene product piping exiting the main exchanger and the JT-Valve loops associated with the BAHE, which are 304 stainless steel.

The BAHE can be cooled down at a rate of approximately 1.5°F per minute. This results in short initial start-up time of slightly over two hours. After a shutdown and start-up/restart, provided the BAHE core is near cryogenic temperatures, normal operation can be obtained within 30 minutes.

During the shutdown, the cold refrigerant slowly warms and the more volatile components vaporize, increasing the pressure in the refrigerant system. This gradual warming and pressure rise can take over a week before the system stabilizes or reaches the "settle out" pressure. In this design, the transfer of

refrigerant to storage is not required for pressure release as the equipment and piping design pressures in the loop are high enough to contain the refrigerant. Venting of the refrigerant is not anticipated because the compressor can be started at settle-out pressure with the use of a suction throttling valve. The design of the system is such that only a small amount of refrigerant is required once the system is charged, so minimal makeup inventories are required. Refrigerant drying beds are included for several components to ensure that the refrigerants entering the closed loop system are free of moisture that can potentially freeze.

For refrigerant make-up, methane is taken from a pipeline or brought to the facility in iso-containers and/or truck transports (LNG). Ethylene is pulled from the pipeline. The source of other refrigerants are from individual storage tanks (bullet type storage tanks) or iso-containers. All refrigerant components are added to the inlet line of the LP MR Compressor Suction Drum, 03-V-01, by circulating a small flow of hot, low pressure refrigerant vapor from the compressor discharge. This bypass flow (sweep gas) is used to moderate the ethylene temperature and vaporize the heavier components. A Refrigerant Drum is provided for any refrigerant liquid taken out of the system for maintenance or due to excess liquid inventories adjustment. This recovered refrigerant can be added back to the system as required, to minimize refrigerant losses.

BASIS OF DESIGN

Ethylene is a colorless gas with a faint “sweet and musky” odor at standard ambient conditions. It is highly flammable and easily ignited. Ethylene is typically transported by pipeline at elevated pressures (80°F at 1000 psig) which places it squarely in the dense phase vapor area of the phase envelope.

For the purpose of this technical comparison, a set of standard parameters were developed to provide guidance in the development of the process simulations. These values are provided in Table 4.

Table 4 – Basis of Comparison

| Basis | Value | Comments |
|------------------------------------|---|--|
| Ethylene Flowrate | 100 metric tons per hour | Approximately 800 gpm |
| Inlet Conditions | 1000 psig @ 80°F | Standard Pipeline Conditions |
| Ethylene Composition | 99.7% Ethylene / 0.3% Methane | Mole Percent |
| End Conditions | -152.1 °F @ 2.0 psig | Saturated Liquid |
| Compressor Efficiency | 77% and 79% | Polytropic Efficiency (1 st /2 nd stage) |
| Pump Efficiency | 75% | Adiabatic Efficiency |
| Approach Temperature | 7°F 4°F | Kettle (BKU or equivalent) Braze Aluminum Heat Exchanger (BAHE) |
| Ambient Conditions | 95°F / 20% Humidity 20' above Mean Sea Level | Gulf Coast Conditions |
| Process Cooling Temperature | 90°F | Air Coolers - 10°F to dew point |
| Maximum Skid Dimensions | 14' x 14' x 40' | Truck-able - Width x Height x Length |

These conditions are set to remove any preconceived technology bias and provide an accurate comparison of the two different technologies. As each individual site and facility is different, adjustments might be required to reflect a true site specific comparison at a defined location.

COMPARISON

Detailed simulations of both processes were developed using UNISIM Design suite 450 simulation software with the Peng-Robinson equation of state and the Lee Kessler enthalpy correlation. The focus of the simulations were inside battery limits (ISBL) only and did not include any ethylene conditioning prior to refrigeration, i.e. drying and filtering/coalescing, or product run-down, i.e. storage and load-out to a gas carrier.

A technology comparison summary is provided in Table 5. This comparison study was undertaken to provide a technology comparison for the inside battery limits (ISBL) facility; it should be noted that availability of peripheral equipment and site specific designs could result in a different design. Key parameters utilized in the comparison include: process efficiency, yearly operating expenses, equipment piece count, number of process skids, overall layout requirement, and capital expenditures.

Table 5 - Process Efficiency Comparison

| Comparison Metrics | Open Cycle | SMR |
|--|------------|---------|
| Total Electrical Consumption | | |
| Horsepower (brake) | 11,300 | 10,600 |
| Kilowatt | 8,400 | 7,900 |
| Electrical Consumption (bhp) ⁽¹⁾ | | |
| Compressor | 10,900 | 10,100 |
| Pumps | N/A | 200 |
| Process Cooling Fan(s) | 400 | 300 |
| Process Efficiency (kWh/tonne) | 84.3 | 78.9 |
| Yearly Electrical Consumption (ISBL) ⁽²⁾ | \$4.3MM | \$4.0MM |
| Equipment Piece Count | 18 | 10 |
| Number of Process Skids | Ten (10) | Six (6) |
| Overall Layout Dimensions (relative) | 1.6 | 1.0 |
| Capital Expenditures (relative) ⁽³⁾ | 1.7 | 1.0 |

Notes:

1. Brake horsepower
2. Electrical consumption based on \$0.06/kWh, operating 350 days/year (~96% availability).
3. Capital expenditures based on budgetary vendor equipment cost factored for installation at site. SMR technology was designated as the base design.

From the preceding table, the refrigeration technology choice is clear: single mixed refrigeration technology requires less capital and operating expenditures, a smaller footprint, and less equipment.

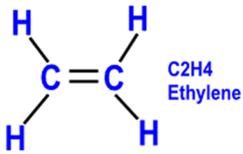
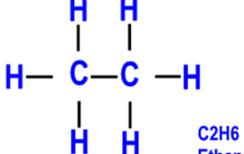
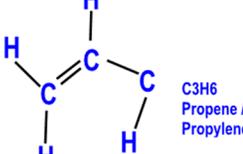
ALTERNATIVE CONFIGURATIONS

Another key advantage of the SMR technology is the flexibility it offers without sacrificing performance. The product side is a once through closed system which is independent of the refrigerant loop. By adjusting the refrigerant composition, provided there is enough compression horsepower and surface area in the BAHE available, the same unit can be utilized to refrigerate other hydrocarbon including propane, propylene, ethane, or methane (production of LNG). In all cases, the inlet product must be free of impurities which can freeze or plug the BAHE.

Additionally, the same equipment can be adjusted to achieve a range of saturated product temperatures (for example, an ethylene SMR unit can be adjusted to refrigerate product between -130°F and -155°F depending on the loading scenarios and storage requirements available). With the open cycle design,

the equipment is designed for certain process conditions and operating outside of that range would be very difficult at best. Relative available refrigeration capacity for a 100 mt/hr ethylene refrigeration unit is shown in Table 6

Table 6 – Relative Refrigeration Capacity – 100MTH SMR Ethylene Unit

| | Ethylene | Ethane | Propylene |
|--|--|---|--|
| Molecular Structure |  <chem>C2H4</chem> Ethylene |  <chem>C2H6</chem> Ethane |  <chem>C3H6</chem> Propene / Propylene |
| MW | 28.06 | 30.08 | 42.09 |
| Boiling Point, °F @ atm press. | -155 | -128 | -54.4 |
| Specific vol, ft³/lb | 13.8 | 12.65 | 9.09 |
| Expansion ratio, Vapor/Liquid [Note 1] | ~ less than 500 : 1 | ~ less than 450 : 1 | ~ less than 350 : 1 |
| Mont Belvieu Spot, \$/mt | 677 | 584 | 882 |
| liquid density, lb/ft³ at 2 psig | 35.23 | 33.77 | 37.78 |
| Relative Liquefaction Production (Ref: 100 MTH Ethylene Unit) | 100 MTH | 110 MTH | 125 MTH |
| <i>Note 1: Compare the expansion ratio with 600:1 for NG to LNG.</i> | | | |
| <i>Note 2: Spot Price of Mont Belvieu, Sep 2017</i> | | | |

Depending on the severity and length of the alternative product chilling, Operations can either operate less efficiently (leave the refrigerant as is) or adjust the refrigerant composition to utilize compression horsepower and surface area effectively.

Additionally, another configuration would allow Operations to purchase multiple BAHE for each service (ethylene, ethane, propylene for example) and operate with one common compression unit. A schematic of this alternative configuration is shown in Figure 6. This configuration would also allow Operations to increase reliability through multiple common compressor units (if desired).

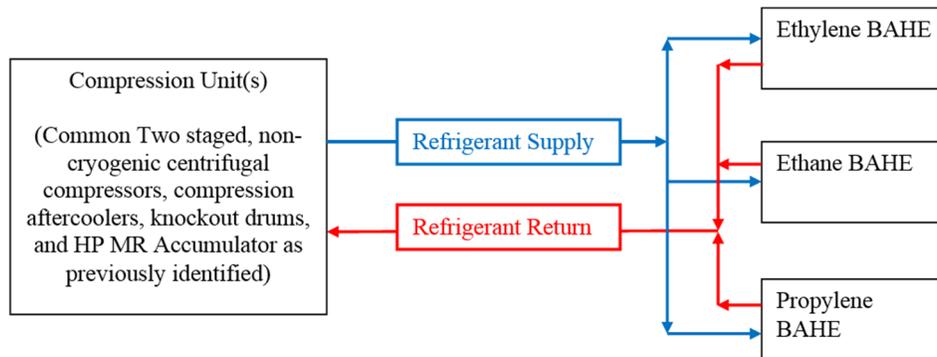


Figure 6 - Simplified Schematic of SMR Multi-Product Refrigeration Unit

CONCLUSION

While the Open Cycle ethylene refrigeration unit is certainly a viable technology for the export of ethylene, the potential future reduction in the ethane to ethylene price spread will require facility operators to look at improving the overall economics of ethylene refrigeration. A SMR Refrigeration unit has improved compression efficiency, smaller footprint, fewer equipment count, reduced installed capital cost, and lower operating expenses compare to the conventional refrigeration technology. Chiyoda International Corporation has designed three (3) different, off-the-shelf, size plants for the refrigeration of ethylene (50 mt/hr, 100 mt/hr, and 150 mt/hr). These units are available for quick integration into an existing facility pending definition of the outside battery limit scope and availability of existing plant infrastructure.

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