Liquefied Natural Gas (LNG) - Thermodynamics and Liquefication Systems Part 3A

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Steven Vitale Ph.D., P.E.

CED CANADA
engineering.ca
CPD FOR THE PROFESSIONAL

Continuing Education and Development, Inc.

P: (877) 322-5800
info@cedengineering.ca

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A Safety Moment

This learning document is meant to be at a technical level, mostly on refrigeration systems. The most important intention of every document I produce is to give you the basic technical knowledge you need to start your study on how to continue making the Liquid Natural Gas Industry a “Safe and Reliable Industry.” You need technical knowledge to do that.

The image to the right is placed here as a reminder that everyone has someone who loves and needs them to come home at the end of their shift.

Reliability is also related to safety because if the LNG plant cannot make LNG into vapor when needed, the consuming public may be out of gas during the worst of cold weather times. This would put the public at severe health risk.

We, as engineers, need to ensure that our designing, planning, operating, and maintenance of LNG facilities help assure safety and reliability.

This will help ensure that everyone comes home at the end of their shift and that gas is supplied when needed by the end-user customers.

Figure ***Error! No text of specified style in document.****.1: Beautiful Granddaughter*

Source: Self-Made photo

Introduction

Two hundred years ago, ice was harvested from frozen rivers in the winter, and large chunks of it were stored in buildings insulated by large bales of hay and sawdust. During the spring and summer, that ice was consumed, but those who could afford it, and once it ran out, there was no way to produce the heat extraction needed to make ice. The only source of that cold product was to wait for the winter weather to produce it!

In 1834 Jacob Perkins invented the first vapor compression system for refrigeration, and in 1876, Carl von Lined patented a new process for liquefying gases. Today nearly every car and home are air-conditioned via various technologies; the most common is the vapor-compression–condensation–pressure-drop-evaporation system. This system is used in household refrigerators and massive liquefaction plants worldwide. The massive systems used in LNG export facilities use the same principles as most home refrigeration systems, except that some enhancements are used to make the large-scale systems more energy efficient. Also, the refrigerants needed to produce very cold temperatures differ from those used in home air-conditioning and refrigeration systems.

We take for granted that when we want a cold soda, it is readily available from the refrigeration system in our house. The amazing thing is that the systems are so well perfected that typically the only reason they are replaced is that they go out of style rather than because they need to be fixed. These systems have been running for many decades with little maintenance. These smaller systems have been so reliable for so many years because, since the late 1920s, these small-scale refrigeration systems have been hermetically sealed. That means the motor and compressor are in a sealed case without the need for shaft seals that could leak and without any possibility of refrigerant contamination.

Over the period of the past 189 years, since Jacob Perkins invented the vapor compression refrigeration system, refrigerant technology has also developed significantly. In the 1800s, refrigerants were extremely toxic, and some were inefficient. These toxic refrigerants included ammonia, methyl chloride, and sulfur dioxide. Refrigeration systems were often installed outside to avoid death from a refrigerant leak.

I had chemical pneumonia for a month due to exposure to anhydrous ammonia from a small refrigeration system. Such exposures have killed many.

In 1928 halogenated hydrocarbons such as chlorofluorocarbons (Trade named Freons) were invented. This revolutionized refrigeration, and various Freon compounds were developed for various temperature applications. However, in the late 1900s, as it became apparent that Freon was harmful to the environment, legal restrictions were placed on using and reusing Freons. With the phasing out of older traditional Freons, newer refrigerants (hydrofluorocarbons, also trade name Freons) were introduced, such as R-134A for automobile applications and R-410a for home air conditioning applications. Even these refrigerants have associated environmental concerns, and newer refrigerants are under development.

For very low-temperature refrigeration systems (LNG production), Freons cannot be used because they cannot achieve the very low temperatures needed to liquefy natural gas. Instead, mixtures of nitrogen, methane, ethane, propane, and iso-pentane are some of the most common refrigerant mixes for attaining ~ -260 F. In a large LNG production facility, the downside of these refrigerants is that tons of them are needed in these systems that cannot be hermetically sealed, and all but nitrogen are highly flammable. Any system that contains large quantities of pressurized flammable liquids and vapors poses a risk to the plant and its operators.

In this work, we will start our study with the simple systems in your automobile air conditioning system and your house household refrigerator/freezer system. Then, we will expand this study to the ultra-large systems used to liquefy natural gas for export terminals (in the 300,000 hp range).

There are billions of small-size air conditioning/refrigeration systems in operation today, but only a few hundred behemoth-size systems are used in the LNG liquefaction industry. There are many other gas liquefying industries, but we will limit our focus to understanding small, simple systems and then learn about the larger systems used for liquefying natural gas.

Although the basic technology is the same between the small-size units and the large units, the complexity of the systems and the refrigerants used differs as the desired temperatures become colder and as the capacity of the units becomes larger.

If the outside environment is at 80 F, it takes little energy, and the technology is simple to achieve the 35 F temperature needed to cool down a soda. Storing frozen food at 0 F takes more energy, but the technology is still simple.

However, if the outside environment is 80 F, it will take a significantly large amount of energy and more complex technology to achieve the ~ -260 F temperature needed to make Liquid

Natural Gas (LNG). To achieve a temperature of ~ -424 F to liquefy hydrogen, the energy and technology required increases many-fold over that needed to make LNG. To take this to the extreme, liquid helium (the very coldest gas liquefied) can be produced at ~ -452 F and is extremely difficult and power intensive. Keep in mind the absolute zero temperature is -459.67 F.

Engineers need some understanding of thermodynamics to better respond to anomalies during plant operation. The thermodynamics presented in this publication are basic and based on application rather than theory. The cases studied are all steady-state (the properties of the fluid at any point do not change with time) and steady-flow (the flow rate does not change with time) type problems. All the solutions are based on some simple calculations and on the use of the pressure-enthalpy chart or thermodynamic software. A large-size pressure enthalpy chart for methane or thermodynamic software should accompany this publication.

Cautionary Note

This document is intended to teach basic concepts. To accomplish this, a simplified approach is taken to explain thermodynamic processes.

Real plants have pressure drops associated with flows through piping, exchangers, and other processing equipment. Such pressure drops are not considered in the simplified examples given herein. Parts of the plant, such as the CO_2 and water removal systems, were not included in the analysis because their study is outside the scope of this document.

Also, rounded-off numbers are often used throughout to allow the reader to focus on the concept without getting bogged down in numerical detail.

Facilities in the United States and Codes that Govern them

The Federal Energy Regulatory Commission (FERC) governs most permanent LNG facilities in the U.S. via the Federal Code of Regulations (code 49CFR193). This code requires the governed facilities to abide by the National Fire Prevention Association (NFPA) 59A consensus code. Many countries around the world also conform to NFPA 59A.

The U.S. Pipeline and Hazardous Material Association (PHMSA) collects data on LNG facilities annually. According to PHMSA, the inventory of LNG facilities as of 10/1/2022 for the 2021 annual reporting year is as follows:

https://www.phmsa.dot.gov/data-and-statistics/pipeline/gas-distribution-gas-gathering-gas-transmission-hazardous-liquids

- 71 Peak Shaver (PS) LNG Facilities (48 with liquefiers) **(almost 70%)**
- 23 Satellite (Sat) LNG Facilities (1 with liquefier – that is how it is reported)
- 26 Base Load LNG (liquefiers - not counted)
- 40 Mobile or temporary LNG facilities
- 8 Other LNG facilities
- Of the 94 Peak Shaver and Satellite LNG facilities, 44 (47%) facilities in the Northeast
- Of the 94 Peak Shaver and Satellite LNG facilities, 72(77%) 1960’s – 1970’s vintage
- Of the 48 PS and Sat in the Northeast U.S., 40 (83%) 1965 – 1975 vintage
- Of the 48 PS and Sat in the Northeast U.S, 12 (25%) have liquefiers

The Northeast is emphasized because it is the country’s area where local distribution companies (LDCs) heavily depend on LNG, as many of these facilities receive LNG via tanker truck from the Everett LNG import terminal.

Terms and Units of Measure for Natural Gas and LNG

Abbreviations

The following abbreviations, terms and units will be used in this document for natural gas and LNG:

U.S.	United States
Peak Shaver	An LNG facility used to supplement the supply of natural gas during times of high gas demand
Satellite	An LNG facility used to supply gas to a localized area
Sendout	Natural gas or vaporized LNG sent out, by a gas utility, via pipelines to customers
Boil-off gas	The gas that boils off from an LNG tank as heat is leaked into the tank from the environment (sometimes just called boil-off)
F	Degree Fahrenheit (a measure of temperature)
Psia	Pounds force per square inch absolute (above absolute zero)
Psig	Pounds force per square inch above atmospheric pressure
Lbm	Pound mass
Lbf	Pound force (the force exerted due to 1 lbm accelerated at 32.2 ft./sec^2)
Cu.ft.	A cubic foot of volume 1 foot x 1 foot x 1 foot (1’ x 1’ x 1’)

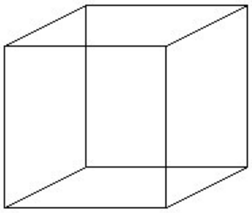

*Figure **Error! No text of specified style in document.**.2: Cubic Foot is a volume 1’ x 1’ x 1’*

Source: Self-Made

BOG	Boil-off gas
SCF	A standard cubic foot is a 1’ x 1’ x 1’ volume of gas at a standard temperature and pressure. This document uses the American Gas Association (A.G.A.) definition of standard pressure and temperature of 14.73 psia and 60 F.
BTU	Btu is the amount of energy needed to raise 1 lbm of water 1 deg F. This is not a precise measure of energy because different industries and countries use a

	different standard temperature for heated water. The heat capacity of water differs with temperature.
HHV	Higher heating value is the heat released from burning a SCF of natural gas at 60 F with air at 60 F and bringing the combustion products down to 60 F.
Therm	A Therm is 100,000 Btu.
Dekatherm	Deca means 10, so a dekatherm is 1,000,000 Btu.
MSCF	In the U.S. Gas Industry, "M" means 1,000. Thus, MSCF is 1,000 SCF.
MMSCF	In the U.S. Gas Industry, "M" means 1,000. Thus, MMSCF is 1,000,000 SCF (one million standard cubic feet)
BSCF	In the U.S. Gas Industry, "B" means billion. Thus, BSCF is 1,000,000,000 SCF (one billion standard cubic feet)
Gallon	Is an imperial unit measure of volume.
m	A meter is a measure of length in the International System of Units
m^3	A volume measurement 1 meter x 1 meter x 1 meter

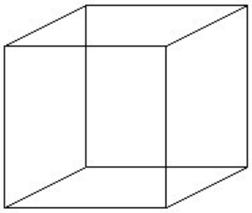

Figure ***Error! No text of specified style in document.***.*3: Cubic Foot is a volume 1' x 1' x 1'*

Source: Self-Made

Nm^3	Normal cubic meter is a cubic meter volume of gas at a defined "Normal" temperature and pressure. Different countries and different industries use different values for "Normal" properties.
Barrel	There are two different barrel terms, one for the Alcohol and Petrochemical industries. For this training, the Petrochemical Industry Barrel will be used. 1 barrel = 42 gallons

Approximations used in this training:

1 m^3 ~ 35.3 ft^3

One cu. ft. of LNG ~ 600 SCF of vapor

One cu.ft. ~ 7.48 gallons

1 gallon of LNG ~ 80 SCF of vapor

Natural Gas Liquefaction Pretreatment

1. General high-level information

Before natural gas can be liquefied, it must be pretreated to lessen the concentration of components that hinder the liquefaction process. The components of natural gas differ from well to well, and more so from country to country. Thus, before a pretreatment system is designed, the expected composition of the gas must be carefully considered.

For this study, the specific capacity of pretreatment systems will not be defined, but instead, reference will be made to the most common types of systems used for pretreatment.

Above, it is stated that it is necessary to lessen the concentration of the components that hinder the liquefaction process. That language was intentionally used, and the word remove was not used. It is important to realize that one cannot "remove" every molecule, so even though bottled water is considered pure, it is far from pure. Thus, in the below, as the word remove or removal is used, understand that it is really reducing the concentration of contaminants to some acceptable level and not totally removing that component.

With natural gas, many components will hinder the liquefaction process. The most obvious are as shown below:

1) Liquids and solids (oils, mill scale, welding rods, etc.) must be removed from the feed gas as a pretreating step. These solid contaminants can damage or plug rotating equipment and heat exchangers. This removal is often accomplished using coalescing filters, knock-out vessels, and screen or media-type strainers and filters.
2) **Water (H_2O)** (will freeze up and plug heat exchangers). Reducing water vapor to less than 1 part per million volume (ppmv) is typical. This is usually accomplished using molecular sieves, which adsorb water molecules on their surface. Passing hot (typically 550 F) dry gas through the bed to drive the water vapor off the adsorbent is typical to regenerate the mole sieve material. This is called temperature swing regeneration. Pressure swing regeneration is also possible but is not typical for LNG facilities.
3) Another method of water removal is via a glycol water-removal system. Glycol absorbs water vapors at high pressures and cold temperatures but rejects water at lower pressure and high temperatures.
4) **Carbon Dioxide (CO_2)** (will freeze up and plug heat exchangers). Reducing CO_2 to less than 50 ppmv is typically accomplished using either a mole sieve or an amine

system. Each system has its pros and cons. For large-scale liquefiers, the process of choice is typically the amine system.

5) **Hydrogen Sulfide (H_2S)** (will freeze up and plug heat exchangers, and excessive H2S will not meet many tariff requirements). Reducing H_2S to less than four ppmv is typically accomplished using either a mole sieve or an amine system. Each system has its pros and cons. For large-scale liquefiers, the process of choice is typically the amine system.
6) **Mercury (Hg) (will corrode aluminum).** Reducing mercury to trace levels is typical when mercury concentration is required. However, some small-scale plants opt not to remove mercury if the feed gas has very little mercury. However, the price paid for not removing mercury is often the need to replace major plant heat exchangers. For an export terminal, the main cryogenic heat exchanger can contain hundreds of miles of aluminum tubing or massive plate-fin heat exchangers which could have a 2+ year lead time for production and cost more than 50 million dollars. Thus, deciding whether to remove or not remove mercury is important.
7) Heavy hydrocarbons (C4+) (typically compounds containing four or more carbon atoms) (heavy hydrocarbons will freeze up and plug heat exchangers). Benzene is one of the more important heavy hydrocarbons to remove, as small amounts of benzene can rapidly freeze in heat exchangers. The typical method to lessen the concentration of heavy hydrocarbons is to chill the gas at high pressure allowing the heavy hydrocarbons to drop out as a liquid. The typical pressure and temperature for such separation is ~ 600 psig and -80 F. However, each plant is different, and the pressures and temperatures used for removal differ from plant to plant. For the effective removal of heavy hydrocarbons, it is critical to ensure that the gas passing through the heavy hydrocarbon removal system is below its critical pressure since the removal process relies on the density difference between liquid and vapor.

These contaminant removal systems are shown at a high level in Figure 2.1 below. As shown in Figure 2.1, heat is added to prevent hydrates from forming downstream of the pressure drop valve. **Hydrates are water/hydrocarbon ice formations that occur at high pressures when water and hydrocarbons are present. Such ice formations can occur at temperatures as high as 60 F.** The pressure is dropped so that by the time the gas flow reaches the heavy hydrocarbon removal vessel, the feed gas will be below the feed gas's critical pressure.

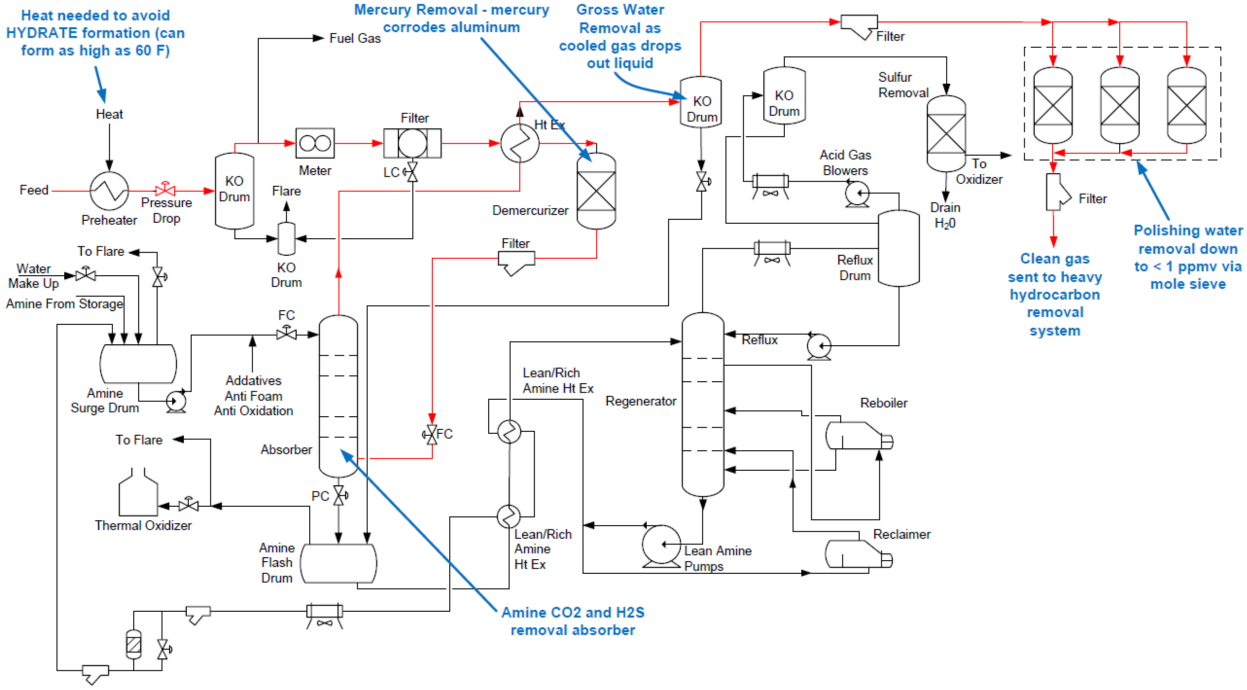

Figure ***Error! No text of specified style in document.*** *.4: Generic LNG plant pretreatment system with pressure reduction of the pipeline feed gas*

Figure 2.2 is like Figure 2.1 except that it shows the feed gas pressure needing to be increased before entering the pretreatment plant. Also, Figure 2.2 shows the heavy hydrocarbon removal system. This system will make more sense once the refrigeration process is explained. **Notice that in Figure 2.2, there is a cooling source to knock out more water before sending the gas to the mole sieves. This extra cooling allows more water to be knocked out before the gas is sent to the mole sieve.** However, the cooling must not drop below ~ 70 F for concern of forming hydrates (the amine system makes the sweet gas (gas with acid gases (CO_2 and H_2S removed)) very wet with H_2O.

After the mole sieves, the feed gas is so dehydrated that cooling it down further is no longer a problem, as hydrates will not form after dehydration because there are just so few water molecules. Thus, the feed gas can be cooled for heavy hydrogen removal.

Figure 2.2 shows reflux at the top of the heavy hydrocarbon removal vessel. This reflux is a very cold liquid that is relatively clean of heavy hydrocarbons. This reflux is used to condense

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out heavy hydrocarbon molecules from the vapors rising in the column. This way, only the most volatile components leave the top of the removal column (nitrogen and methane).

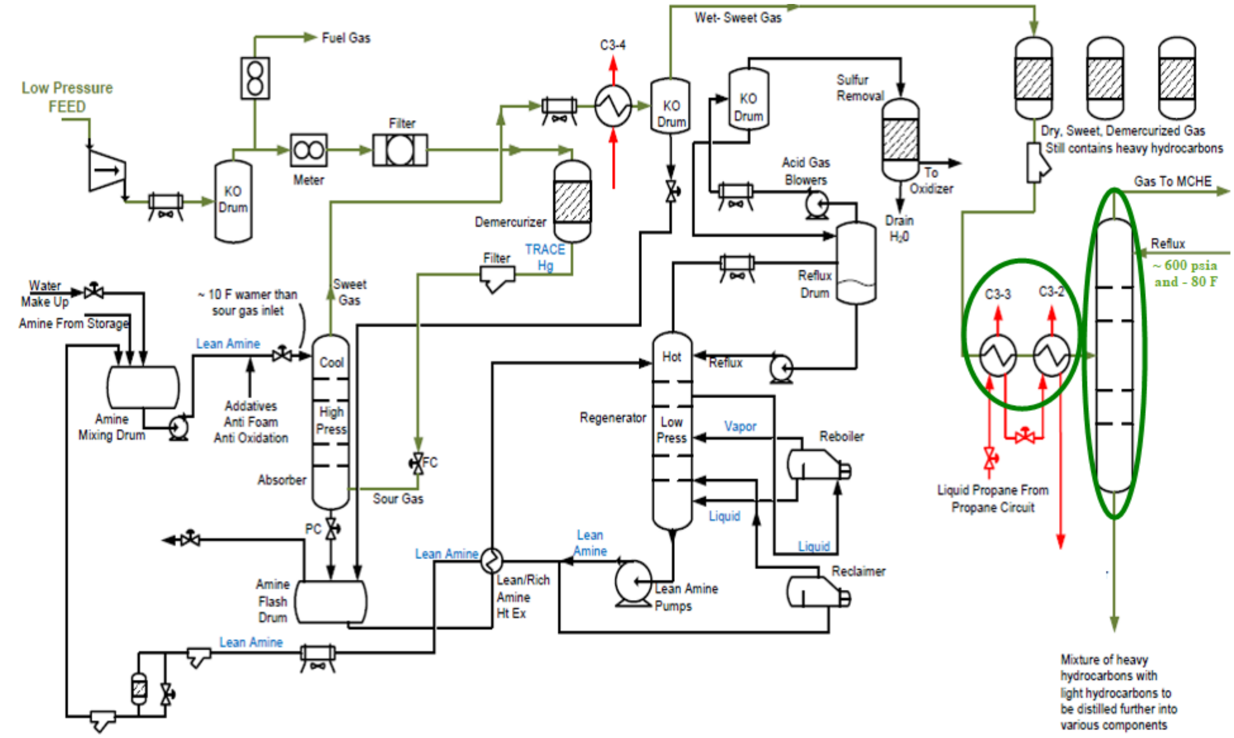

Figure ***Error! No text of specified style in document.****.5: Generic LNG plant pretreatment system with compression of the pipeline feed gas*

2. Additional details on generic feed gas treatment (common to all LNG liquefier plants)

2.1 Components that cannot be removed during pretreatment

- **Nitrogen**. Nitrogen in the feed gas will partially condense into the LNG and mostly stay a vapor through the liquefaction process. If a high nitrogen concentration is present in the feed gas, the nitrogen content in the LNG can become unacceptable. LNG with a content of 1% nitrogen or greater is known to result in nitrogen-induced stratification and subsequent rollover. Nitrogen is typically removed using a Nitrogen Removal Unit (NRU). The nitrogen removal unit is a low low-pressure knock-out drum or distillation tower that separates the nitrogen from the LNG after flashing the LNG across a JT valve. Suppose a higher degree of extraction is required. In that case, the NRU is made into a tray or contact media type distillation column, which can use heating at the bottom distillation column and very cold, nearly nitrogen-free LNG reflux sprayed into the top of the column.

- **Oxygen**. Oxygen in pipeline gas is typically very low in concentration and is not typically a significant problem for liquefaction facilities in the United States at present. The small amount of oxygen in pipeline gas streams does cause the coking of mole sieve materials during regeneration. Some plants have minimized coking by cycling the same gas during regeneration, thereby burning up the oxygen during the first few passes through the mole sieve bed during the regeneration process. QIS is unaware of any LNG plants using oxygen removal systems. This may change in the future as RNG, which may contain a higher oxygen concentration, may be mixed into LNG plant feed gas.
- **Helium**. Helium is extracted from gas wells; it is unknown if it is in natural gas pipelines. Since helium has not been considered an issue, it is not addressed in this learning. However, it should be realized that all helium is obtained from some gas wells.
- **Hydrogen**. Hydrogen has not been a concern in the past because it has not been intentionally injected into pipeline gas. Much discussion has been on the environmental benefits of injecting hydrogen into interstate pipelines. If this does occur, the LNG industry will need to study the effects of such hydrogen on LNG facilities.

2.2 Components of the pretreatment system (common to all LNG facilities)

The following figures show the components used in the pretreatment of feed gas systems:

2.2.1 Pressure letdown or inlet compressor

The feed gas pressure is typically adjusted to higher than four hundred psia for the pretreatment system to function from a technical perspective and cost-efficiently. Still, it must be less than the critical pressure of the feed gas. It must be less than the critical pressure of feed gas so that the heavy hydrocarbon removal column will work. **Above the critical pressure, there is no difference in density between a liquid and a vapor of the feed gas. Thus, liquid and vapor phases do not exist above the critical pressure. Without a liquid and vapor density difference, there is no way to separate the volatile methane from the heavier hydrocarbons. The critical pressure for methane is ~667 psia.**

In Figures 2.3 and 2.4 below, the pressure is shown as < 800 psig, but the intent is for that when accounting for pressure drops, by the time that gas reaches the heavy hydrocarbon removal column, the pressure will be lower than the critical pressure for the feed gas.

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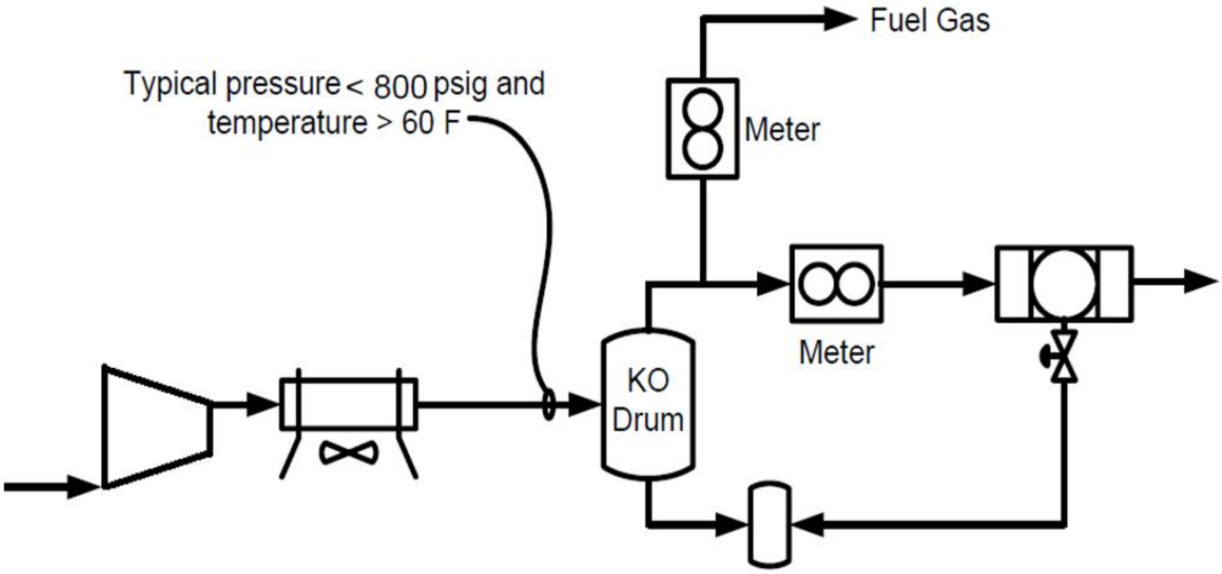

Figure ***Error! No text of specified style in document.****.6: Inlet gas feed gas with compressor and aftercooler on the inlet feed gas line*

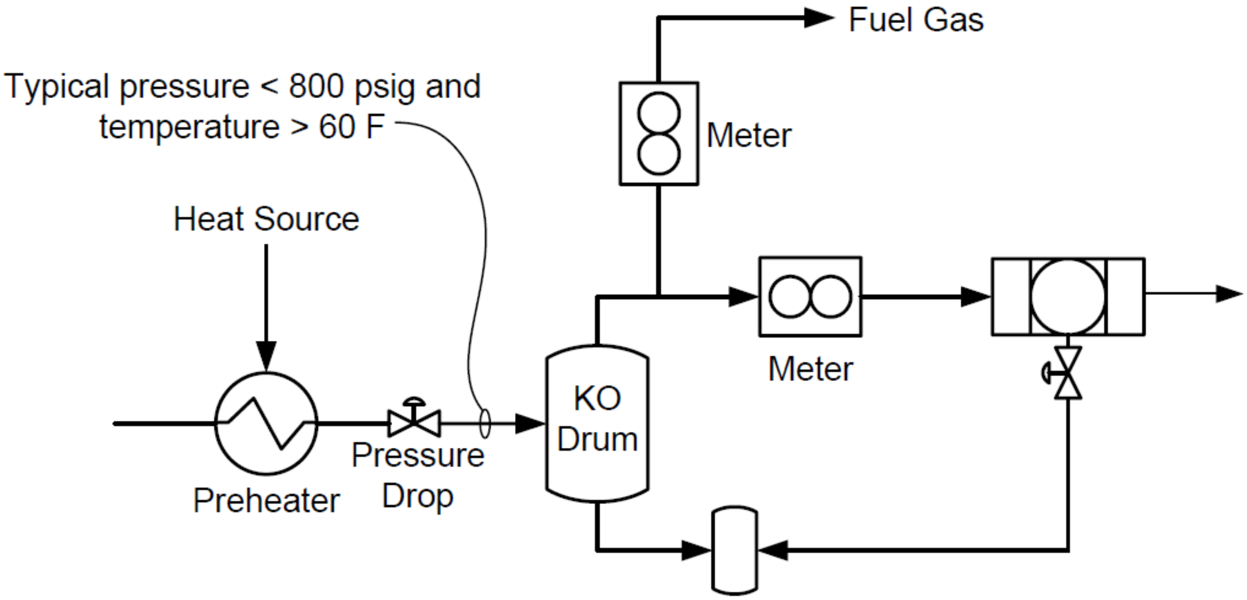

Figure ***Error! No text of specified style in document.****.7: Inlet gas feed gas with preheater and pressure drop valve on the inlet feed gas line.*

2.2.2 Molecular sieve systems

Molecular Sieves are mostly used for water removal to less than 1 ppmv. However, they may also be used in smaller peak-shaving plants to remove CO_2 and H_2S.

Figures 2.5 and 2.6 show the components of a molecular sieve system. Some systems use 2, 3, or even four molecular sieves to accomplish adsorption and desorption. In Figure 2.5, the molecular sieve to the left is adsorbing, the center molecular sieve is cooling down after being regenerated, and the rightmost mole sieve **regenerates at up to 550 F**.

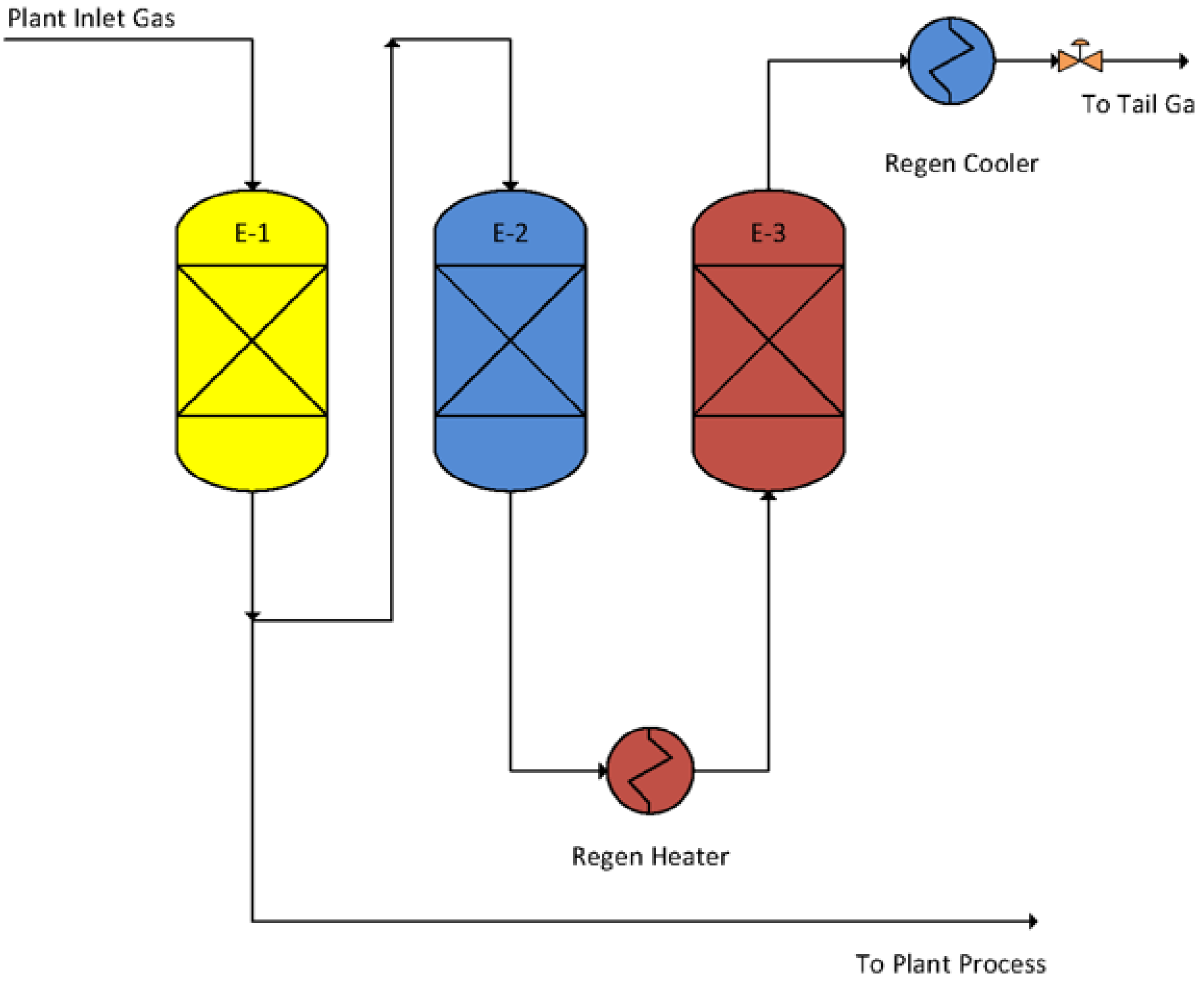

*Figure **Error! No text of specified style in document.**.8: A 3-bed molecular sieve type of adsorption system which operates at 550 F during regeneration*

Figure 2.6 is a two-bed molecular sieve process. Such systems are less energy efficient but lower in capital cost as they do not require a 3rd molecular sieve bed as used in Figure 2.5.

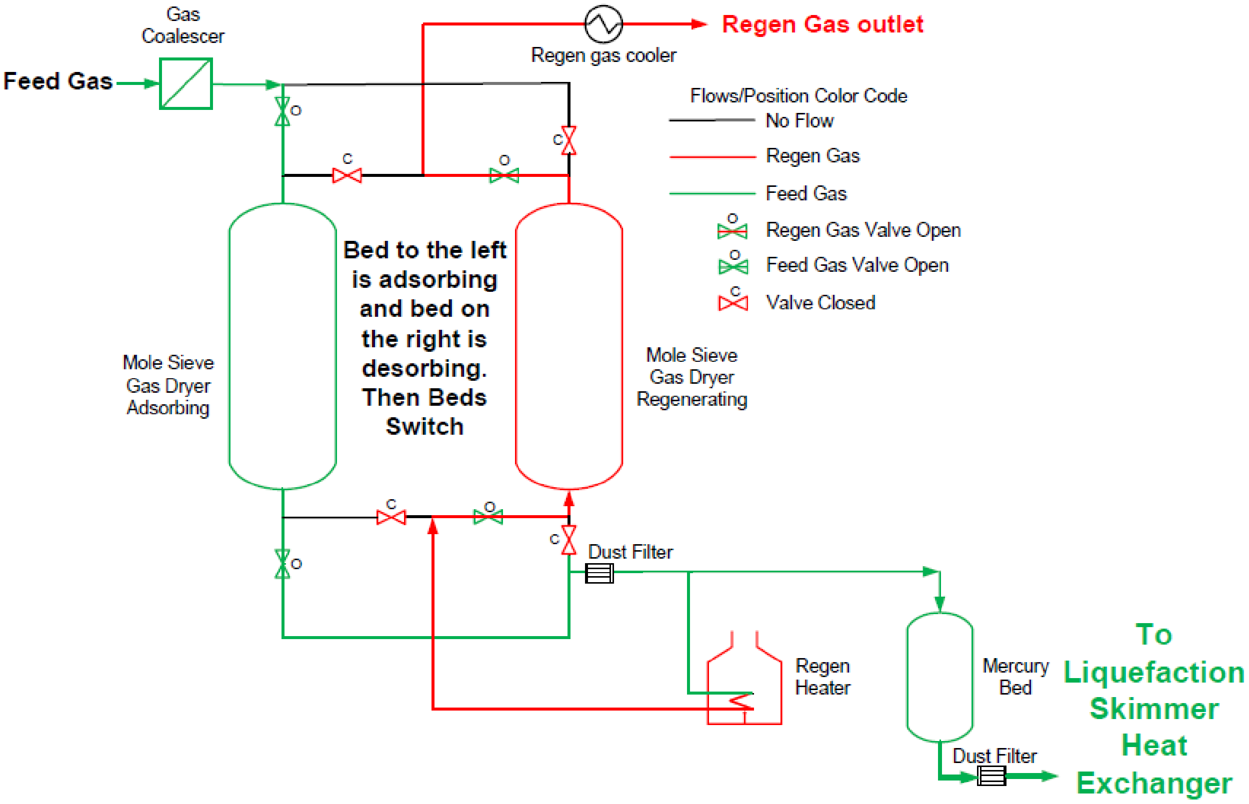

Figure ***Error! No text of specified style in document.****.9: A two-bed molecular sieve*

2.2.3 Glycol water removal system

Some plants use a glycol system for water removal. The system shown in Figure 2.7 uses Tri-ethylene glycol as an absorbent liquid. **The water removal occurs at low temperatures and high pressures, and the glycol rejects the water at high temperatures and low pressure. A clean gas stream strips out water vapor, so the lean glycol is nearly pure.**

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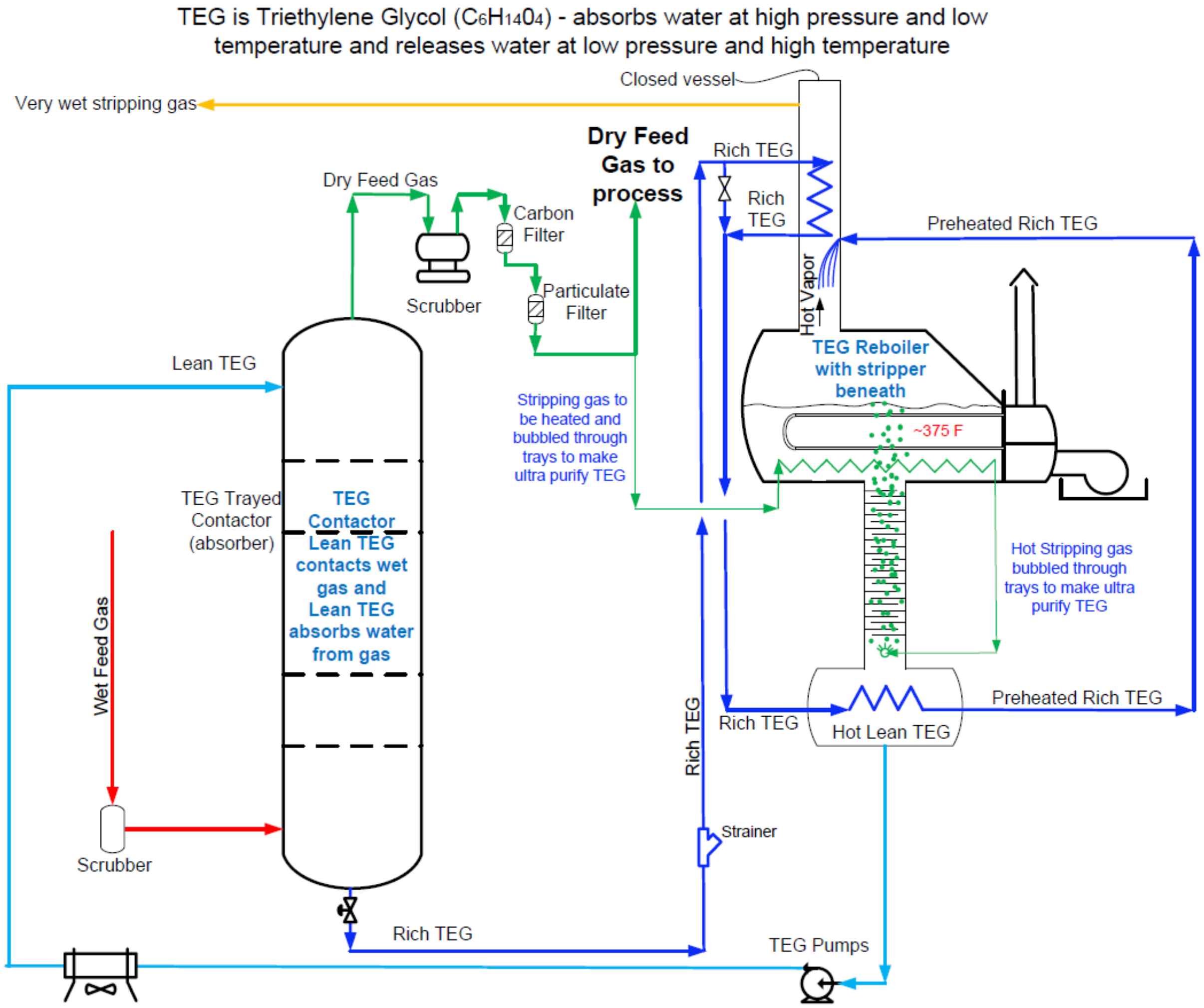


Figure **Error! No text of specified style in document.**.10: Tri-ethylene glycol water removal system

2.2.4 Amine system for acid gas removal

Figure 2.8 shows the components of a typical amine system. The acid gases, CO_2 and H_2S, are are first absorbed and then chemically reacted with the amine. The amine regeneration occurs at low pressure and high temperature in the regenerator. The regenerator uses one or more reboilers to produce boil-up, a top gas condenser, and a knock-out drum to produce reflux.

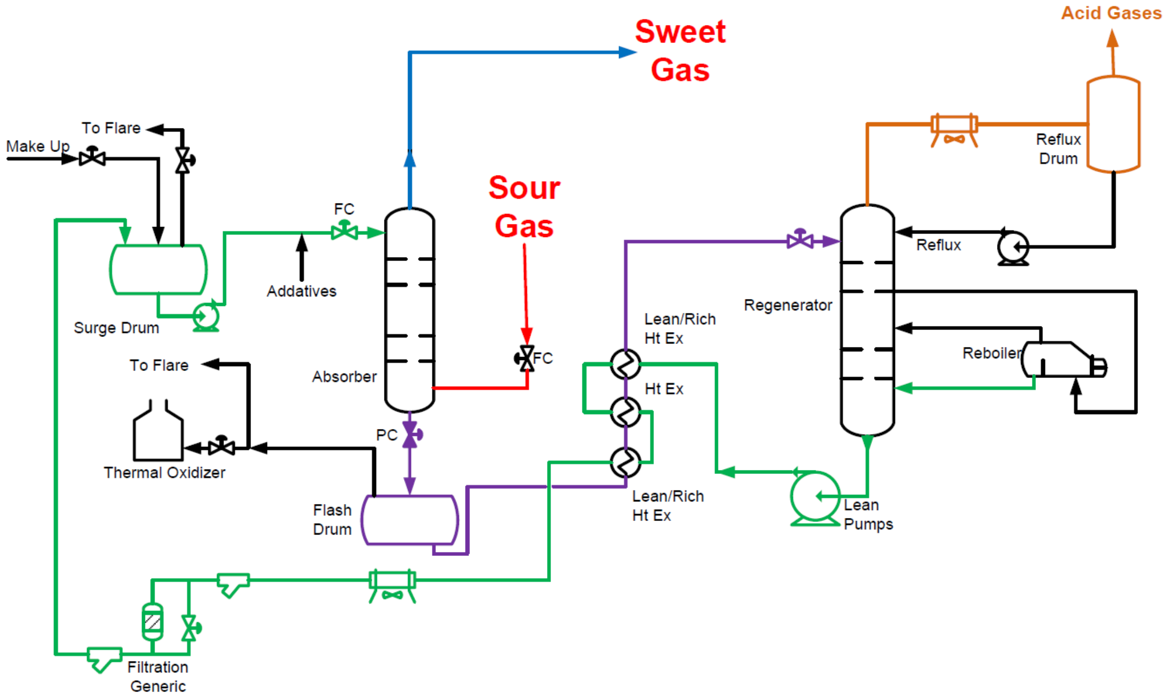
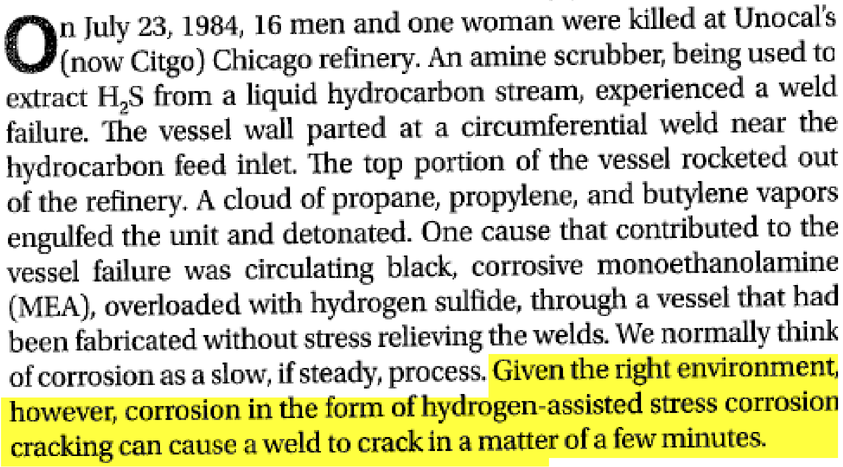


*Figure **Error! No text of specified style in document.**.11: Amine system for removal of acid gases (CO_2 and H_2S).*

It is important to ensure that the amine is maintained clean and properly regenerated. An excerpt from a book titled *Troubleshooting Process Operations* is shown below in Figure 2.9, as the excerpt refers to an acid gas amine system absorber.



On July 23, 1984, 16 men and one woman were killed at Unocal's (now Citgo) Chicago refinery. An amine scrubber, being used to extract H_2S from a liquid hydrocarbon stream, experienced a weld failure. The vessel wall parted at a circumferential weld near the hydrocarbon feed inlet. The top portion of the vessel rocketed out of the refinery. A cloud of propane, propylene, and butylene vapors engulfed the unit and detonated. One cause that contributed to the vessel failure was circulating black, corrosive monoethanolamine (MEA), overloaded with hydrogen sulfide, through a vessel that had been fabricated without stress relieving the welds. We normally think of corrosion as a slow, if steady, process. Given the right environment, however, corrosion in the form of hydrogen-assisted stress corrosion cracking can cause a weld to crack in a matter of a few minutes.

*Figure **Error! No text of specified style in document.**.12: Excerpt from a book*
Source: Troubleshooting Process Operations (4th Edition), Norman P. Liberman, published by PennWell, page 91

2.2.5 Demercurizer (not used in every plant)

Figures 2.10 and 2.11 show the components that clean up the feed gas. Figure 2.10 shows partial pretreatment for a low-pressure supply feed gas and Figure 2.11 shows partial pretreatment for a high-pressure supply feed gas system. In each of these Figures, a demercurizer is shown. Take note that it is typical always to have a strainer downstream of any vessel that contains a granular material like the demercurizer material.

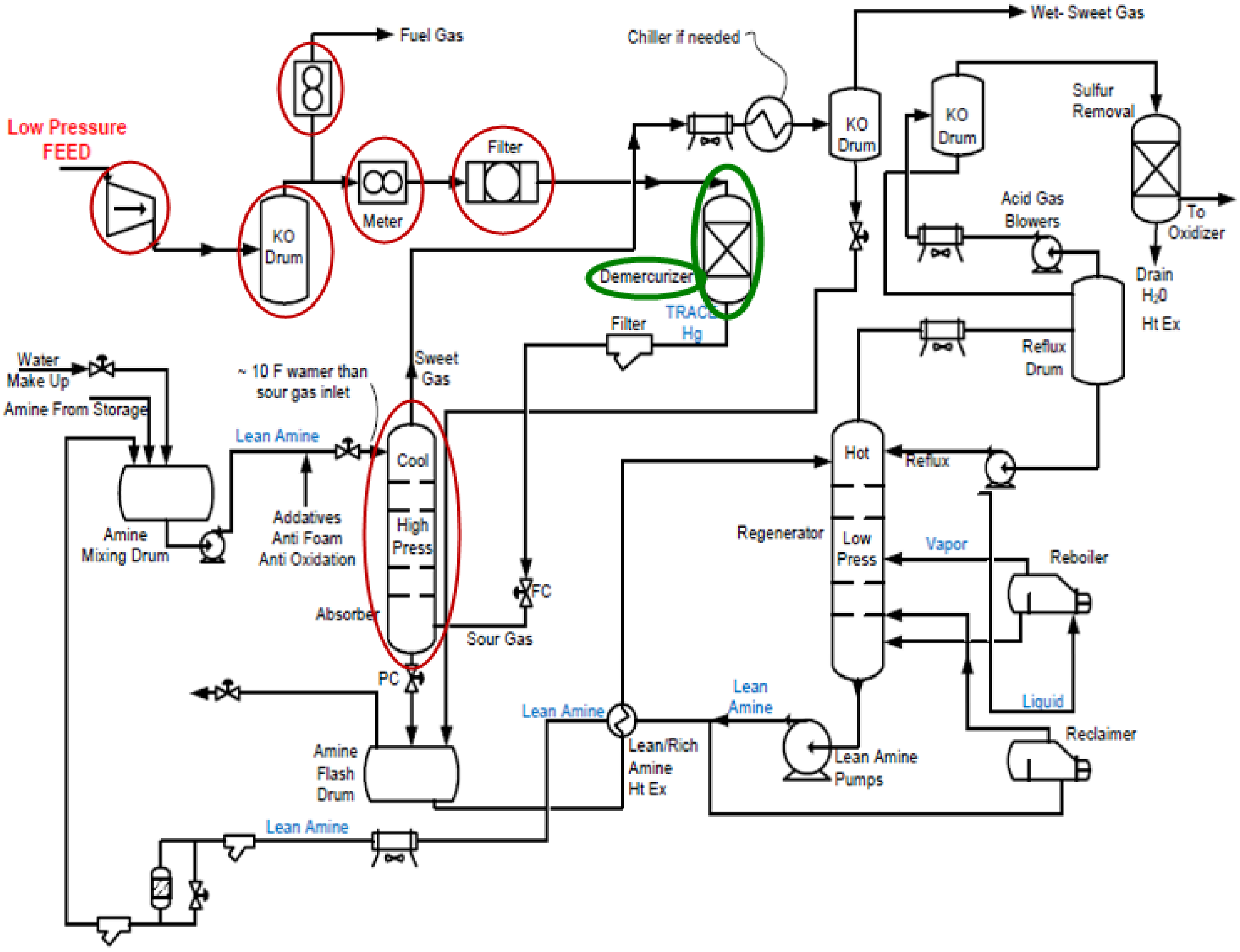


Figure ***Error! No text of specified style in document.****.13: Partial pretreatment system with a low-pressure feed gas. Circled in red are components already discussed. Circled in green is the presently discussed demercurizer.*

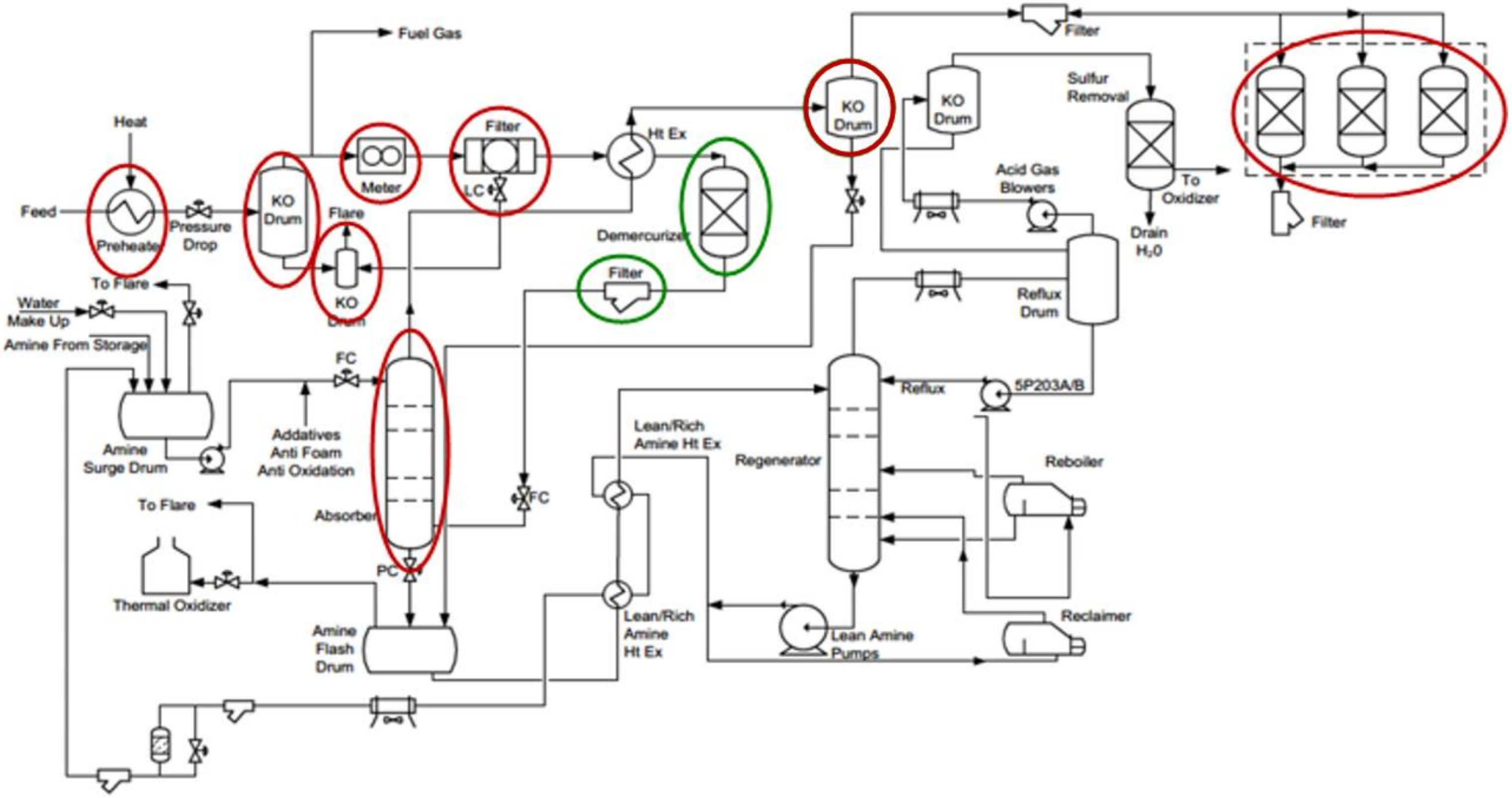


Figure ***Error! No text of specified style in document.****.14: Partial pretreatment system with a high-pressure feed. Circled in red are components already discussed. Circled in green is the presently discussed demercurizer equipment.*

2.2.6 Heavy hydrocarbon removal column or cold separator)

Figure 2.12 shows a heavy hydrocarbon removal unit (distillation column) or cold separator. The difference between a heavy removal unit and a cold separator is that the heavy hydrocarbon removal unit performs a higher degree of separation, requiring less post-treatment of the heavy hydrocarbons. In these systems, the heavier hydrocarbons drop out as a liquid, and the volatile components rise out of the top of the column and are sent to be liquefied. The separation, **which occurs by chilling the feed gas stream,** is imperfect, so it is necessary to process the bottom products further to release most of the methane, ethane, and propane carried along with the heavy hydrocarbons. These released more volatile components are either returned to be liquefied or used as fuel gas. The remaining heavier hydrocarbons are typically trucked out of the plant for other uses.

The heavy hydrocarbon column or separator operates at a relatively cold temperature (order of magnitude -70 to -80 F).

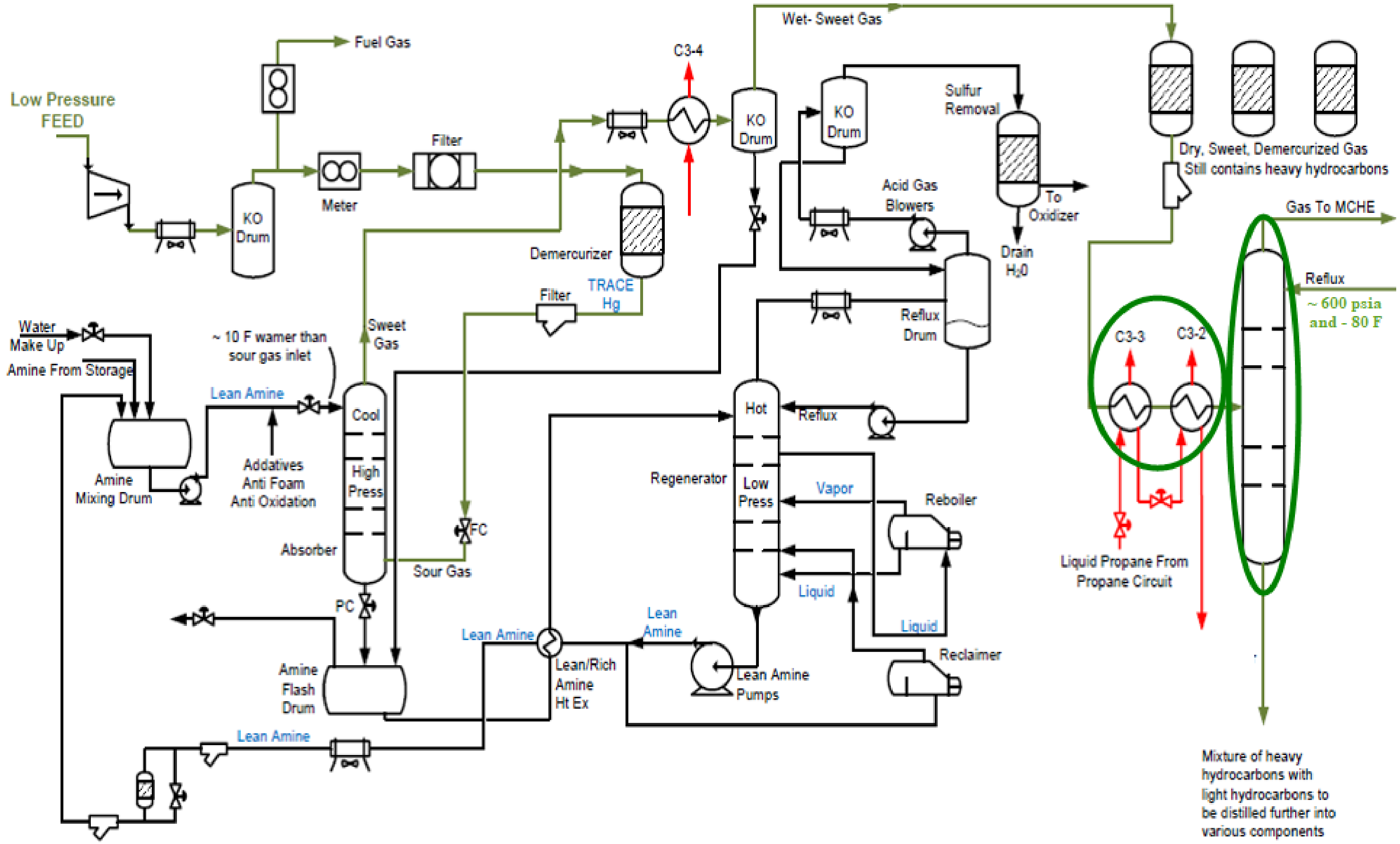


*Figure **Error! No text of specified style in document.**.15: Heavy hydrocarbon removal column or cold separator shown marked in green*

Refrigeration systems (non-expansion-cooling type systems)

With you having already understood the prerequisite courses to this course we get right into using the laws of thermodynamics.

If you understand your car's air conditioning system, you will understand your LNG plant's liquefaction system.

Your car uses a refrigerant that is compressed from low-pressure to high-pressure gas. That gas gets hot as it is compressed. That hot gas (called a superheated vapor) is sent into the radiator in front of the car's water radiator. That radiator is called a condenser.

This is called a condenser because, in the condenser, the outside air cools the hot superheated refrigerant gas to a saturated refrigerant gas, then to a saturated liquid, and finally to a subcooled liquid. The part of the condenser which cools the superheated gas to a lower temperature superheated gas is sometimes called an aftercooler.

The subcooled liquid is approximately 10 F hotter than the outside air temperature. Thus, if it is 90 F outside, this subcooled liquid refrigerant would be approximately 100 F.

This subcooled liquid is flashed across a Joules Thompson valve (JT valve). As we learned earlier, flashing across a JT valve is a constant enthalpy process. At the outlet of the JT valve, the refrigerant exists as both a saturated vapor and a saturated liquid at a much colder temperature. The vapor and liquid temperatures are saturated, which means they are fixed at a temperature directly correlated to the pressure downstream of the JT valve.

A car's air conditioning system is typically adjusted to be no colder than 35 F. The design is for no colder than 35 F to prevent ice from forming in the car's heat exchanger, which is used to cool the air in the car. This heat exchanger is called an evaporator. This is called an evaporator because the liquid refrigerant is boiled off (evaporated) in the evaporator. As the refrigerant is evaporated, it absorbs heat from the car's air. In a car the pressure of the refrigerant in the evaporator and its associated temperature is controlled by turning the compressor on and off via an electric clutch on the air conditioner's compressor. Once the refrigerant saturated liquid is converted to saturated vapor, it is further heated until it becomes a superheated vapor. If the temperature of the car air

entering the evaporator is 70 F, the refrigerant superheated vapor leaving the evaporator would be approximately 50 F (depending on the evaporator coil's efficiency).

The superheated vapor leaves the evaporator and then goes back to the compressor, which is again compressed. The total process has been described as the gas is now at the same point where it was when this description began.

Figure 3.1 is a sketch of the process, and Figure 3.2 plots the process on a pressure-enthalpy Ph diagram. The refrigerant shown in Figure 3.2 is R-134A, commonly used today in car air conditioning systems.

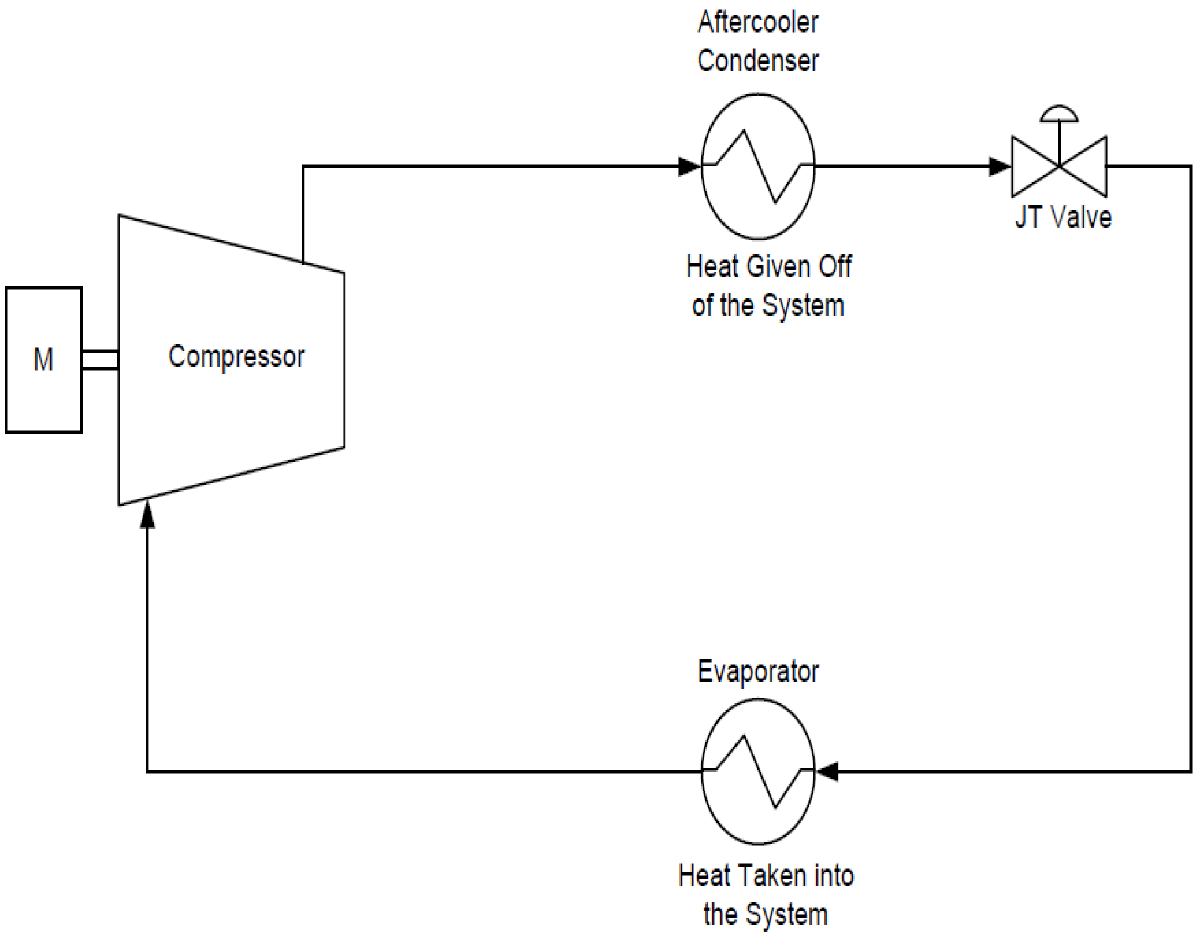


Figure ***Error! No text of specified style in document.****.16: Sketch of a car's air conditioning system*

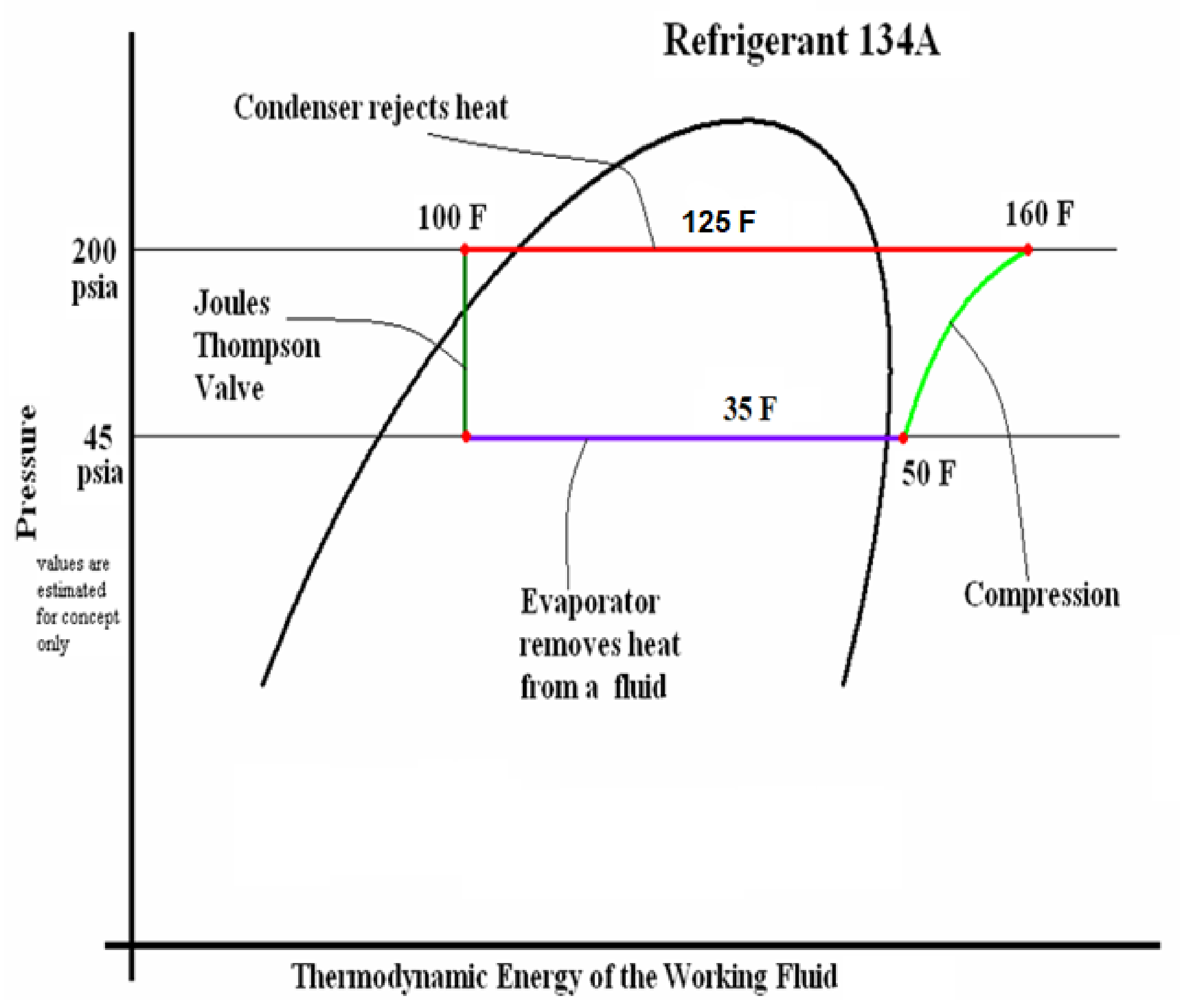


Figure ***Error! No text of specified style in document.****.17: Ph diagram of a car's air conditioning system using R134A refrigerant*

Figure 3.2 neglects pressure drops and shows the JT valve as being adiabatic (without heat transfer). Look closely at the JT valve and analyze it using REFPROP.

Figure 3.3 shows the control volume around the JT valve and the REFPROP output data. As can be seen the enthalpy into the JT valve is the same as the enthalpy leaving the JT valve (see courses 1 and 2). The temperature of the subcooled refrigerant entering the JT valve is 100 F. The temperature of the vapor and liquid refrigerant leaving the JT valve is 35 F. The 35 F liquid refrigerant has a high capacity to remove heat from the car, and the 35 F vapor has a much lower capacity to remove heat from the car. This is shown by the enthalpy of the liquid

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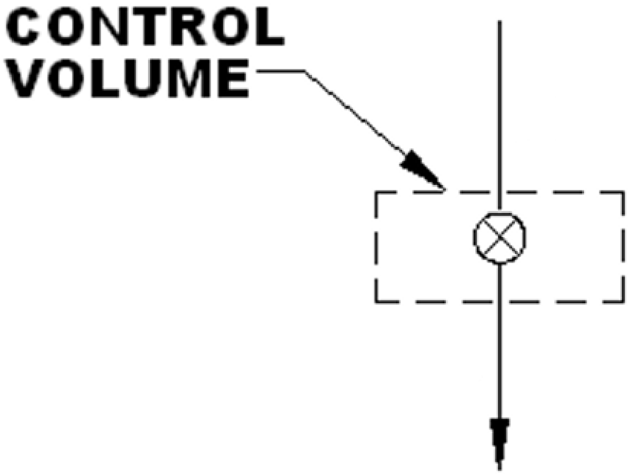
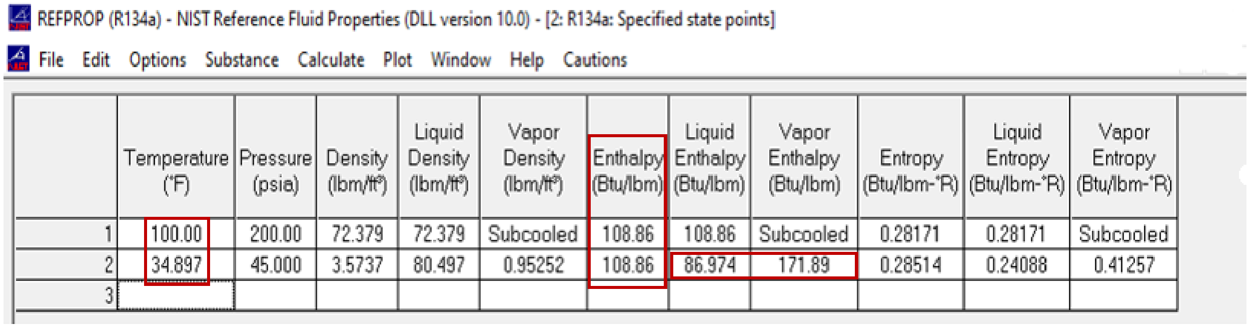
and vapor refrigerant at this pressure. The liquid refrigerant at 45 psia and 35 F has an enthalpy of 86.974 Btu/lbm, and the vapor refrigerant at 45 psia an enthalpy of 171.89 (see Figure 3.3)





	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Density (lbm/ft³)	Vapor Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Enthalpy (Btu/lbm)	Vapor Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)	Liquid Entropy (Btu/lbm-°R)	Vapor Entropy (Btu/lbm-°R)
1	100.00	200.00	72.379	72.379	Subcooled	108.86	108.86	Subcooled	0.28171	0.28171	Subcooled
2	34.897	45.000	3.5737	80.497	0.95252	108.86	86.974	171.89	0.28514	0.24088	0.41257
3											

*Figure **Error! No text of specified style in document.**.18: Control volume and saturation data from REFPROP for R134A at 45 and 200 psia*

As shown in Figures 3.3, 3.4, and 3.5, the actual properties at the outlet of the JT valve consists of the saturated liquid and saturated vapor properties of the R134A. They are two very distinct fluids. Although, they both have identical chemical structures, one is a vapor and the other is a liquid. In the example shown, the liquid and vapor have a difference in enthalpy of 84.961 Btu/lbm. This 84.961 Btu/lbm difference produces most of the cooling in the air conditioning system.

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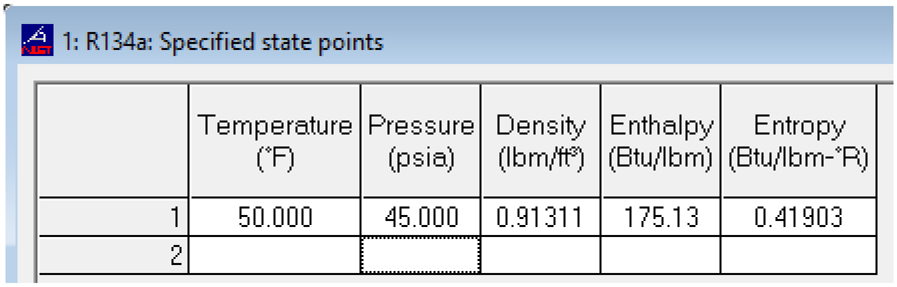
As shown in Figure 3.4 the enthalpy of the vapor entering the compressor is 175.13 Btu/lbm. Using the values of Figure 3.3, the cooling delivered by the liquid and the vapor refrigerant is as follows:

- Heat removed in evaporator by the Liquid R134a is (175.13 – 86.974) = 88.156 Btu/lbm
- Heat removed in evaporator by the Liquid R134a is (175.13 – 171.89) = 3.24 Btu/lbm

Thus, on a per-pound of refrigerant basis, 3.5% of the cooling comes from the saturated vapor refrigerant mass flow, and 96.5% of the cooling comes from the saturated liquid refrigerant mass flow.

How many pounds of refrigerant vapor and how many pounds of refrigerant liquid are delivered for of each pound of refrigerant entering the JT valve is a function of the subcooling temperature of the pre-JT valve subcooled liquid. The greater the subcooling, the higher the ratio of liquid to vapor ratio becomes. With enough subcooling, 100% of the refrigerant downstream of the JT valve can be liquid refrigerant.


1: R134a: Specified state points

	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Enthalpy (Btu/lbm)	Entropy (Btu/lbm-°R)
1	50.000	45.000	0.91311	175.13	0.41903
2					

Figure ***Error! No text of specified style in document.*** *.19: Properties of the refrigerant as it leaves the evaporator and enters the compressor*

Take note in Figure3.5 that although the gross enthalpy of the outlet of the JT valve is 108.86 (see Figure 3.3), the fluids at the outlet of the JT valve are two distinct fluids with enthalpies of 86.947 Btu/lbm and 171.89 Btu/lbm. Thus, for one lbm of refrigerant passing the JT valve, the governing equation can be written as:

108.86 Btu/lbm x (1 lbm) = 171.89 Btu/lbm x (X lbm) + (1-X) (86.947 Btu/lbm) (Solve for X)
Where X is the mass of vapor, and 1-X is the mass of liquid.
This is shown graphically in Figure 3.5.

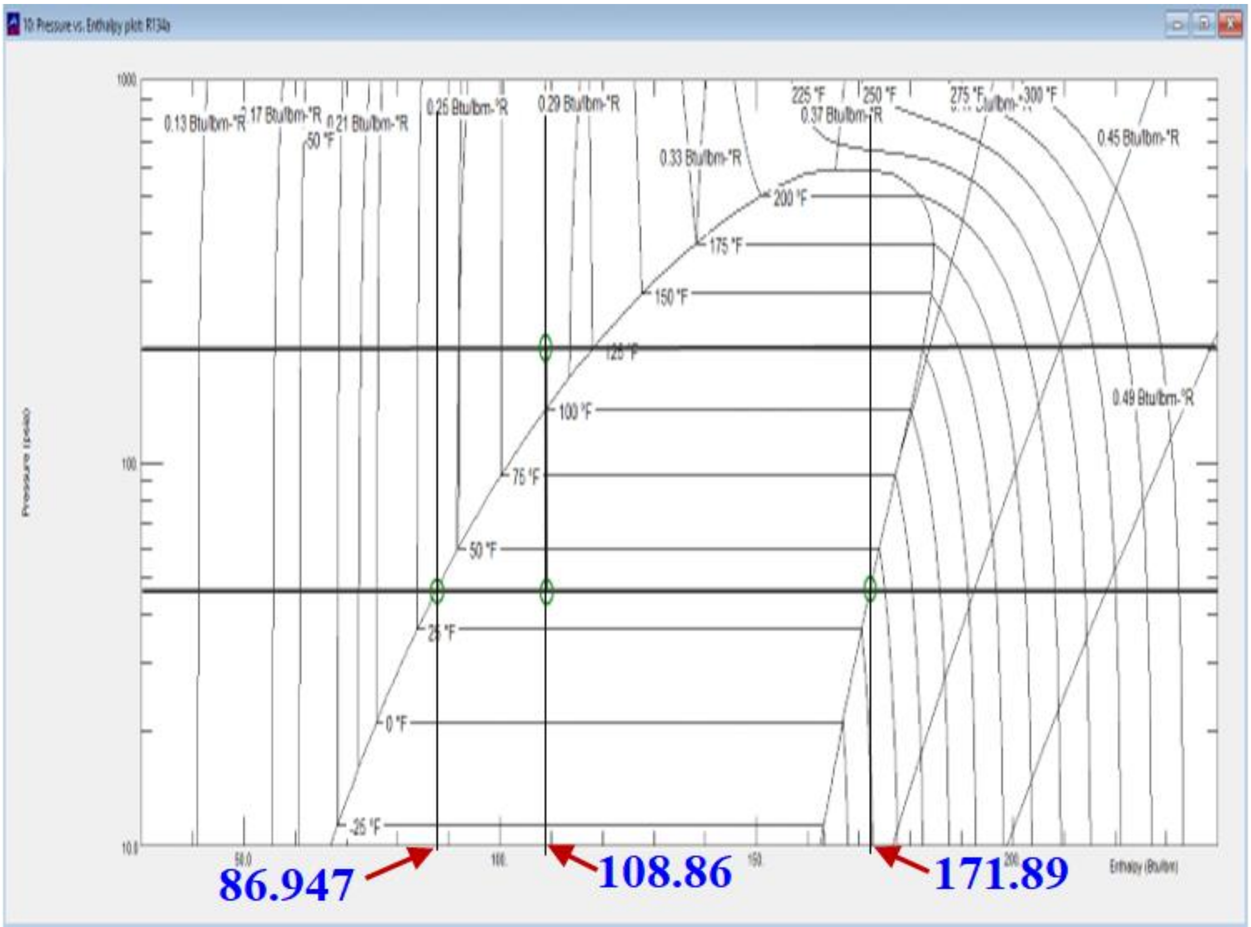


*Figure **Error! No text of specified style in document.**.20: Graphic showing that downstream of JT valve fluid properties are of the saturated liquid and saturated vapor*

As shown in Figure 3.5, the greater the subcooling before the JT valve is, the closer the property of the outlet refrigerant enthalpy is to the saturated liquid value.

As shown in Figure 3.6, downstream of the JT valve, most of the cooling comes from the liquid refrigerant and very little comes from the vapor refrigerant.

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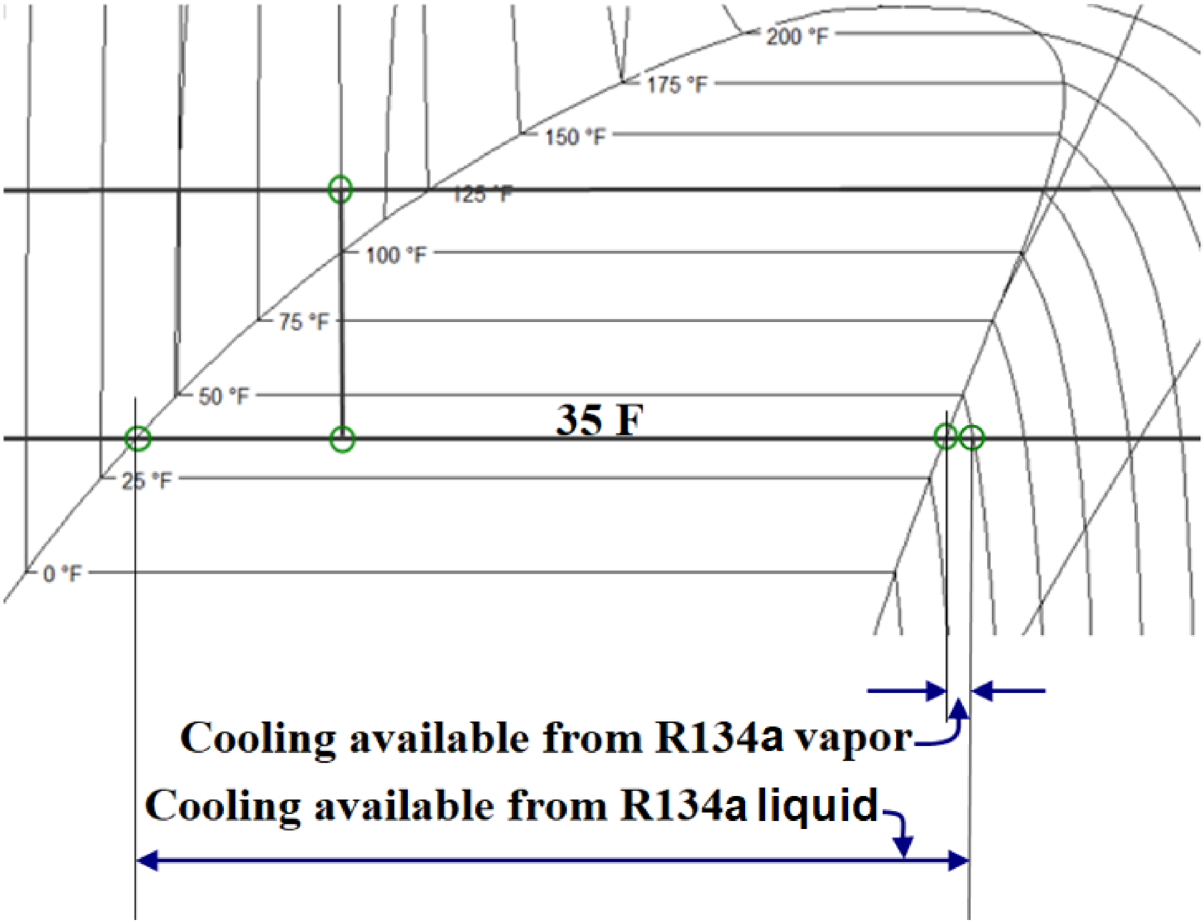

Figure ***Error! No text of specified style in document.****.21: Visual comparison on a per pound of refrigerant vapor*

Figure 3.7 summarizes the car air conditioning process by labeling all the points discussed above on a single Ph diagram.

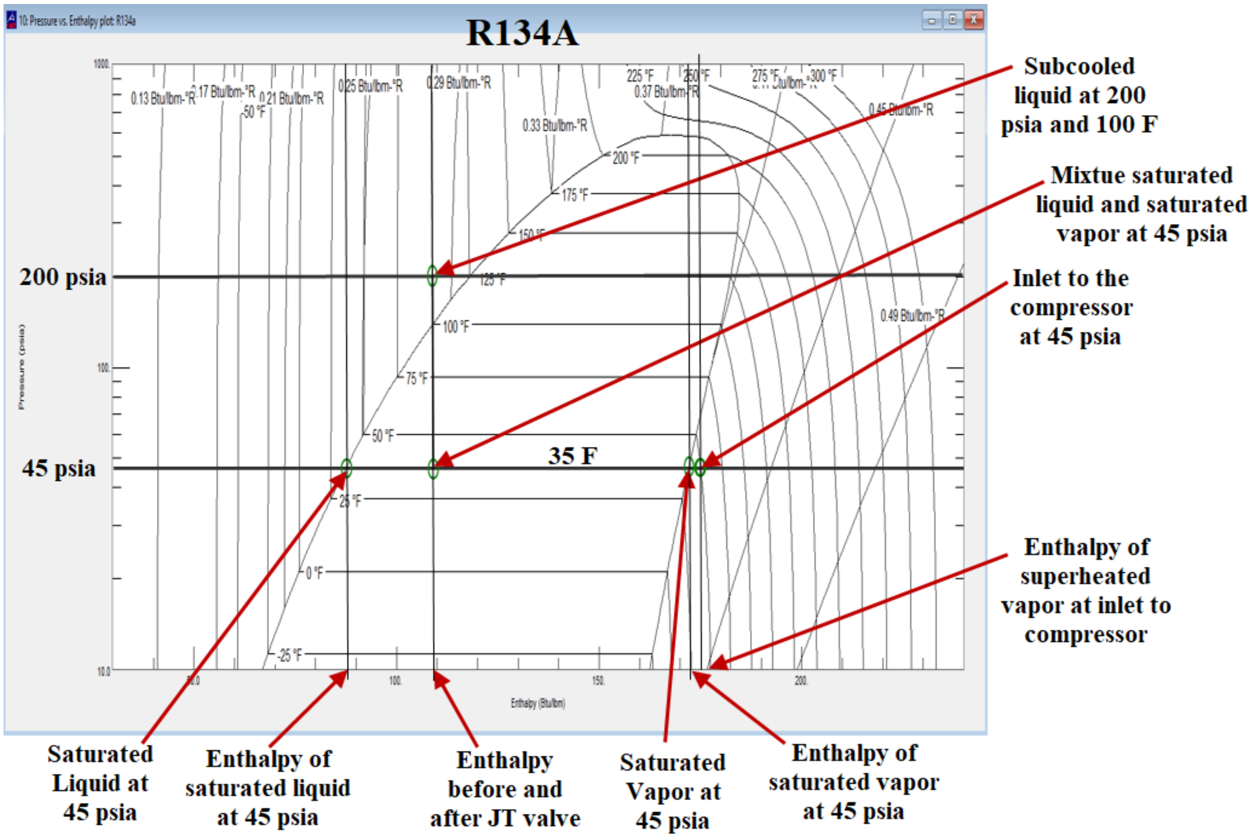

Figure ***Error! No text of specified style in document.****.22: Ph diagram of R134A used in a car air conditioner with data points shown*

Figure 3.8 shows that the compressor work is the change in enthalpy from the inlet to the outlet of the compressor.

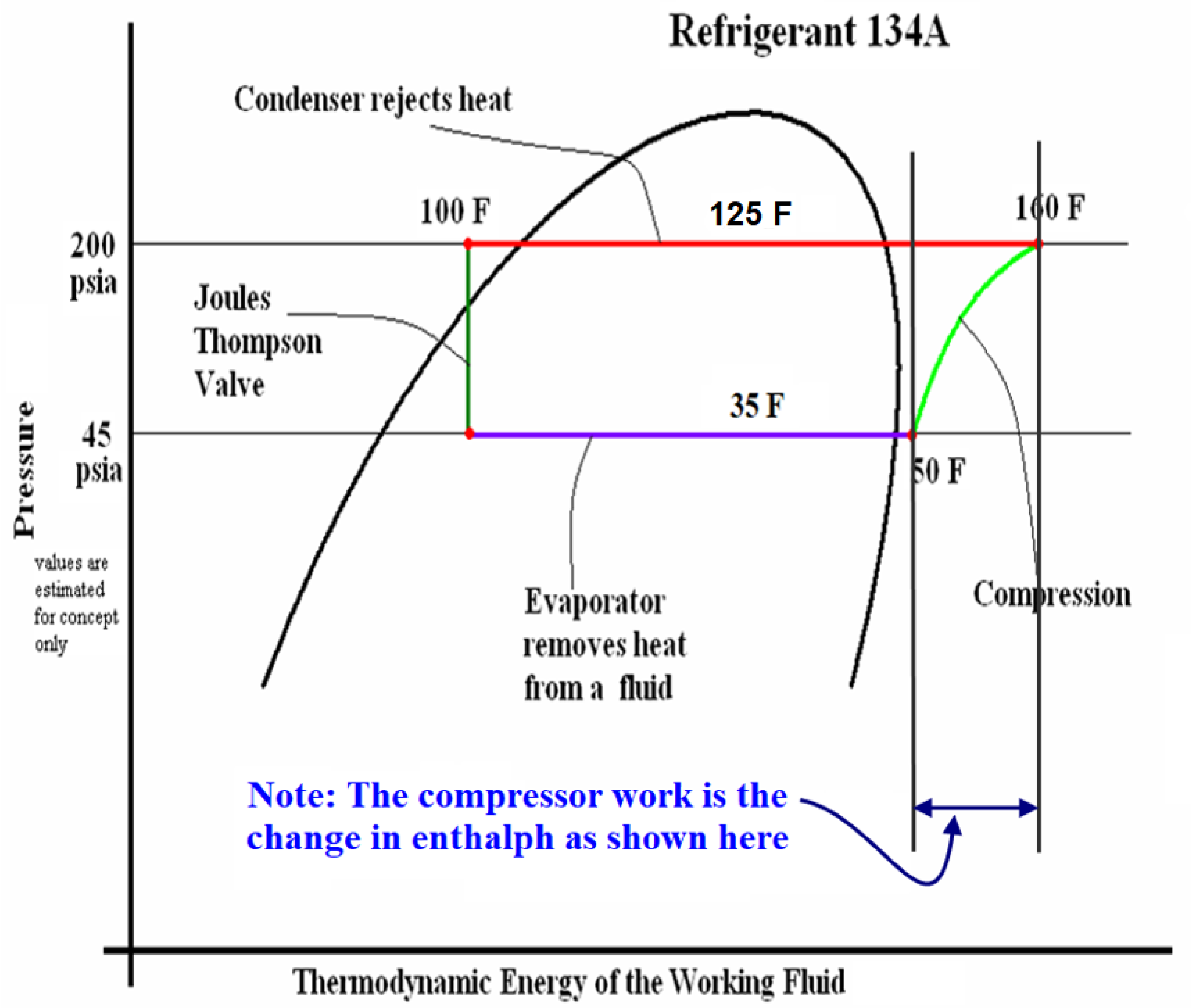

*Figure **Error! No text of specified style in document.**.23: Graphic showing that the compressor work is the change in enthalpy between the inlet and the outlet of the compressor*

In Figure 3.9 it is shown that the heat rejected is the sum of the heat removed from the car by the evaporator plus the work input into the compressor. If numerical values were to be used this would show quantitively as well. In the real world, there would also be heat leaked into or out of the piping as much of the refrigeration piping is uninsulated and under the hood of the car.

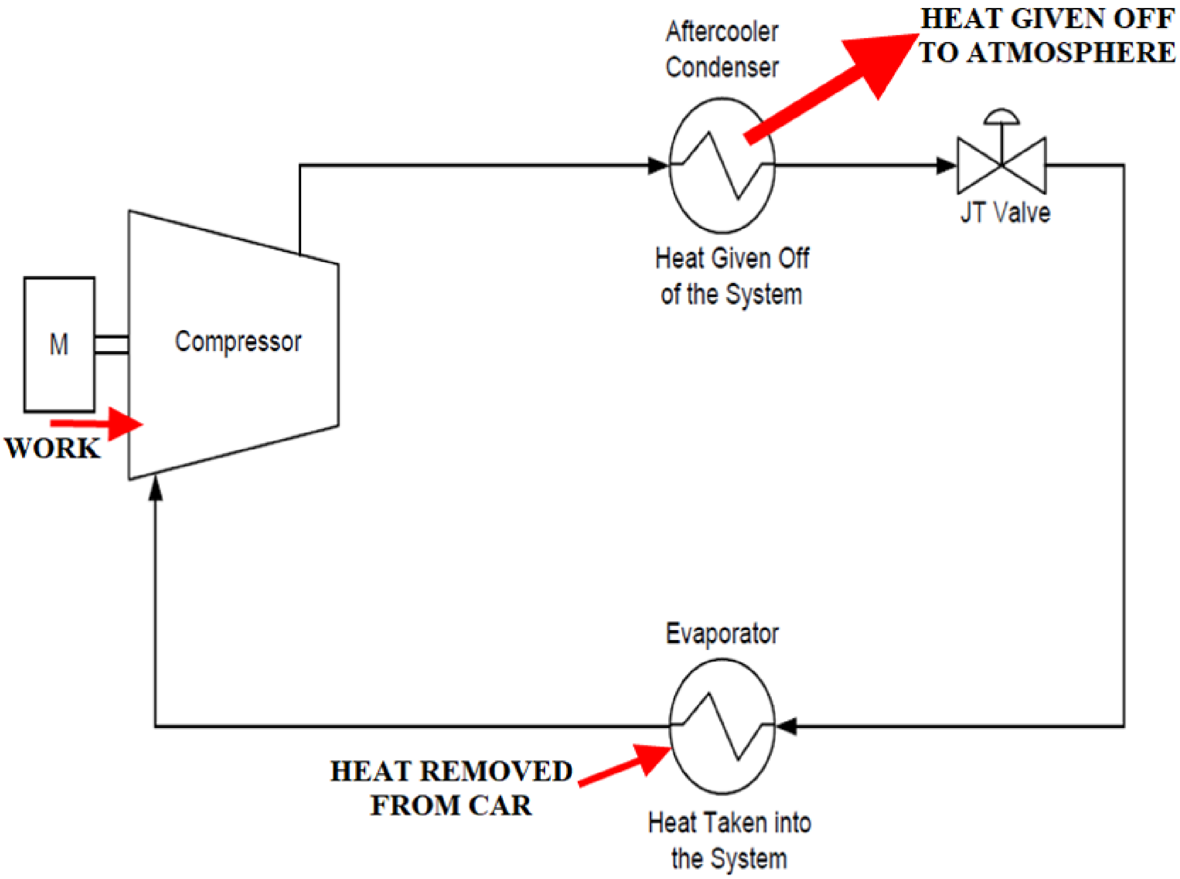

Figure ***Error! No text of specified style in document.****.24: Qualitative representation of heat balance for the total car air conditioning system*

In a vapor compression-liquid expansion refrigeration system like that shown above, there is little benefit for sending the vapor refrigerant through the evaporator. The vapor contributes very little to cooling. The specific volume of the vapor is significantly larger than the specific volume of the liquid refrigerant. Moving the vapor along with the liquid refrigerant causes higher velocities in the evaporator resulting in shorter resonance time for the heat transfer to occur and higher pressure drops within the evaporator. This results in requiring a larger evaporator surface area, adding to the cost of the evaporator, and hindering the process's efficiency.

In many designs, sending the vapor downstream of the JT valve back to the compressor is common practice rather than through the evaporator. However, this may lessen the cost

of the evaporator, but it adds additional piping to the system, which adds cost. This is shown in Figure 3.10

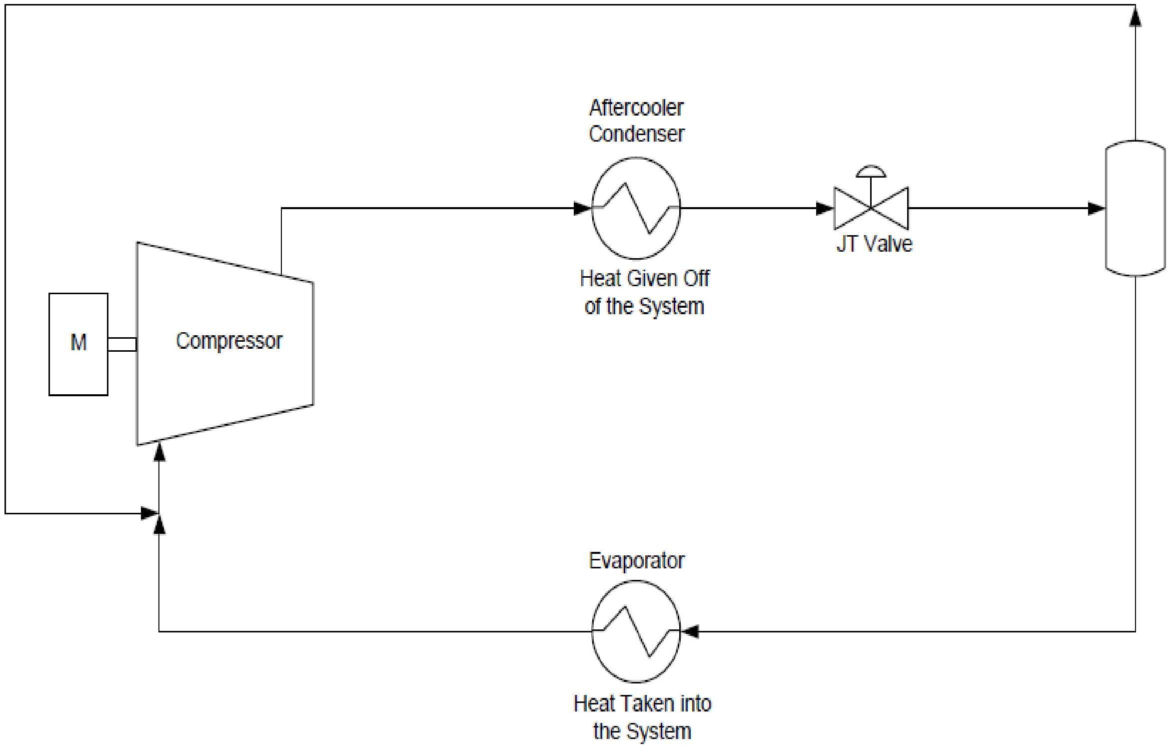

Figure ***Error! No text of specified style in document.****.25: Graphic showing air conditioning system with vapor downstream of JT valve being sent back to the inlet of the compressor.*

To drive the system to lower temperatures, the evaporator pressure can be lowered by further closing the JT valve or by increasing the throughput of the compressor. This will lower the pressure of the evaporator. **For refrigerant R134A one cannot in practicality drop the pressure below 20 psia (which correlates with ~ -2.4 F) for several reasons. The first reason is that it is a poor design practice to ever run any part of the refrigeration loop at less than atmospheric pressure. Running any part of the system below atmospheric pressure would result in air getting into the system if there were a leak. Secondly, the lower the pressure the refrigerant, the larger the equipment must be to manage that refrigerant. Larger compressors become costly. Thus, the refrigerant selection is critical to match the temperature service requirements.**

If a significantly lower temperature is required, obtaining the lower temperature in steps is much more efficient. Theoretically, the more steps, the more efficient the system can be.

However, there are diminishing returns on having too many steps. For instance, making a refrigeration system with 100 pressure drop steps would be very capital-intensive. It would also not be viable to build, and the efficiency hoped to be gained would be lost due to so much additional piping and its associated heat transfer from the environment.

A two-step pressure drops refrigeration system is shown in Figure 3.11

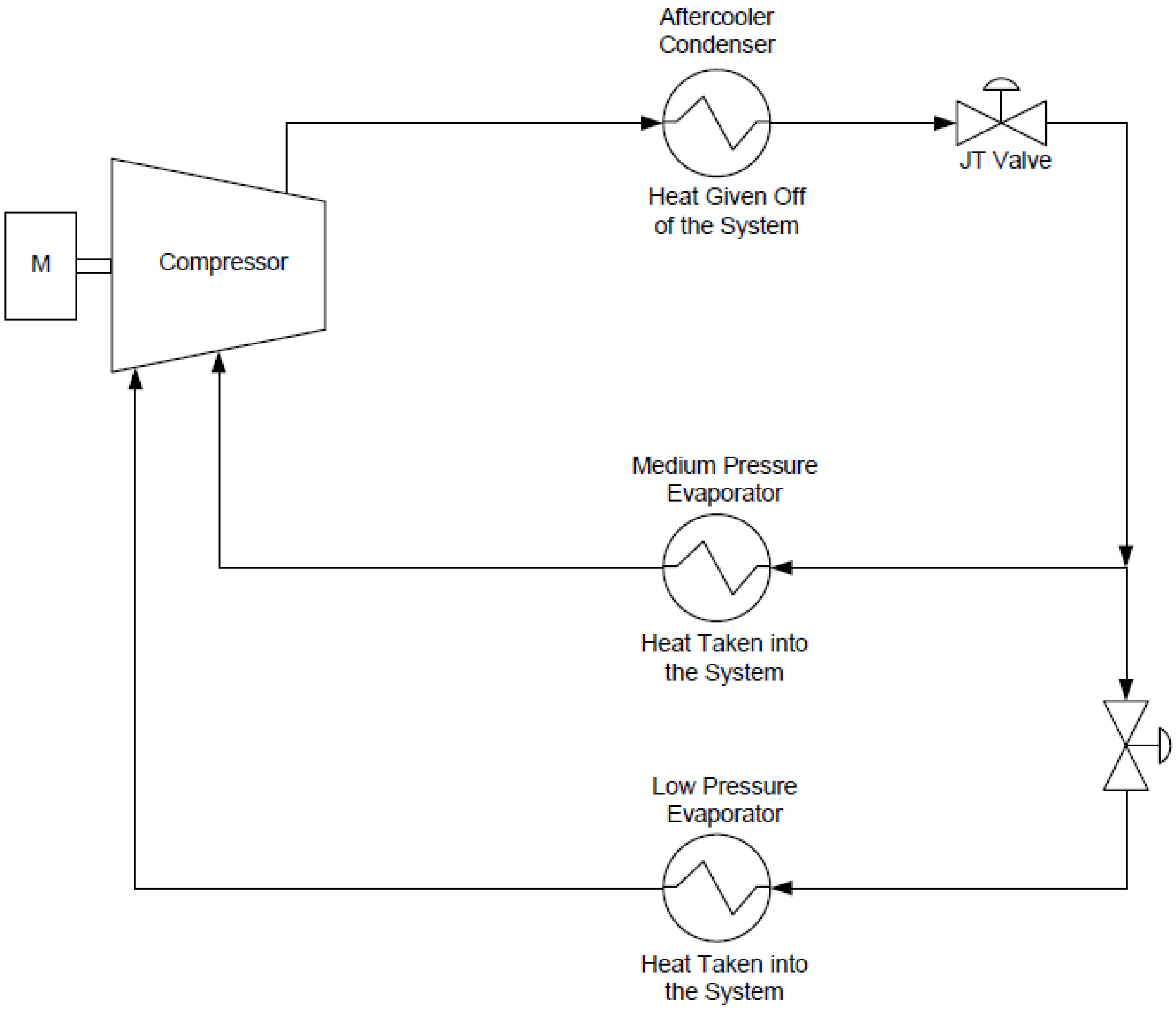

Figure ***Error! No text of specified style in document.****.26: Two step refrigeration process*

As with the earlier example, if is common to send the vapor downstream of the JT valve back to the compressor inlet rather than send it through the evaporator coil. This is shown in figure 3.12.

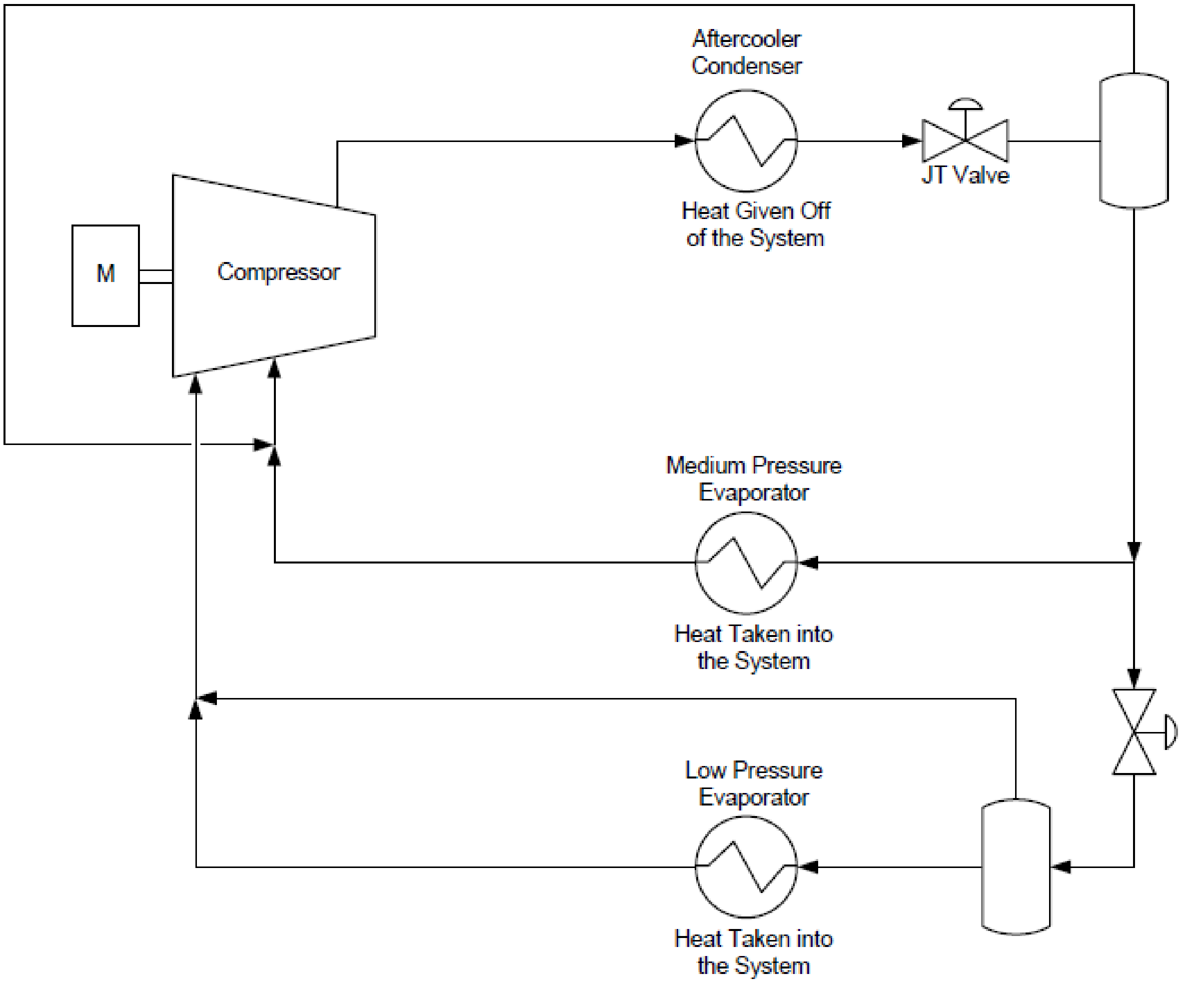

Figure ***Error! No text of specified style in document.****.27: A two-stage JT pressure drop refrigeration system with vapor return to the compressor*

In Figure 3.13 a refrigeration system is shown using propane as the refrigerant and using 4 pressure drops to improve efficiency. Using propane for a refrigerant is right near its limit of producing low temperature as producing 35 F occurs at a pressure of less than 4 psig (18.1 psia). Thus, if a lower temperature were needed, propane would not be a suitable refrigerant. A negative about using propane as a refrigerant is that it is flammable.

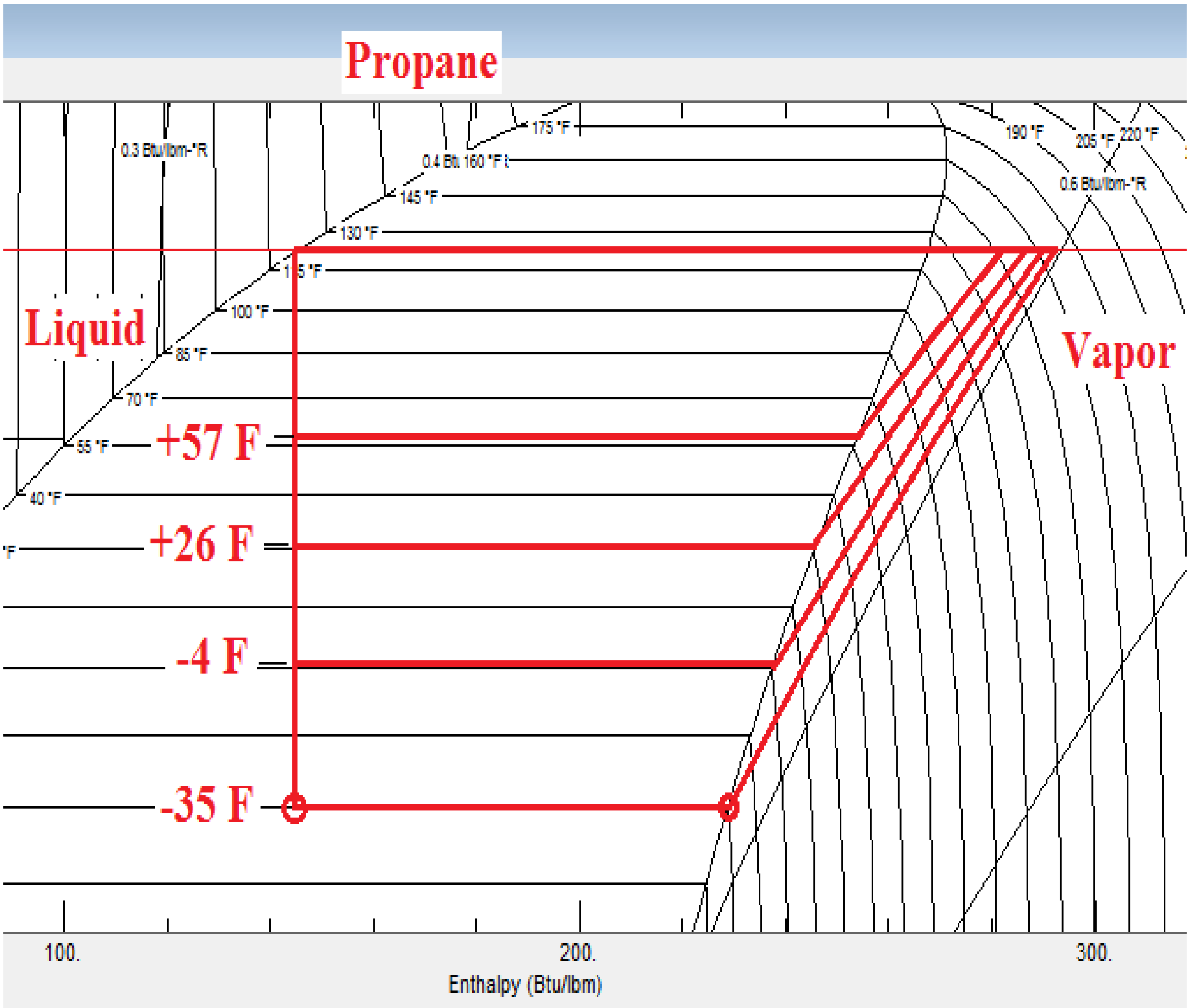

*Figure **Error! No text of specified style in document.**.28: Liquefied natural gas (LNG)*

As shown in Figure 3.13, in order to make liquefied natural gas (LNG) the temperature before the JT valve needs to be brought down to a much colder temperature. The example shown in Figure 3.14, shows the temperature being -180 F (liquid methane was used for this graphic). LNG could be produced at lower temperatures, but the LNG produced becomes richer in heavier hydrocarbons and thus, may not be desirable from a regassification interchangeability perspective in the next section of this series of courses.

Achieving this low of a temperature cannot be accomplished using a single refrigerant. Instead, multiple refrigerants are used along with more complex hardware as will be discussed in the remainder of this study.

Keep in mind, the lower the temperature desired, the higher the energy requirement will be.

1. Making LNG using single component refrigerants

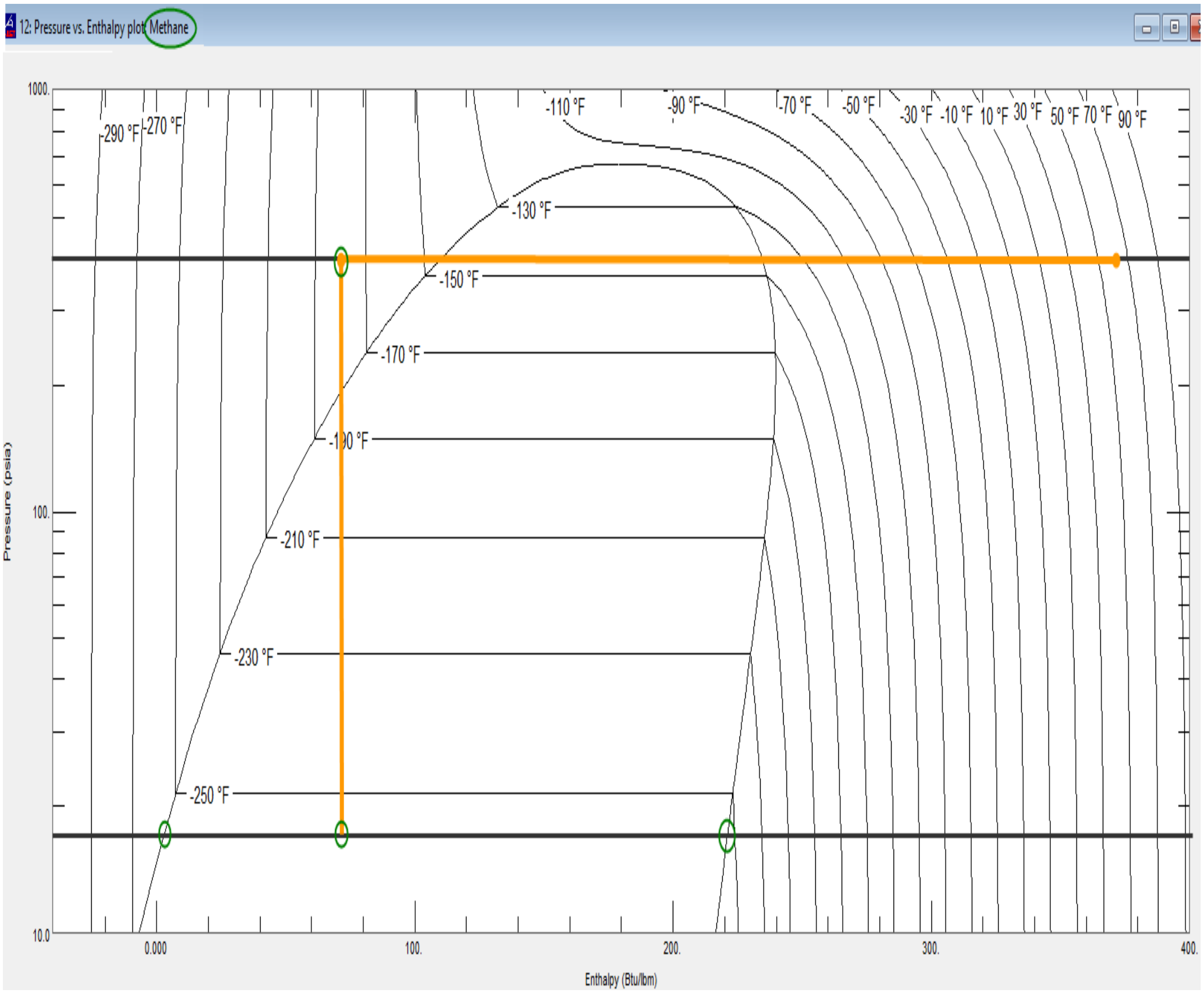

*Figure **Error! No text of specified style in document.**.29: A graphic showing the making of liquid methane*

One method of achieving very low temperatures would be to cascade multiple vapor compression systems using different pure substance refrigerants in a cascaded system (in series). This concept is shown in Figure 3.15. The numerical values shown are conceptual just to give the learner an understanding of how much more energy intensive the system becomes as it needs to reach very low temperatures.

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In Figure 3.15, high pressure LNG would be cooled down to near -180 F and then flashed through a JT valve to a low pressure resulting in a much colder temperature. The LNG itself would be stored at near -260 F in the LNG storage tank.

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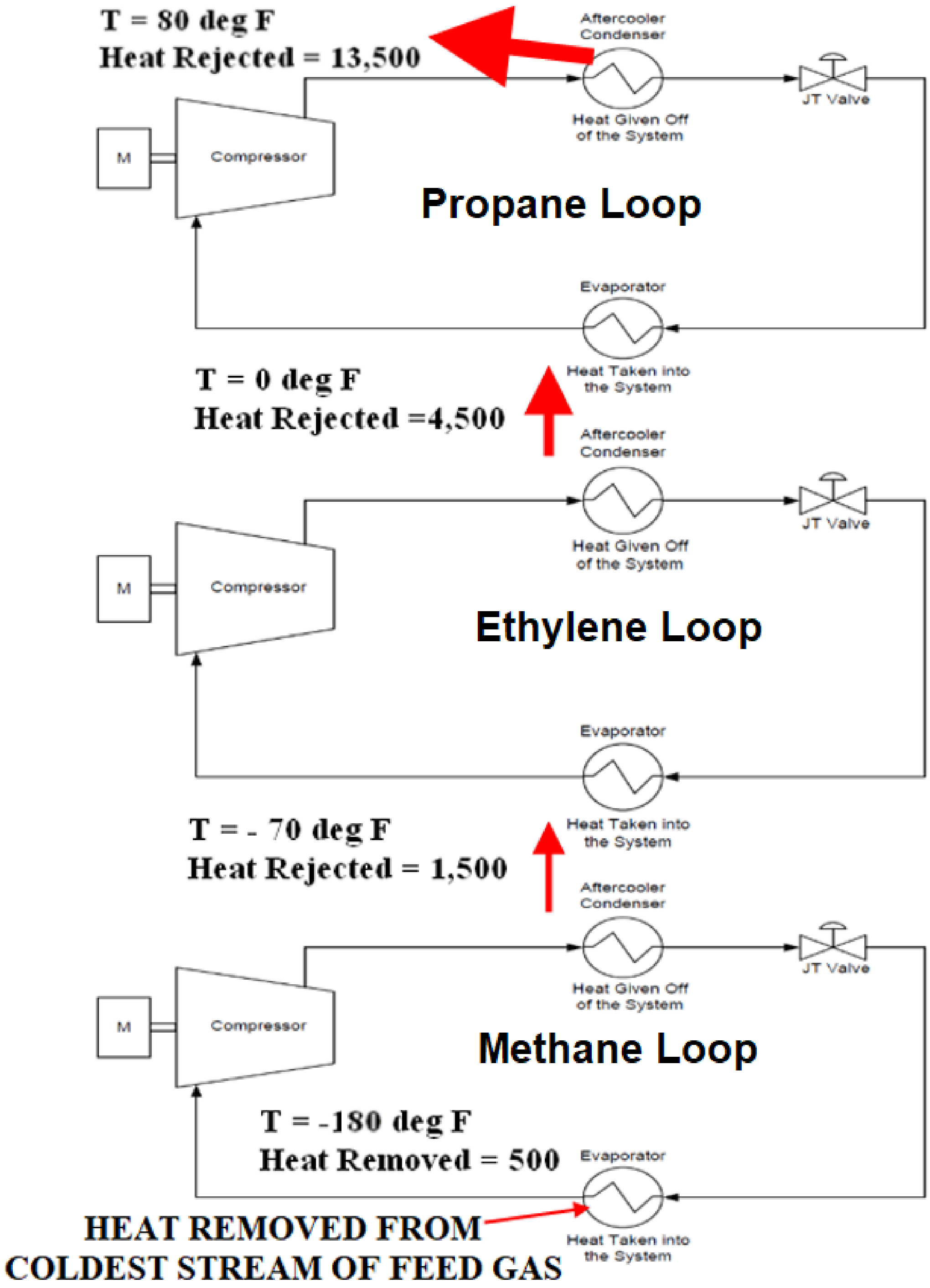

*Figure **Error! No text of specified style in document.**.30: A cascade system used to achieve -260 F. This system would use 3 different refrigerants (the numerical values are Conceptual).*

Obtaining such a low temperature (in Figure 3.15 it is down to -180F) in 3 stages would be very inefficient. This inefficiency is shown below for LNG as the space between the red and the black lines. The black line is the LNG cooling curve, and the red line is the refrigeration curve. The space between them is an indicatorof inefficiency.

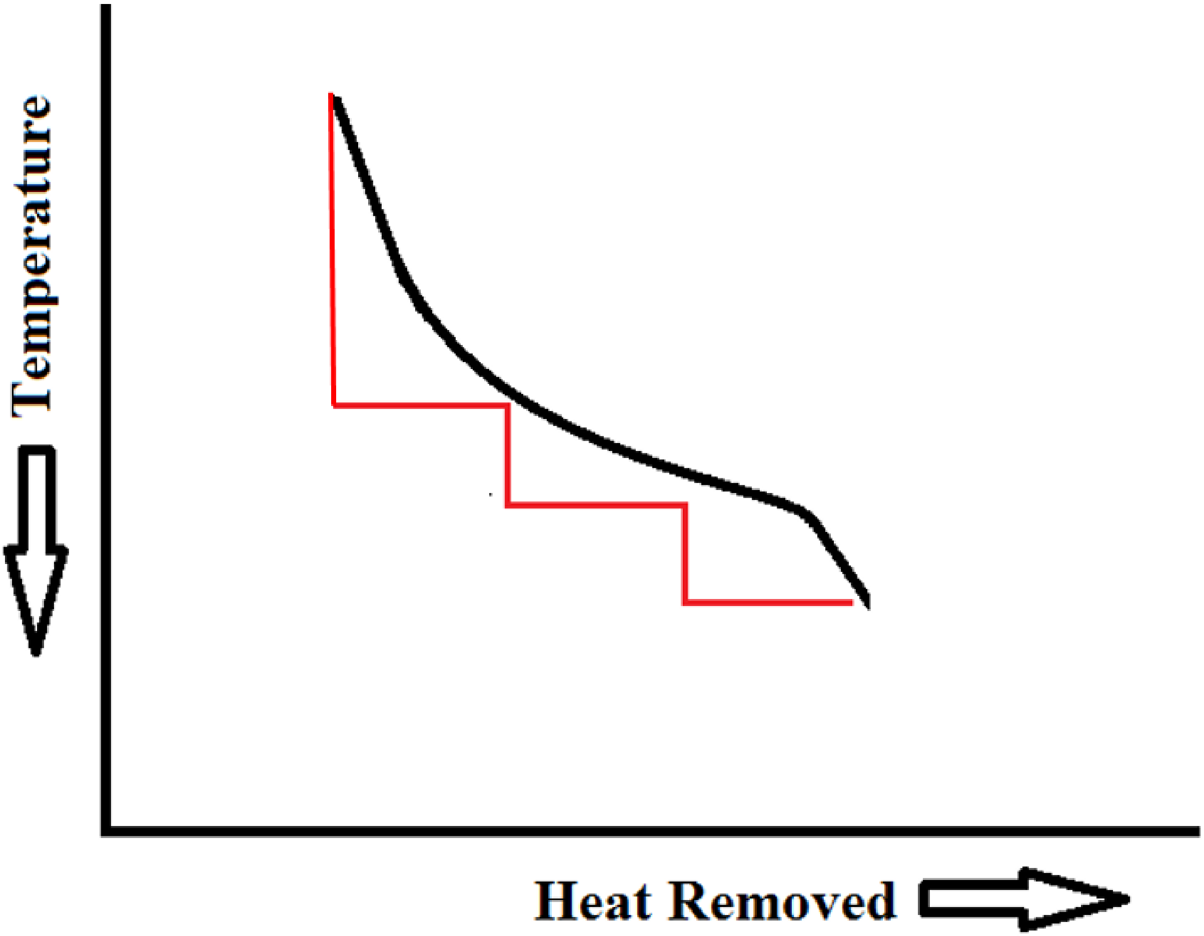

Figure ***Error! No text of specified style in document.****.31: A 3-step cascade system show a high amount of inefficiency (distance between red and black lines is a representation of inefficiency)*

The cascade process efficiency would be improved if each vapor compression cycle had 3 separate pressure drops. This would essentially produce 9 distinct temperature levels, which would match the LNG cooling curve better. For this process propane, ethylene and methane are selected as refrigerants. This process is shown in Figures 3.17 and 3.18.

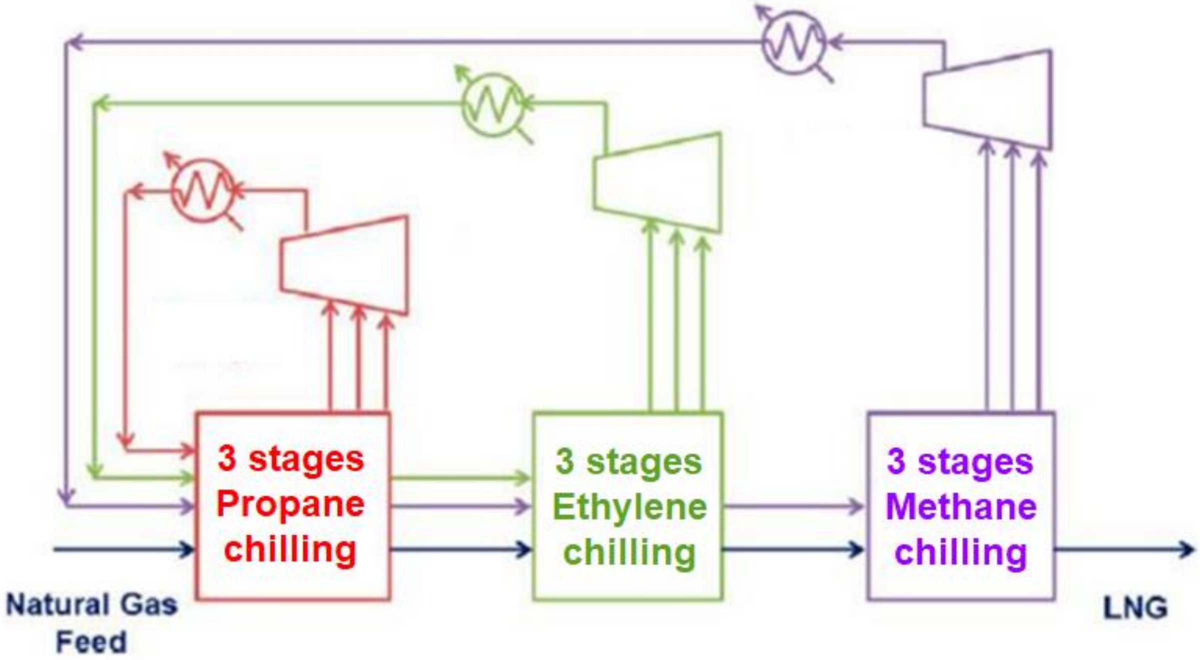

Figure ***Error! No text of specified style in document.****.32: A 3 refrigerant cascade refrigeration system with 3 pressure drops for each refrigerant*

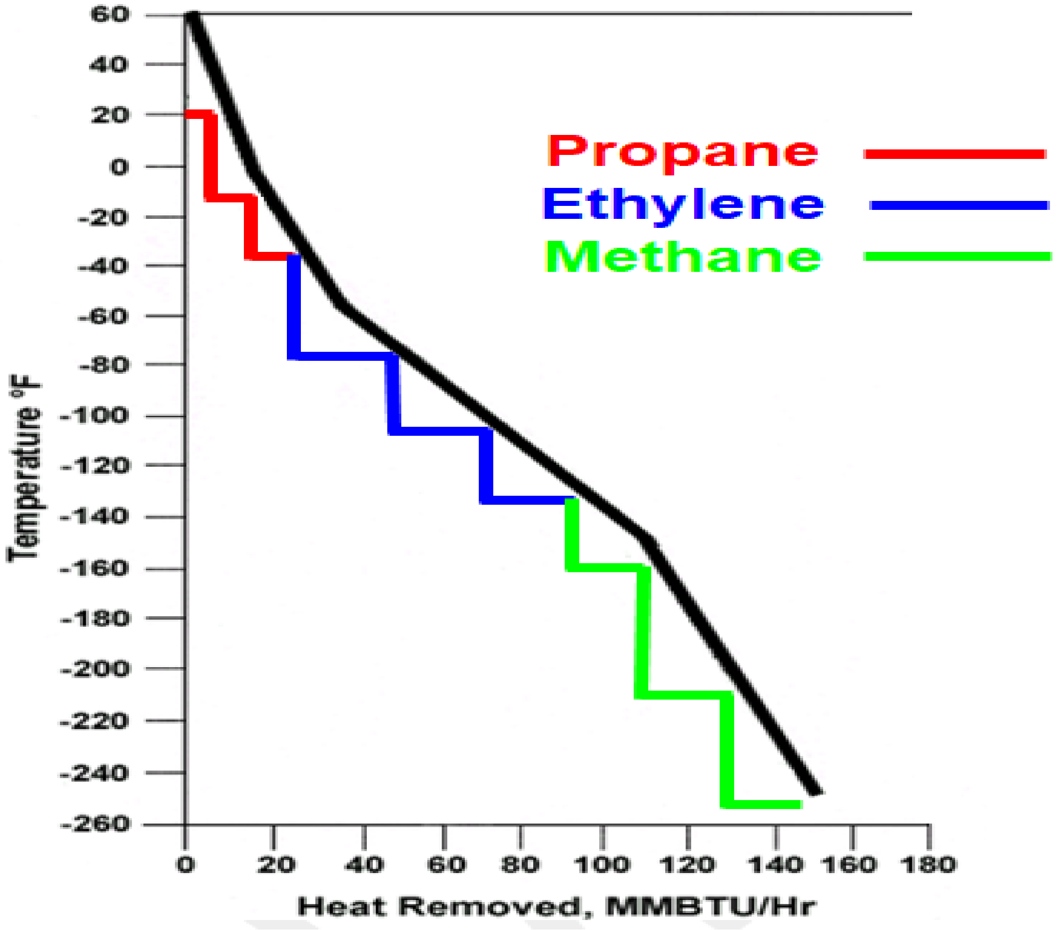

*Figure **Error! No text of specified style in document.**.33: A 3 refrigerant cascade refrigeration system with 3 pressure drops for each refrigerant*

2. Making LNG using multiple component mixed refrigerants

Thus far refrigeration systems shown in this document used single pure substance refrigerants. **A different process for attaining low temperatures is that of using zeotropic mixture of different refrigerants. An example of such a zeotropic mixture would be a mixture of nitrogen, methane, ethane, and propane. Each of these components has a different boiling point and mixing them together makes a refrigerant that changes temperature and composition as it changes phase.** If this mixture is of proper proportions, it would well match the liquefaction cooling curve with less inefficiencies than the earlier systems shown.

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Figure 3.19 shows a mixed refrigerant (MR) used in a vapor compression-liquid evaporation process that changes phase while the temperature of the phase change is not constant, and the composition of the fluid is constantly changing during the phase change. This mixture was randomly selected to conceptually show how the boiling point temperature changes for a given pressure as heat is removed or added to the fluid at two different pressures.

As an example, if a lbm of this mixed refrigerant liquid is brought through a JT valve, initially the nitrogen would “preferentially” boil off, then the methane would “preferentially” boil off, then the ethylene would “preferentially” boil off, and lastly the propane would “preferentially” boil off. The word “preferentially” is important to understand as it does not mean sequentially. Preferentially means that even during the first flashing from high pressure to low pressure occurs, the most volatile component, nitrogen, flashes from liquid to vapor more rapidly than the other components, but some of the less volatile components also flash to vapor. Thus, that initial flash gas will be high in nitrogen content but also contain methane, ethylene, and propane amounts. The initial flash would contain a very small amount of propane.

As the composition of the remaining liquid rapidly loses its nitrogen content, its composition changes, and the boiling point temperature becomes warmer. Then as the composition rapidly loses its methane content, it continues to change, and its boiling point becomes warmer. The same occurs as ethylene boils off. When the last droplets of liquid refrigerant boil off, there are still trace amounts of nitrogen and methane in the liquid refrigerant, but the liquid refrigerant is almost all propane.

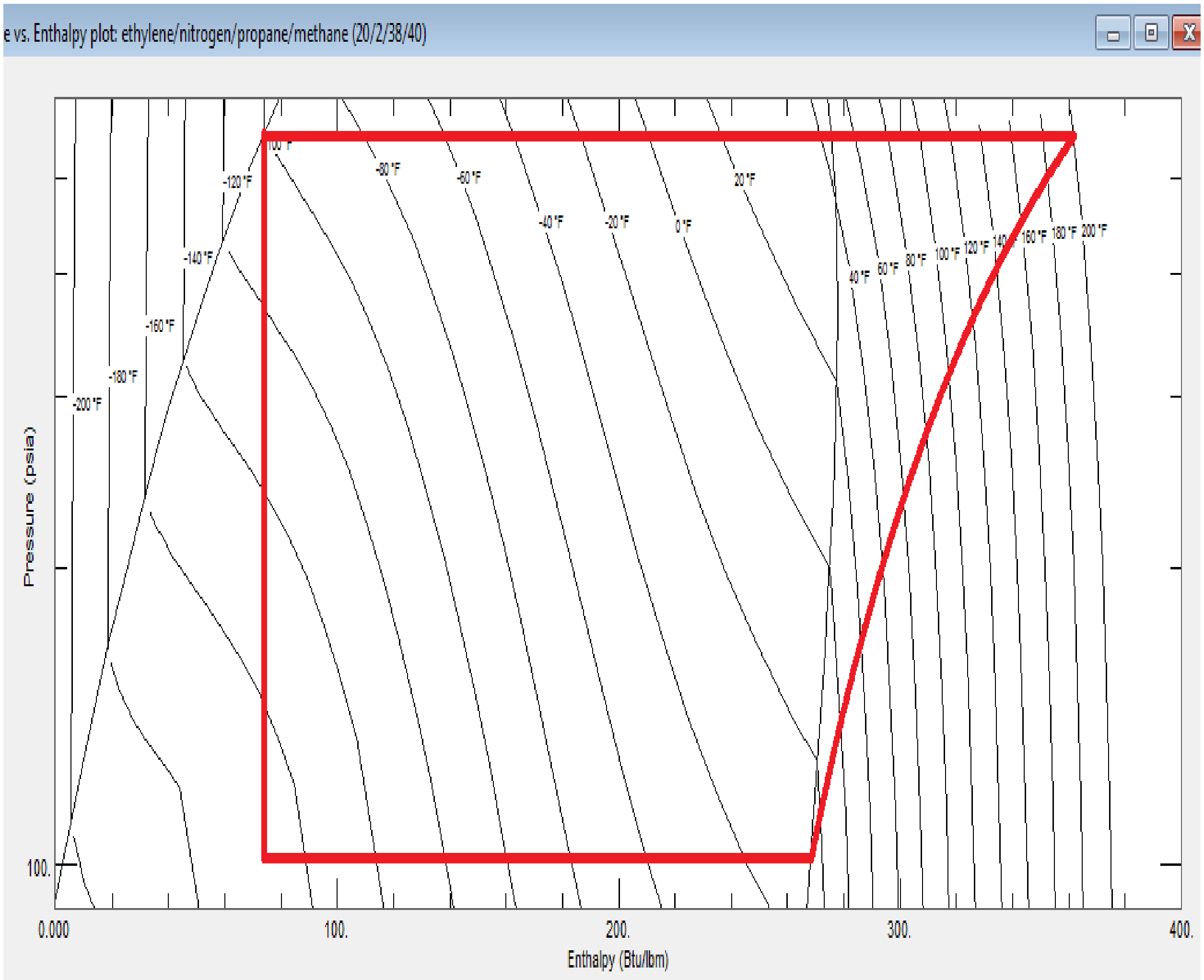

*Figure **Error! No text of specified style in document.**.34: A mixed refrigerant boils off the highest volatile components preferentially at a higher rate than the lower volatile components (preferentially does not mean sequentially)*

In Figure 3.20, a conceptual refrigeration curve is shown beside an LNG cooling curve. Take note, if the mixture is adjusted correctly the space between the red and black lines can be matched in shape and reduced in size, thereby increasing the system's efficiency.

In the real world it is not all that simple. To make a close match, often a dual MR system is used or a pure substance refrigerant with multiple pressure steps is used in concert with single or dual mixed refrigerant systems. This will be shown later in this learning.

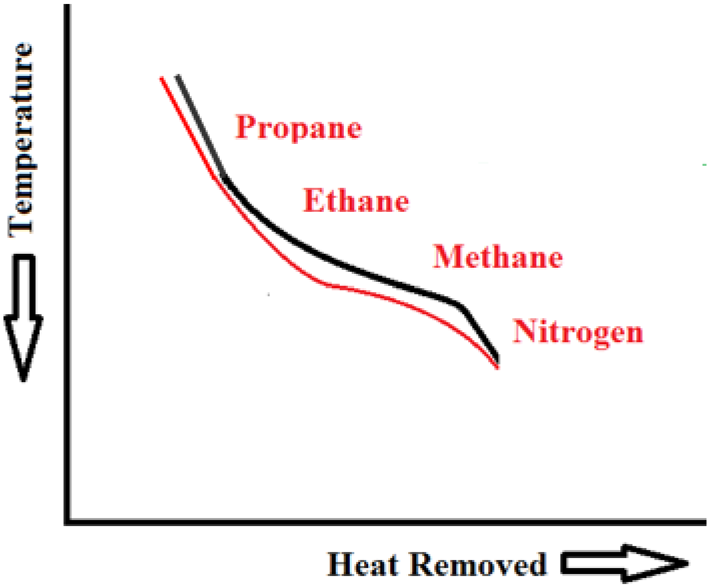

Figure ***Error! No text of specified style in document.****.35: A Conceptual mixed refrigerant refrigeration system well matched to an LNG cooling curve.*

Figure 3.21 shows a simplified sketch of how a mixed refrigerant system works. Note that the refrigeration after the JT valve cools down not only the LNG but also the MR that is fed to the inlet of the JT valve.

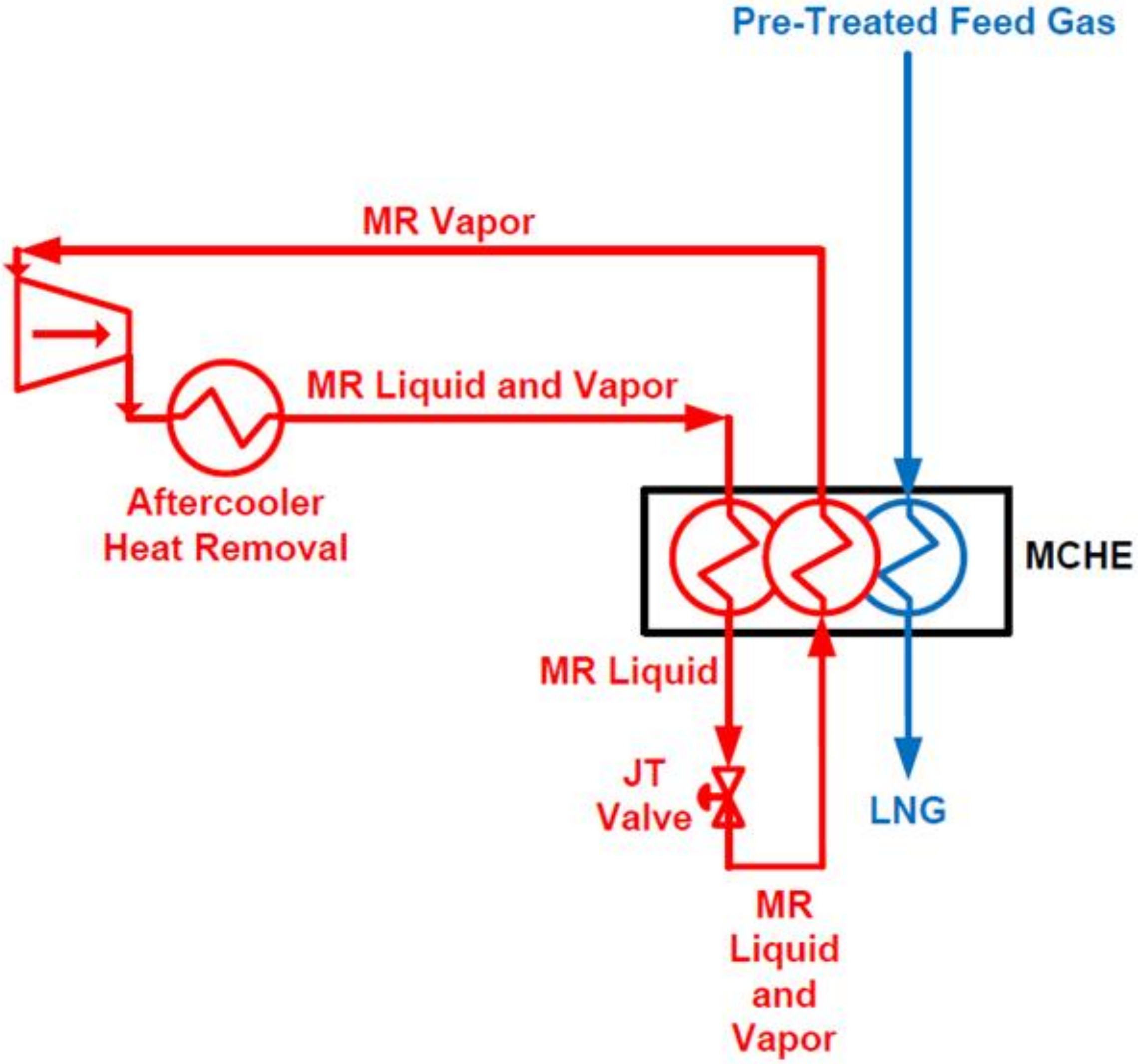

Figure ***Error! No text of specified style in document.****.36: Simplified sketch of how an MR LNG liquefier process operates*

Figure 3.22 is slightly more complex as it shows a separation of Mixed Refrigerant Liquid (MRL) and Mixed Refrigerant Vapor before being recombined and injected into the Main Cryogenic Heat Exchanger (MCHE). Figure 3.22 also shows the flow leaving the MCHE for removal of the heavy hydrocarbons and then returned to the MCHE to be liquefied.

In many plants as the MR enters the MCHE it is both liquid and vapor. It is common to separate the liquid and vapor and then to spray the liquid into the vapor stream at the entrance

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of the MCHE to assure an even distribution of vapor and liquid distributed across the MCHE entrance passages. This avoids channeling of liquid or vapor within the MCHE.

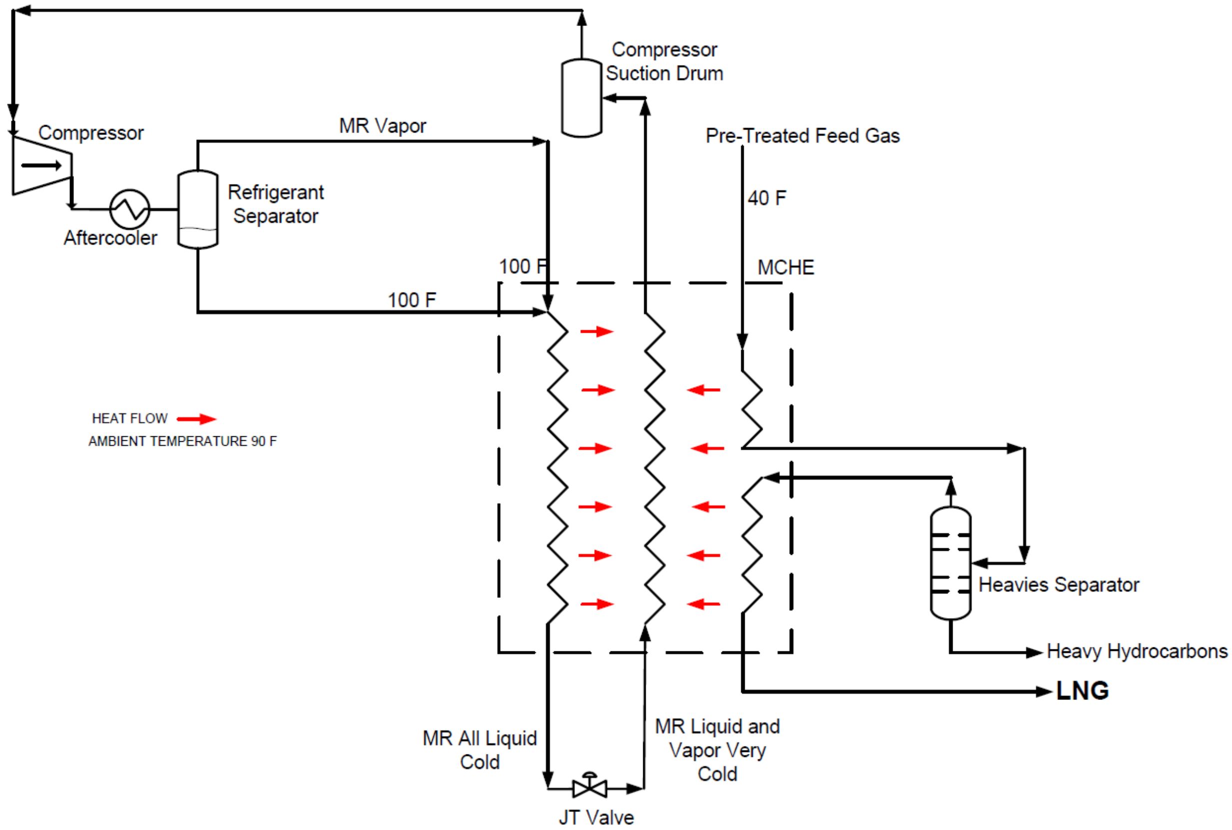


Figure ***Error! No text of specified style in document.****.37: Mixed refrigerant liquefaction process with pre-chilling of MR and feed gas with a takeoff for heavy hydrocarbon removal*

Figure 3.23 shows the above conceptual process overlaid on a Ph diagram for the refrigerant selected. Note: the MR refrigerant selected is15% nitrogen, 20% Methane, 25% ethane, and 30% propane. The ambient temperature for this example is shown as 90 F and pressure drops were neglected since this is a conceptual learning.

There are lines of constant pressure shown at 50, 125, 312, a 781 psia. These are shown on the graph because although this graph shows a single stage compression, the LNG Industry standard is to use multiple compressors in series with each compressor, except the last compressor in the series having an intercooler. The last compressor would have an aftercooler. These specific pressures were selected because they presume an equally spaced compression ratio of 2.5. I.e., 50 x 2.5 = 125, 125 x 2.5 = 312, and 312 x 2.5 = 781.

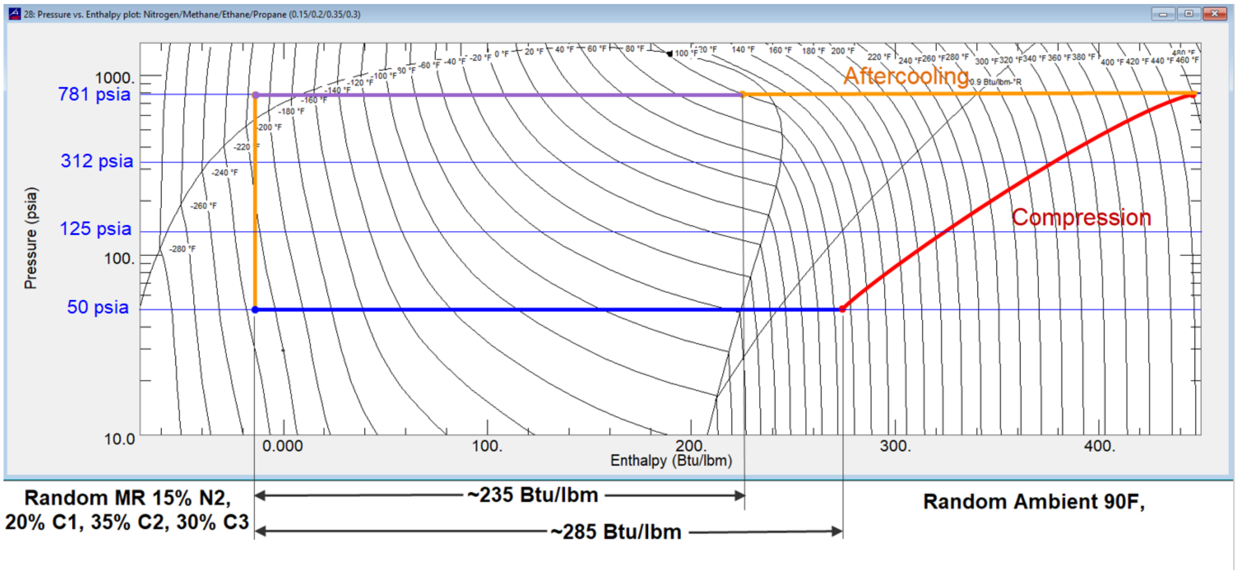


*Figure **Error! No text of specified style in document.**.38: Conceptual MR mixture Ph graph with refrigeration process overlayed*

As can be seen in Figure 3.23, the post-JT valve MR removes more heat than is needed to refrigerate the pre-JT valve refrigerant. The values shown could have been produced using thermodynamic software but were instead estimated by reading the obvious values off of the chart of Figure 3.23. The remaining heat removal (285 Btu/lbm – 235 Btu/lbm) is used to cool down feed gas which in the example shown in Figure 3.24 is brought down to a temperature of -235 F at a pressure of 600 psia. At that temperature and pressure, it is a subcooled liquid. As shown in Figure 3.24 it is flashed to a mixture of saturated liquid and saturated vapor, each with different compositions.

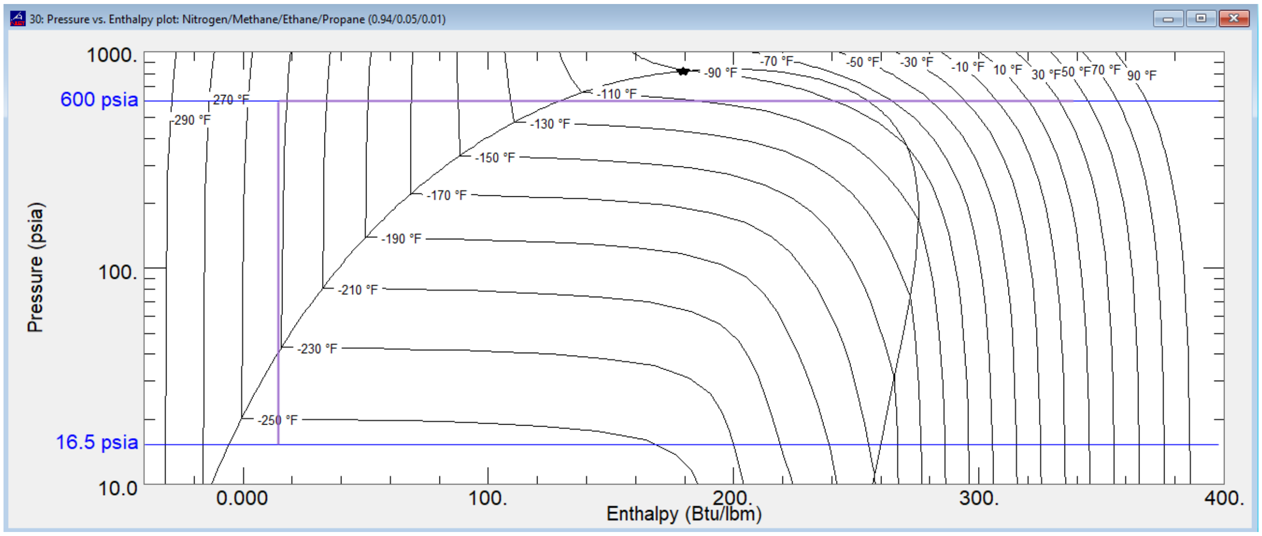
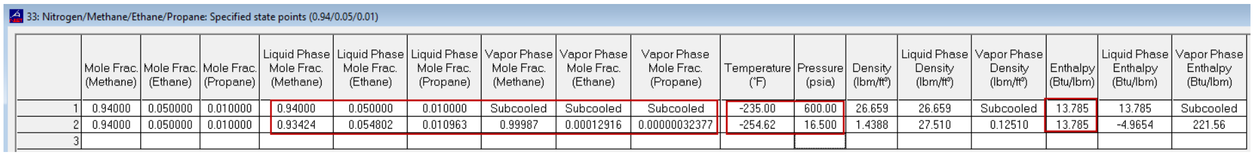


Figure **Error! No text of specified style in document.**.39: Feed gas cooled down to a subcooled liquid and then flashed to become a saturated liquid and saturated vapor at -255 F and 16.5 psia

The feed gas in this example entered the liquefaction plant with a composition of 94% methane, 5 % ethane and 1% propane. After the flash the composition changed slightly to ~93.5% methane, 5.5% ethane and 1% propane as the flash gas is almost 100% methane. This is shown in Figure 3.25.


33: Nitrogen/Methane/Ethane/Propane: Specified state points (0.94/0.05/0.01)

	Mole Frac. (Methane)	Mole Frac. (Ethane)	Mole Frac. (Propane)	Liquid Phase Mole Frac. (Methane)	Liquid Phase Mole Frac. (Ethane)	Liquid Phase Mole Frac. (Propane)	Vapor Phase Mole Frac. (Methane)	Vapor Phase Mole Frac. (Ethane)	Vapor Phase Mole Frac. (Propane)	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)
1	0.94000	0.050000	0.010000	0.94000	0.050000	0.010000	Subcooled	Subcooled	Subcooled	-235.00	600.00	26.659	26.659	Subcooled	13.785	13.785	Subcooled
2	0.94000	0.050000	0.010000	0.93424	0.054802	0.010963	0.99987	0.00012916	0.00000032377	-254.62	16.500	1.4388	27.510	0.12510	13.785	-4.9654	221.56
3																	

*Figure **Error! No text of specified style in document.**.40: Thermodynamic software output of the property changes before and after the JT valve. Note: the enthalpy is the same before and after the JT valve.*

As stated earlier intermediate pressures were shown on the Ph diagram in preparation for improving the efficiency of this MR process. In Figure 3.23 a single stage compression was used. This is an inefficient method of compressing the MR. Adding more stages increases efficiency. The LNG Industry has commonly used 3 stages of compression. There are diminishing returns on investment when adding stages of compression. As an example, in the extreme case, one could not justify using 10 stages of compression. Theoretically, this would reduce the work required to do the compression, but any such gains would rapidly be lost in the additional piping friction pressure drops and the cost would be prohibitive. Thus, most similar cycles use 3 stages of compression as shown in Figure 3.26 below.

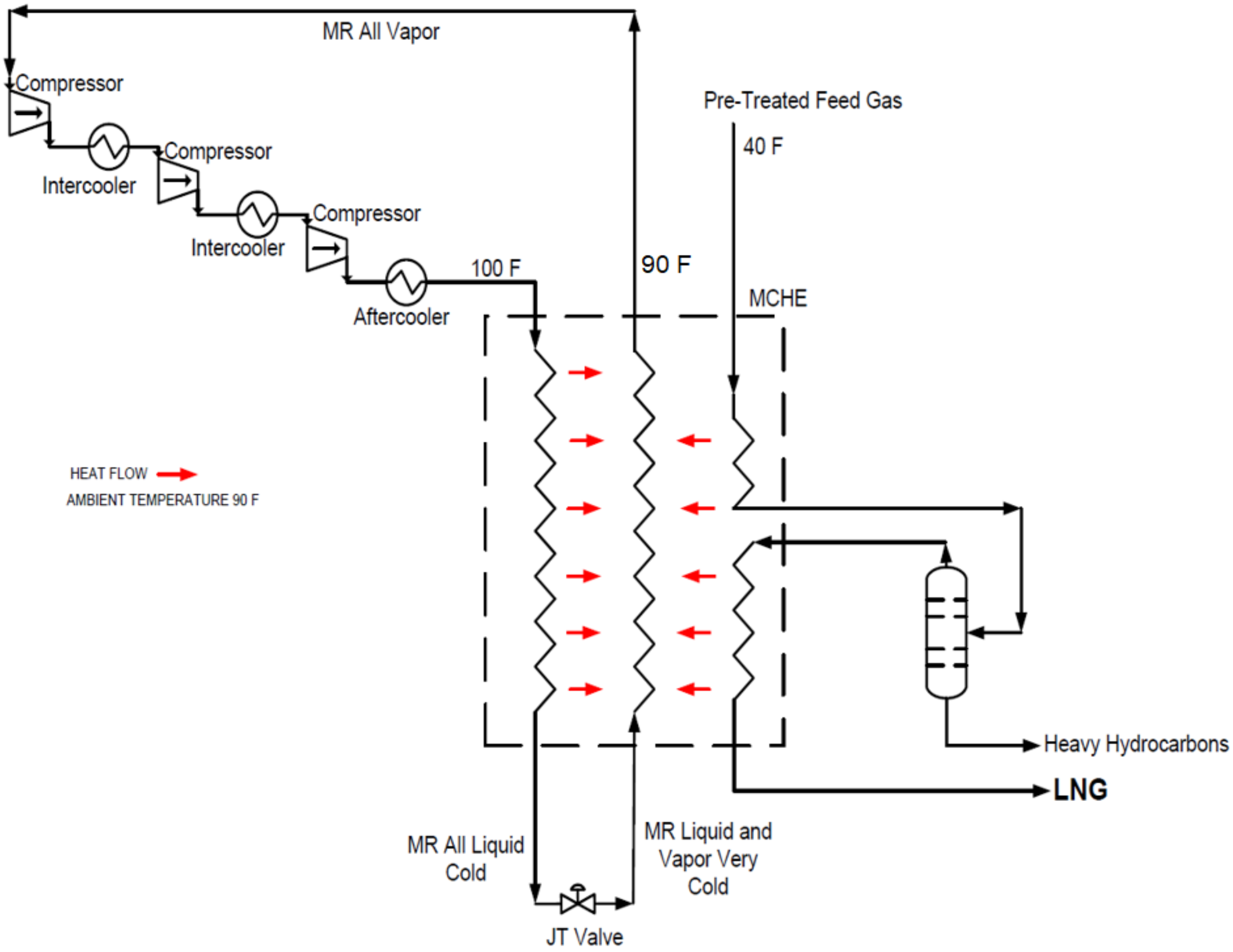


Figure ***Error! No text of specified style in document.*** *.41: An MR liquefaction system using 3 compression stages to improve compression efficiency. Also shown is a takeoff for heavy hydrocarbon removal*

The process shown in Figure is shown plotted on a Ph diagram in Figure 3.27.

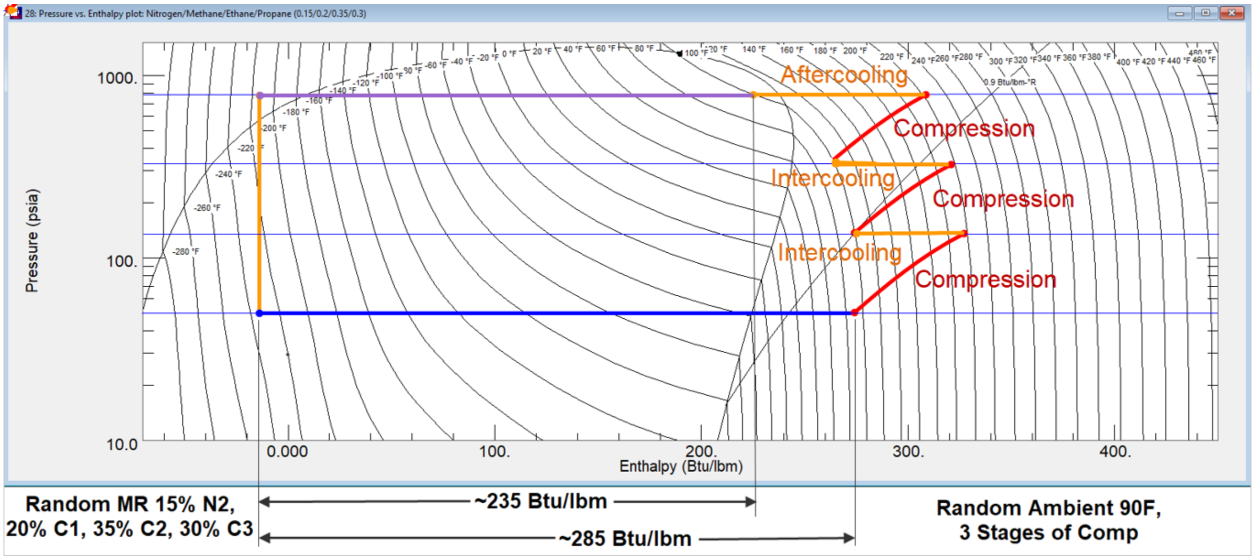


Figure ***Error! No text of specified style in document.****.42: A Ph diagram of an MR system using 3 stages of compression.*

When designing an MR system, it is critically important that the MR composition be such that makes the refrigeration stream is always colder than the stream being liquefied. This is necessary to always transfer heat from the stream being liquefied to the MR stream doing the cooling. The goal is to have the two curves match closely but not to cross each other. If they do cross, the process will not work. Such a condition is called a pinch point in the heater exchanger where the MR stream becomes the same temperature as the stream to be liquefied resulting in no heat transfer. A deeper analysis of this is beyond the scope of this discussion.

A reasonable curve matching is shown in Figure 3.28 below. Take note that in Figure 3.28 most of the very low temperature cooling is accomplished by the boiling off of nitrogen, the next coldest is by the boiling off of methane, and the next by the boiling off of ethane, and the very warmest part of the heat exchange cooling is accomplished mostly by the boiling off of propane. However, as explained earlier, this boiling off MR is a preferential boiling and not a sequential boiling. The amount of boiling of each component is a function of the liquid and vapor composition of each component and the temperature and pressure.

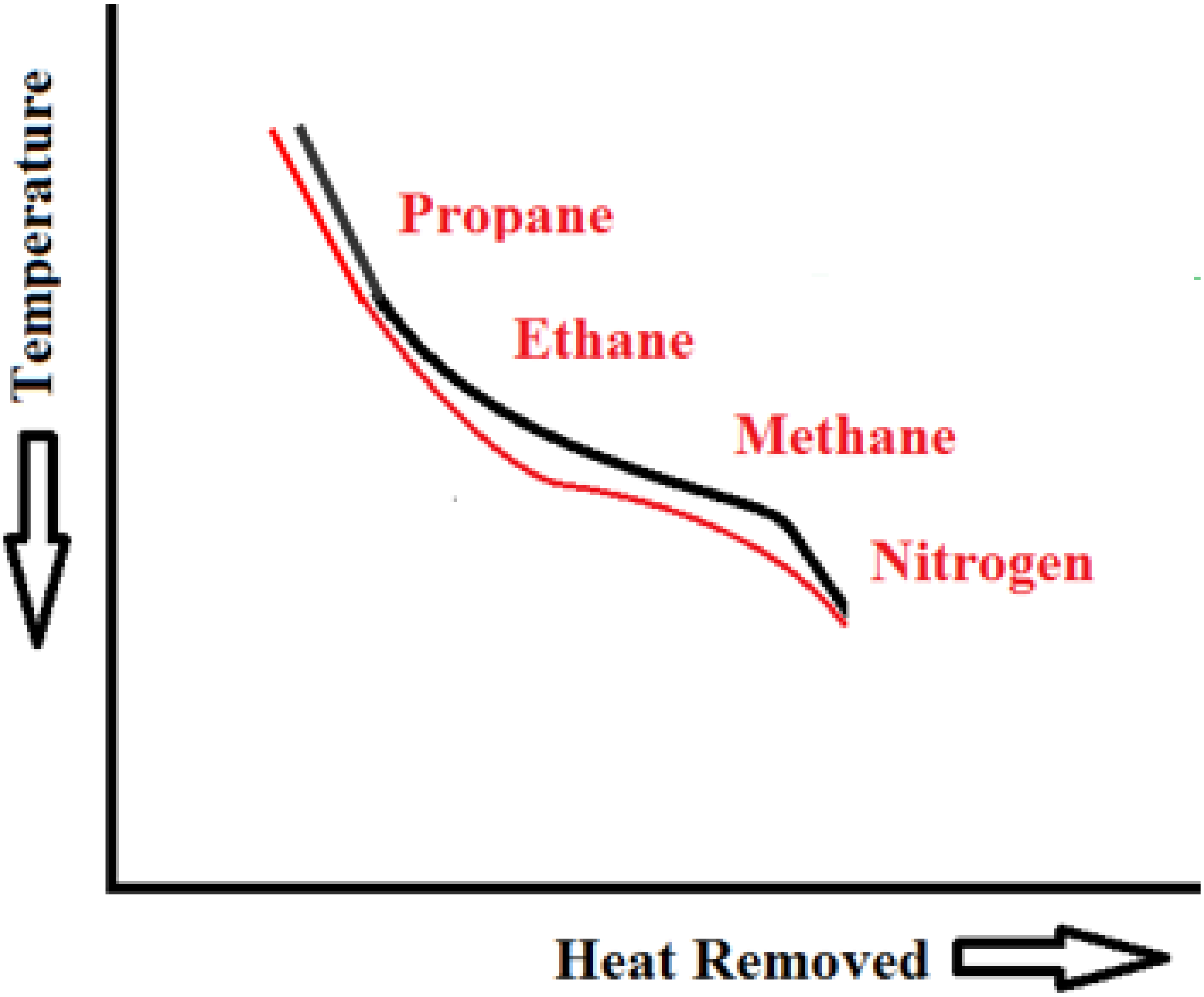


Figure ***Error! No text of specified style in document.****.43: A plot of the MR cooling curve and the feed gas liquefaction curve*

In addition to optimizing an MR process by adding more compression, many designs use a system whereby the liquid and vapor MR is separated and then the liquid is sprayed back into the vapor at the inlet header of the main cryogenic heat exchanger. This spraying is done to ensure an even distribution of both the liquid and vapor into the header inlet of the heat exchanger. This is shown in Figure 3.29.

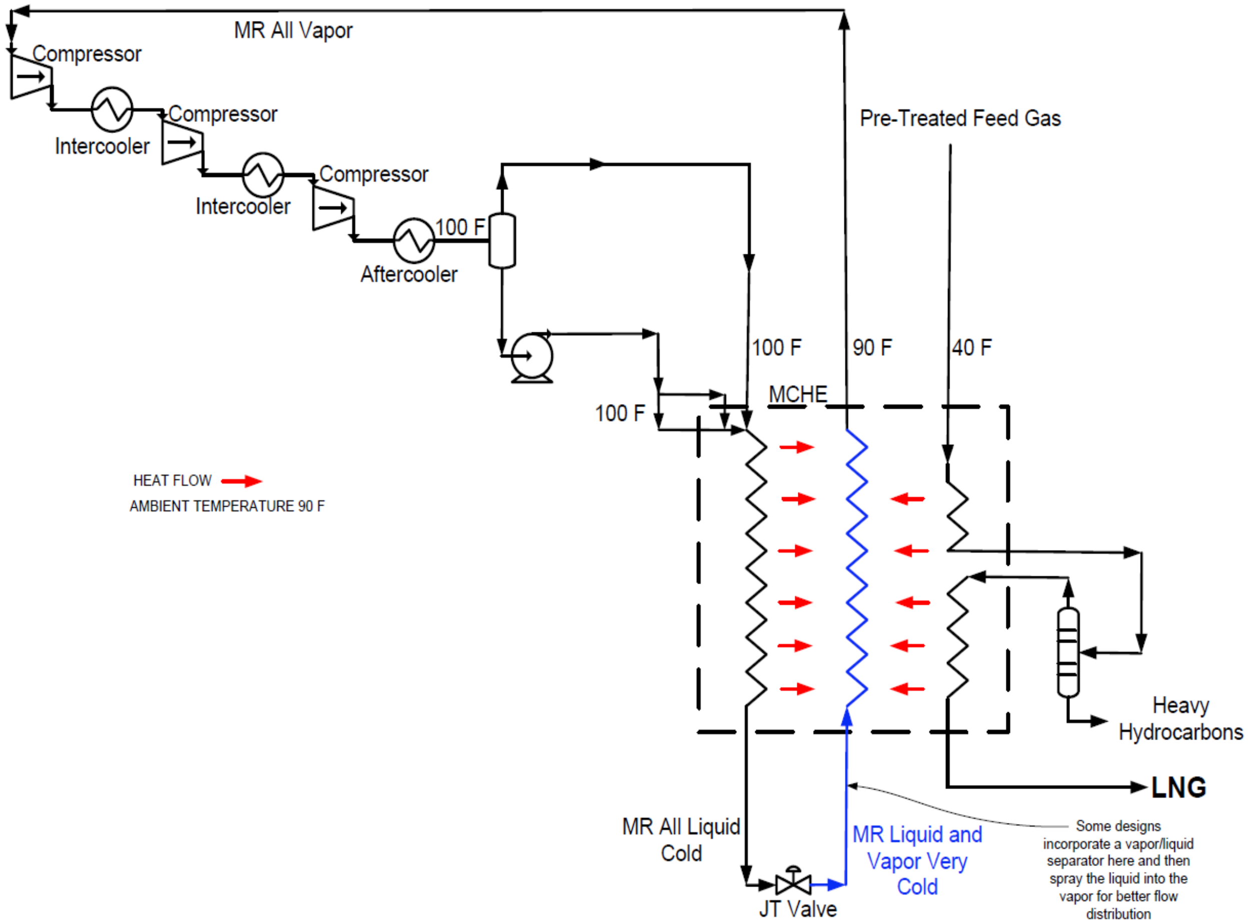


Figure ***Error! No text of specified style in document.****.44: MR system using a liquid separator with reinjection of the liquid as the vapor enters the main cryogenic heat exchanger*

There are several different designs of heat exchanger which could be used to accomplish the MCHE heat exchange. Some plants use brazed aluminum plat fin heat exchangers, and others use spiral wound heat exchangers. Although other types of heat exchangers could be used, these two types are the most popular. Brazed aluminum plat fin heat exchangers are shown in Figures 3.30 and 3.31.

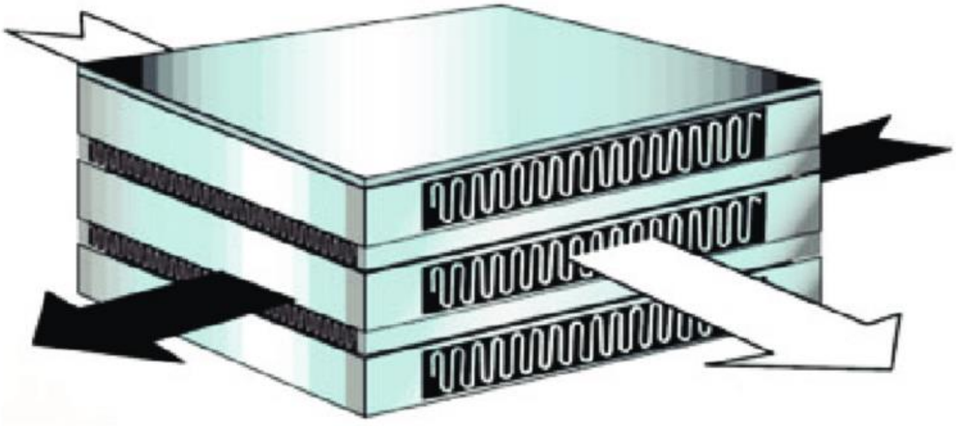


Plate fin heat exchanger Source: https://www.researchgate.net/figure/Basic-structure-of-plate-fin-heat-exchanger-PFHE_fig7_283325770

Figure ***Error! No text of specified style in document.****.45: Conceptual graphic of how a brazed aluminum plate fin heat exchanger exchanges heat*

Plate fin heat exchangers typically made of aluminum and brazed together Source: http://webwormcpt.blogspot.com/2010_07_01_archive.html

Figure ***Error! No text of specified style in document.****.46: A brazed aluminum plate and fin heat exchanger*

Making LNG efficiently is not as simple as shown in the earlier Figures. As the ambient temperature changes and as the natural gas (feed gas) changes composition, the MR composition, pressure, and temperatures may also need to be adjusted. To avoid the hourly effects of temperature, it is common for some larger plants to use a propane pre-chiller process to cool the MR and the feed gas before the MR refrigeration system is used. By doing this, the MR process always receives the same temperature feed gas and MR temperature.

Such a system is shown in Figures 3.32, 3.33 and 3.34. Take note how in Figure 3.32, this prechilling greatly enhances the amount of cooling available from the MR system. In addition to this pre-chilling of the MR it also removes a significant amount of heat that is in the feed gas. As an example, if the propane system brings the MR to -30 F, on a 90 F Day, the MR would have been dropped in temperature by 140F (100 F at the outlet of the compressor aftercooler to the outlet of the propane pre-chiller. In this same example, the feed gas would be cooled by 70 F from a temperature of 40 F to -30 F.

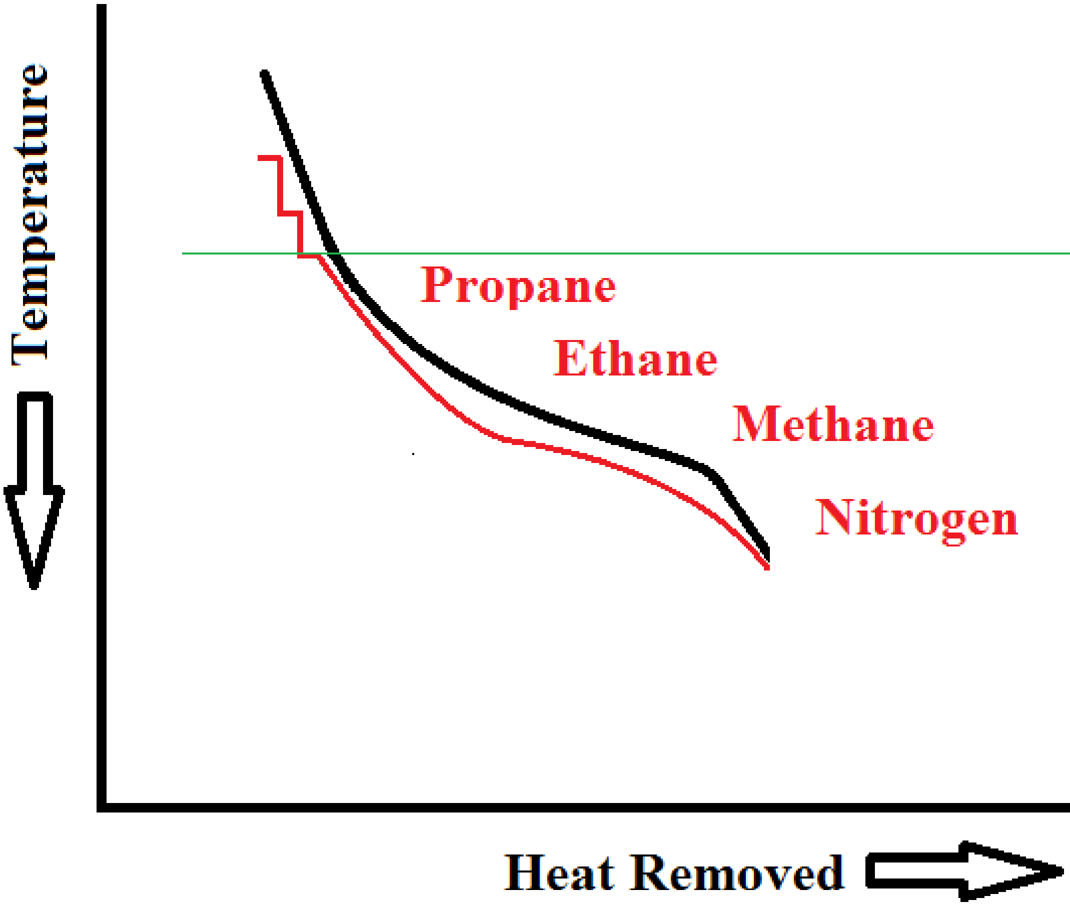


*Figure **Error! No text of specified style in document.**.47: Conceptual refrigeration and LNG load curve for a C3/MR process (propane prechilling is used to maintain the feed gas entering the MR system at a set temperature.*

In Figure 3.33, the C3 cooling effect on the MR process is circled in red. As can be seen, this precooling of the MR allows the MR to provide significantly more refrigeration to the feed gas to be liquefied. It also isolates the MR system from the changes in ambient temperature. Further, the propane pre-chilling also chills the feed gas, thereby increasing the refrigeration needed by MR. This results in an overall higher production rate with an easier to use system.

Figure 3.33 could have been modified further to also show that the MR leaving the cold box would be much colder thereby entering the MR compressor at a temperature near -40 F. This is not shown in Figure 3.33; however, this lower compressor temperature would allow the compressor to operate more efficiently as the inlet MR gas would be denser due to its cold temperature.

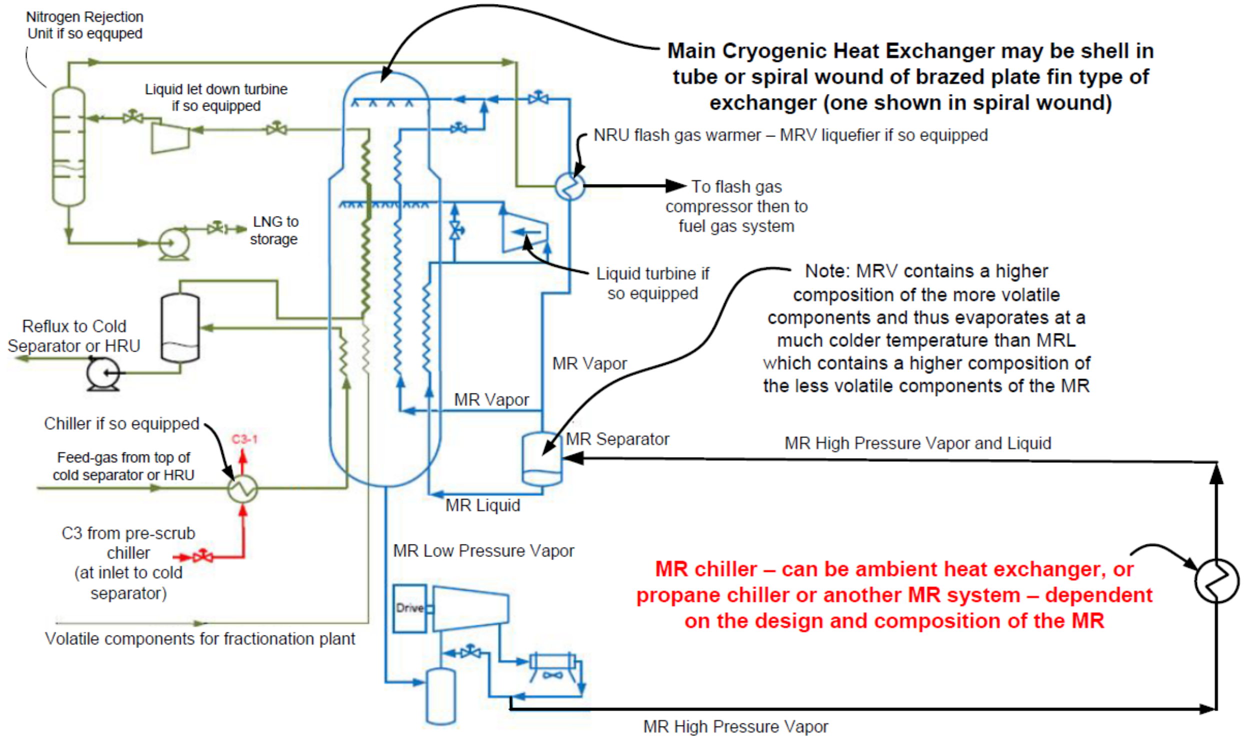


Figure ***Error! No text of specified style in document.****.48 MR Chiller*

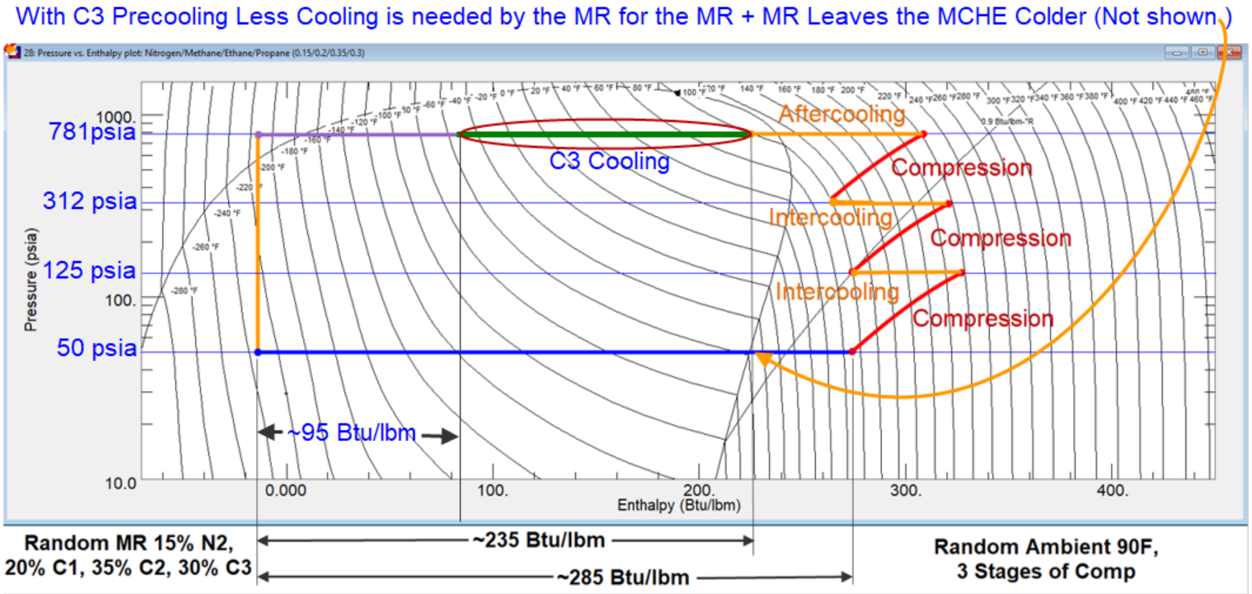


Figure ***Error! No text of specified style in document.****.49: Plot of C3 MR process on a Ph diagram – change to outlet MR temperature not shown*

Many large-scale MR liquefiers use a mixed refrigerant that is cooled to produce two distinct mixed refrigerants, mixed refrigerant liquid (MRL), and mixed refrigerant vapor (MRV). Since the MRL and MRV are two distinct refrigerant compositions, they can be used for providing cooling at two different temperature ranges. Because these refrigerants of MRL and MRV are made by a single stage of distillation the MRV contains more nitrogen and methane, while MRL contains more of ethane and propane. The composition of MRV has a significantly greater composition of the more volatile components, which causes it to change phase from liquid to vapor at a much colder temperature. In the same way MRL contains significantly more of the less volatile components, which causes it to change phase from a liquid to vapor at a warmer temperature. During the phase change of either MRL or MRV the composition and temperature of the MR (L or V) is constantly changing. The plant operators need to adjust the MR concentrations to best match the refrigeration curves to the LNG cooling curve

In Figure 3.35 only a single MR compressor is shown because it is a simplified drawing. However, it is typical to have 3 stages of MR compression with aftercooling after each compressor. Also, any time there is dynamic compressor is used, it is typical to have anti-surge protection that takes gas from the outlet of the aftercooler and brings it back to the suction drum of the dynamic compressor.

Figure 3.35 also shows several other features that may be used in large scale plants to improve plant efficiency or improve final LNG composition. The features shown include a Nitrogen Rejection Unit (NRU) a pressure let down liquid turbine to recover energy and to further subcool the LNG produced in the MCHE. A liquid turbine is also shown at the inlet of the MRL into the MCHE. The Flash gas warmer is also used to recover refrigeration. Not shown in this drawing but another efficiency enhancer would be to use cold boil off gas from the LNG storage tanks as a source of refrigeration.

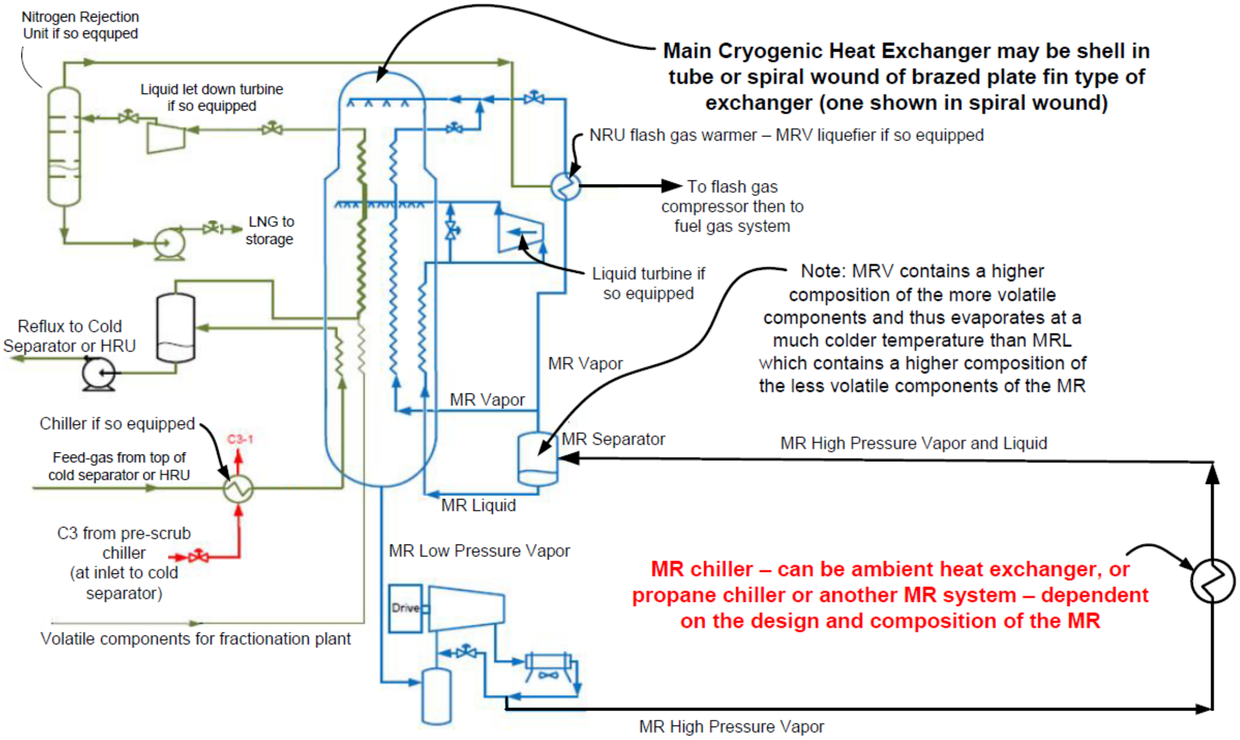


*Figure **Error! No text of specified style in document.**.50: Conceptual drawing of a MR system that uses an MR separator to make MRL and MRV*

Figure 3.36 is another conceptual drawing of a C3/MR process. Many large-scale liquefiers use this process. As shown 4 stages of propane chilling are used to chill the MR converting it to MRL and MRV. In this drawing three stages of MR compression are shown, and a flash gas compressor is used to compress the top outlet gas from the NRU to be used as fuel gas. The flash gas from the NRU can contain a high percentage of nitrogen. Figure 3.36 also shows BOG being used as a source of refrigeration.

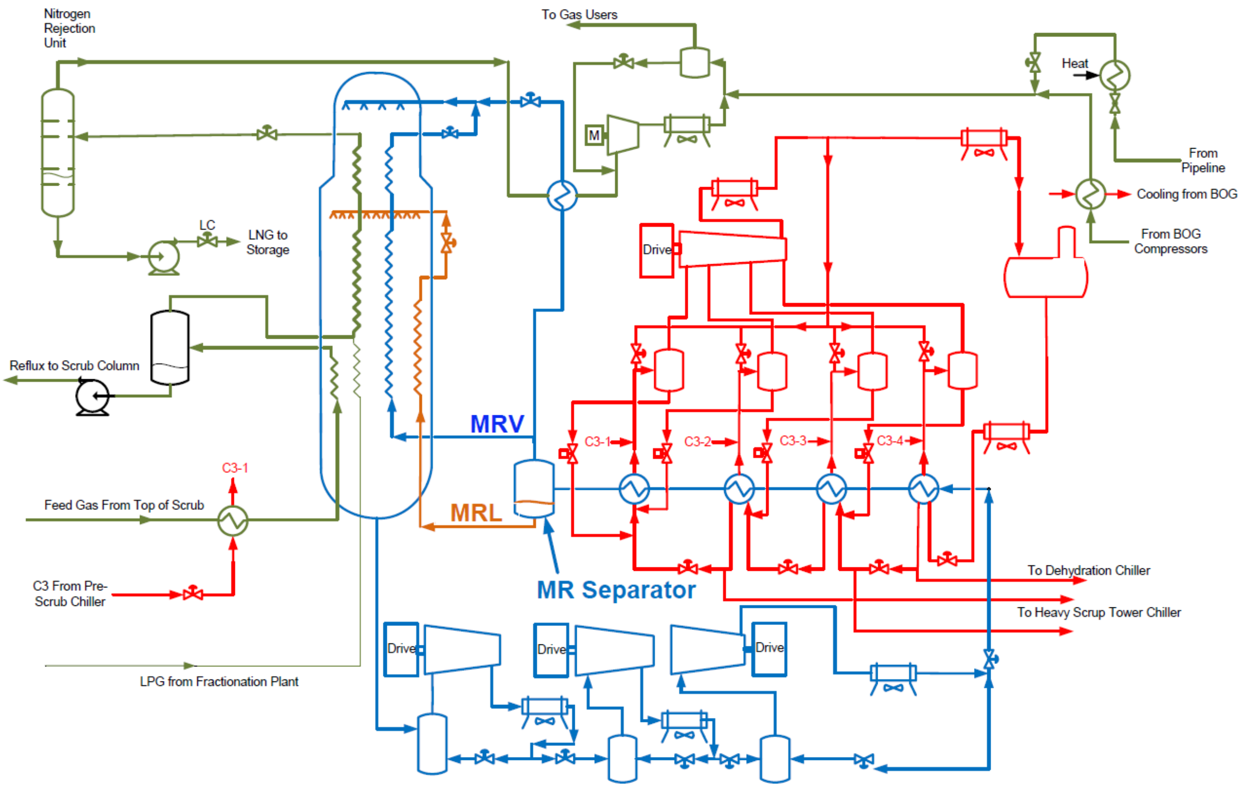


Figure ***Error! No text of specified style in document.****.51: Conceptual drawing of a C3/MR liquefaction system*

To better understand the MR and MRL and MRV relationships, Figures 3.37, 3.38, 3.39 and 3.40 are presented below.

It should be noted that both the MRL and the MRV are converted to a subcooled liquid before being pressure dropped across a JT valve and entering the MCHE. This is shown in Figures

The system shown in Figure 3.36 allows the operator to adjust the composition of the main MR mixture and the MRL and MRV by several optimization methods including, changing the combined MR composition and by adjusting the temperature and pressure of the fluid entering the MR separator. The pressure and temperature of the MR separator as well as the combined MR composition will dictate the composition of the MRL and MRV.

Figure 3.37 shows the relationship of a conceptual MR mixture separated to MRL and MRV.
Figure 3.38 shows the an approximation of the Ph diagram for the MRL shown in Figure 3.37.
Figure 3.39 shows the an approximation of the Ph diagram for the MRV shown in Figure 3.37.

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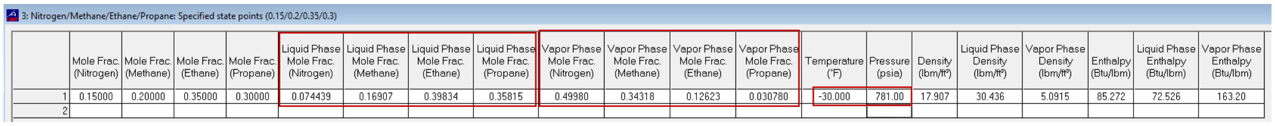
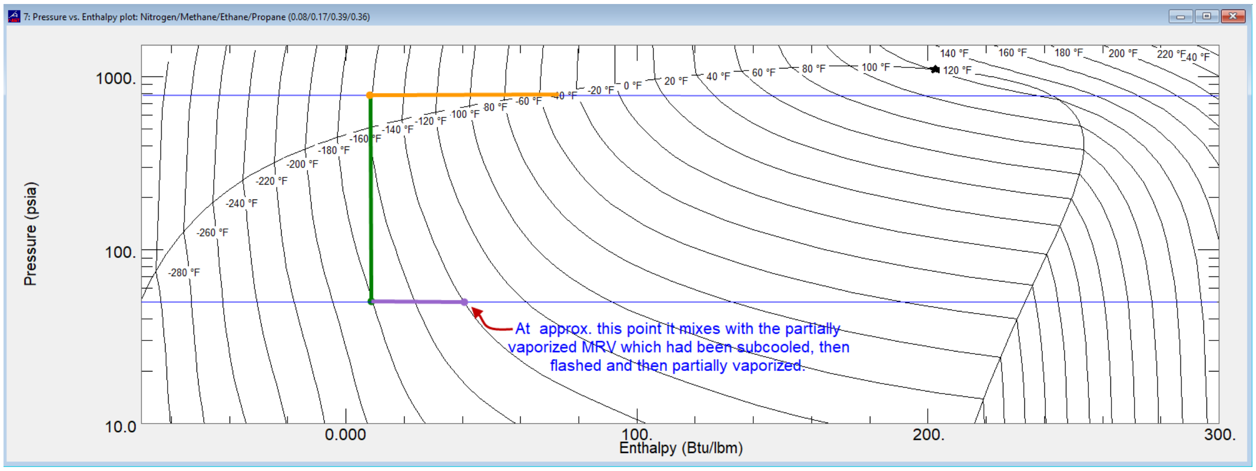
When viewing Figure 3.36, it needs to be understood that the MRV while boiling off is becoming similar to the MRL composition being flashed into the MCHE. By the time the MRV rains down to the point where the MRL is being injected, the composition of the remaining MRV liquid is close to the composition of the post-flash MRL being injected in the midsection of the MCHE. At this midsection, the combined liquid flows continue to rain down on the heat exchanger coils providing cooling to the MRL, MRV and feed gas coils that are in the lower section of the MCHE.



3: Nitrogen/Methane/Ethane/Propane: Specified state points (0.15/0.2/0.35/0.3)

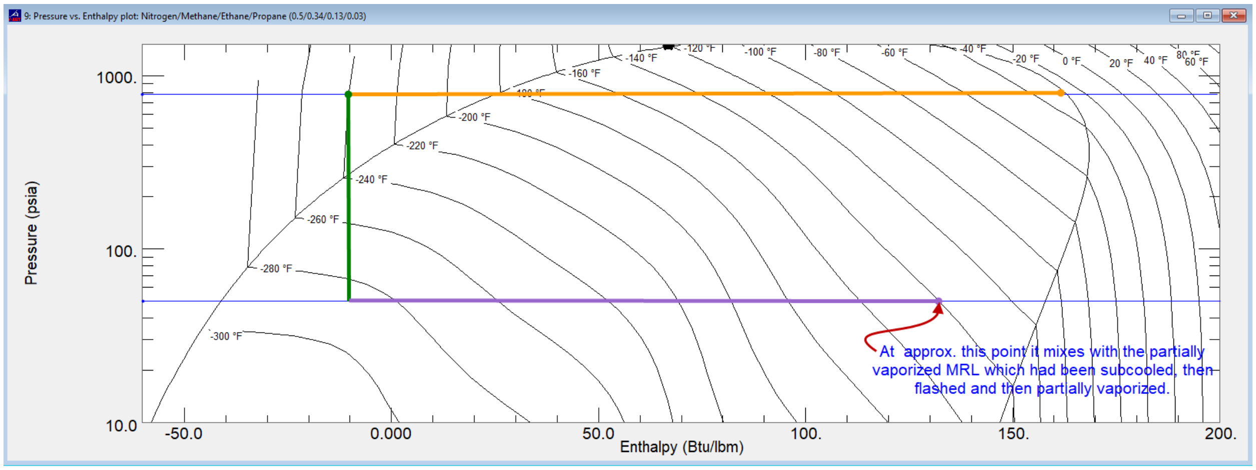
	Mole Frac. (Nitrogen)	Mole Frac. (Methane)	Mole Frac. (Ethane)	Mole Frac. (Propane)	Liquid Phase Mole Frac. (Nitrogen)	Liquid Phase Mole Frac. (Methane)	Liquid Phase Mole Frac. (Ethane)	Liquid Phase Mole Frac. (Propane)	Vapor Phase Mole Frac. (Nitrogen)	Vapor Phase Mole Frac. (Methane)	Vapor Phase Mole Frac. (Ethane)	Vapor Phase Mole Frac. (Propane)	Temperature (°F)	Pressure (psia)	Density (lbm/ft³)	Liquid Phase Density (lbm/ft³)	Vapor Phase Density (lbm/ft³)	Enthalpy (Btu/lbm)	Liquid Phase Enthalpy (Btu/lbm)	Vapor Phase Enthalpy (Btu/lbm)
1	0.15000	0.20000	0.35000	0.30000	0.074439	0.16907	0.39834	0.35815	0.49980	0.34318	0.12623	0.030780	-30.000	781.00	17.907	30.436	5.0915	85.272	72.526	163.20
2																				

*Figure **Error! No text of specified style in document.**.52: MR converted to MRL and MRV in the MR separator*



At approx. this point it mixes with the partially vaporized MRV which had been subcooled, then flashed and then partially vaporized.

*Figure **Error! No text of specified style in document.**.53: A conceptual approximation of an MRL subcooling, flash and heat absorption*



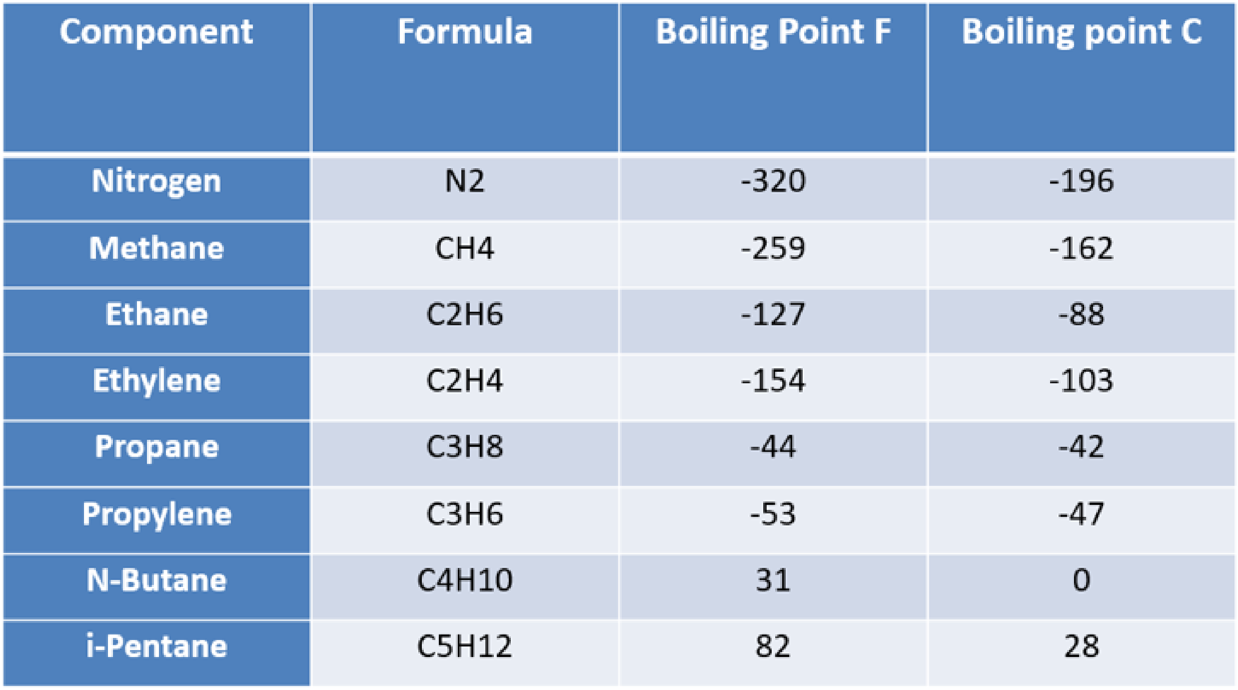
At approx. this point it mixes with the partially vaporized MRL which had been subcooled, then flashed and then partially vaporized.

Figure ***Error! No text of specified style in document.****.54: A conceptual approximation of an MRV, liquefaction, subcooling, flash and heat absorption*

Selecting the correct combination of MR components is not an easy task. Many iterative studies need to be made to optimize the hardware design (compressors, heat exchangers, piping, etc.) and many thermodynamic simulations need to be run to optimize the process. The optimization process needs to take into account, the many variables that the process may undergo during its projected life.

Some of these variables include the feed gas composition changes, temperature changes, heat transfer reductions due to fouling, pressure drops due to fouling etc.

Also the cost of optimization is an important factor. As an example, increasing heat exchanger area may increase heat exchange efficency, however, there is a cost benefit analysis that needs to be considered and a pressure drop concern would also need to be considered. Some of the MR components that are typically used are shown in Figure 3.40 below.



Component	Formula	Boiling Point F	Boiling point C
Nitrogen	N2	-320	-196
Methane	CH4	-259	-162
Ethane	C2H6	-127	-88
Ethylene	C2H4	-154	-103
Propane	C3H8	-44	-42
Propylene	C3H6	-53	-47
N-Butane	C4H10	31	0
i-Pentane	C5H12	82	28

Figure ***Error! No text of specified style in document.*** *.55: Listing of MR components*

Other liquefaction systems

Other liquefication systems include the Nitrogen Expansion system which will be covered in *"What Every Energy Engineer Needs to Know Understanding about the Thermodynamics of Natural Gas Liquefication Systems Part 3B",* the open expansion liquefaction system which was covered in detail in the first course of this series ("*What Every Energy Engineer Needs to Know about Thermodynamics and Liquefication Systems Part (1 of 3)"*).

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Conclusion

In this publication, we have used the conservation of mass and the first law of thermodynamics to understand the basics of liquid methane, methane gas, LNG mixtures and its BOG. It is understood for the reasons stated earlier that the analyses were simplified with the intent of teaching concepts. As you—the engineers of our LNG and propane plants—exercise the concepts described herein, it is hoped that you will gain a hunger for a deeper understanding of thermodynamic concepts.

From this point on, I encourage you to see everything in your day-to-day life with an understanding of thermodynamics:

- As you make a cup of coffee, you are transferring heat (increasing the enthalpy of the water) and to some extent changing phase.
- As that cup of coffee cools, it is transferring heat to the surroundings (its enthalpy is dropping), and its temperature is dropping.
- When you press on the accelerator of your car, there are so many processes that are taking place, each of which has its own thermodynamic phenomenon associated with it.
- When you turn on a methanol or an LNG pump, realize that you are increasing the enthalpy of the fluid as you add work energy to that fluid. As that fluid then flows through the plant piping, realize that, as it gains or loses heat, the fluid is changing in enthalpy. As you vaporize LNG to send gas out to your customers, realize that you are changing phase (if it is sub critical) and then warming the vapor to an acceptable temperature or if you are above the critical point that you are heating a fluid that does not have liquid and vapor phases.
    - Our LNG and propane plants are essential to our industry’s future. Your skill and ability in managing these assets is a critical part of the future. This publication ends with appreciation of you for your technical ability and your dedication to excellence. You are our industry’s greatest asset.

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