

REFRIGERATION CYCLES

Carnot Cycle

We start discussing the well-known Carnot cycle in its refrigeration mode.

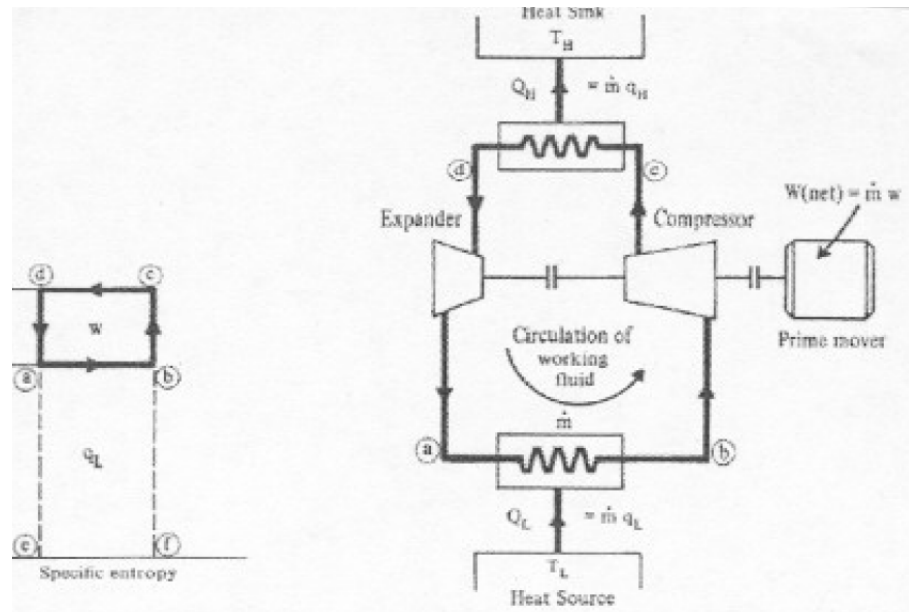


Figure 2-1: Carnot Cycle

In this cycle we define the coefficient of performance as follows:

$$COP = \frac{q_L}{w} = \frac{T_L}{T_H - T_L} \quad (2-1)$$

Which comes from the fact that $w = q_H - q_L$ (first law) and $q_L = T_L \Delta s$, $q_H = T_H \Delta s$ (second law). Note that w is also given by the area of the rectangle.

Temperature differences make the COP vary. For example, the next figure shows how COP varies with T_L (T_H is ambient in this case) and the temperature difference in exchangers.

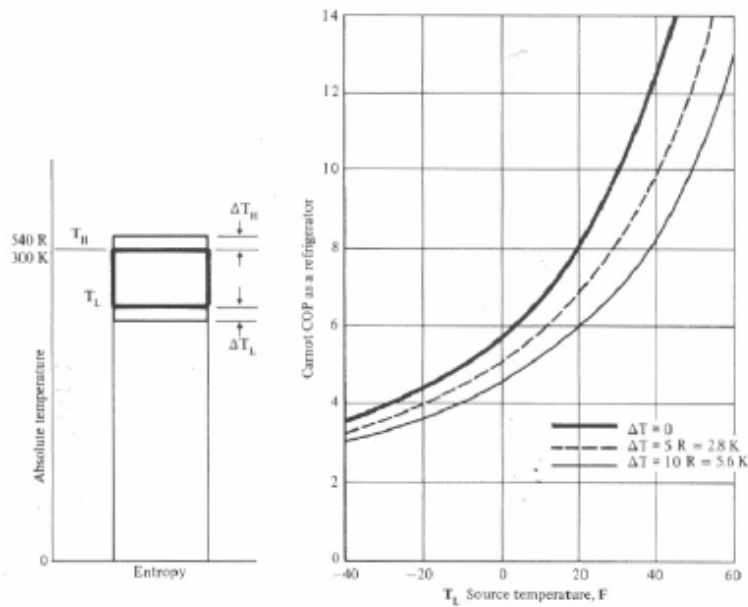


Figure 2-2: COP changes with heat exchanger temperature approximation and T_L (T_H =ambient)

We now turn our attention to a real one stage refrigeration cycle, depicted in the next figure.

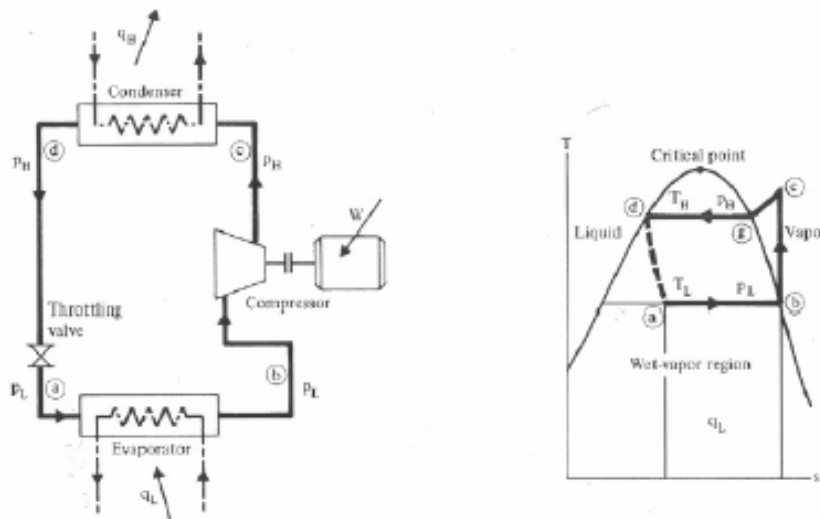


Figure 2-3: Typical one-stage dry refrigeration Cycle

We notice that:

- To be able to achieve the best match possible with the rectangular shape it is necessary to operate inside the two phase region.
- Compression is in this example performed outside the two phase region. Creating a “horn”, which is not thermodynamically advisable, is mechanically better. For this reason, this cycle is called “dry” cycle. A “wet” cycle is shown in the next figure.

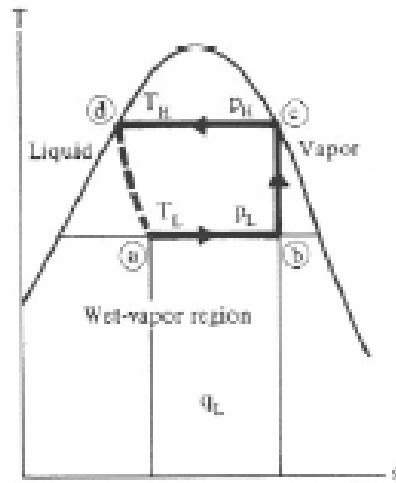


Figure 2-4: *Wet refrigeration Cycle*

- The expander has been substituted by a throttling valve. If an expander had been used the line from **d** to **a** would be a vertical line. This is also done for mechanical reasons.

The refrigeration cycles can also be represented in a P-H diagram.

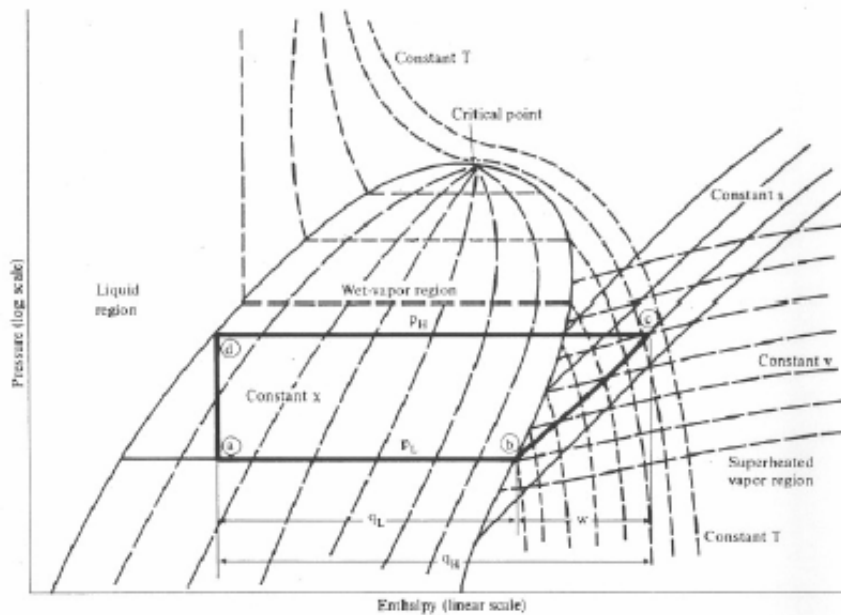
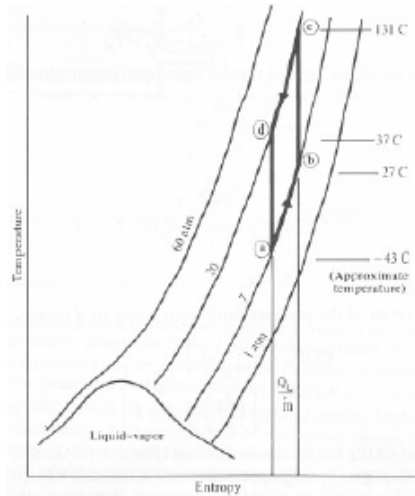


Figure 2-5: *P-H diagram representation of a dry refrigeration cycle*

Exercise 2-1:

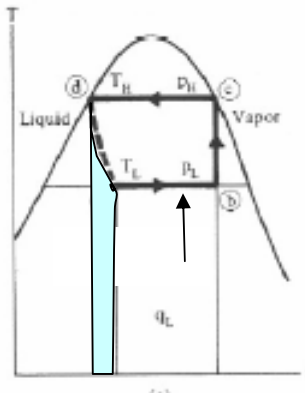
Consider the real cycle taking place outside the two phase region using a compressor and an expander. This is called, the Bryton Cycle.



Prove that this cycle is less efficient than the Carnot cycle. To do this assume constant C_p

Exercise 2-2:

Consider the real dry refrigeration cycle. Prove that the area of inside the cycle plus the shaded area (called throttling loss) is equal to the total work.



Show also that this is less efficient than the pure Carnot cycle.

Refrigerant fluid choice: We now turn our attention to the fluids. Usually, one tends to pick p_L as low as possible, but not below atmospheric pressure. Thus, the refrigerant chosen needs to have a normal boiling point compatible with the lowest temperature of the cycle (usually 10°C lower than the system one wants to cool). The higher pressure needs to be compatible with the cooling media used for q_H . If this is cooling water, then the T_H needs to be around 10°C higher than the available cooling water temperature. The next table shows the existing refrigerants. It is followed by the boiling temperature and rang of selected refrigerants.

Table 2-1: Refrigerants

ASHRAE STANDARD DESIGNATION OF REFRIGERANTS

Refrigerant number	Chemical name	Chemical formula
218	Octafluoropropane	$CF_3CF_2CF_3$
290*	Propane	$CH_3CH_2CH_3$
Cyclic organic compounds		
C316	Dichlorohexafluorocyclobutane	$C_4Cl_2F_6$
C317	Monochloroheptafluorocyclobutane	C_4ClF_7
C318	Octafluorocyclobutane	C_4F_8
Azeotropes		
500	Refrigerants 12/152a 73.8/26.2wt %‡	CCl_2F_2/CH_3CHF_2
501	Refrigerants 22/12 75/25wt %	$CHClF_2/CCl_2F_2$
502	Refrigerants 22/115 48.8/51.2wt %	$CHClF_2/CClF_2CF_3$
Miscellaneous organic compounds		
Hydrocarbons		
50	Methane	CH_4
170	Ethane	CH_3CH_3
290	Propane	$CH_3CH_2CH_3$
600	Butane	$CH_3CH_2CH_2CH_3$
601	Isobutane	$CH(CH_3)_3$
1150†	Ethylene	$CH_2=CH_2$
1270†	Propylene	$CH_3CH=CH_2$
Oxygen compounds		
610	Ethyl ether	$C_2H_5OC_2H_5$
611	Methyl formate	$HCOOCH_3$
Nitrogen compounds		
630	Methyl amine	CH_3NH_2
631	Ethyl amine	$C_2H_5NH_2$
Inorganic compounds (Cryogenic)		
702	Hydrogen (normal and <i>para</i>)	H_2
704	Helium	He
720	Neon	Ne
728	Nitrogen	N
729	Air	$0.21O_2, 0.78N_2, 0.01A$
732	Oxygen	O_2
740	Argon	A

* Methane, ethane, and propane appear in the halocarbon section in their proper numerical order, but these compounds are not halocarbons.

† Ethylene and propylene appear in the hydrocarbon section to indicate that these compounds are hydrocarbons, but are properly identified in the section unsaturated organic compounds.

‡ Carrier Corporation Document 2-D-127, p. 1.

Table 2-1: Refrigerants Continued)

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720	Neon	Ne
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Table 2-1: Refrigerants Continued)

ASHRAE STANDARD DESIGNATION OF REFRIGERANTS

Refrigerant number	Chemical name	Chemical formula
Inorganic compounds (noncryogenic)		
717	Ammonia	NH ₃
718	Water	H ₂ O
744	Carbon dioxide	CO ₂
744A	Nitrous oxide	N ₂ O
764	Sulfur dioxide	SO ₂
Unsaturated organic compounds		
1112a	Dichlorodifluoroethylene	CCl ₂ =CF ₂
1113	Monochlorotrifluoroethylene	CClF=CF ₂
1114	Tetrafluoroethylene	CF ₂ =CF ₂
1120	Trichloroethylene	CHCl=CCl ₂
1130	Dichloroethylene	CHCl=CHCl
1132a	Vinylidene fluoride	CH ₂ =CF ₂
1140	Vinyl chloride	CH ₂ =CHCl
1141	Vinyl fluoride	CH ₂ =CHF
1150	Ethylene	CH ₂ =CH ₂
1270	Propylene	CH ₃ CH=CH ₂

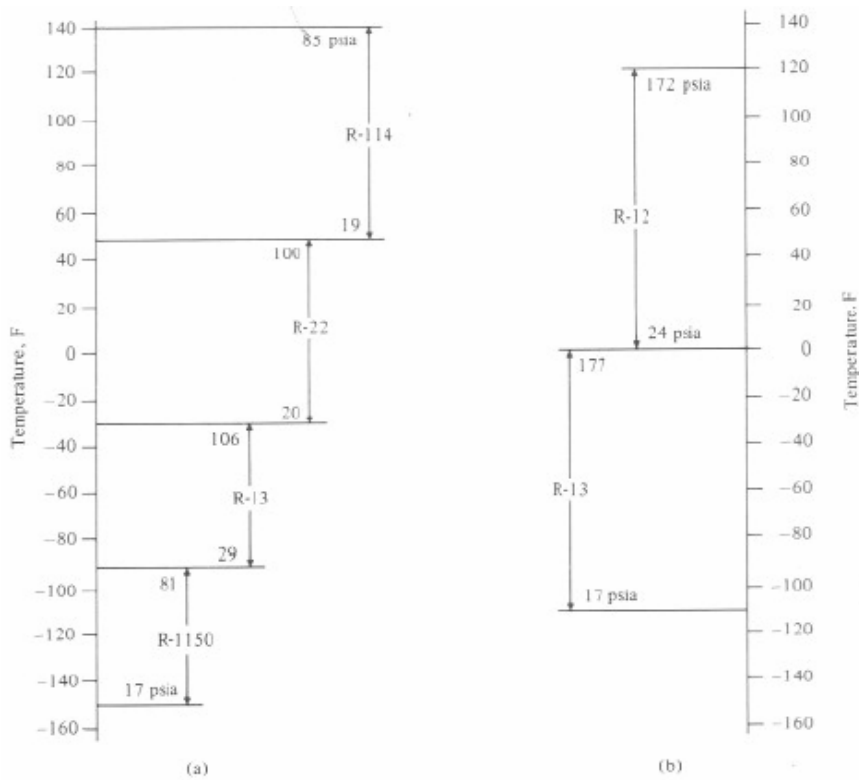
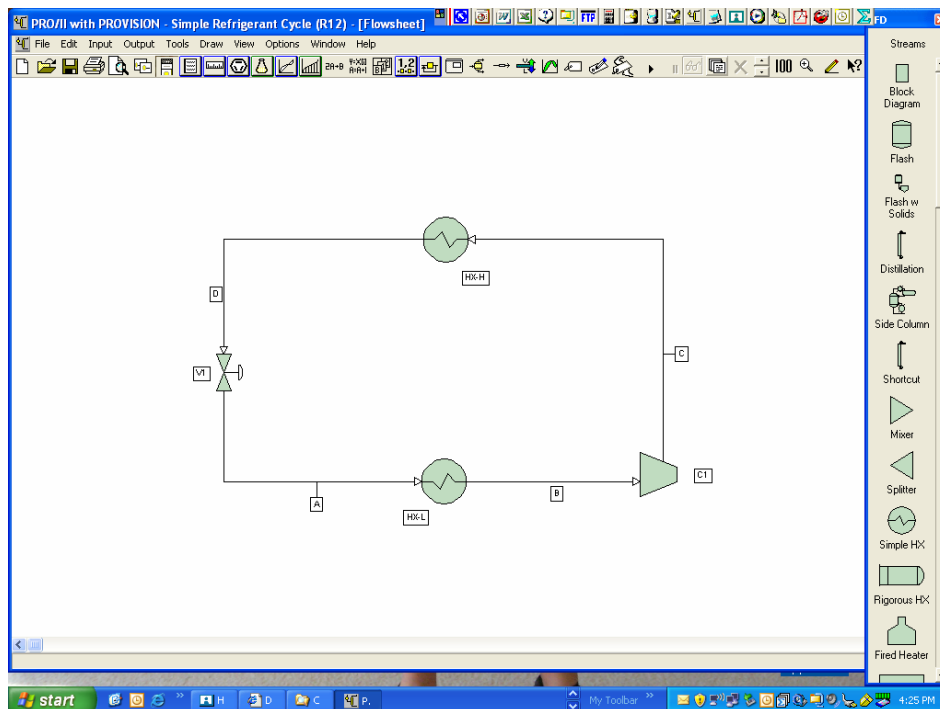


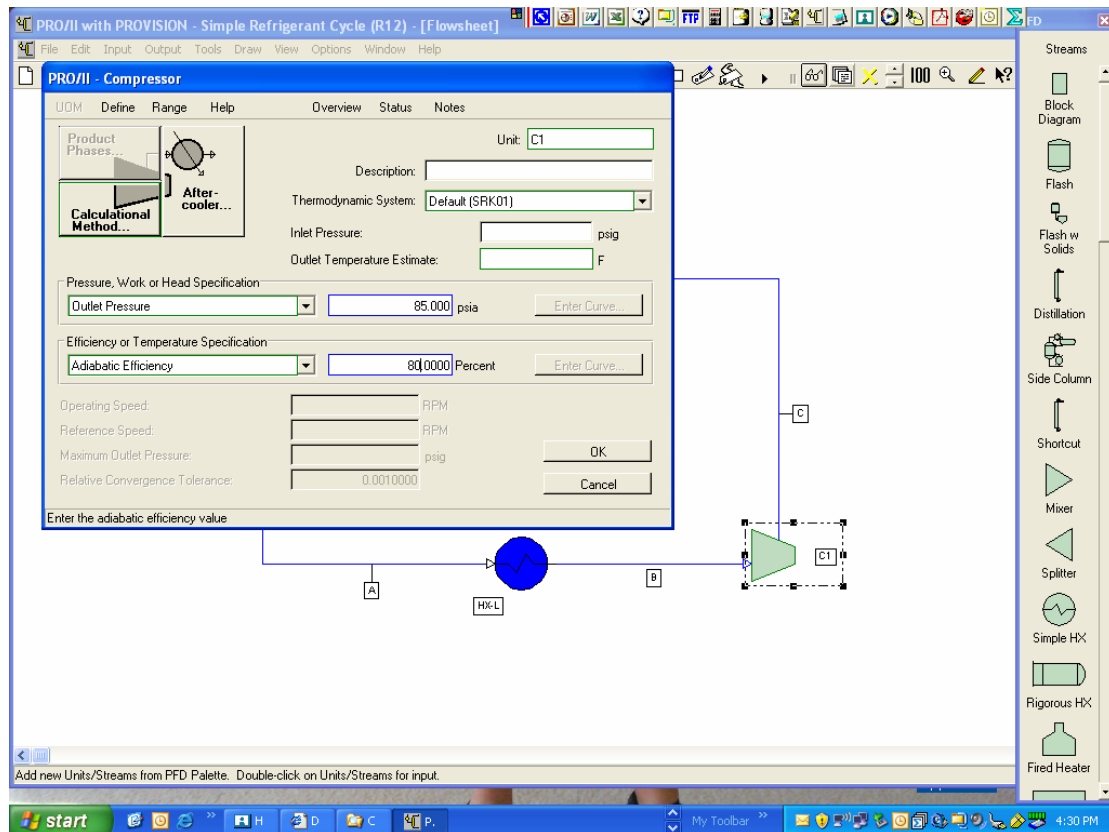
Figure 2-6: Temperature Ranges of Refrigerants

We now turn to Pro II to show how a refrigerant cycle is built. We start with entering the cycle as follows:

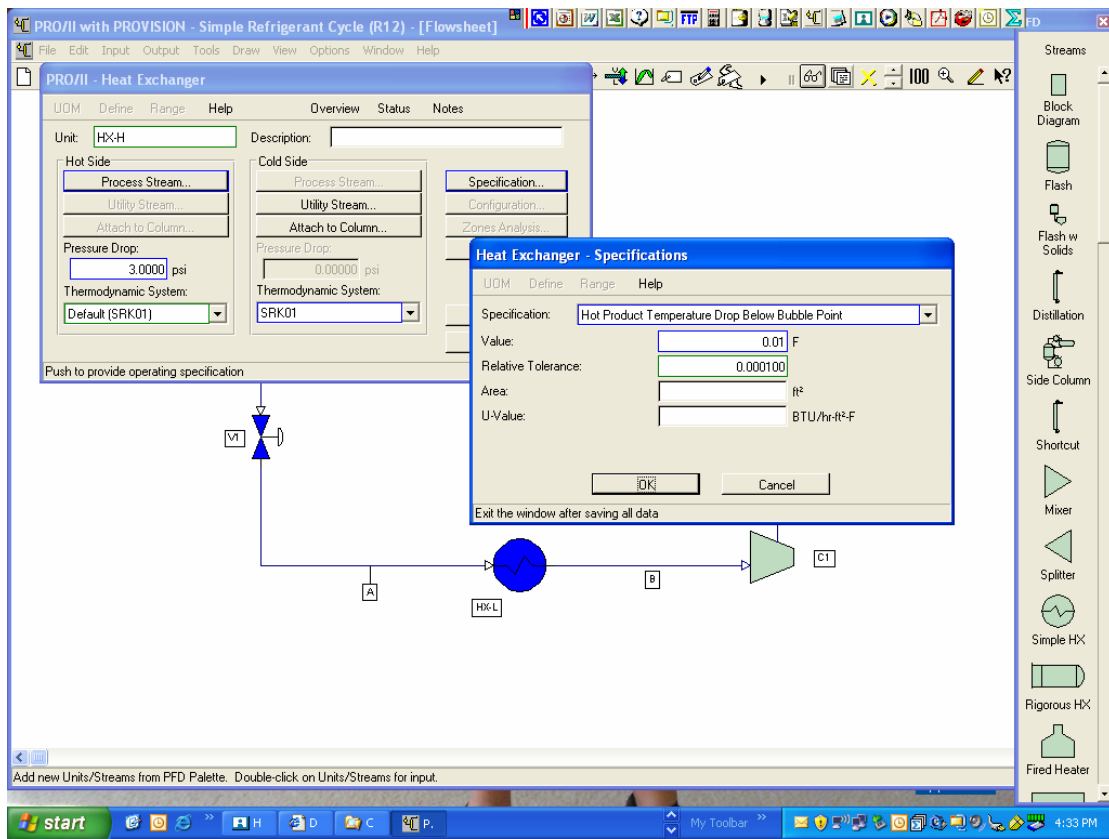


We pick R12, which will allow us to cool down anything to

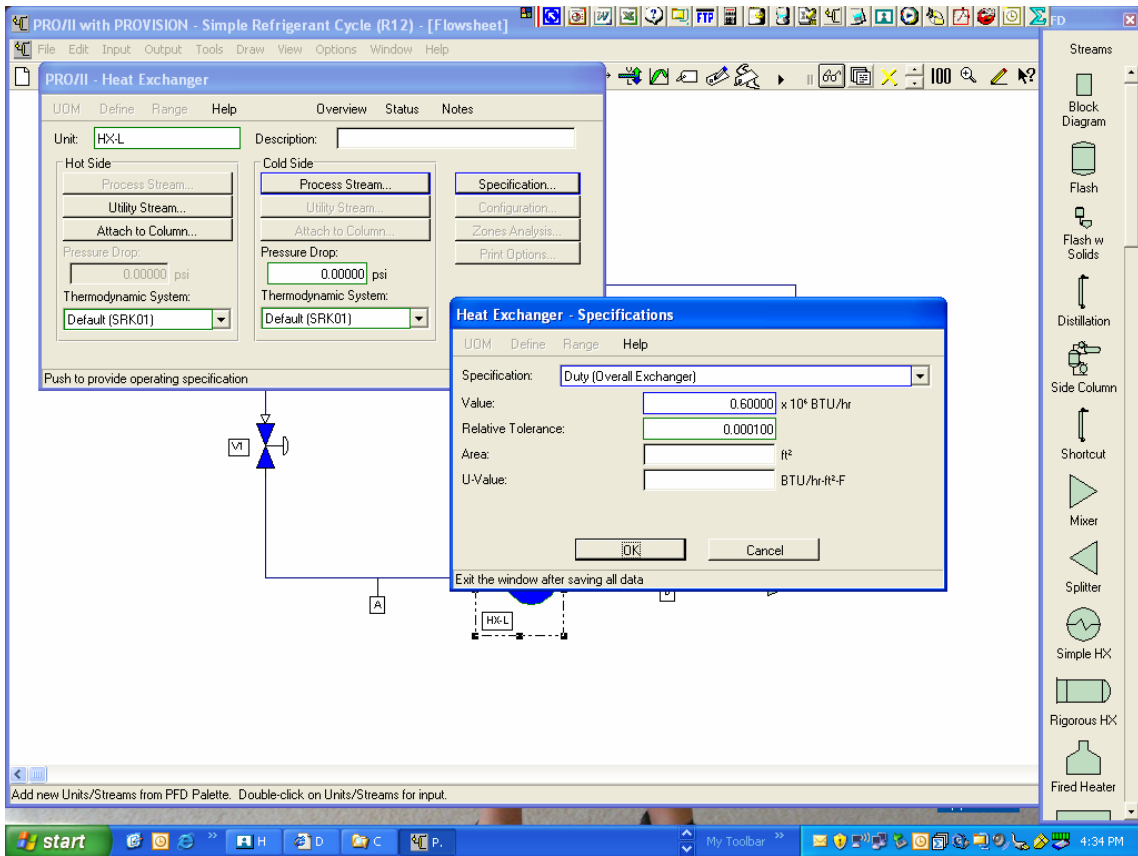
Next we define the outlet pressure of the compressor. This needs to be such that stream C (after the cooler) is higher than 60 °F. To start we choose around 85 psia.



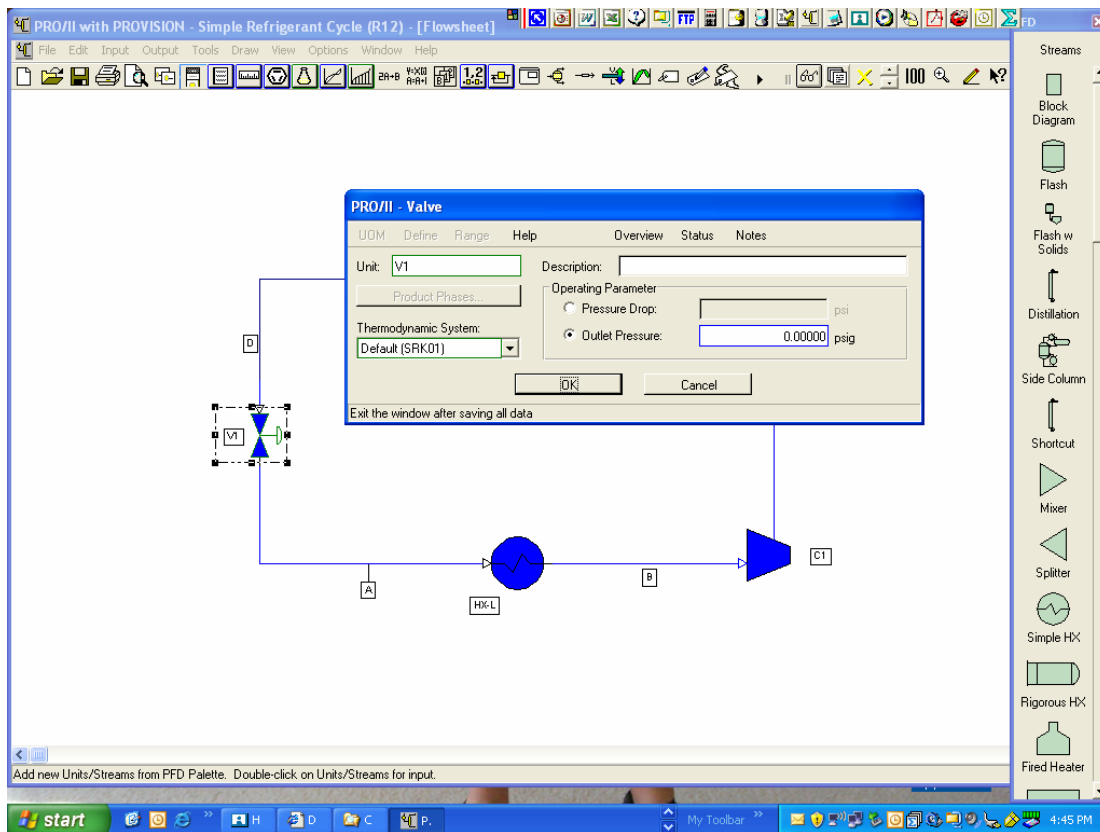
Next we define the top heat exchanger, by specifying an outlet temperature slightly below the bubble point.



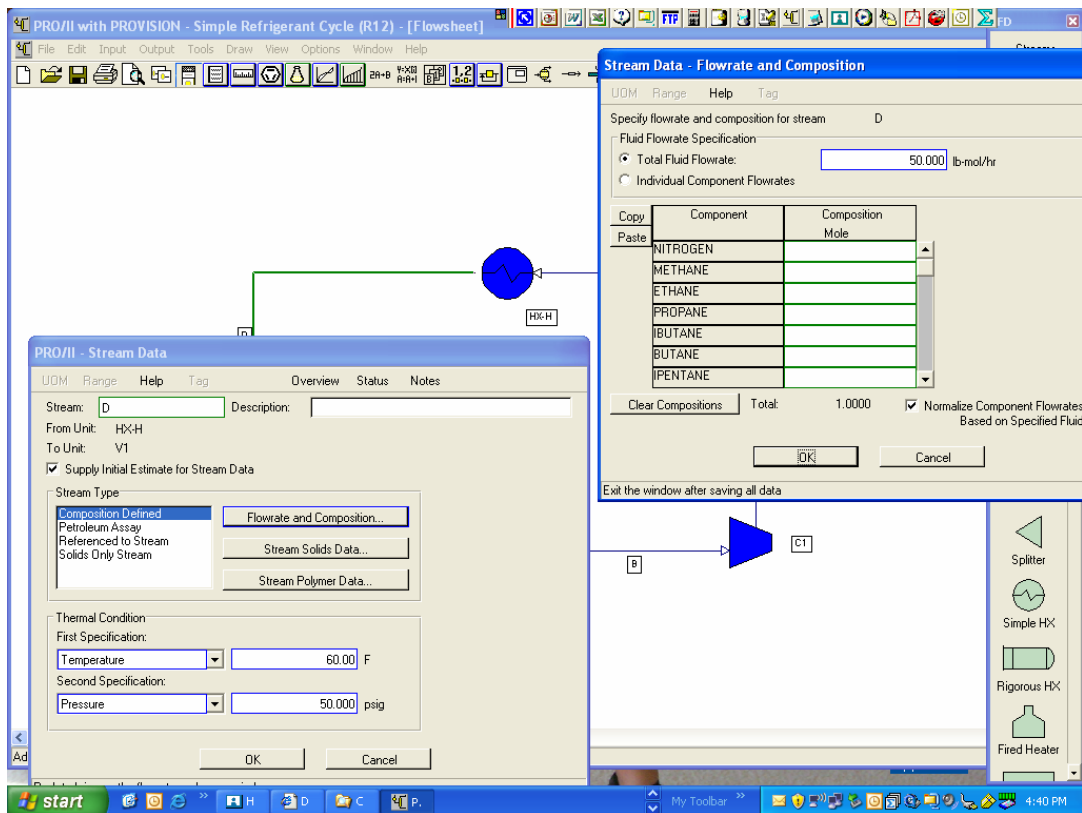
We continue by specifying the duty of the bottom exchanger. This is customary because this is the targeted design goal of the cycle.



We enter the outlet pressure of the valve (atmospheric).

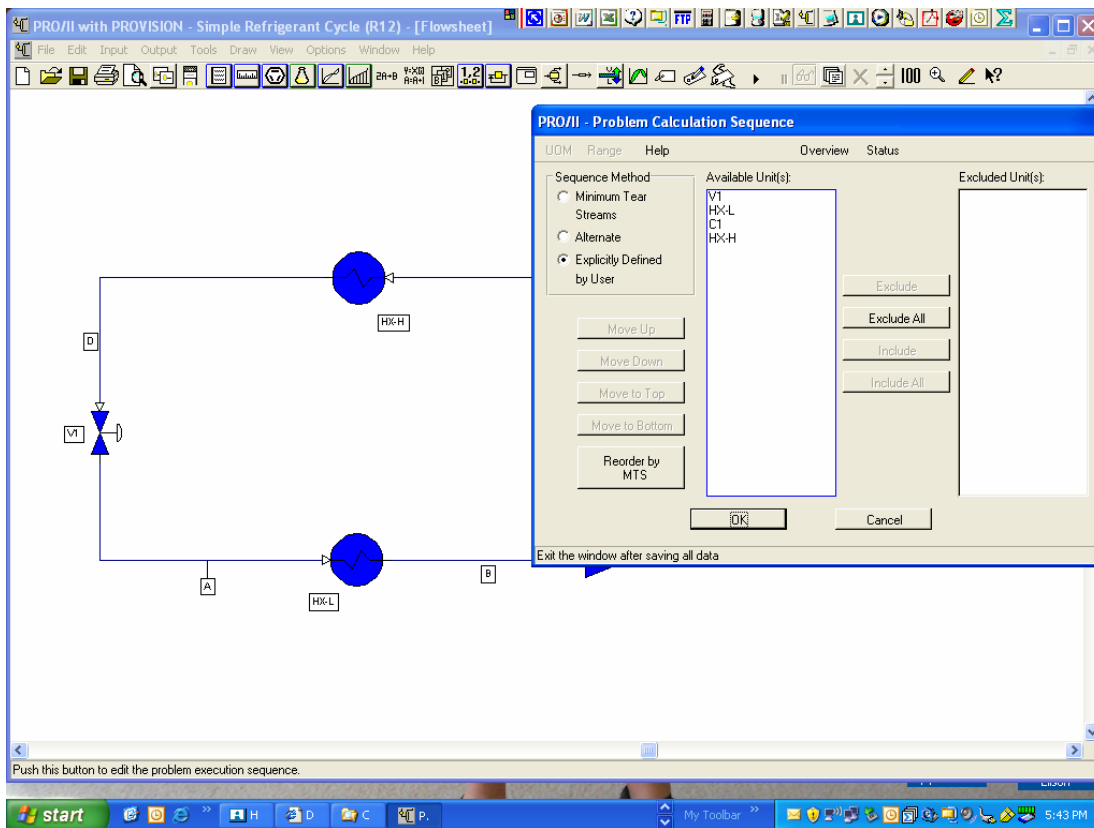


We also realize that this flowsheet does not have input or output streams. Thus, to start the simulation, one needs to give an initial value to a stream. We chose stream D, and initialize with a flowrate that is guessed.



If the flowrate chosen is too high, then the inlet of the compressor will be two phase and this is not advisable. If the flowrate is too low, the cycle will lose efficiency (the “horn” will get larger).

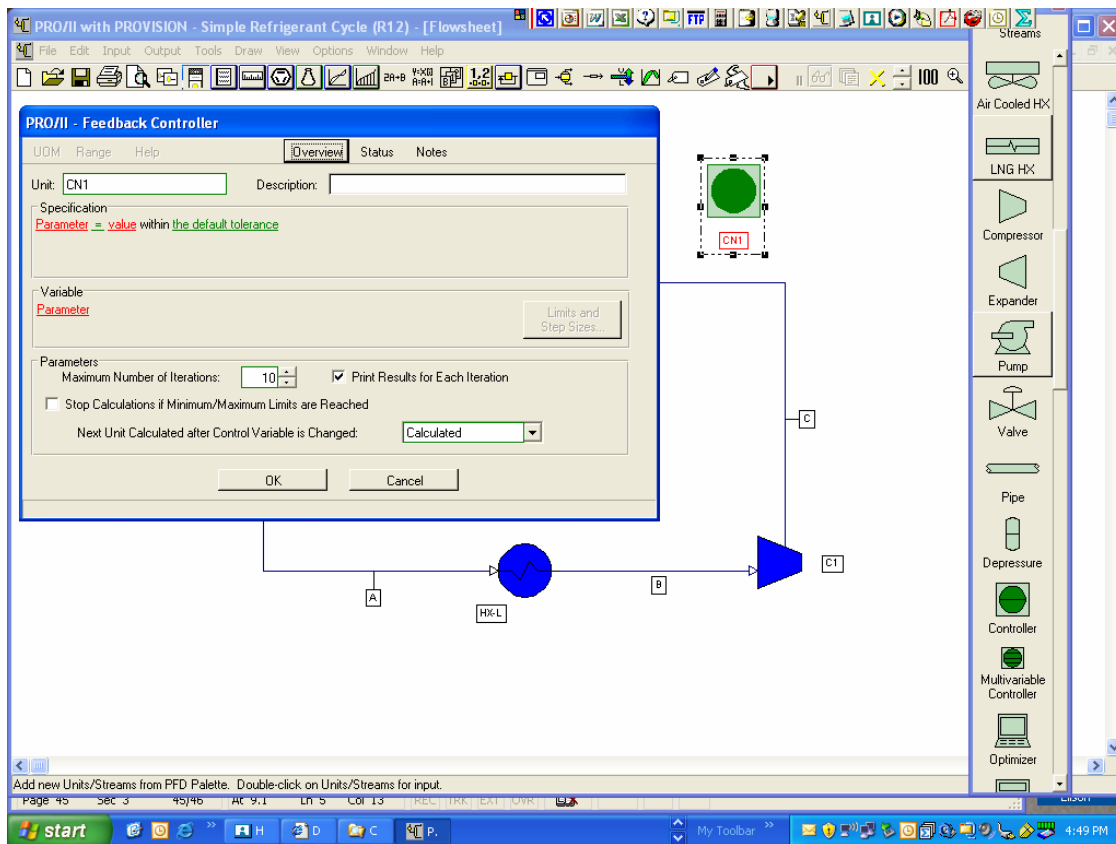
Warning: Pro II may not realize internally that it needs to solve the unit that the initialized stream feeds to and try to continue until it reaches convergence in the loop but it will lose the input data. To avoid problems we specify the order in which we want the flowsheet to solve by clicking in the unit sequence button.



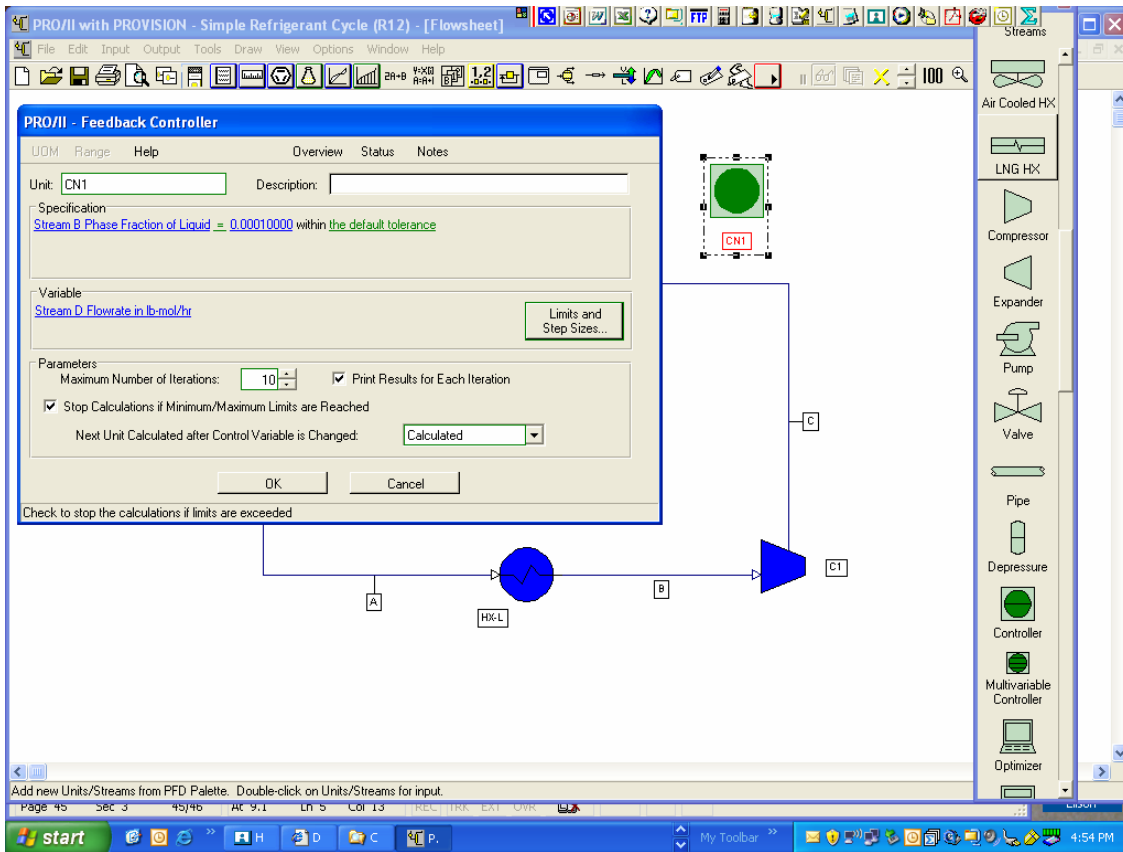
Exercise 2-3:

Construct the simulation above described and determine the right flowrate in the cycle. Determine all temperatures and obtain the COP. Compare it with a Carnot Cycle.

The above exercise can be done automatically using a “controller”, which is a type of “spec and vary” equivalent to “Goal Seek” in Excel. Once the controller is picked, double clicking on it reveals the menu.



Thus, we choose to have the inlet to the compressor just slightly above dew point (specification) and we vary the flowrate, just as we did by hand. It is, however, easier to specify a very low liquid fraction. Make sure the starting point is close to the right value. Sometimes the controller has a hard time converging.



We now turn our attention to a variant where liquid is being sub-cooled:

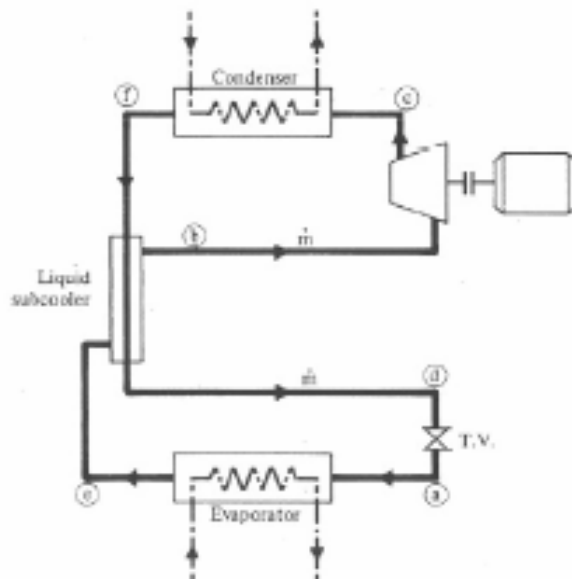


Figure 2-7: Liquid sub-cooling in a refrigeration cycle.

The corresponding TS and P-H diagrams are shown in the next figure. Since we are using the vapor (at the lower pressure) to sub-cool, there is a gain in q_L at the expense of a slight increase in work. Whether there is a gain, it depends on the fluid and the sub-cooled temperature choice.

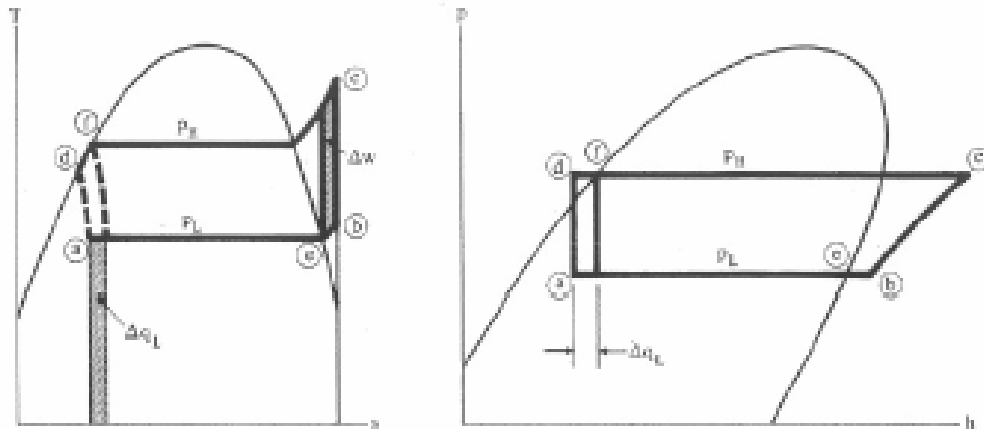


Figure 2-8: TS and P-H diagram for liquid sub-cooling in a refrigeration cycle.

Exercise 2-4:

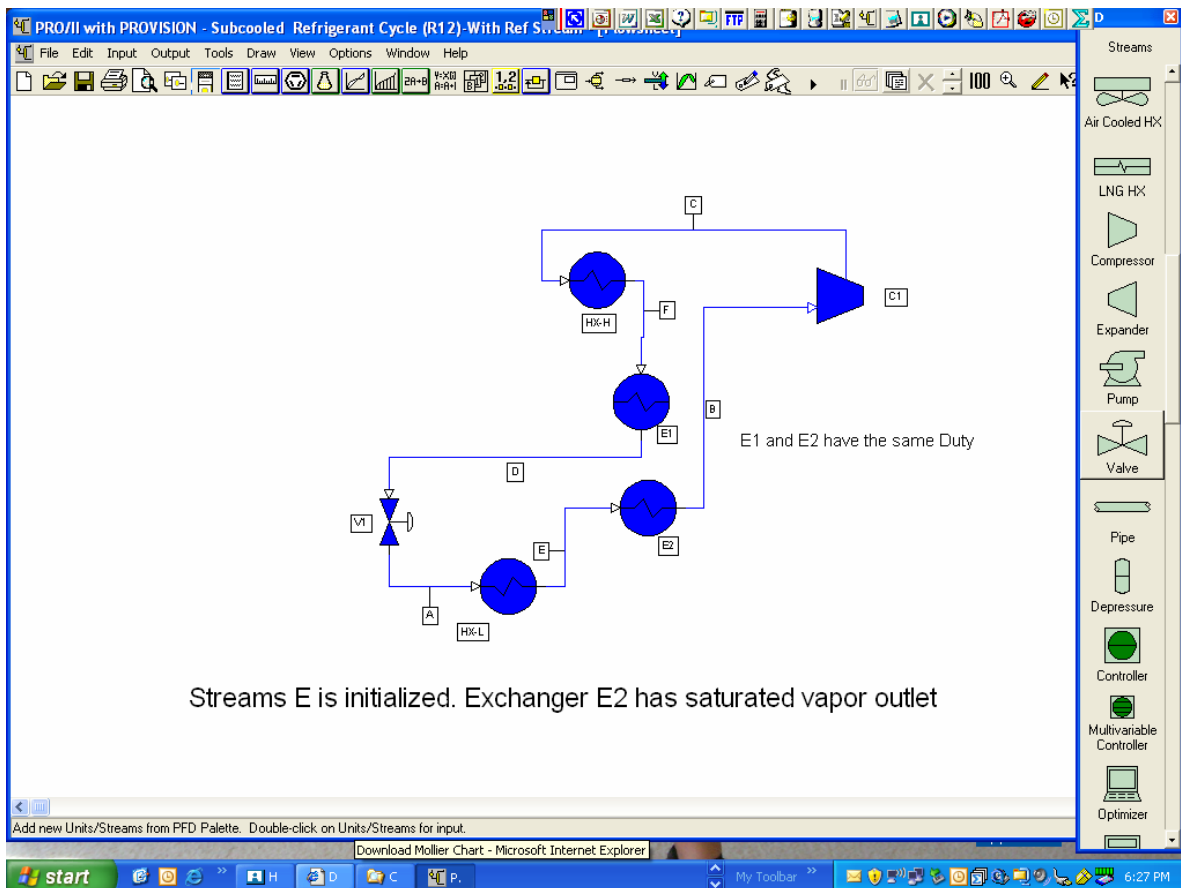
Implement the sub-cooling cycle in Pro II and report the new COP. Compare it with the dry cycle without sub-cooling and the Carnot cycle. Use streams E and F as initial values. The flowsheet has two loops. Once you change the flowrate in BOTH streams, reinitialize the flowsheet (Pro II is a little tricky when recycles are present). Set the sub-cooling to 5°F. Also make sure the sequence is correct. Finally, do not attempt to use a controller here. It will not work.

to loops. Needs two initial streams (E and F)- Update both

Exchanger E1 is set to reduce the temperature by a set amount

- Can one make pints **b** and **e** coincide, i.e. use the cycle without compressing superheated vapor?
- Compare COP for different sub-coolings and flowrates. What about capital costs?

The instructor will also show you another way of implementing this simulation and having only one initial stream.



One cannot put a controller here either. The goal now is to determine sub-cooling **AND** flowrate such that the COP is the largest possible.

Other systems have been proposed, like the sub-cooler and desuperheater combination

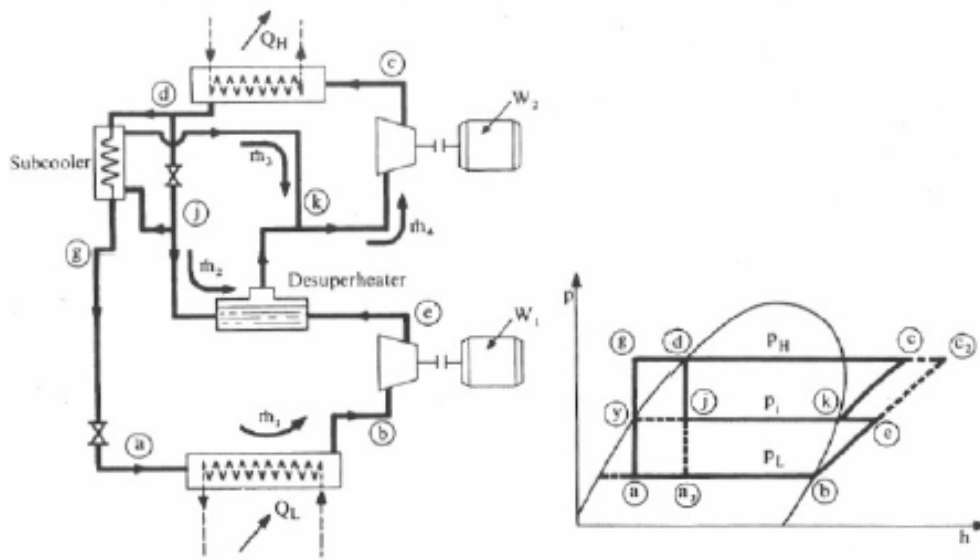


Figure 2-9: One Stage subcooler-desuperheater refrigeration cycle.

Consider now a multistage situation in which two cycles are combined. One reason that multistage cycles are used is because one cycle may require more than one compressor as the compression ratio for one may get to be too high. Instead of putting compressors in series, one could split the work among two compressors and actually increase the COP.

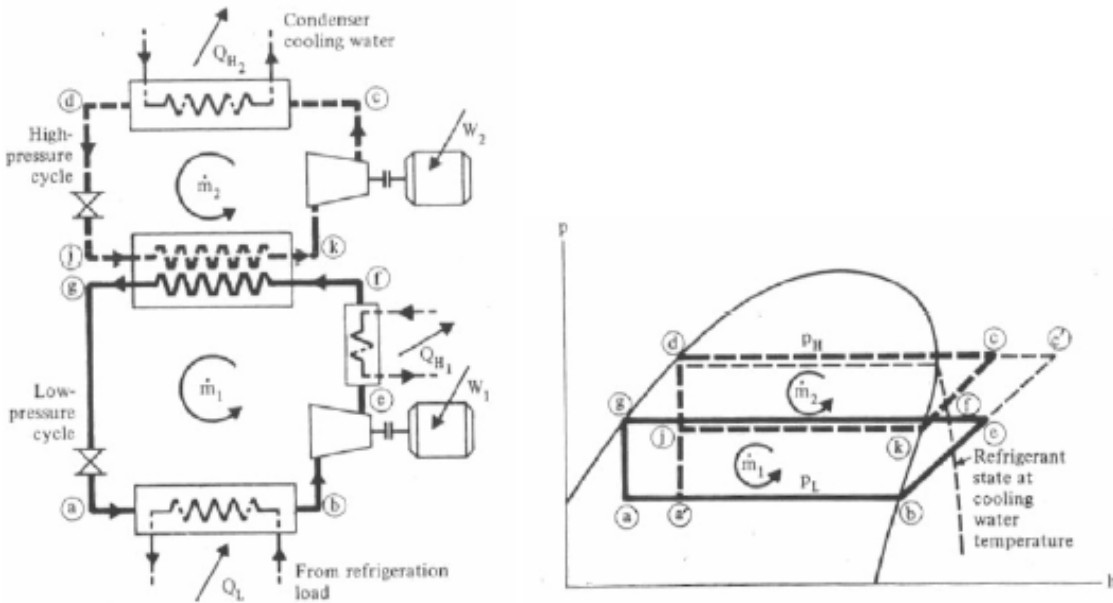


Figure 2-10: Two Stage refrigeration cycle.

Exercise 2-5:

Show, using a T-S diagram why the multistage arrangement increases the COP.

Exercise 2-6:

Pick an intermediate temperature for the cycle of Exercise 2-3 and build a two stage system. Compare COP.

Other systems have been proposed, like the open flash cooler. This actually requires one fluid, but eliminates the need for the upper cycle to have a lower temperature for proper heat exchange, thus reducing work. Besides, a flash tank is cheaper than a heat exchanger.

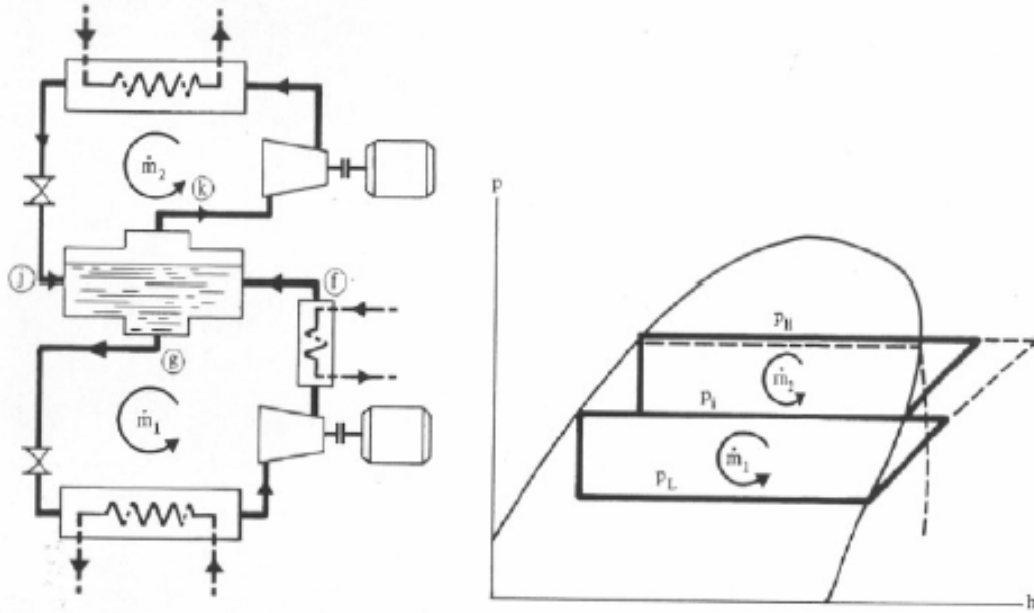


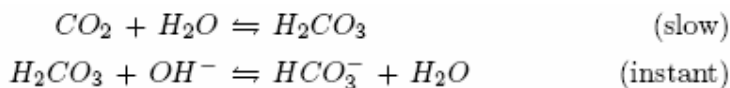
Figure 2-11: Open flash two stage refrigeration cycle.

LNG PRODUCTION

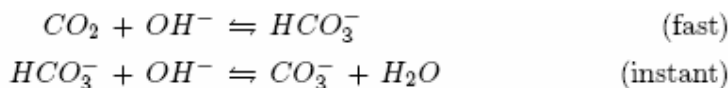
Before natural gas can be liquefied, it must be treated. Treatment involves the removal of CO₂, condensate, organic sulfur compounds, and Hg. This is done to avoid blockage in the liquefaction process, prevent damage done to the equipments, and to meet the heat content standard of the natural gas which differs from country to the other. The pretreatment process consists of four main stages. First, CO₂ and H₂S removal stage which is constructed to assure that CO₂ would not exceed 50 ppm in the natural gas feed. If the composition of CO₂ exceeded that limit it would freeze in the liquefaction process pipelines.

There are two available methods to remove CO₂ from the natural gas. The first method is using sulfinol, which used to be one of the famous methods for gas CO₂ removal in most industrial applications but it started to vanish and few pretreatment plants use sulfinol any more. The reason is that sulfinol does not work well with rich natural gas (rich with heavy hydrocarbons) because it tends to attract or attach to heavy hydrocarbons and then it drags the heavies to the sulfinol pump or circulation which leads to allowing the heavy hydrocarbons to vent into the air. That usually leads to a decrease in the quality and heat content of the natural gas in the feed and according to the new EPA (Environmental Protection Agency) rules heavy hydrocarbons can not be vented to the atmosphere because it would lead to an increase in the air pollution.

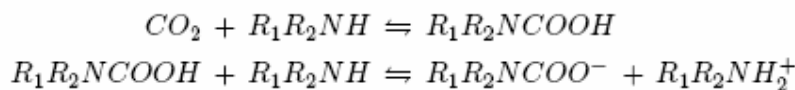
CO₂ dissolves in water as any gas, but it further reacts to form carbonic acid:



At high PH (above 10), the following chemistry takes place:



But the amount dissolved is not large enough. Therefore another method to remove CO₂ is using Amines. The chemistry of this process is:



Since DEA alone cannot remove CO₂ to a ppm level, it is activated by injecting a chemical called Piperazine which activates the DEA to MDEA (Methyl Diethyl Amine).

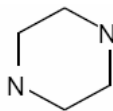


Figure 2-12: Piperazine

MDEA is also used for this pretreatment stage versus sulfinol because the MDEA process is cheaper to install and it has less utility since it requires less rate of solvent circulation compared to sulfinol.

The second stage is dehydration. Water is removed from the natural gas also to avoid freezing in the pipeline of the liquefaction process. The natural gas feed should be completely dry, even from the smallest traces of water molecules ($<0.01\text{Microgram}/\text{m}^3$), before entering the heavy duty cooling section of the liquefaction process. TEG (Triethylene Glycol) is the primary solvent used in gas processing industry to dehydrate gases. Dry TEG contacts the moist natural gas and absorbs the water from it in a contactor tower. The tower contains a structured packing bed to maximize the mixing between the gas and TEG and to increase the contact time between the two substances. The TEG and water mixture is then sent to a TEG recycling system where TEG is separated from water by filtering then heating. The recycled TEG is then sent back to the contactor tower. Although TEG removes H_2O significantly from the natural gas, small amount of water traces still escape this process; so to insure that these traces do not accompany the natural gas feed, molecular sieves are used to serve this purpose. In average, two sieves are needed for every train. Despite all of this, in some processes H_2O in a molecular level still escapes with the natural gas in the feed. A third safety step is taken in the liquefaction process where molecules of water, which accompany the natural gas in the feed, are condensed and flashed in the stage of natural gas pre-cooling.

The third stage is the Hg removal. Hg causes corrosion in the expensive Aluminum LNG heat exchangers used in the liquefaction process. For example, $10\text{ ng}/\text{m}^3$ (nano gram per m^3) are enough to cause a catastrophe. The activated bed filter that is used in the Hg filtration is inexpensive and it is replaced on an average of once every four years.

The fourth and last step is the installation of a Duster in the Pretreatment process outlet to insure that the natural gas feed is free from small solid particles which might cause a clog in the pipes of the liquefaction process or damage the heat exchangers. The figure below shows the overall process flow.

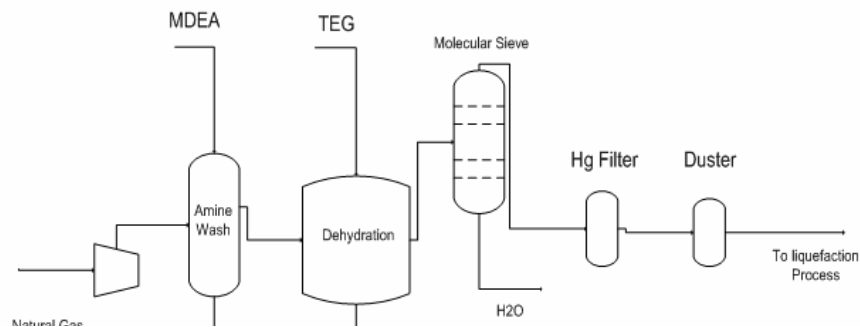


Figure 2-13: *Pretreatment schematics*

After the natural gas has been pretreated and contaminants are removed, it is sent to a liquefaction process where the natural gas is pre-cooled and water traces and heavy hydrocarbons (C_3 & C_4) are knocked off the NG; then, the NG is transformed from a gas phase to a liquid phase and sub-cooled to level where the LNG could be stored at atmospheric pressure. The next figure shows the steps of natural gas liquefaction:

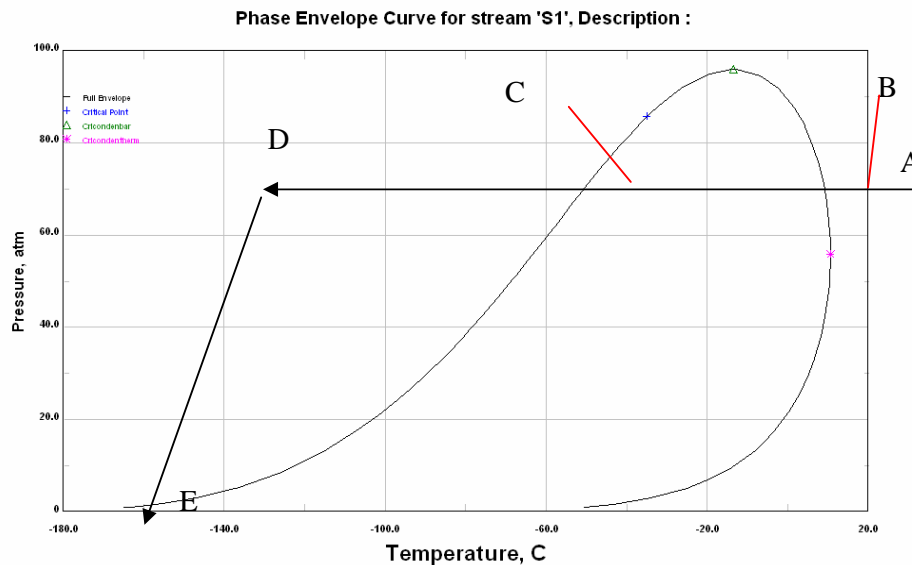


Figure 2-14: Typical Gas Phase envelope

The natural gas usually enters the liquefaction process from pretreatment at about 100 F (above point A) and it is cooled down to about 60 F by either air or water coolers. Propane is usually used to cool the NG to about 40 F and this is where most of the water traces is condensed and knocked out of the NG by flashing. Then the NG is cooled down to its dew point (B) and further to its bubble point (C) and it is sub-cooled to a certain temperature (point D) after which it is depressurized to atmospheric pressure through a valve. The final temperature is about -260 F (point E).

Exercise 2-7:

Consider a south American gas of the following composition: 91.89%, 5.6% ethane, 0.96% propane, 0.02 % n-butane, 0.03% i-butane, 0.1% pentanes, 1.4 % nitrogen. Assume it is available at 800 psia and 77.7 °F. Determine the final temperatures (point D) necessary to achieve a final temperature of -265 °F.

Exercise 2-8:

Gas liquefaction is performed at high pressures (to reduce equipment size). Consider the gas of the previous exercise. Set up a simulation in which the gas is depressurized first to atmospheric pressure and proceed to liquefy it to the target temperature. Compare the duties needed.

One very useful tool in gas liquefaction is the cooling curve. Such curve is shown in the next figure for a capacity of 4.5 mtpa.

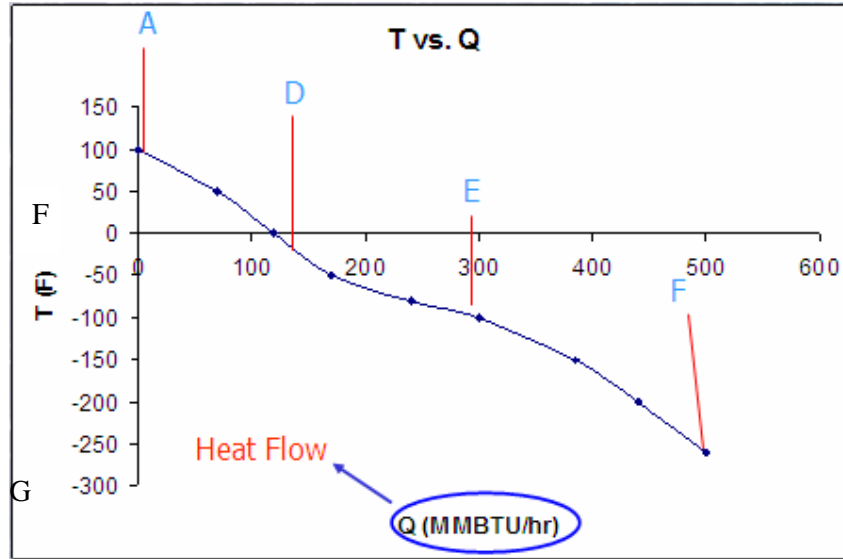


Figure 2-15: LNG cooling curve

From this curve one can infer what is the minimum work needed in the process. Consider a small heat differential dQ at a given temperature. If one runs a Carnot cycle between this temperature and the ambient temperature, one obtains:

$$dW = dQ \left(\frac{T_{Amb} - T_{low}}{T_{Amb}} \right) \quad (2-2)$$

Now an area differential dA is given by $dA = dQ(T_{Amb} - T_{low})$ (see next figure). Therefore, integrating we obtain $W = A/T_{Amb}$. Thus, the bigger the area between the starting temperature (T_{Amb}) and the curve, the more work the system has to perform.

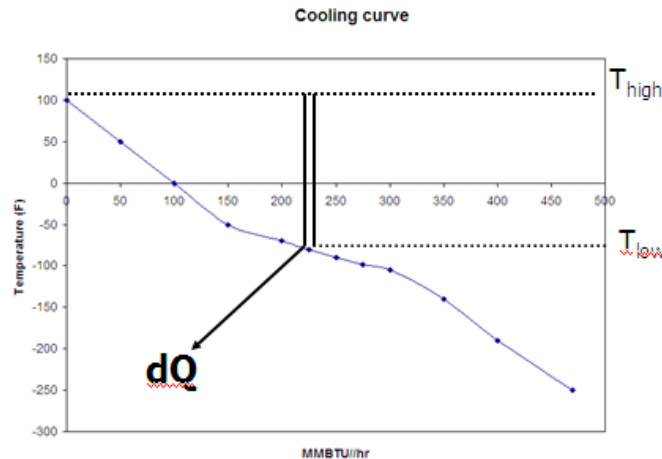


Figure 2-16: LNG cooling curve and work needed

However, real processes cannot be built to exactly follow the cooling curve, and therefore, need to have temperatures below the curve. Thus, the closer the refrigeration heating curve to the LNG cooling curve, the more efficient the process is. This is shown in the next figure.

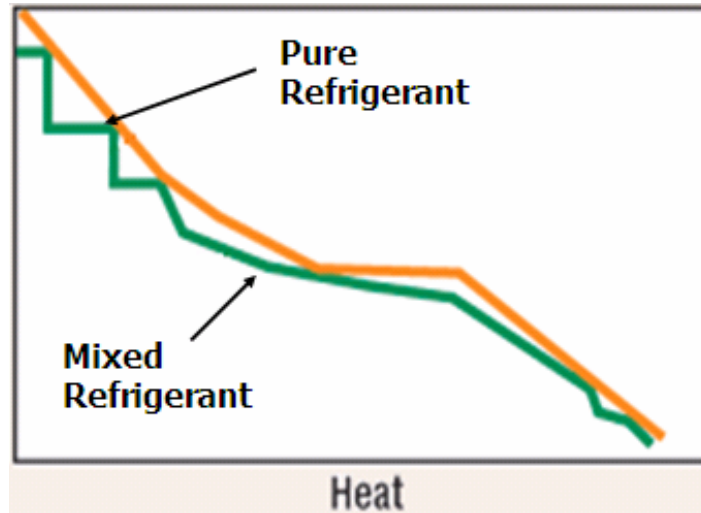


Figure 2-17: Refrigerant vs. LNG cooling curve

The area between the LNG cooling curve (orange line above) and the refrigeration heating curve (green line) represents the amount of heat lost during the liquefaction process. The area above the refrigeration line represents the amount of work done by the system and the closer the lines are to each other the less work the system has to do. The figure above corresponds to the MR process, in which a mixed refrigerant is used. The pure refrigerant-based Phillips cascade is shown below.

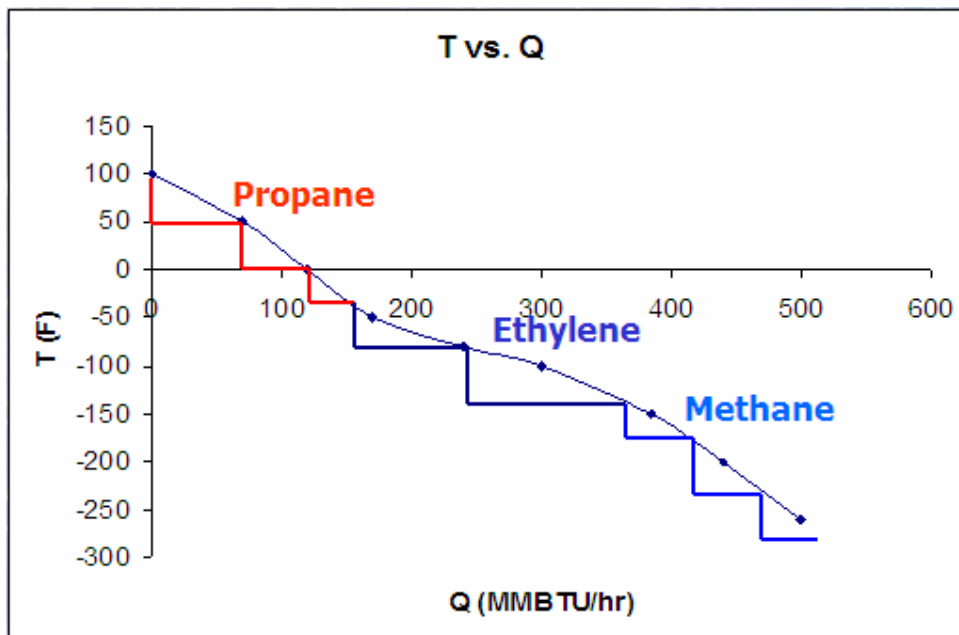


Figure 2-18: Phillips Cascade LNG Cooling Curve

We now show why the above system is more efficient when each refrigerant helps the next refrigerants.

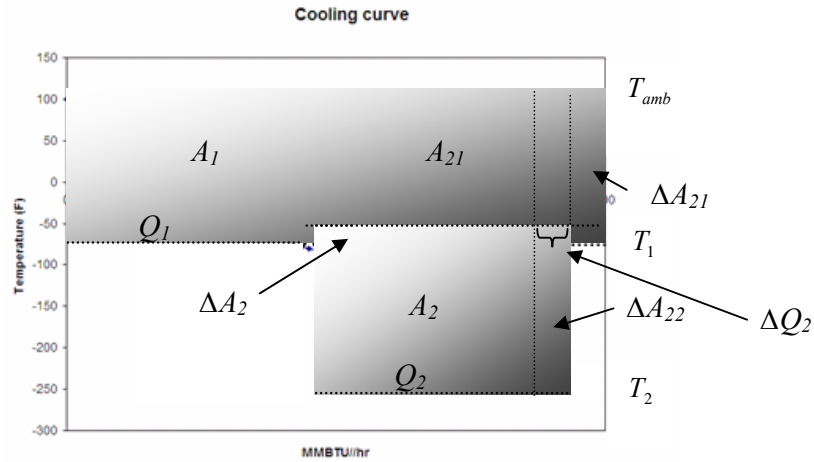


Figure 2-19: Work needed for staged cycles

$$W_2 = Q_2 \frac{(T_1 + \Delta T_{\min} - T_2)}{T_1 + \Delta T_{\min}} + \frac{\Delta A_{22}}{T_1 + \Delta T_{\min}} = \frac{A_2 + \Delta A_2 + \Delta A_{22}}{T_1 + \Delta T_{\min}} \quad (2-3)$$

$$W_1 = (Q_1 + Q_2 + \Delta Q_2) \frac{(T_1 - T_{amb})}{T_{amb}} + \frac{\Delta A_{21}}{T_{amb}} = \frac{A_1 + A_{21} + \Delta A_2 + \Delta A_{21}}{T_{amb}} \quad (2-4)$$

The additional work indicated by the areas ΔA_{21} and ΔA_{22} are the result of the cycles inefficiencies (they are not Carnot cycles). The area ΔA_2 is counted twice. *In turn, both cycles are independent using the ambient temperature as the highest part.*

$$W_1^+ = Q_1 \frac{(T_1 - T_{amb})}{T_{amb}} + \Delta A_{11}^+ = \frac{A_1}{T_{amb}} + \frac{\Delta A_1^+}{T_{amb}} \quad (2-5)$$

$$W_2^+ = Q_2 \frac{(T_{amb} - T_2)}{T_{amb}} + \Delta A_2^+ = \frac{A_2 + A_{21}}{T_{amb}} + \frac{\Delta A_2^+}{T_{amb}} \quad (2-6)$$

The difference is then

$$\Delta W = -A_2 \left[\frac{1}{T_1 + \Delta T_{\min}} - \frac{1}{T_{amb}} \right] - \frac{[\Delta A_2 + \Delta A_{22}]}{T_1 + \Delta T_{\min}} + \frac{[\Delta A_1^+ + \Delta A_2^+ - \Delta A_{21} - \Delta A_2]}{T_{amb}} \quad (2-7)$$

which is negative.

Exercise 2-9:

- a) Show that $\Delta W < 0$
- b) Show using simulations what would be the difference in energy. Make an estimate of the difference in capital involved.

Overview of liquefaction processes

APCI

The APCI (Air Products and Chemicals Inc.) process, also called Propane Pre-cooled Mixed Refrigerant Process (PPMR) currently holds 88% of the liquefaction plants on the market. They currently produce 107.5 mtpa of LNG with 53 trains in operation. Their technology uses a three stage refrigerant cooling powered by two 85 MW Frame 7 compressors. The first stage is a pre- propane cooling stage that cools the mixed refrigerant and inlet treated gas to around – 35 F. The next two cooling stages, held in a heat exchanger tower, use mixed refrigerants (MR) of about 27% methane, 50% ethane, 20% propane, 2% Butane, and 1% nitrogen to cool and condense the natural gas. The flowsheet is shown in the next figure:

Propane chills the gas during pre-treatment. A flash tank is used to separate the mixed refrigerant to a heavy coolant (bottom/red stream) and a lighter coolant (top/green stream). The heavy coolant (propane, butane, and some ethane) takes care of the cooling in the warm bundle (bottom part) of the heat exchanger tower which cools down the natural gas stream (blue stream) to about -50 °C and then the light coolant is sprayed back on the streams of the warm bundle via valves to insure that the refrigerant cooled the natural gas stream to the maximum point possible for this mix. The light coolant (methane, ethane and nitrogen) cools down the natural gas stream to -160 °C in the cold bundle and this temperature is the point where natural gas is converted to LNG. Similarly to the warm bundle, the light coolant is then sprayed on the streams in the cold bundle of the heat exchanger tower and then mixed with the sprayed heavy coolant in the warm bundle and then compressed; that is the end of the cooling cycle. The liquid coming out of the top of the heat exchanger tower is then separated via flash tank to LNG (bottom stream) and light fuel (top stream) which is later sent for fractionation in another sector.

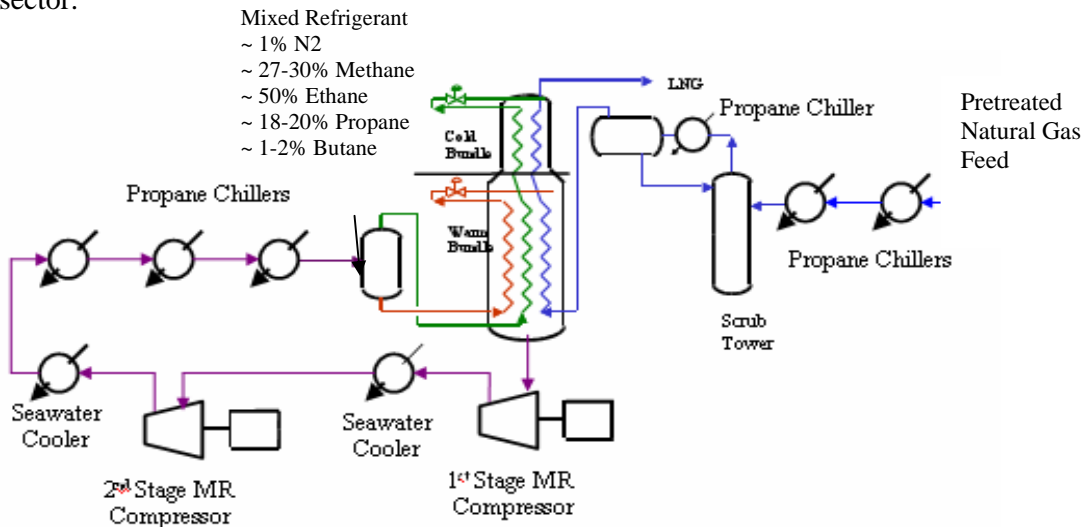


Figure 2-20: APCI process schematics

The overall process requires around 200,000 hp out of the three Frame 7 compressors and the heat exchangers in the tower are Spiral Wound Heat Exchangers (SWHE). A SWH heat exchanger is more flexible and easier to control and it could handle heavy and efficient heat exchanging process, like the liquefaction process, via one big heat exchanger. The MCHE

consists of two or three tube bundles arranged in a vertical shell with the process gas and refrigerants entering the tubes at the bottom which then flow upward under pressure. The overall maximum is 5.0 MMmtpa but it can not go less than 4 MMmtpa.

APCI has also invented their X technology. APCI-X uses nitrogen for the third refrigerant loop instead of MR to cool down the natural gas. The addition of nitrogen to the loop takes some of the compression work off of the propane pre-cooling compressor allowing for increased production. However, while APCI plans on implementing the new technology, production of LNG by APCI-X is not expected for a few years.

While APCI controls the majority of liquefaction plants in operation today, their older designs have limitations. As stated earlier, APCI uses Frame 7 compressors with a rating of about 85 MW. Being so large, Frame 7 compressors only have one vendor that makes them (GE). Additionally, the use of large compressors raises reliability concerns. If one compressor goes down, production halts until the problem is fixed. Another disadvantage of having a large compressor is that it is only sufficient for large flow and it can not handle low flow rates (less than 1000 BCFD). The heat exchanger tower, SWHE are manufactured only by Linde. If any clog or freezing occurs in one of the heat exchanging streams then the whole process is stopped until the problem is fixed.

Exercise 2-10:

Make a Q-T diagram analyzing the APCI process. With the aid of the instructor set up a simulation to find the mixture that will have the right concentration, so that it follows closely the given cooling curve.

DMR

The DMR (Dual Mixed Refrigerant) is very similar to the APCI liquefaction process. The process capacity is about 4.5 MMmtpa and there is only one DMR train in operation. The location of this train is in Sakhalin Island in Russia.

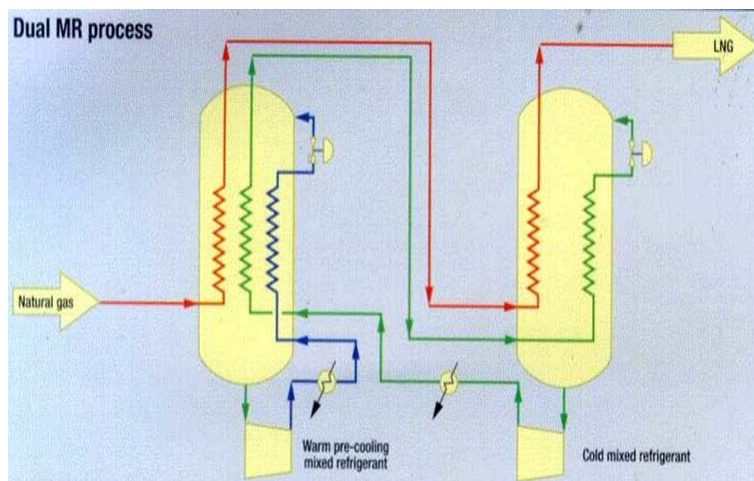


Figure 2-21: Dual mixed refrigerant flow diagram

The process is similar to the APCI, but in this process the heat exchanger tower is divided into two sections rather than one tower and this concept allows the designer to choose the load on each refrigeration cycle through controlling the two compressors work before each column. The first stage, which is the left column, cools the natural gas (red stream) to $-50\text{ }^{\circ}\text{C}$ while the second column cools the natural gas to $-160\text{ }^{\circ}\text{C}$. The composition of the pre-coolant cycle is 50/50 of Ethane/Propane on molar basis and the coolant composition of the cooling cycle is similar to the composition of APCI and that is why it is called the Dual Mixed Refrigerant process (due to having two different refrigerants). The two compressors are frame 7 compressors. The heat exchangers used in this process are also SWHE as used in the APCI. Shell also developed double casing equipment rather than a single casing to optimize the production to 5 mtpa. The advantages and disadvantages of this process is similar to the APCI, but since it has two separate compressors and heat exchangers it becomes more reliable than the APCI: Indeed, if one compressor or heat exchanger goes offline then the rest would do the liquefaction but with a smaller production rate.

Exercise 2-11:

Make a Q-T diagram analyzing the DMR process. With the aid of the instructor set up a simulation to find the mixture that will have the right concentration, so that it follows closely the given cooling curve.

LINDE

This process is also called the Mixed Fluid Cascade process (MFC). It was developed by Linde/Statoil LNG Technology Alliance and it has a capacity of 4 mtpa. Only one Linde train has been constructed with a maximum capacity of 4 mtpa for the Snohvit LNG project in Ekofish (Norway).

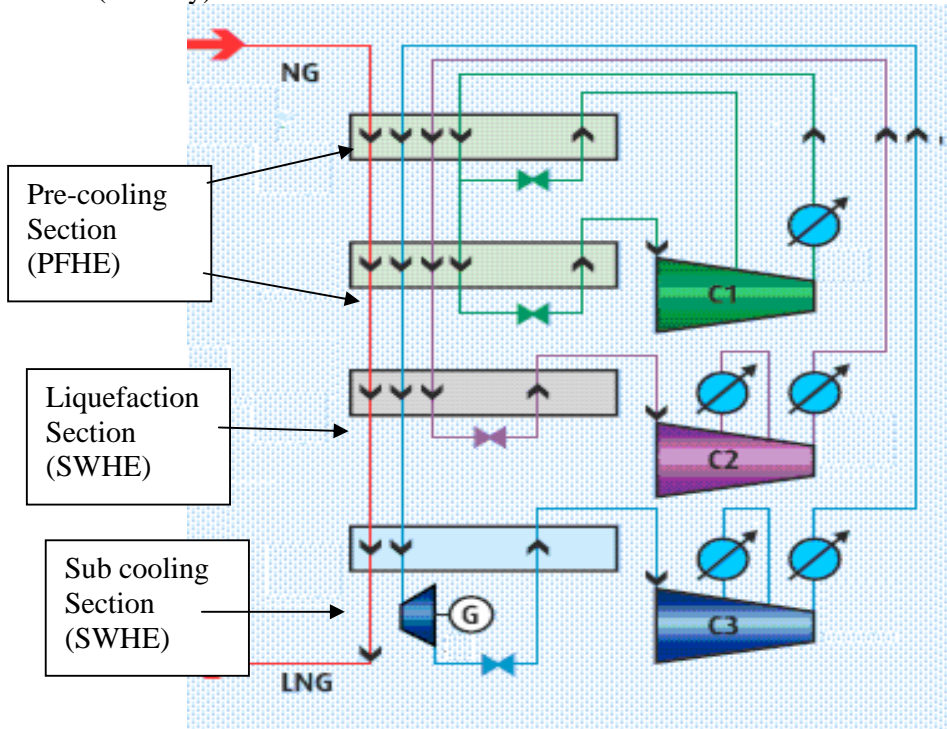


Figure 2-22: Linde process flow diagram

The natural gas (red stream) comes in from the top and goes through three mixed refrigerant cycles. The pre-cooling cycle (green cycle) cools natural gas through two Plate-Fin Heat Exchangers (PFHE) while the liquefaction (purple cycle) and sub-cooling (blue cycle) cycle cool via SWHEs. SWHE is made and patented by Linde and may also be used for the pre-cooling stage. The only possible reason PFHE is used is because it is less expensive than SWHE. The refrigerants are made mainly of methane, ethane, propane, and nitrogen but the composition ratio of the refrigerants would differ among the three stages.

Table 2-2: Composition of Linde MRs

	Propane (%)	Ethane (%)	Methane (%)	Nitrogen (%)
Pre-cooling (Green Cycle)	~60	~28	~10	~2
Liquefaction (Purple Cycle)	~3	~12	~80	~5
Sub-cooling (Blue Cycle)	~7	~10	~80	~3

Frame 7 and 6 compressors have been proposed for this process to optimize it. The MFC has the same advantages and disadvantages of the other MR processes but it has an extra advantage which is the size and complexity of the separate SWHE applied in the MFC are less when compared to the single unit heat exchangers like in the APCI or DMR. That allows larger single compressors to handle refrigerant over a larger temperature range.

Exercise 2-12:

Make a Q-T diagram analyzing the LINDE process.

ConocoPhillips

ConocoPhillips currently has at least two trains in operation: Atlantic LNG, and Egyptian LNG. More trains are being constructed since this process is expanding to compete with the APCI. It shares about 5% of the world's LNG production and it has been in operation for more than 30 years.

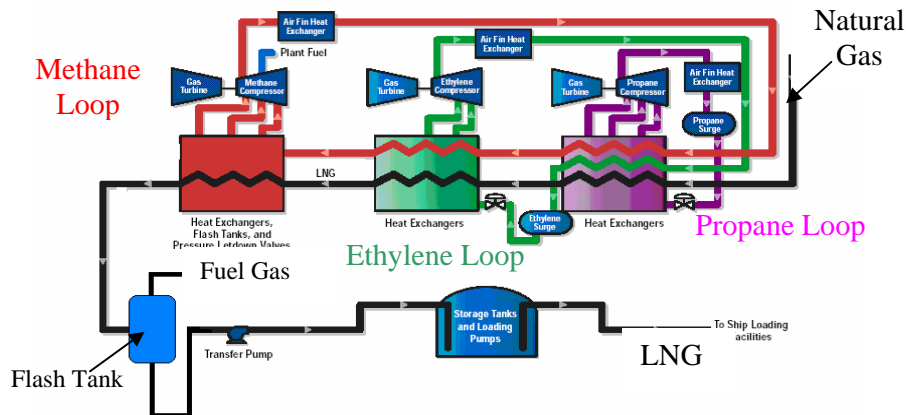


Figure 2-23: ConocoPhillips simple cascade schematic

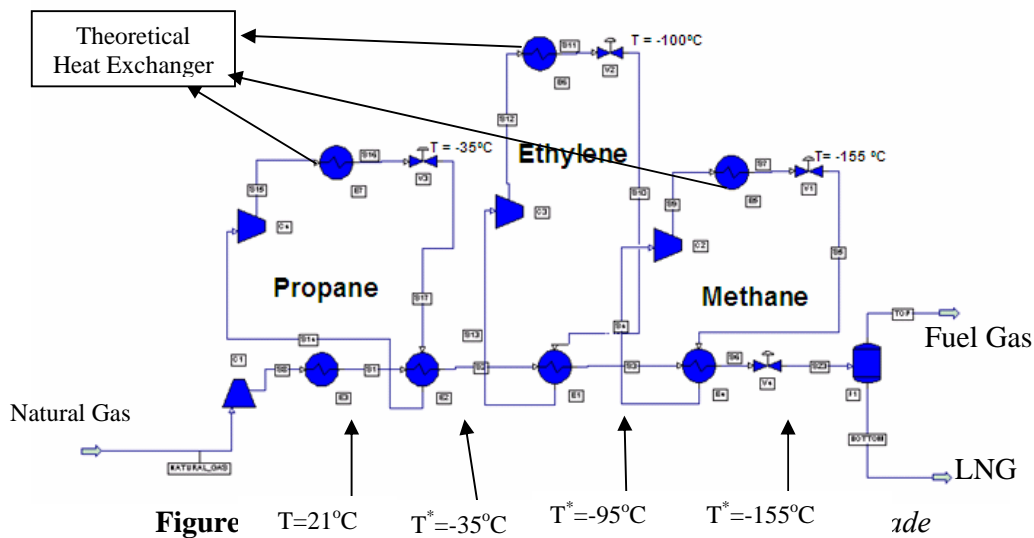
The process uses a three stage pure component refrigerant cascade of propane (purple), ethylene (green), and methane (red). The pretreated natural gas (black stream) enters the first cycle or cooling stage which uses propane as a refrigerant. This stage cools the natural gas to about -35°C and it also cools the other two refrigerants to the same temperature. Propane is chosen as the first stage refrigerant because it is available in large quantities worldwide and it is one of the cheapest refrigerants. The natural gas then enters the second cooling stage which uses ethylene as the refrigerant and this stage cools the natural gas to about -95°C. At this stage the natural gas is converted to a liquid phase (LNG) but the natural gas needs to be further sub cooled so the fuel gas produced would not exceed 5% when the LNG stream is flashed. Ethylene is used as the second stage refrigerant because it condenses methane at a pressure above atmospheric and it could be also condensed by propane. After methane has been condensed by ethylene, it is sent to the third stage where it sub cools the natural gas to about -155°C then it is expanded through a valve which drops down the LNG temperature to about -160°C. Methane is sent back to the first cooling stage and the LNG stream is flashed into about 95% LNG (which is sent to storage tanks) and 5% fuel gas used as the liquefaction process fuel. Methane is used as the sub cooling stage refrigerant because it could sub cools up to -155 °C and it is available in the natural gas stream so it is available at all times and at lower costs.

We will now attempt to perform a simulation of this simple process. We first recognize that the boiling points of each of the refrigerants will limit the temperatures at the outlet of each exchanger.

Table 2-3: *Refrigerants boiling points*

Refrigerant	Boiling Point (°C)
Propane	~ -42
Ethylene	~ -103
Methane	~ -161

We therefore set up a simulation using theoretical exchangers. This will allow figuring out the different duties. The figure below shows a simulation designed with theoretical heat exchanger that cools down the refrigerants to couple of degrees lower than it is boiling point in order to condense it. Then the heat exchangers between the natural gas stream and the refrigeration cycles are designed to cool the natural gas to a temperature (T^*) 10°C lower than the refrigerant boiling point.



Exercise 2-13:

Set up the first simulation for the ConocoPhillips simple cascade to produce 4.5 MTPa of LNG. Determine the appropriate flowrates in each cycle and the load of each compressor. Since you are using fictitious exchangers, these rates will change later. We pick the following pressures for the high pressure portion of the refrigeration loops: Propane: 1.3 MPa, Ethylene: 2.1 MPa, Methane: 3.3 MPa. The LNG is available at 10 atm for this example and is compressed to 3.9 MPa.

After the amounts of heat duties needed for each cycle is determined, the theoretical heat exchangers are replaced by exchangers that will allow real cooling take place.

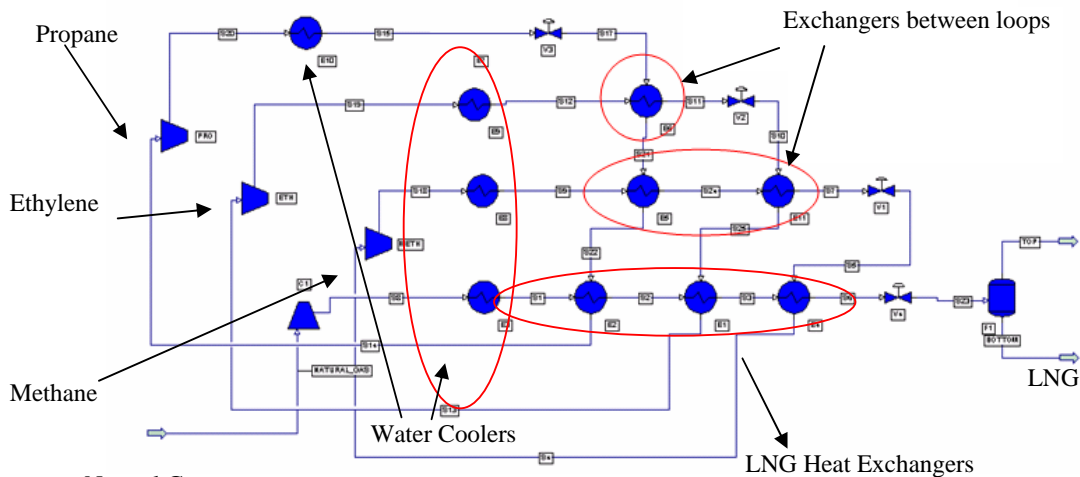


Figure 2-25: ConocoPhillips simple cascade

Exercise 2-14:

Set up the complete simulation for the ConocoPhillips simple cascade to produce 4.5 MTPa of LNG. Determine the appropriate flowrates in each cycle and the load of each compressor.

Exercise 2-15:

Set up the complete simulation for the ConocoPhillips simple cascade to produce 4.5 MTPa of LNG. Use LNG exchangers in this case. Use zone analysis to see the internal temperature profile.

The T-Q profile of the simple cascade is shown in the next figure:

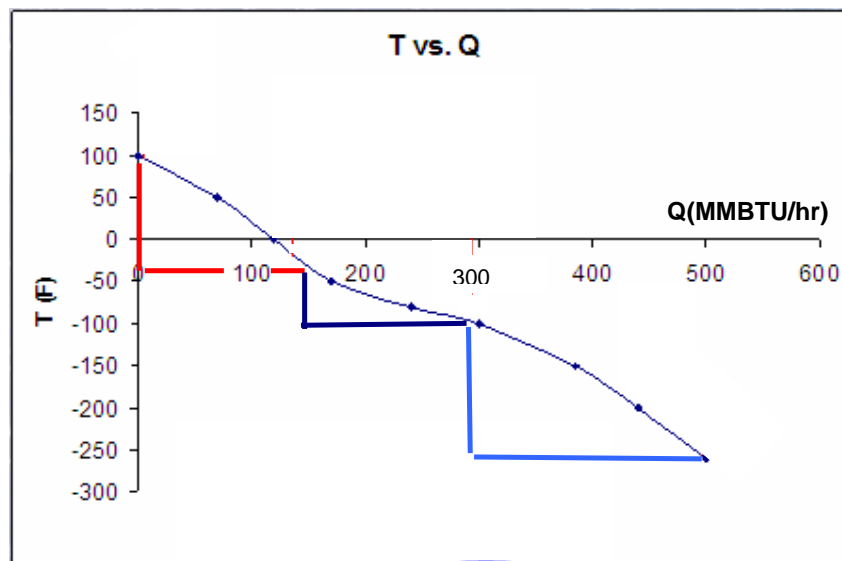


Figure 2-26: Simple ConocoPhillips Cascade LNG Cooling Curve

The optimized Phillips design makes use of complex arrangements with flash tanks to increase efficiency, as shown in figure 2-18. Flash tanks are located before every LNG heat exchangers to separate the liquid refrigerant from the vapor refrigerant and then the vapor phase refrigerant goes to the compressor and the liquid is sent to the next LNG heat exchanger for further cooling of the natural gas stream. This insures that only liquid phase refrigerant would cool the natural gas stream, which will optimize the cooling process and makes it more efficient. The following figure shows the arrangement for a propane loop only.

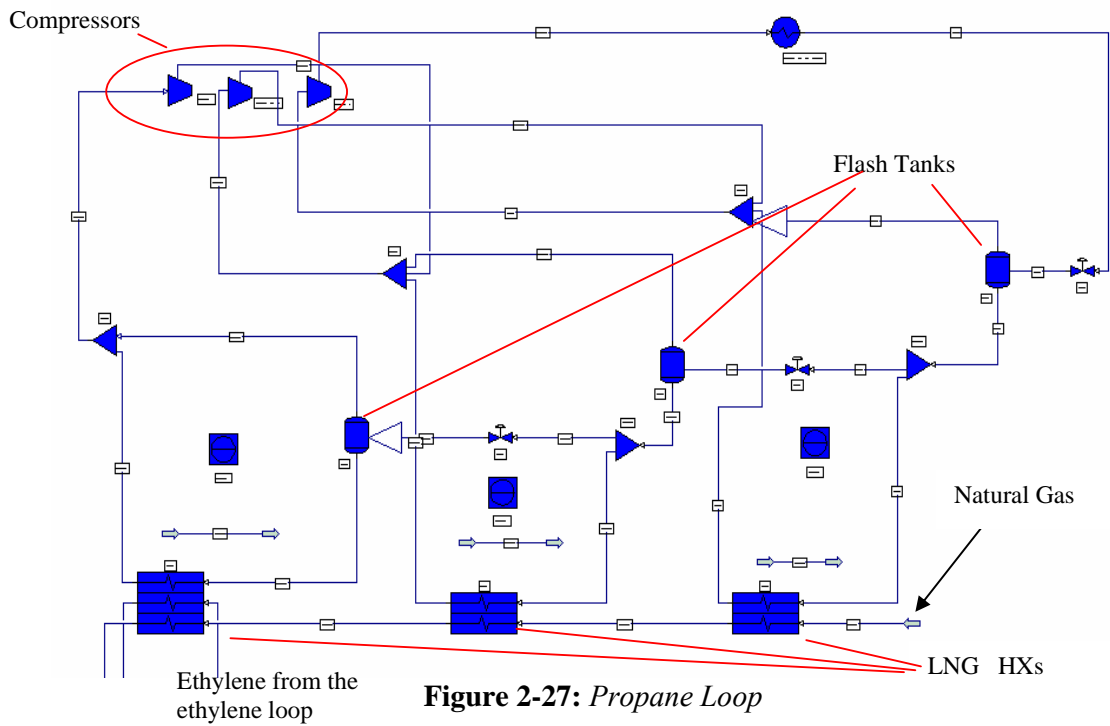


Figure 2-27: Propane Loop

The procedure is explained using the P-H (Pressure-Enthalpy) diagram of propane of next figure:

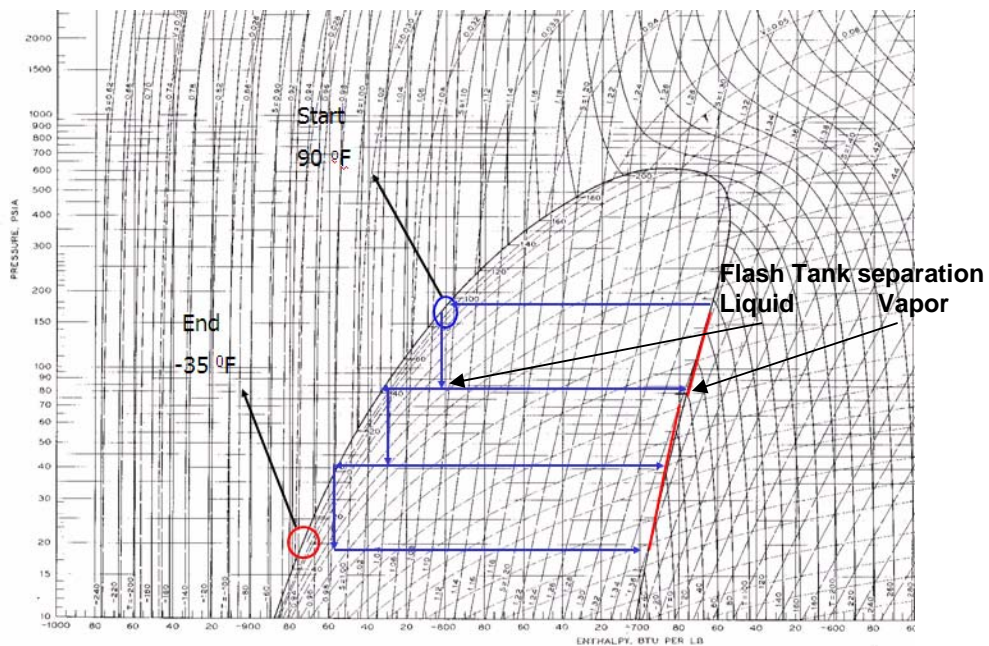
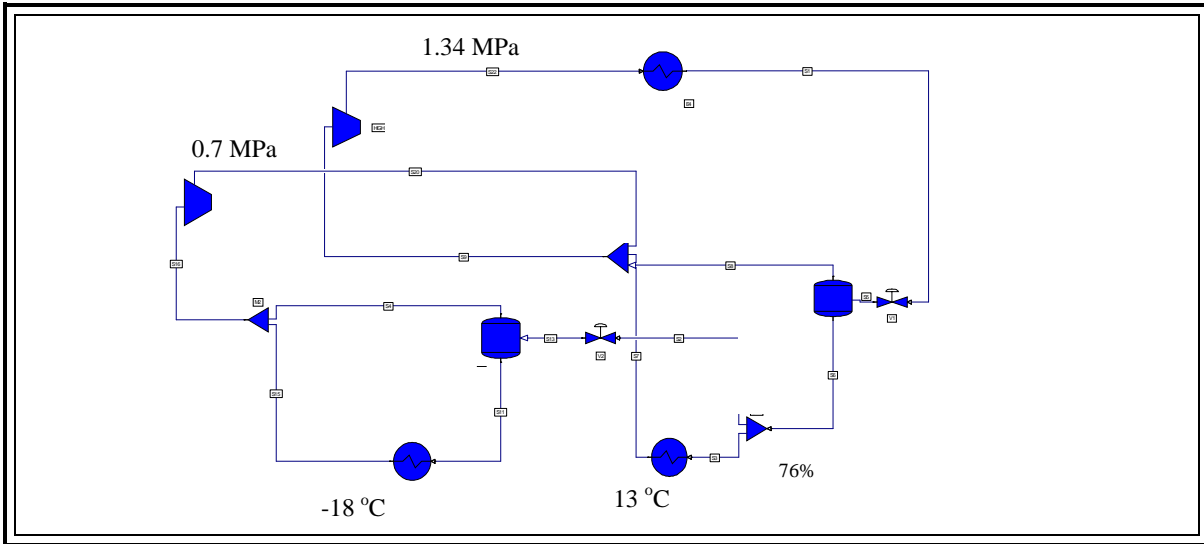


Figure 2-28: Propane Loop P-H diagram

We start at 90 °F (or at a lower temperature) and about 1.35 MPa, flashing across a valve to the new pressure (0.74 MPa). The newly generated saturated liquid is then separated in a flash tank from the vapor which is sent to the first compressor. The liquid is split. A portion (76%) is sent to be further decompressed and sent to a flash, while the rest is put in contact with natural gas and after vaporized it is sent to the corresponding compressor. The process is repeated two more time. The last LNG exchanger is used to cool down the ethylene in the higher pressure portion of the Ethylene loop.

Exercise 2-16:

Set up a propane loop using two flashes as shown below



The next figure shows a complete simulation of the ConocoPhillips optimized process and the following tables give some highlights on efficiencies and work

Table 2-4: *Efficiencies of the ConocoPhillips process*

Overall Plant Production Efficiency = 95%	
Operating Range	Production
Full plant	100%
One Turbine offline	60% to 80%
Three Turbine offline	30% to 60%

Table 2-5: Total work done in refrigeration loops

Loop	Work (hp)(% of total)
Propane	~ 45%
Ethylene	~ 20%
Methane	~ 35%

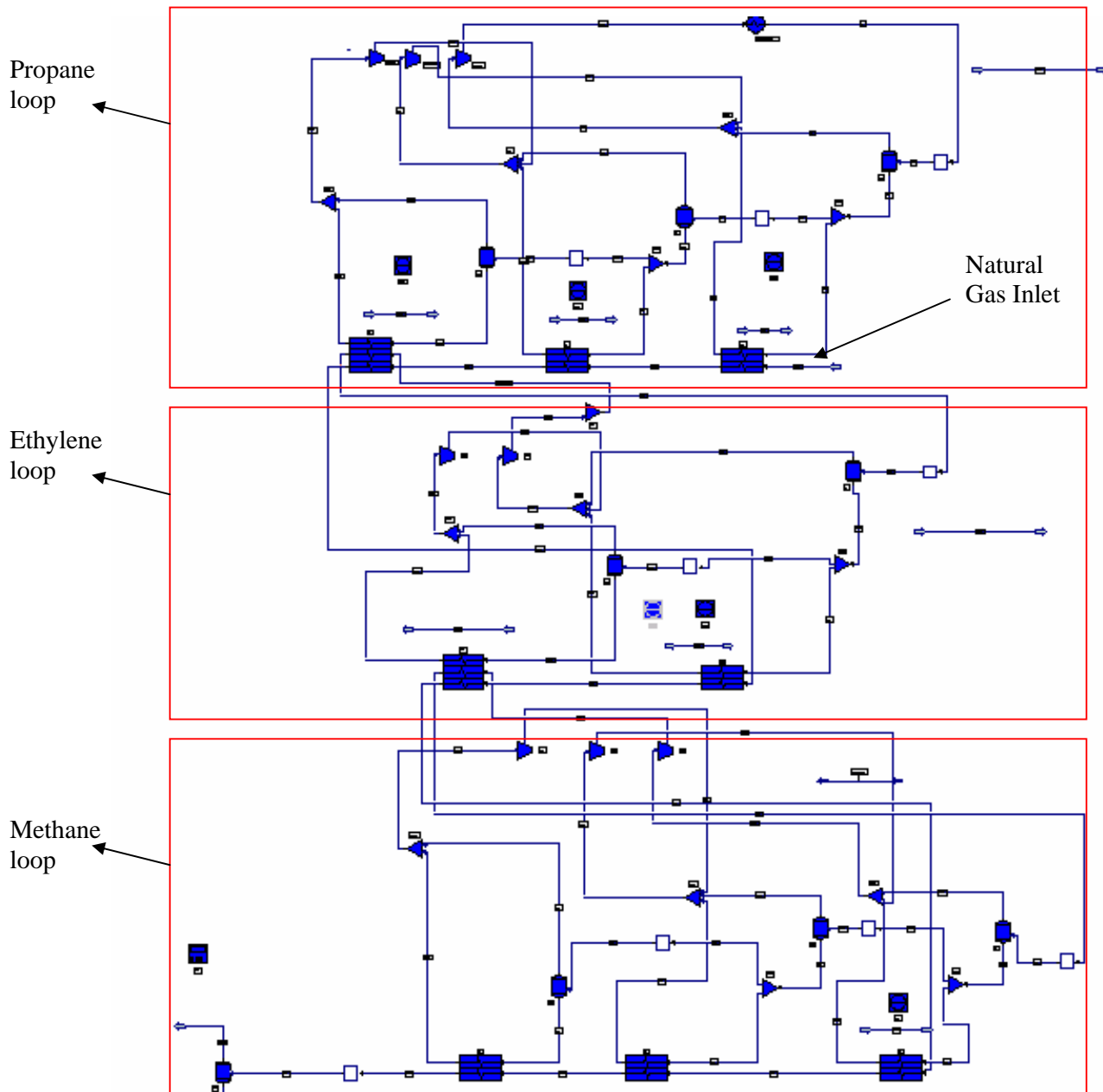


Figure 2-29: *Simulation of the ConocoPhillips Optimized Process.*

It is expected that the ConocoPhillips Cascade Process will come close to the total APCI LNG production rate (in 2010: 35% for Phillips Cascade and 55% for APCI) according to the graph below,

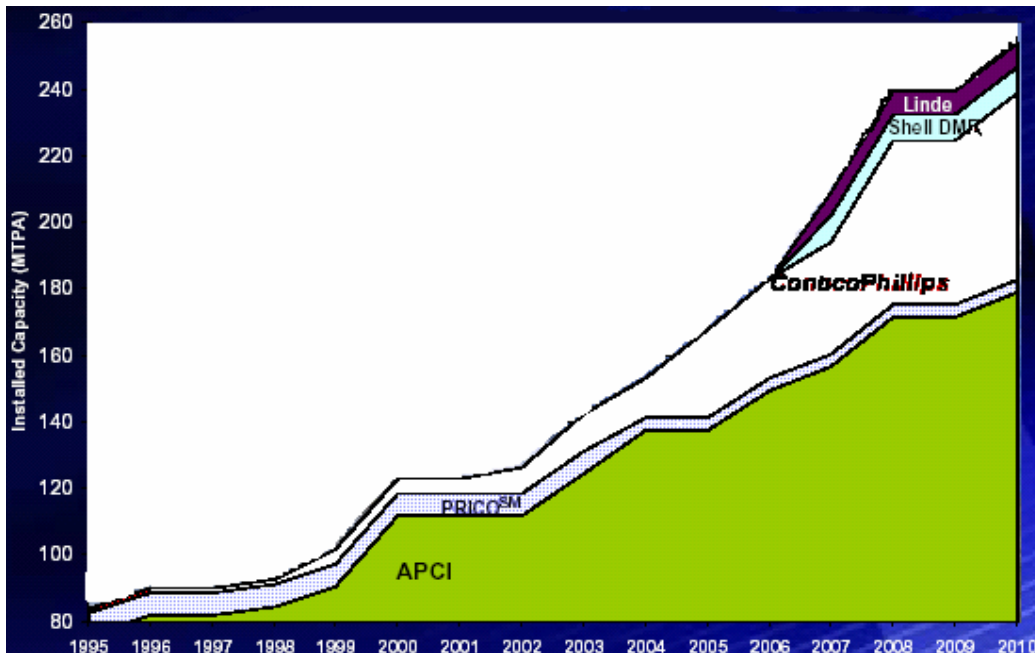


Figure 2-30: Capacity of world LNG (mtpa) vs. year

Table 2-6: Capacities of current and future LNG trains

Licensor	Process Technology	Total Number of Trains	Total Production (MM mtpa)	Percent of Market Production	Start-up Date	Largest Train (MM mtpa)
APCI	PMR	53	107.5	88.1	1972 to present	3.3
APCI	SMR	4	2.6	2.1	1970	0.65
Technip – L’Air Liquide	TEAL (dual pressure SMR)	3	2.85	2.3	1972	0.95
Technip L’Air Liquide	Classical Cascade	3	1.2	1.0	1964	0.4
Pritchard	PRICO (SMR)	3	3.6	2.9	1981	1.2
Phillips	Optimized Cascade	2	4.3	3.5	1969 to 1999	3.0

Ships

Typical ships are shown in the next two figures: The concept of membranes is based on the idea that the forces exerted by the LNG cargo are transmitted by a metallic membrane to the ship’s inner hull (these are double hull ships). The Norwegian company Moss Rosenberg introduced the concept of spherical tanks. The capacity of these ships is between 100,000 to

140,000 m³. The ships are powered with a medium speed 4-stroke diesel engine, which is capable of providing fuel efficiency and operates on burning low pressure gas. It consumes 0.15% of the cargo through what vaporizes of the LNG and that adds up to consuming 2% of the LNG produces over the life of the project.

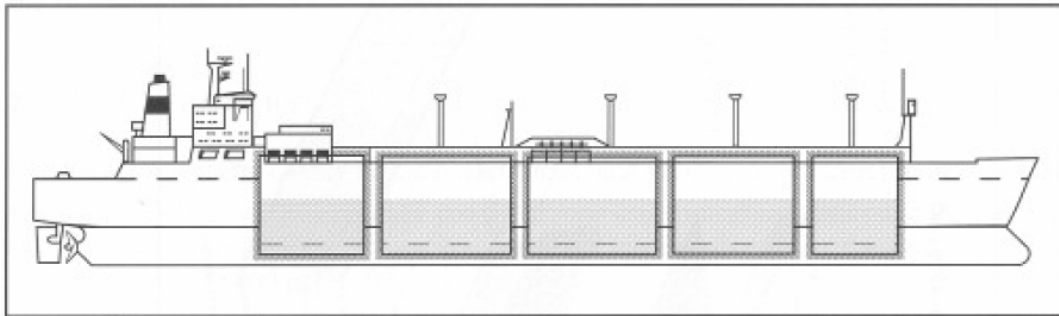


Figure 2-31: LNG carrier with *GAZ Transport Membrane*

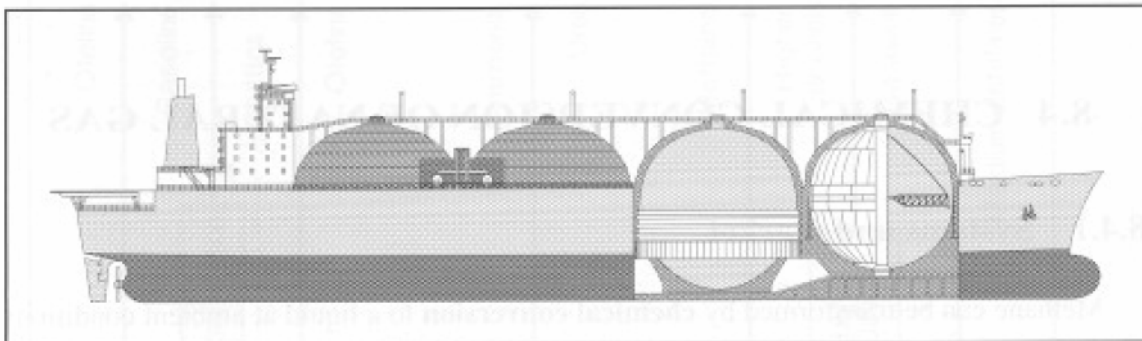


Figure 2-32: LNG carrier with *Moss Rosenberg self-supporting tanks*

Receiving Plants

Once the natural gas has been pumped from the ground, liquefied, and placed in a ship it is now time to deliver the natural gas to its destination and re-gasify it. Receiving plants are normally located near the ocean, either onshore or offshore.

There are many choices out there on how to get the liquefied natural gas back into its natural state, a vapor. There are many tank designs to consider when choosing storage tanks to hold LNG, of these safety ranks among the top. When considering safety, there are 5 designs to choose from; single containment, double containment, full containment, in-ground storage, and underground storage.

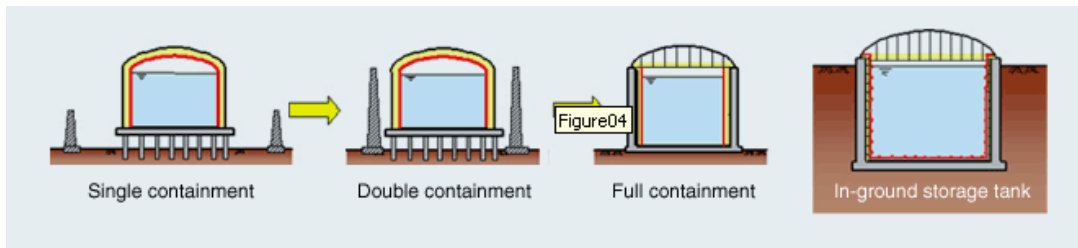


Figure 2-33: LNG Tank designs

Of these, each has their advantages and disadvantages and bearing the location of the prospective plant an in-ground tank would be an excellent choice. The two main reasons to propose in-ground tanks are because they are safer in earthquakes and less space is required because no dikes are needed. Also, in-ground tanks costs roughly the same as above-ground tanks and the construction time is nearly the same as well.

Vapor Handling System

The vapor handling system is a very important part of an LNG receiving terminal for numerous reasons. Inside the storage tank vapor is formed when the LNG is pumped in. This vapor needs to be removed from the tank to make room for the liquid and to keep pressure from building up inside the tank. This is accomplished by pumping the vapor out the top of the tank using a blower.

Vaporizer

The vaporizer network is what turns the liquefied natural gas back into a gas. Various processes are available to accomplish this task and there are pros and cons to each method. These processes will be described in more detail below along with a scheme that will utilize the optimum choice in a way to recover the cold energy.

The submerged combustion vaporization process is the cheapest with regards to capital cost but the annual operating cost is very high. The following schematic illustrates how submerged combustion vaporization works.

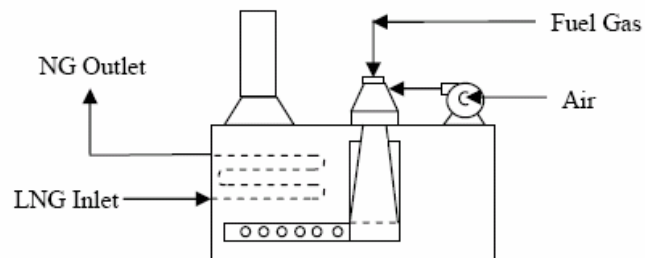


Figure 2-34: LNG submerged combustion vaporizer

Submerged combustion vaporizers use a combustion burner to ignite a mixture of fuel gas and air, which then heats a water bath with submerged tube bundles. The water then provides the heat to the LNG to vaporize it.

The open rack vaporization process (next figure) is the most expensive in capital cost but its operating cost is far smaller than the submerged combustion vaporization process. Here is a schematic of open rack vaporization.

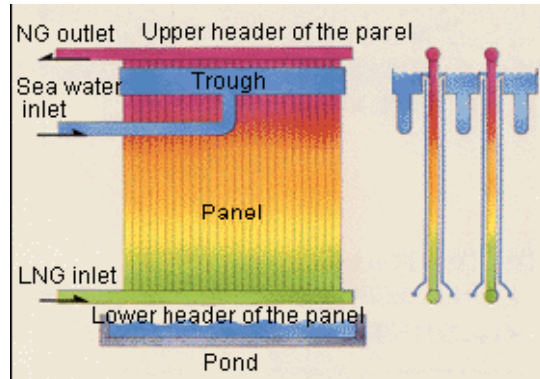


Figure 2-35: LNG Open Rack vaporizer

Open rack vaporization uses sea water to vaporize the LNG by using counter current flow through finned aluminum tubes. Since seawater is corrosive, a zinc alloy coating is used on the outside of these tubes.

The heat integrated ambient air vaporization (next figure) process is the cheapest in both capital and operating cost, making them the optimum choice. One can use natural or forced air convection.

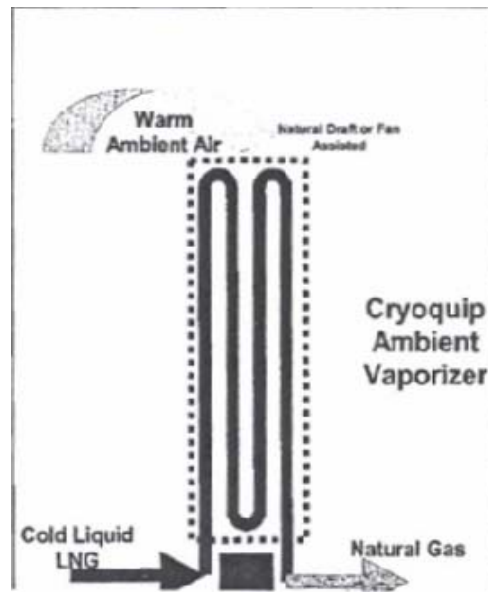


Figure 2-36: LNG Ambient Air vaporizer

The following figure illustrates a process to recover some of the cold energy by using ambient air vaporization and an intermediate fluid.

Table 2-7: Comparison of vaporization methods

Vaporization Choice				
For 1000 m ³ / hr send-out rate	Submerged Combustion Vaporization	Open Rack Vaporization	Forced Draft Heat Integrated Ambient Air Vaporization	Natural Draft Heat Integrated Ambient Air Vaporization
Costs Comparison				
Estimated Capital Costs Factor	1	1.38	1.317	1.258
Capital Costs Comparison	\$107.75	\$148.70	\$141.91	\$135.55
Fuel Gas Usage				
Usage (MMft ³ /d)	6.77	0.00	0.00	0.00
Fuel Gas Cost	12.60	0.00	0.00	0.00
Electrical Usage				
Usage (MW)	1.39	1.88	1.81	0.17
Cost of Power	0.63	0.85	0.81	0.08
Annual Operating Costs (millions)	\$13.23	\$0.85	\$0.81	\$0.08
Environmental Emissions and Effluents				
Chlorine Emissions	No	Yes	No	No
CO Emissions (tpy)	132.39	6.78	6.53	0.43
NO _x Emissions (tpy)	88.44	6.71	6.41	0.43

Finally, since so much work is made to liquefy the natural gas, it makes sense to attempt to recover this work. This can be accomplished with the following propane loop. The loop contains an expander and on the other end a pump, which is intentionally chosen to avoid the purchasing of a compressor.

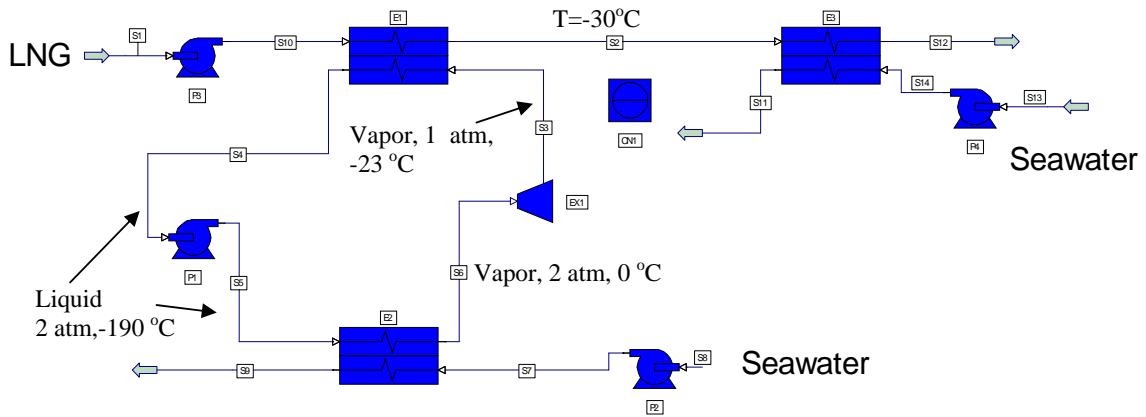


Figure 2-37: Propane Loop re-gasification

Exercise 2-17:

Set up a propane loop re-gasification simulation and determine the amount of work that can be recovered for the South American gas of previous exercises.