Natural gas liquefaction cycles

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Overview

- Liquefaction cycles:
  - 1) Joule-Thomson cycles
  - 2) Expander cycles
  - 3) Cascade cycles for NG liquefaction

- Vapor-compression refrigeration cycle

- Classical cascade cycle

- Mixed refrigerant cascade (MRC) cycles

- Thermodynamic calculations of LNG processes

- Choosing among liquefaction cycles
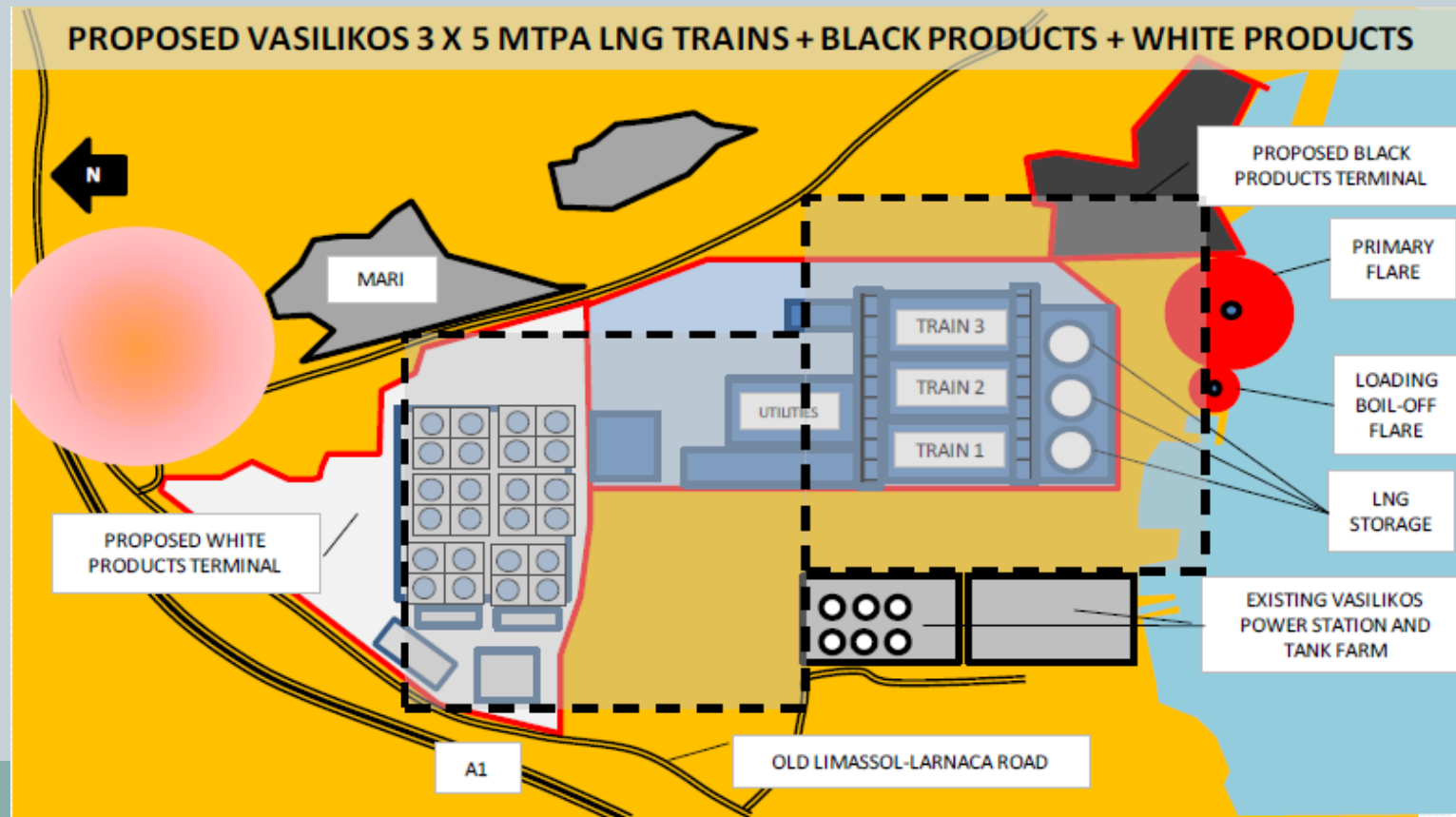
LNG plant flow diagram

- Delivered gas stream at about 1,300 psi
- NG is metered before pre-treatment
- Cryogenic cooling ($<-150\,^\circ$C) usually accomplished in several steps
- Flash vapours either recycled or used as a fuel
- Most LNG contracts specify a range of acceptable heating values
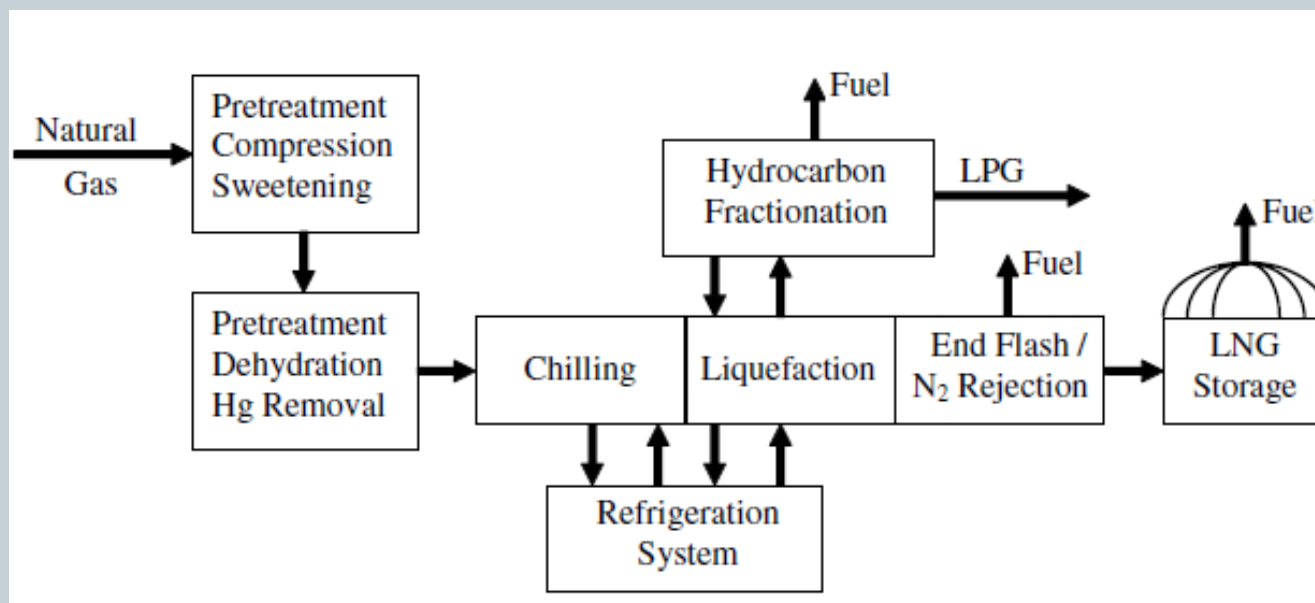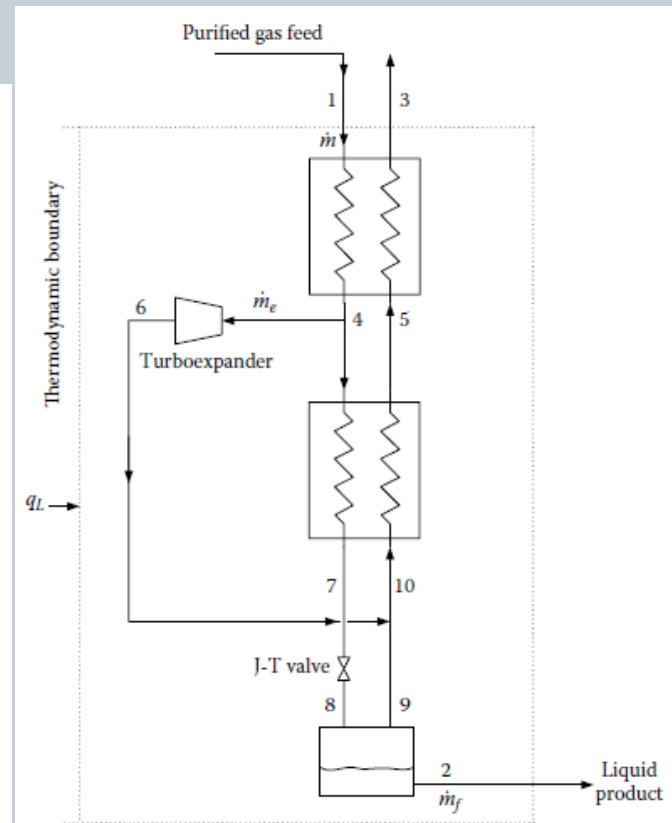
What is an LNG train?

- "Trains" treat & liquefy natural gas and store it in LNG tanks
- Train size governed by: liquefaction process, refrigerant(s), size of compressor/driver combo, size of heat exchangers

PROPOSED VASILIKOS 3 X 5 MTPA LNG TRAINS + BLACK PRODUCTS + WHITE PRODUCTS

Recap: Joule-Thomson & Expander cycles

Recall advantage of (nearly) reversible (ideal) gas expansion over J-T:
– A large part of compression work can be recovered thru heat exchanger → higher η
– Reversible process attains larger cooling effect

Joule-Thomson cycle

Closed-cycle

Open cycle liquefaction

Cascade Cycles

Some definitions

- Thermodynamic cycles consist of *power cycles* & *refrigeration cycles*

- *Refrigeration* is the transfer of heat from a lower temperature to a higher temperature reservoir, facilitated by mechanical work.

- What is a refrigerant?
  It is the working fluid used in a refrigeration cycle eg, R410a, R32, CH_4.

- Sensible heat is the amount of heat required to raise the temp. of a unit mass of a substance by 1K, ($Q = mc_p\Delta T$; $c_{p, H2O}$ = 4,181 J/kg·K @ 20°C)

- Latent heat is the thermal energy *released* or *absorbed* by a body during a phase change at constant temperature eg melting of ice or boiling H_2O. $L_{vaporis.}$ = 2,260 kJ·kg⁻¹ | L_{fusion} = 334 kJ·kg⁻¹

Some definitions

- Entropy (*s*) is the notion tied to the 2nd Law of Thermodynamics. It is defined as the "degree of disorder of a thermodynamic system" or "specific ways in which a thermo system can be rearranged." Stm at equilibrium has max. S. S units: J/K

$$\Delta s = \int \frac{dQ_{Rev}}{T}$$

- Enthalpy (*h*) is the *thermodynamic potential* of a system:

$$h = u + pv$$

where *u* is the internal energy, *p* is pressure & *v* is volume. *h* units: J
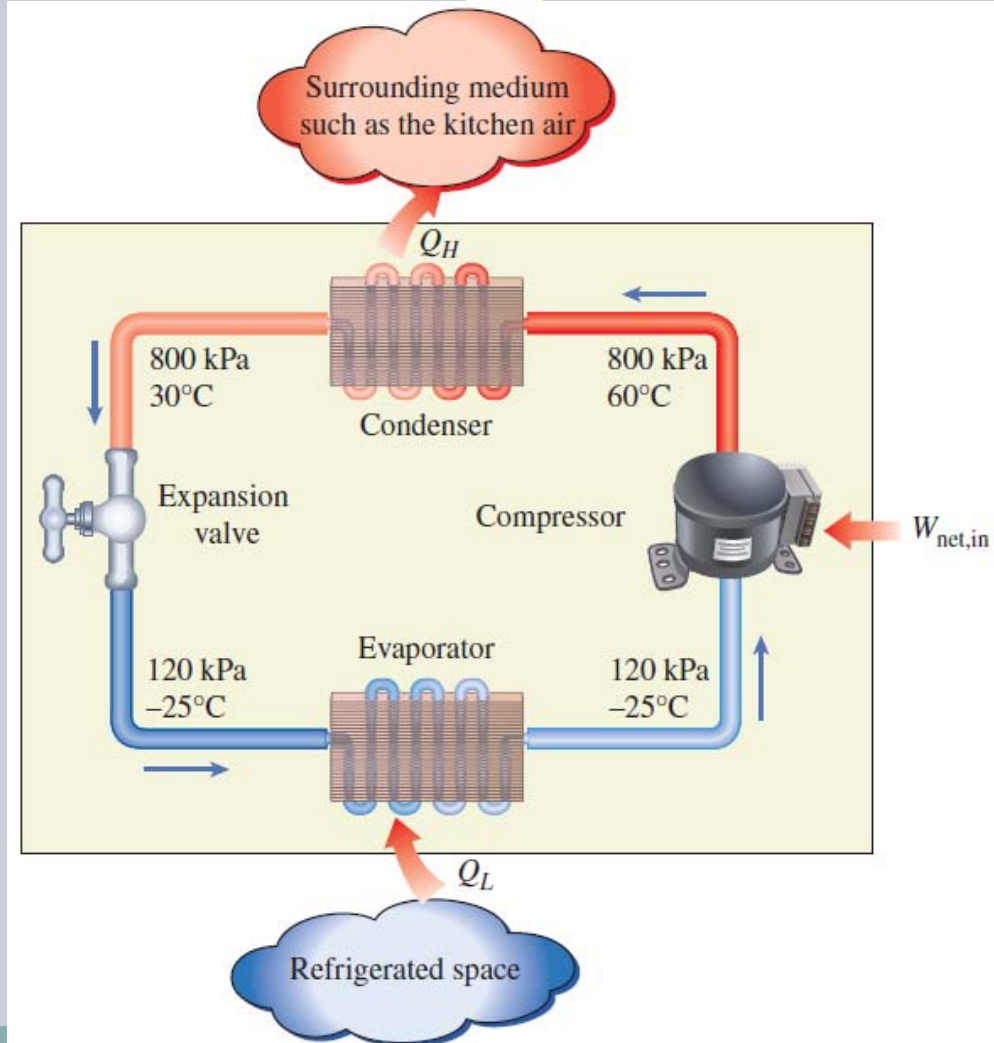
Carnot refrigeration cycle

- Profound societal & economic impacts:
  - Changed the way we process food
  - Expanded agricultural markets & human diet
  - Air-conditioning improves thermal comfort, productivity, standard of living
- Closed loop cycle whose working medium is vapour & liquid
- Processes are internally reversible
- Latent heat absorbs & rejects heat btw colder & hotter environments

- 1→2: isentropic compression
- 2→3: isothermal condensation
- 3→4: isentropic expansion through turbine
- 4→1: isothermal evaporation


Carnot vapour refrigeration cycle
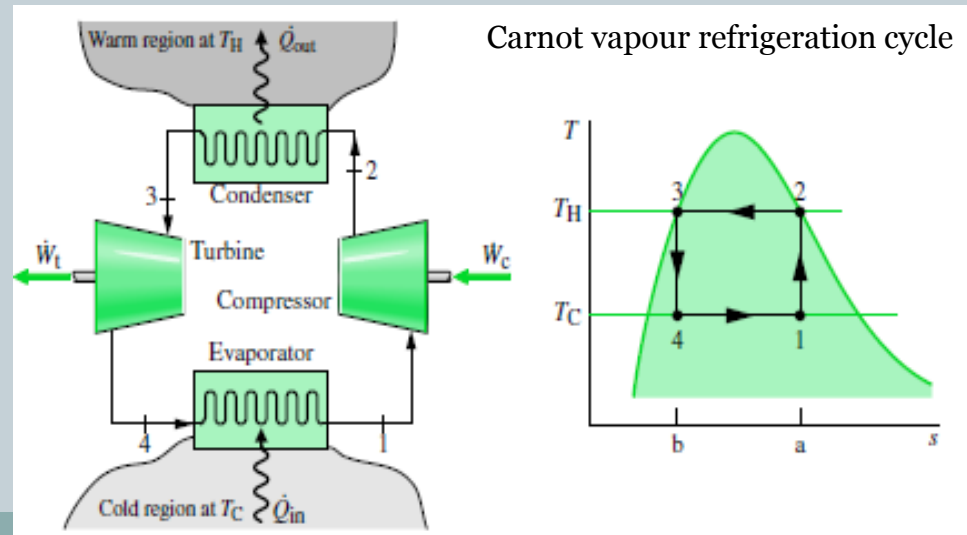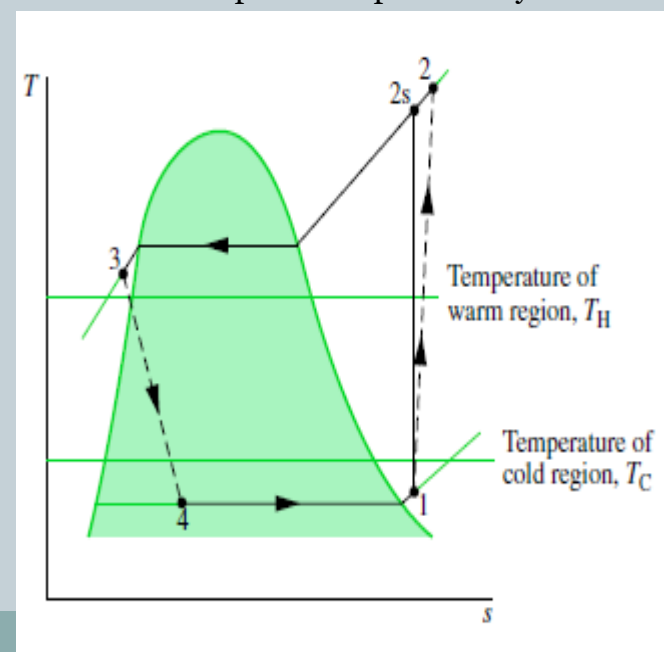
Refrigeration

Vapour compression refrigeration

- Change in phase (or mix %) facilitates heat absorption & rejection
- In an actual vapour-compression refrigeration cycle turbine replaced by expansion valve
- In reality, irreversibilities lower performance.
- Mismatch btw cold & hot regions and refrigerant

Vapour-compression refrigeration system
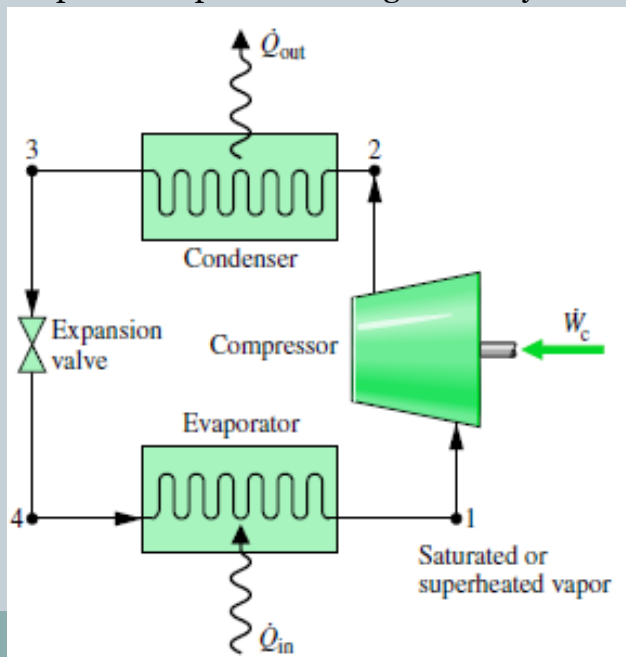
Actual vapour-compression cycle
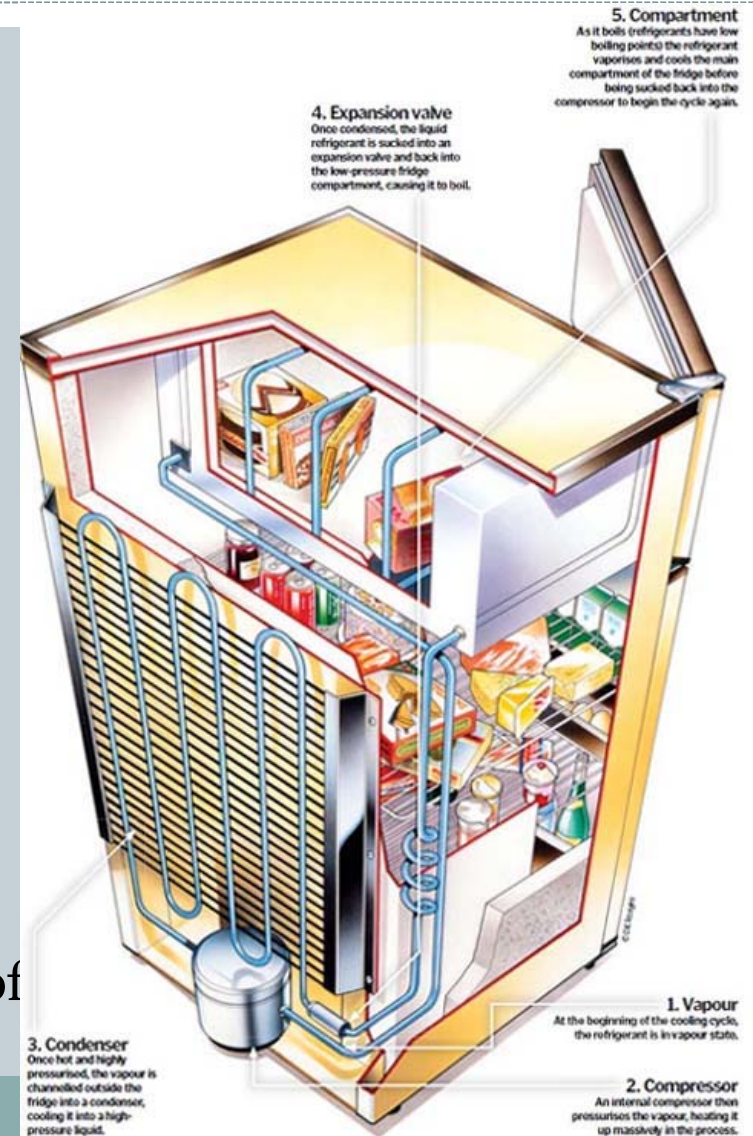
Distinction btw *refrigerators* & *heat pumps*

- A *refrigerator* and a *heat pump* transfer heat from a low-temp. reservoir to a higher temp. region
- They are the same devices but differ in their use
- A refrigerator cools a *cold space*
- A heat pump warms a space (house)
- Both require mechanical work
- Heat pump works on principle of operation of modern air-conditioning systems
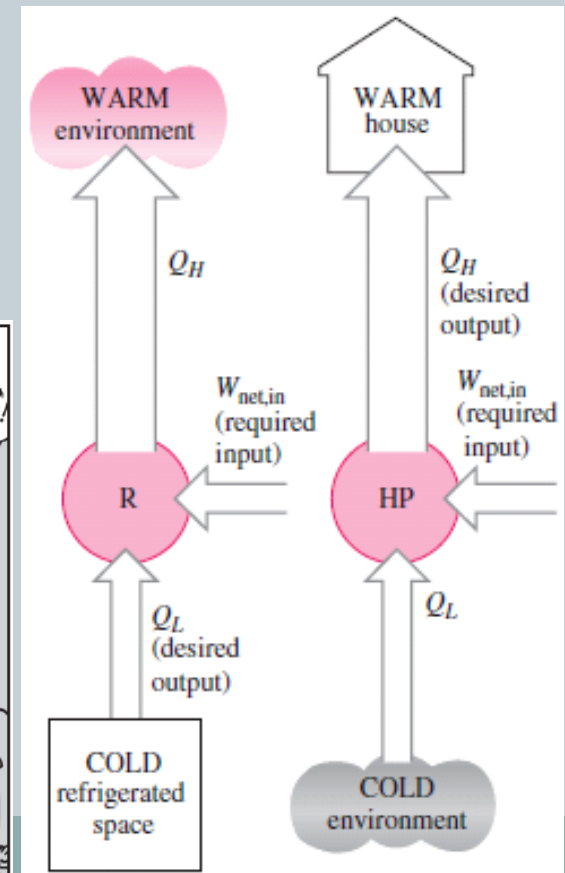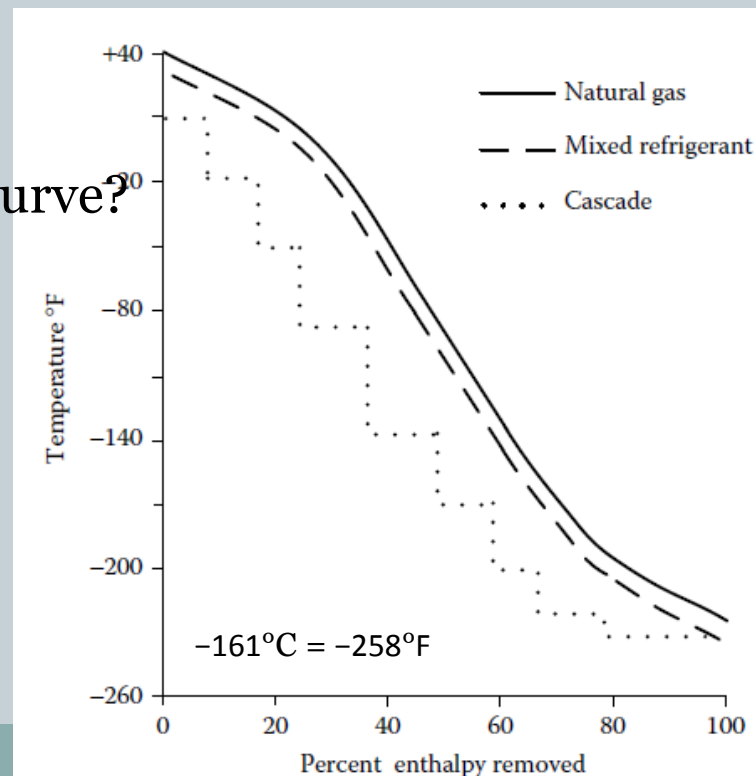
How do refrigerators work

- 1. Vapour. Starting the cooling cycle, the refrigerant is in gaseous state

- 2. Compressor. A compressor then pressurises the vapour, warming it up

- 3. Condenser. Once hot & highly pressurised, the vapour is channelled outside the fridge into a condenser, where it is cooled into a high pressure liquid

- 4. Expansion valve. In liquid form the refrigerant is drawn in an expansion valve & back into the low-pressure fridge compartment

- 5. Compartment. As the refrigerant vaporises it cools the main compartment of the fridge before being directed into the compressor to begin the cycle all over.

5. Compartment
As it boils (refrigerants have low boiling points) the refrigerant vaporises and cools the main compartment of the fridge before being sucked back into the compressor to begin the cycle again.

4. Expansion valve
Once condensed, the liquid refrigerant is sucked into an expansion valve and back into the low-pressure fridge compartment, causing it to boil.

3. Condenser
Once hot and highly pressurised, the vapour is channelled outside the fridge into a condenser, cooling it into a high-pressure liquid.

2. Compressor
An internal compressor then pressurises the vapour, heating it up massively in the process.

1. Vapour
At the beginning of the cooling cycle, the refrigerant is in vapour state.

Cascade cycles

- Maximum thermodynamic efficiency of liquefaction cycle attained if:

  "the heating curve of refrigerant matches the cooling curve of NG"

- Working media: 2 fluids (NG & mixed refrigerant)

- Thermodynamically, the mixed refrigerant emulates a reversible process because it minimizes ΔT (Δh)

- Smaller ΔT less power per kg LNG

- In practice how do u mimic the cooling curve?

- Increase heat transfer efficiency by minimizing ΔT btw refrigerant & NG

- Use a series of refrigerants (usually 3) is a process known as a cascade cycle

- >3 refrigerants can be used but with added costs & complexity

Legend:
- —— Natural gas
- — — Mixed refrigerant
- · · · · Cascade

$-161^{o}C = -258^{o}F$

Temperature ^{o}F axis: +40, -80, -140, -200, -260

Percent enthalpy removed axis: 0, 20, 40, 60, 80, 100

Cascade cycles

- **1**. Classical cascade cycle
- **2**. Mixed-refrigerant cascade cycle
  - Closed cycle
  - Open cycle

Natural gas liquefaction cycles

- Liquefaction cycles:
  - 1. Classical cascade
    - Refrigerants: a) propane, b) ethylene, c) methane in compr.-refrig. cycles
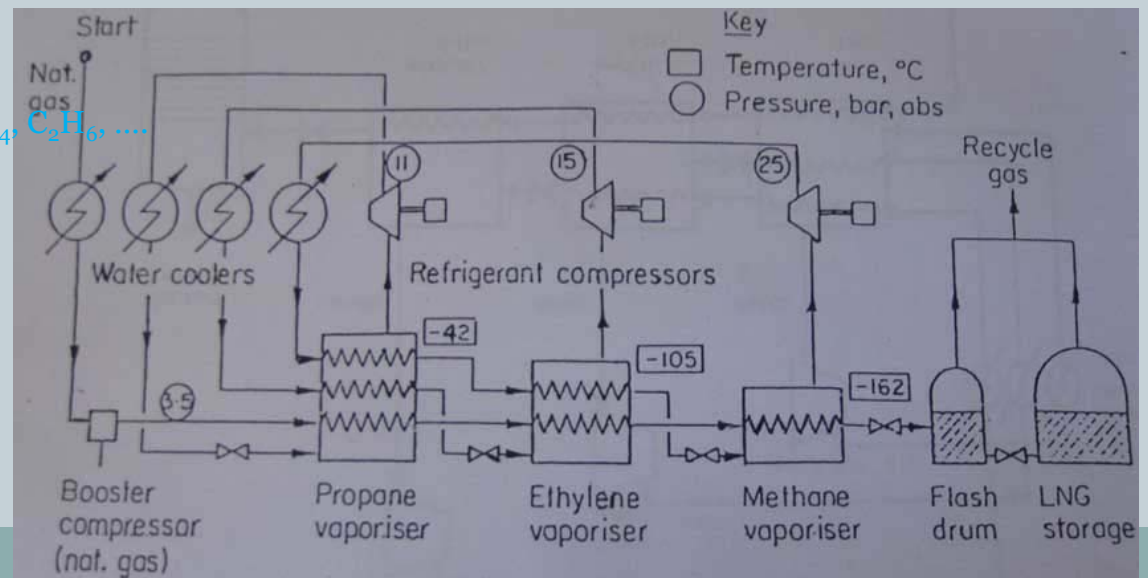 - 2. Modified cascades:
    - Mixed refrigerant
      - Fewer compressors & heat exchangers
      - Less space
      - Less costly to build
   - Costs less to operate
    - Precooled mixed refrigerant
      - Most popular cycle
      - Uses mixed refrigerants: N_2, CH_4, C_2H_6, ...
   - Known as C3MR cycle

1. Classical cascade

- Fig. 1 illustrates a two working fluids cascade cycle
- Working fluid compressed (1) and then cooled in heat exchanger E-1
- *Liquid* from R-1 enters E-2 where it is cooled & expands thru J-T valve
- Vapour directed thru E-1
- Liquid from R-2 cools E-4 gas
- Temp:
  R-1>R-2>R-3>R-4>R-5>R-6
- Feed gas progressively cools until it is expanded through a J-T valve & separated from its vapour


Fig 1. Two-fluid cascade cycle
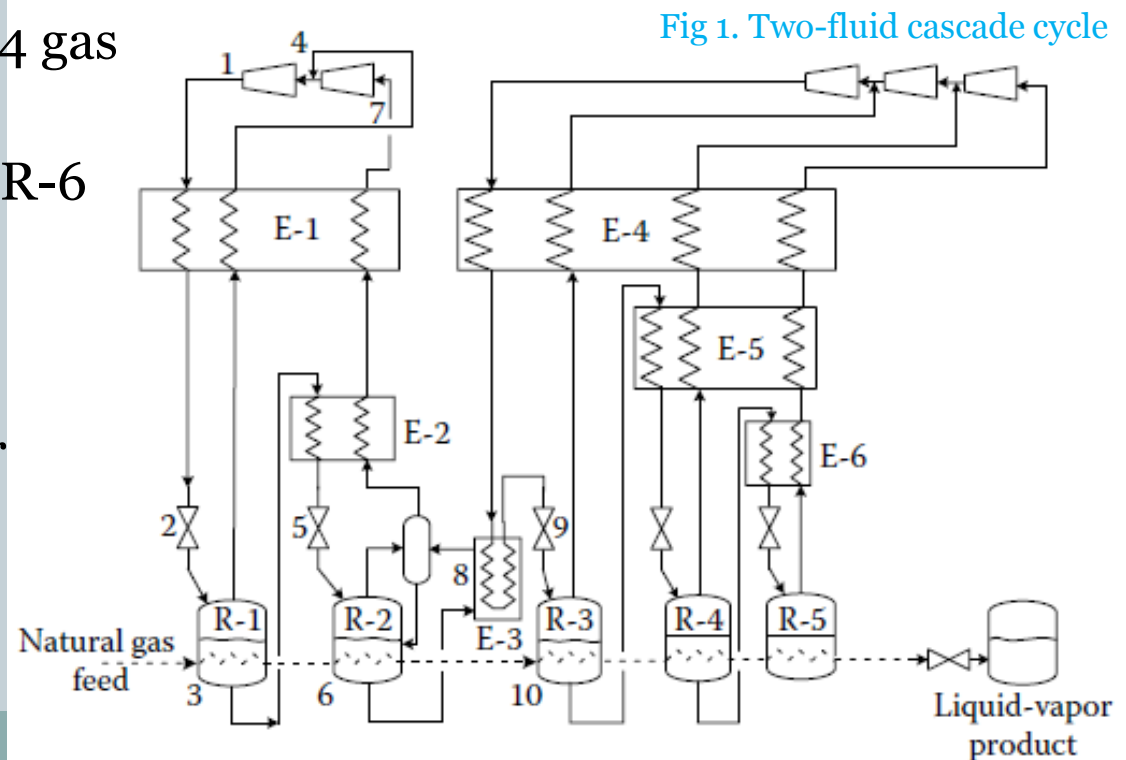
Classical cascade (2)

- NG liquefaction uses 3 refrigerants with 2 or 3 refrigeration stages
- Refrigerants are *pure* fluids (m-e-p):
  1) propane,
  2) ethylene (or ethane)
  3) methane
- Heat exchangers are cooled by refrigeration cycles
- For fluids to *match* part of their vapour pressures must overlap
- Vapour (or equilibrium) pressure
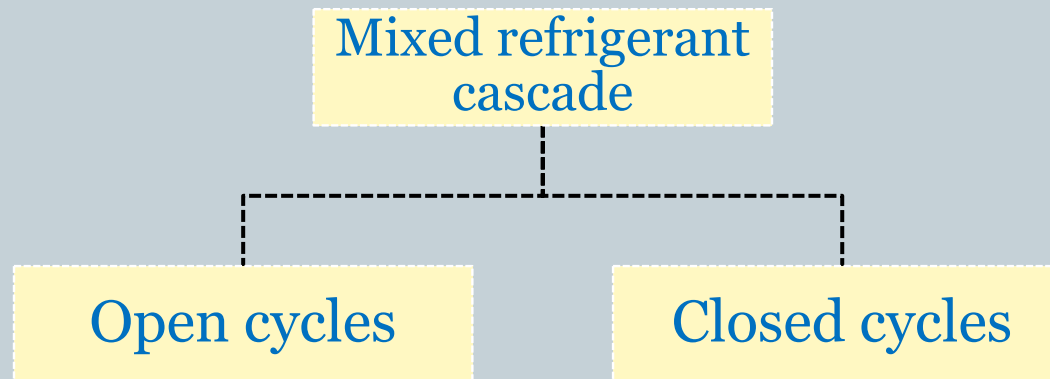- Note: use of 3 compressors is not favourable
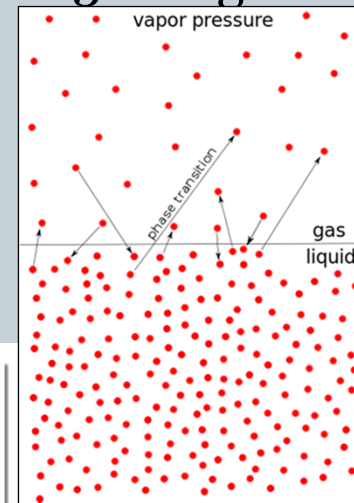
High vapor pressure
=
volatile
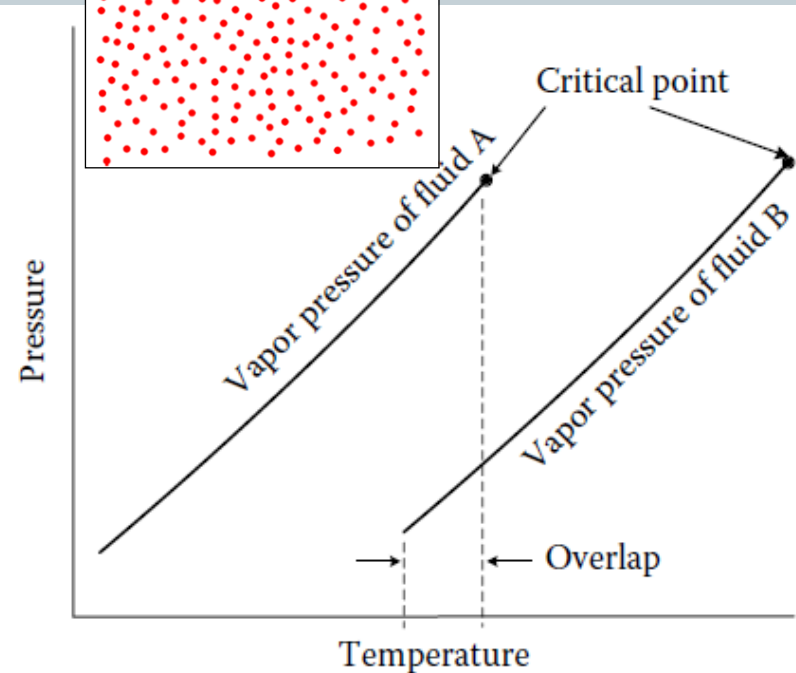
2. Mixed refrigerant cascade

- Principle of mixed-refrigerant cascade (MRC), auto-refrigerated cascade (ARC) & one flow cascade (OFC)
- Aims to mimic the NG cooling curve by using 1 refrigeration loop
- Refrigerant: single fluid whose components liquefy @ varying temps
- Attains closer match btw NG cooling & refrigerant heating
- Only one compressor is needed

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                    Mixed refrigerant
                        cascade
                           |
            ┌──────────────┴──────────────┐
       Open cycles                   Closed cycles
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2. Mixed refrigerant cascade: closed cycle

- Refrigeration mixture = f(NG composition)
- Refrigerant mix may consist of N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, & C_5H_{10}
- Working fluid subject to pressure drops & liquid-vapor separations
- Temp of NG gradually reduced to $-161°C$
- Refrigerant & NG do not mix

Press.bar	1.0	3.4	6.85	17.1	34.2
Methane	-159	-144	-133	-92+15.8	-71
Ethane	-91	-63	-44		
Propane	-46	-12	+12	-	
Ethylene	-104	-80	-62	-8.3	
Propylene	-49	-18	-5.6	-	
Nitrogen	-	-183	-174	-148	-133

Natural gas feed

H_2O cooled condenser

Heat exchangers

Fuel

LNG
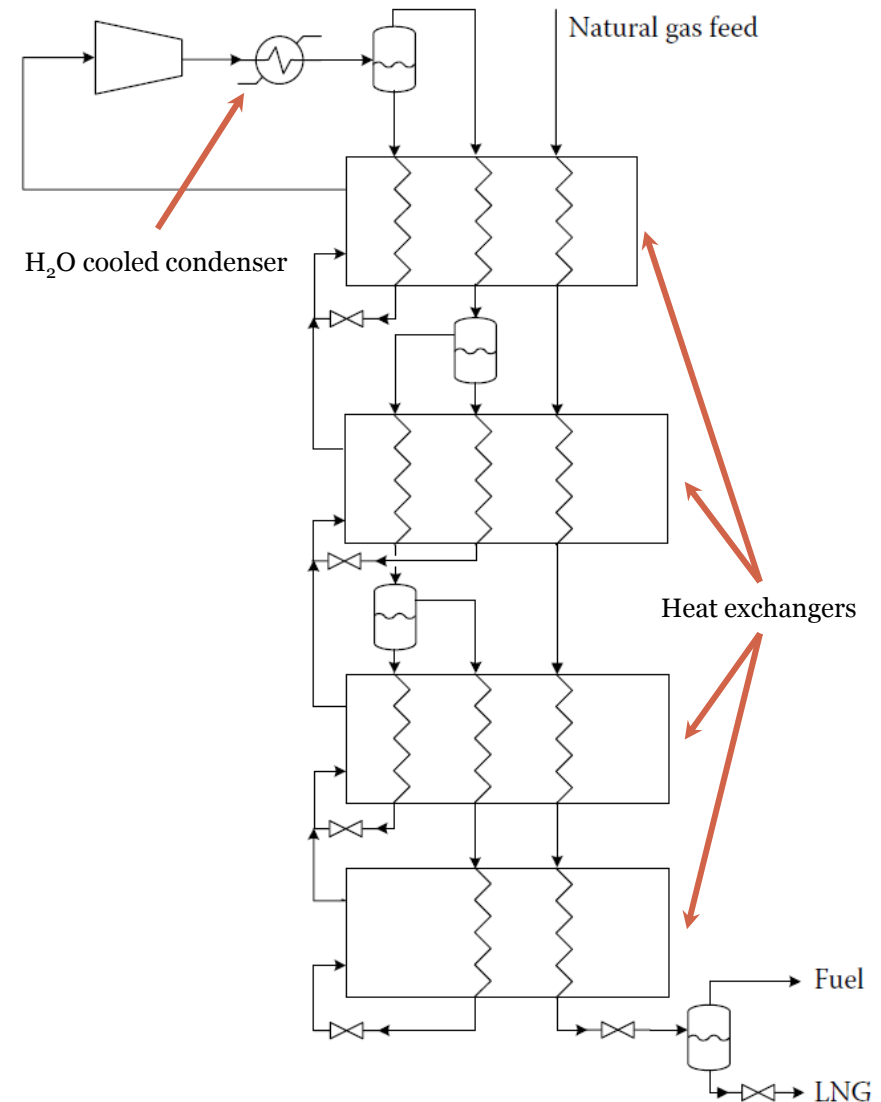
Propane pre-cooled mixed refrigerant (C3MR)

- Most common mixed refrigerant stm for baseload NG plants
- Employs external propane refrigeration & mixed fluid J-T expansion
- Fluid #1: propane, #2: mixed refrigerant, #3: treated NG
- Uses two compressors

Compositional Specifications on Feed to LNG Plant and on Pipeline Gas

Impurity	Feed to LNG Plant[a]	Pipeline Gas[b]
Water	< 0.1 ppmv[c]	150 ppmv, (7.0 lb/MMscf, 110 kg/Sm³)
Hydrogen sulfide	< 4 ppmv	0.25 – 0.30 gr/100 scf (5.7 – 22.9 mg/Sm³)
Carbon dioxide	< 50 ppmv	3 to 4 mole%
Total sulfur (H₂S, COS, organic sulfur)	< 20 ppmv	5 – 20 gr/100 scf (115 – 459 mg/Sm³)
Nitrogen	<1 mol%	3 mol%
Mercury	< 0.01 μg/Nm3	
Butanes	2 mol% max	
Pentanes+	0.1 mol% max	
Aromatics	< 2 ppmv[c]	

[a] Foglietta (2002).
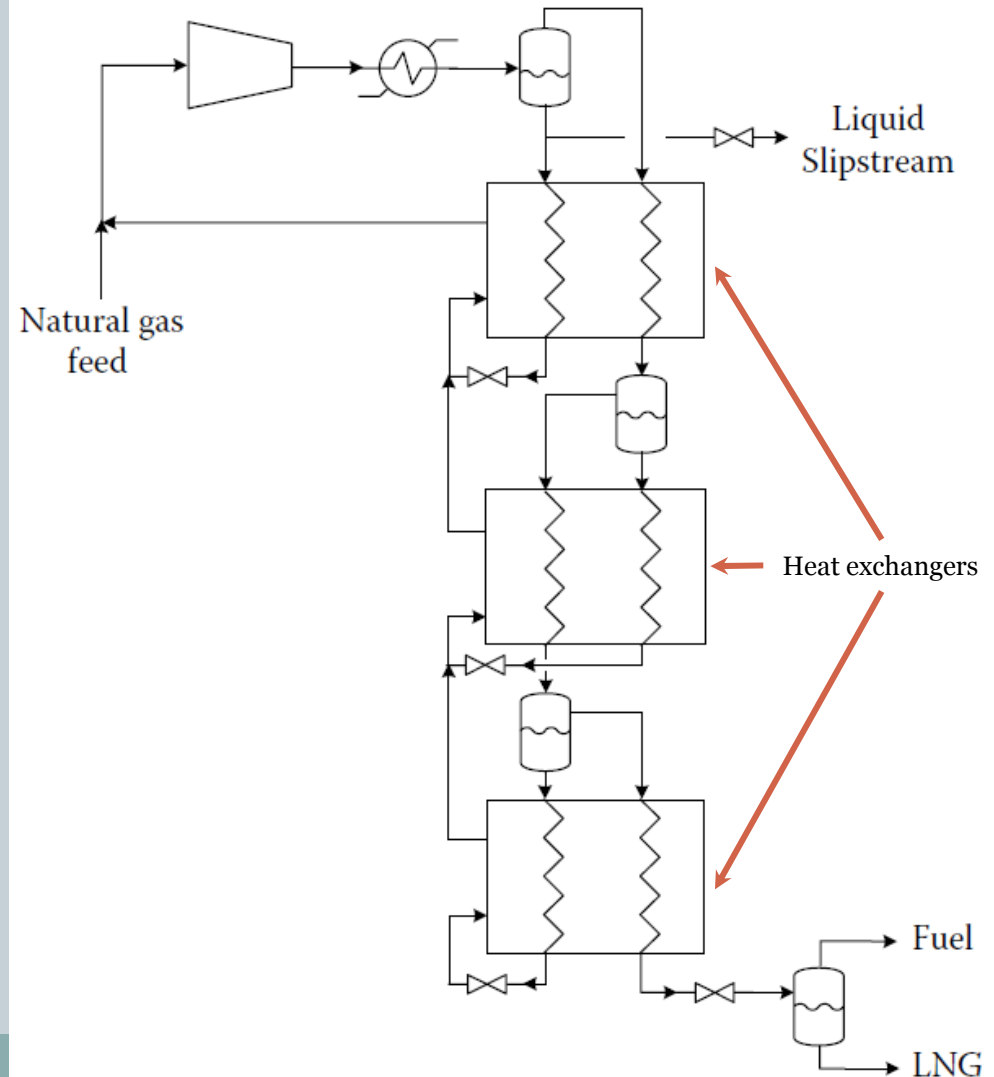[b] Engineering Data Book (2005a).
[c] McCartney (2005).

Propane cooling system
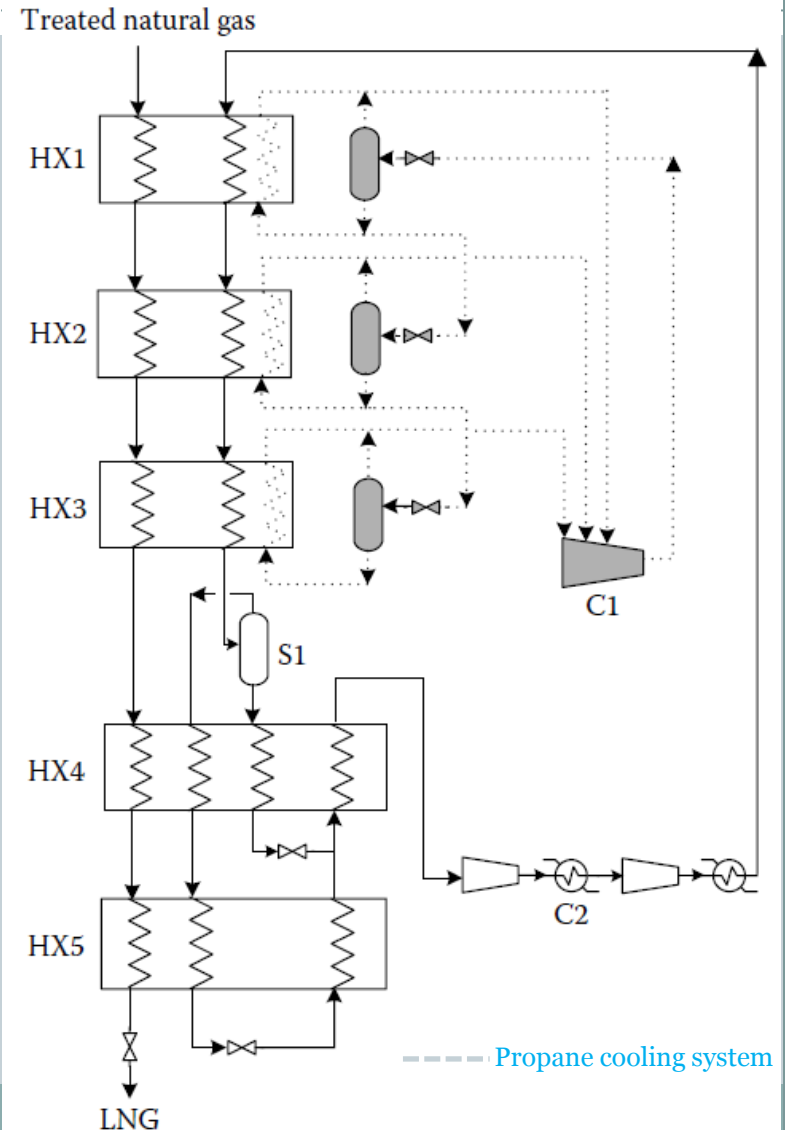
2. Mixed refrigerant cascade: open cycle

- NG stream mixed with refrigeration mix
- Mixing can be done: *before*, *during* or *after* compression
- Final separator divides NG into LNG & flash gas
- Flash gas used to power LNG plant
- Use of a single compressor is advantageous

Mixed refrigerant cascades

- Pros of MRC:
- – Use 1 compressor means:
  - Less complexity
  - Simple pipework
  - Simplification in instrumentation
- – Ability to alter the composition of the refrigerant mix
- – Adjusting the refrigerant mix promotes process optimization
- – Ease of extracting refrigerants from NG stream

- Cons:
- – Facilities for recovering, storing, & blending of refrigerants
- – Refrigerants are flammable but so is NG

Coolers (heat exchangers)

- Two main types of heat exchangers (HE): coil wound heat exchangers & plate-fin HE
- Coil wound (CWHE) can measure 5m in diameter & 70 m in length while weighing 300 tonnes
- Consist of thousands meters of tubing & can handle press. of 1,100 psig
- Note that it can take up to 30 months (ordering to installation)

Plate-fin heat exchangers (PFHE)

- Plate-fin HEs are less expensive than CWHE
- PHFE fabricated by more manufacturers (than CWHE)
- More popular than CHWE (because of few manufacturers for CWHE)

Thermodynamic calculations

Ideal cooling of NG (methane)

- Using the energy balance and mass conservation, the cooling load (Q) is

$$Q_{cool} = m_{out}h_{out} - m_{in}h_{in} \qquad (1)$$

where Q_{cool} is the cooling load (J or BTU), m_{in} & m_{out} is the mass in & out, h_{in} & h_{out} is the enthalpy in & out (J/kg)

- Since $m_{in}=m_{out}$ then $m_{in}=m_{out}=m$. Therefore, eqn(1):

$$\hat{Q}_{cool} = \frac{Q_{cool}}{m} \qquad (2)$$

$\hat{Q}_{cool}$: heat (cooling load)/unit mass (kJ/kg) [Unit cooling load]

- 'Newton's law of cooling' states that for a constant *heat transfer coefficient* (*U*), the rate of heat loss of a body is proportional to the difference in temperature btw the body & its surroundings:

$$\frac{dQ}{dt} = hA(T(t) - T_{env}) = hA\Delta T(t) \qquad (3)$$

Ideal cooling of NG (CH$_4$)

- Heat transfer coefficient (h$_c$) is the proportionality coefficient btw heat flux (heat flow per unit area, q=Q/A) & the thermodynamic driving force for the flow of heat (ie, temp. gradient, ΔT)

- Heat transfer during gas cooling is:

$$\dot{Q} = \frac{Q}{\Delta t} = U_c A \Delta T \qquad (4)$$

where U_c is overall heat transfer coefficient/unit mass (W/m²·C) and $\dot{Q}$ is the heat flux per unit mass (kJ/s)

Ideal vapor-compression cycle (2)

- Distinction btw reversible & ideal V-C cycles: the ideal VC cycle is not internally reversible
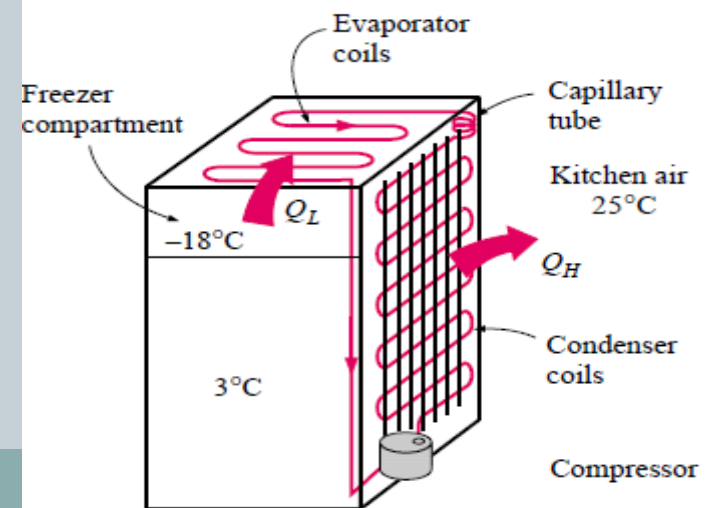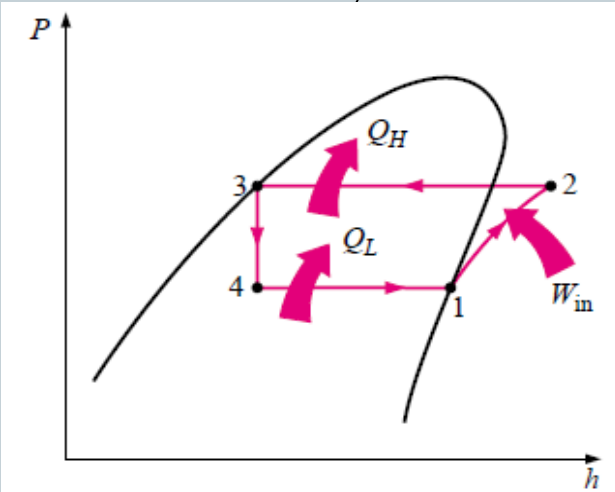- Refrigerant: ethyl ether
- Refrigerator:

$$COP_R = \frac{q_L}{W_{Net,in}} = \frac{h_1 - h_4}{h_2 - h_1}$$

- Heat pump:

$$COP_{HP} = \frac{q_H}{W_{Net,in}} = \frac{h_2 - h_3}{h_2 - h_1}$$
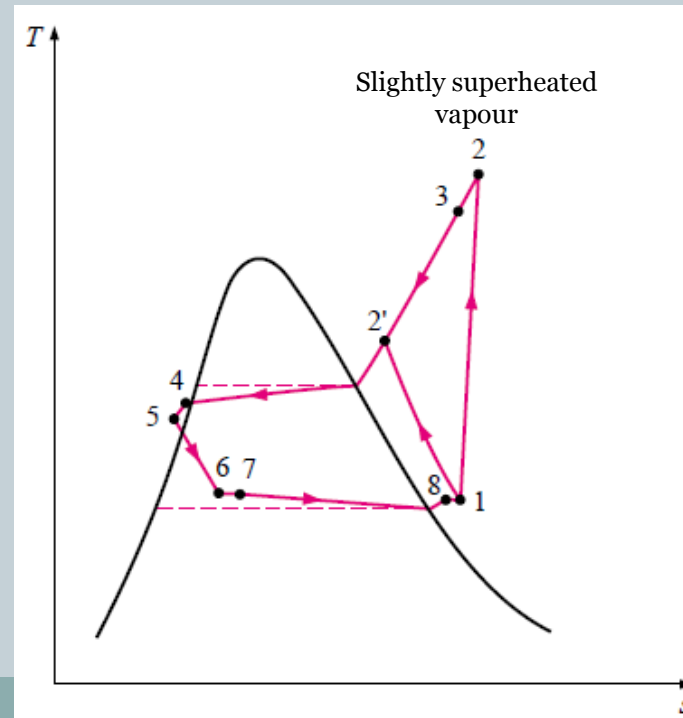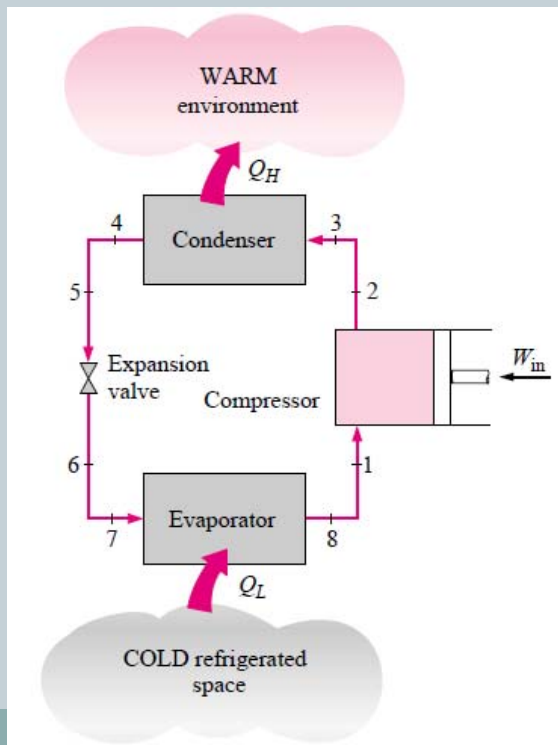
where $h_1 = h_{g@P_1}$ & $h_3 = h_{f@P_3}$

- h values read-off from refrigerant tables (eg, R-134a)

Actual vapor-compression cycle

- In reality, *irreversibilities* plaque the *ideal* VC cycle
  - Fluid friction (induces Δp)
  - Heat transfer *to* & *from* the surroundings

Coefficient of performance (*COP*)

- The efficiency of a refrigerator is expressed in terms of the coefficient of
- performance (*COP*) denoted by COP_R:

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{net,in}} \qquad (6)$$

- The COP of a refrigerator (or heat pump) which operates on the reversed Carnot cycle is termed a **Carnot refrigerator (or a Carnot heat pump)**. The refrigerator efficiency is given by:
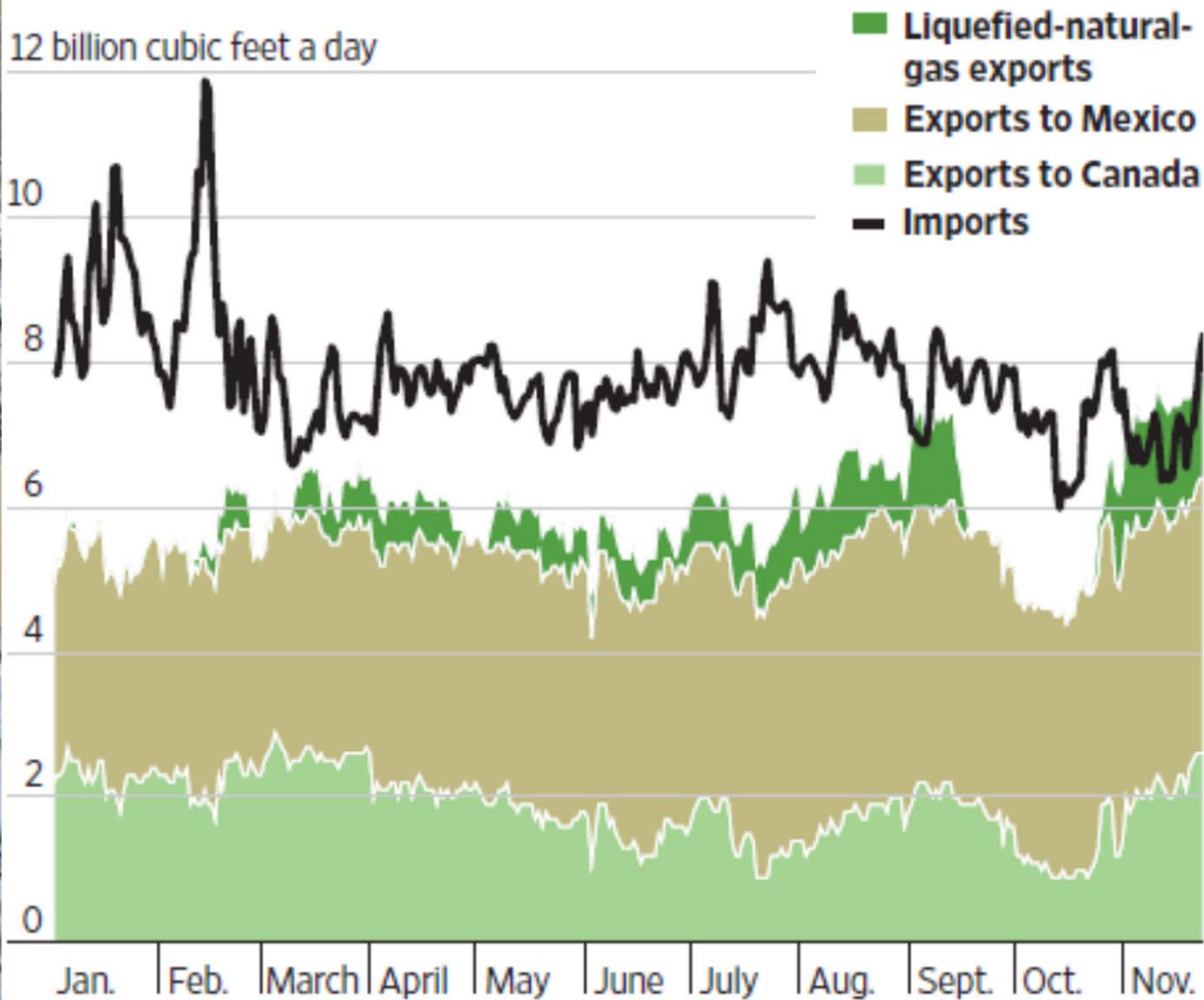
$$COP_R = \frac{1}{Q_H/Q_L - 1}$$

where Q_L is amount of heat absorbed from the low-temperature medium & Q_H *is the amount of heat rejected to the high-temp medium.* For a reversible refrigerator:

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1}$$

$$(7)$$

US a net exporter of natural gas

Natural-gas imports and exports

12 billion cubic feet a day

Legend:
- Liquefied-natural-gas exports
- Exports to Mexico
- Exports to Canada
- Imports

rrier ship in Sabine Pass, Texas

*Through August

882.5 billion cubic feet

| India | 10.2 |
| Other | 29.8 |

Includes Brazil, Portugal, Kuwait, Jordan, United Arab Emirates, China, Dominican Republic, Barbados and others

Sources: Energy Information Administration (data);

Choosing among liquefaction processes

- Note that several of "off the shelf" refrigeration cycles are licensed
- Licensors include: Shell, ConocoPhillips, Air Products CI
- Complicated exercise which factors in:
  - LNG plant throughput (e.g., MTPA)
  - Local (ambient) conditions
  - Gas composition & reserve size
- Trend towards large "trains" (8 mtpa≈ 1.2bcf/d)

Choosing among liquefaction cycles (2)

- Nearly always trade-off between CAPEX & plant efficiency
- Ease of start-up
- Ability to manage changes in feedstock compositions
- Maintenance costs
- Safety considerations
- Previous experience (where it exists)

NG liquefaction costs

- ≈10% of the NG received by an LNG plant is used to condense the gas
- Refrigeration & liquefaction account for:
  - About 35-45% of CAPEX (20-30% of total project costs incl. regas + LNG ships)
  - Around 50% of the plant operating costs
- Why is it so expensive?
  - High cost of steel
  - Often LNG plants are built at remote locations
  - Strict design & safety levels
  - Large volumes of refrigerants are used
  - Redundancy alleviates risk of breakdowns but comes at a cost
  - Greenfields (vs. brownfields) come at a higher cost
- Cost offsets:
  - Exploit economies of scale i.e., larger liquefaction plants

Thanks for your attention!