Hydrogen and Fuel Cells

Fundamentals of cryogenic engineering: liquefaction processes

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Liquefaction processes

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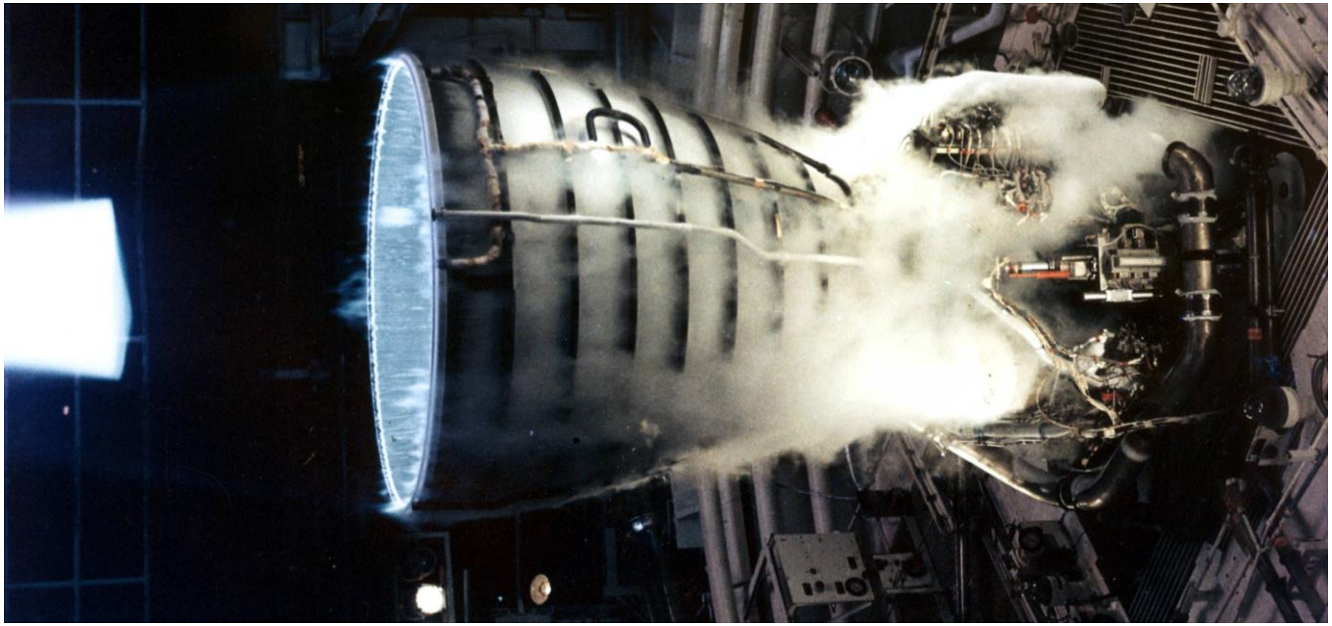
02 Thermodynamic processes at cryogenic temperatures

03 Cryogenic liquefaction processes

04 Exercises with Python and Coolprop

1. Introduction to the cryogenic engineering



The history of cryogenic engineering

1877

Oxygen liquefaction

Engineer Cailletet, expansion of oxygen at 300 atm

1885

Air liquefaction

In Germany, **engineer Linde** patented the first air liquefaction plant

1892

Vacuum double-walled containers

In London, **physicist Dewar** developed the first vacuum jacketed double-walled containers

1907

Neon cryogenic distillation

Engineer Claude achieved the first cryogenic distillation of neon from air separation

1961

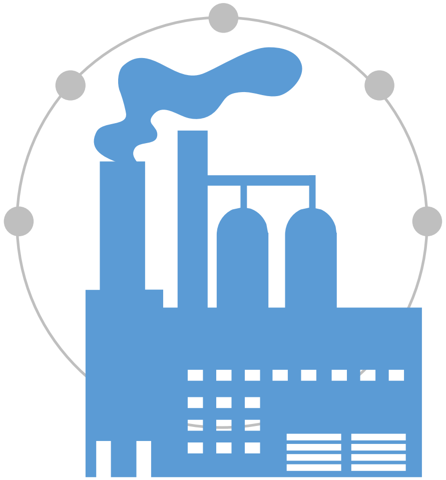
Saturn V

First spacecraft fuelled by both liquid hydrogen and oxygen

Applications of cryogenic engineering

Fuels for transport sectors

In addition to being transported as energy carrier, some cryogenic fluids can be used as fuels. They can be stored in liquid form at low pressure, providing good energy density. Currently, the use of LNG in road and maritime vehicles is widespread. Excellent possibilities lie in the use of LH_2, which would allow the reduction of carbon dioxide emissions.



Aerospace industry

Spacecraft currently use cryogenic fuels for space propulsion. Research focuses on efficiency, robustness, miniaturization and reliability.

Cryobiology

Application on surgery, cryopreservation of embryos and gametes, or the preservation of tissues and blood components

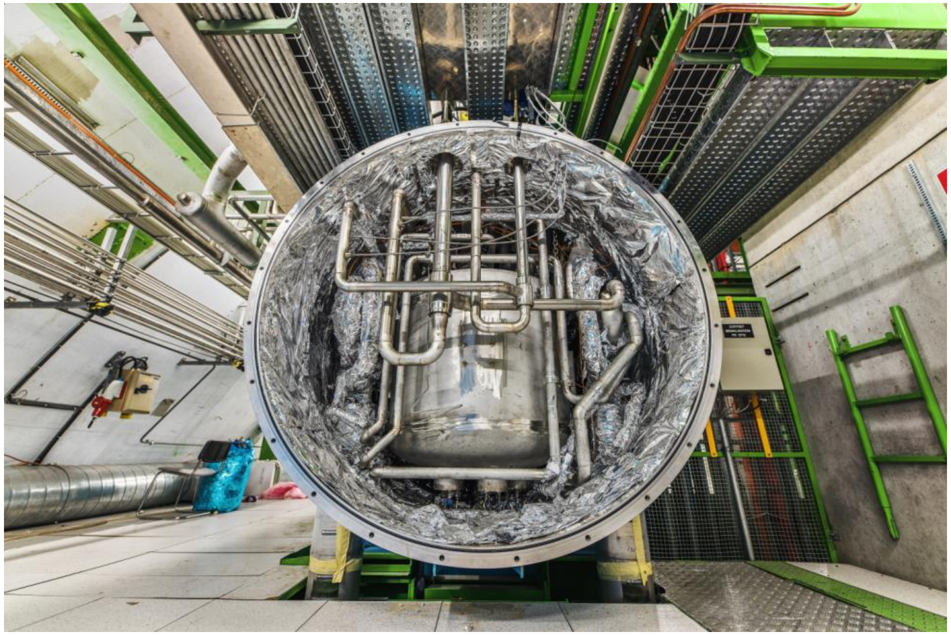
Metallurgy

Some materials are treated with low-temperature hardening processes to improve their physical-technological characteristics.

Superconductivity

At cryogenic temperatures, some materials exhibit negligible electrical resistance. Thanks to these properties, new systems for electrical transmission, high-speed computers and better communication systems are being developed.

2. Thermodynamic processes at cryogenic temperatures



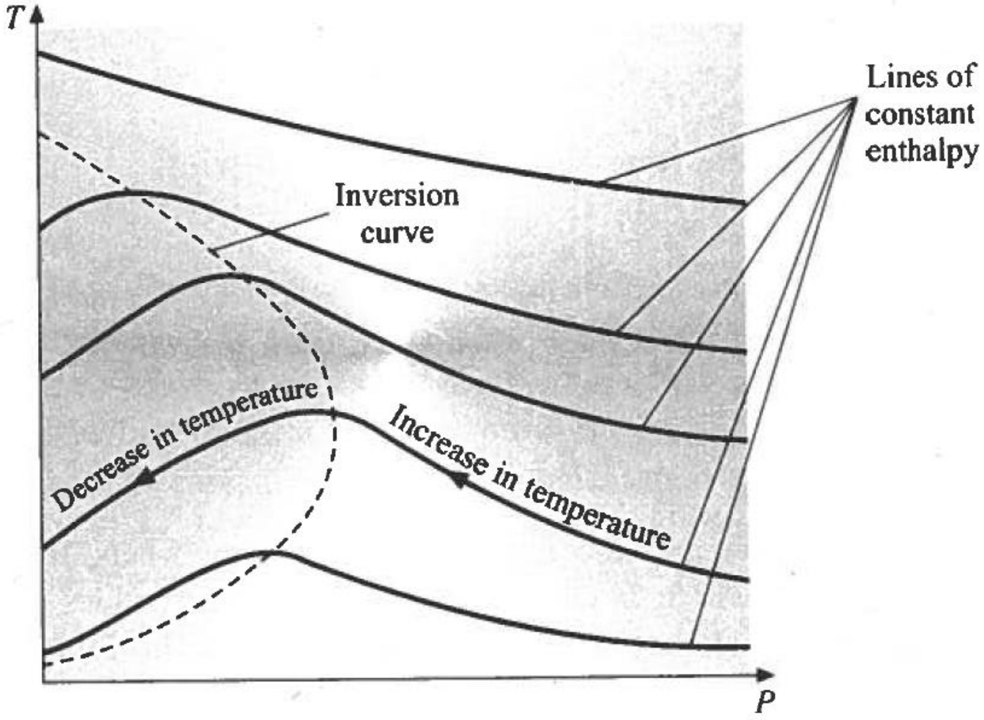
Expansion of Joule-Thomson

Gaseous fluid is subjected to an isenthalpic expansion through a semi-closed orifice or valve. No work is produced but there is an increase in net entropy. Joule-Thomson expansion is usually used in refrigeration cycles to lower the temperature of a gas stream that is proportional to the pressure drop.

Isenthalpic expansion:

Joule-Thomson coefficient

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_h$$



Expansion of Joule-Thomson

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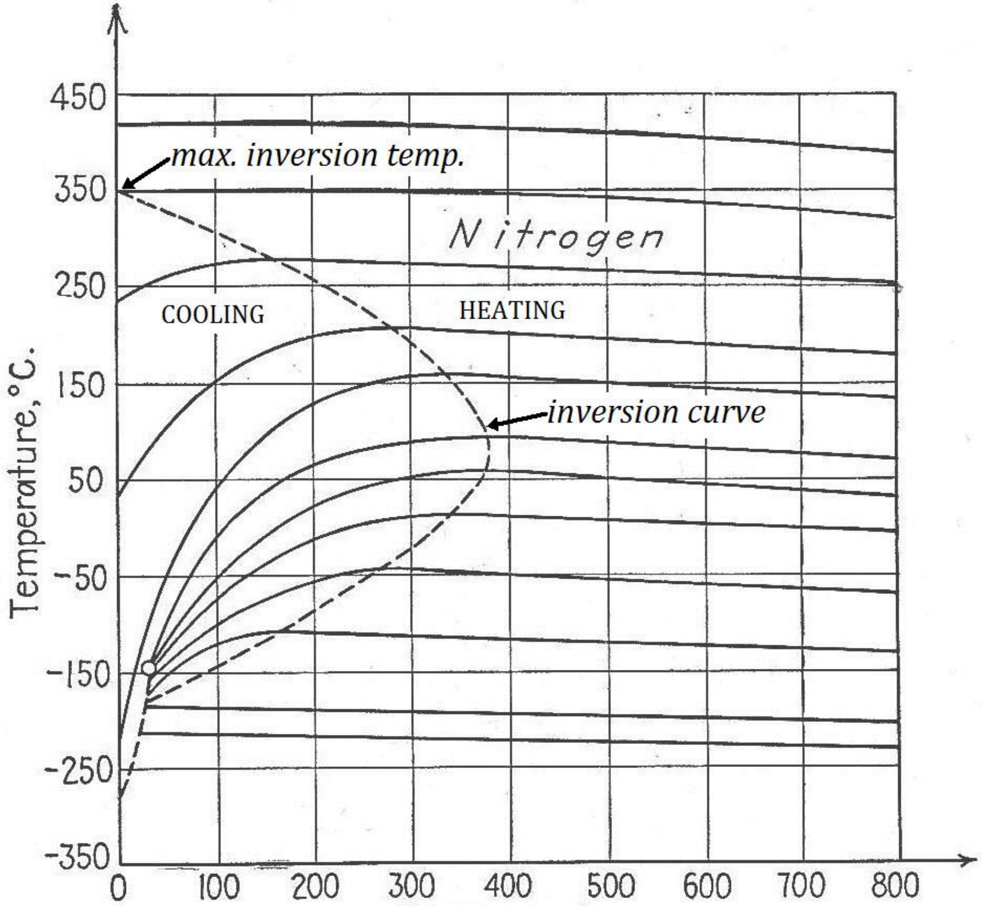
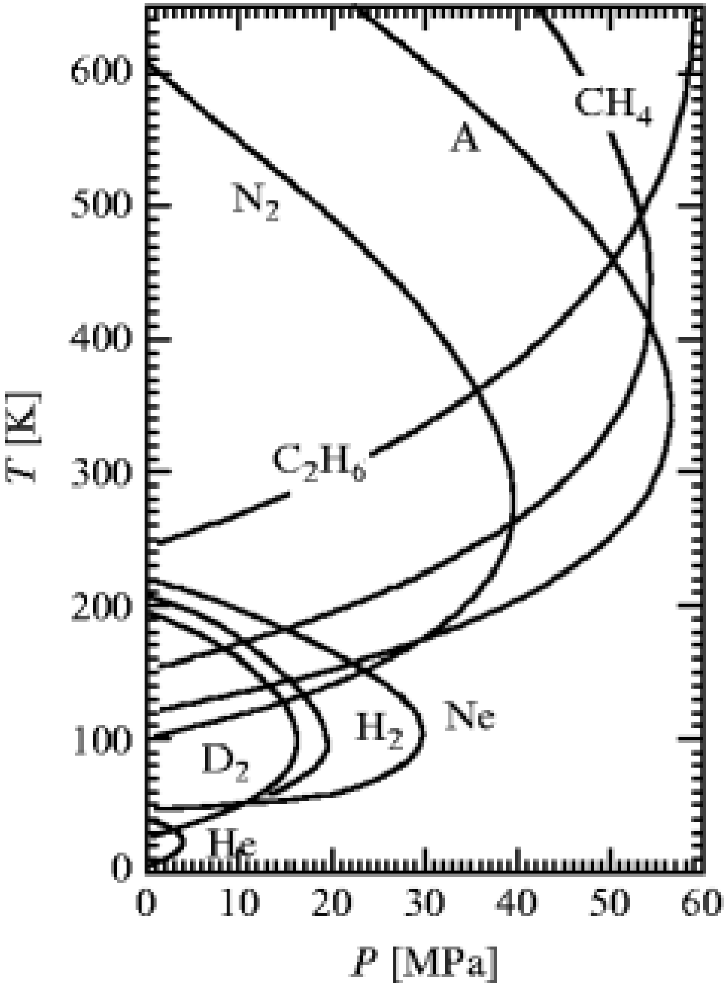


Isenthalpic curves and inversion curve for nitrogen

Expansion of Joule-Thomson

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_h$$

Gas	Maximum Inversion Temperature [K]
Helium-4	45
Hydrogen	205
Neon	250
Nitrogen	621
Air	603
Carbon monoxide	652
Argon	794
Oxygen	761
Methane	939
Carbon dioxide	1500
Ammonia	1994



Expansion of Joule-Thomson

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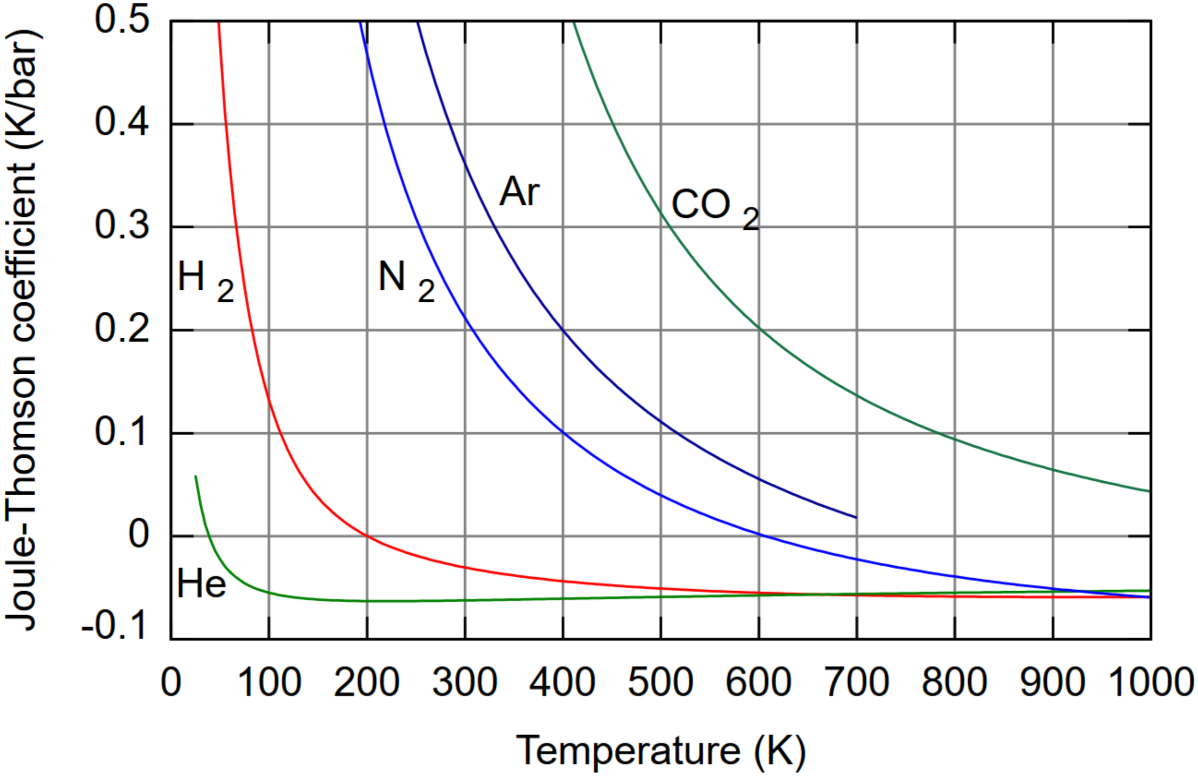
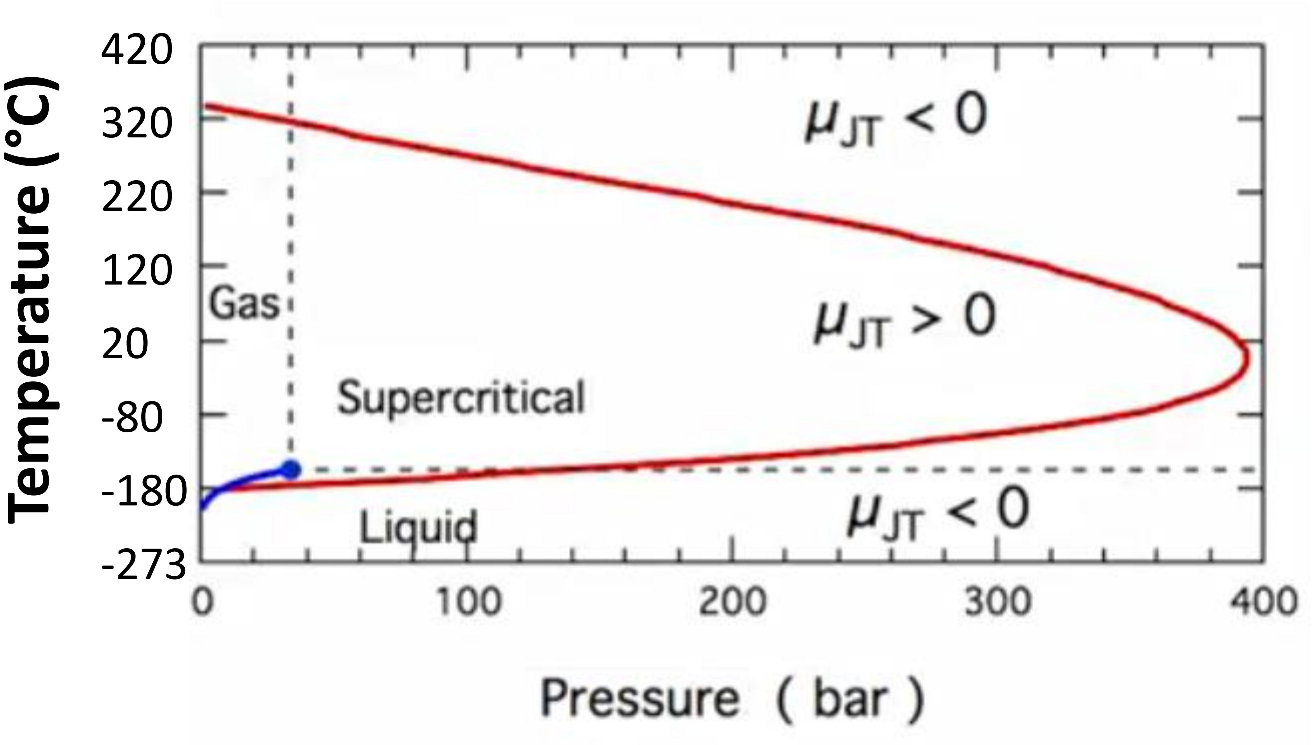


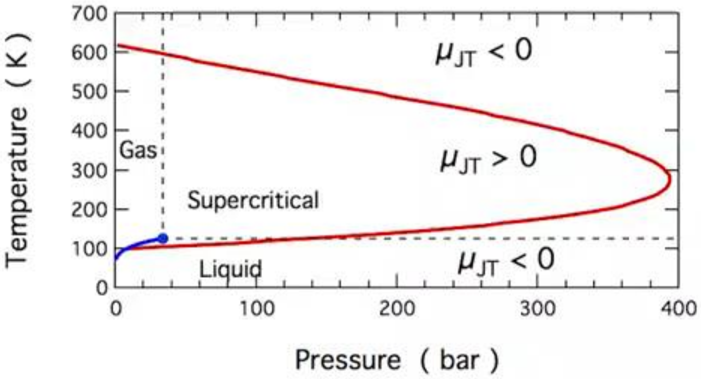
Expansion of Joule-Thomson



Expansion of Joule-Thomson

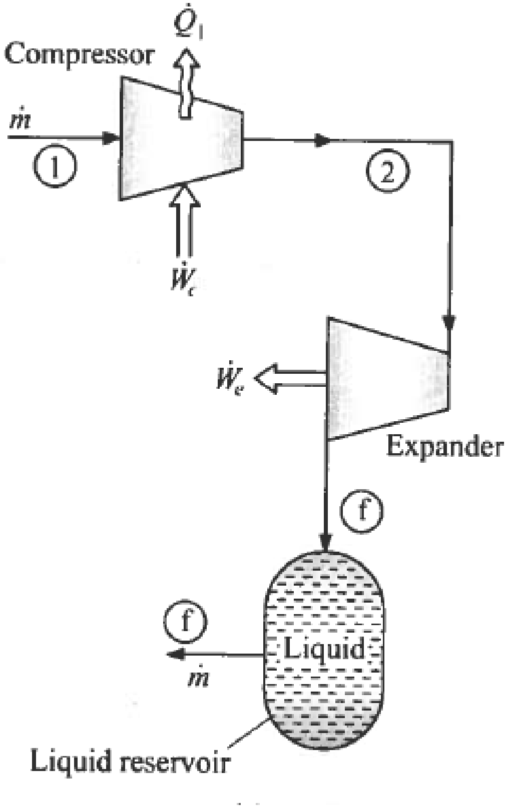
p_{in} = 62 bar
T_{in} = 27 °C
p_{fin} = 14 bar
T_{fin} = -1 °C

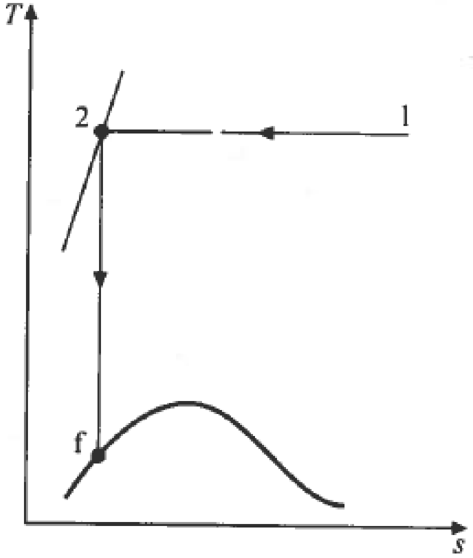
Δp = 7 bar → ΔT = 4 °C



3. Cryogenic liquefaction processes

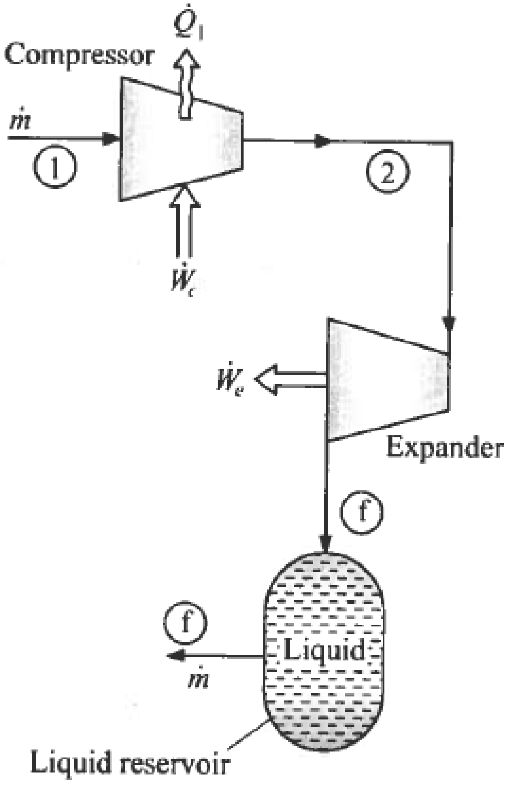
The ideal liquefaction system

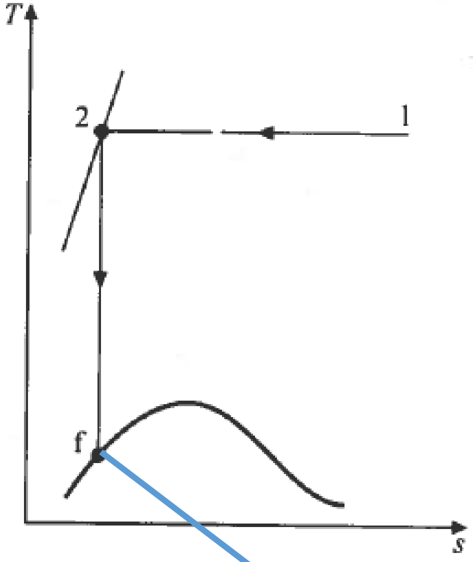




1-2: Isothermal compression;
2-f: Isentropic expansion;

The ideal liquefaction system

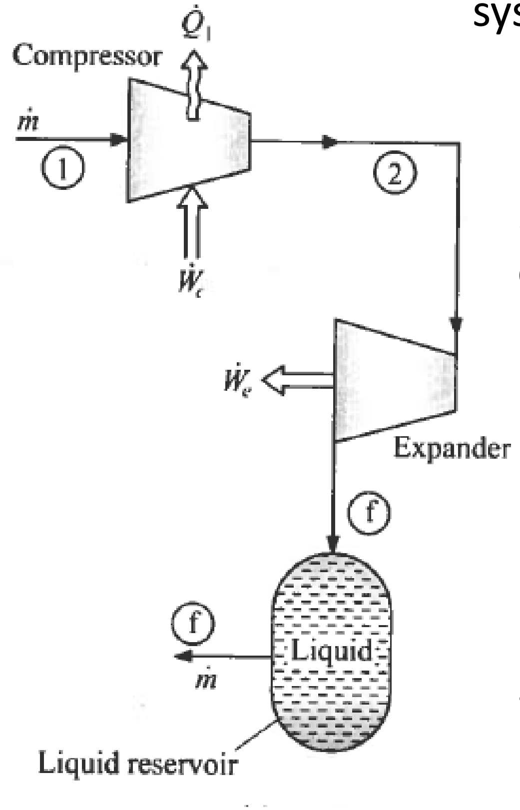




Point f is on the saturated fluid curve, the gas flow rate entering the expander is completely liquefied

1-2: Isothermal compression;
2-f: Isentropic expansion;

The ideal liquefaction system



1) Using first and second principles of thermodynamics for open systems and constant, continuous gas flow, we obtain:

$$\dot{Q} - \dot{W}_i = \sum(\dot{m}_0 * h_0) - \sum(\dot{m}_i * h_i)$$

2) Heat transferred Q for an isothermal and reversible process is defined as:

$$\dot{Q} = \dot{m} * T_1 * (s_2 - s_1)$$

$$\Downarrow$$

$$\dot{m} * T_1 * (s_2 - s_1) - \dot{W}_i = \dot{m} * (h_f - h_1)$$

3) The ideal work per unit flow rate is equal to:

$s_2 = s_f$ → Isentropic expansion

$$-\frac{\dot{W}_i}{\dot{m}} = T_1 * (s_1 - s_f) - (h_1 - h_f)$$

Minimum work for liquefaction

F.O.M. (Figure Of Merit) = calculated as the ratio of ideal liquefaction work to real work

$$\boxed{FOM = \frac{W_i}{W_l}}$$

The ideal work is used as a reference to improve the performance of real liquefaction systems.

$$-W_i = T_0 * \left(s_1 - s_f\right) - \ (h_1 - h_f)$$

T_0 = Ambient temperature

The actual work will be much greater than the ideal work due to thermodynamic limitations and process irreversibility.

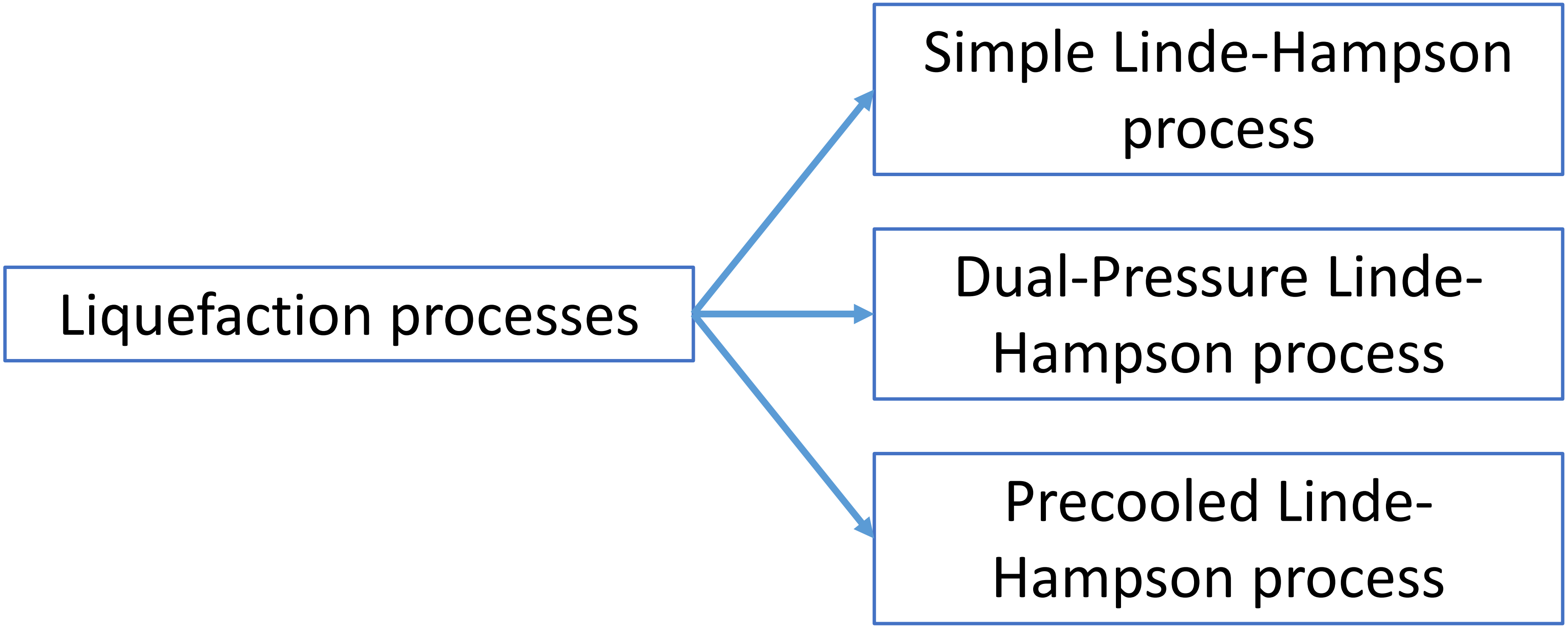
Properties of cryogenic fluids

Objective: to describe the refrigeration processes and systems available for low-temperature production from ambient conditions to temperatures below -150°C..

Fluid	Boiling point (K)	Min. liquefaction work (@ 1 atm)		Min. liquefaction work (@ 1 atm) (kJ/kg)
		Sensible heat	Latent heat	
		(kJ/kg)		
Helium	3.19	-	-	8389
Hydrogen	**20.27**	**6100**	**6090**	**12190**
Neon	27.09	482	859	1341
Nitrogen	77.36	197	580	777
Air	78.8	-	-	739
Argon	87.28	-	-	479
Oxygen	90.18	133	498	631
Methane	**111.7**	**277**	**870**	**1147**
Ethylene	169.4	75	396	471
Ethane	184.5	-	-	353

Liquefaction process for nitrogen, argon and oxygen

These processes are based on the use of Joule-Thomson expansion, efficiently exploiting the heat exchange between flows at different temperatures. J-T expansion facilitates lowering the temperature below the limit imposed by the J-T coefficient. For this reason, some gases must be pre-cooled before throttling (expanded).



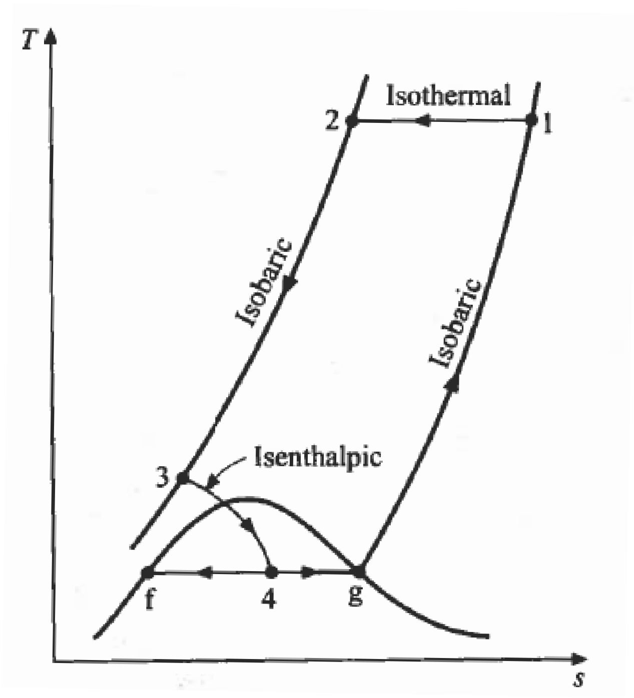
Liquefaction processes

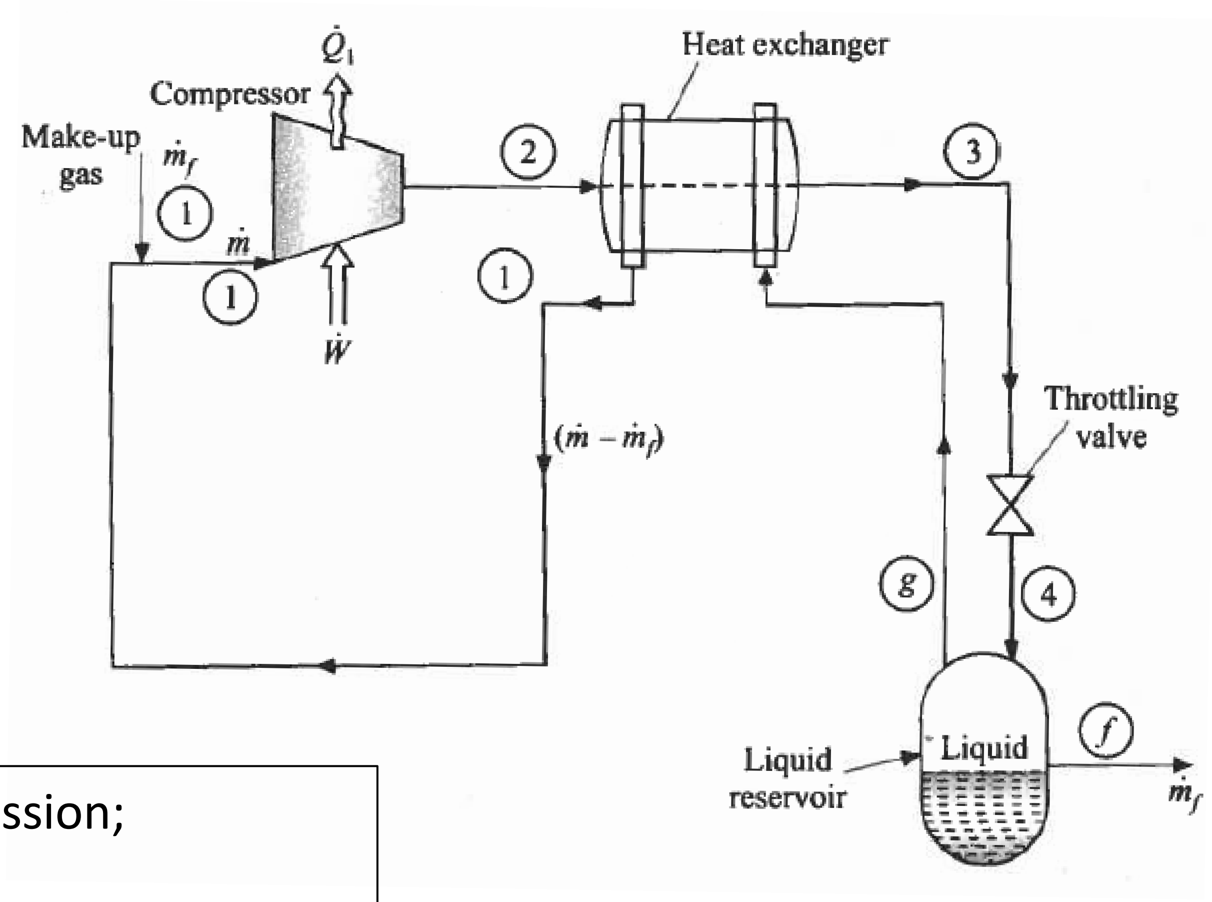
Simple Linde-Hampson process

Dual-Pressure Linde-Hampson process

Precooled Linde-Hampson process

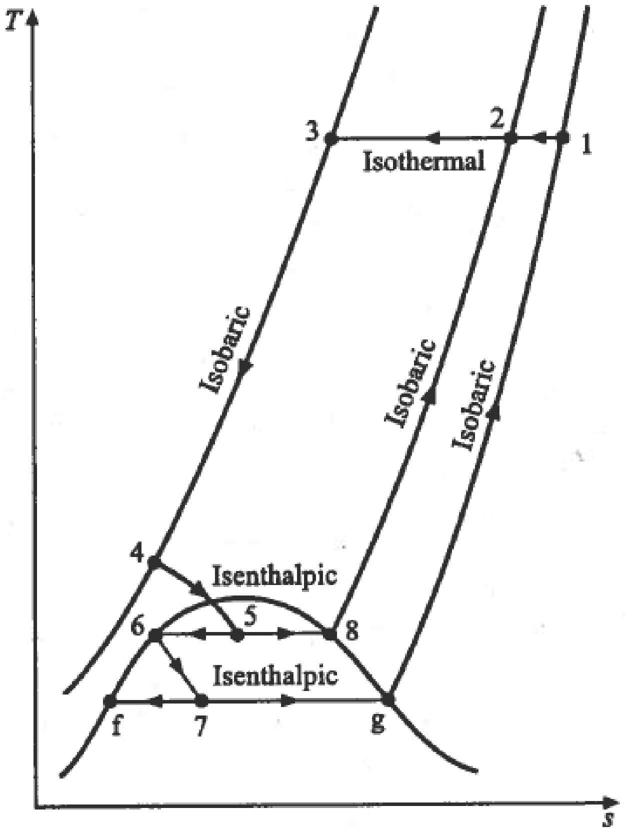
Simple Linde-Hampson process

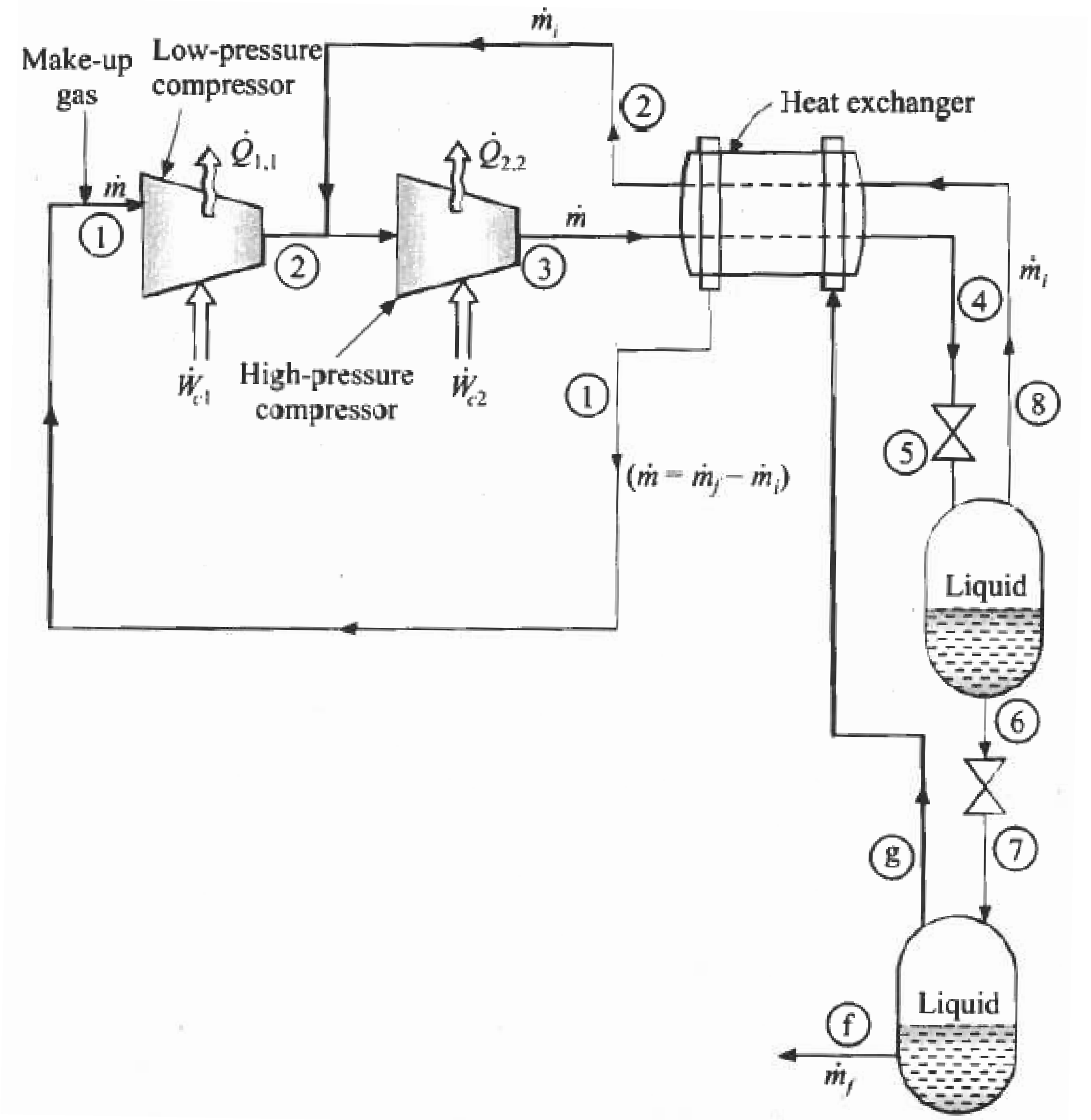




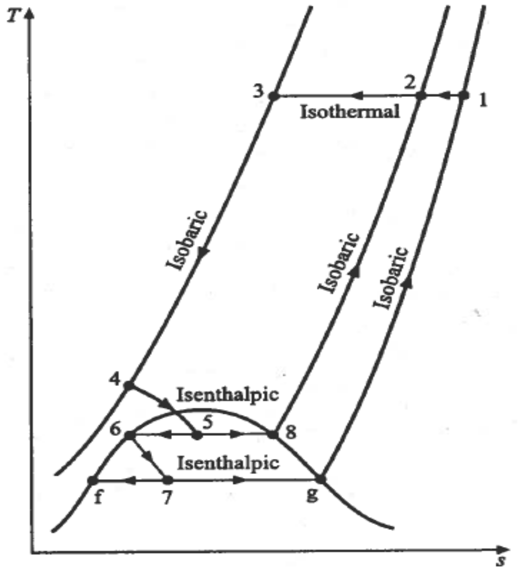
1-2: Isothermal compression;
2-3: Pre-cooling;
3-4: Isentalpic throttling;
4-g: Saturated vapour separation;
4-f: Saturated liquid separation;
g-1: Heat exchanger.

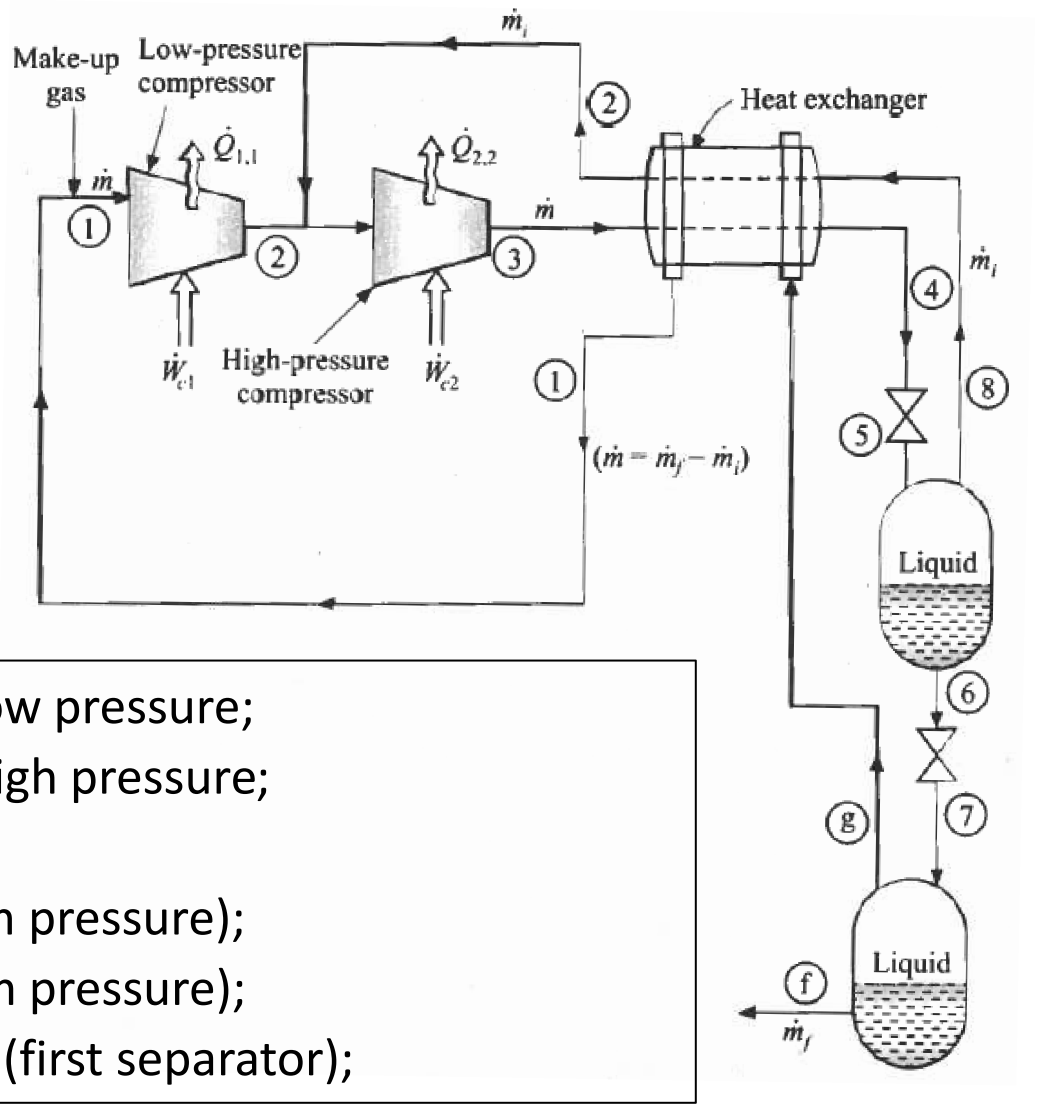
Dual-Pressure Linde-Hampson process





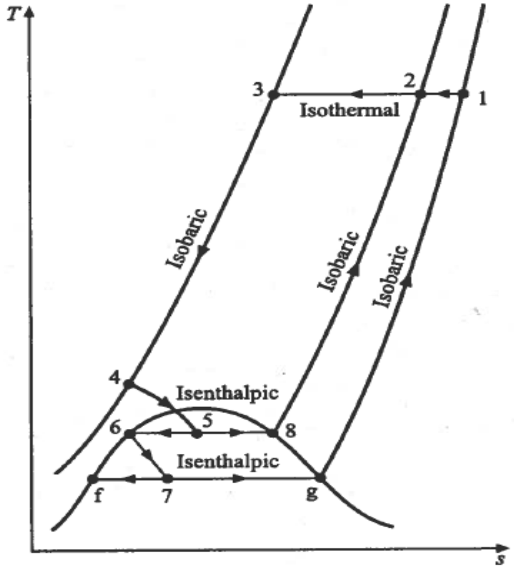
Dual-Pressure Linde-Hampson process

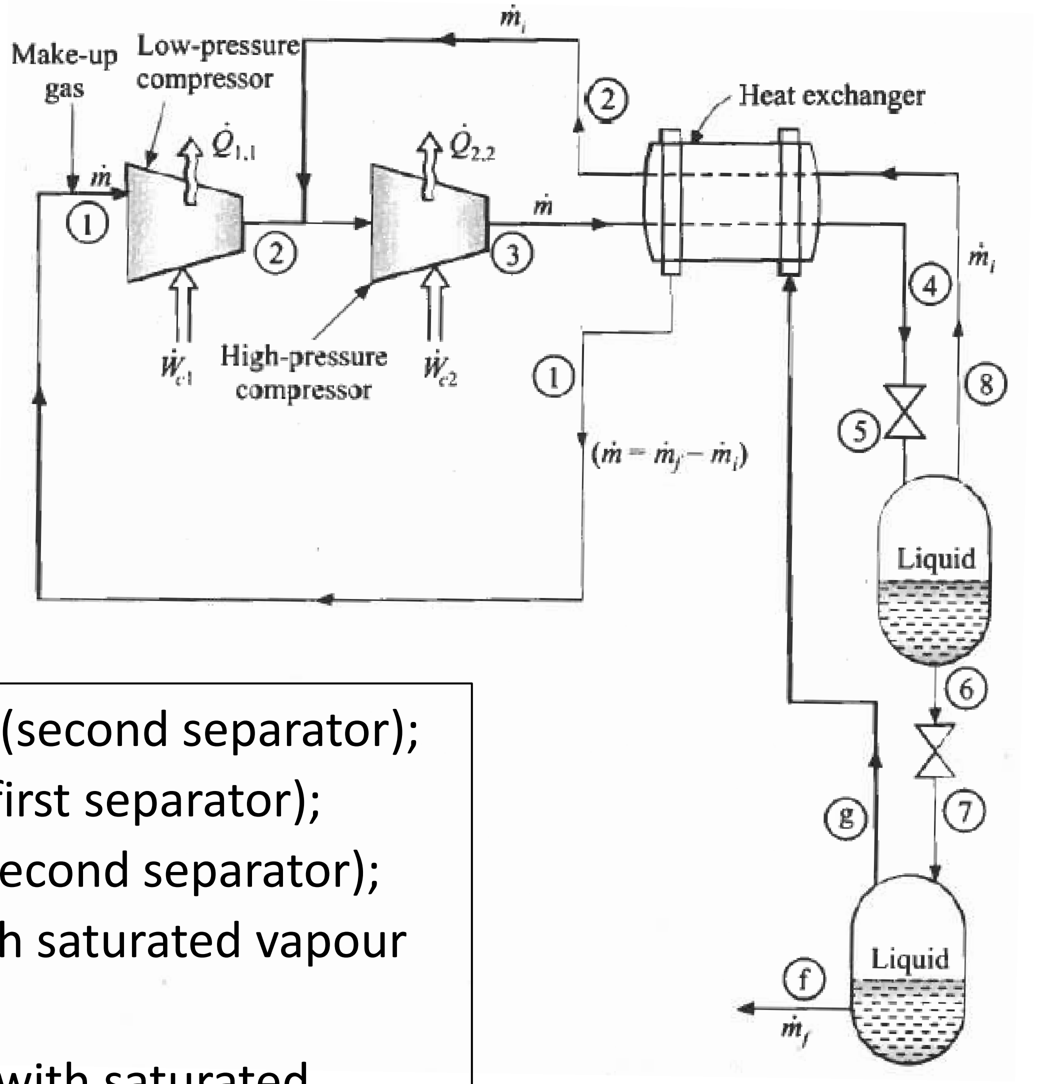




- **1-2**: Isothermal compression at low pressure;
- **2-3**: Isothermal compression at high pressure;
- **3-4**: Pre-cooling;
- **4-5**: First throttling valve (medium pressure);
- **6-7:** Second throttling valve (room pressure);
- **5-8**: Saturated vapour separation (first separator);

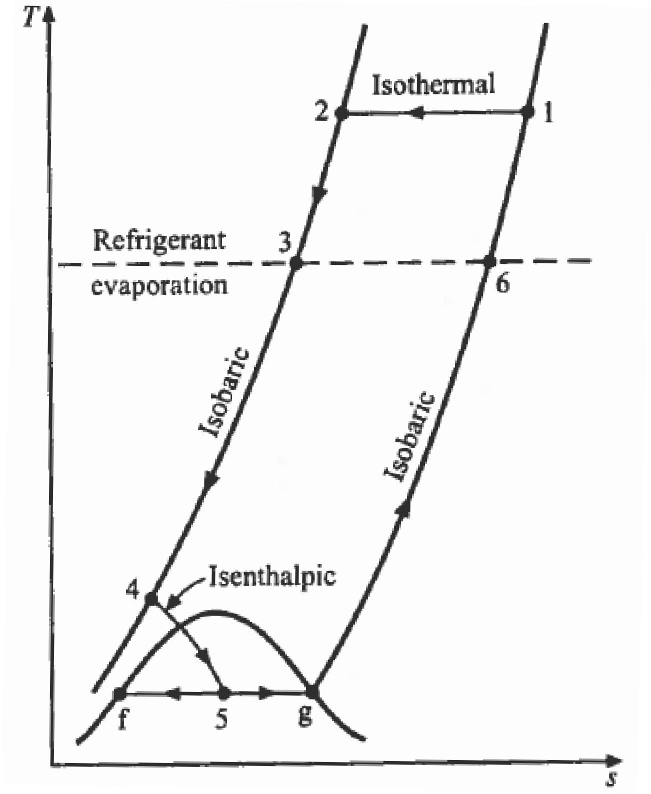
Dual-Pressure Linde-Hampson process

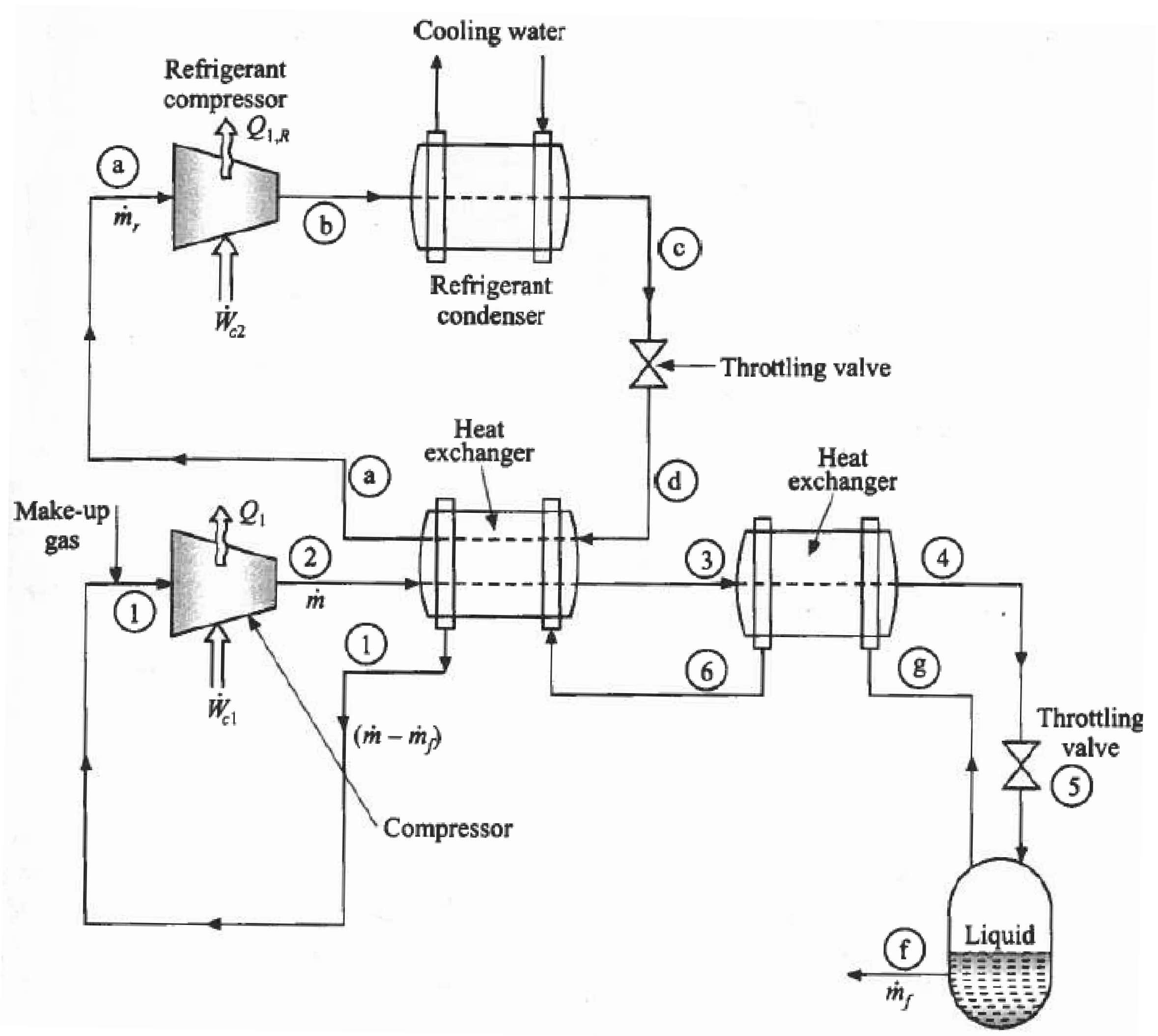




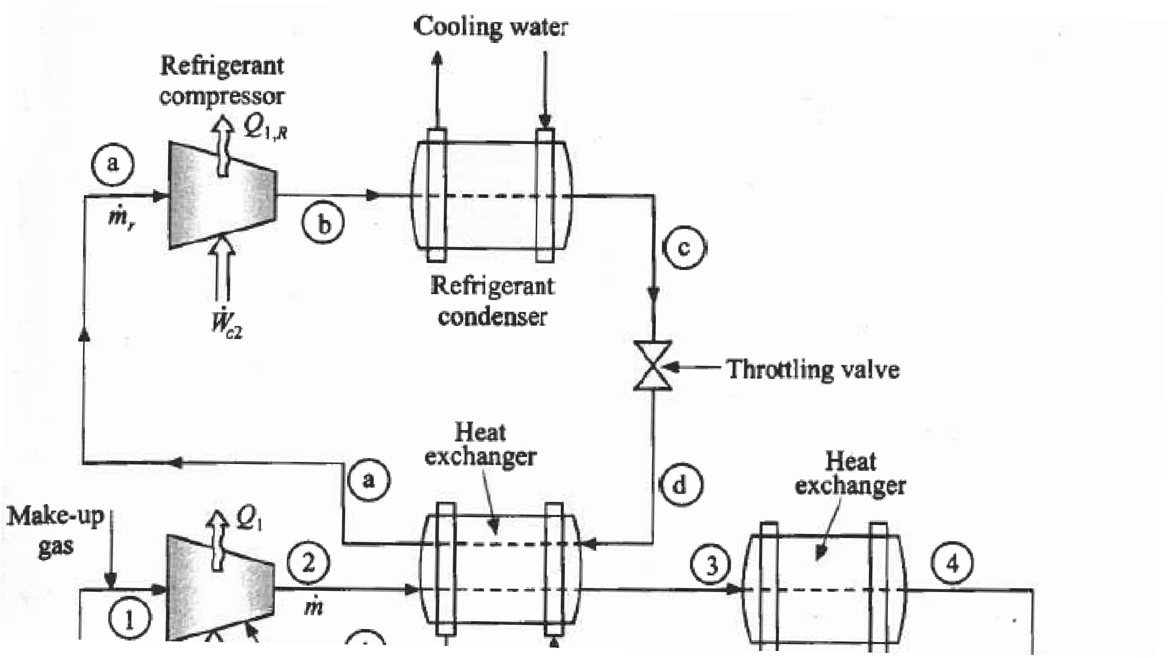
- **7-g**: Saturated vapour separation (second separator);
- **5-6**: Saturated liquid separation (first separator);
- **7-f**: Saturated liquid separation (second separator);
- **g-1**: Cooling at room pressure with saturated vapour from 3-4;
- **8-2:** Cooling at medium pressure with saturated vapour from 3-4;

Precooled Linde-Hampson process



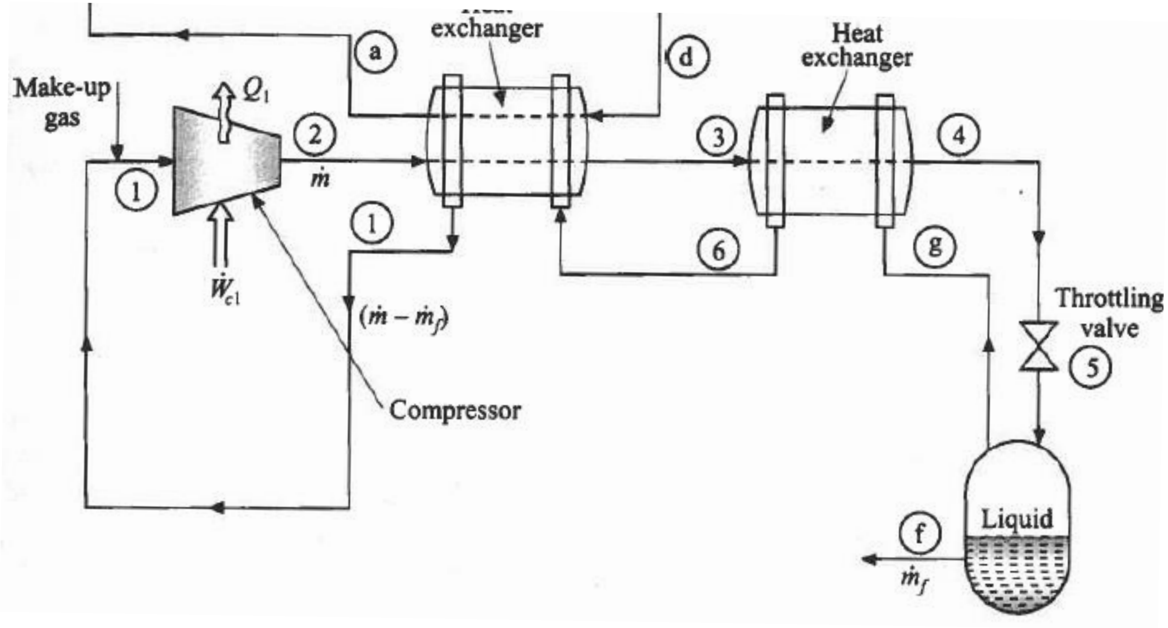


Precooled Linde-Hampson process



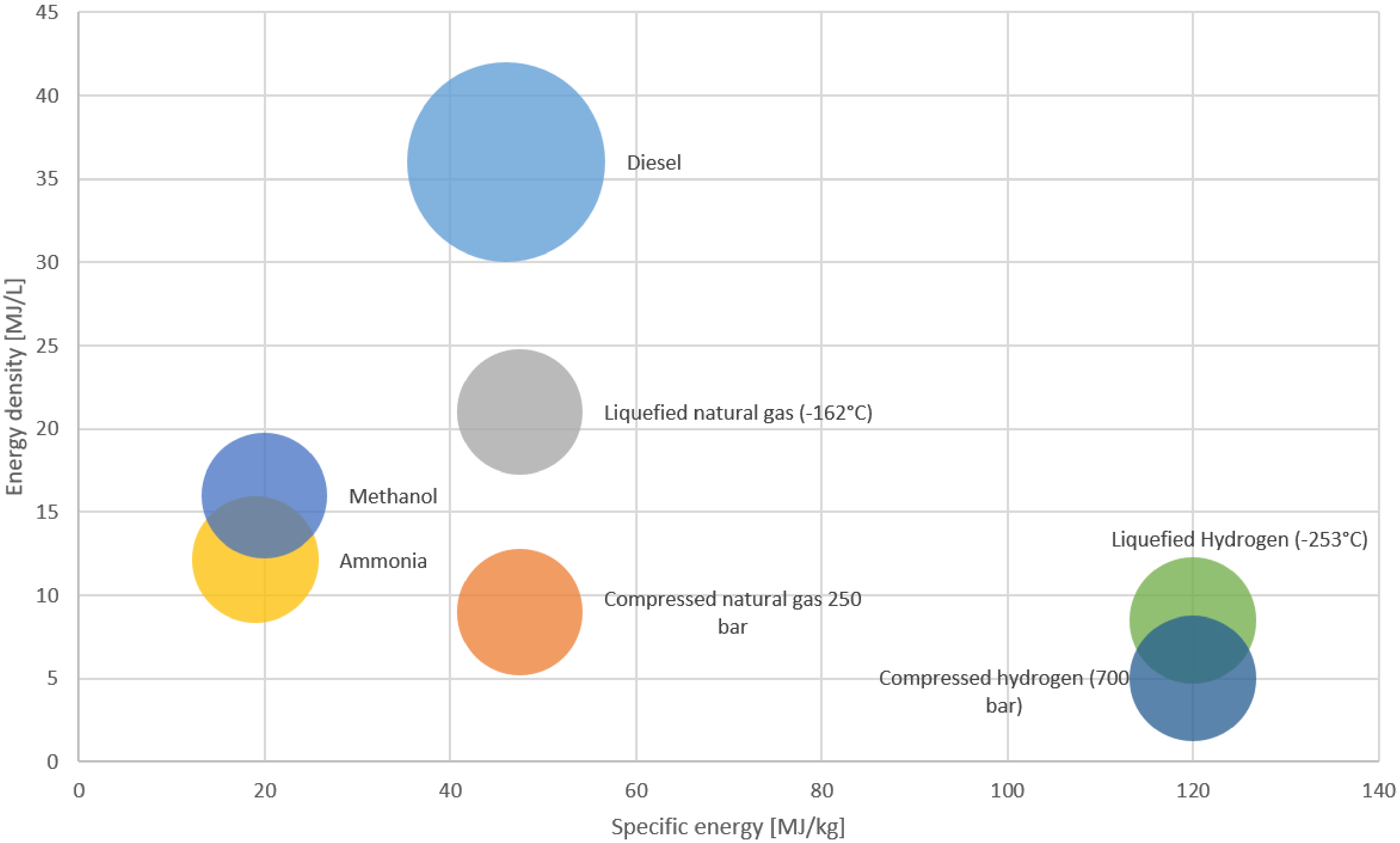
- **a-b**: Compression;
- **b-c**: pre-cooling process with cold water;
- **c-d**: Isentalpic throttling (J-T);
- **d-a**: Evaporating the refrigerant to pre-cool the gas 2 to 3;

Precooled Linde-Hampson process



- **1-2**: Isothermal compression;
- **2-3**: First pre-cooling exchanger;
- **3-4**: Second pre-cooling exchanger;
- **4-5**: Isenthalpic throttling;
- **5-f(g)**: Separation of saturated liquid (vapour);
- **g-1**: Saturated vapour pre-cooling;

Hydrogen



Diesel
Liquefied natural gas (-162°C)
Methanol
Ammonia
Compressed natural gas 250 bar
Liquefied Hydrogen (-253°C)
Compressed hydrogen (700 bar)
Energy density [MJ/L]
0
5
10
15
20
25
30
35
40
45
Specific energy [MJ/kg]
0
20
40
60
80
100
120
140

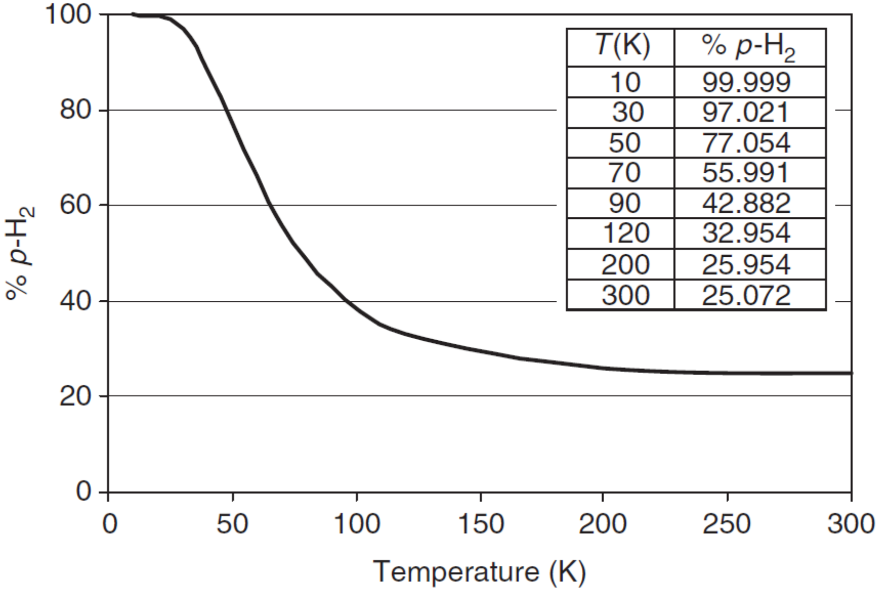
Liquefaction of Hydrogen

1. **Maximum inversion temperature of 204 K:**
   - Cooling from external source required before throttling;

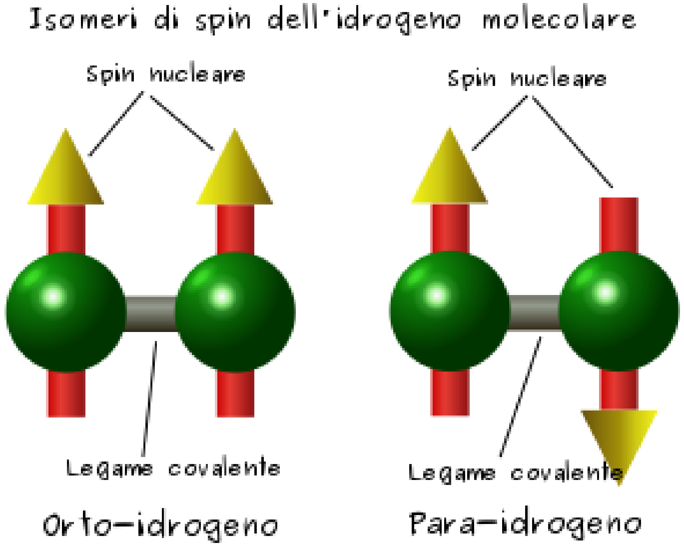
2. **Contains volatile impurities that must be extracted:**
   - For example, methane, oxygen and nitrogen.
   - Silica gel or activated carbon can be used to extract them at a temperature around below 77 K.

3. **Conversione da orto-idrogeno a para-idrogeno:**
   - **Slow**, it will be necessary the use of metal catalysts (chromium oxide in an aluminum support or granular iron hydroxide gel);
   - **Exothermic**, it will be necessary to extract heat at low temperature.

Orto- and para-hydrogen



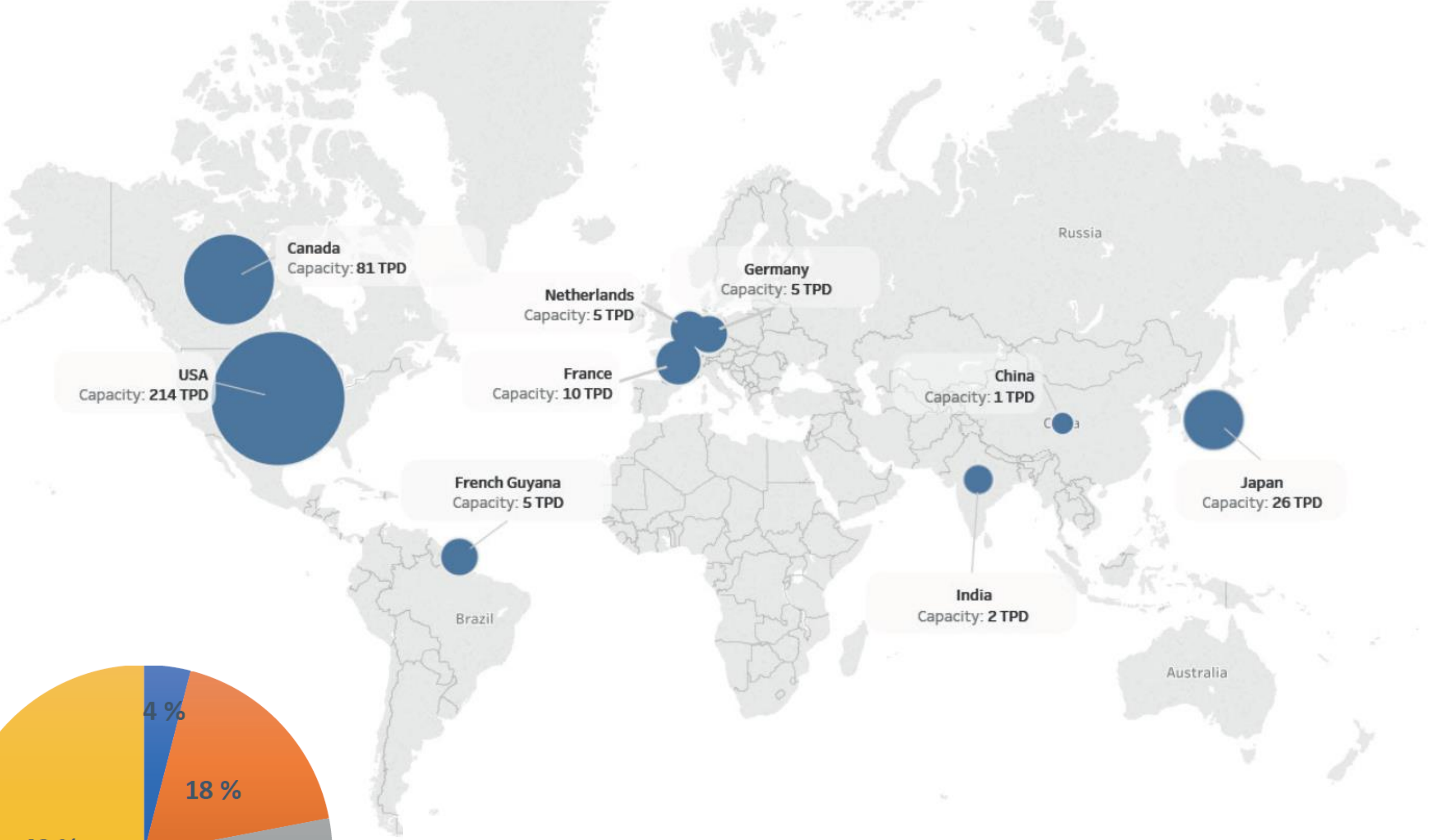
T(K)	% p-H_2
10	99.999
30	97.021
50	77.054
70	55.991
90	42.882
120	32.954
200	25.954
300	25.072

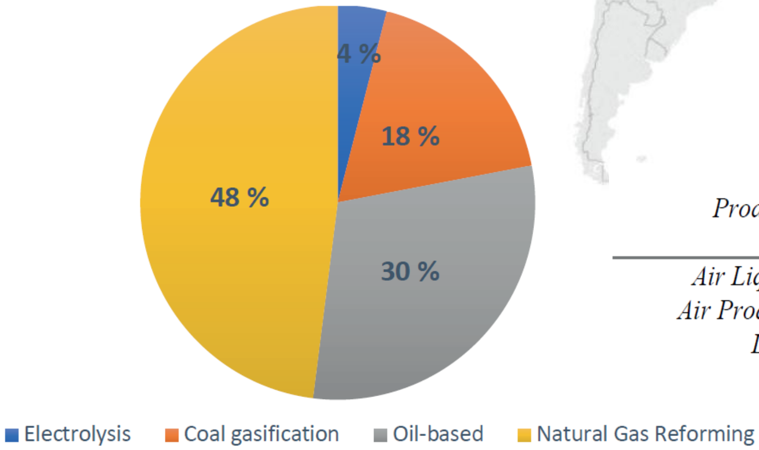


3. Conversione da orto-idrogeno a para-idrogeno:

- **Slow**, it will be necessary the use of metal catalysts (chromium oxide in an aluminum support or granular iron hydroxide gel);
- **Exothermic**, it will be necessary to extract heat at low temperature.

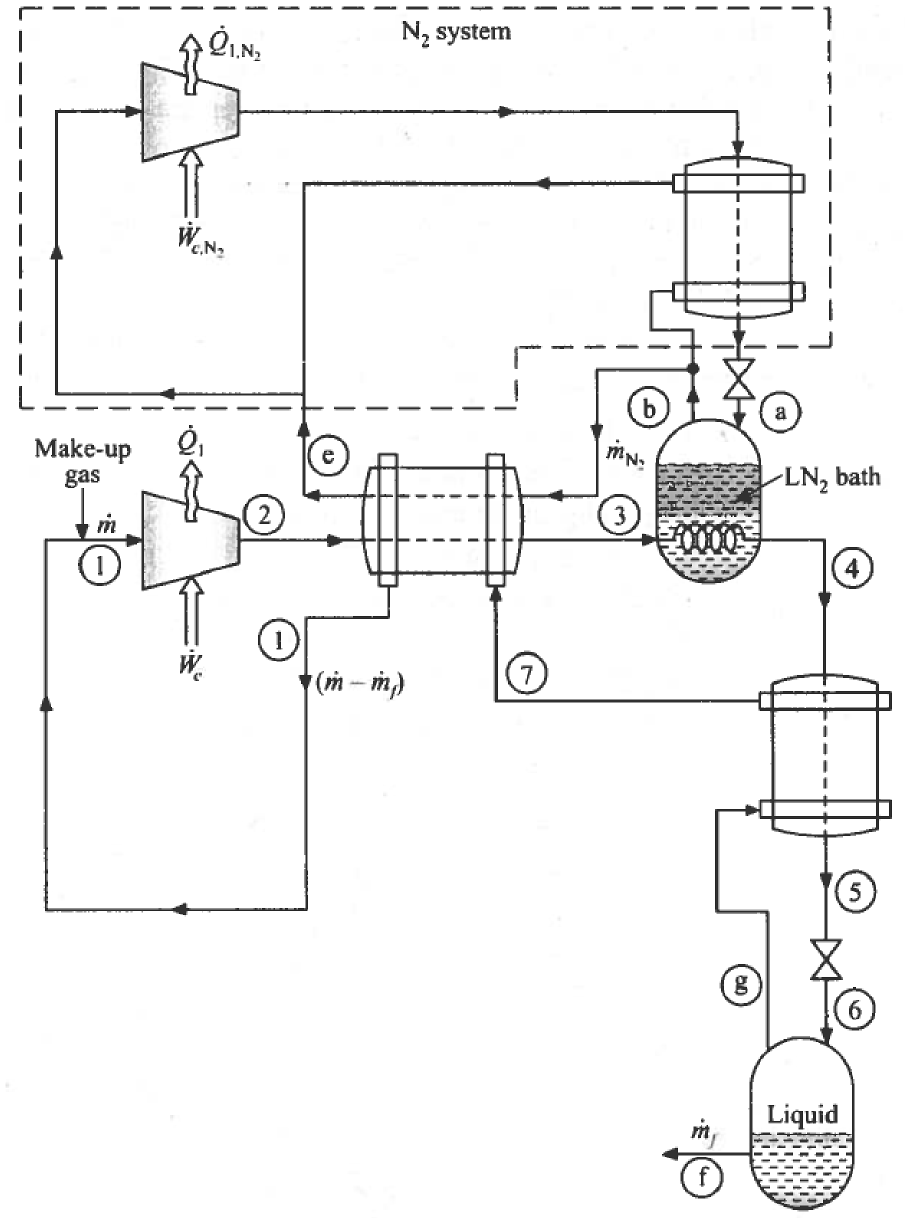
Hydrogen liquefaction plant



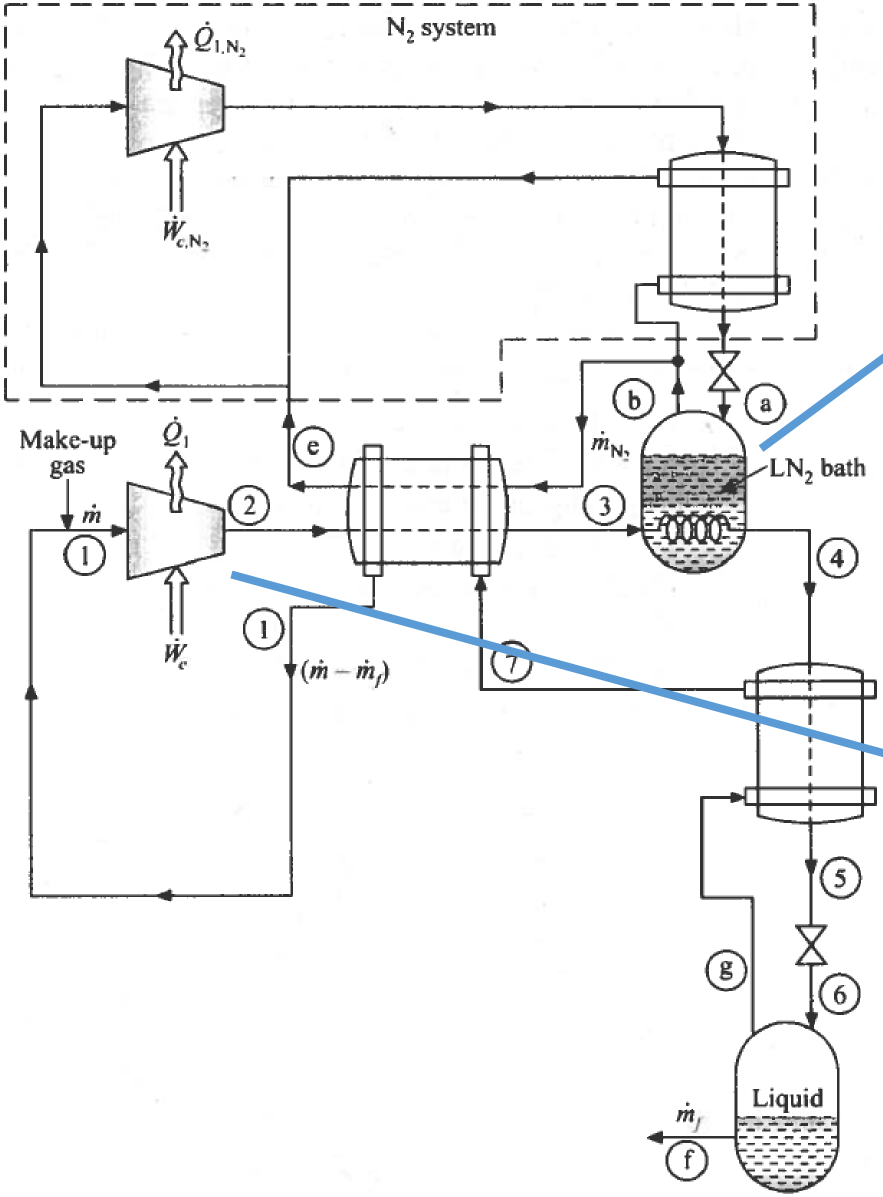


Producer	*City*	*Country*	*Process*	*Capacity (Nm^3/day)*	*Capacity ton/day*	*Year Opened*
Air Liquide	Waziers	France	SMR	4 864	10	1987
Air Products	Rotterdam/Rosenberg	Netherlands	SMR	2 502	5	1990
Linde	Leuna	Germany	SMR	2 038	5 (10)	2007

Precooled Linde-Hampson process



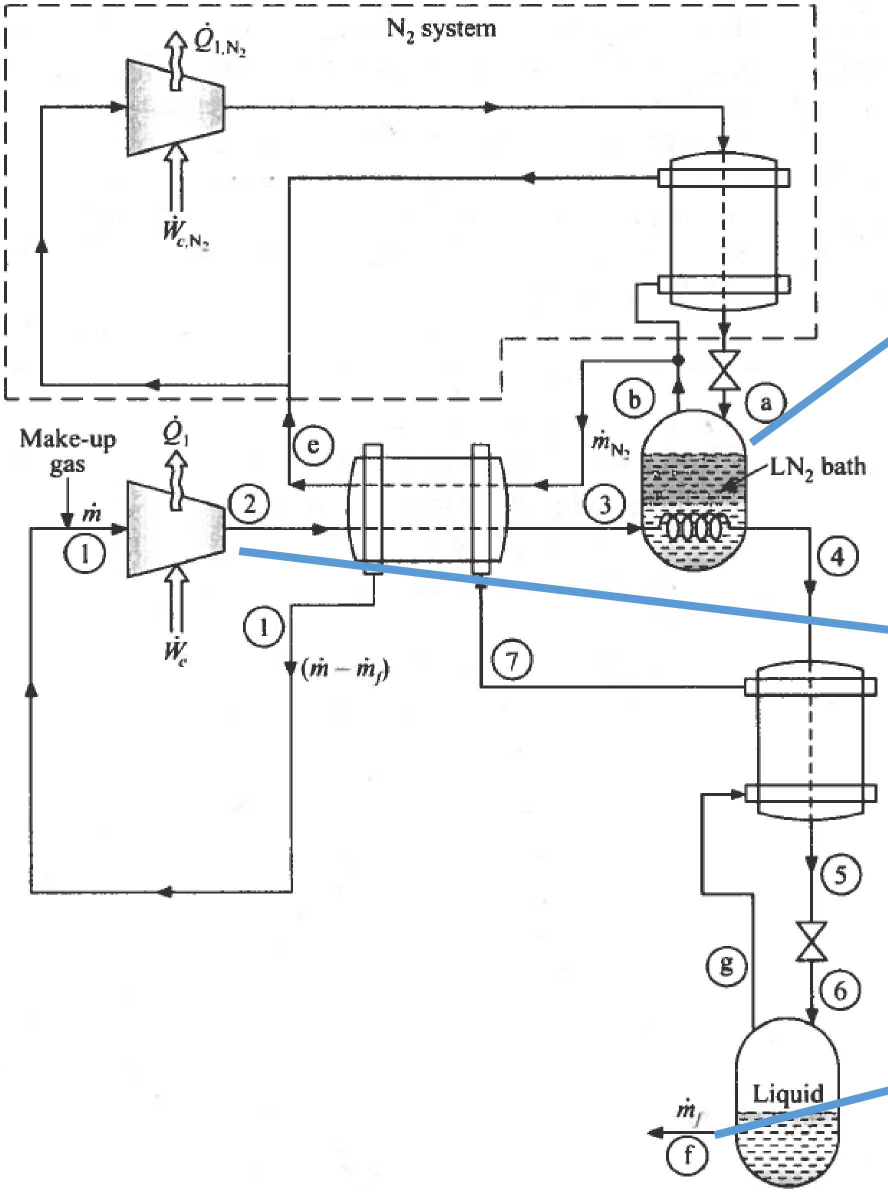
Precooled Linde-Hampson process



Nitrogen at liquid state
@ T=66 K and p=0.2 bar

Hydrogen compressor @ 100 bar

Precooled Linde-Hampson process

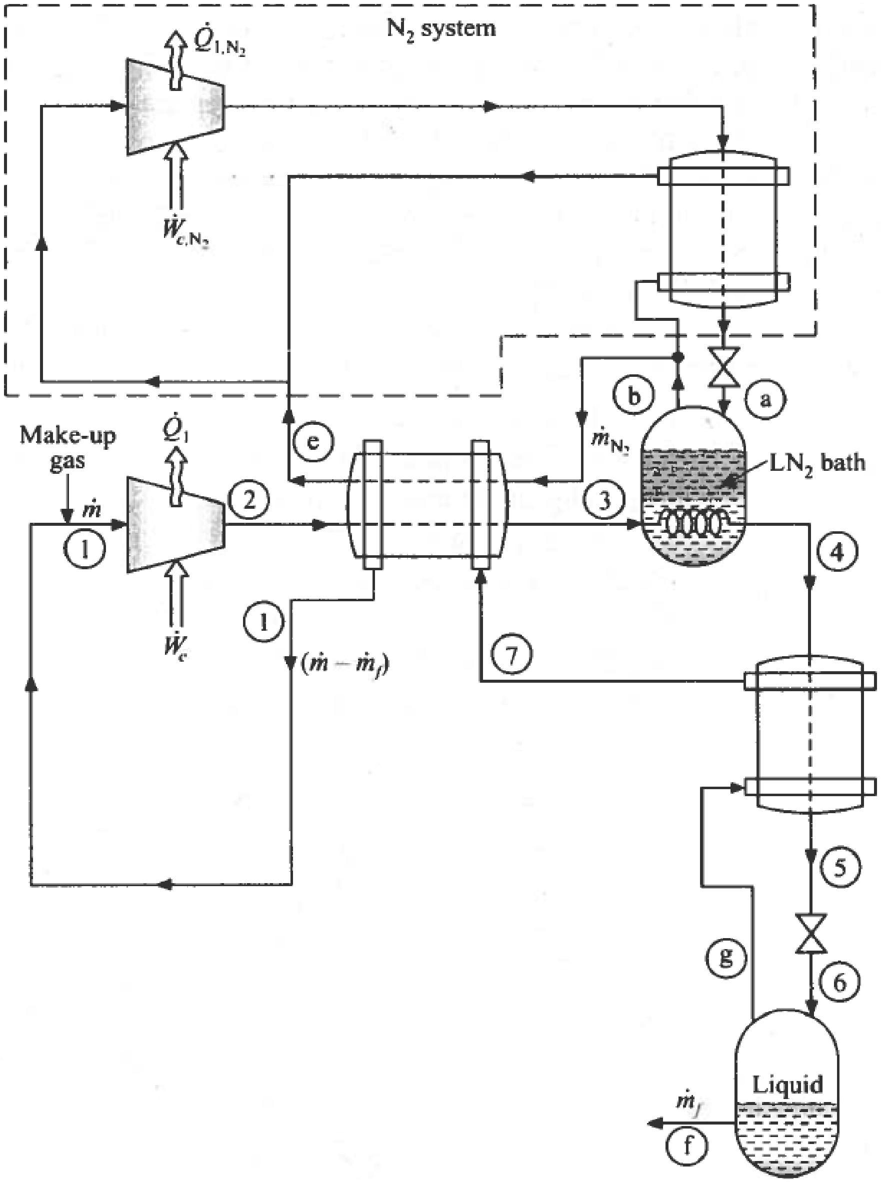


Nitrogen mass flow rate about 340 l/h

Hydrogen compressor capacity 1300 m^3/h

Liquefied hydrogen (95% para-H$_2$) 230 l/h

Precooled Linde-Hampson process



$$z = \frac{\dot{m}_{N_2}}{\dot{m}_{H_2}} = 1.3952 \frac{g_{N_2}}{g_{H_2}}$$

Precooled Linde-Hampson process

Ideal liquefaction work:

$$W_L = \Delta H * \frac{(T_{amb} - T_c)}{T_c}$$

Ideal work → $W_L = 11.62 \frac{MJ}{kg} = 3.228 \frac{kWh}{kg}$

Real work → $W_{L_r} = 30 \frac{MJ}{kg} = 8.3 \frac{kWh}{kg}$

↓

≈ 25% of hydrogen LHV

Precooled Linde-Hampson process

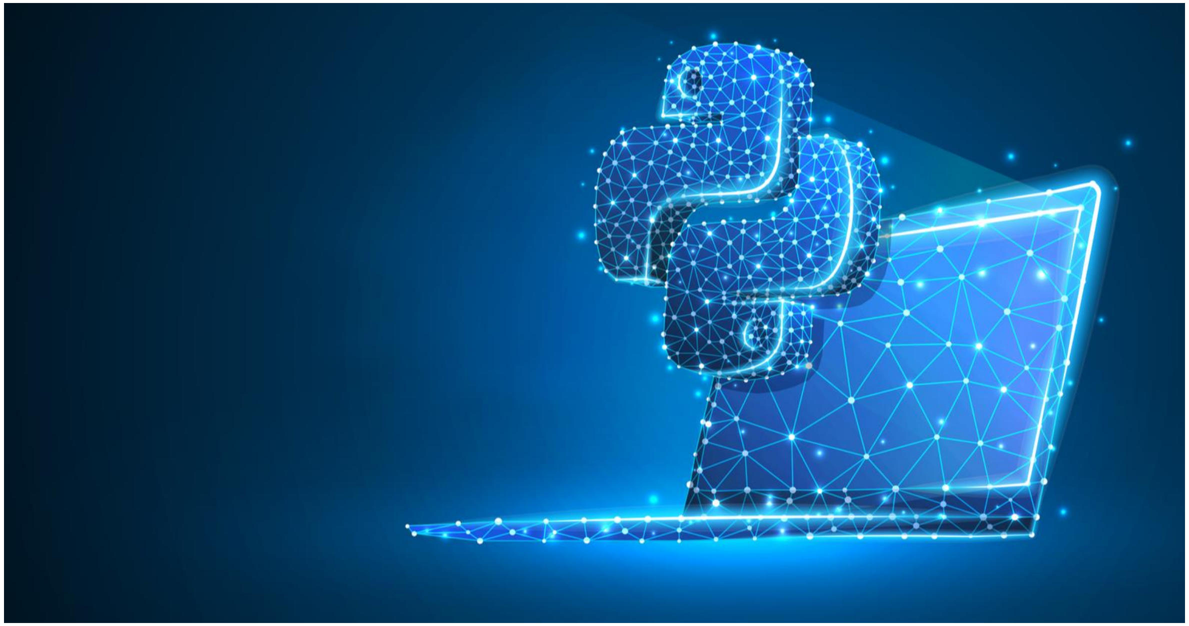
LEUNA (Germany) →

Capacity = 5 t_{LH2}/day

Investment cost = 25 million €

Specific consumption = 11.9 kWh/kg_{LH2}

4. Exercises with Python and Coolprop



Excercise 1: Simple Linde-Hampson process

We assume to use a simple Linde-Hampson cycle to liquefy nitrogen (N_2). Calculate the liquid fraction and the actual work of liquefaction as the pressure changes p_2 .

Assumptions:

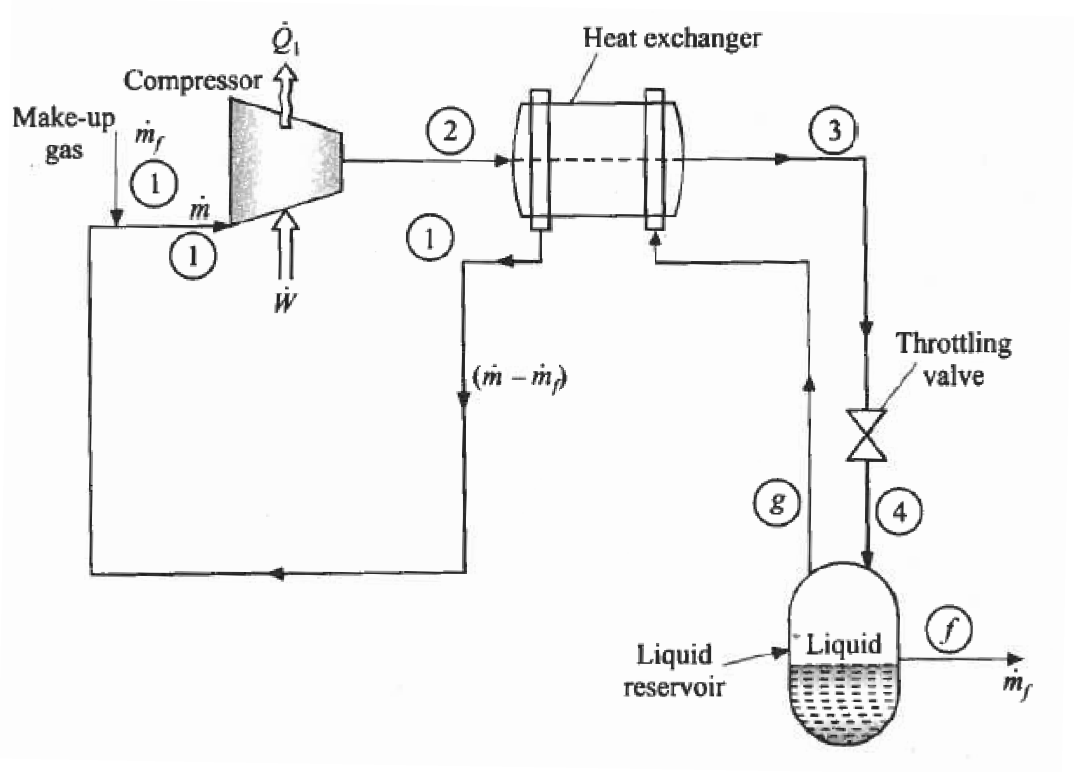
$T_{amb} = T_1 = 300\ K$

$p_{amb} = p_1 = 1\ atm$

$delta_{appr} = T_2 - T_1 = 5\ K$

$p_f = 1\ atm$

$T_f = 77\ K$



Excercise 1: Simple Linde-Hampson process

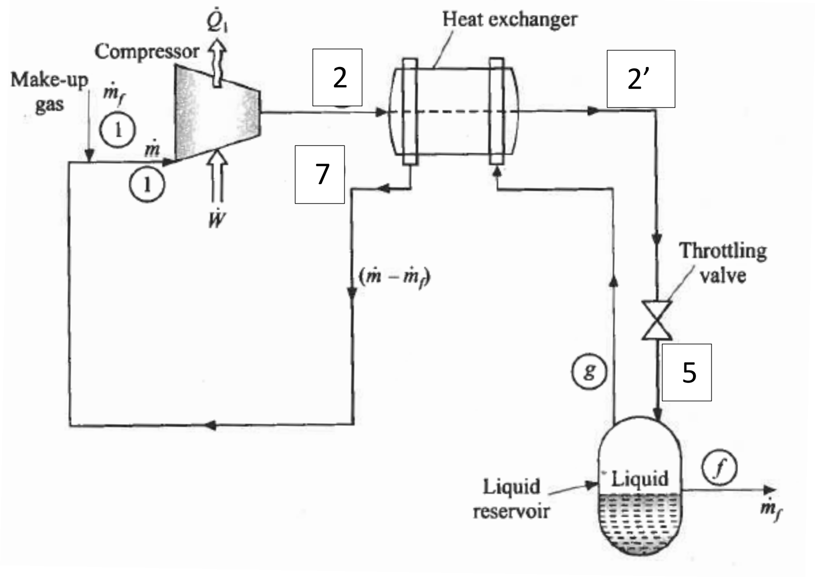
According to the first principle of thermodynamics:

$$m_{TOT} * (h_2) = (m_{TOT} - m_L) * (h_7) + m_L * (h_5)$$

$$m_{TOT} * (h_7 - h_2) = m_L * (h_7 - h_5)$$

$$Liquid\ fraction = y = \frac{m_L}{m_L + m_G}$$

$$y = \frac{(h_7 - h_2)}{(h_7 - h_5)}$$



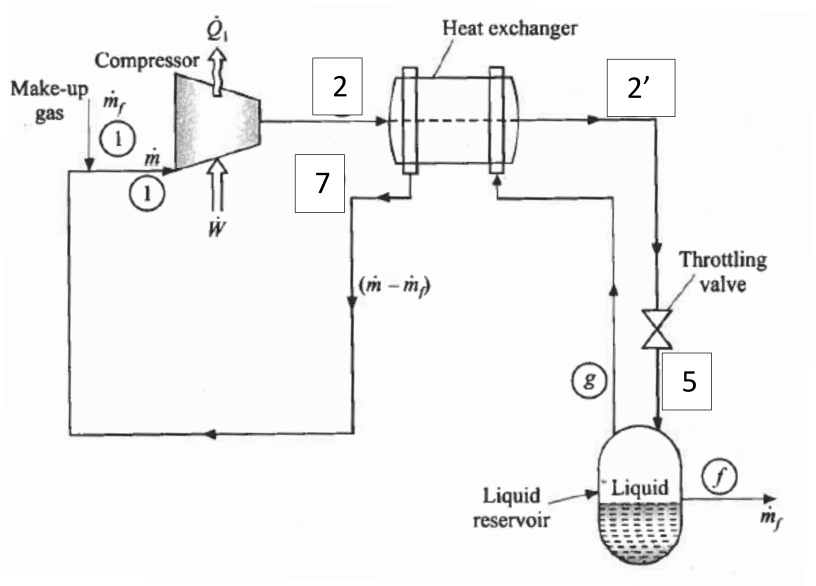
Excercise 1: Simple Linde-Hampson process

The real liquefaction work is calculated as:

$$-\frac{\dot{W}}{\dot{m}_{TOT}} = [T_1 * (s_1 - s_2) - (h_1 - h_2)]$$

Specific energy consumption calculated as:

$$\boxed{-W_L = -\frac{\dot{W}}{\dot{m}_L} = -\frac{\dot{W}}{\dot{m}_{TOT} * y}}$$



Excercise 1: Simple Linde-Hampson process

The ideal liquefaction work is calculated as:

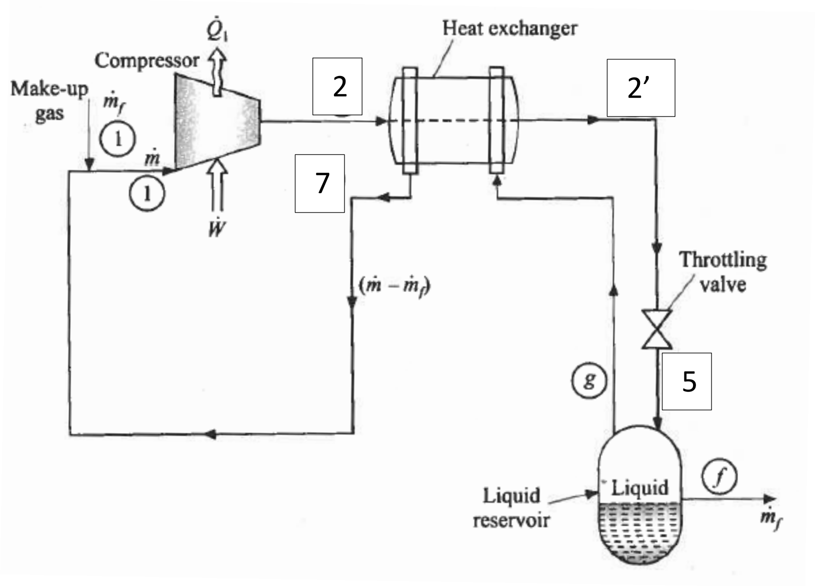
$$\frac{W_{comp}}{m_{TOT}} = [T_1 * (s_1 - s_2) - (h_1 - h_2)]$$

$$W_L = [T_1 * (s_1 - s_2) - (h_1 - h_2)]/y$$

$$W_{id} = [T_1 * (s_1 - s_5) - (h_1 - h_5)]$$

The Figure of Merit (FOM) is calculated as:

$$FOM = \frac{W_i}{W_L}$$



Excercise 2: Precooled Linde-Hampson process

We assume to use a precooled Linde-Hampson process to liquefy hydrogen (H_2), using nitrogen (N_2) as refrigerant. Calculate the liquid fraction (y), the ratio of refrigerant respect to the hydrogen flow rate (z) and the FOM.

Assumptions:

$T_{amb} = T_1 = 300\ K$

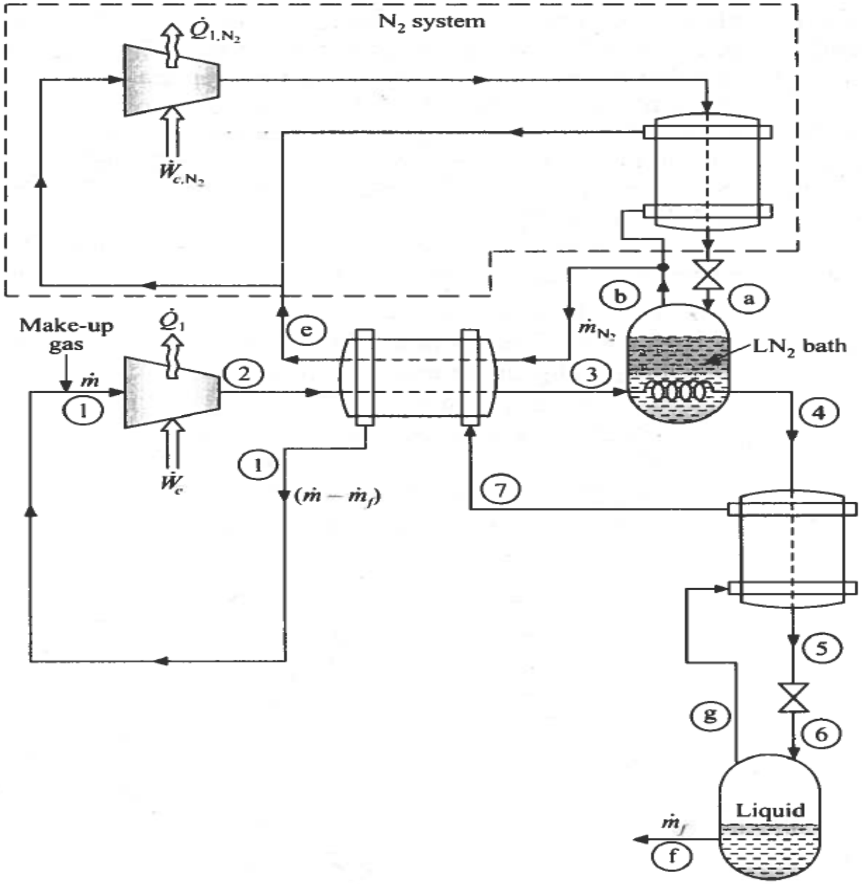
$p_{amb} = p_1 = 1\ atm$

$delta_{appr} = 5\ K$

$p_f = 1\ atm$

$T_f = 20\ K$

$p_2 = p_4 = 50\ atm$



Excercise 2: Precooled Linde-Hampson process

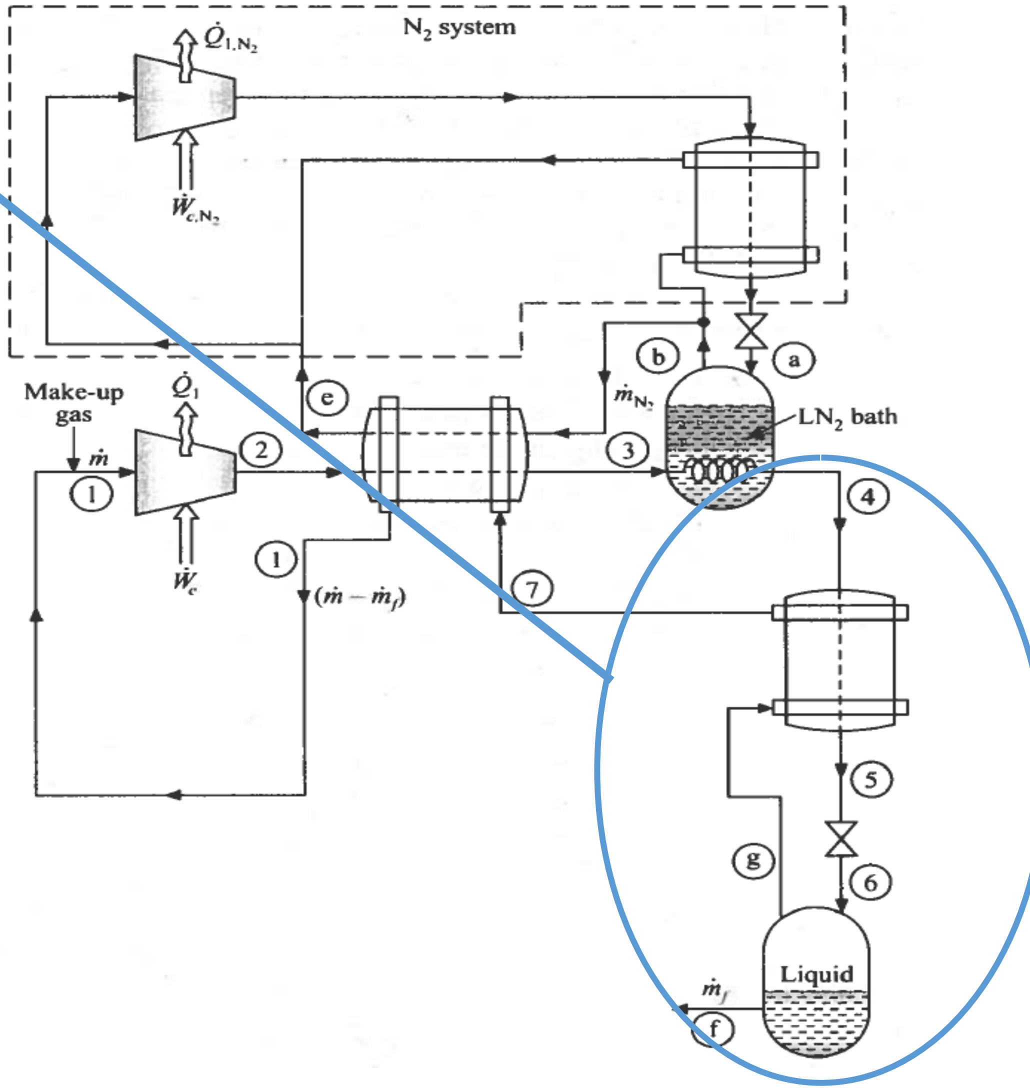
According to the first principle of thermodynamics:

$$m_{TOT} * h_4 = m_L * h_f + m_g * h_7$$

$$m_{TOT} * h_4 = m_L * h_f + (m_{TOT} - m_L) * h_7$$

$$m_{TOT} * (h_4 - h_7) = m_L * (h_f - h_7)$$

$$\boxed{y = \frac{h_7 - h_4}{h_7 - h_f}}$$

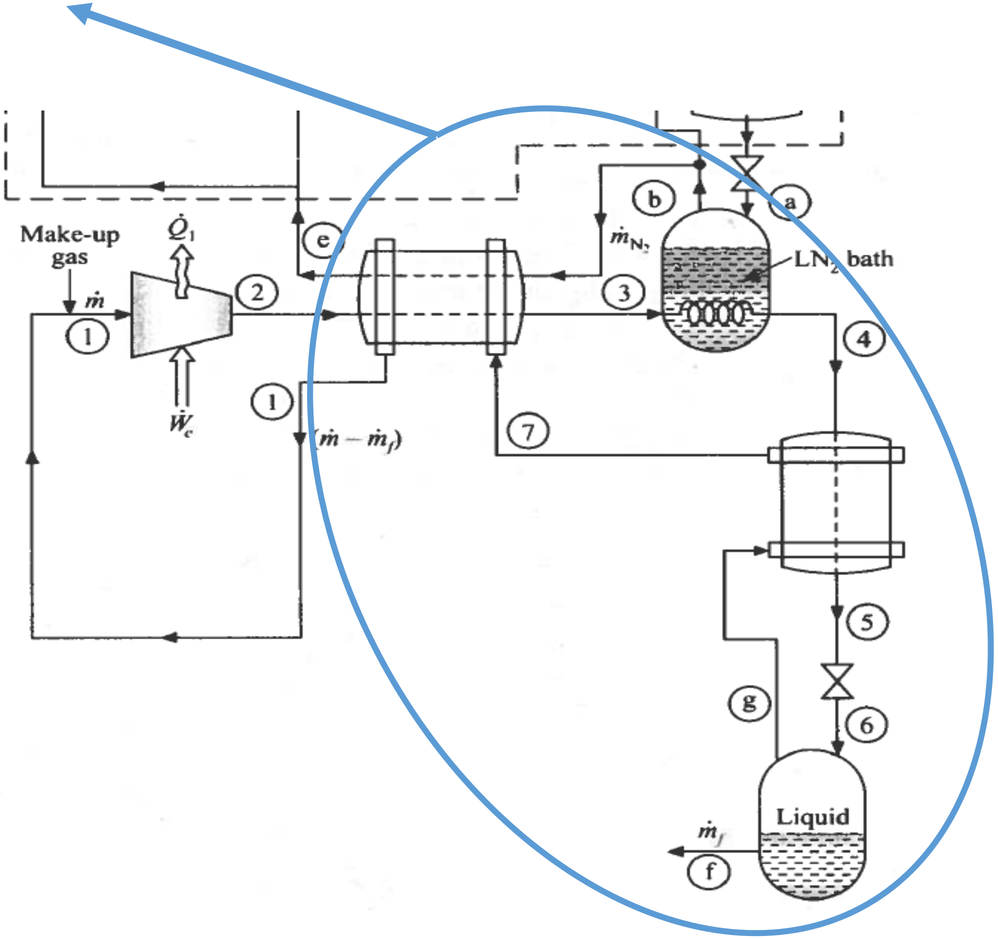


Excercise 2: Precooled Linde-Hampson process

According to the first principle of thermodynamics:

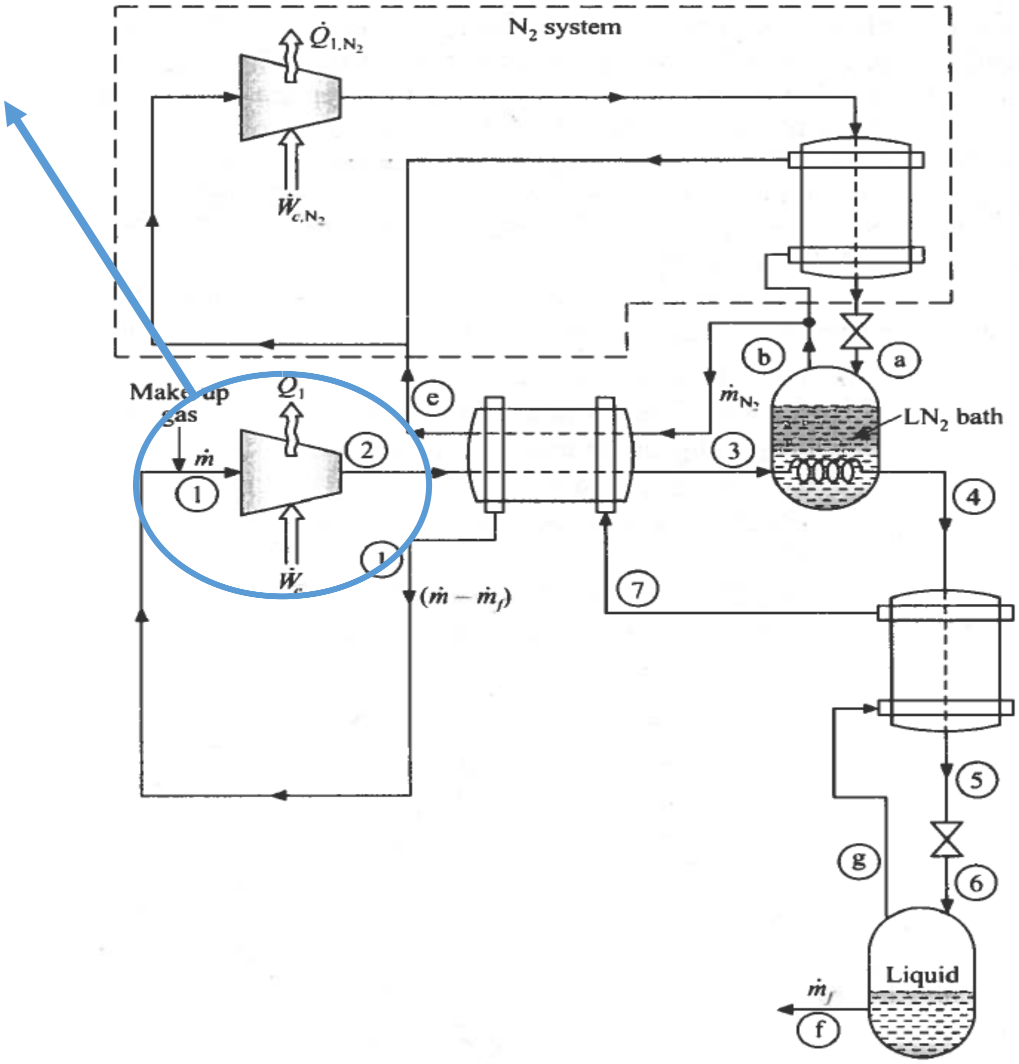
$$m_{TOT} * h_2 + m_N * h_a = \mathrm{m_N} * \mathrm{h_c} + (\mathrm{m_{TOT}} - \mathrm{m_L}) * \mathrm{h_1} + \mathrm{m_L} * \mathrm{h_f}$$

$$\boxed{z = \frac{h_2 - h_{1_{usc}}}{h_c - h_a} + y * \frac{h_{1_{usc}} - h_f}{h_c - h_a}}$$



Excercise 2: Precooled Linde-Hampson process

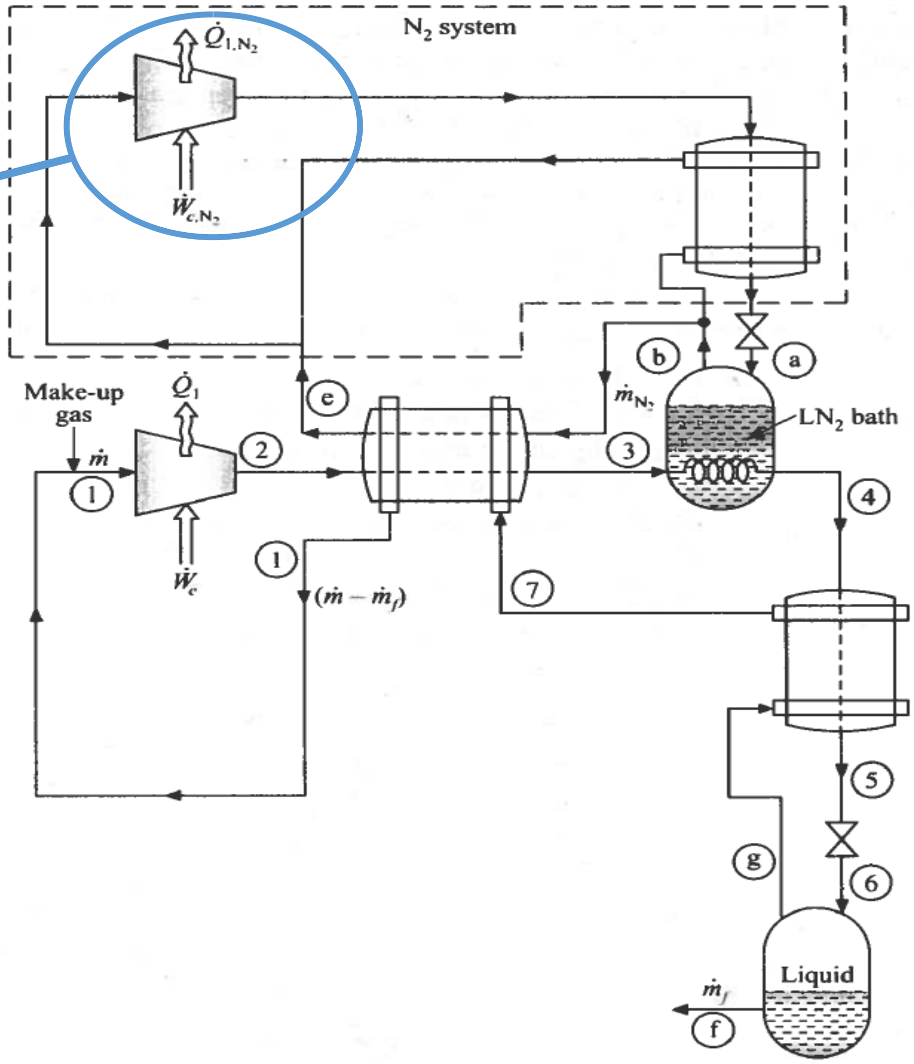
$$\frac{\dot{W}}{\dot{m}_{TOT}} = [T_1(s_1 - s_2) - (h_1 - h_2)]$$



Excercise 2: Precooled Linde-Hampson process

$$\frac{\dot{W}}{\dot{m}_{TOT}} = [T_1(s_1 - s_2) - (h_1 - h_2)]$$

$$\frac{\dot{W}_{TOT}}{\dot{m}_{TOT}} = \frac{\dot{W}}{\dot{m}_{TOT}} + W_{l_{N_2}} * z$$

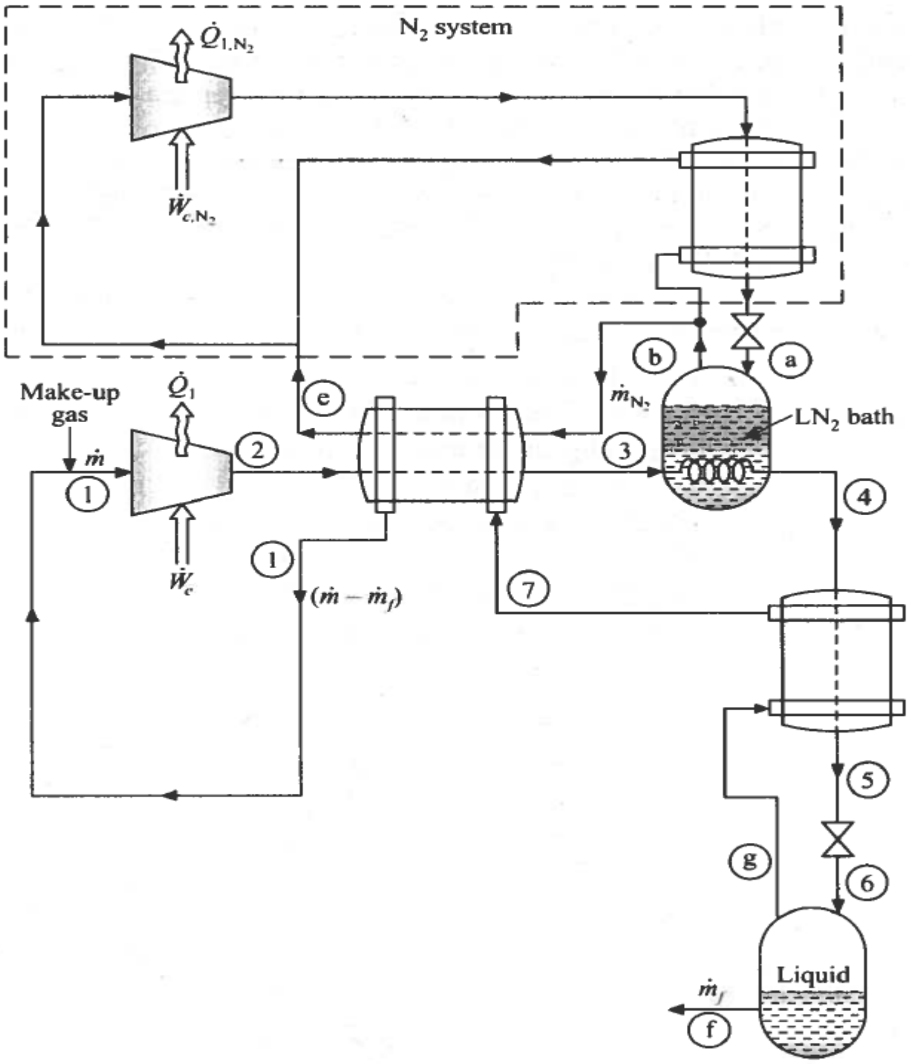


Excercise 2: Precooled Linde-Hampson process

$$\frac{\dot{W}}{\dot{m}_{TOT}} = [T_1(s_1 - s_2) - (h_1 - h_2)]$$

$$\frac{\dot{W}_{TOT}}{\dot{m}_{TOT}} = \frac{\dot{W}}{\dot{m}_{TOT}} + W_{l_{N_2}} * z$$

$$\boxed{\dot{W}_{l_{H_2}} = \frac{\dot{W}_{TOT}}{\dot{m}_{TOT} * y}}$$



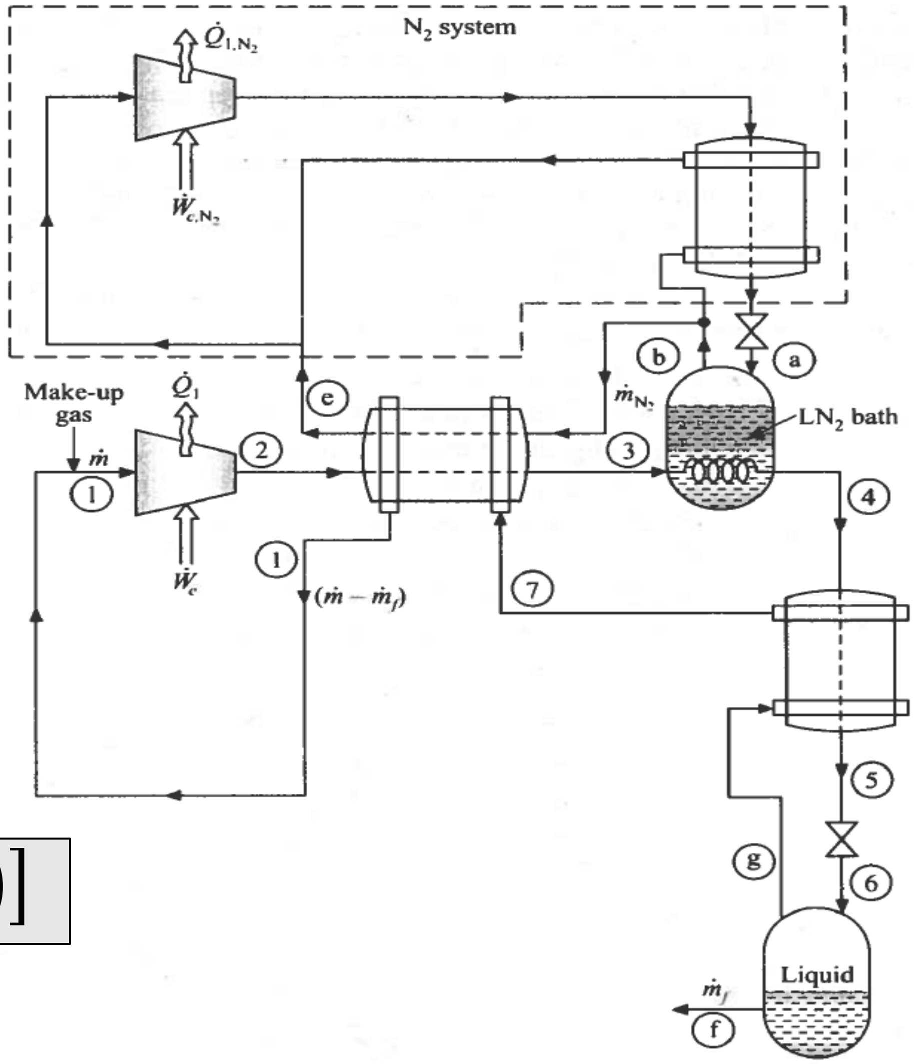
Excercise 2: Precooled Linde-Hampson process

$$\frac{\dot{W}}{\dot{m}_{TOT}} = [T_1(s_1 - s_2) - (h_1 - h_2)]$$

$$\frac{\dot{W}_{TOT}}{\dot{m}_{TOT}} = \frac{\dot{W}}{\dot{m}_{TOT}} + W_{l_{N_2}} * z$$

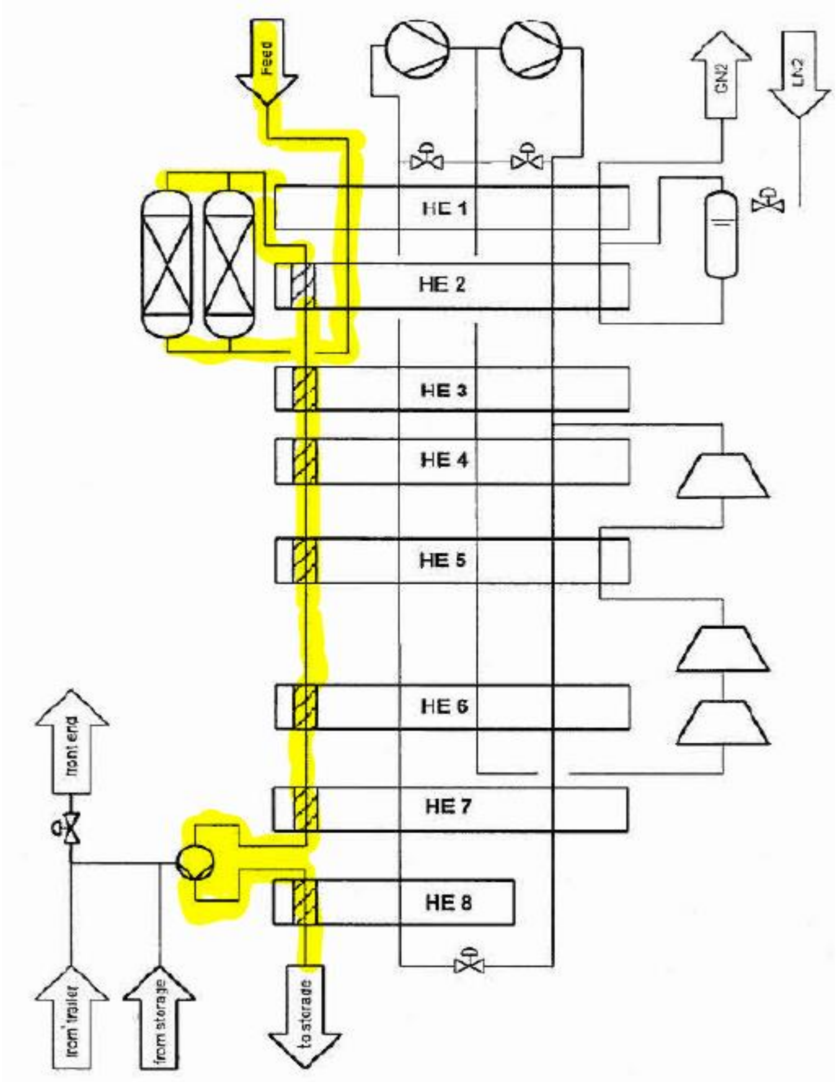
$$\boxed{\dot{W}_{l_{H_2}} = \frac{\dot{W}_{TOT}}{\dot{m}_{TOT} * y}}$$

$$\boxed{\dot{W}_i = [T_1(s_1 - s_f) - (h_1 - h_f)]}$$



Comparison with a real hydrogen liquefaction plant

$$\boxed{W_l = 11.9\,\frac{kWh}{kg_{LH_2}}}$$

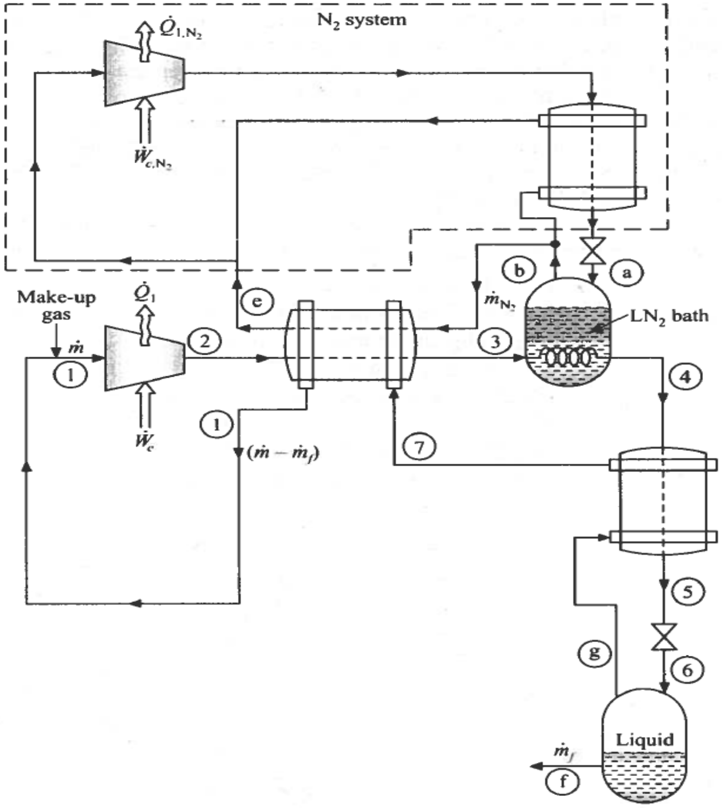


Excercise for the final exam

With reference to the exercise 2 (precooled Linde-Hampson process to liquefy hydrogen, using nitrogen as refrigerant), consider the following assumptions:

- $T_{amb} = T_1 = 300\ K$
- $p_{amb} = p_1 = 1\ atm$
- $delta_{appr} = 5\ K$
- $p_f = 1\ atm$
- $T_f = 20\ K$

Find the optimal plant configuration of the hydrogen liquefaction plant to minimize the work required for hydrogen liquefaction (maximize FOM).



Thank you for the attention!

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