## Lecture # 4

# Liquefaction and Gas Storage

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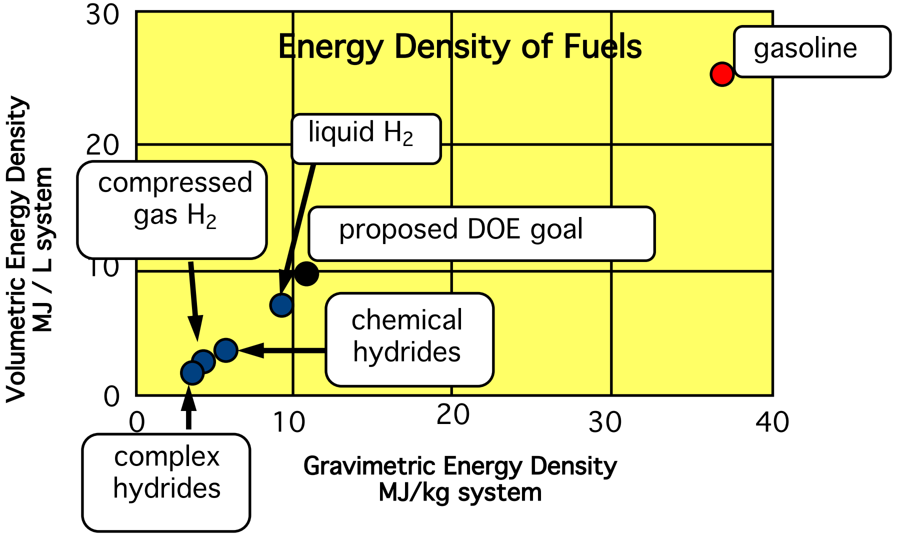
February 12, 2020

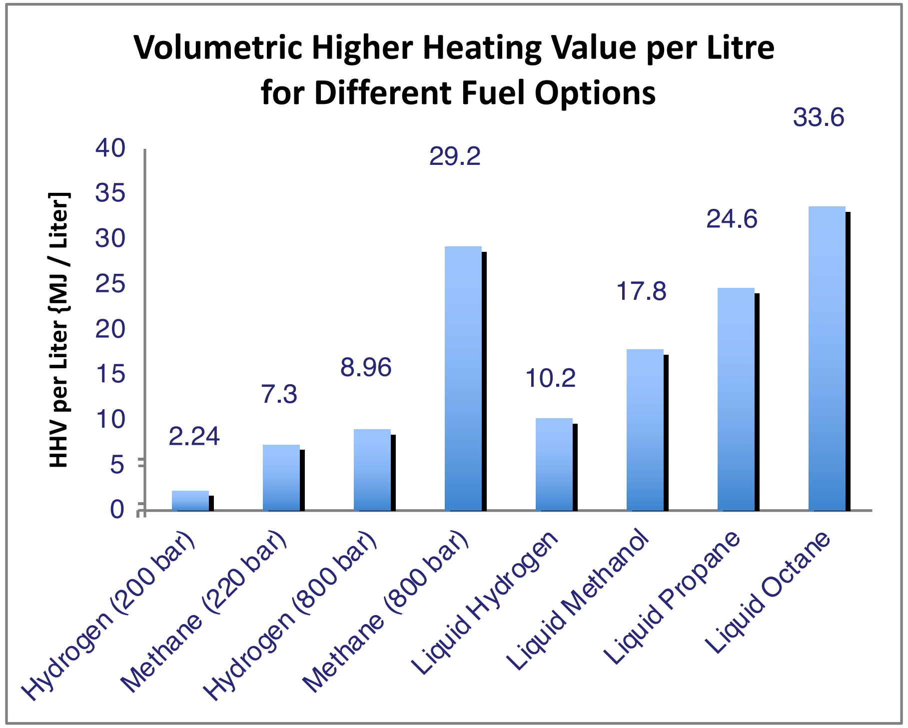
1. Ideal liquefaction work.
2. Liquefaction work for hydrogen and storage
3. Losses in actual processes.
4. Air liquefaction and large scale storage.

# Liquefaction Work, Ideal and “Actual”

- Some gas separation processes require cooling and liquefaction.
- Highest “storage density” for Hydrogen is in the liquid form.
- Liquefied natural gas is becoming important for transporting it.
- For CCS, $CO_2$ must be in liquid form for injection.



Lithium rechargeable Batteries:
0.54 MJ/kg Or 150 Wh/kg



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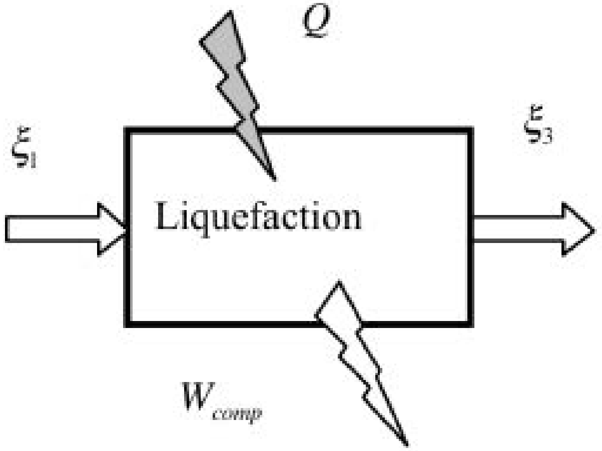
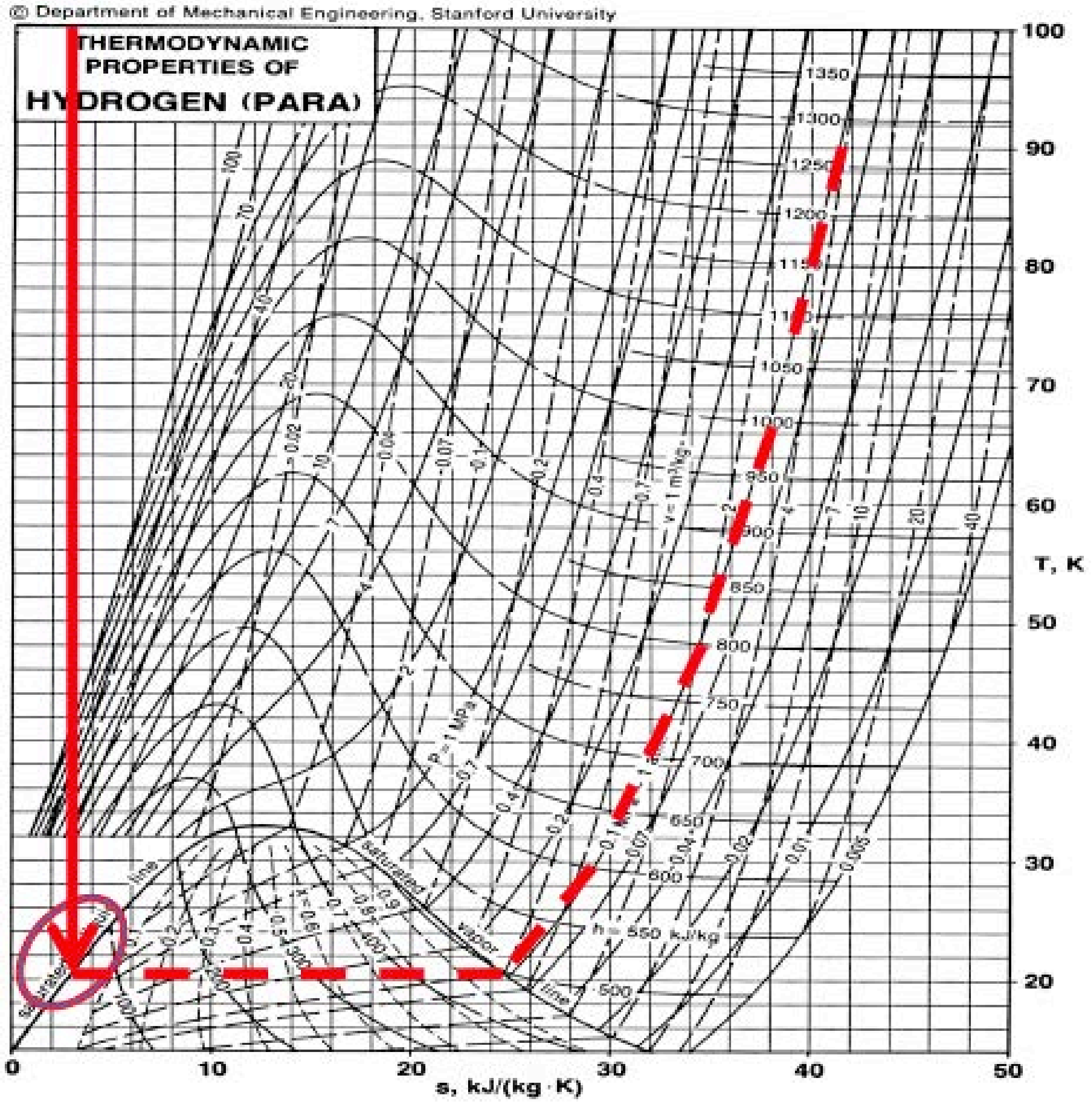
# Minimum Liquefaction Work



Use availability equation :

$$\dot{W}_{cv} = \underbrace{\left(1-\frac{T_o}{T_H}\right)\dot{Q}_H}_{(Q_H=0)} + \dot{m}\left(\xi_{in}-\xi_{out}\right) - \underbrace{\dot{I}_{ir}}_{0 \text{ for min work}}$$

$$\hat{w}_{\min} = -\left[\left(h_3-h_1\right) - T_o\left(s_3-s_1\right)\right]$$



The critical point of hydrogen is 33.3 K, 1.3 MPa

Calculate the ideal liquefaction work for hydrogen starting at1 atm and 298 K:
$s_1 = 53.436\,\text{kJ/kgK}$, $h_1 = 3929.6\ \text{kJ/kg}$,

The liquid hydrogen temperature at 1 atm is 20 K.
$s_3 = -0.02\ \text{kJ/kgK}$, $h_3 = -0.44\ \text{kJ/kg}$

$w_{\min} = 11.870\ \text{MJ/kg}\ H_2$.
Actual values ~ 4-10 times, 40-110 MJ/kg $H_2$
(low second law efficiency).

The lower heating value LHV of hydrogen is 120.9 MJ/kg
Liquefaction work is 30-100% of the LHV (or more)

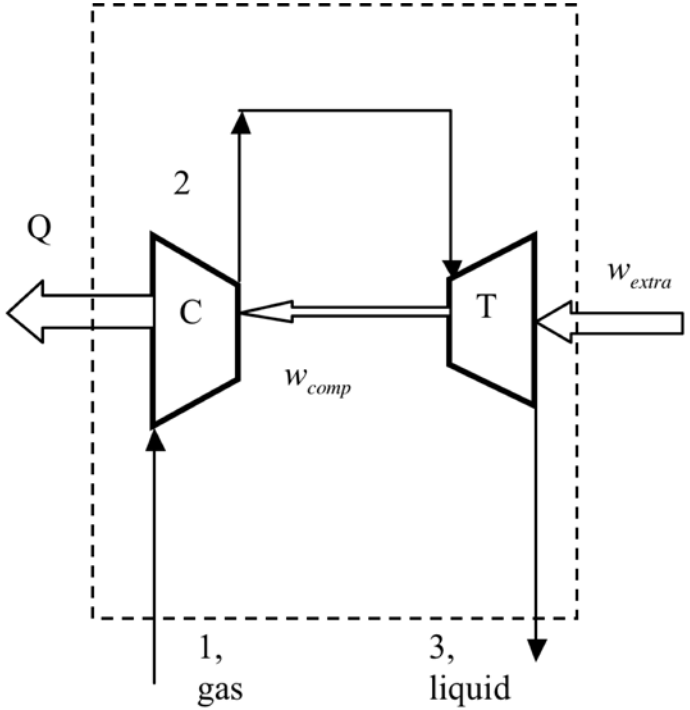
Useful work produced by an engine running at 40% efficiency is ~ 50 MJ/kg
The numbers do not look good!

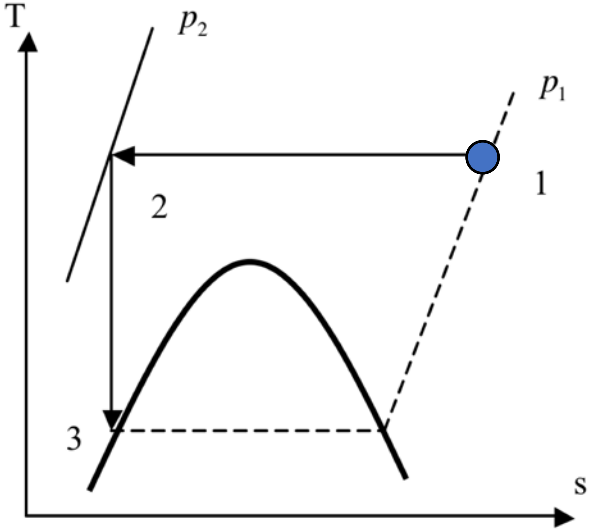
## Minimum Liquefaction Work

$$\hat{w}_{\min} = -\left[\left(h_3 - h_1\right) - T_1\left(s_3 - s_1\right)\right]$$

## Realization of the ideal Linde Liquefaction process:

All processes must be reversible: isothermal heat exchange and isentropic work transfer, thus Isothermal compression and isentropic expansion





# Storage and Packaging of Hydrogen

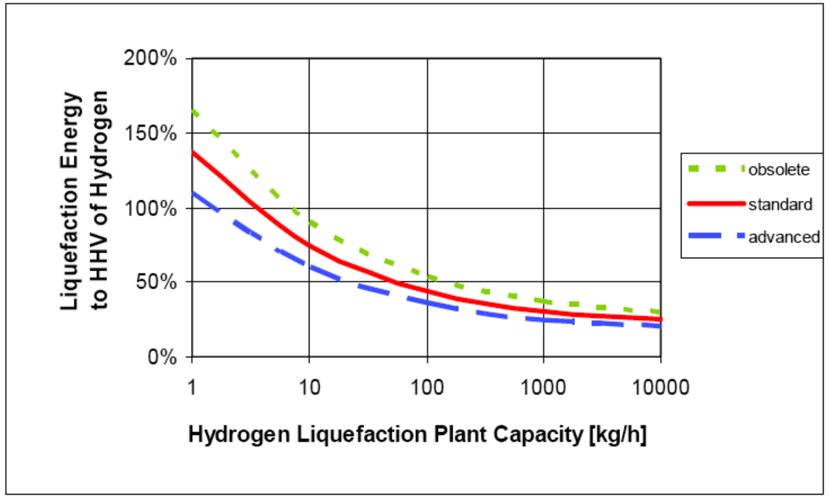
Plant size determines the quality of the equipment and integration of processes

for an ideal gas, the min work is

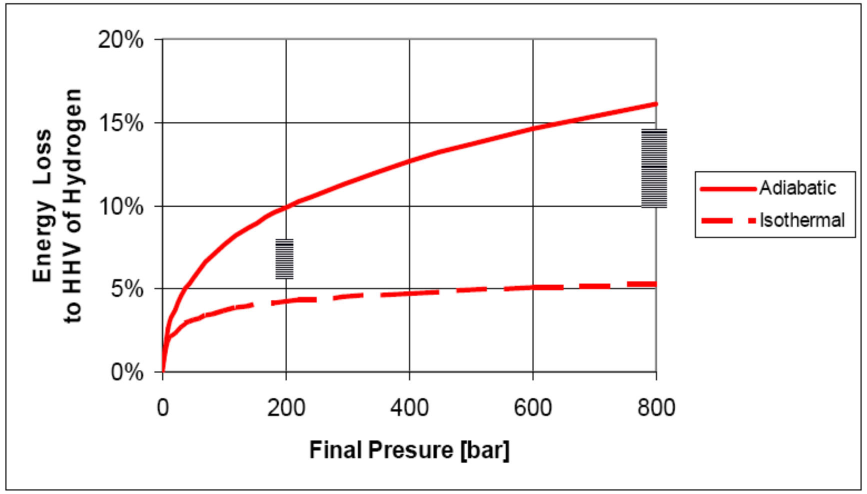
$$w_{isothermal} = \Re T_o \ln\left(p_2 / p_1\right)$$

$$w_{isentropic} = c_p T_o \left( \left(p_2 / p_1\right)^{\frac{k-1}{k}} - 1 \right)$$

**Liquefaction of Hydrogen:**
**Liquefaction Energy in HHV-% of $H_2$**



**Adiabatic and Isothermal Compression:**
**Compression Energy in HHV-% of $H_2$**



Compression energy CE of $H_2$ = 8 x CE of natural gas or 15 x CE of air

The Future of the Hydrogen Economy, Bright or Bleak” Eliasson, and Bossel, 2003.

# Compressed/Liquid $H_2$ Storage

## Compressed $H_2$ Storage

- Composite tanks are available at 5,000 psi (350 bar)
- Prototype 10,000 psi tanks demonstrated

## Liquid $H_2$ Storage

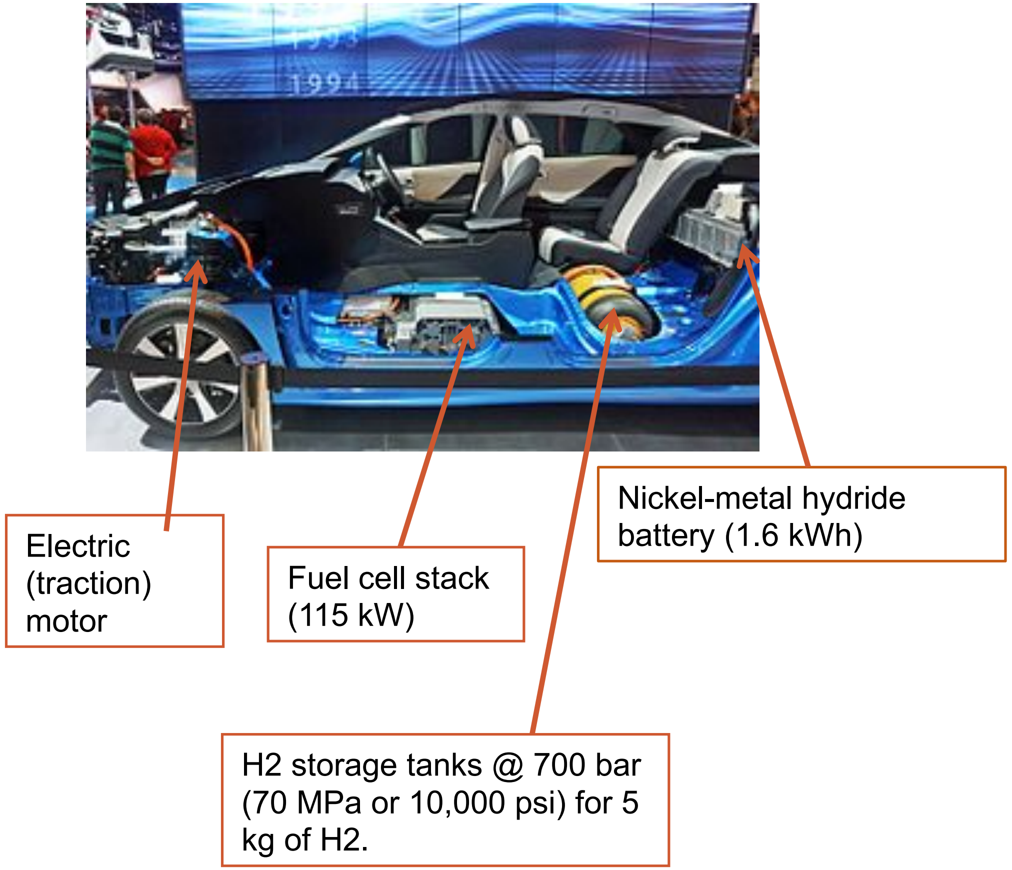
- BMW has demonstrated automotive liquid $H_2$ storage
- Liquefying $H_2$ requires substantial energy (40% of total energy content of $H_2$ fuel)
- Boil-off is an issue for non-pressurized insulated tanks
- Pressurized cryogenic tanks are being developed by LLNL.

**For compressed and liquid storage, packaging volume is still a concern.**

JoAnn Milliken, DOE/EERE, via M. Dresselhaus *web.mit.edu/mrschapter/*

# Leap forward ~ 10 years, Toyota Mirai

| | |
|---|---|
| Fuel cell-powered 113 kW (152 hp) | |
| Battery | 1.6 kWh Nickel-metal hydride |
| Range | 502 km (312 mi) (EPA) |



Electric (traction) motor

Fuel cell stack (115 kW)

Nickel-metal hydride battery (1.6 kWh)

H2 storage tanks @ 700 bar (70 MPa or 10,000 psi) for 5 kg of H2.

# Natural gas is liquefied for its transportation

(Critical point of methane is 191.1 K and 4.74 MPa)

Liquefy methane between $p_1 = 1$ atm, $T_1 = 273\ {}^0$K, and $p_f = 2.6$ atm and $T_f = 110\ {}^0$K

$$w_{\min} = -\left[\left(h_f - h_1\right) - T_0\left(s_f - s_1\right)\right]$$

From NIST web site, the thermodynamic properties of methane:

$h_1 = 854.5$ kJ/kg $\qquad s_1 = 6.48$ kJ/kgK
$h_f = -5.55$ kJ/kg $\qquad s_f = -0.053$ kJ/kgK

$$w_{\min} = -\left[\left(-5.55 - 854.5\right) - 273\left(-0.053 - 6.48\right)\right] = -923.46 \text{ kJ/kg}_{methane}$$

If the second law efficiency of 25%, $w^{actual} = -3693.84 \text{ kJ/kg}_{methane}$
LHV of methane is 50 MJ/kg
Methane engine running at 40% efficiency produces 20 MJ/kg
Number look a lot better!

# Linde-Hampson Process

Replace (expensive) isentropic expansion with a throttle valve

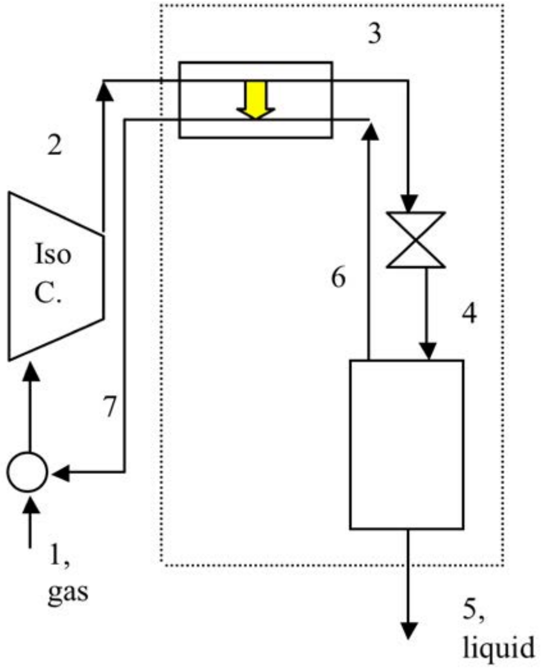
Keep isothermal compression, but use recuperation and (constant enthalpy) throttle valve, also called Joule-Thompson valve

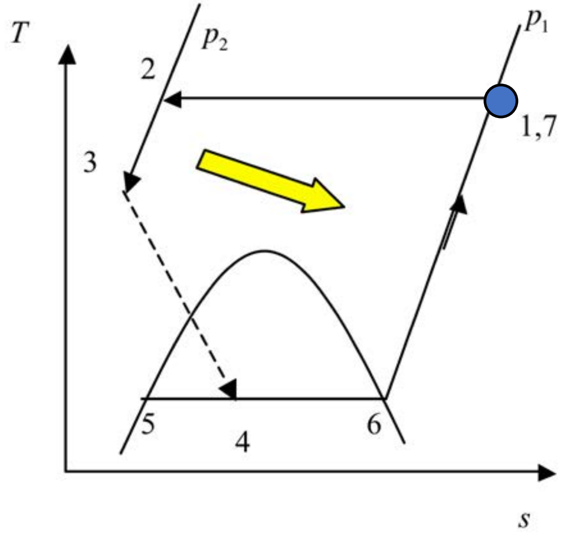
energy balance over (broken line) CV

$$m_2h_2 = m_5h_5 + \left(m_2 - m_5\right)h_1, \quad \rightarrow \quad Y_l = \frac{m_5}{m_2} = \frac{h_1 - h_2}{h_1 - h_5}$$

isothermal compression: $w = T_1\left(s_2 - s_1\right) - \left(h_2 - h_1\right)$

$$w_l = \frac{w}{Y_l} = \frac{h_1 - h_5}{h_1 - h_2}\left[T_1\left(s_2 - s_1\right) - \left(h_2 - h_1\right)\right]$$





# Liquid nitrogen is used extensively …

the critical point of nitrogen is 126.2 K and 3.4 MPa.

The properties of nitrogen at (STP) 1 atm and 298 K $\left(\text{state 1}\right): h_1 = 311.1$ kJ/kg and $s_1 = 6.84$ kJ/kg.K.

the properties of nitrogen at 1 atm at saturated liquid $\left(\text{state 3}\right): h_3 = -122.1$ kJ/kg, $s_3 = 2.83$ kJ/kg.K and $T_3 = 77$ K.

ideal liquefaction work: $w_{\min} = -769.4$ kJ/kg N

Linde-Hampson using: $p_2 = 20$ MPa: $h_2 = 279.0$ kJ/kg and $s_2 = 5.16$ kJ/kg.K

$w = -6354.3$ kJ/kg N

Second law efficiency of Linde Hampson, it or figure of merit,

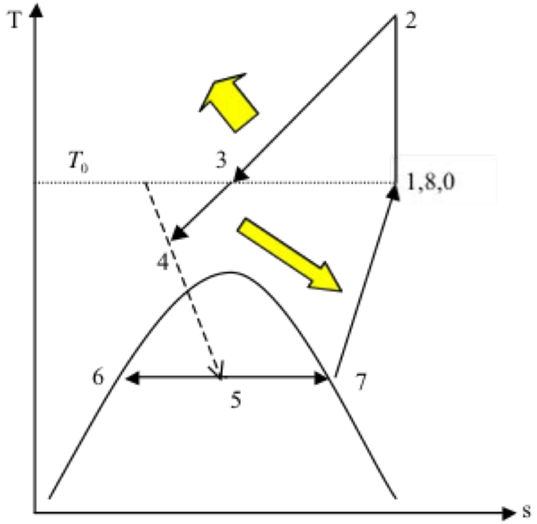
769.4/6354.3 = 0.121 (very low).

Actual Linde-Hampson plants have even lower efficiency because they may use adiabatic instead of isothermal compression

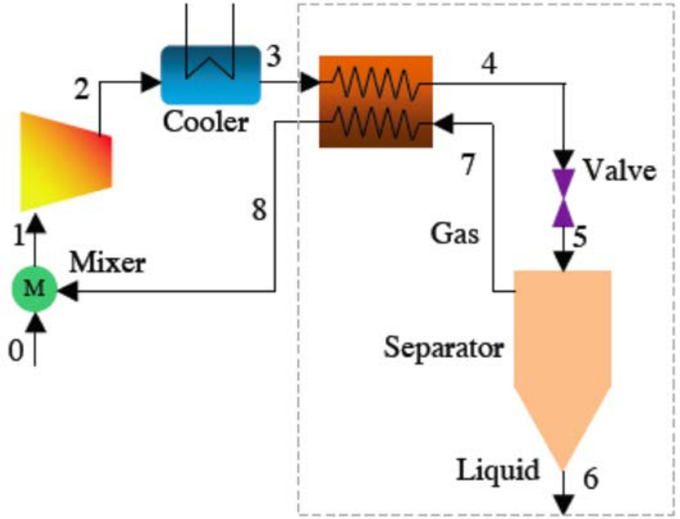
Multi stage compression with intercooling is used to approach the isothermal limit.

An expander can also be used to recover some of the expansion energy

Improvements make sense only in larger plants when larger capital costs are justifiable.



The T-s diagram of the adiabatic-compression liquefaction cycle shown above, utilizing a cooler to reduce the gas temperature between 2 and 3, and a regenerator to further reduce the gas temperature between 3 and 4 (while heating up the separated vapor between 7 and 8).



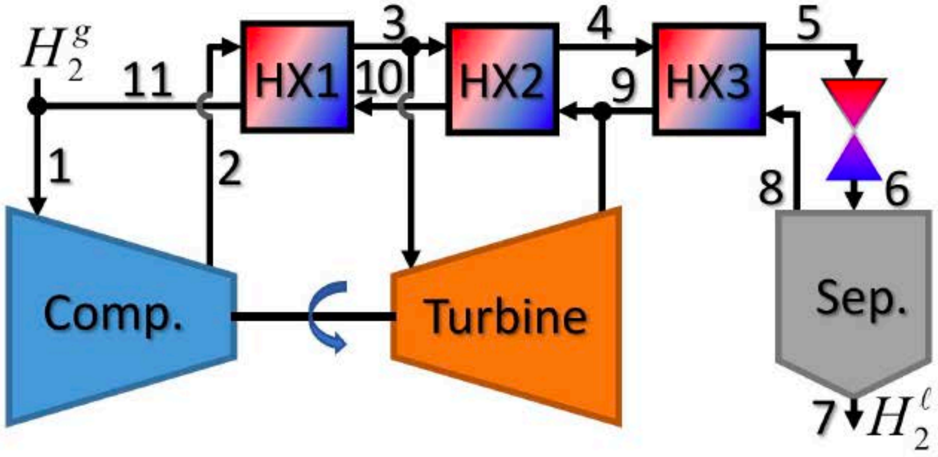
Liquefaction cycle with adiabatic compression and a separate cooler.

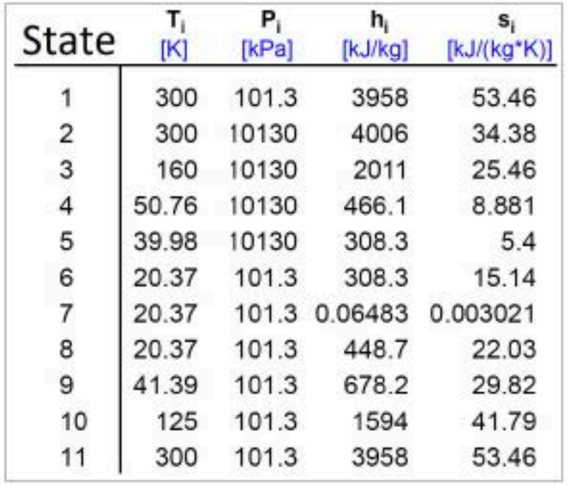
Claude Cycle uses expanded $H_2$ to:

- -reduce work input
- -prechill without $LN_2$

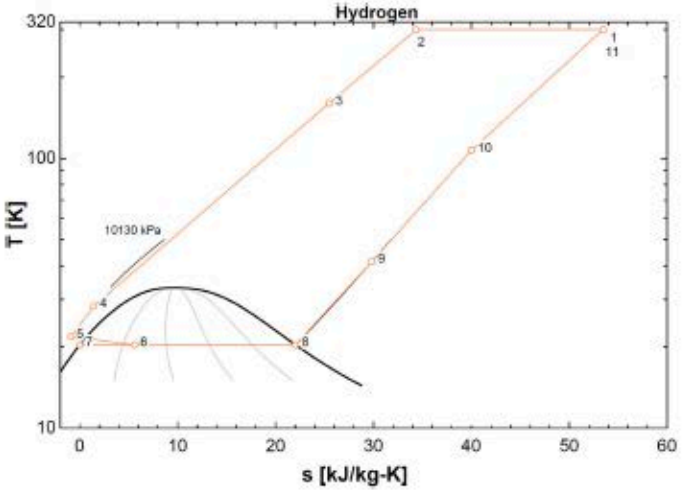
30% Efficient (7% of $H_2$ Exergy)

½ Entropy generation caused by throttling





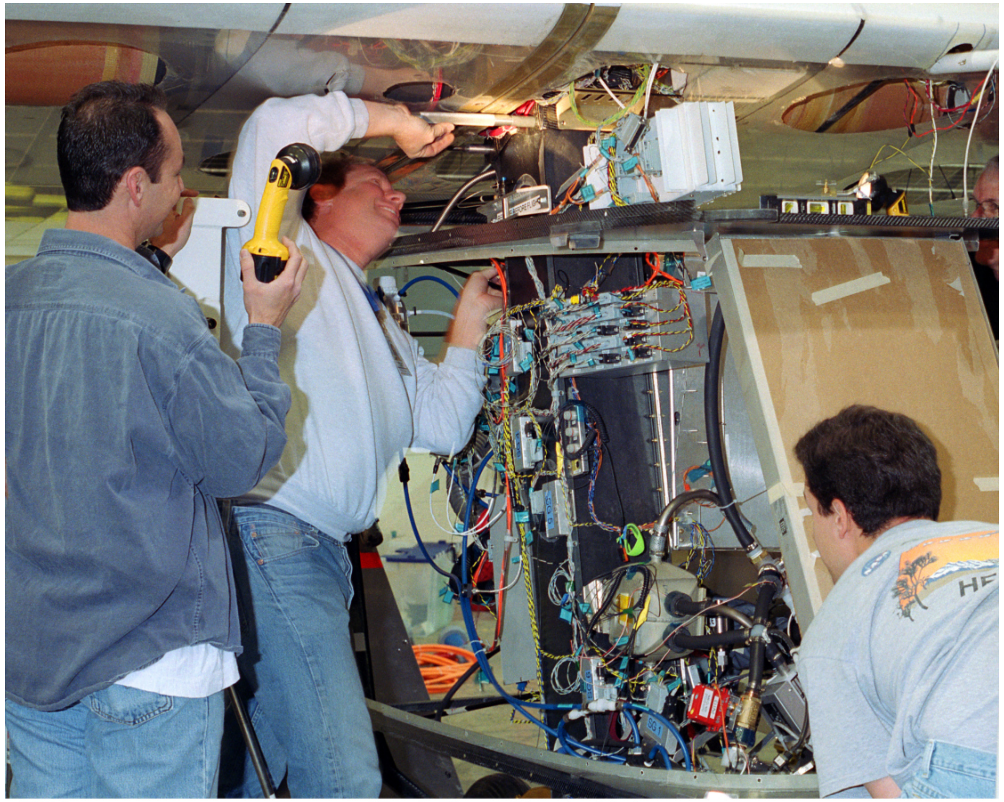
| State | $T_i$ [K] | $P_i$ [kPa] | $h_i$ [kJ/kg] | $s_i$ [kJ/(kg*K)] |
|---|---|---|---|---|
| 1 | 300 | 101.3 | 3958 | 53.46 |
| 2 | 300 | 10130 | 4006 | 34.38 |
| 3 | 160 | 10130 | 2011 | 25.46 |
| 4 | 50.76 | 10130 | 466.1 | 8.881 |
| 5 | 39.98 | 10130 | 308.3 | 5.4 |
| 6 | 20.37 | 101.3 | 308.3 | 15.14 |
| 7 | 20.37 | 101.3 | 0.06483 | 0.003021 |
| 8 | 20.37 | 101.3 | 448.7 | 22.03 |
| 9 | 41.39 | 101.3 | 678.2 | 29.82 |
| 10 | 125 | 101.3 | 1594 | 41.79 |
| 11 | 300 | 101.3 | 3958 | 53.46 |



Baron and Baron, Cryogenic Systems, Oxford, 1985.

## Using $H_2$ to power a fuel cell for Helios

Image courtesy of NASA.



NASA Dryden flight Research Center Photo Collection
http://www.dfrc.nasa.gov/gallery/photo/index.html
NASA Photo: EC03−0058−2 Date: March 4, 2003

Aerovironment technicians line up attachments as a fuel cell electrical system is installed on the Helios Prototype solar powered flying wing.

NASA Dryden flight Research Center Photo Collection
http://www.dfrc.nasa.gov/gallery/photo/index.html
NASA Photo: EC03−0058−6 Date: March 4, 2003

Technicians for AeroVironment, Inc., jack up a pressure tank to the wing of the Helios Prototype solar−powered flying wing.

Images courtesy of NASA.

Liquid Air Energy Storage
Good material in Chris Nutty and Scott Seo
2019 student term report
The Claude cycle, etc.

2.60J Fundamentals of Advanced Energy Conversion
Spring 2020