Hydrogen purification technologies

HyWay Training School

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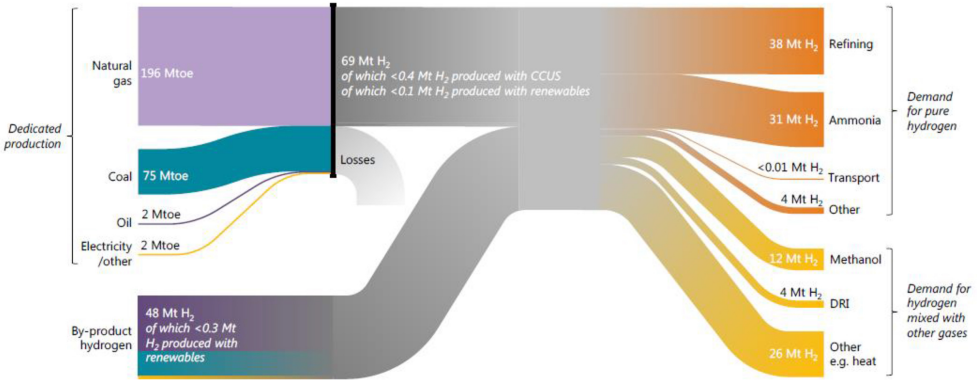
Outline

1 Who are you? Why purify hydrogen? What do you already know?

2 Introduction to molecular separations

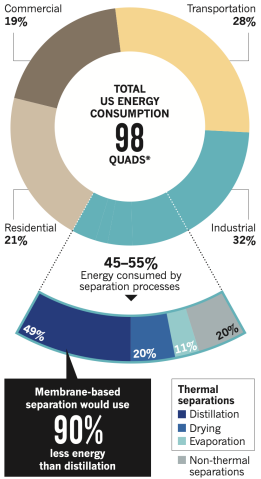
3 Pressure swing adsorption

4 Membrane separations

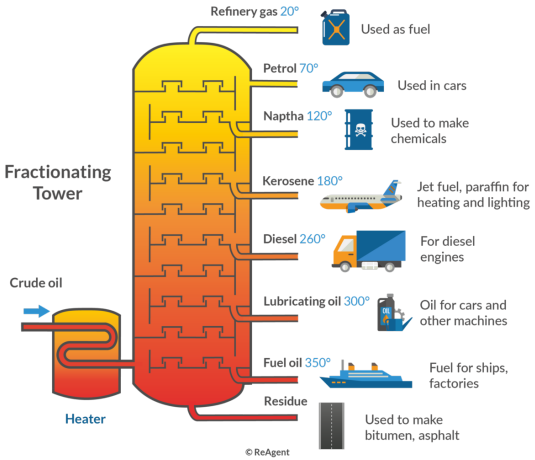

Dedicated production
Natural gas
196 Mtoe
Coal
75 Mtoe
Oil
2 Mtoe
Electricity /other
2 Mtoe
By-product hydrogen
48 Mt H2
of which <0.3 Mt H2 produced with renewables
69 Mt H2
of which <0.4 Mt H2 produced with CCUS
of which <0.1 Mt H2 produced with renewables
Losses
38 Mt H2
Refining
31 Mt H2
Ammonia
<0.01 Mt H2
Transport
4 Mt H2
Other
Demand for pure hydrogen
12 Mt H2
Methanol
4 Mt H2
DRI
26 Mt H2
Other e.g. heat
Demand for hydrogen mixed with other gases

A short Mentimeter poll - join at menti.com with code **4303 4977** or scan the QR code below

- Molecular separations are critically important and very energy intensive
- The major industrial separation technologies (e.g. distillation) account for 10 – 15% of global energy consumption
- At the most fundamental level, to separate two molecules we exploit some difference in properties
- Many differences are available (what are some?)



- Classic and most widely used separation exploits a difference in volatility
- Fractionation of complex hydrocarbon mixture yields a range of different products ranging from high-boiling-point (e.g. bitumen) to low-boiling-point (light gases)
- Heating energy required in the reboiler, cooling required in the condenser



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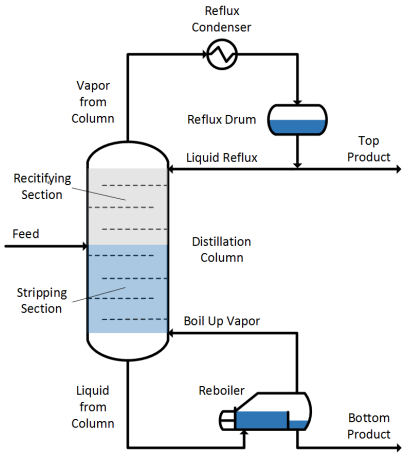
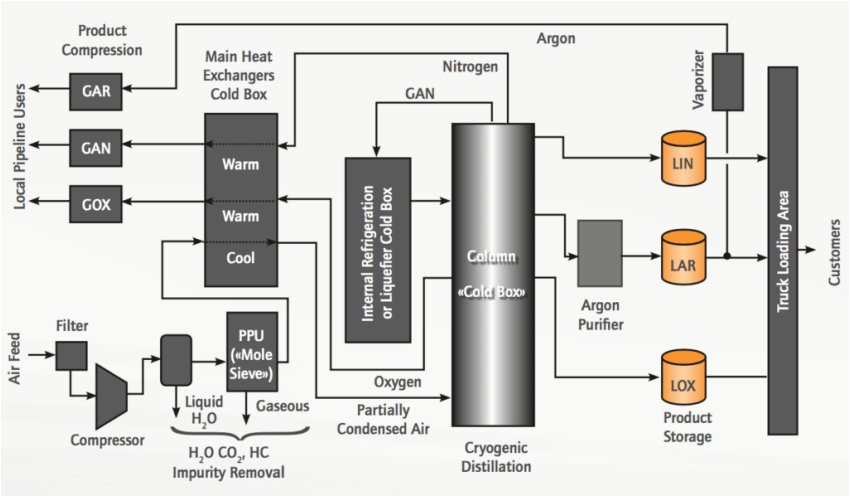
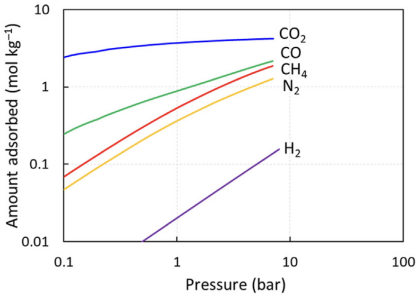
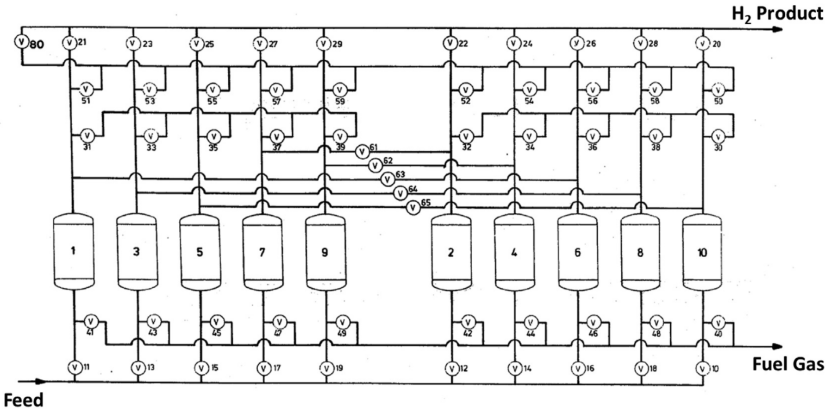


We usually think of distillation in the context of liquid separations, but can we also use distillation to separate gases?


Product Compression
Main Heat Exchangers Cold Box
Argon
Nitrogen
GAN
Vaporizer
GAR
GAN
GOX
Local Pipeline Users
Warm
Warm
Cool
Internal Refrigeration or Liquefier Cold Box
Column «Cold Box»
LIN
LAR
LOX
Argon Purifier
Truck Loading Area
Customers
Filter
Air Feed
PPU («Mole Sieve»)
Liquid H_2O
Gaseous
Oxygen
Partially Condensed Air
Compressor
H_2O CO_2, HC Impurity Removal
Cryogenic Distillation
Product Storage

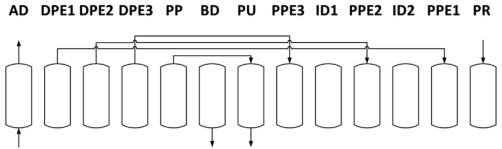
- Fundamental principle is differential adsorption of gases on solid sorbents
- In the simplest sense, adsorber vessels are pressurised and depressurised
- Design, selection of sorbents, equipment selection and operating strategy critically important
- Figure shows adsorption of light gases on Zeolite 5A at 299 K





In reality the flowsheet for hydrogen PSA systems is very complex - this is the UOP Polybed PSA process.

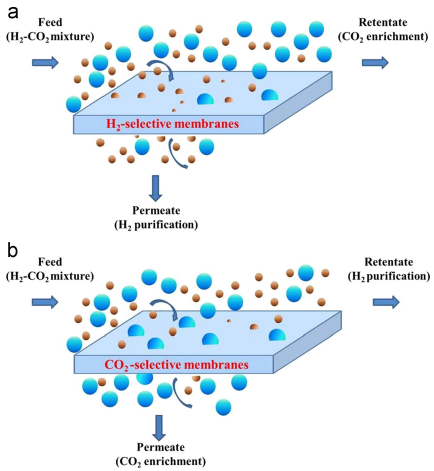
Operation strategies have been extensively simulated and in general, are extremely complex. However the key point is that highly pure hydrogen at good recoveries is possible with PSA systems, for a variety of different feed gas compositions.



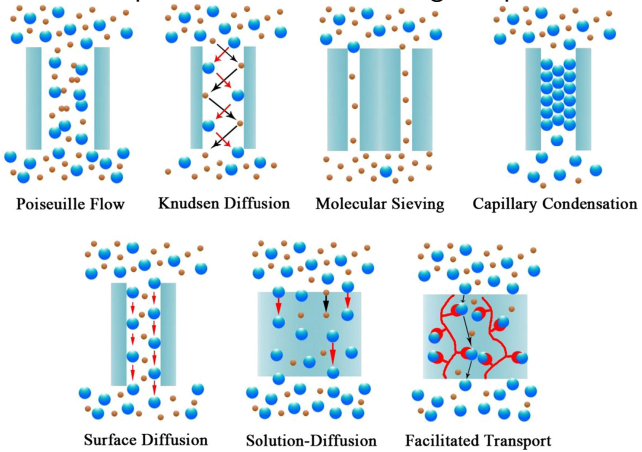
BED	STEP												
1	AD			DPE1	DPE2	DPE3	PP	BD	PU	PPE3	ID1	PPE2	ID2	PPE1	PR
2	PPE1	PR		AD			DPE1	DPE2	DPE3	PP	BD	PU	PPE3	ID1	PPE2	ID2
3	ID1	PPE2	ID2	PPE1	PR		AD			DPE1	DPE2	DPE3	PP	BD	PU	PPE3
4	PU		PPE3	ID1	PPE2	ID2	PPE1	PR		AD			DPE1	DPE2	DPE3	PP	BD
5	PP		BD	PU		PPE3	ID1	PPE2	ID2	PPE1	PR		AD			DPE1	DPE2	DPE3
6	DPE1	DPE2	DPE3	PP		BD	PU		PPE3	ID1	PPE2	ID2	PPE1	PR		AD	

Fig. 6 – Step configuration of a 6-bed H_2 PSA cycle with 3 pressure equalisations and 1 adsorbing bed (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/6$; $t_{PP} = t_{PU} = t_{PR} = t_{cycle}/9$; $t_{BD} = t_{DPE} = t_{PPE} = t_{ID} = t_{cycle}/18$) [97].

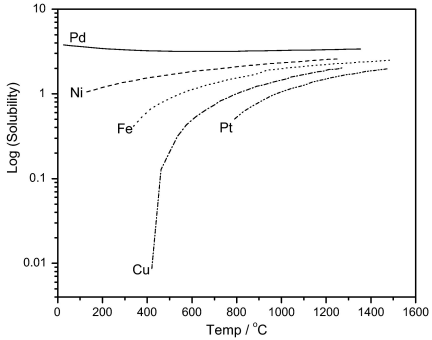
- Membrane separation exploits materials with selective separation properties to purify a gas mixture
- Different mechanisms and materials exist
- When we talk about membranes for hydrogen purification, we need to consider the feed gas mixture
- One example (H_2/CO_2) shows that hydrogen can be purified in the retentate OR the permeate



Range of different separation mechanisms in gas separation membranes.



- Metal membranes, especially palladium and palladium alloys, can provide exceptional purity hydrogen
- Selectivity for H_2 over other molecules almost infinite
- Very high cost, except in niche applications, not suitable
- Overall difficult to create thin, defect-free films, maintain chemical and thermal stability, not a commercial success



- Many other membrane materials have been proposed for H_2 separations
- Inorganic membranes (sol-gel synthesis)
- Polymers, mixed-matrix membranes
- Complex porous materials including metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and more

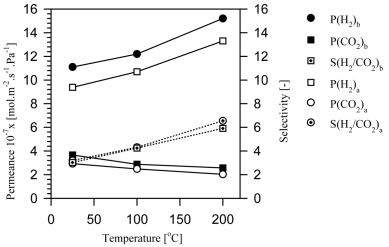
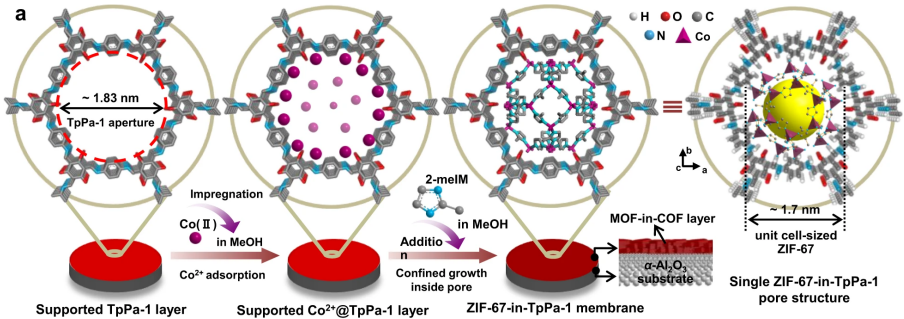


Fig. 2. Temperature dependence performance of the hydrophobic membrane (M1) shown as $(\text{before})_b$ and $(\text{after})_a$ use in PBMR.



Jürgen Caro et al. Nature Communications volume 12, Article number: 38 (2021)