# Sustainable Hydrogen and Electrical Energy Storage
## 22-4-2013

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# Production of hydrogen

- fossil fuels
- biomass
- electrolysis of water
- thermonuclear
- …

# Gupta Ch2 until 2.2.1.5

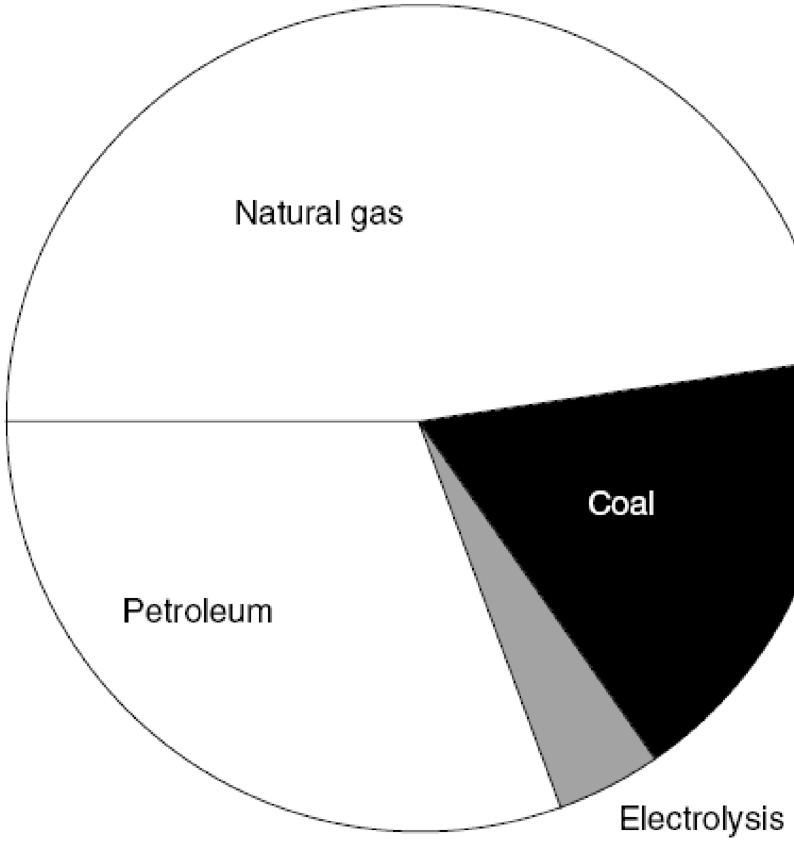


**FIGURE 2.1**
World hydrogen production structure. (Based on the data from The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs, The National Academic Press, Washington, 2004.)

# Current production of hydrogen: from fossil fuels mainly

Hydrocarbons are reformed:

$C_nH_m + n\ H_2O \rightarrow n\ CO + (m/2 + n)\ H_2$ 'synthesis gas'

The case of methane:

1 $CH_4 + H_2O \rightarrow CO + 3H_2 + \Delta H_1$
with $\Delta H_1$= -206 kJ/mol (steam)

This is a strongly endothermic reaction (costs energy) that requires catalysts (Ni or other). It requires more energy if the water is added as liquid.
Process conditions: 850 °C, 25 Bar

Subsequently the CO is used for:

2 $CO + H_2O \rightarrow CO_2 + H_2 + \Delta H_2$

with $\Delta H_2$= +41.1 kJ/mol (steam)

This reaction is called the 'Water-Gas Shift reaction' (WGS).

During 1 and 2 a surplus of $H_2O$ is used to prevent the formation of carbon, and to make sure that all CO reacts.

1+2 combine to

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 + \Delta H_{12}$

Required input heat during these reactions comes from burning some of the fuel:

3 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \Delta H_3$

$\Delta H_3 = 802.4$ (g) or $894.7$ (l) kJ/mol (g/l: gas/liquid)

Lower heating value Upper heating value

1+2+3: $2CH_4 + 2O_2 \rightarrow 2CO_2 + 4H_2 + \Delta H_{tot}$

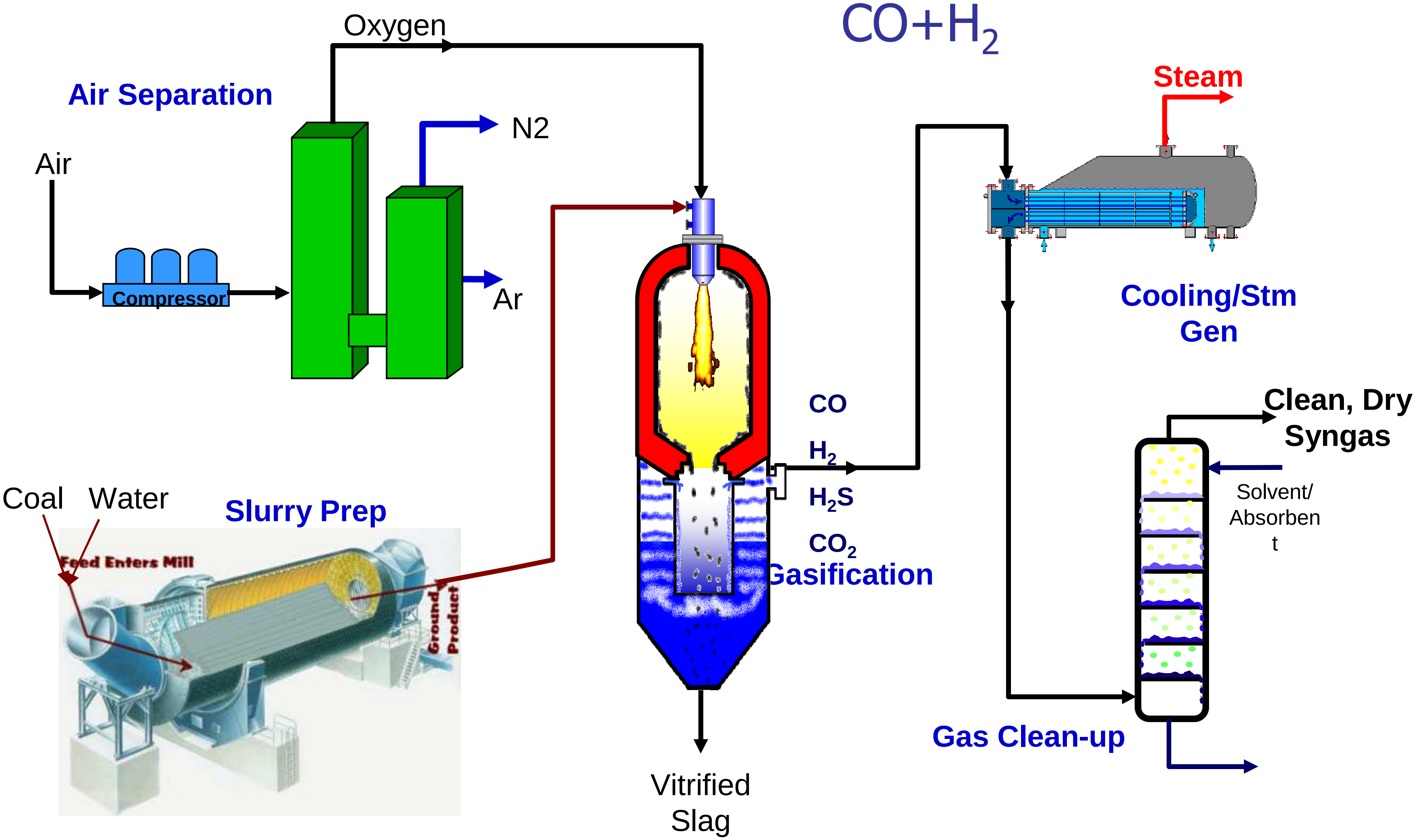
## Chemical conversion efficiency

$$\eta = \frac{E_{\mathrm{H_2}} + E_{\mathrm{steam,\,4.8\,MPa}}}{E_{\mathrm{NG}} + \mathrm{electricity} + E_{\mathrm{steam,\,2.6\,MPa}}} \tag{2.7}$$

This could reach 89% if one could use the energy in the steam. Then the conversion appears to be highly efficient.

# Gasification basics: producing ‘Syngas’ from fossil fuels

↓ $CO+H_2$



# Carbon formation

## Unwanted side reactions:

$CH_4 + 74.9 kJ/mol \rightarrow C + 2H_2$

$2CO \rightarrow C + CO_2 + 172.4\ kJ/mol$ ‘Boudouard reaction’

This C is mainly problematic for the catalysts in the process: they may become covered and blocked by spontaneously growing carbon filaments.

(application of this type of reaction is the production of carbon nanotubes)

Gupta fig. 2.22

The catalyst particles (e.g. Ni) can grow carbon filaments. This is also the way in which carbon nanotubes are produced (using small ~nm Ni particles).

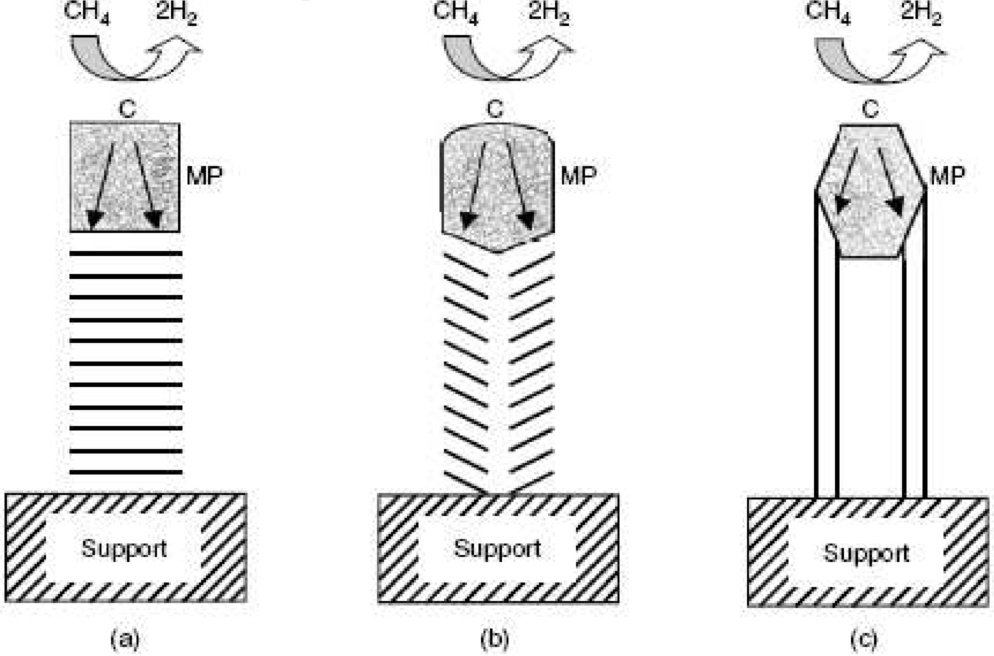
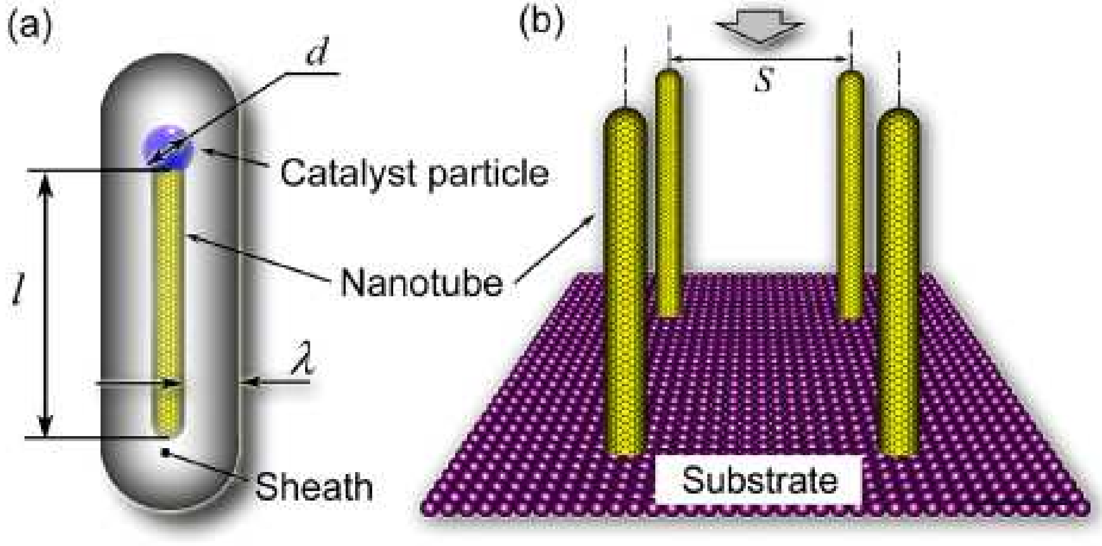
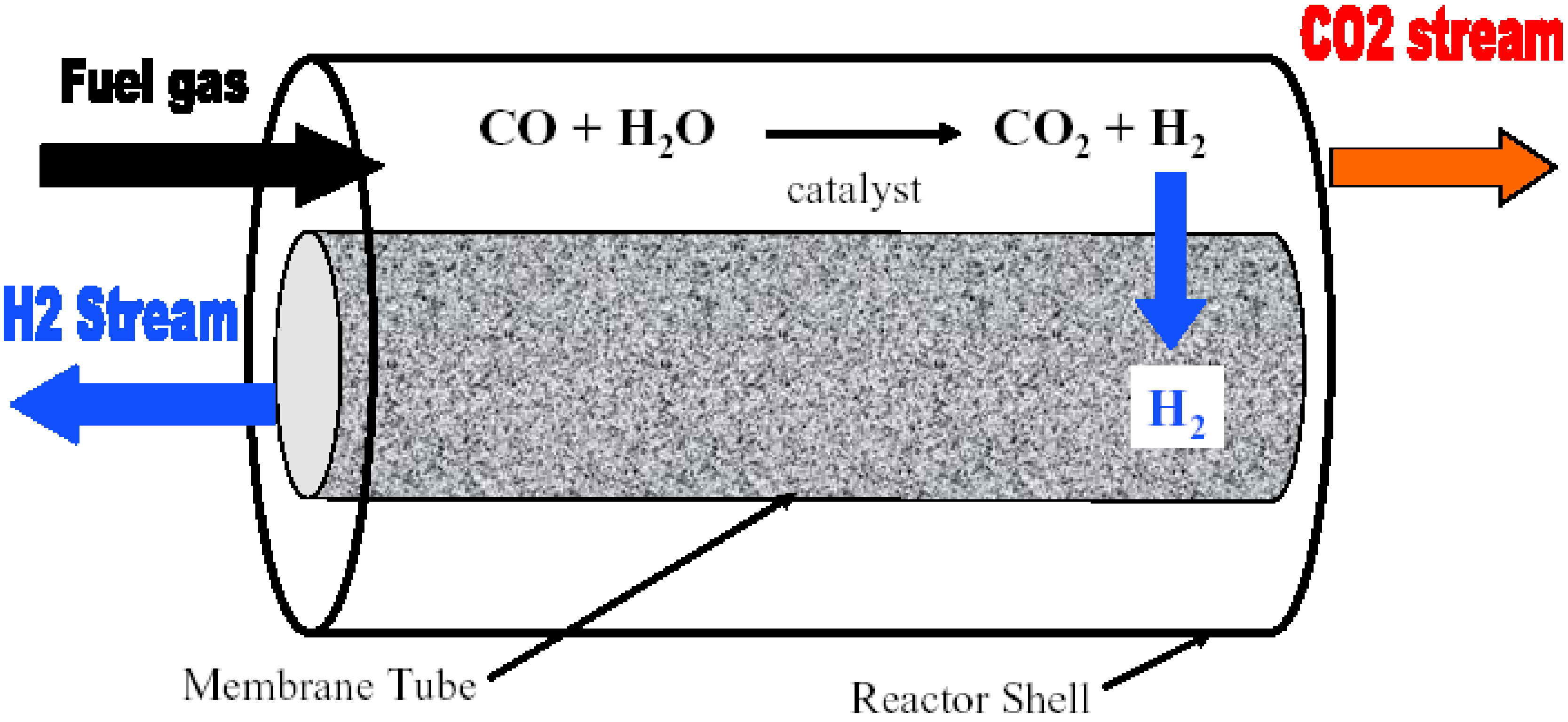


**FIGURE 2.22**
Schematic representation of carbon filaments of different structure produced by metal-catalyzed decomposition of methane. (a) Platelet structure, (b) "herringbone" structure, and (c) ribbon structure. MP denotes a nanosized metal particle.



J. Phys. D: Appl. Phys. **41** No 13 (7 July 2008) 132004

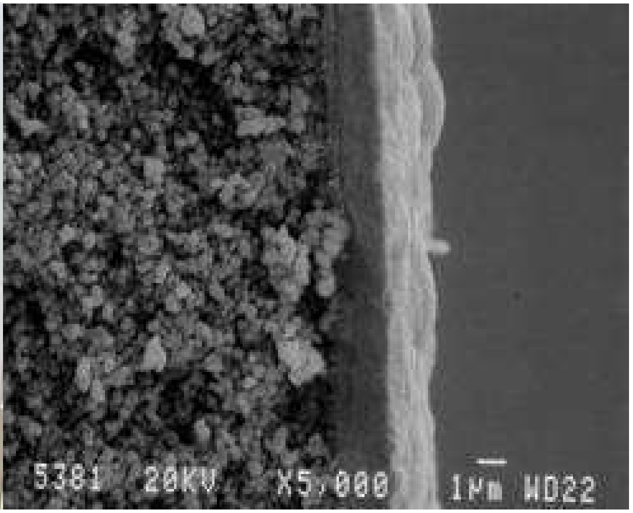
# Driving reaction by $H_2$ removal (Le Chatelier's principle): Membrane hydrogen separation integrated into WGS reactor

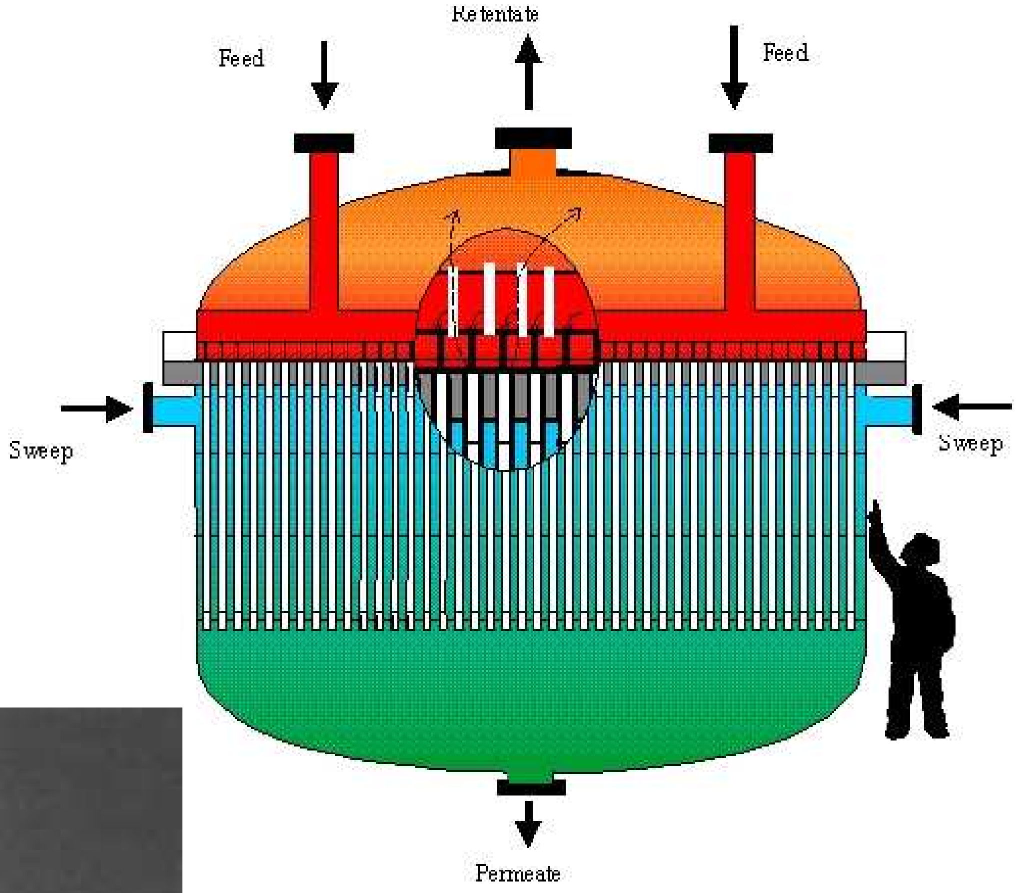


- Removal of $H_2$ drives reactions to completion
- $CO_2$ ready for sequestration?

# Membrane reactor with separation of hydrogen

tubes





Pd 4micron thick on ceramics serves as H filter (Pd: expensive!)
Pd forms $PdH_x$

## Conclusions hydrogen from fossil fuels

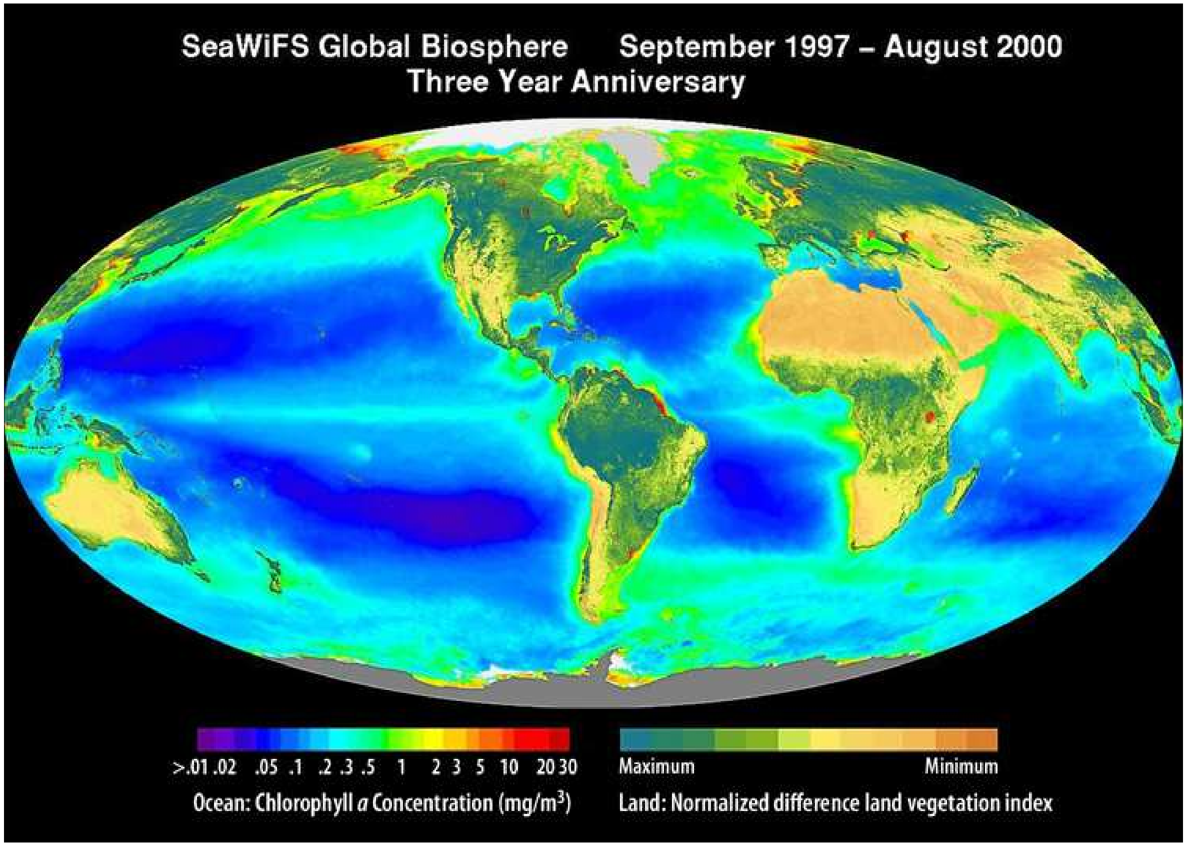
- high efficiency conversion of fossil fuels to hydrogen is possible using gasification.
- the presence of CO and other impurities that come from the fossil fuel pose problems for fuel cell catalysts.
- We will see: high purity of $H_2$ can be obtained by various separation methods.

## Obvious drawbacks

Fossil fuels are depleting and are not renewable (at least on human timescales).

$CO_2$ emissions continue unless large scale sequestration is realized. Capturing the $CO_2$ is relatively straightforward with the various gas separation techniques (but how to store it still needs to be resolved).

# Hydrogen from biomass



Graph: photosynthetic activity on land and in water (NASA)

Source: Ernst Moritz Arndt University

E-coli producing $H_2$ from sugar

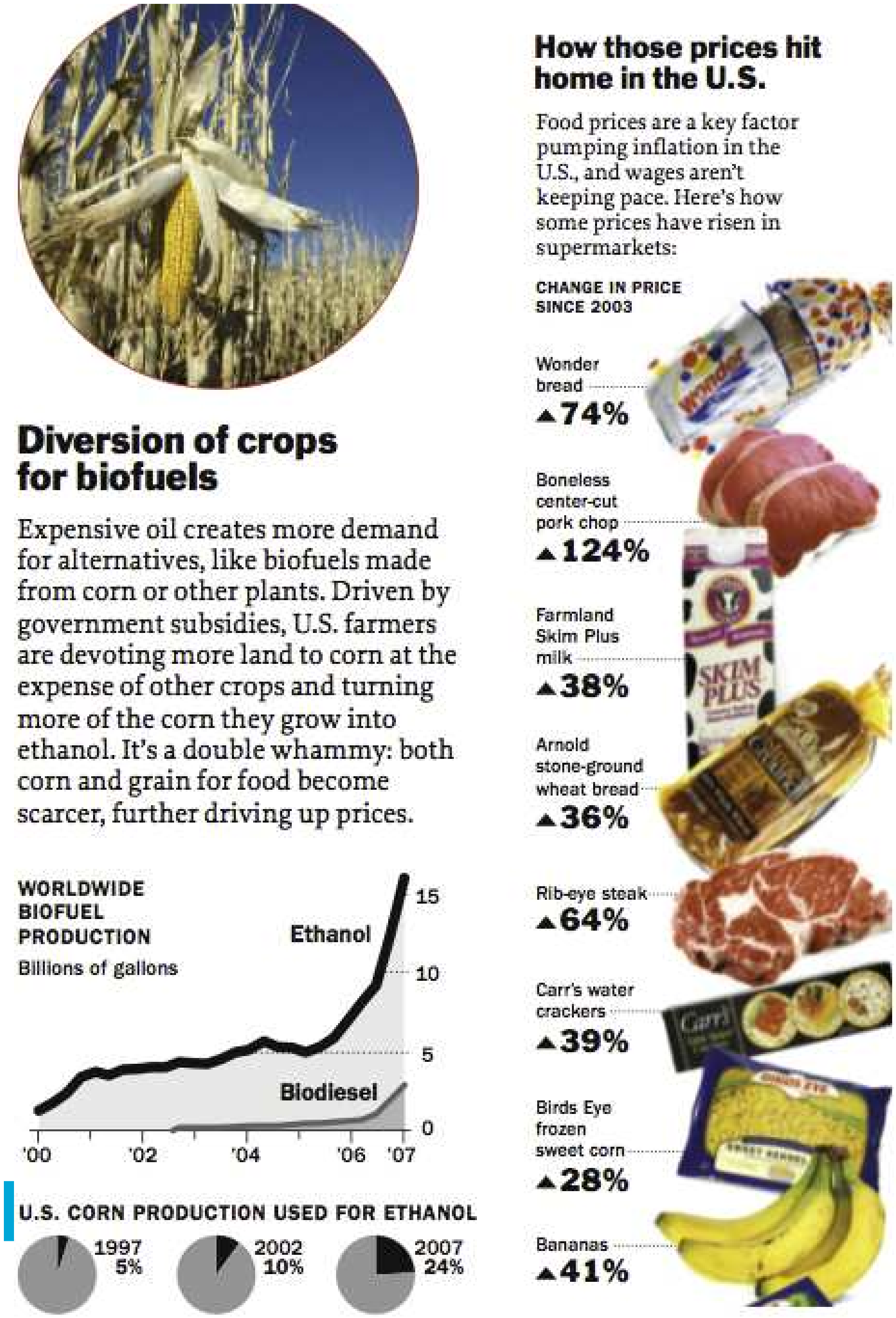
# Production of hydrogen from biomass

## Why?

- $CO_2$ neutral: as much $CO_2$ returned as captured
- Make use of waste streams present from food production
- Make use of waste land or algae in the sea

## Why not?

- possibly better to make ethanol, methanol or methane
- can reduce biodiversity (no ‘apes for oil/$H_2$’)
- competition with food production
- depletion of soils
- low energy yield after all the transportation, processing costs



**Diversion of crops for biofuels**

Expensive oil creates more demand for alternatives, like biofuels made from corn or other plants. Driven by government subsidies, U.S. farmers are devoting more land to corn at the expense of other crops and turning more of the corn they grow into ethanol. It's a double whammy: both corn and grain for food become scarcer, further driving up prices.

**U.S. CORN PRODUCTION USED FOR ETHANOL**

**How those prices hit home in the U.S.**

Food prices are a key factor pumping inflation in the U.S., and wages aren't keeping pace. Here's how some prices have risen in supermarkets:

**CHANGE IN PRICE SINCE 2003**

Wonder bread ▲74%

Boneless center-cut pork chop ▲124%

Farmland Skim Plus milk ▲38%

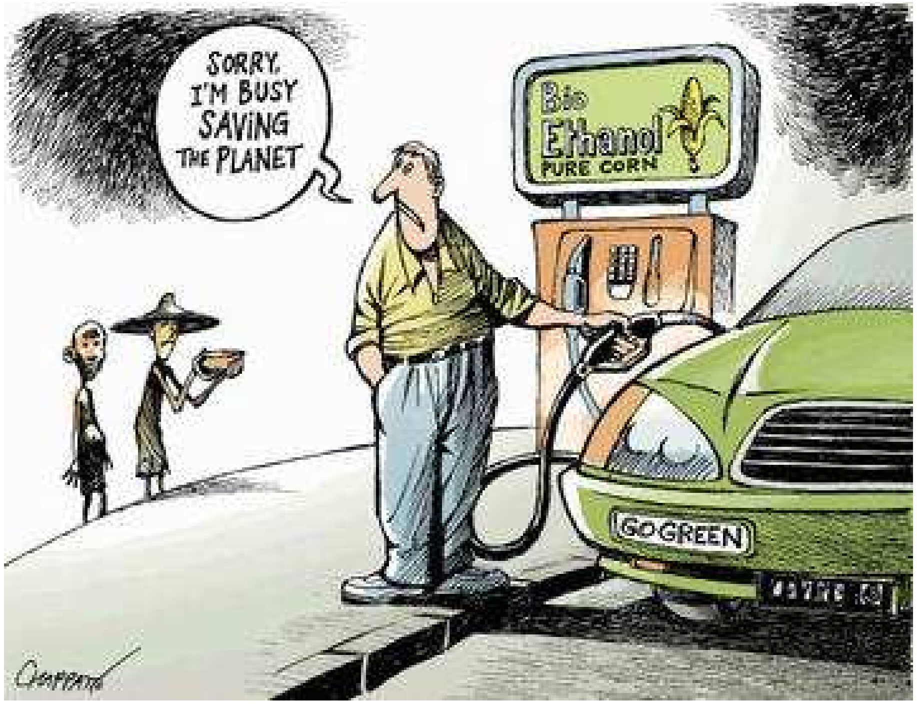
Arnold stone-ground wheat bread ▲36%

Rib-eye steak ▲64%

Carr's water crackers ▲39%

Birds Eye frozen sweet corn ▲28%

Bananas ▲41%



Not only the crop used for fuel becomes expensive, also other crops.

Time Magazine
May 2008

# Production of hydrogen from biomass

- Gasification

- Biological hydrogen production by microbes

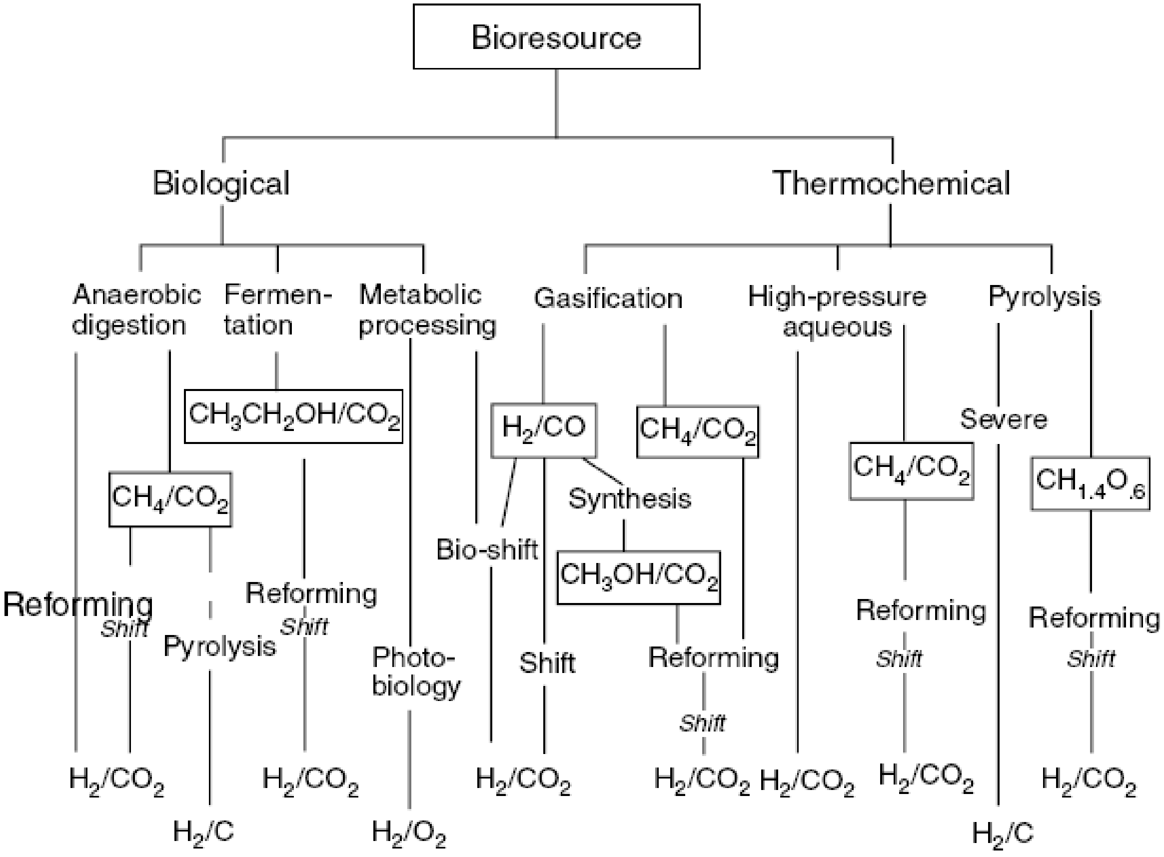


**FIGURE 6.3**

Pathways from biomass to hydrogen. (Adapted from Milne, T.A., Elam, C.C., and Evans, R.J., *Hydrogen from Biomass—State of the Art and Research Challenges*. IEA/H2/TR-02/001, A Report for the International Energy Agency Agreement on the Production and Utilization of Hydrogen Task 16, Hydrogen from Carbon-Containing Materials, Golden, CO USA, 2001.)

# Gasification of biomass

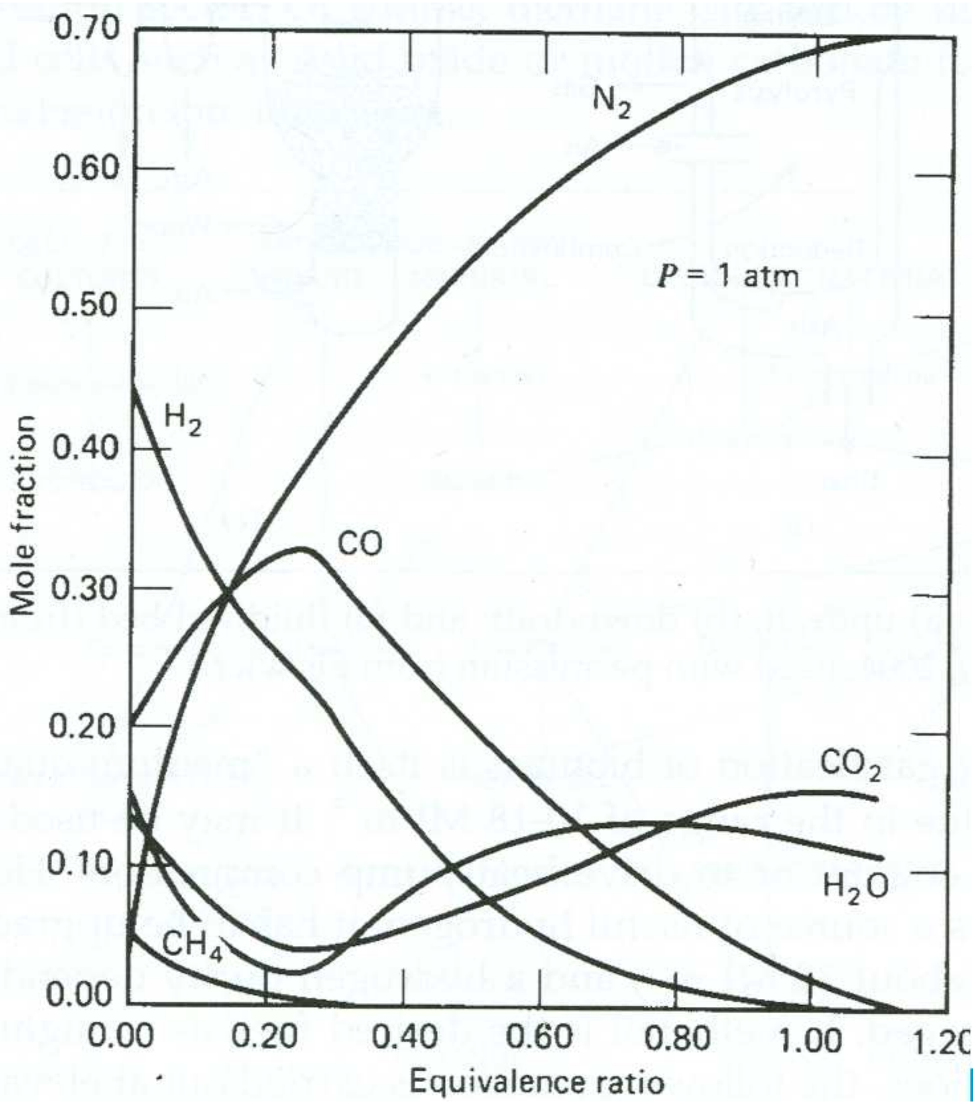
In principle gasification of biomass gives similar products as the gasification of fossil fuels, including hydrogen. Valuable nutrients can be recovered from the ashes and can be used as soil fertilizers.

Gasification may be viewed as a combustion like process where too little oxygen is available to allow burning.

Equivalence ratio (ER): available $O_2$ / $O_2$ required for complete burning

If ER<0.1: process is called pyrolysis
0.2<ER<0.4: good gasification

# Typical output gasses from gasification of biomass



Why is 0.2 – 0.4 good range?

Why is 0.2 – 0.4 good range?

High $H_2$ and CO, low $H_2O$, $CO_2$, $CH_4$.
CO can be used in WGS to produce more $H_2$.

# Pretreatment of biomass

To enable:

reliable feeding systems, transport, storage and handling

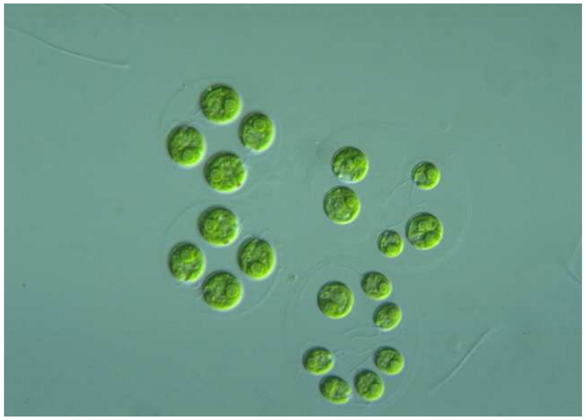
Methods:

drying, chipping, densification, sizing in certain shapes.
Sometimes also leaching to remove salts before gasification.

Maximum water content that is allowable: 35%

# Biological hydrogen production can be classified into five different groups:

(i) direct biophotolysis, or photosynthesis
(ii) indirect biophotolysis,
(iii) biological water–gas shift reaction
(iv) photo-fermentation and
(v) dark fermentation



Algae that can produce hydrogen

An overview of hydrogen production from biomass
Meng Ni, et al., Fuel Processing Technology 87 (2006) 461 – 472

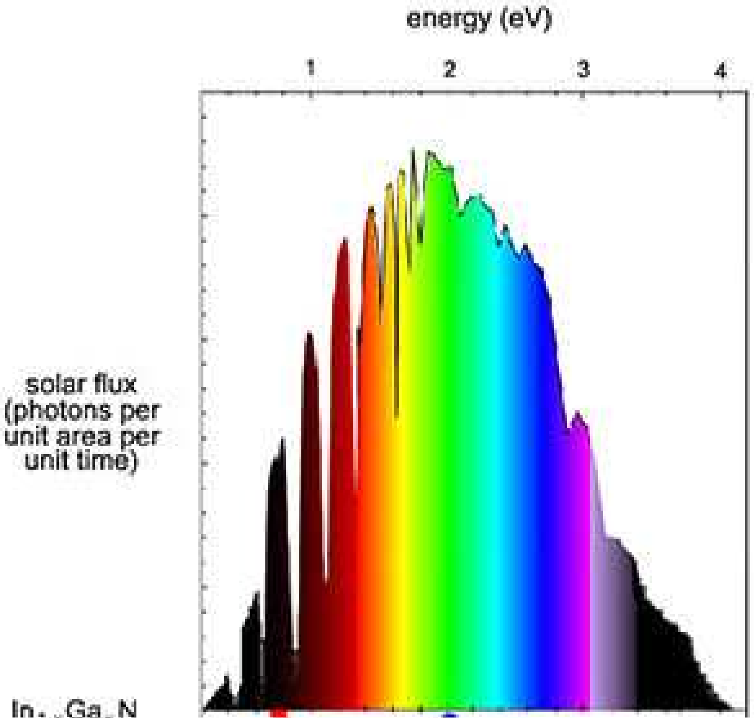
# (i) Direct photosynthesis

See also Gupta 7.5

$2H_2O + 590\ \text{kJ/mol} \rightarrow O_2 + 4H^+ + 4e^-$

$590\ \text{kJ/mol} = 6.16\ \text{eV per}\ 2H_2O$

Basic problem for photosynthesis:
On average ~3 - 4 photons
need to be absorbed to
capture this large amount of energy



Solar spectrum at earth surface

The $H^+$ and $e^-$ can be used to generate $H_2$ or other form of chemically bound H:

| | |
|---|---|
| $2H_2O \rightarrow O_2 + 2H_2$ | hydrogen |

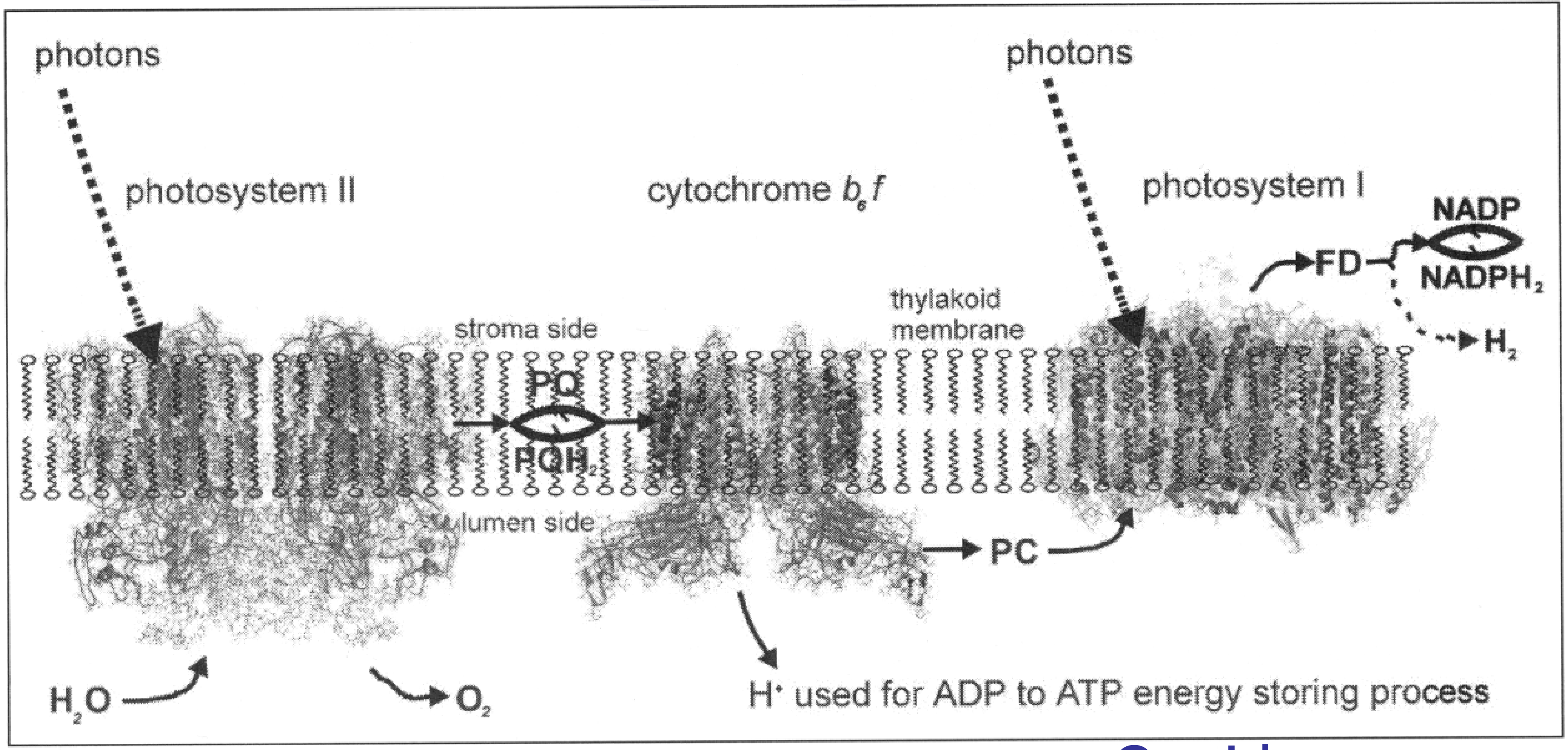
or e.g.

| | |
|---|---|
| $CO_2 + H_2O \rightarrow CH_2O + O_2$ | formaldehyde |

# Direct photosynthesis

## Membrane separates $H_2$ and $O_2$

H2 side

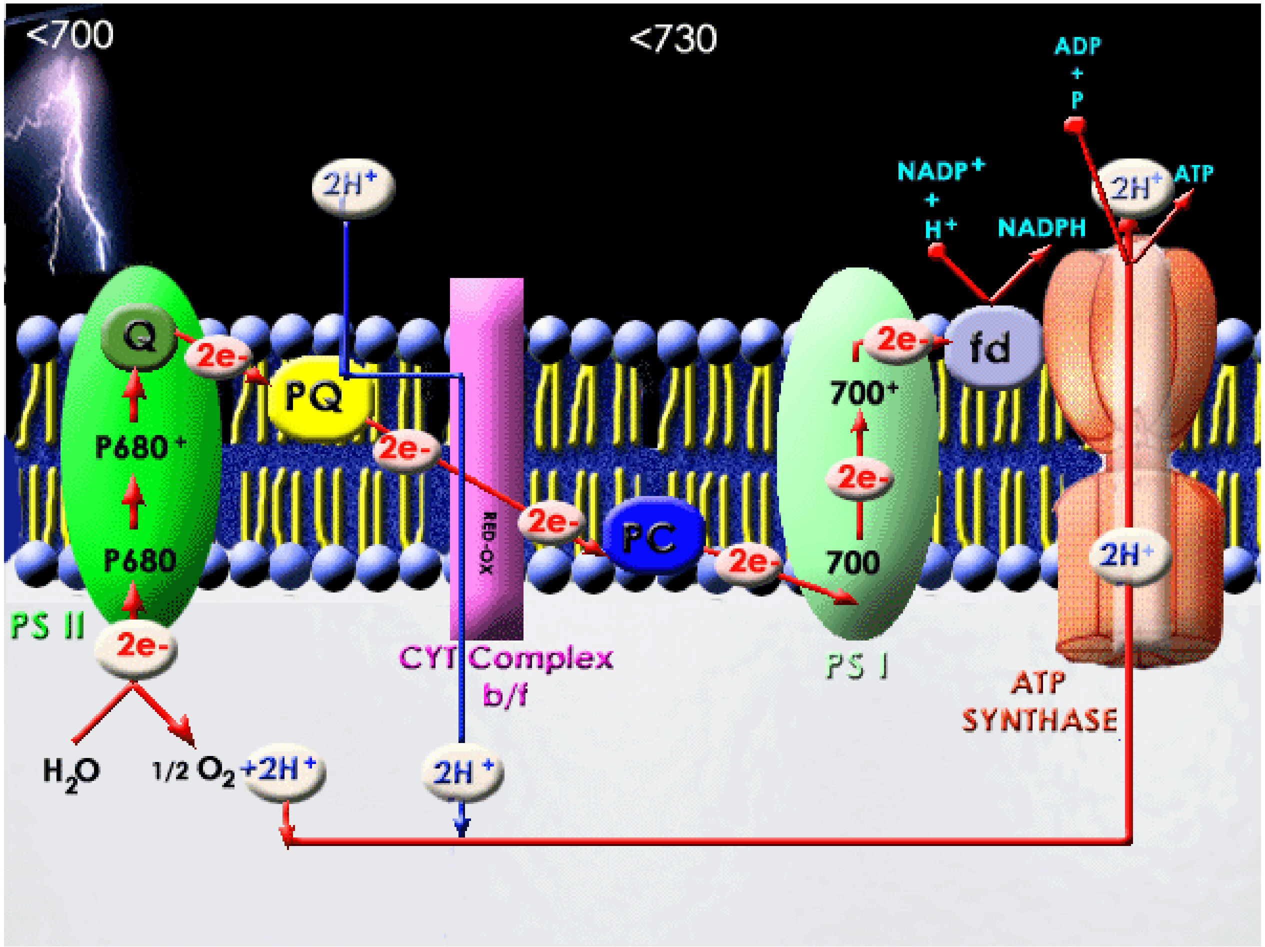


$O_2$ side

Subsequent reaction steps are taking place in different parts of the photosynthetic membrane

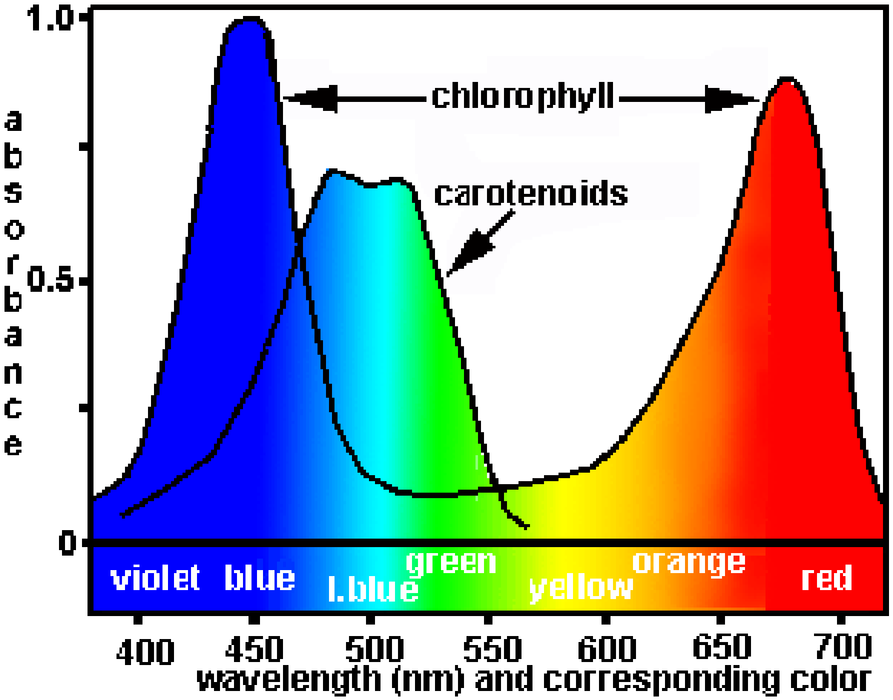
1: Splitting of water using light takes place in photo system II
A $Mn_4O_4$ cluster plays an important role.
2: Hydrogen emerges in the form of $pqH_2$ (pq=plastoquinone)
3: The cytochrome $b_6f$ transfers the energy in $pqH_2$ to plastocyanin pc, and recycles pq to photosystem II
4: pc migrates to photo system I
5: with more light absorption in system I pc is transferred to ferredoxin FD that can convert NADP to $NADPH_2$. Ferredoxin contains $Fe_4S_4$ cluster.
6: $NADPH_2$ can assimilate $CO_2$ to form sugars

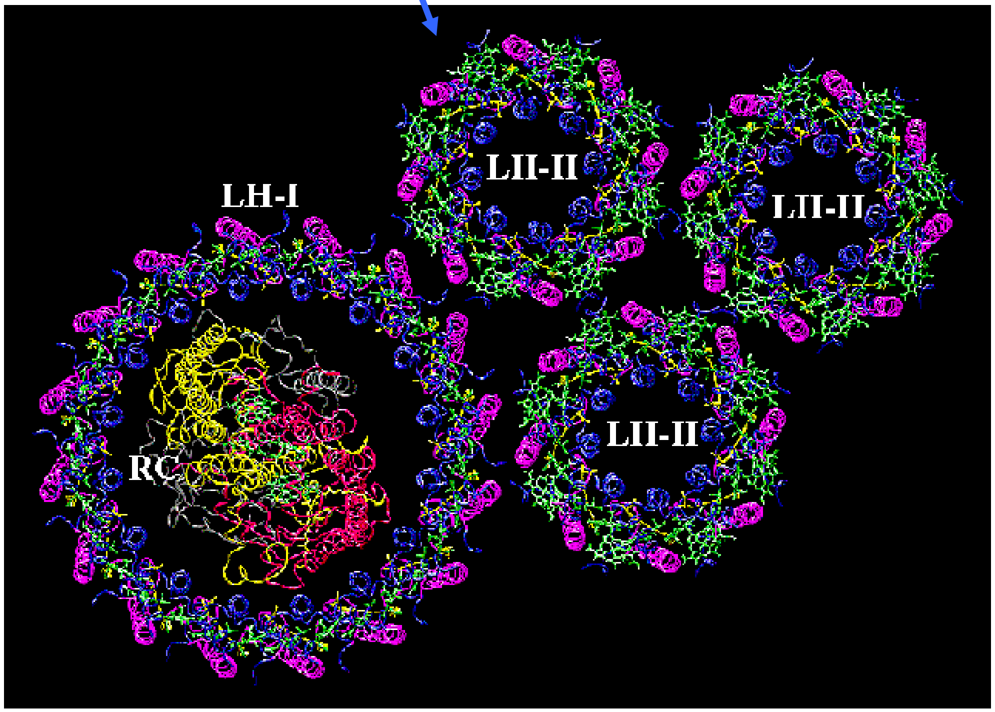
In some bacteria step 5 and 6 can be replaced by the formation of $H_2$. Exploitation of such organisms leads to direct biological $H_2$ production. Genetic modifications may be used.



Steps 1 2 3 4 5 6

# Light is absorbed in molecular antenna systems composed of Chlorophyll aggregates and carotenoids close to the Photo Systems I & II





## Direct photosynthesis possibilities

- biological processes aim to benefit the organism, and produce sugars or also $H_2$ for internal use only, not for our use.

- genetic modification may alter the amount of $H_2$ produced

- solar ray to biomass conversion has 0.2% efficiency as a global average, rising to 2% in coral reefs (*this low compared to PV*)

- solar ray energy to $H_2$ conversion may be 1% efficient in theory
(Compare to normal solar cell (>10%)+ electrolyser (70%): 10*0.7%)

- biomass produced may be used for hydrogen/oil/ethanol

- algae and cyanobacteria are most promising organisms

# (ii) Indirect biophotolysis

Basic idea: bacteria (e.g. cyanobacteria)
- first produce biomass, sugars using photosynthesis
- subsequently the biomass is consumed to produce $H_2$ and $CO_2$
- estimated overall cost is US$10/GJ of hydrogen

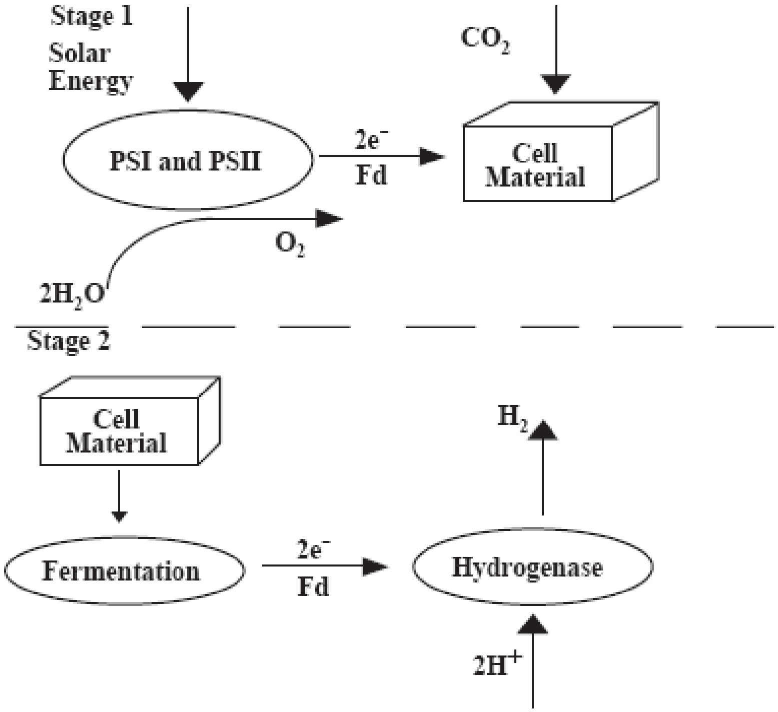


Fig. 5. Indirect biophotolysis for hydrogen production.

$$12H{\pm}_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2.$$

glucose

# (iii) Biological water–gas shift reaction

Some bacteria can live from energy using light (photosynthesis) but still survive in the dark thanks to the ability to feed on C containing feed stocks like CO:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -20.1 kJ/mol$$

These bacteria can thus produce energy and $H_2$.

This is in the research stage: finding organisms, determining feasibility, cost, genetic modification, etc.

# Genetic engineering of bio reactions

Metabolically engineer *Escherichia coli* for hydrogen production. It is one of the easiest strains to manipulate genetically.

Example in Microbial Biotechnology (2008) **1**(1), 30–39:

Modifying genes to switch on:
- 141 x higher $H_2$ production from formate ($CHOO^-$ ion)

$HCOO^- + H_2O \leftrightarrow H_2 + HCO^-_3$
- 50% increase from glucose

Researchers remark that this actually weakens the bacteria because they loose part of their energy to hydrogen production.

# (iv,v) Biological fermentation

Fermentation: production of energy-rich liquid/gas from organic substrate under oxygen-free and dark conditions.

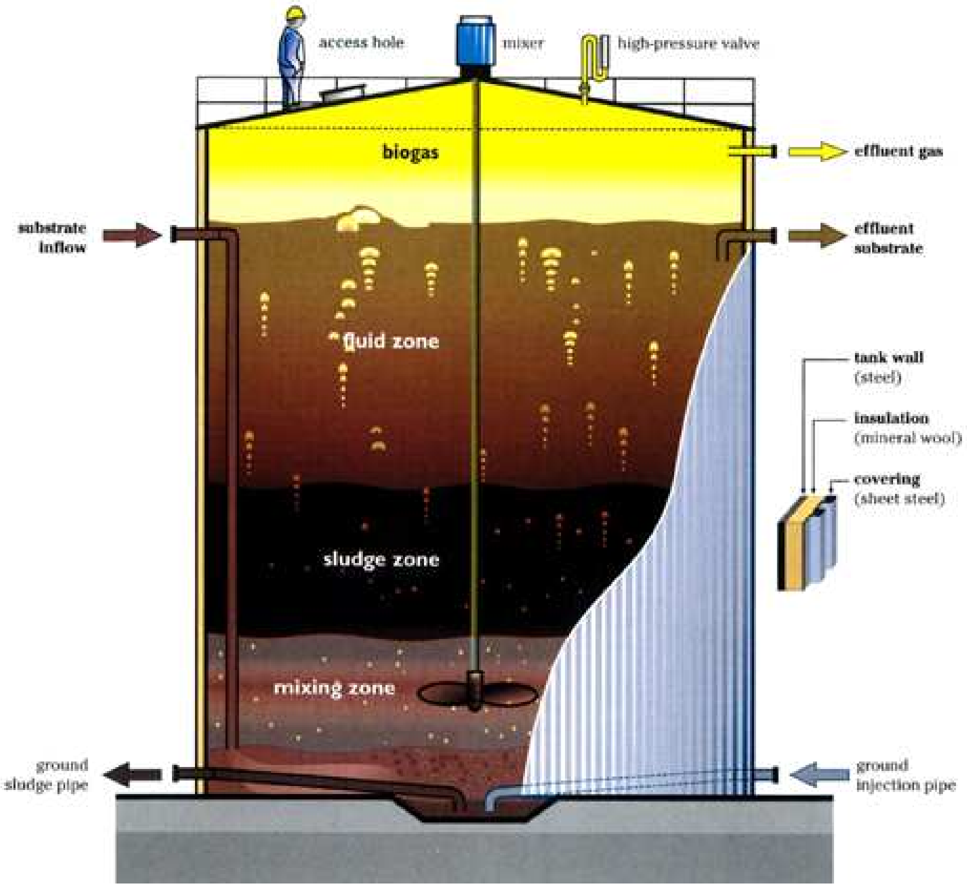
Conversion of glucose to hydrogen (and acids, $CO_2$):

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 + 184.2\ \text{kJ/mol}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 + 257.1\ \text{kJ/mol}$$

# Anaerobic digestion of feedstocks by bacteria

There are two conventional operational temperature levels:
- optimally at 37°C or at ambient temperatures between 20°-40°C using mesophile bacteria
- at elevated temperatures up to 70°C with thermophile bacteria



- When bacteria grow on organic substrates, these substrates are degraded by oxidation to provide building blocks and metabolic energy for growth.

- This oxidation generates electrons which need to be disposed of to maintain electrical neutrality.

- In aerobic or oxic environments, oxygen is reduced and water is the product.

- In anaerobic or anoxic environments, other compounds need to act as electron acceptor and protons that are reduced to molecular hydrogen can fulfill this role.

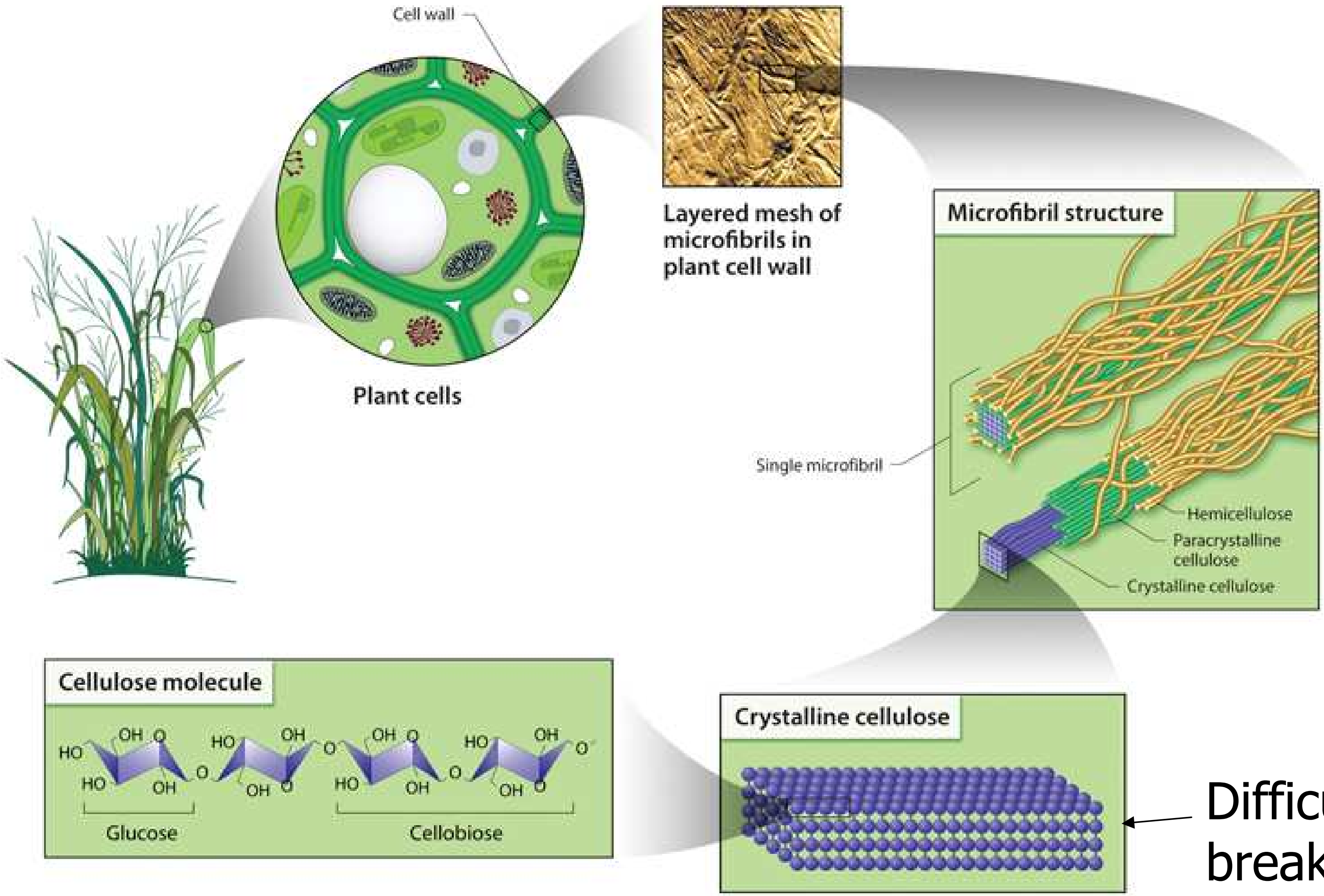
# Main fuel product

$CH_4$ and $H_2$

# Important by-products:

Lignin and chitin. Currently this part is rather indigestible and needs further processing in order to yield useful biofuels. Simplest solution: produce hydrogen by gasification.

- liquid leftovers containing minerals, trace elements, …
Depending on content this should be ingredients for fertilizers required for new crop growth.



Difficult to break down

Lignin is in between cellulose parts, binding the materials together

# Fermentation uses living organisms

Dealing with living organisms means that the conditions of sugar supply, heat, water and the removal of products needs to be optimal. Otherwise the fermentation may be varying in yield or may stop altogether.

Yield of fermentation processes is lower than other processes like the gasification. This makes that improvements are required.

Biotechnology goal:
finding enzymes that can break up lignin, chitin and cellulose to produce alcohols, hydrogen

# Energy yield Gupta 6.1.4

Typical dry mass of biomaterials are:
C: 30 – 60 %
H: 5-7%
O: 30-45%
Due to low C and high O content typical LHV are 10 – 18MJ/kg.
Compare to coal: 30 MJ/kg

Critical assessment is necessary to evaluate energy yield:

- growing, harvesting and transport to hydrogen production sites. Significant logistic operations.
- new crops need to be planted and fertilizer added.

The energy invested for all processing, transport, … needs to be taken into account when determining the overall yield. There still is energy gained.

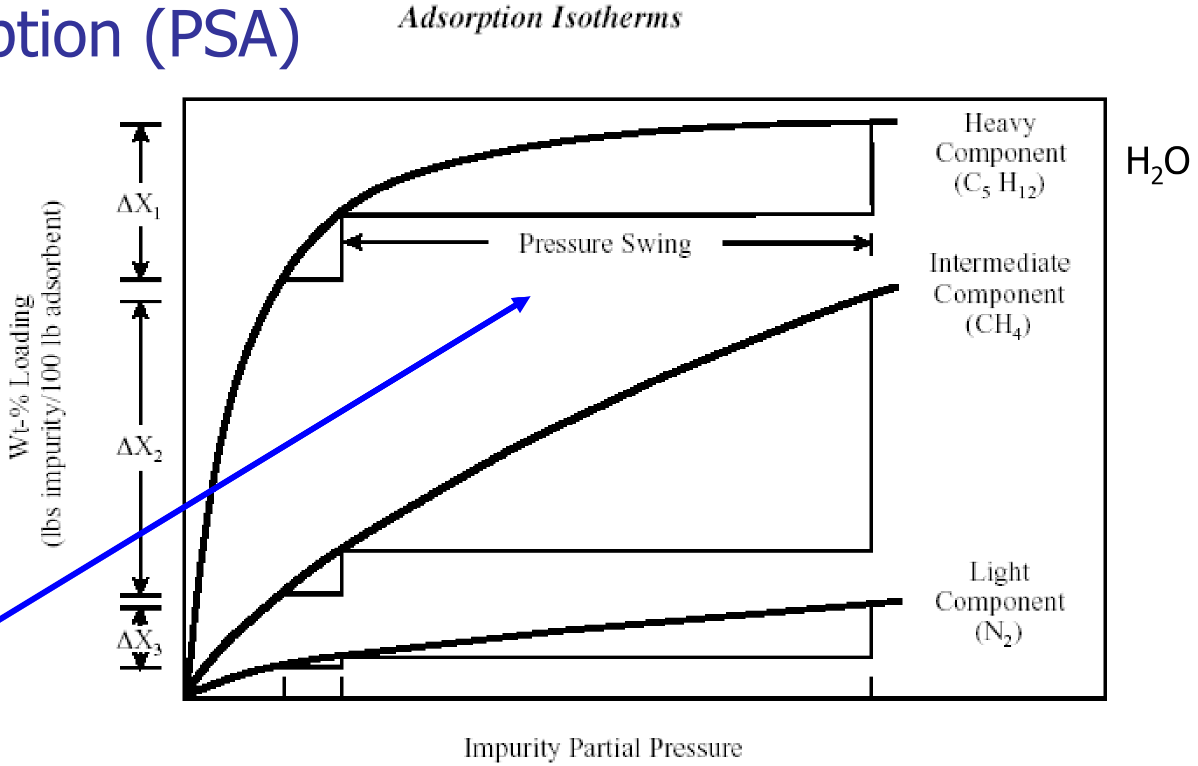
# Hydrogen collection from gas streams; separation and purification Gupta Ch8.3

Various methods exist for the separation of hydrogen from other gases including $CO_2$, $H_2O$, …

| | |
|---|---|
| - Pressure sweep adsorption method | *mature* |
| - Membrane separation | *research* |
| - Cryogenic separation | *mature* |

# Pressure Swing Adsorption (PSA)

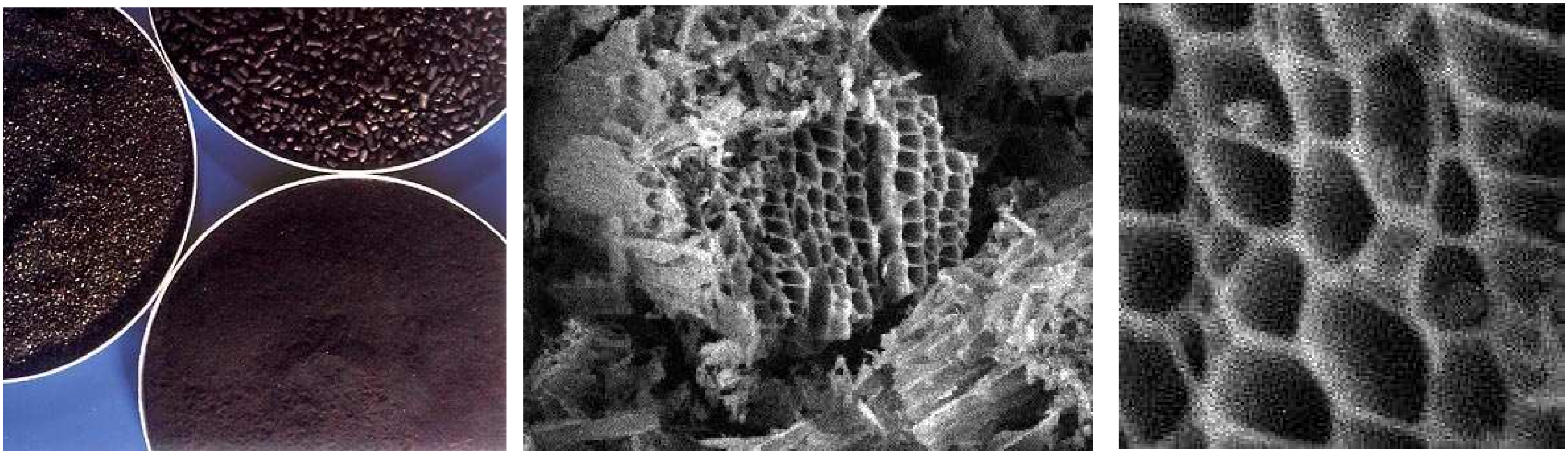
This purification method makes use of the fact that all impurities stick better to a substrate than hydrogen does.



In this region of pressures the impurities mostly remain adsorbed while hydrogen does not. This means that if you release the pressure from the vessel, first ‘only’ hydrogen comes out.
By using many pressure sweep cycles one can obtain pure $H_2$ with impurities reduced to ppm’s.

# Typical adsorber materials: activated carbon, silica gel, alumina,…

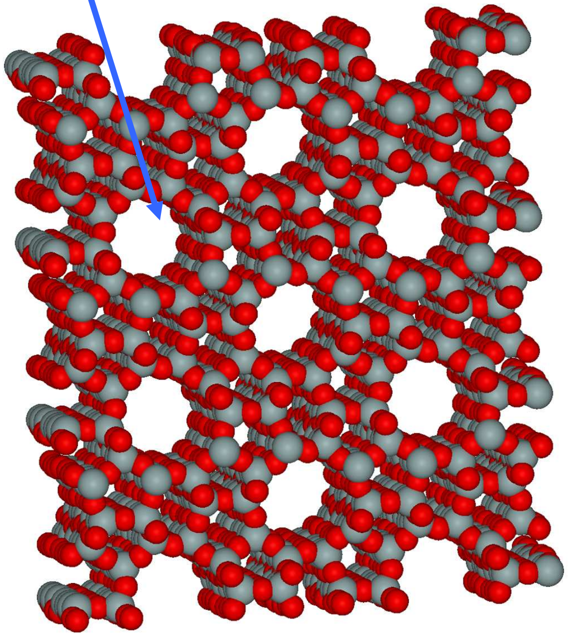
ad, not ab: ‘adsorption’ used for molecules sticking to surfaces



Typical adsorbent materials should have large surface area on which gasses can adsorb. These carbons above can reach 2200 $m^2g^{-1}$

Example of a zeolite based material,
'molecular sieve'

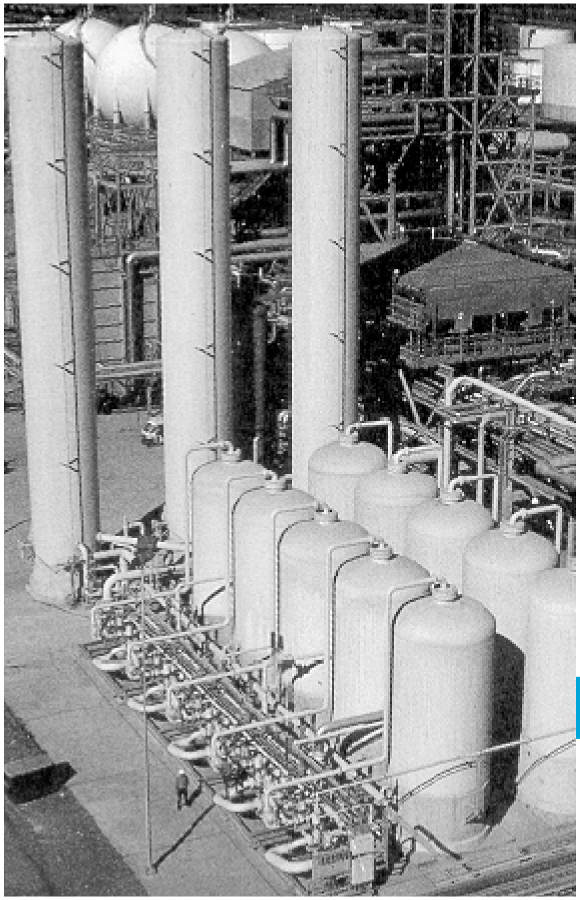
at an atomic scale: small pores in which molecules like can be adsorbed

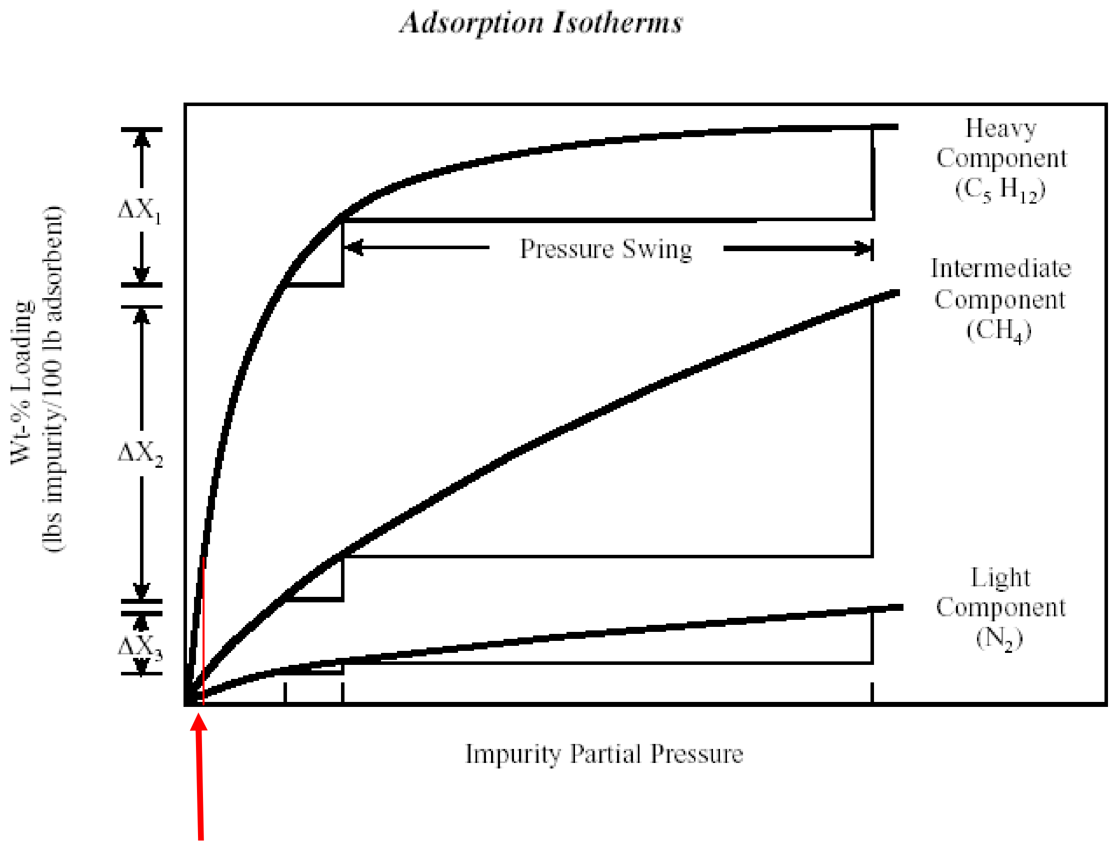


ZSM-5

# *Relative Strength of Adsorption of Typical Impurities*

| Non-Adsorbed | Light | Intermediate | Heavy |
|---|---|---|---|
| $H_2$ | $O_2$ | CO | $C_3H_6$ |
| He | $N_2$ | $CH_4$ | $C_4H_{10}$ |
|  | Ar | $C_2H_6$ | $C_5$+ |
|  |  | $CO_2$ | $H_2S$ |
|  |  | $C_3H_8$ | $NH_3$ |
|  |  | $C_2H_4$ | BTX |
|  |  |  | $H_2O$ |





Regeneration of adsorber is done by reducing the pressure to low levels, gasses coming off then are mostly the waste products, $H_2O$, $CO_2$, … (off-gas)

# Membrane materials for purification:

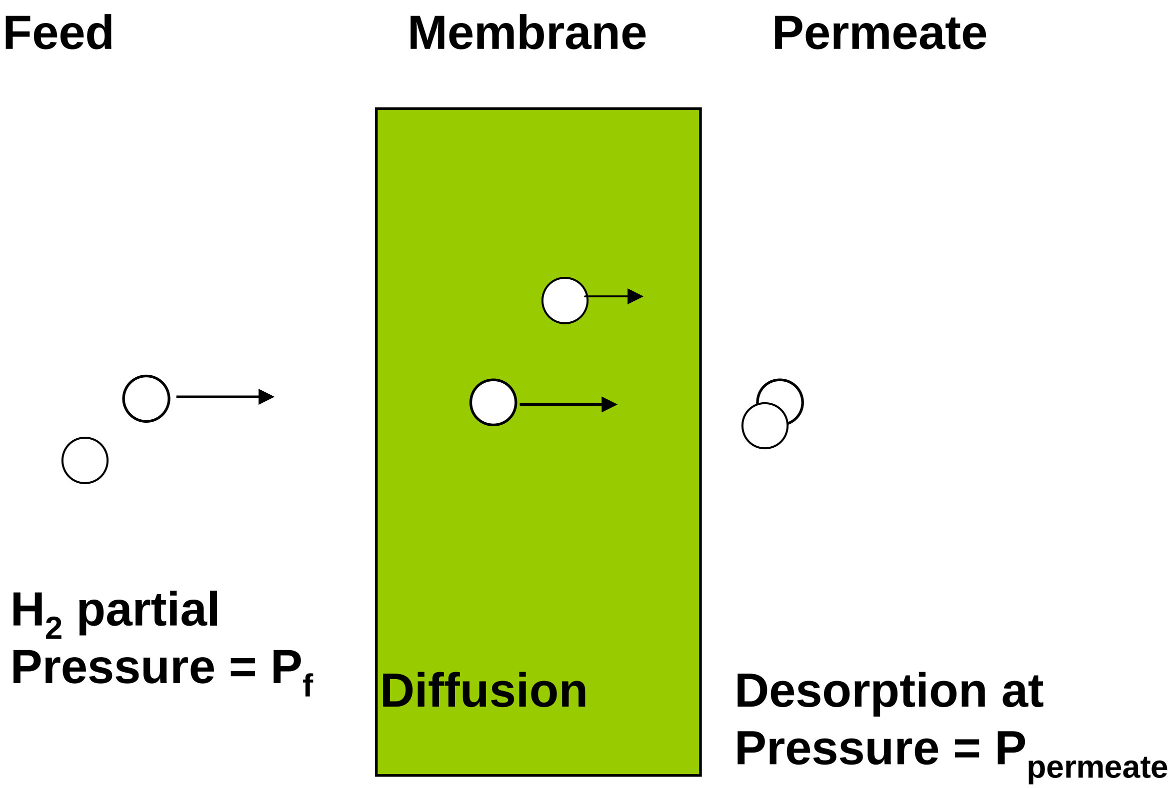
- high temperature ceramics with hydrogen permeable noble metal top layers for inside reactors

- polymer membranes can be used at lower temperatures. The difference in diffusion coefficient for hydrogen compared to other gasses is used as separation mechanism.

These membrane reactors are relatively new developments. Research is required for durability, performance, yield, cost issues.

# Metal membranes for hydrogen separation

Some metals can split $H_2$ in separate atoms and transport them



**Feed**

**Membrane**

**Permeate**

**$H_2$ partial Pressure = $P_f$**

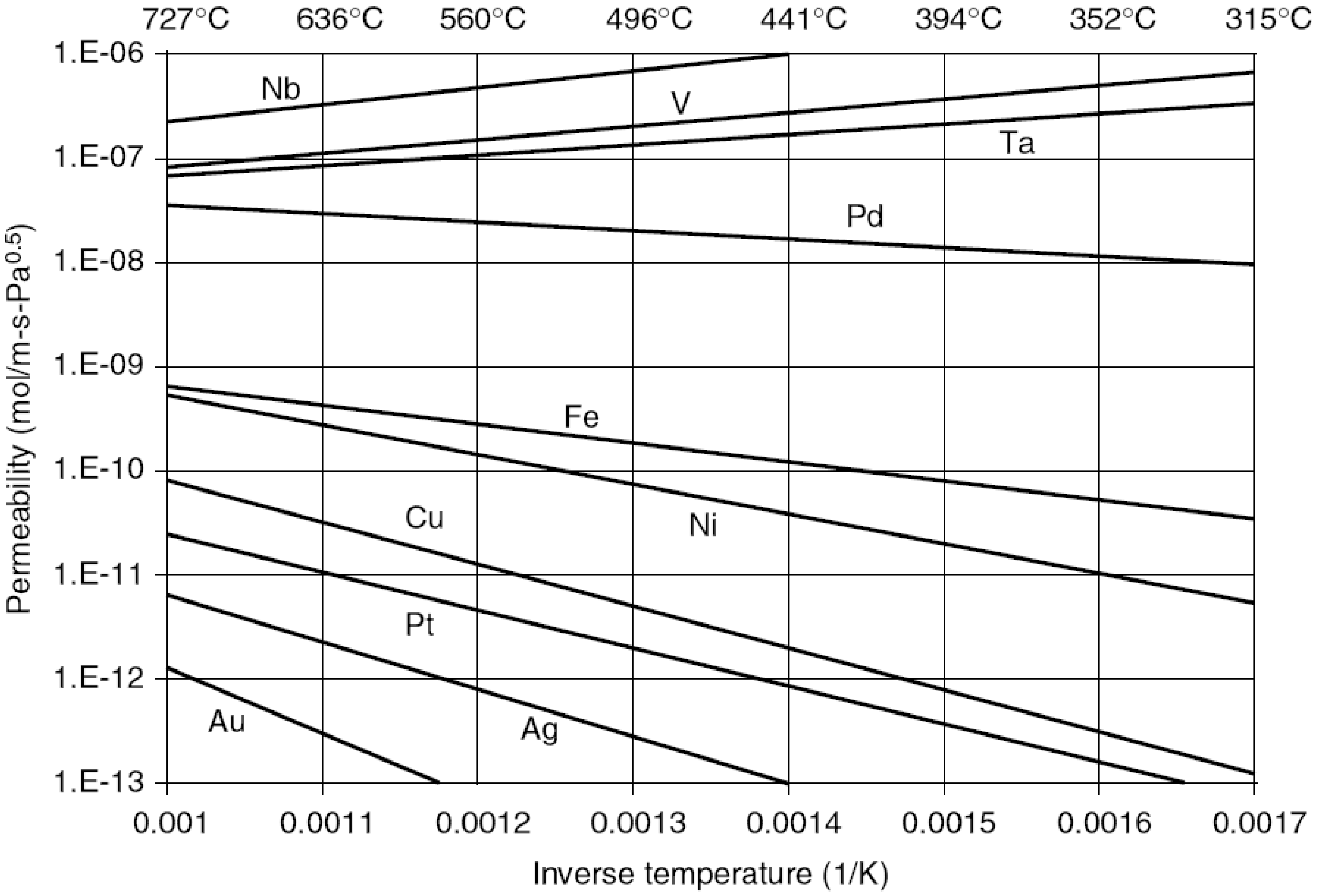
**Diffusion**

**Desorption at Pressure = $P_{permeate}$**

Flux *J* depends on *P* $^{0.5}$ and thickness *L*.
*k*=permeability

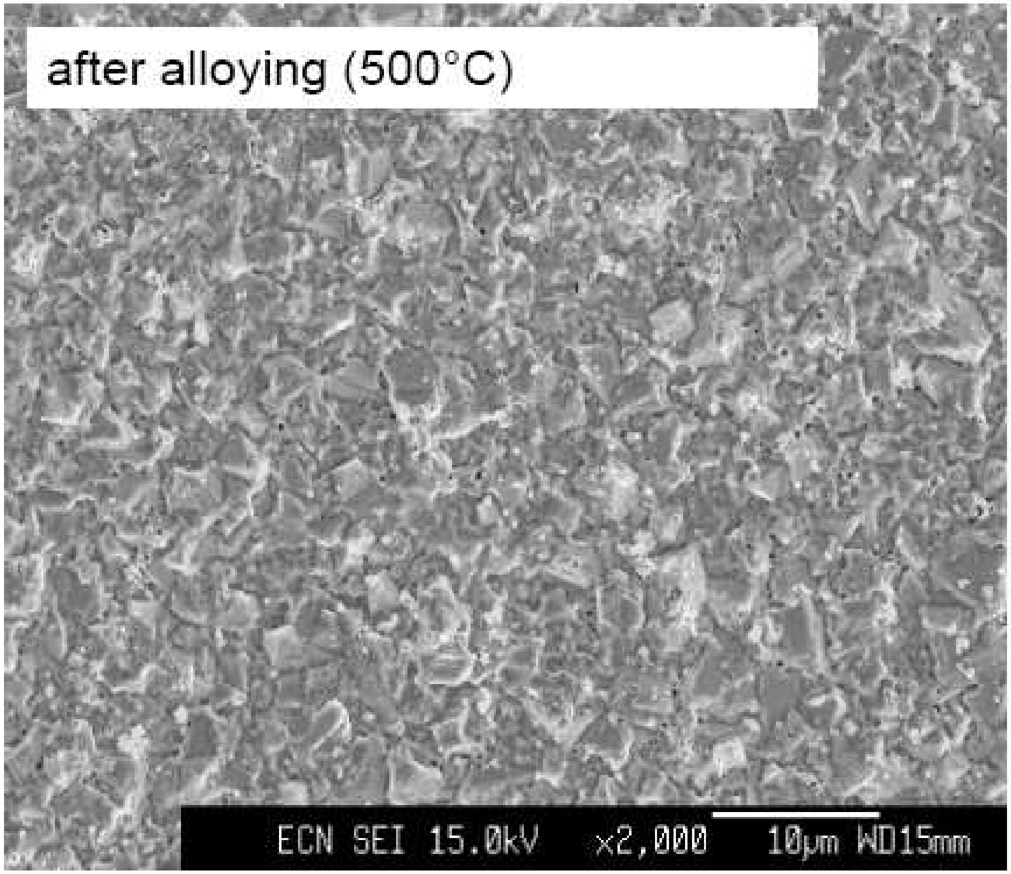
$$J = \frac{-k(\sqrt{P_f} - \sqrt{P_p})}{L}$$

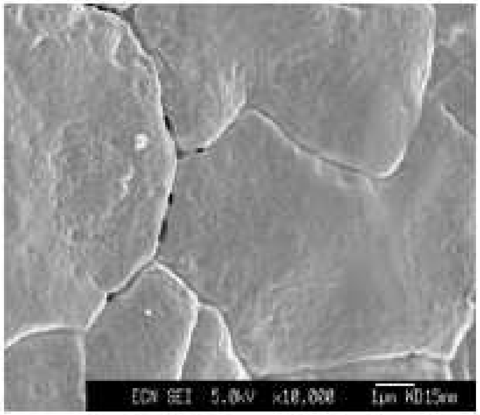
*Only* $H_2$ can get through


727°C
636°C
560°C
496°C
441°C
394°C
352°C
315°C
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-12
1.E-13
Permeability (mol/m-s-Pa$^{0.5}$)
Nb
V
Ta
Pd
Fe
Ni
Cu
Pt
Ag
Au
0.001
0.0011
0.0012
0.0013
0.0014
0.0015
0.0016
0.0017
Inverse temperature (1/K)

# Materials issues: structural change during use

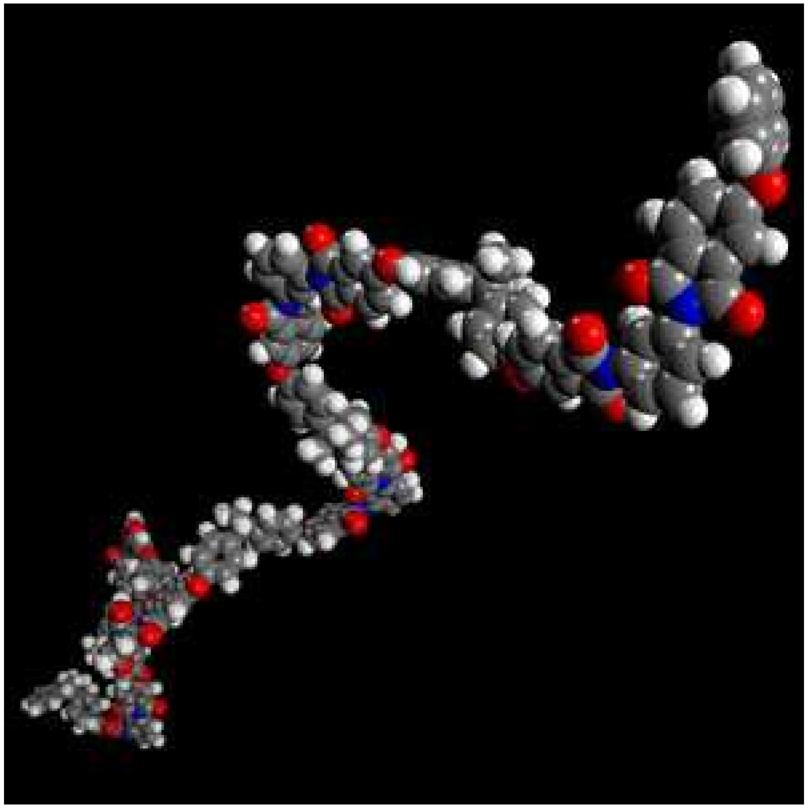
## Coarsening of Pd/Ag membrane during $H_2$ permeation



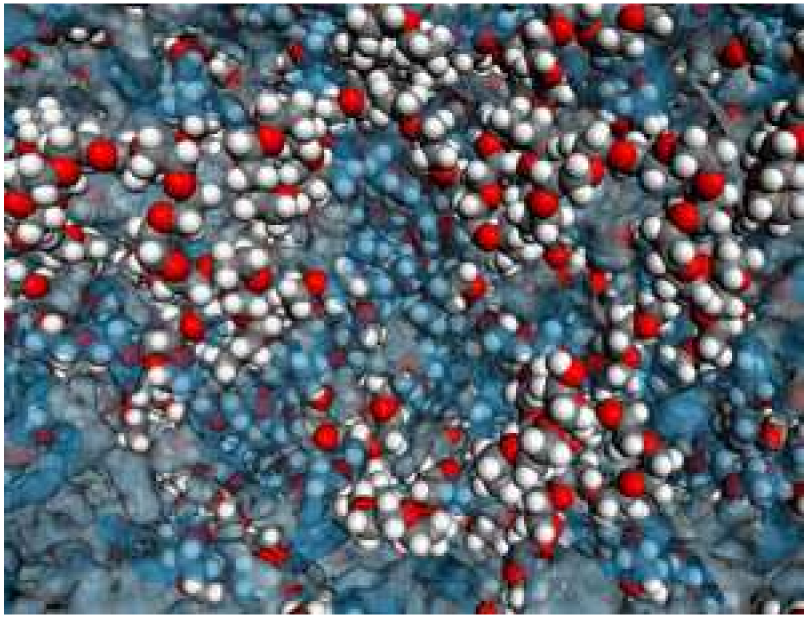


After $H_2$ permeation
meas. (500° C, 100 h)

# Gas permeation (P) through polymer membranes



A polymer looks like this:
a very long molecular strand



A polymer material often looks like this: a rather disordered packing of polymers with ‘free volume’ in between. This free volume leads to uptake and mobility of small molecules like $H_2$. So such material may be a $H_2$ filter.

# Gas permeation (P) through polymer membranes

P=DS

D=diffusion coefficient unit [cm$^2$/s]

S=solubility coefficient [cm$^3$(gas)/cm$^3$(membrane)cm(Hg)]

From gas pressure

Unit of P: Barrer = $10^{-10}$ m$^3$(STP)cm/cm$^2$ s cm(Hg).

m$^3$ of gas at a defined Standard Temperature and Pressure (STP)

Selectivity:
$$\alpha_{H2/CO2} = \frac{P_{H2}}{P_{CO2}} = \frac{D_{H2}S_{H2}}{D_{CO2}S_{CO2}}$$

# $CO_2$ permeability of dense polymer membranes

| Polymer | Permeability (Barrer[*]) |
|---|---|
| Silicone Rubber | 3200 |
| Natural Rubber | 130 |
| Polystyrene | 11 |
| Polycarbonate | 10 |
| Cellulose Acetate | 6.0 |
| Polysulfone | 4.4 |
| Polyetherimide | 1.5 |
| Polyimide (Kapton) | 0.2 |
| PVC | 0.15 |

# Membrane selectivity

| Polymer | Permeability (Barrer) | Selectivity $CO_2/CH_4$ |
|---|---|---|
| Silicone Rubber | 3200 | 3.4 |
| Natural Rubber | 130 | 4.6 |
| Polystyrene | 11 | 8.5 |
| Polycarbonate | 10 | 26.7 |
| Cellulose Acetate | 6.0 | 31 |
| Polysulfone | 4.4 | 28 |
| Polyetherimide | 1.5 | 45 |
| Polyimide (Kapton) | 0.2 | 64 |
| PVC | 0.15 | 15.1 |

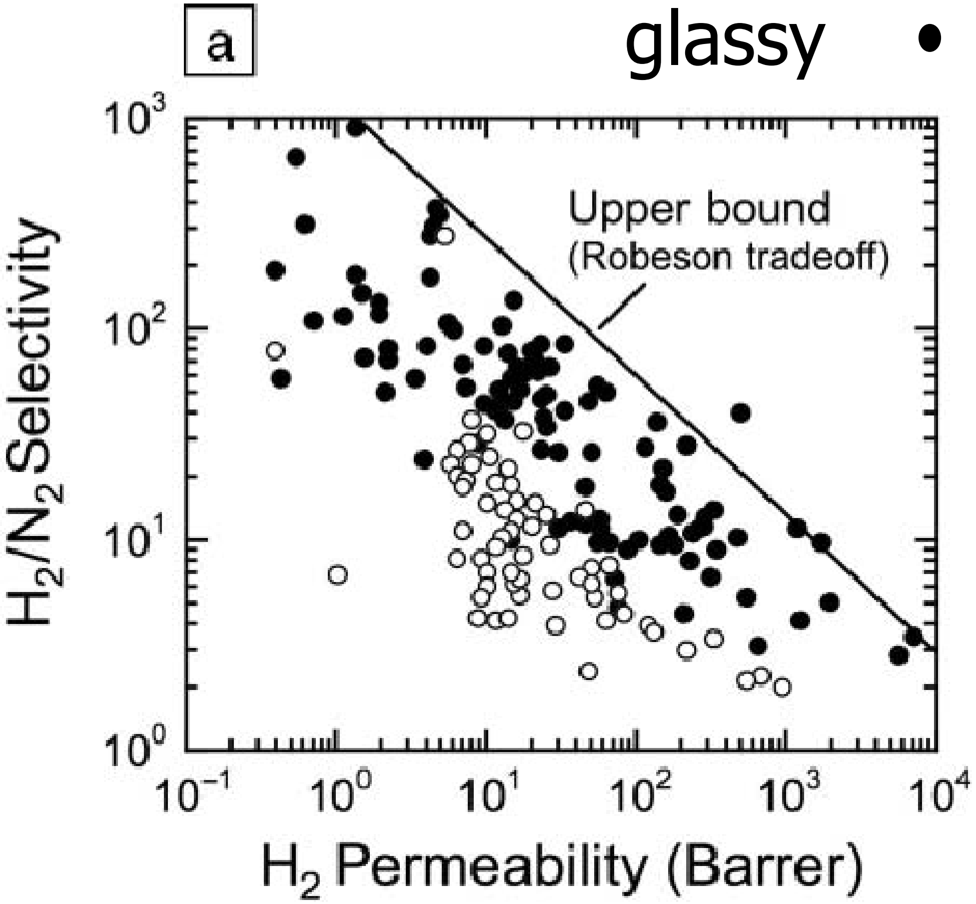
$$P = D * S$$

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{s_i D_i}{s_j D_j}$$

# Gas permeation (P) through polymer membranes

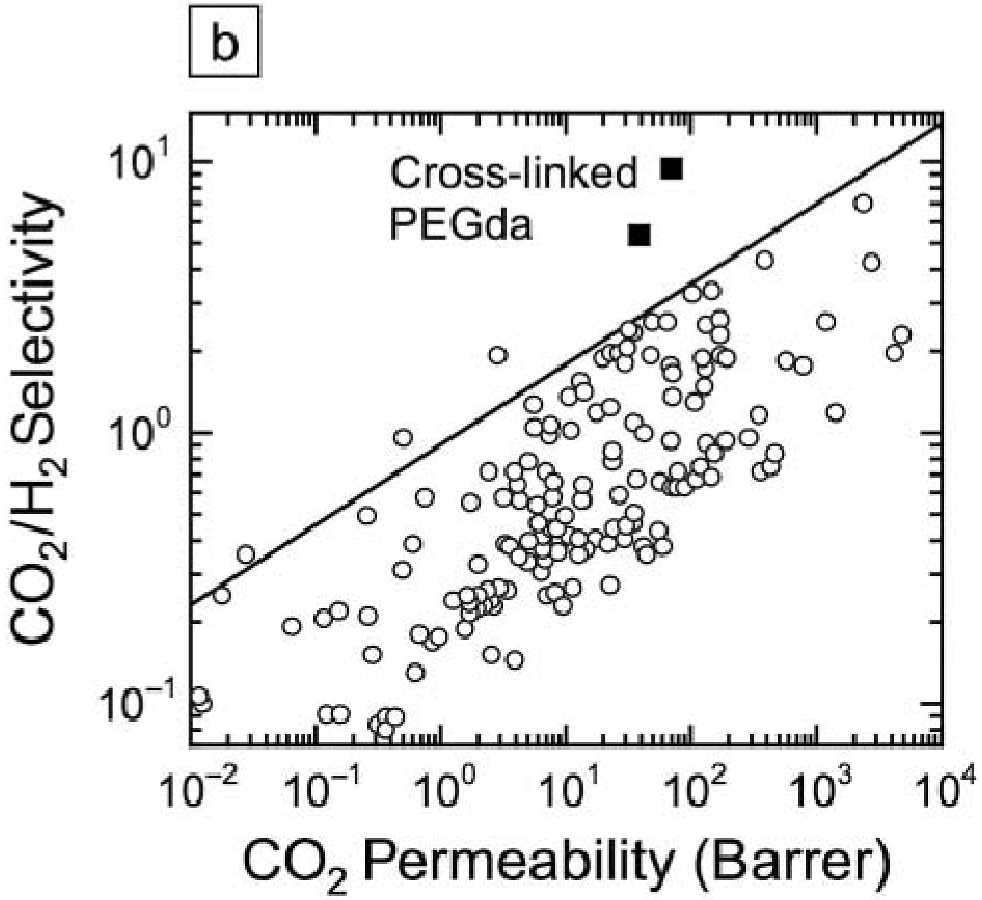
Higher permeability leads to lower selectivity.

rubbery ○
glassy ●

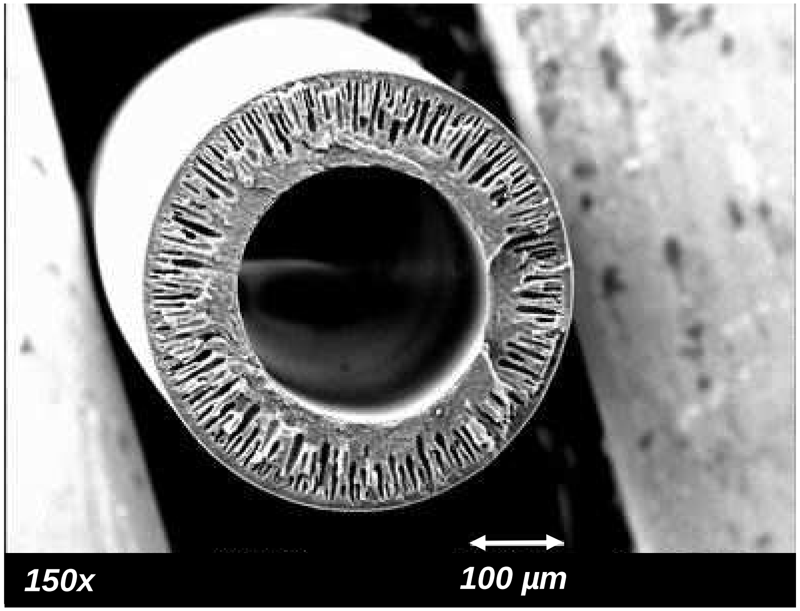


Nenoff et al. MRS Bull. 31 (2006) p735.

Higher permeability leads to higher selectivity.
The permeation of $H_2$ does not increase that much as that of the $CO_2$

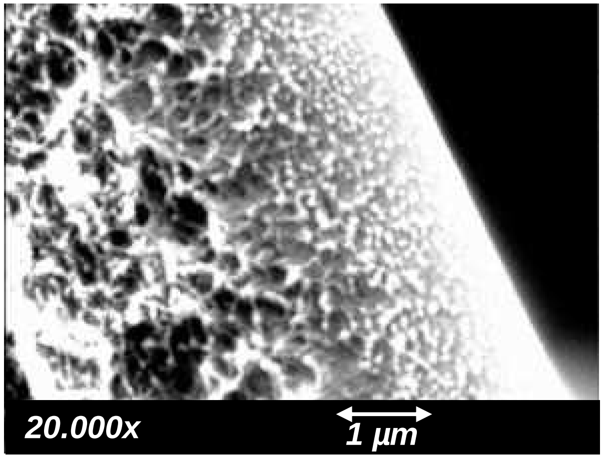


# Polymer membrane development

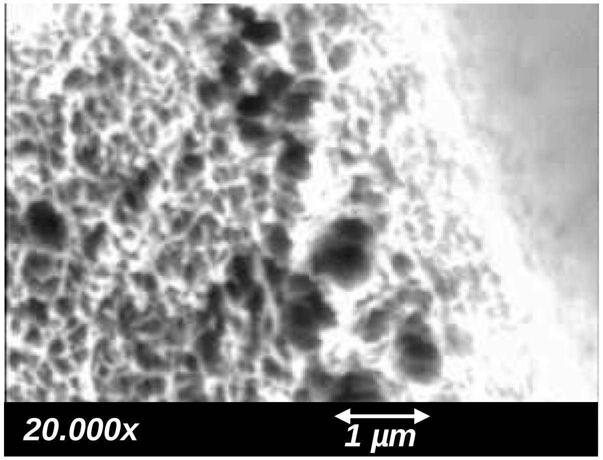


**Geometry**

- **Fiber diameter: 460 µm**
- **Wall thickness: 85-100 µm**



***outside***



***inside***

# Commercial $H_2$-separation membranes

| Membrane (developer) | Selectivity | | | $H_2$-Permeance (GPU) |
|---|---|---|---|---|
| | $H_2/CO$ | $H_2/CH_4$ | $H_2/N_2$ | |
| Polyaramide (Medal) | 100 | >200 | >200 | - |
| Polysulfone (Permea) | 40 | 80 | 80 | 100 |
| Cellulose acetate (Separax) | 30-40 | 60-80 | 60-80 | 200 |
| Polyimide (Ube) | 50 | 100-200 | 100-200 | 80-200 |

What do you expect is the difference in selectivity for $H_2$ between a polymeric filter and a Nb filter?

The Nb has infinite selectivity since it has no $CO_2$ uptake

# Cryogenic separation of gasses

- Uses the difference in boiling temperatures (relative volatilities) of the gas components to effect the separation. Hydrogen has the lowest of all gasses involved.

- Condensation of water is obtained by cooling the gas stream against the fuel gas streams in heat exchangers.

- Refrigeration is obtained by expansion of the compressed hydrogen + exhaust products.

- At low temperature $CO_2$ and impurities condense while $H_2$ does not condense until very low T.

# When to chose what?

**Process considerations for $H_2$ purification**

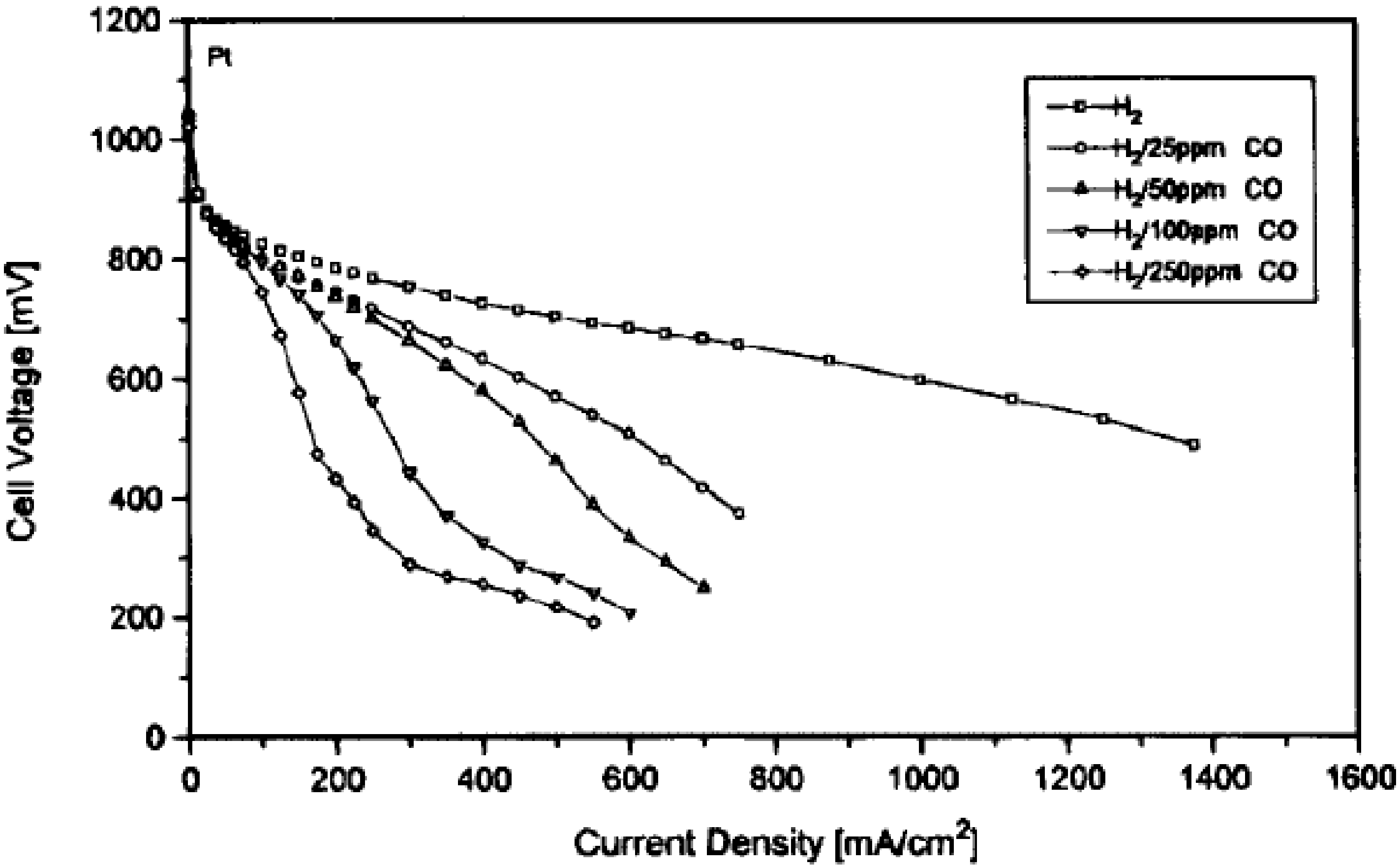
| Factor | Cryogenic | PSA | Membrane (polymeric) |
|---|---|---|---|
| Min. feed $H_2$ (%) | 15 | 50 | 15 |
| Feed pressure (bar) | 10-80 | 10-50 | 10-100 |
| Target $H_2$ purity (%) | 97 | 99.9+ | 98 |
| $H_2$ recovery (%) | Up to 98 | Up to 90 | Up to 97 |
| CO + $CO_2$ removal | No | Yes | No |
| $H_2$ product pressure | Approx. feed | Approx. feed | Less than feed |

# Intermezzo

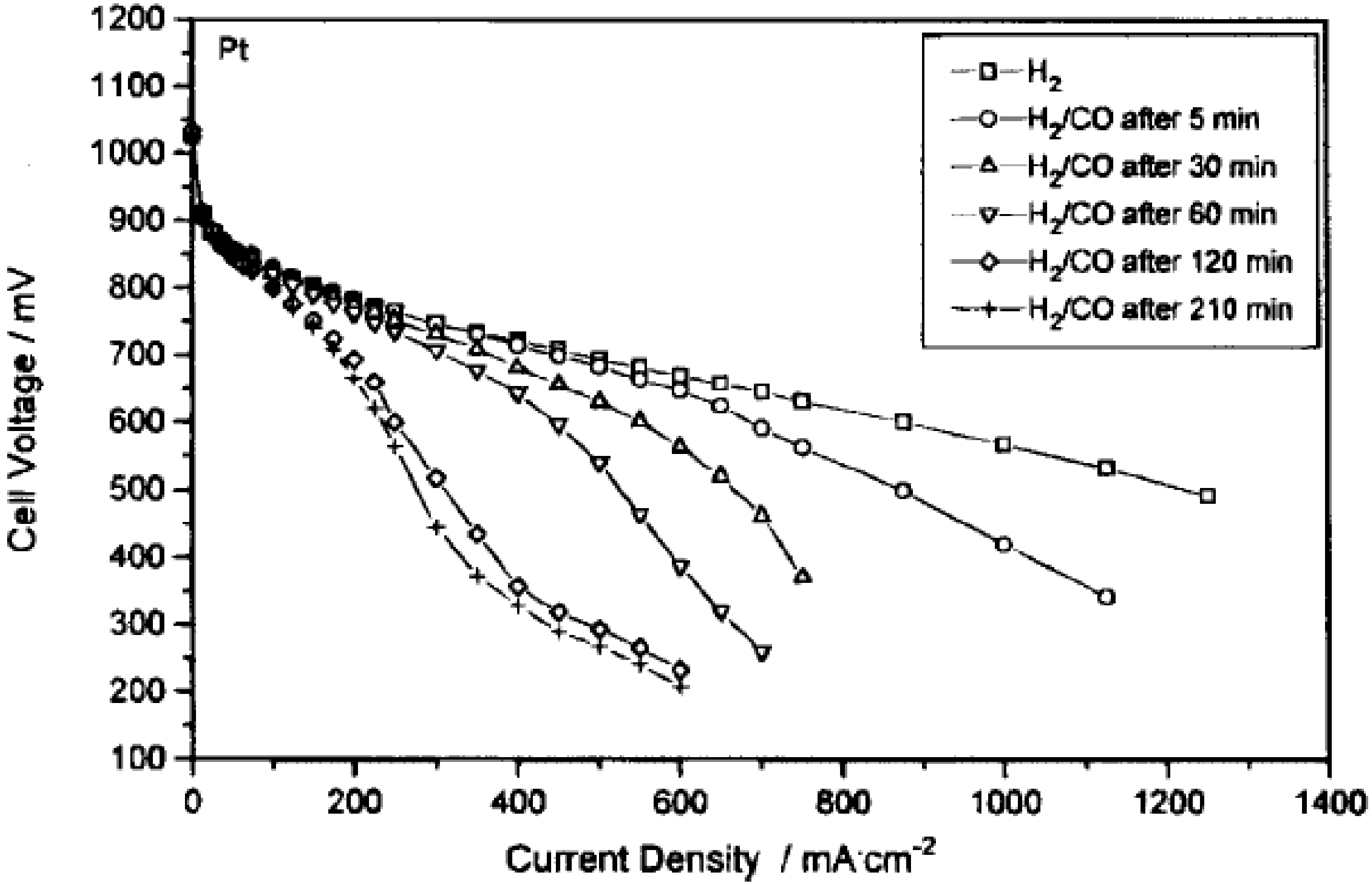
## What level of CO, $CO_2$ impurities can be accepted in hydrogen as a fuel for fuel cells?

CO adsorbs on the Pt catalysts of fuel cells (FC), causing a dramatic reduction of the FC output power. At most ppm levels of CO are allowed.

A trace presence of carbon dioxide can also be detrimental, as this produces carbon monoxide through the reverse water-gas shift reaction: $CO_2 + H_2 \rightarrow CO + H_2O$. And the catalyst for that is the Pt that is already present in the FC electrodes.



Strong reduction of fuel cell output power (P=VxI) when CO is in the gas feed above ppm levels due to catalyst poisoning


Pt
1200
1100
1000
900
800
700
600
500
400
300
200
100
Cell Voltage / mV
0
200
400
600
800
1000
1200
1400
Current Density / mA·cm$^{-2}$
$H_2$
$H_2$/CO after 5 min
$H_2$/CO after 30 min
$H_2$/CO after 60 min
$H_2$/CO after 120 min
$H_2$/CO after 210 min

# Sustainable Hydrogen and Electrical  Energy Storage

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