Intro to Hydrogen Production

Summer School on '*Materials for the hydrogen economy*',
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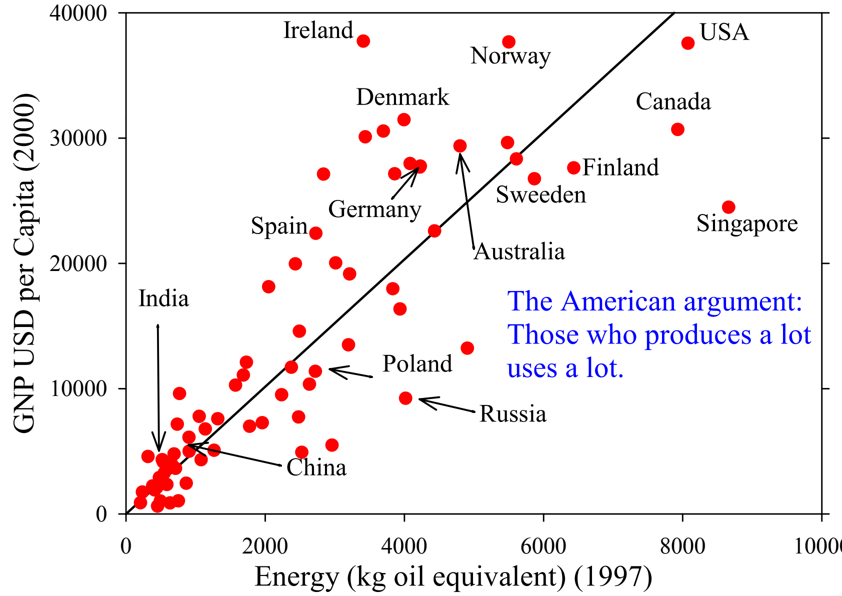
Outline

- Why change anything?
- Do we have problem?
- What is the size of the problem if we have one?
- Where can the sustainable energy come from?
- How can we efficiently convert and store energy?

Is Energy Important?



Why change anything?

What is the problem?

- Lack of fossil resources
- Independence of fossil resource suppliers
- Green house effects

What are the solutions?

Sustainable energy resources like:

- Sun
- Biomass
- Wind

Inherently unstable and here the Hydrogen comes in as an Energy Carrier

Lack of resources ?

Known Fossil Reserves 1997 (1977)

	1997	(1977)
Oil:	141 x 10^9t	(89 x 10^9t)
Natural Gas:	130 x 10^9t	(64 x 10^9t)
Coal:	1030 x 10^9t	

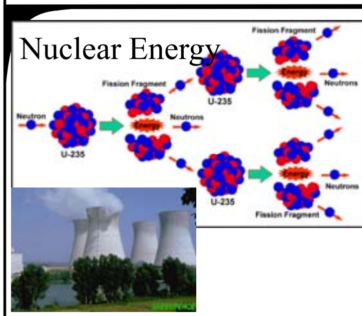
Reserves/production/year

Oil	41 years	(Not really a problem 80$
Natural Gas:	64 years	~90 years
Coal:	219 years	should be maximum.)

The transport sector can run natural gas!
Coal (natural gas) can through Fischer-Tropsch
Be converted to diesel (Nazi-Germany: 700.000 t/år 1944)
Ca. 3% of the natural gas used to be flared
(=200 mio. ton/år CO_2 - DK 53 mio.ton/år.). The FT is realized and increasing in Malaysia, South Africa,Niger, and especially in Qatar – not so much more oil, but plenty natural gas!

Do we have enough to get to the year 2100 ?

Nuclear Energy

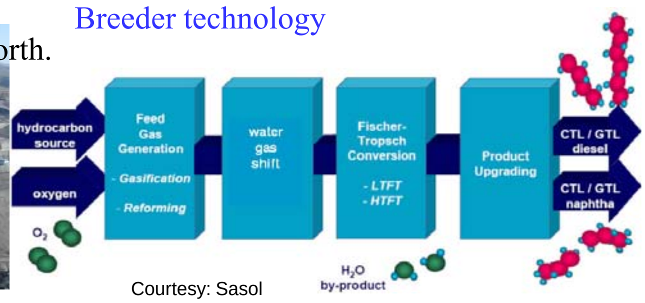


equivalent energy content!

1 kg Uranium-235
But resourceses limited only 0.7%
Breeder technology

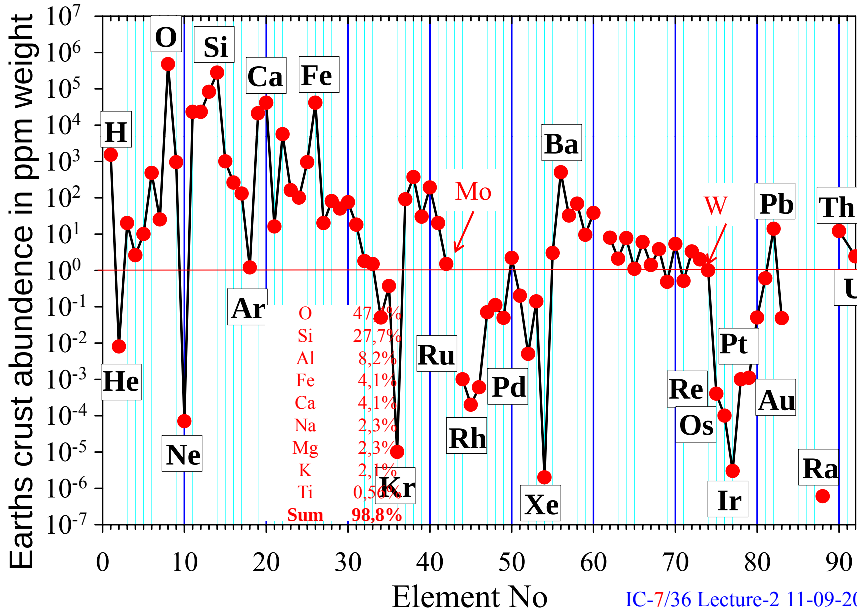
10,000 barrels oil
(~ 100 kg each)

Coal: > 200 years' worth.



Courtesy: Sasol

Composition of Earths Crust



Uranium

Natural abundance of 235 is 0,7% so must be enriched to 3% in order that the process can be self sustained

^{238}U depleted used for kinetic energy penetrators

19,1 g/cm^3 , $T_{1/2}$=4,5 10^9 years

$\alpha - decay$

^{235}U Nuclear Reactors and Bombs

19,1 g/cm^3 , $T_{1/2}$=0,7 10^9 years

Why change anything?

What is the problem?

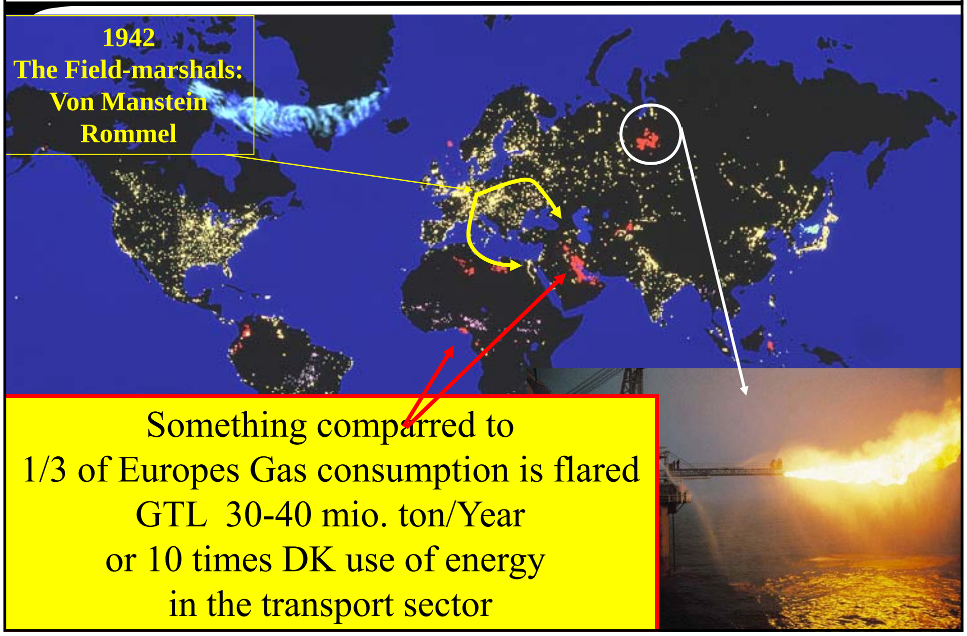
- Lack of fossil resources

  Not a short but a long term problem - YES

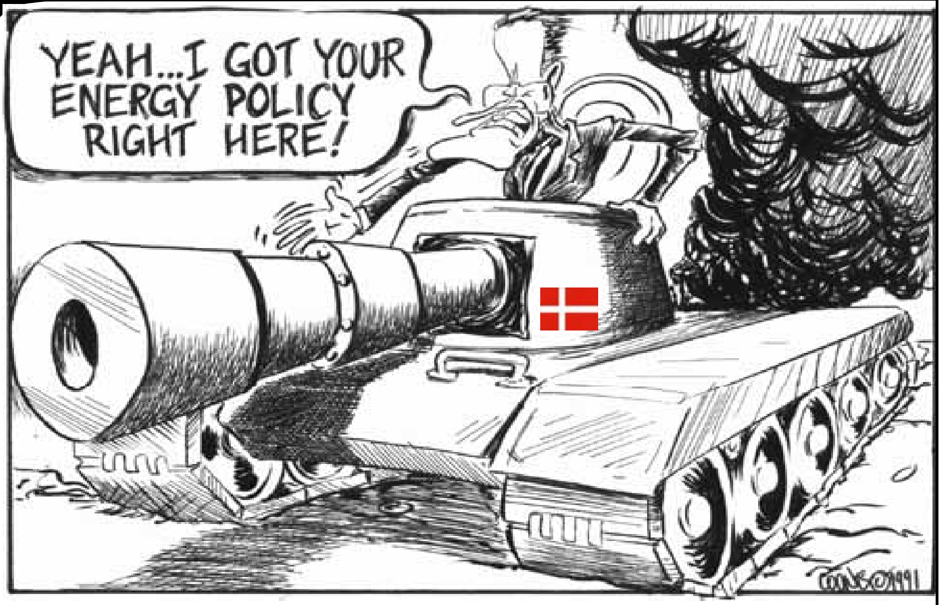
- Independence of fossil resource suppliers

- Green house effects ?

Natural gas to Liquids (GTL)



Supply safety – The Conventional Solution



Why change anything?

What is the problem?

- Lack of fossil resources

  A long term problem - YES
- Independence of fossil resource suppliers

  Certainly worthwhile

  Wars seldom, if ever, produce winners!
- Green house effects ?

The temperature increases

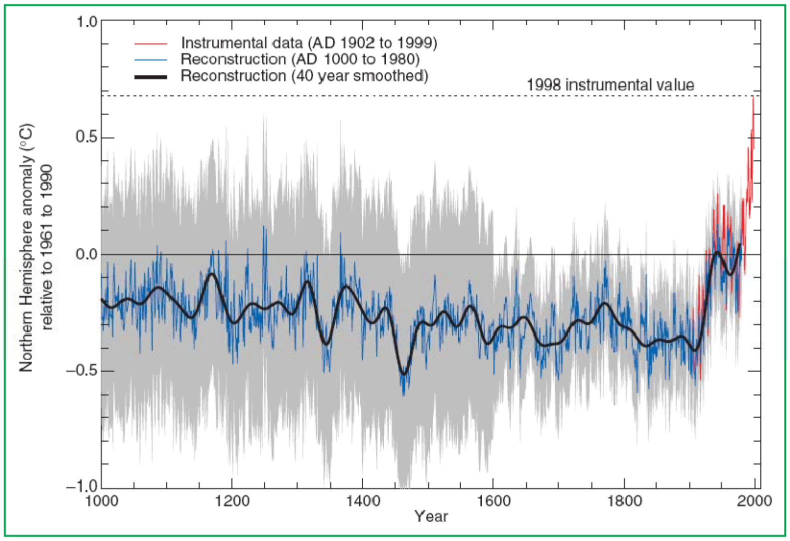
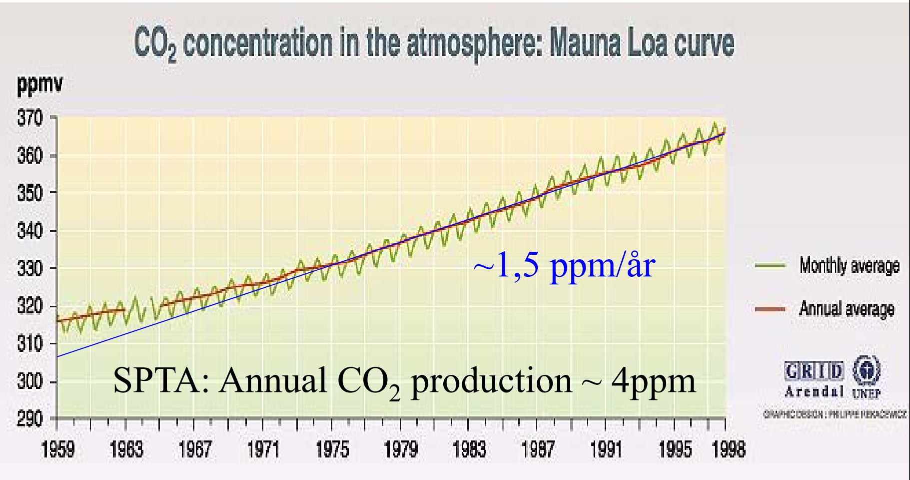


Figure 5: Millennial Northern Hemisphere (NH) temperature reconstruction (blue – tree rings, corals, ice cores, and historical records) and instrumental data (red) from AD 1000 to 1999. Smoother version of NH series (black), and two standard error limits (gray shaded) are shown. [Based on Figure 2.20]

CO_2 Increases!

CO_2 level increases although there are smaller annual variations and we know where some of it is coming from!



Source : Scripps Institution of oceanography (SIO), University of California, 1998.

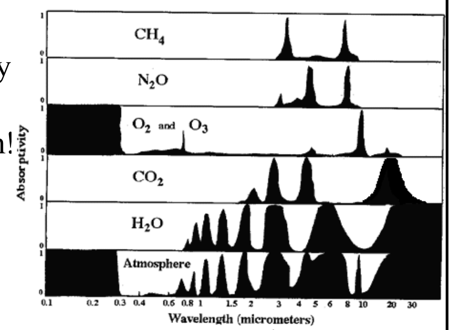
The experiment

We make an experiment:
We introduce a CO_2 in a container increasing the level form 280 to 370 ppm. We know it is a green house gas i.e. and we observe the temperature is increasing. That makes sense. Why is CH_4 20 times worse!

But we already had a much severe green house gas in the container namely H_2O which is present in amounts of 0-3% /average 2% or some 20.000 ppm! Or a factor of 100 higher!

So is it really the CO_2 that's doing all this or is it just a follower?
It is tricky: it would increase the water content and the temperature, but also the coulds ??

Iceage versus Global Heating

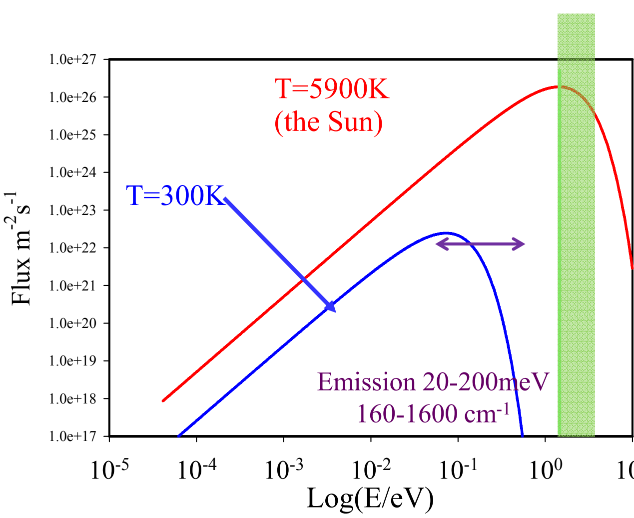


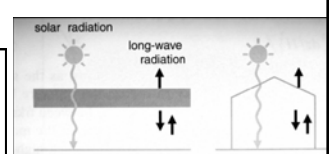
Absorptivity of various gases of the atmosphere and the atmosphere as a whole as a function of the wavelength of radiation. An absorptivity of zero means no absorption while a value of one means complete absorption. The dominant absorbers of infrared radiation are water vapor (H_2O) and carbon dioxide (CO_2). Oxygen (O_2) and ozone (O_3) absorb much of the sun's ultraviolet radiation.

The Planck radiation law

Photon Flux from black bodies

Visible region 1.5- 3.0 eV

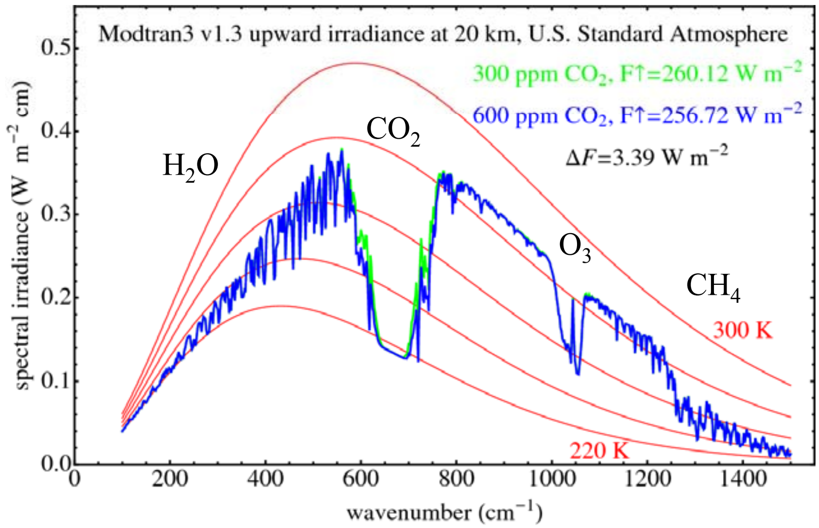




$$\hbar\omega(eV) = \frac{1240eV}{\lambda[nm]}$$

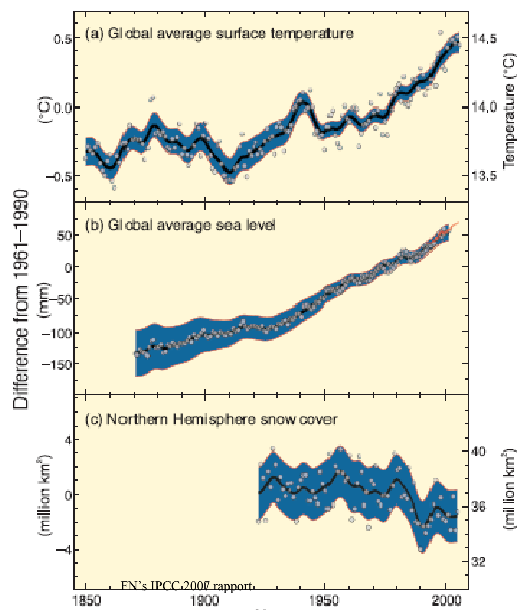
$$1meV = 8cm^{-1}$$

http://en.wikipedia.org/wiki/Radiative_forcing

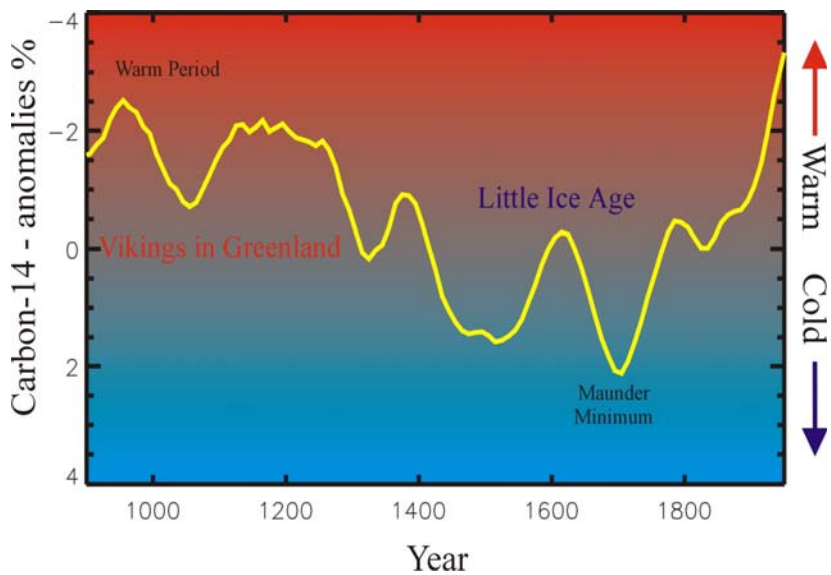


FN's IPCC 2007 rapport:

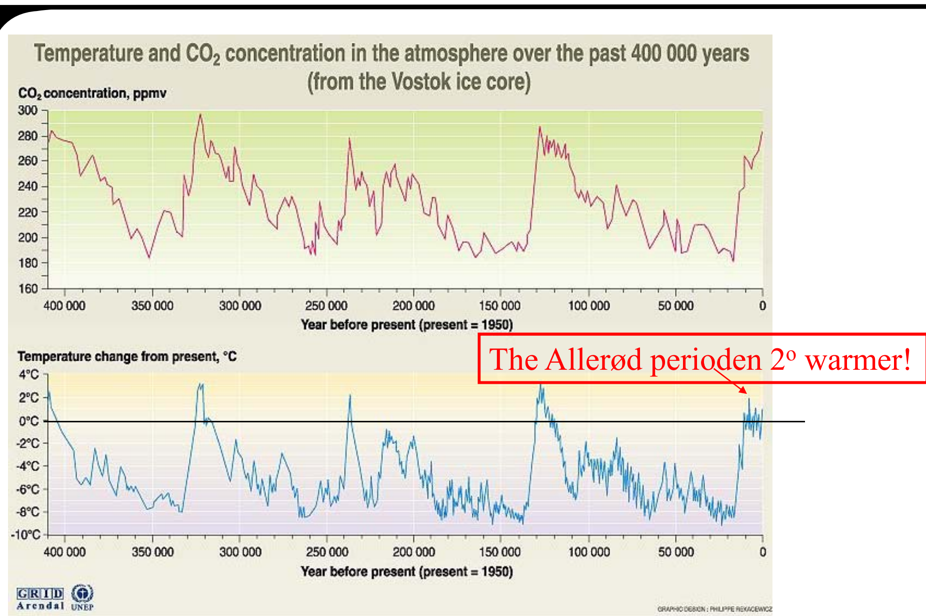
- "Warming of the climate system is *unequivocal*, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice and rising global average sea level"
- "Global GHG emissions due to human activities have grown since pre-industrial times, with an increase of 70% between 1970 and 2004"



Warmer than the last 1000 years

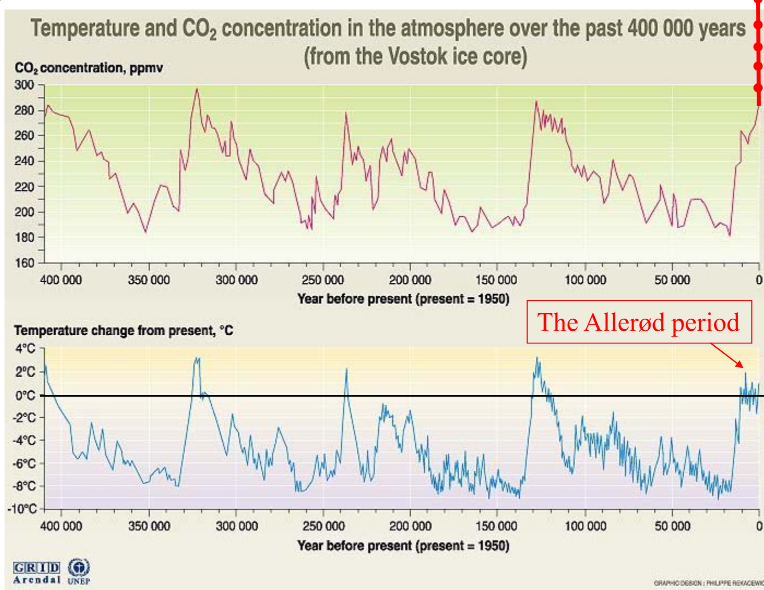


Déjà vu?



Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, Nature 399 (3JUne), pp 429-436, 1999.

The Big Experiment



Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, Nature 399 (3JUne), pp 429-436, 1999.

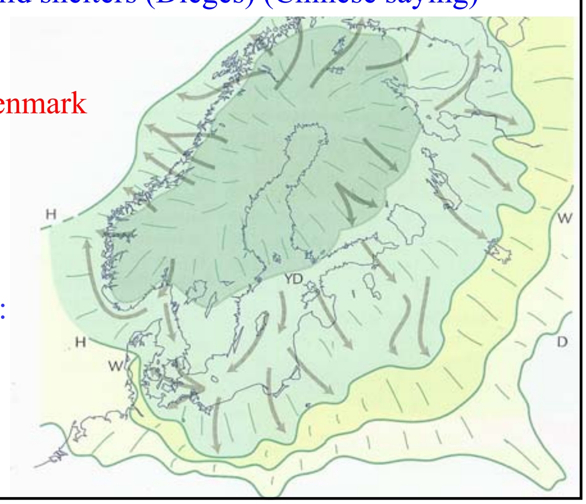
370 ppm CO_2

We are sort of mowing into unknown waters!!

Panta Rhei – “Everything Floats”

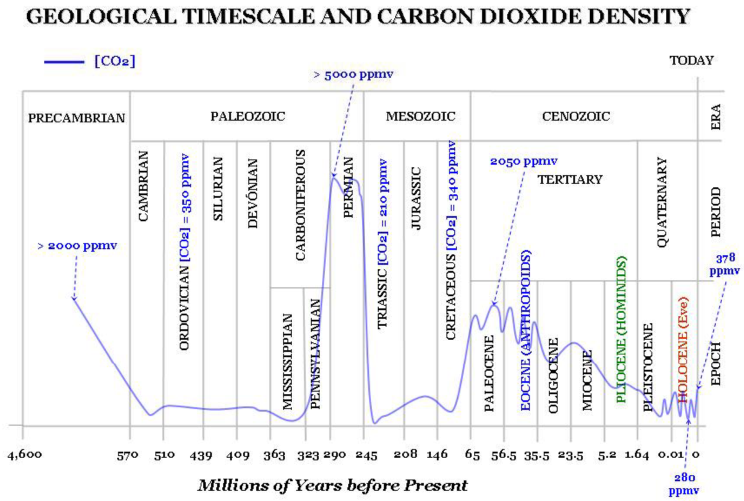
The only thing that is constant is the change (Heraclitus 530-480 BC)
When the wind of change is blowing there those who build wind mills and there are those who build shelters (Dieges) (Chinese saying)

The Standard Climate for Denmark is ca. 2 km Ice cap!!!



The level of concern, however, seems constant:
Nuclear war 1950-80
Meteors 1990ties
Ice age
Green House Effect

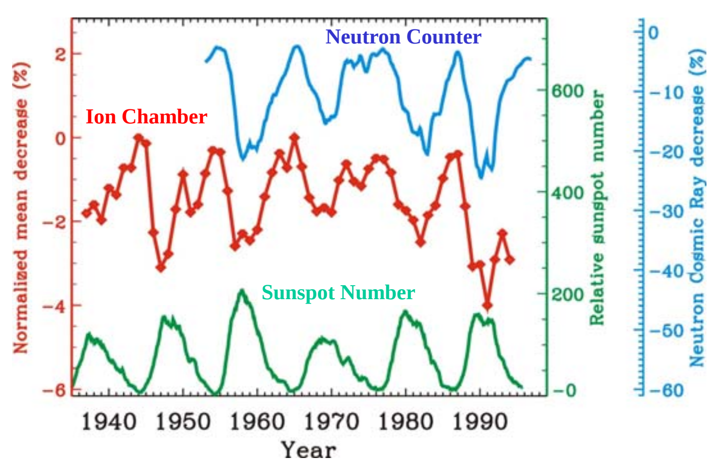
The CO_2 content had huge variations



1- *Analysis of the Temperature Oscillations in Geological Eras* by Dr. C. R. Scotese © *2002*. 2- Ruddiman, W. F. 2001. *Earth's Climate: past and future*. W. H. Freeman & Sons. New York, NY. 3- Mark Pagani *et all*. *Marked Decline in Atmospheric Carbon Dioxide Concentrations During the Paleocene*. Science; Vol. 309, No. 5734; pps. 600-603. 22 July 2005. *Conclusion and Interpretation* by Nasif Nahle ©2005, 2007.

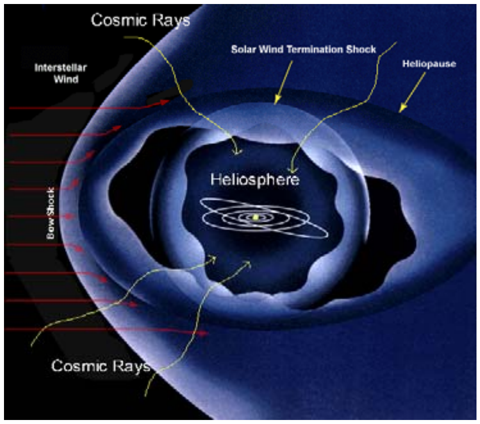
Can the sun influence the climate indirectly

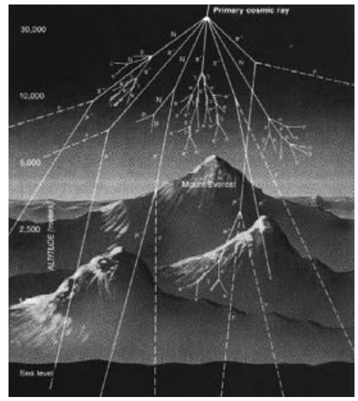
Variation in time of Cosmic Ray flux with Sunspot number



Svensmark, PRL 98

Heliosphere , Cosmic rays and solar activity

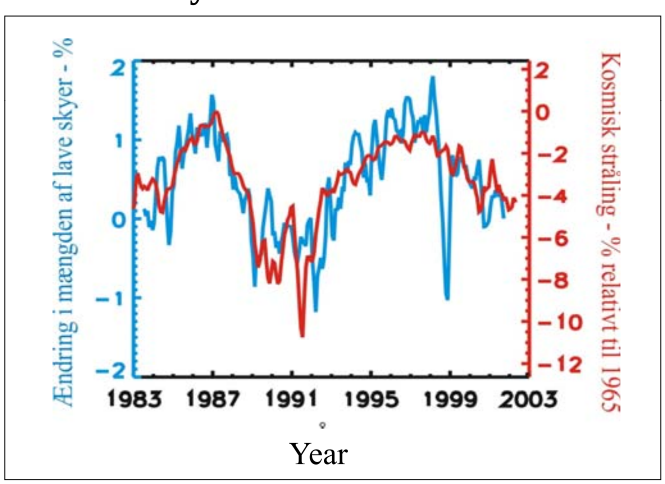




The sun spot activity shield the earth for Cosmic rays reducing the tendency for cloud formation increasing the Temperature. But it is delicate and open for discussion!

A possible link between Cosmic Rays and Climate

Cosmic Rays and Earth's Cloud Cover



N.D. Marsh & H. Svensmark (2003)

But picture not clear for the last cycle

A possible link between Cosmic Rays and Climate

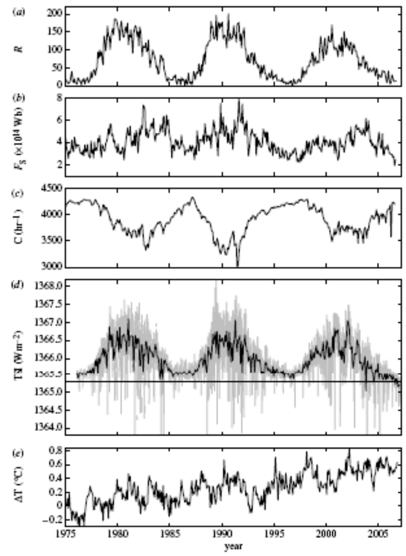
Sunspot

Solar Flux

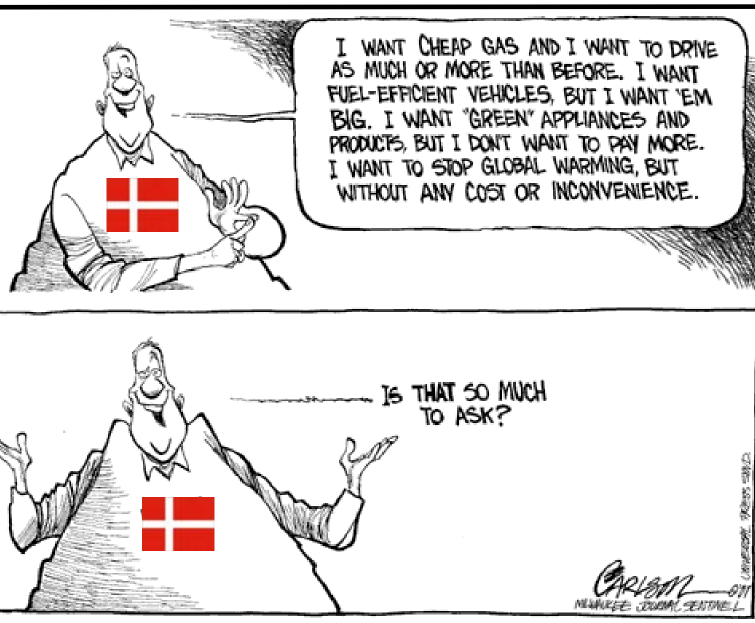
Neutron Count cosmic Rays

Solar Flux

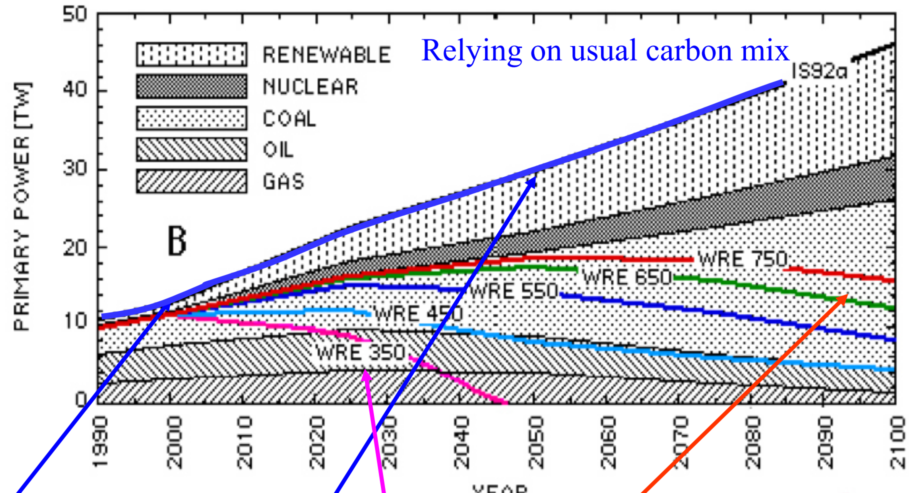
Temparture change



Our expectations ?



The Size of the Problem see Nathan Lewis

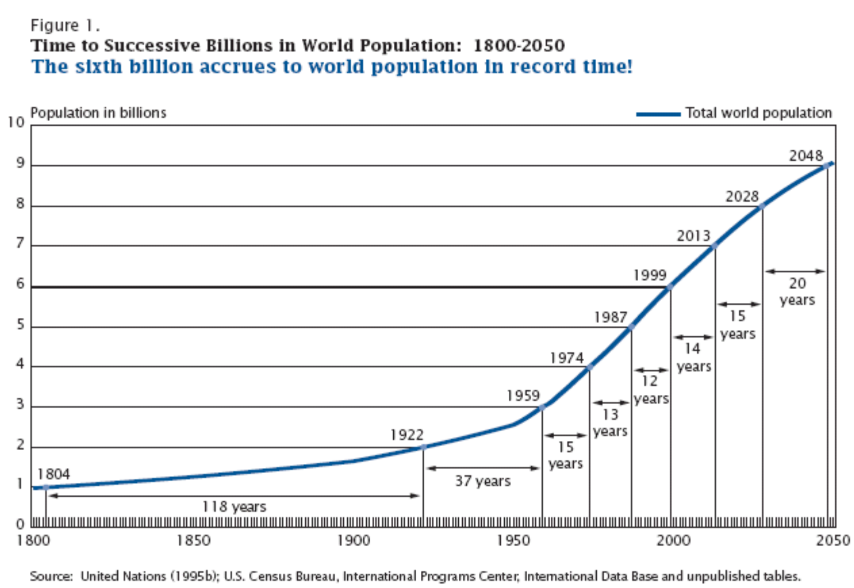


1998: 13 TW
6 billion people

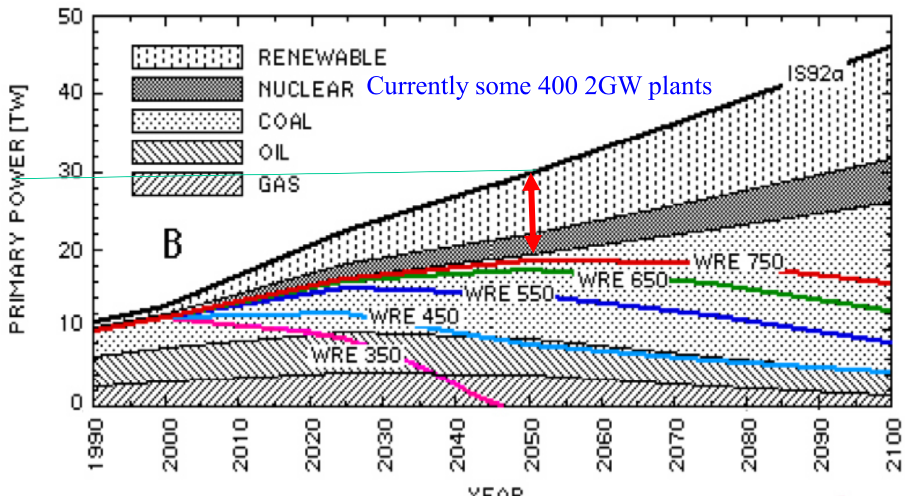
2050: 28 T
~9 billion

The amount of fossil fuel allowed if we want the content of CO_2 to stabilize at 350 or 750 ppm Where are we today?

The success of the homo sapiens

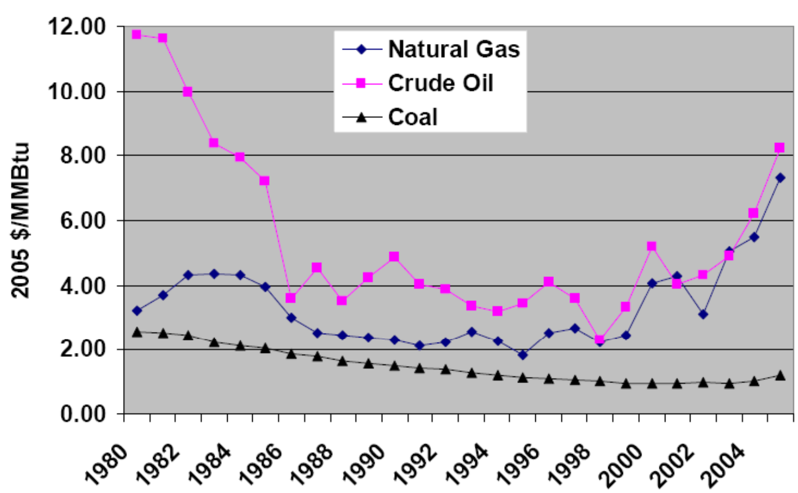


Total Primary Power vs Year



Even we accept the 750 ppm max we must find carbon free replacement energy of 10TW corresponding to three 2 GW nuclear power plant build Per week until 2050!!! NEEDS Breeder reactors (Pu based)

Energy Price (1980 - 2005)



CO2 Sequestration

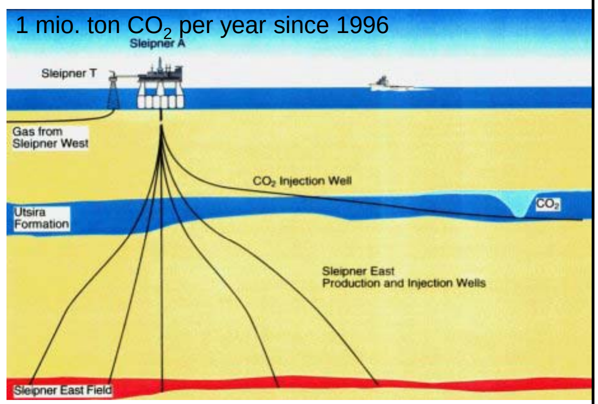
Strongly Endothermic $CH_4 + H_2O \overset{Ni,\ 1000\ ^oC}{\longleftrightarrow} CO + 3H_2$

Exothermic $CO + H_2O \overset{Cu,\ 200\ ^oC}{\longleftrightarrow} CO_2 + H_2$

Coal/gas

CO2 sequestration

Energy and H_2 for transportation without CO_2

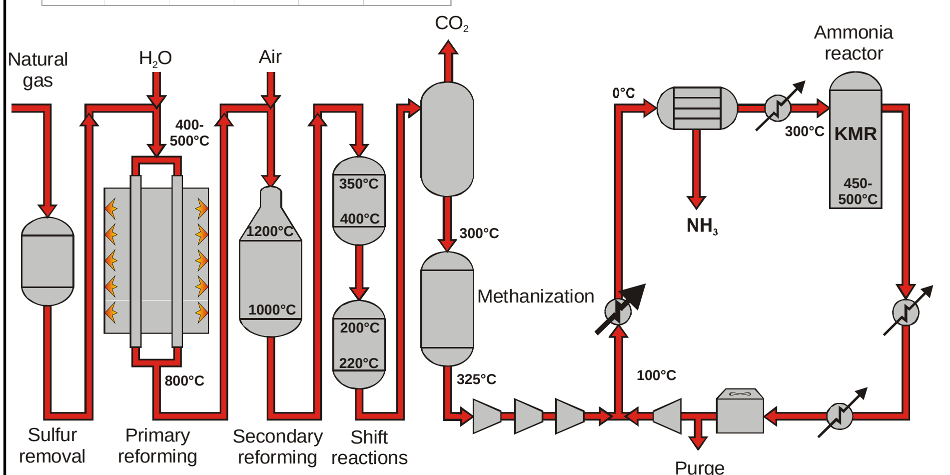


The Capacity of Utsira is ~ 800 billion ton CO_2 or 200 years from Europa
But the method is disputable:will it stay down there ?

Clean Hydrogen -The ammonia plant

Gas	N_2	H_2	CH_4	Ar	CO
%	74.3	24.7	0.08	0.03	1-2ppm

$CH_4 + H_2O \leftrightarrow CO + 3H_2$



"Concepts of Modern Catalysis and Kinetics" by Ib Chorkendorff and Hans Niemantsverdriet

Why change anything?

What is the problem?

- Lack of fossil resources

  A long term problem - YES

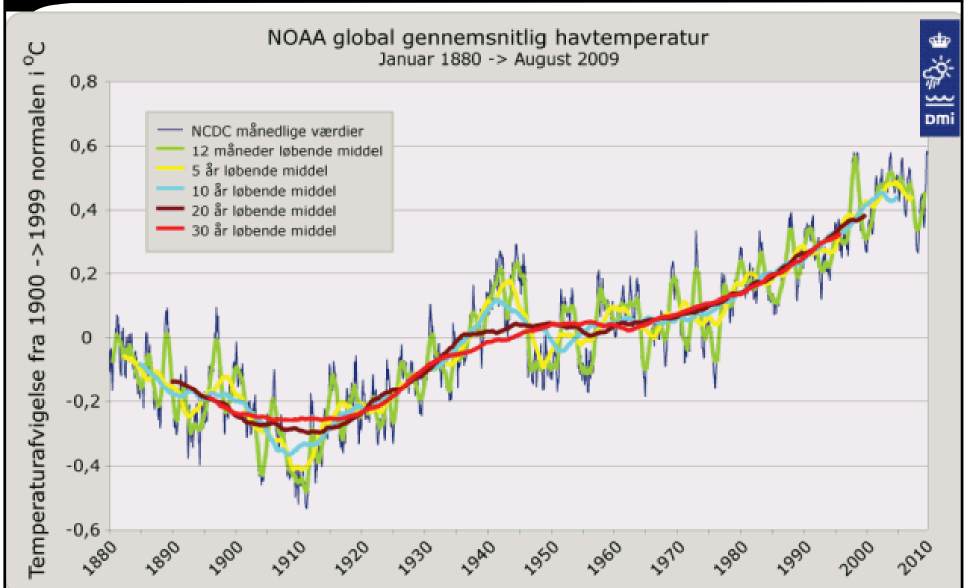
- Independence of fossil resource suppliers

  Certainly worthwhile

  Wars seldom, if ever, produce winners!

- Green house effects ?

  The effect is probably there and unfortunately we do not seems to be able to do anything about it so…..get used to higher temperature!



Exercises

Exercise 1: Are we Guilty?

We use some $3,8*10^{20}$ J/year
Say 80-90 % is fossil fuels say 80%
Average lets say 80 kg CO_2/GJ
How much does that contribute to if it all goes into the atmosphere?

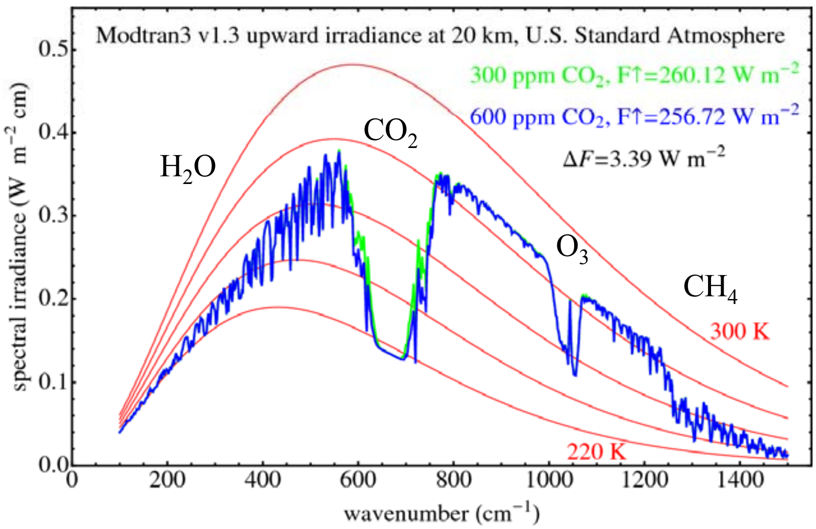
Exercise 2: Why is methane such a bad green house gas?

20 times worse than CO_2?

Exercise: Are we Guilty?

We need some $3,8*10^{20}$ J/year
Say 80-90 % is fossil fuels say 80%
Oil between 70-80 kg CO_2/GJ
Natural gas 57,3 kg CO_2/GJ
Coal products 95-105 kg CO_2/GJ
Average lets say 80 kg CO_2/GJ
CO_2 outlet per year $=3.8*0.8*10^{20}*80/10^9 = 2,4*10^{13}$ kg/year
$=(2,4*10^{13}/0.044)*0,024m^3 = 1,3*10^{13}m^3$
Earths atmosphere say 6 km average pressure 1 bar
$R=6.371*10^6$m
$V=4*3.14*R^2*6\ km=317*10^{16}\ m^3=4,1*10^{18}m^3$
Annual outlet rate = 3,2 ppm!

http://en.wikipedia.org/wiki/Radiative_forcing



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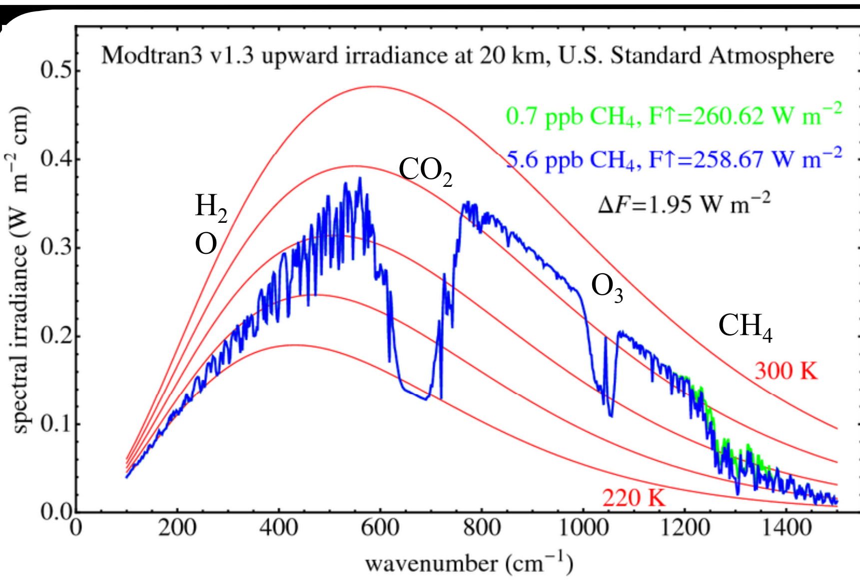


The sun supplies plenty of energy

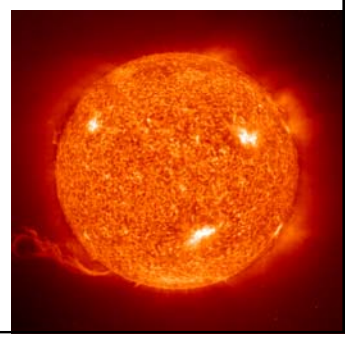
Some data on energy consumption and sources

	Total Earth	DK
Human related energy consumption:	3,8E20 J/year	8,4E17 J/year
Total incoming sun energy:	3,8E24 J/year	ca. 1,6E20 J/year
Total power production:	4,6E19 J/year	1,2E17 J/year

Roughly 10% of the area in DK must be used if we should get all the energy from solar cells or wind mills.

Now: ~3% (20% of electric power) from wind and 8% from bio-mass (wood/straw) Bio-mass not enough by it self!

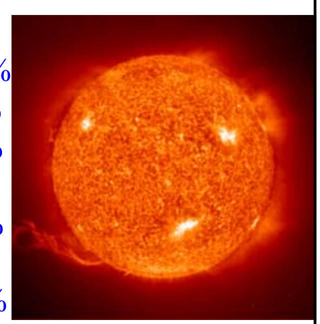
We are still relying massively on fossil fuels for decades to come



The Long term approach (DK)

We will have to use energy from any source we can find:

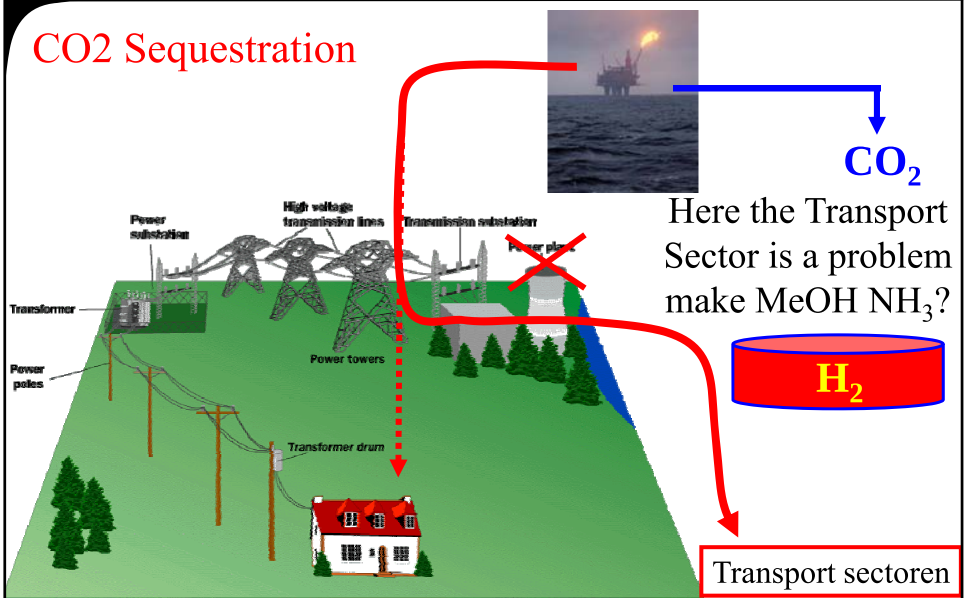
- Fossil fuel (global 80% - nuclear 6%) 85%
- Biomass (Max at 75%) 8%
- Garbage (not really sustainable) 4%
- Solar energy (comes as the sun shines) 0%
- Wind energy (75 times as many WM) 3%
- Wave energy (unstable) 0%
- Geothermal energy (stable) 0%
- ….? Fusion would solve our problems 0%



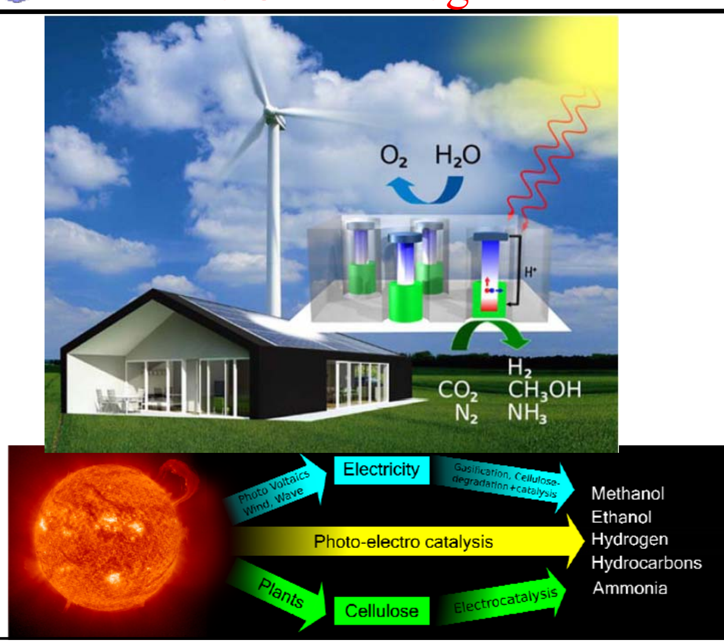
We need an energy buffer i.e. Hydrogen has been suggested.
Electricity is converted to hydrogen (electrolysis), which then can be either transported in a net or stored.

We need to have some technology ready before the last drop of oil is used

The Future Energy Distribution



The UNIK Program

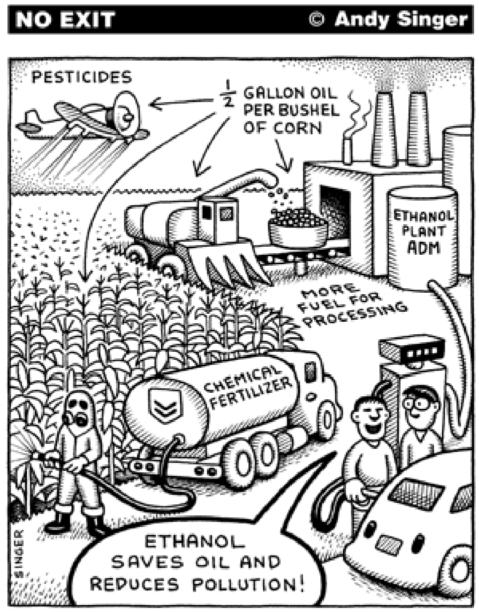


Bio-mass – An Important Contribution

Bio-mass is today the only sustainable energy source that is contributing significantly
DK ca. 8%, Globally 10%.

But even if the entire Danish arable land is utilized only some 2/3 can be covered and then we have no food.

Bio-ethanol have currently no future. It competes with food and even second generation is better utilized by combustion in the power plants as long as it can replace fossil fuel, but it can be used for transport.



Biomass Denmark

DK area = 43.560 km^2

15.500km^2 9,2 mio. tons grain and 6,3 mio. tons straw (1996 data)
It cost roughly 15GJ to fertilize, sow, and harvest per Ha
1 ton grain or straw produces some 15GJ/ton
1 ha =10 tons straw + grain=(10-1)ton*15GJ/ton=135GJ ~ 4,3kW
Price???
Other way: one Dane use 125 GJ/year~0,9 Ha or 50.000Km^2/year

18 % not potential farm land
16 % forest
66 % Farm land =2.890.000 Ha =3,9*10^{17}J/year or 46% of total
Even if we include the forests = 4,8*10^{17}J/year or 58% of total
Total= 8,4*10^{17}J/year
And then there is no food for 5,4 mio Danes and 12,5 mio pigs

Biomass Energy Potential

Global: Top Down

- Requires Large Areas Because Inefficient (0.3%)
- 3 TW requires ≈ 600 million hectares = $6\text{x}10^{12}$ m^2
- 30 TW requires ≈ $6\text{x}10^{13}$ m^2
- Total land area of earth: $1.3\text{x}10^{14}$ m^2
- Hence requires 6/13 = 50% of total land area

Remember DK max 75% and no Food !!
The earths biosphere requires 90 TW

Global: Bottom up

- Land with Crop Production Potential, 1990: $2.45\text{x}10^{13}$ m^2
- Cultivated Land, 1990: 0.897 $\text{x}10^{13}$ m^2
- Additional Land needed to support 9 billion people in 2050: $0.416\text{x}10^{13}$ m^2
- Remaining land available for biomass energy: $1.28\text{x}10^{13}$ m^2
- At 8.5-15 oven dry tonnes/hectare/year and 20 GJ higher heating value per dry tonne, energy potential is 7-12 TW
- Perhaps 5-7 TW by 2050 through biomass
- Possible/likely that this is water resource limited

Some methods to synthesize solar fuels

Photobiologic → organisms that split water

Photochemical → metallorganic absorbers and redox mediators

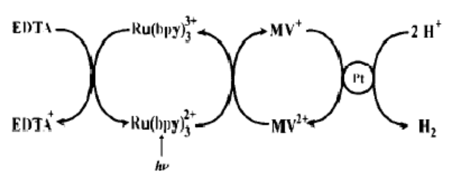
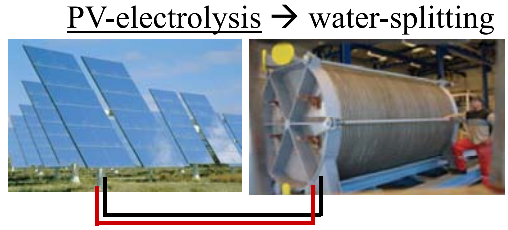


Fig. 3. Scheme for the photochemical generation of hydrogen in a reduction half reaction.

Solar thermal → heterogeneous catalysis.

PV-electrolysis → water-splitting



Solar Energy Potential

- Theoretical: 1.2×10^5 TW solar energy potential
  (1.76×10^5 TW striking Earth; 0.30 Global mean albedo)
  Energy in 1 hr of sunlight = annual consumption for a year

- Practical: ≈ 600 TW solar energy potential
  (50 TW - 1500 TW depending on land fraction etc.; WEA 2000)
  Onshore electricity generation potential of ≈60 TW (10% conversion efficiency):

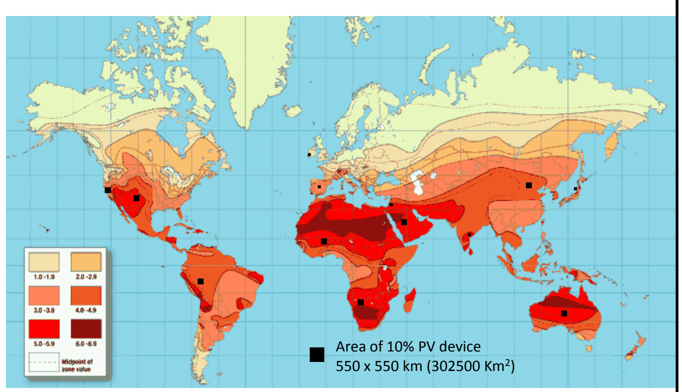
- Solar energy is the only source that has the potential for covering our entire energy requirement, but the technology is way to expensive and inefficient

Sun light is somewhat uneven distributed

Can we make fuels from a renewable energy source in a cost competitive way?

$50-70/GJ
η~10–20%

$10-30/GJ



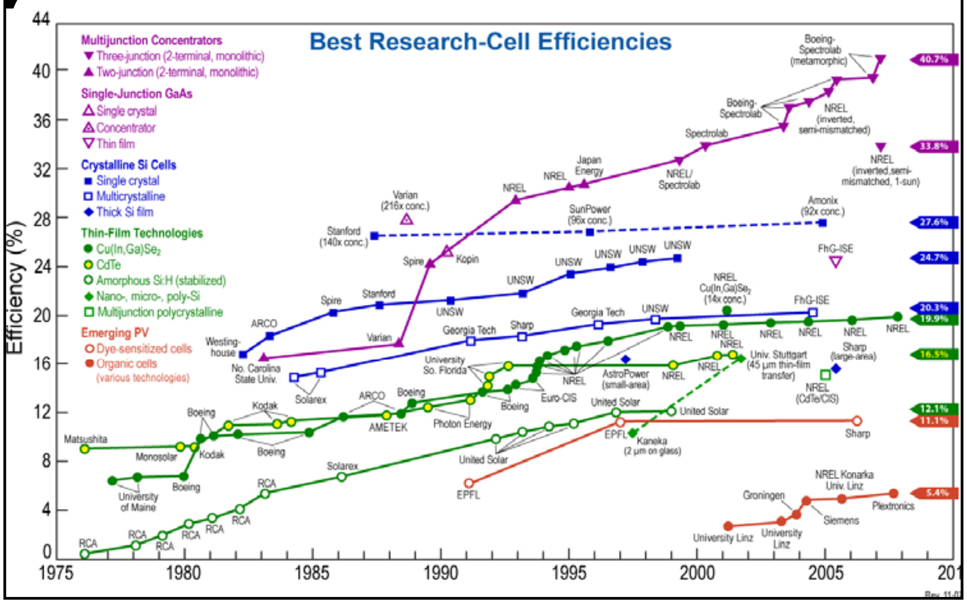
6.1GJ/barrel oil

$6-24/GJ

~46,000 Kg H_2O/day

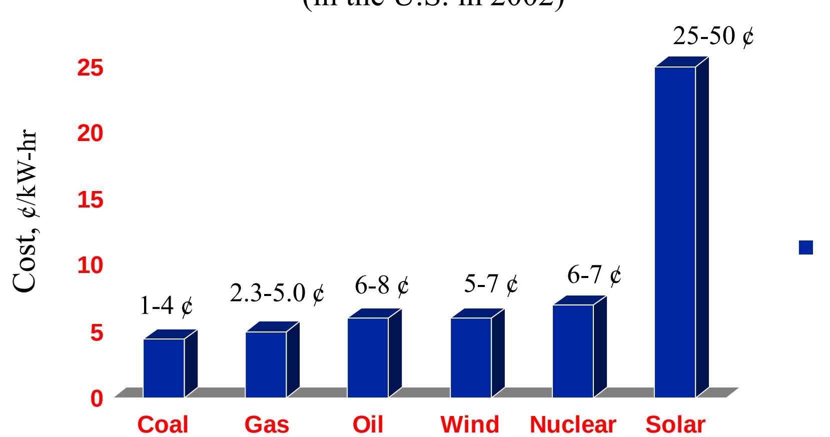
50

Materials in Photo



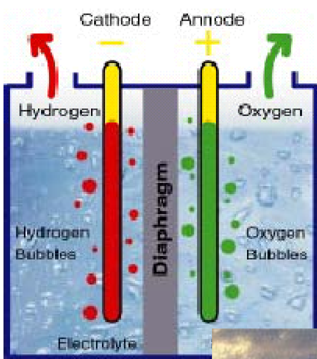
Production Cost of Electricity

(in the U.S. in 2002)



Remember that electricity is a high value for of energy, but cannot be stored without additional costs

Electrolysis



Cathode: $2(H^+ + e^-) \rightarrow H_2$

Anode: $H_2O \rightarrow \frac{1}{2} O_2 + 2H^+$

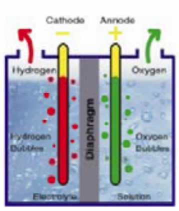
Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

Could be a route for averaging out sustainable energy production i.e. from wind

Electrolysis- Efficiency

Efficiency Considerations



- Energy efficiency of electrolysis =

$$\frac{\text{Chemical potential}}{\text{Electrolysis potential}} = \frac{1.23}{1.9} = 65\%$$

- Coupling to a 12% PV array gives a solar-to-hydrogen efficiency of:

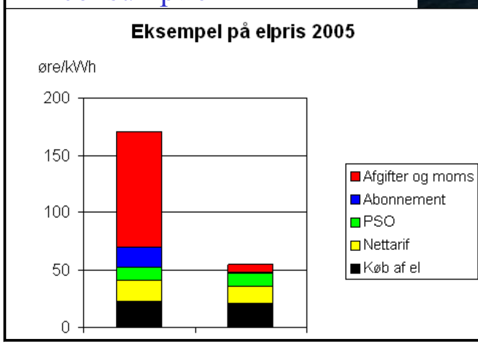
.12*.65 = 7.8%

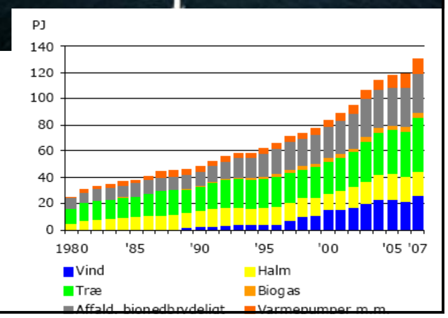
Coupling to a PEMFC
With 45% efficiency
= 3.5%

Wind Power – Is it subsidiced ??

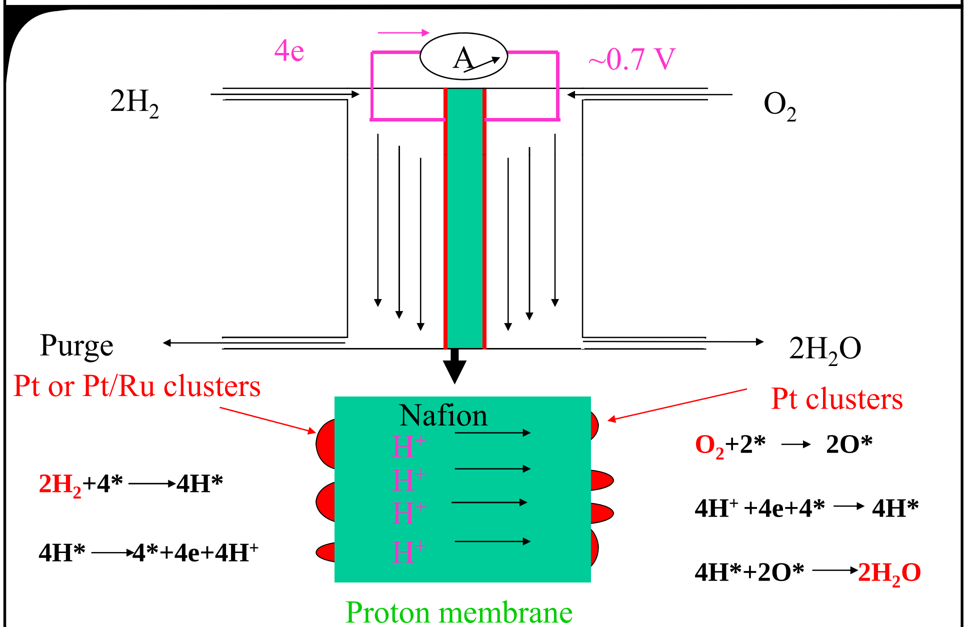
In DK ~ 20%
25,8PJ out of
141PJ power
from wind alone
~3 % of total energy
consumption

314.000 per Wind Mill!
5200 mills,
1.6 Billion from PSO

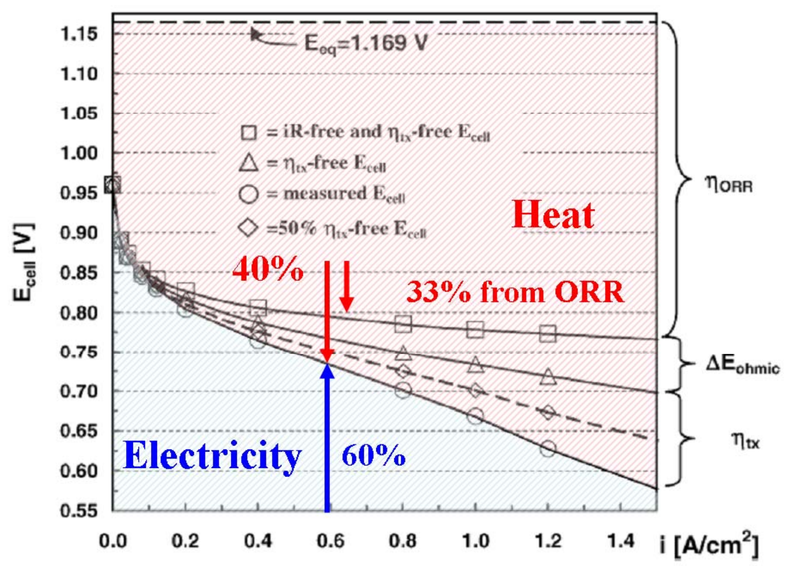




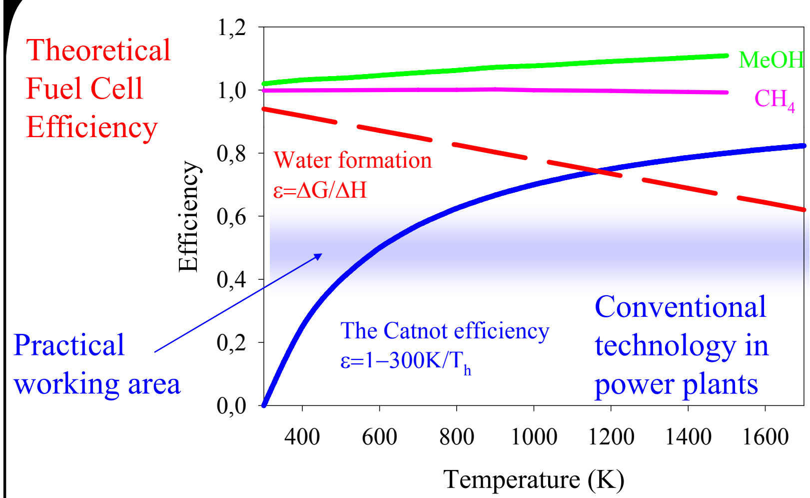
Working Principles PEM fuel cell



The Major loss in ORR and OER



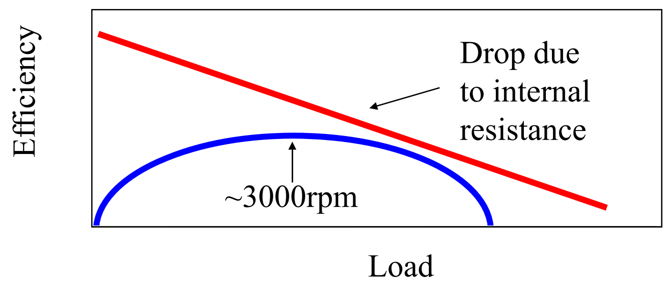
Fundamental differences in efficiencies



Still Fuel Cells are **not** more efficient than conventional power plants, but they have a potential for being it! Electrolysis 70% efficiency

Why interesting for automobiles

- Hydrogen based fuel
- Efficiency conventional engine versus fuel cell engine
- Clean technology (and cost)



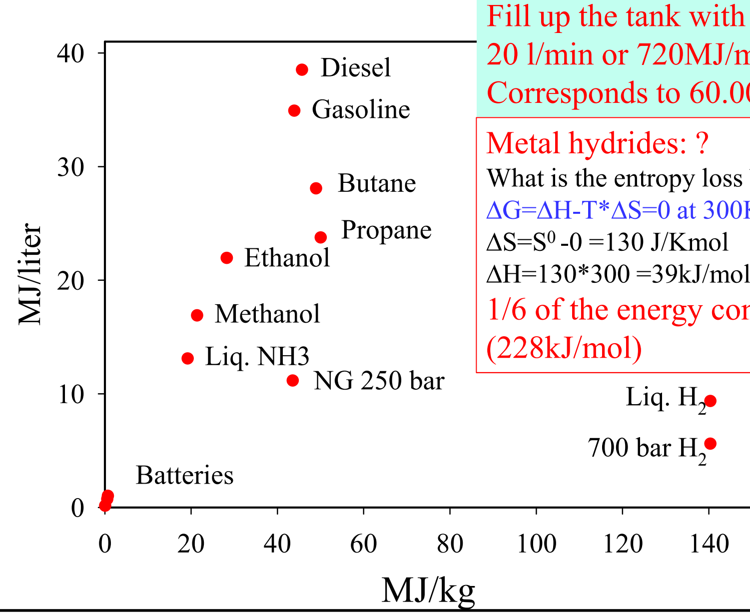
Outstanding problems is overall weight and fuel storage (H_2)

NECAR 90mph, 280 miles on one tank and 75 HK (55kW)
DailmerChrysler

Energy content of fuels

Fill up the tank with gasoline!
20 l/min or 720MJ/min
Corresponds to 60.000A @ 200V

Metal hydrides: ?
What is the entropy loss by adsorption?
$\Delta G=\Delta H-T*\Delta S=0$ at 300K
$\Delta S=S^0 -0 =130$ J/Kmol
$\Delta H=130*300 =39$kJ/mol or
1/6 of the energy content!!
(228kJ/mol)



Challenges in the Transport Sector

Probably electricity will be the major form of sustainable energy, but it is impractical to store (in particular in the transport sector- require long cables?). Who much energy is used in the transppot sector??

Brint Fuel Cells

- Electrolyse 70%
- Compression 90%
- Distribution 90%
- Fuel cell 45%
- Can be improved

Total efficiency
0,7*0,9*0,9*0,45= 25%
Hard to store Hydrogen
No Infrastructure

Batteries

- Distribution 90%
- Local transformation 90%
- charging/decharging 80%

Total effektivitet
0,9*0,9*0,8 = 65%
Capacitet is a problem
Charging is slow

Conclusion

- We have pleanty of fossil resources for 100 years plus
- We seem to heat up climate Hopefully this not bad because
- We shall need fosile fuels for many years to come! Maybe CO_2 free?
- We shall need all available sources: Wind, Solar, Waves…
- We need averaging Hydrogen is an energy carrier, i.e. there are No Hydrogen ressources!
- The transport sectore is trouble: Energy efficiency ~0,3
- Fuel cells are potentially more effective and environmental friendly. (If the hydrogen is produced correctly)
- Lack for metal resources could be a show stopper