Fakultet kemijskog inženjerstva i tehnologije
Sveučilište u Zagrebu

Diplomski studiji **PRIMIJENJENA KEMIJA**
EKOINŽENJERSTVO

Kolegij:

VODIKOVA ENERGIJA I EKONOMIJA (2)

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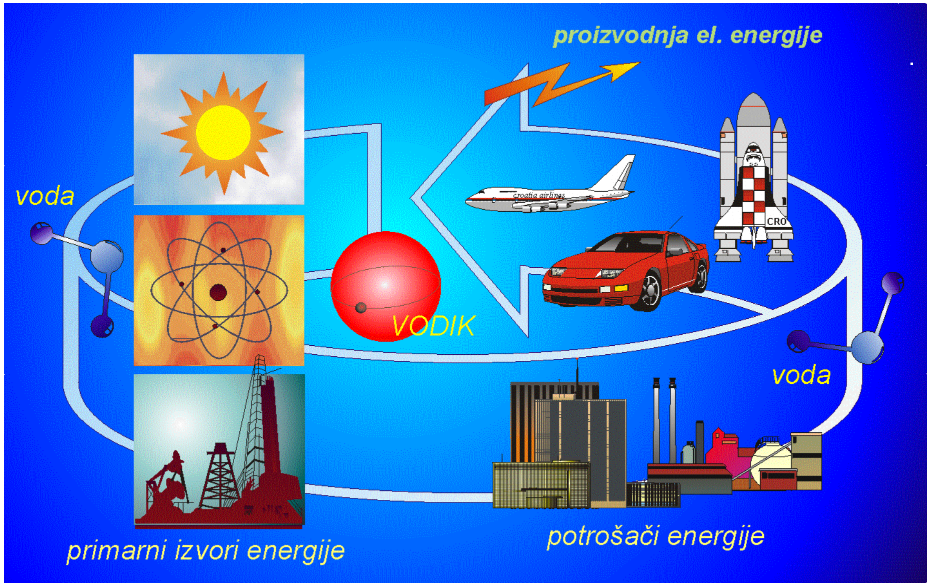
V O D I K

(hydrogen)

- ekološki prihvatljivo gorivo: izgaranjem ne nastaje CO_2
- nije primarni izvor energije, već je nosilac energije (poput ⚡)
- u prirodi ga nalazimo u spojevima s drugim elementima:
s kisikom / voda (H_2O), s ugljikom / ugljikovodici (CH)
- proizvodnja elementarnog vodika zahtijeva utrošak energije



$$2\ H_2\ (g) + O_2\ (g) \rightarrow$$
$$2\ H_2O\ (l) + 572\ kJ\ (286\ kJ/mol)$$

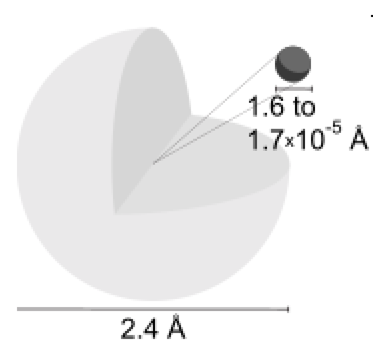
v • d • e **Periodic table**

H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca	Sc															Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y															Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

Alkali metals	Alkaline earth metals	Lanthanoids	Actinoids	Transition metals	Other metals	Metalloids	Other nonmetals	Halogens	Noble gases

General properties	
Name, symbol, number	hydrogen, H, 1
Element category	nonmetal
Group, period, block	1, 1, s
Standard atomic weight	1.00794(7) g·mol^{-1}
Electron configuration	1s^1
Atomic properties	
Oxidation states	1, -1 (amphoteric oxide)
Electronegativity	2.20 (Pauling scale)
Ionization energies	1st: 1312.0 kJ·mol^{-1}
Covalent radius	31±5 pm
Van der Waals radius	120 pm

The ground state energy level of the electron in a hydrogen atom is −13.6 eV, which is equivalent to an ultraviolet photon of roughly 92 nm wavelength.



Most stable isotopes					
Main article: Isotopes of hydrogen					

iso	NA	half-life	DM	DE (MeV)	DP
^{1}H	99.985%	^{1}H is stable with 0 neutrons			
^{2}H	0.015%	^{2}H is stable with 1 neutron			
^{3}H	trace	12.32 y	β^{-}	0.01861	^{3}He

Physical properties	
Color	colorless
Phase	gas
Density	(0 °C, 101.325 kPa) 0.08988 g/L
Melting point	14.01 K, -259.14 °C, -434.45 °F
Boiling point	20.28 K, -252.87 °C, -423.17 °F
Triple point	13.8033 K (-259°C), 7.042 kPa
Critical point	32.97 K, 1.293 MPa
Heat of fusion	(H_2) 0.117 $kJ \cdot mol^{-1}$
Heat of vaporization	(H_2) 0.904 $kJ \cdot mol^{-1}$
Specific heat capacity	(25 °C) (H_2) 28.836 $J \cdot mol^{-1} \cdot K^{-1}$

Hydrogen gas forms explosive mixtures with air in the concentration range 4-74% (volume per cent of hydrogen in air) and with chlorine in the range 5-95%.

The mixtures spontaneously detonate by spark, heat or sunlight.
The hydrogen autoignition temperature, the temperature of spontaneous ignition in air, is 500 °C.
Pure hydrogen-oxygen flames emit ultraviolet light and are nearly invisible to the naked eye, as illustrated by the faint plume of the Space Shuttle main engine compared to the highly visible plume of a Space Shuttle Solid Rocket Booster.

Hydrogen is the most abundant element in the universe, making up 75% of normal matter by mass and over 90% by number of atoms.

Under ordinary conditions on Earth, elemental hydrogen exists as the diatomic gas, H_2. However, hydrogen gas is very rare in the Earth's atmosphere (1 ppm by volume) because of its light weight, which enables it to escape from Earth's gravity more easily than heavier gases.
However, hydrogen is the third most abundant element on the Earth's surface.
Most of the Earth's hydrogen is in the form of chemical compounds such as hydrocarbons and water.
Hydrogen gas is produced by some bacteria and algae and is a natural component of flatus.
Methane is a hydrogen source of increasing importance.

Production
Laboratory

In the laboratory, H_2 is usually prepared by the reaction of acids on metals such as zinc with Kipp's apparatus.

$$Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$$

Aluminium can also produce H_2 upon treatment with bases:

$$2\,Al + 6\,H_2O + 2\,OH^- \rightarrow 2\,Al(OH)^{4-} + 3\,H_2$$

The electrolysis of water is a simple method of producing hydrogen.
The theoretical maximum efficiency (electricity used vs. energetic value of hydrogen produced) is between 80–94%.

$$2H_2O(aq) \rightarrow 2H_2(g) + O_2(g)$$

In 2007, it was discovered that an alloy of aluminium and gallium in pellet form added to water could be used to generate hydrogen. The process also creates alumina, but the expensive gallium, which prevents the formation of an oxide skin on the pellets, can be re-used. This has important potential implications for a hydrogen economy, since hydrogen can be produced on-site and does not need to be transported.

Production
Industrial

Hydrogen can be prepared in several different ways, but economically the most important processes involve removal of hydrogen from hydrocarbons.
Commercial bulk hydrogen is usually produced by the steam reforming of natural gas. At high temperatures (700–1100 °C), steam (water vapor) reacts with methane to yield carbon monoxide and H_2.

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

This reaction is favored at low pressures but is nonetheless conducted at high pressures (2.0 MPa, 20 atm) since high pressure H_2 is the most marketable product. One of the many complications to this highly optimized technology is the formation of coke or carbon:

$$CH_4 \rightarrow C + 2\ H_2$$

Consequently, steam reforming typically employs an excess of H_2O.
Additional hydrogen can be recovered from the steam by use of carbon monoxide through the water gas shift reaction (WGS), especially with an iron oxide catalyst.
This reaction is also a common industrial source of carbon dioxide:

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

Production
Industrial

Other important methods for H_2 production include partial oxidation of hydrocarbons:

$$2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$$

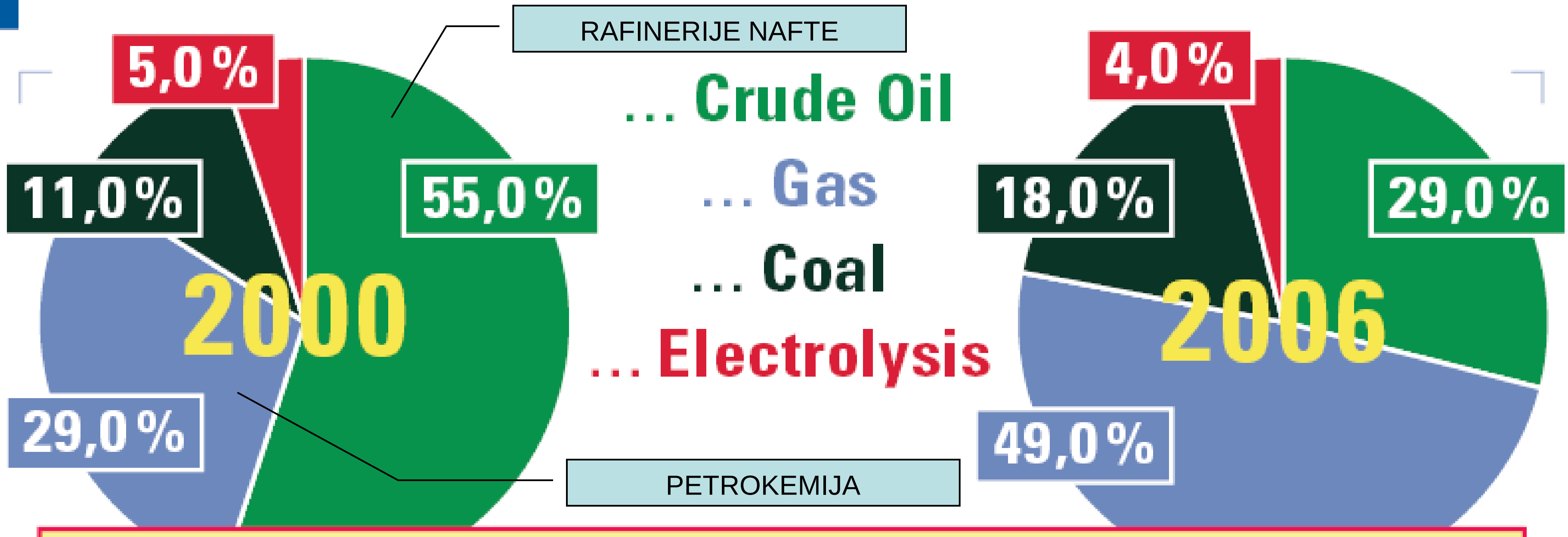
and the coal reaction, which can serve as a prelude to the shift reaction above:

$$C + H_2O \rightarrow CO + H_2$$

Hydrogen is sometimes produced and consumed in the same industrial process, without being separated.
In the Haber process for the production of ammonia, hydrogen is generated from natural gas.
Electrolysis of brine to yield chlorine also produces hydrogen as a co-product.

"brine" – zasićena vodena otopina soli (najčešće NaCl)

Actual Worldwide Hydrogen Production from …



The world hydrogen production is not monitored, but estimated at 45 million tons (500 million cubic metres) per year.

Sources: Chemical Economics Handbook, SRI – July 2001 and
Industrial Gases by the Chemical Economics Handbook, SRI – October 2007

Electrolysis had and still has a minimal impact.
As long as the electricity for the electrolysis does not come from renewable energy sources, no hydrogen produced at present is clean and "green" respectively.

Applications

Large quantities of H_2 are needed in the petroleum and chemical industries.

The largest application of H_2 is for the processing ("upgrading") of fossil fuels, and in the production of ammonia.

The key consumers of H_2 in the petrochemical plant include hydrodealkylation, hydrodesulfurization, and hydrocracking.
H_2 has several other important uses.
H_2 is used as a hydrogenating agent, particularly in increasing the level of saturation of unsaturated fats and oils (found in items such as margarine), and in the production of methanol.
It is similarly the source of hydrogen in the manufacture of hydrochloric acid.
H_2 is also used as a reducing agent of metallic ores.

Applications

Hydrogen is highly soluble in many rare earth and transition metals and is soluble in both nanocrystalline and amorphous metals.

Hydrogen solubility in metals is influenced by local distortions or impurities in the crystal lattice.
These properties may be useful when hydrogen is purified by passage through hot palladium disks, but the gas serves as a metallurgical problem as hydrogen solubility contributes in an unwanted way to embrittle many metals, complicating the design of pipelines and storage tanks.

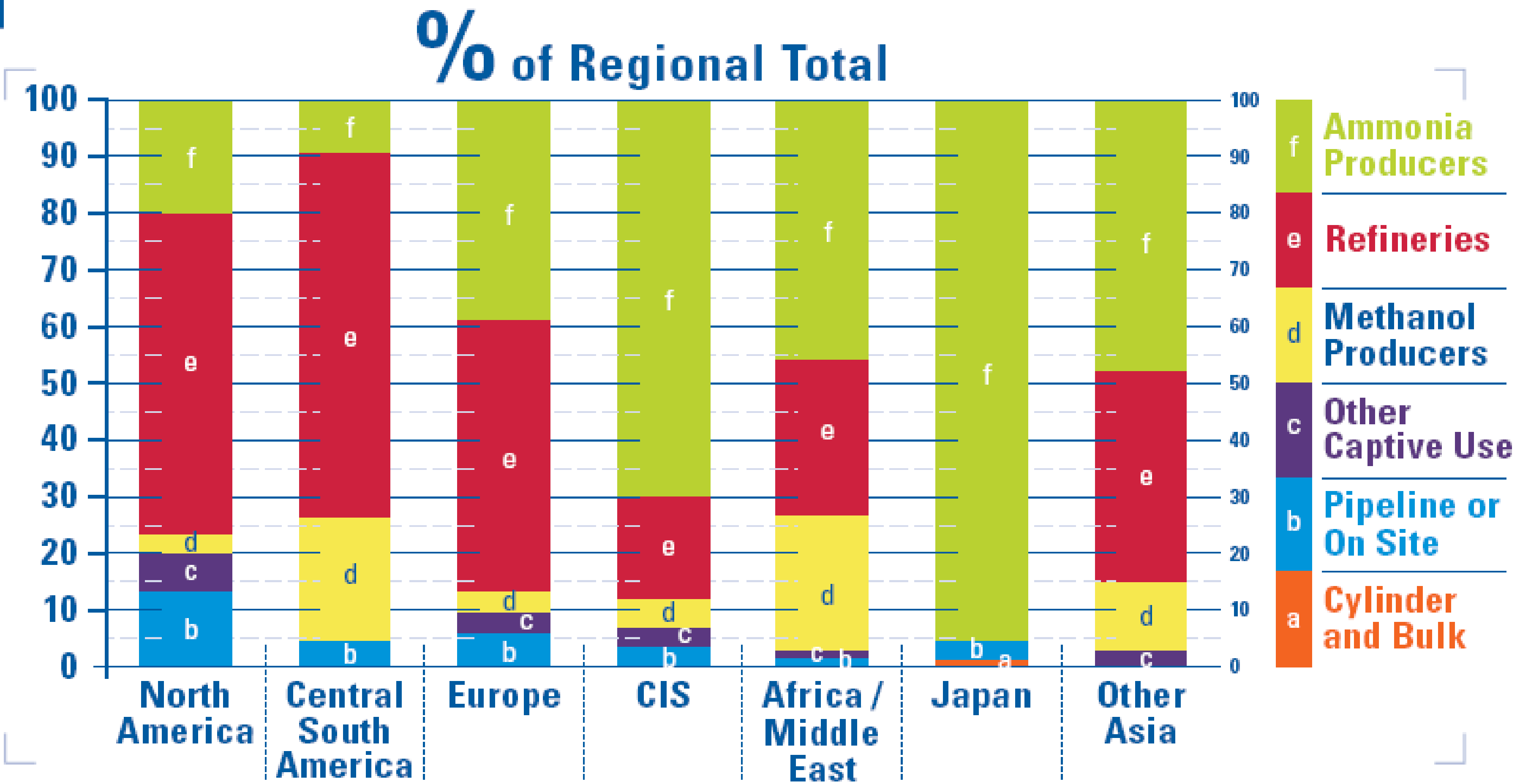
Applications

Apart from its use as a reactant, H_2 has wide applications in physics and engineering. It is used as a shielding gas in welding methods such as atomic hydrogen welding. H_2 is used as the rotor coolant in electrical generators at power stations, because it has the highest thermal conductivity of any gas. Liquid H_2 is used in cryogenic research, including superconductivity studies. Since H_2 is lighter than air, having a little more than 1⁄15 of the density of air, it was once widely used as a lifting gas in balloons and airships.

In more recent applications, hydrogen is used pure or mixed with nitrogen (sometimes called forming gas) as a tracer gas for minute leak detection. Applications can be found in the automotive, chemical, power generation, aerospace, and telecommunications industries. Hydrogen is an authorized food additive (E 949) that allows food package leak testing among other anti-oxidizing properties.

Hydrogen's rarer isotopes also each have specific applications. Deuterium (hydrogen-2) is used in nuclear fission applications as a moderator to slow neutrons, and in nuclear fusion reactions. Deuterium compounds have applications in chemistry and biology in studies of reaction isotope effects. Tritium (hydrogen-3), produced in nuclear reactors, is used in the production of hydrogen bombs, as an isotopic label in the biosciences, and as a radiation source in luminous paints.

Consumption of Hydrogen by End Use – 2006



Source: www.sriconsulting.com

Energy carrier

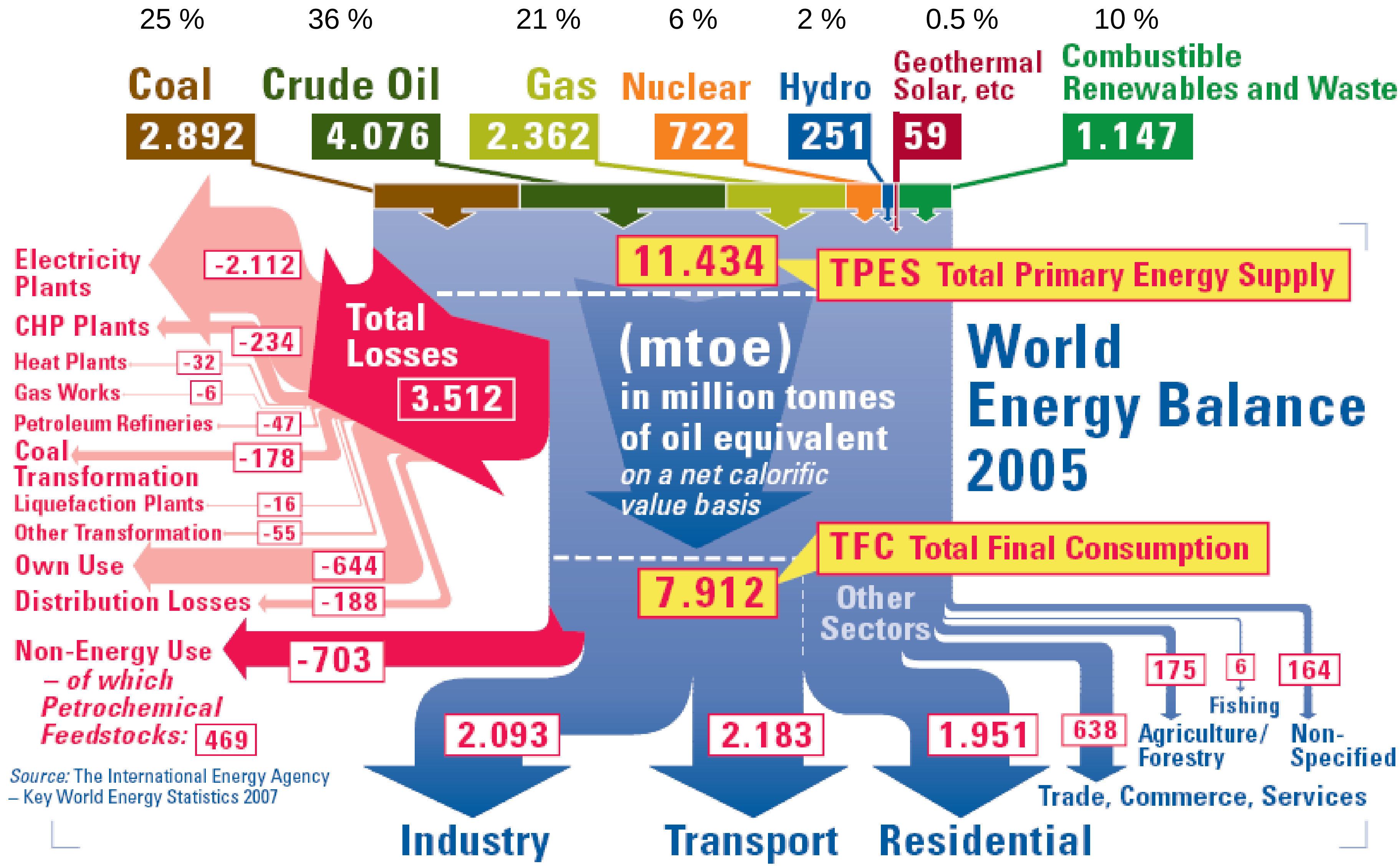
Hydrogen is not an energy resource, except in the hypothetical context of commercial nuclear fusion power plants using deuterium or tritium, a technology presently far from development. The Sun's energy comes from nuclear fusion of hydrogen, but this process is difficult to achieve controllably on Earth.
Elemental hydrogen from solar, biological, or electrical sources require more energy to make it than is obtained by burning it, so in these cases hydrogen functions as an energy carrier, like a battery. Hydrogen may be obtained from fossil sources (such as methane), but these sources are unsustainable.
The energy density per unit *volume* of both liquid hydrogen and compressed hydrogen gas at any practicable pressure is significantly less than that of traditional fuel sources, although the energy density per unit fuel *mass* is higher. Nevertheless, elemental hydrogen has been widely discussed in the context of energy, as a possible future *carrier* of energy on an economy-wide scale.

For example, CO_2 sequestration followed by carbon capture and storage could be conducted at the point of H_2 production from fossil fuels.
Hydrogen used in transportation would burn relatively cleanly, with some NOx emissions, but without carbon emissions.
However, the infrastructure costs associated with full conversion to a hydrogen economy would be substantial.

Semiconductor industry

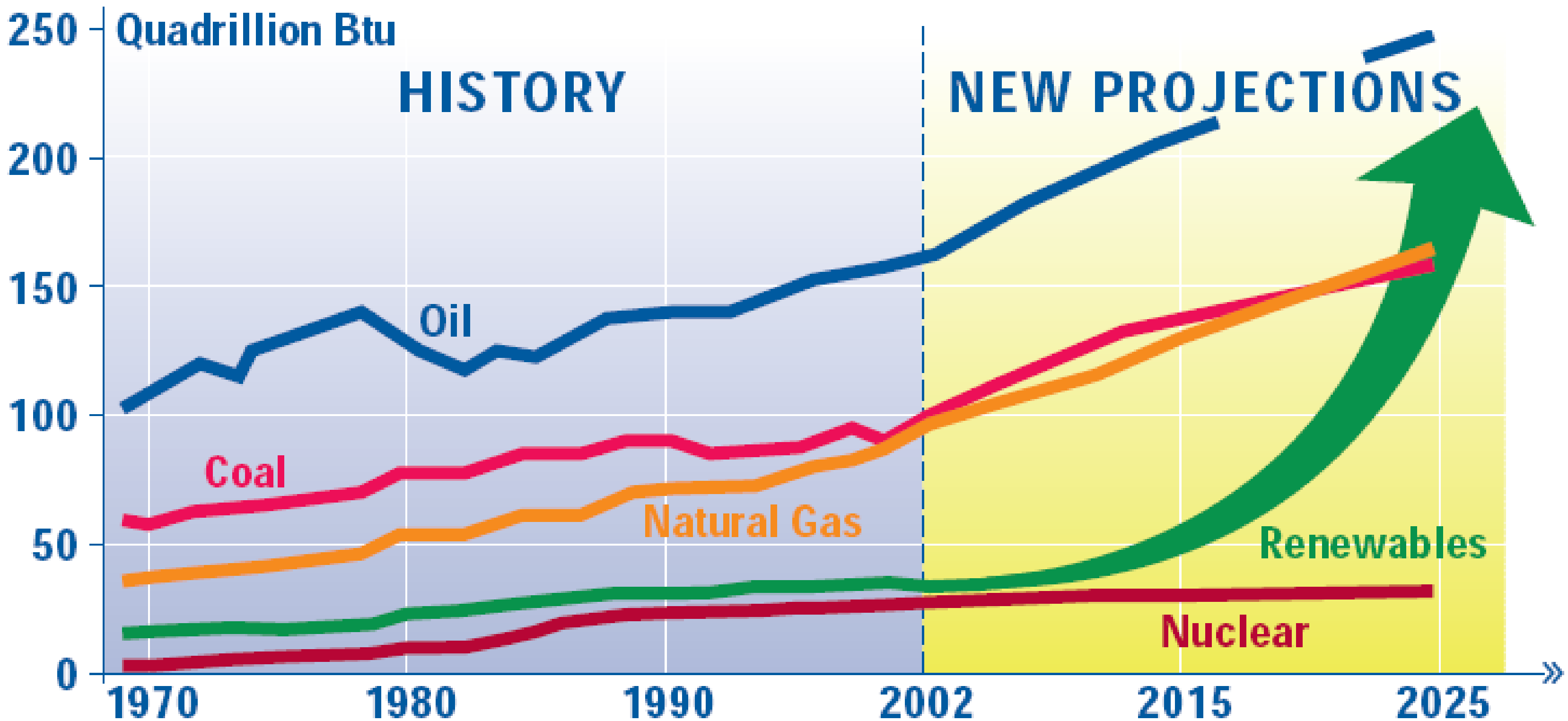
Hydrogen is employed to saturate broken ("dangling") bonds of amorphous silicon and amorphous carbon that helps stabilizing material properties.

It is also a potential electron donor in various oxide materials, including ZnO,[100][101] SnO_2, CdO, MgO,[102] ZrO_2, HfO_2, La_2O_3, Y_2O_3, TiO_2, $SrTiO_3$, $LaAlO_3$, SiO_2, Al_2O_3, $ZrSiO_4$, $HfSiO_4$, and $SrZrO_3$.



The proportion of total final consumption reflects the large amount of total losses: approx. 31 (!) % of the total primary energy supply dwindle away by distribution and transmission losses, transformation, power plants' own consumption etc.
Only 69 % of the total primary energy supply can finally be consumed by the end-users which is dominated by the transport, industry and residential sector. This situation can only be overcome by fundamental changes: converting to a decentralized energy system, harvesting all renewable energies.

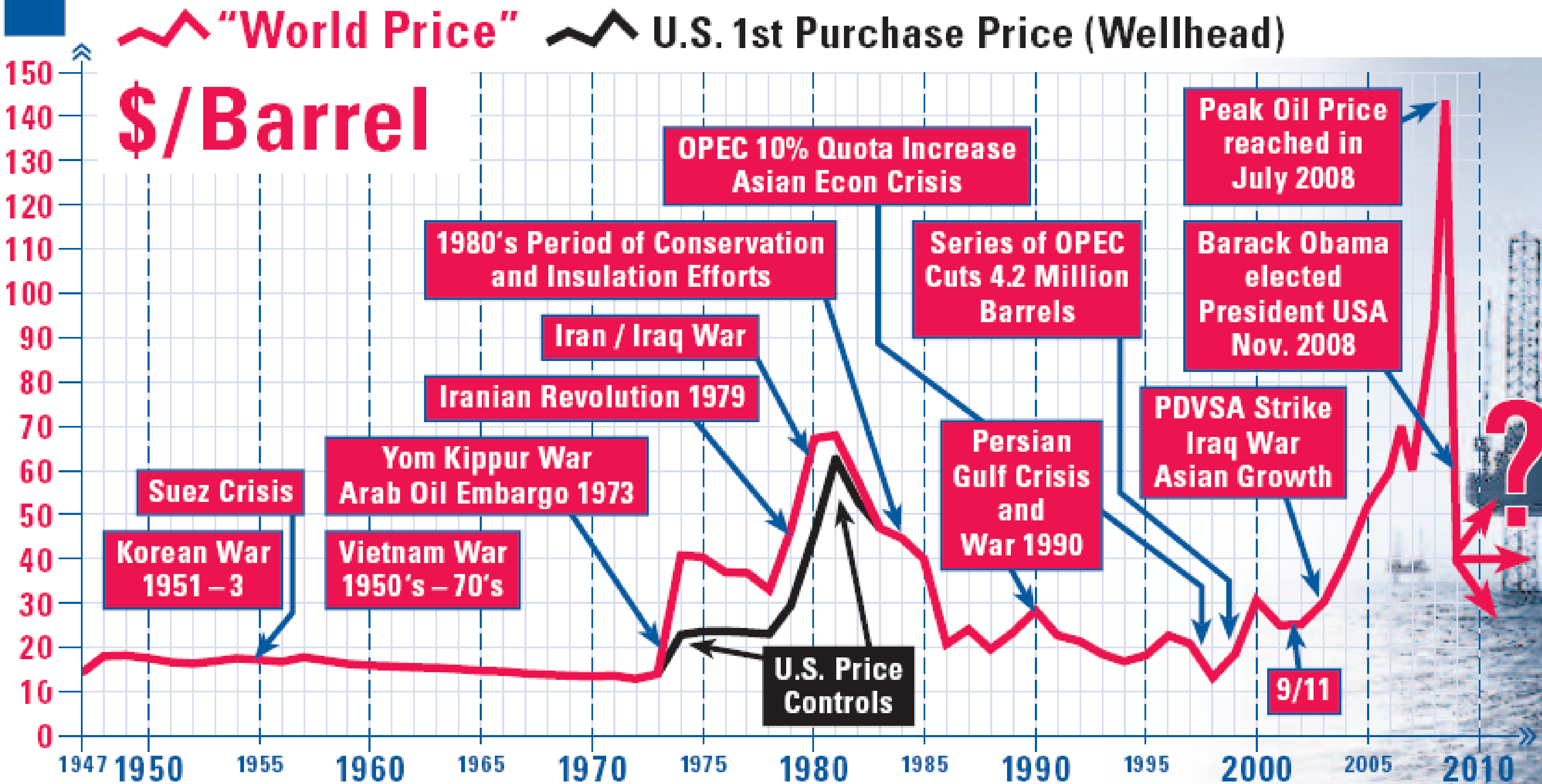
Worldwide Energy Use by Energy Type, 1970 – 2025



Source: History: Energy Information Administration (EIA)
Projections: EIA, System for the Analysis of Global Energy Markets (2005)

Own Research

Crude Oil Prices 1947 – 2008

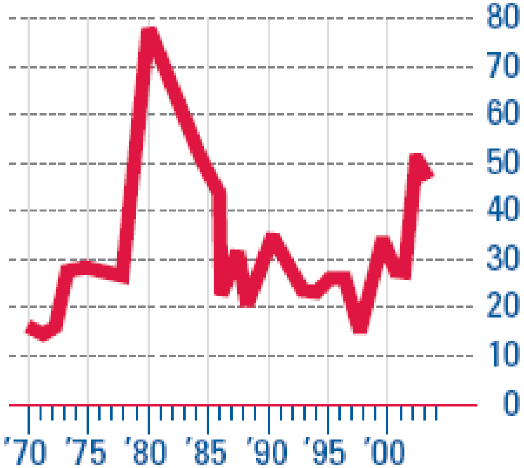


Source: WTRG Economics © 1998 – 2007
www.wtrg.com / ASPO - USA, Vol. 3 No.13, March 31, 2008
and www.tecson.de/prohoel.htm

First released: Oct. 2002; latest update: Jan. 2009

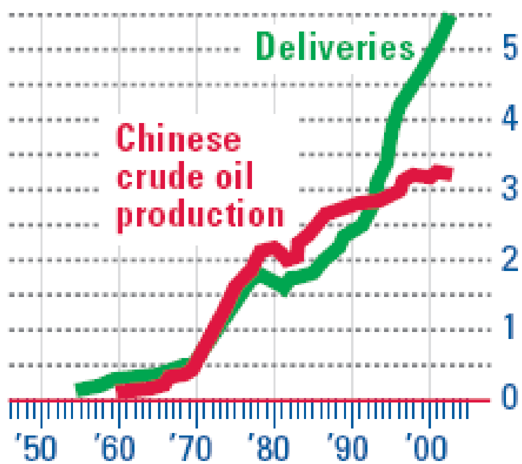
Crude oil at $50 US a barrel is really a bargain

Development of crude oil in $US a barrel in 2003 constant $US



Source: Canaccord Capital

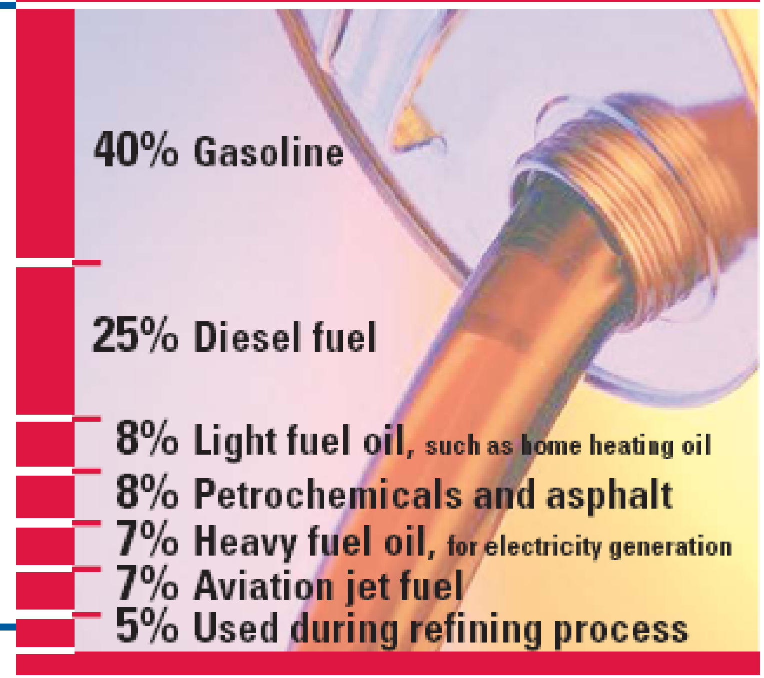
Development of crude oil in China in million barrel per day



Source: The Globe and Mail

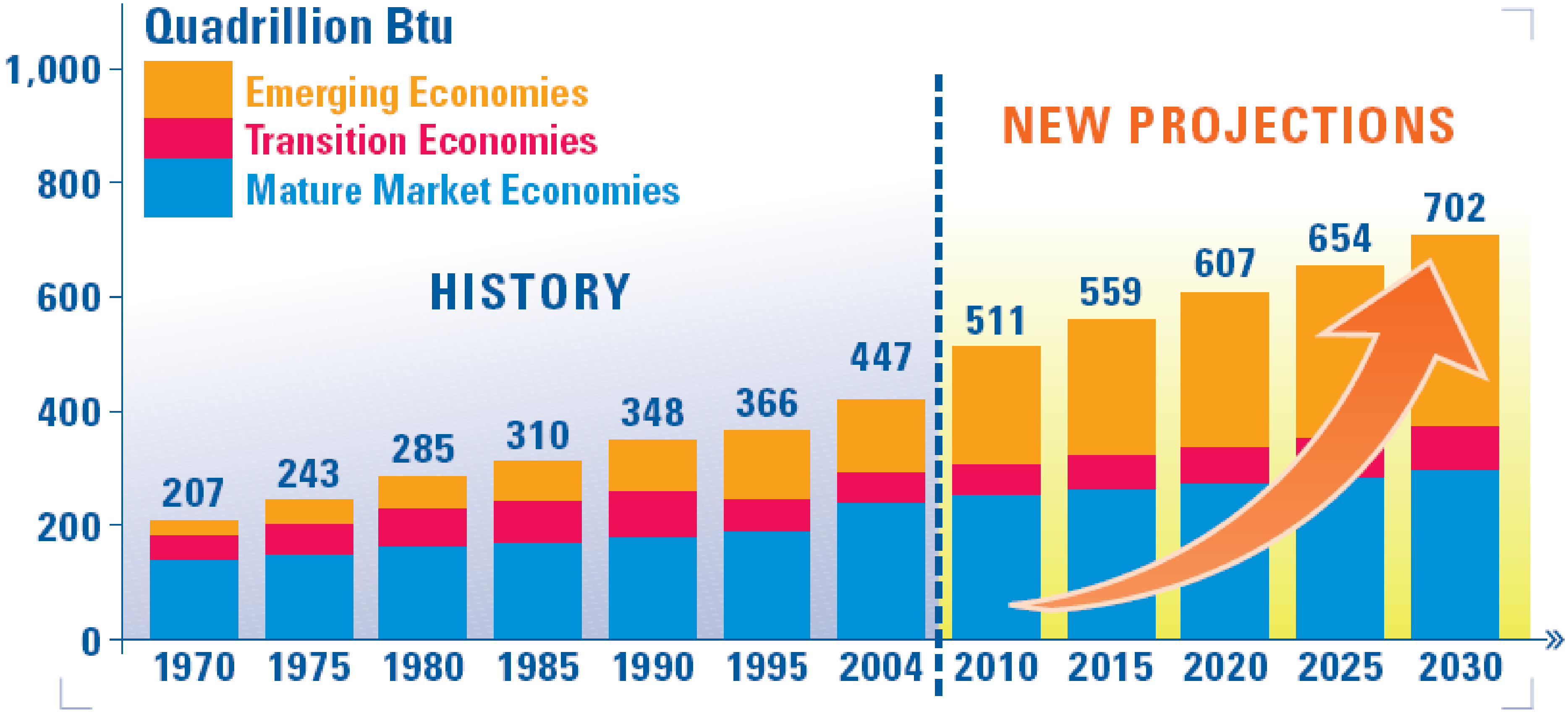
China's annual per-capita oil consumption is about 1,5 barrel – roughly the same as in the US 100 years ago.

Percentage breakdown of products from refining a barrel of crude oil



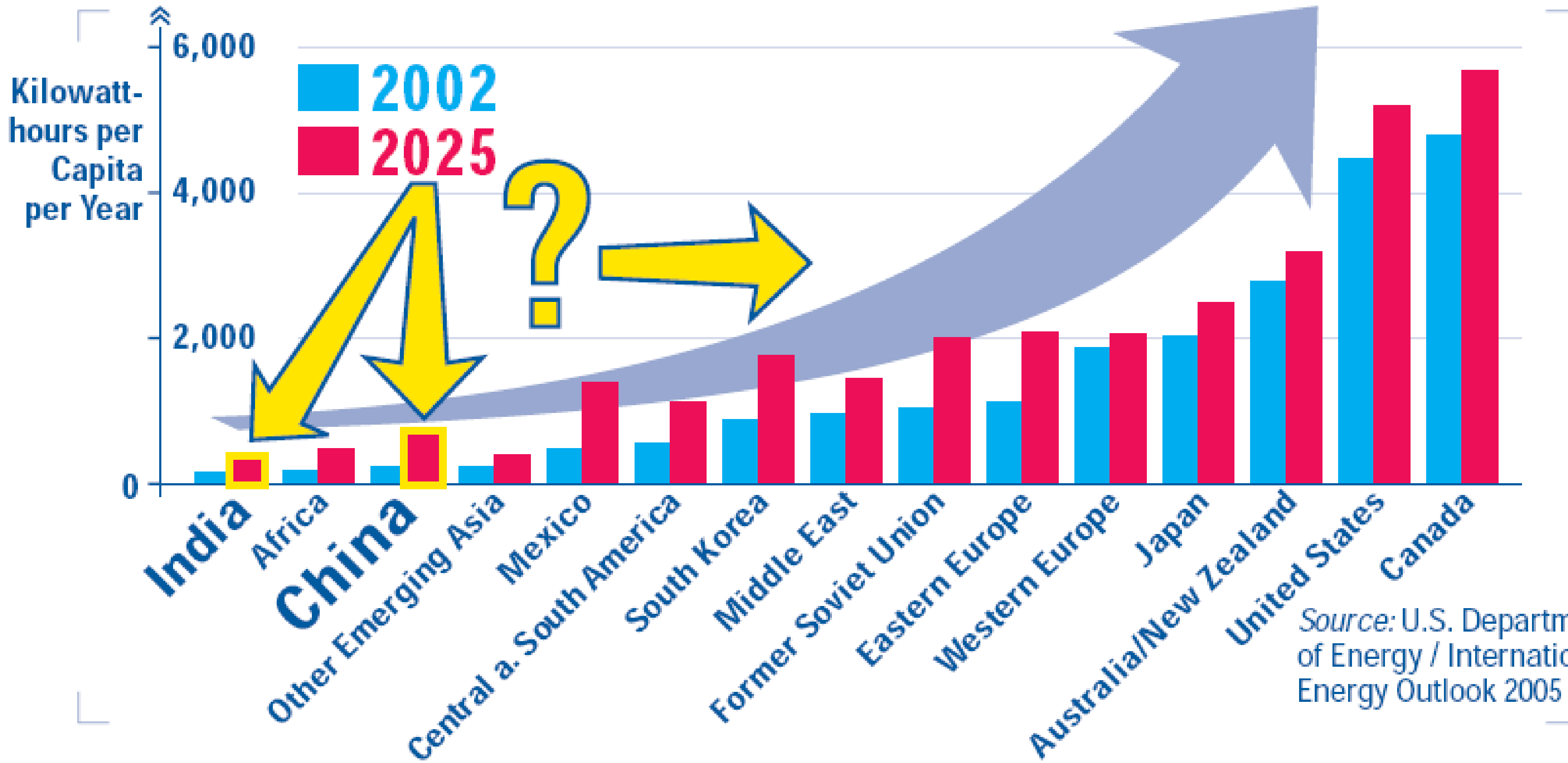
Source: The Globe and Mail, Sept. 2004

Worldwide Energy Consumption by Region, 1970 – 2030



Source: **History:** Energy Information Administration (EIA)
Projections: EIA, System for the Analysis of Global Energy Markets 2007

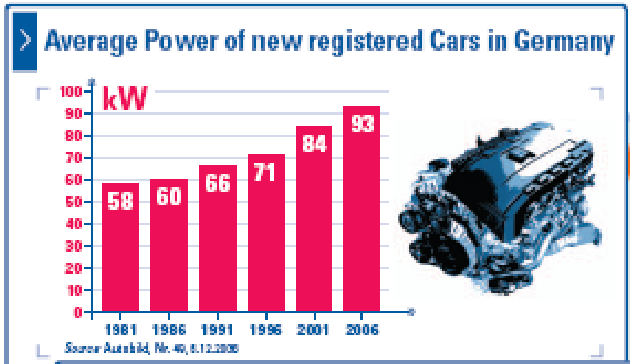
Residential Sector Electricity Consumption per Capita by Country Group, 2002 and 2025

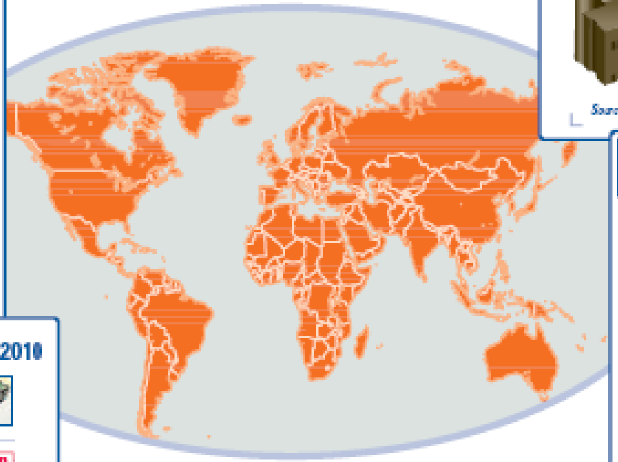


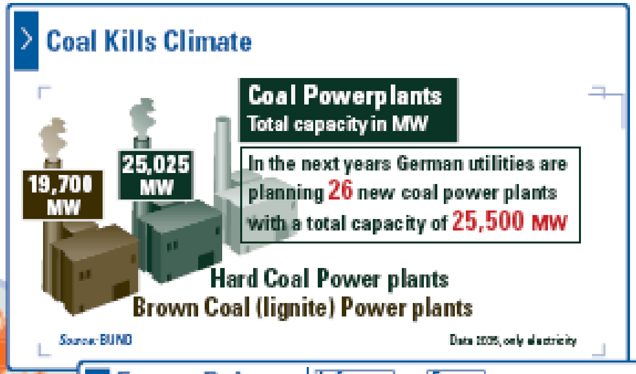
Source: U.S. Department of Energy / International Energy Outlook 2005

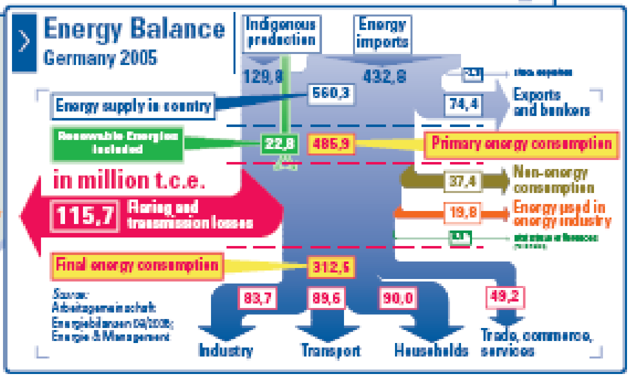
Today's Energy Situation

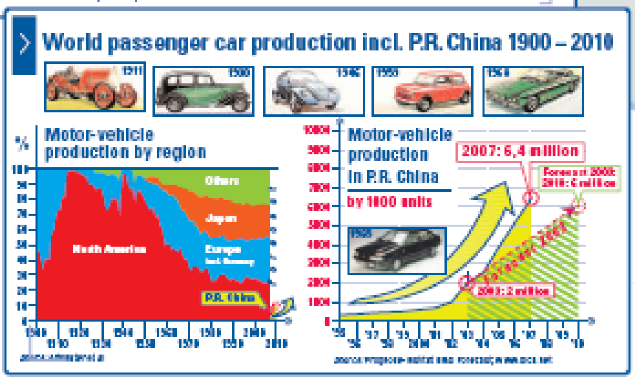
» More than 800.000.000 Cars on the road «



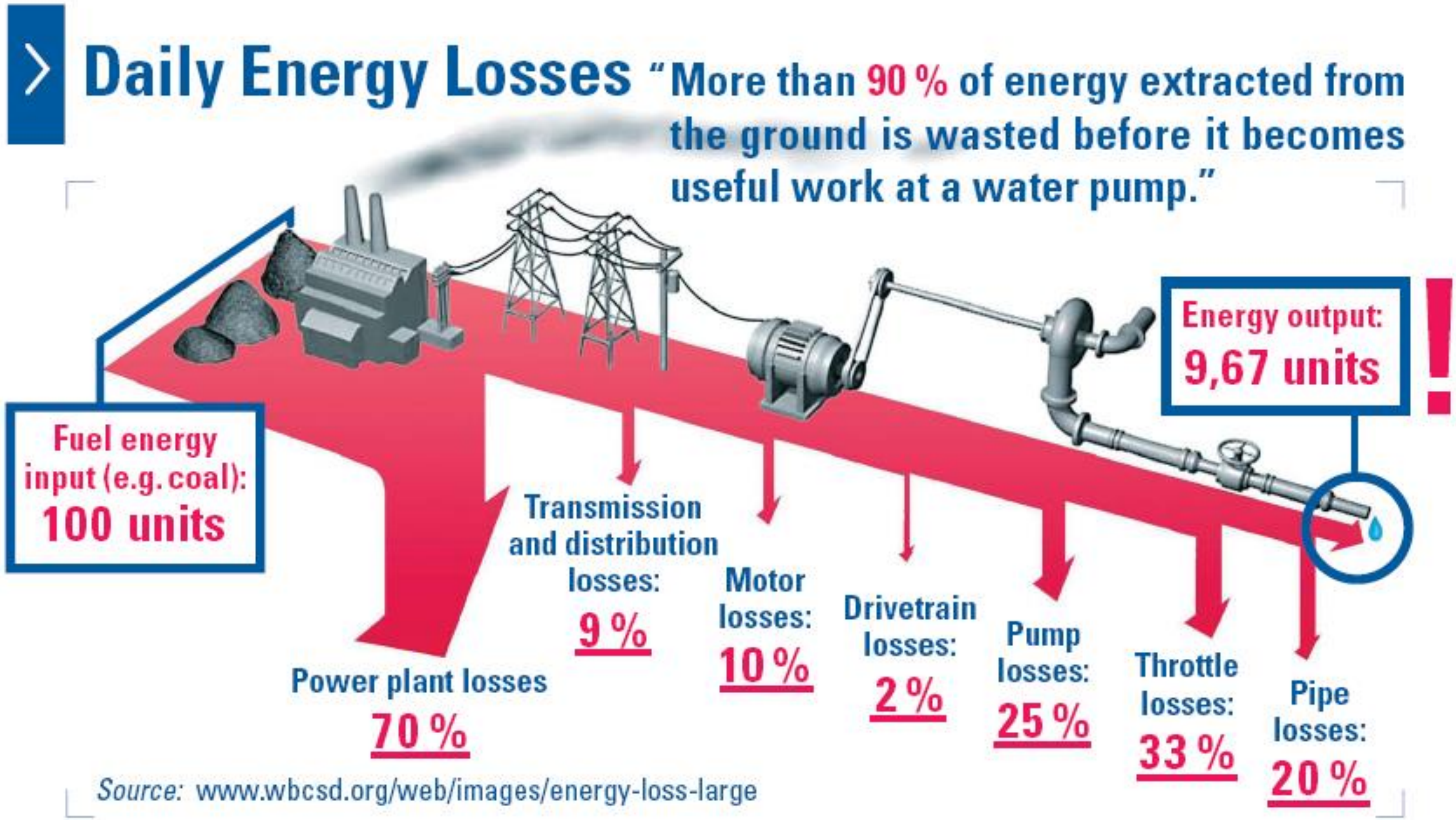








»1.152.840.000 Cellular Phones sold in 2007«



Today's Energy Balance, especially the production and distribution of electricity, is rather uneconomical worldwide, creating high flaring and transmission losses.

Energy effiency – one example

Source: Own research

German high voltage network

Electric circuit distances in Germany in km

> Low voltage [0,4 Kilovolt]	1.070.000
> Base voltage [6 bis ≤ 60 Kilovolt]	494.000
> High voltage [> 60 bis < 220 Kilovolt]	74.700
> Extreme voltage [220 und 380 Kilovolt]	36.000
total:	1.674.700

Voltage connection

- 380 kV
- 220 kV
- HVDC transmission link
- Converter stations
- Substations
- Cities

Numbers of substations/transformers*

> Base voltage [6 bis ≤ 60 Kilovolt]	557.700
> High voltage [> 60 bis < 220 Kilovolt]	7.500
> Extreme voltage [220 und 380 Kilovolt]	1.100
total:	566.300

Substations/transformers rated power [Mega-Volt-Ampere]*

> Base voltage [6 bis ≤ 60 Kilovolt]	268.200
> High voltage [> 60 bis < 220 Kilovolt]	260.000
> Extreme voltage [220 und 380 Kilovolt]	311.000

* estimated

Source: VDN, Verband der Netzbetreiber, 2006;
VDEW, Verband der Elektrizitätswirtschaft

Hydrogen is already on the market worldwide, but ....

45 Mio tons p.a.

Hydrogen Production worldwide

H_2

USD 280 billion p.a.

Produced by:

> Steam methane reformers (SME)
> partial oxidation of heavy fractions of hydrocarbons
> large (hydro) electrolyzers
> coal and biomass gasification

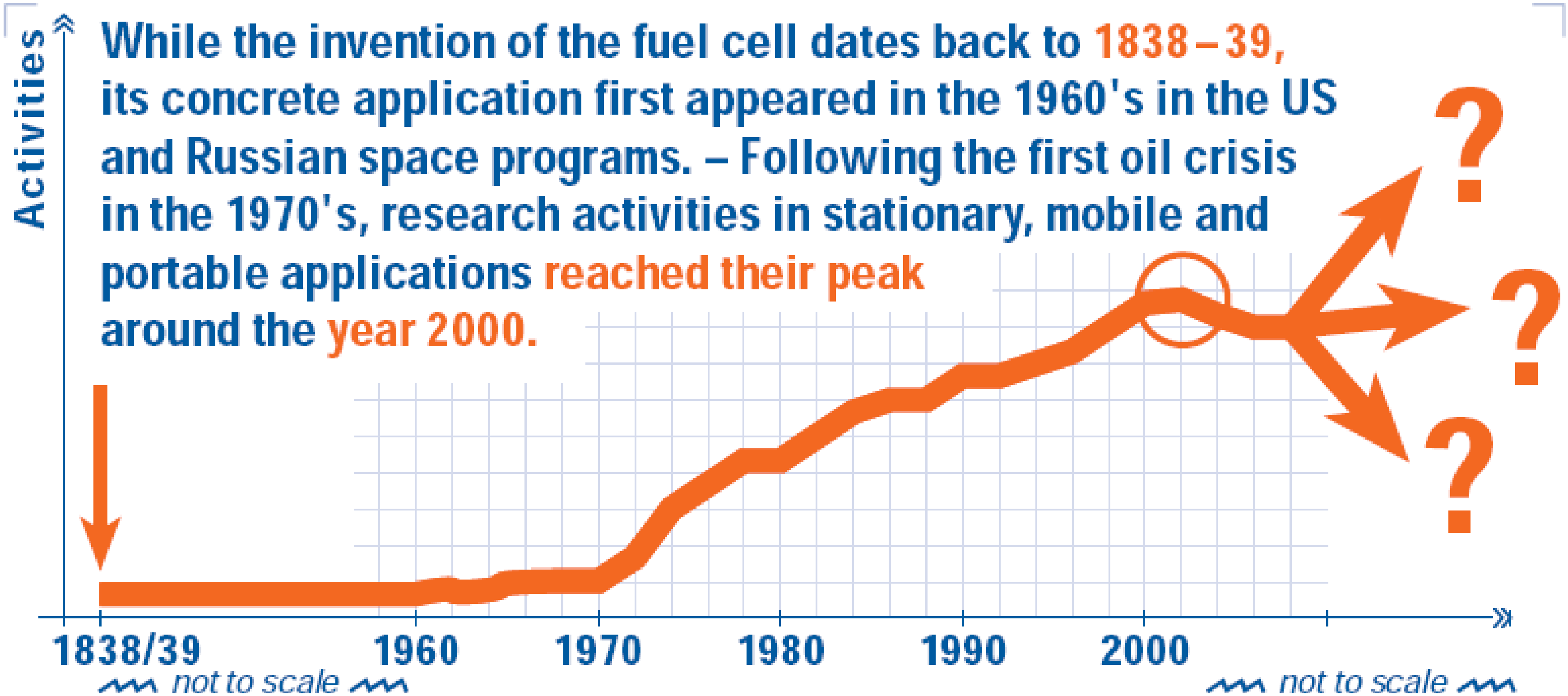
Utilized for:

> Space flight business (NASA et al.)
> making of ammonia for fertilizer
> removing sulphur from gasoline
> production of semiconductors
> glass and food manufacturing

By far the largest amounts of hydrogen are produced and utilizd captively in methanol and ammonia synthesises, and used in the refining industry for hydrogen treatment of heavy crude and the production of reformulated gasoline and desulphurization of middle distillate diesel fuel!

Source: Carl-Jochen Winter, First released: July 2009

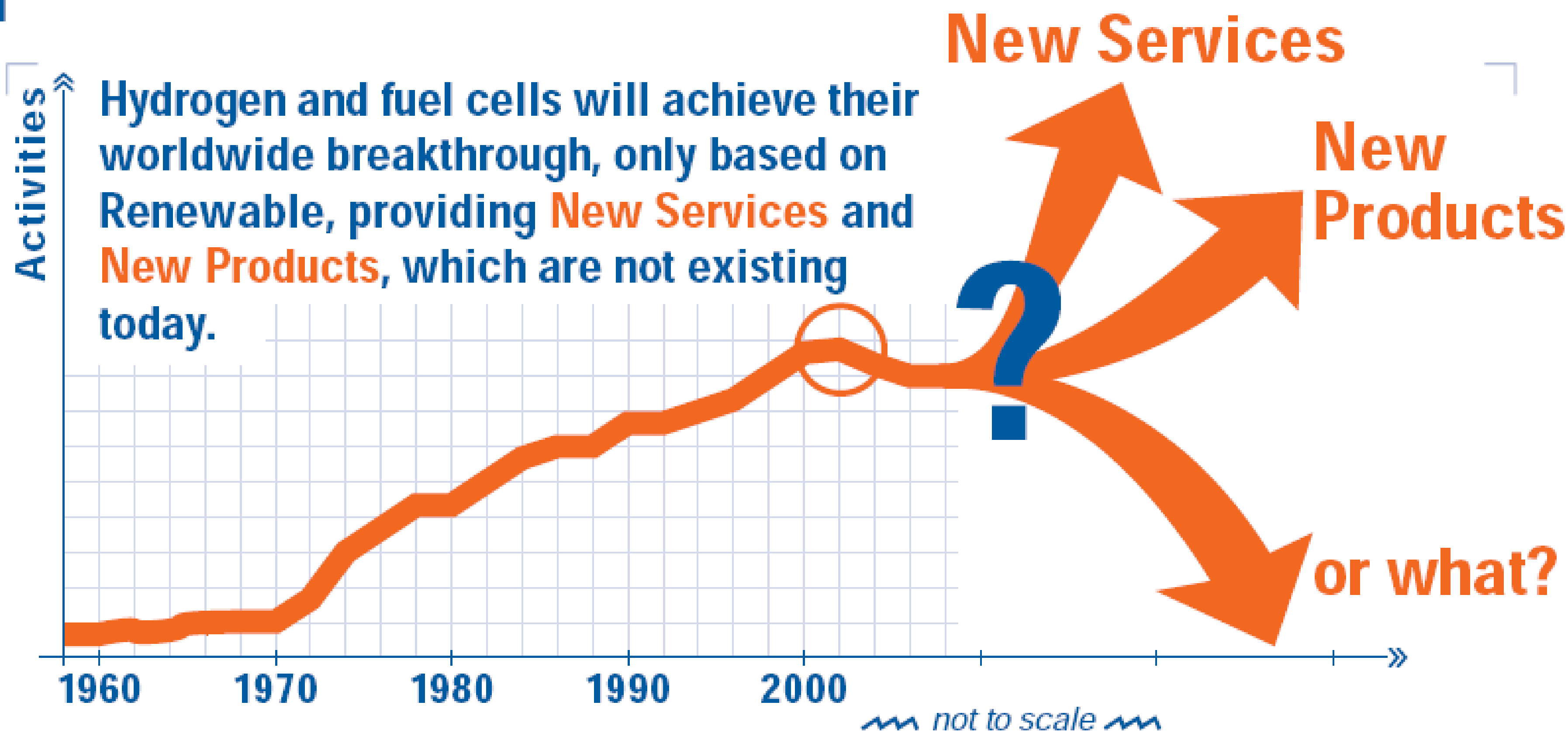
Worldwide breakthrough for Hydrogen + Fuel Cells



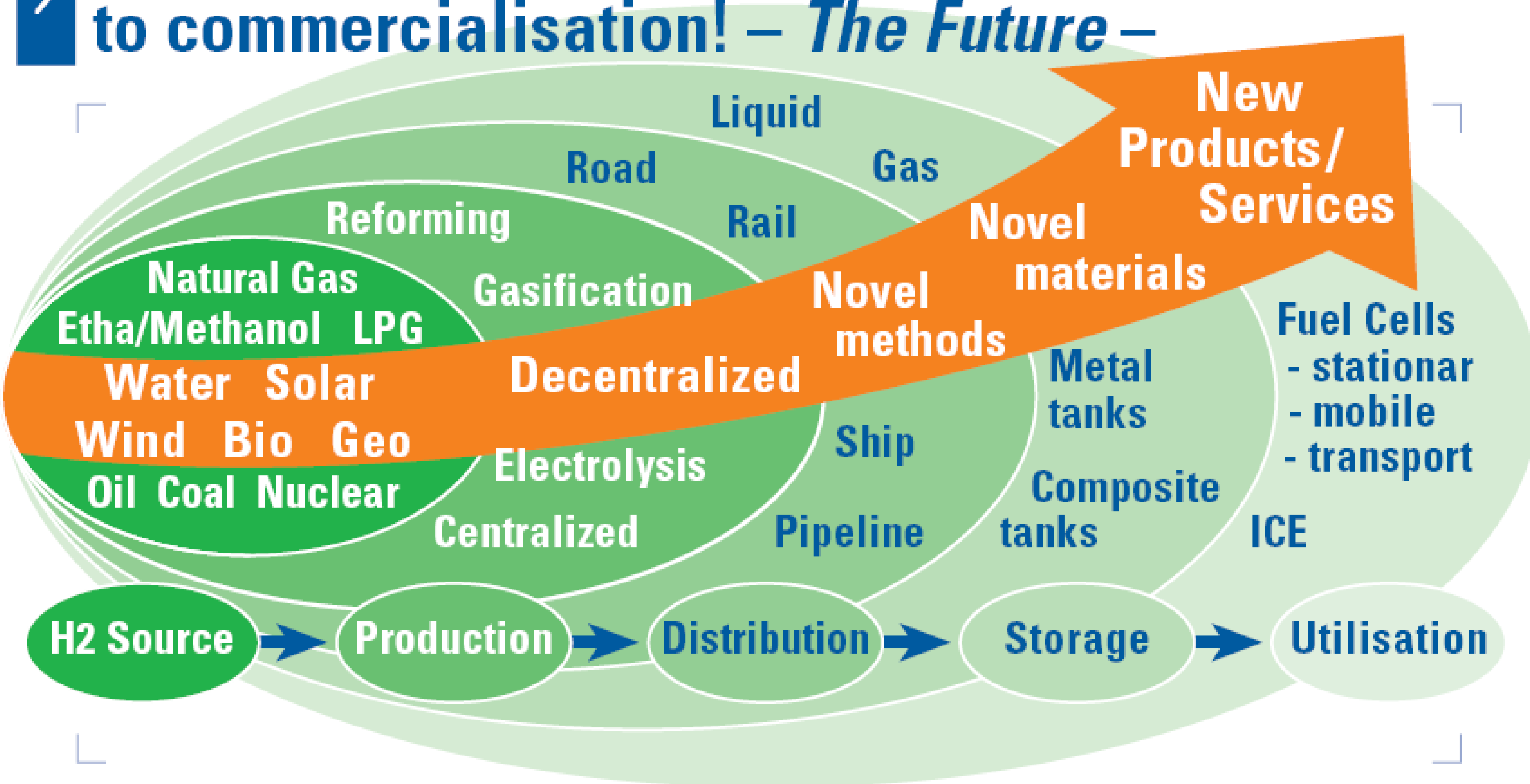
EVERS

Worldwide breakthrough for Hydrogen + Fuel Cells

Hydrogen and fuel cells will achieve their worldwide breakthrough, only based on Renewable, providing New Services and New Products, which are not existing today.

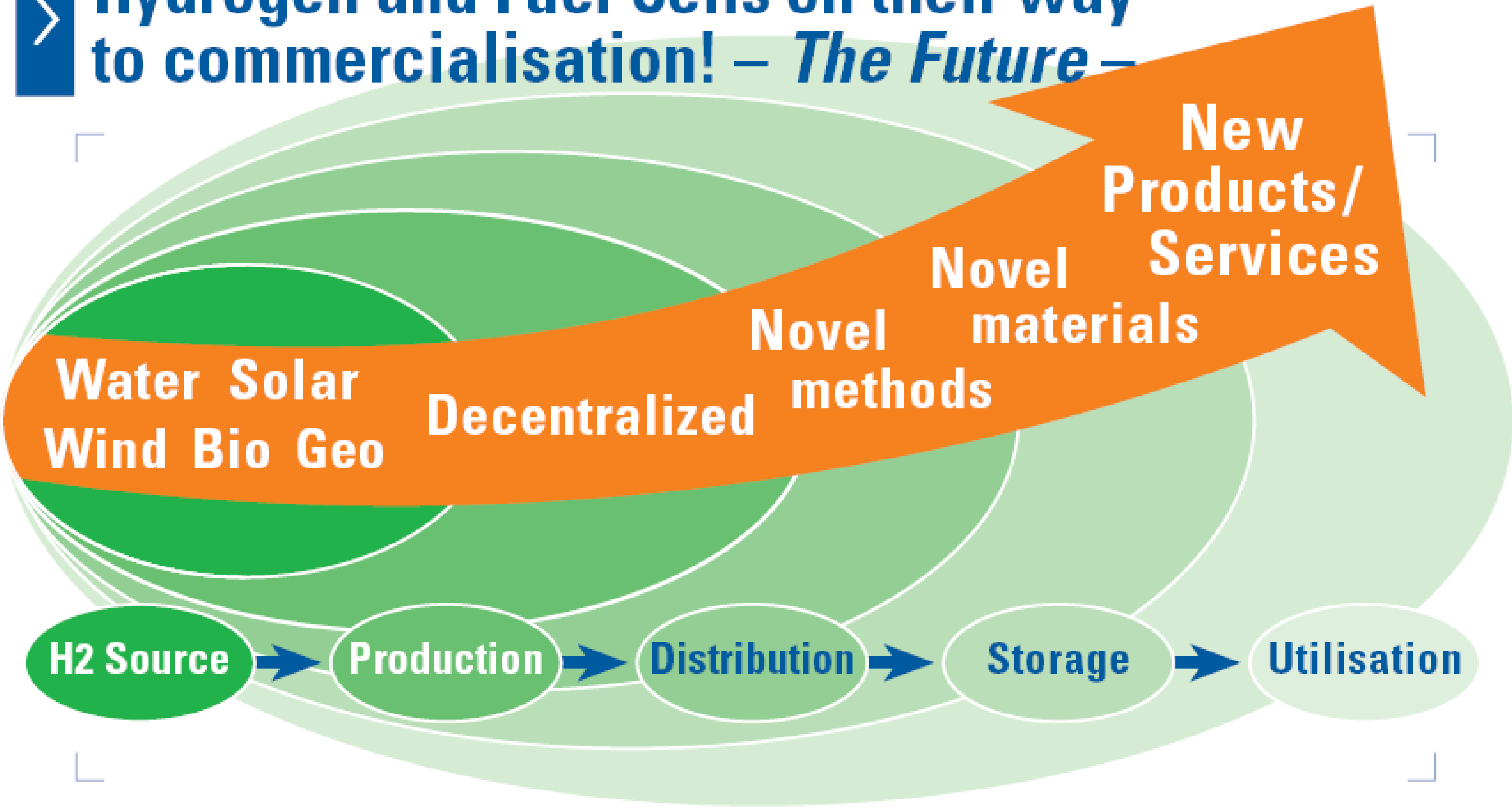


Hydrogen and Fuel Cells on their way to commercialisation! – *The Future* –



EVERS

Hydrogen and Fuel Cells on their way to commercialisation! – *The Future* –



How can we create the sustainable hydrogen society?

Hydrogen Vision:

1) Hydrogen has to become a common commodity
2) Hydrogen has to be produced free of pollution and losses
3) Hydrogen has to be traded localy, based on supply and demand
4) Hydrogen has to be used for electrification, transportation and convenience

Fuel Cells Vision:

Fuel Cells have to utilize their advantages in connecting the markets for:

→ 1. Electricity → 2. Heat → 3. (clean) water

Fuel Cells have to be used as decentralised, personal power systems

The existing methods to produce hydrogen (1) (Conventional)

Hydrogen is the most abundant element in the universe, most of it occurs in chemical combination with oxygen in water, so it has to be produced:

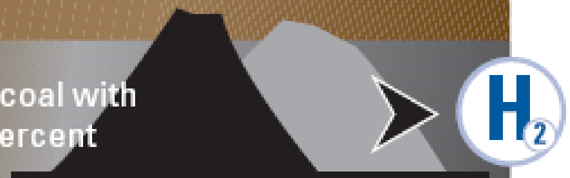
1. Hydrogen production from fossil fuels

1.1. Steam reforming of natural gas at this time the most efficient, economical and widely used process for hydrogen production

1.2. Partial oxidation converts hydrocarbons heavier than naphtha, using natural gas, ethanol or even gasoline as feedstock

1.3. Thermal cracking of natural gas has been practised for many years using a methane-air flame in tandem furnances or fixed bed reactors

1.4. Coal gasification (Koppers-Totzek process) oxidizes pulverized coal with oxygen and steam, to produce hydrogen with purity higher than 97.5 percent

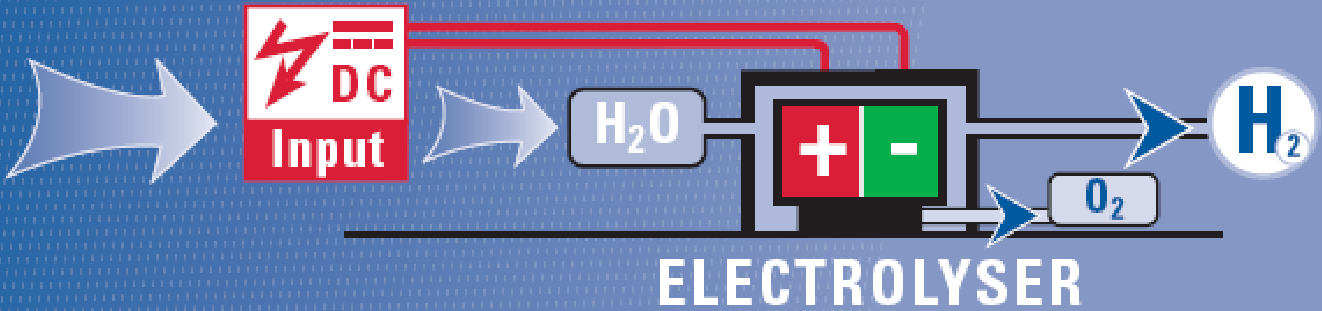


The existing methods to produce hydrogen (2) (Conventional)

Hydrogen is the most abundant element in the universe, most of it occurs in chemical combination with oxygen in water, so it has to be produced:

2. Hydrogen production with electrolyser

Electrolysis seems still to be the best method used for large-scale hydrogen production in a post-fossil-fuel era, however has very bad efficiency



The future role of hydrogen as energy carrier (1)

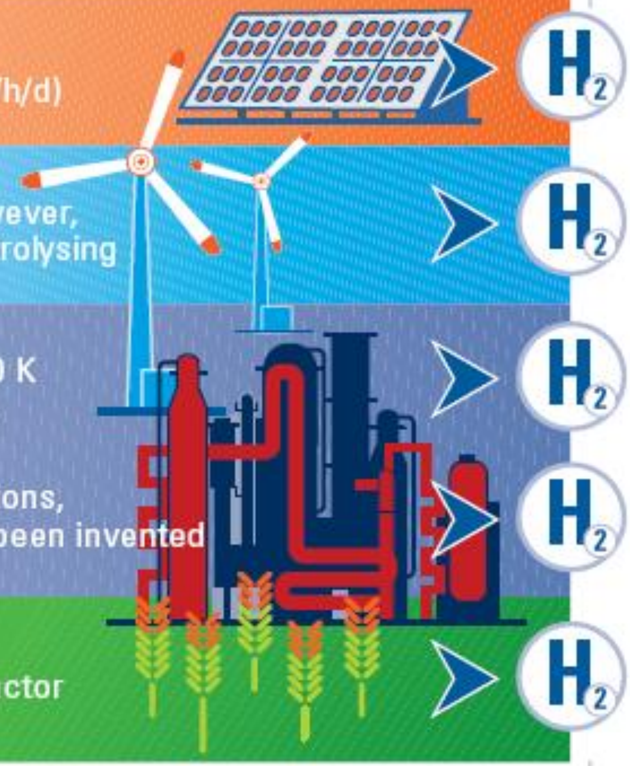
1\. **Photo Voltaic** has the highest potential with solar insolation of up to 6,5 kWh per square meter per day (Avg. in the U.S. 3,0 kWh/d)

2\. **Wind Power** can already produce electricity up to 6 MW, however, the electricity generated is immiment and not very suitable for electrolysing

3.1 **Thermolysis** splits water thermally at temperatures up to 3000 K raising problems with the material resitance to high temperatures

3.2 **Thermochemical** produces hydrogen through cyclical reactions, on trial since the mid-1960, with thousands of cycles which have been invented

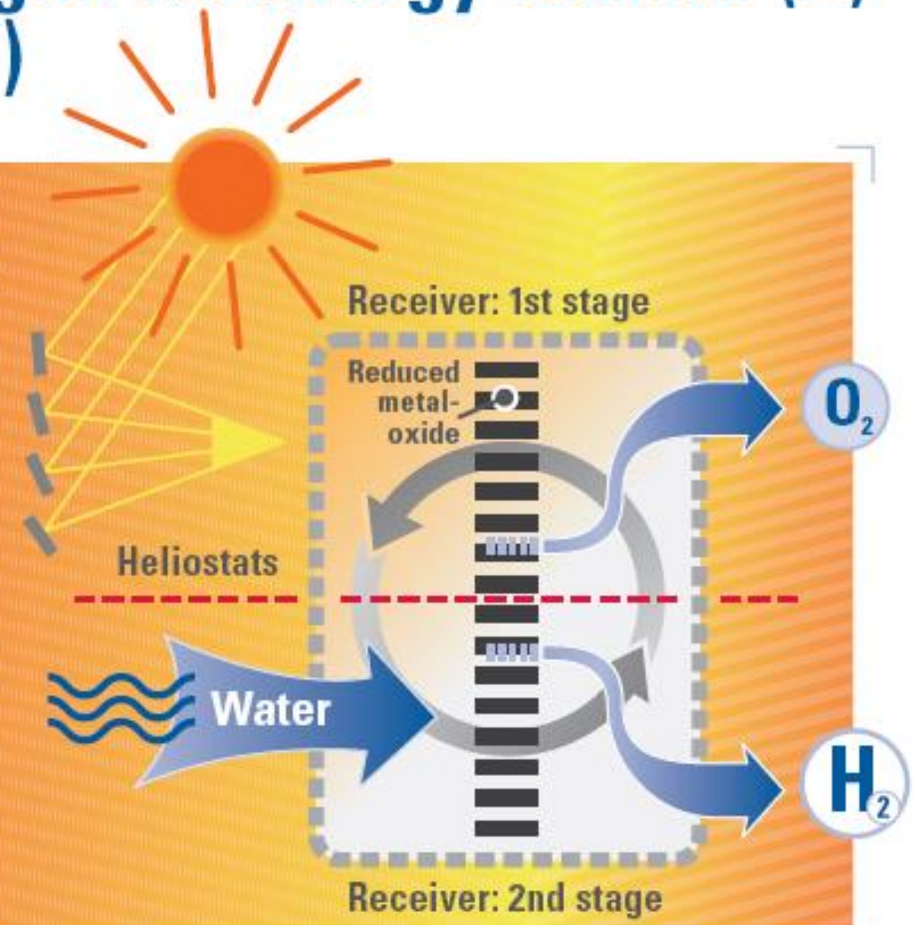
4\. **Biomass** can produce hydrogen by a pyrolysis/gasification process, heating the biomass/water slurry under pressure in a reactor



The future role of hydrogen as energy carrier (2) (direct solar production)

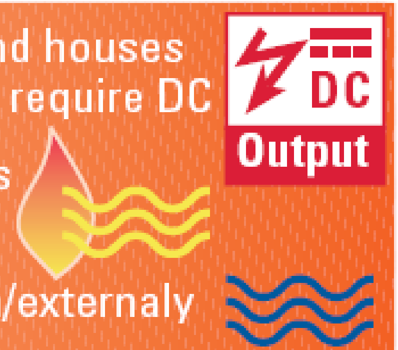
5. Photolysis direct extraction of hydrogen from water. Uses only sunlight in photobiological, photochemical or photo-electro-chemical conversions

All processes have to be developed and complemented with novel methods. Down-scaled to be used in decentralised mass-markets, the user of hydrogen and electricity will become their producer!

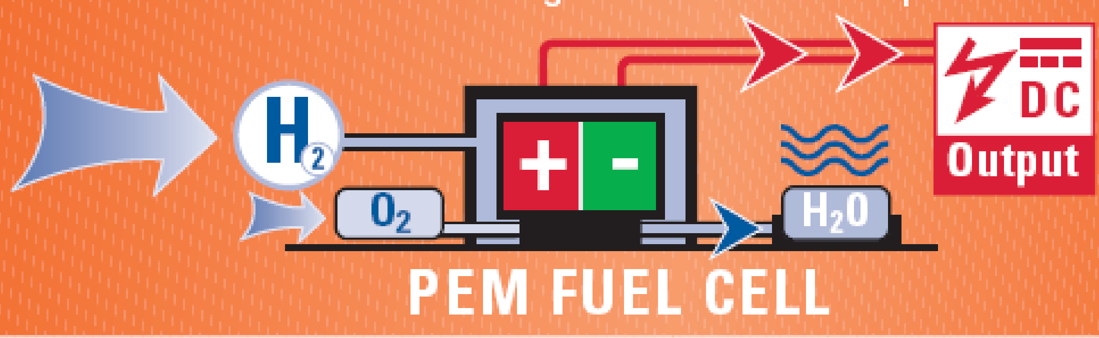


The future roles of fuel cells in decentralised power centers

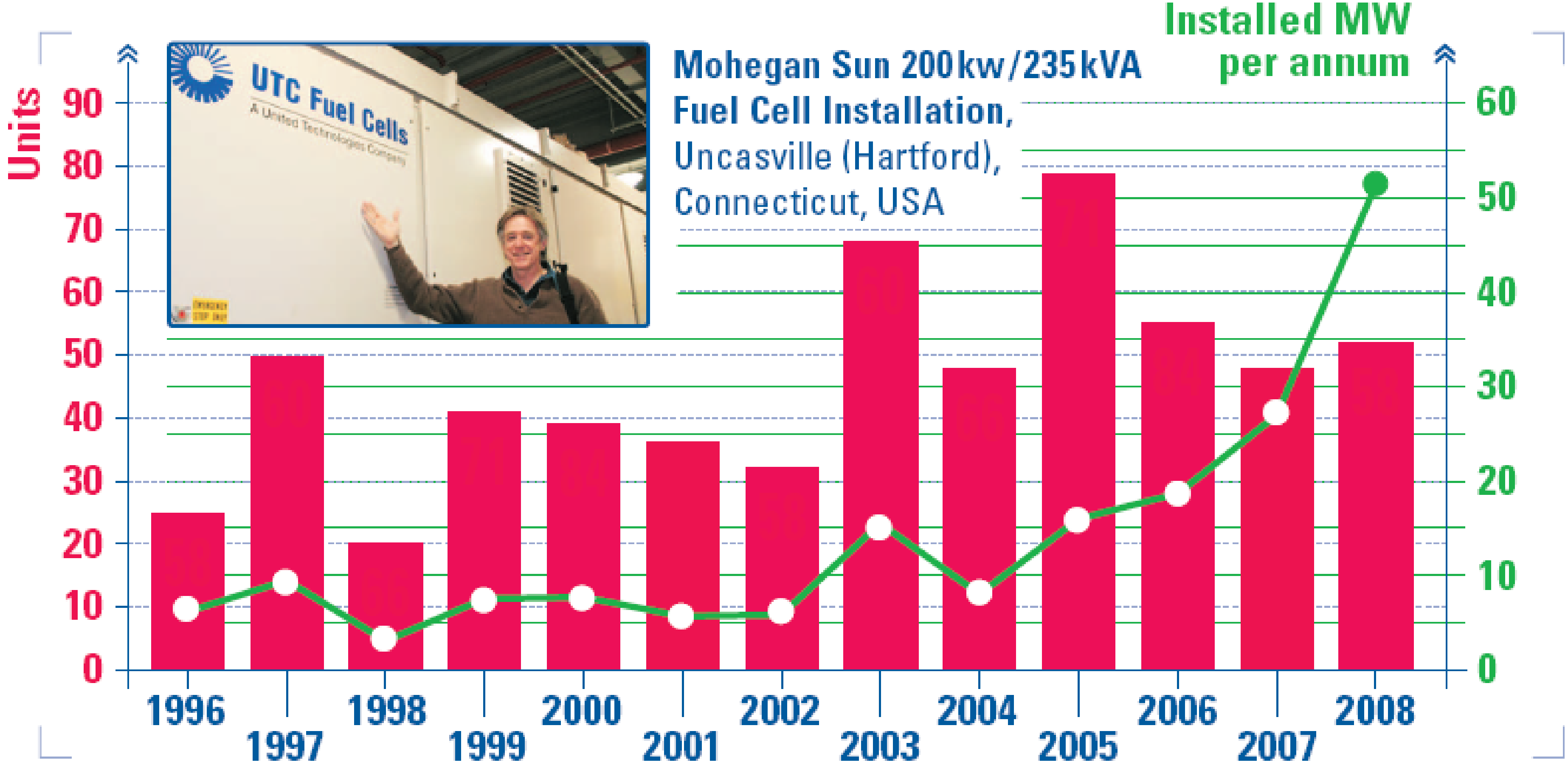
Fuel Cells have the ability to work for three tasks:



1. **Electricity** will be utilized in buildings like hospitals, offices and houses as DC (Direct Current), as nearly all home and office appliances require DC
2. **Heat** is not being wasted or flared, but captured in the process and used for heating (in winter) or cooling (during summer)
3. **(clean) Water** is produced while making electricity and used in/externaly or sold on the local market at the hightest achievable price

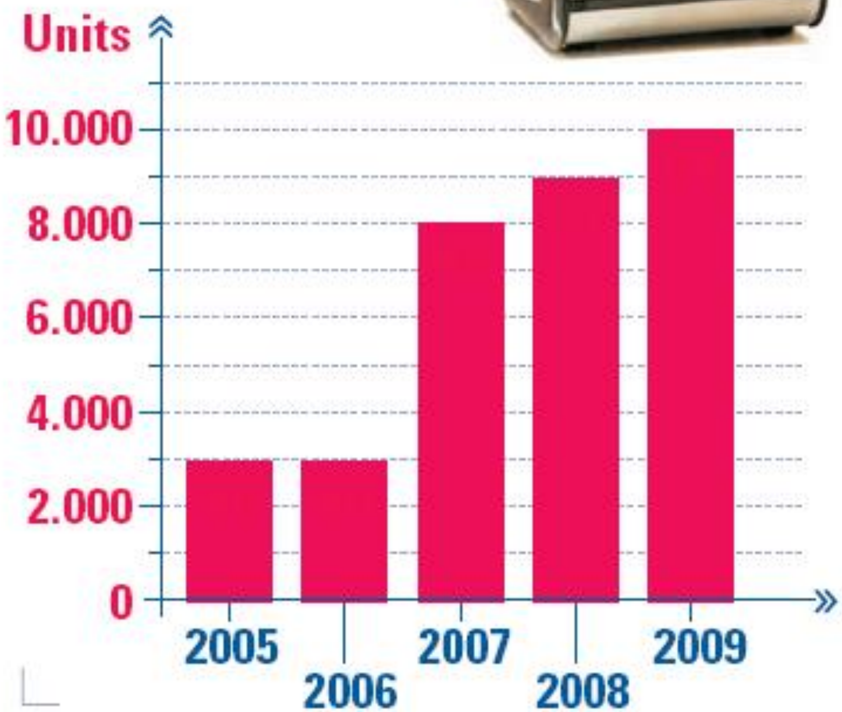


Annual number of large stationary fuel cells above 10kWe and MW installed

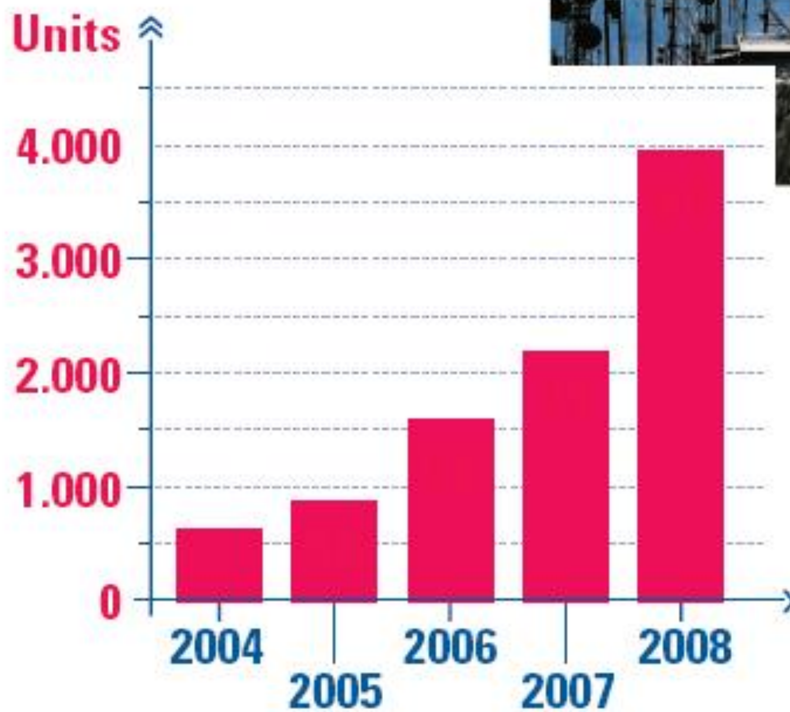


Source: Fuel Cell Today

Annual new portable fuel cell units 2005 – 2009

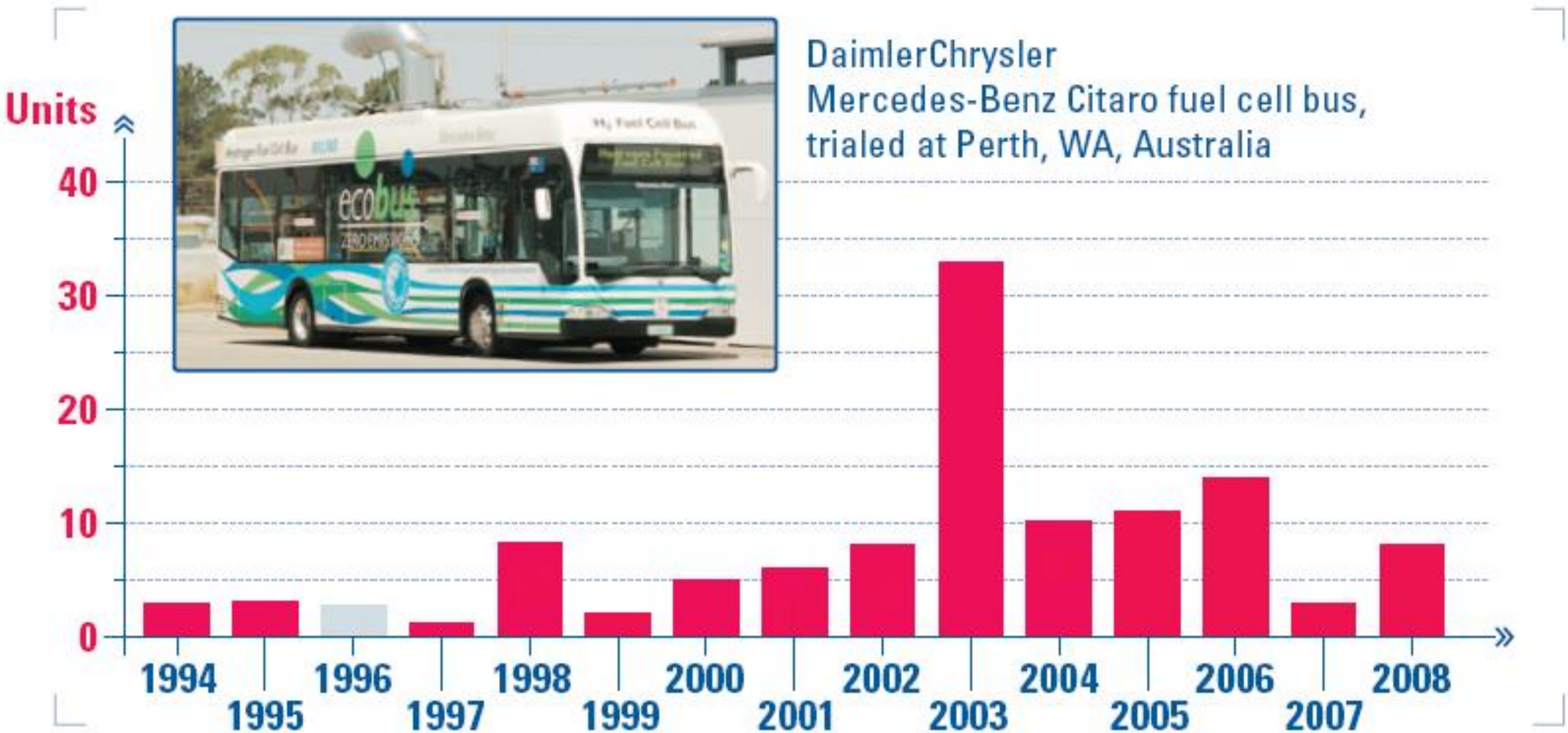


Annual new small stationary H2/FC units for CHP and UPS *(under 10kW)*



Source: Fuel Cell Today

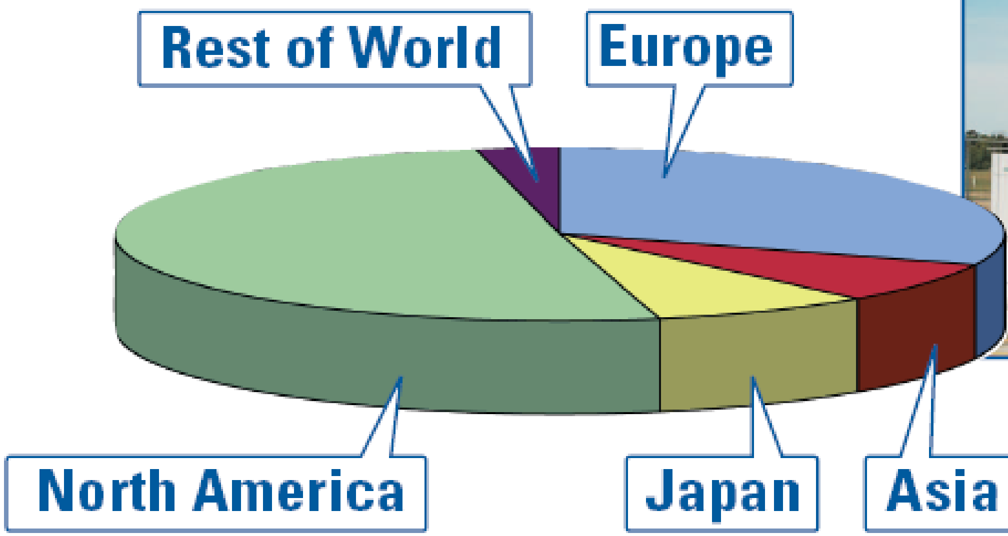
Annual new fuel cell buses produced from 1994 through 2008



Source: Fuel Cell Today

Distribution of hydrogen fueling stations by region

There will be over 150 hydrogen fueling sites in operation worldwide by the end of 2009

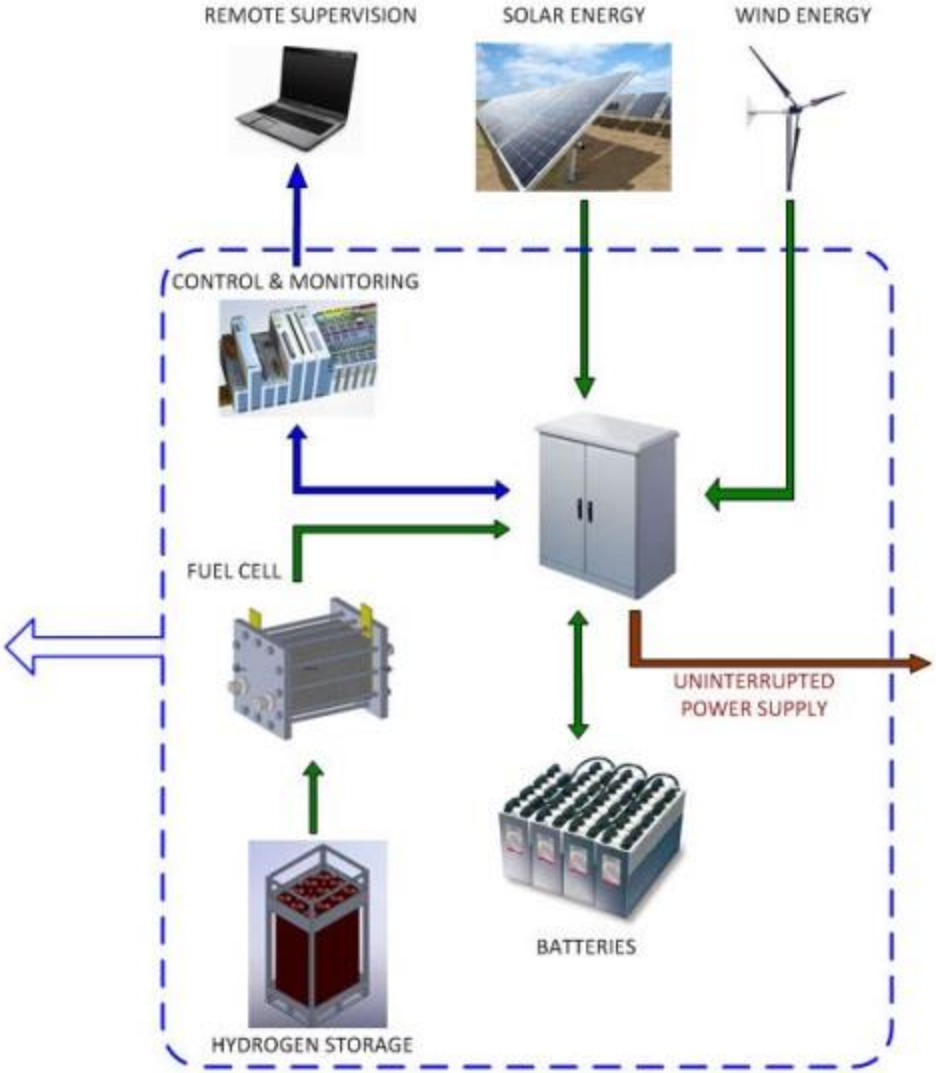


Hydrogen Fueling Station, University of California Davis, CA, USA

Source: Fuel Cell Today

Autonomni sustavi napajanja

Autonomni sustav napajanja predstavlja zaokruženi, cjeloviti sustav koji **objedinjuje uređaje za proizvodnju električke energije iz obnovljivih izvora (vjetroagregati, fotonaponski članci), pohranu energije u baterijama, spremnik vodika i gorivne članke za proizvodnju električke energije iz vodika, zaštitne sustave mjerenja i upravljanja**.
Sustav omogućuje komunikaciju prema udaljenom korisniku te uvid u stanje radnih parametara, upozorenja i alarma.
Ovisno o energetskim potrebama lokacije, potencijalu sunca i vjetra, autonomni sustav napajanja se konfigurira s određenim brojem vjetroagregata, fotonaponskih članaka i potrebnom veličinom spremnika energije.
Spremnici energije su baterije i vodik ili dizel koji služi kao podrška trošilima u slučaju nemogućnosti proizvodnje električke energije iz sunca i vjetra te praznih baterija.
Napredni algoritmi sustava upravljanja osiguravaju optimalno iskorištavanje pojedinog obnovljivog izvora ovisno o njegovoj trenutnoj raspoloživosti.
Visoka sigurnost osigurana je nizom procedura implementiranih u sustavu upravljanja te tzv. fail-safe konfiguracijom.
Autonomni sustav napajanja je razvijen u skladu sa svim relevantnim normama i propisima te se isporučuje sa izjavom o sukladnosti pojedinih komponenti.



KONČAR INSTITUT za elektrotehniku

50 GODINA