MINISTERO DELL'INTERNO

Vigili del Fuoco

ICHS International Conference on Hydrogen Safety

Ministry of the Interior

Department of Firefighters, Public Rescue and Civil Defence
Central Directorate for Prevention and Technical Safety

Hydrogen: use and fire prevention in Italy

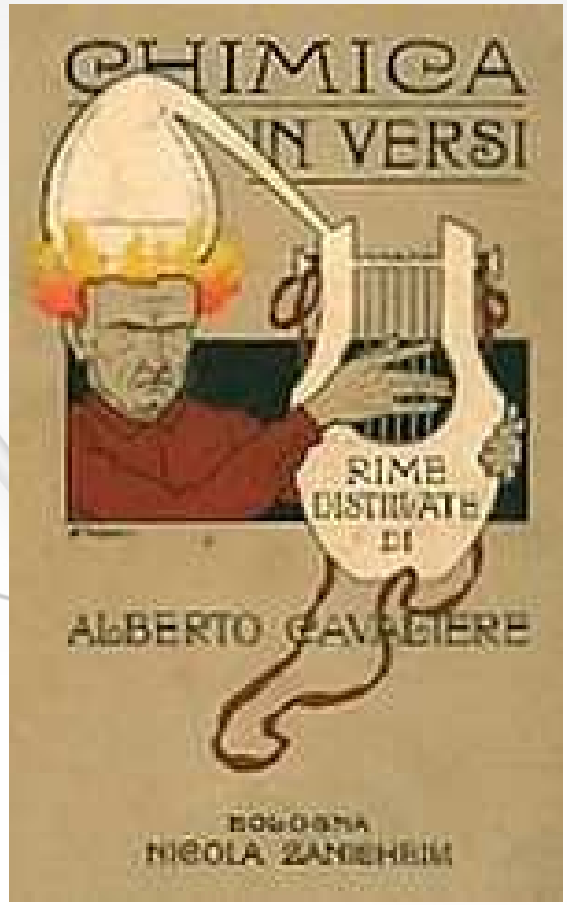
Fabio Dattilo
Central Director for
Prevention and Technical Safety

Bruxelles, 10 September 2013

- From the beginning to nowadays
- The industrial production of H2: potential risks
- Hydrogen and renewable energy sources
- Legislation and safety aspects

Alberto Cavaliere

Chemist, poet, journalist…
Born in 1897, he wrote “Chemistry in verses”
(published in 1926)
after failing a chemistry exam
at school...



Since it was even more arid in the summer heat
I wanted to make chemistry brighter
So, in verses translated, I learnt it all by heart
And in october I answered that scholar
A miracle happened: that maniac mind,
Used to seeing only ammonia,
sulphuric acid, lead and cyanid,
laughed, just for once, and approved.

IDROGENO

Con ferro e un acido
già sviluppato,
aria infiammabile
venne chiamato

quando, nel secolo
decimosesto,
a un noto chimico
fu manifesto.

Chimica in versi"-Alberto Cavaliere, 1926

HYDROGEN

With iron and acid

already formed,
flammable air
it was called

when, in the 16th century,
by a famous chemist

it was discovered.

Chemistry in verses"-Alberto Cavaliere, 1926

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IDROGENO

Pur diffusissimo,
libero, in fondo,
è in parte minima
sul nostro mondo, (…)

ma combinato

è abbondantissimo / quest'elemento,
formando -dicono- / l'uno per cento

di tutto il tragico / peso che, ansante,
grava su l'inclite / spalle d'Atlante; (…)

però, fra i metodi / per prepararlo
oltre ai moltissimi /di cui non parlo,

lo scopo in pratica
meglio è raggiunto
con l'elettròlisi
dell'acqua appunto, (…)

E' un gas insipido,
senza colore,
di peso minimo,

buon conduttore.

Anche, volendolo, si liquefà,
ma con grandissima difficoltà

Chimica in versi"-Alberto Cavaliere, 1926

HYDROGEN

Although abundant,
free is rare
in our world.

No odour,
no colour,
small weight,
good conductor

Chemistry in verses"-Alberto Cavaliere, 1926

The misterious Island - Jules Verne (1874)

In 1874 Jules Verne wrote "The mysterious Island"

When the sailor Pencroff asks:

"What will we burn in the future instead of coal?"

engineer Cyrus Smith answers:

" Water, because water, decomposed in its components…

decomposed, without any doubt, by means of electricity…

Yes, my friends, I believe that water one day will be used as a fuel, that HYDROGEN and oxygen that form water, used separately or simultaneously, will offer an inexhaustible source of **heat and light,** of an intensity that coal can't give…

….. water could be the coal of future

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The production of hydrogen

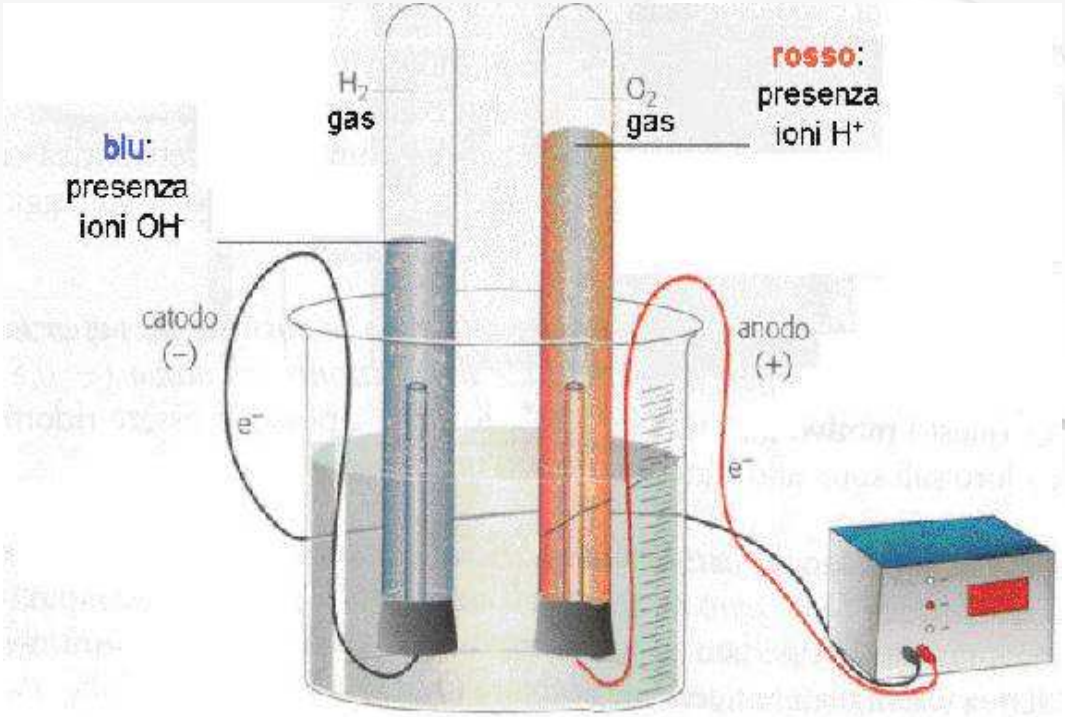
The main industrial methods used to produce hydrogen

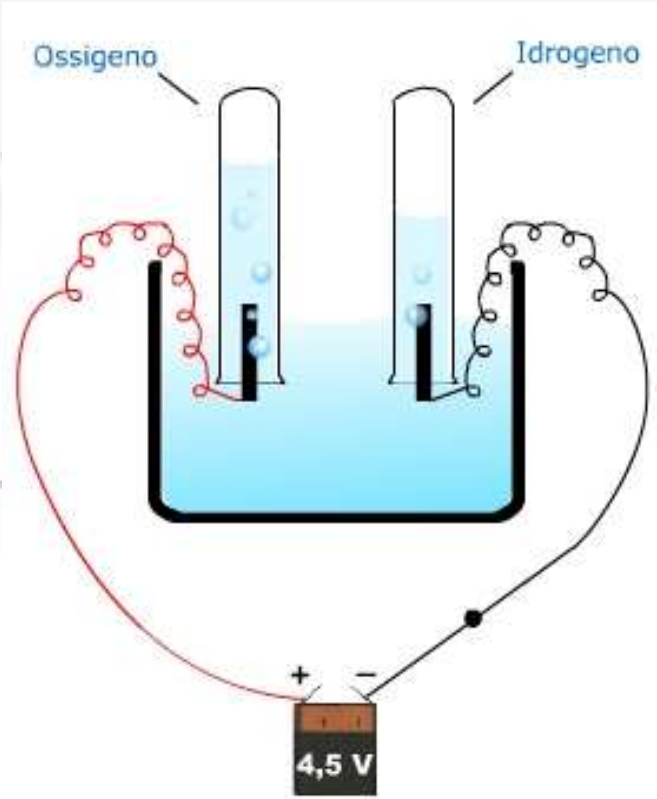
are:

- Electrolysis of water
- Reforming Process
- Oxydation of hydrocarbons – Gassification process
- Photosynthesis
- Fermentation
- Reactions water-hydride (=idruro)

Electrolysis of water (fuel cells)

By means of electrolysis, water is divided into hydrogen and oxygen



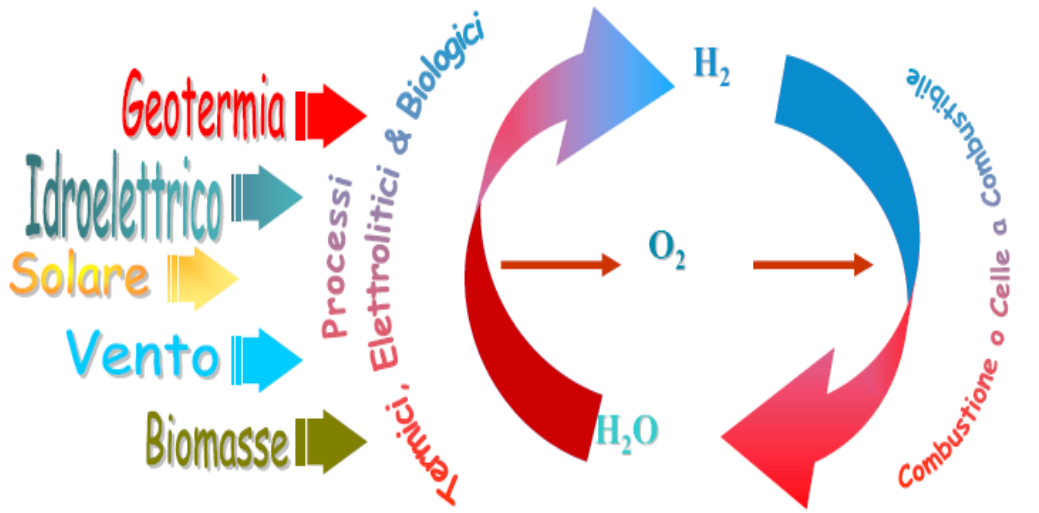


Electrolysis of water

Production of hydrogen by means of electrolysis is cheap if, the necessary electric power comes from a renewable source: wind, sun, water, geothermic heat, bio-masses.

Hydrogen is an "energy vector" or an accumulator (battery).

Potential risks connected to the energy storage could be lower than the risks of Na-S (Sodium-Sulphur) batteries, used to store energy from renewable sources



Reforming process

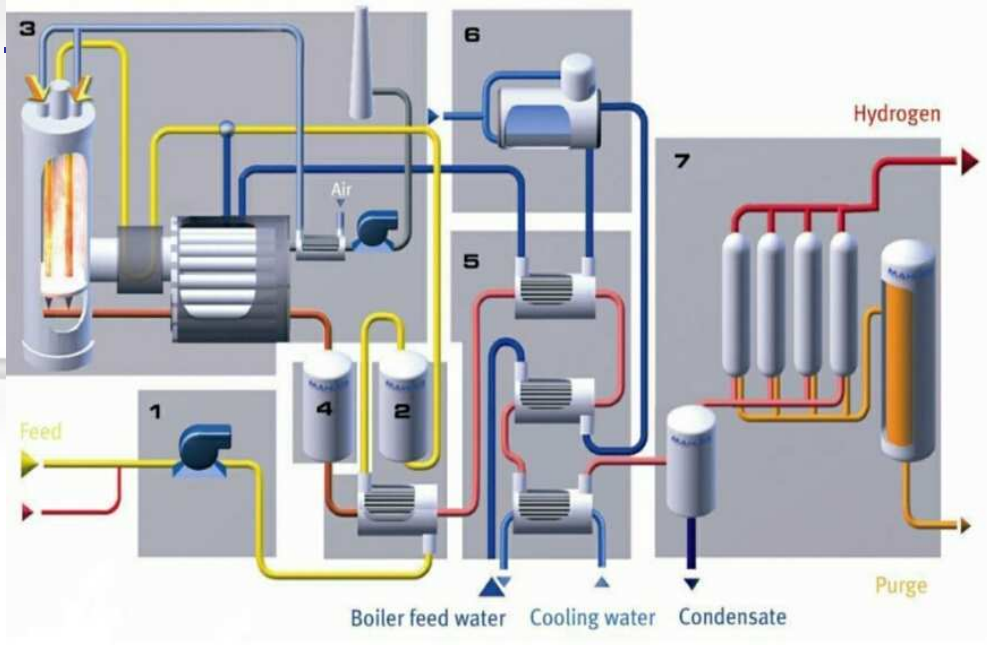
Steam reforming

In this industrial process an hydro-carbon (usually methane or light gasoline) reacts with steam and produces hydrogen, often with a catalyst. Reaction products are H_2, CO, CO_2 (hydrogen, carbon monoxide and carbon dioxid).

Energetic efficiency (rendimento) about 65%.

Endothermic reaction at the temperature of 700° C.

Because of this high temperature, a risk analysis is needed.



1: Feed compression unit
2: Feed pretreatment
3: Reforming and steam generation
4: High temperature conversion
5: Heat exchanger unit
6: Pretreatment of boiler feed water
7: Purification unit – HYDROSWING® system

Partial oxidation of hydro-carbons (1/3)

It’s a reaction between hydrocarbons and oxygen, that produces hydrogen.

Products of the reaction are:

H2 and CO (hydrogen and carbon monoxide), and smaller quantities of CO2 and CH4 (carbon dioxide and methane).

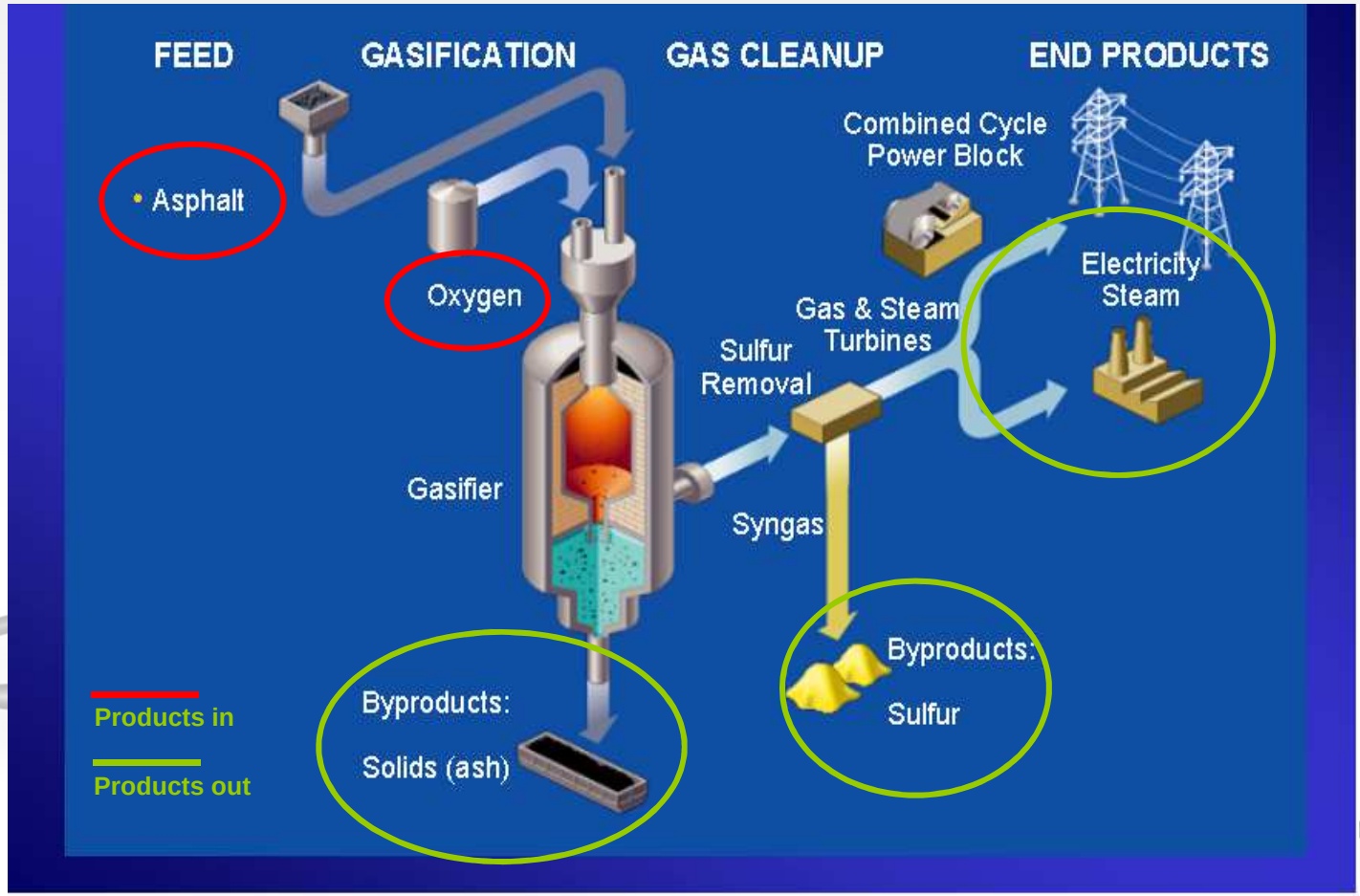
Exothermic reaction, Temperature above 1000 ° C.

Risk analysis necessary.

Partial oxidation of hydro-carbons (2/3)
IGCC plant (Integrated Gassification Combined Cycle)

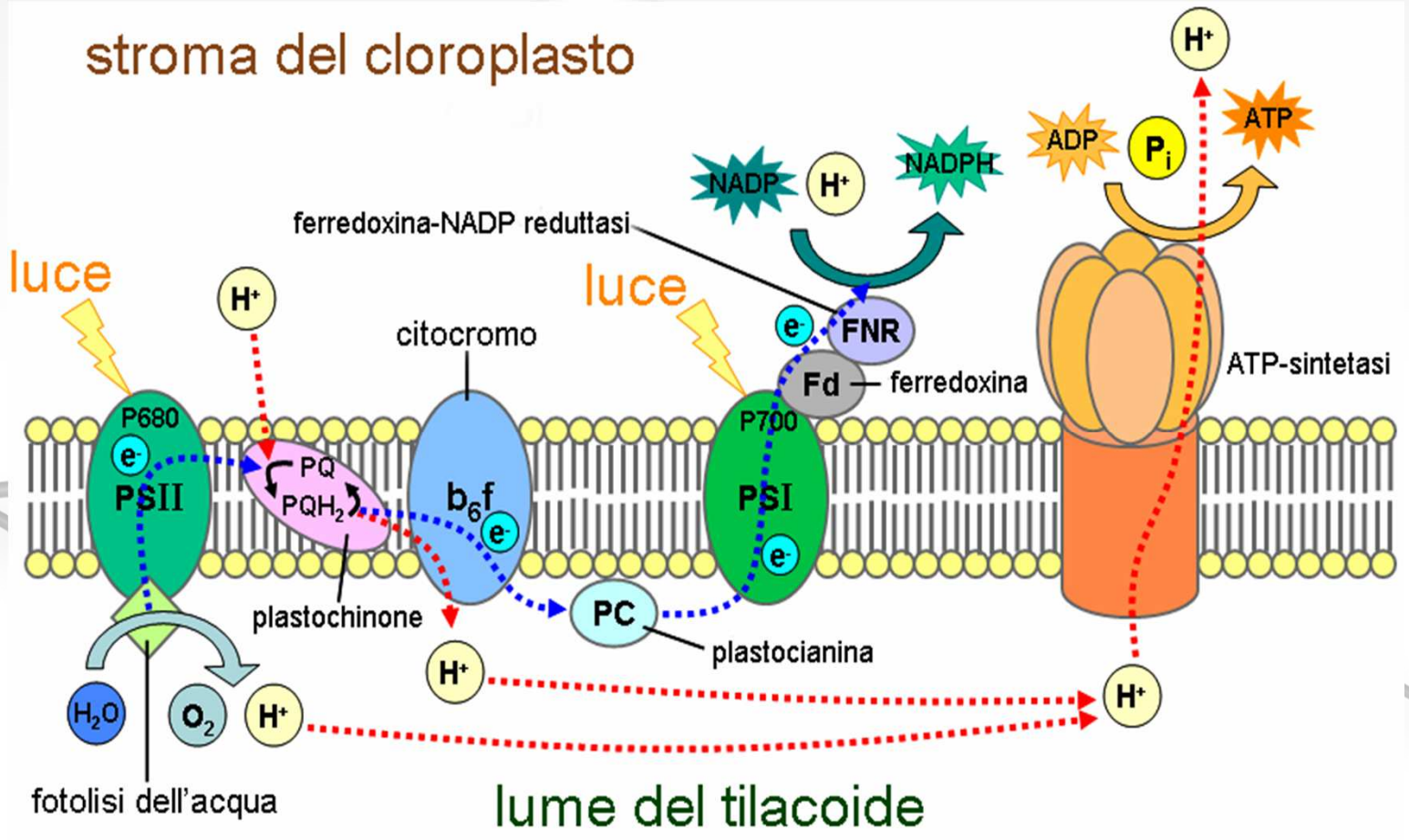
This reaction is used in IGCC plants – Integrated Gasification Combined Cycle: coal or the waste of refining of crude oil are transformed into electric power and hydrogen

Partial oxidation of hydro-carbons (3/3)
IGCC plant (Integrated Gassification Combined Cycle



Photosynthesis

Using CO2 and water, in the presence of light, plants produce organic substances (es glucose, C6H12=6) and oxygen.
Byologic production of hydrogen is made by mean of algae (alghe).



Fermentation

Production of hydrogen by means of fermentation is very convenient for industrial applications.
Bacteria (hydrogen – bacteria) generate fermentation, with a high speed of the reaction:

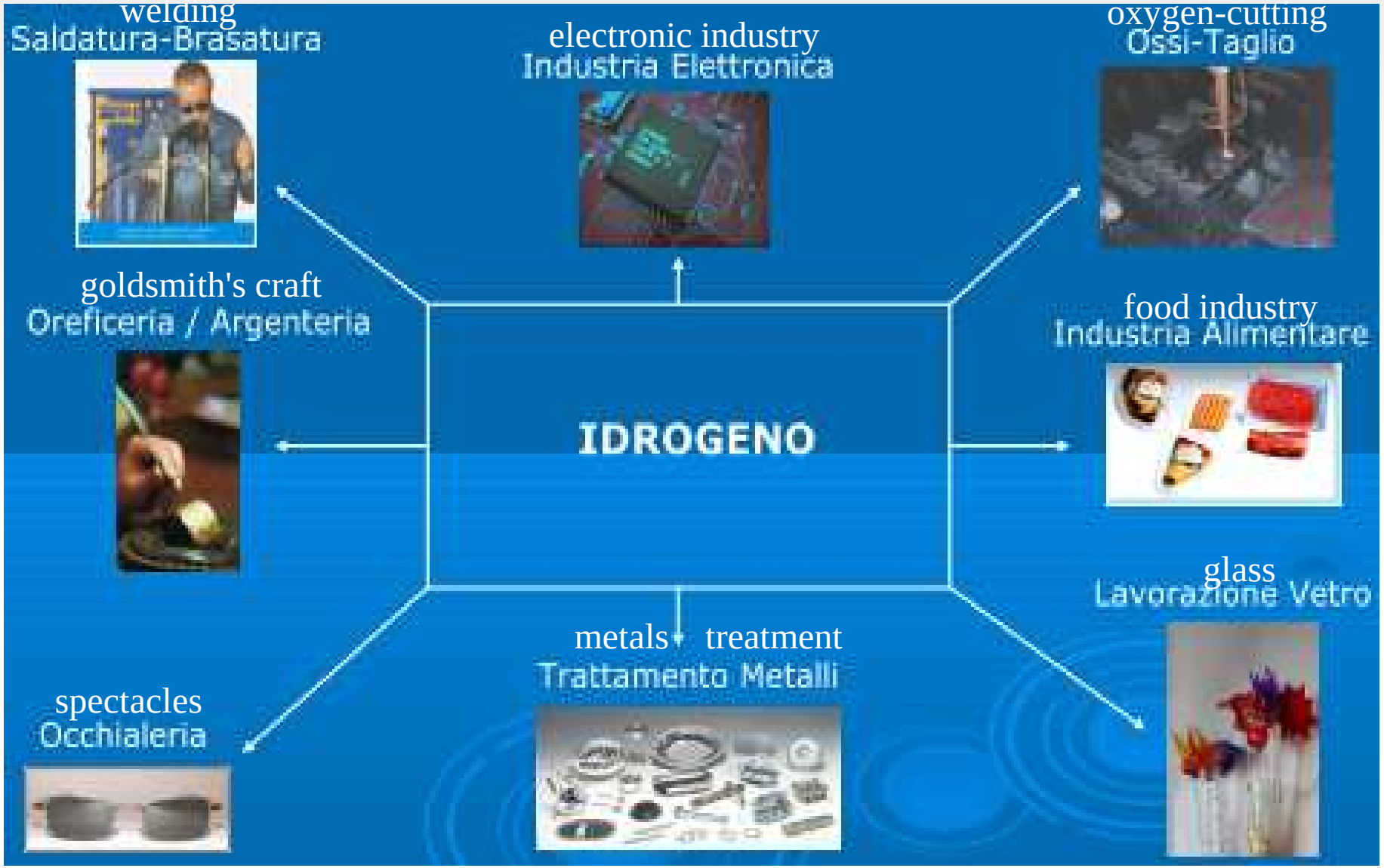
$$HCOOH = H_2 + CO_2$$

Production is continuous (day and night).

At the moment, different bio-masses are used: they contain saccharin, starch (=amido), or cellulose.

Problem connected to photosyntesis and fermentation: energy storage

Some industrial uses of hydrogen



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Renewable energy sources and Hydrogen

Production of hydrogen from renewable sources has some handicaps:

- DISCONTINUITY
- not possible to SCHEDULE the production

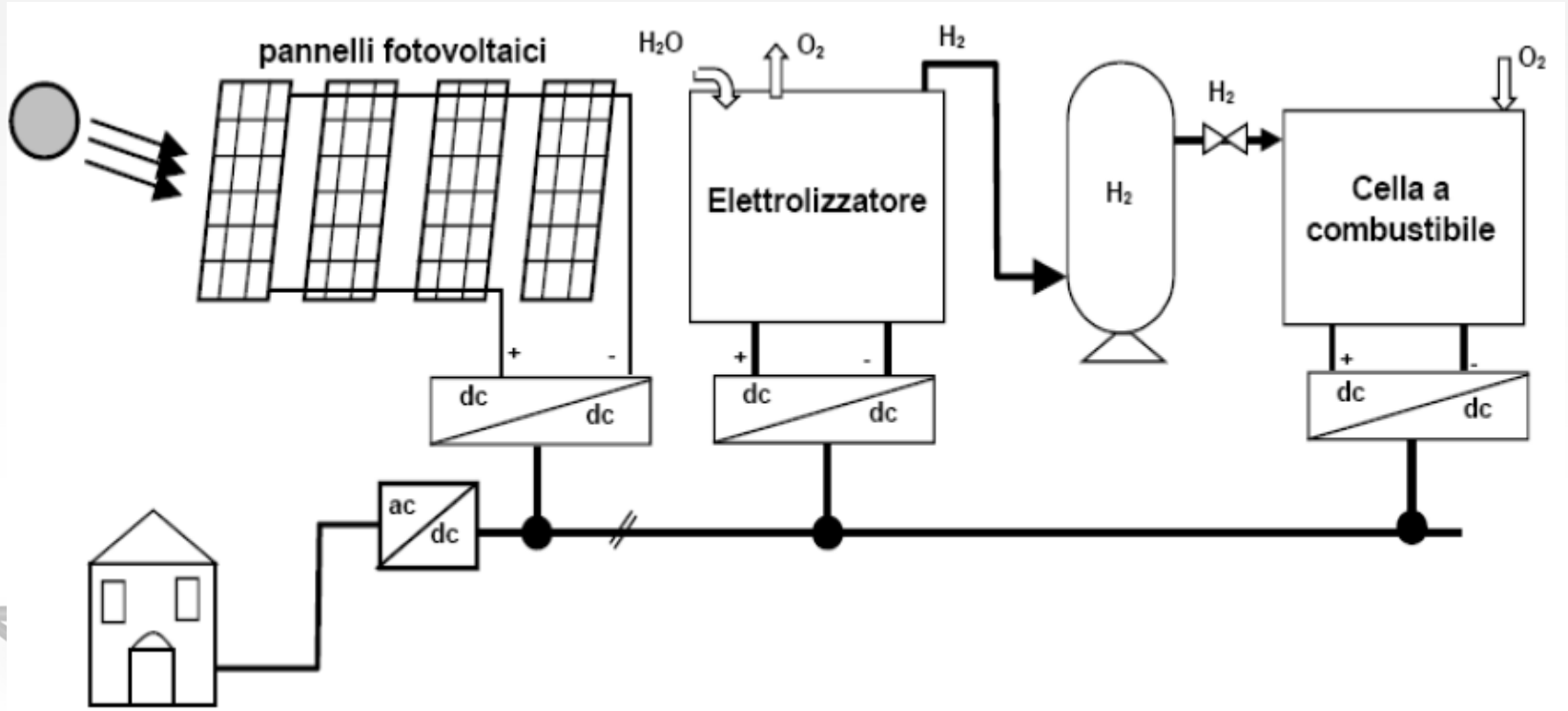
Instead, production of H2 from hydrocarbons (the method now used for industrial uses) has the disadvantage to generate CO2 (carbon dioxide).

Future is already here

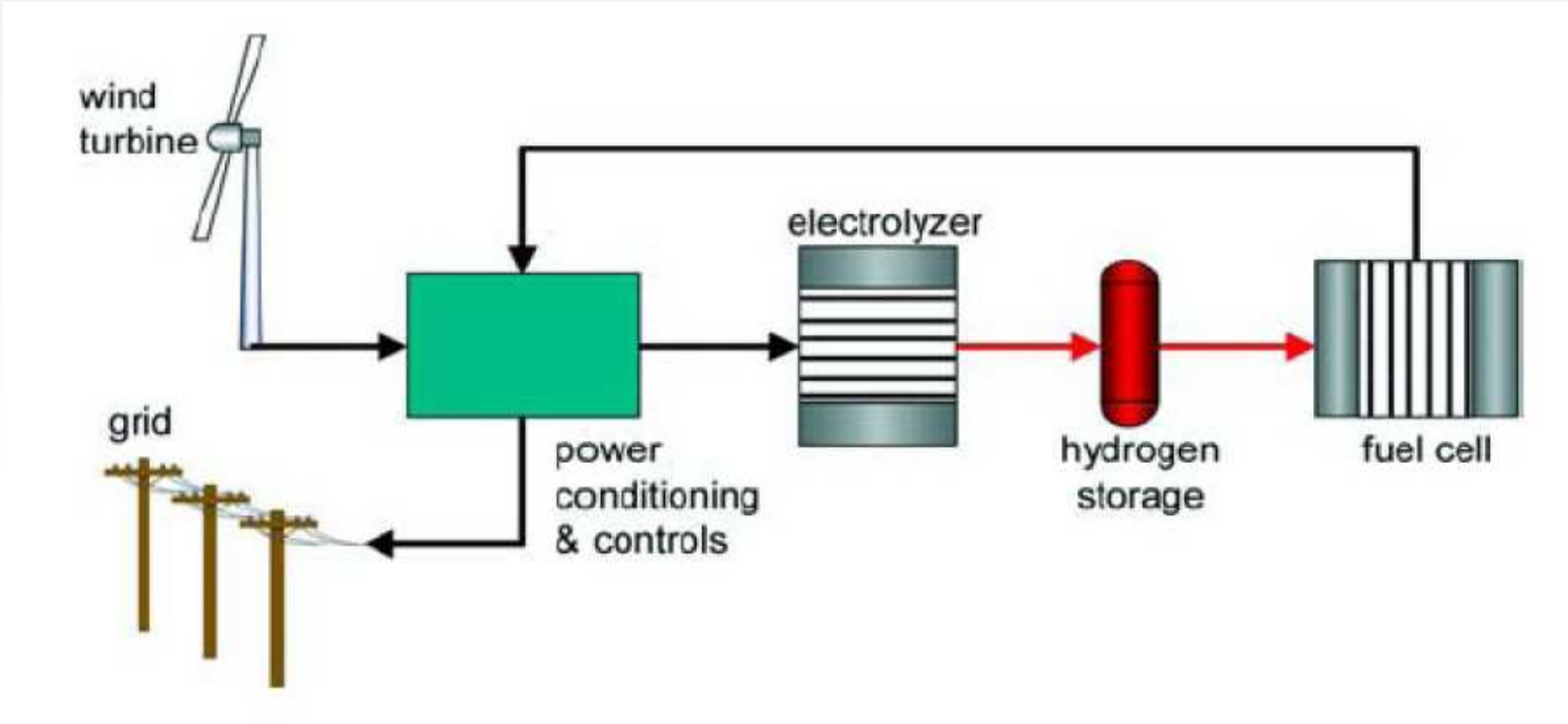
Hydrogen: producers and consumers

From solar power to hydrogen

from PV to H2



From wind power to hydrogen



Use of hydrogen for transport

The problem:
Pollution due to micro-dusts

Access forbidden to vehicles,
in the centre of town

A possible solution:
progressive introduction (in the centre of town) of eco-friendly vehicles:
- electric cars
- hydrogen cars

Mobility with hydrogen

Many research project about innovative locomotive systems

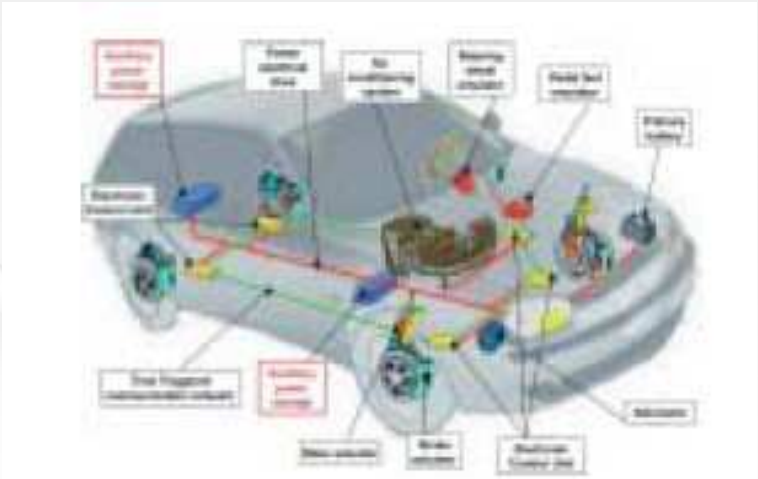
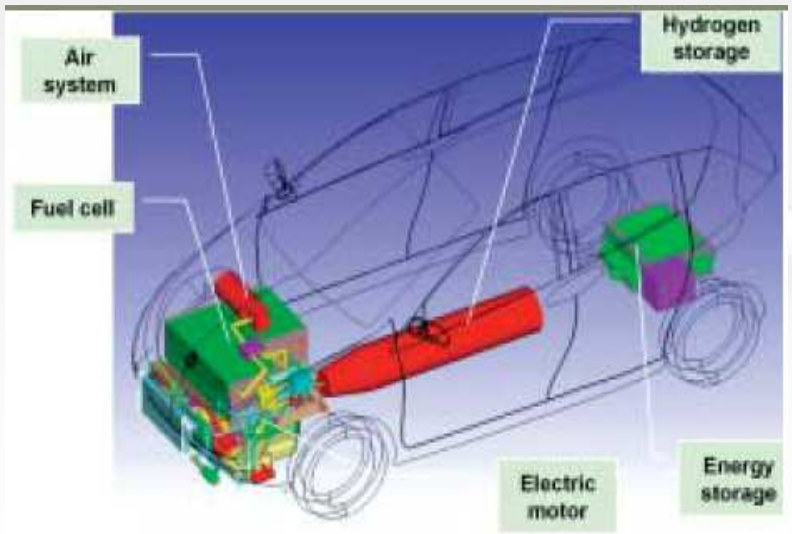
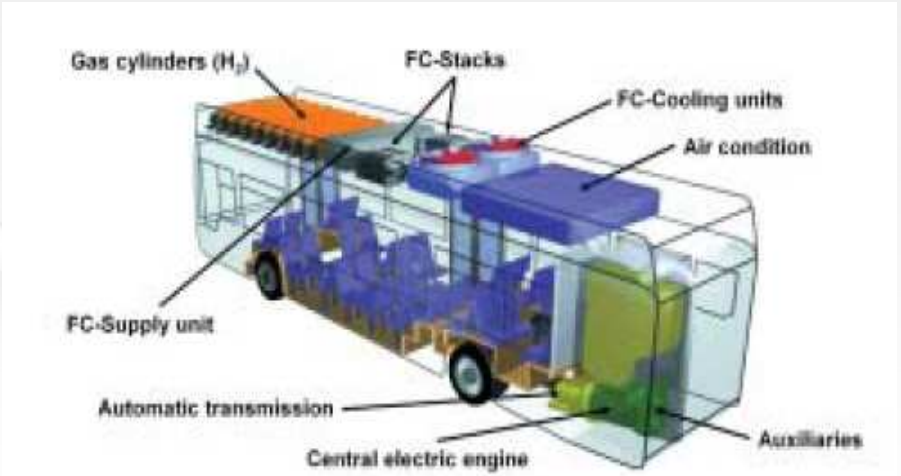


Figure 1: Future architecture using new auxiliary FC power supply for air-conditioning system, lighting systems and x-by-wire systems.

The main car and motorcycle industries have designed vehicles fuelled by hydrogen

Vehicles fuelled by hydrogen





A hydrogen fuel cell engine in the rear of a bus.

A fuel station for the distribution of hydrogen

Source: www.trasportando.com

Mobility with hydrogen

The key problems, still to be solved, to develop the mobility with hydrogen, are:

- design, installation and management of Hydrogen logistics (the european hydrogen-net)
- distribution net of hydrogen in towns
- production of vehicles with an electric engine, fuelled by an hydrogen fuel-cell
- lack of regulations and standards for the use of hydrogen, with the consequence that we sometimes use standards not fit for H2

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Hydrogen:
many good qualities
and some…dangerous ones

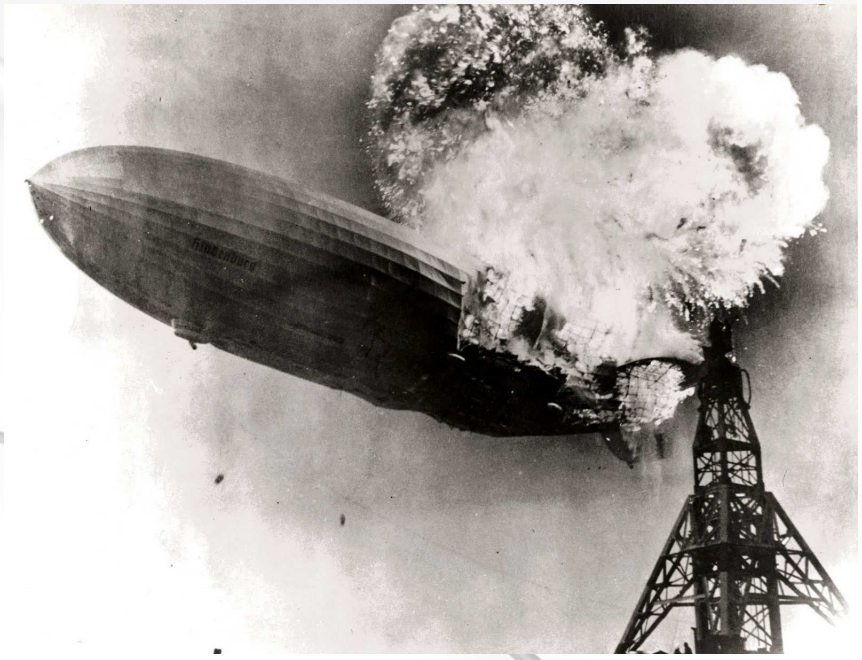
- highly flammable

- wide flammability

range: 4-76 %

- wide detonability

  range: 13-65%

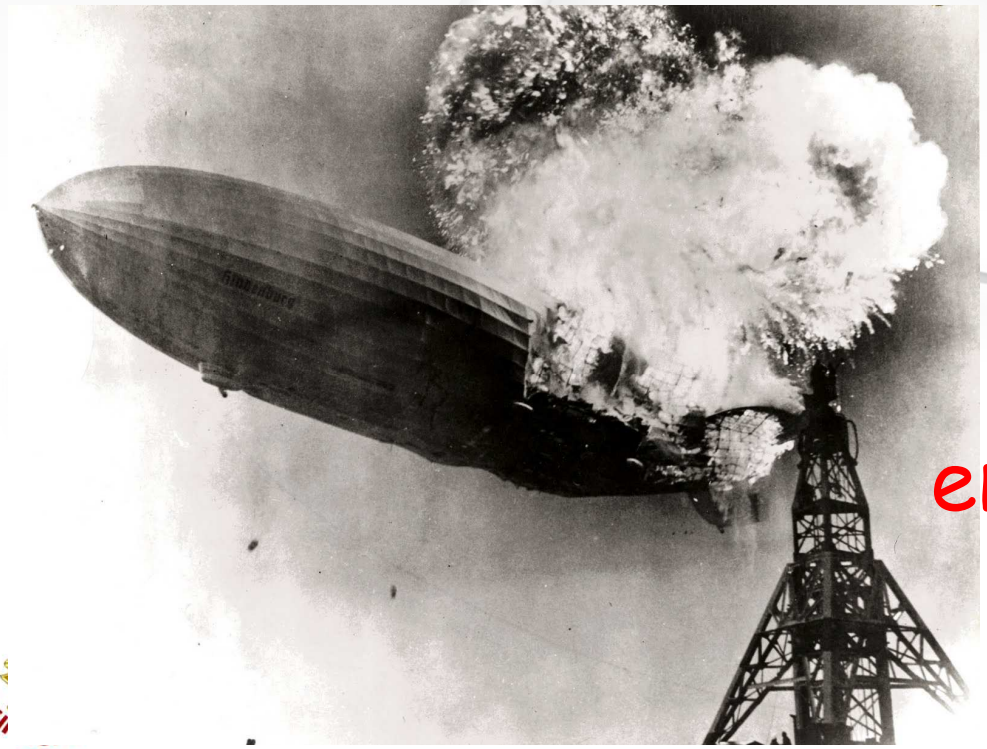


Zeppelin Hindeburg - 1937

- small ignition energy: 0,02 mJ in air

Accidents involving Hydrogen

A famous accident involving Hydrogen: the Zeppelin Hindenburg, 6th May 1937



Possible causes:
- release of hydrogen

- electrostatic energy, that primed the coating

Accidents involving Hydrogen

MARS=Major Accidents Reporting System, the European database of accidents in Seveso establishments, reports several events involving hydrogen. Among the others:

- 21 December 2006: during maintenance works on a tank, the suspected hydrogen in the tank was ignited by hot works
- 5 October 1991: in a ceramic manufacture, a valve of a tank containing 370 Kg of Hydrogen leaked and the released gas exploded; 23 people lightly injured, damages outside the establishment
- 21 October 1993: in a chemical manufacture, during repair works, there was an accident in an Hydrogen high-pressure condenser, 2 people injured
- 15 July 1998: in a chemical manufacture, there was a release of hydrogen and immediate ignition of the mixture, involving an adsorber. The cause was an assembly error
- 14 September 2005: in an electrolytic metal coating plant, release and fire of hydrogen (100 kg). Cause: increased heat production during a process

Source: http://emars.jrc.ec.europa.eu

Risks connected to Hydrogen

- Physiologic risks: freezing, asphyxia, breathing problems
- Physical risks: phase changes, failure in components, propensity to leak (because of: low viscosity, high diffusivity, high buoyancy), fragile behaviour of materials (enbrittlement)
- Chemical risks: propensity to ignite (because of: wide flammability range, low ignition energy, spontaneous ignition);

  after ignition: invisible flames and rapid burning rate; explosion (propensity to detonation in a confined or congested space)

Risks connected to liquid Hydrogen

- Low temperature: hydrogen has to be cooled below its critical T=-240°C and stored below its boiling point = -253 °C at atmospheric pressure

- Boil-off = transition from liquid to gas and consequent increase of pressure; cryogenic tanks usually designed for low pressure, no more than 5 bar

The solidified air can plug pipes and orifices and jam valves.

- Condensation of all gases (excluded helium) that come in contact with liquid hydrogen, because of its low temperature. Solidified air can plug pipes, valves, etc.

Some ways to reduce risks

- Separation distances
- Assessment of material compatibility
- Minimise probability of hydrogen releases
- Quick and reliable detection systems – gas and fire
- Shutdown, isolation and depressurisation of system
- Prevent accumulation of hydrogen gas in pockets
- Avoid high levels of confinements
- Promote natural ventilation and gas release to safe location

Safety of hydrogen pipelines

- A specific regulation doesn't exist, yet

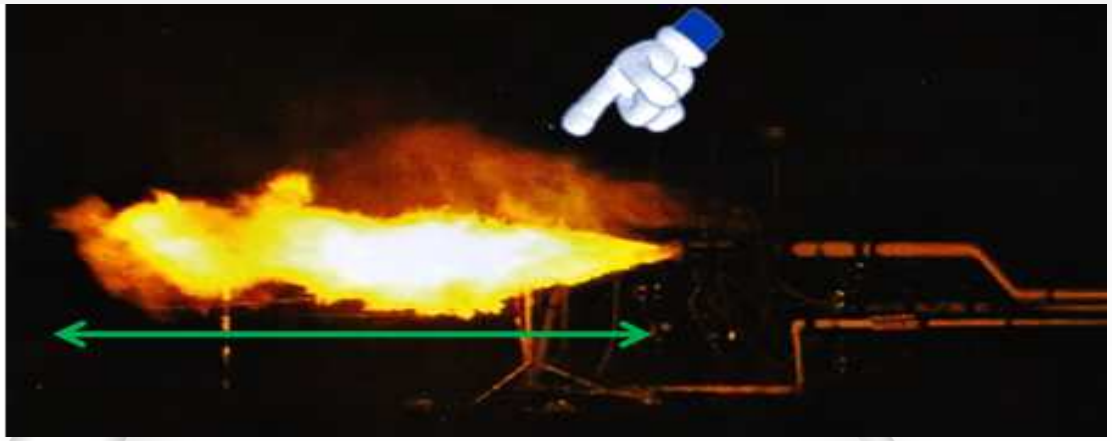
- Hypothesis: use of the natural gas net, to transport hydrogen

- At the moment, the control Authorities give permits for hydrogen nets, using as a guide-line the regulation for natural gas or for LNG liquefied natural gas

- The Italian Forum of Hydrogen is developing reserchs, in order to support the elaboration of specific regulation:
  Universities, Department of Firefighters and private firms participate in H2 Forum

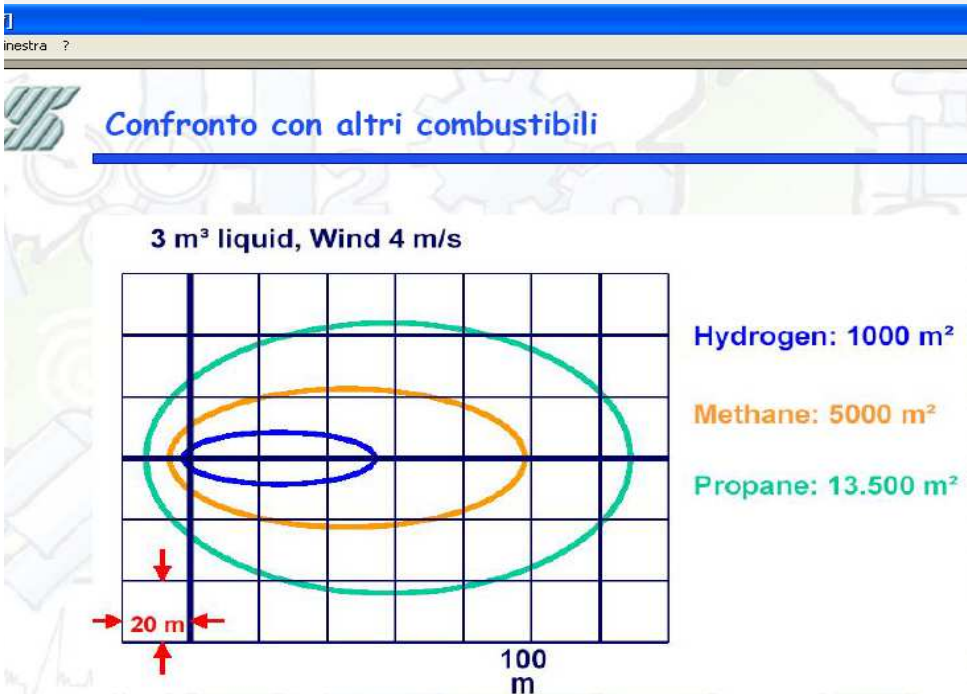
Safety

The University of Pisa, Department of mechanical engeneering, has developed tests on hydrogen releases, with different fuels, and dimensions of the jet fire. Results in the table



Dimensioni del jet fire							
Test	P [bar]	Diametro [mm]	Lunghezza [m]	Larghezza [m]	LH2 [m]	L CH4 [m]	%
HPBT-JF-1	10	2,5	1,15	0,15	1,36	1,74	**21,84**
HPBT-JF-2	5,5	2,5	0,95	0,15	1,06	1,35	**21,48**
HPBT-JF-3	5	2,5	0,9	0,15	1,02	1,3	**21,54**
HPBT-JF-4	2,2	2,5	0,6	0,13	0,76	0,95	**20,00**
HPBT-JF-5	10,2	11	4.30	0,7	5,43	6,87	**20,96**
HPBT-JF-6	5,1	11	3,6	0,6	4,07	5,19	**21,58**
HPBT-JF-7	2,3	11	2,4	0,45	3,01	3,89	**22,62**
HPBT-JF-8	6,8	11	3,9	0,7	4,57	5,81	**21,34**
HPBT-JF-9	5,6	11	3,75	0,7	4,24	5,37	**21,04**

Safety of hydrogen pipelines



The picture shows iso-concentration curves, in case of leakage of different fuels.
The area relative to Hydrogen is the smallest.

Hydrogen: the European legislative frame

- Transport: international standars (ADR for roads, RID for railways)

- As fuel for vehicles: UNECE regulations, CE regulations for approval of engine components

- Fuel stations: Italian specific regulation

- Storage: in Italy, no specific regulation

- Pipelines: in Italy no specific regulation

- Transport: ADR/RID
- As fuel for vehicles: as in Europe (regulation CE-79-2009 of 14 Genuary 2009) and specific approval by MIT= Ministry of Infrastructure and Transport

- Filling station:
Italian Ministerial Decree 31 August 2006

-Storage: general regulation for flammable liquid or gas

-Firefighters have recently elaborated a guide-line: "Fire prevention for electric power production plants, with cells fuelled by gas hydrogen, to supply mobile telephony aerials"

Why is Hydrogen under the control of Firefighters in Italy ?

DPR 151-2011 contains a list of 80 activities, under the control of Firefighters

Hydrogen corrisponds to activities n°:

1: production and use of flammable gas
2: storage of flammable gas in mobile tanks
3: storage of flammable gas in tanks
13: filling stations

Hydrogen and Seveso legislation (Risk anlaysis)

An establishment that stores or uses Hydrogen falls under the scope of Seveso directives (DIR 96-82-CE as amended by DIR 2003-105-CE and, from 1 June 2015, DIR 2012-18-UE) if

the quantity of Hydrogen is
>= 5 ton (lower tier)
>= 50 ton (upper tier)

Hydrogen fuel stations in Italy

- Collesalvetti (LI) - AGIP Grecciano Sud (2006)
- Roma - AGIP Magliana Sud on highway Rome-Fiumicino (2007
- Milano - Tecnocity Bicocca (opened but then closed)
- Mantova, industrial area Valdaro (project "Zero Regio" financed by European Community, opened on 21 September 2007)

Collesalvetti (Livorno)- Grecciano Sud

Hydrogen fuel stations:
Decree of Ministry of Interior 31 August 2006

In this case, regulation as come before the building of the fuel stations

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- Art. 2. - Obiettivi
- Art. 3. - Disposizioni tecniche
- Art. 4. - Ubicazione
- Art. 5. - Commercializzazione CE
- Art. 6. - Disposizioni complementari e finali

Hydrogen fuel stations: DM 31 August 2006 Technical Annex

I – General provisions
II - Design characteristics (=modalità costruttive)
III – Safety distances
IV – Operation rules
V – Plans for fuelling of Society fleets
VI – Mixed fuel stations:

hydrogen+gas (methan o LPG)+gasoline+diesel

THANK YOU FOR YOUR ATTENTION