UNIVERSITÀ DEGLI STUDI DI MILANO

DIPCHI
DIPARTIMENTO DI CHIMICA

La produzione di Idrogeno da fonti alternative

Pirola Carlo
carlo.pirola@unimi.it
Tel +39/02-50314283

SusCheOpe Lab

LA TUTELA DELL'AMBIENTE

Intelligenza Artificiale e nuove tecnologie per un futuro ecosostenibile

Sabato 13 Aprile 2024 dalle 9,30 alle 12,30

Palazzo Marino – Sala Alessi – Piazza della Scala, 2 - Milano

OCF ORDINE INTERPROVINCIALE DEI CHIMICI E DEI FISICI DELLA LOMBARDIA

FCP FONDAZIONE CARLOPERINI 60 ANNIVERSARIO

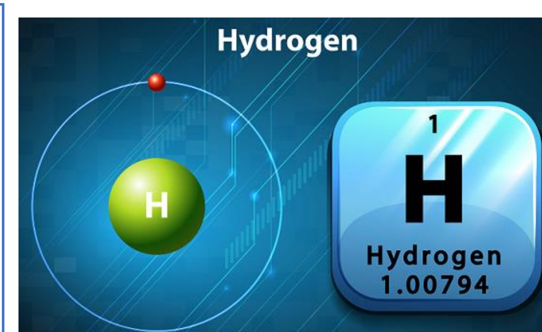
ORDINE DEGLI INGEGNERI DELLA PROVINCIA DI MILANO

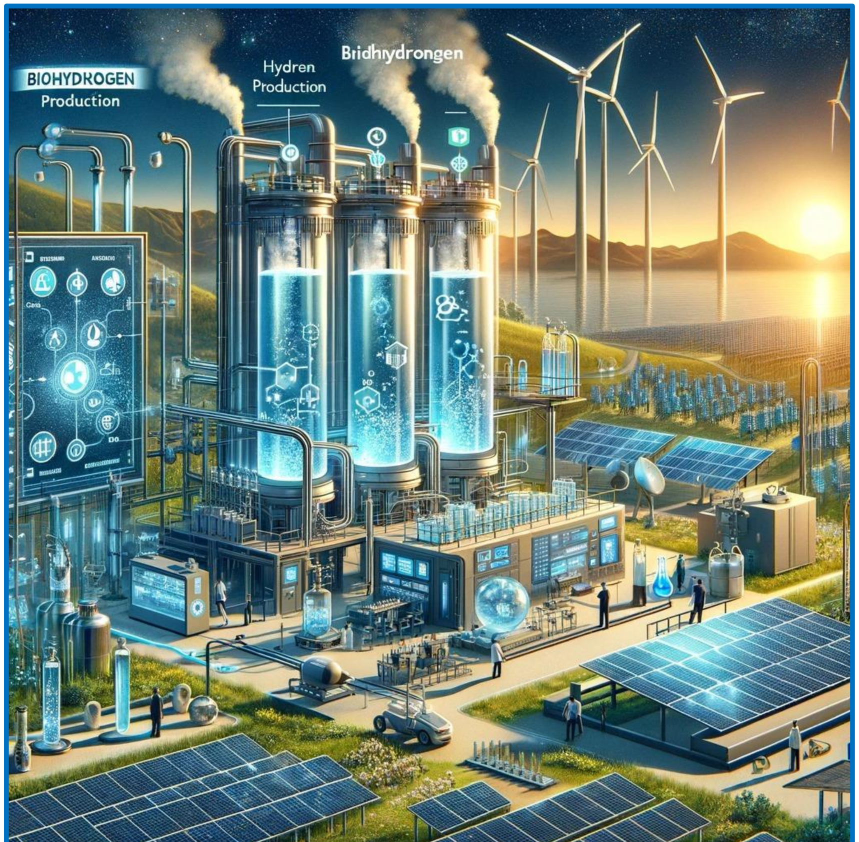
Two photos from the future?

- The industrial processes of the future?
- A mix of IA and H_2?
- Why not?

The crucial point is to be able to produce hydrogen:

- From renewable resources
- In a sustainable economic way
- In a sustainable environmental way
- With a zero carbon footprint

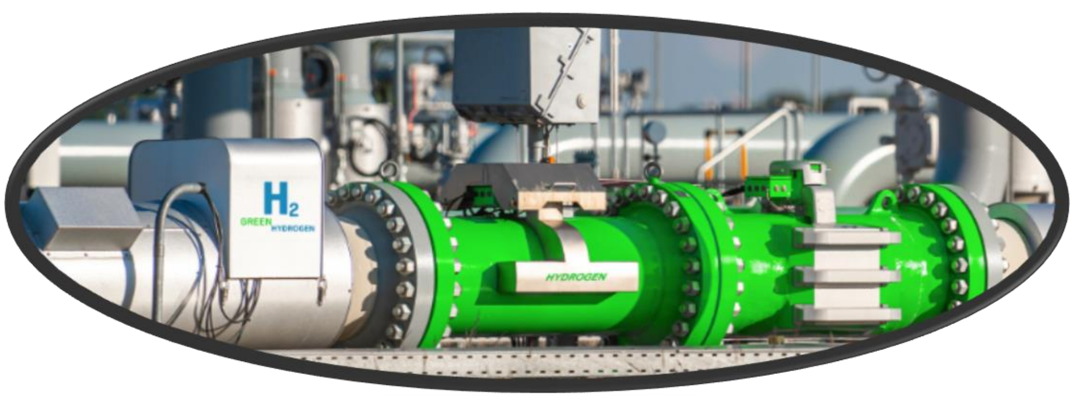




We need (more) hydrogen (green)!

The main industrial uses of hydrogen:

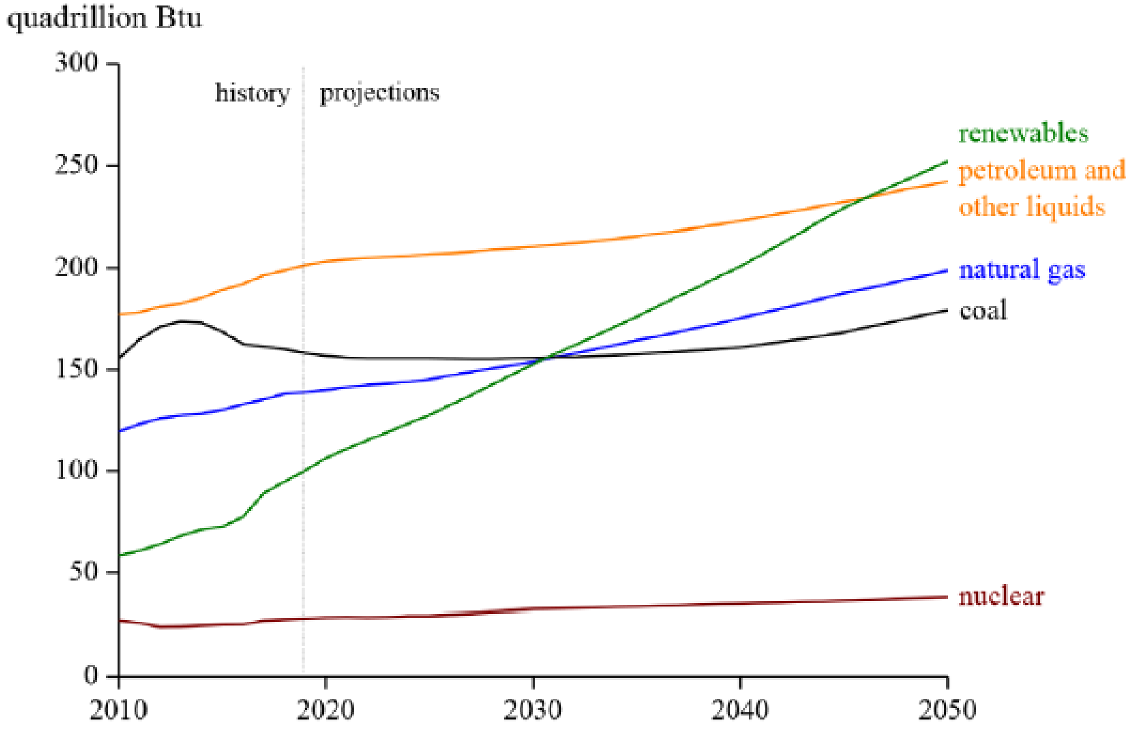
1. <u>Production processes</u> (ammonia, methanol, hydrogenation)
2. <u>Electronics manufacturing</u> (semiconductors, silicon and titanium production)
3. <u>Fuel cells and Energy vector</u>: The ability of hydrogen to store, transport, and deliver energy from various sources makes it a promising energy vector for a wide range of applications, particularly in a future where renewable energy sources are increasingly integrated into the energy system



Let's start considering where we are:

Global demand for primary energy rises by 1.3% each year to 2040.

Currently, carbon-based fuels supply 85% of the entire world's energy demand.

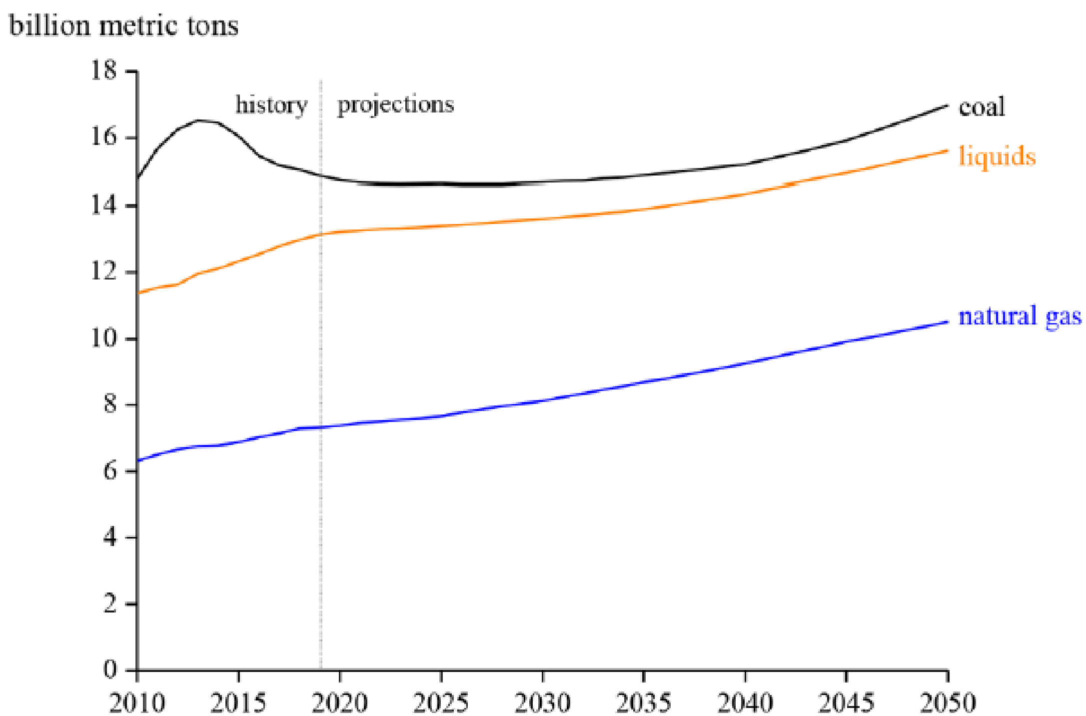


World primary eneergy consumption by energy source (2019 U.S. Energy Information Administration)

Fossils are projected to remain the dominant energy source until at leat 2050

Consequently… CO_2 emissions:

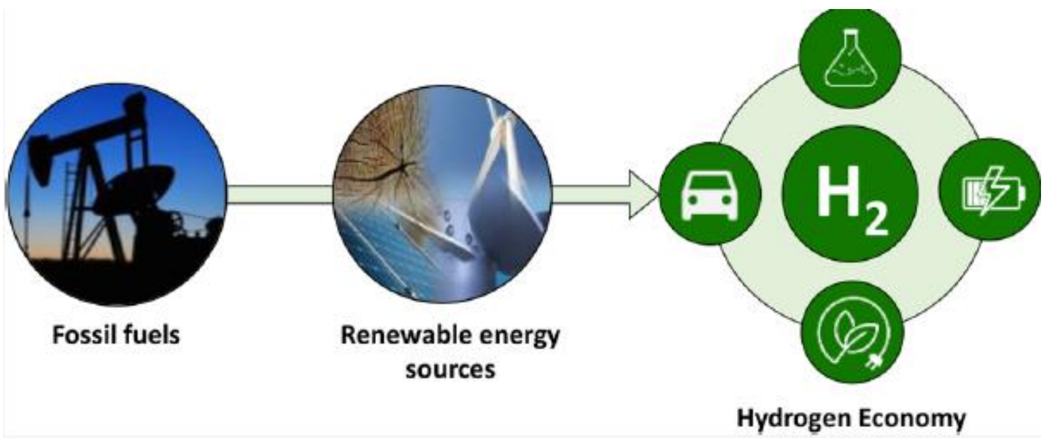
Approximately 36 billion tons of CO_2 are emitted into the atmosphere every year to meet the energy demand. Of these emissions, over 90% comes from fossil fuels



Energy-related carbon dioxide emissions Energy-related carbon dioxide emissions (2019 U.S. Energy Information Administration)

The hydrogen transition

Nowadays, hydrogen is mainly produced by thermochemical processes using fossil fuels



Hydrogen from renewable resource, a possible solution:

- Most abundand gas in the universe
- Maximum energy content per unit of weight
- Using H_2 for energy production does not result in pollutant emissions
- already used, as reactant, in many industrial processes
- Not available in free form in nature!

The hydrogen production from fossil

Process/ Technology	Feedstock	Operating conditions	Maturity
Steam reforming (*endothermic, with steam*)	light hydrocarbons (less frequently from liquefied petroleum gas and naphtha)	800−1000 °C	Commercial
Partial oxidation (*Exothermic, with O_2*)	hydrocarbons, heavy fuel oil, and coal	>1000 °C	Commercial
Autothermal reforming (with steam and O_2)	light hydrocarbons (less frequently from liquefied petroleum gas and naphtha)	>1000 °C	Early Commercial
Pyrolysis (*thermal degradation*)	hydrocarbons	500−800 °C in the absence of oxygen	Commercial
Gasification (*coal with steam and O_2*)	Coal, high production of CO_2	700−1200 °C	Commercial

Fossil feedstocks:

Hydrogen from Petroleum: **15** %

Hydrogen from Natural gas: **48** %

Hydrogen from Coal: **18** %

International Energy Agency (2015)

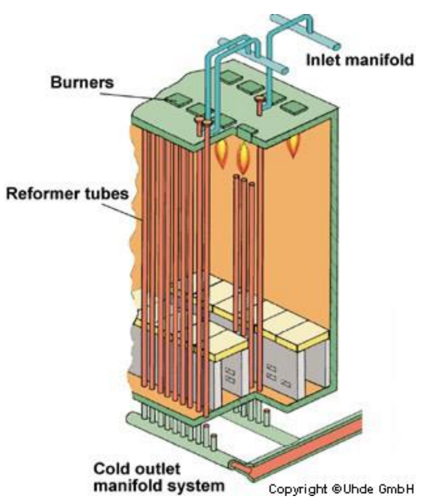
Some details more on:

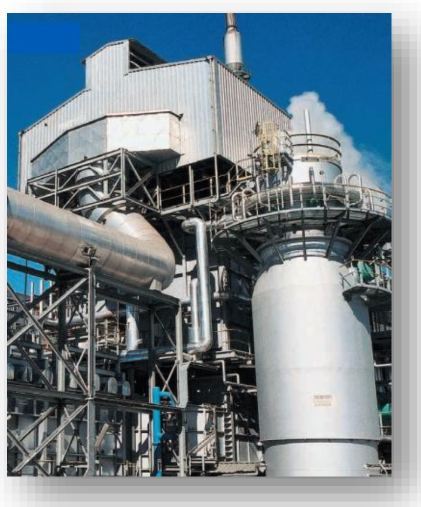
Methane steam reforming

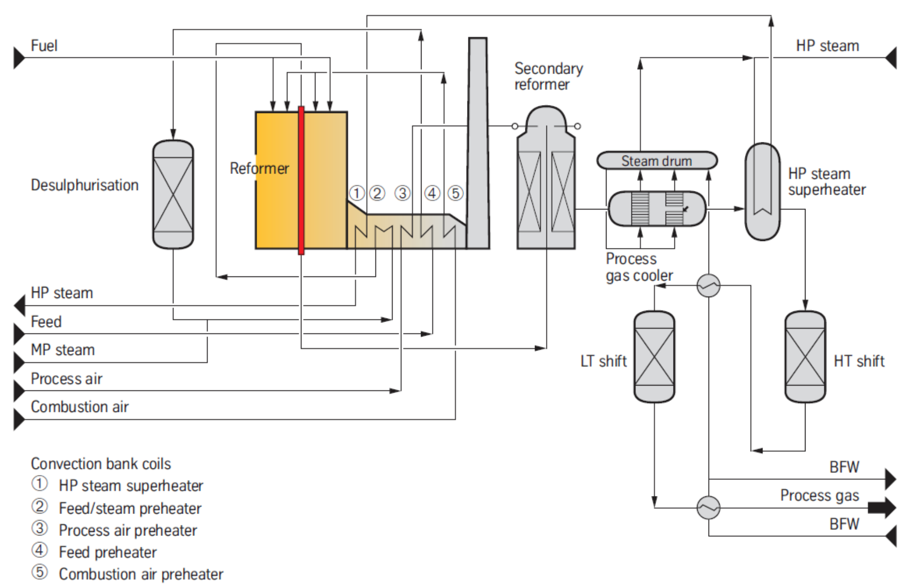
The steam reforming of methane is the main source of hydrogen today:

$$CH_4 + H_2O \rightarrow 3\,\mathbf{H_2} + CO$$
$$H_2O + CO \rightarrow H_2 + \mathbf{CO_2} \quad (WGS)$$

The steam reforming of methane is highly endothermic and then energy intensive. This energy is presently generated by the combustion of fossil fuels which simultaneously produces carbon dioxide. This emission can be minimized if it is perfomed in the presence of gaseous oxygen (autothermal reforming).







The hydrogen production from renwable

WATER

BIOMASS

The hydrogen production from water

Process/ Technology	**Energy source**	**Operating conditions**	**Maturity**
Electrolysis	Electricity	50-900°C (depending on the method) and up to 30 bar	Commercial
Thermolysis	Heat	Temperature of >2500 °C (<1000 °C for thermochemical cycles)	Research and development
Photoelectrolysis	Solar	ambient conditions	Research and development
Biophotolysis	Microorganism Metabolism (*hydrogenase enzime*)	ambient conditions	Research and development

Some details more on:

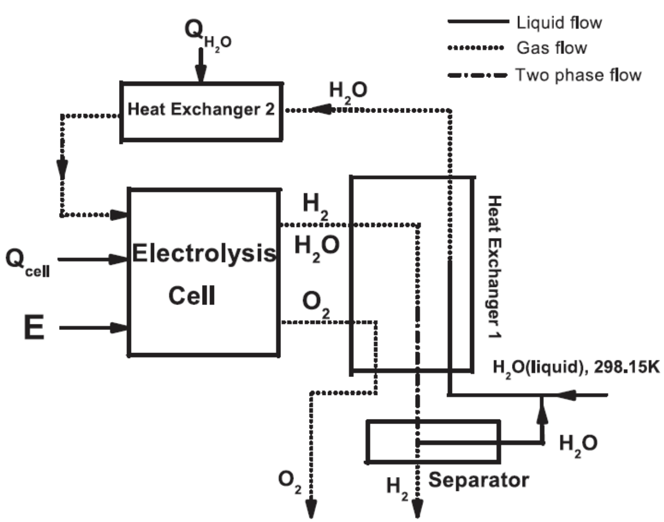
Water electrolysis

Water electrolysis is industrially applied to produce H_2 and oxygen, eliminating expensive separation costs, with efficiencies in the range 50-70%.

$$2H_2O \rightarrow 2H_2 + O_2$$

Electricity production is the dominant cost, and also contributes to air pollution if it is generated from fossil fuel.

Water elctrolysis is free from CO_2 emissions only when electricity is produced by wind or sunlight sources.



From Zhang et al., Int. J. Hydrogen Energy, 2010

anode

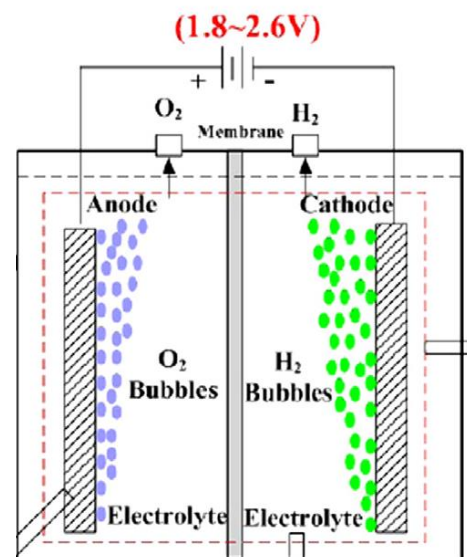
$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$$

cathode

$$2H^+ + 2e^- \rightarrow H_2$$

overall process

$$H_2O \rightarrow H_2 + 1/2O_2$$



From: M. Wang et al. Ren. Sust. Energy Rev., 2014

Some details more on:

Water electrolysis

1. **Alkaline Water Electrolysis** uses concentrated electrlyte and non-noble metal-based electrodes (e.g. nickel)

2. **Proton-exchange membrane electrolysis** uses humidifiedpolymer membranes as the electrolyte and noble metals aselectrocatalysts, such as platinum or iridium oxide

3. **Solid Oxide Electrolysis** converts water into hydrogen and oxygen at high temperatures (700–900°C), increasing the thermal demand.

Water electrolysis powered by renewable energysources (e.g., wind, sea wave, and biomass) is expected to enable the scale-up of hydrogen production

Some details more on:

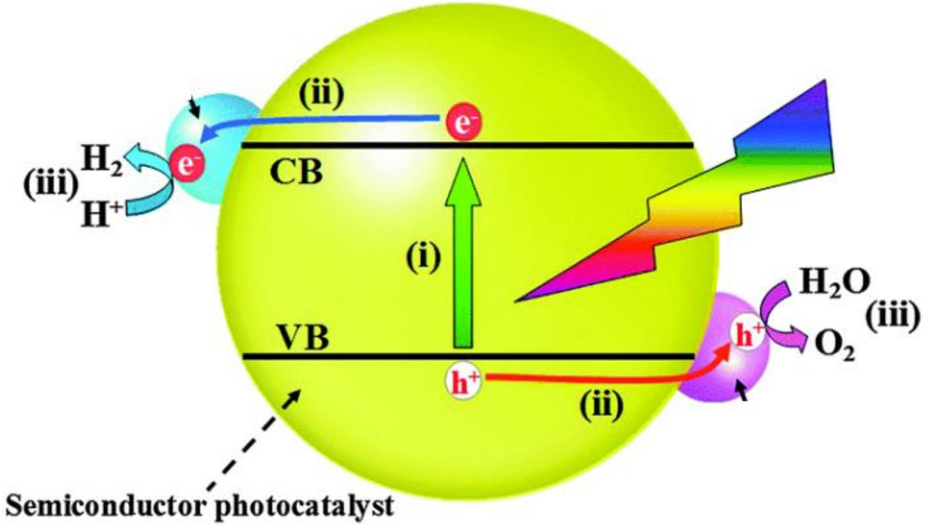
Photocatalysis

Water splitting can be perfomed also by photocatalysis, i.e. using a semiconductor activated by UV or visible light.

At the moment, no industrial application of this technology are working.

Catalytic material are required to:

- Provide a solar-to-hydrogen suitable efficiency
- To be stable against oxidation and then produce hydrogen for longer time than 15000 hours



From Ran et al., Chem. Soc. Rev., 2014

The hydrogen production from biomass
(biological and thermochemical processes)

Process/ Technology	Principle	Operating conditions	Maturity
Fermentative (dark)	Biological	anaerobic bacteria and conditions (BM to H_2 and CO_2)	Research and development
Fermentative (photo)	Biological	anaerobic conditions and photobacteria (BM to H_2 and CO_2)	Research and development
Pyrolysis	Thermochemical	300−1000 °C in the absence of oxygen	Commercial
Gasification	Thermochemical	800−900 °C	Commercial
hydrothermal liquefaction	Thermochemical	250−370 °C, 4-22 Mpa to break down the BM polymers	Research and development
Steam reforming	Thermochemical	800-1000°C	Commercial

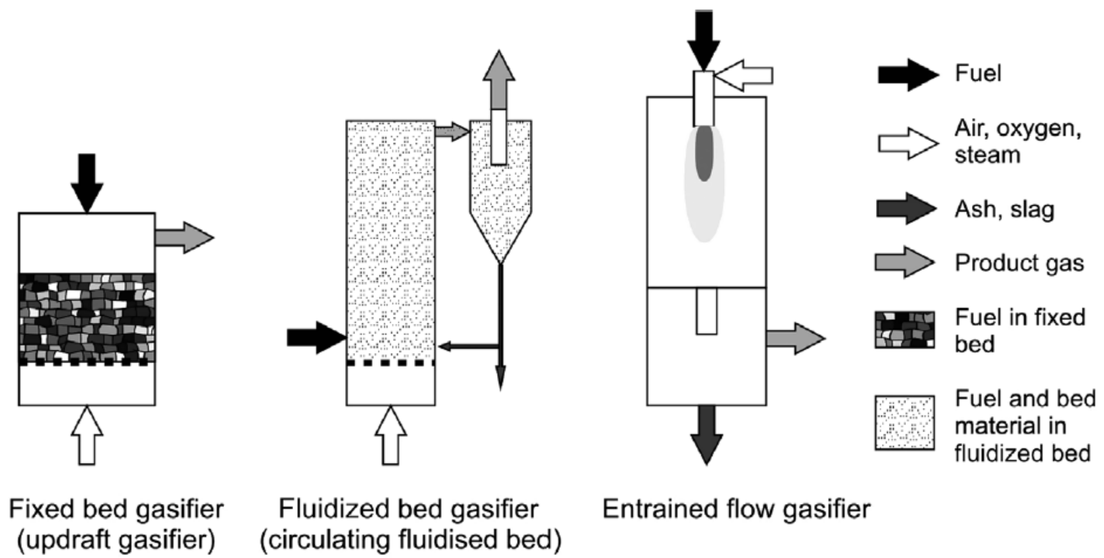
Some details more on:

Biomass to hydrogen: gasification

Biomass can be converted to hydrogen through liquifaction, pyrolisis and gasification. Gasification is most attractive. It occurs above 1000 K in presence of oxygen and/or water:

$$C_xH_yO_z + O_2 + H_2O \rightarrow H_2 + CO + CO_2 + C_nH_m + tar$$

Taking into account the renewable nature of biomass, this H_2 production can be considered as CO_2 neutral.
It is also possible to combine the biomass gasification with coal gasification, by minimising the environmental impact of this last process.



From Heidenreich et al. Advanced Biomass Gasification, Elsevier, 2016

	Idrogeno MARRONE	Idrogeno GRIGIO	Idrogeno BLU	Idrogeno TURCHESE	Idrogeno GIALLO	Idrogeno ROSA	Idrogeno VERDE
Processo	Gassificazione	Steam reforming	Steam reforming o gassificazione con CCUS	Pirolisi	Elettrolisi	Elettrolisi	Elettrolisi
Fonte energetica	Carbone	Gas metano	Gas metano Carbone	Gas metano	Energia elettrica dalla rete	Energia elettrica nucleare	Energia elettrica rinnovabile

Drawbacks and efficiecy of the technolgies from water

Process/ Technology	Drawback	Energy efficiency (%)	H_2 cost ($/kg H2)
Electrolysis	Energy storage Low efficiency High capital costs	55-80	**4,15-10,30**
Thermolysis	Separation step is required High capital costs	20-50	**7,98-8,40**
Photoelectrolysis	Low efficiecy High surface for the light	0,06-14	**4,98-10,36**
Biophotolysis	High surface for the light Difficult to control	10-15	**1,42-2,13**

Production capacity is another point to carefully evaluate

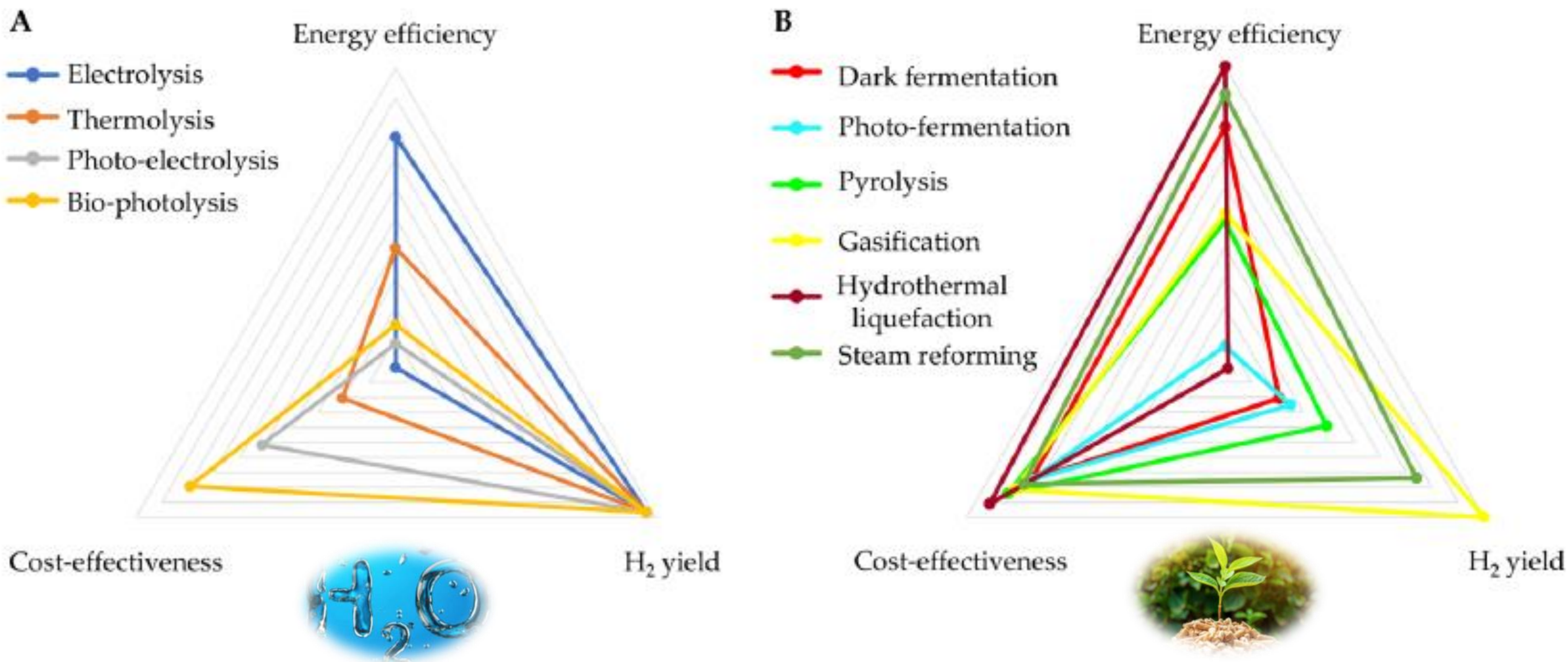
Elaborated from From [Energy Fuels 2021, 35, 16403−16415]

Drawbacks and efficiecy of the technolgies from biomass

Process/ Technology	Drawback	Energy efficiency (%)	H2 cost ($/kg H2)
Fermentative (dark or photo)	Byproduct generation Large reactor volume	0,1-50	**1,68-2,83**
Pyrolysis	Tar formation Dependent from the feedstock Produce carbon co-pruducts	35-50	**1,5-2,20**
Gasification	Dependent from the feedstock Require oxidation agent Produce carbon co-products	30-60	**1,77-2,05**
hydrothermal liquefaction	Dependent from the feedstock Presence of nitrogenated compounds Produce carbon co-products	85-90	**0,54-1,26**
Steam reforming	Produce carbon co-products	74-85	**1,83-2,35**

Elaborated from From [Energy Fuels 2021, 35, 16403−16415]

Comparison of the technolgies



Normalized ranking comparison of different hydrogen production technologies from (A) water and (B) biomass. From [Energy Fuels 2021, 35, 16403−16415]

- ✓ Water is the ideal source of hydrogen for reducing CO_2 emissions
- ✓ Hydrogen generation from fossil fuels and biomass leads to the co-production of CO_2 and CO
- ✓ For this reason, CO_2 neutrality can only be realized if the cogenerated CO_2 is hydrogenated in subsequent process steps in the same process

Cost of production of 1 kg of hydrogen using various technologies
(*from Aresta et al., Chem. Rev. 2014*)

Gas reforming	Electrolysis with nuclear	Electrolysis with electricity from oil powered station	Electrolysis with photovoltaic cells	Electrolysis with wind
1,10-1,15 euro	1,45-1,50 euro	2,20-3,50 euro	2,8-4,0 euro	3,8-5,20 euro

Methanol synthesis: some economic considerations

(from Aresta et al., Chem. Rev. 2014)

- If we consider H_2 produced by water electrolysis using perennial primary energy sources the cost is about **3 euro/kg H_2**.
- Considering the reaction $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$ it is possible to calculate that **1 kg of H_2** will allow conversion of **7.3 kg of CO_2** producing **5,3 kg of methanol**.
- In the best case, considering CAPEX and OPEX, methanol can be produced from electrolytic hydrogen at a cost of **0,3 euro/kg**, that is **4 times higher than methanol produced from fossil (0,08 euro/kg)**.

Cost of production of 1 kg of hydrogen using various technologies

Gas reforming	Electrolysis with wind
1,10-1,15 euro	3,8-5,20 euro

Are we starting?

Il gruppo MAIRE realizzerà un impianto di produzione di idrogeno per la nuova bioraffineria Eni di Livorno

Febbraio 21, 2024 · redazione · eni, Kinetics Technology, Maire

Idrogeno 'verde': elettrolizzatore PEM da 54 MW per BASF

3 Gennaio 2024 · Tempo di lettura: 4 minuti

Production of hydrogen as a clean fuel from waste

9 Gennaio 2024 · Tempo di lettura: 4 minuti

Waste-to-hydrogen company Compact Syngas Solutions (CSS) has demonstrated the viability of producing hydrogen gas from syngas generated from the gasification of waste.

ANALISI

Transizione energetica, perché l'Europa deve puntare su nucleare e idrogeno

AMBIENTE • ENERGIA

Questa invenzione potrebbe rivoluzionare la produzione di idrogeno verde

ILARIA ROSELLA PAGLIARO

Pubblicato il 07/02/2024

Le ultime innovazioni nel campo della produzione di idrogeno verde: come la ricerca del Technion - Israel Institute of Technology sta lavorando per ridurre i costi e superare le sfide tecniche

Al via, entro il prossimo giugno, alla realizzazione dell'impianto per la produzione di idrogeno rinnovabile a Cerignola, in provincia di Foggia. Si tratta di un progetto finanziato dalle risorse del bando regionale Hydrogen Valley, destinatario dei 40 milioni di euro previsti dal PNRR.

"As a result of the environmental implications with the use of fossil fuels for hydrogen production, their use must decrease; however, ***even though numerous studies are focused onobtaining green hydrogen, its production is still far from being competitive" (Energy and Fuels, 2021, Prof. P. J. Megia)***

The challenges to overcome:

1) Optimize the **production processes**, in particular from water

2) H_2 is a gas, with a volume of more than 3000 times higher than liquid fuels. Its volume must be reduced to be **easily storable and transportable**

3) **Safety issues** (H_2 flammability is higher than other fuels)

4) **Social acceptance**: hydrogen is considered as a very dangerous gas, more than the traditional fuels

DIPCHI
DIPARTIMENTO DI CHIMICA

UNIVERSITÀ DEGLI STUDI
DI MILANO

I gruppi di ricerca del Dipartimento di Chimica sono attivi nello studio di nuove tecnologie per la transizione a idrogeno verde (produzione e utilizzi)

Sustainable Chemical Operations
SusCheOpe Lab

https://sites.unimi.it/pirolacarlo/

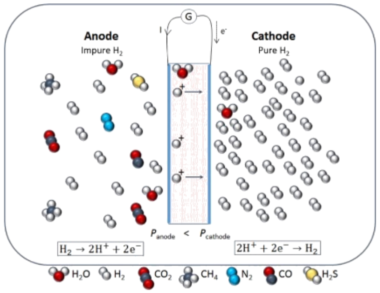
ISMER
Innovative Sustainable Materials for Environmental Remediation

https://sites.unimi.it/ClaudiaLBianchi/it/

Prof. Claudia Bianchi, Prof. Ermelinda Falletta, Prof. Carlo Pirola

Sustainable Chemical Operations

SusCheOpe Lab



1) Separazione e compressione dell’idrogeno da miscele idrogeno/metano tramite elettrocompressori

2) Utilizzo dell’idrogeno per la produzione di metanolo e biocarburanti a partire da CO_2

3) Utilizzo dell’idrogeno nella produzione di acido adipico (nylon 6) a partire da biomasse

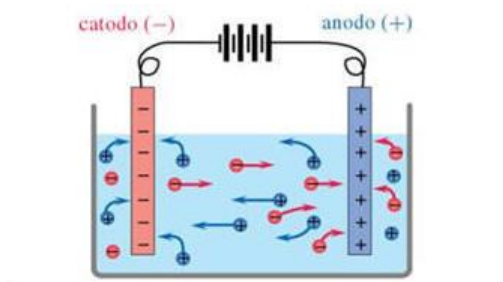
Scientific publications are available:
https://expertise.unimi.it/get/person/carlo-pirola

ANSA.it › Ambiente&Energia › Inquinamento › Legambiente, il 60% dell'acqua di fiumi e laghi è chimicamente inquinata

Legambiente, il 60% dell'acqua di fiumi e laghi è chimicamente inquinata

Tra il 2007 e il 2017 gli impianti industriali hanno **immesso 5.622 tonnellate** di sostanze chimiche **nei corpi idrici**.
(Fonte E-Prtr*)

Pesticidi, farmaci e microplastiche sono alcuni dei principali composti organici presenti nelle acque inquinate.



Il trattamento elettrochimico di acque reflue rappresenta un opportunità per la produzione di idrogeno verde

Vantaggi

- ✓ Evoluzione di idrogeno favorita
- ✓ Disinquinamento delle acque
- ✓ Recupero energetico

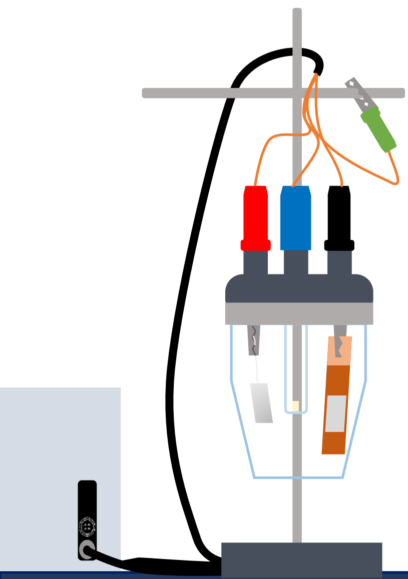
*European Pollutant Release and Transfer Register

Processo di produzione H_2 e purificazione delle acque in **2 STEP:**

ISMER
Innovative Sustainable Materials for Environmental Remediation

STEP 1

Trattamento elettrochimico di acqua inquinata:

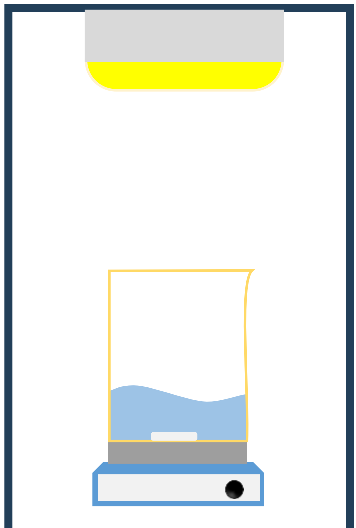


- ✓ **Elettrodi** economicamente sostenibili a base di **metalli non nobili**
- ✓ L'ossidazione delle **sostanze organiche favorisce** la produzione di **idrogeno**

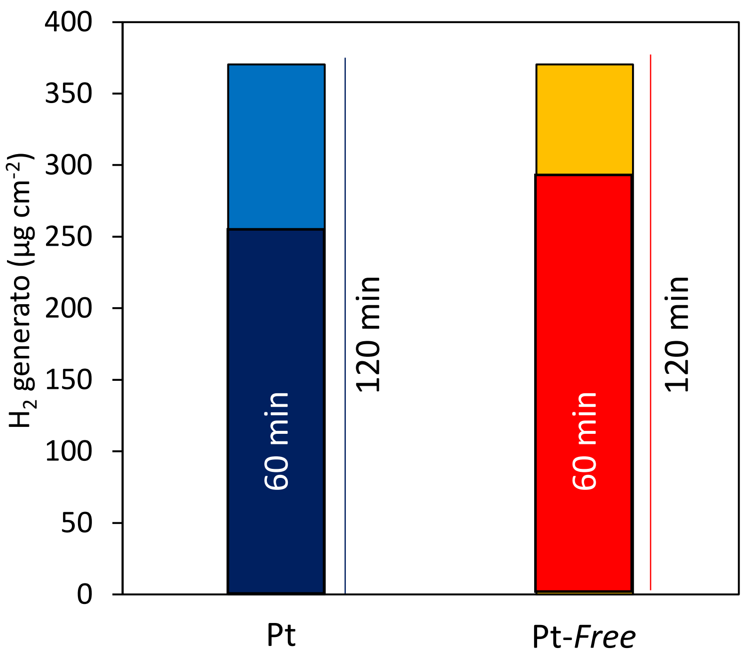
STEP 2

Trattamento fotocatalitico dell'inquinante residuo in acqua

- ✓ Uso di **catalizzatori** innovativi **TiO_2-free**
- ✓ Disinquinamento completo dell'acqua con **incremento** della **mineralizzazione**



Risultati



Il processo in 2 step garantisce un **disinquinamento del 90%** c.a. con una **riduzione della domanda di ossigeno** necessaria per ossidare le sostanze organiche del **60%** (conversione della sostanza organica in CO_2)

Conclusions and take-home messages

- Hydrogen can be produced from water or biomass
- These technologies are still more expensive than the traditional based on fossil feedstocks
- The first demostration plants are appearing in the market
- New improvements are requested to scale up successfully the production of hydrogen from renewable sources
- AI and the digitalization of the process can contribute in this work in a crucial way

Sustainable Chemical Operations

SusCheOpe Lab

https://sites.unimi.it/pirolacarlo/

Prof. Pirola Carlo
Dipartimento di Chimica – Università degli Studi di Milano
Via Golgi, 19 – Milano
Italy
Phone +39 0250314283

DIPCHI
DIPARTIMENTO DI CHIMICA

Thermolysis for water splitting

The **sulfur–iodine cycle** (S–I cycle) is a three-step thermochemical cycle used to produce hydrogen.

$I_2 + SO_2 + 2\ H_2O$ - heat⟶ $2\ HI + H_2SO_4$ (120 °C (250 °F)) (Bunsen reaction)

The HI is then separated by distillation or liquid/liquid gravitic separation.

$2\ H_2SO_4$ + heat⟶ $2\ SO_2 + 2\ H_2O + O_2$ (830 °C (1,530 °F))

The water, SO_2 and residual H_2SO_4 must be separated from the oxygen byproduct by condensation.

$2\ HI$ + heat⟶ $I_2 + H_2$ (450 °C (840 °F))

Iodine and any accompanying water or SO_2 are separated by condensation, and the hydrogen product remains as a gas.

Net reaction: $2\ H_2O \rightarrow 2\ H_2 + O_2$