How can green molecules contribute to a safe and competitive energy transition ?

Francegaz

The context of the energy transition in France

- **A debate focused in France, so far, on the electrical issue and on nuclear** in particular (respectively 1/4 and 1/6th of energy consumption) culminating in the decision of the President of the Republic to relaunch the nuclear power program to compensate for the aging of the fleet (6 EPR2 + 8?)
- **A weakening of energy systems** linked to the drop in electrical capacities, for instance those that can be controlled in France and in neighboring countries (between 70 and 110 GW by 2035 depending on the sources)
- **Extremely proactive energy saving** programs whose level of ambition may call into question the closure of the provisional balance sheets

Able to learn from our mistakes ?…

- Political Stop and go : Nuclear, …
- Betting on a single idea (and not the same one depending on the moment)
- Not being technology neutral
- Imagining 2050 with what we know today
- Underestimating research capacity
- Disconnecting political and industrial time
- Considering Europe as an obvious model the world will follow
- Considering CO2 emissions and not CO2 impact
- Lack of communication on energy transition costs and constraints
- Forgetting how key competencies are and will be
- Focusing on means and not on objective with a to linear approach
- Underestimating the crucial role of infrastructures

The conditions for the success of a competitive and safe transition

- **Express a clear and unequivocal political will** to no longer oppose energies but to make the best use of their complementarities and the use of existing means with the objective of controlling costs
- **Accelerate energy efficiency programs**
- **Betting on technologies of the future**, a factor in strengthening the sovereignty of our country and creating local added value
  - EPR2 and SMR
  - Floating offshore wind turbines
  - **New technologies to produce renewable and carbon-free gases**
  - Tandem solar panels (perovskite/silicone)
  - High temperature electrolysers
  - …

The potential of new gases: an asset for France

- A potential for renewable and carbon-free gases far greater than current consumption, which will contribute to:
  - The resilience of energy systems
  - The reindustrialization of the country and in particular of the rural areas
  - Strengthening the country's energy independence and sovereignty
  - The development of a circular economy at the heart of the territories and the creation of non-relocatable jobs
  - Support for the development of sustainable agriculture
  - The development of high-performance solutions for waste treatment

New gases allow a gas transition for the benefit of the community

- Renewable and carbon-free gases are vectors of reindustrialization and strengthening of our sovereignty
  - 75% of the added value created by anaerobic digestion benefits the French economy, as do the wind (40%) and solar (44%) sectors
  - The sector generates jobs that cannot be relocated to the territories; in addition to the 60,000 direct and indirect jobs that will be generated by 2050 by the renewable and carbon-free gas production sector, approximately 200,000 local jobs will be sustained
  - The production of renewable and carbon-free gases strengthens the energy independence of the territories and has a positive impact on the French trade balance: by 2030, a reduction of around 4 billion euros in gas imports is envisaged with our script

The gas industry can count on 5 main technologies (+1) to decarbonize its supply chain

Francegaz

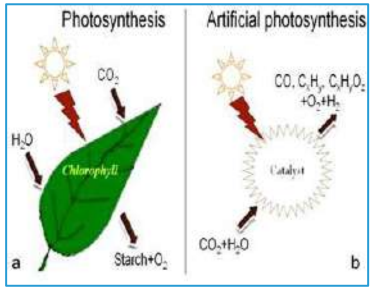
Anaerobic digestion: biomethane based on wet biomass

Pyrogasification: synthetic methane from thermo-chemical process of wastes rich in carbon

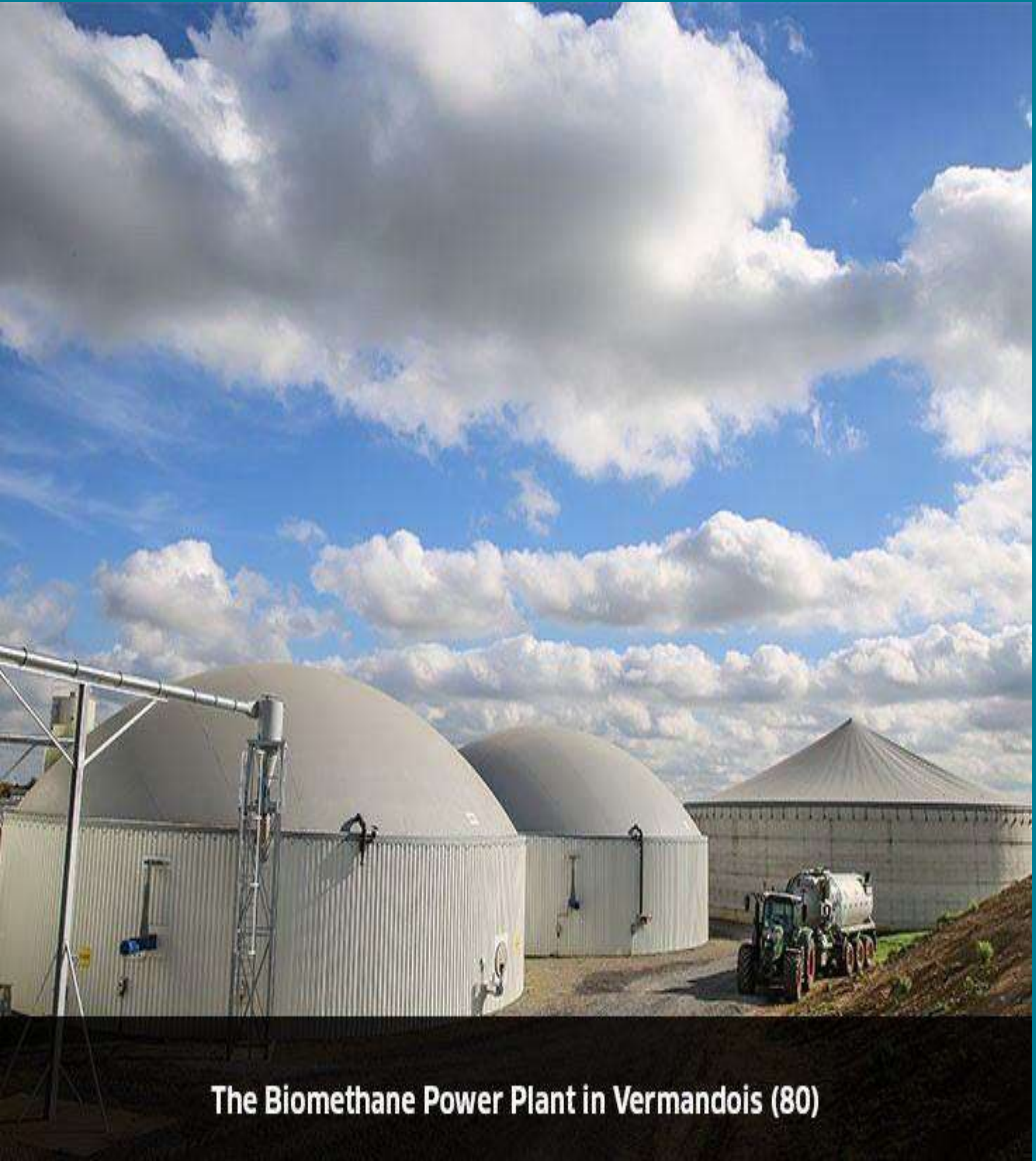
Hydrothermal gasification: synthetic methane based on liquid biomass treatment at high temperature

Methanation: synthetic methane with CO_2 as a feedstock

Natural gas/Synthetic gas + CCS



Emerging technologies: solar photocatalytic processes…

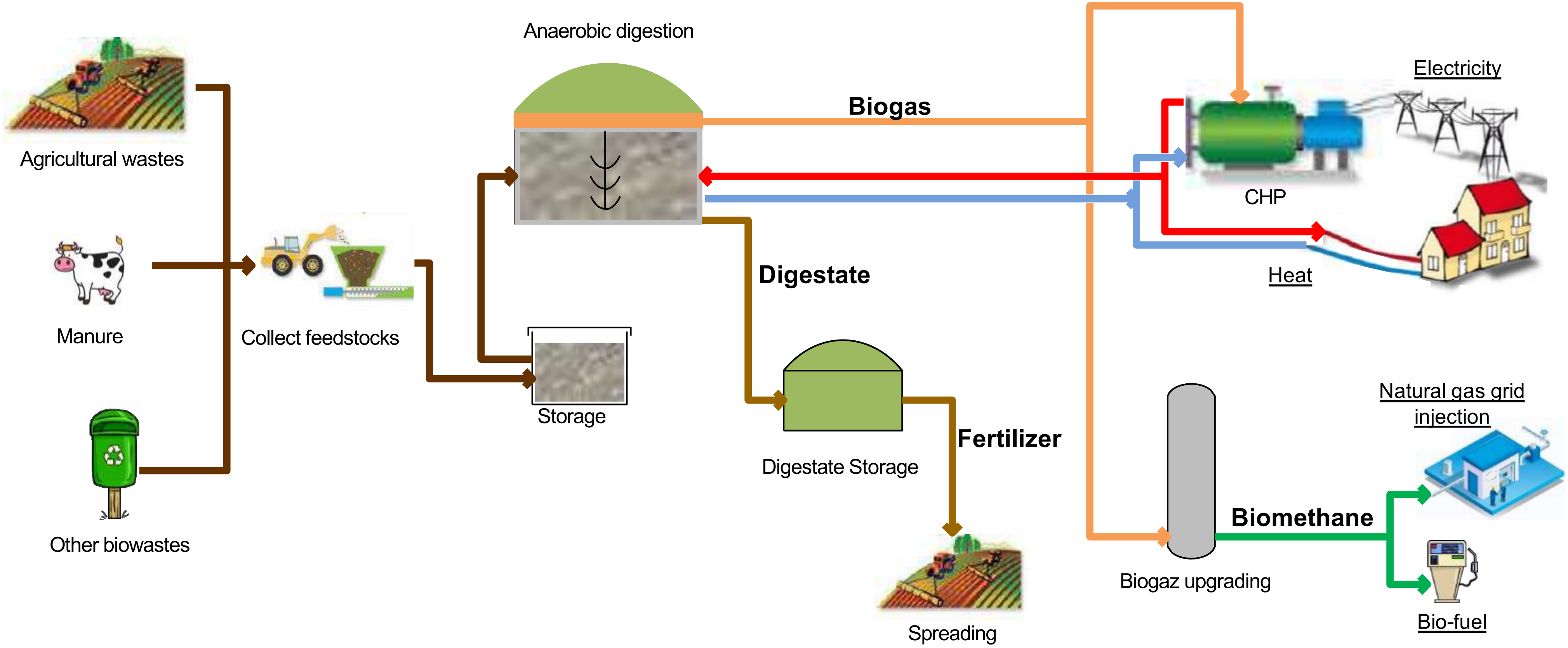

The Biomethane Power Plant in Vermandois (80)

1

Anaerobic digestion of wet biomass

How biogas is produced?

Feedstocks Production, Storage and Physical Pretreatment | Production | Digestate valorisation | Biogas / Biomethane Valorisation



What are the inputs ?

Food and feed industry wastes

Manure and slurry

Sewage sludges

Inputs=
Wet organic wastes

Green wastes

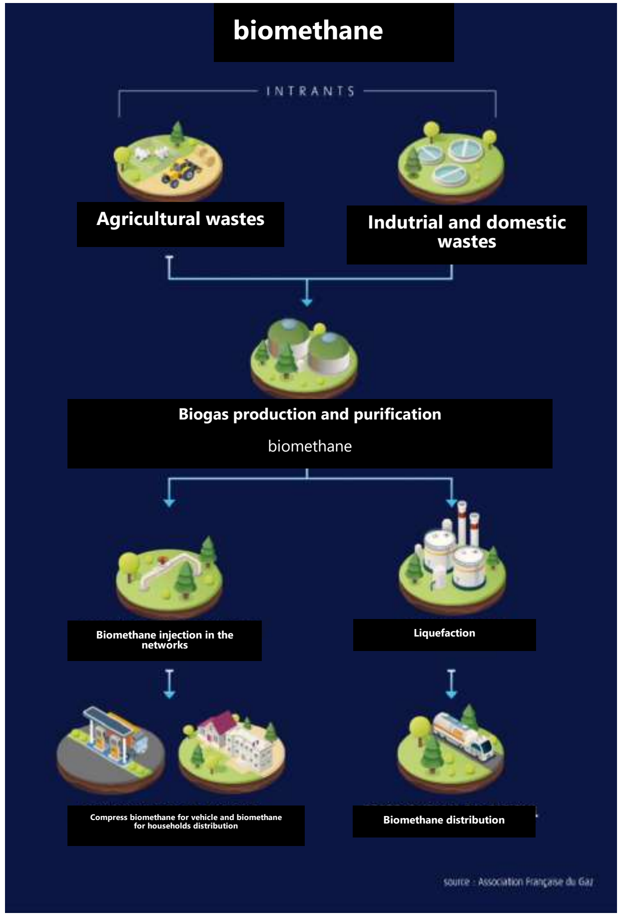
Intermediate crops for energy purposes

Food wastes

The potential and the levers of anaerobic digestion

- **A potential estimated at 190 TWh**

- Today, 1,200 installations listed in the capacity register for production estimated at 26 TWh
- The implementation of biogas production certificates will lead to an increase in the number of these small installations
- Hypothesis of reinforced use of intermediate crops for energy purposes (CIVE)
- In 2050 we can estimate
  - Between 5000 and 5500 installations
  - For a production of around 135 TWh



source : Association Française du Gaz

The levers to be implemented

- Continue production support to achieve the expected scale effects
- Launch the call for tender system for larger installations and publish the biogas production certificate system
- Have a stable regulatory framework
- Enable the development of a demand policy
- Promote the use of CIVEs

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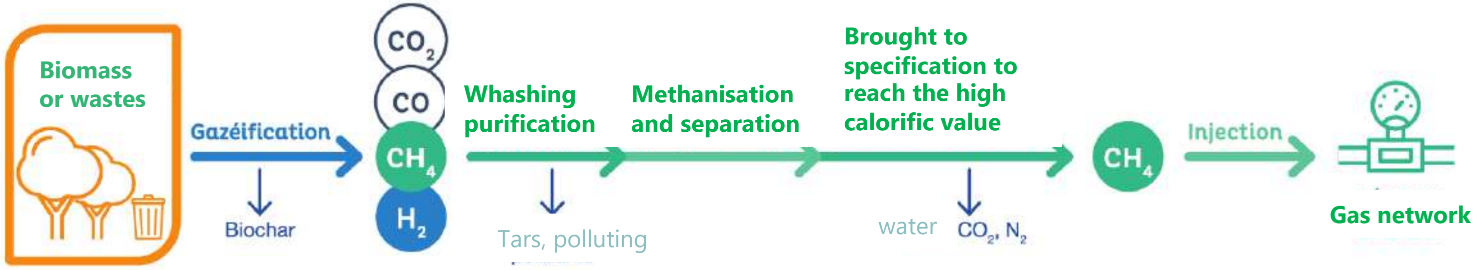
2

Pyrogasification of biomass or waste (Solid Recovered Fuel)

The pyrogasification process



- Based on pyrolysis and gasification processes by heating relatively dry carbonaceous material at high temperature (400 to 1,500°C) in the absence or lack of oxygen. This material is then transformed into methane

- Pyrogasification recovers dry inputs, namely a wide variety of resources that are difficult to recover: wood residues, non-hazardous demolition wood (doors, windows, old furniture, industrial panels, etc.) and solid recovered fuels

Pyrogasification of dry wood is a mature technology also flexible to turn various waste into valuable end-products in the future

ADVANTAGES

- It reduces waste dumping and its impact on **Health & Environment**
- SRF are **low cost** materials: from -20 to + 90 €/ton depending on the country and the quality
- SRF represents a **large, increasing**, and **available resource** ➔ Lowering the stress on biomass supply
- Mix of **SRF** with **conventional biomass** can be valorized in pyrogasification plants
- Small (2 MW_{th}) to high (<100 MW_{th}) unit capacities can be addressed by pyrogasification

CHALLENGES

- Costly p**retreatments** due to heterogeneity of waste
- Higher content of heteroatoms in SRF than in biomass, resulting in **higher pollutants content** in syngas and/or in fluegas (H_2S, HCl, NH_3)
  - **Corrosion issues**
  - **Syngas cleaning** process to adapt
- **Higher ash content** than in biomass: **15-35%** for SRF from Municipal Solid Waste, **2-20%** for SRF from Ordinary Industrial Waste.
  - Large quantity of **solid residues** to landfill in Hazardous Waste centers if no other valorization way is developed
- **Fouling** of apparatus (such as heat exchangers) due to **high alkaline and particle contents**
- Emerging market ➔ competition for quality and quantity of SRF

Source:2020, Le Cadre E., Mertens J., Emerging Sustainable Technologies

Biomass pyrogasification has been widely proven worldwide and industrialisation of the supply chain has started

Canada
Energir:
100 KW_{SNG}
expecting industrialize the technology by 2020
(TLR 6)

USA
Pacific National Laboratory:
1 MW_{SNG}
expecting industrialize technology by 2020
(TLR 7)

USA - California
GTI :
94 MW_{SNG}
Engineering phase
(TLR 7)

France
SALAMANDRE:
30 MW_{SNG}
Commissioning planned for 2023
(targeted TLR = 7)

France
SYNTHANE:
2 MW_{SNG}
Start construction planned in 2019.
(TLR 5)

France
TITAN V:
2 MW_{SNG}
Commissioning planned for 2021
(TLR 5)

France
GAYA project :
400 kW_{SNG}
Operational since 2019
(TLR 7)

Delfzijl Project :
25 MW_{SNG} (2* 12,5 MW)
Engineering phase
Start construction planned in 2019.(TLR 6)

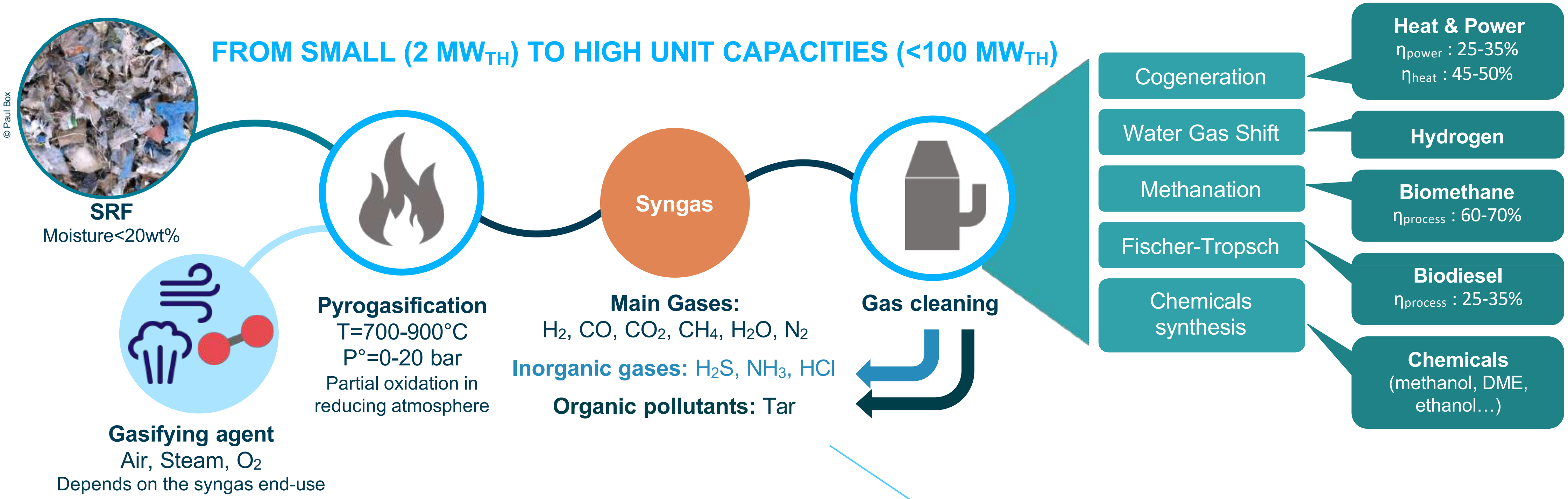
SEWDEN
Bio2G Project :
100 MW_{SNG}
Stand-by, looking for investment resources
(TLR 8)

SEWDEN
ProBioStål Project
(Woodroll process) :
6 MW_{SNG}
Commissioning planned for 2020
(TLR 7)

UK
Go Green Gas Project 1:
3 MW_{SNG}
Stand-by, looking for investment resources
(TLR 8)

UK
GoGreenGas Project 2:
40 MW_{SNG}
Commissioning planned for 2023
(TLR 8)

Pyrogasification of Solid Recovered Fuel (SRF) is an efficient way to convert dry waste into several energy carriers



FROM SMALL (2 MW_{TH}) TO HIGH UNIT CAPACITIES (<100 MW_{TH})

© Paul Box

SRF
Moisture<20wt%

Gasifying agent
Air, Steam, O_2
Depends on the syngas end-use

Pyrogasification
T=700-900°C
P°=0-20 bar
Partial oxidation in reducing atmosphere

Syngas

Main Gases:
H_2, CO, CO_2, CH_4, H_2O, N_2

Inorganic gases: H_2S, NH_3, HCl

Organic pollutants: Tar

Gas cleaning

Cogeneration	**Heat & Power** η_{power} : 25-35% η_{heat} : 45-50%
Water Gas Shift	**Hydrogen**
Methanation	**Biomethane** $\eta_{process}$: 60-70%
Fischer-Tropsch	**Biodiesel** $\eta_{process}$: 25-35%
Chemicals synthesis	**Chemicals** (methanol, DME, ethanol…)

Syngas from SRF contains much more **pollutants** than syngas from clean biomass.
Conventional **inorganic gases** removal processes must be adapted before valorising syngas.

SRF are complex and **heterogeneous** materials, strongly dependant on initial waste, production method, and season

Solid Recovered Fuels (SRF) are a mixture of:

- Plastics
- Waste wood
- Paper/carton
- Textiles…
- Carpet/matress
- Rocks
- Glass
- …

Source:2020, Le Cadre E., Mertens J., Emerging Sustainable Technologies

The potential and levers of pyrogasification

The mobilizable potential is significant

- Energy deposit from the forest of 120 TWhLCV/PE* which takes into account compliance with the hierarchy of uses and recovery of the residual share after lumber and industrial wood after allocation to priority uses
- With regard to non-forest resources, the potential is distributed as follows:
  - Solid recovered fuels: 90 TWhLCV/EP
  - Wood outside the forest: 35 TWhLCV/EP
  - Wood-waste: 8 TWhLCV/EP
  - Lignocellulosic cultures: 50 TWhLCV/EP
- As a precaution, lignocellulosic crops that raise questions in terms of land use change are not retained.
- The overall mobilisable potential respecting the hierarchy of biomass uses and waste recovery amounts to approximately 255 TWhLCV/EP or 180 TWhHCV/EF
- For 2050 we retain a realistic production of 90 TWh including 60% CSR, 20% wood waste and 20% biomass
- Use limited to non-recyclable waste, competing uses of waste are priced into account

The levers to be implemented

- Recognize the role of these technologies for the recovery of certain waste and residues with no outlet (CSR, wood B)
- Quickly deploy calls for projects to set up experimental contracts for the production of gas using innovative technologies
- Launch calls for projects to support methane production units from the pyrogasification of non-renewable waste
- Extend the CPB system to pyrogasification facilities
- Optimize the supply and logistics of inputs

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*Lower calorific value in primary energy

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3

Hydrothermal gasification of biomass and waste

Hydrothermal Gasification converts liquid organic waste into green gases in contrast to pyrogasification processes which valorize dry organic waste

What is a liquid organic waste?

- Biomass or waste having a dry matter range of 5-50 wt%
- Organic fraction in the dry matter is higher than 50 wt%
- Liquid organic waste must be pumpable to reach high pressure required by the process

Digestates from anaerobic digestion

Sewage sludge from industrial or municipal wastewater treatment plant

Food industry residues and by-products

Inputs= Waste or residues difficult to valorize

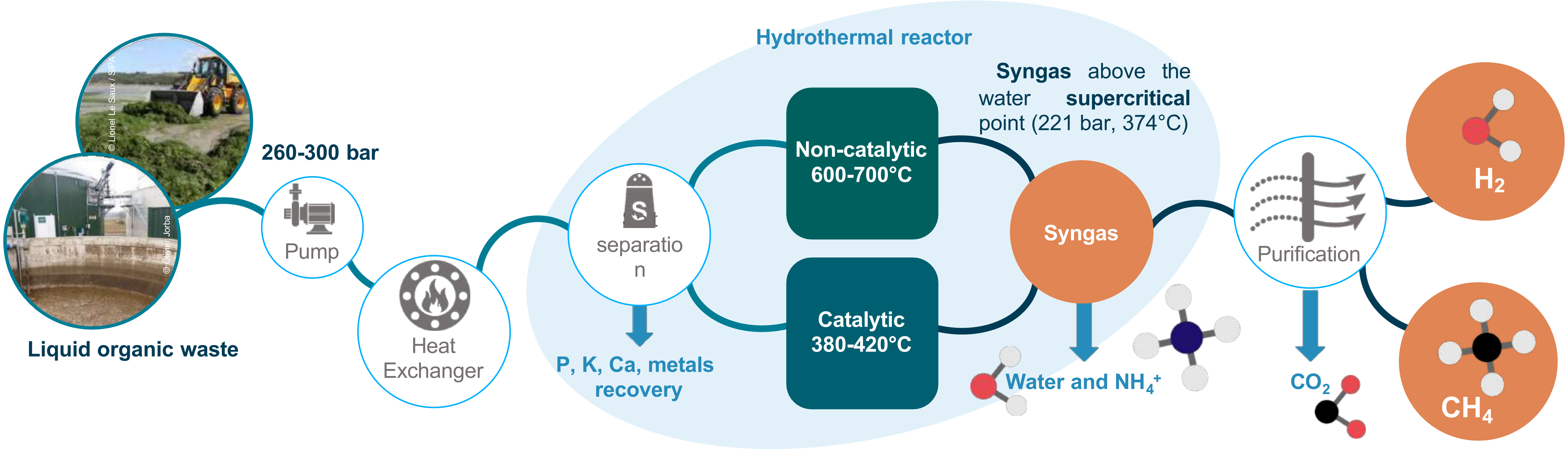
Macro and micro-algae

Liquid industry, effluents

Liquid and solid farming waste

Source:2020, Le Cadre E., Mertens J., Emerging Sustainable Technologies

Hydrothermal Gasification is gasification in hot compressed water which uses water in a supercritical state



Production of syngas, CH_4, H_2, or chemicals

- Raw syngas can be valorized either directly for heat and/or electricity production, or purified to clean CH_4 or H_2, or converted into **chemicals.**
- CH_4 content reaches 50-60% in catalytic conversion, and up to 90% when H_2 is co-injected in the gasifier
- H_2 concentration can achieve 50-75% in syngas

Sources [43], [44], [45]

Source:2020, Le Cadre E., Mertens J., Emerging Sustainable Technologies

Hydrothermal Gasification is either a complementary or competitive alternative pathway for green gas production from organic waste

ADVANTAGES

- Complementary to **pyrogasification process** which valorizes dry organic waste and to **anaerobic digestion (AD)** by valorizing liquid digestates in saturated spreading zones
- Efficient production of **CH_4 or H_2** depending on the operating conditions and process chain (CH_4 production is doubled compared to **AD**)
- Fast conversion (<10min) ➔ **compact units** (10 times more compact than AD)
- Co-production of minerals (P, K, Ca) and NH_4+ possibly valorized as fertilizer ➔ **extra-revenues**
- Low quantity of **final solid residue** generated
- No problem by using only one type of feedstock contrary to AD

CHALLENGES

- Operating with high pressure and high temperature
- **Optimisation of minerals separatio**n to avoid plugging of the gasification reactor
- Preventing from catalysts **deactivation by poisoning** (sulfur compounds) and **plugging** (minerals precipitation)
- Scaling-up and simplifying the installation operation
- Potentially in competition with anaerobic digestion since both sectors valorize **liquid organic fuels**
- Uncertainty on profitability due to costly alloys for reactor and equipment to withstand operating conditions and corrosion

Sources [45], [46], [47], [48], [49], [50], [51], [52]

Source:2020, Le Cadre E., Mertens J., Emerging Sustainable Technologies

The potential and levers of hydrothermal gasification

The potential between 58 TWh and 138 TWh

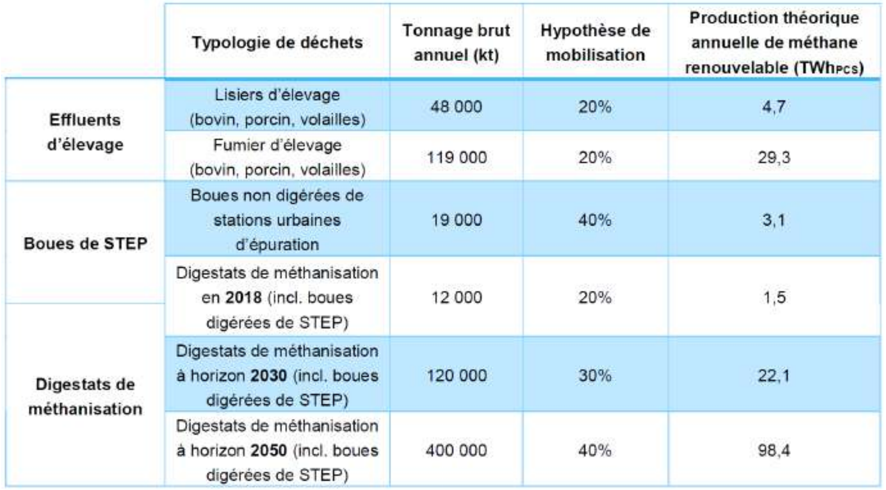
- Agricultural methanisation digestates that cannot be composted, spread or in excess or from WWTP sludge and digestates (40%)
- Sludge from cleaning and dredging (ports, rivers and canals) whose discharge into the sea will be prohibited in 2025 (9%)
- Animal by-products (carcasses) and plants (vinasses) not recovered in methanization (2%)
- Black liquors from the paper industry burnt because there is no outlet, of which 60% recovered (9%)
- Other inputs: industrial sludge, industrial waste (sugar beet pulp co-produced from biodiesel and bioethanol, landfill leachate) in search of alternatives (40%)

- A production of 50 TWh in 2050 is realistic

The levers to be implemented

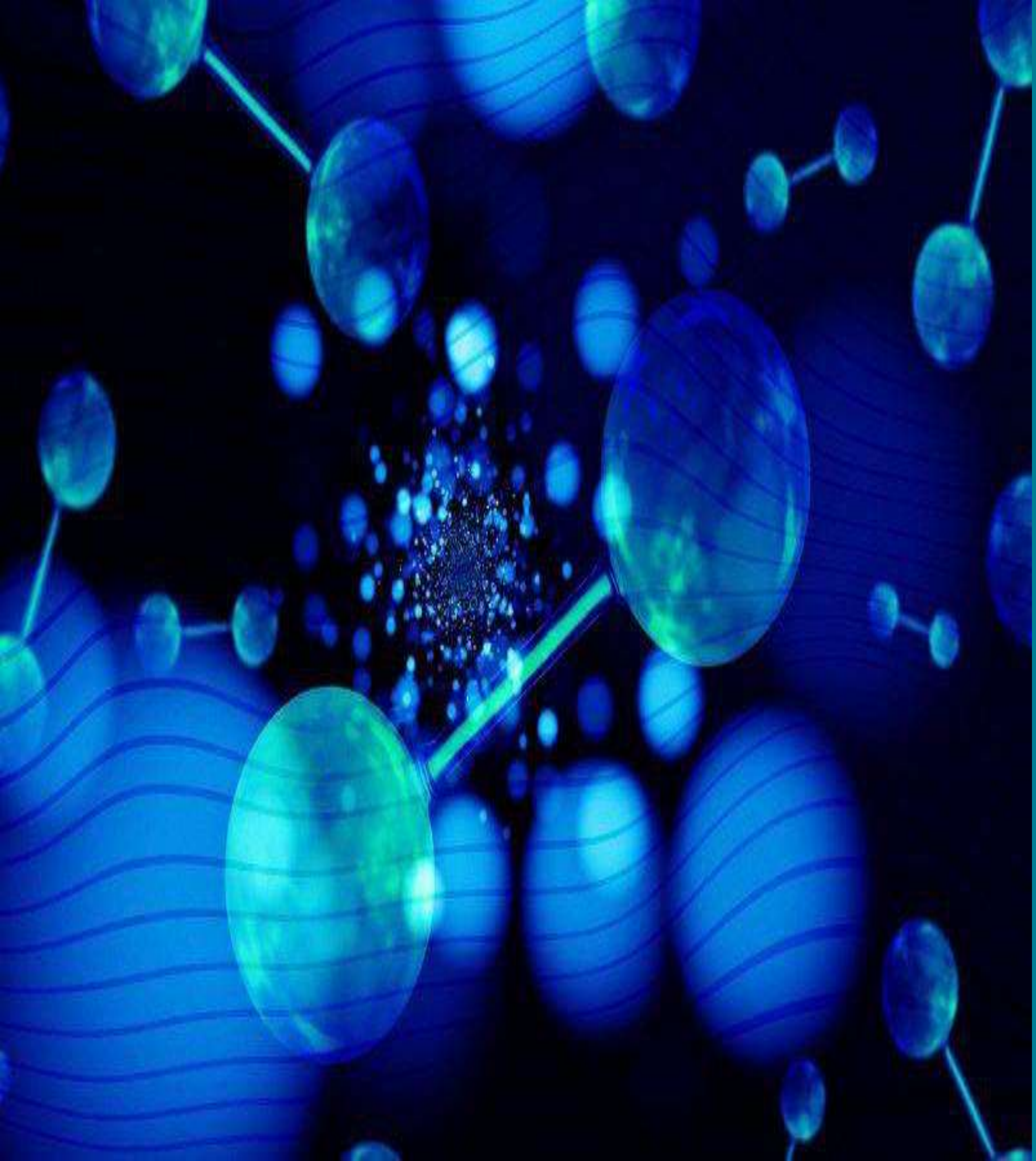
- Launch experimental contracts to bring out the sector
- Extend existing support schemes for biomethane (CPB type)

It should be noted that the increase in the constraints of recovery of sludge and liquid waste will be favorable to the deployment of this technology



	Typologie de déchets	Tonnage brut annuel (kt)	Hypothèse de mobilisation	Production théorique annuelle de méthane renouvelable (TWh_{PCS})
Effluents d'élevage	Lisiers d'élevage (bovin, porcin, volailles)	48 000	20%	4,7
	Fumier d'élevage (bovin, porcin, volailles)	119 000	20%	29,3
Boues de STEP	Boues non digérées de stations urbaines d'épuration	19 000	40%	3,1
	Digestats de méthanisation en **2018** (incl. boues digérées de STEP)	12 000	20%	1,5
Digestats de méthanisation	Digestats de méthanisation à horizon **2030** (incl. boues digérées de STEP)	120 000	30%	22,1
	Digestats de méthanisation à horizon **2050** (incl. boues digérées de STEP)	400 000	40%	98,4

Tableau 2 Potentiel de production de méthane renouvelable par gazéification hydrothermale



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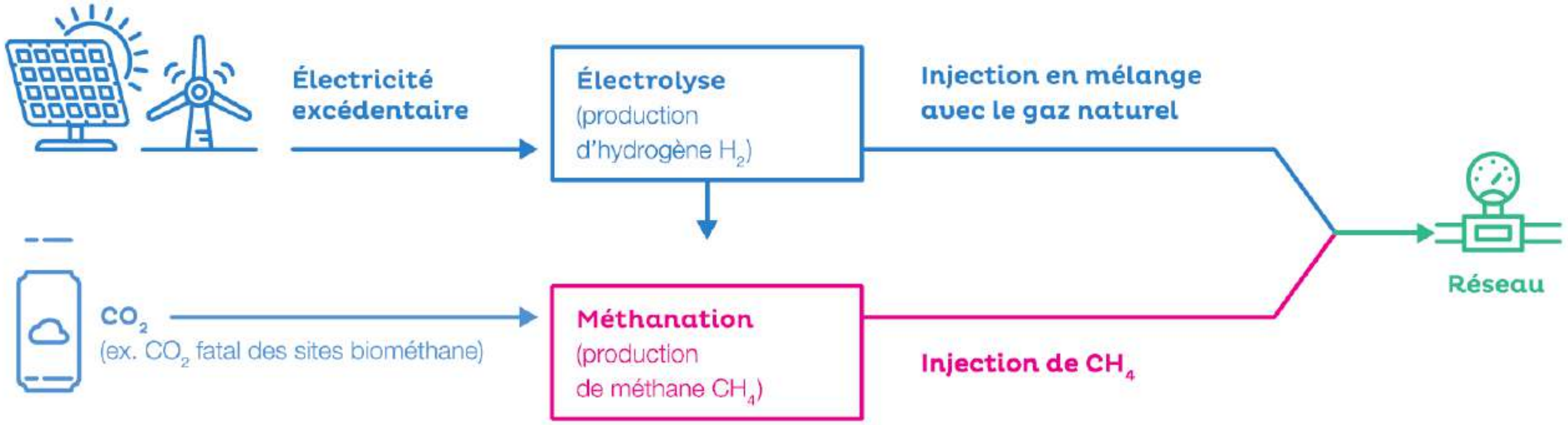
E-methane: Synthetic methane with CO_2 as feedstock

The methanation process



Électricité excédentaire

Électrolyse (production d'hydrogène H_2)

Injection en mélange avec le gaz naturel

Réseau

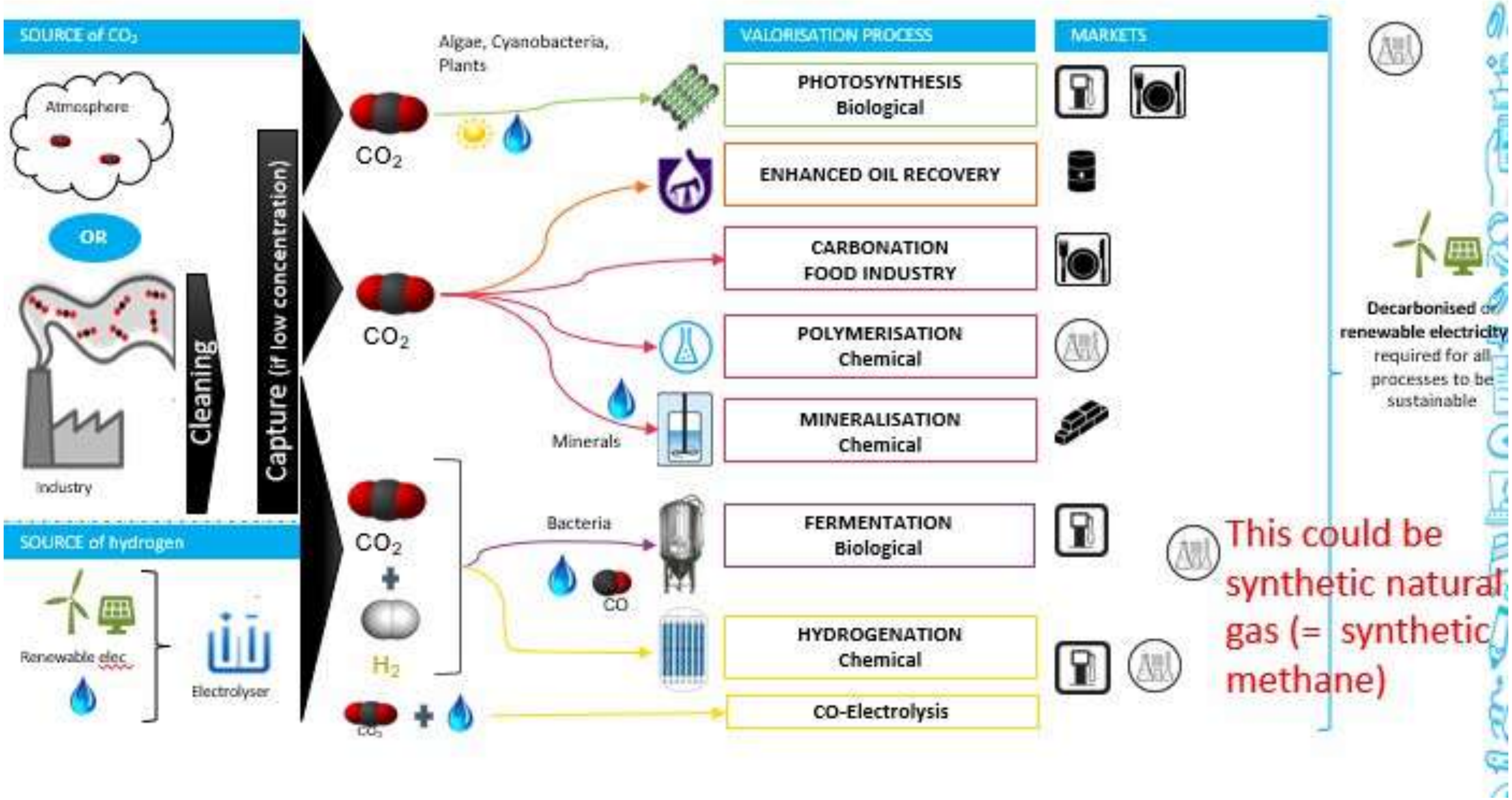
CO_2 (ex. CO_2 fatal des sites biométhane)

Méthanation (production de méthane CH_4)

Injection de CH_4

- Methanation allows the production of synthetic methane by combining CO2 and green hydrogen
- A sector with multiple advantages:
  - Electricity-gas coupling and recovery of surplus renewable energy production
  - Decarbonization of gas uses
  - Recovery of biogenic CO2 (methanization, combustion of organic matter) or industrial

CO2 can be used as building blocks for high added-value fuels like e-methane



This could be synthetic natural gas (= synthetic methane)

The potential and methanation levers

A trajectory of 60 TWh is realistic

- This trajectory is identified by evaluating the possible optimizations of CO2 recovery according to two sources:
- CO2 from agricultural methanation: recovery of biogenic CO2 from agricultural methanation with electrolyzers, systematic implementation of such recovery on all methanation facilities from 2028, on the basis of operation at 4000 hours

  => 50 TWh
- Industrial CO2 (food industries in particular)

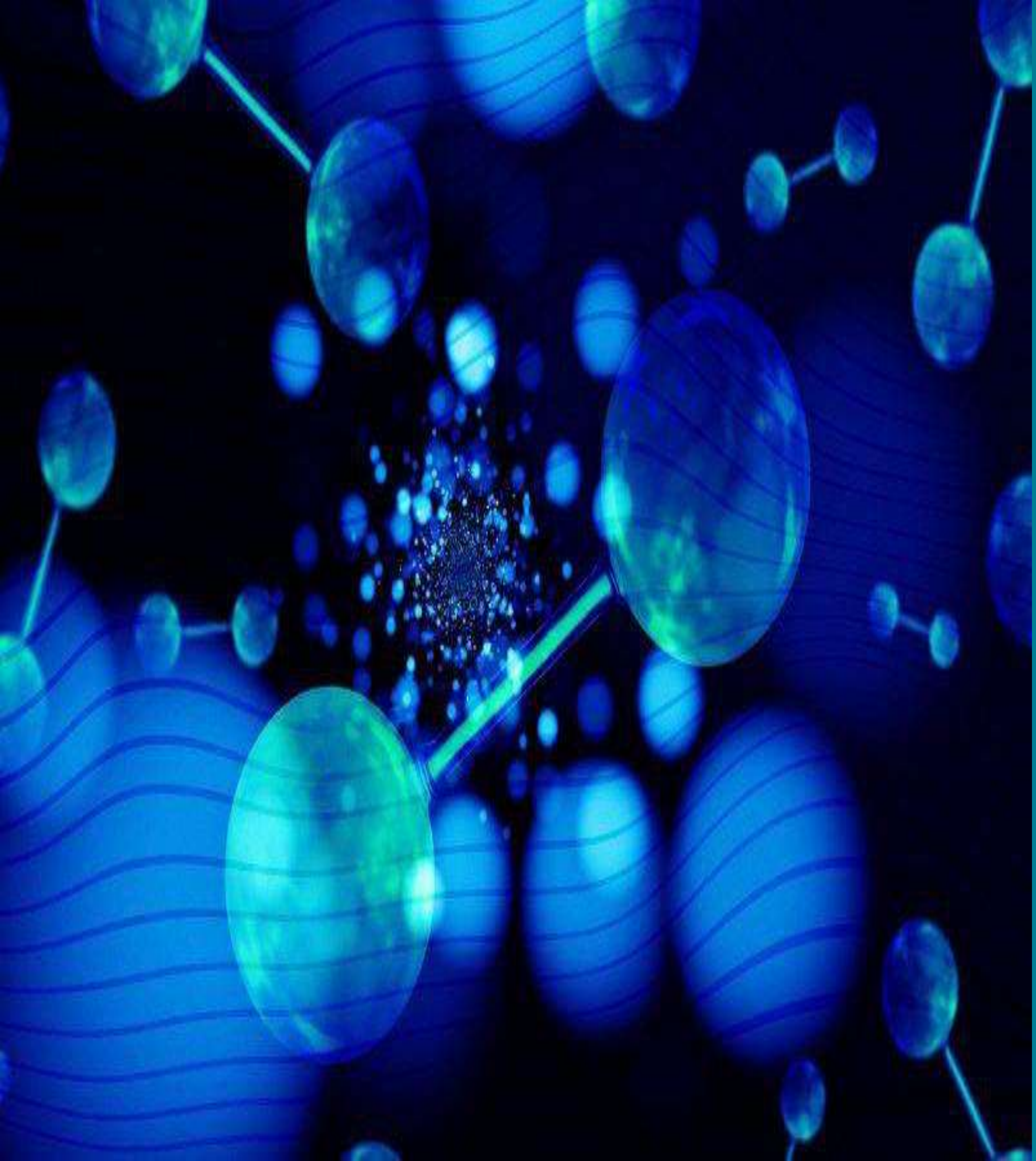
  => 10 TWh

- The potential is estimated at 120 TWh

The levers to be implemented

- Define a regulatory framework (definition) for methane produced by methanation as a renewable gas and a development trajectory in the PPE
- Set up an aid system (OPEX) for the first projects to produce methane produced by methanation

A specific support mechanism for the production of renewable H2 will be decisive



5

Emerging technologies: solar fuels...

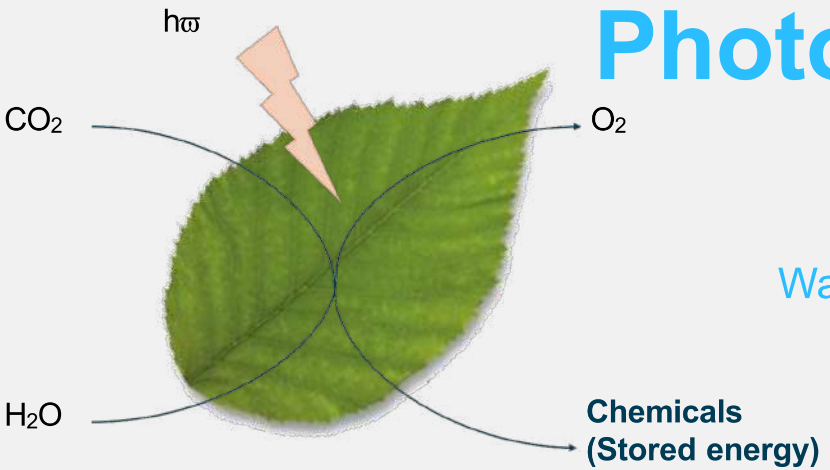
ENGIE University

Solar photocatalytic processes also called artificial photosynthesis (AP) could produce synthetic methane

Principle : When hit by photons, some semiconducting materials will generate charges (e^- / h+) that exhibit an electrochemical potential high enough to split the water molecule. Those materials can be metal oxides (TiO_2, Fe_2O_3, WO_3, …) bulk or nanostructured, nanoparticles immerged in an electrolyte.

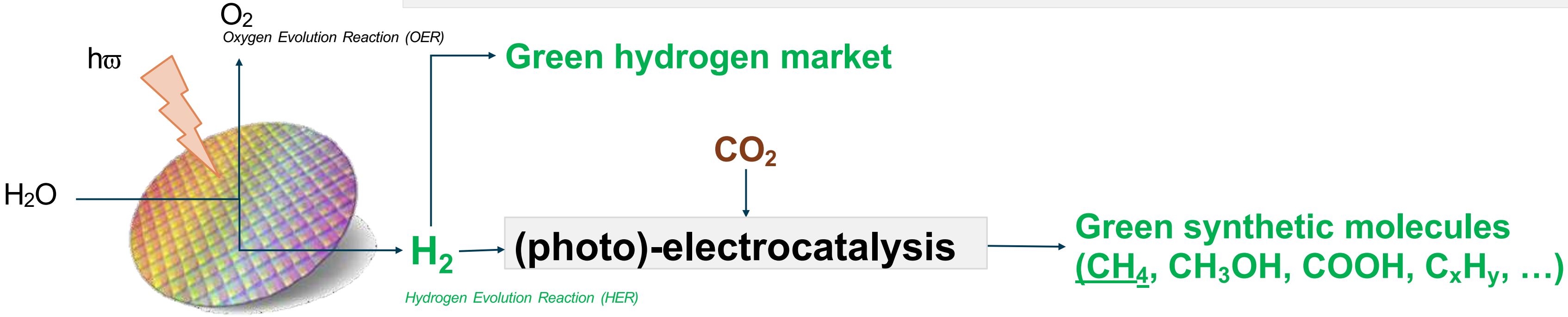
Through the use of photo-electrocatalysis, AP seeks to replicate the photosynthesis process. It widely uses semiconductors as photocatalyst and often splits the process in two steps:

1) Production of hydrogen by water splitting using photocatalysis
2) CO_2 reduction and subsequent reaction with hydrogen to form light weight hydrocarbons through different approaches



Photosynthesis :

- Natural storage of solar energy
- Two reactions: Water splitting & CO_2 reduction
- Storage of energy in molecular bonds



Green hydrogen market

CO_2

(photo)-electrocatalysis

Green synthetic molecules (CH_4, CH_3OH, COOH, C_xH_y, …)

A trajectory with significant renewable gas volumes is realistic

	Potential	Realistic production trajectory		
		2030	**2040**	**2050**
Methanisation	190 TWh	49 TWh	100 TWh	135 TWh
Pyrogazeification	180 TWh	6 TWh	30 TWh	90 TWh
Hydrothermal Gazeification	100 TWh	2 TWh	25 TWh	50 TWh
Methanation	120 TWh	3 TWh	30 TWh	60 TWh
Total	**>> 335 TWh**	**60 TWh**	**185 TWh**	**335 TWh**

- In addition to these figures, there are various options that allow for flexibility Carbon capture and storage solutions
- A bio-propane potential exists: estimated at 4 TWh in 2030 and 10 TWh in 2050
- France could also be a hub for e-methane in transit or imported if the economic conditions are favorable: volumes estimated to be significant from 2040 to 2050, of which more than 70% transit
- Finally, renewable and low-carbon hydrogen will be present

These potentials are the subject of numerous studies, the results of which are consistent

Francegaz

TWh	Potential 2050				Production 2030
	Methanisation	Pyrogazification	Hydrothermal gazification	Methanation	Methanisation
SNBC / PPE (2020)	130 à 140	24 à 85		6	22 (2028)
ENGIE (2021)	158	49 à 94		179	45
ADEME / Solagro (2018)	140	180		140	
CRE (2019)	39 à 42				39 à 42
ADEME (2021)	104 à 141	0 à 180		0 à 40	42 à 51
France Stratégie (2021)	109 à 138				
négaWatt (2021)	139	51		20	
Fraunhofer Institut					41 (4 pyro)
Trinomics (2020)	125	60			
EC JRC (2015)	125	65			
Imperial College	300	221			301
Prospective Gaz Territoires	130	50	37	9 (local)	30-49
GRDF- GRTgaz	142	189	58	50 (local)	42-49
ENEA			58 à 138		


FRANCE STRATÉGIE

Quelle place pour le gaz dans la transition énergétique ?

Imperial College London Consultants

Sustainable biomass availability in the EU, to 205

EUROPEAN COMMISSION

COMMISSION STAFF WORKING DOC

IMPACT ASSESSMENT REPORT

Stratégie nationale bas-carbone

La transition écologique et solidaire vers la neutralité carbone

PROJET

LE VERDISSEMENT DU GAZ

JOINT RESEARCH CENTRE


Fraunhofer

ACTUALISATION DU SCÉNARIO ÉNERGIE-CLIMAT ADEME 2035-2050

TRANSITION(S) 2050 CHOISIR MAINTENANT AGIR POUR LE CLIMAT

Synthèse

Impact of the use of the biomethane and hydrogen potential on trans-European infrastructure

Trinomics

APESA

teurs

enea

État des lieux du biométhane en France

Rte

Futurs

Scénario négaWatt 2022

JRC SCIENCE FOR POLICY REPORT

The JRC-EU-TIMES model. Bioenergy potentials for EU and neighbouring countries.

ENGIE

Quelles solutions pour une transition énergétique efficace et résiliente ?

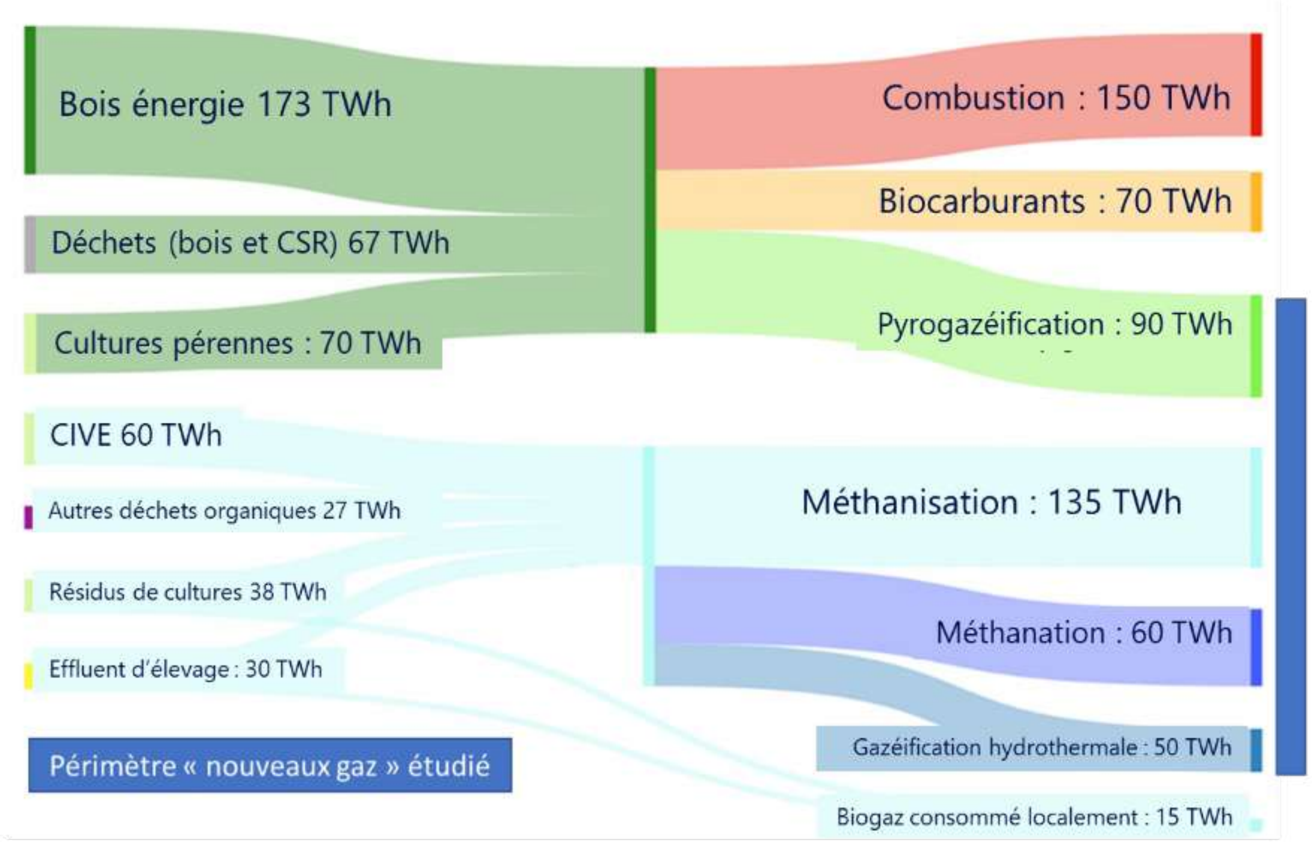
Potentiel de la Gazéification Hydrothermale en France

Perspectives Gaz 2020

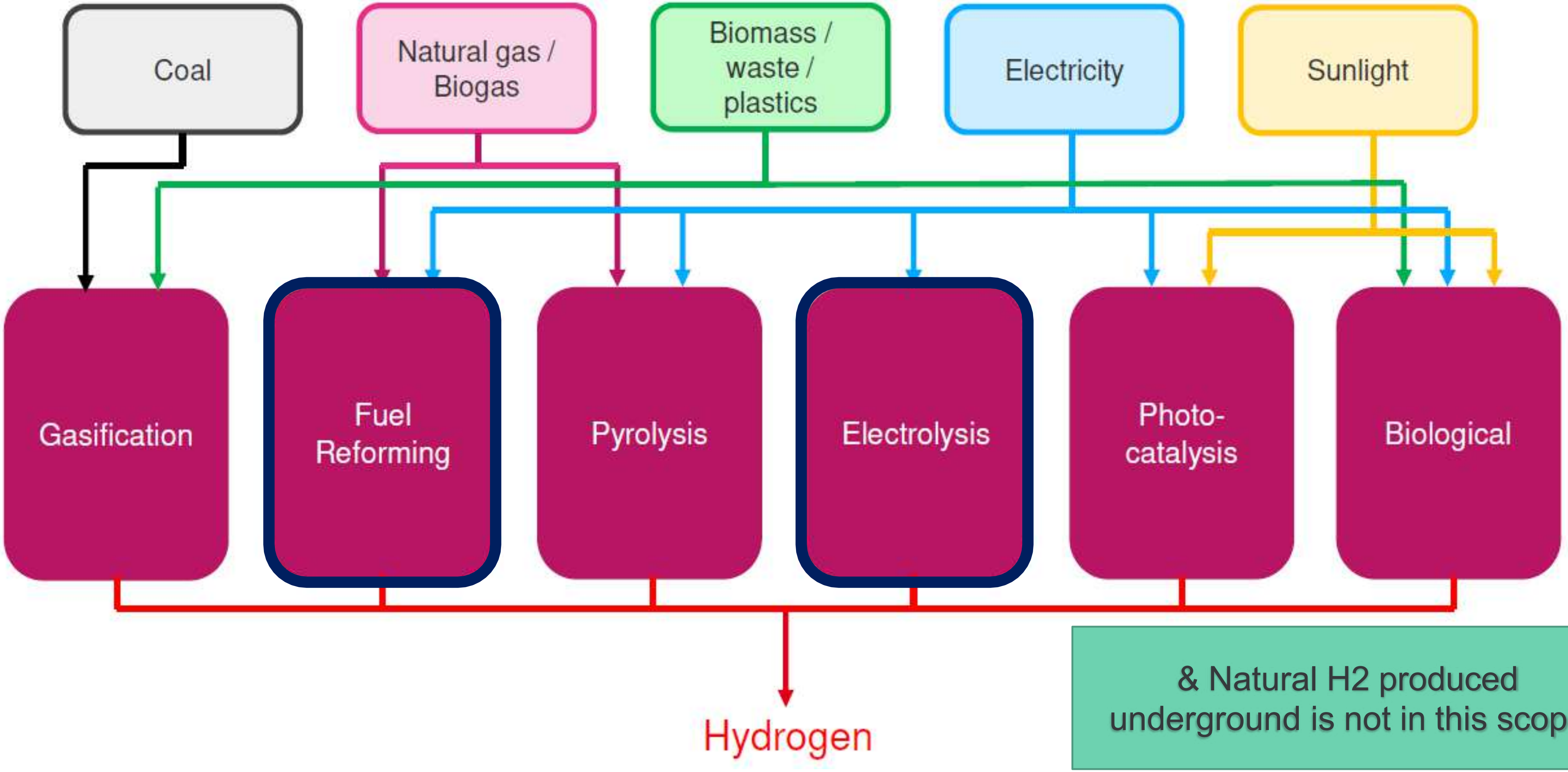
Gaz naturel & renouvelables 2020 - 2030

An association of uses rather than conflicts of use

- An overview shows that the potential identified is part of a complementarity of the different uses



OVERVIEW OF H2 PRODUCTION TECHNOLOGIES AND THIER ENERGY SOURCES

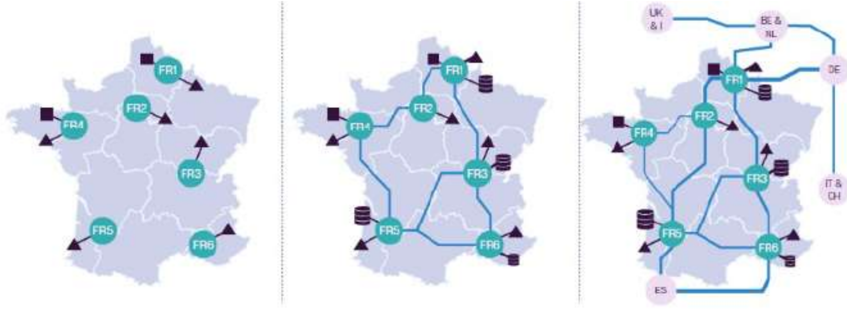


& Natural H2 produced underground is not in this scope

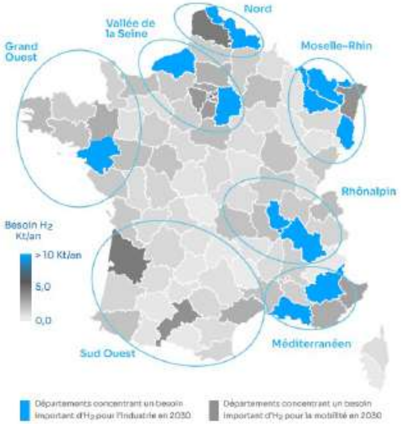
The deployment of a competitive renewable and low-carbon hydrogen economy

- Hydrogen will play an important role in the transition of industry (refining, chemicals, steel) or energy (long-term storage), it should remain marginal for domestic uses
- **It could represent ≈ 100 TWh by 2050**
- A bouquet of technologies is necessary to meet the demand for carbon-free hydrogen: renewable or network electrolysis, gas and CCS coupling, biomass pyrogasification

- The role of infrastructure (transport, storage) is key for the development of hydrogen: economic optimization, security of supply, multiplication of outlets
- The development will take place in 3 phases: emergence, connection, integration
- Converting existing gas infrastructure to hydrogen is the most economical option (about 10 times more than laying a new pipeline)



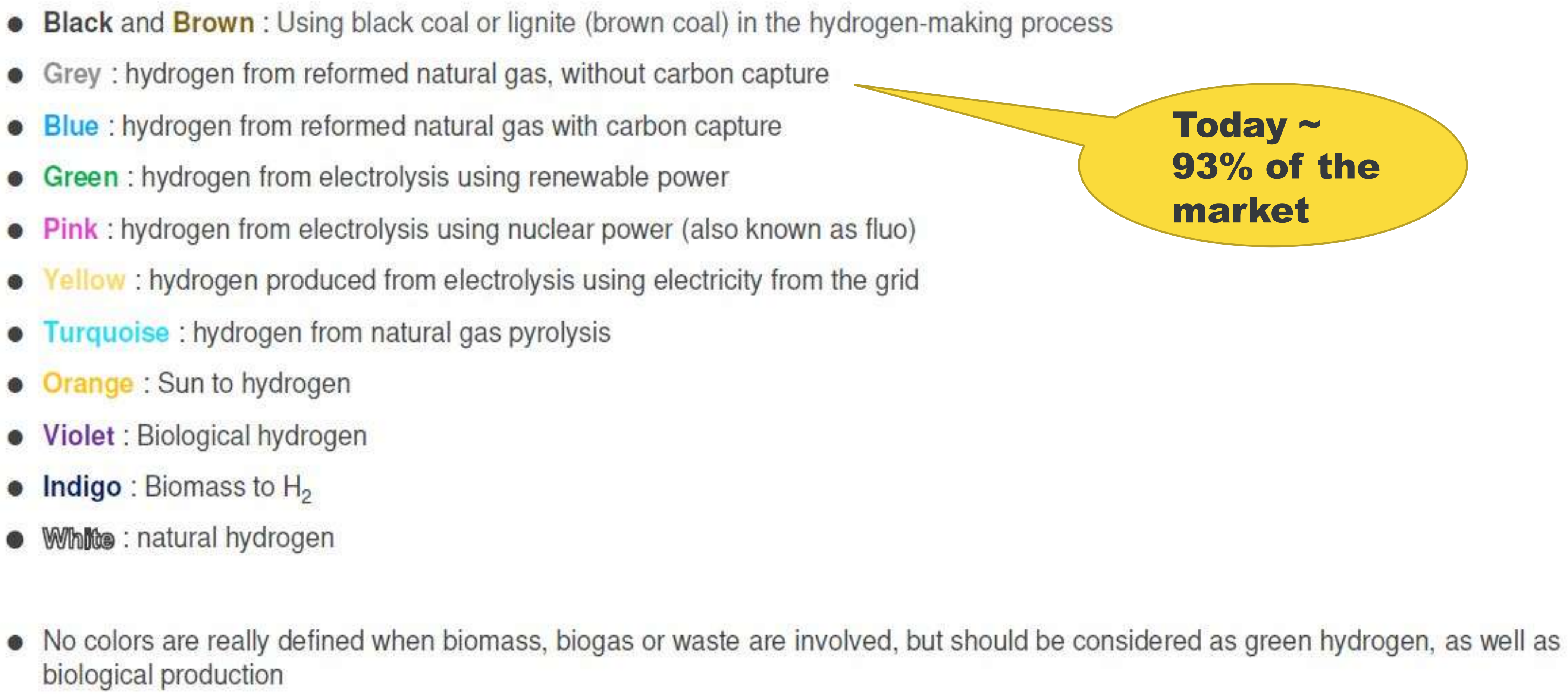
Source: Guidehouse



A large-scale and integrated system, based on national and interconnected hydrogen infrastructures, in this analysis reduces the cost of delivered hydrogen by around 30% in 2040.

HYDROGEN COLORS : ALTHOUGH USED BY MANY OF US, IT'S NOT A STANDARD DEFINITIONS

THESE COLORS ARE TO BE USED WITH CAUTION, BECAUSE ENVIRONMENTAL IMPACT DEPENDS ON BOTH TECHNOLOGY AND ENERGYSOURCES



- **Black** and **Brown** : Using black coal or lignite (brown coal) in the hydrogen-making process
- Grey : hydrogen from reformed natural gas, without carbon capture
- Blue : hydrogen from reformed natural gas with carbon capture
- Green : hydrogen from electrolysis using renewable power
- Pink : hydrogen from electrolysis using nuclear power (also known as fluo)
- Yellow : hydrogen produced from electrolysis using electricity from the grid
- Turquoise : hydrogen from natural gas pyrolysis
- Orange : Sun to hydrogen
- Violet : Biological hydrogen
- **Indigo** : Biomass to H_2
- **White** : natural hydrogen

- No colors are really defined when biomass, biogas or waste are involved, but should be considered as green hydrogen, as well as biological production

Today ~ 93% of the market

HYDROGEN PRODUCTION: TOWARDS TO DECARBONED HYDROGEN

- **Existing /available technologies (TRL 8-9)**

  1. ***Methane reforming**: Most common method of hydrogen production. High temperature process to produce CO_2 and H_2 from CH_4 (natural gaz) and Steam. **CO_2 Emissions, unless CCS***
  2. ***Water electrolysis**: Use of electricity to separate water molecules into hydrogen and oxygen using electrolyzer technologies and electricity. **Renewable H_2, if the electricity is renewable***

- **Other technologies in development (TRL 3-6/7)**:

  3. ***Biomass gasification or SFR (pyro-gasification):** high-temperature thermal process consisting of breaking down hydrocarbon's molecules into (CO, CO2, CH4, H2O, H2 and impurities). Renewable H_2 if (Biomass) and low carbon (SFR).*
  4. ***Pyrolysis of methane**: High temperature thermal process breaking methane into hydrogen and carbon black. Use of Plasma, Combustion and catalytic systems.*
  5. ***Solar thermochemical hydrogen production**: use of concentrated solar energy to drive the dissociation of water. Renewable process, at the pilot stage. Decentralized uses*
  6. ***Biological processes**: use of micro-organisms, such as algae or bacteria, which are capable of producing hydrogen by bio photolysis. Renewable, but still low maturity*

- *And **Natural H2**: Direct emanations of H2 from under the earth's crust. Renewable H_2.*

Renewable and carbon-free gases combine, at the heart

- of the territories,
- circular economy,
- sustainable agriculture,
- waste treatment,
- creation of local jobs.

They will make the energy transition a lever

- of reindustrialization
- strengthening France's sovereignty

Thank you for your attention

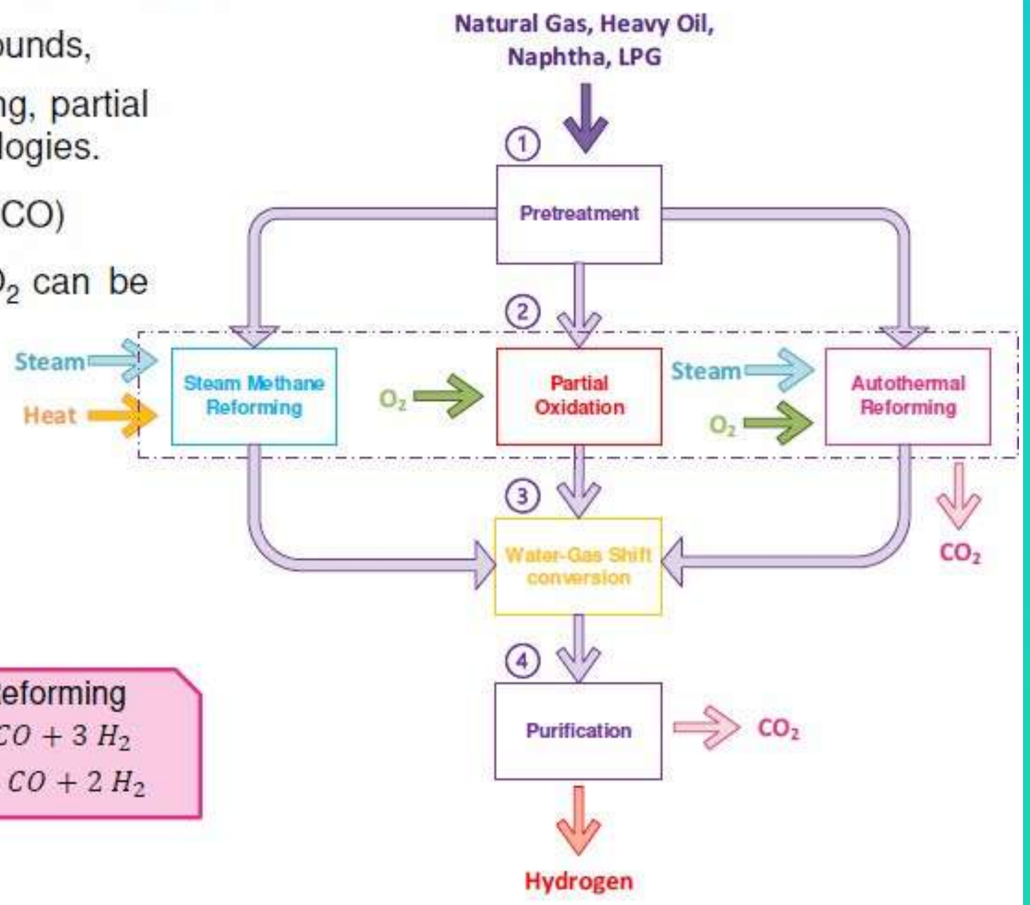
Lab Crigen
RESEARCH & INNOVATION

TECHNOLOGIES DESCRIPTION

1- METHANE REFORMING: 3 MAIN TECHNOLOGIES

- **Process steps:** Methane Reforming process for pure H_2 production consists of four stages:
  ① Pretreatment unit to pre-reform feedstock and to eliminate Sulphur compounds,
  ② Reforming step to produce syngas using either: steam methane reforming, partial oxidation or autothermal reforming. It is possible to combine these technologies.
  ③ Shift reactor(s) to convert syngas and (increase H_2 content and decrease CO)
  ④ Purification unit separates the hydrogen from the product stream. CO_2 can be captured through Carbon Capture technologies.

- **Catalysts:**
  - The relative catalytic activity of metals in the SMR reaction: Ru > Rh > Ir > Ni > Pt > Pd
  - Conventional iron-chromium for high temperature WGS and copper alloys for low temperature WGS



Steam Methane Reforming
$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2$$
$$\Delta H = 206 \text{ kJ/mol}$$

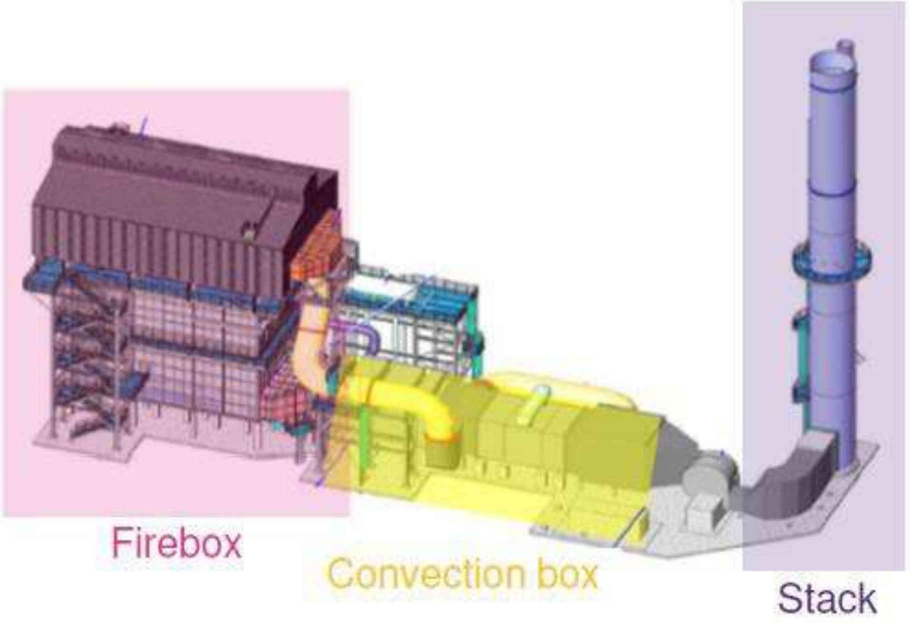
Partial Oxidation
$$CH_4 + {}^1/_2\,O_2 \leftrightarrow CO + 2\,H_2$$
$$\Delta H = -36 \text{ kJ/mol}$$

Autothermal Reforming
$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2$$
$$CH_4 + {}^1/_2\,O_2 \leftrightarrow CO + 2\,H_2$$

Water-Gas Shift
$$CO + H_2O \leftrightarrow H_2 + CO_2$$
$$\Delta H = -41 \text{ kJ/mol}$$

1- STEAM METHANE REFORMING

This energy-intensive steam reforming process takes place inside hundreds of catalyst-packed reaction tubes placed vertically in a large-scale refractory lined furnace called the **firebox**. Heat is recovered from the flue gases through several tube banks arranged in a **convection box**. This section preheats gas, steam and combustion air. Flue gases are then evacuated through a **stack**.



Plant owner	Location	Capacity [kgH$_2$/day]	SMR licensor
Tuapse Refinery	Sao Francisco do Conde	5.10^5	TechnipFMC
Kuwait National Petroleum	Mina Abdulla	4.10^5 (x3 trains)	HALDOR TOPSOE
JSC Bashneft NOVOIL	Ufa	4.10^5	amec foster wheeler
TUPRAS	Izmit	3.10^5	TechnipFMC
Abu Dhabi Oil Refining	Ruwais	3.10^5	HALDOR TOPSOE

World's largest single-train SMR plants

2- WATER ELECTROLYSIS : FIVE MAIN TECHNOLOGIES

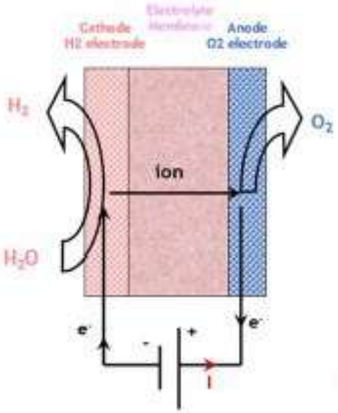

+

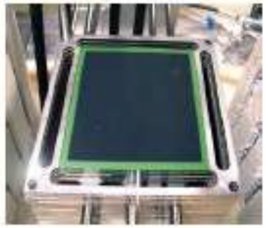
→ $H_2 + O_2$

Water electrolysis consists in the **production of hydrogen from water and electricity**. H_2O is electrochemically split into H_2 and O_2 using electric power **at a voltage of ~1.2 – 1.8 V**.

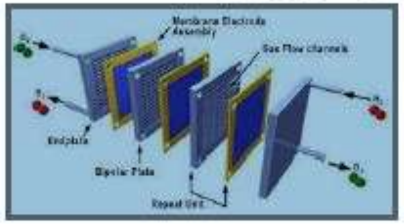
A **cell** (electrolyte + two electrodes) can be piled into **stacks** (adding bipolar plates and sealants) that will be integrated in a **system**. There are **five main technologies** that **differ in terms of materials** (electrolyte, electrodes, bipolar plates, etc…), **operating conditions** (T, current density, gas inlet, etc.), reaction mechanisms, etc. This induces **specific characteristics** for each technology (power density, lifetime, fuel flexibility, etc.) **suitable for specific applications**.

Cell = electrolyte + two electrodes





Stack = cells' piling



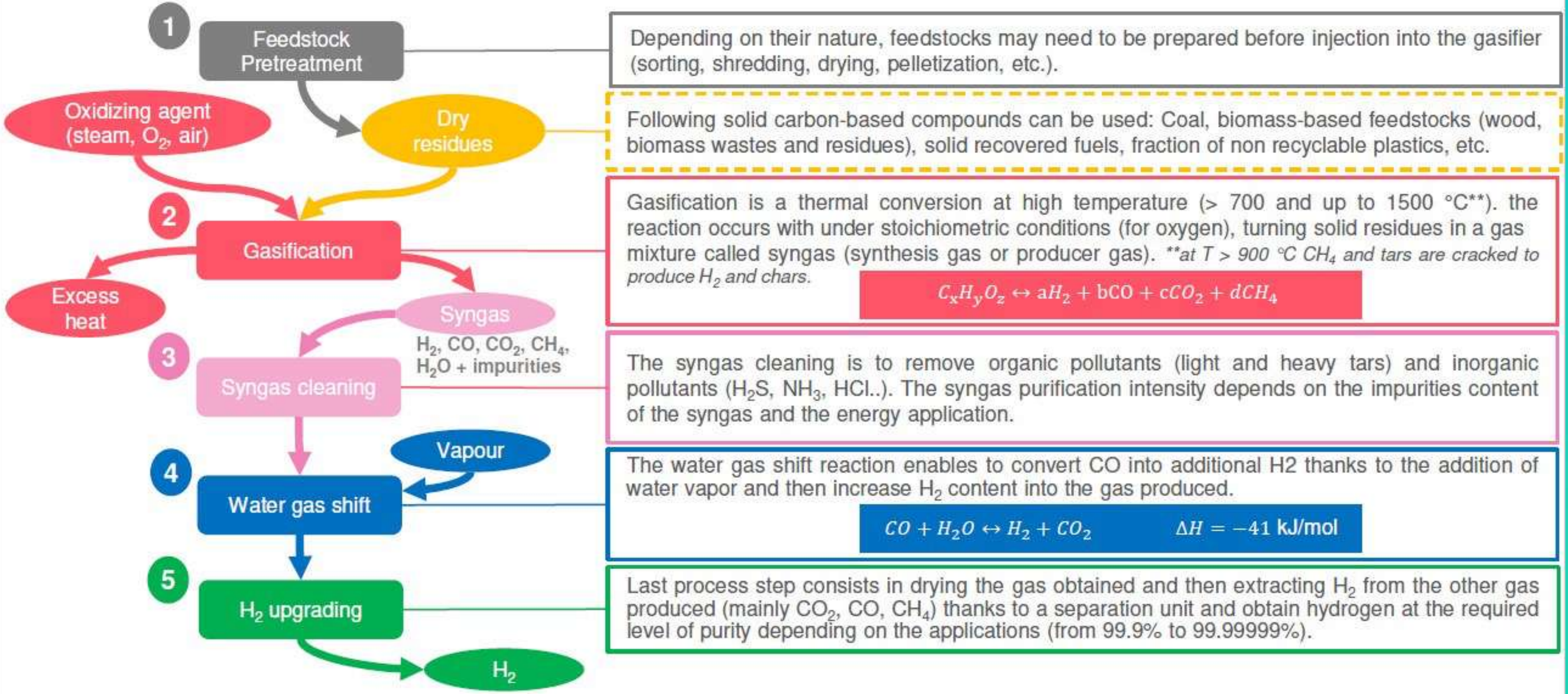
	PEM	Alkaline	AEM	PCEC	SOEC
T (°C)	50 - 80	60 - 80	50 - 70	500 - 600	700 - 850
ion	H^+	OH^-	OH^-	H^+	O^{2-}
electrolyte	Nafion (*) (polymer)	KOH (liquid)	QAPS (polymer)	BaCeZrYYb (ceramic)	YSZ (ceramic)
Catalyst cathode	Pt	Ni	Ce/La	Ni	Ni
Catalyst anode	Ir/Ru	Ni/Co/Fe	Co	BaCoFeZrY perovskite	LaSrCrFe persovskite
Development Status	Commercial	Commercial	R&D	R&D	Pre-commercial pilots

(*) Discussions on possible ban of this product in EEC

2- WATER ELECTROLYSIS : FIVE MAIN TECHNOLOGIES

	Alkaline	PEM	SOEC	AEM	PCEC
Track record	100+ years	20+ years	10+ years	10- years	5- years
TRL	9	9	6-9	3-9	3-5
System/plant size (max)	5.10^4 kg H_2/day ~100's MWe	5.10^3 kg H_2/day ~10's MWe	10^3 kg H_2/day ~ 1's MWe	5 kg H_2/day (~10's kWe)	No system (only lab test)
Stack size	Up to a few MWe	100's kWe to a few MWe	10's kWe	10's kWe	From W to kW
Stack view					
Actors	Nel Hydrogen, ThyssenKrup, Asahi Kasei, Hydrogenics, Mc Phy, John Cockerill (Suzhou), Peric, THE, Sunfire (IHT)	Plug Power (Giner Elx), ITM, H-TEC, Nel Hydrogen, ELOGEN, Cummins (Hydrogenics), Siemens Energy	Sunfire, Elcogen, FuelCell Energy, Solid Power, Haldor Topsoe, CEA, DTU, IKTS, …	Enapter, Alchemr, Nel Hydrogen, Evonik, Ionomr, Dioxide Materials, Sintef, Fraunhofer, KIST, …	Coorstek, FuelCell Energy, HyET, Sintef, Idaho National Lab, Colorado School Mines, University of Oslo, …

3- THERMAL GASIFICATION (BIOMASS, SFR, COAL, WASTES ….)



1 Feedstock Pretreatment

Depending on their nature, feedstocks may need to be prepared before injection into the gasifier (sorting, shredding, drying, pelletization, etc.).

Oxidizing agent (steam, O_2, air)

Dry residues

Following solid carbon-based compounds can be used: Coal, biomass-based feedstocks (wood, biomass wastes and residues), solid recovered fuels, fraction of non recyclable plastics, etc.

2 Gasification

Excess heat

Gasification is a thermal conversion at high temperature (> 700 and up to 1500 °C**). the reaction occurs with under stoichiometric conditions (for oxygen), turning solid residues in a gas mixture called syngas (synthesis gas or producer gas). ***at T > 900 °C CH_4 and tars are cracked to produce H_2 and chars.*

$$C_xH_yO_z \leftrightarrow aH_2 + bCO + cCO_2 + dCH_4$$

Syngas

H_2, CO, CO_2, CH_4, H_2O + impurities

3 Syngas cleaning

The syngas cleaning is to remove organic pollutants (light and heavy tars) and inorganic pollutants (H_2S, NH_3, HCl..). The syngas purification intensity depends on the impurities content of the syngas and the energy application.

Vapour

4 Water gas shift

The water gas shift reaction enables to convert CO into additional H2 thanks to the addition of water vapor and then increase H_2 content into the gas produced.

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H = -41 \text{ kJ/mol}$$

5 H_2 upgrading

H_2

Last process step consists in drying the gas obtained and then extracting H_2 from the other gas produced (mainly CO_2, CO, CH_4) thanks to a separation unit and obtain hydrogen at the required level of purity depending on the applications (from 99.9% to 99.99999%).

3 - THERMAL GASIFICATION (BIOMASS, SFR, COAL, WASTES ….)

	Coal gasification	**Biomass gasification**	**Waste gasification**
Main actors	CHN Energy (80 coals gasifier, China), KHI (Carbonet, Australia)	CORTUS, HAFFNER, ENGIE*, HYMOOV, QUAIROS, WAYS2H	ENGIE*, ETIA
Status	Commercial plants	Advanced demonstrators	First demonstrators
TRL	9	6 - 8	5 - 7
Capacity or equivalent capacity	10^5-10^7 kg H_2/day	In operation: 10 – 50 kg H_2/day Planned: up to 400 kg H_2/day	In operation for CH_4 production: equivalent to 50 kg/day H_2
Photos			

** Coal or fossil fuels gasification will available only if coupled with CCS * Acceptance as renewable will depend on the type of waste and local legislations

4 - METHANE PYROLYSIS –THERMOCHEMICAL DECOMPOSITION OF METHANE MOLECULE INTO H_2 & SOLIDE CARBON

Methane pyrolysis

0 kg CO_2 (direct emission)

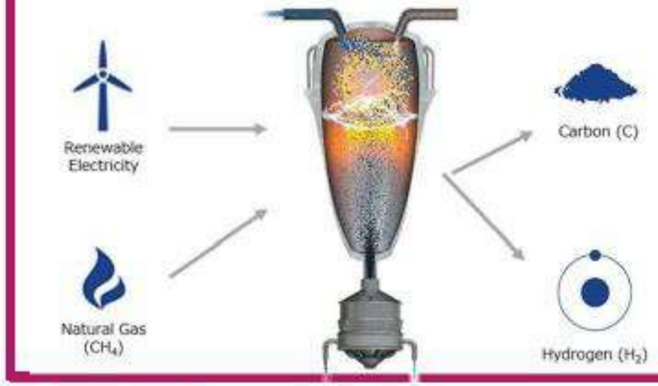
37 kJ/Mol H_2

- The reaction requires less energy input than electrolysis
- GHG footprint is low due to the absence of CO_2 emission
- Main feedstock is NG, allowing the integration to the current NG infrastructure
- Solid carbon might be valorized or considered as a waste
- Water consumption is intrinsically low

Carbon waste for 1 kg of H2	Pyrolysis	SMR+CCS
Mass	3 kg of solid carbon	9 kg of CO_2

Plasma Pyrolysis

Electric power to ignite a plasma in CH_4 gas generating $H_2 + C$

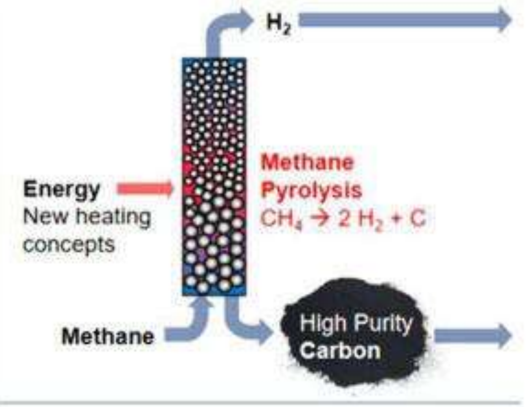


Thermal Pyrolysis

Molten salts or metals baths to decompose CH_4 into $H_2 + C$

Catalytic Pyrolysis

Catalytic decomposition of CH_4 in a fluidized bed



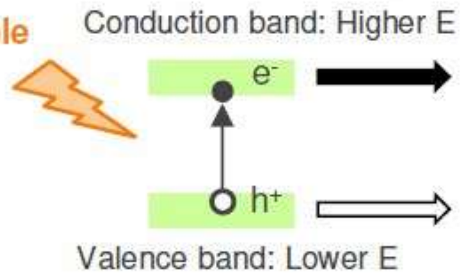
4 - METHANE PYROLYSIS –THERMOCHEMICAL DECOMPOSITION OF METHANE MOLECULE INTO H_2 & SOLIDE CARBON

	Plasma pyrolysis	Thermal pyrolysis	Catalytic pyrolysis
Development status	Commercial demonstrator (for Carbon black prod)	Lab scale	Demonstrator
TRL	5-9	3-5	4-7
Current max. H_2 capacity	~10^4 kg H_2 / day (MONOLITH)	~10 kg H_2 / day (lab) (C-ZERO)	~ 10^3 kg H_2 / day (HAZER)
Main actors	MONOLITH wintershall dea PLENESYS Plasma Energy Systems GAZPROM spark decarbonizes MITSUBISHI HEAVY INDUSTRIES	POLITÉCNICA KIT Karlsruher Institut für Technologie DBI GUT Gas- und Umwelttechnik GmbH C ZERO TNO engie	BASF We create chemistry Linde thyssenkrupp hte BFI tu technische universität dortmund HazerGroup

5 - SOLAR PHOTOCATALYTIC PROCESSES : DECREASE OR AVOID ELECTRICAL POWER NEED AND GHG EMISSIONS

In such a system, a photoabsorber (typically a semiconductor) **absorbs light, which** leads to the **separation** of positive (h^+) and negative charges (e^-)…

UV-visible light



Conduction band: Higher E

e^-

h^+

Valence band: Lower E

Reduction:

$4\,H^+ + 4\,e^- \rightarrow 2\,H_2$

Oxidation:

$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^-$

(Reactions in acidic or neutral media)

… making them available for **redox reactions** to produce H_2 from water.

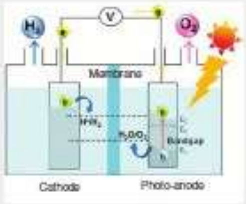
This basic concept is utilized in several technologies:

PhotoCatalysed (PC) water splitting

This system is the simplest and consists typically in a photocatalyst immersed in a solution at the surface of which the reactions take place. O_2 and H_2 must be further separated.

Photo-ElectroChemical (PEC) water splitting

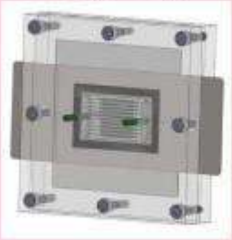
The system is based on electrolysis principle, where anode and/or cathode are implemented with photocatalysts. Compared to the photocatalysed water splitting, this system is electro-assisted, which allows to increase the current for higher yields.



Photovoltaic-ElectroChemical (PV-EC) water splitting

This last one is often associated to PC and PEC processes. It consists of an electrolyzer equipped with an integrated III-V PV cell.

5 - SOLAR PHOTOCATALYTIC PROCESSES : DECREASE OR AVOID ELECTRICAL POWER NEED AND GHG EMISSIONS

	Domen et al.	**XJTU**	**Engie Nanoptek**	**Sun Hydrogen**	**JCAP**	**KU LEUVEN**	**EPFL SoHHytec**
Technology	**PC** (PhotoCatalysis)		**PEC** (Photo-ElectroChemical) water splitting		**PV-EC** (Photovoltaic-ElectroChemical) water splitting		
TRL	3	4	6	4	3	5	5
Demonstrator Capacity (*)	4.10^{-4} kg/day	2.10^{-3} kg/day	2.10^{-1} kg/day	n.a.	n.a.	2.10^{-2} kg/day	3.10^{-1} kg/day
Catalyst known stability	Few hrs	> 1 year	> 10 year	> 1 month	> 1 month	n.a.	> 1 month
Dimensions	1 m²  	Few m² 	5 panels of 1.8 m² each 	~0.2 m² joined units 	Lab cell 	~1.3 m² 	Lab cell + 7m solar concentrator 

(*) Considering 1760 h of sun illumination per year

6 - BIOLOGICAL PROCESSES : USE MICROORGANISMS AND LOW-COST INTRANT AS BIOMASS, WATER OR LIGHT TO PRODUCE HYDROGEN

Fermentation processes

Macro-nutrients from biomass
Carbohydrates,
Proteins,
Lipids

Bacteria

H_2 + short molecules (alcohols, simple sugars, Volatil Fatty Acids…)

There are different technologies of fermentation :

- **Dark fermentation** (fermentation without light), substrate used is complex organic matter. A large scale of bacteria can perform dark fermentation.
- **Photo fermentation** (fermentation assisted by light) ; substrate used is small organic acid
- **MEC** (fermentation assisted by a low electrical current) : substrate used is simple carbon source : short molecules from C2 to C6 (Volatile Fatty Acids, single sugar, alcohols…)

➔ Photofermentation and MEC have to be coupled with a first step of dark fermentation in a two-step process.

Biophotolysis

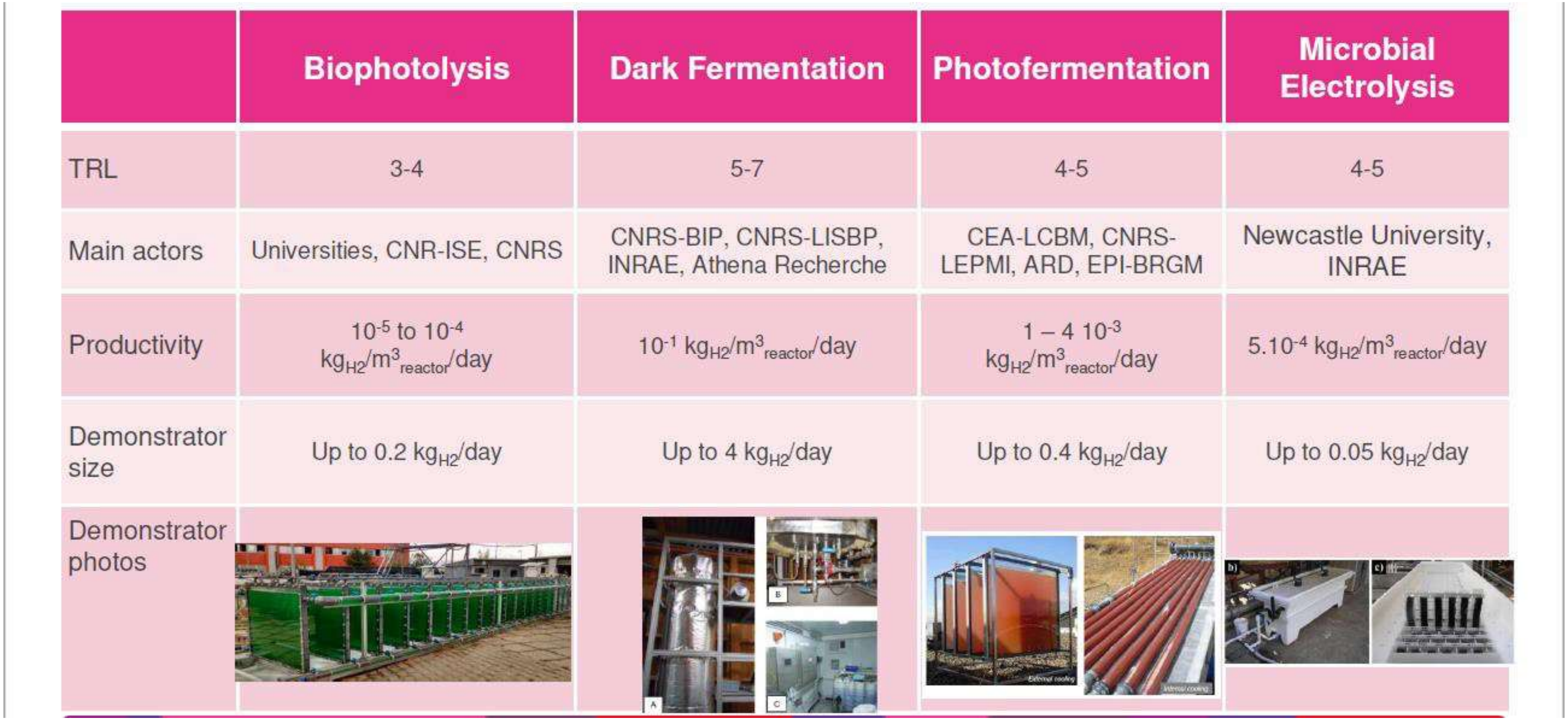
Cyanobacteria

Green Algae

Biophotolysis (direct or indirect) :
H_2 production from light and water.

Cyanobacteria & Green Algae are able to split water into H_2 and O_2 through their hydrogenase or nitrogenase enzyme system.

6 - BIOLOGICAL PROCESSES : USE MICROORGANISMS AND LOW-COST INTRANT AS BIOMASS, WATER OR LIGHT TO PRODUCE HYDROGEN



	Biophotolysis	Dark Fermentation	Photofermentation	Microbial Electrolysis
TRL	3-4	5-7	4-5	4-5
Main actors	Universities, CNR-ISE, CNRS	CNRS-BIP, CNRS-LISBP, INRAE, Athena Recherche	CEA-LCBM, CNRS-LEPMI, ARD, EPI-BRGM	Newcastle University, INRAE
Productivity	10^{-5} to 10^{-4} $kg_{H2}/m^3_{reactor}/day$	10^{-1} $kg_{H2}/m^3_{reactor}/day$	$1 - 4\ 10^{-3}$ $kg_{H2}/m^3_{reactor}/day$	5.10^{-4} $kg_{H2}/m^3_{reactor}/day$
Demonstrator size	Up to 0.2 kg_{H2}/day	Up to 4 kg_{H2}/day	Up to 0.4 kg_{H2}/day	Up to 0.05 kg_{H2}/day
Demonstrator photos		A B C		b) c)