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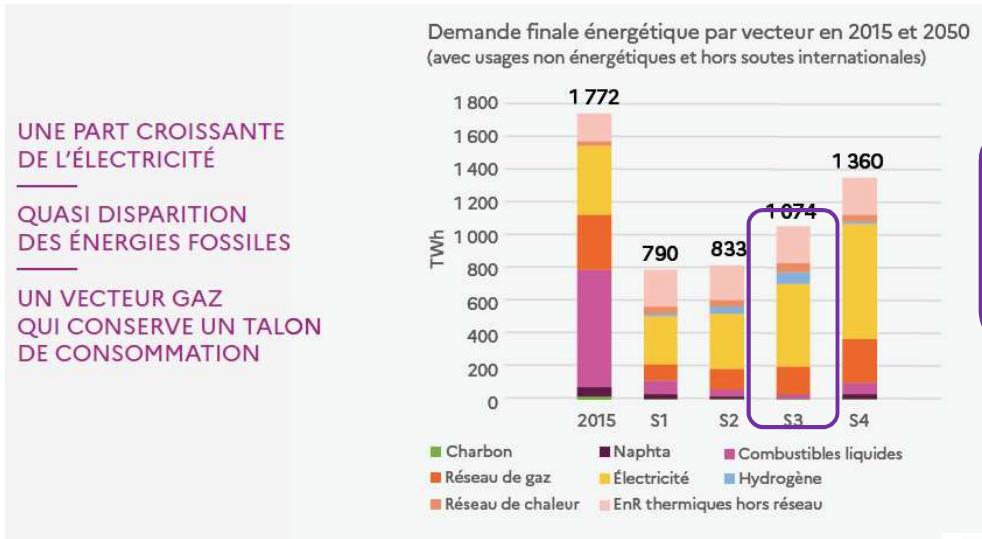
Club Pyrogazéification

Présentation des technologies de méthanation : grands principes et caractéristiques techniques, quelques exemples d'acteurs et développement

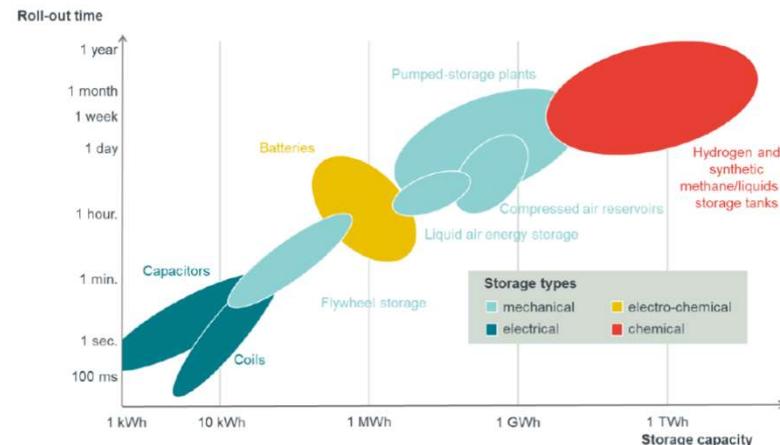
3 / 6 / 2022

**F. Ducros
G. Geffraye**

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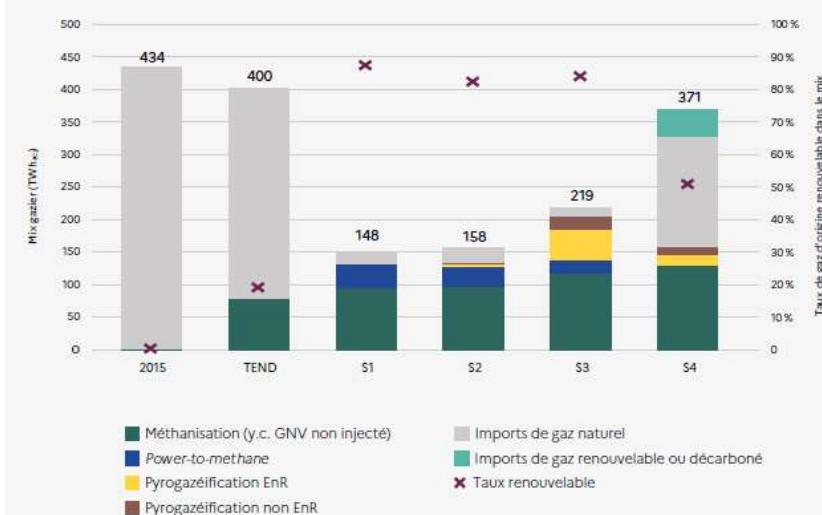
sources: INTERNATIONAL ASPECTS OF A POWER-TO-X ROADMAP A report prepared for the World Energy Council Germany



En 2050 – Scénario 3 :

Le mix de la consommation d'énergie finale est composé de 517 TWh d'électricité, 290 TWh de chaleur, **161 TWh de gaz** et 36 TWh de combustibles liquides.

Graphique 18 Mix gazier en 2015 et en 2050 pour les cinq scénarios ADEME (référence et variante gaz haut)



METHANE SYNTHESIS

Sabatier reaction : **equilibrated, highly exothermic, and catalyzed by metals :**



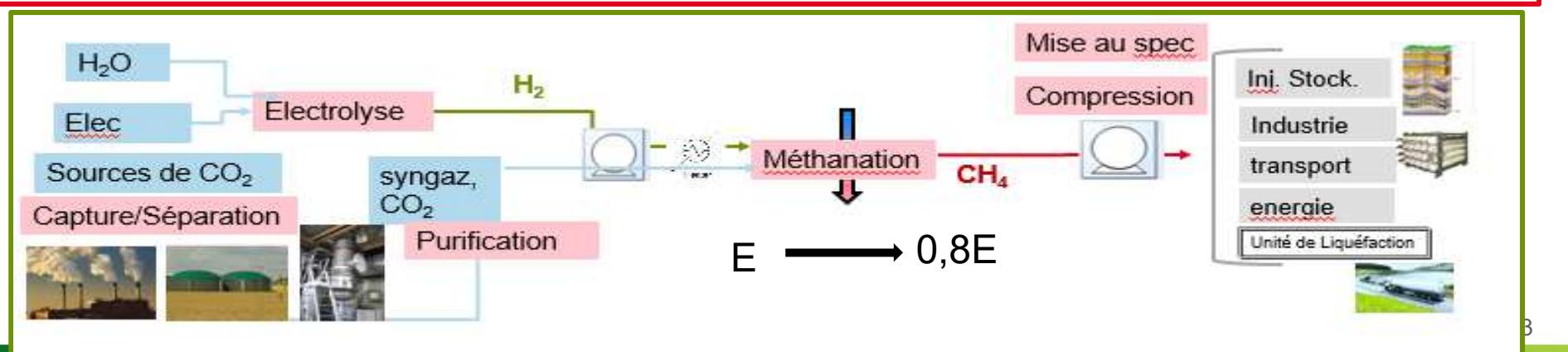
Direct path



Indirect path



- 1902: CO and CO₂ methanation processes discovered by Sabatier et Senderens
- 1970s: CO methanation applied for the production of SNG using syngas from coal gasification.
→ several methanation concepts developed. (Kopyscinski, Schildhauer, et Biollaz 2010)
- 1980s: CO₂ methanation processes focused on the use of coke oven gas or blast furnace gas
→ Due to high efforts for the gases cleaning, few concepts reached a commercial scale.
- Beginning 21st century: CO₂ methanation processes gained new attention at research institutions and in industry
Over the last 50 years, several methanation concepts have been developed.



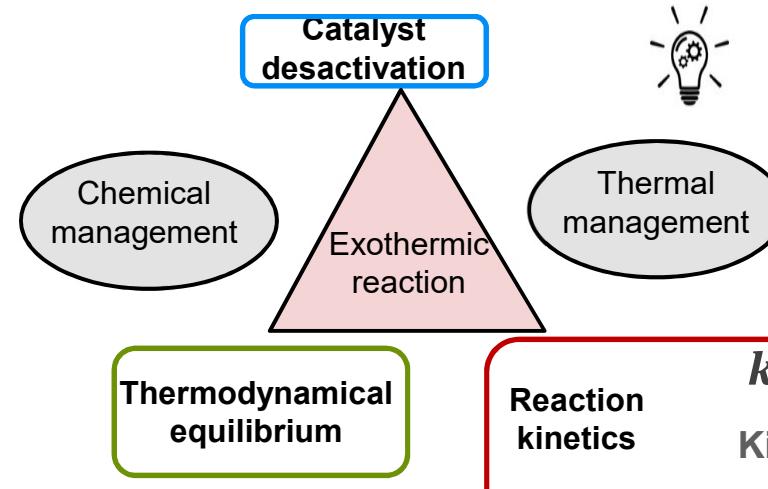
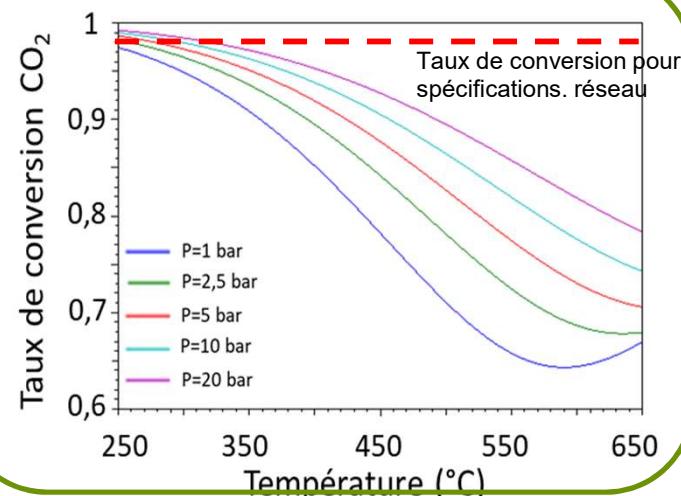
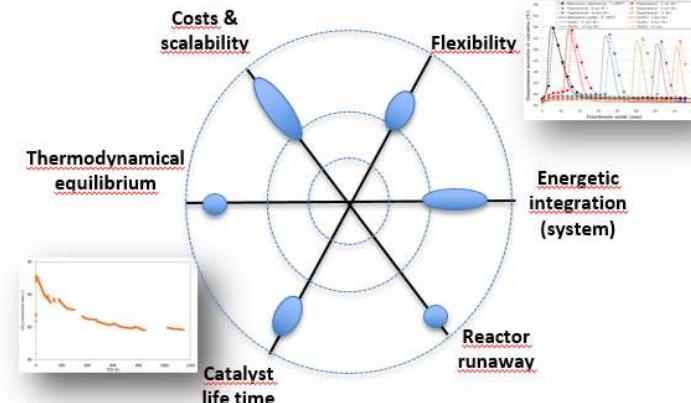
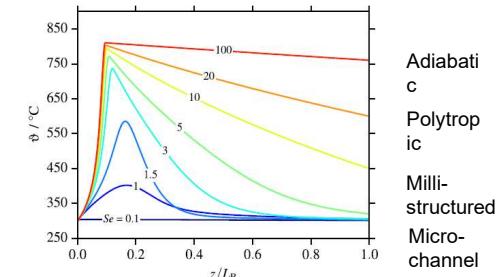
CATALYTIC METHANE SYNTHESIS : a trade-off between

$\text{Ni}/\text{Al}_2\text{O}_3$

CO and CO_2 methanation : **finely dispersed nickel on an oxide support with a large specific surface area (alumina)**

Deactivation issues (leading to unwanted shut-down of the PtG unit and an increase of the maintenance costs)

- **Poisoning** : (chemisorption of poisons on reactive sites (H_2S , SO_2))
- **Thermal degradation (Sintering)**
- **Fouling** (Carbone deposition)



$$k = k^\circ \cdot e^{-E_a/RT}$$

Kinetics enhanced at high temperature

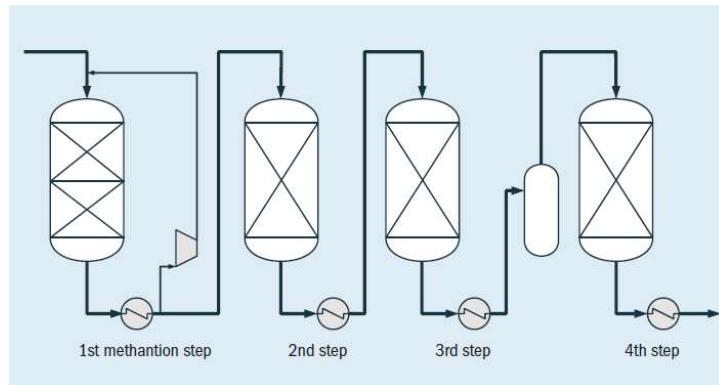
Interest to control T,P as much as possible

METHANE SYNTHESIS & REACTORS

The catalytic methanation reactors are either state of the art technologies adapted from large scale stationary Coal-To-SNG systems, or new concepts designed to reach the specific requirements for smaller scale, more compact units and unsteady operation due to fluctuating availability of renewable hydrogen.

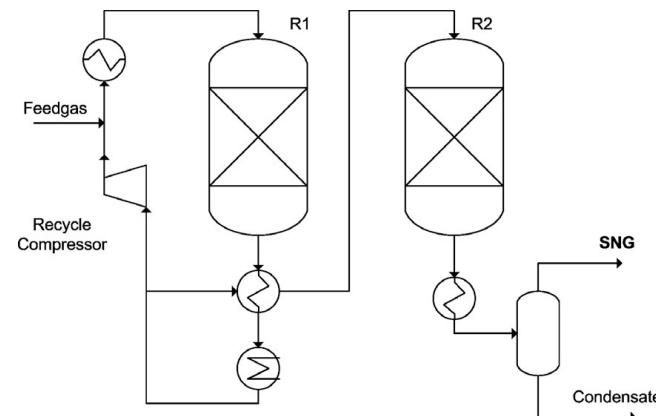
The main difference between the methanation technologies is the temperature profile inside the reactor.

Réacteurs adiabatiques en série



TREMP (Haldor Topsøe) :

- ✓ Topsoe's Recycle Energy-efficient Methanation Process
- ✓ Gestion température dans le premier réacteur par recyclage des gaz ($\approx 70\%$)
- ✓ Température dans les réacteurs : 700°C (1^{er} réacteur)
→ 250°C (dernier réacteur)
- ✓ Valorisation chaleur en électricité
- ✓ Durée de vie du catalyseur ≈ 3 ans



Procédé Lurgi

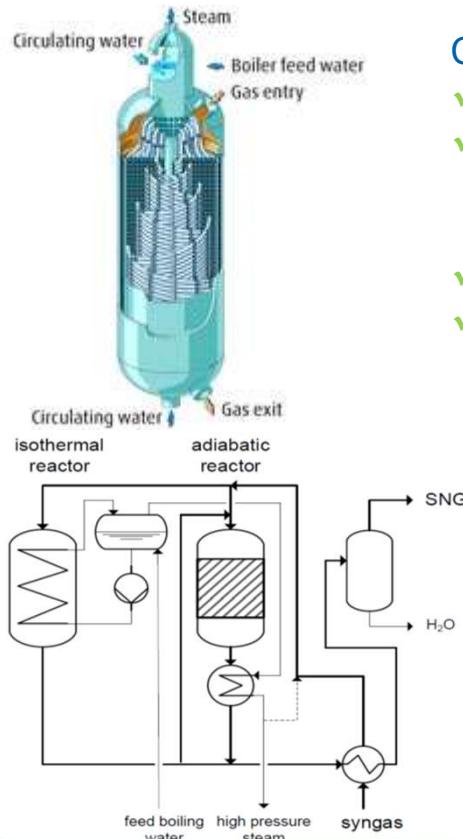
- ✓ Gestion température dans le premier réacteur par recyclage des gaz ($> 85\%$)
- ✓ Température plus faible dans le premier réacteur
- ✓ Valorisation chaleur en électricité

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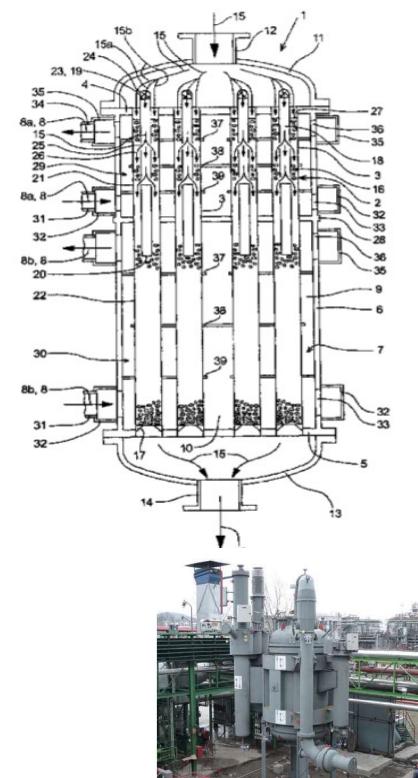
Réacteurs tube-calandre



Cooled fixed bed reactors (Linde process)

- ✓ Simple manufacturing (up to 10000 tubes)
- ✓ Lit de catalyseur refroidi par circulation d'un fluide thermique pour contrôler la température
- ✓ → need reactants dilution/staged injection
- ✓ Better thermal management when decreasing the tube diameter

réacteur DWE (MAN)



METHANE SYNTHESIS & REACTORS

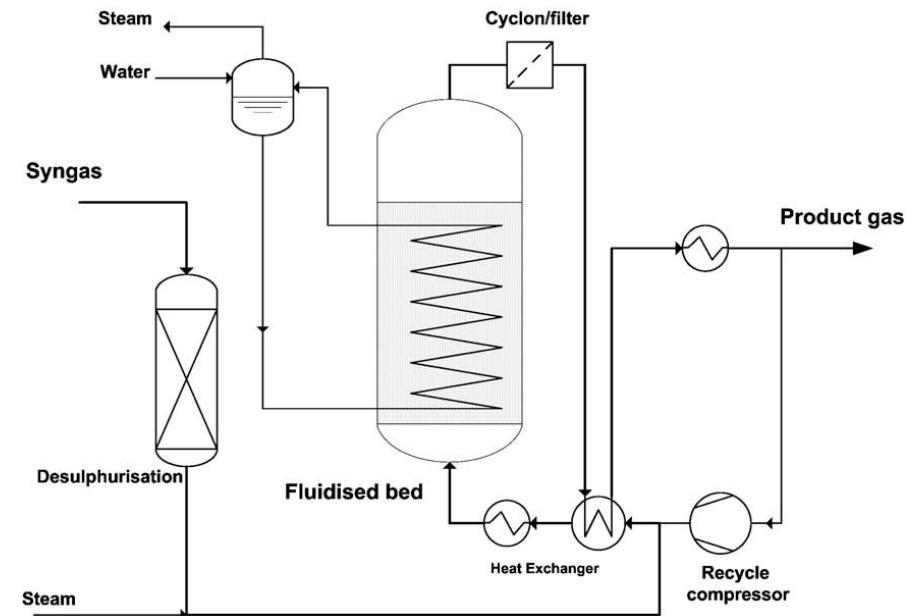
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Réacteurs lits fluidisés

- ✓ Procédé Comflux : Thyssengas et Univ. Karlsruhe
- ✓ Température isotherme dans le lit
- ✓ Gamme de débit pour le contrôle de la fluidisation
- ✓ very good heat exchange at the walls.
- ✓ catalyst may suffer from attrition
- ✓ not well adapted to load variations

- ✓ Technologies dans des démonstrateurs (Gussing et GAYA)



METHANE SYNTHESIS & REACTORS

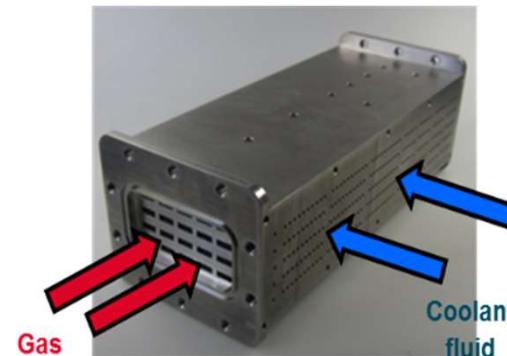
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Réacteurs structurés

Micro-structured reactors

- ✓ Intensification of heat and mass transfer
- ✓ High catalyst density and easy loading
- ✓ Intensification cross flow cooling
- ✓ Complexity for large scale appli



METHANE SYNTHESIS & REACTORS

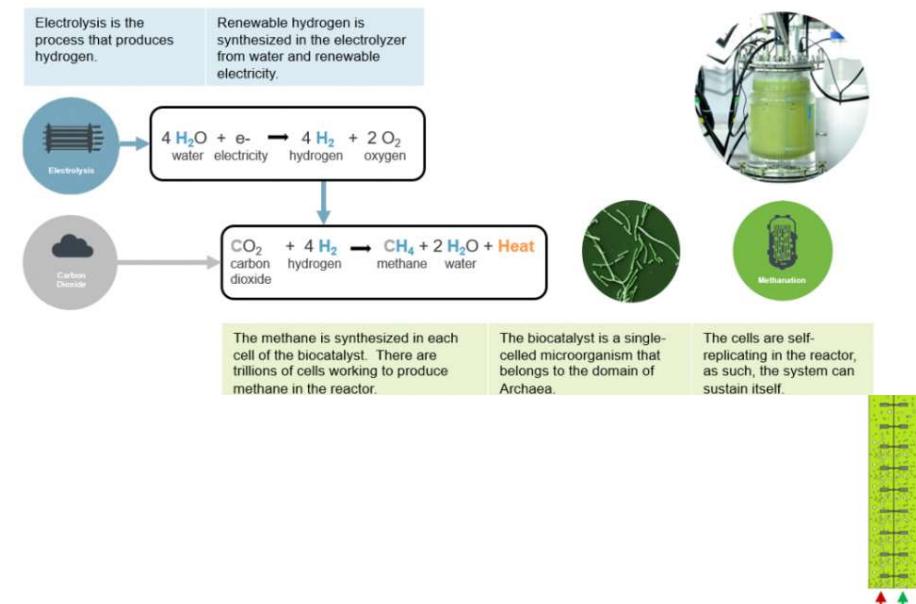
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Réacteurs biologiques (bactéries)

- ✓ Production de méthane à basse température
- ✓ CAPEX potentiellement plus faible
- ✓ Tolère mieux les impuretés
- ✓ Conversion de H₂ et CO₂ par des bactéries en milieu aqueux vers 60°C (refroidissement car réaction exothermique)
- ✓ Solubilité du CO₂ et l'H₂ limitée en phase aqueuse
- ✓ Energie d'agitation nécessaire pour assurer un transfert de masse suffisant (Pas d'information validée sur l'énergie d'agitation par Nm³ CH₄ produit)
- ✓ VVH ≈ 10-50 h⁻¹ : faible compacité

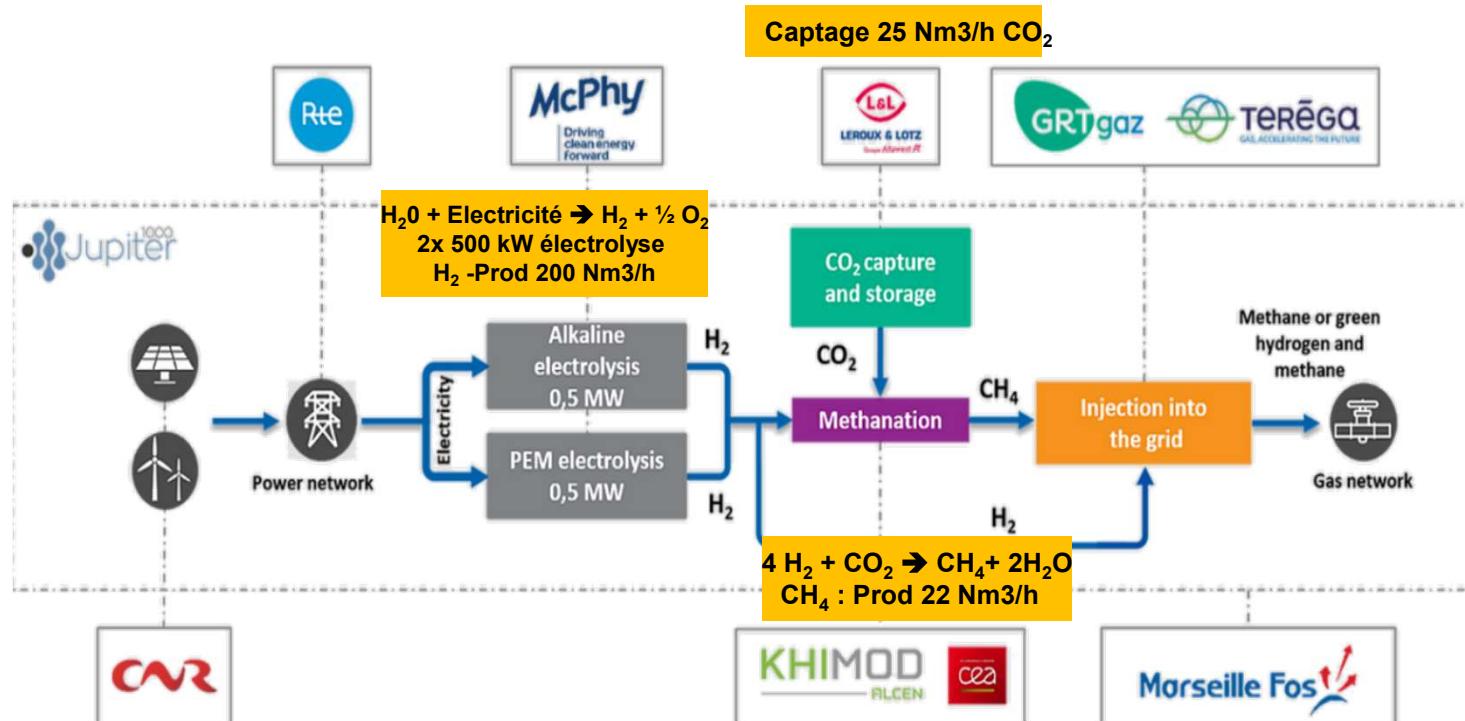
<https://www.electrochaea.com/technology/>



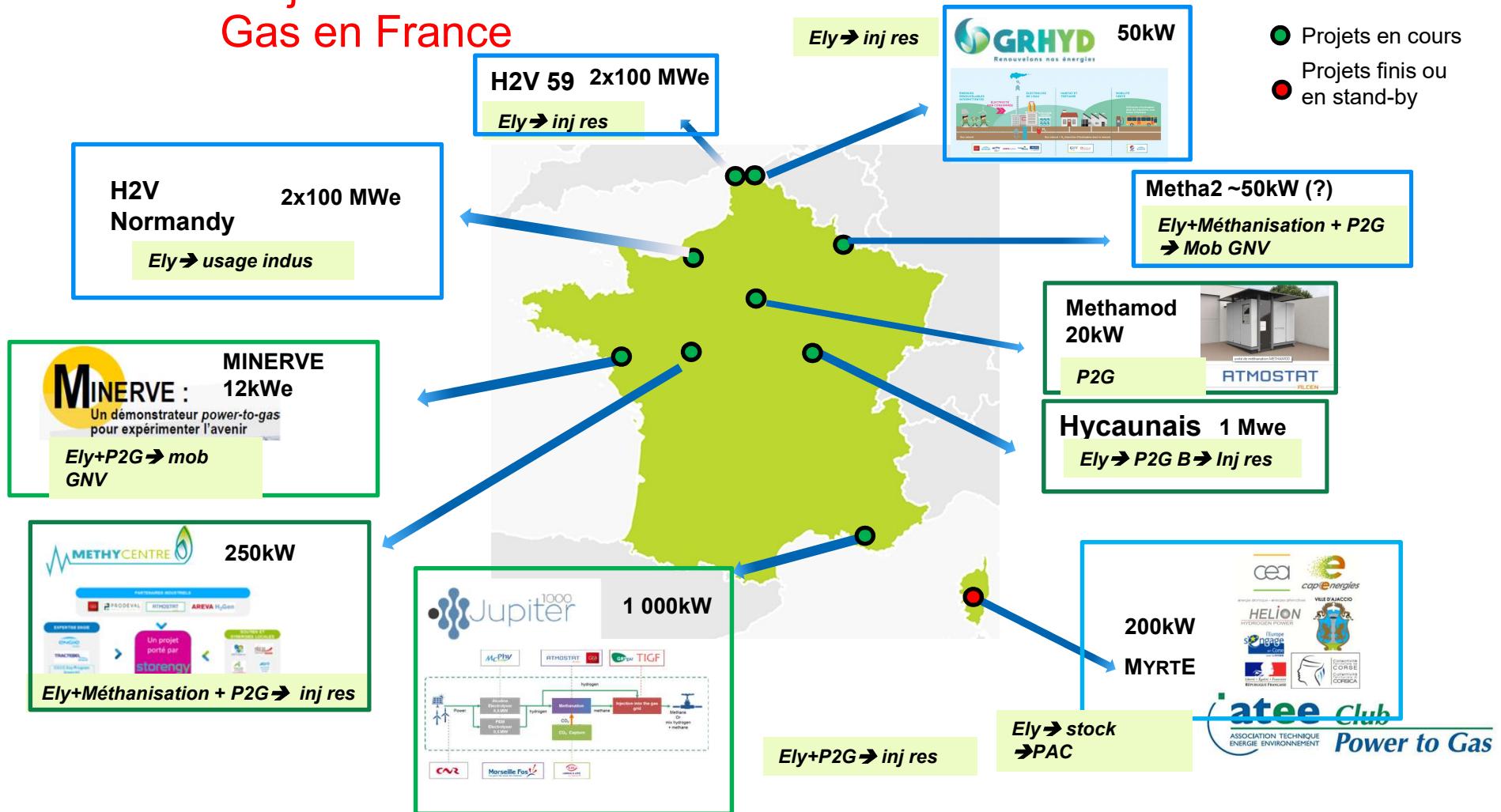
METHANE SYNTHESIS & POWER TO METHANE PROJECTS

Project	Country	Power Mwe	year	Methanation type / concept	Constructor	H2	CO ₂
e-Gas-AUDI	DE	6	2013	One tubular Catalytic Molten salted cooling	MAN	Alkaline electrolysis	Biogas Amine absorp
CO ₂ _SNG	PL	0.12	2018	Millistructured reactors (2 stages)	Atmostat	Alkaline electrolysis	Flue
Biocat	DK	1	2016	biologic	Electrochea	Alkaline electrolysis	Biogas
SUNFIRE-HELMET	DE	15kW	2017	Two catalytic fixed bed	KIT design	SOEC	
STORE&GO Falkenhagen	DE	1	2016-2020	2 catalytic reactors: Honeycomb and tubular	Thyssenkrupp	Alcalin	From bioethanol
STORE&GO Solothurn	CH	0.7	2016-2020	Biologic	Electrochea	PEM	From waste water
STORE&GO Troia	It	0.2	2016-2020	Millistructured catalytic reactor (recycling)	KHIMOD	PEM	DAC
JUPITER 1000	Fr	1	En cours	Millistructured catalytic reactor	KHIMOD	Alkaline and PEM	Flue
Great Plains Synfuels Plant	USA	1500		Lurgi methanation	Air liquid (lurgi)		
GOBIGAS	Sweden	20		TREMP	Haldor Topsoe		
				Vesta	Clariant and Foster wheeler		
Fuxing and Xinwen projects	China	4billion m3/y		HICOM	JM		
				Linde isothermal reactor	Linde		

METHANE SYNTHESIS & JUPITER 1000



- Projets de démonstration de Power to Gas en France



CONCLUSIONS

Méthanation – méthaneurs

- Système de conversion (Matures, ... Améliorables...)
- Plusieurs marchés : réseaux / stockage / mobilité ?
- Intégrant plusieurs filières potentielles
- Power 2 Gas \leftrightarrow Jupiter 1000
- Power&Biomass 2 Gas
 - Méthanisation/Méthanation \leftrightarrow Méthycentre
 - Pyrogazéification/Méthanation \leftrightarrow GoBiGas

Coûts de production dépendant des hypothèses mais couramment « autour de 100-150 Euros / MWh » avant 2021.

...ACV...

