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**“Catalytic hydrogenation of carbon dioxide (CO<sub>2</sub>) to  
methane (CH<sub>4</sub>): Current status and perspectives”**

CHANIA

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## **“Catalytic hydrogenation of carbon dioxide (CO<sub>2</sub>) to methane (CH<sub>4</sub>): Current status and perspectives”**

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## Περίληψη

Η αλόγιστη χρήση των ορυκτών καυσίμων έχει οδηγήσει σε μια άνευ προηγουμένου αύξηση της συγκέντρωσης του διοξειδίου του άνθρακα ( $\text{CO}_2$ ) στην ατμόσφαιρα. Αυτή η αύξηση παίζει τον σημαντικότερο ρόλο για την επίταση του φαινομένου του θερμοκηπίου και την επικείμενη κλιματική αλλαγή. Με τις επιπτώσεις της κλιματικής αλλαγής να γίνονται όλο και πιο φανερές, η ανάγκη μιας βιώσιμης λύσης βρίσκεται στην κορυφή των επιστημονικών και πολιτικών προτεραιοτήτων. Πολλές από τις προτεινόμενες λύσεις, συνεπάγονται με την αντικατάσταση των συμβατικών μορφών ενέργειας και την αναζήτηση περιβαλλοντικά φιλικών και ενεργειακά αποδοτικών νέων τεχνολογιών. Ανάμεσα στις λύσεις βρίσκεται και η μετατροπή του  $\text{CO}_2$  σε χρήσιμα χημικά προϊόντα ή/και καύσιμα όπως το μεθάνιο ( $\text{CH}_4$ ) ή αλκοόλες.

Η παρούσα Διπλωματική Εργασία (ΔΕ) εστιάζει στη καταλυτική μεθανοποίηση του  $\text{CO}_2$  ως μία εναλλακτική λύση. Ο σκοπός αυτής της έρευνας είναι να αναλύσει την αποδοτικότητα της διεργασίας χρησιμοποιώντας χαμηλού κόστους υλικά και υψηλής δραστηριότητας καταλύτες. Σε αυτό το πλαίσιο, οι παράμετροι που επηρεάζουν την απόδοση της αντίδρασης του Sabatier εξετάζονται. Έπειτα, η συλλογή  $\text{CO}_2$  και παραγωγή  $\text{H}_2$  αξιολογούνται, με έμφαση στις τεχνολογίες που δεν απαιτούν χρήση ορυκτών καυσίμων. Σε αυτήν την εργασία εξετάζεται επίσης η απόδοση της αντίδρασης για διάφορα καταλυτικά υλικά, καθώς και το περιβαλλοντικό της αντίκτυπο και η οικονομική της βιωσιμότητα. Τα ευρήματα αυτής της έρευνας παρέχουν πολύτιμες πληροφορίες για τις δυνατότητες της καταλυτικής μεθανοποίησης του  $\text{CO}_2$  ως μια βιώσιμη λύση για την μείωση των εκπομπών  $\text{CO}_2$  και στην άμβλυνση των επιδράσεων της κλιματικής αλλαγής.

## Abstract

The excessive use of fossil fuels has led to an unprecedented increase in the concentration of CO<sub>2</sub> in the atmosphere. This increase plays the most important role in exacerbating the greenhouse effect and contributing to imminent climate change. As the irreversible effects of climate change become increasingly apparent, the need for a sustainable solution is now at the forefront of both scientific and political agendas. Many of the solutions suggested, entail the substitution of conventional energy sources and the development of environmentally friendly and energy-efficient technologies. Among these solutions is the idea of converting CO<sub>2</sub> into useful chemical products and/or fuels, such as methane (CH<sub>4</sub>) or alcohols.

This diploma thesis focuses on CO<sub>2</sub> catalytic methanation as an alternative solution. The objective of this research is to analyze the efficiency of the process using low-cost materials and highly active catalysts. Within this context, the parameters that affect the efficiency of the Sabatier reaction are examined. Then, CO<sub>2</sub> capture and H<sub>2</sub> production are reviewed, by focusing on technologies that are not powered by fossil fuels. The study also examines the performance of the reaction over various catalytic materials, as well as its environmental impact and financial sustainability. The findings of this research provide valuable insight into the potential of CO<sub>2</sub> catalytic methanation as a sustainable solution to reduce CO<sub>2</sub> emissions and mitigate the effects of climate change.

## 1. Introduction

Last decades, the intensification of industrial activities, urbanism and increase in human population have led to a surge of energy demand around the globe. Since the dawn of the first industrial revolution, humans have developed the exploitation of fossil fuels in order to cover our energy demands, as even in modern times they make up to 80% of global energy production. The consumption of fossil fuels however is the driving force for greenhouse gas (GHG) emissions in the atmosphere, mostly CO<sub>2</sub>, triggering a domino effect of consequences. GHG effect is responsible for global temperature rise, leading to climate change, influencing ecosystems and the varieties of plants, animal species and seasonal events timing in them, affecting human health and economy through extreme weather conditions.

To get a better grip of the surge of CO<sub>2</sub> emissions in the atmosphere, in 1960 the annual emissions were 11 billion tons [1], where in 2022 reached 36.8 billion tons [2]. Future projections are pessimistic as they estimate an increase to 43.08 billion tons of CO<sub>2</sub> emissions in 2050 [3], as for energy consumption, a 50% increase in global demand is projected, with industrial consumption reaching 305 quadrillion Btu [3].

With the GHG effects becoming more remarkable as the years go by, the Paris Agreement, which came into effect in 2016, is binding 196 parties to face climate change. More precisely, the main objective of the agreement is to maintain global temperature increase below 2°C from pre-industrial levels, setting the limit at 1.5°C. This agreement has motivated researchers to focus on carbon capture and utilization (CCU) technologies that aim to recycle CO<sub>2</sub> and potentially produce energy.

With these into perspective, production of alternative fuels from CO<sub>2</sub>, have been in the spotlight. CO<sub>2</sub> methanation have quickly gained ground as potential solution, producing CH<sub>4</sub>, which has one of the highest calorific values among fuels (50-55 kJ/kg[4]), in a process capable of being powered solely by renewable energy sources (RES) and the product can potentially be injected into the natural gas (NG) grid, using the existing infrastructures for storage and transportation [5].

Over the last years, several studies investigate the means and the opportunities of this process. Multiple catalytic systems have been assessed, regarding their capability of enhancing methane production. Alongside the catalysts, the thermodynamic conditions, side reactions, components concentrations and reactors play a significant role in the process outcome, leading to extensive literature reviews. Beside the maturity of the technology through research, the environmental impact of the process, the economics of such facilities and their socio-political impact must be reviewed in order for the technology to capture the attention of energy production industry.



In this thesis, CO<sub>2</sub> catalytic methanation is reviewed, with refers to the latest advances, limitations and potential. Section 2 is mainly focused on the thermodynamics of the reaction, combined with a brief reference to the timeline of the process. Section 3 and 4 analyze the CO<sub>2</sub> capture and hydrogen production respectively, followed by a detailed breakdown of the CO<sub>2</sub> catalytic methanation process in section 5. Lastly, section 6 takes a look beyond the process, reviewing Life Cycle Assessment (LCA) results, techno-economic analyses and sociopolitical reports.

## 2. Reaction analysis

### 2.1 Brief history of the reaction

In 1902, the French novelist Paul Sabatier and the chemist Jean-Baptiste Senderens were the first to document CO and CO<sub>2</sub> methanation. Using hydrogen and the oxides of carbon as reactants, combined with reduced nickel at 250 degrees Celsius, methane and water were formed.

These methanation techniques have seen numerous applications the past century. The first and most significant application was to eliminate traces of CO and CO<sub>2</sub> from production of gases like ammonia. Later in the 20<sup>th</sup> century, due to the oil crisis in the 1970's, these techniques were resurfaced, focusing on the production of synthetic natural gas (SNG) from coal and biomass [6]. In the early stages of this process, there were experiments regarding CO<sub>2</sub> methanation, using coke oven gas or blast furnace gas. However, only a few of these concepts found application.

As the environmental awareness grew in late 20<sup>th</sup> century, with the effects of CO<sub>2</sub> emissions from fossil fuels usage in the spotlight, institutes reinstated their interest to its methanation, thus reviving the most recent discoveries. In this context, Hashimoto proposed the groundbreaking concept of reforming CO<sub>2</sub> to CH<sub>4</sub>, with hydrogen extracted from seawater, as a measure to prevent global warming [7].

With no viable large-scale option to prevent the accumulation of CO<sub>2</sub> in the atmosphere up to this day, accompanied by the need of storing energy surplus, the carbon oxides methanation techniques are lately examined as a solution for converting energy surplus from renewable sources into gas, named Power-to-Gas (PtG).

Recently, the application of these methods is also examined for long-term extraterrestrial explorations in order to provide energy and water in manned missions [8] and eliminating CO emissions from proton exchange membrane (PEM) fuel cells, making them a possible source of clean and efficient power [9].

### 2.2 Thermodynamics

Carbon oxides methanation is a complex process, with many reactions taking place simultaneously. Studying the thermodynamic aspect of these reactions can hint an easier path for specific products, making reactions stand out depending on their

parameters. Moreover, readjusting reaction conditions such as pressure, temperature and components ratio can lead to a thermodynamic equilibrium of the chemical system, which achieves higher concentrations of specific products [10]–[16].

From experimental thermodynamic analyses conducted, regarding this reaction [10]–[13], [16], the optimal conditions for the reaction, are determined by the analysis of the chemical system in thermodynamic equilibrium. The estimation of the systems composition was measured with the Gibbs free energy minimization, a method based on the principle that minimum value of Gibbs free energy is achieved when the system reaches equilibrium [13].

### 2.2.1 Reactions and thermodynamic parameters

In this process several reactions take place simultaneously (Table 2.1), each defined by different thermodynamic parameters. In order to meticulously study these reactions, besides Gibbs free energy change ( $\Delta G$ ), the natural logarithm of the equilibrium constant ( $\ln(K)$ ), alongside with the enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) change are taken into consideration. These parameters interact with each other through the second law of thermodynamics and the thermodynamic equilibrium formula.

$$\Delta H = \Delta G + T\Delta S \quad (1)$$

$$K = \exp \left[ \frac{\Delta G}{RT} \right] \quad (2)$$

Table 2.1: Reactions involved in CO<sub>2</sub> methanation, thermodynamically studied at T=25°C and P = 0.1 MPa [13]

No.	Reactions	Reaction description	$\Delta H$	$\Delta S$	$\Delta G$	$\ln(K)$
1	$\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	CO <sub>2</sub> methanation	-164.747	-214.497	-141.932	24.868
2	$\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{C} + 2\text{H}_2\text{O}(\text{g})$	CO <sub>2</sub> reduction	-90.147	-91.722	-62.800	11.003
3	$2\text{CO}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) + 4\text{H}_2\text{O}(\text{g})$	CO <sub>2</sub> hydrogenation to CH <sub>3</sub> OH	-49.321	-177.109	3.484	-0.61
4	$\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$	Reverse water gas shift	41.138	42.045	28.602	-5.011
5	$2\text{CO}_2(\text{g}) + 7\text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g}) + 4\text{H}_2\text{O}(\text{g})$	CO <sub>2</sub> hydrogenation to C <sub>2</sub> H <sub>6</sub>	-264.978	-357.361	-158.43	27.759

6	$\text{CO}_2(\text{g}) + \text{CH}_4(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + 2\text{H}_2(\text{g})$	Dry reforming of $\text{CH}_4$	247.023	256.542	170.535	-29.879
7	$2\text{CO}(\text{g}) \rightleftharpoons \text{C} + \text{CO}_2(\text{g})$	Boudouard reaction	-172.423	-175.812	-120.004	21.026
8	$\text{CH}_4(\text{g}) \rightleftharpoons \text{C} + 2\text{H}_2(\text{g})$	$\text{CH}_4$ cracking	74.6	80.73	50.53	-8.853
9	$\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$	CO methanation	206	-172.452	-113.330	19.857
10	$\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$	CO hydrogenation to $\text{CH}_3\text{OH}$	-90.459	-219.153	-25.118	4.401
11	$\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{C} + \text{H}_2\text{O}(\text{g})$	CO reduction	-131.285	-133.767	-91.402	16.015
12	$2\text{CO}(\text{g}) + 5\text{H}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	CO hydrogenation to $\text{C}_2\text{H}_6$	347.254	-441.45	-215.635	37.782

According to Figure 2.1, combined with the results of the parameters that are shown at the Table 2.1, it is obvious that different groups of reactions are feasible and dominate the mixture in different temperatures.  $\text{CO}_2$  methanation (1),  $\text{CO}_2$  reduction (2), Boudouard reaction (7), CO methanation (9), CO reduction (11) are reactions with high  $\ln(K)$  values, highly spontaneous due to negative  $\Delta G$  values and besides reaction (9) are exothermic (negative  $\Delta H$  values). Consequently, these reactions are feasible and most likely to dominate during the methanation process. On the contrary, Reverse water gas shift (4), Dry reforming of  $\text{CH}_4$  (6),  $\text{CH}_4$  cracking (8) are endothermic reactions (positive  $\Delta H$ ) with positive  $\ln(K)$  values, evincing their infeasibility. From temperatures between 450 and 500°C  $\text{CO}_2$  and CO hydrogenation to  $\text{C}_2\text{H}_6$  (5,12) are becoming feasible, with them becoming infeasible again after 500°C.  $\text{CO}_2$  and CO hydrogenation to  $\text{CH}_3\text{OH}$  (10,3) are favored from lower temperatures.

In order to assess the performance of the reaction, in different conditions and with different catalysts, the following performance parameters will be examined.

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} = \left( 1 - \frac{I_{\text{CO}_2}^{\text{out}}}{I_{\text{CO}_2}^{\text{out}} + I_{\text{CH}_4}^{\text{out}} + I_{\text{CO}}^{\text{out}}} \right) \times 100\% \quad (3)$$

$$\text{CH}_4 \text{ yeild: } Y_{\text{CH}_4} = \frac{I_{\text{CH}_4}^{\text{out}}}{I_{\text{CO}_2}^{\text{out}} + I_{\text{CH}_4}^{\text{out}} + I_{\text{CO}}^{\text{out}}} \times 100\% \quad (4)$$

$$\text{CH}_4 \text{ selectivity: } S_{\text{CH}_4} = \frac{Y_{\text{CH}_4}}{X_{\text{CO}_2}} \times 100\% \quad (5)$$

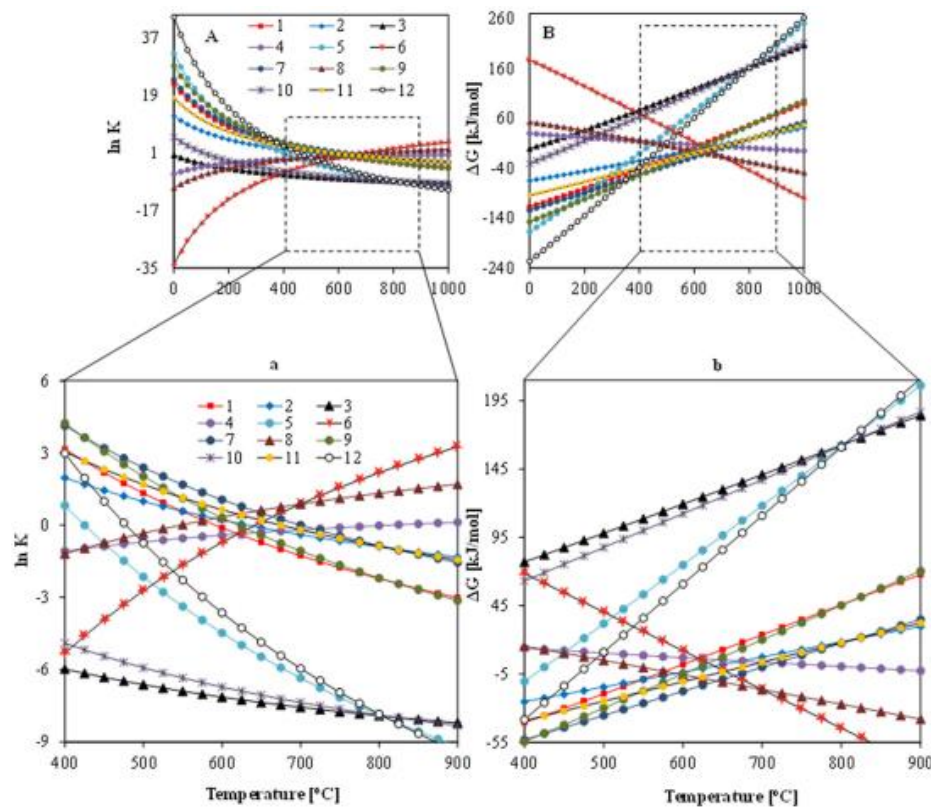


Figure 2.1 Equilibrium constant (A,a) and Gibbs free energy (B,b) graphs for different temperature values [13]

### 2.2.2 Effect of pressure and temperature

Despite the parameters mentioned above, pressure and temperature play a significant role in the concentrations that form the mixture. By increasing the pressure of a mixture that contains at least one gas reactant, it simultaneously increases the molecular concentration of the reactant, with more particle collisions taking place, accelerating the reaction. Studies prove that higher pressure favors CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity, with pressure values up to 100 bar standing out the most [10], [12], [17], [18]. On the contrary, CO selectivity decreased with the increasing pressure. By modifying the temperature with certain pressure applied, the CH<sub>4</sub> yield, and selectivity and CO<sub>2</sub> conversion are decreasing dramatically, while CO selectivity increases with reaction 4 dominating as an endothermic reaction. Meng et al. [16] studied the carbon yield produced from reactions 2,7,8 and 11, with reaction 7 account for the largest amount of carbon deposition, due to higher value of ln(K). Additionally, for 1 bar and around 575°C the carbon yield reaches the maximum value of 23%. All in all, as Hussain et al. [13] mention, carbon oxides methanation is optimized in low temperature and high pressure, where in industrial scale high temperature and low pressure is favored due to precautionary reasons. Thus, the

temperature of 300- 500°C and pressure of 3 to 10 bar are ideal for commercial application of carbon oxide hydration to  $\text{CH}_4$ .

### 2.2.3 Effect of reactants concentrations

Besides temperature and pressure, the ratio of  $\text{H}_2$  to  $\text{CO}_2$  strongly influence on the product concentrations. Figure 2.2 depicted by Miguel et al. [12] prove the correlation of  $\text{H}_2/\text{CO}_2$  feed ratio with temperature and pressure, in influencing  $\text{CO}_2$  conversion,  $\text{CH}_4$  selectivity, as  $\text{CH}_4$  and C yield as well. As it is shown, for  $\text{H}_2/\text{CO}_2$  ratio of 4,  $\text{CO}_2$  is the favored reaction, as the ratio obeys the reaction stoichiometry, with  $\text{H}_2\text{O}$  molar flow being double compared to  $\text{CH}_4$ . However, for feed ratio mentioned, for temperatures higher than 300°C and for pressure lower than 5 bar  $\text{CO}_2$  selectivity and  $\text{CH}_4$  yield drops with a small fraction of CO forming (yield of  $\text{CO} < 1\%$ ) through reaction 4. With ratios decreasing, so does  $\text{CO}_2$  conversion,  $\text{CH}_4$  yield and selectivity percentages. This derives from surplus of unconverted  $\text{CO}_2$ , since  $\text{H}_2$  is less than required from the stoichiometry of the reaction. Moreover, for the feed ratios of 2 and 3, methane yield peaks around 200-250°C, with  $\text{CO}_2$  selectivity decreasing for lower pressure and higher temperature, while  $\text{CH}_4$  selectivity increases with higher temperature. The most interesting observation is that for the feed ratios of 2 and 3, coke formation is notably increased, with the smaller ratio leading to C yield around 55% for 150°C.

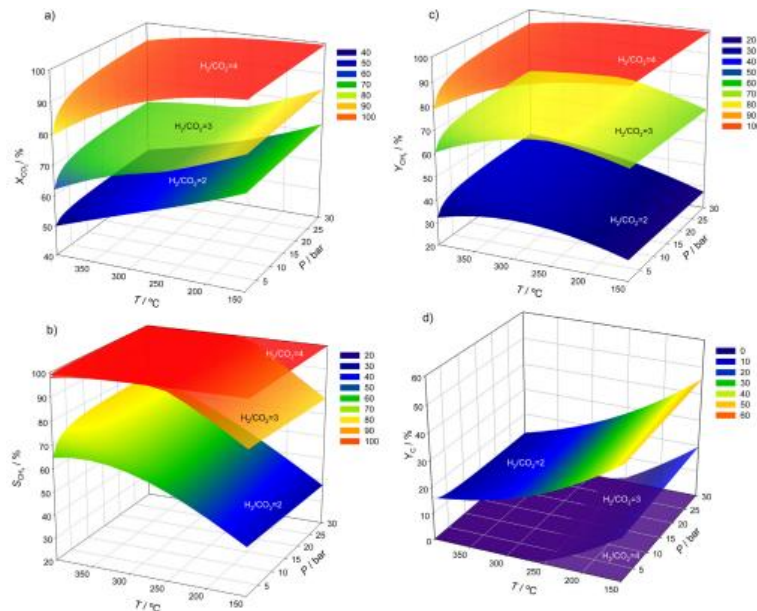


Figure 2.2 Contour graph of temperature, pressure and  $\text{H}_2/\text{CO}_2$  ratio effect on a)  $\text{CO}_2$  conversion, b)  $\text{CH}_4$  selectivity, c)  $\text{CH}_4$  yield, d) Carbon yield [12].

### 2.2.4 Products and other gases effect

Studies also examine the effects of individual and conjoint content of  $\text{H}_2\text{O}$  and  $\text{O}_2$  in the reaction. Steam with absent  $\text{O}_2$ , as a product of  $\text{CO}_2$  methanation decreases the  $\text{CO}_2$  conversion, as it is one of the products of reaction 1. For the  $\text{H}_2/\text{CO}_2$  ratio of 4,  $\text{CO}_2$  selectivity decrease is not as noticeable as for the ratio of 3, while  $\text{CH}_4$  selectivity reaches almost 100% for  $\text{H}_2/\text{CO}_2$  ratios examined. According to Miguel et al. [12] the existence of water decreases coke formation at temperatures below  $250^\circ\text{C}$ , alongside with the ability of controlling the heat produced of the exothermic reaction of methanation. Small concentration of oxygen is found in coal gasification and emanating flue gas.  $\text{O}_2$  has the ability of reacting with  $\text{H}_2$  and  $\text{CH}_4$ , leading to a decay in  $\text{CO}_2$  and  $\text{CO}$  conversion especially in temperatures higher than  $500^\circ\text{C}$ . Similar results found for  $\text{CH}_4$  selectivity as for pressure equal to 1 bar, selectivity plummeted for increasing temperature and  $\text{O}_2$  concentration values, while for pressure set at 30 bar  $\text{CH}_4$  selectivity dropped steadily for the same modifications. As  $\text{O}_2$  reacts with  $\text{H}_2$  and  $\text{CH}_4$  forming  $\text{H}_2\text{O}$ , having  $\text{O}_2$  and  $\text{H}_2\text{O}$  simultaneously in the feed leads to further decay in carbon oxides conversion, with temperatures above  $300^\circ\text{C}$  in atmospheric pressure a slight  $\text{CO}$  is noted ( $\text{CO}$  yield  $<1\%$ ), which can be avoided with an increase of pressure.

### 3 Carbon Dioxide Capture

#### 3.1 Capture technologies

Carbon dioxide is crucial for methane production, as the only carbon containing reactant. Its production is mostly associated with fossil fuel combustion, providing energy for human activities throughout the centuries. However, it is mostly contained in a mixture of gases and usually released to the atmosphere. Thus, CO<sub>2</sub> must be collected from either an emitting source or from the atmosphere. Such technologies have been under the academic and the industrial microscope the last decades, with numerous plants operating globally. CCU and Carbon Capture and storage (CCS) technologies include a plethora of methods for CO<sub>2</sub> capture, separation and transportation [17]. However, the high cost of these technologies and the CO<sub>2</sub> produced to meet the energy demands of such facilities, referred as energy penalty, are the most challenging parameters.

CO<sub>2</sub> formed as a result of combustion and in order to efficiently extract it, a different removal process is being implemented for every type of combustion process. There are many available technologies, but they usually make up 70-80% of the total CCS project cost, with the majority of studies focusing on the reduction of the overall operating cost [18]. There main CO<sub>2</sub> technologies are the options associated with combustion processes (post-combustion, pre-combustion, oxyfuel).

Post-combustion process, is usually applied to already existing power plants, removing CO<sub>2</sub> from flue gasses after combustion has taken place. The CO<sub>2</sub> concentration in combustion flue gas is scarce (for coal-fired plant is 7-14% v/v, while for gas-fired boilers is as low as 7-8% and for gas-fired turbines is 2-4%), leading to limited CO<sub>2</sub> capture efficiency while capturing large quantities of dust and impurities, combined with a high energy penalty and operational cost. However, this technology can extract high purity CO<sub>2</sub> from enhanced oil recovery, urea production and food/beverage plants, with the largest operating unit capable of recovering up to 800t/day. Kanniche et al. [19] reported an estimated 32% increase in electricity cost for gas fired plants and 65% increase in coal fired plants.

In pre-combustion process, the fuel in use, usually coal or NG is pre-treated before the combustion. In this process, the fuel is being converted into syngas. For NG, CH<sub>4</sub> is reformed (Eq.6) with H<sub>2</sub>O, producing CO and H<sub>2</sub>, while coal is being gasified (Eq.7) under low oxygen level. Then syngas is taking part in the water gas shift reaction (Eq.8), reacting with steam and producing CO<sub>2</sub> and H<sub>2</sub>.





The flue gas produced contains a CO<sub>2</sub> concentration greater than 20% v/v, the absence of N<sub>2</sub> provides a clean CO<sub>2</sub> source, while the gas mixture is under pressure making the process more energy and consequently financially efficient [19]. After CO<sub>2</sub> separation, H<sub>2</sub> is burnt, reacting with O<sub>2</sub> and producing H<sub>2</sub>O, generating energy for the plant. Studies prove the high efficiency of this process, with an efficiency loss of 7-8% for its application to Integrated Gasification Combined Cycle (IGCC) coal power plant, while pre-combustion application on advanced combined cycle gas turbine plants, operating with NG achieved 80% CO<sub>2</sub> capture efficiency [20].

In oxyfuel combustion, cryogenic air separation provides the system with pure oxygen mixed with flue gases, eliminating nitrogen products generated from combustion with air, producing CO<sub>2</sub> with higher partial pressure in coal combustion. The products are primarily CO<sub>2</sub>, H<sub>2</sub>O, with particulates and SO<sub>2</sub> often found in the flue gases, which are eliminated through electrostatic precipitation and desulphurization methods respectively. Then CO<sub>2</sub> and H<sub>2</sub>O are being separated after water condensation leading to 98% CO<sub>2</sub> purity which then is transported in supercritical state. On the downside, air separation is increasing the energy demands and the operational cost of the plant, leading to an energy penalty potentially over 7%, compared to a plant without CCS, as leftover impurities in the CO<sub>2</sub> streamline may cause vibrations and shock loads in the pipe, which can be avoided with further dehydration [20], [21].

After sidetracking the flue gas from the plant, and capturing a rich CO<sub>2</sub> gas mixture, a separation process takes places, producing pure CO<sub>2</sub>. The technologies developed are primarily studied are absorption, adsorption, cryogenic distillation, membrane separation, hydrate-based separation and chemical looping combustion.

### 3.2 Separation technologies

In absorption process, an amine liquid sorbent or solid matrix is used to separate CO<sub>2</sub> from the product gas. This process relies on absorbing only CO<sub>2</sub>, which later can be obtained from the solution and the sorbent residue is recycled to absorb CO<sub>2</sub> from newly produced flue gas. Monoethanolamine (MEA), Diethanolamine (DEA), Diglycolamine (DGA), Methyl diethanolamine (MDEA), Piperazine (PZ), K<sub>2</sub>CO<sub>3</sub> or mixture of amines are typically used [22], with MEA being the most favored solvent for this process, as it is efficient and economic. Moreover, MEA finds applications in the chemical industry for over 60 years, with extensively studied properties and easy regeneration process. However, oxygen and sulfuric acid leftovers can corrode the infrastructure and lead to limited solvent regeneration, while high temperatures can degrade the solvents, forming nitrosamines and nitramines, posing a threat to human health and the environment. Consequently, alternative solvents are being studied, with aqueous ammonia posing as the most efficient solution in matters of energy and cost [17], [20], [23].

In the adsorption process, a heterogeneous process captures gas CO<sub>2</sub> molecules from flue gases, as they get trapped by a solid sorbent or physi-sorbed [23]. Flue gases, consists of multiple nitrogen, carbon and sulfur gases, in varying concentrations. Multiple materials have proven ability of selectively adsorbing CO<sub>2</sub> in cracks, pores or on their surface, under specific thermodynamic conditions.

In order to determine the optimum sorbent, which is characterized with high selectivity, low cost, capability to regenerate, combined with mechanical and chemical strength, countless materials have been tested. Recent studies focus on activated carbon (AC), activated carbon fiber (ACF), carbon nanotubes (CNT), organic polymers, molecular sieves, zeolites, metal organic frameworks (MOFs), microporous coordination polymers (MCPs), zeolitic imidazolate frameworks (ZIFs), metal oxides and graphene and graphene-based materials [24]. However, every material has parameters limiting their large-scale application, with surface modifications necessary for process optimization.

Multiple adsorption methods have been studied with pressure swing adsorption (PSA), temperature swing adsorption (TSA) and electrical swing adsorption (ESA). In TSA the solvent column is cooled during the adsorption process, favoring CO<sub>2</sub> adsorption as flue gas flows through the adsorbent pores, followed by a raise in temperature, purging the adsorbed CO<sub>2</sub> [25], with studies calculating obtained CO<sub>2</sub> purity of 96.22%, recovery of 86.5% and productivity of 0.279 kg/hour [26]. PSA takes place in constant temperature, with adsorption being carried out at typically 10-40 bar, with desorption taking place with pressure slightly above atmospheric and as a sequence the solvent is being regenerated. This method on average achieves 79.8-99.4% CO<sub>2</sub> purity and 94-97.7% recovery rate. ESA is similar to TSA, with the honeycomb solvent column being regenerated through Joule effect application, as electricity passes through a conductor, lowering desorption time [27]. The application of this method offers 89.8% overall CO<sub>2</sub> purity.

Adsorption methods stand out for their simplicity and low capital needs. The sorbents can be reused multiple times, providing a financially sustainable solution for multiple industries, with operational circumstances are not characterized as dangerous, with pressure and temperature fluctuating in controllable ranges. On the contrary, large amounts of CO<sub>2</sub> cannot be easily handled with this method. Moreover, the solvents pores usually adsorb amounts of N<sub>2</sub> leading to product impurities [23].

In cryogenic distillation, CO<sub>2</sub> is distilled from feed gas, which is assumed that consists of CO<sub>2</sub> and N<sub>2</sub> with the prior liquified under extreme conditions. After combustion, flue gas produced is filtered, with CO<sub>2</sub> and N<sub>2</sub> remaining, sent into a chamber where high pressure and temperatures lower than -73.3°C lead to CO<sub>2</sub> liquification (triple point of CO<sub>2</sub> is -56.6°C) with N<sub>2</sub> escaping as a gas, leading to CO<sub>2</sub> purity higher 99.95%.

Cryogenic distillation has multiple advantages and disadvantages. First and foremost, this method is capable of handling CO<sub>2</sub> concentrations higher than 50% v/v. Moreover, it leads to a liquid product which can be transported easier, while it does not require

chemical additives throughout the process. These advantages however, come with a high capital cost due the high energy requirement in order to achieve low temperatures. Additionally, a further removal of potentially freezing components must take place, for the process to be efficient [28], [29].  $\text{CO}_2$  is distilled from feed gas, which is assumed that consists of  $\text{CO}_2$  and  $\text{N}_2$  with the prior liquified under extreme conditions. After combustion, flue gas produced is filtered, with  $\text{CO}_2$  and  $\text{N}_2$  remaining, sent into a chamber where high pressure and temperatures lower than  $-73.3^\circ\text{C}$  lead to  $\text{CO}_2$  liquification (triple point of  $\text{CO}_2$  is  $-56.6^\circ\text{C}$ ) with  $\text{N}_2$  escaping as a gas, leading to  $\text{CO}_2$  purity higher 99.95%.

Membranes can act as sieves, concentrating  $\text{CO}_2$ , excluding other components from flue gases. Membranes used for these applications can be distinguished in two layers, a thin reactive layer responsible for  $\text{CO}_2$  selectivity, made of composite polymer, metal or ceramics and a thicker neutral layer that offers mechanical support [30].

As combustion takes places, product gas enters a chamber, which is separated by a membrane, which can have four potential methods of separating  $\text{CO}_2$  from flue gas. The first is solution-diffusion mechanism where flue gas is absorbed by the membrane, diffused and  $\text{CO}_2$  gets desorbed downstream. Another mechanism is the facilitated transport, with biological membranes interacting with  $\text{CO}_2$  molecules, transporting them through the membrane. The most common concept is the mechanical sieving, where porous membranes are applied filtering  $\text{CO}_2$  molecules from other gases with larger molecules. At last, preferential adsorption-monomolecular surface diffusion mechanism has also been examined, as membranes with pores walls covered with a material which attracts and absorbs only  $\text{CO}_2$  molecules through [31]. After separation takes place, or before flue gas enters the chamber nitrogen and sulfur oxides are removed improving  $\text{CO}_2$  purity.

Different reactive types of polymer membranes have emerged, with ether oxygen-rich polymers, polymeric ionic liquids, perfluoropolymers, thermally rearranged polymers, iptycene-containing polymers, facilitated transport membranes (FTMs) containing amine or other carriers, at the epicenter of academic reviews [30]. The selective layer plays essential role to the process with its dimensions varying for every mechanism and material used, typically range between  $0.1\text{--}10\text{ }\mu\text{m}$  [32].

Membrane separation is the simplest concept in terms of equipment, with limited energy needs compared to other methods. However,  $\text{CO}_2$  selectivity of the membranes, the poison of the selective layer from  $\text{SO}_x$  and  $\text{NO}_x$ , combined with clogging of the pores from vapor or other gases are commonly encountered problems.

Hydrate application is also a considerable option. Gas hydrates are ice like structures called clathrates, formed from gas molecules, which are getting trapped within cavities of hydrogen bonded water molecules [33]. Small nonpolar carbon gases like  $\text{CO}_2$  are favored occupants of this method, forming hydrates in contact with water and possibly cyclopentane, when temperature is lower than equilibrium temperature and pressure higher than equilibrium pressure. The optimum mole fraction of this method

is 0.148 with weight fraction of 0.31 gCO<sub>2</sub>/H<sub>2</sub>O, as 8 CO<sub>2</sub> molecules can be caged by 46 H<sub>2</sub>O molecules under optimal conditions [34] with hydrates having at least four times greater CO<sub>2</sub> concentration compared to its gas phase [33].

Shifeng Li et al. [35] mention the increased density of hydrate state of a gas, provide this mechanism with the ability to store large amounts of gas with more than 99% CO<sub>2</sub> collected from flue gas, after a three-stage hydration process. The first step is the formation of solid hydrates under high pressure and low temperature, capturing CO<sub>2</sub>, followed by leftover gas and hydrate slurry separation. Then the hydrates are dissociated releasing high purity CO<sub>2</sub> for further processing.

Hydrate process leading to a hydrate product rich with CO<sub>2</sub>, with high density, offering an efficient transportation option. On the other hand, in order to form CO<sub>2</sub> hydrates the extreme conditions of approximately 89 bar and 0°C are required, with Tajima et al [36] conducting a study on a hydrate-based carbon capture 100 MW thermal power plant, with 7000 m<sup>3</sup> reactor reaching the energy penalty of 15.8% and other methods reaching as high as 35% [23]. Moreover, this method demand for increased efficiency for CO<sub>2</sub> capture as 35.29% of CO<sub>2</sub> entering the chamber is in hydrate state for water cyclopentane emulsion [35].

Chemical looping combustion is a promising process, which substitutes pure oxygen with a metal oxide, in oxyfuel combustion. During combustion, CO<sub>2</sub> and water vapor is produced, which can be easily removed through condensation, providing pure CO<sub>2</sub> without energy consumption of separation.

Multiple metal oxides find application in this process. Fe<sub>2</sub>O<sub>3</sub>, NiO, CuO, Mn<sub>2</sub>O<sub>3</sub> and CoO are some of the metal oxides reviewed [37], [38]. After combustion, the reduced metal, enters an air chamber, regenerating metal oxide for further CO<sub>2</sub> capture, with product released in the atmosphere as the concentrations of the pollutants produced can be disregarded [39]

The limited energy needs of this process, decreasing the operational costs, combined with high efficiency CO<sub>2</sub> capture make this process stand out. Another notable advantage is the low toxicity of the products, while being biodegradable. On the other hand, the continuous recycle of the metal impracticable, due to components degradation. Another effect of the metal oxidation taking place, is the potential corrosion to the equipment.

### 3.3 CO<sub>2</sub> transportation

As CO<sub>2</sub> is captured and separated from the flue gases, a sufficient CO<sub>2</sub> transportation method to storage or industrial utilization is required. The most crucial parameters for a reliable CO<sub>2</sub> transportation system, are safety and cost. Depending on the volume of the gas and the type of transportation (onshore, offshore), various methods have been developed, ranging from pipeline transportation to road tanker and ships [20].

Pipeline transportation is the most used medium. Carbon dioxide is similar to NG in terms of transportation form, while it is non-toxic and non-flammable. NG pipeline transportation is an already mature process, with some modifications required to transport CO<sub>2</sub>. Another characteristic is the efficiency, with large volumes being transported with low cost. Moreover, CO<sub>2</sub> leakage does not pose a threat of explosion, but it bears a toll to plants humans and marine ecosystem, thus monitoring is required [40]

This method has some obstacles to overcome regarding its application. It requires temperature and pressure monitoring, reassuring CO<sub>2</sub> maintains the same phase throughout the process (liquid, gas, dense-phase, supercritical), leading to a well-tempered transportation, as phase transition in the pipeline may lead to clogging [41]. Moreover, impurities must also be monitored, in order to avoid corrosion or damage to the equipment. Regarding capital investment, the volume of initial cost to construct the pipeline facilities, is momentous, making these methods available to limited industries.

The optimal CO<sub>2</sub> phase for pipeline transportation is either liquid or supercritical. Johnsen et al. [42] studied the optimal conditions, with supercritical phase standing out, leading to operational temperature of 32.1°C and 74 bar, with typical pipeline conditions varying from 13-44°C and 85-150 bar reassuring single-state CO<sub>2</sub> flow [20] with compressors placed periodically maintaining a constant pressure value. Pantoleonatos et al. [43] conducted a transportation and cost optimization analysis, of a 34,000 km pipeline facility, connecting 17 plants from central Europe, with 16 utilization facilities in the Mediterranean coastline based on solar energy. The operational cost estimated reached 9 billion euros/year, with approximately 2 billion dedicated to the 93 Mt CO<sub>2</sub> transported yearly.

Other options for smaller and scattered CO<sub>2</sub> sources are marine, motor and railway transportation, usually connecting storage tanks to a pipeline system. Marine transportation consists of a liquefaction facility, stored in tanks and transferred with a ship and with CO<sub>2</sub> being loaded to storage tanks in a new location. Already existent LPG marine transportation ship can be utilized with CO<sub>2</sub> capturing 60% of its total capacity [44]. This method is already established for various industrial purposes, has a high operational cost but a low capital cost, and an approved marine environment alteration. Motor and railway transportation are onshore options, not preferred due to limited capacity, incapability of transferring efficiently large amounts of CO<sub>2</sub>.

## 4 Hydrogen

Besides  $\text{CO}_2$ ,  $\text{H}_2$  is the other reactant of Sabatier reaction (Table 2.1, reaction 1). Consequently, obtaining  $\text{H}_2$  is a crucial part of the methanation process chain. Throughout the years, multiple hydrogen production processes have been developed and have been classified according to the energy source used, the emissions and costs. Different colors have been used to distinguish every class, with green, blue and grey hydrogen predominantly studied, while purple and yellow can also be found in scientific literature [45]. In addition, Yu et al. [46] reviewed a subterranean method of hydrogen production, developed by University of Calgary and Proton Technologies [47], [48], classified as aqua hydrogen. The color separation regarding energy sources powering hydrogen production is depicted in Figure 4.1.

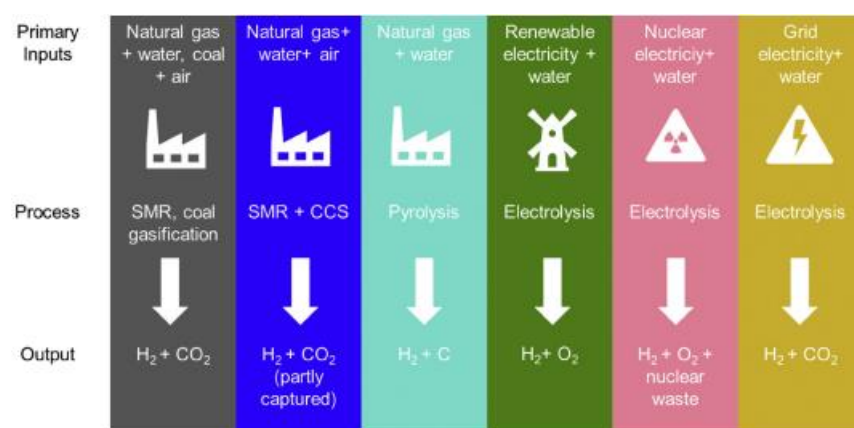


Figure 4.1 Hydrogen production colors [45]

Hydrogen is a versatile element with multiple applications in industry, electricity, transportation and other fields. The hydrogen production consists of upstream hydrogen production, followed by midstream storage and transportation and lastly the downstream applications [45], [49]–[52]. Some hydrogen production methods are quite mature, while others are still under research. Hydrogen production based on fossil fuels, using NG, coal, oil or biomass, as a source, produces  $\text{H}_2$  through steam methane reforming (SMR) or gasification, emitting  $\text{CO}_2$  which can potentially be captured and stored (CCS) or utilized (CCU). Other developed methods are methane pyrolysis, based on methane thermal cracking (Table 2.1, reaction 8) leading to pure carbon by-products [53] with potential substitution of methane with biomass.

Another well-established method is water electrolysis with industrial applications before the 20<sup>th</sup> century reported. This method is environmentally sustainable, producing  $\text{H}_2$  and  $\text{O}_2$ . Additionally, electrolysis can potentially lead to a zero-carbon  $\text{H}_2$  production, powered by renewable energy sources (RES), while nuclear energy can be an alternative, mostly overlooked due to its notoriety, with only a handful of countries examining it. Furthermore, water electrolysis can be powered by a low-carbon option,

or using energy produced from the grid. This method however cannot be considered green, since the electrical power is mostly produced by a mixture of sources, with fossil fuels being the primary energy source for electricity production, making up to 63.3% of global electricity production in 2019 [54].

## 4.1 Water-based hydrogen production

Water is the most common hydrogen containing element on the surface of Earth, making it an inexhaustible source of hydrogen, with the application of certain processes. There are three processes developed for water dissociation, with electrolysis being the most well-established, as thermolysis and photo-electrolysis techniques emerging. According to Martinez-Burgos et al. [55] from 2000 until 2019, 199 patents have been filed, where 3% are referring to thermolysis, 27% to photolysis and 70% electrolysis, with electrolysis being the only process applied to industrial scale.

### 4.1.1 Electrolysis

Electrolysis is a process, in which  $H_2O$  surrounds an electrolyzer, which circulates in direct current, splitting  $H_2O$  to  $H_2$  and  $O_2$ . The electrolyzer consists of the anode and the cathode operating two half reactions, which are responsible for oxygen evolution reaction and hydrogen evolution reaction respectively [39]. Electrolyzer module types are divided between monopolar and bipolar. Monopolar modules are being characterized by robustness, simpleness and considerable size, while bipolar modules are more complex, yet have a more compact structure [56]. In general, industrial electrolyzers usually consist of bipolar electrolyzers, with multiple cells connected in series, generating the desired  $H_2$  amount. In addition, a separating layer is placed between the electrodes. Depending on the electrolyzer operating principle there are three main types of electrolysis: Alkaline Water Electrolysis (AEL), Proton Exchange Membrane (PEM) and Solid Oxide Electrolysis (SOEL) [39], [57].

AEL is the electrolysis technology with the most applications globally, invented in the 19<sup>th</sup> century and by 1902 more than 400 electrolyzers were providing hydrogen commercially [58]. In this method, an aqueous solution, containing 30%wt of diluted potassium hydrate (KOH) or sodium hydroxide (NaOH) leading to increased ionic conductivity. The operating temperatures vary between 60-100°C as the conductivity of the solutions in use, peaks in this range of concentration and temperature [59], with pressure typically in the range of 1-30 bar, where some models reach even 448 bar [57].

Electrolysis cells, consists of two porous electrodes, made from low-carbon steel with or without nickel-coating. The cell is divided by a diaphragm, made typically from asbestos, with an electrode in each tank. As direct current flows in the electrodes, it forms the negatively charged cathode and the positively charged anode, which are reacting with water according to Eq.9 and Eq.10 respectively. In the cathode water is reduced, releasing  $H_2$  gas and hydroxide anions, which circulate the diaphragm to the anode, where the anions recombine, forming  $O_2$  gas bubbles as two electrons are closing the circuit [57]. A detailed AEL electrolyzer can be seen in Figure 4.3.

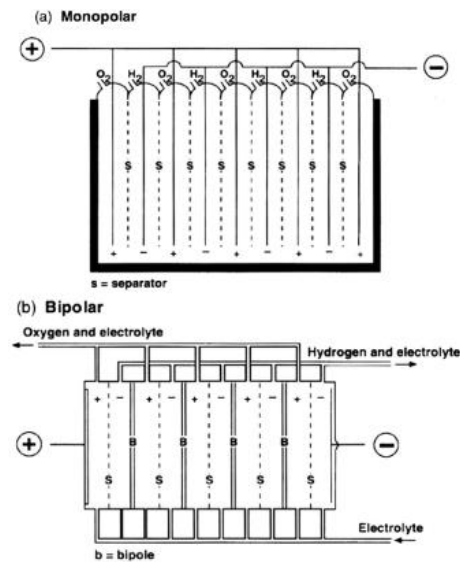
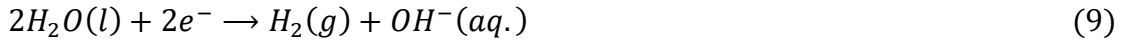


Figure 3.2 Alkaline electrolysis cell module a) monopolar b) bipolar [56]

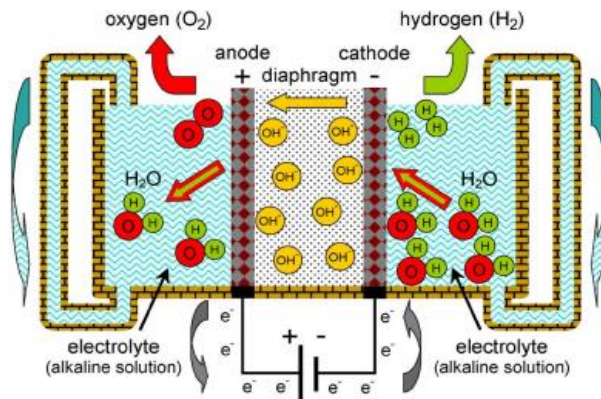


Figure 4.3 Design and operating principle of an AEL electrolyzer [57]



The efficiency of an AEL electrolyzer depends on multiple parameters. The design of the electrodes plays a significant role, as they are responsible for the evolution of the gas products. An efficient electrolyzer design, contains electrodes with maximized interfacial contact with the solution [57]. Besides that, as cathode consumes water and the anode reforms water from anions, the recirculation of the electrolyte is crucial, maintaining a constant concentration of electrolytes in the solution, leading to uncontaminated product gases. Moreover, the proper concentration reassurance, under constant control is crucial, as gas contamination can lead to flammable mixtures, especially when part load is low [60]. Lastly, ohmic losses occur as gas bubbles develop on the electrode surface, as their sizes correlates directly with an increase on the electrical resistance of the system, insulating the electrodes from the solution. Recent studies focus on the addition of substances, preventing the gas from being attached to the electrode [61], [62].

High purity is characterizing the gas products. Hydrogen purity percentage can reach 99.9% and oxygen 99.7% without further purification process applied [57]. The AEL applications are based on freshwater, as seawater electrolysis is being studied extensively, leading to an inexhaustible source of water as only 0.5% of global water reservoirs is available fresh water, while 97% of global water is found in oceans [63].

The development of PEM for ion exchange is a nearly commercialized technology, developed in 1960s by General Electric [64]. This technology is based on a proton exchange membrane, also referred as solid polymer electrolyte (SPE). In general, polyfluorosulfonic, a highly acidic material (mostly Nafion®, a DuPont trademark [65]) with width between 50-250µm[66]) , separating two electrodes made from primary noble metals like platinum or iridium. The application of noble metals is preferred, as the acidic environment would dissolve non-noble metals [66], [67]. The cell consists of a bipolar module, with the electrodes attached to the membrane, forming the so-called MEA (membrane electrode assembly) [39]. The anode oxidizes water, with protons closing the circuit as they move through the membrane to the cathode, reducing to hydrogen bubbles. The PEM electrolyzer configuration is depicted in Figure 4.4. The reactions of the anode and the cathode are written in detail below:



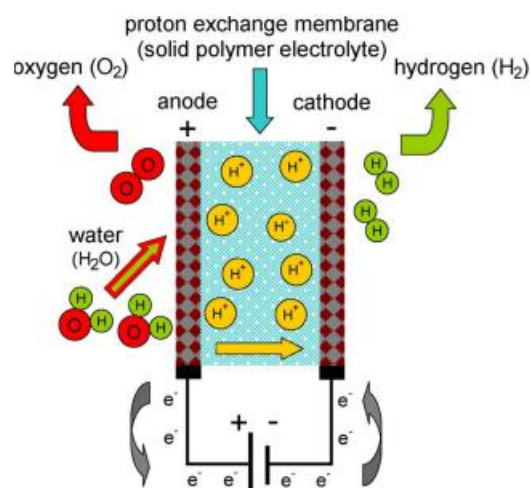


Figure 4.4 Design and operating principle of an PEM electrolyzer [57]

PEM electrolysis finds low-scale application for the time, as indicated in Table 4.1 below. The cells are operating below 80°C, as ambient operating pressure is common, the pressure value ranges up to 20-30 bar and in some instances to 85 bar [57]. The optimal operating temperature increases proportionally with the current density, following an analytically solvable function as Scheepers et al. [68] proved. The modules operating this type of electrolysis are characterized by a compact design, with the ability of handling different pressure values on each side of the MEA configuration, producing gases in different pressures.

Table 4.1 Leading manufactures of PEM electrolyzers [69]

Manufacturer	Series and Operating pressure	Hydrogen Flow Rate ( $\text{Nm}^3 \cdot \text{h}^{-1}$ )	Energy Consumption ( $\text{kWh} \cdot \text{Nm}^{-3} \cdot \text{H}_2$ )	Load Range (%)	Electrolyte	Power
Proton OnSite	S Series 13.8 bar	0.265–1.05	6.7	0–100	SPE	No details
Proton OnSite	H Series 15–30 bar	2–6	6.8–7.3	0–100	SPE	No details
H-TEC Systems	H-TEC Series-S	0.22–1.1	No details	No details	SPE	1–5 kW
H-TEC Systems	ME unpressurised 30 bar	13–210	4.9	No details	SPE	225 kW–1 MW
Areva H <sub>2</sub> gen	E series Up to 35 bar	10–200	4.7–5.3	No details	SPE	80–1600 kVA
Hydrogenics	HyLYZER 7.9 bar	0–1–2	6.7	0–100	SPE	No details

ITM Power	HPac, HCore, HBox, HFuel 15 bar	0.6–35	4.8–5.0 (system)	No details	SPE	2 MW
Siemens	SILYZER 35 bar	200 225	No details	No details	SPE	1.25 MW
Green Hydrogen	P-series/15– 50 bar	1	No details	25– 100	SPE	4.95 kW
NEL	M Series bar	30 103–413	4.53	0–100	SPE	0.5–2 mW

A PEM cell bare the ability of producing high purity gases. In most cases hydrogen produced from these technologies, has purity above 99.99%, without further filtration, due its wide load range. Additionally, the membrane structural characteristics make it almost impenetrable from gases, thus eliminating the risk of forming flammable mixtures [57]. Moreover, PEM electrolyzers are capable of handling fluctuating power feed.

The study of solid oxides for electrolysis first appeared in Germany at Brookhaven National Laboratory and in General Electric laboratories [70]. The principal of solid oxides application in quite complicated, with the academic community studying its properties the last 15 years. The increased temperature, usually between 700 and 1000°C, increases the hydrogen production efficiency as the division of water molecules is thermodynamically and kinetically favored. The operating principle is groundbreaking, with the reactant now in gas state, mixed with hydrogen, reacting with the cathode with more hydrogen generated (Eq. (13)). Oxide anions are attracted to the anode where they deposit the electron surplus forming oxygen (Eq. (14)) [39], [71].



A common cell design, consist of two electrodes, separated by a dense ionic conductivity electrolyte, with the total thickness of the cell varying from 200-300 µm. There are two basic SOEL electrolyzer designs, the electrolyte-supported cell (ESC) and the cathode-supported cell (CSC). The first concept is based on a thick electrolyte layer where thin anode and cathode mounted to each side. On the contrary, in the second design, both a thin electrolyte and a thin anode are based on a thick cathode. The difference in the architecture of the cell, leads to different properties and efficiency rates for every cell type [71]. A typical ESC electrolyzer is shown below in Figure 4.5.

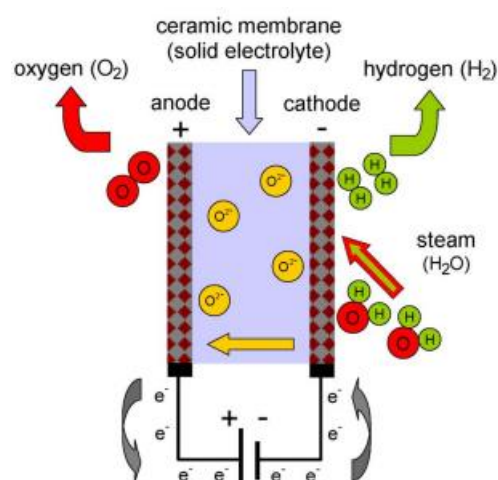


Figure 4.5 Design and operating principle of an SOEL electrolyzer [57]

The evolution of the product gases takes place on an electrode reacting with steam, making the gas separation and the maximization of the reacting surface area of the electrode the most valuable parameter. In general, the electrode materials have to be good electricity conductors with high ionic conductivity and adequate porosity in order to efficiently react with the products and the reactants. They typically are coated by multiple yttria( $\text{Y}_2\text{O}_3$ )-stabilized zirconia (YSZ), with the cathode usually consisting of ceramic YSZ and nickel and the anode consisting of YSZ and perovskites like  $\text{LaMnO}_3$ ,  $\text{LaFeO}_3$ ,  $\text{LaCoO}_3$  [57]. The electrode materials are being intensively studied, in order to maximize the efficiency of SOEL and become industrially feasible [72].

SOEL technology is considered to outpace the well-established AEL technologies soon. The power efficiency of this technology, in elevated temperatures is noteworthy, as the ability of producing multiple gas mixtures from co-electrolysis (e.g., syngas) [71], [73] or even generate electricity, operating in reverse [74]. This great potential however is restricted by the short lifespan of the cells, compared to other methods.

The typical characteristics and a brief comparison of the three electrolysis technologies available, are listed in Table 4.2 below.

Table 4.2 Comparison of electrolysis methods [57], [71], [75]–[78]

Technology	AEL	PEM	SOEL
Operating conditions	60-100°C 1-20 bar	>80°C 20-30 bar	700-1000 °C Ambient pressure
Cathode material	Ni alloys	Pt/Pb Carbon black Carbon multiwalled nanotubes	Ni-YZC Perovskites

Anode material	Ni>Co>Fe oxides Perovskites	IrO <sub>2</sub> , RuO <sub>2</sub> Supports: TiO <sub>2</sub> , ITO, TiC	Ir <sub>x</sub> Ru <sub>1-x</sub> O <sub>2</sub> , La <sub>x</sub> Sr <sub>1-x</sub> MnO <sub>3</sub> + Y-Stabilized ZrO <sub>3</sub>
Lifespan (years)	20-30	10-20	2-3
Efficiency	59-70%	62-82%	≤100%
Electricity demand (kWh/kg(H <sub>2</sub> ))	51.8	54	42.3
Production size (kg(H <sub>2</sub> )/h)	19.3	18.5	23.6
Applicability	Commercial	Near-term commercialization	Demonstration
Advantages	Well-established. Non-noble catalysts. Low cost/Cost effective. Long lifespan.	Compact design. Good partial load range. High gas purity. Dynamic operation.	Efficiency up to 100%. Non-noble catalysts Enhanced thermodynamics and kinetics. Low energy demands. Low costs
Disadvantages	Gas products contamination. Restricted dynamics. Corrosive liquid electrolyte. Low pressure.	High cost Highly corrosive, low pH (~2) environment. Iridium is scarce.	Not mature yet. Susceptible to leaking. Bulky design. Not extensive cost information for commercial scale.
Challenges	Improve durability. Improve kinetics with electrolyte additives/catalysts. Gas bubble management.	Reduce cost. Reduce/substitute noble materials. Improve membrane characteristics.	Multiple stream management. Cell operation optimization. Minimize electrode rapid degradation.

#### 4.1.2 Thermochemical cycles

The process known as water thermolysis or thermochemical water splitting, is a hydrogen producing process with water as raw material. This process is divided in two techniques, the one-step process where water is heated in a temperature high enough

(pressure up to 1 bar and temperature over 2500°C [79], [80]) for water molecules to split, while in the thermochemical cycles process, water reacts with different additives, which are then exposed to high temperature, where they dissociate to H<sub>2</sub> and O<sub>2</sub> gases with the substances added recycled. In thermochemical cycles the temperature for the dissociation of these elements is significantly lower than the temperature in one-step thermolysis, leading to decreased energy demands and increase in the overall efficiency [81], [82].

One-step thermolysis is based on a simple principal. Water is exposed to an enormous amount of heat, which thermodynamically leads to water molecule schism, producing hydrogen and oxygen (Eq. (15)) [82]. Although in order to fully separate water molecules, temperature must exceed 4,000°C, which consequently leads to excessive energy demands to power this process. This process can be powered by renewable, nuclear, biomass and thermal heat sources [82]. However, the management of this process is complicated, as the materials capable of enduring temperatures that high, also have a high cost. Moreover, when the temperature is high enough to decompose water, the gas product is a mixture of H<sub>2</sub> and O<sub>2</sub>, tending to reform water at a gradual temperature drop [82]. Thus, due to its complications, this method is not taken into consideration for large scale applications, with the literature focusing on thermochemical multi-step cycles, in order to overcome the one-step thermolysis obstacles.



Thermochemical cycles are processes based on the principle of thermolysis. These processes consist of multiple chemical reactions, with the first reaction involving water reacting usually with metal oxides, leading to products which in their dissociation release O<sub>2</sub> and H<sub>2</sub> under high temperatures (500-2000°C), with a value notably lower than one-step thermolysis [79], [82]. The extensive research on these methods has led to the study of approximately 3000 cycles, with only a few of them capable of meeting large scale hydrogen production needs [80]. Recent studies focus on sulfur-iodine, zinc-sulfur-iodine, cooper-chlorine and magnesium-chlorine multi-step processes, as they pose as the most promising reaction chains.

Sulfur-Iodine (S-I) cycle developed in USA in 1970s, immediately capturing the interest of researchers in eastern Asia, becoming the most studied thermochemical hydrogen production process [79], [82], [83]. This thermochemical cycle consists of the 3 reactions given below.





The concept of this hydrogen production method is depicted in Figure 4.6. The first reaction, also known as Bunsen reaction, occurs as an aqueous mixture of  $SO_2$  and excess  $I_2$  reacts, producing heat and leading to the formation of two immiscible acids at ambient conditions. These acids are separated in two different chambers, with HI exposed to temperatures as high as  $400^\circ\text{C}$  and  $H_2SO_4$  at temperatures close to  $900^\circ\text{C}$ , where the bonds of the acids collapse, to form  $H_2$  and  $O_2$  alongside with the regeneration of the reactants of the initial reaction [83]. The heat, in order Eq (16) and Eq (17) to take place, has been produced typically in High Temperature Gas-cooled Reactor (HTGR), with multiple other patents capable to cover the heat needs [84], as Modular Helium Reactor (MHR), Very High-Temperature Reactor (VHTR), Supercritical water-cooled nuclear reactor (SCWR) and others.

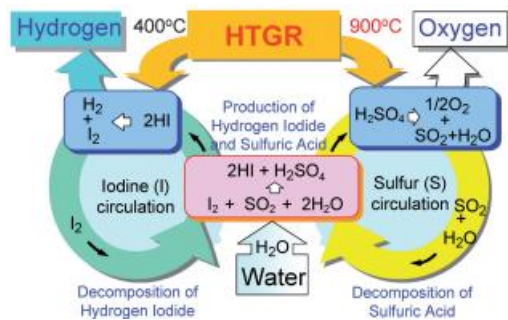


Figure 4.6 Operational principle of S-I cycle [85]

Theoretically the reactants (besides  $H_2O$ ) are inexhaustible, are being regenerated along the reaction chain, however, it is possible for the Bunsen reaction products to react, forming sulfur or hydrogen sulfide, which can potentially restrict the process by clogging the equipment. Consequently, excess concentration of Iodine, with concentration even eight times greater than the stoichiometric, acts as a barrier between the acids separating them into light and heavy phases, minimizing the potential of unwanted reactions. The light phase liquids as  $H_2SO_4$  and  $H_2O$  are separated from the heavy phase liquids as HI,  $I_2$  and  $H_2O$ . The collected liquids are purified, reformed to the initial reactants with additional  $O_2$  and  $H_2$  sidetracked, consequently purifying the reactants.

The separation of the substances is not the only challenge this method is facing. The highly corrosive  $H_2SO_4$  product, leads to demand of durable materials. Moreover, heat must be combined with the existence of a catalyst, as  $H_2SO_4$  has restricted kinetics limiting its decomposition [82]. Additionally, HI dissociation is a reversible reaction, making the simultaneous separation of  $H_2$  and  $I_2$  products a necessity. As a result, the

application of a membrane able to endure the acidic environment has been studied, trapping  $H_2$  and  $I_2$ , increasing the production rate from the decomposition of the acid.

The development Zinc-Sulfur-Ionic (Zn-S-I) thermochemical water dissociation method, is based on the same principle with S-I cycle, with the difference of the simultaneous production of CO. This cycle consists of 6 reactions (Number 1-3), their equations are as follows.

Table 2.3: Zn-S-I cycle steps [83]

Number	Equation
1	$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2H$
2	$2HI \rightleftharpoons I_2 + H_2$
3	$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2$
4	$Zn + CO_2 \rightarrow ZnO + CO$
5	$2HI + ZnO \rightarrow H_2O + ZnI_2$
6	$ZnI_2 \rightarrow Zn + I_2$
7	$ZnI_2 + CO_2 \rightarrow ZnO + CO + I_2$
8	$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$
9	$I_2 + 2H^+ + 2e^- \rightarrow 2HI$

The Zn-S-I (Table 4.3) cycle consists of the S-I cycle, under the same condition parameters, with the addition of 3 more reactions (number 4-6) in order to recycle the initial reactants and produce CO. Zinc oxidation is the outcome when Zn is paired with  $CO_2$  (number 4) in roughly  $780^\circ C$ , releasing CO as a final product and ZnO. Then, ZnO reacts spontaneously, when paired with remaining HI (number 5) in ambient conditions. The outcome of number (5) is a mixture of  $ZnI_2$  and  $H_2O$ , which later is dehydrated forming  $ZnI_2$  crystals, which are decomposed to approximately  $740^\circ C$ , closing the process cycle, reforming the initial reactants [83], [86].

As this cycle is an enhanced version of S-I cycle, the same challenges have to be encountered, where additional obstacles surface with the existence of 3 more reactions. Additional equipment is required, as more reactions and more complex processes take place. Moreover, the low yields of HI and  $ZnI_2$  conversion, indicate the need of catalysts, primarily noble metals [86]. As a result, the overall investment capital and operating cost increases significantly. Consequently, modified cycles have been studied, as an open cycle, five-step cycle combining reactions number 4 and 6 to form 7 and lastly, electrochemical five-step cycle, which has captured the attention of the researchers as a concept [86]. An electrochemical reactor substitutes the conventional one, leading to higher production rate without the need of excessive concentrations of reactants [87]. The anode and cathode reaction are written in detail in reactions number 8 and 9 respectively.



Alongside with S-I cycle and its variants, the Cooper-Chlorine cycle (Cu-Cl) is under intense research. The reduced heat needs of this process, offers a flexibility on the potential energy sources, which can power this process. Multiple Cu-Cl pathways achieve water dissociation, with the number of steps varying from two to five [82]. As a result, the operational cost and processes complexity correlate with the number of reactions taking place in the thermochemical cycle.

Table 4.4 Cu-Cl cycles reactions [82]

Number	Equation	Temperature (K)
1	$nH_2O(l) + 4CuCl(s) \rightarrow 2Cu(s) + 2CuCl_2 \cdot nH_2O(aq)$	350
2	$H_2O(g) + 2CuCl_2 \cdot mH_2O(s) \rightarrow CuO \cdot CuCl_2(s) + HCl(g) + mH_2O(g)$	650
3	$H_2O(g) + 2CuCl_2(s) \rightarrow CuO \cdot CuCl_2(s) + 2HCl(g)$	673
4	$H_2O(g) + 2CuCl_2 \cdot nH_2O(s) \rightarrow \frac{1}{2}O_2(g) + 2HCl(g) + 2CuCl(l) + nH_2O(g)$	823
5	$H_2O(g) + Cl_2(g) \rightarrow \frac{1}{2}O_2(g) + 2HCl(g)$	1073
6	$2Cu(s) + 2HCl(g) \rightarrow H_2(g) + 2CuCl_2(l)$	723
7	$2CuCl(s) + 2HCl(aq) + nH_2O(l) \rightarrow H_2(g) + 2CuCl_2 \cdot nH_2O(aq)$	473
8	$2CuCl_2(s) \cdot nH_2O(g) \rightarrow CuO \cdot CuCl_2(s) + 2HCl(g) + (n - 1)H_2O(g)$	650
9	$CuO \cdot CuCl_2(s) \rightarrow \frac{1}{2}O_2(g) + 2CuCl_2(l)$	800
10	$2CuCl_2 \cdot nH_2O(g) \rightarrow 2CuCl_2(l) + Cl_2(g) + nH_2O(g)$	773
11	$2CuCl_2 \cdot nH_2O(aq) \rightarrow 2CuCl_2 \cdot mH_2O(s) + (n - m)H_2O(g)$	550

Table 4.5 Cu-Cl cycles [82]

Cycle	Reactions included
Two-step cycle	4-7
Three-step cycle a	4-6-1
Three-step cycle b	7-9-8
Three-step cycle c	5-7-10
Four-step cycle a	1-6-9-8
Four-step cycle b	3-7-9-11
Five-step cycle	2-6-9-1-11

The cost of the application of different thermochemical Cu-Cl cycles (Table 4.4 & Table 4.5) is relatively the same. However, studies conducted on these cycles, prove that cycles with less steps restrict solid deposition, maintaining efficient heat and mass transfer. However, higher temperature values are required, and the separation

process is complex [83]. The efficiency of the processes depends on the power source, but in general an increase in both temperature and flow rate, increases the efficiency of every cycle. Another notable aspect of these cycles is the extensive literature on this topic, proposing groundbreaking methods in order to provide enough heat for these systems, even with heat recovery from industrial systems as iron furnace [88].

Another low-temperature thermochemical hydrogen production method is the Magnesium-Chlorine cycle (Mg-Cl) shown in Table 4.6 & Table 4.7, with competitive characteristics among other thermochemical cycles. As in Cu-Cl cycle, the decreased heat demand, widens the range of the potential power sources, that this process can be paired. Multiple Mg-Cl cycles have been developed for hydrogen production, with their equations written in detail in the table below.

Table 4.6 Mg-Cl cycles reactions [83]

Number	Equation	Temperature(°C)
1	$MgCl_2(g) + H_2O(g) \rightarrow MgO(s) + HCl(aq)$	450-550
2	$MgO(s) + Cl_2(g) \rightarrow MgCl_2(s) + \frac{1}{2} O_2(g)$	450-500
3	$2HCl(aq) \rightarrow H_2(g) + Cl_2(g)(1.8V)$	70-90
4	$2HCl(g) \rightarrow H_2(g) + Cl_2(g)(1.4V)$	70
5	$2MgCl_2(g) + 2H_2O(g) \rightarrow 2MgOHCl + 2HCl(aq)$	240-300
6	$2MgOHCl + Cl_2(g) \rightarrow 2MgCl_2(s) + H_2O(g) + \frac{1}{2} O_2(g)$	450
7	$MgCl_2(g) + H_2O(g) \rightarrow MgOHCl + HCl(aq)$	280
8	$MgOHCl \rightarrow 2MgO(s) + HCl(g)$	450

Table 4.7 Mg-Cl cycles [83]

Cycle	Three-step a	Three-step b	Four-step a	Four-step b
Reactions	1-2-3	5-6-3	7-8-2-3	7-8-2-4

This process utilizes heat and electricity and water. It consists of 4 types of reactions, hydrolysis reactions (number 1 & 5 in Table 4.6), chlorination reactions (number 2 & 6 in Table 4.6), decomposition reaction (number 8 in Table 4.6) and HCl electrolysis (number 3 & 4 in Table 4.6). According to Mehrpooya et al. [83] energy and exergy efficiency ratios vary from 16.3% to 50.3% and 17.6% to 63.7% respectively. These ratios depend on the power sources and the thermodynamic cycles applied to the system (typically Rankine).

According to Ozcan et al. [89] the Mg-Cl cycle does not involve the typical problems of other thermochemical cycles. Heat requirements for this process are reduced to approximately 400-450°C from other thermochemical hydrogen production cycles. The lower heat demands of this process, leads to a plethora of potential equipment

materials, alongside with the potential utilization of nuclear waste heat to power the system, lead to a decrease in the overall cost of the system [89].

Moreover, HCl electrolysis plays a significant role in this process. Hallet Air Products had experimentally studied hydrogen production through HCl electrolysis, with exceptionally low hydrogen production yields. In Mg-Cl cycle however, the reaction mechanics of HCl electrolysis are enhanced, as the consumption of chlorine gas in O<sub>2</sub> production reactions (reaction number 2 & 6 in Table 4.6), pushes the electrolysis equilibrium towards HCl dissociation, preventing it from reforming. The electrolysis step is a groundbreaking factor, especially with a membrane cell application, removing anhydrous HCl (number 4) with efficiency close to 100% [89], [90].

In conclusion, hydrogen production from thermochemical cycles is a process capable of potential industrial applications. The characteristics of multiple hydrogen production cycles have been studied, with reviews evaluating the efficiency of the energy and exergy of this process, the overall cost, and the power needs of the processes. According to Mehrpooya et al. [83], variations of the S-I cycle are the highest energy and exergy efficiency, a result correlated by the greater volume of literature surrounding this method, when compared to others. However, the overall cost of the S-I cycles is competing with this of Cu-Cl, with the second cycle only providing a hundredth of the production rate of the first cycle.

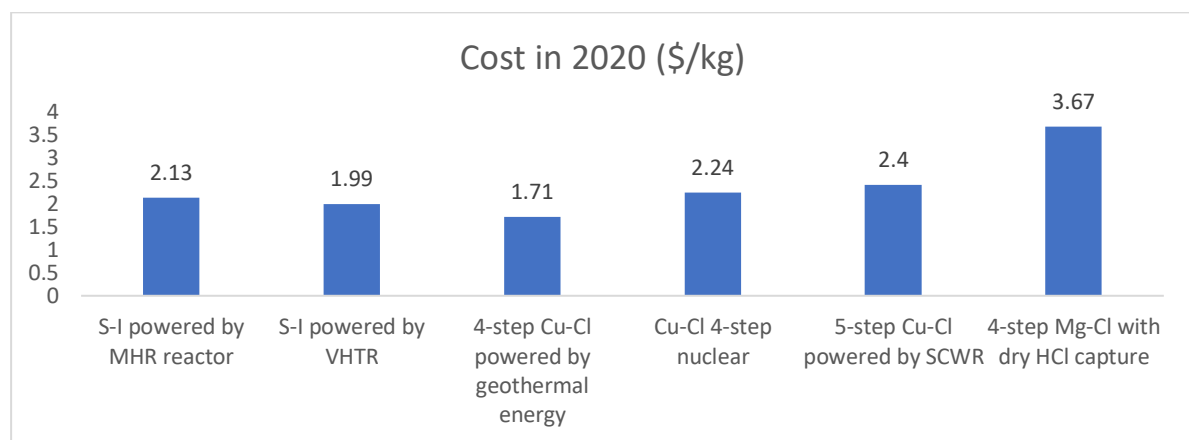


Figure 4.7 Cost comparison of different thermochemical cycles [83]

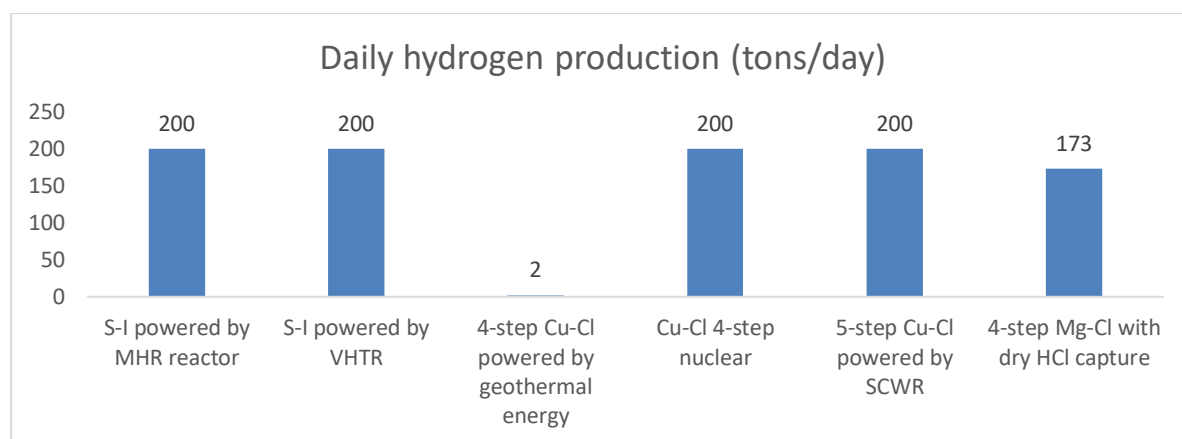


Figure 4.8 Hydrogen production rate comparison of different thermochemical cycles [83]

### 4.1.3 Photolysis and photo-electrolysis

Other interesting pathways for hydrogen production are those associated with solar energy. The inexhaustible solar energy found in the surface of earth can be utilized to dissociate water, producing hydrogen and oxygen, with two methods. The first one direct photolysis and the second one is photo-electrolysis.

In water photolysis or photodissociation, water molecules exposed to ultraviolet radiation, can theoretically dissociate a single water molecule, when exposed to 285.57kJ. Beside the fact that this method is direct and it only needs light, it is characterized by low efficiency, with photocatalyst, micro-organisms and dyes studied, aiming to improve the overall efficiency of the process [91].

Photo-electrolysis on the other hand is a promising renewable energy hydrogen production method, merging electrolysis operating principle with photovoltaics photon absorption. Two semiconductors are combined to form a p-n junction with a permanent electric field, which when it gets exposed to photons with a greater or equal bandgap compared to this of the material, an electron hole is formed to the junction. The deficit of electrons on the positive end, assisted by a complimentary voltage, leads to oriented electron movement, closing a circuit. When this configuration is immersed in an aqueous solution, a photon powered electrolysis takes place [81].

## 4.2 Biomass

Biomass is a hydrocarbon material, formed from organic wastes, which can be exploited to produce energy, with the powering of basic household needs, except electricity, being its most common application. Processes to extract hydrogen from biomass have been developed over the years, based on two different hydrogen production principles [81], [92]–[94]. The first is thermochemical processing, where biomass is exposed to high temperatures under certain conditions, releasing  $H_2$ . The second is based on biological process, utilizing enzymes.

Thermochemical hydrogen production from biomass is divided in 3 techniques. Gasification and pyrolysis are the two methods primarily studied, with biomass liquefaction mostly being overlooked, due to low hydrogen yield and operating conditions (250-330°C and 5-20 MPa in absence of ambient air) are too demanding for industrial application.

Pyrolysis of biomass takes place in temperatures ranging between 380-530°C, and pressure of 0,1-0,5 MPa without the presence of ambient air. When biomass is exposed to these conditions, is converted into oils, gases and charcoal [92]. The speed of the transition from ambient to operating conditions, combined with phase instability play a significant role on the production yields, with rapid transitions favoring the production of  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $CO$  gases, with restricted tar, oils and solid byproducts. Biomass is a versatile energy producing compound, with multiple potential catalysts capable of enhancing the production. With further processing hydrogen yields can overcome 90% [92].

In biomass gasification, like in pyrolysis, biomass molecules are exposed to heat, with the presence of oxygen being the main difference. Biomass of moisture percentage below 35%, is exposed to temperatures higher than 730°C, where particles are getting oxidized with the presence of oxygen, forming charcoal with is latter reduced to a mixture of gases containing  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $CO$ . Besides the main products however, light and heavy hydrocarbons as tar are produced, alongside with ash. These byproducts can obstruct the production of hydrogen. The formation of tar can form polymers or aerosols inside the reactor restricting hydrogen from being released. Various additives have been examined, which can eliminate its formation, or even enhance the formation of hydrogen. Ash accumulation through the process, can degrade the equipment, decreasing the efficiency of the process. When moisture content exceeds 35%, the method differs, as water at these temperatures is supercritical. The violent conditions, biomass is gasified rapidly, gases are formed rapidly, achieving gasification ratio up to 100% and hydrogen makes up to half of the total volume of the gas mixture produced [92]. The cost of the hydrogen produced cost varies between 1.77-2.5\$/kg [81].

## 4.3 Bio-based

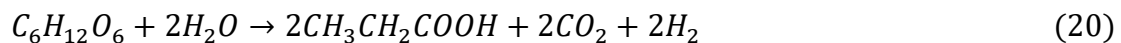
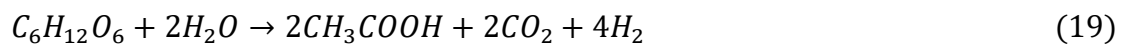
Among alternative hydrogen production methods, biological hydrogen obtained from biomass, stands out as a financially competitive and environmentally friendly technique. Microorganisms capable of splitting water and carbohydrates are applied, with hydrogenase and nitrogenase enzymes releasing hydrogen. These methods can produce  $H_2$  via three routes: (i) direct & indirect bio-photolysis, (ii) photo-fermentation and (iii) dark-fermentation [95], [96]. These methods are complex, depend on multiple parameters, with the extensive literature available on these methods is incapable of proving their availability for large scale hydrogen production. However, the ability of utilizing waste to produce a methanation reactant is noteworthy.

### 4.3.1 Direct and indirect bio-photolysis

Direct and indirect bio-photolysis microorganisms are powered by light, with the only difference that direct bio-photolysis separating hydrogen molecules directly [95], when the indirect alternative cultivates organic compounds which are later converted into hydrogen, while hydrogenase and nitrogenase content of the microorganisms and anaerobic conditions are the common parameters. In direct bio-photolysis cyanobacteria and green algae are cultivated in the largest possible area, producing hydrogen and oxygen with light absorption. Oxygen production is directly correlated with the efficiency of these methods, as higher than 0.1% content of this gas inactivates the enzymes, thus restricting the hydrogen production [92]. A cost estimation per kilo of product is 2.62\$ according to Ni et al. [92], with potential substitution of oxygen with argon in order to avoid the enzyme deactivation, increasing the operating cost and consequently the product cost significantly [95]. In indirect bio-photolysis, water, light and carbon dioxide react with microorganisms to produce glucose dextrose ( $C_6H_{12}O_6$ ) and oxygen, with the first is divided in hydrogen and carbon dioxide when it illuminated with the presence of water. Microalgae and cyanobacteria, which are responsible for hydrogen production are not exposed to oxygen in this method, overcoming the oxygen content obstacle. Genetically modified cells are finding application in this method, as they are modified to store more glycose, which effects positively the hydrogen yields [95]. An approximate estimation regarding the hydrogen cost is 1.31\$/kg [92]. However, this technique is not yet mature for any application, requiring further research [95]. The common disadvantage of these methods is the low efficiency of light conversion and hydrogen yield.

### 4.3.2 Dark fermentation

Under light and oxygen absence, heterotrophic bacteria can ferment organic wastes, producing  $H_2$  and  $CO_2$  gases alongside with volatile fatty acids (VFAs) [97] with the following reactions, which describe the release acetic and butyric acid, dominating the process [98].



This hydrogen production method depends on multiple parameters, with extensive literature examining and experimenting on the conditions and bacteria cultures taking place. With the chemical reactions above taking place, microorganisms reduce organic waste through oxidization, with the reactor maintaining a neutral electron load through hydrogen evolution. According to Akhalgi et al. [95] the *Clostridium* sp., *Enterobacter* sp. and *Bacillus* sp. are the most commonly implied bacteria in this process, with every bacteria culture following a different hydrogen production pathway, leading to various hydrogen yields, and byproducts. In order to exploit the most versatile waste mixtures, multiple bacteria cultures can be merged in order to maximize the hydrogen production yields and make the technology financially attractive. In terms of hydrogen yield achieved, sucrose and acetate have achieved the highest molar ratio of hydrogen to raw material, which however leads to increased operational costs. At last, minerals and trace metals can act as catalysts and enhance hydrogenases activity, while pH and temperature are crucial parameters for the process, correlated with the environment that the cultures live and thus with their efficiency. Optimal pH ranges between 5.5 and 6.5, while temperature conditions are separated to 3 categories: mesophilic (25-40°C), thermophilic (40-65°C), hyper-thermophilic (>80°C), with the first mostly implied due to restricted energy demands and the second as the most efficient in terms of hydrogen production [95], [97], [99]].

### 4.3.3 Photo fermentation

Photo fermentation takes place in anaerobic environment with the presence of light. Photosynthetic non-sulfur bacteria (PNS) convert VFAs or carbon compounds to hydrogen and  $CO_2$ . According to Akhalgi et al. [95] *Rhodobacter* spheroids, *Rhodobacter capsulatus*, *Rhodobacter sulfidophilus*, *Rhodopseudomonas palustris* and *Rhodospirillum rubrum* are some of the PNS bacteria that can be used to photo-ferment organic waste. Through the bacteria nitrogenase and hydrogenase bacteria catalyze the process, leading to hydrogen production.

The process starts with the organic compound oxidization to  $\text{CO}_2$ , hydrogen cations and electrons which are evolved to hydrogen through nitrogenase. Nitrogenase typically metabolizes  $\text{N}_2$ , leading to  $\text{NH}_3$  production and  $\text{H}_2$  as a byproduct, with  $\text{N}_2$  absence however, nitrogenase compliments hydrogenase, which catalyzes the formation of hydrogen in protons and electrons [95]. According to Argun et al. [97] optimal pH range is 6.8-7.5 and temperature conditions to be mesophilic (more especially ranging between 31-36°C), with light wavelengths between 400-1000 nm and with light intensity from 6 to 10 klux. The maximum theoretical photochemical light efficiency is 10%, with experiments able to achieve as high as 9.3%, while hydrogen production can reach up to 80% of the theoretical yield. Organic acids are responsible for high conversion efficiency, which leads to a preference of food industry wastes as a raw material, which also come with a low cost.

#### 4.4 Hydrogen from fossil fuels

Current hydrogen production is based almost entirely on dissociating hydrocarbons. Almost half of hydrogen produced is a product of methane reforming, while coal gasification and partial oxidation of oil make up the rest of hydrogen production. Globally only 4% of hydrogen is derived from sources other than fossil fuels. The production of this gas from fossil fuels is highly efficient and with a luring cost for the industry. A detailed graph of the hydrogen production partition is depicted below in Figure 4.9.

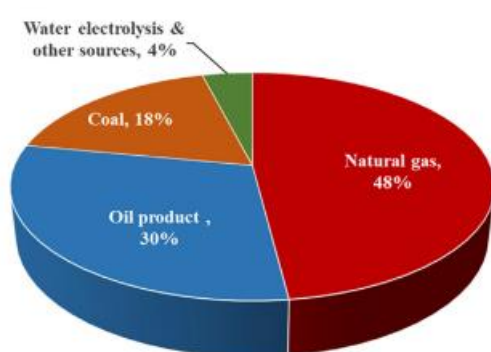


Figure 4.9 Main sources for hydrogen production [82]

The implementation of such methods on the other side, have carbon oxides as byproducts and most commonly apply Sabatier reaction in reverse. Thus, the



examination of such methods, aiming to intergrade them in a potential methanation plant is contradicting with the concept of CCU technologies. A brief analysis concerning these methods is taking place in the paragraphs below, providing a holistic view of the current state of hydrogen production, while setting the threshold of the product cost renewable sources have to comply in order to become more competitive.

As previously mentioned, NG is providing the majority of hydrogen across the globe. Methane can be reformed with steam in a highly energy consuming process, exposed to temperatures between 800-1100°C and catalyzed by Ni-based materials (reaction number 1 & 2 in Table 4.8). Moreover, it can be partially oxidized when exposed to oxygen in temperatures as high as 650-1500°C, releasing H<sub>2</sub> in an exothermic reaction (number 3) without a catalyst needed. These two techniques can be combined with the second providing heat loads to the first, leading to a cycle called autothermal reforming (ATR). Moreover, NG can be dissociated, releasing H<sub>2</sub> and solid carbon, in a reaction called methane pyrolysis, also known as methane cracking. This reaction has been studied in three different directions, the thermal and plasma pyrolysis, which are non-catalytic processes, and catalytic pyrolysis. In catalytic pyrolysis, the reaction can be triggered in temperatures lower than 500°C, however temperatures above 800°C achieve higher efficiency. In thermal pyrolysis, NG is exposed to temperatures above 700°C, with higher yields reported above 1000°C. At last plasma pyrolysis occurs at extreme conditions, above 2000°C (number 4) [53], [81], [82], [100], [101].

Besides methane, coal and oil products play a significant role in the hydrogen production industry. Coal gasification (GC) utilizes both mined coal (surface gasification) and unmined coal (underground gasification). Grinded coal is first exposed to air, releasing CO<sub>2</sub> (number 5) and then is exposed to steam, leading to H<sub>2</sub> formation (number 6). At last, oil products can be oxidized in a similar process as methane oxidation, with the only difference being the higher temperatures (1200-1500°C) their oxidization reaction (number 7) takes place [81], [82], [100], [102].

*Table 4.8 Hydrogen producing reactions with fossil fuel reactants, their efficiency rates and the cost of the produced hydrogen [81], [82], [100], [102]*

Process	No.	Reaction	Efficiency	Cost (\$/kg)
Steam Methane Reforming (SMR)	1	$CH_4 + H_2O \rightarrow CO + 3H_2$	70-85%	2.08-2.27
	2	$CO + H_2O \rightarrow CO_2 + H_2$		
Partial Methane Oxidation (POM)	3	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	55-75%	1.34-1.48
Coal Gasification (CG)	4	$C + O_2 \rightarrow CO_2$	60-75%	1.63-1.34
	5	$C + H_2O \rightarrow CO + H_2$		
Partial oil product oxidation (POX)	6	$C_nH_m + 0.5nO_2 \rightarrow nCO + 2mH_2$	63-72.8%	0.84
Methane Pyrolysis	7	$CH_4 \rightarrow C + 2H_2$	14-91%	2.2

## 4.5 Hydrogen pallet

Traditional hydrogen production technologies are based on methane pyrolysis, oil product oxidation and coal gasification, with these technologies often referred as grey hydrogen. As mentioned in Figure 4.9, 96% of global hydrogen production comes from fossil fuels. These technologies have a heavy toll at the environment, with large amounts of carbon oxides released annually. Countries with large oil or carbon reserves, like China, meet their hydrogen needs with conventional methods. With environmental concerns, about greenhouse gases like carbon oxides, growing globally and with nations committed to neutralize their carbon footprints,  $H_2$  has to be obtained without the burden of  $CO_2$ .

Green hydrogen principal is carbon neutral  $H_2$  production, as the process powers typically water dissociation or biogas processes, solely from renewable energy sources. Green hydrogen can act as the trojan horse for excess energy long-term storage through Power-to-Gas (PtG) projects [103], pairing water-based hydrogen production with wind, solar, hydro, biomass and geothermal energy sources, often paired with nuclear energy [104]. However green hydrogen production correlates with an increase in demand for renewable energy production, as excess renewable energy alone, cannot substitute the energy demands for hydrogen production, which are met by fossil fuels. Replacing all grey hydrogen production globally would save annually 830 million tons of  $CO_2$  from being released to the atmosphere, requiring 3,000 TWh/year from new renewables [105], 500TWh/year less than 2020 European power demands [106]. The assumption of a complete grey hydrogen substitution from green hydrogen in the near future is utopic, however multiple countries motivate their industry to refrain from traditional energy sources, increasing carbon tax, with the largest  $CO_2$  producer globally, China aiming to produce 10% of their overall system energy from hydrogen, with 70% of it being produced from renewable sources. For the transition from grey to green hydrogen take places, blue hydrogen will be the crucial link between these technologies, providing a carbon-free yet sufficient production.

Blue hydrogen technologies are the evolution of grey hydrogen, as they are based on fossil fuels with integrated carbon capture utilization and storage (CCUS) technologies. The implementation of these technologies is a crucial step towards the transition to completely carbon-free methods [45]. However, a plant can be considered blue if there is a carbon capture installation, without the capturing efficiency playing a role. The efficiency rates vary from 65-85%, even 90% according to some reports [45], [107], considering however the energy consumed by the capture facility decreases the overall  $CO_2$  captured when powered non-renewably. Blue hydrogen has attracted attention from multiple nations, with EU subsidizing CCUS with 587M euros. The toll

of CCUS application in hydrogen production, however, lead to a decrease in overall production efficiency, with SMR efficiency for example being decreased 5-14% [45].

Another option to power hydrogen production, is the overlooked nuclear energy, labeled as purple hydrogen. Nuclear energy has a notorious reputation, connected with almost clean and efficient power production alongside with tragic accidents, permanently marked in modern history. Besides its reputation, it is still a viable option for multiple nations as Russia and China, to power water electrolysis, thermochemical and thermoelectrochemical processes, or even utilize the escaping heat from the plant for fossil fuel conversion to  $H_2$  [45], [104], [108]. Nuclear energy can complement intermittent renewable sources, stabilizing the energy input to each process [104], [108].

Additional colors standing out in the hydrogen spectrum are turquoise, yellow and aqua hydrogen. Turquoise hydrogen is  $H_2$  release from methane pyrolysis with the carbon produced as a byproduct, divided into coke (150-400 €/t), black carbon (500-1000 €/t), filaments (~1M €/t) and activated carbon (1500-1800 €/t). These products can be reapplied in industry without releasing  $CO_2$ . Yellow hydrogen is produced with energy consumed from the grid, mostly through electrolysis. This method releases  $CO_2$ , yet it is preferred from grey, in terms of overall pollution. However according to a report with research conducted on the electricity mix of 2008 in Denmark, a high operating cost was noted [109]. At last, a state-of-the-art method was developed from University of Calgary in Canada, and Proton Technologies which first was applied in February of 2021, ejecting pure oxygen to bitumen and oil reservoirs trapped underground. The in-situ gasification of bitumen is conducted under a complex system of reactions, which is triggered by an exothermic reaction caused by oxygen ejection. The heat produced separated oil from water, releases  $H_2$  without the burden of  $CO_2$  [46]–[48].

## 4.6 Hydrogen storage and transportation

For  $CO_2$  methanation to take place, sufficient hydrogen supply and storage must be taken into consideration. The means applied can directly affect the capital investment, the operating cost and the production rate of the methanation plant.

Hydrogen storage is divided into three categories, with each category being characterized by the conditions and phases  $H_2$  is stored. It can be stored compressed in gas phase, liquified in cryogenic conditions or stored in materials. Each method besides the different conditions that  $H_2$  is stored, is also described by safety, storage cost, volumetric ratio and energy consumed to store hydrogen.

The most popular storage technique is compressing hydrogen in vessels. Four distinct types of vessels have been studied, with varying structures, able to store the gas under different pressure values, hence different volumetric ratios. The first and most common type of vessels is made entirely by metal, usually aluminum or steel, capable of withstanding up to 50 MPa of pressure. This design is the heaviest among compressed hydrogen storage vessels, with poor mass storage efficiency, while achieving the lowest cost. The second type of vessels consist of steel reinforced cylindrically with fiber resin, capable of maintaining immense pressure amounts, thus bearing the highest volumetric ratio. The cost of this design is increased by half, with overall weight decreased 30-40%, compared to the first type of vessels. Another type has vessels are fully constructed by fiber, typically carbon fiber, reinforced by metal. In this design, the enclosed metal relieves only 5% of the total mechanical load, with fiber substituting the majority of metal, significantly lowering the weight of the structure, weighting almost half of the previously mentioned vessel. This vessel can withstand pressure up to 45 MPa, incapable of maintain structural integrity for values greater than 70 MPa. The overall cost is elevated, being as expensive as three fully metal vessels. The last type of vessels is fully composite, as high-density polyethylene substitutes the metal skeleton of the previous design, leading to a nonporous and extremely light design and a hefty price. This composition can store hydrogen at pressure up to 1000 bar [110], [111].

Another technology developed to store  $H_2$ , is its liquefaction in cryogenic temperature of  $-253^\circ\text{C}$ , with density of  $70\text{kg/m}^3$  at 1 bar. Gas hydrogen gets compressed and cooled, in accordance with Linde cycle, followed by a an enthalpic Joule-Thompson expansion, becoming a liquid. The liquid is stored in a vessel bearing an insulating layer, reassuring that a certain temperature is maintained. Energy content loss equals 40%, four times as much as in compression technologies, with potential obstruction of the equipment by the extreme conditions. However, this method is safer than compression, as hydrogen can explode only upon ignition [112], [113]

Other technologies utilize materials which can chemically and physically absorb hydrogen. The solid materials used are usually found in powder form, thus must reformed so hydrogen can be embedded efficiently. The materials responsible for hydrogen storage takes up the whole tank, alongside with a heat exchanger responsible for manipulating the conditions of the chamber, whether charge or discharge of the material takes place [111], [113].

In chemical processes, hydrogen reacts with the material, thus getting intergraded in the structure. Metal hydrides display good characteristics for such applications, with liquid organic hydrogen carriers (LOHCs) also being considered by researchers, as they can carry  $H_2$  in ambient conditions without the burden of carbon production.

However, LOHCs are incapable of carrying large amounts of  $H_2$ . The most vital parameters of these processes are cost, overall tank weight, operating temperature, charge and discharge kinetics and the presence of unwanted gases being released, adulterating hydrogen [111], [113].

Physical means of storage consist of porous materials where hydrogen adhere. These techniques show a great potential in terms of capacity and safety. Additionally, the high surface area, combined with good process kinetics, low binding energy and cost are making these methods competitive. On the other hand, thermal management issues, weight of the configuration and the density of the hydrogen stored, are some parameters that must be studied, in order for these methods to find large-scale applications. The materials with the greatest potential for physical hydrogen storage are MOFs, carbon porous materials and zeolites [111], [114].

Beside storage, the methods of transportation of this energy dense gas must be examined, in order for a methanation plant to be supplied sufficiently. Hydrogen transportation is vital for a methanation plant, influencing the operating cost of the plant directly, depending on the mean used. Different means of transportation are used, depending on the transportation network characteristics. For distances greater than 1,500 km, gas hydrogen carrying pipelines are the most effective option for terrestrial transportation [114], while seaborne transportation of liquid hydrogen can serve the intercontinental  $H_2$  trade. Giacomazzi [115], offered tanker designs, capable of transporting liquid  $H_2$  as early as 1989. Moreover, another onshore transportation method, is the transportation of hydrogen gas, compressed under high pressure, stored in tube trailers. Similar methods have been applied to serve mass transportation of other gases, hence there is experience considering the operating principle and safety regulations. In addition, this method has the lowest gas losses, while having the highest safety risk [113]. The options that minimize safety concerns are the methods transferring hydrogen absorbed from materials, which however come at a high cost and transfer significantly lower hydrogen quantities [111].

*Table 4.9 Hydrogen transportation methods, their characteristics and costs [111], [113]*

<b>Hydrogen transportation</b>	<b>Pressure</b>	<b>Temperature</b>	<b>Quantity</b>	<b>Cost (\$/kg)</b>
Tube trailers	200-500 bar	Ambient	420-666 kg/tube	2.86
Liquid hydrogen	Typically ambient	-253°C	0.7-4 t/tanker	1.4-2.42
Pipelines	10-20 bar	Ambient	~1000 t/day	2.73

## 5 CO<sub>2</sub> catalytic hydrogenation to CH<sub>4</sub>

The conversion of the CO<sub>2</sub> released abundantly through the exploitation of fossil fuels, into higher hydrocarbons is not a new process. The documentation of the process dates back more than a century. However, the complexity of the process mechanisms has prevented it from finding commercial applications in the past. Currently, the process is being thoroughly studied, as it enables the controlled conversion of a greenhouse gas to CH<sub>4</sub>, a useful gas which price is soaring the last years, while avoiding the risks of underground or underwater CCS. This process can be approached through different pathways, with the thermochemical process standing out. Besides that, the type of the reactor and the use of a catalysts is crucial for the efficiency of the reaction with the active metal, support material and promoter combination offering different product yields, requiring different preparation techniques and facing different limitations.

### 5.1 Methanation methods

The thermochemical hydration of CO<sub>2</sub> to CH<sub>4</sub> has been meticulously studied, posing as the methanation process which potentially has the most effective industrial applications. In a typical thermochemical process, CO<sub>2</sub> and H<sub>2</sub> enter a chamber, in which lies an active catalyst. The reactor is exposed to temperatures ranging between 150-500°C and pressure up to 100 bar, demanding high energy consumption in order for the reaction to be efficiently carried out. This thesis focuses on the thermochemical CO<sub>2</sub> hydration, with the aforementioned reaction thermodynamics revolve around it. However, the literature available expands to the study of other CO<sub>2</sub> methanation techniques, which are worth mentioning [116], [117].

The photosynthesis process is an alternative, capable of reforming CO<sub>2</sub> to CH<sub>4</sub> without the presence of H<sub>2</sub>. In this technique, highly purified CO<sub>2</sub> enters a vacuumed reactor, alongside with a metal oxide (ZnO, TiO and others) which is typically in powder or pellet form, suspended in water. After the system is left to settle for a few hours, it gets exposed to ultraviolet, visible or infrared light. When the reaction is conducted in a normal pressure, CH<sub>4</sub> is the only product. The reaction principle is based on the surface excitation mechanism of the catalyst, which is triggered by the light exposure, leading to H<sub>2</sub>O dissociation and formic acid formation, which react with hydrogen atoms, releasing CH<sub>4</sub> and O<sub>2</sub> molecules [118]–[120].

Another method that does not require H<sub>2</sub> is the electrochemical CO<sub>2</sub> hydration. In this process, CO<sub>2</sub> dissolves in H<sub>2</sub>O, leading to carbonic acid formation as the aqueous CO<sub>2</sub> solution reaches its equilibrium. Then the solution enters the electrolysis cell, which

carries two electrodes coated with an electrocatalyst, where CO<sub>2</sub> adheres and the electric current forces anions and cations to migrate and form methane. This process utilizes electrical energy, is carried out in ambient conditions and is characterized as an easily controlled process [121].

In biological CO<sub>2</sub> hydration, microorganisms are responsible for the production of CH<sub>4</sub> from a CO<sub>2</sub> and H<sub>2</sub> gaseous mixture. The bio-methanation process takes place in ambient conditions and can occur either directly (Eq. (21)) or indirectly (Eq. (22) & (23)).



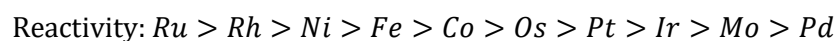
The reactions above are a result of the hydrolysis, acidogenesis and methanogenesis occurrence, which are the outcome of the synergistic action of hydrolytic-fermentative bacteria, acetogens and methanogens. These bacteria typically exist in anaerobic systems, with the reactants being fed to liquid or wet solid medium, while they are constantly stirred, improving the overall efficiency of the process [120], [122].

## 5.2 CO<sub>2</sub> thermal methanation

Over the years various methanation catalysts have been examined, with extensive literature reviewing different metals, support materials and novel catalysts combinations. The composition of a heterogeneous catalyst usually has an active metal dispersed on a metal oxide supporting material. Recently, structured catalysts and MOFs have gained popularity among the methanation research as they can be designed to deliberately enhance specific aspects of the process. W.K Fan and M. Tahir [120] have classified in detail an overview of the active metals and supports for CO<sub>2</sub> methanation.

## 5.3 Active metals

Noble and non-noble metals of groups 8-10 in the periodic table, have exhibited great ability of activating CO and CO<sub>2</sub> methanation, as can be seen in the reactivity and selectivity order below. Generalized reactivity and selectivity orders of the metals has been reported over several studies. However, the support materials implemented, the conditions inside the reactor, the type of the reactor and other factors play a significant role on the catalyst activity.



Selectivity:  $Pd > Pt > Ir > Ni > Rh > Co > Fe > Ru > Mo$

Kuznecova et al [123] carried out a preliminary rating report, assessing some of the most applied active metals. Four parameters of the metals are assessed, with selectivity, activity and stability rating the operation performance and the cost parameter rating the economic aspect of the catalyst. The performance parameters depend also in various other parameters, however, this evaluation is not considered an authority on the catalyst activity, as it highlights the metals that have the biggest potential to form a high-performance catalyst that find industrial application. The results have Ni as the best overall option, with Fe and Ru closely following and with Co and Mo being the least favorable options.

Table 5.1 Active metals assessment [123]

Catalyst	Catalyst properties			Cost
	Selectivity	Activity	Stability	
Ru	3	5	4	1
Fe	2	4	5	5
Ni	4	3	3	4
Co	1	2	1	3
Mo	5	1	2	2

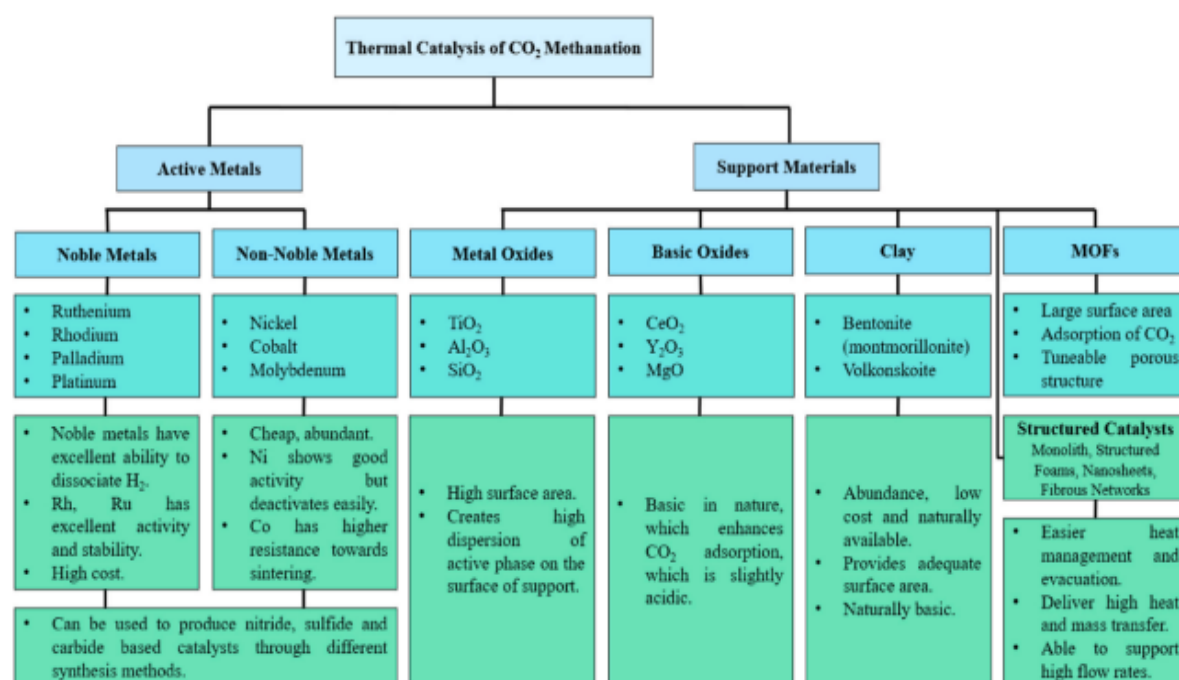


Figure 5.1 Summary of the active metals and support materials for thermal catalytic CO<sub>2</sub> methanation [120]



### 5.3.1 Noble metals

#### 5.3.1.1 Ruthenium

Ruthenium is a noble metal that stands out as an active metal for CO<sub>2</sub> methanation, due to its properties. It has demonstrated an outstanding catalytic performance, with multiple ruthenium catalysts typically exhibiting the highest activity and methane selectivity, which heavily depend on the metal dispersion. Higher dispersion of ruthenium over the catalyst surface leads to improved methanation result with decreased energy demands [124]. Additionally, catalyst based on this metal show long-term thermal stability, alongside with the ability to accelerate the reaction even in low temperatures and with low loads [5]. Pressure also affects the reaction equilibrium, with a slight increase the pressure value enhancing the reaction kinetics and favoring methane production [125]. Extensive literature is available, studying the effects of ruthenium catalysts. However, the excessively high price of the metal (costs more than hundred times the cost of Nickel) has made the implementation of a Ruthenium based catalyst in commercial plants not feasible [5].

#### 5.3.1.2 Rhodium

Rhodium is a platinum group metal, showing similar properties as ruthenium, characterized by high activity and CO<sub>2</sub> selectivity. Moreover, rhodium catalyst exhibit stability while being able to dissociate H<sub>2</sub> molecules effectively. Another noteworthy ability that rhodium catalyst bare is the product selectivity which can be tuned by the particle size, the element doping and nanoparticle environment [120]. The performance of such catalysts, however, depends on the reactor thermodynamic conditions and the feed composition. Increasing the pressure and reducing the operating temperature the methane yield is increased, a sequence derived from the exothermic nature of the reaction. As other precious metals, Rhodium is an expensive material, with its price limiting its potential for large-scale applications [126] Even though this metal can form highly active methanation catalysts, it has not attracted much attention, with limited literature around the rhodium methanation catalysts.

#### 5.3.1.3 Palladium

Catalysts based on palladium demonstrate the ability to effectively dissociate H<sub>2</sub> molecules and abundantly distribute hydrogen atoms across the catalyst surface. Palladium catalysts have an acceptable activity, stability, and CO<sub>2</sub> conversion rate.

Nonetheless, it has poor properties when compared to other noble metals and when its cost is considered, it is taken out of competition for industrial applications [120], [124]. However, in a section below the effect of multimetallic catalysts will be analyzed where the synergistic action of palladium with other metals is noteworthy.

### **5.3.2 Non-noble metals**

#### **5.3.2.1 Nickel**

The catalytic performance of this material combined with the low cost and the plentiful resources worldwide make it the protagonist of CO<sub>2</sub> methanation catalysts. Nickel catalysts have adequate methanation properties, with their main ability being the dissociation of H<sub>2</sub> molecules, which can be combined with a support material which effectively absorbs and activates CO<sub>2</sub> [124]. Wang et al. [127] bibliometric analysis has China as the leading nickel CO<sub>2</sub> methanation catalyst researcher, with 30.2% of the total papers published from Chinese institutes with Chinese Academy and International Journal of Hydrogen Energy intensely researching the catalysts properties. According to the abovementioned analysis, the benefits that nickel catalysts offer is the increase in catalyst specific area, formation of oxygen vacancies and moderately basic sites, which are accountable for improved CO<sub>2</sub> activation and adsorption. Additionally support materials monitor nickel particle size and dispersion, in order to avoid catalyst deactivation due to particle agglomeration while enhancing low temperature methanation yields. At last, resistance to oxidation is improved, leading to higher catalysts stability and higher material circulation. All in all, nickel-based catalysts will be able to industrialize carbon oxides methanation processes, once they can perform in a steady rate after many cycles and bare antioxidant properties without the need of precious metals.

#### **5.3.2.2 Molybdenum**

This transition metal has been studied as a complimentary element primarily to nickel and iron catalysts. The first studies classified the catalysts derived from this metal as negligible [128]. However, contemporary reports, have molybdenum as a part of complex structures which provide more than decent yields [129]. According to Hussain et al. [5] molybdenum has exhibited high sulfur tolerance during methanation process, finding hydrodesulfurization and hydrodenitrogenation applications. Additionally, the coexistence of Mo and Ni has reportedly promoted the carbon deposition tolerance of the catalysts, alongside with the prevention of Ni particles sintering [130]. However,

besides the poor performance of the metal by itself, it favors higher hydrocarbons production reducing methane yields [5].

### 5.3.2.3 Iron

Iron catalysts are another example of an active metal, exhibiting interesting results. Iron based catalysts can endure temperatures higher than 700°C, while it has lower price than the majority of the other metals used [5]. Catalysts solely based on iron as active metal have low reactivity and high methane selectivity, however the formation of alloys containing iron and other metals exhibit intriguing results, providing enhanced CO<sub>2</sub> conversion, CH<sub>4</sub> selectivity and catalyst tolerance over time [131]. On the contrary, iron catalysts are heavily influenced by the CO<sub>2</sub> feed, leading to various carbon species formation, without being capable to maintain their catalytic activity over time due to particle oxidation and surface sintering and coke formation [5], [132], [133].

### 5.3.2.4 Cobalt

Cobalt is a highly reactive transition metal, with similar or even higher activity than nickel with lower risk of deactivation [120]. The strong adsorption of CO<sub>2</sub> favors its catalytic activity, being better alternative than noble metals cost-wise, although it is more expensive than nickel, thus it is not that practical for large scale applications [116]. Literature extents to its combination with MOFs and organic acids as supports materials, with satisfactory results [120].

## 5.4 Bimetallic

As mentioned above, many metals showed improved catalytic activity for CO<sub>2</sub> methanation, with the presence of a complementary active metal in the catalyst. Metals such as Fe, Pt, MgO, Al, Co and other complementary metals, have been implied predominantly in already studied Ni catalysts, exhibiting better CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity most of times. For instance, the formation of Ni<sub>3</sub>Fe over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, can achieve methanation in lower temperatures with higher activity compared to the Ni catalysts [134]. Moreover, cobalt can get integrated easily in the lattice of metallic nickel, while cobalt oxides can alter the electronic properties of Ni catalysts. High Co loading drastically improve the catalyst activity and potentially improve stability [135], [136].

## 5.5 Reactor design

Reactors are also another crucial part for carbon oxides methanation. The reaction conditions often require high temperatures, which combined with the exothermic nature of the CO<sub>2</sub> methanation can lead to excessive heat being released, thus the primary parameter of the reactor design is the adequate heat management and distribution among the reactor, which is responsible for the integrity of the reactor, to avert the deactivation of the catalyst, the uncontrolled shift of equilibrium or prevent side reactions from taking place. Over the years multiple designs have been developed, some of them capable of commercial applications, others still in the research and development phase. In this thesis, emphasis is given to fixed-bed, fluidized bed, three phase, microreactors, monolith, membrane and sorption enhanced reactors.

Fixed-bed reactors are the most common type of reactors applied to the methanation process. Overall, they bare sufficient exposure of the inlet gases to catalyst molecules even for long periods. There are two types of fixed bed reactors, the adiabatic and the polytropic.

In adiabatic fixed-bed reactors, the inlet gas reacts on the surface of a static catalytic bed. Usually, for high methanation efficiency, a series of adiabatic reactors or a recirculation system is used, with the outlet gas being exposed an intercooling system, feeding the outlet stream to a reactor for further hydrogenation. This process leads to high CO<sub>2</sub> conversion rates, with this type of reactors being considered an affordable solution, capable to manage a high gas hourly space velocity (GHSV) feed. Nonetheless, the formation of hot-spots and poor load management, alongside with the potential demand of multiple reactors in order to achieve satisfactory results are the main problems of this configuration [137].

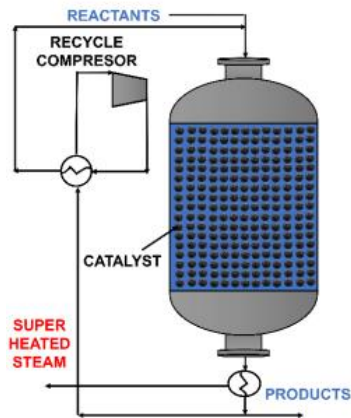


Figure 5.2 Fixed bed reactor [138]

Polytropic reactors on the other hand are based on cooled fixed-bed tubes, with the most common configuration being the multitubular fixed-bed exchanger reactor. This design consists of multiple catalyst carrying tubes, responsible for the hydrogenation of  $\text{CO}_2$ , with the rest of the reactor being filled with a cooling medium, for instance oils, water, steam, or molten salts, which are responsible for the heat management. This configuration can carry out high temperature reactions without jeopardizing the integrity of the reactor. This ability, however, is limited to certain temperatures and pressure values, which vary with the medium used, depending on the available capital of the investment. Another limitation is the amount of inlet gas that can be processed, as the tube diameters are usually small. Compared to adiabatic reactors however, multitubular reactors have longer lifespan [138].

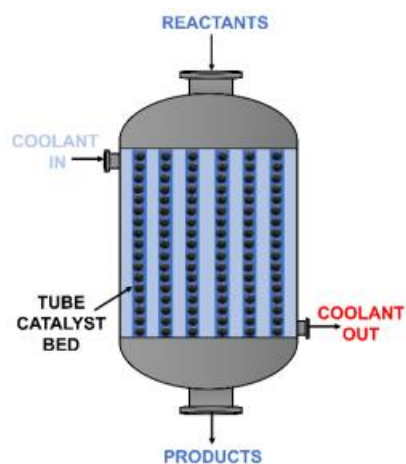


Figure 5.3 Multitubular fixed-bed reactor [138]

Fluidized bed reactor is roughly the reverse design of multitubular reactor. The steam of the reactants flows upwards, fluidizing the catalyst particles, with cooling mean, typically water, circulating inside a tube, extending inside the reactor. The surface of the catalyst practically is maximized, leading to improved efficiency heat exchange and

temperature control, compared to fixed bed reactors. This reactor is susceptible to degeneration due to high speeds of catalyst fluidization; thus, it has limited GHSV.

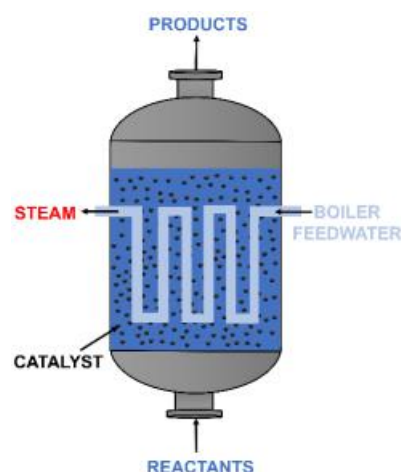


Figure 5.4 Fluidized bed reactor [138]

A reactor which still under development is the three-phase reactor. In this reactor, solid catalyst particles with diameter smaller than  $100\mu\text{m}$  are suspended over liquid dibenzyltoluene, with the inert gas steam flowing upwards. The catalyst and the suspension medium are constantly renewed, ensuring the stable isothermal conditions of the reactor. This design is based on the fluidized bed principal, with a complimentary catalyst renewal system and a different fluidizing mean. This reactor, however, is prone to backmixing, dibenzyltoluene decomposition and evaporation, while a catalyst and liquid separation step is mandatory. This configuration favors  $\text{CO}_2$  methanation over catalyst that quickly deactivates [138].

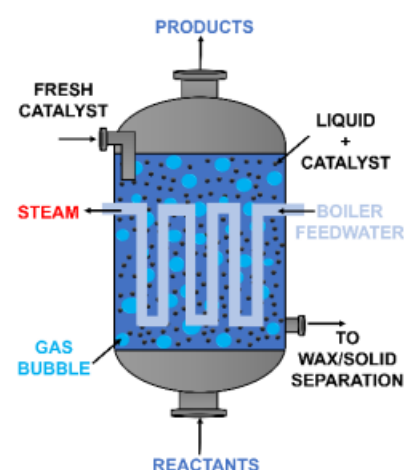


Figure 5.5 Three-phase reactor [138]

A revolutionary concept is the implementation of microreactors for  $\text{CO}_2$  hydrogenation. The compact designed microreactors consist of microchannels coated or filled with catalyst, with diameter from  $50\text{-}5000\mu\text{m}$ . The architecture of this heat exchanger and reactor hybrid, offers a high catalyst to reactor volume ratio, with its

high heat transfer preventing catalyst deactivation. Nonetheless this reactor is costly, has single-use application and the catalyst removal is almost impossible [137], [138].

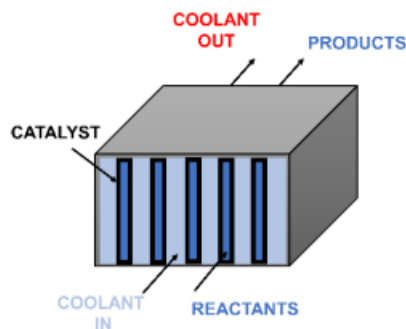


Figure 5.6 Microreactor [138]

A common reactor design, with a monolith catalyst, bares a large catalyst surface, adequate heat and pressure management and quick response time. The catalyst has holes giving it a honeycomb appearance, with the honeycomb walls with thickness from 0.05-0.3mm playing a significant role, as does hole density, in the catalyst activity. As the monoliths are primarily ceramic, they are characterized by poor mechanical properties and difficulty to be applied to large scale reactors. There is also the metallic option, which however has limited lifespan [137], [138].

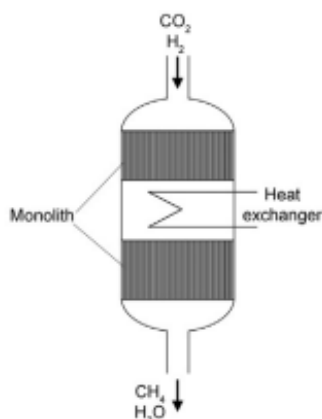


Figure 5.7 Monolith reactor [137]

Membrane reactors are based on a separate reactants feed. The hydrogen and the carbon dioxide are fed to different sides of H<sub>2</sub>O selective membrane, which expels H<sub>2</sub>O produced, forcing the methanation equilibrium to shift towards methane production. Membranes also exhibit the ability to distribute heat evenly among the reactor and producing a mixture of gases which requires less effort to be converted to SNG. On the other side of the coin, the short lifespan of the membrane, along with their cost should be further developed [137].

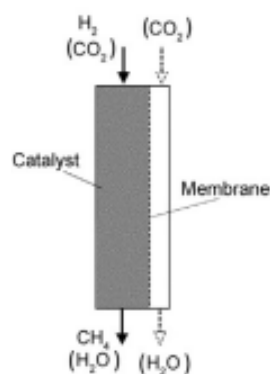


Figure 5.8 Membrane reactor [137]

Another reactor concept is sorption enhanced, which also follows Le Chatelier's principle as the membrane reactors. In this configuration, the catalyst is combined with an adsorbent which has high selectivity towards some reactants, pushing the equilibrium towards products formation in an outstanding rate. The adsorbent can regenerate through pressure or thermal swing adsorption, which however limits the reaction's operating time. Even though it is considered a complex reactor, studies report its ability to achieve up to 100% CO<sub>2</sub> conversion rate [137].

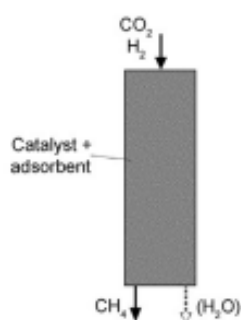


Figure 5.9 Sorption enhanced reactor [137]

## 5.6 Support materials

Support materials are a crucial part of the development of an effective catalyst. The primary objective of such materials is to enhance the active metal dispersion and complement its impact on the reaction. Support materials, often improve the reaction kinetics, reacting and forming anions or cations and stabilizing the active metal crystallites [120], [139].

The nature of the support material varies, from metal oxides to minerals and MOFs. The metal oxides like Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, have primarily been studied, with perovskites, zeolites, carbon materials and various novel support materials properties being examined [5].



### 5.6.1 Metal oxides

As mentioned above, metal oxides are the most common support materials reported. Among them,  $\text{Al}_2\text{O}_3$  stands out, as the most studied support. The effect this oxide bears to the catalytic process is correlated with its crystallographic modifications ( $\gamma, \kappa, \delta, \theta, \alpha$  phases).  $\gamma\text{-Al}_2\text{O}_3$  exhibits the best properties among the other phases, with higher porosity, surface area, pore structure and satisfactory acid-base surface properties [5], [139].

More specifically, Jaffar et al. [140] investigated the differences between various active metals, supported by  $\text{Al}_2\text{O}_3$ . According to this report, the alumina supported catalyst exhibited uniform dispersion of the active metal catalyst, as well as forming smaller particles. However various studies have reported a vulnerability to coke formation at high temperatures and particle agglomeration [5].

$\text{SiO}_2$  (silica) is another metal oxide that finds application as supporting material for  $\text{CO}_2$  methanation. It is characterized by large pore size, high surface area significant thermal stability and inert properties [120]. Besides pure  $\text{SiO}_2$ , structured catalyst supports based on this metal oxide, have also found applications on  $\text{CO}_2$  methanation, showing interesting results. Such supports will be discussed in a later section.

Another metal oxide for similar application, is  $\text{TiO}_2$ , which is one of the most effective Ni catalyst supports. Nickel can be absorbed by  $\text{TiO}_2$ , forming oxide vacancies, which combines with the high hydrogen adsorption nature of Ni. Additionally, titanium oxides often achieve their high activity by supplying Ni with electrons, increasing the catalyst performance by improving the CO dissociation [139].

Cerium and zirconium oxides ( $\text{CeO}_2$ ,  $\text{ZrO}_2$ ) influence catalysts is noteworthy. These oxides, have a redox property, which allows them to store and release oxygen, forming an environment which activates carbon oxides. This property, combined with an active component that attracts hydrogen can form a high-performance catalyst even in low temperatures [5], [139]. According to the examples of catalysts below,  $\text{ZrO}_2$  and  $\text{CeO}_2$  have excellent  $\text{CH}_4$  selectivity, with catalysts achieving close to 100%, often demonstrating higher rates than other metal oxide supports, for the same active metal loadings.

### 5.6.2 Metal organic frameworks

Over the last years, the introduction of MOFs has revolutionized the catalytic studies, opening new diodes to carry out complex processes. These synthesized compounds are a result of organic ligands and metal cluster interaction. They are characterized by

high surface area ( $1,000\text{--}10,000\text{ m}^2\text{g}^{-1}$ ), stability, porosity, recyclability and multiple active centers. Besides that, MOFs have the discrete ability of being modified, due to their structural flexibility, forming compounds with precise characteristics. Other aspects of these frameworks, is their high crystallinity, improving their  $\text{CO}_2$  adsorption and the high surface porosity, leads to increased gas transfer along their structure, making these materials strong candidates for  $\text{CO}_2$  methanation catalysts [141].

A perfect example of a MOF as support material is Pd/UiO-66 catalyst. UiO-66 is strongly basic, which lead to  $\text{CO}_2$  to adhere, due to its mildly acidic nature. The material loading played a significant role to the process, with Pd 6wt% posing as the optimum active metal load, with higher loads leading to particle agglomeration and nonuniform particle dispersion. The UiO-66 support, was responsible for the decrease of byproducts concentrations [142].

### 5.6.3 Zeolites

Zeolites are hydrated aluminosilicate minerals, with interesting properties that can be tuned according to the reaction demands. Such minerals can be found in nature, but can also be manipulated, consisting of oxygen tetrahedra, which are surrounded by Si, Al, P, Be, Zn, Mg, Co, B and other metal cations. They are characterized by a large surface area, while considered a microporous material, capable of filtering ions [13], [143]. Additionally, zeolites have found industrial applications to NG “sweetening” from hydrogen sulfide, an ability that can benefit the methanation reaction, by avoiding product poisoning.

Chen et al [144] studied the properties of beta zeolite as a catalyst support, combined with Na cations, carrying Ni and La active metals. The sodium cations addition improved the  $\text{CO}_2$  adsorption on the surface, where the addition of lanthanum significantly improved  $\text{CO}_2$  conversion and  $\text{CH}_4$  selectivity.

### 5.6.4 Carbon

Among the catalysts supports, multiple carbon materials have been implemented, providing different properties to the catalysts compared to the supports mentioned above. The effect of these supports in essence, is the enhanced hydrogen adsorption, primarily providing the reduced  $\text{CO}_2$  with hydrogen atoms to form methane. More specifically, according to W.J Lee et al. [139], these supports provide high thermal conductivity, high hydrogen storage, easily manipulated surface properties, while avoiding coke formation.

Feng et al. [145] studied the effect of carbon nanotube (CNT) and  $\text{Al}_2\text{O}_3$  supported nickel catalysts. According to this report, CNT support proved beneficial, improving the process overall outcome. The effects exhibited, are a result of CNT larger specific area, compared to  $\text{Al}_2\text{O}_3$  support, which leads to higher Ni dispersion, combined with high hydrogen storage, providing enough hydrogen for the process.

## 5.7 Promoters

Multiple reports have examined the influence of adding compounds that complement or manipulate the catalyst in the methanation process. These compounds are referred in the literature as promoters, with alkali metals, alkaline earth metals, cerium oxide and rare earths being mostly examined.

According to literature, several studies observed that alkali metals can sometime obstruct the process, as a result of the alkali-carbonate formation, however, small quantities of alkalis were suggested to replace portion of costly active metals, decreasing the overall cost without reducing the activity of the catalyst [5]. More specifically, Panagiotopoulou et al [146] reported that alkali metal promotion favored the CO dissociation and carbon species hydrogenation on  $\text{Ru}/\text{TiO}_2$  surface.

Alkaline earth metals have also showed great potential, as it improves active metal dispersion, increasing the amount of surface oxygen vacancies, enhancing catalytic performance. On the contrary, every promoter reacts differently with the catalyst, leading to different results for each combination or even activity decrease in  $\text{Ni}/\text{Al}_2\text{O}_3$  and alkali earth metals case [5].

Cerium oxide (IV) besides its role as a support material, it is also added as a promoter, with noteworthy results. More specifically, the addition of  $\text{CeO}_2$  in the 0.25wt% Ru-2.5wt%  $\text{Fe}_3\text{O}_4$ /13wt%  $\text{CeO}_x$ - $\text{SiO}_2$ -2 catalyst stabilized nanoparticle size throughout the process, improved the rate of product formation, due to the  $\text{CO}_2$  absorbing and enhanced reduction ability, while improving the oxygen storage of mesoporous silica [147]. In  $\text{Ni}/\text{Al}_2\text{O}_3$  case,  $\text{CeO}_2$  promotion was responsible for increasing the number of active  $\text{CO}_2$  and  $\text{CH}_4$  sites, with higher loads of the promoter improving the  $\text{CH}_4$  selectivity. Moreover, it was noticed that it prevented the disposition of carbon on the catalyst [148].

Other promoters include lanthanum oxide and lanthanide series. The effect of lanthanum oxide on a nickel catalyst supported by different types of zeolites, is characterized by an increase in the active sites along the catalysts surface, due to a decrease in Ni particle size, combined with an improved particle dispersion, thermal stability of the active metal and methane formation yields. Furthermore, an increase in  $\text{La}_2\text{O}_3$  load contributes to higher  $\text{CO}_2$  conversion, by aiding Ni to absorb more  $\text{CO}_2$  at

higher rates [149]. Ahmad et al [150] studied the addition of lanthanide series elements, reporting that their addition promoted metal dispersion, maintained average particle size and stabilized support materials particles. It is worth noting that Praseodymium in particular increase the active sites of the catalyst.

## 5.8 Catalysts summary

This section contains Table 5.2, with multiple potential combinations of active metals, support materials and promoters, in different conditions and reactors. They are characterized by their reaction conditions, performance rates, reaction type, GHSV (Gas Hourly Space Velocity), which expresses the volume of gas entering the reactor per hour and promoters. Furthermore, the catalysts are classified based on the support material used.

Table 5.2 Overview of various methanation catalysts and their performance.

Catalyst	T (°C)	P(bar)	X <sub>CO2</sub> (%)	S <sub>CH4</sub> (%)	Reactor	GHSV (mL/g*h)	Promoters	Ref.
Metal oxide support								
2.5 wt% Ru/TiO <sub>2</sub> (001)	325	1	>80	100	fixed-bed	-	-	[151]
Ru/CeO <sub>2</sub>	300		83	99	fixed-bed	7,640	-	[143]
0.25 wt%Ru- 2.5 wt%Fe <sub>3</sub> O <sub>4</sub> /13 wt%CeO <sub>x</sub> -SiO <sub>2</sub> -2	300	20	82	32	fixed-bed	3,000	CeO <sub>x</sub>	[147]
3.54wt% Ru/[Ca <sub>12</sub> Al <sub>12</sub> O <sub>33</sub> :OH <sup>-</sup> ]	375	1	>80	>99	fixed-bed	-	-	[152]
Rh/Al <sub>2</sub> O <sub>3</sub>	150	1	21	100	fixed-bed	-	-	[153]
0.5wt% Rh/TiO <sub>2</sub>	350	1	76-80	100	fixed-bed		-	[154]
1wt% Rh/ZrO <sub>2</sub>	300	1	61.8	98.3	tubular fixed-bed	-	-	[155]
0.5wt% Pd/TiO <sub>2</sub>	440	1	<10	~0	fixed-bed	-	-	[154]
5wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub>	240-300	1	-	22-40	tubular fixed-bed	45,000	-	[156]
Pd- MgO /SiO <sub>2</sub>	300	-	59	95	fixed-bed	-	MgO	[157]

10wt% Ni/Al <sub>2</sub> O <sub>3</sub>	360	-	83	98	fixed-bed	6,000	-	[140]
27wt% Ni/MgO	325	1	91.2	99	fixed-bed	-	-	[158]
10wt% Ni/CeO <sub>2</sub>	350	1	~90	100	tubular fixed-bed	10,000	-	[159]
Ni/ZrO <sub>2</sub>	300	1	79.1	69.5	fixed-bed	60,000	-	[160]
Fe/Al <sub>2</sub> O <sub>3</sub>	250		11.2	96.5	down-flow	-	-	
Ru-Mn-Ni/Al <sub>2</sub> O <sub>3</sub>	400	1	99.74	72.36	microreactor	-	Ru-Mn	[5]
Ni-MgO/ZrO <sub>2</sub>	300	1	85.6	100	fixed-bed	-	MgO	
Co-Ni/ZrO <sub>2</sub>	250	5	93	90	fixed-bed	-	Co	
10wt% Ni-0.5wt% Pd/Al <sub>2</sub> O <sub>3</sub>	300	1	75	97	-	5,700	-	[138]
10wt% Ni-0.5wt% Pt/Al <sub>2</sub> O <sub>3</sub>	300	1	67	97	-	5,700	-	
Ni/Al <sub>2</sub> O <sub>3</sub>	300	5	95	≥99	fixed-bed	-	La <sub>2</sub> O <sub>3</sub>	
17 wt % Ni <sub>3</sub> Fe/γ-Al <sub>2</sub> O <sub>3</sub>	358	6	71	>98	microchannel packed bed	13,400	-	[134]
Mineral support								
Ru/ZSM-5	350	1	100	100	tubular microreactor	-	-	[162]
Zeolite 13X	320	1	79	100	fixed-bed	-	-	[5]
Ni-Ce/USY	305	1	78	99	fixed-bed	-	Cs+	
15Ni-20La/Na-BETA	400	-	84	97	fixed-bed	-	La	[144]
FS@SiO-BEA	~500	1	61	65	tubular fixed-bed	45,000	-	[13]
10Ni-10La <sub>2</sub> O <sub>3</sub> /Na-BETA	800		65	99	tubular fixed-bed	10,000	La <sub>2</sub> O <sub>3</sub>	[149]
11.25 wt Ni/r-La <sub>0.5</sub> Ce <sub>1.5</sub> NiO <sub>4</sub>	350	-	78.9	99.3	tubular fixed-bed	10,000	-	[163]
50wt% Ni/AlCeO	200	1	83.2	99.5	fixed-bed	-	-	[164]

10wt% Ni-CaTiO <sub>3</sub>	325	1	80	100	fixed-bed	48,000	-	[165]
Carbon support								
2wt% Rh/PSAC	207	1	52.6	77.8	fixed-bed	-	-	[166]
0.8wt% Rh/ACZ	402	1	~50	~100	tubular fixed-bed		-	[167]
Fe/CNT	440	20	35	26	fixed-bed	-	K <sup>+</sup>	[168]
Ni-Ca/AC	360	1	76	100	fixed-bed	-	Ca	[5]
MOFs support								
Ni-xCeO <sub>2</sub> /MCM-41	380	1	85.6	99.8	fixed-bed	-	-	[5]
6wt% Pd/UiO-66	340	40	56	97.3	fixed-bed	15,000	-	[169]
Ni <sub>20</sub> -Al <sub>2</sub> O <sub>3</sub> /MIL-53	350	1	70-75	99	fixed-bed	1,435		[170]
Hydrotalcite support								
N-I-V2.0	300	1	74.7	100	quartz U-type tubular	12,000	V	[169]
Ni <sub>0.73</sub> Zr <sub>0.03</sub> Al <sub>0.24</sub> -R	300	20	95	97.5	fixed-bed	-	-	[171]
0.25wt% Fe-Ni-Al O <sub>2</sub> -HT	362	20	100	96.8	fixed-bed	-	Fe	[126]
Other support								
Ru/Ni NW	179	1	100	100	fixed-bed microreactor		-	[172]
Ni/F-SBA-15	400	1	99.7	98.2	tubular fixed-bed	24,900	-	[173]
Ni-Mg-Al/UH	300	-	82.3	99.8	U-shape quartz reactor	12,000	-	[174]
75wt% Ni-YSZ	300	9	>90	>99	Fixed-bed	15,700	-	[175]
15wt%Ni/Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub>	350	1	~81	~99.5	fixed-bed	12000	-	[176]
OMA-1Co8Ni	400	1	79.9	97.5	tubular fixed-bed	15,000		[135]
6wt% Ni/MoO <sub>x</sub> -La <sub>2</sub> O <sub>3</sub> /SiO <sub>3</sub>	362	1	96.8	100	fixed-bed	15,000	-	[129]

Co-Al-O-600	250	20	74	99	microreactor fixed-bed	5,000	-	[177]
8wt% Ni-2wt% Co	300	1	18	90	-	15,000	-	[138]

Table 5.2 shows the plethora of material combinations forming a catalyst. In this table multiple catalyst exhibit excellent performance in the methanation process. Even though Ru/ZSM-5 is the catalyst with the best catalytic performance, 27wt% Ni/MgO, 10wt% Ni/CeO<sub>2</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/F-SBA-15, 6wt% Ni/MoO<sub>x</sub>-La<sub>2</sub>O<sub>3</sub>/SiO<sub>3</sub> are catalyst that are better contenders overall, considering their performance to cost ratio, as Ni is far cheaper than Ru.

Practically, the assessment of the catalyst is vague, considering that their industrial implementation will be based on weights that will be assigned to various the performance capabilities of the plant, which will fluctuate in order to maximize the net profit of each plant. Thus, a precise catalyst classification will also depend on the expense to operate in the required conditions, the reactor cost, plants environmental impact and other parameters that demand specific structural, environmental and economic parameters to be taken into account. Some detailed technoeconomic assessments will be studied in the following section.

Complimenting the table, Figure 5.10 and Figure 5.11 depict the effect of different catalysts in the same reaction. Both catalysts are characterized by high CH<sub>4</sub> selectivity and CO<sub>2</sub> conversion, however each catalyst follows different pathways to carry out the reaction. These examples highlight the importance of the effective combination of the catalyst materials.

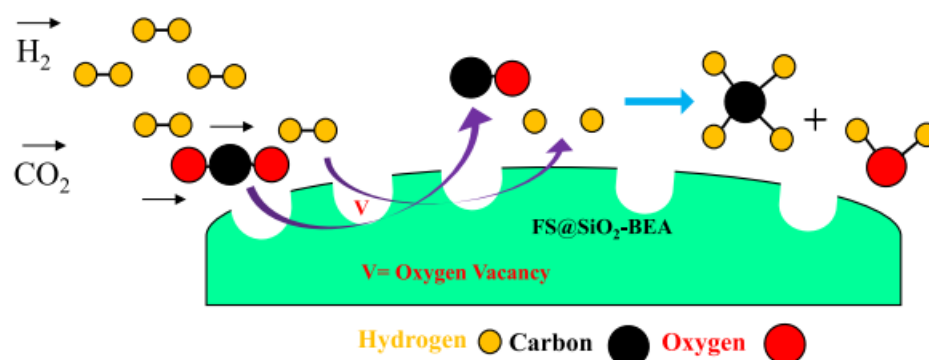


Figure 5.10 Silica Beta Zeolite catalyst setup and mechanism [13]

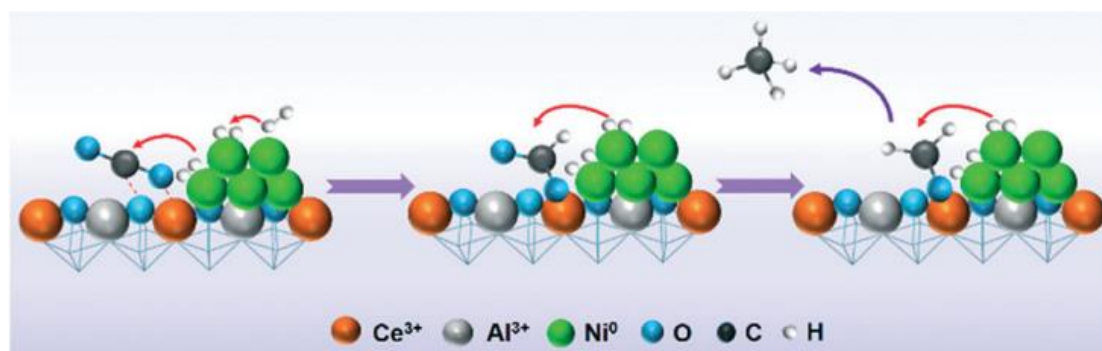


Figure 5.11 Nickel catalyst with  $\text{AlCeO}_3$  support setup and mechanism [164].

## 5.9 Catalyst preparation methods

The combination of the active metal with the support material is vital for the catalyst activity. The catalyst preparations methods are responsible for the metal dispersion and loading on the catalyst surface, particle size and crystal structure.

The most simple and widespread method for heterogeneous catalyst formation is the impregnation process. Impregnation can be achieved with two methods, with the first being wet impregnation and the second being dry or incipient wetness impregnation. The overall process starts with the diluting mean evaporation after a certain period, leading to an inactivated catalyst [178]. The difference between the two methods is the proportion of active solution to the pore volume of the support. In the first method, the solution is in abundance, contrary to dry impregnation, where the solution volume barely meets the pore volume. Each method has its defects, as the wet impregnation has active solution runoff, due to the high volume of the active solution. To minimize the active metal loss, a recycle and filtration step is required. The second method lacks the filtration of unwanted particles that may form, demanding a removal step if filtration is needed. Additionally, the simultaneous impregnation of a support by two metal solution is called co-impregnation [179].

Another popular preparation method is the sol-gel technology, where a metal salt or alkoxide is exposed to a solvent, forming a colloidal solution. This solution is then hydrolyzed and condensed, becoming liquid that surrounds a gel network. This method has drawn attention over the last years, due to its simplicity, allowing particle size and catalyst surface monitoring at low temperatures and the ability to adjust the properties of the catalyst [180].

Other preparation methods include the well-established method of microemulsion, which can form nanoparticle catalysts. In this technology, an aqueous solution of nanoparticles is dispersed over oil, forcing the particles to orientate and then integrate



with the support powder. This method forms catalysts with high thermal stability, metal dispersion, surface area and porosity [181]. Deposition precipitation process is a complex method, where metal salt is reduced and gets activated when it reacts with the support material, however this method forms catalysts with nonuniform particle dispersion [179].

## 5.10 Catalyst deactivation

Through the methanation process, catalysts are exposed to high temperatures and impurities that can decrease their impact through physical or chemical deactivation. More precisely, the most common issues that occur are catalyst fouling, sintering and poisoning. These phenomena can decrease the catalyst activity or even cause complete deactivation.

The fouling of a catalyst is the deposition of solids on its surface, interrupting the process. More specifically, in CO<sub>2</sub> methanation, carbon (also referred to as coke) deposition takes place during the Boudouard reaction, which blocks the pores and the active sites of the catalyst. However, this problem can be solved by increasing H<sub>2</sub> feed, or by adding steam in the reactor [5], [182], [183].

Catalyst poisoning is a big threat for the industrial carbon dioxide hydrogenation processes. Flue gases that can be fed to the reactor as CO<sub>2</sub> stream, often contain impurities as tars, NH<sub>3</sub>, sulfur, zinc, chlorine and other compounds. Primarily, studies examine the addition of H<sub>2</sub>S due to its high toxicity and concentration in flue gases. H<sub>2</sub>S addition in the reaction deactivated the catalyst by getting absorbed by it [182]. The poisoning is considered almost permanent, with the conventional anti-poisoning methods aiming attacking the sulfur concentration before the CO<sub>2</sub> stream enters the reactor [5], or by adding Ce or Mo as promoters, which are elements with the ability to absorb sulfur [183]. A state-of-the-art solution has been developed by Bayer Material Science AG, capable of reviving Ru catalyst [182].

High temperatures in the reactor for certain periods can lead to metal particle fusion on the catalyst, leading to catalyst deactivation. This phenomenon is called sintering and is characterized by active surface decrease, due to metal particle agglomeration, while the occurrence of sintering can be found also in the support materials lattice [183]. The most significant parameter is the reactor type, as fixed bed reactors are prone to sintering. Additionally, sintering is prevented at operation temperatures around 30-40% of the active metal melting point [182].

Other mechanism that causes catalyst deactivation is the thermal stress of sudden temperature changes, damaging the catalyst. Moreover, in fluidized bed reactors, the

collision of the catalyst molecules with each other, or with the reactor walls, leads to deactivation, in a phenomenon called attrition [182].

To conclude, an effective PtG plant is strongly based on the catalyst chosen. The active metal combination with the support material plays the biggest role in the catalyst efficiency, while parameters like reactor type, preparation method and others, not only influence the effectiveness of the catalyst to convert  $\text{CO}_2$  to  $\text{CH}_4$ , but also the lifetime of the catalyst and its uniform activity throughout its surface.

## 6 Opportunities and challenges

Despite the ability to produce SNG from CO<sub>2</sub>, PtG technology study has to extend to other dimensions. The study of the general effects, its potential and its limitations must be put under the microscope. Firstly, in this section, its environmental impacts reviewed, reporting the problems that its implementation may generate. Later, its financial feasibility is examined, as it directly correlates with its potential. Lastly, the process is studied from a sociopolitical standpoint, putting the humanitarian aspect into perspective.

### 6.1 Life cycle assessment

As environmental issues escalate, the need for a viable solution to the environmental crisis is bigger than ever. PtG processes are the most promising way to store renewable energy and excess energy produced from conventional means, while treating CO<sub>2</sub> as a valuable gas rather than a waste product. Nevertheless, CO<sub>2</sub> methanation demands energy supply not only for the main reaction but also for the acquisition of the reactants, with questions rising around its environmental sustainability.

Through various environmental assessment methodologies developed LCA is the most precise tool. The main principle of LCA is to examine most of the traces left from a product, taking into consideration the environmental impact of the raw materials production, up to the last stage of waste treatment. The whole methodology is based on the goal of the assessment, with the scope setting the limits for the detail that the life cycle will be studied. Afterwards, an inventory analysis step studies the energy and material flows, followed by an impact assessment, which determines the value of every category of environmental impact and concluding with the interpretation of life cycle, where the data are reviewed and presented [184]. Different variants of LCA exist, with the most known being cradle-to-grave, cradle-to-cradle and cradle-to-gate.

Many researchers have conducted LCA for Power-to-Methane (PtM), mostly assessing the environmental effects of different catalysts implemented in thermal methanation, with some also looking into the biological methanation alternative. In this thesis, the assessment of biological methanation will not be put into perspective.

Sayyah et al. [185] conducted LCA on CO<sub>2</sub> methanation, evaluating the environmental impact that different catalyst bares on this process. The process evaluated included a H<sub>2</sub> production unit (AEL), a CO<sub>2</sub> capture and purification unit (amine absorption), a catalyst synthesis unit and a CO<sub>2</sub> hydrogenation unit. The power plants studied produce energy with a combined cycle NG turbine and pulverized lignite coal (C) (400

MW and 800 MW produced respectively, without CO<sub>2</sub> sequestration), with the CO<sub>2</sub> capture process providing 95.6% molar purity of CO<sub>2</sub> while operating with 90% efficiency. Alongside with conventional energy production, wind turbines (WT) and 3 types of photovoltaics (PV), the amorphous silicon solar (SS) cell, copper indium selenide (CIS), CH<sub>3</sub>NH<sub>3</sub>SnI<sub>3</sub> perovskite (PS) are being considered.

The goal of the analysis is to assess 5 catalysts based on their lab scale reports and evaluate their total environmental impact. In this cradle to grave analysis the functional unit implemented in this is the production of 1 m<sup>3</sup> of CH<sub>4</sub> in one hour, while the system boundaries expand until raw material extraction, energy acquisition, transportation and production.

Table 6.1 below contains the cases and the LCI reported. Case E is considered to have the biggest environmental impact, with the highest electricity usage, case D is responsible for the highest environmental toxicity, while case A is considered the greenest option, with the highest CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity. Besides catalysts evaluation, Sayyah et al. [185] proceed to evaluate the overall impact of cases A, B, C for different power sources. Wind turbines are the most environmentally viable powering choices, while providing the following order of environmental friendliness of renewables and NG energy mixture.

$$WT + NG > CSI + NG > SS + NG > NG > PS + NG \quad (24)$$

Table 6.1 Environmental impact breakdown per catalyst [185]

Cases	Catalysts	Life cycle impact outline
A	20 wt% Ni/Al <sub>2</sub> O <sub>3</sub>	<ul style="list-style-type: none"> <li>Alumina preparation plays significant role in fossil depletion.</li> <li>H<sub>2</sub> production tetrachloromethane emissions make up most of ozone depletion.</li> <li>Nickel nitrate is responsible most of the impact of the rest of the categories.</li> </ul>
B	15 wt% Ni/TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>TiO<sub>2</sub> carbon emissions for the catalyst production are responsible for 32% and 46% of total climate change and ozone depletion respectively.</li> <li>Conventional electricity production has significant influence in fossil depletion and terrestrial acidification.</li> </ul>
C	10 wt% Ni/ZSM-5	<ul style="list-style-type: none"> <li>High energy demands for catalyst production make CO<sub>2</sub> and energy production are the main contributors in the climate change category.</li> <li>N<sub>2</sub> substitution of Ar reduces overall impact almost 80%.</li> </ul>
D	Rh@HZSM-5 core@shell	<ul style="list-style-type: none"> <li>Production of Rh causes high levels of toxic elementary flow emissions into the environment (e.g. 97,650 kg CO<sub>2</sub>, 0.0044 kg CFCs, and 2229 kg SO<sub>2</sub> per 1 kg of Rh).</li> </ul>

		<ul style="list-style-type: none"> <li>• Ar production has the second highest impact due to its use as an inert gas in catalyst reduction.</li> <li>• Catalyst synthesis and Ar production effects significantly outweigh H<sub>2</sub> and CO<sub>2</sub> acquisition.</li> </ul>
E	Rh@KZSM-5 core@shell	<ul style="list-style-type: none"> <li>• Worst scenario environmentally wise.</li> <li>• Requires more Rh and electricity to achieve the efficiency yields of other cases.</li> <li>• Significantly lower CO<sub>2</sub> conversion (55%) than other cases.</li> </ul>

Another study [186] offers a simpler LCA, evaluating catalytic and biological from biogas methanation scenarios. The goal of this assessment is to quantify the environmental impact of Power-to-Methane (PtM) in a cradle to gate analysis, with the functional unit being 1 MWh worth of synthetic methane produced, based on the higher heating value (HHV). The data used are based on the Belgian NG grid, with EU and global data complementing any missing data. Additionally, only electricity produced from WT (1-3MW energy output) is considered in the system studied, no CO<sub>2</sub> sequestration, distribution or combustion is examined. It is assumed that the methanation is a continuous process without fluctuations nor halts in production of synthetic NG (SNG), with ideal production conditions (no leaks, heat losses, or pressure drops) and converting all CO<sub>2</sub> and H<sub>2</sub> isometrically. Finally, only operational consumption of raw materials is considered, while infrastructure is considered as a background process.

The overall global warming potential of catalytic CO<sub>2</sub> methanation is 26.93 kg CO<sub>2</sub>-eq/MWh of SNG produced. Hydrogen production is 94.2% responsible for the total environmental impact of PtM, from which 98.8% is a result of WT energy consumption. Thus 1.58 kg CO<sub>2</sub>-eq/KWh are produced from other parts of the process, most of which is due to the compressor, dryer and sulfur removal. Other impact categories were also assessed with total mineral resource depletion being calculated at 0.64 kgCu-eq/KWh mainly caused by the compressor and the electrolysis, the freshwater ecotoxicity is more than 0.45 kg 1.4-DCB-eq/MWh almost solely caused by sulfur removal and water consumption (0.7 m<sup>3</sup>water/MWh) is mainly generated by electrolysis and the water consumption in the background process, which is the water consumed for electricity and material production. Moreover, an interesting suggestion is the utilization of waste heat, which can save 156.5 kWh of electricity, with temperatures at 270 °C can be useful for industrial chemical activities, avoiding additional emissions, where upgrades on the process design can utilize the residual heat in different steps of the process, like CO<sub>2</sub> sequestration.

In a different approach, LCA is combined with JRC-EU-TIMES energy system model (ESM), offering a more holistic view on the PtM potential [187]. ESM offer an insight into the cost and feasibility of an energy system, with the specific model focusing on

analyzing energy systems in EU countries, UK and others, offering predictions about the technology performance, with the results also including the optimum investment portfolio [188]. ESM combination with LCA can be proven fruitful, as ESM takes into consideration the evolution of the process, materials and electricity mix, while integrates the financial aspect, by making assumptions about the market, leading to different energy mixes and impact. Lastly, ESM can predict the effect of policies and assess their consequences.

Despite the combination with ESM, LCA methodology remained the main, with the authors setting as a goal the assessment of 18 environmental impact categories for future methanation EU energy systems, from 1990-2050, primarily focusing on the assessment of PtM environmental impact and predict its effect. The functional unit is the satisfaction of all energy services demand, including residential, commercial, industrial, mobility and agriculture needs. Multiple CO<sub>2</sub> sources are considered, with a gradual dominance of air capture and biogenic technologies. In the scenarios the combustion emissions have not been calculated, a supply mix of liquid and gas fuels have been considered (with a gradual reform) and biofuels have been assigned neutral emissions. Furthermore, simplifications are made, as only processes with greater than ~1% contribution to total CO<sub>2</sub> emissions, only representative processes (e.g., 3/10 gas turbines), few heating and cooling methods and merge of value chains have been examined.

Six scenarios were studied in this LCA. The first two studied the reduction of total CO<sub>2</sub> by 80%, from 1990 to 2050, one with Carbon Capture and Storage (CCS) technologies and one without. The first is set as the lower limit for decarbonation, detecting trends and technologies, while the second has no CCS, examining the decarbonization feasibility if CCS meets sociopolitical barriers. The other four scenarios have 95% CO<sub>2</sub> reduction, with the first scenario evaluating the impact of a more intense decarbonization, the second without CCS, examining the effect of CCS for higher decarbonization demand, the third one is an optimum scenario, setting the higher bound for capacity and environmental impact, and the last scenario does not consider PtM, in order to evaluate the difference this process makes in the European decarbonization.

The results of this study are separated between the entire system impact and methanation impact. The indirect CO<sub>2</sub> emissions make up half of the emissions in 80% scenarios and two thirds in 95% scenarios. In the first case, 50% of these emissions are a result from upstream fossil fuel production, while on the second case the emissions are evenly distributed to manufacturing, power and industrial categories. In the 80% reduction scenario the total CO<sub>2</sub> emissions are 914 Mt CO<sub>2</sub>eq, where in 2016 the average EU emissions from combustion and heat were 1000 Mt CO<sub>2</sub>eq, with the supply sector being the most impactful sector. The power sector has the largest share

of overall impact, where 75% of electricity come from PV and WT. In general, the 80% CO<sub>2</sub> reduction scenarios have been found to have a higher toll for the environment, compared to 95% scenarios, terrestrial ecotoxicity impact is 50-80% higher in no CCS scenarios due to larger demand for electricity, marine and freshwater eutrophication impact increases, but all the other categories have a 5-10% impact reduction. Additionally, the most industry and transportation sectors cost the most to decarbonize.

Beside the main system impact results, PtM influence is the most notable outcome. The maximum allowable impact of PtM was estimated between 122.6-180.9 g CO<sub>2</sub>eq/kWh, where its allowable electricity footprint should be between 3.8-62.2 g CO<sub>2</sub>eq/kWh to be preferred over NG. Additionally, it has performed better than NG in 10 out of 18 categories, with the most energy consuming part being the electrolyzer. Methanation highest impact categories are metal and water depletion, ionizing radiation and lastly terrestrial, marine and human toxicity. In the model applied, PtM by 2050 was covering 75% of EU gas demands. Comparing the prediction with the technology available, with a prediction of not having this technology, climate change become approximately 4% worse and fossil depletion 9% worse.

In another literature review, Garcia-Garcia et al. [189] delve into the result of LCA studies in Power-to-X methods. The main findings of their research include that other than PEM electrolyzers, generate more greenhouse gas emissions than current NG production and electrolysis is beneficial for the environment only if it is powered by renewable energy sources (RES). Moreover, based on a research that analyzed Swiss data, they report that the upper bound for methanation emissions is 113 g CO<sub>2</sub>eq/kWh without CCS and 73 g CO<sub>2</sub>eq/kWh with CCS, while PtM powered by RES has higher impact than conventional NG production in human toxicity (cancer and non-cancer effects), freshwater ecotoxicity, mineral, fossil and renewable resource depletion, due to CO<sub>2</sub> capture and the wear and tear of the system.

## **6.2 Cost estimations and Techno-economic analyses**

In recent years, the need for sustainable energy, processes and materials has been developed into a necessity. Beside the environmental aspect of sustainability, which shows the direction in which modern society must move towards, the economic aspects define the paths available. Especially in the energy sector, companies have already integrated RES energy development, expanding their interests in energy transition. However, the options that will prevail are the ones that are financially viable. Consequently, for PtM processes, the economical perspective has to be studied in order to evaluate their viability as a CCU option.

Baier et al. [190], studied the cost of CO<sub>2</sub> methanation plant in 2017, capturing CO<sub>2</sub> directly from Swiss cement industry flue gases, with the SNG produced reused on site. The reason that the Swiss cement industry is specifically studied, is its high energy consumption and CO<sub>2</sub> emissions. More specifically, in 2015, it was accountable for 5% of total energy consumption and for 36% of the total CO<sub>2</sub> industrial emissions [191]. Additionally, another reason for applying CO<sub>2</sub> methanation in this industry in Switzerland, is that its centralized and continuous activity, leading to a steady production of flue gases, while making the collection of the majority of carbon oxides emissions from this sector feasible. Moreover, the high calcination temperature can provide the heat required for the SNG production.

Beside the characteristics of the industry, additional parameters have to be noted in order to understand the depth of the analysis. Firstly, this analysis aims to convert 2.5 million tons of CO<sub>2</sub>, alongside with 0.46 million tons of H<sub>2</sub> (ratio of H<sub>2</sub>/ CO<sub>2</sub> is 4:1), producing 2.04 million tons of H<sub>2</sub>O and 0.9 million tons of CH<sub>4</sub> per year, for 30 years. For the Sabatier reaction to achieve the conversion of 2.5 million tons of CO<sub>2</sub>, 503 GWh annually are required, while H<sub>2</sub> demand is covered by AEL (efficiency is set to 64%), requiring 4.1 million tons of fresh H<sub>2</sub>O and 23,900 GWh per year, with approximately 3.6 million tons of O<sub>2</sub> as a byproduct. The entire plant is powered by photovoltaics, assumed to have 16% efficiency, with 20% output loss and 5% losses of the inverter system. Thus, the power production system is designed to produce 27,604 GWh annually to offset the system losses.

After defining the parameters, the authors proceeded to estimate the cost of such an installation, using net present value (NPV) formula with interest rate of 3% and a 10% discount to PV and AEL installation due their large size. The results of the capital expenditures (CapEx) and operational expenses (OpEx) are reported in the Table 6.2 below.

Table 6.2 Costs per infrastructure in detail [190]

Infrastructure	Expenditure	Value
Photovoltaics installation	Investment cost (million CHF)	20,703
	Investment cost/power (CHF/kW)	900
	Operational cost (million CHF/year)	1,982
	Cost/energy consumption (CHF/kWh)	0.09
Alkaline Electrolysis plant	Investment cost (million CHF)	13,471
	Investment cost/power (CHF/kW)	636
	Operational cost (million CHF/year)	1,397
	Cost/energy consumption (CHF/kWh)	0.11
Methanation plant	Investment cost (million CHF)	4,405
	Investment cost/power (CHF/kW)	208



Overall plant	Operational cost (million CHF/year)	457
	Cost/energy consumption (CHF/kWh)	0.04
	Investment cost (million CHF)	38,579
	Investment cost/power (CHF/kW)	900
	Operational cost (million CHF/year)	3,836
	Cost/energy consumption (CHF/kWh)	0.24

According to the findings of the abovementioned report, PV installation has the highest CapEx and OpEx, being responsible for the 53.66% of the total investment cost and 51.67% of the total annual operational expenses. On the other hand, the methanation plant makes up 11.41% of total investment cost and 11.91% of the total annual operational expenses, being the least expensive both operational and investment wise. It worths noting that there is no SNG and H<sub>2</sub> transportation and storage cost taken into consideration. Additionally, the SNG produced translates to one third of the Swiss annual NG consumption, which was evaluated 3.6 times more expensive than conventional NG, projected to generate 1.059 billion CHF per year if consumed concluding to a feasible investment.

Another interesting techno-economic assessment [192] was conducted in 2021, evaluating PtM plant feasibility in Greece, capturing CO<sub>2</sub> from cement plant flue gases with MEA scrubbing combined with AEL H<sub>2</sub> production powered by PV and WT. The system that they studied was defined by the capture of the entirety of the cement industry flue gases, the H<sub>2</sub> production was fixed for ratio of H<sub>2</sub>/ CO<sub>2</sub> of 4, the methanation was carried out by the most efficient catalyst, the existence of heat management alongside with pressure drops, heat loses and other equipment not having optimum efficiency (e.g for pumps and compressors efficiency is approximately 75-80%). Lastly, the useful life of the plant was expected to be 25 years, the discount rate was set at 4% and the regional tax rate on the net profit is 24%.

The system studied has also defined infrastructure parameters. The MEA unit was assumed to have 88% efficiency, capturing flue gases containing 13.7 v/v% CO<sub>2</sub>. The renewable powered 2200 MW AEL is expected to produce 32.4 t/h, is powered annually by 7043 GWh and 2032 GWh power produced by PV and WT respectively, with 303 GWh/yr of surplus power being stored in lead acid batteries. The efficiency of the AEL was expected to be 75%, producing also O<sub>2</sub> of more than 99% purity at 10 bar, which is sold. For the CO<sub>2</sub> methanation, CO<sub>2</sub> is compressed to 10 bar, and heated with H<sub>2</sub> to 300°C, producing SNG of 90.5% purity, with H<sub>2</sub> making up most of the byproducts. The catalyst consists of nickel, supported by ceria nanorods, with CO<sub>2</sub>

conversion of 93% and ~92% CH<sub>4</sub> yield. The projected expenses for the entire plant and the market value for the products are presented in the Table 6.3 below.

Table 6.3 Cost breakdown [192]

Type of value	Value
Total Utilities Cost (€/yr)	28,734,500
Total Fixed Capital Investment (€)	9,707,703,950
Total Annual Production Cost (€/yr)	145,479,100
Produced Oxygen Value (€/yr)	156,409,600
Produced SNG Value (€/yr)	239,191,800
Electricity Surplus Value (€/yr)	12,400,000

Cost breakdown is the most significant aspect of the cost analysis. The costs take into perspective all the systems used, with Total Fixed Capital Investment and Total Annual Production Costs also considering the support systems. The AEL plant powered by renewables is accountable for the majority of the Total Fixed Capital Investment and the Total Utilities Cost, as it comprises 93.33% and 54.26% of the costs respectively. Additionally, the 75% of H<sub>2</sub> production plant investment cost is made up by the renewables and 23% of the AEL unit. The Total Annual Cost is more evenly distributed as the CO<sub>2</sub> sequestration plant is responsible for the biggest portion of the cost (34.61%). In general, CO<sub>2</sub> methanation plant has the less significant cost among all categories, besides the Total Annual Production cost where the support system costs the least. Taking the products value into perspective, the produced SNG produces the most revenue with the electricity surplus producing the least significant revenue.

To study the feasibility of the assessed plant, three scenarios were developed. The first scenario (scenario A) is the base case scenario, considering 25 €/t carbon penalty, without SNG redirected in the cement industry, the second scenario (scenario B) explores the recycle of 200tn/h of SNG in the cement industry (equivalent to 30-35% of this industry energy needs), partial financing of the renewables for H<sub>2</sub> production and the effect of different CO<sub>2</sub> penalty costs. The last scenario (scenario C) assumed that the AEL plant is powered by the grid and the SNG is recycled in the industry. Table 6.4 below, puts the main findings into perspective.

Table 6.4 Results per scenario [192]

Scenario A	Scenario B	Scenario C
<ul style="list-style-type: none"> <li>Non-feasible scenario (NPV&lt;0)</li> <li>SNG adapted price to break-even is 1500 €/t (SNG assumed cost is 500 €/t).</li> </ul>	<ul style="list-style-type: none"> <li>SNG recycle reduces SNG and O<sub>2</sub> price to achieve break even, by 31% and 35% respectively.</li> <li>The CO<sub>2</sub> penalty increase to 100 €/t has the most</li> </ul>	<ul style="list-style-type: none"> <li>Price per kWh is set at 0.02€ where market value ranges between 0.04€ to 0.06€ per kWh.</li> </ul>

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<ul style="list-style-type: none"> <li>• O<sub>2</sub> adapted price to break even is 366 €/t (O<sub>2</sub> assumed cost is 80 €/t).</li> </ul>	<p>significant effect to break effect prices (38.5% for SNG and 54.3% for O<sub>2</sub>).</p>	<ul style="list-style-type: none"> <li>• SNG break even prices is 1079€/t for 25€/t of CO<sub>2</sub> penalty, 954€/t for 50€/t of CO<sub>2</sub> penalty, 711€/t for 100€/t of CO<sub>2</sub> penalty.</li> </ul>
	<ul style="list-style-type: none"> <li>• For 25€/t of CO<sub>2</sub> penalty, 10% and 30% of renewables capital reduction, translates to 41.1% and 61.7% break even SNG price reduction respectively.</li> </ul>	<ul style="list-style-type: none"> <li>• O<sub>2</sub> break even prices is 237€/t for 25€/t of CO<sub>2</sub> penalty, 204€/t for 50€/t of CO<sub>2</sub> penalty, 138€/t for 100€/t of CO<sub>2</sub> penalty.</li> </ul>
	<ul style="list-style-type: none"> <li>• For 25€/t of CO<sub>2</sub> penalty, 36% of renewables capital reduction, leads to SNG and O<sub>2</sub> market values.</li> </ul>	
	<ul style="list-style-type: none"> <li>• For 50€/t of CO<sub>2</sub> penalty, 28% of renewables capital reduction, leads to SNG and O<sub>2</sub> market values.</li> </ul>	
	<ul style="list-style-type: none"> <li>• For 100€/t of CO<sub>2</sub> penalty, 13% of renewables capital reduction, leads to SNG and O<sub>2</sub> market values.</li> </ul>	

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Such endeavors, however, cannot find the same application in every country across the globe, due to geological and legal limitations. Morimoto et al. [193] studied the ways that PtM could be implemented in Japan and the prospect of cooperation with another country. This study aims to evaluate the carbon footprint of Japan and economic feasibility of a methanation plant powered by various energy sources and partner with trading countries. Five different scenarios were examined, with the first (scenario A) assuming SNG was imported, CO<sub>2</sub> and H<sub>2</sub> without any CO<sub>2</sub> captured in Japan, the second scenario (scenario B) studies CO<sub>2</sub> capture in Japan combined with H<sub>2</sub> and CH<sub>4</sub> production overseas, the next scenario (scenario C) studies CO<sub>2</sub> capture and CH<sub>4</sub> production in Japan transported with pipelines, with H<sub>2</sub> produced overseas, scenario D is the same as C with LNG transport instead of pipelines and lastly, scenario E examines the whole process in Japan.

In order to review this study, the system studied has to be defined. CO<sub>2</sub> sources examined where flue gases of coal fired exhaust gases, from LNG powered plants and

from blast furnace gas from steel plants, which are absorbed by MEA with 90% efficiency. CO<sub>2</sub> catalytic hydrogenation was carried out by an adiabatic reactor at 649.7°C and 13.5 bar. Heat produced from the methanation reaction can power the electrolysis and methanation pumps and compressors, while steam produced from the reaction can generate 2.95 MWh/t CH<sub>4</sub> which is sufficient for MEA regeneration. When the methanation plant is not adjacent to CO<sub>2</sub> sequestration plant the MEA regeneration is conducted with LNG. The runoff heat is utilized only in scenarios A, C, D, E. The life cycle of CO<sub>2</sub> examined 3 different powered sources, uses CO<sub>2</sub>/t CH<sub>4</sub> as the function unit and did not include the construction phase in the assessment. Six different overseas locations were studied (UAE, Indonesia, Australia, Malaysia, Qatar, Russia)

The outcome of this study classifies scenario B for Indonesia and scenario 5 as the best options. Firstly, life cycle of CO<sub>2</sub> results suggests that SNG is environmentally viable over imported LNG, only when H<sub>2</sub> production is powered by renewables for the scenarios A and B, while for the rest of scenarios the whole process must be powered by renewables. The main comparison for the scenarios was done assuming coal plants as the CO<sub>2</sub> source. Scenario A was found to be the cheapest PtM option when paired with Indonesia (420,5 USD/t CO<sub>2</sub>), where scenario E costs 510,9 USD/t CO<sub>2</sub>. The low cost of scenario A was a result of the lack of liquefaction process, combined with the low renewable energy cost in Indonesia and the close distance between Indonesia and Japan. On the other side of the coin, scenario A is not preferred for CO<sub>2</sub> reduction, as it does not consume Japan's CO<sub>2</sub>. The CO<sub>2</sub> reduction optimal scenario was scenario E. Moreover, comparison between scenario B and C suggests that importing H<sub>2</sub> is less profitable than exporting CO<sub>2</sub>, while comparison of scenario C and D found that pipeline transportation is the cheapest option.

The report proceeded to examine further scenario B and E, with the assessment of CO<sub>2</sub> sources, showing that the lowest CO<sub>2</sub> reduction value occurred for coal produced CO<sub>2</sub> in scenario B (473.3 USD/t CO<sub>2</sub>), blast furnace produced CO<sub>2</sub> in scenario E (511.8 USD/t CO<sub>2</sub>) and LNG produced CO<sub>2</sub> in scenario E (471.5 USD/t CO<sub>2</sub>). The option with the highest cost to potential was found to be scenario E utilizing LNG produced CO<sub>2</sub>, which has the potential of converting 143.9 Mt CO<sub>2</sub>/yr with 3.0-5.1 billion USD/yr total annual cost. However, this number is far from reality, as it assumes that all the renewable power available in the island would power the PtM process.

### 6.3 Existing plants

Theoretical studies of scenarios, no matter how detailed they are, usually lack some aspects that may play a role in reality. Thus, studying existing PtM plants offers a complete view of the plant operations, accompanied with the preferred technologies

in the field, market development and leading countries experimenting with this technology on industrial level.

Thema et al. [194] analyzed data collected from 153 CO<sub>2</sub> methanation plants and their H<sub>2</sub> production technologies. The data collected are from completed, current and planned plants, some dating back to 1988, considering the plant size, shares and amount of H<sub>2</sub> and SNG produced, plant allocation and plant power development. Results from this publication are separated to H<sub>2</sub> production and PtM, using CapEx data for H<sub>2</sub> and PtM obtained from literature, paired with data collected from experts through a survey conducted in 2017.

Putting H<sub>2</sub> production under the microscope, Thema et al. [194] forecasted H<sub>2</sub> technologies prices through exponential approximation. AEL cost is expected to decrease from 1300 €/kW in 2017 to 700 €/kW in 2030 and 500 €/kW by 2050, PEM cost is expected to decrease from 1900 €/kW in 2017 to 600 €/kW by 2030 and 500 €/kW by 2050 and SOEC price is projected to drop from 3570 €/kW to 535 €/kW. These prices projections are susceptible to policies and legislations that may be enforced in the future.

Regarding CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, most aspects of the study cover the technologies used and the growth of PtM. Firstly, only 57% of the studied plants cover H<sub>2</sub> production, while when the electrolysis technologies preferred were AEL and PEM, approximately in a 50/50 ratio, where SOEC and combination of electrolysis technologies were rarely tested. The number of biological and catalytic methanation plants was evenly distributed, with the majority located in Central Europe with Germany, Denmark and The Netherlands being the frontrunners. Their potential is directly correlated with the electrical power of their installed electrolyzers, with the first having 40 MW, the second 20 MW and The Netherlands was looking to set at 12 MW. The most common type of reactor is fixed bed, followed by fluidized bed, while roughly 45% of the produced SNG was injected in the grid, probably due to standard limitations. Furthermore, the number of plants soared between 2012 and 2015, with the average plant increasing from 118 kW to 390 kW in the same timeframe.

On top of the reported results, other interesting results include plant characteristics. Mean hydrogen and methanation unit size is estimated to be 0.7 MW, where mean methanation unit power is estimated to be 1.56 MW and mean H<sub>2</sub> plant size is 0.45 MW due to small projects. Mean efficiency of methanation plants is 41% and H<sub>2</sub> plant is 77%. Additionally, only 10% of plants manages heat produced from the reaction. Considering plants lifespan, projects that were reported between 1998 and 2018 has one to three years of life, taking usually up to 1.5 year to be constructed. Lastly, mean cost of powering CO<sub>2</sub> methanation costs 800 €/kW in 2017, decreasing to 500 €/kW in 2030 and ranging between 130-440 €/kW in 2050, with methanation and electrolysis cost aligning with the progression of the years.

Some plants stand out from others due to their size, or innovation in CH<sub>4</sub> synthesis. Bailera et al. [195] reviewed the objectives and future plans for some plants in 2017. The plants reviewed were converting CO<sub>2</sub> either catalytically or biologically. As this thesis studies catalytic methanation, most of the plants reported will regard catalytic methanation, as one biological plant will be analyzed in order to provide a more complete view in the alternative PtM processes and market. The main outlook of the plants is given in Table 6.5 below.

Table 6.5 Detailed review of existing PtG plants [195]

Plant	Details
ETOGAS - Audi e-gas plant Location: Werlte, Germany	<ul style="list-style-type: none"> <li>• Longest plant in the world, with three 2 MW EAL, powered by offshore WT park in the North Sea.</li> <li>• Catalytic methanation of pure H<sub>2</sub> and CO<sub>2</sub> (obtained from biogas with amine scrubbing) in a single isothermal fixed bed reactor.</li> <li>• The project is funded primarily by AUDI AD and the local power company.</li> <li>• Runs on 54% efficiency and lacks heat management system.</li> <li>• Produces approximately 1000t of SNG and consumes 4,000 hours of renewable power annually.</li> <li>• Mature plant, which has steadily expanded, experimenting with various reactor types, CO<sub>2</sub> sources and product refinement methods.</li> <li>• Main goal is to produce SNG with 80% efficiency, while expanding to commercialized PtM systems of approximately 20 MW.</li> </ul>
Sunfire – HELMETH Location: Karlsruhe, Germany	<ul style="list-style-type: none"> <li>• PtM system with 85% efficiency, paired with 15 kW SOEC operating at 800°C and 15 bar.</li> <li>• Two methanation reactors in series, operating at 300°C and 30 bar with intermediate water removal methanation.</li> <li>• Total project funds are 3.8 million €, with 2.5 million funded by EU, with Karlsruhe Institute of Technology, Sunfire and other institutes and universities.</li> </ul>
Haldor Topsoe – El-Opgraderet Biogas Location: Foulum, Denmark	<ul style="list-style-type: none"> <li>• Demonstration plant, which upgrades biogas through CO<sub>2</sub> methanation, with H<sub>2</sub> produced from a 40 kW SOEC.</li> </ul>

	<ul style="list-style-type: none"> <li>• Total budget is 5.3 million €, with 3.5 million € funded by EU</li> <li>• Haldor Topsoe leads the project, partnered with Aarhus University which received a fund covering 70% of the construction expenses. Other institutes, power and NG companies also participate</li> </ul>
Aarhus University - MeGa store Location: Lemvig, Denmark	<ul style="list-style-type: none"> <li>• Two step biogas upgrade, with biogas purification and methanation in an air cooled reactor, using bottle H<sub>2</sub>.</li> <li>• Launched in 2013 with a lifespan of two years, produced SNG with methane content higher than 97% at 270°C and 8 bar</li> </ul>
Enagas – RENOVAGAS Location: Spain	<ul style="list-style-type: none"> <li>• First methanation plant in Spain, launched in 104 and with the first phase ending in 2017, upgrading biogas to SNG capable of being injected into the existing gas network.</li> <li>• H<sub>2</sub> produced from a 15 kW AEL unit, with the CO<sub>2</sub> conversion taking place in a multichannel reactor with a Ni or Ru catalyst based on Al<sub>2</sub>O<sub>3</sub>, oil-based cooling, operating at 25 bar, 275-300°C and GHSV of 2000-20000 per hour.</li> <li>• The goal is to build a 5MW commercial scale plant.</li> </ul>
DNV GL – Power to Gas in Rozenburg Location: Rozenburg, Netherlands	<ul style="list-style-type: none"> <li>• Basic objective is to produce SNG capable of being injected in the existing gas network.</li> <li>• Operates since 2014, providing SNG to 30 nearby apartments.</li> <li>• The unit consists of a 7 kW PEM electrolyzer, a four reactor methanation system, 2 CO<sub>2</sub> tanks and 4 solar panels on the container roof combined with power from the grid, cover the energy demands.</li> <li>• The reactors use different reaction of Ni, with the first two having 11%w, the third 37%w and the last 54%w, exhibiting optimum results at 377°C and 8 bar.</li> </ul>
Hitachi Zosen – CO <sub>2</sub> Conversion to Methane project Location: Rayong, Thailand	<ul style="list-style-type: none"> <li>• CO<sub>2</sub> conversion project based on Hashimoto [7] studies, with multiple universities and institutes being recruited to develop the technology.</li> </ul>

	<ul style="list-style-type: none"> <li>• A CO<sub>2</sub> conversion plant, collecting CO<sub>2</sub> from NG extraction sites.</li> <li>• 5 meters long tubular reactors, bearing Ni supported by zirconia-samarium catalyst.</li> <li>• H<sub>2</sub> produced from AEL.</li> <li>• A consortium of Hitachi Zosen corporation and other technology and petroleum companies.</li> </ul>
EMPA – catalytic methanation of industrially-derived CO <sub>2</sub> Location: Switzerland	<ul style="list-style-type: none"> <li>• Experimental sorption enhanced CO<sub>2</sub> methanation reactor, with high CO<sub>2</sub> conversion, while absorbing water through a Ni, supported by a zeolite, catalyst.</li> <li>• This plant has 3 different projects carried out, one for catalyst development, one for biogas upgrade and one for CO<sub>2</sub> methanation.</li> <li>• Experiments are performed at 1.2 bar GHSV is 1000 per hour, with an output of 1 kW.</li> <li>• Research is focused on renewable fuels, photo-electrolysis of water, utilization CO<sub>2</sub> from cement plant flue gases and sulfur poisoning.</li> </ul>
Tauron – CO <sub>2</sub> – SNG Location: Poland	<ul style="list-style-type: none"> <li>• Launched in 2014, aiming to produce SNG in order to store power surplus.</li> <li>• CO<sub>2</sub> is collected from Tauron coal power plant.</li> <li>• Tauron has partnered up with Atomic Energy, Alternative Energy commission and Atmosstat, which developed a reactor with 95% CO<sub>2</sub> conversion rate.</li> <li>• AGH University has developed and tested and tested the catalyst.</li> <li>• The plant potential is still examined.</li> </ul>
Electrochaea – BioCat Location: Avedøre, Denmark	<ul style="list-style-type: none"> <li>• Biological PtM plant, which aims to be the biggest biomethanation plant globally, producing SNG at 4 bar which gets injected in the gas grid.</li> <li>• It operates in dynamic mode, capable to store Danish energy surplus, converting CO<sub>2</sub> from an anaerobic digester (60% CH<sub>4</sub>, 40% CO<sub>2</sub>), or pure CO<sub>2</sub> from a conventional biogas upgrading system.</li> </ul>



- 
- $H_2$  is produced by a 1MW AEL unit, powered by excess wind power, with  $O_2$  and heat produced reused at wastewater treatment.
  - Methanation is carried out by methanogenic archaea, single-celled microorganisms, evolved by *Electrochaea GmbH*, metabolizing  $H_2$  and  $CO_2$  to  $CH_4$ , with 98.6%  $CO_2$  conversion at 60-65°C.
  - The microorganisms exhibit tolerance to  $H_2S$ ,  $NH_3$ , nitrogen oxides and other particles.
  - The overall budget is 6.7 million €, with the plant managed by the danish energy supply company *Energinet.dk*, in cooperation with multiple other companies.
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## 6.4 Sociopolitical aspect

Sociopolitical acceptance is key requirement towards a successful PtM technologies implementation. As every technology available to date however, it is not perfect, as it is clear through LCA that has an environmental impact, regarding fossil depletion, human health and freshwater ecotoxicity. Consequently, introducing a new, groundbreaking technology, with certain risks for the local ecosystem, has to be examined in terms of social acceptance and the way its benefits and risks can be communicated.

Public opinion, especially in EU does not stand with similar technologies. As  $H_2$  production and occasionally  $CO_2$  conversion is examined to be paired with renewable energy, it may face social backlash, as renewables have not been totally accepted, as many regions still disagree with their application. Additionally, CCU is often confused for CCS by the public, while CCS technologies have met resistance from stakeholders and the public in multiple European countries, CCU may be more easily accepted, as it can be regarded as waste recycling [196]. The same study assessed Power-to-X (PtX) technologies, with PtG being the method with the highest social acceptance.

Other studies suggest that CCU technologies should differentiate their approach to the general public and the local communities that they will find applications, as the first will emphasize on the benefits of their implementation and the latter will focus on the environmental risk lurking. As a matter of fact, a survey between France and Spain public opinion of CCU and CCS technologies, in regional and national level are

noteworthy. In general, CCU was approximately 10-15% more acceptable than CCS technologies, while the French were more open-minded in regional level compared to nation-wide, in contrast with Spanish where the opposite occurred [197]. Detailed graph of the result is presented in Figure 6.1.

The perspective of the public is momentous for a successful technology industrial development. Understanding the criteria in which the technologies will be assessed by the public is mandatory, as psychological, cultural and technological perception aspects are crucial for a successful implementation strategy [198]. A study conducted in 2015 in UK, suggested that stakeholders, policymakers, media and politicians are the means that are responsible for setting the tone for the social acceptance of such technologies [199].

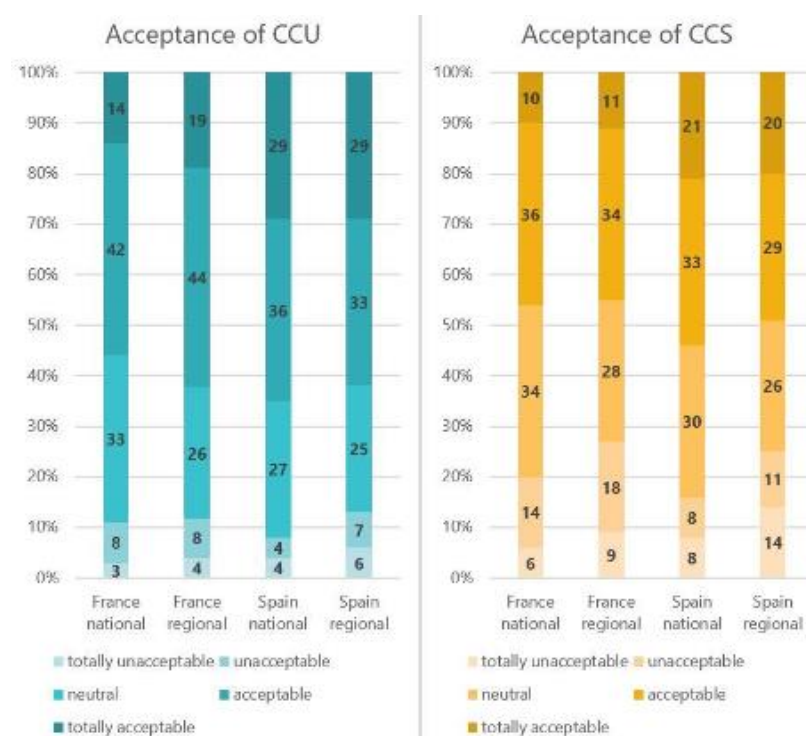


Figure 6.1 Survey regarding CCU social acceptance in France and Spain [197]

## 7 Conclusions

The purpose of this thesis was to review the catalytic CO<sub>2</sub> methanation status and potential, as a mean to restrict GHG effects, while producing an alternative fuel, capable to cover a portion of human energy demands.

CO<sub>2</sub> concentration in the atmosphere of the earth is increasing annually, with its effects being more noticeable than ever. At the same time, human activities are mostly based on fossil fuel consumption, a depleting resource which has to be substituted, while renewable sources are not capable of providing energy consistently. In this framework, significant research has been conducted on alternative energy sources, especially alternative fuels, produced by renewable sources and potentially storing their surplus. One of the most promising alternatives is SNG production as it has high calorific value and there is already existing infrastructure for its exploitation.

In this context, the present thesis studies the processes surrounding CO<sub>2</sub> methanation, followed by an analysis of their opportunities. Firstly, there is a thermodynamic analysis of the reaction, followed by a review of the CO<sub>2</sub> sequestration and separation methods, an examination of literature around the alternative hydrogen production methods and their energy sources, alongside with a detailed analysis of the CO<sub>2</sub> methanation processes, the importance of the catalysts and the details in the infrastructure and the report of current breakthroughs. Regarding the future of the technology, its environmental impact, financial viability and socio-political acceptance are reviewed in depth.

Notable findings mostly revolve around H<sub>2</sub> production, CO<sub>2</sub> methanation. H<sub>2</sub> produced globally, is almost solely powered from fossil fuels, due to the reduced cost compared to renewable powered production. However, utilizing H<sub>2</sub> produced with fossil fuels in order to convert CO<sub>2</sub> is sisyphism. Additionally, mostly electrolysis is mostly studied as an alternative hydrogen production method, due to its maturity and ability to be paired with renewable sources. However, for this specific process thermochemical H<sub>2</sub> production may have an effective contribution on CO<sub>2</sub> methanation, utilizing its excess heat produced. Beside H<sub>2</sub> production, the most promising catalyst for CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, is Ni based on Al<sub>2</sub>O<sub>3</sub>, due to its low cost, exceptional performance and according to LCA limited environmental impact.

The above sections, suggest that CO<sub>2</sub> catalytic methanation is a promising technology, capable to produce SNG relatively close to NG prices in certain occasions. However, there are plentiful obstacles that this process has to overcome, mostly regarding the immense cost of investment if the process is paired with water electrolysis and the impact of human health, caused by the catalyst.

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