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Master Thesis

Review of CO_2/H_2-methanation within power-to-gas processes

carried out for the purpose of obtaining the degree of Master of Science

(MSc or Dipl.-Ing. Or DI)

submitted at TU Wien, Faculty of Mechanical and Industrial Engineering

Rouhollah Ahmadi

Mat.Nr: 01528645

under the supervision of

Ass.Prof. Dipl.-Ing. Dr. techn. Michael Harasek

Dipl.-Ing. Dr. techn. Martin Miltner

Institute of Chemical Engineering - E166

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Abstract

The global warming phenomenon caused a revelation (transition to renewable energies such as wind or photovoltaic power) in the energy supply progress during last decades. Consequently, these changings have been dictating some challenges, so that required new technologies such as **Power to Gas** to overcome them. Because renewable energies due to their fluctuating and intermittent nature essentially need to store surplus produced power.

Power to gas is based on the conversion of power to hydrogen firstly by water electrolysis and finally synthetic natural gas (SNG) within methanation reactor. Natural gas has much more advantages than power itself. Most important ones are the portable and storable properties in a gas state (SNG) and even liquid state (LNG). Also, it can be applied as fuel for different requirements (vehicles, settlements, industries) or as feed for petrochemical units, especially it has a higher purity than fossils resources.

This investigation is primarily discussed the theoretical fundamentals of methanation reactions and its concepts, though some of these technologies are not commercially available more. The advantage of these considerations is especially remarkable for new researchers because it can help them with huge amounts of studies to find a correct path.

The core scope of this work is an investigation of commercial plants and pilot projects. European countries especially Germany are leading Power to Gas technology, with attention to a number of these plants that are operating currently within them. Attention to the production efficiency of methane and hydrogen plants caused to be created many hydrogen plants or some plant by presenting both products simultaneously beside methane plants. Although, hydrogen has the advantage of production with higher efficiency but the suitable infrastructures for storage and transfer (gas grids) and customary consumption targets (common engines) motivating to choose methanation plants for energy suppliers.

The robust plant modeling and simulation tools particularly Aspen Plus (with Object Oriented Simulation capability) and Matlab (with Simulink Environment) are applied as a trustable advisor in cost and plants efficiency and concepts comparison fields. But, in other fields such as concepts developments (e.g. novel reactors such as three phase and fluidized reactors), computational fluid dynamic (CFD) methods have truly been helping researchers. But, for simple requirements is not necessary to apply the complicated software. For example, the state of reaction system (reactant, product) can be monitored even using a basic model for methanation reactor in Excel.

The most important research fields in power to gas are, improvement of temperature control in FB reactors or development of structural reactors with high heat transfer property, enhancement of transient operation flexibility of plants against feed (CO_2, Electricity) fluctuations, development of novel catalysts with especial specification (e.g. high temperature resistance, longer life cycle in sulfur environments or high stress conditions) and development of suitable kinetic with an acceptable results in comparison with experimental data in a wide range of conditions (e.g. Xu and Froment).

This work is aimed to display, as a review study, a clear picture of CO_2-methanation fundamentals and its development progress since exploration by Sabatier et al. (1902) till now, as it is applied within the power to gas technology.

Kurzfassung

Das Phänomen der globalen Erwärmung verursachte ein Umdenken (Übergang zu erneuerbaren Energien wie Wind oder Photovoltaik) in der Energieversorgung in den letzten Jahrzehnten. Die veränderten Gegebenheiten haben neue Herausforderungen geprägt und erfordern folglich auch neue Technologien wie **Power to Gas** um sie zu lösen. Weil erneuerbare Energien aufgrund ihrer fluktuierenden und intermittierenden Natur im Wesentlichen überschüssige produzierte Energie speichern müssen.

Power to Gas basiert auf der Umwandlung von Energie in zunächst Wasserstoff durch Wasserelektrolyse und schließlich in synthetisches Erdgas (SNG – synthetic natural gas) im Methanisierungsreaktor. Erdgas hat viele Vorteile gegenüber der Energie selbst, die wichtigsten sind die tragbaren und lagerfähigen Eigenschaften in einem Gaszustand (SNG) und sogar in flüssigem Zustand (LNG). Auch kann es als Brennstoff für unterschiedliche Anforderungen (Fahrzeuge, Ansiedlungen, Industrie) verwendet werden oder als Grundlage für petrochemische Einheiten, insbesondere hat es eine höhere Reinheit als fossile Ressourcen.

In dieser Arbeit werden vor allem die theoretischen Grundlagen von Methanisierungsreaktionen und ihre Konzepte diskutiert, wobei einige dieser Technologien kommerziell nicht mehr verfügbar sind. Der Vorteil dieser Überlegungen ist besonders für neue Forscher bemerkenswert, weil es ihnen bei einer großen Anzahl von Studien helfen kann, einen korrekten Weg für die eigene Forschung zu finden.

Der Kernbereich dieser Arbeit ist eine Untersuchung von kommerziellen Anlagen und Pilotprojekten. Europäische Länder, insbesondere Deutschland, führen die Power-to-Gas-Technologie an, wobei die Aufmerksamkeit auf einige dieser Anlagen gerichtet ist, die derzeit in diesen Ländern betrieben werden. Die Aufmerksamkeit auf die Produktionseffizienz von Methan- und Wasserstoffanlagen führte dazu, dass viele Wasserstoffanlagen oder einige Anlagen geschaffen wurden, indem beide Produkte gleichzeitig neben Methananlagen präsentiert wurden. Wasserstoff hat zwar den Vorteil einer Produktion mit höherer Effizienz, aber die notwendige Infrastruktur für Speicherung und Transfer (Gasnetze) und übliche Verbrauchsziele (Common Engines) motivieren zur Wahl von Methanisierungsanlagen für Energieversorger.

Bewährte Anlagenmodellierungs- und Simulationstools, insbesondere Aspen Plus (mit objektorientierter Simulationsfähigkeit) und Matlab (mit Simulink-Umgebung), werden als vertrauenswürdiger Berater in den Bereichen Kosten- und Anlageneffizienz- und für Konzeptvergleiche eingesetzt. Auf anderen Gebieten, wie etwa bei der Entwicklung von Konzepten (z. B. neuartige Reaktoren, wie dreiphasige und fluidisierte Reaktoren), haben rechnergestützte fluiddynamische (CFD) -Verfahren den Forschern wirklich geholfen. Für einfache Anforderungen ist die Anwendung komplexer Software allerdings nicht notwendig. Zum Beispiel kann der Zustand des Reaktionssystems (Reaktant, Produkt) sogar unter Verwendung eines Basismodells für den Methanisierungsreaktor in Excel überwacht werden.

Die wichtigsten Forschungsgebiete im **Power to Gas** Bereich sind die Verbesserung der Temperaturregelung in FB-Reaktoren oder die Entwicklung von Strukturreaktoren mit hoher Wärmeübertragungseigenschaft, Verbesserung der transienten Betriebsflexibilität von Anlagen gegen Fluktuationen (CO_2, Elektrizität), Entwicklung neuer Katalysatoren mit spezieller Spezifikation (z.B. hohe Temperaturbeständigkeit, längere Lebensdauer in Schwefelumgebungen oder hohe Spannungsbedingungen) und Entwicklung geeigneter Kinetik mit akzeptablen Ergebnissen im Vergleich zu experimentellen Daten unter verschiedensten Bedingungen (z. B. Xu und Froment).

Diese Arbeit zielt darauf ab, als Übersichtsarbeit ein klares Bild der Grundlagen der CO_2-Methanisierung und ihrer Entwicklungsfortschritte seit der Exploration durch Sabatier et al. (1902) bis jetzt über die angewandte „Energie-zu-Gas“-Technologie zu geben.

Nomenclature

Abbreviations

Abbreviation	Denotation
ACM	Aspen Custom Modeler
ADAM	Anlage mit Drei Adiabaten Methanisierungsreaktoren
Cat.	Catalyst
CHP	Combined Heat and Power
Conoco	The Continental Oil Company (today: ConocoPhilips,United States)
DBFZ	Deutsches Biomasseforschungszentrum
DRI	Desert Research Institute
DVGW	Deutsche Vereinigung des Gas- und Wasserfaches
dyn.	Dynamic
EU	European Union
ECN	Energy Research Centre of the Netherlands
ER	Eley-Rideal
ESME	ECN System for Methanation
EWE	Ems-Weser-Elbe Netz GmbH
FB	Fixed-bed
Ger.	Germany
GHG	Greenhouse Gas
GL mass transfer	Liquid-Gas mass transfer
HICOM	High Combined Shift Methanation
HSR	Hochschule für Technik Rapperswil
i.s.	In series
isoth.	Isothermal
ICI	Imperial Chemical Industries
IMR	Institute for Material Research
IWES	Fraunhofer-Institut für Windenergie und
Jap	Japan
KIT	Karlsruhe Institute of Technology
LH	Langmuir-Hinshelwood
LNG	Liquid Natural Gas
n.s.	Not specified
ORC	Organic-Rankine-Cycle
PSI	Paul Scherrer Institut
PEM	polymer electrolyte membrane
PtG	Power-to-gas
PV	photovoltaic
RDS	Rate-Determining Step
2nd Law	The second law of thermodynamics
SGC	Swedish Gas Centre
SNG	Synthetic Natural Gas
SNO	Semenov number optimization
SOEC	Solid Oxide Electrolyzer Cell
STP	Standard Temperature Pressure
stat.	Stationary
S.S.	steady state
therm.	Thermal
TPR	Temperature Programmed Reduction
TREMP	Topsøe Recycle Energy-efficient Methanation
ZSW	Zentrum für Sonnenenergie- und Wasserstoff-Forschung

Symbols

Symbol	Unit	Denotation
A_i	[-]	Species i that entering in reaction
B	[-]	Heat production potential
C_F	m	Forchheimer coefficient
c_p	$[Jkg^{-1} K^{-1}]$	mixture specific heat
Da_I	[-]	Damköhler number (first order)
D_t	[m]	tube diameter
E_a	$Jmol^{-1}$	activation energy
G	[J]	Gibbs free enthalpy
G	$[kgm^{-2} s^{-1}]$	gas load
GHSV	$[h^{-1}]$	Gas Hourly Space Velocity
ΔG°_R	[J]	Gibbs free enthalpy of reaction at standard condition
H	[J]	Enthalpy
ΔH_R	$[Jmol^{-1}]$	enthalpy of reaction
K	m^2	bed permeability
K_P	[-]	Equilibrium Constant
L_R	[m]	reactor length
pδ_eq(p_i,T)	[-]	Distance to equilibrium
p_0	[bar]	Total pressure at standard condition
p_i	[bar]	Partial pressure of species i
p_i^*	[bar]	Partial pressure of species i, representing equilibrium state
R	8.314 [J/mol.K]	Ideal Gas Constant
R_u	8.314 [J/mol.K]	universal gas constant
$r^{(V)}$	$[molm^{-3} s^{-1}]$	volumetric reactionrate
Re	[-]	Reynolds number (Convective momentum transport rate/viscous momentum transport rate)
S	$[J.K^{-1}]$	Entropy
Se	[-]	Seminov number (Heat production rate/cooling rate)
St	[-]	Stanton number (Cooling rate/convective transport rate)
T	[K],[°C]	Temperature
$U_{w,0}^{(eff)}$	$[Wm^{-2} K]$	effective wall heat transfer coefficient
v_i	[-]	Stoichiometric Coefficients of species i
x_i	[-]	Concentration fraction of species i
η	[-]	effectiveness factor
γ	[-]	Activation energy/thermal energy

Chapter 1

Introduction

1. Introduction

As we have been observing for the past two decades, the supply of energy is obviously changed, otherwise, our conservation on the earth is not going to be possible more (Figure 1.1). For a long time, we had just been using the fossil sources of energy, but at the beginning of the Industrial revolution between 1760 and 1820 [1] this process was accelerated (Figure 1.2), and it caused rising the emission of greenhouse gases including CO_2, which is seen as a major driver of the greenhouse effect and global warming.

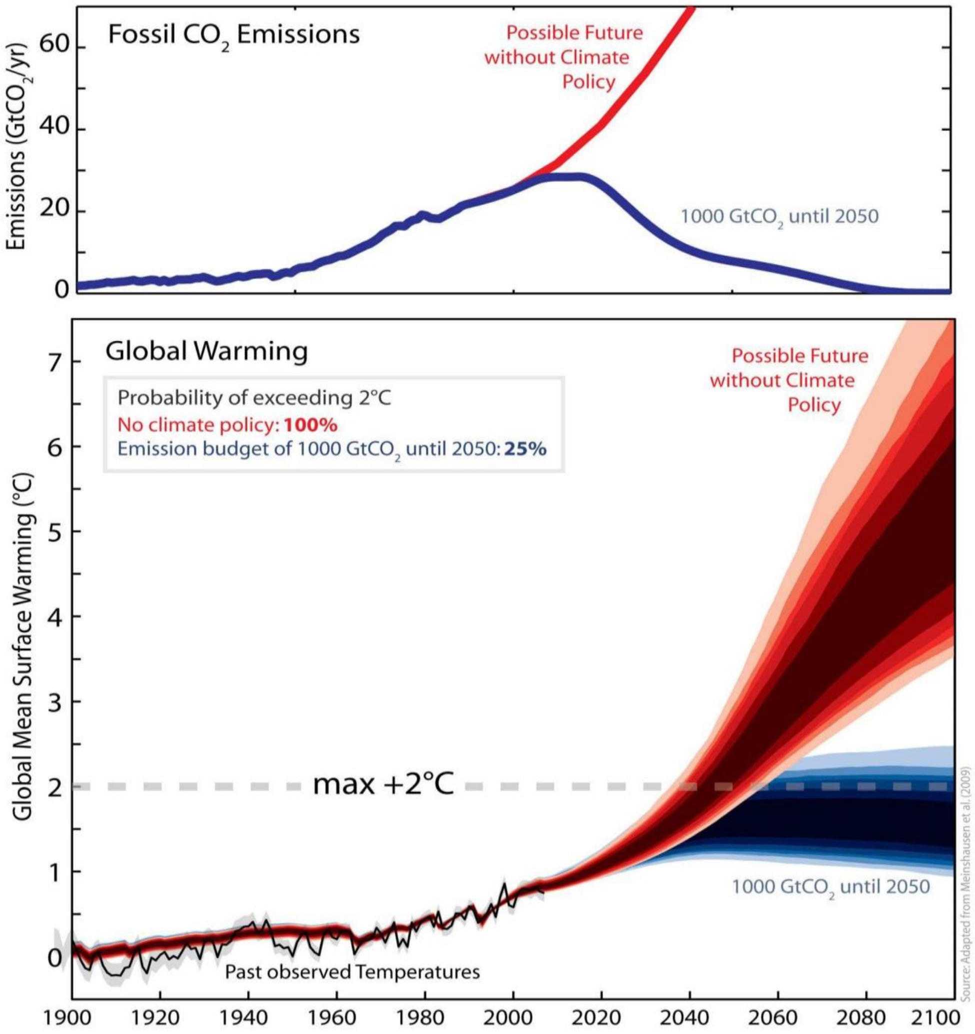


Figure 1.1 Two possible future scenarios: *One in which no climate policies are implemented (red), and one with strong actions to mitigate emissions (blue). Shown are fossil CO_2 emissions (top panel) and corresponding global warming (bottom panel). The shown mitigation pathway limits fossil and land-use related CO_2 emissions to 1,000 billion tons CO_2 over the first half of the 21st century with near-zero net emissions thereafter. Greenhouse gas emissions from this pathway in the year 2050 are ~70% below 1990 levels. Without climate policies, global warming will cross 2°C by the middle of the century. Strong mitigation actions according to the blue route would limit the risk of exceeding 2°C to 25%. Source and ©: Nature* [2].

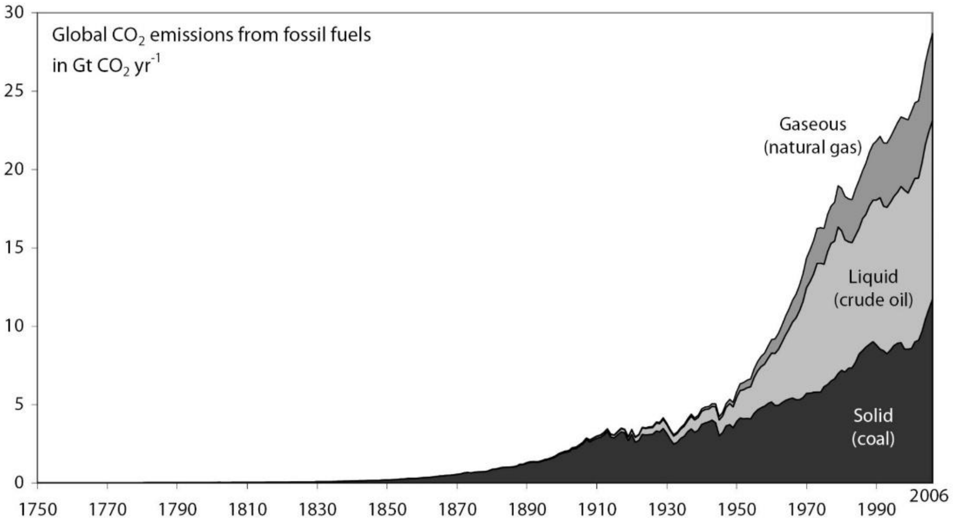


Figure 1.2 Growth of global CO_2 emissions from fossil fuels in Gt CO_2 per year (1750-2006), [7,3].

For Example, in order to keep climate change below 2ºC, the European Council reconfirmed in February 2011 the EU objective of reducing greenhouse gas emissions by 80-95% by 2050 compared to 1990, in the context of necessary reductions according to the Intergovernmental Panel on Climate Change by developed countries as a group 3. This is in line with the position endorsed by world leaders in the Copenhagen and the Cancun Agreements. These agreements include the commitment to deliver long-term low carbon development strategies [4].

Figure 1.3 illustrates the pathway towards an 80% reduction by 2050, shown in 5-year steps. The upper "reference" projection shows how domestic greenhouse gas emissions would develop under current policies.

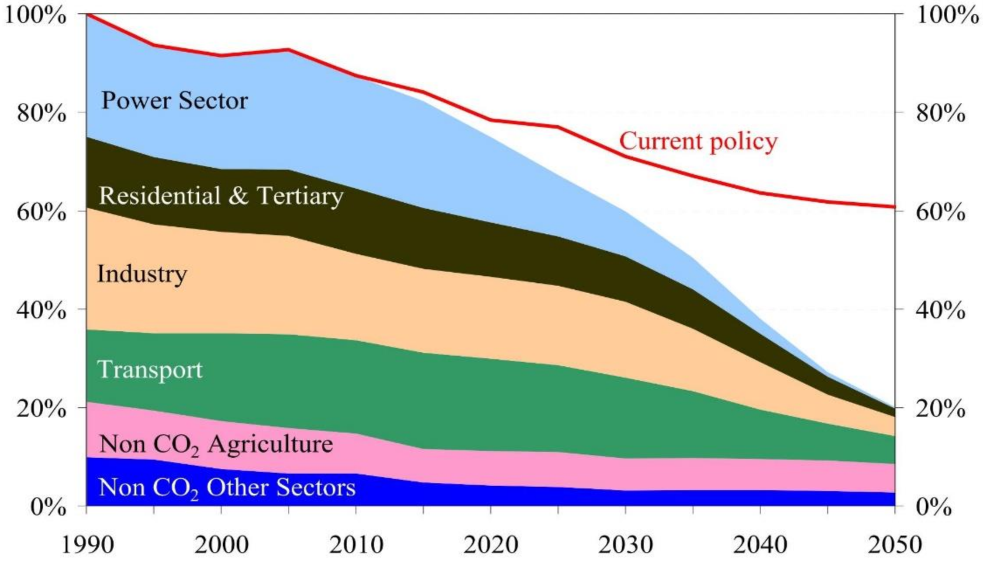


Figure 1.3 EU GHG emissions towards an 80% domestic reduction (100% =1990), [4].

The best way to control and reverse these process is a transition to renewable and clean energy sources, such as wind power and photovoltaic cells. But this strategy will lead to some challenges that the most important ones are going to be reported here:

- In contrast to conventional power plants, renewable energies are known as fluctuating and intermittent energy sources and they depend on atmospheric conditions, day and night or season etc. Consequently, there is a need to store energy (electricity) when it is available, to provide and apply it immediately on demand and to transport it cheaply and efficiently for other customers with different requirement.
- Also, if it is going to replace renewable energy with 40% of required fossil energy by 2050 according to Figure 1.3, one might anticipate about converting renewable energy to transportable fuels for mobile applications that be able to use by combustion engines.

Scientists and researchers have been looking for a way to overcome these challenges and they have introduced a number of methods, which are based on mechanical or chemical processes [5], such as:

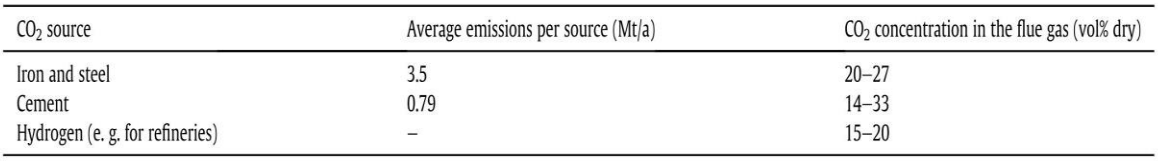
1. Mechanical electrical storage systems (Compressed air, Flywheel energy storage, Hydroelectric pumped)
2. Flow battery
3. Thermal storage system
4. Thermochemical (called solar fuel also and different fuels can be generated by solar systems such as hydrogen, hydrocarbons and heat pipes).
5. Hydrogen system
6. **Power to gas system**

In the following will be explained some reasons caused power to gas systems have particularly been considered today in the energy market.

1.1. Motivation

The chemical storages by means of so-called chemical energy carriers and in particular of synthetic natural gas (SNG) are capable to overcome the mentioned challenges (in the previous chapter), due to transition from conventional energy system to renewable energy systems. Hence, available renewable energy can be consumed to electrolyze water to hydrogen and oxygen. The produced hydrogen can then be synthesized with carbon dioxide separated for instance from off-gas of **fossil power plants** (Figure 1.4), cement industry, biomass conversion or from the atmosphere to methane (Table 1.1) [6,8]. This methane can easily be stored in the gas reservoirs, or transported via the gas grid and consumed as power resources or even feed for petrochemical plants, using already existing infrastructure (gas grid).

As shown in figure (1.4), the power to gas plants has been creating a closed loop between electricity and natural gas networks. Where, the balance between these networks can be the most important role of power to gas plants in the future, while the infrastructure of this two networks have completely been structured before.



CO_2 source	Average emissions per source (Mt/a)	CO_2 concentration in the flue gas (vol% dry)
Iron and steel	3.5	20–27
Cement	0.79	14–33
Hydrogen (e. g. for refineries)	–	15–20

Table 1.1 Properties of different industrial large scale carbon sources [6,8].

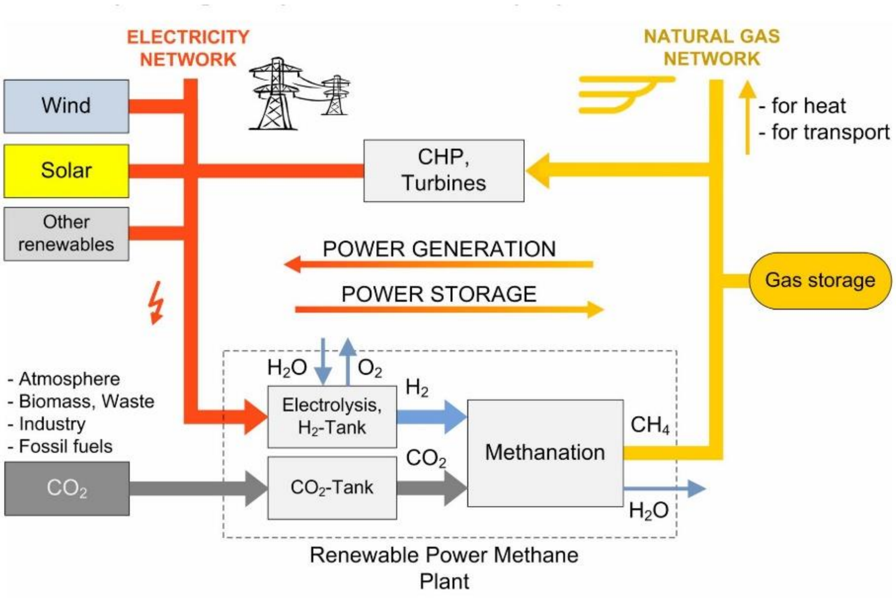


Figure 1.4 Basic concept of a renewable power to methane plant (Wind/Solar-to-SNG) with concentrated CO_2 from a tank, integrated into power and gas grid. Optionally, Surplus heat from methanation can be used in an ORC-CHP-plant to generate power [7].

1.2. Chapters overview

This thesis consists of six chapter. The **first chapter** describes the reasons, which justify the application of power-to-gas systems and cause the research groups in energy section expenditure time to develop its concepts. shortly there are going to be expressed the place and the role of **Power to Gas** technology in the future of energy industry.
Chapter 2 is organized in a way, that readers can easily catch theoretical subjects about methanation reactions such as their fundamentals, concepts (history of more than one-century development) and catalysts. According to the title of thesis, methanation of CO_2 and H_2 is supposed to be the axis of subjects in this article but due to a clear connection between CO and CO_2 methanation especially in methanation concepts and catalysts, CO methanation is advantageously considered along with the second chapter, also.
Chapter 3 is dedicated to the power-to-gas demonstration projects that particularly are operational or planned at this moment. Pilot plants are considered during the investigations also. despite, the subject of this article is limited to the CO_2 methanation within the power to gas plants, the other power to gas projects including hydrogen-methane, and hydrogen plants are briefly mentioned in the separated parts.
Chapter 4 contains a comprehensive discussion of simulation and modeling and its applications in the power to gas processes. Also in this chapter, a basic model is developed for methanation reactors using Excel. This model is able to calculate the working state and the equilibrium state of methanation reactors and compare them with presenting the Distance to Equilibrium State (DES) parameter.
Chapter 5 is concentrated on the research topic and trying to introduce the investigations and research groups based on the subjects belong to the power to gas subcategories.
Chapter 6 is presented a summary of discussed subjects. Especially, as a conclusion of this chapter is tried to illustrate for new researchers a comprehensive overview about the CO_2 methanation concepts within the power to gas technology to accompany and facilitate more comfortable new developments in this field.

Chapter 2

Theoretical Background

2. Theoretical Background

2.1. Methanation fundamentals

The debate of the finiteness of fossil resources and climate change results in the research expenditures approximate to **Thermochemical (catalytic)** and **biological** methane production from carbon oxide-rich sources (methanation) during the last decades. According to the comparison between these methods on Table (2.1), due to the higher process temperature and the resulting higher reaction velocity, Thermochemical methanation requires much lower reactor volumes for a constant feed gas flow than biochemical methanation. The Biological methanation method proceeds at a temperature range of (<70 °C) in the stirred tank or trickle-bed reactor [3,8]. Vice versa, catalytic methanation is essentially occurred at temperature conditions above 250 °C, so that is the main subject of this article. Mainly, research into catalytic methanation processes focuses on two options, CO methanation, and CO_2 methanation.

Methanation Method	**Biological**	**Thermochemical (catalytic)**	
Reactor Type	Isothermal CSTR	Isothermal slurry bubble column (Figure 2.19)	Fixed Bed adiabatic
Catalyst	the enzyme of microorganism	Ni-based	Ni-based
Stages	1	1 - 2	2 - 6
T in °C	40 - 70	300 - 350	300 - 550
P in bar	> 4	> 20	> 5 - 10
Stage of development	lab scale/pilot	lab scale	commercial
GHSV in h^{-1}	< 100	500 - 1,000	2,000 - 5,000
Limitation	GL mass transfer	GL mass transfer	equilibrium
Tolerance of impurities	high	medium	low
Electricity demand in kWh/m^3 SNG (injection pressure of 16 bar)	0.4 - 0.8	< 0.4	< 0.4
Process materials	nutrients, buffer solution	heat transfer liquid, (catalyst)	(catalyst)
Reaction Heat Utilization	poor	good - very good	very good

Table 2.1 Comparison of biological and thermochemical methanation processes ([8], adapted).

Methanation processes achieve to produce methane from the reaction between hydrogen and carbon oxides. The reaction of carbon monoxide is recognized as CO methanation (Eq. (1)), the reaction of carbon dioxide and hydrogen as CO_2 methanation, respectively (Eq. (2)).

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O\ (g) \qquad -206\ \text{kJ / mole} \qquad (\text{at } 298\ \text{K}) \qquad (1)$$

$$CO_2 + 4H_2 \longleftrightarrow CH_4 + 2H_2O\ (g) \qquad -164\ \text{kJ / mole} \qquad (\text{at } 298\ \text{K}) \qquad (2)$$

Both reactions are essentially known exothermic. The stoichiometric methanation of carbon monoxide is known with releasing 206 kJ heat per mole (Eq. (1)), but the conversion of carbon dioxide discharges 164 kJ per mole (Eq. (2)). Hence, production of each 1 m3 methane (STP) per hours results in 2.3 and 1.8 kW heat, respectively.

The hydrogen and carbon monoxide are fed in CO methanation reaction (Eq. (1)) as educt gases for the catalytic production of methane and water, which they are normally supplied by coal or biomass gasification at synthetic fuel production plants (Figure 2.1) [9].

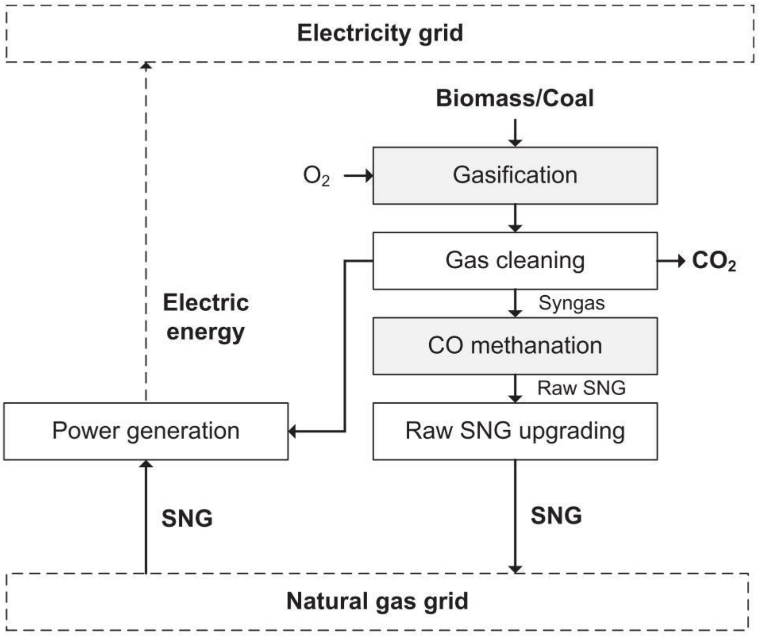


Figure 2.1 Exemplary biomass/coal-to-SNG plant setup with CO methanation, [10].

Educt gases in CO_2 methanation plants are carbon dioxide and hydrogen (Eq. (2)). As shown in figure (2.2), CO_2 methanation unlocks the doors to the chemical storage of electrical energy (**Power to Gas**), when an electrolysis supplies hydrogen into the feed stream [11].

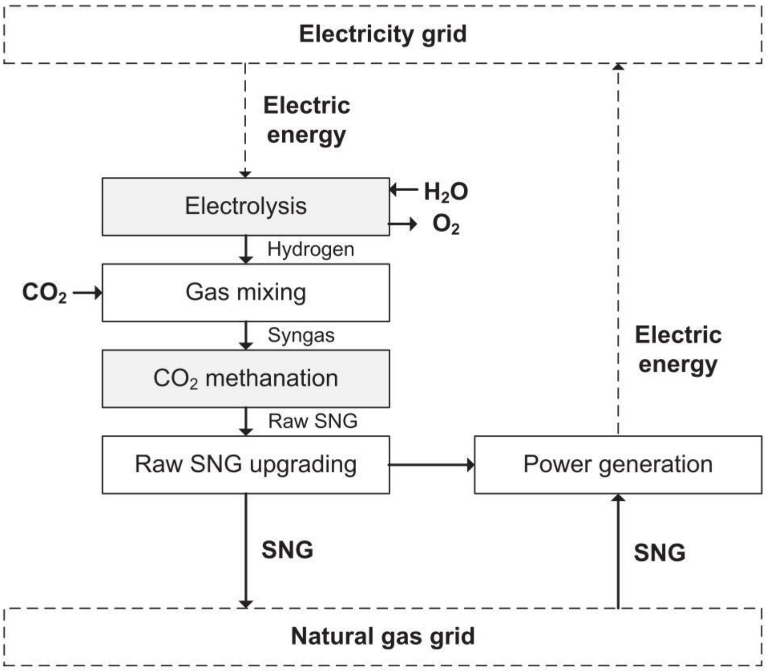


Figure 2.2 Exemplary PtG plant setup with CO_2 methanation [10].

In power to gas plants the central role is played by the CO_2 methanation, so consequently this article is dedicated to cover all aspects of CO_2 methanation, but CO methanation is slightly considered also because, it is one of the side reactions in CO_2 methanation reactors, therefore it effectively is capable to change the efficiency of reactor and plant. On the other hand, CO_2 methanation (Eq. (2)) is a linear combination of CO methanation (Eq. (1)) and reverse water-gas shift reaction (Eq. (3)), which always attends the CO methanation reaction using nickel catalysts in practical operation (section 2.1.2.2). However, conversion of CO_2 can be inhibited, if the CO concentration overpasses a certain threshold [12].

$$CO_2 + H_2 \text{<--------->} CO + H_2O\ (g) \quad 41\ kJ / mole \quad (at\ 298\ K) \qquad (3)$$

2.1.1. Equilibrium

The chemical equilibrium will occur, when the state properties of the system (temperature, pressure, concentration, etc...) as a function of time are constant. The practically equilibrium state is impossible to fulfill. In other words, a system requires infinite time to reach an equilibrium state, hence researchers try to define a particular kinetics equation for every reaction, by that they can predict the state of the system and consequently it's properties such as composition as a function of time.
The Second Law of Thermodynamics (2nd Law) has been explained in different ways. Here two practical declarations are presented:

- Heat will always flow from the hot to the cold side, never the other way.
- Chemical reactions always proceed towards an equilibrium state (with respect to temperature, pressure, and composition).

These considerations impose some limits to processes comparable to balances [13]. The second expression of the 2nd Law above can answer this question:

- how can the chemical equilibrium point be estimated for mixtures of species with the chemical reaction?

If, without derivation of the principle, we introduce the so-called Gibbs free enthalpy (G):

$$G = H - T.S \qquad (4)$$

All involved quantities are properties of the state. The formal expression of the second law can now be made using the Gibbs free enthalpy:

$$G \text{ -------> } Min \qquad (5)$$

The 2nd Law in this form is also called the principle of ***Minimization of Gibbs Free Enthalpy*** and It means that:

- *Equilibrium is fulfilled if any further change in composition due to chemical reactions would lead to an* ***increase*** *of the intensive Gibbs free enthalpy (typically the molar quantity is used to work with)* [13].

A chemical reaction is generally defined by:

$$\Sigma\, v_i \cdot A_i = 0 \qquad (6)$$

Where A_i are all species taking part in the reaction and v_i are their stoichiometric coefficients (v_i are negative for reactants and positive for products).

The equilibrium constant for partial pressures is defined as a dimensionless parameter of the partial pressures relative to standard pressure as follows:

$$K_p = \Pi \left(p_i^*/p_0\right)^{v_i} \qquad (7)$$

The superscript asterisk in (7) indicates that the partial pressures represent the equilibrium state. In the case of ideal gases, the equilibrium constant is a function of temperature only and can straightforward be calculated from standard pressure Gibbs free enthalpy of reaction:

$$Ln\,(K_p(T)) = -\,\Delta G^{\circ}_R\,(T) \,/\, R.T \qquad (8)$$

$\Delta G°_R$ (T) is the Gibbs free enthalpy of reaction at standard pressure (1 bar) [13].

2.1.1.1. Chemical equilibrium of the Sabatier reaction

As discussed above, one way to determine the equilibrium is Gibbs free energy where K_p, the equilibrium constant, is a substantial variable. The equations (9) and (10) below are related to K_p for the Sabatier reaction (Eq. (2)) that are resulted from equations (7) and (8) respectively [14,15]:

$$K_p = (X^2_{H2O} * X_{CH4})\,(X_{CO2} * X^4_{H2})^{-1}(p/p_0)^{-2} \qquad (9)$$

$$K_p = \;Exp\,(-\,\Delta G^o_T \,/\, R.\,T) \qquad (10)$$

The K_p at different temperatures for the reaction are calculated with equation (10) and they are presented in table (2.2).

Temperature		K_p
K	° C	[-]
400	127	2,70e+12
600	327	7,15e+4
800	527	7,70
1000	727	0,03

Table 2.2 K_p of the Sabatier reaction for the temperature range 127-727 °C [14].

2.1.1.1.1. Composition

Knowledge of the K_p of the reaction and equation (9) gives an understanding of how different parameters like composition, temperature, and pressure affects the reaction [14,15].

According to Le Chatelier's principle "*If a system at chemical equilibrium changes pressure, temperature or concentrations, then the equilibrium will shift to the side that would reduce the effect of the changes*" [16]. In the Sabatier reaction, if more products (water or CH_4) are interred to the mixture the production of methane will be disfavored. But higher concentrations of CO_2 would positively increase the production of methane, the forward reaction. Equation (9) proofs that adding H_2 will be much more effective than adding CO_2 to the equilibrium mixture, because of the H_2-fraction contribution with the higher power of four. Consequently, adding water will be more unfavorable than adding CH_4 on the methane production, because of the squared power of the H_2O-fraction in the equation (9).

2.1.1.1.2. Temperature

As shown in figure (2.3), high temperatures, by contrast, decreases the formation of methane, because K_p has an inverse proportion to temperature. This understanding is also proved by Equation (10) and Table (2.2).

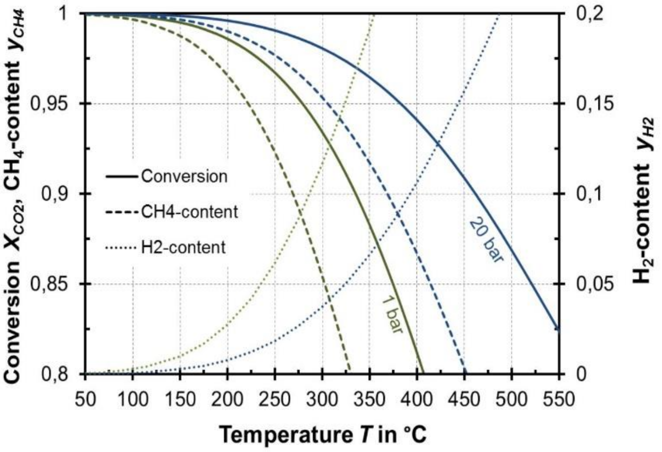


Figure 2.3 Thermodynamic equilibrium of the Sabatier reaction at different temperatures and pressures [8].

2.1.1.1.3. Pressure

In thermodynamic equilibrium, high pressures favor the production of methane, respectively conversion of hydrogen (Figure 2.3), because the number of moles of the reactants is higher than the number of moles in the products. Therefore, increasing the pressure will move the equilibrium to the products side. This can also be seen in equation (9) where the $(p/p_0)^{-2}$ factor explains the pressure dependency behavior of K_p [14,15].

2.1.1.2. Comparison of the equilibrium conditions between CO and CO_2-Methanation

As discussed before, the equilibrium of both CO and CO_2 methanation reaction, (Eq. (1)) and (Eq. (2)) depend on composition, temperature, and pressure (K_p is also a function of state).

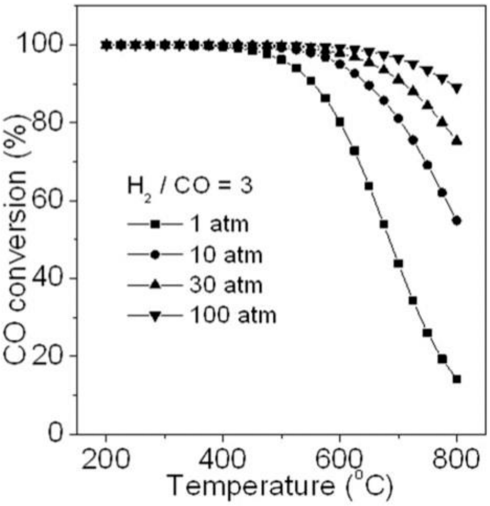


Figure 2.4 Effects of pressure and temperature on CO conversion [17].

The commercial process modeling software, such as Aspen Plus and Chemcad are easily able to model these reactions in equilibrium states and compare the influences of temperature, pressure, and composition of reactant species or even composition of non-reaction species in detailed graphs and charts [17]. The influence of pressure and temperature on the conversion of CO and CO_2 methanation at the chemical equilibrium states are shown in figure (2.4) and figure (2.5) respectively, by way of example.

Since methanation reactions are exothermal (section 2.1.1.1.2), temperature enhancement in methanation reactor decreases the conversion of hydrocarbons in both CO and CO_2 reactions. This prediction is also appeared in figures (2.4) and (2.5), in addition, according to these figures CO conversion shows a larger drop in comparison with CO_2 conversion because CO methanation releases more heat (206 kJ/mole) than CO_2 methanation (164 kJ/mole). Vice versa, the pressure increase has a positive effect on the conversion of carbon oxides (Figures (2.4) and (2.5)). However, the same differences between the stoichiometric factor or reacting substances, for equation (1) {4 moles_{in} - 2 moles_{out} = **2** moles} and for equation (2) {5 moles_{in} – 3 moles_{out} = **2** moles}, that taking part in both reactions caused similar behavior against changing of pressure (concentration) within reactors.

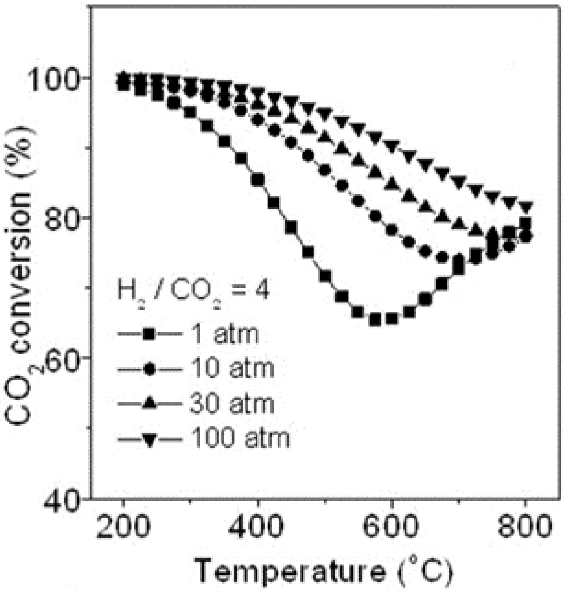


Figure 2.5 Effects of pressure and temperature on CO_2 conversion [17].

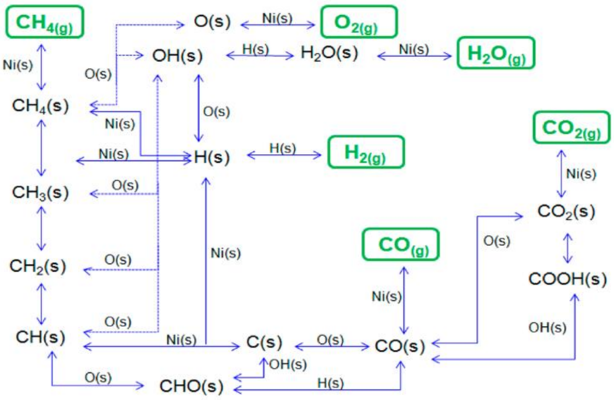
2.1.2. Mechanism

Developing and improving methanation technology would be impossible if researchers have not considered the mechanism of reactions. This subject seems to be particularly essential for developing the Kinetic of reactions and catalysts and at the same time very controversial. The researchers in this field try to discover the paths that, the reactants should go through to form the products. For example, in figure (2.6) is demonstrated reaction pathways for methane oxidation and reforming [18].

In fact, scientists try to define, choose, investigate and develop these pathways with respect to particular specifications for each reaction. After this progress, they can estimate the Rate-Determining Step (RDS) through each reaction to develop a reliable kinetic.

The mechanism of a reaction tightly depends on the catalyst using the reaction. Hence, the most common catalysts in the methanation processes are based on nickel (section 2.3), here the mechanism of CO and CO_2 methanation on nickel-basis catalysts will be presented below.

Although CO-methanation is not supposed to investigate in the current article, in the next section it is briefly considered.

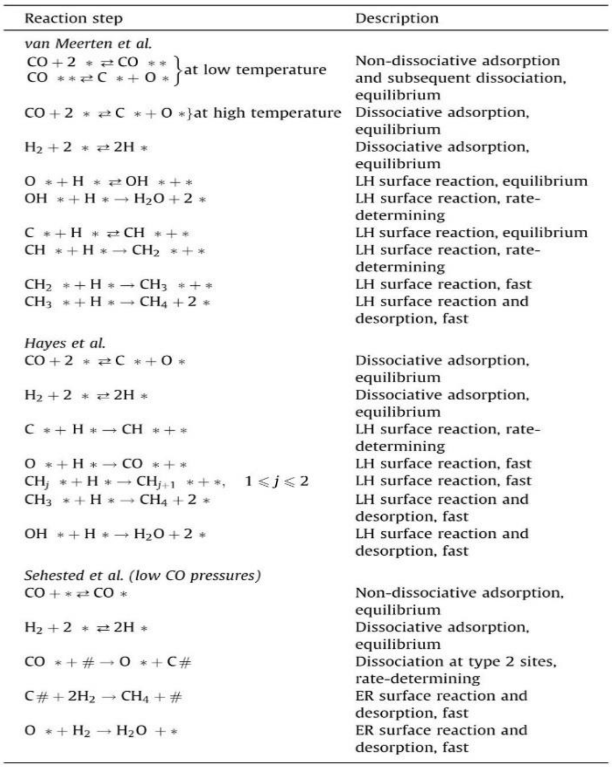


2.6 Reaction pathways for methane oxidation and reforming [18].

2.1.2.1. CO methanation

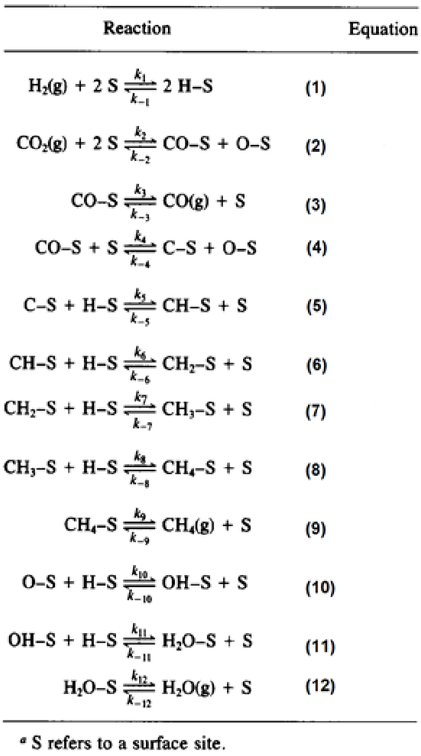
There are several reviews and studies about CO-methanation (e.g. [19,20]). A selection of CO methanation mechanisms in the literature is collected in figure (2.7) [10].

Vander Meerten et al. [21] investigated CO-methanation on a 5% Ni/Alo$_2$ catalyst in a differential flow micro-reactor. They expressed with increasing temperature the reaction order for carbon monoxide increased from -1 to +1 and the reaction order for hydrogen decreased from +1 to almost zero. Also, they understood that the reaction order of both reactants influenced on each other. They defined the adsorption of carbon monoxide on Nickel and addition of a hydrogen atom to adsorbed CH$_x$ (Figure 2.5) as RDS and suggested Langmuir-Hishelwood (LH) type of kinetic rate reaction.



Reaction step	Description
van Meerten et al.	
$\left.\begin{array}{l} CO + 2\ * \rightleftarrows CO\ ** \\ CO\ ** \rightleftarrows C\ * + O\ * \end{array}\right\}$ at low temperature	Non-dissociative adsorption and subsequent dissociation, equilibrium
$CO + 2\ * \rightleftarrows C\ * + O\ *\}$ at high temperature	Dissociative adsorption, equilibrium
$H_2 + 2\ * \rightleftarrows 2H\ *$	Dissociative adsorption, equilibrium
$O\ * + H\ * \rightleftarrows OH\ * + *$	LH surface reaction, equilibrium
$OH\ * + H\ * \rightarrow H_2O + 2\ *$	LH surface reaction, rate-determining
$C\ * + H\ * \rightleftarrows CH\ * + *$	LH surface reaction, equilibrium
$CH\ * + H\ * \rightarrow CH_2\ * + *$	LH surface reaction, rate-determining
$CH_2\ * + H\ * \rightarrow CH_3\ * + *$	LH surface reaction, fast
$CH_3\ * + H\ * \rightarrow CH_4 + 2\ *$	LH surface reaction and desorption, fast
Hayes et al.	
$CO + 2\ * \rightleftarrows C\ * + O\ *$	Dissociative adsorption, equilibrium
$H_2 + 2\ * \rightleftarrows 2H\ *$	Dissociative adsorption, equilibrium
$C\ * + H\ * \rightarrow CH\ * + *$	LH surface reaction, rate-determining
$O\ * + H\ * \rightarrow CO\ * + *$	LH surface reaction, fast
$CH_j\ * + H\ * \rightarrow CH_{j+1}\ * + *, \quad 1 \leqslant j \leqslant 2$	LH surface reaction, fast
$CH_3\ * + H\ * \rightarrow CH_4 + 2\ *$	LH surface reaction and desorption, fast
$OH\ * + H\ * \rightarrow H_2O + 2\ *$	LH surface reaction and desorption, fast
Sehested et al. (low CO pressures)	
$CO + * \rightleftarrows CO\ *$	Non-dissociative adsorption, equilibrium
$H_2 + 2\ * \rightleftarrows 2H\ *$	Dissociative adsorption, equilibrium
$CO\ * + \# \rightarrow O\ * + C\#$	Dissociation at type 2 sites, rate-determining
$C\# + 2H_2 \rightarrow CH_4 + \#$	ER surface reaction and desorption, fast
$O\ * + H_2 \rightarrow H_2O + *$	ER surface reaction and desorption, fast

Figure 2.7 Mechanistic schemes for the catalytic hydrogenation of carbon monoxide. The symbols ⁄ and # represent ordinary (type 1) and 5-fold coordinated reaction sites (type 2) respectively [10].



Reaction	Equation
$H_2(g) + 2\,S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,H{-}S$	(1)
$CO_2(g) + 2\,S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO{-}S + O{-}S$	(2)
$CO{-}S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CO(g) + S$	(3)
$CO{-}S + S \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C{-}S + O{-}S$	(4)
$C{-}S + H{-}S \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} CH{-}S + S$	(5)
$CH{-}S + H{-}S \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} CH_2{-}S + S$	(6)
$CH_2{-}S + H{-}S \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CH_3{-}S + S$	(7)
$CH_3{-}S + H{-}S \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} CH_4{-}S + S$	(8)
$CH_4{-}S \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} CH_4(g) + S$	(9)
$O{-}S + H{-}S \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} OH{-}S + S$	(10)
$OH{-}S + H{-}S \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} H_2O{-}S + S$	(11)
$H_2O{-}S \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} H_2O(g) + S$	(12)

[a] S refers to a surface site.

Figure 2.8 Proposed Sequence of Elementary Steps in CO$_2$ Methanation [12].

Hayes et al. [22] used chemical and physical techniques to investigate the nickel-catalysts reactions. They introduced the NiΞC—H complex as RDS. Also, they introduced the best possible rate reaction using power law method.

Sehested et al. [23] investigated CO-methanation at low CO concentration and the H_2-pressure a little higher than the atmosphere. The dissociation of CO on the nickel surface was chosen as RDS and the proposed kinetic by them is a first-order expression.

2.1.2.2. CO_2 methanation

Weatherbee and Bartholomew published (1982) a comprehensively report [12] regarding the investigation of CO_2-hydrogenation, comprising:

- Set up an experimental facility based on CO_2-methanation.
- Collecting operational data during the experimentation phase.
- Developing a series of reaction pathways and estimation the RDS steps.
- Developing a kinetic-based on LH method, which can fit the experimental data.

They run the experiments with 3% Ni/SiO_2 catalyst at temperatures between 227 and 327 °C, total pressures between 140 and 175 kPa, and space velocities between 30000 and 90000 h^{-1} with a maximum CO_2 conversion of 10% in an isothermal, one-pass differential reactor. H_2 and CO partial pressures varied between 2% and 10% and 0.2% and 2% of total pressure, respectively.

They suggested the mechanism (Figure 2.8), with CO_2 being adsorbed dissociative on Ni, thus forming adsorbed CO and O species. After analyzing the results, they found a simple power law since the rate could not be fitted to the experimental data. Instead, an LH rate equation (Figure 4.2) was used for data fitting. Further conversion of adsorbed CO into CH_4 was expected as in the case of CO hydrogenation (Eq. (2) from figure 2.8). Based on this, it was tried to fit the experimental data with LH rate equations. The assumption of the dissociation of adsorbed CO being the RDS was the only one that resulted in physically meaningful rate and adsorption equilibrium constants. This is also supported by the observation of comparable specific reaction rates in CO_2 and CO methanation on Ni/SiO_2. The mentioned RDS is applicable at moderate temperatures between 252 and 302 °C. At higher temperatures (>302 °C), hydrogenation of carbon (Eq. (5) from figure 2.8) might be rate-controlling.

Also, Stefan Rönsch, et al. [10] explained very well the CO_2 methanation reaction mechanism based on some useful studies, (e.g. [24,25,20,26-28]) that could be useful on this subject for more details.

2.2. Methanation concepts

2.2.1. History

Sabatier and Senderens in 1902 were the discoverers of the methanation processes [29]. These reactions have been investigated and developed by researchers during more than a century (Figure 2.9). During this period, different circumstances had been motivated researchers to apply these processes in the industry (e.g. Oil crisis, Global warming). Historically, the CO-methanation could firstly take part in the industry. The most important applications of the CO-methanation have included cleaning the carbon monoxide from syngases such as ammonia production Plants and proton-exchange membrane fuel cells. The energy crisis in the late 1970s motivated the researcher to use CO methanation for the production of SNG. They were going to produce natural

gas using produced syngas from coal gasification as an educt, [10]. At the 1970s and 1980s, several CO methanation concepts were developed [30].
The growth of CO_2 methanation process was built on the CO-methanation concepts. First exclusive CO_2-methanation was developed in the 1980s [31]. These studies aimed to use coke oven gas or blast furnace gas as an educt for CO_2 methanation. But just a few of those concepts were implemented in the commercial plants because they required some complicated operations to clean gases before feeding to reactors [32].

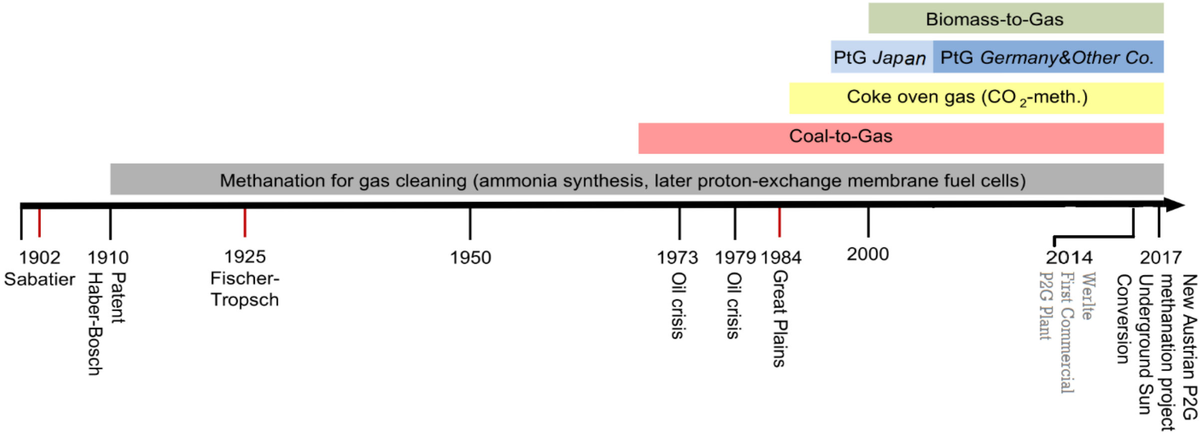


Figure 2.9 History of methanation; Abbreviations: meth. - methanation ([10] updated).

As explained in the first Chapter a result of growing environmental worries was the decisions to reduce greenhouse gas emissions, accordingly research into CO methanation processes was accelerated again at the beginning of the 21st century. Hence, methanation projects have predominantly been developed the concepts from the 1970s and 1980s to fulfill new requirements. On the other hands, CO_2 methanation was detected at research institutions and in the industry as a process with the reasonable ability of the electricity storage, which was needed by increasing contributions of wind and solar power (Power-to-Gas). What become famous as "power to gas" was firstly done by Hashimoto et al. [33] in the 1980– 1990s to recycle CO_2 using an electrolysis plant that feeds from seawater and later in 2009 this opinion was again revived by Sterner [34] for the storage of generated renewable electricity in methane formation.

2.2.2. Established methanation concepts

There are several different possibilities (reactor concepts) to actualize the thermochemical (catalytic) methanation processes. Fundamentally, these concepts can be sub-categorized by the geometry of the reactor and its accessories (Micro-channel, Honey-combs), the temperature profile (section 2.2.3) during the reaction (isothermal, adiabatic, polytropic) or the phases involved in reaction (two-phase vs. three-phase reactions), etc.
As demonstrated in figure (2.10), over the last 50 years, several methanation concepts have been established and developed in different criterion (commercial, demonstration scale, research). Also, these concepts are arranged with respect to the working temperature profile [10].

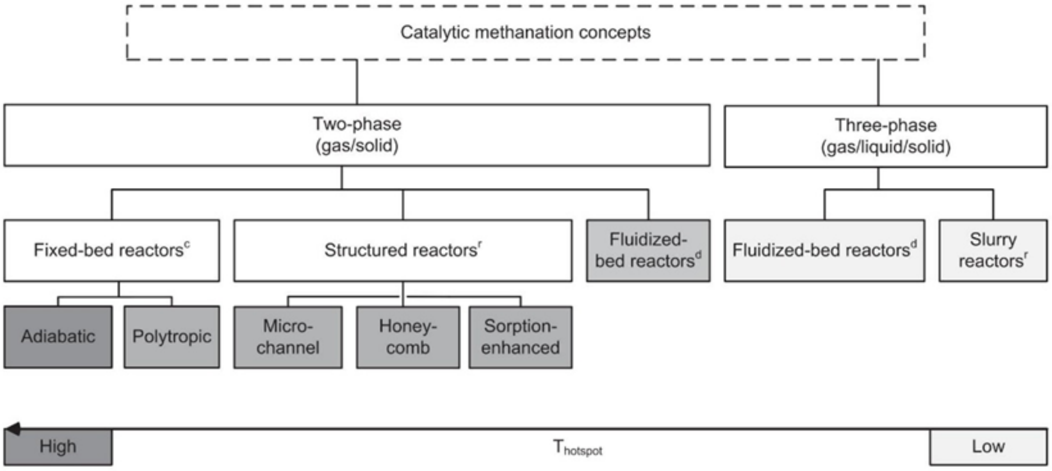


Figure 2.10 Overview of different methanation concepts; State of development: c – commercial, d – demonstration scale, r – research [10].

2.2.2.1. Adiabatic fixed-bed methanation

Currently, adiabatic fixed bed methanation is highly developed and became the most applied method of Thermochemical methanation concept. In fixed bed methanation, the reactor is filled with the catalyst, the particle which sizes in the range of millimeters. The primary challenges in fixed bed methanation are related to the temperature control in the reactor, which results from the high exothermic reaction. The temperatures above 550 °C can cause catalyst decomposition and deactivation, so it is vital to be avoided. Furthermore, as discussed in section (2.1.1.1.2), the methane production has reverse relation with temperature (Figure 2.3). Therefore, usually a number of series reactors with interstage cooling equipment are considered in order to control temperature during operation, or even some concepts also use recycle streams as a high safety factor. In the following, these concepts will be introduced one by one.

2.2.2.1.1. Air Liquide (formerly Lurgi)

In the 1930s, the Lurgi engineers in Germany designed and developed a methanation technology based on two fixed-bed reactors with intermediate cooling system and gas stream recycling (Figure 2.11).

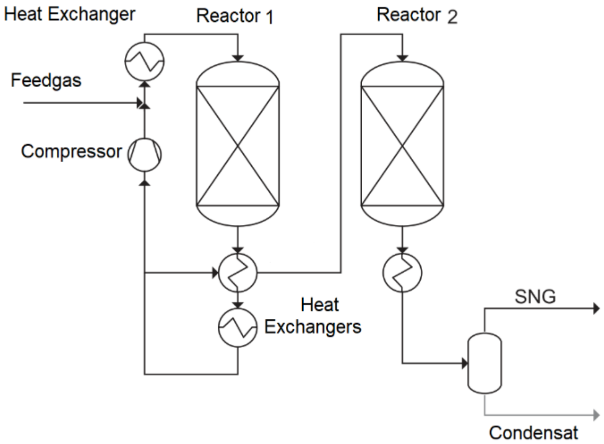
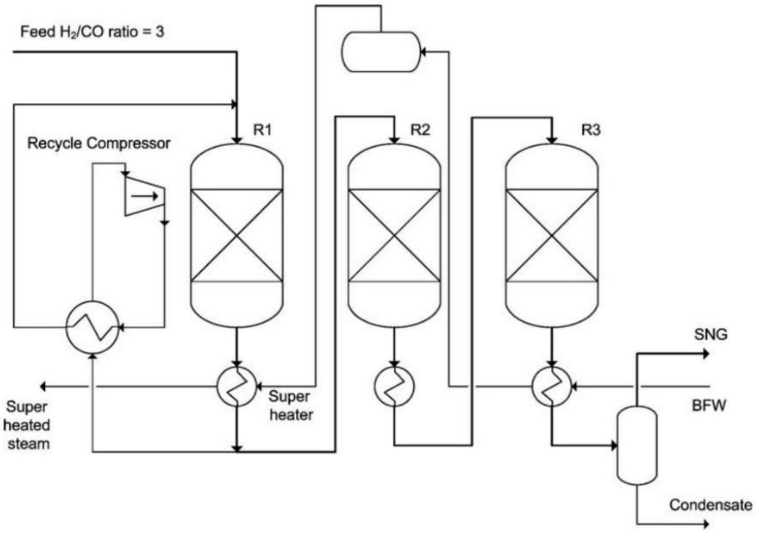


Figure 2.11 Simplified flow schemes of Lurgi SNG process [30].

This concept was in the 1960s and 1970s the only commercially available technology for the production of SNG and is currently commercially operated still. Besides that, this successful experience was inspired to many similar applications for example, in crude oil refineries (Schwechat, Austria) or coal gasification plants (Great Plains Plant, USA) [10].

2.2.2.1.1. Haldor Topsøe

In the 1970 and 1980s, the research center Jülich (Germany), the Rheinische Braunkohlewerke (Germany) and Haldor Topsøe (Denmark) combined steam reforming of methane and methanation of the synthesis gas as a cycle process designed to store and distribute over long distance process heat from nuclear high-temperature reactors (<700 °C). Steam reforming was investigated in the bench-scale unit EVA I and the methanation in the bench-scale unit ADAM I.

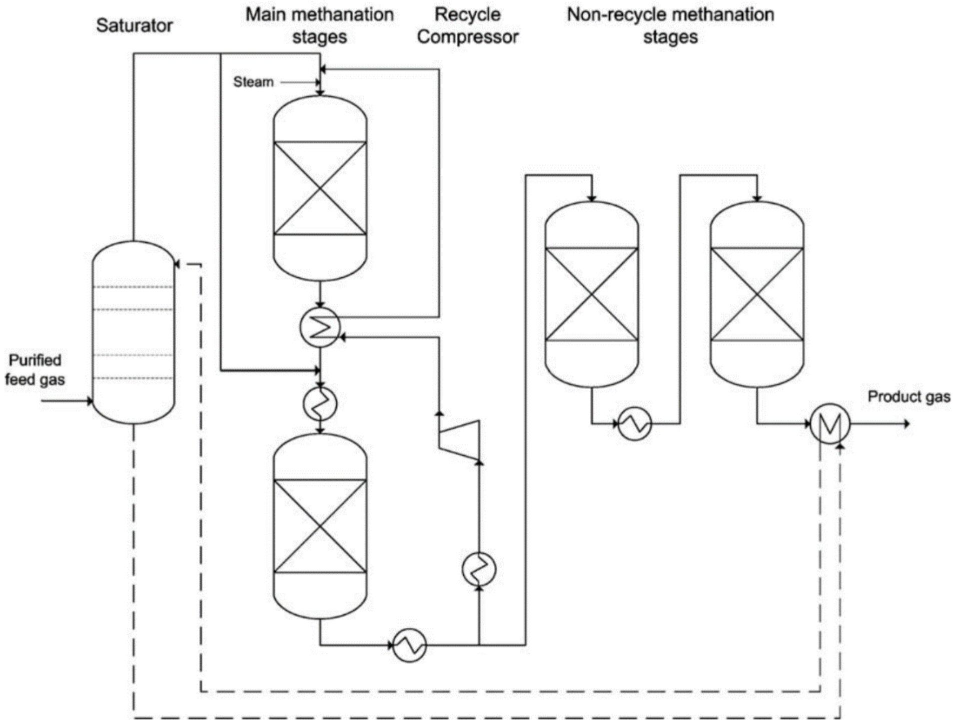


2.12 Scheme of the TREMP™ process, [30].

The methanation plant ADAM I (Anlage mit Drei Adiabaten Methanisierungsreaktoren) consisted of three adiabatic fixed bed methanation reactors including recycling according to the TREMP™ process of Haldor Topsøe (Figure 2.12). It is important to mention that this concept is currently operated still. The TREMP technology began operation recently at the GoBiGas plant in Gothenburg (Sweden) [15,30].

2.2.2.1.2. British Gas and Conoco

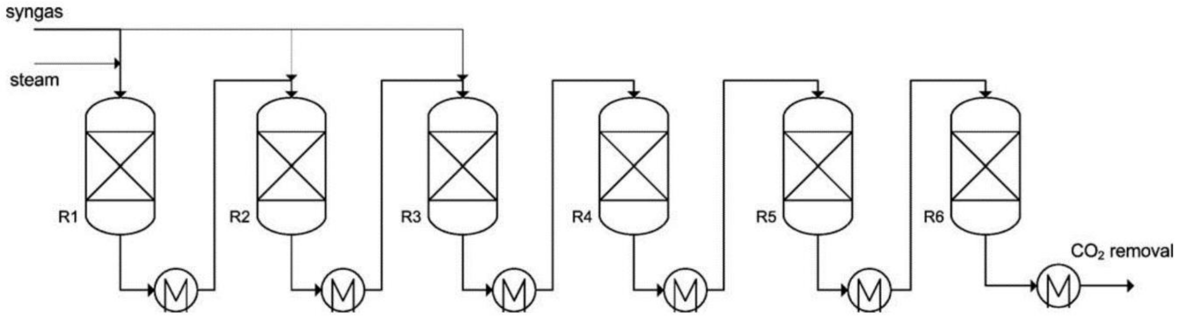
In 1972 on the Westfield Coal Gasification plant (Scotland), the first worldwide demonstration plant had been accomplished, which has proven the complete process chain from coal to SNG. It is similar to the former process, intermediate cooling and gas recycling, but with three adiabatic fixed-bed reactors developed by British Gas (BTG) and Conoco (Figure 2.13) [35]. This technology is known today HICOM (High Combined Shift Methanation) and is presented in the market by the company of Johnson Matthey (Davy Technologies) [10]. **Johnson Matthey (Davy Technologies)** is an example of HICOM technology and has the same specification (three FB reactors, gas recycling, intermediate cooling).



2.13 Simplified process flow diagram for the HICOM process [30].

2.2.2.1.3. Ralph M. Parsons (RMP)

A high-temperature methanation without gas recycle and no separate shift conversion unit, the Ralph M. Parsons company introduced a new concept with 4-7 adiabatic fixed-bed reactors in series (Figure 2.14). The intermediate gas coolers with a staged gas feed system into the reactors were combined to improve the temperature control of the methanation reactor with highly exothermic reaction [35]. Nevertheless, a commercial plant of this technology has not been realized.

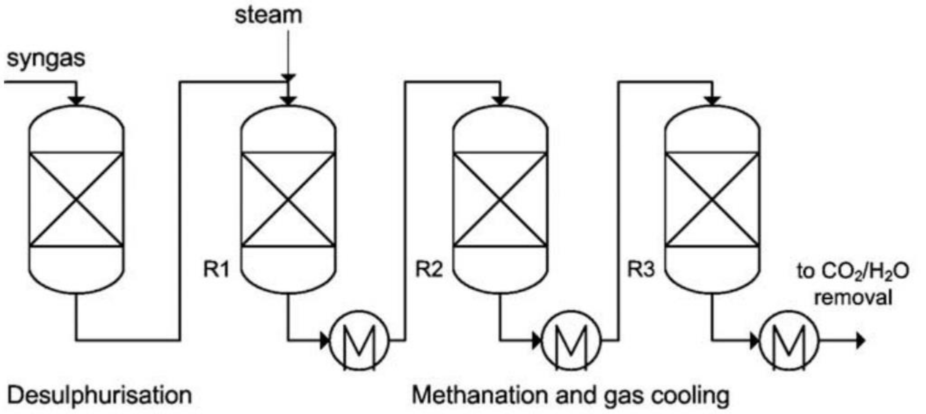


2.14 Fixed bed methanation in the RMP process [30].

2.2.2.1.4. Imperial Chemical Industries (ICI) and Koppers

This technology was developed by ICI (Imperial Chemical Industries, England) and it was supposed to feed by the Koppers-Totzek gasifier system to produce syngas. Although the newly introduced process was similar to RMP without gas recycling (once-through) with intermediate cooling, it consisted of three fixed-bed reactors in series (Figure 2.15) [30].

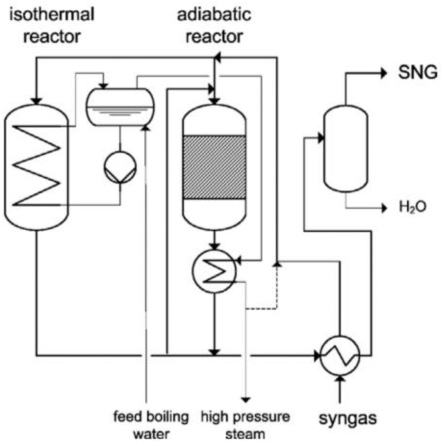
Clariant and Foster Wheeler is an updated example of ICI technology applying modern catalyst. This concept is available now (**Vesta** methanation (Table 2.4)).



2.15 ICI high temperature once-through methanation process [30].

2.2.2.2. Cooled fixed-bed methanation

The Linde company developed a novel concept (the 1970s) based on the combination of one adiabatic and one isothermal reactor for the methanation process (Figure 2.16).



2.16 Process flow diagram of the Linde SNG process with one isothermal and one adiabatic fixed bed reactor [30].

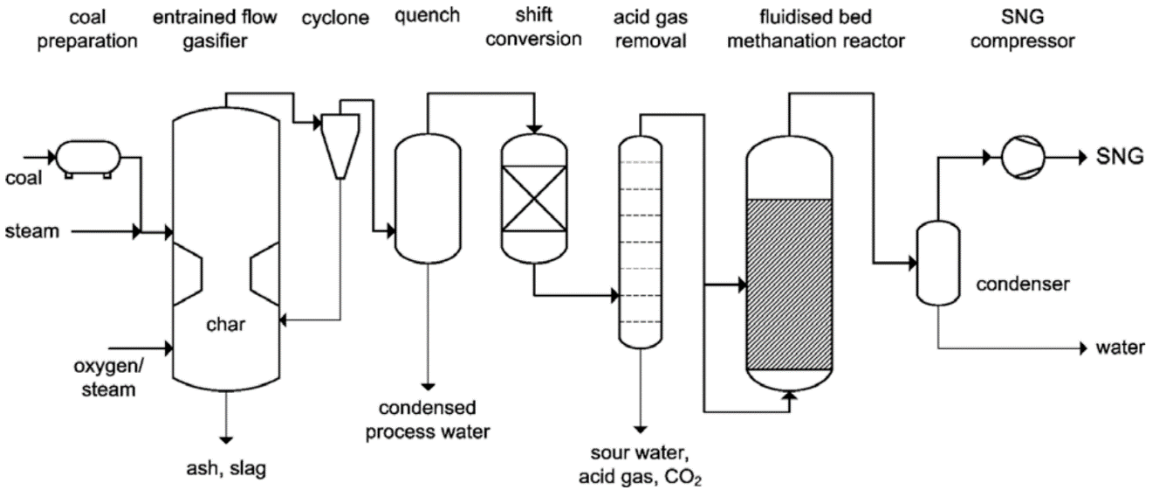
The feed gas ratio was adjusted between reactors to control the carbon monoxide conversion and temperatures inside the reactors. This concept cannot be presented in the commercial application, unfortunately. Although there is no report about the commercial operation of this technology, the Linde group was successful in applying isothermal reactor for Methanol production [10,30].

2.2.2.3. Fluidized-bed methanation

As an alternative for fixed bed methanation, fluidized bed reactors also are established between other technologies for methanation, that efficiently operated in large-scale plants. In this technology, fine catalyst particles are fluidized by the gaseous reactants. Hence, the operation is closest to the isothermal condition and the possibility of using a single reactor is the most important advantage of this method. Negative aspects of this process include attrition and breakage of the catalyst due to the high physical stresses between catalyst particles and reactor walls. Incomplete conversion because of bubbling is also an issue [8].

2.2.2.3.1. Bituminous Coal Research Inc.

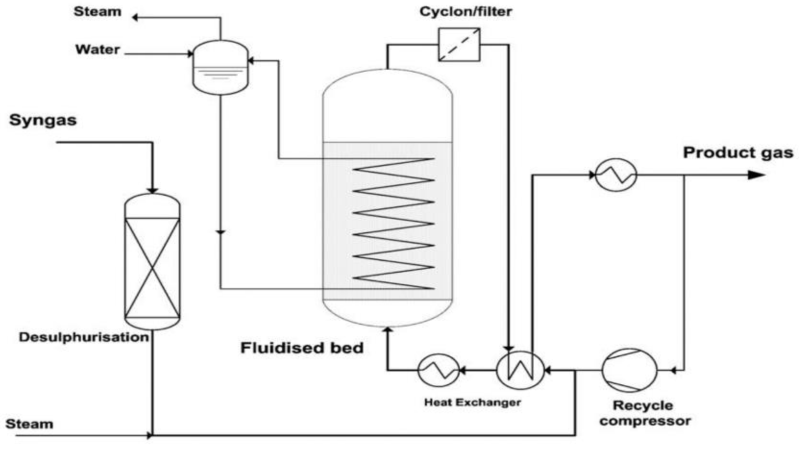
Due to the sophisticated process control, fluidized-bed methanation processes were primarily investigated by research institutions (e.g. the Synthase process of the Bureau of Mines's Fuel Technology Division). One of the first fluidized-bed methanation processes developed by industry was the Bi-Gas-Process of Bituminous Coal Research Inc. (Figure 2.17). The reactor contained two internal heat exchangers in the bed. The development started in 1963 and the reactor was tested at the laboratory for several thousand hours [30].



2.17 Bi-gas process flow diagram, adapted from [30].

2.2.2.3.2. Thyssengas

Another fluidized-bed reactor concept with internal heat exchanger was developed by Thyssengas GmbH (Figure 2.18), Didier Engineering GmbH, and the DVGW-Forschungsstelle in Karlsruhe (Germany). A first test plant of this COMFLUX process was constructed in 1977, and a pilot plant was commercially operated at the Ruhrchemie plant site in Oberhausen (Germany) [10,30].



2.18 Thyssengas process flow diagram [30].

The Comflux process was developed by Engler-Bunte-Institut in conjunction with Thyssengas GmbH from which a demonstration plant was built to produce 2,000 m3/h SNG. In 2009, the Comflux process was used to produce SNG from solid biomass in a 1 MW plant in Güssing, Austria [8].

2.2.2.4. Three-phase methanation

In three-phase methanation (Figure 2.19), a solid catalyst (powder < 100 µm) is fluidized in a temperature stable inert liquid (mineral oil, due to its high heat capacity (C_p)) such as dibenzyltoluene. The first three-phase methanation concept was developed by Chem Systems Inc., from 1975 – 1981. The concept was based on a single three-phase fluidized bed reactor operated up to 70 bar.

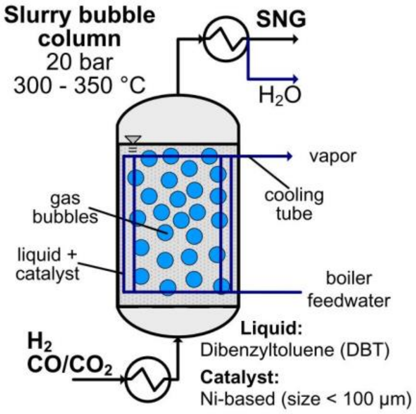


Figure 2.19 Schematic diagram of the three-phase reactor concept [8].

Currently, the three-phase methanation in a slurry bubble column reactor is under verifying at laboratory scale at the Engler-Bunte-Institut, Germany and at the Institute of Coal Chemistry, China. Good heat rejection of the reaction is a remarkable advantage for this method, as it allows for good heat control of the reaction. This is particularly important in the PtG process since the high heat capacity of the liquid phase makes it easier for the methanation process to handle the fluctuations/downtime. Moreover, the catalyst can be replaced during operation. However, a major disadvantage of the three-phase methanation is the liquid side mass transfer limitation, which reduces the effective reaction rate.

In the same way with the CO methanation, the recent CO_2 methanation process innovations (last decades) are based on methanation concepts from the 1970s and 1980s. Nevertheless, some vital adaptations regarding e.g. temperature controlling of the reactor and dynamic operation behavior had to be exerted [8].

2.2.2.5. Market availability

As explained, methanation research and its developed concepts look back on a history of more than 100 years, nevertheless, not all concepts are commercially available now. Here is given an overview of commercially available technologies for the CO_2 and CO-methanation in Tables (2.3) and (2.4) respectively. The technologies listed in (Table 2.4) can be practically employed at CO_2 methanation plants [10].

Supplier	Concept	Technology name
Outotec	Staged fixed-bed reactor with intermediate cooling	Outotec methanation
Etogas	Fixed-bed reactor or plate reactor with steam cooling	Etogas methanation
MAN	One isothermal fixed-bed reactor with molten salt cooling	MAN methanation

Table 2.3 CO_2-Methanation technologies available on the market [10].

Supplier	Concept	Technology name
Air Liquide (formerly Lurgi)	2 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	Lurgi methanation
Haldor Topsøe	3–4 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	TREMP
Clariant and Foster Wheeler	3 fixed-bed reactors with steam addition and without gas recycle	Vesta
Johnson Matthey (Davy Technologies)	3 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	HICOM
Linde	One isothermal fixed-bed reactor with an internal contorted heat exchanger	Linde isothermal reactor

Table 2.4 CO methanation technologies available on the market [10].

2.2.3. Temperature Comparison (Semenov number)

Sabatier reaction is strongly exothermic according to Equations (1) and (2) and, furthermore they are gas phase reactions with high speed, therefore they normally create hot spots within the reactors. Hence, the temperature control in the methanation process is an essential challenge. For successful controlling, several parameters (Table 2.5) should simultaneously be considered to monitor the heating and cooling rates in reactors. Kiewidt and Thöming [36] defined the dimensionless **Seminov number** (Eq. (11)) to classify methanation reactors by the temperature profiles during the reaction.

$$Se = \text{Heat production rate/ Cooling rate} = (Da_I * B / St) \qquad (11)$$

In theory, three types of temperature profiles are known: adiabatic, isothermal, and polytropic. In the following, the Seminov number is applied to describe these temperature profiles.

Parameter	Symbol	Definition	Interpretation/ratio
Arrhenius number	γ	$E_a/(R_u T_0)$	Activation energy/thermal energy
Heat production potential	B	$-\Delta H_{R,0}\,\gamma / (M_0 c_{p,0} T_0)$	Heat production/thermal storage capacity
1st Damköhler number	Da_I	$M_0 \eta_0 r_0^{(V)} L_R / G_0$	Reaction rate/convective transport rate
Stanton number	St	$4U_{W,0}^{(eff)} L_R / (G_0 c_{p,0} D_t)$	Cooling rate/convective transport rate
Reynolds number	Re	$GK / (\mu_0 c_F)$	Convective momentum transport rate/viscous momentum transport rate
Semenov number	Se	$Da_I B / St$	Heat production rate/cooling rate

Table 2.5 Summary of dimensionless parameters used within Semenov number [36].

- Adiabatic reactors (Se ---> ∞)

Fixed bed reactors without heat exchanging and high rate of the produced heat due to the reaction, typically display adiabatic temperature profile with a distributed hot spot in the bed and high-temperature levels.

- Isothermal reactors (Se ---> 0)

When the cooling rate is extremely bigger than produced reaction heat, then the isothermal temperature profile will be indicated. Fluidized-bed reactors and three-phase reactors ideally are isothermal reactors.

- Polytropic reactors ($0 < Se < \infty$)

If the cooling rate and produced heat rate have been well-balanced during the reaction process, the polytropic temperature profile will be recorded. Cooled fixed-bed and structured reactors (e.g. microchannel, honeycomb) are the best examples of these reactors.

2.3. Catalysts, activation, and deactivation

The catalyst is the place where the reaction occurs, hence, its material and shape directly effect on the design and operation of the reactor and its up- and downstream equipment and they should be coordinated with catalyst specification (such as activation, deactivation, and selectivity). In the following, an overview of methanation catalysts and its specifications is presented.

2.3.1. Catalysts

2.3.1.1. Active compound

Sabatier and Senderens introduced nickel as the catalyzer for the methanation reaction (Eqs. (1) and (2)) [29]. It is very interesting that after more than 100 years many metals have been identified as an active material for the methanation reaction, but still due to its activity, selectivity and price in comparison with other materials the researchers are suggesting nickel as the optimal option for commercial applications [37]. For example, Vannice et al. [38] considered activity and selectivity of (Ru, Fe, Ni, Co, Rh, Pd, Pt, Ir) and published the following order:

Activity: Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir

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

In terms of metals important for methanation, Mills and Steffgen [37] *limited the candidates for the investigation to Ru, Ni, Co, Fe, and Mo*.

Activity: Ru > Fe > Ni > Co > Mo

Selectivity: Ni > Co > Fe > Ru

2.3.1.2. Support

Beside the active metal also other parts of a catalyst such as support, promoter and the skill of their preparation and conditions of putting them together are very important for a catalyst to be formed that promises high selectivity and activity [37].
The active metals are normally dispersed on metal-oxide supports (e.g. Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2), however, Al_2O_3 is more frequently applied than others [39].
Beside the supported catalysts, also unsupported catalysts such as Raney-Nickel [40] are known.

2.3.1.3. Promoters

The promoters are the materials (e.g. MgO, La_2O_3, V_2O_3, CeO_2, K), which based on its structures are able to create positive or negative effects on the performance of the catalyst in a particular reaction (e.g. methanation) [10].
For example, the addition of (MgO) to Ni/Al_2O_3 improves the interaction between nickel atoms and the neighboring cations and support of the $MgNiO_2$ though the particle size of NiO is constant [41]. But potassium (K) decreases the formation of methane and increases the formation of heavy hydrocarbons on pure Ni (100) catalysts and Ni/Al_2O_3 with high nickel concentration [42].

2.3.2. Reduction and activation

The nickel-based methanation catalysts, in contrast to many other catalytic processes (e.g. Fischer–Tropsch-Synthesis) do not need any separate activation step instead of reduction step. The reduction of nickel-based methanation catalysts requires floating in hydrogen at temperatures ranging from 300 to 600 °C [10].
The TPR (temperature-programmed reduction) measurements are applied monitoring the behavior of a catalyst under reductive conditions (increased temperature and hydrogen atmosphere) [41]. For example, TPR-profile of unsupported NiO and supported NiO/SiO_2 catalysts are given in the Figure 2.20. The H_2 consumption (Y-axis) is displayed as a function of temperature (X-axis). The considerable H_2 consumption in the Figure 2.20 is indicating, where main reduction process takes place. Each mutation on the profile of H_2 consumption can probably be related to a portion of the catalyst that is reduced at the specific temperature.

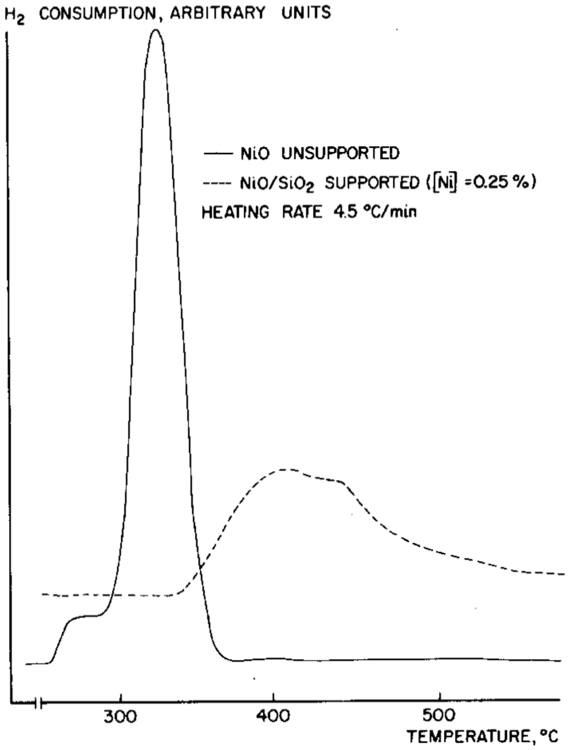
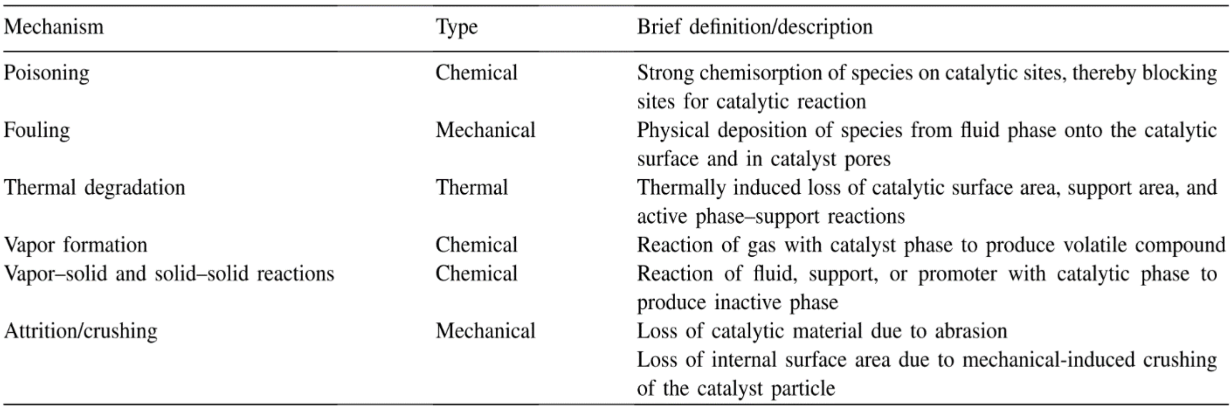


Figure 2.20 Exemplary TPR profile of unsupported NiO and supported NiO/SiO_2 catalysts [41].

2.3.3. Deactivation

Bartholomew et al. [43] comprehensively investigated the deactivation subject of nickel-based catalysts (table 2.6) and categorized them into three main groups (Chemical, Mechanical and Thermal mechanism). In the following will be discussed this mechanism one by one.



Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

Table 2.6 Mechanisms of catalyst deactivation [43].

2.3.3.1. Poisoning

Poisoning is the undesired reaction between catalyst and reactant, product or impurities, so it leads to chemisorption and inactivation of total or parts of the catalyst surfaces [43]. Every reaction requires suitable conditions to occur, what exactly is also tried to achieve in the catalytic methanation reactors but the challenge is a suitable condition for one reaction may comparatively be suitable for other reactions. Particularly, if the gas phase feed carries some impurities such as *chlorine compounds, tars, particles, ammonia, sulfur compounds or alkalis*. Nickel-based catalysts are prone to poisoning by sulfur compounds and must be considered by designers [44,45].

Rönsch S. [46,10] suggests Rectisol washing and adsorption with Zinc Oxide methods in methanation plants to protect them against catalyst poisoning by sulfur compositions.

Hydrogen sulfide by the chemical reaction equation (Eq. (11)) converts nickel oxide to nickel sulfide that shows no activity for the methanation reaction [10].

$H_2S\ (g) + NiO\ (s) \longleftrightarrow NiS\ (s) + H_2O\ (g)$ (11)

2.3.3.2. Vapor–solid reactions

Vapor-solid reaction (Eq. (12)) transfers applied solid nickel in the catalyst to gas phase nickel carbonyls in methanation plant at low temperature. Hence, it is an undesired reaction [47]. *Then at startup and shutdown phases (dynamically or periodically operation) of the methanation plant, any contact between catalyst and carbon monoxide should be avoided because of this reaction* [48,10].

$Ni\ (s) + 4CO\ (g) \longleftrightarrow Ni(CO)_4\ (g)$ (12)

2.3.3.3. Thermal degradation

Sintering of the active catalyst causes loss of area and finally a reduction of catalyst efficiency. The temperature threshold of catalysts depends on their materials, but they must normally be kept away from temperatures above 500 °C. However, some catalysts for high-temperature between 600 and 700 °C are available on the market [49].

2.3.3.4. Fouling

Against vapor-solid reaction, catalyst fouling means transferring some species from the gas phase onto catalyst material (solid phase) due to the chemical or physical transactions during operation. *In methanation plants, especially the deposition of carbon and coke must be avoided. Carbon deposits are formed by the Boudouard reaction (Eq. (13)). Adding steam or rising the* H_2/CO*-ratio* is applied in methanation plants to prevent catalyst fouling by carbon or coke [10].

$2CO\ (g) \longleftrightarrow CO_2\ (g) + C\ (s)$ (13)

2.3.3.5. Attrition

The attrition of active catalyst material by abrasion is a troublous drawback reported often in *operation of moving-bed, slurry-bed, or fluidized-bed reactor*s [79]. That is a harmful subject because it leads to *financial expenditures for make-up catalysts and shouts down the operation*. To prevent any failures on downstream equipment (e.g. pumps and compressors), it is vital to separate the abraded catalyst from the product gas [10].

2.3.3.6. Crushing

The crushing of catalyst particles is also one of a number of different mechanical deactivation mechanisms. Crushing can be created either by sudden thermal stresses (due to very fast heating or cooling) or by mechanical stresses (due to pressure fluctuations in the reactor) [43]. Simultaneously, both situations can be accompanied by a startup and shutdown and as well as during operation of the plant. In addition, *feed rate fluctuation by flexible methanation operation particularly of Power-To-Gas or poly-generation plants* (an interdependent chain production plant), *i.e. inconstancy of the syngas flow rate*, may result in mechanical stressing crushing [10].

Chapter 3

Review of commercial plants and pilot projects

3. Review of commercial plants and pilot projects

This chapter is dedicated to the power-to-gas demonstration projects that particularly are operational or planned at this moment. According to the fact that power to gas is very young technology (Figure 3.3), prototype plant (Japan, 1996) and first commercial plant (Germany, 2013), during the investigation the pilot plants are considered also. Due to the subject of this article is limited to the catalytic CO_2 methanation within the power to gas plants, here I focus on the investigation of Thermochemical (catalytic) methanation plants, nevertheless, the other power to gas projects including hydrogen-methane and hydrogen plants are briefly mentioned in separated parts.

As a preliminary overview of the information that is going to be presented in the following, Figures 3.1 and 3.2 clearly illustrate the distribution of the projects between worldwide and European Union countries classified by type of process, respectively [50,51]. Germany is the leader of nations in applying and propounding PtG systems, due to an increasing requirement for chemical storage of produced electricity by fluctuating wind and solar energy sources. The projects in Germany mostly concentrate on CO_2 catalytic methanation [50].

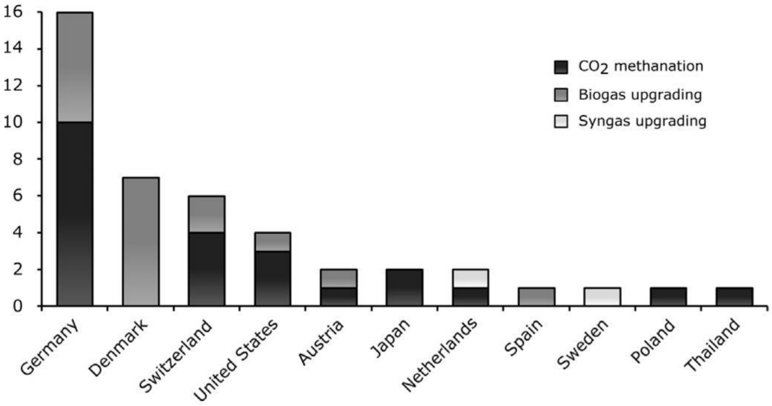


Figure 3.1 Existing PtG projects distributed by country and technology (2017) [50].

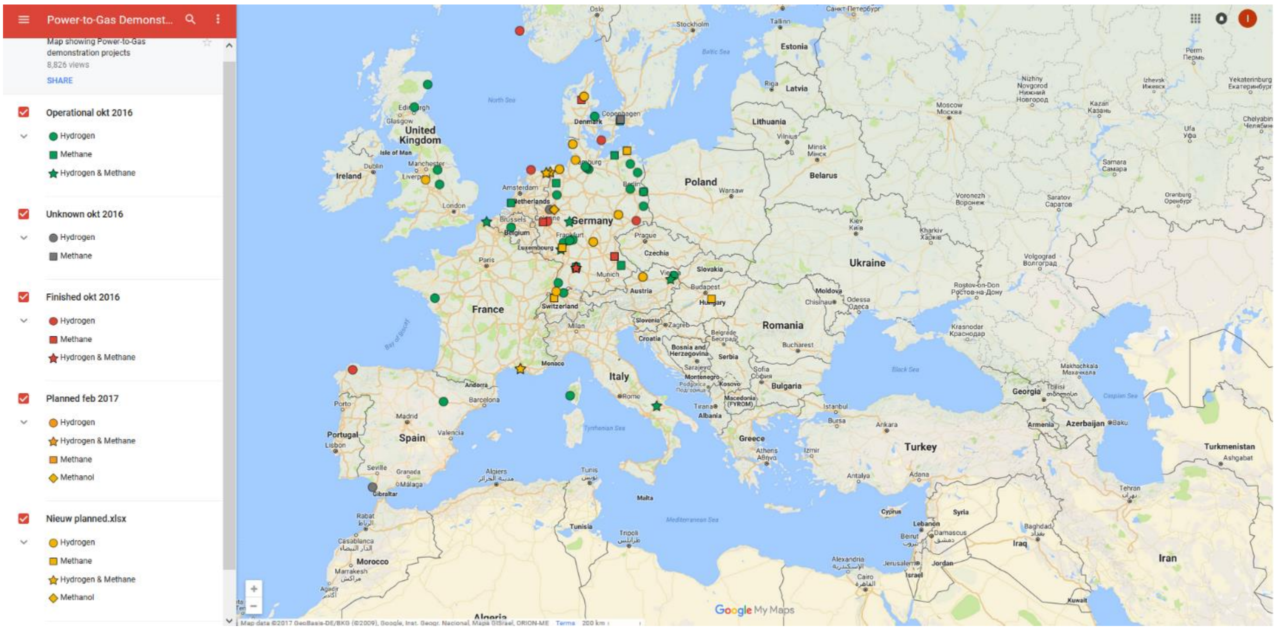


Figure 3.2 Power-to-gas (demonstration) projects in Europe, the symbols (□, ○, ⋇, ◊) represent the type of PtG plant (Methane, Hydrogen, Hydrogen&Methane, Methanol) and the color of these symbols (Green, Gray, Red, Deep yellow, Light yellow) indicate the life cycle of project (Operational okt. 2016, Unknown okt. 2016, Finished okt. 2016, Planned feb. 2017, Nieuw planned.xlsx) respectively (2017) [51].

For a technology like PtG using a timeline of evolutions can be more effective to investigate it, because it is possible to see what has been done from start to end based on time. The timeline in Figure 3.3 has been prepared to represent the progress of the global PtG technology. As mentioned, Tohoku University and Hitachi Zosen initiated research in PtG systems in 1996, [52,53]. It seems very interesting, that most of the projects are initiated to be built by 2011, 2013 and 2014.

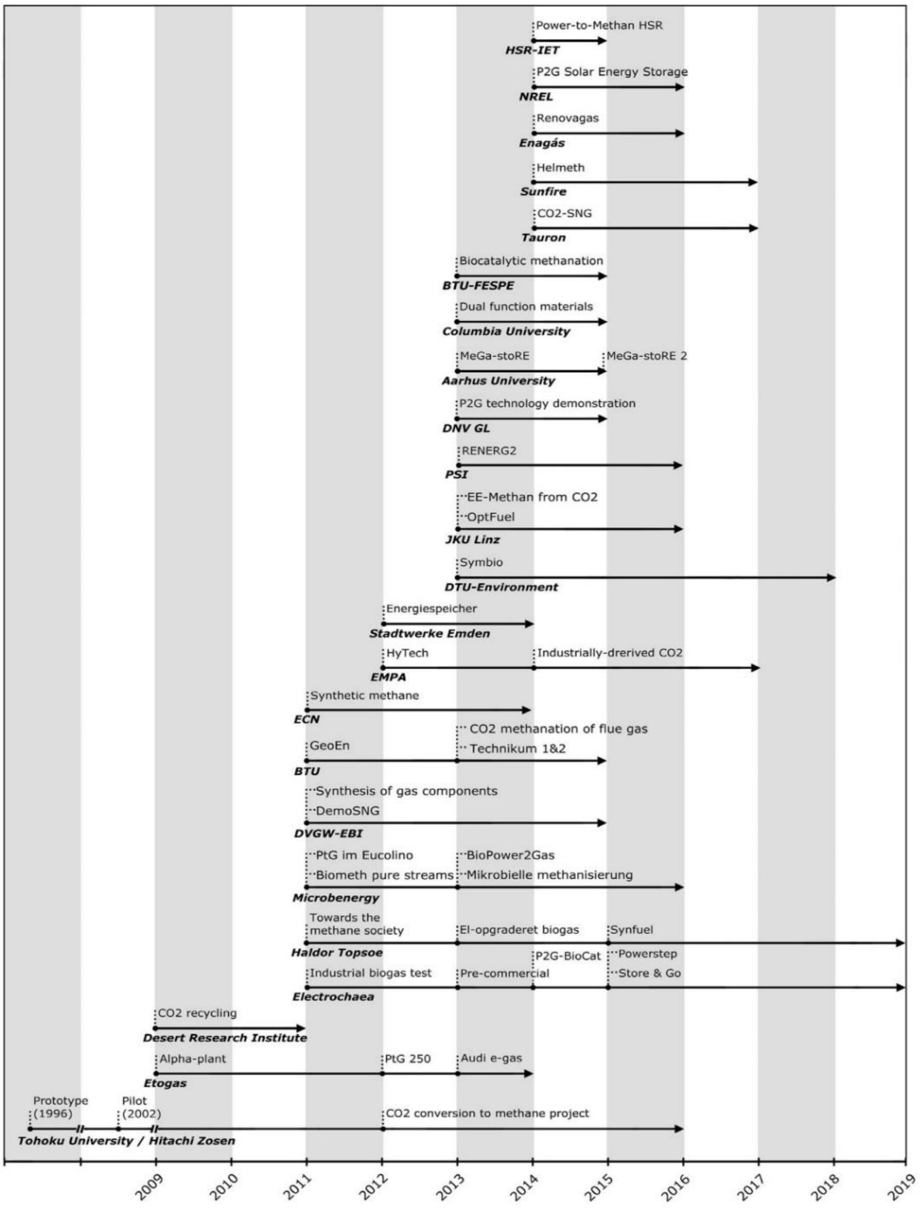


Figure3.3 Timeline of worldwide existing PtG projects [50].

Based on the categorization for PtG projects in the Figure 3.2, that is applied by The European Power to Gas Platform [51], in the same way, this chapter is divided also into three sub-categories, namely:

- Methanation projects
- Hydrogen projects
- Methane-hydrogen projects

3.1. Methanation projects

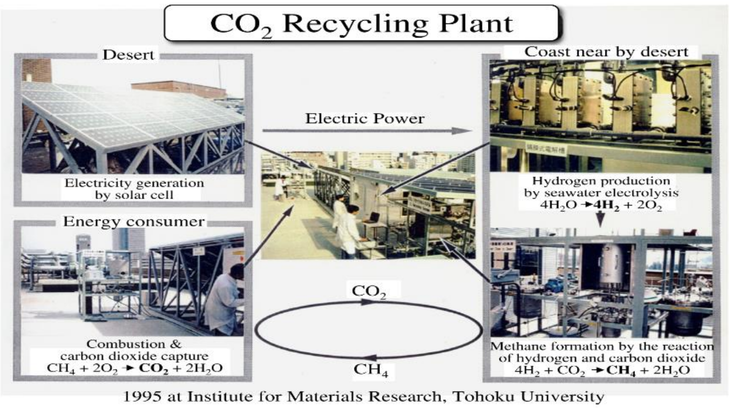
As discussed before (section 2.1), methanation projects can mainly be subdivided into catalytic and biological methanation. These two concepts in most of the reviews on methanation plants are considered together. But due to the defined scope, this investigation is reviewing just the catalytic methanation projects. An overview of catalytic methanation projects at pilot (Alpha) and commercial (Beta) scale is arranged in the table (3.1).

No.	**Project Name** Location	**Application**	**Period**	**Institutions**
1)	**Prototype plant – Tohoku University** Tohoku, Japan	Research	1996	Tohoku University, IMR, TohTech, Hokudai, DAE, NRIM, MES, Ryoka
2)	**Pilot plant – Tohoku Institute of Technology** Tohoku, Japan	Research	2002–2005	Tohoku University, TohTech, Hokudai, DAE, NRIM, MES, Ryoka
3)	**CO_2 recycling via reaction with hydrogen** Reno, United States	Research	2009	DRI, RCO$_2$ AS
4)	**Audi e-gas** **(First commercial Plant)** Werlte, Germany	Gas grid, mobility	2013	ETOGAS, ZSW, Fraunhofer IWES, EWE Biogas, Audi
5)	**Alpha-plant** Stuttgart, Germany	Research	2009	ETOGAS, ZSW
6)	**Alpha-plant** Werlte, Germany	Research	2010-2011	ETOGAS, ZSW, EWE Biogas
7)	**Alpha-plant** Morbach, Germany	Research	2011	ETOGAS, ZSW, EWE Biogas, Juwi AG
8)	**Alpha-plant** Bad Hersfeld, Germany	Research	2012	ZSW
9)	**Power to Gas 250** Stuttgart, Germany	Research	2012-2014	ETOGAS, ZSW, Fraunhofer IWES
10)	**SEE project** Baden- Wurttemberg, Germany	Research	2011-2014	DVGW-EBI, EnBW, Fraunhofer ISE, H-Tec, IoLiTec, Outotec
11)	**HyTech** Dübendorf, Switzerland	Research	2012-2015	EMPA, ZHAW, EPFL, PSI
12)	**CO_2-Methanation of flue gas** Brandenburg, Germany	Research	2013-2015	BTU, Panta Rhei, Vattenfall
13)	**Technical assumptions, technology demonstration and results P2G project** Rozenburg, Netherlands	Research	2013-2015	DNV GL, TKI Gas, Stedin, Rotterdam Council, Ressort Wonen
14)	**Pilot- und Demonstrationsanlage Power-to-Methane HSR** Rapperswil, Switzerland	Research	2014–2015	HSR-IET, HSR, Audi, Climeworks, Erdgas Obersee, Erdgas Regio
15)	**CO_2 Conversion to Methane Project** Rayong, Thailand	Research (phase 1) Gas grid (phase 2)	2012–2016	Hitachi Zosen, DAE, PTTEP
16)	**JKU Linz-EI – PtG in Austria** **(EE-Methan from CO_2)** Leoben&Linz, Austria	Research	2013-2016	JKU Linz, MU Leoben, TU Wien, Christof Group, Profactor, ÖVGW, FGW
17)	**Catalytic methanation of industrially-derived** Dübendorf, Switzerland	Research	2014-2017	EMPA, ZHAW
18)	**HELMETH** Sunfire	Research	2014-2017	Sunfire, KIT, PoliTo, ERIC, TS-Torino, NTUA, DVGW

Table 3.1 catalytic methanation projects at pilot (Alpha) and commercial (Beta) plant [50,51].

3.1.1. Prototype plant (1996)

As shown in the figure (3.4), the birthplace of PtG is the roof of the material institute of Tohoku University. This plant consists of an electrolysis that is powered by a photovoltaic screen and two reactors in series [52].



3.4 First worldwide PtG prototype, Japan, 1996 [53].

3.1.2. Pilot plant (2002–2005)

Due to the obtained positive results from the prototype, the research was followed by the assembling of its pilot plant in the Tohoku Institute of Technology (TohTech) (Figure 3.5).

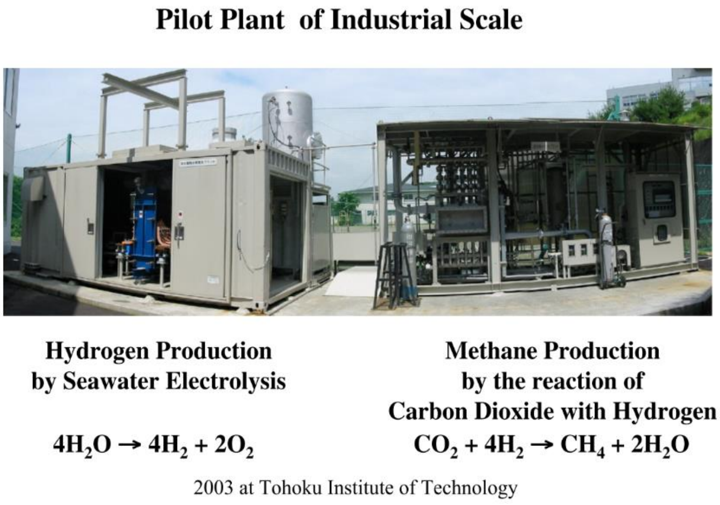


Figure 3.5 First worldwide PtG pilot plant, Japan, 2003 [53].

It produced up to 4 Nm^3/h *of* H_2 *and 1* Nm^3/h *of* CH_4 [52]. *This second project was funded through a 3-year grant for developing revolutionary technologies within the Millennium Projects framework [53].*

3.1.3. Desert Research Institute – CO_2 recycling via reaction with hydrogen

The Desert Research Institute (DRI), in 2009, started a pilot PtG project to estimate its limitations and challenges against benefits of catalytic methanation (foundation by RCO_2 AS). *The system was installed in a portable trailer in Reno, United States*.

The pure hydrogen (99.999%) was supplied by a 5kW PEM electrolyzer, which was powered by a *1.0kW Siemens PV array* and located in a trailer. This unit was able to supply H_2 up to 600 cm^3/h at 200 psi. The carbon dioxide was fed to the reactor via a mixture of 2% CO_2 and N_2, due to achieving various experimental operation with maximal temperature controlling.

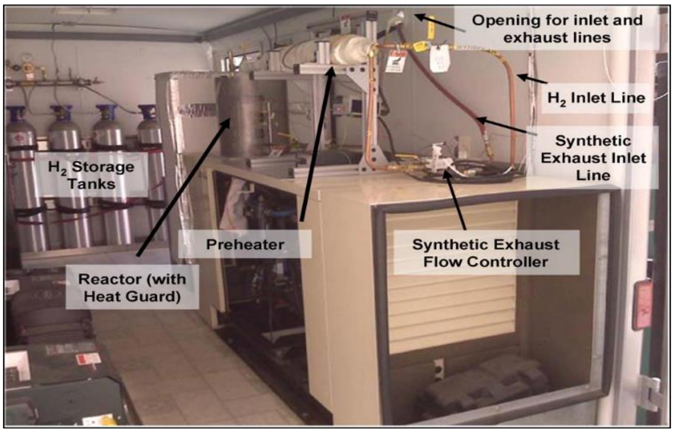


Figure 3.6 The portable pilot plant of PtG structured by DRI into a trailer [54].

The feed gas after preheating flowed through the reactor (with Heat Guard) from top to bottom. The temperature of reactor was monitored by three transmitters, two transmitters checked the top and bottom of catalyst temperature and the third transmitter checked combustion chamber (Figure 3.6).

During the operation the feed ratio 4/1 between H_2/CO_2 was kept constant and the feed total flow rate was varied. The baseline parameters for experiments were considered as the reactor temperature of 300 °C and the space velocity approximately 9000 h^{-1}, but the Space velocities were changed in steps of 25% of the baseline during experiments. The maximum conversion of CO_2 recorded 60% in the temperature range of 300–350 °C and 10,000 h^{-1} space velocity [54].

3.1.4. ETOGAS – Audi e-gas plant

The Audi e-gas plant is located in Werlte (Germany) and is the first and biggest (6 MW) commercial PtG plant. It was the result of a successful collaboration between *Audi AG, ETOGAS GmbH (formerly known Solar Fuel GmbH), the Centre for Solar Power and Hydrogen Research Baden-Württemberg (ZSW), the Fraunhofer Institute for Wind Energy and Energy System Technology (Fraunhofer IWES) and EWE Biogas GmbH & Co. KG* (2009-2013) [55]. As a manufacturer in this collaboration, ETOGAS designed the research plant of this project in Stuttgart and ZSW was the chief developer [56].

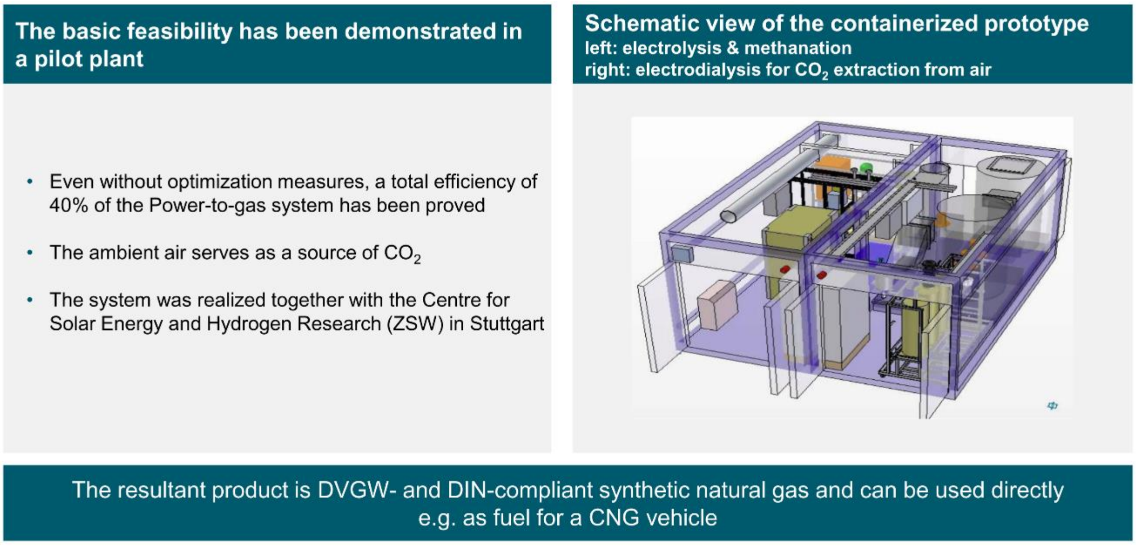
The required hydrogen is supplied by *3×2.0 MW alkaline electrolyzers* that are powered by generated electricity from an *offshore wind park in the North Sea*.

The required CO_2 is supplied by EWE Biogas GmbH & Co. KG. Amine scrubbing technology was applied to separate CO_2 from raw biogas [57].

A single ***Isothermal fixed-bed reactor*** was recruited for the catalytic methanation [58,50].

3.1.5. Power to Gas α-plant with air purification (Stuttgart, 2009)

The first research (α-plant) step of Audi e-gas project was done by ZSW (Figure 3.7). It was aimed at the *basic feasibility of the PtG process*. Hence, a 25 kW electrolyzer and a *CO_2 ambient air purification system* was installed as a mobile plant in a container [59].



The basic feasibility has been demonstrated in a pilot plant

- Even without optimization measures, a total efficiency of 40% of the Power-to-gas system has been proved
- The ambient air serves as a source of CO_2
- The system was realized together with the Centre for Solar Energy and Hydrogen Research (ZSW) in Stuttgart

Schematic view of the containerized prototype
left: electrolysis & methanation
right: electrodialysis for CO_2 extraction from air

The resultant product is DVGW- and DIN-compliant synthetic natural gas and can be used directly e.g. as fuel for a CNG vehicle

Figure 3.7 The 25kW α-plant shows the feasibility of the P2G process [59].

3.1.6. Power to Gas α-plant with CO_2 from biogas purification (Werlte,2010–2011)

The second research (α-plant) step of Audi e-gas project was supposed to investigate the methanation using carbon dioxide that was produced by *pressure swing adsorption (PSA) from the EWE Biogas plant*. Hence, in this research phase *Audi AG, ETOGAS GmbH, EWE Biogas GmbH & Co. KG* cooperated at Werlte, Germany [60,50].

3.1.7. Power to Gas α-plant with raw biogas (Morbach, 2011)

The third research (α-plant) step of Audi e-gas project was aimed to determine the feasibility of methanation using raw biogas instead of pure CO_2. With joining Juwi AG to the previous partners at Werlte, it was proved that direct methanation of biogas is technically possible in a PtG plant [60,50].

3.1.8. Power to Gas α-plant in long period operation with raw biogas (Bad Hersfeld, 2012)

The fourth research (α-plant) step of Audi e-gas project was in collaboration with ZSW. It was aimed to test locally long period methanations with *raw biogas from an agricultural biogas plant* *located in the Hessian Biogas Research Centre (HBFZ)*, despite the fluctuating the feed raw biogas composition [50].

3.1.9. Power to Gas 250 kW test facility (Stuttgart, 2012–2014)

ZSW, Fraunhofer IWES, and ETOGAS implemented the last plant before beta plant (Audi e-gas project). It was aimed to assess different fixed-bed methanation concepts [61] (*plate versus tubular reactor construction*). The plant contained two reactors with 50-liter catalyst capacity. The cooling system for reactors was differently designed (one of them water-cooling, another molten salt) [50].

The 250 kW alkaline electrolyzer had the ability to supply hydrogen even in a dynamic and intermittent condition, due to fluctuating solar and wind energy supplies. The methane is indicated 99% purification using Gas-Purification-Membrane technology after methanation. [56,59].

3.1.10. SEE project (2011 – 2014)

The research project (SEE) has been implemented in collaboration with DVGW and EBI. It was proposed to compare fixed-bed and slurry methanation concepts at lab-scale and also an investigation of the dynamic behavior of electrolyzers [62].

6 kW PEM electrolyzer was provided by H-Tec Systems to supply required hydrogen.

The fixed-bed reactor was investigated by Outotec with *different catalysts by varying the inlet and reaction temperatures as well as the gas space velocity*. At least this reactor was indicated up to 70% CO_2 conversions in some conditions [63].

The slurry reactor was designed by DVGW-EBI. The novel reactor used Ionic Liquids Technologies GmbH (IoLiTec). *This fluid distributed finely catalyst and dissipates efficiently the reaction heat, thus enabling an accurate temperature control under fluctuating feed streams*. *Energie Baden-Württemberg AG (EnBW) evaluated the economic viability [50]*.

3.1.11. EMPA – catalytic methanation of industrially-derived CO_2

EMPA performed this project in partnership with ZHAW, EPFL and Zeochem AG [64]. The costs for experimental facility have funded by the *Swiss Federal Office of Energy (SmartCat project) and the SNSF (Catalytic methanation of the industrially-derived CO_2 project)*. *The Swiss Federal Laboratories for Materials Science and Technology* aimed to improve CO_2 conversion using zeolite-nickel catalyst due to its water adsorption properties through this project. The geometry of stainless steel reactor was reported 45 cm long and 1.8 cm in diameter with the available volume for 13 g of catalyst and the operating condition of 1.2 bar and 1000 h^{-1} space velocity [65].

3.1.12. BTU – CO_2-methanation of flue gas

The Brandenburg University of Technology (BTU) investigated the methanation of oxyfuel CO_2 and underground-stored CO_2.

The required hydrogen was transferred by storages to the research place. The geometry of reactors was reported *153 mm in diameter, 870 mm high and 15 slots for temperature measurements also the reactor volume was measured 30 dm^3 that settled up to 2 kg of* *catalyst (Silica/Alumina covered by Ni 66%w)*. *The operation conditions of 350 °C and 10 bar and an input capacity of 1000 Nm^3/day led to approximately 200 Nm^3/day of CH_4* [66,50].

3.1.13. DNV GL – Power to Gas in Rozenburg

The DNV GL Group was the first company working on Power to Gas facilities in Rozenburg, Netherlands [67]. This project was aimed to assess the feasibility of PtG as SNG source in gas grids. This project was run in cooperation with *DNV GL, the Rotterdam Council and Ressort Wonen with funding from Stedin (grid operator) and TKI Gas [50]*.
The main equipment (Figure 3.8) was distributed in three separate containers [68], comprising:

- 7 kW PEM electrolyzer (first container).
- The four methanation reactors in series (Figure 3.9) that was structured of *stainless steel 316 L with a capacity of 1.06 L for each, filled with different commercial catalysts depending on H_2 and CO_2 concentrations. The two first reactors use 11%w Ni catalysts to avoid exceeding the temperature requirements, whilst the third and fourth reactors use 37%w and 54%w Ni contents, respectively*. Hence, with this strategy the reactors can operate at a temperature range *between 150–700 °C and pressures below 15 bar, although the best results are obtained at 377 °C and less than 8 bar* (second container).

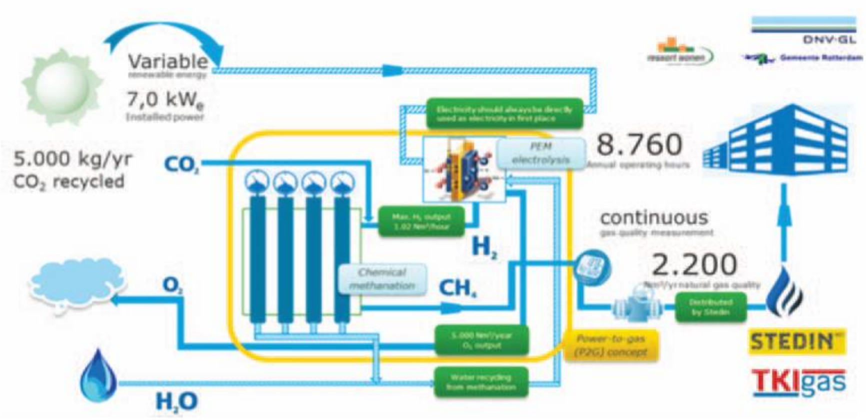


Figure 3.8 Schematic overview of the P2G project in Rozenburg [67].

- Two CO_2 tanks, located in third container.
- Four solar panels, that were installed on the containers' roofs can't completely generate the required power for electrolyzer, therefore the electricity grid supplies the remaining demand. The carbon dioxide porches from an industrial distributor [68].

Figure 3.9 Reactors of methanation [68].

3.1.14. HSR-IET – Power-to-Methane HSR

The Institute for Energy Technology of the Hochschule für Technik Rapperswil (HSR-IET) defined and developed the first Power to Gas plants in Swiss, Rapperswil (Figure 3.10). The pilot project was aimed for developing simulation models to estimate the future role of Power to Gas in the Swiss energy supply. In this project, for the first time within PtG plants, the methanation heat was conducted and applied in an ambient-CO_2 absorption process [69].
The hydrogen was provided by the local power company *Elektrizitätswerk Jona-Rapperswil AG (EWJR)* and the CO_2 was separated from the air and collected up to 4 kg/day [70].

Die Hochschule für Technik in Rapperswil produziert in einer eigenen Anlage Methangas. HSR

Figure 3.10 The pilot and demonstration Power-to-Methane plant HSR [69].

3.1.15. Hitachi Zosen – CO_2 Conversion to Methane Project

The first facility in Thailand approaching CO_2 Conversion to Methane launched in 2012. The results were supposed to apply in the simulation and design of the main plant with a methane production of 1000 Nm^3/h. The partner's group in this research were *Hitachi Zosen Corporation, Daiki Ataka Engineering Co. and PTT Exploration and Production Public Company Limited (PTTEP).* The CO_2 generated during extraction of natural gas from natural reservoirs was considered as the main source for this project [71].
The required hydrogen was supplied by alkaline electrolyzers fed with desalinated seawater. The first phase of the project was designed using tubular reactors that operated at 200 °C. *The catalyst based on zirconia-samarium, with nickel as an active material, which was developed by Hashimoto et al.* [72].

3.1.16. JKU Linz-EI – PtG in Austria

The Energy Institute of the Johannes Kepler University Linz (JKU Linz-EI) took part in four connected projects for developing a complete chain of Power to Gas systems in Austria. These projects have been running in cooperating with the *Vienna University of Technology (TU Wien), the Austrian Association for Gas and Water (ÖVGW), the Association of Gas and District Heating Supply Companies (FGW), Montan University of Leoben and the Christof Group*.

- Wind2Hydrogen (2014– 2016) built a 100 kW pilot plant with 12 PEM electrolyzers (section Hydrogen projects, Table 3.2) [73].
- EE-Methan aus CO_2 (2013–2016) develops catalytic methanation [74].
- OptFuel (2013–2016) focuses on hydrogen production through fermentation and on the purification requirements for its later conversion into methane (partly biological methanation, so it won't investigate more) [75].
- Underground Sun Storage (2013–2016) studies the storage of the generated gas (section methane-hydrogen projects, Table 3.3).

The main goal of EE-Methan project is to develop a ceramic honeycomb catalyst adapted to industrial CO_2 sources for increasing the lifetime about 10% with respect to commercial catalysts [74].

3.1.17. Paul Scherrer Institute – RENERG2

The RENERG2 project (Renewable Energies for Future Energy Supply) was defined to investigate electrolysis, methanation, combustion fundamentals, refueling and economics for using renewable energy surplus in mobility sector [76]. The project's partners included *EMPA, the Swiss Federal Institute of Technology Zurich (ETH Zurich), the Zurich University of Applied Sciences (ZHAW), and EPFL*. This project was funded by the *Competence Centre for Energy and Mobility (CCEM)* [76,50].
The methanation research was dedicated to the Paul Scherrer Institute using its bubbling fluidized bed methanation process (GanyMeth) [50].

3.1.18. Sunfire – HELMETH

The *HELMETH* project (*Integrated High-Temperature Electrolysis and Methanation for Effective Power to Gas Conversion*) was in cooperating with *Sunfire GmbH (administrative), KIT (project conductor), Politecnico di Torino* (*PoliTo), the European Research Institute of Catalysis AISBL (ERIC), Turbo Service Torino spa (TS-Torino), National Technical University of Athens (NTUA), DVGW*. This project was aimed to reach efficiencies above 85% in Power to Gas technologies by *uniting high-temperature electrolysis and* CO_2 *methanation* [77].
The electrolysis research was supposed to be done by the ERIC using a 15 kW SOEC, working at 800 °C and 15 bar [50].
The methanation process consisted of two reactors in series at 300 °C and 30 bar and *intermediate water removal* and also adding *composite oxides to the* γ-Al_2O_3 *substrate,* as catalyst stabilizer [78,79].

3.2. Hydrogen projects

The hydrogen plants have from efficiency aspect (Figure 3.4) more advantages than methanation plants. This fact has created enough motivation for energy suppliers. Therefore, they have been structuring also many hydrogen plants beside the methanation plants. The following presents an overview of hydrogen plants in European Union countries (Table 3.2), [51].

Project Name Location	**Application**	**H_2production** (Nm^3/h)	**Installed power** (kW)	**Electrolys is technique**	**Involved parties**
Auersthal (AT) - Wind2Hydrogen Auersthal, Austria	Mobility Gas grid	Unknown	100	PEM	OMV Gas & Power, Fronius, EVN AG, HyCentA Research GmbH und das Energieinstitut der Johannes Kepler Universität Linz
Brugg (CH) - PostBus Hydrogen Bus Stuttgart, Germany	Mobility	60	315	Alkaline	Carbagas (Swiss sibsidiary of Air Liquide), Hydrogenics, PostBus
Aragon (E) – ITHER Brugg, Switzerland Aragon, Spain	Mobility	Unknown	4070	Alkaline & PEM	unknown
Corsica (F) - MYRTE Ajaccio, Corsica, France	Power generation, Power storage	23	150	PEM	AREVA, CEA, University of Corsica, CNRS
Abalone Energie Nantes (F) Nantes, France	Power generation, Power storage	Unknown	0	unknown	Regio Pays de la Loire
Don Quichote (BE) - Colruyt Halle, Belgium	Mobility (forklifts)	30	150	PEM	WaterstofNet, Colruyt, Hydrogenics, Thinkstep, Icelandic New Energy, FAST, TÜV Rheinland
Leicestershire (UK) – Hari project Leicestershire, United Kingdom	Power generation, Power storage	Unknown	36	Alkaline	Loughborough University
Rotherham (UK) - hydrogen **mini-grid project** Rotherham, United Kingdom	Power generation, Power storage	Unknown	30	unknown	Unknown
Fife (UK) - Levenmouth Community Energy Project Fife, Scotland	Mobility		370	Alkaline & PEM	Bright Green Hydrogen Ltd,Fife Council, Toshiba, Leven Valley Development Trust, Fife College, BOC (for hydrogen transport), Green Business Fife, Community Energy Scotland and the Scottish Hydrogen and Fuel Cell Association (SHFCA).
Aberdeen (UK) - Hydrogen Bus Project Aberdeen, Scotland	Mobility	180	1000	Alkaline	BOC, Scottish & Southern Energy Power Distribution (SSEPD), Scotland Gas Networks (SGC), Van Hool, Ballard Power Systems, Dantherm, First, Stagecoach, Scottish Government, Scottish Enterprise, Element Energy, Planter Energie, Innovate UK, Aberdeen City Council
SamsØ (DK) SamsØ, Denmark	Mobility	Unknown	20	Alkaline	SamsØ Energy Academy
Freiburg (D) – H_2Move Freiburg, Germany	Mobility	6	40	PEM	Fraunhofer ISE, Ministerium für Umwelt, Klima und Energiewirtschaft Baden-Württemberg, Stadt Freiburg, badenova, NOW GmbH
Mainz (D) Mainz, Germany	Mobility, Power generation, Power storage, Industry	1000	3900	PEM	Stadtwerke Mainz AG, Linde AG, Siemens AG, Hochschule RheinMain
Frankfurt am Main (D) - Thuga Frankfurt am Main, Germany		60	315	PEM	
Hanau (D) Hanau, Germany	Power generation	4	35	PEM	SolviCore GmbH & Co. KG, Mainova AG, Stadtwerke Hanau GmbH, Hochschule RheinMain aus Rüsselsheim
Ibbenburen (D) – RWE Ibbenbüren, Germany	Gas grid, heat	30	150	PEM	WESTNETZ GmbH
Hamburg-Schnackenburgallee (D) Hamburg-Schnackenburgallee, Germany	Mobility	30	185	PEM	Shell, NOW GmbH, CEP-Clean-Energy-Partnership
Hamburg-Hafencity (D) – Vattenfall Hafencity, Hamburg, Germany	Mobility	120	630	Alkaline	Bundesministerium für Verkehr, Bau und Stadtentwicklung, CEP-Clean Energy Partnership, NOW GmbH, Shell
Hamburg-Reitbrook (D) – WindGas Hamburg Reitbrook, Hamburg, Germany	Gas grid	290	1000	PEM	Uniper, Hydrogenics, GmbH, SolviCore GmbH & Co. KG, Fraunhofer Institute for Solar Energy, Systems ISE and German Aerospace Center (DLR), NOW GmbH, Greenerity
Grapzow (D) – RH_2 WIND Grapzow, Germany	CHP & gas grid	210	1000	Alkaline	NOW GmbH, Haas Engineering, Architekturbüro Karsten Klünder. Hydrogenics, Senergie
Prenzlau (D) – ENERTRAG AG Prenzlau, Germany	Mobility & power generation / storage	120	600	Alkaline	Vattenfall Europe Innovation GmbH, Total, DB Mobilty Network Logistics, Bundesministerium für Verkehr, Bau und Stadtentwicklung, European Union, Land Brandenburg, PTJ, Investitionsbank des Landes Brandenburg, Fachhochschule Stalsund, Brandenburgischer Technischer Universität
Berlin Airport (D) - H_2BER Berlin Airport, Germany	Mobility, Power generation, Power storage, anticipates CHP(combined heat and power plant)	90	500	Alkaline	Total Deutschland GmbH, Enertrag AG, Linde AG, McPhy Energy, 2G Energy
Cottbus (D) Cottbus, Germany	Unknown	20-30	150	Alkaline	Wassertoff-Forschungszentrum Brandenburgische Technische Universität Cottbus

Table 3.2 The operating hydrogen PtG plants in European Union countries [51].

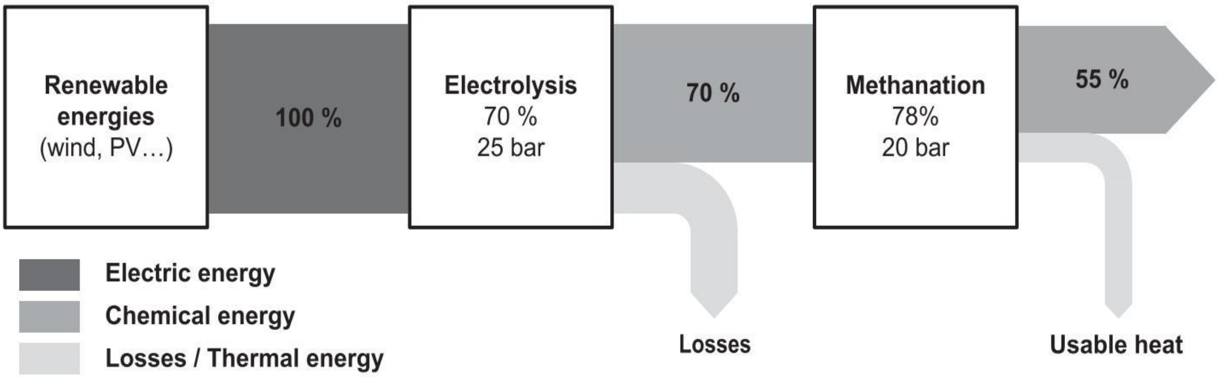


Figure 3.4 Sankey diagram of the PtG process efficiency, [11].

3.3. Methane-hydrogen projects

As expressed before, some of the plants are designed by engineers in a way, which can simultaneously provide methane and hydrogen as products for customers (Figure 3.2). In the following, the methane-hydrogen plants (Table 3.3) in European Union countries [51] are listed.

Project Location	Target	H_2/SNG production (Nm^3/h)	**Electrolysis technique** Installed power (kW)	**Methanation principle** CO_2 Source	Involved parties
Vienna (AT) - Underground Sun Storage [108] Vienna, Austria	Storage	120 /Unknown	**Alkaline** 600	**Chemical** Atmosphere, biogas or industrial plant	RAG, University of Leoben, University of Natural Resources and Life Siences Vienna, Energy Institute at Johannes Kepler University Linz, Verbund, Axiom Angewandte Prozesstechnik, Nafta, Etogas, German Technical and Scientific Association for Gas and Water or DVGW, Hychico
Puglia region (I) - INGRID Project Troia, Pulgia, Italy	Gas grid (Regional distribution)	Unknown/Unknown	Alkaline 1000	**Chemical (Modular mili-structured catalytic methanation reactors)** atmosphere	McPhy Energy S.A. Hydrogenics, Tecnalia, RSE, Enel Distribuzione, Arti
Dunkerque (F) - GRHYD project Dunkerque, France	Mobility, Gas grid	10-15/Unknown	Unknown Unknown	**n/a** Unknown	GrDF, NVERT, AREVA Hydrogène et Stockage de l'énergie, CEA, McPhy Energy, INERIS, CETIAT and CETH2
Kirchheimbolanden (D) - RegEnKibo Kirchheimbolanden, Germany	Gas grid	Unknown/Unknown	Unknown Unknown	**Unknown** Unknown	e-rp GmbH, KIT, DVGW-Forschungstelle am Engler-Bunte-Institut des KIT, Transferstelle für Rationelle und Regenerative Energienutzung Bingen (TSB), Viessman Gruppe, Stadt Kirchheimbolanden
Allendorf, Eder (D) - BioPower2Gas Allendorf, Eder, Germany	Gas grid	60-220/15-55	PEM 1100	**Biological** Unknown	MicrobEnergy GmbH, EnergieNetz Mitte GmbH, EAM EnergiePlus GmbH, CUBE Engineering GmbH

Table 3.3 The operating methane-hydrogen PtG plants in European Union countries [51].

Chapter 4

Modeling and simulation

4. Modeling and simulation

4.1. Introduction

Models are applied to investigate a system more accurate and predict its technical behavior and drawbacks and also to improve it based on simulation results. The life cycle of a modeling prototype is demonstrated in Figure 4.1. Starting from the real system that is going to be investigated, an abstract model structure is created. This step has the greatest impact on the modeling results because the incorrect understanding of the real system will be transferred into incorrect model. In the second step, the model parameters are calibrated by the real system behavior in different scenarios (experiments data). Finally, an authentic model is anailable to estimate the behavior of the real system in various situations. In the third step, the proven model is able to simulate new systems based on accurate parameters gained from the investigations.

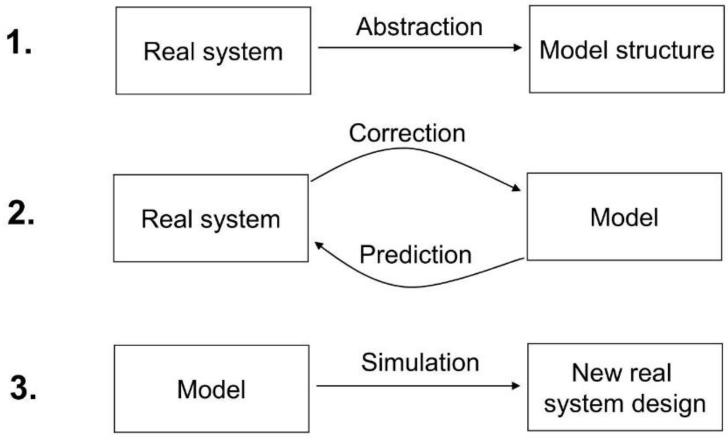
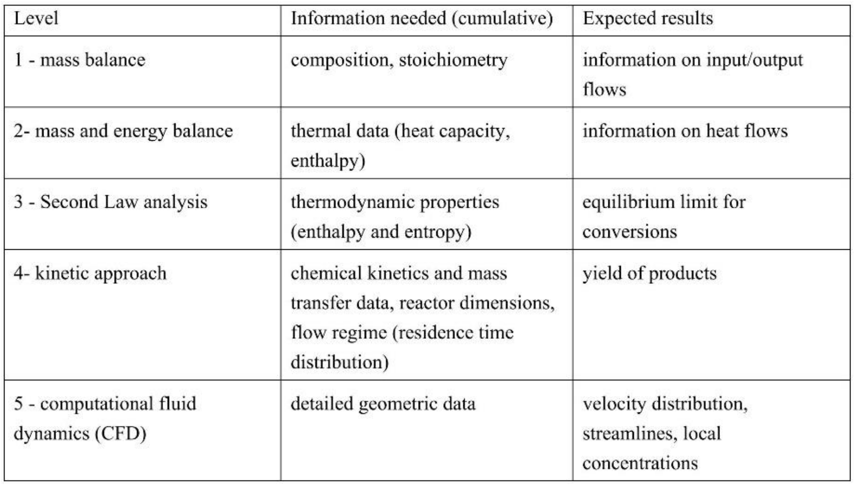


Figure 4.1 Stages of development and application of models [13].

Table 4.1 is presenting possible degrees of modeling approaches. As a basic rule, *it is constantly represented to walk through the list in the table (4.1) top-down with a critical evaluation of the work after each stage* [13].



Level	Information needed (cumulative)	Expected results
1 - mass balance	composition, stoichiometry	information on input/output flows
2- mass and energy balance	thermal data (heat capacity, enthalpy)	information on heat flows
3 - Second Law analysis	thermodynamic properties (enthalpy and entropy)	equilibrium limit for conversions
4- kinetic approach	chemical kinetics and mass transfer data, reactor dimensions, flow regime (residence time distribution)	yield of products
5 - computational fluid dynamics (CFD)	detailed geometric data	velocity distribution, streamlines, local concentrations

Table 4.1 Levels of itemization in modeling [13].

4.2. Modeling and simulation in methanation

Today, modeling and simulation are an essential phase of research and development not only in methanation concepts, even all chemical engineering branch and science. Practically, modeling and simulation works apply in the four scopes including *process design,* ***process evaluation****, process optimization, and process adaptation [10]*.

- Process design

The computer-aided process design is a major task of engineers in chemical engineering. As discussed in chapter 2, the exothermal identity of the methanation reactions causes the reactor temperature to be especially noteworthy. The temperature behavior of a designed reactor is depending on *reactor design (e.g. diameter, length, cooling, and insulation), process design (residence time, the composition of the feed gas), and the catalyst (activity, dilution)* [10].

- **Process evaluation**

The evaluation of an equipment like methanation reactor is quantitatively translated to the performance of reaction from different aspects (e.g. selectivity [80]). The simulation-based evaluation studies require process parameters such as temperature profile, production rate, composition, and transferred heat rates of reactor and exchangers. Also, these evaluations can be done for a whole process (e.g. PtG plant). In section 4.4 a novel simulation-based evaluation (**Distance of Equilibrium State**) for a sample methanation reactor using programming capabilities in Microsoft ® Excel ® is presented.

- Process optimization

As mentioned before, with increasing demand for applying methanation concepts as a chemical storage of renewably-generated power (**Power to Gas**), simulation studies try to optimize the reactor dynamic performances. Hence, simulation models are used to predict the consequences caused by power or feed fluctuations [81,82]) and also to improve control strategies [83].

- **Process adaptation**

This subject has practically been applied within the recent CO_2 methanation processes (**Power to Gas** plants). Therefore, the past methanation concepts (particularly CO-methanation) is adapted to the customized CO_2-methanation processes, which are adequated for applying in PtG plants by modeling and simulation developments [84,85].

4.3. Reactor modeling

The industrial methanation reactor is known as a complex process because of the simultaneous occurrences of gas phase reaction that happen very quickly. Hence, simulation and modeling of such a process before the industrial plant designing seems to be vital. According to Table 4.1, to simulate a reactor system, its issues like mass transfer, heat transfer (exothermic reaction), the occurrence of secondary reactions such as water gas shift reaction, the kinetic approach, etc. must be considered. Therefore, the characteristics of models very clearly depend on the purposes of modeling and simulation task. Main characteristics are known to be *the time resolution of the model, the reactor dimension, the phase modeling, the temperature characteristics, the kinetic approach, and the software* [10]. In Tables 4.2, 4.3, and 4.4 a selection of the models is presented with respect to their main characteristics concerned to the fixed-bed, the three-phase, fluidized-bed, the fixed-bed tube bundle, and the fixed-bed structured methanation reactors respectively.

4.3.1. Time analysis

Due to defined requirements, steady state (S.S.) or dynamic reactor models can be approached. The dynamic reactor models include also derivations of time instead of spatial derivatives equations only in the stationary models. Accordingly, these models can be applied to analyze the methanation reaction.

4.3.2. Reactor dimensions

Briefly, reactor models may be considered with zero to three spatial dimensions.

- If designers create situations within reactors that mentioned specifications are just a function of time, not geometry, then they can apply zero-dimensional models to describe the real system, such as continuous stirred tank reactors when being perfectly mixed. However, a chain of zero-dimensional models can be placed in series to obtain a one-dimensional (axial) profile.

- For fixed-bed reactors particularly, the one-dimensional reactor models are normally implemented. It is clear, that the axial profile of gas species and temperature will especially be investigated as the only geometrical characteristic in case of plug flow reactors. The radial property changes are often neglected because the plug flow reactors assumption of constant radial temperature and concentrations will practically be acceptable.

- Two-dimensional models require much more computational effort for solving the differential equations. The one-dimensional models are more efficient to evaluate qualitative attitudes of the real system. However, the two-dimensional models reflect more detailed picture that is more suitable for quantitative evaluations [86].

- To solve the equations of three-dimensional models highest level of computational calculations has to be applied. They are vital especially for detailed optimization and design. But there are not necessarily big differences between two and three-dimensional simulations in some cases [87,88].

4.3.3. Phase modeling

The conventional fixed bed methanation reactors and three phase reactors are categorized as heterogeneous reactors in this science because they contain gas phase (reactants and products) solid phase (catalyst) and a liquid phase (just for three-phase reactors) that usually are inert heat transfer fluids.

But in contrast, fluidized-bed reactors with some assumption and estimations (e.g. *effect of external mass transfer and pore diffusion are negligible [10]*) can suppose as a two or even one continuum (pseudo-homogeneous) phase because these assumptions have the advantages of easier modeling process, however it will include certainly the inaccuracy in the outputs from model. The criteria of Mears [90] are usually considered by engineers to realize the acceptable assumptions for each system [89].

4.3.4. Temperature characteristic

As discussed before, control of the temperature due to a high-exothermic heat of the reactions is a very significant issue that must be considered from the designing phase of the methanation processes and reactors. For methanation modeling, the temperature profile often is estimated by an ideal temperature profile. *Ideal fixed-bed reactors without cooling typically display adiabatic temperature profiles, also, ideal fluidized-bed and three-phase reactors with cooling mechanisms are demonstrated isothermal temperature profiles* (section 2.2.3) [10,8].

4.3.5. Kinetics approach

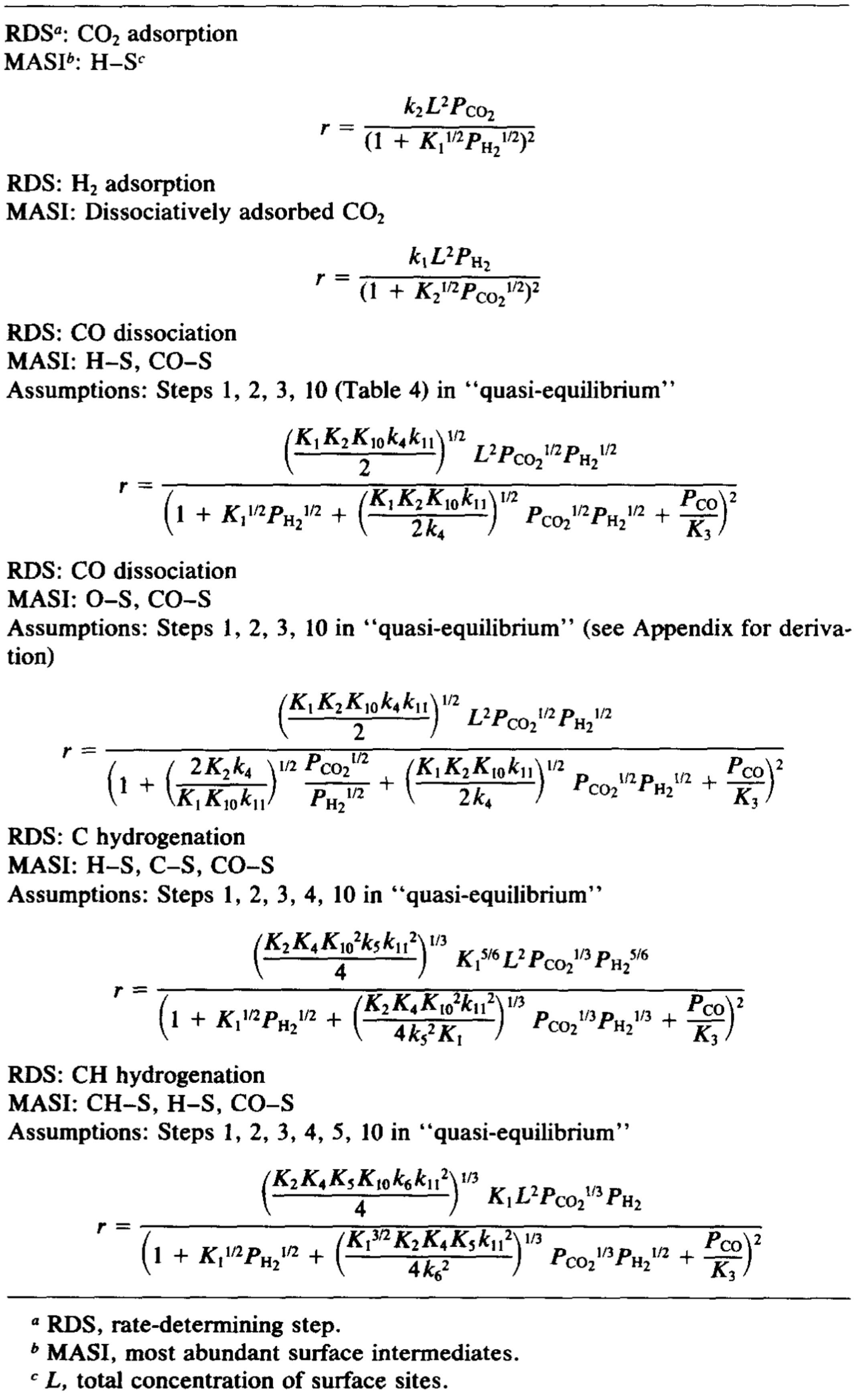
As mentioned in section (2.1.1), because processes cannot practically fulfill the equilibrium states during the reaction (requirement of infinite time or very slow interactions progress), kinetics descriptions have been developed to describe the system through the non-equilibrium states. Additionally, there are infinite non-equilibrium states that every reaction with a particular catalyst and condition (i.e. temperature, pressure, composition, etc.) is able to show. There are several methanation kinetics in the literature that useing a particular mechanism and method (e.g. power law, Langmuir-Hinshelwood etc.) developed by researchers. For example, in Figure 4.2 the developed CO_2-hydrogenation kinetic by Weatherbee and Bartholomew [12] (1982) is illustrated. As described in section 2.1.2, this kinetic was developed based on their mechanism (Figure 2.8) to fit the determined experimental data. Also, useful *overviews about different kinetic approaches are presented by Kopyscinski [91], Mills and Steffgen [49], and Vannice [38]*.

Xu and Froment kinetic [92] for FB-reactors and Kopyscinski kinetic [91] for fluidized and three phase reactors seems to be the best chooses, according to Tables 4.2, 4.3 and 4.4.

Franz Koschany et al. [93] developed several kinetics as rate equations using power law and Langmuir–Hinshelwood–Hougen–Watson (LHHW) approaches for a series of $NiAl(O)_x$ catalysts with varying Ni/Al ratio.

4.3.6. Software

As it is observable from tables 4.2, 4.3 and 4.4 a group of simulation and modeling software is available to be applied for solving the differential equations due to methanation reactor modeling. These tools include Aspen Plus, Aspen Dynamics, Modelica Fluid, Femlab, Fortran, ACM, Matlab, etc. Matlab is the most common software for this purpose.



RDS[a]: CO_2 adsorption
MASI[b]: H–S[c]

$$r = \frac{k_2 L^2 P_{CO_2}}{(1 + K_1^{1/2} P_{H_2}^{1/2})^2}$$

RDS: H_2 adsorption
MASI: Dissociatively adsorbed CO_2

$$r = \frac{k_1 L^2 P_{H_2}}{(1 + K_2^{1/2} P_{CO_2}^{1/2})^2}$$

RDS: CO dissociation
MASI: H–S, CO–S
Assumptions: Steps 1, 2, 3, 10 (Table 4) in "quasi-equilibrium"

$$r = \frac{\left(\frac{K_1 K_2 K_{10} k_4 k_{11}}{2}\right)^{1/2} L^2 P_{CO_2}^{1/2} P_{H_2}^{1/2}}{\left(1 + K_1^{1/2} P_{H_2}^{1/2} + \left(\frac{K_1 K_2 K_{10} k_{11}}{2k_4}\right)^{1/2} P_{CO_2}^{1/2} P_{H_2}^{1/2} + \frac{P_{CO}}{K_3}\right)^2}$$

RDS: CO dissociation
MASI: O–S, CO–S
Assumptions: Steps 1, 2, 3, 10 in "quasi-equilibrium" (see Appendix for derivation)

$$r = \frac{\left(\frac{K_1 K_2 K_{10} k_4 k_{11}}{2}\right)^{1/2} L^2 P_{CO_2}^{1/2} P_{H_2}^{1/2}}{\left(1 + \left(\frac{2K_2 k_4}{K_1 K_{10} k_{11}}\right)^{1/2} \frac{P_{CO_2}^{1/2}}{P_{H_2}^{1/2}} + \left(\frac{K_1 K_2 K_{10} k_{11}}{2k_4}\right)^{1/2} P_{CO_2}^{1/2} P_{H_2}^{1/2} + \frac{P_{CO}}{K_3}\right)^2}$$

RDS: C hydrogenation
MASI: H–S, C–S, CO–S
Assumptions: Steps 1, 2, 3, 4, 10 in "quasi-equilibrium"

$$r = \frac{\left(\frac{K_2 K_4 K_{10}^2 k_5 k_{11}^2}{4}\right)^{1/3} K_1^{5/6} L^2 P_{CO_2}^{1/3} P_{H_2}^{5/6}}{\left(1 + K_1^{1/2} P_{H_2}^{1/2} + \left(\frac{K_2 K_4 K_{10}^2 k_{11}^2}{4k_5^2 K_1}\right)^{1/3} P_{CO_2}^{1/3} P_{H_2}^{1/3} + \frac{P_{CO}}{K_3}\right)^2}$$

RDS: CH hydrogenation
MASI: CH–S, H–S, CO–S
Assumptions: Steps 1, 2, 3, 4, 5, 10 in "quasi-equilibrium"

$$r = \frac{\left(\frac{K_2 K_4 K_5 K_{10} k_6 k_{11}^2}{4}\right)^{1/3} K_1 L^2 P_{CO_2}^{1/3} P_{H_2}}{\left(1 + K_1^{1/2} P_{H_2}^{1/2} + \left(\frac{K_1^{3/2} K_2 K_4 K_5 k_{11}^2}{4k_6^2}\right)^{1/3} P_{CO_2}^{1/3} P_{H_2}^{1/2} + \frac{P_{CO}}{K_3}\right)^2}$$

---

[a] RDS, rate-determining step.
[b] MASI, most abundant surface intermediates.
[c] *L*, total concentration of surface sites.

Figure 4.2 Kinetic Rate Expressions for CO_2-Methanation Based on Langmuir-Hinshelwood Kinetics [12].

Time resolution	Reactor dimensions	Phase modeling	Temperature characteristic	Kinetic approach	Software	Authors
dyn.	1D	Heterogeneous (therm.)	Adiabatic (supposed)	– (equilibrium)	Modelica Fluid	Bader et al.
stat.	3D	Pseudo-homogeneous	Polytropic	Measured (1st order)	Femlab	Cao et al.
dyn.	1D	Pseudo-homogeneous	Adiabatic	n.s.	Fortran	Dissinger et al.
dyn.	1D	Pseudo-homogeneous	Adiabatic	van Herwijnen et al.	n.s.	van Doesburg et al.
stat.	1D	Pseudo-homogeneous	Isothermal	Kopyscinski	Aspen Plus	Er-rbib et al.
dyn.	1D	Pseudo-homogeneous	Isothermal	Kopyscinski	ACM	Güttel
stat.	1D	Heterogeneous (cat. isoth.)	Adiabatic	Xu and Froment	Matlab	Khorsand et al.
dyn.	1D	Pseudo-homogeneous	Polytropic	Xu and Froment	Aspen Dynamics	Li et al.
dyn.	1D	Heterogeneous (therm.)	Polytropic	Measured	n.s.	Lunde
dyn.	1D	Heterogeneous (therm.)	Adiabatic	Xu and Froment	Matlab	Matthischke and Rönsch
stat.	1D	Heterogeneous[a]	Adiabatic	Xu and Froment (refit)	n.s.	Parlikkad et al.
dyn.	0D	Heterogeneous (therm.)	Adiabatic	– (equilibrium)	Matlab	Rönsch et al.
stat.	1D	Heterogeneous	Polytropic	Xu and Froment	Matlab	Schlereth and Hinrichsen
stat.	2D	Pseudo-homogeneous	Polytropic	Xu and Froment	Matlab	Schlereth and Hinrichsen
stat.	1D	Pseudo-homogeneous	Adiabatic	van Doesburg. (refit)	–	Wedel and Luss

Table 4.2 Model characteristics of fixed-bed methanation reactors [10].

Time resolution	Reactor dimensions	Phase modeling	Temperature characteristic	Kinetic approach	Software	Authors
stat.	1D	Three phases, pseudo-homogeneous	Isothermal	Measured (1st order)	Matlab	Götz
stat.	1D (0D i.s.)	Two phases, pseudo-homogeneous dense phase	Isothermal (supposed)	Measured (1st order)	n.s.	Cobb and Streeter
stat.	1D	Two phases, pseudo-homogeneous dense phase	Defined profile	Kopyscinski	Athena	Kopyscinski et al.
dyn.	2D/3D[a]	Two phases, heterogeneous dense phase	Isothermal	Kopyscinski	Open FOAM	Liu and Hinrichsen

Table 4.3 Model characteristics of three-phase and fluidized-bed methanation reactors [10].

Time resolution	Reactor dimensions	Phase modeling	Temperature characteristic	Kinetic approach	Software	Authors
stat.	1D	Pseudo-homogeneous	Polytropic	Xu and Froment	AMPL	El Sibai et al.
stat./dyn.	1D	Pseudo-homogeneous	Polytropic	Kopyscinski	Aspen Dynamics	Jürgensen et al.
dyn.	1D (0D i.s.)	Pseudo-homogeneous	Polytropic	Xu and Froment	Matlab	Kang and Lee
dyn.	1D	Heterogeneous (cat. isoth.)	Defined profile	Lunde (refit)	LIMEX	Brooks et al.
dyn.	1D	Heterogeneous	Polytropic	Sughrue and Bartholomew and Weatherbee and Bartholo- mew	gProms	Sudiro et al.

Table 4.4 Model characteristics of the fixed-bed tube bundle and structured methanation reactors [10].

4.3.7. Plant modeling

Generally, plant modeling can be done for several purposes, e.g. *concepts comparison and development, process and thermal integrations, efficiency estimations, and data collection for economic and environmental assessments* or even politics decisions [10]. Also, researchers in SNG production fields (e.g. PtG plants, biomass, coal to SNG) have performed several plant simulations. The studies mostly aimed at concept comparisons for different SNG systems according to efficiency calculations. An overview of selected studies is given in Table 4.5.
Aspen Plus as commercial modeling software has been applied most frequently (Table 4.5) in SNG plant analysis, due to its advantages (e.g. robust databank, comprehensive offered concepts and equipments, the capability of implementation of customized equipment via coding in Fortran or Excel, etc.). Some studies tried to estimate production costs [94,96] or greenhouse gas emissions [95,96].

Authors	**Plant concept**	**Focus**	**Methanation reactor**	**Software**
De Saint Jean et al.	Power to gas	Process assessment: efficiency	1D fixed-bed, kinetic	ProSimPlus
Seyedmehdi Sharifian	Power to gas	Process assessment: efficiency	1D fixed-bed, kinetic	Aspen Plus
Fendt et al.	Biomass to SNG	Concept comparison: efficiency, costs	0D n.s., equilibrium	Aspen Plus
Heyne et al.	Biomass to SNG	Process optimization and concept comparison	0D, fixed-bed, equilibrium	Aspen Plus
Koytsoumpa et al.	Coal to SNG	Technology assessment: acid gas removal	0D n.s., equilibrium	Aspen Plus
Nagumo et al.	Biomass to SNG	Process optimization: process integration	0D n.s. equilibrium	Aspen Plus
Rehling et al.	Biomass to SNG	Process optimization: heat integration	0D fluidized-bed, equilibrium	IPSEPro
Rönsch et al.	Biomass to SNG	Concept comparison: efficiency	0D fixed-bed, equilibrium	Aspen Plus
Rönsch and Kaltschmitt	Biomass to SNG	Concept comparison: efficiency, costs, GHG emissions	0D fluidized-bed equilibrium	Matlab Simulink
Swedish Gas Centre	Biomass to SNG	Concept comparison: efficiency	0D fixed-bed, equilibrium	Aspen Plus
Tremel et al.	Biomass to SNG	Process optimization: process integration	0D fluidized-bed, equilibrium	Aspen Plus
van der Meijden et al.	Biomass to SNG	Concept comparison: efficiency	0D fixed-bed, equilibrium	Aspen Plus
Zwart et al. [	Biomass to SNG	Concept comparison: efficiency, costs	0D fixed-bed, equilibrium	Aspen Plus

Table 4.5 Selected simulation studies for SNG plant simulation ([10] adapted).

4.4. Basic simulation of the methanation reactor in Excel

4.4.1. System introduction

The final purpose of this novel simulation-based work is the evaluation of the reactor working state and comparison with equilibrium state using the Distance to Equilibrium State (DES) parameter (pδ_eq(p_i,T)). This kind of simulation is able to evaluate the working reaction's state that in concept development or catalyst and mechanism investigation is very important.

The catalytic methanation reactor which is going to be investigated is an adiabatic reactor (Figure 4.3) with one feed (S_2) and product (S_3) stream that operates in a steady state profile and isobaric process. Also, the components comprising CO_2, CH_4, CO, H_2, and H_2O are reported as the substances in the gas form that ideal gas mixture theories can well define their properties during the reaction process.

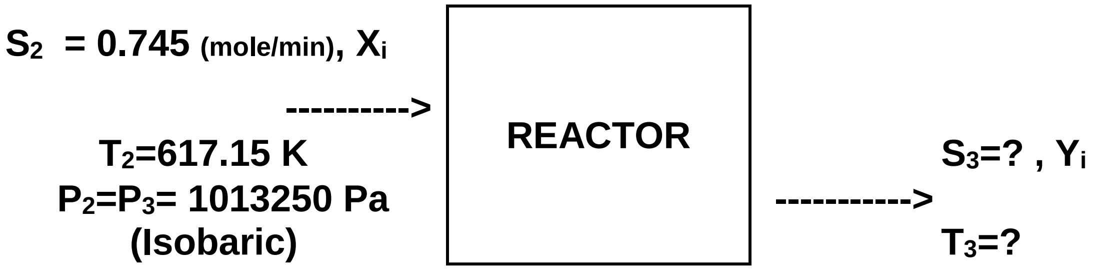


Figure 4.3 The catalytic adiabatic methanation reactor.

The composition of substances in the feed stream (H_2/CO_2=11.6952) is presented in Table 4.6.

Species	x_i (mole/mole)	X_i(kg/kg)
CO_2	0,0771	0,6060
CH_4	0,0058	0,01662
CO	0,0018	0,009004
H_2	0,9017	0,3246
H_2O	0,0136	0,04376
Sum	1,0000	1,0000

Table 4.6 composition of the feed stream of the sample reactor, (Experimental Data) [109].

4.4.2. Thermodynamic property

The thermodynamic properties (e.g. molecular weights (M), conventional enthalpy H*, conventional entropy (S*)) of the component in this modeling will be calculated by NASA polynomial macro in Excel based on International Standard Temperature 25 °C and SI unit system. The generated properties by excel for the feed stream (S_2) are collected in Table 4.7. The advantage of conventional properties (Eq. (14)&(15)) is the easier calculations without entering the reaction enthalpy in the heat balance and equilibrium constant (K_p) equations [13,97].

$$h^* (p,T) = \Delta h^\circ_{f,298} + h (p,T) - h (p_0,T_0) \quad , T_0=298°C \qquad (14)$$

$$h^* (p,T) = \Delta h^\circ_{f,298} + \int_{T0}^{T} Cp(T)\, dT \quad , \quad T_0=298°C \qquad (15)$$

Species	M [kg/mol]	h*_i(J/mol)
CO_2	0,04401	-29280,3941
CH_4	0,0160	-352,8637
CO	0,0280	-181,9018
H_2	0,002016	8407,2513
H_2O	0,01802	-3137,3751
SUM (S_2)	**M_gas (S_2) = 0,005599**	-24545,2834
Conv. Enthalpy S_2 (J/min)		**-18286,23617**

Table 4.7 Calculated property for the feed stream by Microsoft ® Excel ®.

4.4.3. Mass Balance

After comparisons between the unknown parameters (S_3, Y_{CO2}, Y_{CH4}, Y_{CO}, Y_{H2}, Y_{H2O}) and the available balance equations (Total, C, H, and O mass balances) it can be concluded that the freedom degree of this system is +2, hence, to reach a solvable system with the freedom degree of zero, there are two required assumptions about the compositions of the methane and carbon monoxide in product stream (Y_{CH4}, Y_{CO}).

Working point number (Wpn) →			**1**	**2**	**3**
Component	**Balance Data**	**Y_i (kg/kg)**	**No reaction point**	**Operation point**	**Almost Ideal Point**
CO_2	Mass Balance C	kg/kg	0,6060	0,1166	0,1261
CH_4	Set Point	kg/kg	0,01662	0,1982	0,195
CO	Set Point	kg/kg	0,009004	0,003495	0,003
H_2	Mass Balance H	kg/kg	0,3246	0,2338	0,2354
H_2O	Mass Balance O	kg/kg	0,04376	0,4480	0,4405
Sum Y_i		kg/kg	1,00	1,00	1,00
M_gas (S_3)		kg/mol	0,005560	0,006412	0,006396
Mole Flow (S_3)		mol/min	0,7450	0,6506	0,6522
Mass Flow (S_3)	Total Mass Balance	kg/min	0,004172	0,004172	0,004172

Table 4.8 The results of the system mass balances in three point. In the Wpn (1) the set-point is chosen same as their feed stream amounts, also Wpn (3) have the set points of normal operation amounts, and the Wpn (5) has the best results based on calculated DES parameter.

In fact, when the assumption in the system are changed, consequently other parameters will be calculated differently and actually, the working state of the system has been changed. The table (4.8) display the calculated parameters in this progress for three interested set points or working point of the methanation reactor.

4.4.4. Energy Balance

The temperature of the operating reactor (T_{S3}) is the most important property, which will be obtained from energy balance. Due to the adiabatic reactor operation ($\Delta Q = 0$), the principle of conservation energy ($H^*\_S_2 = H^*\_S_3 \pm \Delta Q$) is arranged according to equation (16).

$$H^*\_S_2 = H^*\_S_3 \qquad (16)$$

Where:

$$H^* = \sum y_i \, . \, H^*_i(T) \qquad (17)$$

The temperature will be calculated using the solver extension of excel if the error function of equation (16) is limited to zero. The table (4.9) is represented the calculated temperatures for the mentioned three working point (Wpn) in the table (4.8).

Working point number (Wpn) →	Unit	1	2	3
Conv. Enthalpy S2	J/min	-18286,23617	-18286,23617	-18286,23617
Conv. Enthalpy S3	J/min	-18286,23617	-18286,25303	-18286,23627
Energy balance error	J/min	-9,62E-07	-1,69E-02	-1,01E-04
Temperature	K	617,15	1000,395	993,74

Table 4.9 The resulted temperatures using the system energy balances around the three working point.

4.4.5. Distance to Equilibrium State (DES)

According to the subjects, which were investigated in section (2.1.1.1) the equilibrium constant for Sabatier reaction (Eq. (2)) using the equation (9) and (10) is achievable. Therefore, with the definition, the distance to equilibrium state (DES) according to the equation (18), the comparisons between different operating conditions and the equilibrium operation point in the methanation reactor will be possible.

DES [13]:

$$p\delta\_eq(p\_i,T) = Log_{10} \left[\prod (P\_i/P°)^{vi} / K_P(T) \right] =$$

$$Log_{10} \left[(X^2_{H2O} * X_{CH4}) (X_{CO2} * X^4_{H2})^{-1} (p/p_0)^{-2} / Exp(- \Delta G^o_T / R. T) \right] \qquad (18)$$

The Table (4.10) summarizes the calculations and results for the considered three working points (Wpn), also, was drawn the figure (4.4) for analyzing these results.

Methanation Reaction			
X_CH4	**x_CH4**	**DES**	**Reactor Temperature**
(kg/kg)	(mole/mole)	pδ_eq(p_i,T)	T(K)
0	0		
0,01662	0,005800	-11,0909	617,1500
0,195	0,07774	-0,03186	993,7411
0,1982	0,0792	0,1578	1000,3951
0,3	0,1		

Table 4.10 The calculated DES parameter for the considered three working point.

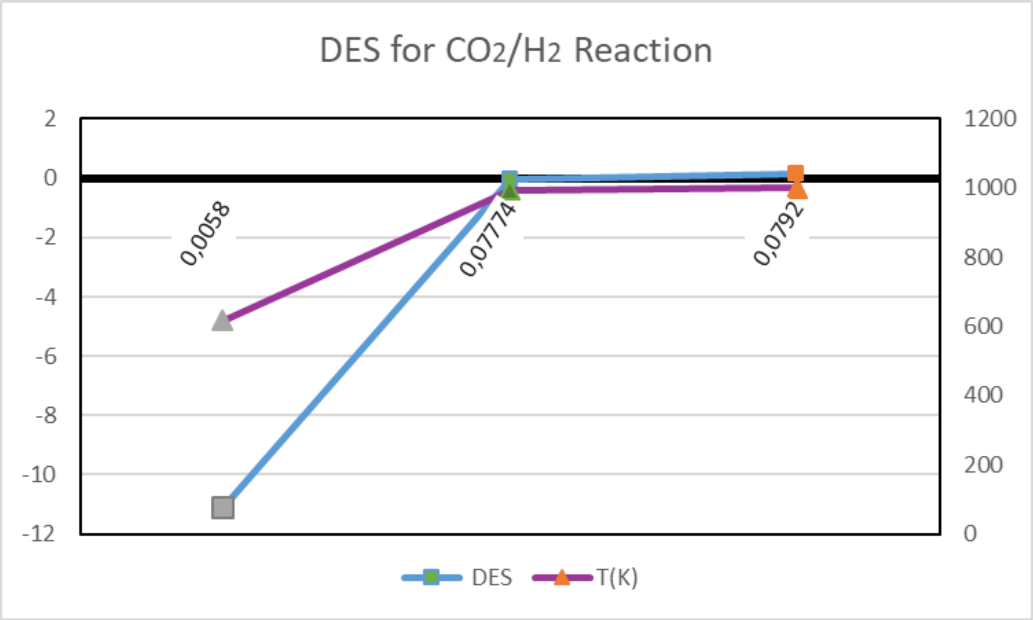


Figure 4.4 the drawn plot based on the calculated DES for three considered the Working point.

According to the Equation (18) the best working point will be the nearest one to the equilibrium (DES = 0), therefore, the green point in the chart with the DES-parameter’s amount of (-0.03186≈ 0.00) has advantages than other points to be approached.

Chapter 5

Research activities

5. Research activities

Although methanation technologies have been applied in several commercial plants during last decades, new applications and requirements (e.g. PtG) lead to the continuous optimization and development of methanation technologies. Current research efforts relating to CO and CO_2 methanation primarily focus particularly on temperature control, limiting process costs (efficiency) and increasing the process flexibility in the possible fluctuation due to syngas feed and renewably generated power.

A list of research groups that work on a section of methanation concepts can be observed in table 5.1, where almost 30 groups were identified by Götz et al. [11] in methanation field.

Fixed-bed	Fluidized-bed	Three-phase methanation	Structured reactor
Montan Universität, Leoben, Austria Unite de Catalyse et de Chimie du Solide, Villeneuve d'Ascq, France Deutsches Biomasseforschungszentrum, Leipzig, Germany DVGW and KIT, Karlsruhe, Germany Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany TU Clausthal, Germany TU München, Germany Zentrum für Sonnenenergie-und Wasserstoff-Forschung, Stuttgart, Germany Tokyo Institute of Technology, Japan Energy Research Centre of the Netherlands, Petten, Netherlands HSR Hochschule für Technik Rapperswil, Switzerland Pacific Northwest National Laboratory, Richland, USA	Beijing University of Chemical Technology, China Chinese Academy of Sciences, Beijing, China Engie SA (former GDF Suez), Paris, France Paul Scherrer Institute, Villigen, Switzerland	Chinese Academy of Sciences, Taiyuan, China DVGW and KIT, Karlsruhe, Germany	Montan Universität, Leoben, Austria Tsinghua University, China Brandenburg University of Technology, Cottbus, Germany DVGW and KIT, Karlsruhe, Germany Karlsruhe Institute of Technology (KIT),Germany Energy Research Centre of the Netherlands, Petten, Netherlands Instituto Superior Tecnico,Portugal Zurich University of Applied Sciences with Laboratory for Hydrogen & Energy, Switzerland Colorado School of Mines, Golden, USA Columbia University, USA Pacific Northwest National Laboratory, Richland, USA

Table 5.1 Overview of research groups working on catalytic methanation reactor concepts (sorted by country in alphabetical order) [11].

5.1. Fixed-bed reactors

The particular research field in the fixed-bed methanation reactor is related to improve the reactor temperature control and development of new catalysts with high-temperature resistance specifications (heat cracking, sintering). Due to the temperature control flexibility is directly related to a cost-justification in the process design by type, number or size of applied equipment (e.g. recycle compressor, heat exchanger, reactor etc.), hence, there are a number of useful simulation works (Chapter 4.4), that investigated these issues together (e.g. [98]).

5.2. Fluidized-bed reactors

Also, some research groups concentrate on fluidized bed reactors (Table 5.1). The main advantage of fluidized-bed reactors is operating with effective heat removal, hence in this plant, just one single reactor is applied. But these reactor concepts have also disadvantages, e.g. fluidization of catalyst particles lead to a strong mechanical clash between the particles and reactor walls and cause destructed catalyst and reactor walls corrosion and consequently shorter life period for both. To reduce this problem, the Chinese Academy of Sciences tries to develop a specially designed catalyst for fluidized-bed reactor conditions [99,100]. In these works, syngas methanation over Ni-W/TiO2-SiO2 and Ni–Mg/Al2O3 catalysts were investigated in a fluidized-bed reactor (FBR).

5.3. Three-phase reactors

In three-phase methanation, the liquid phase due to high heat capacity (c_p) has the capability to create isothermal process conditions even at high load variations (against what is a disaster in FB reactors). Particular drawbacks about this kind of reactor concept are high gas-liquid mass transfer resistance and the decomposition and evaporation of the heat transfer fluids. Hence, Götz et al. [11] study on the hydrodynamics and heat transfer fluid stability within three-phase reactor concepts [101].

Additionally, the Key Laboratory of Coal Science and Technology of Taiyuan (China) focus on the improvement of catalyst specifications for three-phase methanation processes [102].

5.4. Structured reactors

There are some new approaches such as monolith reactors to solve *high-temperature spots and high-pressure drops* in adiabatic fixed-bed reactors using structured reactor concepts. These novel reactor concepts develop in an away to have better heat transfer and less pressure drop. In fact, their structure improves radial heat transport *by two to three orders of magnitude due to heat conduction through the metallic structure (depending on the metallic material)*, [103,104,105]. Examples of these reactors are:

- Honeycomb reactors with catalyst coating [106].
- Thermo-oil cooling [106].

One special research topic of structured honeycomb reactors is the improvement of reactor partial load behavior. Significant research in this field is performed by Montan University Leoben [74,75]. The sorption-enhanced reactor concept is another structured reactor [107]. The innovation matter about these reactors is water (liquid) adsorption ability of the catalyst support.

Chapter 6

Summary and conclusions

6. Summary and conclusions

Methanation looks back on a history of more than 100 years and is presently attracting new attention because of climate change, finiteness of fossil fuels, and a changing energy system with a high share of renewables. Two different catalytic methanation processes are fundamentally discussed: CO methanation for the production of natural gas substitutes in combination with coal or biomass gasification and CO_2 methanation for the chemical storage of electric energy (Power to Gas).

CO methanation projects in Europe primarily focus on the use of gases from biomass gasification. Additionally, a significant increase in methanation activities in Asia (mainly China) can be reported. These activities basically concentrate on large-scale (>500 MW fuel input) coal-to-SNG plants to complement China's limited natural gas resources [10].

CO_2 methanation projects generally focus on Europe and especially Germany, the objective being to contribute to a flexible energy system. For this reason, they are combined with electrolysis units for the production of hydrogen [51]. A remarkable increase in technology deployment in terms of ongoing projects PtG processes started after 2010.

Power to Gas was like a child, however, it was born in Japan, but it has well been developed in Europe and today it is a strong man, hence, *the current leadership holds in Europe, mainly thanks to the support of the governments of Germany, Denmark, and Switzerland*. The USA has also contributed to the deployment of the technology with up to four projects since 2009. Data show that the average budgets for demo-plants projects are around one million Euro per year in most cases [50].

6.1. Methanation concepts and research

A multitude of methanation concepts was produced in the pilot and commercial scale in the past. But only a few of them are currently available on the market (section 2.2.2.5). All of those commercially available concepts are fixed-bed reactor concepts that are predominantly equipped with gas recycling and intermediate cooling (TREMP, HICOM, Lurgi methanation). However, to reduce investment and operational efforts, there is the trend to avoid recycle gas compressors in future applications (e.g. Vesta, TREMP modified) [50]. Table 6.1 introduces obviously different methanation concepts and their specifications.

Concept	Adiabatic FB reactors	Cooled FB reactors	Micro-reactors	Fluidized-bed reactors	Three-phase reactors
Operation mode	Adiabatic	Polytropic	Polytropic	Isothermal	Isothermal
Reactor stages	2–7	1–2	1–2	1–2	1–2
Gas recycling	Usually	Sometimes	No	Sometimes	No
Temperature range	250–700	250–500	250–500	300–400	300–350
Arrangement/State of cat.	Packing	Packing	Coated	Fluidized	Fluidized or suspended
Particle size	Millimeters	Millimeters	<200 lm	100–500 lm	<100 lm
Mechanical stress of cat.	Low	Low	Low	High	Moderate
Thermal stress of cat.	High	Moderate	Moderate	Low	Low
Complexity of process setup	High	Low	Low	Low	Low
Reactor costs	Medium	High	Very high	Low	Low–medium
GHSV	Medium–high	High	High	Medium–high	Low–medium
Technology readiness level	9	7	4–5	7	4–5

Table 6.1 Comparison of different methanation concepts [10].

Although methanation processes are commercially operating now, there is still research demand to understand the mechanism of reaction for new catalysts and varying educt gas compositions, to improve methanation catalysts (especially for fluidized reactor concepts) and to develop reactor as well as process models. This is, in particular, true for future methanation concepts with dynamic operating conditions. Process temperature control, improvement of cost efficiency and flexibility, i.e. dynamic operation scenarios, are in the focus of research.

6.2. Catalysts

The price, activity, and selectivity have been considered as a most important criterion to choose catalyst. Hence, nickel catalysts are commonly applied in commercial methanation plants, as Sabatier had early introduced. Current research is focused on the improvement of the thermal and sulfur resistance specifications of methanation catalysts.

6.3. Mechanism

The dissociation of carbon on the catalyst surface (surface carbon) and its hydrogenation has mostly been reported by the researchers as RDS reaction intermediate in the catalytic CO and CO_2 methanation reaction. These reactions in the investigated mechanisms are formulated as below (Figure 2.7) and (Figure 2.8).

For CO-Reaction: CO + 2-Cat. ↔ C-Cat. + O-Cat. (surface reaction)
C-Cat. + H-Cat. ↔ CH-Cat. + - Cat. (hydrogenation)

For CO_2-Reaction: CO_2 + 2-Cat. ↔ CO-Cat. + O-Cat. (surface reaction)
C-Cat. + H-Cat. ↔ CH-Cat. + -Cat. (hydrogenation)

6.4. Modeling

Design, evaluation, optimization, and adaptation are known as the main fields of the modeling and simulation works in the methanation technology. Matlab ® and Aspen Plus ® have mostly been applied by researchers in the investigations about methanation concepts.

The simulation-based investigations about FB-reactor are recently focused on improving the control flexibly of the process using dynamic-models and increasing the efficiency of methanation process (cost, heat, environmental aspect, etc.) using plant-simulations works. Aspen Plus seems to be the best option for this purpose.

For fluidized-bed and three phase reactors, the investigations are mostly attempted to optimize the hydrodynamic behavior of the fluids inside the reactors (fluidization progress).

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