CONVERSION OF CO₂ TO SYNGAS AND SYNTHETIC NATURAL GAS (SNG): TECHNOLOGIES AND MARKETS

A techno-economic investigation commissioned by the members of the Carbon Dioxide Capture & Conversion (CO₂CC) Program

Client Private
December 2013
The Carbon Dioxide Capture & Conversion (CO₂CC) Program

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CONVERSION OF CO₂ TO SYNGAS AND SYNTHETIC NATURAL GAS (SNG): TECHNOLOGIES AND MARKETS

Dr. Danielle Ballivet-Tkatchenko
Dr. Riitta Keiski

A techno-economic investigation
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Carbon Dioxide Capture and Conversion (CO₂CC) Program

managed by:

The Catalyst Group Resources, Inc.
P.O. Box 680
Spring House, PA 19477
-USA-

Phone: +1.215.628.4447
Fax: +1.215.628-2267

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PEER REVIEW SECTION

Description

This section includes two essays written independently of the actual Report. Each essay represents a critical review of the report’s contents. By definition, the review is authored by a technical or commercial expert who is a peer to, but in no other way affiliated with, any of the experts who authored the Report.

Each Peer Review represents the professional judgment of its respective author. In its entirety, this section provides the perspective of an independent team of technical or commercial experts. This independent team has evaluated the work of the report’s authors in an effort to judge the relevance and implications of the technical and economic findings. Where appropriate, each Peer Reviewer may have cited additional references and if necessary, critiqued aspects of the report.

The Peer Reviewers evaluated a draft edition of the final report presented here. In a few instances, comments by the Peer Reviewers may reflect these circumstances.
This document details relevant technologies and recent developments related to the conversion of carbon dioxide to syngas and synthetic natural gas (SNG). This is an especially timely report since CO$_2$ represents an inexpensive and abundant feedstock that can be used to produce many value added produces. In particular, the use of CO$_2$ in thermochemical upconversion schemes is incredibly topical since the storage of renewable and other non-petroleum based energy sources via fuels is an extremely promising strategy. As such, this report’s focus on the conversion of CO$_2$ to syngas and SNG should be of interest to those working in a variety of fields involving energy use, transfer and storage, including industrialists and investors that are pursuing carbon capture and energy conversion.

This report is written by experts in the fields of catalysis and syngas production. The authors have provided detailed scientific descriptions for the various technologies covered in the report. Up to this point, the industrial scale conversion of carbon dioxide to fuels and fuel precursors has not been carried out on a scale comparable to that for other thermochemical upconversion schemes and therefore the experience base for commercialization of such technology is very limited. Nonetheless, there have been several important developments over the last several years that may make the commercial conversion of CO$_2$ to fuels a viable possibility and future commercialization ventures will become more likely as the road for carbon capture, sequestration and utilization becomes better defined.

The use of CO$_2$ in thermochemical upconversion schemes promises to be an important area of development over the next decade. In particular, the reaction of CO$_2$ with natural gas to produce syngas mixtures is a prime strategy that may allow low quality natural gas deposits that contain high levels of carbon dioxide to be converted to a valuable commodity chemical (carbon monoxide) that can be used for the production of liquid petroleum (via Fischer–Tropsch methods) and other carbon based liquid fuels (i.e., methanol, etc.). Indeed, as shown in sub-section 2.2 of this report (Figure 2.2.1), CO$_2$ conversion to syngas via dry reforming of low quality natural gas has been an area of growing interest and commercial development over the last five to ten years. Much effort has been directed toward the development of nickel catalysts on a variety of oxide supports, which are competent platforms for this chemistry. The major issue with these systems is the deposition of carbon deposits during catalysis, a process that leads to catalyst deactivation.

Although nickel based catalysts for CO$_2$ conversion to syngas via dry reforming of methane have been heavily relied upon for this process, these platforms are not nearly as active as ruthenium or rhodium containing reactors. Moreover, the general mechanism by which these bifunctional catalysts function is still poorly understood. Accordingly, there is much room for fundamental
research in this arena in order to better understand the pathway by which these platforms drive
the production of syngas. The development of alloyed nanoparticles that are primarily comprised
of nickel but also contain other metals or other materials would appear to be a worthwhile
strategy for the production of inexpensive catalysts that have activities for syngas production that
more closely approach those displayed by noble metals.

Although the production of syngas from CO$_2$ and a fossil fuel such as methane or bitumen may
make commercial sense, one must be careful not to overstate the environmental benefits that are
associated with this approach. Although this strategy may allow for syngas production with lower
levels of sulfur and heavy metal side products, it does not significantly mitigate CO$_2$ emissions.
The production of fuels with significant environmental benefits can only be accomplished if the
reducing equivalents needed for this chemistry come from renewable/carbon neutral energy
inputs. In this regard, the direct photochemical and electrochemical reduction of CO$_2$ is of prime
importance and commercial interest.

A significant portion of this report focuses on the photochemical and electrochemical conversion
of CO$_2$ to SNG. In general, this transformation is of questionable commercial relevance given the
current pricing for natural gas. Since methane prices are at near historic lows and current supplies
of this gas are burgeoning, it is difficult to understand why one would target “power to gas” as
opposed to targeting CO$_2$ reduction products with higher price points. Similarly, the thermal
hydrogenation of CO$_2$ using hydrogen gas is also specious, since this transformation would serve
to convert a valuable energy carrier (H$_2$) to one of much lower value (CH$_4$). Moreover,
hydrogenation of CO$_2$ to SNG requires 4 equivalents of this more valuable reductant (H$_2$) per
equivalent of SNG produced, which hardly makes economic sense. A more viable option is the
reduction of CO$_2$ with hydrogen to deliver methanol. Although this process requires three
equivalents of H$_2$ for every equivalent of the alcohol, it at least generates a reduced carbon
product of significant value to merit the transformation be pursued when electricity or hydrogen
are inexpensive. Accordingly, hydrogenation of CO$_2$ to methanol has been a more important
target for industrialists over the last decade than the “power to gas” route.

One topic, which was not thoroughly addressed was the electrochemical reduction of CO$_2$ to
value added products other than SNG. The electrochemical/ photoelectrochemical reduction of
CO$_2$ to carbon monoxide (CO) is one such route that generates an energy rich, valuable and
versatile commodity chemical that can be converted to syngas, methanol and other products.
Although the electrochemical reduction of CO$_2$ to CO has historically only been possible using
precious metals such as gold and silver catalysts (Hori 2008), recent work has detailed the
development of more cost effective platforms (DiMeglio 2013). These systems, which are based
upon environmentally benign and inexpensive bismuth materials, can drive the conversion of
CO$_2$ to CO with exceptional selectivity and energy efficiency (Jacoby 2013). As such, these
architectures are promising and potentially very cost effective candidates for the electrochemical
production of CO and syngas from carbon dioxide streams.
References


A native of New York City, **Joel Rosenthal** received his bachelor’s degree from New York University, where he conducted undergraduate research as a Pfizer fellow with Prof. David I. Schuster. He completed a Ph.D. in Inorganic Chemistry from the Massachusetts Institute of Technology as a Fannie and John Hertz doctoral fellow. His thesis work, with Prof. Daniel G. Nocera focused on the mechanistic study of proton-coupled electron transfer reactions as applied to energy conversion processes. Rosenthal studied bioinorganic chemistry and metalloneurochemistry with Prof. Stephen J. Lippard at MIT as an NIH postdoctoral fellow, where he developed detection methods for reactive nitrogen species and neuronal signaling agents.

In 2010, Rosenthal joined the faculty in the Department of Chemistry and Biochemistry at the University of Delaware. His group is active in the fields of energy, catalysis, chemical synthesis, electrochemistry and photochemistry and is focused on developing systems for alternative fuel production and renewable energy conversion. Specifically, Rosenthal’s work aims to identify the molecular design principles necessary to drive the energetically demanding conversion of carbon dioxide to liquid fuels. He is also a faculty member of the Center for Catalytic Science and Technology at UD and is a faculty trainer for the UD Chemical Biology Interface Program.

Rosenthal’s honors include an MIT Sustainable Chemistry Award and the MIT Davison Thesis Prize. In 2007 he received a Young Investigator Award from the American Chemical Society and he was recognized with a Ralph E. Powe Junior Faculty Enhancement Award from Oak Ridge Associated Universities in 2011. Rosenthal also received a DuPont Young Professor Award in 2012 and was named a Camille and Henry Dreyfus Environmental Chemistry Mentor in 2013.
PEER REVIEW
by
Dr. Eckhard Dinjus

Part 1: Introduction
Part 2: CO₂ conversion to syngas
Part 3: CO₂ conversion to synthetic natural gas (SNG)
Part 4: CO₂ utilization in “power to gas”

The contributions in parts 2 and 3 are compact materials on conventional syngas production and conversion of CO₂ to syngas and synthetic natural gas and give an overview on the different methods and technologies via steam methane reforming (SMR), gasification and partial oxidation of methane.

The contribution in part 2 CO₂ conversion to syngas is divided into three major sections. The first section summarizes the traditional state-of-the art syngas production technology by steam methane reforming (SMR), partial oxidation of fossil fuels and carbonaceous materials like biomass and partial oxidation of methane to prepare the reader with basic knowledge on traditional gasification technologies. This subject is adequately and systematically covered in textbooks on technical chemistry and handbooks of chemical engineering (e.g., Ullmann). These references should be consulted to complement the short treatment in this contribution, which does not yet cover the real and special aim of CO₂-conversion to syngas.

The sets of key gasification reactions given are over determined: with 6 species C, CO, CO₂, H₂, H₂O CH₄, only three key reactions are needed; e.g. from the set of 5 chemical equations from 2.1 – 2.5, equation 2.3 and 2.5 are linear combinations of (2.1 minus 2.2) and (2.3 minus 2.4) respectively. Also, the 8 equations in set 2.6 to 2.13 can be reduced to 4 real key reactions, which allow a correct and complete stoichiometric description; e.g. equation 2.8 is (2.7 minus 2.6)

The second section deals with the real subject: CO₂-conversion to syngas via dry reforming of methane (DRM) and lower hydrocarbons. The role and efficiency of different catalysts is described in detail from the synthesis of catalysts over structure parameters to processes. The rather broad research on suitable catalysts, mainly at laboratory scale, and thermodynamic and mechanistic aspects are well reported and referenced. This material is of large interest for basic research. The results from scale-up from lab scale to pilot scale and the first industrial applications are discussed. Actual technical applications (e.g. the “Calcor” technology and others) are described and a final outlook identifies potential catalyst improvement in the future.

Other development routes in 2.3 describe the catalyst bireforming and trireforming processes for CO₂-conversion with mixtures of H₂O, CH₄ and O₂ as well as electrochemical routes, CO₂-
conversion based on solar energy, plasma technology and technologies under development in the chemical industry (e.g., Haldor Topsoe, Korea Gas Corporation, BNL USA, BASF Germany). The main incentive for market introduction is to reduce CO₂ emissions via utilization of CO₂ as C₁-feedstock. Yet the production of organic fuels and chemicals from CO₂ does not reduce CO₂ emissions, since the carbon products are reoxidized to CO₂ after use with a delay of few years or decades. To maintain a huge CO₂-recycle technology on a large world-wide scale requires a huge amount of renewable energy and a huge amount of capital investment and operating costs. Such economic aspects are decisive for market introduction. A significant but limited amount of reduced CO₂ is already available sustainably in the form of biomass in its most abundant type: lignocellulose like wood or straw.

Interestingly, CO₂-reforming with steam and oxygen allows the direct processing of flue gas, so you can expect that these alternatives will increase the CO₂ market to syngas as attested by on-stream technologies and demonstration units. Some studies have shown that the availability of cost effective electricity is crucial for economic competitiveness. In such a scenario synthetic fuels could be produced at a cost comparable to biomass to liquid (BTL) processes, based on Fischer–Tropsch or methanol-to-gasoline (MTG) processes.

The next contribution (part 3) deals with the CO₂-conversion to synthetic natural gas (SNG). Technologies for SNG production from fossil and biomass carbon resources are well known and technically mature. To reduce the huge amounts of anthropogenic CO₂ emission in the flue and exhaust gases of combustion (power stations) and gasification plants by conversion into organic fuels or chemical requires huge amounts of hydrogen and renewable energy for hydrogen production. SNG produced from bioresidues is considered as a second generation biofuel and can also be used as motor fuel or for heat and power generation. The pipeline networks for distribution are already available for natural gas. This also includes large extended SNG storage sites for excess renewable energy from solar wind or hydropower.

Expensive carbon capture and storage (CCS)-technologies that really contribute to CO₂ emission reduction are compared to carbon capture and utilization technologies (CCU) which can be more attractive than CCS in specific areas. At present only pilot scale facilities are in operation but there is potential and economic viability for future technical applications. The already existing processes for CO₂-utilisation are described; the main CO₂-user is ca. 114 Mt/a for urea production in ammonia plants.

The economics of SNG production via reduction of CO₂ is strongly influenced by the cost of hydrogen. For an industrial process the economics in comparison to the cost for natural gas plays an important role, independent of the decrease in CO₂ emissions.

For SNG production from CO₂ and H₂, a number of different catalysts have been investigated and tested and it seems nearly impossible to say which type of catalyst will be the favorite, because the reported process parameters are quite different and longtime tests are not available.
By the way, using H\textsubscript{2} from “power to gas” the carbon effectiveness for synthetic fuels can be increased (factor 2) because the H\textsubscript{2}/ CO ratio can be increased from 1:1 to 2:1 and a WGSR for CO conversion to H\textsubscript{2} is no longer necessary and simultaneously lowers the plant investment costs.

The contribution in part 4 CO\textsubscript{2} utilization in “power to gas” is focused as expected on different kinds of water electrolysis and the applications of hydrogen for energy storage. The “power to gas” contribution gives a good overview on the H\textsubscript{2}-production via water electrolysis and the possible reactions with CO\textsubscript{2}. The hurdles for using this process to decrease of CO\textsubscript{2} emissions via production of valuable compounds are considerably higher from the economic point of view, as the additional continuous production is not mentioned in the most of the processes. More basic research is necessary.

In summary, the report is of high quality, since nearly all aspects of CO\textsubscript{2} -use are discussed on a high scientific level. This is especially true for all aspects concerning the production, application, efficiency and sensitivity of the catalysts involved and includes also discussion of mechanism, which is a basis for further catalyst improvements. Existing hurdles and market problems are described in a serious way. Each chapter finishes with an outlook and is accompanied by critical remarks which are helpful for future research and development and market introduction. The report gives a realistic overview about future R&D and perspectives in this field.

Reference

Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH.

Prof. Dr. Eckhard Dinjus was born in 1944 in Saalfeld/Saale and was trained as Chemical Technical Assistant in 1962/63. After his Chemistry Studies from 1963-1968 at the Friedrich-Schiller-University in Jena, he worked at the Institut for Inorganic Chemistry (1968-1987). At the Institut für Technische Chemie he became leader of the group, ‘Chemietechnikum’ in 1987. Following that, he participated in the Joint Venture at Jenapharm (1988-90), was Guest Professor at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (1990-91), and served as Leader of the research group, ‘CO\textsubscript{2}-Chemie’ of the Max-Planck Gesellschaft at the Jena University (1991). From 1996-2012 he has held a professorship at the Institute of Technical Chemistry at the University Heidelberg and has served as Director of the Institute of Catalysis Research and Technology at the KIT (Karlsruhe Institute for Technology). Since 2012, he has had a consultancy contract with the Institute Catalysis Research and Technology at the KIT – Campus North.
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EXECUTIVE SUMMARY

At present, there is growing social pressure to mitigate the effects of climate change by reducing the emission of greenhouse gases (GHG) such as carbon dioxide (CO₂). However, rather than simply capturing and sequestering such emissions, CO₂ can instead be harvested and used as feedstock to produce a number of marketable fuels and chemicals. This third report of The Catalyst Group Resources’ (TCGR’s) Carbon Dioxide Capture & Conversion (CO₂CC) Program in 2013 provides:

• An analysis of the technology and economic potential of CO₂ conversion to syngas and synthetic natural gas (SNG); and

• A discussion of potential technologies to convert excess electrical energy into usable gas.

The chapters on CO₂ conversion to syngas and SNG analyze the technical and economic aspects of existing and new conversion technologies, with particular attention paid to the catalytic materials being developed to improve production. The third chapter discusses the electrolytic production of H₂ using excess electricity produced at power plants, and its potential storage through conversion with CO₂ to syngas or SNG.

CO₂ CONVERSION TO SYNGAS

Broadly speaking, there are three main routes either in use or in development for producing syngas:

• **Methane reforming** – Using steam or CO₂;
• **Oxidation** – Partial oxidation of carbon-containing materials or methane; and
• **Autothermal reforming** – Processes combining methane reforming and oxidation.

Steam methane reforming (SMR) is the most common industrial process used for syngas production, producing a H₂/CO ratio of one for the resulting syngas stream. SMR is a catalytic thermal process in which nickel is the most commonly used catalyst as it provides the best balance of performance and price. Gasification is a feed-flexible technology mainly used to produce CO, H₂, CO₂, and CH₄ from feedstocks such as coal, petroleum, and biomass. The disadvantage of gasification compared to SMR is that its outlet H₂/CO ratio is usually lower than one. The third benchmark technology, partial oxidation of methane (POM), results in almost complete methane conversion and provides syngas with a H₂/CO molar ratio of about two that is useful as feedstock to produce synthetic natural gas, methanol, and long-chain Fischer−Tropsch...
products. Autothermal (ATR) POM reactors incorporate steam reforming, again with Ni as the most commonly used catalyst. ATR has become the most commonly used syngas production process for large-scale syngas plants because of economies of scale provided by the process.

The only commercial process technology using CO$_2$ as the feedstock for syngas production, and which has seen the most interest over the last two decades, is dry methane reforming. Like SMR, dry (or CO$_2$) reforming produces a H$_2$/CO ratio of one, which is suitable for downstream production of oxo-products and short-chain Fischer–Tropsch products. Also like SMR, low pressures and high temperatures (i.e., above 800°C) improve conversion of CO$_2$ and CH$_4$ and decrease carbonaceous deposits. The last feature is particularly crucial as carbon deposits are a major cause of CO$_2$ reforming catalyst deactivation.

Researchers have studied the effectiveness of both noble and non-noble metal catalysts for dry reforming, with nickel-based catalyst studies accounting for half of all reports on the subject. Work is ongoing to improve catalyst design through optimizing the interrelated characteristics of catalytic properties, physical characteristics, and physicochemical properties. For instance, the high temperatures required for maximum efficiency of the process also requires catalysts with a high thermal stability. Alternatively, adding Boron to a 10 wt% Ni/$\gamma$-Al$_2$O$_3$ catalyst can decrease carbon deposits by 90%, while adding noble metals such as ruthenium to Ni-based catalysts can also inhibit deposits. Using supports such as ordered mesopores materials can improve performance of nickel-based catalysts by confining small particles, as smaller nickel particles are more resistant to carbon formation, while Ni supported on MgAl$_2$O$_4$ spinel possesses a high resistance to sintering and high mechanical strength..

The most successful dry reforming technology to date is Caloric Anlagenbau GmbH’s Calcor process, which uses a proprietary catalyst to generate high purity CO at low pressure in small- to medium-scale plants. The syngas created during the process has a H$_2$/CO molar ratio of 0.42. The gas is then separated in most plants to provide high purity CO as an end product. A total of 4,137 Nm$^3$h$^{-1}$ of the Calcor process technology has been installed worldwide since the late 70's.

Apart from dry reforming, there are a number of other routes to syngas production via CO$_2$ in development. One of the most promising is the co-electrolysis of CO$_2$ and steam using high temperature solid oxide electrolysis cells (SOEC), which simultaneously dissociates H$_2$O and CO$_2$ to H$_2$ and CO on the cathode and O$_2$ on the anode. A typical SOEC consists of a porous Ni/yttria stabilized zirconia cermet (YSZ) cathode, a dense YSZ electrolyte, and a porous $(La_1-xSr_x)MnO_3$/YSZ composite anode. This type of electrolyzer reaches a CO$_2$ and H$_2$O conversion of 93% and a H$_2$/CO molar ratio of 2.1 using a current of -25 A.

Bireforming combines CO$_2$ and steam reforming in two parallel processes, using similar catalysts to those in steam and dry reforming. However, the combined process minimizes catalyst deactivation because it is thermodynamically possible to suppress carbon deposits with ratios of CH$_4$/CO$_2$ > 1.5 at temperatures at and above 800°C. Bireforming also provides a tunable H$_2$/CO
ratio without additional process units. The process can also be modified by deliberately introducing oxygen into the dry reforming process, referred to as oxidative dry reforming. Syngas production in this technique is a two-part process consisting of a one-step partial oxidation pathway and a two-step combustion and bireforming pathway. Oxidative dry reforming also has the potential for processing biogas into syngas.

The trireforming process combines both steam and dry reforming with the partial oxidation of methane in a three-step process in a single reactor. The main advantages of this process are a lack of coke formation, good energy efficiency, a tunable H₂/CO molar ratio, and its ability to process a variety of feedstocks including flue gases and biogas. Korea Gas Corporation (KOGAS) is furthest along commercializing this technology, with development of its trireforming process for syngas use in dimethyl ether (DME) production. Two other processes still very much in the developmental stage are a two-step thermochemical redox cycle to convert CO₂ and H₂O into CO and H₂ using concentrated solar power, and CO₂ dissociation by plasma through either thermal decomposition or energy transfer through the vibrational modes of the reactants.

CO₂ CONVERSION TO SYNTHETIC NATURAL GAS (SNG)

While commercial production of SNG does exist, high production costs have limited its adoption. The typical thermochemical method used to create SNG from a carbon source (typically coal) is a four-step process: first feedstock is gasified to syngas or producer gas, followed by cleaning and conditioning of the gas, then fuel synthesis by CO methanation, and finally removal of H₂O and CO₂ from the SNG stream. The only commercial-scale plant producing SNG is the 1.5 billion m³ Great Plains Synfuels Plant, which uses a fixed bed gasifier with coal feedstock. A few pilot scale plants have been built using fluidized bed technology for gasification to produce SNG from biomass, but no commercial-scale facilities are under construction.

There are three different routes being actively investigated for production of SNG through the hydrogenation of CO₂ to methane: catalytic conversion, photocatalytic conversion, and electrochemical conversion. In addition to these routes, there is also research into membrane assisted CO₂ conversion reactors, using materials such as microporous zeolite for selective H₂O removal or H₂ addition into the reactor. At the time of writing, the only SNG plant in production using CO₂ as feedstock employs catalytic conversion to produce SNG, while the other two technologies are still confined to laboratory-scale operations.

The methanation of CO₂ is a highly exothermic reaction that is thermodynamically favorable at low temperatures (i.e., 400°C). For catalytic conversion of CO₂ to SNG, most methanation studies have focused on metal-based catalytic systems, with a preference towards heterogeneous catalysts because of their improved stability, separation, handling, and reusability over homogeneous catalysts. The catalysts used for the methanation of CO₂ are similar to those used for CO₂ reforming to produce syngas. Nickel-based catalysts supported on metal oxides the most widely studied. All commercial methanation catalysts at the time of writing are nickel-based
because they provide the best methanation activity per unit cost while still exhibiting a high selectivity towards methane. However, Ni-based catalysts are prone to deactivation due to the formation of mobile nickel carbonyls and solid carbon deposits. Just as with dry reforming catalysts, CO₂ methanation catalysts work best with supports possessing high surface areas, with zeolites considered a very suitable support because of this feature as well their thermal stability and affinity to carbon oxides.

The photocatalytic reduction of CO₂ to produce synthetic methane is a multistep process consisting of parallel and series reactions; CO₂ adsorbed on the photocatalyst’s surface interacts with photogenerated electrons and hydrogen to yield an entire series of C₁ and C₂ products. Photocatalytic reactions are an endothermic process that can run under low temperature and pressure conditions, where sunlight provides the required energy. The most important characteristic of a suitable photocatalyst is its ability to generate electron-hole pairs by adsorbed irradiation energy and possessing an appropriate band gap. However, CO₂ is a very stable molecule that does not absorb visible or ultraviolet radiation, so development of an efficient photocatalyst is crucial. This is also the reason why photoreduction of CO₂ has only been successful at laboratory scale, particularly as the reaction mechanisms are not yet fully understood.

The third route for SNG production is electrochemical reduction of CO₂ (ERC). The ERC process exhibits high selectivity, recyclability of electrolytes and water, is low cost, and can potentially use renewable energy to supply the required voltage. In this process, CO₂ is reduced at the cathode to form CO₂⁻, while an O₂-/H⁺ evolution takes place at the anode with H₂O to form intermediates and end products such as SNG. Note that temperature dictates the amount of methane formation in the reaction, which decreases as temperature increases. The reaction also requires a high electrode potential; in fact, it is much easier to produce formic acid and CO through electrochemical reduction of CO₂ than it is to produce methane and ethylene.

The three factors dictating the conversion efficiency of an ERC system are high current density, high faradaic efficiency, and high energy efficiency. These characteristics are based on electrode composition, electrolyte solution, the operating conditions of the process, and external factors such as CO₂ purity and solubility. A significant part of the literature investigates copper as the electrode of choice, but other materials such as carbon nanotubes and Ni-YSZ are also being studied. The biggest challenge in ERC processes is in reducing higher overpotentials that significantly effect efficiency and current density. This challenge, among others, must be addressed before ERC can become a commercially viable synthetic methane production process.

**CO₂ UTILIZATION IN “POWER TO GAS”**

Wind and solar power installations produce electricity at irregular intervals, and as the number of renewable energy installations increases, so will the separation between the amount of electricity produced at any given moment and the amount actually required on the electrical grid. The most
common energy storage systems used to harness this potentially wasted energy include pumped hydro, compressed air, flywheels and batteries.

Another way to store this excess electrical energy is to produce hydrogen through electrolysis from water, then store the hydrogen for later use. The hydrogen can be stored as a gas by injecting it into existing natural gas or hydrogen pipelines, as a solid such as magnesium hydride, or it can be reacted with CO₂ through a catalytic Sabatier process to produce methane that is then stored in the existing natural gas pipeline infrastructure.

The key to commercializing an effective power to gas strategy is to improve hydrogen production by increasing the efficiency of the electrolysis system. Alkaline electrolyzers are available commercially and can last for years, but use a caustic liquid electrolyte requires an additional gas-liquid separation unit for H₂ production, and does not adapt well to fluctuating power sources. Proton exchange membrane (PEM) electrolyzers have high efficiency, but are expensive as they are still primarily at the demonstration stage, and must operate at low temperatures to avoid drying out the membrane. In contrast, SOEC cells can operate at temperatures of 800–1,000°C, have a total energy efficiency of 50–90%, and are already under development to produce SNG from CO₂.

Table ES.1 lists a number of demonstration projects making use of power to gas systems in Europe. These projects then use the hydrogen for everything from providing electricity to homes to powering vehicles with SNG produced from the hydrogen and CO₂ from biogas. However, for such power to gas technologies to move to commercial scale use, electrolyzer costs and water purification and electricity costs must become low enough to make the technology economical.

Table ES.1
Selection of Power to Gas Demonstration Projects in Europe (Grond et al., 2013)

<table>
<thead>
<tr>
<th>Project</th>
<th>Power installed</th>
<th>Electrolysis Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Werlte D) - Audi AG</td>
<td>6000</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Aragon (S) - IOTHER</td>
<td>4000 &amp; 70</td>
<td>Alkaline &amp; PEM</td>
</tr>
<tr>
<td>Falkenhagen (D) - E.ON AG</td>
<td>2000</td>
<td>PEM</td>
</tr>
<tr>
<td>Puglia region (I) - INGRID project</td>
<td>1200</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Grapzow (D) - RH2 WIND project gruppe</td>
<td>1000</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Grabenn (D)</td>
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<td>Alkaline</td>
</tr>
<tr>
<td>Hambourg (D) - Vattenfall</td>
<td>900</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Prenzlau (D) - Enetrag AG</td>
<td>500</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Frankfurt (D) - Thuga &amp; ITM Power</td>
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<td>PEM</td>
</tr>
<tr>
<td>Foulum (DK) Electrochaea</td>
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<td>PEM</td>
</tr>
<tr>
<td>Stuttgart (D) – Solar Fuel &amp; Fraunhofer IWES</td>
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<td>PEM</td>
</tr>
<tr>
<td>Karlsruhe (D) - DVGW &amp; KIT</td>
<td>200</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Xermade (S) - Sotavento Project</td>
<td>200</td>
<td>Alkaline</td>
</tr>
</tbody>
</table>
Table ES.1 (cont’d)
Selection of Power to Gas Demonstration Projects in Europe (Grond et al., 2013)

<table>
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<tr>
<th>Project</th>
<th>Power installed</th>
<th>Electrolysis Technique</th>
</tr>
</thead>
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<tr>
<td>Herten (D) - Stadt Herten &amp; Evonic Industries</td>
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<td>PEM</td>
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<tr>
<td>Leverkusen (D) - CO2RECT Project: Siemens &amp; RWE</td>
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<td>undisclosed</td>
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<td>Schwandorf (D) - Eucolino: Schmack &amp; Viessmann</td>
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<td>undisclosed</td>
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<tr>
<td>Ibbenburen (D) - RWE, CERAM Hyd</td>
<td>100</td>
<td>undisclosed</td>
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<td>Utsira (N)</td>
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<td>Alkaline</td>
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<td>Freiburg (D) - H2Move: Fraunhofer ISE</td>
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<td>undisclosed</td>
</tr>
<tr>
<td>Tahivilla (S) - Hidrolica Project</td>
<td>40</td>
<td>PEM</td>
</tr>
<tr>
<td>Stuttgart (D) - Solar Fuel &amp; Fraunhofer ZWS</td>
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<td>PEM</td>
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<tr>
<td>SamsØ (DK) - SamsØ Energy Academy</td>
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<td>Groningen (NL) - DNV KEMA</td>
<td>7</td>
<td>PEM</td>
</tr>
<tr>
<td>France - GDF Suez GRHYD project</td>
<td>new project</td>
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</table>

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CONCLUSIONS

There is still considerable work needed to improve the efficacy of catalytic materials to realize the economic potential of syngas and SNG production from CO₂. Dry reforming for syngas production and catalytic conversion of CO₂ to produce SNG are close to being competitive to produce these gases, but processes such as the electrolysis of water to produce hydrogen, and the co-electrolysis of CO₂ and water to produce syngas, require significant advances in technology to become economically feasible.
1. INTRODUCTION

This is the third report delivered as part of the 2013 membership, and the twelfth report overall, in The Catalyst Group Resources’ (TCGR’s) Carbon Dioxide Capture & Conversion (CO2CC) Program. The scope and content of the report reflect both the evolving interests of the members as well as the changing factors being considered in the utilization/conversion of CO2 as a chemical feedstock. The report goes beyond the earlier studies of 2010-2012, which presented predominantly techno-economic information and benchmarks on CO2 capture/conversion, and instead addresses the important scientific and commercial developments in the conversion of CO2 to syngas and synthetic natural gas (SNG).

The CO2CC Program is a membership-directed consortium whose members are involved in the development, monitoring and utilization of the “state-of-the-art” in technological progress and commercial implementation of carbon dioxide capture and utilization/conversion. By the direction of the member companies (through balloting and other interactive means), the program delivers a range of timely and insightful information and analyses which are accessible exclusively to members and protected by confidentiality agreements. The objective is to document technically and commercially viable options for CO2 capture/clean-up as well as its utilization/conversion in products which meaningfully address the challenges posed by CO2 lifecycle and overall sustainability issues.

1.1 SCOPE AND OBJECTIVES

The objectives of this report are to comprehensively cover the technology and economic potential of CO2 conversion to syngas (synthesis gas) and synthetic natural gas (SNG), and to analyze the technology available to use excess electrical power from renewable energy sources to produce H2, syngas and SNG. For each process, this report describes and analyzes potential conversion routes for their technical and economic status, and factors affecting efficiency and performance. Catalysts play a key role in high energy CO2 conversion processes, and this report provides a detailed discussion of the latest results from literature on the performance of new catalytic materials.

The first main chapter on CO2 conversion to syngas analyzes a number of different process technologies based on methane reforming, oxidation, and combinations of the two, and also takes a close look at the co-electrolysis of CO2 and steam for syngas production. The second main chapter on (SNG) investigates the catalytic, photocatalytic, and electrochemical conversion routes for conversion of CO2. The report finishes with a chapter analyzing the potential for “power to gas” technologies that make use of excess electricity production to generate H2, and discusses the potential ways to store this gas, including conversion syngas and SNG.
1.2 OVERVIEW OF CO₂ CONVERSION OPTIONS

The largest commercial use for CO₂ at present is in the production of urea (i.e. fertilizer), which accounts for over half of the estimated 200 million tonnes of CO₂ usage per year. About 50 million tonnes is used each year for enhanced oil recovery (EOR), the production of inorganic carbonates uses another 50 million tonnes each year, and much of the rest of goes towards production of technological fluids. The remaining CO₂ utilization is split between production of tert butyl methyl ether (TBME), methanol, and other chemicals.

Virtually all CO₂ conversion processes currently in use are low energy, with only a few catalytic high energy CO₂ conversion facilities in operation. More importantly, use of these low energy CO₂ conversion processes will not substantially increase CO₂ consumption in the coming years due to limited demand for the end products. Thus, new strategies are required to promote CO₂ use for chemical and fuel production. There are two potential use cases with the greatest potential impact for using CO₂ as a feedstock. The first is developing SNG as an alternative fuel in the transport sector. The second possibility is to make use of excess electricity produced at wind and solar power installations to produce hydrogen through electrolysis, then using the CO₂ and H₂ streams to produce syngas or SNG. However, considerable work is still needed to make these conversion technologies commercially competitive.

1.3 MARKET & TECHNOLOGY DRIVERS FOR CO₂-BASED SYNGAS AND SNG

The major drivers affecting market adoption of CO₂-based syngas and SNG can be broken out into three types: environmental, societal, and economical. At present, the environmental factors have the largest impact on encouraging development of CO₂ conversion to syngas and SNG because the state of existing conversion technology is considerably more expensive than commercial production costs for these gases from fossil fuels. The major environmental factor is decreasing anthropogenic CO₂ emissions to reduce the effects of climate change. Of course, this awareness of the link between anthropogenic CO₂ and climate change is also behind societal factors such as the European Union’s 20-20-20 goal to reduce greenhouse gas emissions by 20% from 1990 levels (Decision 406/2009/EC). Increasing production of SNG from CO₂ can also improve the energy security of countries such as China and India by reducing their dependency on imported oil.

Economic factors include the potential revenue derived from using waste CO₂ at power plants, major manufacturing facilities, and at remote gas sites to produce new revenue streams. The growing use of renewable energy from sources such as wind and solar is also an important factor. In countries such as Germany, renewable energy sources now account for a considerable fraction of national electricity production and can result in a significant amount of surplus production. Finding a cost effective way to store this excess electrical energy is essential to increasing the competitiveness of such renewable resources.
1.4 CHALLENGES TO USING CO₂ AS A FEEDSTOCK

The single biggest factor limiting use of CO₂ as a feedstock is the process costs associated with converting CO₂ into syngas or SNG. More research and development is required to improve the efficacy, stability, impurity tolerance, and reusability of the catalysts used in processes such as dry reforming for syngas production and catalytic conversion of CO₂ to SNG to make these technologies economically competitive. For this to happen, however, there must be sufficient political impetus regarding issues surrounding CO₂ “costs” to justify further research and development on effective catalytic materials, as well as a willingness to ensure the sustainable development of such technologies. This is a complex issue requiring funding and support from both the corporate sector and from all levels of government.

A second challenge is to minimize the emissions and energy requirements of CO₂ conversion technologies. In order to successfully promote CO₂ as a more environmentally friendly and viable feedstock for gas and chemical production, energy inputs and emitted pollutants must be reduced as much as possible. However, this is difficult to do and still keep process costs low. While CO₂ conversion technologies have the potential to limit CO₂ emissions, the sustainably of these processes must be verified to maintain the political and social support needed to develop CO₂ as a viable feedstock for syngas and SNG production.

1.5 REPORT CONTRIBUTORS

In order to complete this report, TCGR sought external contributors with expertise in the field who delivered independent, value-added assessments as well as real-world, commercially relevant insights.

The report’s Chapters 2 and 4 were authored by Prof. Danielle Ballivet-Tkatchenko of the University of Bourgogne (France). Chapter 3 of the report was authored by a team headed by Prof. Riitta Keiski of the University of Oulu (Finland), who was assisted by colleagues Mika Huuhtanen, Satu Pitkäaho, Prem Kumar Seelam, Esa Turpeinen and Rauli Koskinen. Chapter 1 of the report, as well as its Executive Summary, were authored by Norman Deschamps of Rogue Thought Consulting (Canada). Mr. John J. Murphy of The Catalyst Group Resources, Director of the Carbon Dioxide Capture & Conversion (CO₂CC) Program, served as the report’s editor.

Biographical and professional information, as well as contact details, for each of the external contributors are presented below.

Danielle Ballivet-Tkatchenko

Danielle Ballivet-Tkatchenko gained her Doctorat ès Sciences Physiques from the University of Lyon (France) in 1970 and spent one-year as a post-doctoral CNRS fellow at the Corporate Research Center of Elf Aquitaine (now Total) in Lacq, France. She came back to the CNRS Research Institute on Catalysis (IRC, Lyon-France) as project leader. In 1985, she was
appointed CNRS Directeur de recherche, project manager, at the CNRS Laboratory on Coordination Chemistry (LCC, Toulouse-France). She moved back to IRC Lyon in 1995, and in 2000 to the Institut of Molecular Chemistry, a joint research CNRS-University unit at the University of Bourgogne (Dijon-France). Meanwhile, visiting professor positions at the University of Bari (Italy, 1989), FZK Karlsruhe (Germany, 2003) and the University of Oulu (Finland, 2005) permitted her to manage common research projects. Danielle is presently CNRS Directeur de recherche émérite at the Institut of Molecular Chemistry (Dijon-France).

The tour of France as a CNRS fellow has allowed her to gain a multicultural approach to fundamental and applied catalysis from oil refining with heterogeneous catalysts to specialty chemicals with soluble catalysts. Most of the research projects were conducted in cooperation with industry which have led to seminal contributions to acid-catalyzed reactions with zeolites and to carbon-carbon bond formation with cationic organometallic catalysts. The CO₂-related projects started in the early 1980's in collaboration with industry aiming at developing electrochemical and catalytic technologies. As a member of the International Scientific Board of the International Conferences on Carbon Dioxide Utilization (ICCDUs), Danielle chaired the 11th edition (ICCDU XI) held in Dijon-France (June 27-30, 2011) which gathered more than 360 participants from academia and industry. She is a member of the international board of the new "Journal of Carbon Dioxide Utilization" recently launched by Elsevier. Danielle is also a member of the French and American Chemical Societies and acted as an expert in panels of the EU research programs. She can be reached at ballivet@u-bourgogne.fr or +33.3.80.39.3770.

Riitta Keiski

D.Sc.(Tech.) Riitta L. Keiski is the Professor in Mass and Heat Transfer at the University of Oulu (UOulu, since 2001). She is a Docent in Chemical Process Engineering, especially in Heterogeneous Catalysis and Environmental Engineering. She has gained her doctoral degree in 1991 and has earlier hold Acting professor posts in Bioprocess engineering in 1998-2000 and Chemical process engineering in 1994, and an Assistant professor post in 1989-1994. In education and research, Prof. Keiski’s fields are process and environmental catalysis, air and water pollution control, reactor and separation unit design and modelling, mass and heat transfer, sustainability and research ethics. Carbon dioxide utilization (CCU), environmental catalysis and membrane studies have been the key research for more than a decade. Prof. Keiski is leading a research group of more than 25 doctoral students and 11 senior researchers. So far she has supervised more than ten PhD theses, and 110 M.Sc. and Lic.Tech. theses, and has published more than 180 articles in peer-reviewed journals and eight book chapters. Between 2007-2012 the research group lead by Prof. Keiski has had totally 37 research projects funded by the Academy of Finland, Tekes, EU FP7 and EU Regional Development Fund, and Foundations. She is leading the ProChemE Research Community (Sustainable Solutions for Production Processes and Environmental Applications) and the ADMA Doctoral Programme (Advanced Materials DP) at the University of Oulu.
In addition, she is actively taking part in the steering committees of research programs, and planning of research programs and research strategies in national and University of Oulu contexts. She is also evaluating research, research proposals, projects and programs, and research groups and researchers in national and international forums. She has been the Vice-Rector of the UOulu (2006-2009) and a Member (1998-2000) and the Chair (2001-2006) of the Research Council for Natural Sciences and Engineering at the Academy of Finland (AF) and a Member of the Board of the AF (2001-2006). She has been nominated as the Professor of the Year 2011 in Finland. She can be reached at rkeiski@sun3.oulu.fi and +358.40.7263018.

Mika Huuhtanen

D.Sc.(Tech.) Mika Huuhtanen is a Docent in Chemical process engineering, especially in Applied heterogeneous catalysis. He defended his doctoral thesis in 2006, continued as a postdoctoral researcher, and has been a coordinator and a responsible leader in projects funded by Academy of Finland and Tekes. In addition, he is currently a steering group member in two national CSTI programmes. Since 2011 he holds the university lecturer position. He is an author of around 50 international journal articles and five book chapters. His expertise areas are heterogeneous catalysis, pollution prevention and mitigation, energy production, and surface characterisation techniques.

Satu Pitkäaho

D.Sc.(Tech.) Satu Pitkäaho defended her doctoral thesis work in June 2013 dealing with catalytic oxidation of VOC emissions, especially emissions containing chlorinated VOCs. Since 2006 she has been involved in several research projects dealing with industrial air emission measurements and abatement. Since 2008 she has been coordinating SkyPro Oulu Clean Air Cluster which is an active collaboration network between academia and industry conducting research assignments arising from industry.

Prem Kumar Seelam

M.Sc.(Eng.) Prem Kumar Seelam is finishing his Ph.D (process engineering) in December 2013. His research topic was hydrogen production from alcohols via steam reforming using conventional and membrane reformers. His research interest is to study the catalysis and membrane phenomena integration. He has been involved in reforming and CO₂ utilization research projects and actively participating in international collaboration.

Esa Turpeinen

M. Sc.(Eng.) Esa Turpeinen is doing his doctoral thesis dealing with reforming of CO₂ containing flue and process gases. His field of expertise covers thermodynamics, the technologies for CO₂ utilization, synthesis gas/hydrogen production (reforming, gasification and pyrolysis) and gas upgrading to valuable products. He has been involved in several CO₂ utilization and reforming related projects since 2005.
Rauli Koskinen

M. Sc.(Eng.), M. Sc.(Chem.) Rauli Koskinen is working on doctoral thesis focusing on utilizing of carbon dioxide in chemical reactions. His expertise areas are CO₂ utilization and heterogeneous catalysts and reactions. He has been involved also with plastic, resin and rubber composites and economic evaluation of industrial production. He has been working in several positions first in rubber product industry and then in biofuel and oil refining industry. Since 2011 he has worked as a university teacher.

Norman Deschamps

Norman Deschamps is the owner of Rogue Thought Consulting (RTC), a market research firm providing insightful analysis on a variety of global markets since 2007. Based in Moncton, New Brunswick, Canada, RTC’s mission is to provide top quality research, analysis, and writing to every single client. As a dedicated analyst, Norman provides market intelligence and forecasting to companies within the renewable energy and biorenewable sectors, and has written over a dozen market research reports on topics such as biofuels, bio-based chemicals, energy storage technologies, wind, and solar. He holds a Bachelor of Science in Physics from Dalhousie University and a Master of Applied Science from the University of Toronto. He can be reached at deschamps@rtconsulting.ca and +1.780.669.4445.

1.6 REFERENCES

2. CO₂ CONVERSION TO SYNGAS

The term syngas (or synthesis gas) is herein used for gas mixtures consisting of CO and H₂ in various ratios suitable for the production of synthetic fuels and chemicals such as methanol, hydrocarbons, and higher aldehydes/alkohols. Basically, H₂/CO ratio of 2 is needed for the synthesis of synthetic natural gas, methanol, long-chain Fischer–Tropsch products, whereas a ratio of 1 is preferred for oxo-products and short-chain Fischer–Tropsch products. Syngas is also the main intermediate currently for hydrogen production in refinery hydrotreating/hydrocracking to fuels, ammonia synthesis, hydrogenation of various organic substrates, and fuel cell applications. Pure carbon monoxide is obtained as well from syngas for the production of organic acids, organic carbonates, and phosgene as examples.

The manufacture of syngas originally arose from coal gasification, then from reforming of crude oil fractions and natural gas (predominantly methane). Nowadays, other feedstocks including peat, wood, and agricultural or municipal solid waste are being examined. The major on-stream technologies to syngas are allothermal and autothermal reforming, gasification, and partial oxidation. The water gas shift reaction is also practiced to complement the aforementioned reactions in tuning H₂/CO ratios for specific applications. A brief overview of these technologies is reported in the following section as an introduction to discussing challenges and opportunities of innovative technologies in the context of CO₂ to syngas. It is, therefore, not intended to give an exhaustive coverage of the vast literature. The given references are recent reports in which additional information can be found.

2.1 STATE OF "BENCHMARK" TECHNOLOGIES FOR SYNGAS PRODUCTION

2.1.1 Steam Methane Reforming (SMR)

Steam reforming involves the reaction of hydrocarbons with steam in the presence of a catalyst. In modern industrial practice, when higher hydrocarbons are used as feedstock, a pre-reformer is installed upstream in order to get methane to feed the steam reformer. This setup allows flexibility in the carbon resource which is nowadays extended to biomass. SMR has a long and proven history. Its related technology is well developed and has been improved over the years thanks to fruitful integration of industry and academia inputs.
2.1.1 Key reactions

When methane is reacted with steam, several reactions in equilibrium are taking place according to equations (2.1-2.5). Therefore, product gas composition at the outlet of the reformer is controlled by thermodynamics. In other words, maximum methane conversion achievable in the catalytic process is dictated by thermodynamics.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3 \text{H}_2 & \Delta_r H^0 = +206 \text{ kJ mol}^{-1} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 & \Delta_r H^0 = -42 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{CO}_2 & \rightleftharpoons 2 \text{CO} + 2 \text{H}_2 & \Delta_r H^0 = +247 \text{ kJ mol}^{-1} \\
\text{CH}_4 & \rightleftharpoons \text{C} + 2 \text{H}_2 & \Delta_r H^0 = +75 \text{ kJ mol}^{-1} \\
2 \text{CO} & \rightleftharpoons \text{C} + \text{CO}_2 & \Delta_r H^0 = -173 \text{ kJ mol}^{-1}
\end{align*}
\]

The given standard enthalpy values, $\Delta_r H^0 \ (T = 298 \text{ K}, P = 0.1 \text{ MPa})$, refer to gaseous CH$_4$, CO, H$_2$ and CO$_2$, vapor H$_2$O, and graphite C states.

Steam reforming itself, reaction (2.1), is endothermic. Hence, methane conversion at equilibrium increases with temperature. The coexistence of H$_2$O and CO leads to the slightly exothermic water gas shift reaction (WGSR) (2.2), and to the more endothermic CO$_2$ reforming reaction (2.3). Methane cracking (2.4) and Boudouard reaction (2.5) are side reactions forming undesirable carbon in the context of SMR. Thermodynamics also indicates that the pressure effect is negative on syngas yield as major reactions (2.1) and (2.3) lead to a net increase in molecules (Le Chatelier's principle). For example, at 1,000°C total consumption of methane (reaction (2.1)) occurs at 0.1 MPa whereas only 70% conversion is achieved at 3 MPa (Aasberg-Petersen et al., 2004; Urréjola et al., 2011).

2.1.1.2 Catalysts

Numerous studies have been carried out on SMR catalysts due to the industrial relevance of the topic. The catalysts must have high activity to quickly approach the thermodynamic equilibrium thus keeping reformer wall temperature as low as possible to ensure long life. Carbon deposition according to equations (2.4) and (2.5) has to be minimized to avoid catalyst deactivation as well as reformer plugging. Transition metals such as Fe, Ru, Co, Rh, Ir, Ni, Pd, and Pt are active in SMR. It is usually agreed that Rh and Ru have the highest activity as shown in Figure 2.1.1.1 (Jones et al., 2008). However, Ni is chosen for industrial SMR reformer, being the good compromise between performance and price.
The recent review of Aasberg-Petersen et al. (2011) provides an in-depth analysis of the methodologies applied over the years to tackle the different facets of the surface chemistry involved: nature of the active site, reaction mechanism, deactivation by sintering and carbon formation. For the time being, there is a general consensus that at high temperature with Ni-based catalysts methane partial order is close to unity and its dissociative chemisorption is the kinetically controlling step (Wei and Iglesia, 2004). Under industrial conditions, the catalytic reaction is fast and the overall kinetics is controlled by heat and mass transfers. The good performance of the catalysts also relies on the prevention of carbon deposit which is best achieved with an over stoichiometry of steam depicted in reaction (2.1). The counter-effect is the acceleration of sintering of the active metal particles leading to a loss of surface area. Therefore, the selection of the catalyst support play an important role. At high SMR temperature, typically in the range 750-1,000°C, the support must be both chemically and physically stable. Oxides like Al₂O₃, MgAl₂O₄, MgO, ZrO₂ and mixtures thereof are convenient candidates with a typical nickel loading of around 15 wt% Ni (Rostrup-Nielsen, 1984). For steam reforming of higher hydrocarbons, the reaction temperature is lower (350-550°C) due to higher reactivity of the feed. Well dispersed nickel particles on support with high specific surface area ensure the highest rate.

2.1.1.3 Process concepts/reactors

The steam reforming process was first developed by Standard Oil of New Jersey (Byrne et al., 1932), and has been optimized over the years. Nowadays, reformers operate under pressure as high as 6 MPa in the temperature range 750-1,000°C, and are integrated into the value chain units (Rostrup-Nielsen and Christiansen, 2011). Operating at high pressure has two main advantages: downsizing the reformer and lowering syngas compression costs as most applications require high pressure. But, total methane conversion is not reached due to thermodynamics limitation. Steam/CH₄ molar ratio commonly >2 helps to minimizing methane
content at reactor outlet with additional benefit of less carbon deposit. Aasberg-Petersen et al., (2011) have reviewed in detail the present status of the catalytic technologies involved in syngas production from natural gas.

The steam methane reformer is part of a train of reactors. As a rule of thumb, deep feed purification, e.g. free from sulfur-containing compounds, is mandatory prior to any reforming to ensure optimum activity and long lifetime of the catalysts. Then, a prereformer may be installed where the feedstock is made of higher hydrocarbons. Downstream the steam methane reformer, a secondary reformer boosts methane conversion. Final syngas purification and composition may be adjusted by the water gas shift reaction and other technologies.

Three main types of steam reactors are currently in use: adiabatic prereformer, tubular steam reformer, and heat exchange reformer. Their respective role depends not only on the feed but also on the specific utilization of syngas that can be defined by three criteria: H2/CO ratio, purity, and production scale.

- The adiabatic prereformer ensures feed flexibility for syngas production. It includes Ni-based catalyst and operates at low steam/carbon ratio with inlet temperatures between 350 and 550°C, the kinetics being controlled by mass diffusion. Hydrocarbons are converted into CH4-rich mixture of CH4, H2, CO2, and CO that feeds the steam methane reformer.

- The tubular steam reformer, also called primary reformer, is heated by external fired furnace. Thus, heat transfer to the catalyst pellets is the limiting kinetics parameter. It is best achieved with narrow reactor tubes set in parallel to getting high productivity. At the outlet of the reformer, the temperature lies in the range 750-1,000°C. The H2/CO molar ratio is >3, too high for most applications, and unconverted methane remains. Some CO2 may, therefore, be added to the reformer inlet to promote reaction (2.3) or a secondary reformer based on adiabatic oxy-steam reforming installed downstream. In the latter configuration, heat is generated in situ by combustion of part of the feed with oxygen.

- The heat exchange reformer is a variant of the fired-furnace reformer. Heat is provided with any hot gas which can be process gas. Therefore, this type of reformer is installed with an other reformer from which heat is transferred to.

2.1.2 Gasification

Gasification is the common term to describe partial oxidation of carbon-containing materials with oxygen (air or oxygen-enriched air) and steam to produce syngas. Gasification has been used since the 19th century, at first for street lighting and heating applications (town gas). Nowadays, the commercialized technologies are producing mainly CO, H2, CO2, and CH4 from a wide range of feedstocks such as coal, pet coke, petroleum, biomass and waste. It is, therefore, a feed-flexible technology.
2.1.2.1 Key reactions

The main oxidation reactions with oxygen and the carbon substrate consist in the formation of CO and CO$_2$ as shown by equations (2.6)-(2.8). These reactions are exothermic providing heat to the process. The reactions producing CO$_2$ are minimized by a controlled introduction of oxygen and by the addition of steam as milder oxidant. The reactions with steam are endothermic, producing CO, CO$_2$, H$_2$ and CH$_4$. Therefore, the oxygen demand for gasification is mainly determined by the heat requirements of these two sets of reactions. Reduction of carbon with hydrogen (2.13) is also observed in oxygen-depleted zone of the gasifiers.

\[
\begin{align*}
C + 0.5 \text{ O}_2 & \rightarrow \text{ CO} & \Delta_r H^0 = -111 \text{ kJ mol}^{-1} \quad (2.6) \\
C + \text{ O}_2 & \rightarrow \text{ CO}_2 & \Delta_r H^0 = -393 \text{ kJ mol}^{-1} \\
\text{CO} + 0.5 \text{ O}_2 & \rightarrow \text{ CO}_2 & \Delta_r H^0 = -283 \text{ kJ mol}^{-1} \\
C + \text{ CO}_2 & \leftrightarrow 2 \text{ CO} & \Delta_r H^0 = +173 \text{ kJ mol}^{-1} \\
C + \text{ H}_2\text{O} & \leftrightarrow \text{ CO} + \text{ H}_2 & \Delta_r H^0 = +131 \text{ kJ mol}^{-1} \\
2 \text{ C} + 2 \text{ H}_2\text{O} & \leftrightarrow \text{ CH}_4 + \text{ CO}_2 & \Delta_r H^0 = +105 \text{ kJ mol}^{-1} \\
\text{C} + 2 \text{ H}_2\text{O} & \leftrightarrow 2 \text{ H}_2 + \text{ CO}_2 & \Delta_r H^0 = +90 \text{ kJ mol}^{-1} \\
\text{C} + 2 \text{ H}_2 & \leftrightarrow \text{ CH}_4 & \Delta_r H^0 = -75 \text{ kJ mol}^{-1} \\
\end{align*}
\]

Reactions with oxygen are nearly complete under reaction conditions which means there are no thermodynamics restrictions. The other reactions are under thermodynamic control. The balance between partial oxidation, steam reforming and the hydrogen content of coal dictates the outlet H$_2$/CO ratio which is usually lower than unity, contrasting with the SMR's one.

2.1.2.2 Process concepts/reactors

Basically, oxygen-blown gasifier needs upstream air separation unit (ASU) mostly achieved by cryogenic separation, better fitting large-scale processes due to high investment costs. Smaller scale gasifier for biomass and waste feedstocks are commonly air-blown. The three types of reactor technologies, developed at first for coal gasification, are the Winkler fluidized bed (1926), the Lurgi moving bed (1931) and the Koppers-Totzek entrained flow (1940) gasifiers. They operate with different coal particle sizes at different temperatures and pressures in the range 980-1,730°C and 2-8 MPa, respectively, and carbon conversion is essentially complete (Cornils, 1987; Higman and van der Burgt, 2008). Different syngas compositions are therefore obtained, depending also on the origin of coal. The higher temperature of entrained flow gasifier leads to nearly complete removal of hydrocarbons. Further purification steps involve sulfur, nitrogen compounds, mercury and particulates. As the resulting H$_2$/CO molar ratios is most often
CO\textsubscript{2} can be used as carrier for feedstock transport to the gasifier, thus also acting as mild oxidant in gasification reaction (Irfan et al., 2011). Several positive effects have been identified. The thermodynamics indicates higher conversion of carbon and enhanced CO yield which allows operation at lower temperatures (Renganathan et al., 2012; Kwon et al., 2013). The reverse Boudouard reaction (2.9) to CO is also kinetically favored (Hanaoka et al., 2013). In addition, CO\textsubscript{2} promotes the formation of micropores in the carbon structure favoring, therefore, the kinetics of gasification (Butterman and Castaldi, 2009).

### 2.1.3 Partial oxidation of methane

Partial oxidation of methane (POM) is carried out homogeneously at high temperature for getting almost complete methane conversion with limited soot formation (Lurgi, 2003; Liu et al., 2010). The preferred on-stream technologies consist of homogeneous partial oxidation of methane (POM) that may be combined with steam reforming to run the reforming process autothermally (ATR).

#### 2.1.3.1 Key reactions

Partial oxidation has two main advantages over steam reforming. Partial oxidation is midly exothermic (2.13) and provides syngas with H\textsubscript{2}/CO molar ratio of about 2 that fits for methanol and long-chain Fischer–Tropsch products.
\[ \text{CH}_4 + 0.5 \text{ O}_2 \rightarrow \text{CO} + 2 \text{ H}_2 \quad \Delta_r H^0 = -36 \text{ kJ mol}^{-1} \quad (2.13) \]
\[ \text{CH}_4 + 1.5 \text{ O}_2 \rightarrow \text{CO} + 2 \text{ H}_2\text{O} \quad \Delta_r H^0 = -520 \text{ kJ mol}^{-1} \quad (2.14) \]

Most often, reaction (2.13) is accompanied by over oxidation reactions that are strongly exothermic. For example, reaction (2.14) corresponds to the oxidation of hydrogen into water leading to a decrease in \( \text{H}_2/\text{CO} \) molar ratio.

ATR technology operates at sub-stoichiometric O\(_2\)/C molar for providing heat necessary for the endothermic steam reforming (2.1) to occur along with WGSR (2.2). Due to the high temperatures in the combustion zone, other reactions are occurring homogeneously mainly based on the chemistry of radicals. Finally, the gas mixture is catalytically steam-reformed by the main set of reactions presented under heading 2.1.1.1. Overall ATR reactors are nearly thermo-neutral. The \( \text{H}_2/\text{CO} \) molar ratio is dictated by thermodynamics: temperature, mass balance and enthalpies of reactions at the outlet pressure. This ratio is commonly around 2 at steam/carbon molar ratio of 0.6, contrasting with the SMR process (Aasberg-Petersen et al., 2001).

### 2.1.3.2 Process concepts/Reactors

POM and ATR processes have in common burner and combustion chamber in a pressurized vessel.

![Figure 2.1.3.1 Basics of (a) multi-purpose gasification and (b) autothermal reforming reactors (adapted from Lurgi, 2003).](image)
To control the process, oxygen is the limiting reactant that is totally consumed. But with POM technology, reactor capacity is limited to about one-tenth that of ATR for safety reasons. Increasing operating pressure from 3 up to 10 MPa may boost the productivity (Lurgi, 2003). Moreover, H₂/CO molar ratio is dictated by the feed composition that implies catalytic downstream technologies to be installed whenever H₂/CO ratio should be adjusted. Nevertheless, not only gas but also liquid/viscous carbonaceous feeds can be gasified. Operating at temperatures above 1,200°C, almost complete feed conversion can be achieved with limited soot formation.

ATR reactor has the same compact design with a catalyst bed installed in the pressurized vessel below the combustion chamber (Figure 2.1.3.1b). Operating at around 3–4 MPa and 1,000°C (outlet gas temperature), the presence of a catalyst implies desulfurized feedstock. As for SMR, supported nickel is the best compromise between cost and activity. Supports such as α-Al₂O₃ and MgAl₂O₄ ensure thermal strength and stability (Aasberg-Petersen et al., 2011). ATR reactor is part of a train of reactors. Upstream prereformer and tubular SMR reactors may be installed. Oxygen is provided by a cryogenic air separation unit (ASU). Downstream, syngas upgrading is performed according to the targeted use. Nowadays, ATR is the key technology for large-scale syngas plants to benefit from economy of scale providing high productivity using a single reactor. Major licensors are Haldor Topsoe and Lurgi-Air Liquide companies.

2.1.4 Others

Other technologies have been suggested or demonstrated to improve the economics of the aforementioned processes. Some are incremental due to the high maturity of the technologies while others target new markets. They are mainly based on physical and chemical exergy optimization.

Catalytic partial oxidation of methane, CPO, is a flameless technology early recognized as an alternative to homogeneous oxidation. A number of research groups are active in the area (York et al., 2003; Choudhary, 2008; Chin et al., 2011; Boullosa-Eiras et al., 2011). Even though catalyst development has progressed, main engineering challenges have to be overcome such as avoiding hot spots formation and runaway reaction for the technology to be transferred to an industrial scale.

The membrane technology for air separation in the oxygen-blown gasifier can be cost-effective compared to the cryogenic technology (IEA, 2007). Catalytic membrane-assisted steam reforming selectively removes hydrogen from the reaction medium, thereby enhancing methane conversion and lower reaction temperatures (Sarić et al., 2012).

Unworked underground coal can be gasified in situ with lower plant costs and no coal transportation (www.worldcoal.org). Moreover, valorization of unmineable coal is estimated to increase coal reserves by 70% according to the World Energy Council. In addition, CO₂ could be stored in the coal cavity after gasification.
As opposed to large-scale syngas processes for chemicals and fuels markets, aforementioned technologies are being developed for fuel cells and on-board applications. Compactness, fast startup, load variations, and high production rates are important criteria to consider. SMR-derived and CPO technologies are envisioned (Palo et al., 2007; Silveira et al., 2009; Avci et al., 2010; da Silva et al., 2011; Xu et al., 2013).

Finally, catalytic conversion of different grades of coal, petroleum coke and biomass in the presence of steam \((2C + 2H_2O \leftrightarrow CH_4 + CO_2)\), so-called hydromethanation, to produce methane and CO\(_2\) in a 1:1 ratio is attractive as being nearly autothermal without adding oxygen. Then, CO\(_2\) reforming of methane can lead to syngas. Figure 2.1.4.1 shows the catalytic hydromethanation process developed by GreatPoint Energy.

![Figure 2.1.4.1](image.png)

**Figure 2.1.4.1** The hydromethanation process developed by GreatPoint Energy.

### 2.1.5 Outlook

Each of the commercial technologies for syngas production results in a specific H\(_2\)/CO ratio that may not fit the downstream syngas utilization. Therefore, technologies that tune product outcomes have to be integrated, adding complexity to the train of reactors, therefore also adding cost in the overall process.

Steam reforming to syngas is a catalytic thermal process with the most industrial practice. It gives the highest H\(_2\)/CO molar ratio, commonly >3, and oxygen is not required. The main
disadvantage lies in the requirement of external heat for energy transfer to the chemical reactions to occur. Large-scale units are also preferred for the oxygen-blown gasification technology due to the capital-intensive separation of oxygen from air. Gasification is a non-catalytic process that operates autothermally with co-injection of oxygen and steam. The H$_2$/CO molar ratio is close to unity. The main advantage lies in the different types and grades of carbonaceous feedstocks, and being non-catalytic, there is no need for upstream feed purification. The most compact on-stream technology to syngas involves partial oxidation which provides H$_2$/CO molar ratio close to two. Nevertheless, the exothermicity of the process has to be controlled. Combined with catalyzed endothermic steam oxidation lead to an overall autothermal process with the same H$_2$/CO molar ratio. This last technology, less mature than the others, is developing because it provides the right H$_2$/CO ratio for some fuels synthesis with high production capacity due its compactness and the economy of scale in the air separation unit (Aasberg-Petersen et al., 2001).

### 2.2 CO$_2$ Conversion to Syngas Via Dry Reforming of Methane (DRM)

There has been considerable interest in the dry reforming of methane (DRM) during these last two decades motivated by environmental issues. DRM technology, also called CO$_2$ reforming, allows two major greenhouse gases to be converted into chemicals, playing therefore a key role in energy storage strategies. In spite of this incentive, the implementation of DRM technology on an industrial scale has not been very successful contrasting with the SMR one. Nonetheless, research on the topic has been very active since the mid 1990s as highlighted in Figure 2.2.1 which reports the number of publications and patents per year.

![Figure 2.2.1](image.png)

**Figure 2.2.1** Number of publications (blue) and patents (red) published per year dealing with CO$_2$ reforming of methane or dry reforming. Source: SciFinder database, last accessed September 18, 2013).
2.2.1 Processes/ Catalysts/ Other Factors

2.2.1.1 Processes

CO\textsubscript{2} reforming of methane gives H\textsubscript{2}/CO molar ratio of unity (reaction (2.3)). Being endothermic, it can only proceed at high temperature, above 700°C, and is primarily accompanied by methane cracking (2.4), Boudouard reaction (2.5) and reverse WGSR (CO\textsubscript{2} + H\textsubscript{2} \rightarrow CO + H\textsubscript{2}O). Therefore, these three latter reactions constitute a loss of carbon and hydrogen with respect to CO and H\textsubscript{2} production, respectively.

Nikoo et al. (2011) recently performed thermodynamics calculations on multi-reaction network taking into account feasible side-reactions that might occur. Starting from an equimolar ratio of CO\textsubscript{2} and CH\textsubscript{4}, conversion at equilibrium reaches 85 and 95%, respectively, at 0.1 MPa and 800°C, and carbon formation amounts to 15%. Carbon formation drastically increases at the expense of CO at lower CO\textsubscript{2}/CH\textsubscript{4} ratios, whereas negligible amount is found at temperature over 900°C leading to H\textsubscript{2}/CO molar ratio close to unity. Like SMR reaction (2.1), pressure increase provides lower conversion due to the net increase of molecules. Hence, on a thermodynamic basis low pressure and high temperature are beneficial to CO\textsubscript{2} and CH\textsubscript{4} conversions, and to H\textsubscript{2} and CO selectivity with H\textsubscript{2}/CO close to unity. Another thermodynamic study shows complete conversion of the reactants above 1,000°C with 100% selectivity into H\textsubscript{2} and CO at a 1/1 molar ratio (Raudaskoski et al., 2009).

In the presence of a catalyst, the kinetics of the individual reactions of the network may influence the overall conversion and selectivity. Experimental results usually show that catalysts deactivate by coke formation according to reactions (2.4) and (2.5). There has been, therefore, a great deal of studies for mastering this major issue. It is worth noting coke formation may also arise from homogeneous reactions, according to reaction conditions and reactor design, leading to plugging which is detrimental on an industrial scale (Rostrup-Nielsen, 1984; Kahle et al. 2013).

Concerning the mechanism of the metal-catalyzed reaction, there is a general agreement that the more demanding reaction step is methane dissociation into adsorbed carbon species CH\textsubscript{x} (x = 0-3) and H species on all catalysts. CO\textsubscript{2} activation and oxygen transfer to adsorbed CH\textsubscript{x} species to form CO is controversial. Several mechanisms have been proposed based on experimental evidences with different metal-supported catalysts (Wei et al., 2004; Navarro et al., 2007; Enger et al., 2012; Kahle et al., 2013; Sadykov et al., 2013). Basically, CO\textsubscript{2} may react either directly in the gas phase with CH\textsubscript{x} species (Eley-Rideal mechanism) or may dissociate at first on the catalyst into CO and O (Langmuir-Hinshelwood mechanism) as shown in Scheme 2.2.1.1.
Then, $O_{\text{ads}}$ and/or OH species migrate towards CH$_x$ ones to form CH$_x$O and/or CH$_x$OH species that break down to CO and H$_2$. Adsorbed CO$_2$ might also react by the reverse water-gas shift reaction to CO and H$_2$O via an adsorbed COOH intermediate. Alternatively, the support if basic enough may activate CO$_2$ through bifunctional mechanism as shown in Figure 2.2.1.1). Accordingly, the extent of carbon accumulation relies not only upon thermodynamics but also on the kinetics of CO formation.

### 2.2.1.2 Catalysts

Catalysts based on both noble and non-noble metals have been extensively studied for CO$_2$ reforming. All of the reactions being similar to those of the steam reforming process, the same supported metals were found active. For economic reasons, much attention has been paid to non-noble metal catalysts, among which nickel-based accounts for half of the literature on the topic. As nickel is prone to more severe deactivation by coke deposits, various methodologies have been deployed for better catalyst design to control carbon formation, sintering and mechanical strength, and, thereby, get more active and robust systems fitted for industrial development shown (Scheme 2.2.1.2). In brief, catalyst optimization over the years has been a combination of interrelated physical characteristics, physicochemical and catalytic properties.
It has been shown that deposited carbon has structure, morphology and reactivity depending on the specific reaction conditions and catalyst. Authoritative studies published by Trimm (1997) and Rostrup-Nielsen (1984) identified several types of carbon on nickel catalysts: adsorbed carbon that may dissolve into nickel lattice leading then to nickel carbide and whiskers, as well as nickel encapsulation (Scheme 2.2.1.3).

![Scheme 2.2.1.3](image)

**Scheme 2.2.1.3**  Schematic reaction network of carbon formation and TEM image of encapsulated nickel catalyst into whisker (adapted from Trimm, 1997).

Dissolved carbon and whiskers formation are irreversible processes, whereas the other types can be gasified by CO₂ under the reforming conditions. Dissolved carbon has been recently identified as graphene-like structure that may either encapsulate catalyst particles or even remove nickel from its support for further growth into filamentous and nanotube morphologies as shown in the micrograph of Scheme 2.2.1.3 (Abild-Pedersen, 2006).

A wide range of catalysts have been screened such as metal carbides and supported metals on oxides (Fan et al. 2009). Various basic oxides such as Al₂O₃, MgO, TiO₂, ZrO₂, CeO₂, La₂O₃, and binary or ternary oxides have been used. Basicity, either intrinsically or promoted by alkali or alkaline earth addition, generally increase nickel performances through better dispersion and higher gasification rate. However, suppressing the formation of carbonaceous deposits is still challenging. The most relevant developments are presented in the following with a focus on supports and promoters involving nickel as the active species as well as cobalt.

The support should not only be thermally stable but should also prevent the active metal from sintering. Whereas metal-support interaction is acknowledged, a strong interaction can lead to complete deactivation like Ni on alumina which forms inactive NiAl₂O₄ spinel phase.

Supports with ordered mesopores such as mesoporous silicas (SBA-15, MCM-41, TUD-1) have been shown to improve nickel activity through confinement of small particles, thereby avoiding sintering and carbon deposits. Wang et al. (2013) report on a new series of ordered mesoporous materials made of 7 wt% of nickel, alumina and various amounts of cerium. The best result was obtained with a Ce/(Ce + Al) ratio of 1 mol%. At 700°C and CO₂/CH₄ = 1, the conversion of CO₂ and CH₄ was 70 and 68%, respectively, and provided H₂/CO close to unity. The activity remained quite stable during a 50 h run. Characterization of spent catalyst showed an average Ni particle size of 6.6 nm with no evidence of sintering and graphitic carbon formation, contrasting with samples either without cerium or prepared by nickel impregnation. The authors proposed
that the rates of carbon gasification and coke formation are nearly equal, thus establishing a steady-state concentration of Ni-C species (2.15).

\[
\text{CH}_4 + \text{Ni} \rightarrow \text{Ni-C} + 2\text{H}_2 \quad (2.15)
\]

\[
2 \text{CeO}_2 + \text{Ni-C} \rightarrow \text{Ce}_2\text{O}_3 + \text{Ni} + \text{CO} \quad (2.16)
\]

\[
\text{Ce}_2\text{O}_3 + \text{CO}_2 \rightarrow 2 \text{CeO}_2 + \text{CO} \quad (2.17)
\]

The mechanism behind relies on the well-known redox process \(\text{Ce}^{IV} \Leftrightarrow \text{Ce}^{III}\) which may account for the stepwise redox process of carbon gasification to CO (2.16) and CO\(_2\) activation to CO (2.17). The oxygen mobility of CeO\(_2\) promotes gasification, then CO\(_2\) reoxidizes the support (Mars Van Krevelen mechanism).

Bifunctional catalysis is not restricted to the reduction of the support by CO\(_2\). The basic properties of the support lead to CO\(_2\) chemisorption forming carbonate species that take part in the catalytic cycle as confirmed by Bachiller-Baeza et al. (2013). Performing temporal analysis of products (TAP) experiments at 500°C with Ni (5 wt%) supported on ZrO\(_2\)-La\(_2\)O\(_3\) doped with 2 wt% of CaO allowed to propose the following bifunctional process. CaO is transformed into CaCO\(_3\) with acts as the major supplier of gaseous CO and adsorbed OH species. The latter migrates towards the nickel particles to gasifying the adsorbed CH\(_x\) species (Figure 2.2.1.1). Noteworthy, in the absence of CaO, both CH\(_4\) an CO\(_2\) have been found to be activated on nickel.

**Figure 2.2.1.1** Schematic representation of bifunctional catalysis on basic support (adapted from Bachiller-Baeza et al. 2013).

The effect of additives such as K, Sn, Mn and Ca on Ni-Al\(_2\)O\(_3\) catalyst have been reported to slightly decrease the activity compared to the original Ni-Al\(_2\)O\(_3\) while less carbon deposits was evidenced with 0.5 wt% of potassium (Castro-Luna et al., 2008). A following study dealt with the effect of 0.5 wt% Li and K on Ni supported on Al\(_2\)O\(_3\), CeO\(_2\), La\(_2\)O\(_3\), and ZrO\(_2\). The 10% Ni/ZrO\(_2\) sample promoted with potassium showed stable activity and lower coke deposition (Castro-Luna et al., 2010). Nagaraja et al. (2011) also highlighted that addition of 0.5 wt% potassium to Ni (10wt%) supported on mixed MgO-ZrO\(_2\) exhibits better performances than without K addition.

Boron has been reported to promote the reforming process. Fouskas et al., (2013) studied the effect of boron addition on a 10 wt% Ni/γ-Al\(_2\)O\(_3\) catalyst. The alumina was co-impregnated with
nickel and different amounts of boron. At atmospheric pressure and 700°C, using a feed of undiluted equimolar of CO$_2$ and CH$_4$, their respective conversion does not depend very much upon boron content. Conversion of CO$_2$ and CH$_4$ reaches 65 and 55%, respectively, while CO and H$_2$ yield is 60 and 50%, respectively. Therefore, CO$_2$ conversion is 10% higher than that of CH$_4$, and the H$_2$/CO ratio of 0.8 is less than the stoichiometry of reaction (2.3). This result strongly suggests reverse WGSR to occur without any specific role of boron. All catalysts exhibited stable activity over 24 h runs. However, the analysis of carbon by H$_2$ titration and electron microscopies (SEM, TEM, HRTEM) indicated carbon accumulation, the amount and nature of which were found boron-dependent. A spectacular decrease of 90% in carbon deposits can be observed with an increase of the B/(B+Ni) atomic ratio up to 0.5 (Figure 2.2.1.2)

![Figure 2.2.1.2](image)

**Figure 2.2.1.2**  Ni particles diameter (blue) and amount of coke (red) on NiB$_x$/Al$_2$O$_3$ catalysts (adapted from Fouskas et al., 2013).

Determination of the mean diameter of the nickel particles indicates smaller nickel particles as the B/(B+Ni) atomic ratio increases up to 0.5 as also shown in Figure 2.2.1.2. These observations confirm that carbon formation is structure sensitive, smaller nickel particles being more resistant to carbon formation. Most of the previous studies correlating carbon deposits with nickel particles size define a critical size of about 7-10 nm, corroborated by this work. It was also demonstrated an electron transfer interaction from boron to nickel to occur that is beneficial to nickel dispersion.

The addition of noble metals to Ni-based catalysts has been reported to promote nickel reduction and to inhibit carbon deposits. Therefore, initial activity should be increased and deactivation limited. Addition of 0.5 wt% of ruthenium to Ni (5wt%) supported on CeO$_2$-ZrO$_2$ mixed oxide has been found to be very active compared to the sample without ruthenium, reaching the thermodynamic equilibrium at 800°C with H$_2$/CO ratio of 1.1 (Pietraszek et al., 2011).
Ni catalyst supported on MgAl₂O₄ spinel exhibits high resistance to sintering and high mechanical strength and is utilized in industrial steam reforming. Other spinel-type structure incorporating nickel such as Ba₀.₇₅Ni₁.₀Al₁₁.₀O₁₉.₃ leads to high CH₄ and CO₂ conversion at 900°C and 0.2 MPa, approaching the thermodynamic equilibrium (Gardner et al., 2013). However, metallic Ni and BaO that segregate from the bulk phase are responsible for the catalytic activity which is fairly constant over 18 h on stream, although 30 wt% carbon did accumulate. Perovskite-type oxides (ABO₃, A = lanthanide, B = transition metal) are also good catalyst precursors to getting high metallic dispersion after the H₂ reduction pretreatment preceding the reforming process. As an example, LaNiO₃ perovskite is transformed into supported Ni on La₂O₂CO₃ (Gallego et al., 2008). The catalytic activity has been correlated with the oxygen storage capacity of the support that provides oxygen to gasify CHₓ species adsorbed on nickel via a bifunctional mechanism similar to that shown in Figure 2.2.1.1 (Sadykov et al., 2013).

The synthesis protocol for preparing the catalyst precursors is of paramount importance. For example, impregnation of the support or coprecipitation of all the constituents may afford different materials. Even nonthermal plasma technique have been very recently applied for supporting nickel particles on ceria (Odedairo et al., 2013). By utilizing the coprecipitation technique followed by different water-washing workup procedures, Chen et al. (2013) have obtained Ni-CaO-ZrO₂ (0.4/0.2/1) materials exhibiting different catalytic behavior. Mesoporous solid could be obtained with an increase in pore volume with Soxhlet-treated (hot water) sample compared with the non-Soxhlet one. Activity runs carried out at 850°C with an undiluted mixture of CO₂ and CH₄ (1.2/1) point out that Soxhlet washings afford a catalyst with the highest activity, that is constant over 800 h on stream. Conversion of CH₄ and CO₂ is 97 and 90%, respectively, with H₂/CO = 0.87. In addition, the amount of carbon is reported to be very low.

An interesting system based on Ni-Co bimetallic catalyst, associated with MgO-Al₂O₃ mixed oxide, has been reported (Zhang et al. 2007). Not only is activity high but stability is excellent. This catalyst was claimed to be the most stable that has ever been developed for CO₂ reforming of CH₄ since activity decrease was less than 3% over a 2,000-h run at 750°C. Several specific physicochemical properties of the catalyst have been identified to account for the outstanding performances, including good metal dispersion, synergy between Ni and Co, and strong metal support interaction. Other Ni-Co bimetallic supported on CeO₂-ZrO₂ mixed oxide are not as good at the same reaction temperature (Djinović et al., 2012).

Monometallic Co-supported catalysts are active in CO₂ reforming. Different oxides, preparation techniques, and reaction conditions have been evaluated and very recently summarized by Budiman et al. (2012). Deactivation by carbon deposits is also present to various extent. Interestingly, Choudary et al. (2005) have reported NdCoO₃ perovskite-type precursor to convert, at 850°C and 0.1MPa, around 92% of CH₄ and CO₂ from an undiluted equimolar mixture affording a selectivity of 96% for syngas with a H₂/CO molar ratio of 0.91. After a 15-h catalytic run, no carbon deposition has been evidenced by oxygen titration. The observed inhibition to carbon formation was ascribed to strong Co-Nd₂O₃ interaction, showing that the perovskite structure fell apart into efficient catalyst.
2.2.1.3 Other factors

It is worth noting that syngas production is being opened to small-scale units convenient for biomass feedstocks. Biogas, the composition of which is commonly over 30 v% in CO₂, is well suited to dry reforming processing (Mota et al., 2011). Alternatively, the concept of modular mobile units is being developed to valorizing associated gas in oil production and at gas well sites in remote areas (GTL Technology Forum, July 30-31, 2013, Houston, Texas, USA). Sasol, Shell, BP, Velocys, and R3 Sciences are among companies that have projects. At CO₂-rich sites, CO₂ reforming may be an alternative for syngas production to transportable liquids.

2.2.2 Enabling technologies

2.2.2.1 Calcor technology

The Calcor process generates high purity CO from the CO₂ reforming technology at low pressure for medium- to small-scale plants. The corresponding units are installed on-site with the CO utilization ones making chemicals via carbonylation reactions (Teuner et al., 2001). Typically, syngas is obtained with a H₂/CO molar ratio of 0.42 and CH₄ content of 0.0005 v%. A schematic overview of the process is shown in Figure 2.2.2.1.

![Schematic flow diagram for Calcor Standard process](image)

**Figure 2.2.2.1** Schematic flow diagram for Calcor Standard process

The heat necessary for the endothermic reforming reaction is generated by a high velocity burner firing into the reformer made of circular tubes containing the catalyst. The nature of the catalyst...
as well as reaction conditions are undisclosed. The gas mixture leaving the reformer is composed of CO, H₂, H₂O, CO₂, and traces of CH₄. Cooling to ambient temperature allows CO₂ recycling to the reforming process by passing through a monoethanol amine (MEA) solution. Further CO purification step is best achieved by membrane technology that simultaneously separates H₂ and remaining CO₂.

As shown in Table 2.2.1, the Calcor technology has operated worldwide since the end of the 1970s with productivity up to 850 Nm³ h⁻¹ per unit.

### Table 2.2.1
Installed Calcor Technology Around the World

<table>
<thead>
<tr>
<th>Country</th>
<th>Capacity (Nm³ h⁻¹)</th>
<th>Year delivered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulgaria</td>
<td>220</td>
<td>1990</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>160</td>
<td>1998</td>
</tr>
<tr>
<td>Germany</td>
<td>40</td>
<td>1978</td>
</tr>
<tr>
<td>Germany</td>
<td>77</td>
<td>1978</td>
</tr>
<tr>
<td>Germany</td>
<td>250</td>
<td>1986</td>
</tr>
<tr>
<td>Germany</td>
<td>300</td>
<td>1991</td>
</tr>
<tr>
<td>India</td>
<td>450</td>
<td>1990</td>
</tr>
<tr>
<td>Japan</td>
<td>160</td>
<td>1984</td>
</tr>
<tr>
<td>Korea</td>
<td>330</td>
<td>1990</td>
</tr>
<tr>
<td>Korea</td>
<td>330</td>
<td>1996</td>
</tr>
<tr>
<td>Middle East</td>
<td>400</td>
<td>2001</td>
</tr>
<tr>
<td>Singapore</td>
<td>850</td>
<td>2006</td>
</tr>
<tr>
<td>Spain</td>
<td>40</td>
<td>2005</td>
</tr>
<tr>
<td>Spain</td>
<td>530</td>
<td>2008</td>
</tr>
<tr>
<td><strong>Total Capacity</strong></td>
<td><strong>4137</strong></td>
<td></td>
</tr>
</tbody>
</table>

The final CO purity is between 99.25 and 99.98%. The H₂-rich tail gas stream obtained from the CO purification step is sold as technical grade hydrogen with a yield of 37 Nm³ per 100 Nm³ of CO produced. Moreover, the reforming process is highly carbon-efficient as 97-99% of the carbon contained in the feed as well as in the fuel is converted to CO. Consequently, CO₂
emissions to the atmosphere are low, and have been estimated to be 15 kg of CO₂ per tonne of CO.

2.2.2.2 Carbon Sciences technology

Carbon Sciences (http://www.carbonsciences.com/) is developing the dry reforming process for gasoline production from methanol. Although catalyst and process are undisclosed, setting the dry reforming technology for syngas production is claimed to be energy-saving as it eliminates steam feed and/or oxygen production. Moreover, the technology makes economical use of gas fields with high CO₂ content. Small-scale units are targeted with production of liquid fuel amounting to 1,000 to 2,000 barrels per day. Hence, CO₂-rich small to medium size gas fields could be valorized. Noteworthy, they represent nearly 40% of worldwide known gas reserves.

2.2.2.3 Others

Shell Global Solutions International B.V. (Shell), Shanghai Advanced Research Institute of Chinese Academy of Sciences (SARI-CAS) and Shanxi Lu’An Group (Lu’An) signed an agreement in 2011 to demonstrate a novel dry reforming technology that recycles methane and CO₂ formed as side-products in Fischer–Tropsch process to alcohols. The proprietary catalyst stays active for a prolonged period of time, becoming a commercially attractive way to increase the process carbon efficiency. This technology is undergoing pilot testing at a commercial site of Lu’An, before it can be made available to the market.

There is also a project funded by the Japanese government which aims to develop dry reforming technology for the gas-to-liquids value-chain (Yagi, 2009).

2.2.3 Outlook

Thermodynamics tells that the CO₂ reforming of methane should be performed above 800°C to get reactants conversion and H₂/CO yield at a maximum. The higher the temperature, the lower carbonaceous deposits on the catalyst will be. At the operating pressure of the synthesis gas plant (>2 MPa), temperature should even be higher as the conversion of CH₄ decreases with pressure. This imposes to design catalysts with high thermal stability. The same stands for the reformer itself which benefit from technological learnings of the other processes to syngas. Dry reforming process is always accompanied by the reverse water gas shift reaction which means hydrogen loss into water and lower H₂/CO ratio.

The fundamental studies on nickel-catalyzed dry reforming highlight the reaction is structure sensitive for both methane activation and carbon formation. Small particles are preferred for high yields of syngas. They can be successfully stabilized by tuning the electronic and textural properties of the support. Inhibiting total carbon accumulation is still an issue although proof-of-concepts have been demonstrated. Supports exhibiting basic properties and/or oxygen storage capacity greatly accelerate the gasification process. However, a comparison between the described catalysts is a difficult task, just because conditions used for each investigation are
different in catalyst weight, contact time, reactor geometry, temperature, etc. In addition, conversion of CO$_2$ and CH$_4$ are often close to equilibrium values. Despite these hurdles, the dry reforming technology is implemented on an industrial scale.

2.3  CO$_2$ CONVERSION TO SYNGAS VIA OTHER DEVELOPMENTAL ROUTES

Other developmental routes for CO$_2$ conversion to syngas are being evaluated via two different approaches. The first one consists of promoting synergy between the afore-described technologies in combining CO$_2$ reforming with steam reforming and/or partial oxidation. The second approach aims at developing alternative technologies for CO$_2$ activation to syngas such as electroreduction, thermochemical splitting and plasma-assisted routes.

2.3.1  Bireforming

2.3.1.1  Processes

Bireforming, or mixed or combined reforming, couples CO$_2$ and steam reforming to overcome catalyst deactivation by carbon deposition in the DRM process and to tune the H$_2$/CO ratio without additional process units.

Demidov et al. (2011) published thermodynamics calculations aiming at defining optimal CH$_4$/CO$_2$/H$_2$O feed ratio to get CO$_2$ and CH$_4$ conversion at a maxima, free from carbon deposits, at a given pressure and temperature. Table 2.2.2 provides selected values together with the H$_2$/CO molar ratio and enthalpy of reaction.

<table>
<thead>
<tr>
<th>T $^\circ$C</th>
<th>P MPa</th>
<th>CH$_4$/CO$_2$/H$_2$O molar ratio</th>
<th>CO$_2$ %</th>
<th>CH$_4$ %</th>
<th>H$_2$/CO molar ratio</th>
<th>$\Delta H$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.1</td>
<td>1/0.31/0.83</td>
<td>1.68</td>
<td>1.46</td>
<td>2.18</td>
<td>220.7</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1/0.42/1.03</td>
<td>6.08</td>
<td>5.85</td>
<td>2.19</td>
<td>184.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/0.58/1.30</td>
<td>13.96</td>
<td>14</td>
<td>2.19</td>
<td>131.6</td>
</tr>
<tr>
<td>900</td>
<td>0.1</td>
<td>1/0.27/0.78</td>
<td>0.46</td>
<td>0.53</td>
<td>2.18</td>
<td>229.6</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1/0.32/0.91</td>
<td>2.16</td>
<td>2.17</td>
<td>2.18</td>
<td>214.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/0.43/1.22</td>
<td>6.51</td>
<td>6.35</td>
<td>2.18</td>
<td>181.3</td>
</tr>
<tr>
<td>1,000</td>
<td>0.1</td>
<td>1/0.26/0.76</td>
<td>0.15</td>
<td>0.2</td>
<td>2.18</td>
<td>232.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1/0.28/0.84</td>
<td>0.84</td>
<td>0.82</td>
<td>2.19</td>
<td>226.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/0.34/1.07</td>
<td>2.93</td>
<td>2.75</td>
<td>2.18</td>
<td>209.7</td>
</tr>
</tbody>
</table>
Table 2.2.2 shows that the optimal CH₄/CO₂ and CH₄/H₂O feed molar ratios increase with temperature, the opposite stands with pressure. At 0.5 MPa, methane and carbon dioxide contents in syngas are lower than 6 and 1% at 800 and 1,000°C, respectively. Increasing the pressure at 2 MPa decreases conversion. At 900°C, methane and carbon dioxide contents are at around 2%. The H₂/CO molar ratio has a rather constant value close to 2.2. The enthalpy of the process decreases with pressure and increases with temperature. Comparison with the 1/1/1 feed composition, the optimized CH₄/CO₂/H₂O mixtures decrease the upper temperature limit of coke formation by 150°C. In fact, the optimized values and the H₂/CO ratio are very close to the theoretical ones considering the overall reaction to syngas (2.18).

$$3 \text{CH}_4 + 2 \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons 8 \text{H}_2 + 4 \text{CO} \quad (2.18)$$

Another thermodynamic study confirmed the same trends (Sun et al., 2011). Suppression of carbon deposits is thermodynamically possible at CH₄/CO₂ greater than 1.5 and $T \geq 800°C$. And carbon deposits are always in equilibrium with an equimolar amount of CH₄ and CO₂ in the temperature and pressure range of 700-1,000°C and 0.1-3 MPa, respectively.

### 2.3.1.2 Catalysts

The catalysts for bireforming can be those used for the separate steam and dry reforming. The two processes may be run in parallel, then the downstream syngas may be mixed to get the appropriate H₂/CO ratio of 2. Nevertheless, it may be simpler to coupled the two reactions in a single reactor one-step. Olah et al. (2013) showed that 15 wt% Ni/MgO exhibits a stable activity at 830°C and 0.7 MPa over a 320-h run. As shown in Figure 2.3.1.1, conversion of CH₄ and CO₂ is about 71%.

![Figure 2.3.1.1](image)

**Figure 2.3.1.1** CO₂ and CH₄ conversion in bireforming of methane over 15 wt% Ni/MgO at 0.7 MPa and 830°C. 100 mL min⁻¹ of CH₄/CO₂/H₂O with a molar ratio of 3/1.2/2.4 and GHSV of 6 $10^4$ mL h⁻¹ g⁻¹ catalyst. Reprint from permission of Olah et al., 2013 (American Chemical Society).
The obtained H2/CO molar ratio amounted to two, and selectivity to H2 and CO is 98 and 100%, respectively. Changing the initial relative CH4/CO2/H2O feed ratio from 1/0.33/0.66 to feed 1/0.8/1.6, i.e. doubling the amounts of CO2 and H2O, increased CH4 conversion to 85%. The same catalyst was also evaluated for the bireforming of natural gas. Stable CO2 and CH4 conversion was again observed over a 160-h run with a natural gas conversion of 70%.

Other nickel-based catalysts such as Ni/Al2O3 and Ni/Al2O3-La2O3 have been evaluated in a microchannel reactor aiming at process intensification for small-scale syngas production (Al-Nakoua et al., 2012). Although the activity was stable for 140-h time on stream at 700°C and atmospheric pressure, a decrease was evidenced with prolonged reaction time which is likely due to carbon accumulation. A microchannel reactor may be envisioned as a replica of multi-tubular steam reformer. Such downsizing may open to new small-scale technologies. Nevertheless, good adherence and thermal stability of catalyst coating to the inside reactor walls should be optimized for long-term operation.

2.3.2 Oxidative dry reforming

2.3.2.1 Processes

Deliberately introducing oxygen into the dry reforming process significantly reduced the overall enthalpy to syngas in combining the exothermic partial oxidation process with the endothermic dry reforming one. For oxidative dry reforming of methane, thermodynamics analysis indicates CH4/CO2/O2 molar ratio should be in the range of 1.0/0.5-1.0/0.2-0.4 for high CH4 and CO2 conversion, and high H2 and CO yield, while minimizing H2O and coke formation at a preferred temperature above 800°C (Nematollahi et al., 2012).

The process is performed in the presence of metallic catalysts similar to those for SMR and DRM. Basically, the same adsorbed species, CHx from methane and Oads from either H2O, CO2 or O2, are producing H2 and CO. Documented studies on the mechanism of partial oxidation to syngas highlights that two process pathways may operate according to the catalyst and reaction conditions (Prettre et al., 1946; Enger et al., 2008). As shown in Scheme 2.3.2.1, syngas can be produced through a one-step as well as a two-step process.

\[
\begin{align*}
4 \text{CH}_4 + 2 \text{O}_2 & \rightarrow 3 \text{CH}_4 + 2 \text{H}_2\text{O} + \text{CO}_2 \\
3 \text{CH}_4 + 2 \text{H}_2\text{O} + \text{CO}_2 & \rightarrow 8 \text{H}_2 + 4 \text{CO}
\end{align*}
\]

\textbf{Scheme 2.3.2.1} Reaction pathways for methane partial oxidation to syngas.
The one-step partial oxidation corresponds to the direct pathway. The two-step process consists at first in CH₄ combustion providing CO₂ and H₂O and 75% of unreacted CH₄, then bireforming takes place. Hence, under oxidative CO₂ reforming bireforming may contribute to the overall process.

The net heat of the oxidative CO₂ reforming process can be estimated taking into account the co-feed CH₄/CO₂/O₂ relative ratio and the H₂/CO syngas ratio. On a Co/MgO-based catalyst with CH₄/CO₂/O₂ = 1/0.2/0.4, the H₂/CO ratio was 1.75 and 1.55 at 750 and 900°C, respectively, while the process was slightly more endothermal, from +20 to +65 kJ mol⁻¹, with temperature (Choudary and Choudary, 2008). Optimized heat flow for a biogas reformer has also been calculated and experimentally checked for keeping the reaction temperature at 800°C (Jahn et al., 2013).

### 2.3.2.2 Catalysts

According to participants in the field, only catalysts exhibiting high activity in the separate CO₂ reforming and partial oxidation process should be considered for the mixed process. Moreover, the active form of the catalyst in dry reforming being in the metallic state, the partial oxidation process should not stabilize higher oxidation states. Supported noble metals are, therefore, good candidates (Choudary and Choudary, 2008). Bimetallic noble metals such as Pt-Ru supported on Al₂O₃-CeO₂ and Pt-Rh on CeO₂-ZrO₂ have been studied for biogas processing into syngas (Lai et al., 2012). One application is envisioned for the automotive market in upgrading biogas by the so-called Exhaust Gas Fuel Reforming process (Lau et al., 2012). The concept of exhaust gas fuel reforming consists of incorporating a reformer reactor in the exhaust gas recirculation system. In this way, the engine is co-fed with a recirculating exhaust gas which is enriched in H₂.

Besides noble metals, molybdenum and tungsten carbides have been reported to be active. One may also operate the process with two-stage catalysts, one being very active for combustion, e.g. BaMn₂Al₁₀O₁₉, transferring maximum heat to the reforming catalyst such as Co₀.₂W₀.₈Cₓ (Xia et al., 2009). The activity was shown to be stable for five days. No carbon formation was observed in the reactor and no carbide catalyst oxidation was evidenced.

### 2.3.3 Trireforming

#### 2.3.3.1 Processes

The trireforming concept (TRM) is a three-step process that combines dry reforming, steam reforming and partial oxidation of methane in a single reactor. This process scheme can be compared to the indirect route of partial oxidation (Scheme 2.3.3.1). The main advantage of the trireforming concept lies in resolving the coke formation issue and promoting an energy-efficient process by introducing oxygen in the feed. Moreover, the H₂/CO molar ratio can be tuned by
changing the relative amounts of the co-reagents. It can, therefore, be used in the production of liquid fuels and chemicals as well as in fuel processing for fuel cells.

The proof-of-concept has been first demonstrated by Song (2001) in showing trireforming may operate with co-feed synthetic mixture of CO₂/H₂O/O₂ mimicking flue gases composition. Although there is no need to separate and concentrate the individual feed components, SOₓ, NOₓ, and other toxic substances should be eliminated as they are strong catalyst inhibitors. In addition, flue gases from pure oxygen-powered plants would be preferred to avoid stream dilution by nitrogen.

**Scheme 2.3.3.1**  Flue gases value chain by the trireforming process.

The composition of flue gases depends on the types of fuels used in power plants. From natural gas-fired power plants, the flue gases typically contains 8-10% CO₂, 18-20% H₂O, 2-3% O₂, and 67-72% N₂, whereas from coal-fired plants a composition of 12-14% CO₂, 8-10% H₂O, 3-5% O₂, 72-77% N₂, is commonly found.

Thermodynamics calculations have been performed for a near thermoneutral process with complete consumption of oxygen (Halmann and Steinfeld, 2006). Figure 2.3.3.1 reports the composition in H₂, CO, CO₂, H₂O and CH₄ at equilibrium at different temperatures from an initial feed of 8.4 v% CO₂, 12.9 v% H₂O, 5.8 v% O₂, and 60 v% N₂.

**Figure 2.3.3.1**  Thermodynamic equilibrium with temperature at 0.1 MPa from a feed of 8.4 v% CO₂, 12.9 v% H₂O, 5.8 v% O₂, and 60 v% N₂ (Halmann and Steinfeld, 2006).
As shown in Figure 2.3.3.1, the H₂/CO molar ratio is around 2 between 800 and 1,000°C, fitted for methanol synthesis and Fischer–Tropsch products. In the case of methanol production, it has been estimated that setting upstream a trireformer may avoid 50% of the CO₂ emissions and save 32% of natural gas as fuel when compared to the conventional technologies. Fuel savings may even reach 75% for hydrogen production.

An innovative integrated trireforming power plant (ITRPP) for co-generation of electrical power and syngas has been recently modeled to assess the overall energy efficiency and CO₂ emissions. It is concluded that trireforming process does not decrease the power plant efficiency contrasting with the conventional CO₂ capture by the amine technology. Moreover, the reduction in CO₂ emissions is about 83%. Therefore, there is a clear advantage of the trireforming process over the amine one to capture CO₂ (Minutillo and Perna, 2009). In addition, trireforming is directly valorizing CO₂ into the value chain of fuels and chemicals.

Zhang et al. (2013) reported a modeling study with the trireforming process for optimizing syngas production rate, which is then converted to methanol. The best conditions of the trireformer were identified as 850°C, 0.1 MPa, and CH₄/CO₂/H₂O/O₂/N₂ feed composition of 1/0.25/0.5/0.075/1.67. Under these conditions, CO₂ conversion of 99% and H₂/CO of 2 can be achieved. However, carbon and oxygen are found in trace amounts in the simulation.

Tirereforming is not restricted to flue gases treatment. Biogas, the composition of which lies in the range of 50-75 v% CH₄, 25-45 v% CO₂, 2-7 v% H₂O, 2 v% N₂, has been reformed for fuel cell application. Upstream to solid oxide fuel cell (SOFC), biogas trireforming, after elimination of H₂ (<1%) and trace amounts of H₂S, O₂, NH₃, halides and siloxanes, allows to convert CH₄ for preventing the risk of carbon deposition at the Ni-based anode, therefore increasing cell stability (Lo Faro et al., 2013). Trireforming of biogas has also been evaluated with fixed-bed reactor and microreactor (Izquierdo et al., 2013). The catalytic activity measured using the microreactor was one order of magnitude higher and catalyst stability was greatly improved, likely due to the technique used for loading the catalyst onto the walls of the microreactor. It has also been demonstrated that fluidized bed reactor is superior to fixed-bed configuration with Ni₀.₁₅Mg₀.₈₅O solid solution catalyst (Tomishige, 2004). The origin may stem from catalyst particles circulating between reducing and oxidizing zone. Reforming and carbon gasification proceed in the reducing and oxidation zone, respectively.

### 2.3.3.2 Catalysts

For the time being, the trireforming catalysts are commonly those reported for steam and dry reforming as attested by the pioneer work of Song and Pan (2004) with flue gases mixture. The objective is to approach the thermodynamic equilibrium with low carbon deposition. High CH₄ conversion (≥ 97%) and high CO₂ conversion (around 80%) for producing syngas with H₂/CO ratio in the range of 1.5-2.0 could be obtained over supported nickel on MgO, ZrO₂, CeO₂ and their mixed oxides, at 800-850°C under atmospheric pressure. No carbon formation was evidenced over some hours on stream, contrasting with the same catalysts tested in CO₂ reforming. Therefore, the presence of steam and oxygen is beneficial to carbon gasification.
More recently, Garcia-Vargas et al. (2012) reported on a new support, $\beta$-SiC, for the reforming catalysts. The $\beta$-SiC porous form of silicon carbide exhibits high thermal conductivity and mechanical strength, and chemical inertness. High thermal conductivity is of special interest for highly endo- and exothermic reactions, where the temperature inside the catalyst bed should be precisely controlled. Over a 4-h on stream, 4 wt% Ni/$\beta$-SiC was as active, and resistant to coke formation, as 4 wt% Ni on CeO$_2$ with the same average nickel particle size.

### 2.3.4 Electrochemical route

#### 2.3.4.1 Processes

The carbon dioxide (CO$_2$) to syngas process can be accomplished by electrochemistry according to different strategies: (a) electroreduction of H$_2$O to H$_2$ followed by the reverse water gas shift reaction; (b) separate electroreduction of CO$_2$ to CO and H$_2$O to H$_2$; and (c) co-electroreduction of CO$_2$ and H$_2$O. Both electroreduction of H$_2$O and CO$_2$ can be achieved in solution at room temperature (Windle and Perutz, 2012). However, for the usage of syngas as intermediate to fuels and chemicals it is simpler to design a solventless single process according to reactions (2.19) and (2.20), that provides the required H$_2$/CO molar ratios.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &\rightarrow \text{CO} + \text{H}_2 + \text{O}_2 \\
\text{CO}_2 + 2 \text{H}_2\text{O} &\rightarrow \text{CO} + 2 \text{H}_2 + 1.5 \text{O}_2
\end{align*}
\]

(2.19) (2.20)

Co-electrolysis of (CO$_2$) and steam with high temperature solid oxide electrolysis cells (SOECs) is currently gaining increasing interest worldwide due to the opportunity in renewable electricity utilities. Using renewable electricity sources, e.g. solar, wind, tidal, etc., will avoid consuming fossil fuels and emitting greenhouse gases. Noteworthy, SOEC and SOFC (solid oxide fuel cells) are the same technology operating either as power to gas or vice versa (Scheme 2.3.4.1).

![Scheme 2.3.4.1](image)

**Scheme 2.3.4.1** Basic principle of SOEC for the co-electroreduction of CO$_2$ and steam.

As shown in Scheme 2.3.4.1, steam electrolysis involves the reductive dissociation of H$_2$O to H$_2$ and O$^{2-}$ on the cathode. Subsequent diffusion of O$^{2-}$ across the solid electrolyte is driven by the external applied DC voltage, and the oxidation of O$^{2-}$ to O$_2$ occurs on the anode. A similar process may occur with CO$_2$ electroreduction forming CO on the cathode and O$_2$ on the anode.
Moreover, catalytic reactions may occur during the course of electroysis. In line with, it has been proposed that the predominant CO\textsubscript{2} to CO process does occur catalytically by the reverse water gas shift process (Stoots et al., 2009). High temperature SOEC operates in the temperature range of 750-1,000°C, which is beneficial for fast electrode kinetics and high efficiency. The materials used are typically porous Ni/yttria stabilized zirconia cermet (YSZ) for the cathode, dense YSZ for the electrolyte, and porous (La\textsubscript{1-x}Sr\textsubscript{x})MnO\textsubscript{3}/YSZ composite for the anode.

### 2.3.4.2 Performances

Sulfur-free CO\textsubscript{2} and deionized H\textsubscript{2}O should be used to keep the cathode efficiency. It should also be emphasized that electroreduction of CO\textsubscript{2} benefit from the presence of steam in avoiding carbon deposition, as for the bireforming process. The total energy input is supplied by electrical and thermal energy. The electrical energy demand, i.e. voltage, decreases with temperature increase due to faster O\textsuperscript{2-} diffusion across the electrolyte. At the same time, thermal energy increases with temperature. Moreover, CO\textsubscript{2} and H\textsubscript{2}O electroreduction have the same kinetics between 750 and 900°C (Hansen, 2011).

According to Fu et al. (2010), thermoneutral process is obtained at 800°C for a co-feed stoichiometry corresponding to equation (2.20). Experiments showed CO\textsubscript{2} and H\textsubscript{2}O conversion and CO and H\textsubscript{2} yield increased with the applied current. Under a current of -25 A, CO\textsubscript{2} and H\textsubscript{2}O conversion reached 93% and H\textsubscript{2}/CO molar ratio was 2.1. High current density of -1.46 A cm\textsuperscript{-2} could be obtained, and optimizing the operating voltage led to a value of 1.343 V. In another study, an optimized value of 1.37 V was found by energy and exergy modeling with flue gases from a simulated power plant (Stempien et al., 2012). The corresponding calculated energy and exergy required to convert one kg of CO\textsubscript{2} was found to be 16.4 and 7.2 kJ, respectively.

SOEC durability was studied by Chen et al. (2013) in a Topsøe Fuel Cell (TOFC®) 10-cell stack, containing Ni/YSZ electrode supported cells with a footprint of 12 x 12 cm\textsuperscript{2}. Co-electrolysis of CO\textsubscript{2} and steam was performed at 800°C and -0.75 A cm\textsuperscript{-2}, from a 1/1 mixture of CO\textsubscript{2} and H\textsubscript{2}O. Conversion based on Faradic yield was 60% and the working potential remained almost stable over 1,000-h electrolysis for one type of cell, the composition of which is undisclosed. However, long-term stability over five years and more will be required before commercialization.

### 2.3.5 Solar-based Thermochemistry

#### 2.3.5.1 Processes

Comparison between the energy from the sun reaching the earth per hour and that consumed by humans, 4.3 10\textsuperscript{20} J h\textsuperscript{-1} and 4.7 10\textsuperscript{16} J h\textsuperscript{-1}, respectively, highlights unlimited amounts of energy that may be beneficial to a variety of endothermic chemical transformations ( Izumi Y, 2013). However, 1 kW m\textsuperscript{-2} is the maximum of direct insolation that can be reached in regions including Australia, southern Europe and the Mediterranean basin, southwestern United States, and parts of
the developing countries (Kodama and Gokon, 2007). Therefore, solar power concentrator technologies have been developed over the years and temperature can now exceed 1500°C for operating highly endothermal processes such as steam and CO\textsubscript{2} reforming (Agrafiotis et al., 2014). Figure 2.3.5.1 shows the principle and a picture of solar power concentration.

![Solar power concentration](image)

**Figure 2.3.5.1** Solar power concentration: the principle (left), picture of heliostats and furnace at PROMES-CNRS, France (right).

Despite the advantage of lower CO\textsubscript{2} emissions than conventional reforming, thermochemical reforming process is far from being mature. Kirillov (1999) has reviewed the technical characteristics and results of methane reforming acquired during international projects in the period 1987-1996. The author concluded industrial application is a long-term alternative due to the unfavorable economics in comparison with the on-stream technologies. Since then, solar thermal conversion of CO\textsubscript{2} and H\textsubscript{2}O into CO and H\textsubscript{2} has emerged as a concept for fuel-free pathway to syngas.

The developed technology for solar thermal conversion of CO\textsubscript{2} and H\textsubscript{2}O is a two-step thermochemical cycle using metal oxide redox properties (Kodama and Gokon, 2007). The redox systems considered so far are based on Fe, Mn, Co, Nb, Zn, In, Sn, and Ce oxides. The thermochemical properties of ceria have been recently reported for the first time (Abanades and Flamant, 2006). The recognized advantage over the other metallic redox systems lies in the reduction creating oxygen vacancies without significant reorganization of the crystal lattice. Therefore, lattice oxygen ions are reversibly stored and released. Additionally, CeO\textsubscript{2} is thermally stable with a high melting point (2,400°C), and displays faster kinetics.

As shown in equations (2.21-2.23), the reaction sequence based on CeO\textsubscript{2} redox cycle involves the endothermic reduction of CeO\textsubscript{2} followed by its exothermic oxidation by H\textsubscript{2}O:

\begin{equation}
\text{CeO}_2 + \text{H}_2 \rightarrow \text{CeO}_2 + \text{H}_2
\end{equation}

\begin{equation}
\text{CeO}_2 + \text{H}_2\text{O} \rightarrow \text{Ce}_2\text{O}_3 + \text{H}_2
\end{equation}
2 CeO₂ → 2 CeO₂₋ₓ + x O₂ (g)  \hspace{1cm} (2.21)

CeO₂₋ₓ + x H₂O → CeO₂ + x H₂ (g)  \hspace{1cm} (2.22)

CeO₂₋ₓ + x CO₂ → CeO₂ + x CO (g)  \hspace{1cm} (2.23)

2.3.5.2 Performances

Le Gal et al. (2011) observed that upon CeO₂ reduction at 2,000°C partial sublimation did occur leading to the decrease of reactivity upon several successive redox cycling. Introduction of zirconium as dopant allowed to decrease the reduction temperature below 1,400°C. The reduction yield was also increased together with that of CO and H₂. However, the rate of reoxidation by CO₂ and H₂O was slower with Zr₀.2₅Ce₀.₇₅O₂ with an optimum temperature at 1,100°C. This effect is consistent with the reoxidation of the surface of CeO₂, whereas with Zr₀.2₅Ce₀.₇₅O₂ reoxidation of the bulk is operative.

Furler et al. (2012) reported on CeO₂ being reduced at 1,527°C to an oxygen deficient state. Re-oxidation at 827°C with a mixture of CO₂ and H₂O in the range of 0.8-7.7 produced syngas with H₂/CO molar ratio of 0.25-2.34. Ten consecutive cycles within 8 h have been performed giving a stable gas composition and yield, although cerium oxide sublimation did occur Figure 2.3.5.2.

![Figure 2.3.5.2](image)

**Figure 2.3.5.2** Ceria temperature profile, CO, H₂ and O₂ production rate, and H₂/CO molar ratio during ten consecutive splitting cycles. Experimental conditions: 3.6 and 0.7 kW radiation power input during reduction and oxidation steps, respectively; H₂O/CO₂ = 6.7; reduction and oxidation steps performed at constant time intervals of 30 and 15 minutes, respectively (Furler et al., 2012)

To optimize the potential of such redox cycles, more materials should being tested focusing on higher re-oxidation rate by CO₂ and H₂O at lower temperature for increasing the productivity in syngas, with long-term stability over extended cycle operation.
2.3.6 Plasma route

According to "The 2012 Plasma Roadmap", CO₂ dissociation by plasma technology is attractive if the price of electricity is at the lowest (Samukawa et al., 2012). The technology can be even more attractive where over-production of fluctuating renewable electricity leads to negative prices on the spot market. Despite this economic criterion, the plasma technique is currently developed in particular for valorizing various feedstocks into valuable products.

2.3.6.1 Processes

The concept of plasma technology lies in the generation of high-energy electrons that impact molecules to produce radicals that rearrange to the final products. Under thermal quasi-equilibrium plasma conditions, thermal decomposition is the main process. The technology is being applied, for example, to organic waste gasification to syngas (Fabry et al., 2013). Accordingly, up to 80% of the chemical energy contained in the initial organic waste can be recovered.

Under non-thermal plasma conditions, the predominant energy transfer is through the vibrational modes of the reactants. Non-thermal plasma intrinsically contributes to energy conservation when it eliminates or minimizes fuel combustion for providing thermal energy to the process (Nozaki and Okazaki, 2013).

2.3.6.1 Performances

The thermal plasma technology has been applied to CO₂ reforming processes and CO₂ dissociation into CO and O₂. Tao et al. (2011) recently reviewed the CO₂ reforming of methane assisted by different plasma technologies. The general trends are variable conversion in CO₂ and CH₄ according to the reaction conditions, and variable selectivity to syngas due to C₂-product formation which commonly amount to over 8% together with coke deposition.

The integration of 20 wt% Ni on alumina in the plasma discharge zone was evaluated in CO₂ reforming (Mahammadunnisa et al., 2013). The schematic setup is shown in Figure 2.3.6.1

Figure 2.3.6.1 Schematic representation of the catalyst-packed dielectric barrier discharge reactor for dry reforming of methane. Reprint from permission of Mahammadunnisa et al., 2013 (American Chemical Society).

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At a specific energy input (SEI, defined as the amount of electrical energy delivered into the system divided by the reactants flow rate) of 5.2 kJ L\(^{-1}\) and a CH\(_4\)/CO\(_2\) mixture ratio of 2, the catalyst increases CH\(_4\) conversion from 38 to 49% while CO\(_2\) conversion did not change. Both selectivities for H\(_2\) and CO were in the range of 40%, giving an H\(_2\)/CO of 1.2.

Liu et al. (2013) carried out the oxidative reforming of simulated biogas (CH\(_4\)/CO\(_2\)/O\(_2\) = 3/2/2) in a novel plasma shade arrangement shown in Figure 2.3.6.2a and b. Test stability over 8 h on stream shows stable consumption of O\(_2\) close to 97%, while stable CH\(_4\) and CO\(_2\) conversion reached 80 and 35%, respectively (Figure 2.3.6.2c).

![Figure 2.3.6.2](image)

**Figure 2.3.6.2**  (a) Schematic representation of the shade reactor, CH\(_4\)/CO\(_2\)/O\(_2\) fed at room temperature and atmospheric pressure from the bottom; (b) Picture of the 2.5 cm\(^3\) shade reactor at gas residence time of 0.1 s and SEI of 84 kJ mol\(^{-1}\); (c) CH\(_4\), CO\(_2\) and O\(_2\) conversion with time on stream (Liu et al., 2013).

Selectivities to CO, H\(_2\), and H\(_2\)O close to 92, 48 and 48%, respectively, have been calculated leading to H\(_2\)/CO ratio of 0.8. Hydrocarbons, i.e. C\(_2\)H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\), have also be analyzed with selectivity amounting to 8%. Investigation of the chemical reaction pathways highlighted the major contribution to CH\(_4\) and CO\(_2\) conversion arose from the partial oxidation of methane and the reverse water gas shift reaction (WGS), respectively.

Lebouvier et al. (2013) have assessed the potential of non-thermal plasma CO\(_2\) dissociation processes compared to currently available technologies. The most efficient noncatalytic plasma-assisted CO\(_2\) dissociation experiment, which is currently at laboratory scale, has an energy cost of 123 and 55% higher than the most efficient catalytic natural gas reforming and coal gasification plants, respectively. Plasma-based dry reforming is 27% more efficient than plasma CO\(_2\) dissociation likely due to more research efforts on dry reforming over the past decade. For CO\(_2\) dissociation to be competitive, a breakthrough has to be made to obtain sufficient energy.
efficiency with an acceptable conversion rate and mass flow rate. Moreover, an industrial scale-up would require increasing the capacity of the processes.

2.3.7 Enabling Technologies

2.3.7.1 SPARG technology

In the 1980’s, Haldor Topsøe company developed the SPARG technology, Sulfur PA ssivated Reforming (Rostrup-Nielsen, 1984; Undengaard et al., 1992). It consists of the reversible adsorption of sulfur on the catalyst (TOPSOE R 67) as well as on the reactor walls to inhibit carbon deposition and growth in the reformer process. Operating bireforming conditions of H₂O/natural gas (H₂O/C = 0.93) and CO₂/natural gas (CO₂/C = 0.65) result in a H₂/CO molar ratio of 1.8-1.9, a value suitable for acetic acid, oxo alcohols and dimethyl ether production.

Later on, a plant of 3030 t per day of methanol was planned also based on bireforming but no details were given except that the process is feasible where cheap CO₂ is available (Aasberg-Petersen et al., 2001).

2.3.7.2 KOGAS technology

Korea Gas Corporation (KOGAS) is developing trireforming technology for syngas use in dimethyl ether production (Cho et al., 2009). Here, trireforming is defined as combination of combustion, steam and CO₂ reforming in a single reactor. Therefore, the reformer is similar to the ATR one, with a burner and H₂O and CO₂ as co-oxidants (Figure 2.3.7.2).

![Figure 2.3.7.2 Schematic flow diagram of KOGAS trireforming process.](image)

A prereformer is installed upstream for reforming, at 350°C and 3 MPa, C₂ and C₃ fraction contained in natural gas. Carbon dioxide stream comes from recyclings after syngas cleanup and dimethyl ether synthesis. At the outlet of the trireformer which is run autothermally, syngas temperature and pressure is at around 1,000°C and 2 MPa, respectively. Two main operational
issues have been solved: the H2/CO ratio lies in the range 1.2-1.5 and coke deposition is limited. The appropriate H2/CO ratio for operating downstream dimethyl ether production avoids installing water gas shift technology and is therefore cost-effective. With Ni catalyst supported on Al2O3 promoted with CeO2, ZrO2 and MgO, reactor optimization led to methane conversion close to the equilibrium value with H2/CO2 = 1.2. The demonstration plant produced 10 tons per day (TPD) of dimethyl ether and the commercial scale of 3,000 TPD was scheduled in 2012 with three trains of prereformers/trireformers set in parallel.

2.3.7.3 Carnol technology

Steinberg (1996) at Brookhaven National Laboratory, USA, developed the deep cracking of methane to produce carbon and hydrogen (reaction (2.4)) followed by the hydrogenation of CO2 to afford methanol. Named as the Carnol process, CO2 mitigation could be effective if it can be recycled from power plant stack gas. It is worth noting that, when comparing the endothermal enthalpy for hydrogen production by methane deep cracking process with that for steam and CO2 reforming (reactions (2.4), (2.1), (2.3)), there is a net energy gain of around 50 and 70%, respectively.

2.3.7.4 BASF technology

The Carnol concept is being reconsidered as environmentally-friendly and competitive utilization of CO2 to produce syngas on an industrial scale. Since 2013, BASF has been teaming with Linde and ThyssenKrupp for a 3-year project to develop closely-related Carnol concept. The new technology is based on two successive processes. In the first process, an innovative high-temperature reactor will operate to thermally transform natural gas into hydrogen and carbon, and the heat generated will be recycled into the process. Compared with current hydrogen production, this technology is expected to lower CO2 emissions by about 50%, and carbon black will be valorized by steel industry. In the second process which is catalytic, H2 will be reacted with CO2 sourced in part from industrial production facilities to produce syngas as a raw material for chemical production. The technology is fitted for large-scale industrial production.

2.3.7.5 Haldor Topsøe technology

According to Hansen's presentation at the 11th International Conference on Carbon Dioxide Utilization (2011), Haldor Topsøe company is developing the SOEC technology for methanol synthesis from CO2 and steam. This approach is integrated into the 2050 energy vision of Denmark for fossil fuel free energy, and may be extended to those countries intensely developing fluctuating renewable electricity sources.

2.3.8 Outlook

Dry reforming has been combined with steam reforming and/or oxygen providing solutions to drastically decrease coke accumulation and external heat required to perform endothermic
reactions. Concommitantly, H2/CO ratio could be tuned at values equal or lower than 2. Flue gases can be directly processed to syngas avoiding energy-intensive CO2 concentration. Alternative technologies that provide energy into the system to get syngas include electroreduction and solar thermochemistry of CO2-H2O mixtures bypassing hydrocarbon co-feed. Plasma-assisted processes have also been demonstrated but energy efficiency for the dissociation reaction is much higher for CH4 than for CO2. The enabling technologies are based on combined CO2 reforming, CO2-H2O electroreduction, and CH4 deep cracking to H2 that is further processed with CO2.

2.4 COMMERCIAL/MARKET SIZE(S) AND OPPORTUNITIES

2.4.1 Value chain of CO2

The worldwide strong incentive to slow down CO2 emissions from stationary and mobile energy production brings to the forefront the utilization of CO2 as C1 feedstock. Additionally, one may argue that nature solely uses CO2 as carbon resource for biomass production. Hence, designing synthetic procedures to convert CO2 into chemicals for different markets is a worthwhile approach that should contribute to moving forward to non-fossil carbon resources.

Carbon dioxide is already a commodity chemical with various usages. Of the 200 million tons per year (Mt/y) consumed by the industry from natural sources, the major markets are by far urea and enhanced oil recovery (EOR) amounting to around 110 and 50 Mt/y of CO2, respectively (Ballivet-Tkatchenko and Dibenedetto, 2010). Although market growth is foreseen for urea as fertilizer, it will stay at the level of millions of tons for a while, unless other applications are found. The development of EOR technology is tightly linked to CO2 capture and storage from industry emitters. Therefore, its expansion will depend on the development of CO2 capture, including but not restricted to anthropogenic emissions. The benefits of EOR are substantial according to NETL/DOE (2012). It is estimated that in the United States, 17 billion tons of CO2 would be needed to produce 60 billion barrels of oil by 2100 using EOR technology. Moreover, enhanced recovery is not limited to oil. Gas recovery has been shown feasible in enhanced coal bed methane (ECBM) technology (Locke and Wirschel, 2013). The timeframe to commercial deployment can be potentially accelerated through demand for natural gas supply.

The main issue in designing new strategies for promoting the market of CO2 into chemicals is to balance emission and consumption due to the large energy input intrinsically needed to operate the processes. Obviously, low-carbon energy sources are well adapted to the issue, but their development will depend on local situations. The 2011 energy-related CO2 emissions are shown in Figure 2.4.1.1 by regions from data of EIA (2011). Overall, it corresponds to a total of 32.5 gigatons (Gt) emitted. Hence, the current market for CO2 cannot counterbalance its emissions, being less than 1%.
New concepts are, therefore, necessary to assess which technologies would have a stronger positive impact on CO₂ transformation. At a first glance, making chemicals for the energy sector should greatly improve CO₂ utilization. Syngas as intermediate represent a huge potential market as fossil fuels become further depleted, and syngas production from CO₂ may play a key role. More benefits could arise from avoiding CO₂ to be flared and from new opportunities in full use of CO₂-rich gas field, biogas and biomass in general.

2.4.2 Syngas market

Syngas has been recognized as a flexible intermediate to produce hydrogen, fuels and chemicals. The mature technologies in use are based on steam reforming, partial oxidation, and gasification of various carbonaceous feedstocks. It has also been recognized that addition of CO₂ into the processes tunes H₂/CO molar ratio, which is beneficial to downstream technologies such as methanol, dimethyl ether and hydrocarbons products production.

According to Aasberg-Petersen et al. (2011), the volume of syngas required for the production of ammonia (133 Mt/y in 2008) and methanol (45 Mt/y in 2010) amounts to about 100 billions Nm³/y. Additional 5 and 100 billions Nm³/y are estimated for hydrogen and Fischer–Tropsch fuels, respectively. These figures correspond to around 10% of the 3,282 billions Nm³/y of natural gas produced in 2010 (IAE, 2011). It is worth mentioning syngas is also produced from other carbonaceous sources as described previously in this report.

Opening widely the fuel market to these chemicals will boost their production capacities. One can roughly estimate that replacing motor gasoline, aviation fuels and fuel oil originating from petroleum refining will generate a worldwide demand amounting to over 1, 0.2 and 0.5 Gt/y, respectively (IAE, 2011). Moreover, consistent growth in automobile industries due to the economic growth of regions such as Asia could foster further expansion of syngas market for either carbon- or hydrogen-based fuel.

Figure 2.4.1.1  CO₂ emissions percentage by regions (EIA, 2011).
2.4.3 Syngas production capacity

Syngas production capacity of a plant and the downstream process to fuels or chemicals are interlinked as syngas continuously feeds the downstream process. In single train units, capacities of typically 35,000 barrels per day can be reached for liquid fuel production by the Fisher-Tropsch process, and 10,000 tons per day in mega-scale methanol plants (Aasberg-Petersen et al., 2001).

According to Udengaard (2005), the shift in methanol market from conventional to future energy carrier will change the location of the new plants from close to the end users to areas with abundant low cost feed and fuel. It will also change the production scale and the technology for syngas. The ATR technology is best fitted for high-capacity reformer due to the economy of scale in oxygen production, whereas steam reformer is best optimized for production up to 2,500 tons per day.

Small-scale units can be foreseen for biogas and biomass valorization to syngas as well as where carbon-free decentralized energy production is available. Stationary and on-board processes may also be envisioned.

2.4.4 CO₂ to syngas

Mature technologies in syngas synthesis and its purification for methanol production emits 1 ton of CO₂-eq per ton of methanol from natural gas, and twice more from coal (IEA, 2013). This example justifies the strong incentive for developing CO₂ to syngas routes for being implemented on an industrial scale to decrease net emissions. The sources of CO₂ vary from dilute stream, such as flue gases, to concentrated ones. The latter can originate from either capture/separation processes, oxy-combustion, or CO₂-rich natural gas fields. Developing CO₂ to syngas routes can be achieved through two strategies. The first one takes advantage of the mature technologies adapting them to CO₂ as co-feed. The second strategy focusses on technologies derived from new concepts.

Among the benchmark technologies described under heading 2.1, the introduction of pure CO₂ in the co-feed provides a better adjustment of syngas composition suitable for a given downstream application. Derived-benchmark technologies are based on CO₂ reforming combined or not with steam reforming and/or partial oxidation. The contribution of CO₂ to syngas is there high. Nearly half of the co-feed may be made of CO₂. The processes, therefore, are of interest for CO₂-rich natural gas sources as they can be processed directly without upstream separation step. This permits to exploit new reserves previously considered as uneconomical. The other interest of CO₂ reforming lies in the deployment of biogas which can be valorized one-step to syngas. Interestingly, operating CO₂ reforming with steam and oxygen allows the direct processing of flue gases. These alternatives will increase the CO₂ market to syngas as attested by on-stream technologies and demonstration units.
New concepts to convert CO₂ to syngas are best based on the use of renewable energies for providing electricity along with heat. In these cases, either CH₄ or H₂O is the hydrogen source. The processes converting CO₂ and H₂O into syngas do not anymore involve carbonaceous feedstocks and may open to new technologies free from constraints on carbon reserves and CO₂ emissions.

2.5 REMAINING HURDLES

The implementation of CO₂-based processes that can be considered as quasi carbon-neutral, depend on their economic competitiveness and environmental impact. According to Oyama et al. (2012), the only scenarios where dry reforming might be considered is where the supply of methane is contaminated with carbon dioxide, and that there are no facilities for separation, or where syngas with a H₂/CO ratio of unity is desired.

Gangadharan et al. (2012) evaluated the economic and environmental impact of combining CO₂ reforming with steam reforming of methane. The results indicate that combined reforming process has a lower carbon footprint. The total capital investment, utility costs and energy consumption of the combined process is higher than those of the steam methane reforming. The overall environmental impact is about the same for the two technologies but the global warming potential of combined reforming is lower. In another study, a 67% reduction in CO₂ emissions was calculated when comparing optimized combined reforming and steam reforming (Lim et al. 2012).

Zhang et al. (2013) compared bi- and tri-reforming economics for methanol production. The tri-reforming and bireforming processes require 19.0 kWh and 11.5 kWh per kg of CO₂ converted, respectively. But, the methanol production rate was much higher from the tri-reforming process, which suggests trireforming process will be more economical and profitable for CO₂ utilization from flue gases in industrial scale.

Minutillo and Perna (2009) carried out an extensive investigation on the treatment of CO₂ from fossil-fuel-fired power plants, using the tri-reforming process integrated with electrical power co-generation. An impressive estimated reduction in CO₂ emissions close to 85% was calculated.

Fu et al. (2010) reported on the economics of high-temperature steam/CO₂ co-electrolysis process and compared to the biomass process to Fischer–Tropsch fuel. Although it is not yet a mature technology, the study showed the availability of cost-effective electricity is crucial for its economic competitiveness. As an energy-intensive process, preferred electricity sources are nuclear and surplus wind power with which synthetic fuels could be produced at a cost comparable to biomass to liquid (BTL) process. However, the by-product of the electrolysis process, pure O₂, can be sold to reduce the production cost of syngas. In addition, when the electrolyser operates at thermoneutral voltage, only a small amount of extra heat (4% of the total energy input) is needed as it is thermally self-sustainable.
Lebouvier et al. (2013) assessed CO₂ dissociation by plasma-based technologies and made a comparative review of the energy involved per mole of syngas. The comparison shown in Figure 2.5.1 highlights the challenges to be overcome for CO₂ dissociation to be a competitive technology.

![Figure 2.5.1](image)

**Figure 2.5.1** Energy cost for the production of 1 mol of syngas through different processes. (A) Perfect CO₂ dissociation-100% conversion, 100% chemical energy efficiency; (B) CO₂ dissociation by dielectric barrier discharge; (C) CO₂ dissociation by thermal plasma jet; (D) CO₂ dissociation by DC corona discharge; (E) CO₂ dissociation by gliding arc plasmatron; (F) CO₂ dissociation by dielectric barrier discharge with catalyst; (G) CO₂ dissociation glow discharge with catalyst; (H) perfect dry reforming; (I) dry reforming by glow discharge; (J) dry reforming by microwave discharge; (K) dry reforming by binode thermal plasma; (L) perfect steam reforming; (M) partial oxidation-pilot plant (Texaco Shell); (N) partial oxidation by gliding arc Tornado; (O) autothermal reforming-pilot plant; (P) coal gasification-fixed bed, bituminous (Sasol-Lurgi); (Q) coal gasification-fixed bed, lignite(Sasol-Lurgi); (R) coal gasification-fixed bed, anthracite (Sasol-Lurgi); (S) coal gasification-slagging bed, bituminous. Reprint from permission of Lebouvier et al. 2013 (American Chemical Society).

However, the technologies presented are at a different level of maturity. Learning by doing may be expected to decrease the cost of SOEC and plasma-based technologies in the future. Globally, the usage of CO₂ to syngas is an economic driver for producing fuel with the transport sector as the main market. A potential barrier for its development is alternative transport systems such as electric vehicles that may be a more competitive solution with low cost of off-peak grid electricity.
2.6 CONCLUSIONS

The usage of CO$_2$ for syngas synthesis implies the reforming process of methane or the co-reduction with water. However, other reforming, partial oxidation and gasification technologies are also producing syngas. Therefore, the viability of the CO$_2$-economy to syngas depends on a number of factors, including feedstock price and availability along with those of energy sources. All the processes are energy-intensive due to the chemical energy involved in breaking C-O and C-H bonds. Moreover, high feedstock conversion require operation at high temperatures due to thermodynamics. Therefore, the efficiency of energy converters and heat recovery units in the train of reactors is of paramount importance for the process to be competitive. Economy of scale is also a key factor for the choice between the allothermal and autothermal technology.

Separation, purification and additional units add complexity and cost to the syngas process. Syngas of the right composition can be produced by combining CO$_2$ and H$_2$O reforming. In such a way, large amounts of CO$_2$ can be consumed while at the same time the downstream WGSR units are avoided. Combining CO$_2$ and H$_2$O reforming with partial oxidation can produce syngas directly from flue gases.

In the CO$_2$ conversion processes described in this chapter, net CO$_2$ consumption is better achieved where renewable energy use is made possible. Dry reforming is not an efficient means of producing hydrogen because part of it goes into water via the reverse WGSR. The scenarios where dry reforming can be considered are where CO$_2$-rich methane feedstock is available. This can be encountered for biogas and for natural gas fields, the exploitation of which is currently uneconomical due to the cost of separation.

The choice of the technology for syngas production depends on the scale of operation. The renewed interest in biomass as a carbon resource fosters the development of gasification technology, which is an indirect conversion of CO$_2$ to syngas. Technologies best suited for small-scale operation will allow low-scale sources to be exploited. These technologies should be simpler than those of conventional reformers, and modular to be removed from one place to the other after the resource is exhausted. The SOEC technology is being implemented with the advantage of a feedstock composed of CO$_2$ and H$_2$O for producing syngas and O$_2$ as by-product which can be sold bringing additional profit to the process. The plasma technology is also developing but still at the laboratory scale.

The current different possible routes to syngas are summarized in Scheme 2.6.1.
Scheme 2.6.1  Schematic representation of the network of processes to syngas.

2.7  REFERENCES


3. CO₂ CONVERSION TO SYNTHETIC NATURAL GAS (SNG)

3.1 SNG PRODUCTION: INTRODUCTION

The production of synthetic natural gas (SNG) from synthesis gas was of considerable interest in the 1970s as a shortfall of natural gas supplies was anticipated (Satterfield, 1991).

There are several existing ways to produce SNG from fossil raw materials, and biomass also offers several advantages when considering it as a raw material in SNG production. The utilization of CO₂ to produce synthetic natural gas which can further be converted to value added chemicals and fuels are reported in many literature reviews (Aresta, 2007 and 2010; Appel et al., 2013). It is also advised that in order to reduce significant amounts of anthropogenic CO₂ emissions, CO₂ in flue and exhaust gases must be converted into fuels rather than chemicals (Centi et al., 2009). Thus, technologies that enable a highly efficient and environmentally benign conversion of climate-damaging CO₂ and hydrogen from biomass into – storable – methane are of crucial need (PR&D 2013).

3.1.1 Needs for SNG Production

SNG production is currently considered to be commercialized and the research interest towards this matter has increased worldwide due to the rising price for natural gas and the tendency for diminishing the dependency of fossil based natural gas in general. Coal, crude oil, and naphtha can be considered as conventional feedstocks for synthesis gas production which can be further converted to SNG. Besides fossils limited reserves, the need for decreasing greenhouse gas emissions is another main motivation in increasing the usage of alternative feedstock such as renewable biomass and other feedstock such as CO₂. The production of synthetic natural gas (SNG) to replace natural gas as a fuel has advantages such as the already existing gas distribution infrastructure (e.g. pipelines) and the established and efficient end use technologies (e.g. compressed natural gas cars, heating systems, and power stations). Upgraded methane (both synthetic and from natural sources) can be used as an engine fuel or in heat and power generation, but presently it represents only local markets. (Kopyscinski et al., 2010; Zhang, 2010, Kopyscinski et al., 2013; Bidart et al., 2013) When the feedstock in SNG production is lignocellulosic biomass from forest or agricultural residues, SNG is considered a second generation biofuel. Harvesting second generation feedstock interfere the food economy and strain land, air and water resources much less than the first generation biofuel production. (Zhang, 2010).
An innovative process for storing electricity generated from renewable energy sources has come to the market by Austrian company Krajete GmbH. The process is based on microorganisms that enable a highly efficient and environmentally friendly conversion of CO$_2$ to methane of high purity. The demand for this type of a process for the manufacture of ultra-pure methane is important in numerous application areas. The process is useful for the storage of excess renewable energy from solar, wind and hydropower plants, the so called "power to gas" approach (see Chapter 4) and it is also suitable for the purification of raw biomass to produce pure methane and the production of 5th generation biofuels. The conversion of CO$_2$ and H$_2$ to natural gas takes place in a bioreactor over special strains of Archaea microorganisms (PR&D 2013).

### 3.1.2 CCS and CCU

Carbon capture and storage (CCS) is considered as one of the possible technologies in the portfolio of mitigation options that can contribute to emission reductions. Regardless of promises, the research and project experience in recent years have shown that significant flaws are related to the CCS concept. Capturing of CO$_2$ means high investment costs, notable variable operating costs and in most cases leads to a significant energy penalty for a power plant.

Rather than considering CO$_2$ as waste, it can take a role as a chemical feedstock for the syntheses of valuable chemicals and fuels. Although such carbon capture and utilization (CCU) options are still in the research phase, with the current estimated costs therefore high, strategic research can make these options more feasible. It is necessary to develop processes and technologies for a resource- and energy-efficient process industry (Aresta, 2010; Centi and Perathoner, 2013). These processes can build upon current post-combustion CCS technologies to generate value-added products that can in theory compensate the costs of plant investment or even make the process profitable. Currently, only pilot scale installations are in operation but they have a potential and economic viability to be scaled-up (Styring et al., 2011). The reactor technology and novel active selective and stable catalysts will need to be developed if this CCU option is to play a significant role at a commercial scale. It is possible and even likely that costs can be brought down so much that in specific areas, CCU can be more attractive than the storage of CO$_2$. This is demonstrated in the case studies where synthetic liquid fuels and cyclic carbonates are considered as commercial products from CO$_2$ in flue gas (Styring et al., 2011).

Carbon dioxide is considered to be a thermodynamically and chemically stable molecule. The carbon atom in CO$_2$ is in its most oxidized state. So, CO$_2$ is the lowest in energy of all carbon-containing binary neutral species and is therefore relatively unreactive (Aresta and Dibenedetto, 2007). Its Gibbs free energy of formation has a large negative value ($\Delta G_f = -394.6$ kJ/mol) (Lide, 1993), which contributes to the high inertness of CO$_2$ and renders its reactions energetically unfavorable. However, it can under certain conditions react with other chemical feedstocks given sufficient energy or using a catalyst to produce value-added commodity chemicals. In general, if CO$_2$ is incorporated as the entire moiety into a compound, the energetic of the process is around to be favorable, while if one reduces carbon, energy will be required. Thus, the reactions in which CO$_2$ is involved can be divided into two main categories (Aresta et
Low energy processes, in which C maintains its +4 oxidation state or is lowered by only one unit (a C–C bond is formed). Such processes bear to the formation of carboxylates, carbamates, carbonates, ureas, polymeric materials, inorganic carbonates and hydrogen carbonates, and any similar compounds. These reactions do not need much additional energy and hence occur at lower temperatures (240 – 400 K). High energy processes, in which C goes down to oxidation states lower by at least two units below +4 are the formation of HCOOH, CO, H₂CO, CH₃OH, CH₄, hydrocarbons and similar compounds. Because they require a large amount of energy, they typically occur at high temperatures (600 – 1,000 K).

At the moment, carbon dioxide consuming synthetic organic chemicals production was estimated to be globally about 200Mt (Aresta et al., 2013). Only a few industrial processes utilize CO₂ as a raw material today (Table 3.1.2.1). However, if new catalytic processes are developed that may bring to new polymers or new chemicals, the amount of CO₂ used will grow but will stay at around 300–500 Mt/y, at the best (Aresta and Dibenedetto, 2007; Aresta et al., 2013). The potential catalytic reactions for carbon dioxide can be for example reforming of CH₄, hydrogenation to methanol, synthesis of dimethyl carbonate with methanol, reaction with propylene glycol and synthesis of cyclic carbonates with epoxide or ammonium salt (Ma et al., 2009).

### Table 3.1.2.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Production (Mt)</th>
<th>CO₂ used (Mt)</th>
<th>2016 forecast (Mt)</th>
<th>CO₂ required (Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>155</td>
<td>114</td>
<td>180</td>
<td>132</td>
</tr>
<tr>
<td>Methanol</td>
<td>50</td>
<td>8</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Organic carbonates</td>
<td>0.2</td>
<td>0.005</td>
<td>&gt;2</td>
<td>0.5</td>
</tr>
<tr>
<td>Polycarbonates</td>
<td>4</td>
<td>0.01</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Carbamates</td>
<td>5.5</td>
<td>0</td>
<td>&gt;6</td>
<td>1</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>&gt;8</td>
<td>0</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Acrylates</td>
<td>2.5</td>
<td>0</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.6</td>
<td>0</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>Inorganic carbonates</td>
<td>200</td>
<td>~50</td>
<td>250</td>
<td>70</td>
</tr>
<tr>
<td>Technological fluids</td>
<td>28</td>
<td>28</td>
<td>~300</td>
<td>~300</td>
</tr>
<tr>
<td>DME</td>
<td>11.4</td>
<td>3</td>
<td>&gt;20</td>
<td>&gt;5</td>
</tr>
<tr>
<td>TBME</td>
<td>30</td>
<td>1.5</td>
<td>40</td>
<td>3</td>
</tr>
<tr>
<td>CH₂O</td>
<td>21</td>
<td>3.5</td>
<td>25</td>
<td>5</td>
</tr>
</tbody>
</table>

**Higher alcohols**

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

Bolded numbers mean actual values, italics are estimates, empty cells - no information

CO₂ Conversion to Synthetic Natural Gas (SNG) | 55
3.2 TECHNOLOGIES FOR SNG PRODUCTION FROM SYNGAS

Production of SNG from solid carbon sources, such as coal requires thermo-chemical processes which can reach up to 65% over all chemical efficiency (i.e. chemical energy output of SNG compared to chemical energy input of feedstock). In comparison, wet biomass converted to methane by anaerobic digestion can reach 20-40% overall chemical efficiency. Another route to produce SNG from wet biomass more efficiently is via the hydrothermal gasification process which is suitable to convert wet biomass into a fuel gas with a high heating value. These processes are operated under high pressures (> 220 bar), but at much lower temperatures (~ 670 K) than temperatures (1073-1173 K) required of the typical gasification. (Kopyscinski et al., 2010; Rabou and Bos, 2012)

The production of SNG via the thermo-chemical process consists of several conversion steps as shown in Figure 3.2.1. The first step is the gasification to produce syngas or producer gas. Both consist of H₂, CO, CO₂, and H₂O but the producer gas also contains CH₄, and other hydrocarbons. The next step is the gas cleaning and conditioning step to remove impurities and catalyst poisons. The most common conditioning steps are steam reforming and water gas shift reaction. The third step is the fuel synthesis which is a heterogeneously catalyzed process to produce methane from carbon oxides, main reaction being CO methanation. The loss of heating value is higher with syngas than with the producer gas because producer gas needs only partial conversion. The fourth step is the fuel upgrading to remove water and carbon dioxide in order to fulfil the quality specifications of gas grid or biofuel (Kopyscinski et al., 2010; Rabou and Bos, 2012).

![Figure 3.2.1 General scheme of the process chain from a solid carbon source to SNG (modified from Kopyscinski et al., 2010).](image)

Technologies and catalysts for producing SNG based on coal have been intensively studied in the sixties and seventies mainly in the United States, Germany and Great Britain. Several methanation processes have been developed including fixed bed and fluidized bed systems and other concepts such as synthane process (Pennline et al., 1980), catalytic coal gasification (Gallagher and Euker, 1980), and liquid phase methanation (ChemSystemInc, 1979). The developed fixed bed methanation processes include Lurgi, TREMP, Conoco/BGC, HICOM, Linde, RMP, and ICP/Koppers processes. The developed fluidized bed methanation processes are Bureau of Mines, Bi-Gas, and Comflux processes. Both methods, fixed and fluidized bed concepts, allow combining water gas shift and methanation reactions in the same device to adjust the H₂/CO ratio leading to high flexibility in the composition of the feed gas. Fluidized
bed methanation allows isothermal operations due to high heat transfer coefficients while the catalysts need to stand attrition. In the fixed bed reactors heat is usually removed by combining intermediate gas cooling and gas recycle leading to higher number of reactors, heat exchangers etc. From the catalytic point of view, sintering due to high reaction temperatures has to be taken into account. (Kopyscinski et al., 2010)

During these earlier studies, demonstration and pilot plants were set up but only one commercial syngas based SNG plant was built. In 1984 the Great Plains Synfuels Plant, now operated by the Dakota Gasification Company, started its operation and ever since has been producing 1.53 billion m$^3$ SNG every year. The plant consists of 14 Lurgi Mark IV fixed bed gasifiers, shift conversion units, Rectisol scrubbers (CO$_2$ and sulphur removal), fixed bed methanation units with recycle, a SNG compressor and a dryer. The compressed gas with a heating value of 36.3 MJ per cubic meter leaves the facility for sale (Kopyscinski et al., 2010; Dakota Gas, 2013).

Recently several new processes for SNG production have been developed, concentrating mainly on biomass feedstock where the main challenges are in process gas production and gas cleaning steps. The main components in biomass based process gas include H$_2$, CO, CO$_2$, H$_2$O and CH$_4$ (depending on the gasification temperature). Minor components such as sulphur compounds, ammonia, tars and dust loads must be removed from the gas. New SNG process concepts need to consider the biomass logistics resulting in either a few big plants (>400 MW$_{SNG}$) at sites where biomass can be easily transported (e.g. harbors) or a higher number of smaller plants (<100MW$_{SNG}$). In the smaller plants down-scaling the technology from SNG-from-coal processes, especially integrating the traditional cold gas cleaning, is not possible due to efficiency and financial limitations. In consequence, simpler gas cleaning strategies are needed (Rabou and Bos, 2012; Kopyscinski et al., 2013).

An additional challenge in biomass based SNG production is the catalyst’s stability in the methanation step since methane rich producer gas contains also unsaturated (e.g. 2-4% ethylene) and (poly)-aromatic hydrocarbons (= tar), which are converted into solid carbon over Ni catalysts causing deactivation. Excess steam can be used to reduce tar, but at the same time the heat demand grows and the efficiency of gasification reduces. To prevent problems, hydrogenation and pre-reforming of hydrocarbons into ethane, CH$_4$, CO and H$_2$ is needed. An alternative is to separate these harmful compounds from the producer gas and find a different application for them but e.g. selling them as chemical feedstock would be an attractive option only at large scale. A totally different approach is to use isothermal fluidized bed technology where the catalyst is internally regenerated during the methanation enabling catalysts stability without ethylene removal (Rabou and Bos 2012; Kopyscinski et al., 2013).

In 2002 the Energy Research Centre of the Netherlands (ECN) began its studies in the feasibility of SNG production from biomass and development of indirectly heated MILENA dual fluidized bed gasifier technology for SNG production from biomass targeting at least 70% energy efficiency. In the MILENA process warm gas cleaning technology OLGA (oil gas wash) is used to remove tar efficiently while light aromatic compounds and unsaturated hydrocarbons remain in the gas representing a significant part of the producer gas heating value. In order to reach the desired high efficiency process, the producer gas has to reach high benzene conversion into
methane and to achieve this, efficient sulfur removal e.g. without the loss of valuable benzene and toluene is needed. The ongoing activity focuses on the construction of an 800 kWth pilot plant. In Figure 3.2.2 it is shown how the future SNG-from-biomass system could look like (Rabou and Bos, 2012; Kopyscinski et al., 2013; ECN 2013).

Figure 3.2.2 High-efficiency SNG production system (modified from Rabou & Bos, 2012).

The Center for Solar Energy and Hydrogen Research (ZSW) in Stuttgart, Germany has developed the Adsorption Enhanced gasification/Reforming (AER) process where low temperature gasification in dual bed gasifier is utilized to produce hydrogen-rich gas from biomass. Then this AER producer gas is turned to SNG by fixed bed methanation over a commercial nickel catalyst in a molten salt cooled multi-tubular reactor. (Kopyscinski et al., 2010; US Patent Application, 2013)

At Paul Scherrer Institute (PSI) in Switzerland research about the conversion of dry biomass to SNG has been carried out for about ten years. As a consequence the construction of 1 MW_SNG semi commercial Process Development Unit (PDU) was completed in 2009 allowing the demonstration of the complete process chain from wood to SNG. The PDU consists of Fast Internally Circulating Fluidized Bed (FICFB) gasification, gas cleaning, Comflux® fluidized bed process methanation, and gas purification producing 100 m³/h of high quality synthetic natural gas (Kopyscinski et al., 2010).

At PSI a new technology, called SunCHem, is under study. In this process bio-methane is produced via hydrothermal catalytic gasification of microalgae, where the produced nutrients, water and CO₂ are recycled. The two main parts of this process are growing of microalgae and hydrothermal gasification of biomass, which both have been previously studied independently but now in this technology these two parts are joined into a new concept. The experimental work is e.g. about the investigation of the supercritical catalytic gasification of different species of microalgae, and about the influence on the growth of algae of nickel, which is a trace contaminant that may be present in the effluent recycled from the gasification to the methanation step (Haiduc et al., 2009).
3.3 SNG PRODUCTION FROM CO₂

The reaction of CO₂ methanation that is the hydrogenation of CO₂ to methane (Eq. (3.1)) has been known for over a century as the Sabatier reaction but has received renewed interest recently for the development of new CO₂ fixation technologies.

\[
\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad (3.1)
\]

Carbon dioxide turns out to be an important C₁ building block to obtain high added value molecules from a safe, economic and renewable carbon source, and its utilization also contributes to the mitigate global warming. Moreover, renewable hydrogen should be used as a co-reactant to synthesize SNG by hydrogenation of carbon dioxide from different sources. Methane can be stored and distributed safely in huge quantities through infrastructures that already exist for natural gas (Park and McFarland, 2009).

It is important to convert CO₂ to fuels or raw materials which are easily transportable. However, there are not yet many commercial plants established using CO₂ as feedstock, in our best knowledge at the moment, the first SNG plant has just been started to operate in Werlte, Germany. The new plant will produce around three million m³ of renewable synthetic methane per year (NGVA Europe, 2013; Clariant, 2013; Park and McFarland, 2009).

3.3.1 Catalytic CO₂ conversion

The methanation of carbon dioxide is thermodynamically favorable at low temperatures (ΔG²⁹₈K = -130 kJ/mol). Thus, the methanation process generally operates at around 670 K (Gao et al., 2009). The methanation reaction is highly exothermic (ΔH²⁹₈K = -165 kJ/mol). However, an eight-electron transfer process is needed to reduce the most oxidized form of carbon to methane and due to the kinetic limitations an effective catalyst is needed to achieve acceptable reaction rate and selectivity (Park and McFarland, 2009).

3.3.1.1 Catalysts

Most of the methanation studies have been focused on metal-based catalytic systems. Both homogeneous and heterogeneous catalysts have been applied to CO₂ hydrogenation. Although homogeneous catalysts display suitable activity and selectivity, the regeneration of catalysts is not straightforward. In contrast, heterogeneous catalysts are preferred considering stability, separation, handling and reuse. (Jessop et al., 2004, Centi and Perathoner, 2009)

The methanation of CO₂ has been extensively studied and reviewed using numerous catalytic systems based on the group VIIIB transition metals (e.g. Ni, Co, Pd, Pt, Ru and Rh) supported on various metal oxides (e.g., Al₂O₃, SiO₂, TiO₂, ZrO₂ and CeO₂). The catalysts used have many similarities to those for CO₂ reforming (dry reforming). CO₂ hydrogenation has been studied and described recently by using various catalysts including Ni/γ-Al₂O₃ (Rahmani et al., 2013), Ni/SiO₂ (Chang et al., 2001), Ni/TiO₂ (Liu et al., 2013), Ni/ZrO₂ (Perkas et al., 2009), Ni/CoO₂ (Tada et al., 2012), Ni/La₂O₃ (Song et al., 2010), Ni-Mo/Al₂O₃ (Aksoylu et al., 1999), Ni-Al
alloys (Abello et al., 2013, Lee et al., 2005), Ni-Fe alloys (Sehested et al., 2007), Ni-Zr alloys (Yamasaki et al., 2006), Ni-Fe-Ru alloys (Hwang et al., 2013), Ni/CEZrO2 (Ocampo et al., 2009), Ni/ZrO2-Al2O3 (Mengdie et al., 2011), Raney nickel (Sane et al., 1984), Ni/zeolite (Jwa et al., 2013), Ni/HNaUSY zeolites (Graca et al., 2014), LaNiO3 perovskites (Gao et al., 2009), Ni/SiC (Zhang et al., 2013), Ni/MCM-41 (Du et al., 2007), Ni/MSN (Aziz et al., 2014), Ni, Co, Pd, or Ru doped CeO2 (Sharma et al., 2011), Co/SiO2 (Guilin et al., 2013), Co/KIT-6 (Guilin et al., 2013), MoO3/CoO-Al2O3 (Jiang et al., 2013), Pd-MgO/SiO (Kim et al., 2010), Pd-Mg/SiO2 (Park and McFarland, 2009), Pt/Tnt (Yu et al., 2008), Rh/γ-Al2O3 (Beuls et al., 2012), Rh/SiO2 (Kusama et al., 2000), Rh/TiO2 (Abe et al., 2009), Rh/Y zeolites (Bando et al., 2000), Ru/Al2O3 (Kusmierz, 2008), Ru and Pd doped MnNi/Al2O3 (Wan Abu Bakar et al., 2013), Ru/C (Kowalczyk et al., 2008), Ru/CNT (Jimenez et al., 2010).

Supported nickel catalysts remain the most widely studied materials (Abello et al., 2013). Nickel based catalysts have been mostly used for methanation reaction because of their relatively low cost, high activity, and the best selectivity to methane as compared to other metals. All commercial methanation catalysts are Ni-based (Nguyen et al., 2013). Nickel is not the most active methanation catalyst but provides the best methanation activity per unit cost while maintaining a high selectivity towards methane (Bligaard et al., 2004). However, a high activation temperature (above 620 K) is generally needed to achieve the maximum CO2 conversion, which results in undesirable influences on the stability/lifetime of the catalysts as well as increased energy consumption (Park and McFarland, 2009, Chang et al., 2003, Yamasaki et al., 2006). Many studies have focused on improving the stability of nickel catalysts by varying support materials, promoters, and preparation methods (Liu et al., 2011, Gao et al., 2012, Yu et al., 2011, Zhao et al., 2012, Hu et al., 2012, Bartholomew et al., 1983). It has previously been shown that the methanation reactions are highly sensitive to the structure of the catalyst (Andersson et al., 2008), and that methanation only occurs on Ni step sites, which account for only a small fraction of the total active Ni sites (Rostrup-Nielsen, 1975). The exact fraction varies greatly depending on the catalyst preparation method and characteristics, but an averaged level for a number of Ni catalysts is in the order of 5% (Rostrup-Nielsen, 1975).

RANEY nickel (alloy of aluminum and nickel), which is well-known as an active catalyst for hydrogenation appears to have high reactivity in the methanation reaction. The notable catalytic performance is attributed to its unique thermal and structural stability as well as a large BET surface area (Sane, 1984).

One of major problems of Ni-based catalysts is the deactivation due to the interaction of the metal particles with CO and formation of mobile nickel carbynls that are extremely poisonous and can easily leads to sintering of metal particles due to the very exothermic nature of the methanation reaction (Agnelli et al., 1994, Ocampo et al., 2011). In addition, nickel catalysts are susceptible to solid carbon formation occurring at low temperatures in the methanation reaction. Instead, noble metals catalysts (e.g. Ru, Pd, Pt and Rh) are stable at operating conditions, more tolerant against solid carbon and more active for CO2 methanation than nickel catalysts. However, noble metal catalysts are notably more expensive than nickel based catalysts limiting their use in the catalytic hydrogenation of CO2. The Ru catalyst has an excellent low temperature CO2 catalytic methanation activity compared to other studied precious metal catalysts,
exhibiting high CO₂ conversion at 673 K (Lu et al., 2005). It has been found that Ru and Rh are much more active hydrogenation catalysts as compared to Pt and Pd, which promote the undesired reverse water gas shift reaction (Jimenez et al., 2010).

Supports with high surface area, usually oxides, have been applied extensively for the preparation of metal catalysts. The nature of support plays a crucial role in the interaction between nickel and support, and thus determines catalytic performances towards activity and selectivity for CO₂ methanation (Chang et al., 2003). Presently, various materials are used as the support for nickel catalysts such as γ-Al₂O₃, SiO₂ (amorphous and mesoporous silicas), ZrO₂, CeO₂ and zeolites. (Rahmani et al., 2013, Zhou et al., 2013, Tada et al., 2012, Wang and Gong 2011)

CeO₂ is generally used to improve the performance of alumina. CeO₂ can affect the thermal and structural stability of alumina, the degree of dispersion of active ingredients on the Al₂O₃ carrier, and the storage and release of oxygen by the catalyst. (Gao et al., 2009b) ZrO₂ is another support of interest due to its acidic/basic features and CO₂ adsorption ability. Ni/ZrO₂ catalysts with various amounts of ZrO₂ polymorph can be prepared from amorphous Ni–Zr alloys (Yamasaki et al., 2006). Zeolites are among attractive support materials since they normally have high thermal stability, affinity to carbon oxides and large surface area (Jwa et al., 2013).

Supports such as carbon nanofibers could be an alternative to the classical support materials (alumina, silica, TiO₂, etc.) widely studied on the literature due to their excellent characteristics such as the high purity of the material, high mechanical strength and mesopore nature which results in low internal mass-transfer resistances (Díaz-Taboada et al., 2009).

The co-precipitation method has been considered as the most conventional method for the preparation of mesoporous nickel–alumina catalysts due to its high reproducibility. The co-precipitation method has also advantages such as high metal loading and high metal dispersion compared to the impregnation method (Lok, 2009).

### 3.3.1.2 Reaction mechanism

Although the methanation of CO₂ is a comparatively simple reaction, its reaction mechanism appears to be difficult to establish. There are different opinions on the nature of the intermediates and the methane formation process. Reaction mechanisms proposed for CO₂ methanation fall into two main categories. The first one involves the conversion of CO₂ to CO prior to methanation, and the subsequent reaction follows the same mechanism as CO methanation (Beuls et al., 2012, Eckle et al., 2010, Fischer and Bell, 1996). The other one involves the direct hydrogenation of CO₂ to methane without forming CO as an intermediate.

### 3.3.1.3 Reaction and process technology

Methanation is a highly exothermic reaction. From a thermodynamic point of view, the methanation reaction is favored at low temperature and high pressure. Operating at high pressures generates a large amount of heat per reactor volume compared with the low-pressure condition. The major objectives in the development and optimizing of a methanation reactor are...
the efficient removal of heat from the reactor to prevent the methane yield from being reduced and to minimize deactivation of the catalyst due to the thermal stress at hot spots (Kopyscinski, 2010).

Since the 1970s a number of methanation processes have been developed, comprising both fixed bed and fluidized bed methanation (Kopyscinski, 2010). Most of the units for the catalytic methanation of CO$_2$ have been fixed-bed reactors. A number of current SNG plant designs are based on a series of adiabatic fixed bed reactors with inter-bed cooling. A fluidized bed is inherently suitable for the highly exothermic reaction systems due to the excellent heat transfer and removal capabilities. Moreover, a fluidized bed technique particularly fits the mass production of chemicals in industry. A challenging problem is inevitably encountered for the methanation process that high conversion and selectivity of the reactor performance is difficult to be implemented in a fluidized bed, in which gas and solids back-mixing plays a negative role in the overall reactor performance. Up to now, the fluidized bed methanation reactor is still under-development in a lab or a pilot-plant scale (Martin et al., 2010, Kopyscinski et al., 2011a, Kopyscinski et al., 2011b).

### 3.3.2 Photocatalytic CO$_2$ conversion

Photocatalytic conversion of CO$_2$ to synthetic methane has been studied since decades by several research groups, as the conversion of CO$_2$ to C$_1$ products have been demonstrated first time in 1979 by Honda and co-workers (Mao et al., 2013; Varghese et al., 2009). However, recently the interest towards methane production has again increased as there is a growing need for SNG and the photocatalytic reactions can be done under mild conditions (low temperature and pressure), which is encouraging the development of this technique (Tahir and Amin, 2013a, Mao et al., 2013).

In photocatalytic CO$_2$ reduction the catalysts have a significant role as several multistep reactions and processes are occurring at the same time on the catalyst surface. At the first step CO$_2$ adsorbed on a photocatalysts’ surface, then interacts with photogenerated electrons and hydrogen, yielding finally a set of various products mainly C$_1$ (such as CO, methane, methanol, formic acid, formaldehyde) but possibly also C$_2$ and higher hydrocarbons. (Wu et al., 2013; Varghese, 2009). As the reaction is endothermic the energy required must be provided and one possibility is to use sunlight as the energy source. The development of photocatalysts using solar energy may provide an energy efficient way to produce chemicals from CO$_2$ (Tahir and Amin, 2013a, Mao et al., 2013).

The overall reaction for the photocatalysis of CO$_2$ with water (Eq. 3.2) or with protons (Eq. 3.3) is as follows. It has been noted that the methane formation reaction requires eight photons. The thermodynamic reduction potential ($E^\circ_{\text{reaction}}$) of CO$_2$ to methane at pH 7 is determined to be -0.24 V vs. normal hydrogen electrode (NHE) (Tahir and Amin, 2013a, Hong et al., 2013, Mao et al., 2013, Varghese et al., 2009):
Recently there are studies which have been concentrated to find out the detailed mechanistic steps to improve the efficiency of the CO₂ conversion. Some of the studies have utilized the surface intermediate detection by e.g. DRIFT for identification of the reaction mechanistic steps. In addition, the mechanistic approach could help to develop visible light driven reaction routes (Wu et al., 2013, Look and Gafney, 2013). For example, Look and Gafney (2013) have proposed a more detailed reaction mechanism for methanation of CO₂ via the Fischer–Tropsch sequence (Eq. 3.4):

\[
\text{CO}_2\text{ads} + 2\text{H}^+ \rightarrow \text{HCOOH} \rightarrow \text{H}_2\text{CO} + 2\text{H} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4 \tag{3.4}
\]

The most crucial challenge to meet in the CO₂ conversion to methane and other C1 products is that CO₂ is a very stable molecule which does not absorb visible or ultraviolet radiation. So, efficient photocatalysts are needed to be developed. Some of the developed and studied photocatalytic materials for SNG production are summarised in Table 3.3.2.1.

<table>
<thead>
<tr>
<th>UV light</th>
<th>Visible light</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-C (&lt;280 nm)</td>
<td>Ni-NiO/InTaO₄, AgBr/TiO₂, CeSe/Pt/TiO₂, Cu/Pt/TiO₂</td>
</tr>
<tr>
<td>UV-B (280–315 nm)</td>
<td>TiO₂, ZrO₂, Ag/TiO₂, TiO₂-P25, K/Y-zeolite, MgO, Zn/Ce-LDH, Zn/Ti-LDH</td>
</tr>
<tr>
<td>UV-A (315–380 nm)</td>
<td>TiO₂, Cu/TiO₂, Ti-MCM-41, Ti-MCM-48, Ag/TiO₂, ZnS-MMT</td>
</tr>
<tr>
<td>Wavelength of UV-irradiation not specified</td>
<td>TiO₂/SiO₂, Ti/Si-h-c, TiSBA-15, Ru-RuO/Ti-NPs, Li₂O/TiO₂ over MgO and/or Al₂O₃, Cu/ZnO, TiO₂/Pd/Al₂O₃, Au/Ti/SBA-15, Ti/SBA-15, K Nb₃O₈, HNb₃O₈</td>
</tr>
</tbody>
</table>

LDH = layered double hydroxide, MMT = montmorillonite modified TiO₂, NP = nanoparticle
The studied materials for CO₂ activation and conversion to fuels in general are e.g. semiconductors and metal complexes, such as various oxides (e.g., Ti, Mg, Zr, Cu, In, W), sulphides (Cd, Bi) and halides (Br, Cl) both in powder and immobilized forms. In addition, decoration of active metals (Ag, Au Cu, Ru, Pt, Rh, etc.) on the photocatalytic supports has been studied widely. Besides the materials, various irradiations from the UV-range (>254 nm) to visible (>420 nm) with Xe, W and Hg-lamps has been studied to activate CO₂. UV-C (250-350 nm) range is the most energetic; however, the most suitable irradiation (i.e. UV-C, UV-B, UV-A, visible) is dependent on the catalytic material and reaction conditions used. It has also been noticed that the CO₂ reduction is accelerated in alkaline solutions. The hole scavenger formation is observed to be promoted in alkaline solutions, thus, increasing the rate of photoactivation on CO₂ (Mao et al., 2013; Tahir and Amin, 2013a; Cybula et al., 2012).

It is worth mentioning that all the studied materials may and/or will promote also several other possible reaction routes which favor production of methanol, formic acid and formaldehyde as well as ethane, CO, and H₂ besides methane. (e.g., Tahir and Amin, 2013a; Mao et al., 2013)

The most important phenomenon is the catalyst’s ability to generate electron-hole pairs by adsorbed irradiation energy. Thus, there is also a need to develop catalytic materials which have the band gap (E_{bg}) between the conductivity and valence bands in a reasonable level to promote the electron-hole pairs formation and, at the same time, prevent the recombination of these. An illustration of the possible reactions over the photocatalyst is presented in Figure 3.3.2.1 (Varghese et al., 2009).

Figure 3.3.2.1  Carbon dioxide conversion to hydrocarbon fuels by sunlight-driven routes (based on Varghese et al., 2009).

The photoreduction of CO₂ and formation of hydrocarbons especially methane is still in the level of experiencing in the laboratory scale. The amounts of CH₄ (and other hydrocarbons) formed during the photocatalytic reactions are in many studies quite low, being from few (<1 μmol g⁻¹h⁻¹) up to around one hundred (100 μmol g⁻¹h⁻¹) at the maximum over the studied catalysts depending on the used irradiation source (wavelength, energy) and catalyst (type and metal). (Mao et al., 2013; Tahir and Amin, 2013a; Varghese et al., 2009, Tan et al., 2006). However, the amount of CH₄ has also been reported to be reached the formation level being at around 350 μmol g⁻¹h⁻¹ over the 20%MMT/TiO₂ catalyst (Tahir and Amin, 2013b).

As a summary, the photocatalytic CO₂ reduction and conversion to SNG and higher hydrocarbons contains a series of reactions both parallel and in series. These reaction mechanisms are not yet fully understood and further research is still needed. Thus, efficient
materials and catalysts are needed to achieve the reasonable levels of the selectivity and the yield of the desired products.

### 3.3.3 Electrochemical CO₂ conversion

In CO₂ utilization one important conversion technology is the electrochemical reduction of CO₂ (ERC). Electrochemically CO₂ is converted into a wide variety of products such as CO, HCOO⁻, CH₄, C₂H₄, CH₃OH, etc. (Halmann and Steinberg, 1999) at different reaction conditions. The ERC is widely studied using different electrocatalysts, and operating conditions. The electroreduction of CO₂ generally takes place in aqueous, and non-aqueous solutions and also in metal mediated complexes (Aresta, 2010). In the ERC process, CO₂ is reduced at cathode electrode to form CO₂⁻ anion and the O₂⁻/H⁺ evolution (Equation 3.5) takes place at the anode by H₂O to form intermediates and products. The balanced reactions with standard potentials (E<sub>o</sub>) versus standard hydrogen electrode (SHE) at anode and cathode are presented as follows.

**Anode:** \[ \text{H}_2\text{O(l)} \rightarrow 2\text{H}^+ (\text{aq}) + 0.5\text{O}_2 (g) + 2e^- \] \[ E_o = 0.0V \text{ vs. SHE} \ (3.5) \]

**Cathode:**
\[ \text{CO}_2 (g) + 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{CO} (g) + \text{H}_2\text{O(l)} \] \[ E_o = -0.103V \text{ vs. SHE} \ (3.6) \]
\[ \text{CO}_2 (g) + 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{HCOOH(aq)} \] \[ E_o = 0.225V \text{ vs. SHE} \ (3.7) \]
\[ 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{H}_2 (g) \] \[ E_o = 0.0V \text{ vs. SHE} \ (3.8) \]
\[ \text{CO}_2 (g) + 6\text{H}^+ (\text{aq}) + 6e^- \rightarrow \text{CH}_3\text{OH(l)} + \text{H}_2\text{O(l)} \] \[ E_o = -0.38V \text{ vs. SHE} \ (3.9) \]
\[ \text{CO}_2 (g) + 8\text{H}^+ (\text{aq}) + 8e^- \rightarrow \text{CH}_4 (g) + 2\text{H}_2\text{O(l)} \] \[ E_o = 0.169V \text{ vs. SHE} \ (3.10) \]
\[ \text{CO}_2 (g) + 12\text{H}^+ (\text{aq}) + 12e^- \rightarrow \text{C}_2\text{H}_4 (g) + 4\text{H}_2\text{O(l)} \] \[ E_o = 0.079V \text{ vs. SHE} \ (3.11) \]

The electrolysis cell (or electrolyzer) mainly consists of two compartments i.e. cathode and anode electrodes with and without gas diffusion layers, and electrolytic solutions (aqueous and/or non-aqueous). The advantages of ERC over other conversion technologies are as follows: operated at ambient conditions, high selectivity, low cost, recycling electrolytes and water (minimal waste), highly possible to use renewable energy (e.g. intermittent sources), commutable, compact design and easy in scale-up (DNV, 2011). The three main parameters which determine the ERC technology’s viability and the performance evaluation are the current densities (J<sub>e</sub>), faradaic (η<sub>e</sub>), and energetic (ε<sub>e</sub>) efficiencies (Equations 3.12-3.14, respectively) (Jhong et al., 2013). The parameters are defined as follows (where, E<sub>k</sub><sup>o</sup> is the equilibrium potential (E<sup>o</sup> <sub>cathode</sub> – E<sup>o</sup> <sub>anode</sub>) and η is the cell overpotentials (cathode + anode)).
Current density: \[ J_e = \frac{\text{Total current produced (A)}}{\text{Total electrode area (m}^2)\text{}} \quad (3.12) \]

Faradaic efficiency: \[ \eta_e = \frac{(\text{no. of electrons exchanged,}\ z)}{(\text{no. of moles of product,}\ n)} \times \frac{\text{Faradays' constant,}\ F}{(\text{charge passed,}\ Q)} \quad (3.13) \]

Energetic efficiency: \[ \varepsilon_e = \sum \frac{E_k^0 \eta_e}{E_k + \eta} \quad (3.14) \]

An efficient ERC electrolyzer should have high current density as well as, high energetic and faradaic efficiency (Jhong et al., 2013). To obtain high efficiency many factors will influence such as

- CO₂ purity
- Optimal electrodes composition
- Electrolyte solution
- Gas diffusion layers
- Optimal operating conditions
- Selectivity and stability.

The list of various metal electrodes, electrolytes, and selective product formation are presented in Figure 3.3.3.1 (with different efficiencies and current densities). In this section, the topic is restricted to ERC to methane (or SNG) formation.

**Figure 3.3.3.1** Electrochemical reduction of CO₂ to methane and ethylene on various studied electrodes, electrolyte solutions (aqueous and non-aqueous) (modified from Halmann and Steinberg, 1999; Jhong et al., 2013).

3.3.3.1 Electrodes for methane production via ERC

The ERC to methane was first reported by Hori et al. (1985 and 1986), a faradaic efficiency was dependent on temperature, at 273K, 70% of efficiency was achieved with 5 mA/cm². The temperature has a significant effect on the products formation at ambient pressure. As reported by Hori et al. (1986) the methane formation decreases as the temperature increases due to presence of intermediates at longer residence times. Electrochemical conversion of CO₂ to methane takes place by eight electron transfers. This multi-electron transfer requires a high electrode potential. Formate and CO are preferentially produced with high current efficiencies compared to methane.
formation via ERC (Whipple and Kenis, 2010). Many authors reported and suggested that producing formic acid and CO with a high yield is much easier than methane and ethylene formation (DNV, 2011, Li, 2010). In ERC, the nature of electrode and its composition are strongly affecting the product distribution and selectivity. A strong interaction and adsorption of CO₂ on the metal is needed in order to undergo the desired reaction path to form CH₄ species (Gattrell et al., 2006 and 2007). The solubility of CO₂ is a very crucial factor which determines the CO₃ads formation on metal electrode, which further undergoes hydrogenation to form methane (Li et al., 2010). Most of the works are reported on ERC using aqueous media but there are a few disadvantages like low solubility of CO₂, deactivation, poor kinetics, by-products formation, and low tolerance to impurities (Li, 2010). In aprotic organic solvents (e.g., methanol) CO₂ has a better solubility compared to water. Even though a few authors have reported excellent efficiencies low current densities have been obtained (Kuhl et al., 2012).

Copper catalyzes CO₂ into hydrocarbons (i.e. CH₄, C₂H₄ etc.) and this topic is well addressed in the scientific literature using different Cu materials (Peterson et al., 2010). A comprehensive review on ERC to hydrocarbons at Cu electrodes was published in 2006 (Gattrell et al., 2006; Kuhl et al., 2012). The mechanism of CO₂ reduction on a Cu catalyst undergoes series of consecutive steps to form various products. First, CO₂ is adsorbed on the electrode to form an anion radical and then it is reduced to CO₃ads. Further, the adsorbed CO is catalyzes on Cu to a more reduced form to hydrocarbons and oxygenates (Kuhl et al., 2012). Peterson et al. (2012) have studied ERC on transition metal catalysts, and found that the protonation of CO is the most critical step in operating at lower overpotentials. At low overpotentials, H₂, CO and formate are formed with high current densities. The CO₃ads, is the main intermediate which is further protonated to form methane (Li, 2010). The copper surface roughness, crystal structure and pre-treatment are the main parameters in methane formation. The deactivation of a Cu electrode was a serious problem which can be solved through various techniques e.g. pulsed electrodeposition (Aresta, 2010). Some authors have reported that efficiencies greater than 75% with reasonable current densities can be achieved but the biggest challenge was the overpotentials (e.g., Kuhl et al., 2012; Peterson et al., 2010).

Another promising route into hydrocarbon fuels is ERC using solar energy on carbon nanotube based electrodes (Genovese et al., 2013). Decorating mono-, bi- and trimetallic (Fe, Cu, Co) compounds on CNTs as electrodes have been investigated and different metal catalysts have been used to form different products. Moreover, the inhibition of surface reactivity toward H₂ evolution is the crucial step to avoid. Recently Li et al. (2013) have reported CO₂-H₂O electrolysis in a solid oxide Ni-YSZ based cell operating at 550-750 °C. They found that, operating at higher voltage (> 2V, 750 °C), methane production was significantly increased and Ru promoted Ni-YSZ promoted hydrogenation of carbon to methane formation.

As proposed by Whipple et al. (2010) that the biggest challenge in ERC is to reduce the higher overpotentials which significantly effecting the efficiency and current density. In order to solve these problems, a new class of Cu based materials and hybrid materials should be designed and tested. It is important to understand the CO₂ interface with Cu electrode in atomic level and a better mechanistic approach is needed. Controlling and optimizing the conditions and improving the durability of Cu need also to be taken into consideration. ERC to methane is foreseen as a
promising way to utilize CO₂ but many technical challenges and economical constrains should be addressed before the process can be commercially applied.

### 3.3.4 Membrane assisted CO₂ conversion

Membrane technology is a well-established and widely studied in gas separation and purification (Kenarsari et al., 2013). There are potential application areas for membranes in SNG production for example in SNG upgrading. The list of possible options to use membranes and membrane based reactor systems are illustrated in Figure 3.3.4.1.

![Figure 3.3.4.1](image)

**Figure 3.3.4.1** Possible configurations for the membrane applications in the framework of SNG production. A) Upgrading and purification of raw SNG via membrane system. B) Three potential options for membrane applications in CO₂ conversion to SNG, membranes for CCS to purify the raw CO₂ gas to high purity gas before feeding it into a methanation reactor, membrane assisted reactor for selective removal of by-product water-vapor and distribution of pure H₂ for example in a Pd-based membrane to control the reaction.
There is a substantial need to develop membranes and membrane based reactor systems for CO2 methanation. As illustrated in Figure 3.3.4.1B, a membrane assisted reactor can be applied in two ways in a methanation reaction loop or a dual membrane mode can be introduced into the reactor system. In the dual mode module, one part will be an extractor type membrane for perm-selective water vapor removal and the second being the distribution and feeding of pure H2 (i.e. a distributor type MR) gas into the methanation reactor (H2 can be produced from renewable energy source). Henceforth, by applying a dual mode membrane type, the exothermic methanation reaction can be controlled and can be operated at low temperature. Furthermore, by continuous H2O removal the reaction will shift towards the product side (i.e. an extractor type MR) which also avoids the catalyst deactivation (Rohde et al., 2008; Hwang, 2009). Hydrophilic membranes like microporous zeolite can be good materials for the perm-selective H2O removal in the methanation membrane assisted reactor (Rohde et al., 2008).

3.4 COMMERCIAL/MARKET SIZE ANALYSIS

3.4.1 Commercialization

Synthetic natural gas (SNG) production has the potential to reduce CO2 emissions by replacing liquefied natural gas (LNG) consumption. Local SNG production can be also considered to increase national security and national economy. SNG has a great potential for fuel consumption in the transport sector and it can replace even about 72% of gasoline and about 40% of the total motor fuel consumption (Naqvi et al., 2012). For example some LNG using ships are already constructed for environmentally conscious sea transporting. Methane is an excellent fuel for Otto-engines (Johansson, 1999). The rapid growth in the number of vehicles in China has given more pressure for environmental protection and energy security due to the oil demand. This shows a great potential for the use of gas as an automotive fuel (Ma, 2013).

When considering the costs of producing SNG directly from carbon dioxide then the market price of carbon dioxide also needs to be predicted. Carbon dioxide will obviously be one of the most interesting feedstocks in the future. Due to numerous carbon capture plannings in the near future, large amounts of CO2 will be available almost free or even with compensation for innovative industrial use (Centi and Perathoner, 2009). The possible compensation is strongly dependent on the future market price of emission permits i.e. carbon credits.

Catalytic steam gasification has several advantages: it does not need any air separation unit and therefore it is more energy efficient and costs are lower also due to low temperature gasification and methanation (Chandel, 2009). Disadvantages in this technique are the need for separation of the catalyst from the reactor ash and the loss of catalyst reactivity. In the methanation process steam is removed from gas by condensation and then the product is ready for commercial use. (Chandel, 2009).

SNG production directly from carbon dioxide can compete with petroleum-based fuels, coal to liquid (CTL) fuels, natural gas to liquid (GTL) fuels and biomass-based SNG gasification fuels
e.g. black liquor gasification (Naqvi et al., 2012; Fu et al., 2010). It can also be predicted that the more important the control of carbon dioxide emissions becomes in the future the broader acceptance the techniques of producing SNG directly from carbon dioxide (or from biomass) can be achieved in the energy and fuel markets.

According to the Fu et al. (2010) the cost for syngas production via high-temperature steam/CO₂ co-electrolysis was 0.775 €/kg from which the capital and maintenance costs were 9.3% and electricity consumption 57.3%. They calculated that the feedstock cost was 31.6% due to carbon dioxide price 160 €/t but this can be predicted to become cheaper depending the CO₂ legislation. The costs were for a plant when syngas productivity was calculated to be 1,845 331 kg/a. Fu et al. (2010) estimated also that if syngas is converted through the Fischer–Tropsch process to provide diesel then the cost would be 1.02 €/l. This was calculated for costs of 44 €/MWh for nuclear electricity and of about 20 €/t for CO₂ from ammonia plants. When oxygen obtained from the plant was calculated to be sold the diesel cost was estimated to be 0.86 €/l (Fu et al., 2010).

Production of syngas from methane via dry reforming has achieved interest because it can be used in a remote natural gas fields for changing LNG to liquid fuel that can be transported more easily and economically than gas (Aresta, 2007). One of the most interesting possibilities in the future can be storing renewable electricity during overproduction and utilizing that energy to SNG production. Oversupply in electricity production periods of renewable sources such as wind, geothermal, ocean waves or sun the production goes waste but in the future it could be a potential way to store the extra energy temporarily by using chemical feedstocks e.g. methane, hydrogen, methanol, ammonia or iso-octane (Pickard, 2013).

### 3.4.2 Markets

SNG consists mainly of methane and the markets can be estimated by considering both LNG and methane markets in the world or also locally. Natural gas prices often drive e.g. electricity market prices and affect the value of all energy producing plants (Costello, 2010). For example if the gas prices are high the energy source can be changed from gas to coal with CCS. Currently 10% i.e. 53 Exajoules of world energy consists of biofuels that includes wood, straw, charcoal, ethanol and methane rich biogas, but potential for it is at least up to 25% of the estimated energy consumption by the year 2035 (Kopetz, 2013). Higher production costs can slow down the use of biofuels but that can be overpassed with e.g. incentives, subsidies or mandanting a minimum percentage of use, as EU has done. These can also create economically lucrative markets for CO₂ to SNG production.

The found and proven LNG reserves are over 56 years and its availability does not seem to be a problem (Lochner and Bothe, 2009). On the other hand LNG is still a fossil fuel so its resources are limited and a production peak could be expected in the future and afterwards the use of it is forced to decrease. If in the near future the growing share of energy will be produced with LNG then the growing demand of SNG could be expected after the LNG resources starts to run dry. Changing the use from LNG to SNG can be done easily when facilities already exist.
The share of gas in the world energy production is growing in the future (World Energy Outlook, 2011). LNG markets are globalizing and three essential changes affecting the markets will be the use of less carbon-intensive fossils, new emerging demands without enough production e.g. China and India, and also declining LNG reserves close to the major demand regions (Lochner and Bothe, 2009). Even though gas is the least carbon-intensive fossil fuel its increasing use will not be enough for sustainable carbon emissions without CCS (World Energy Outlook, 2011).

The European Commission is considering the implementation of a single natural gas market and this could include regulated provision for security of supply and with strategic stocks, and this would increase costs via unutilized arbitrage profits from the unavailable gas stocks (Ejarque, 2011). Therefore, in that situation the commercial SNG producer could achieve some arbitrage profits from the gas markets.

Gas prices in the future in Europe can be dependent also on the strategic behavior of the biggest gas producers due to the growing dependendency on imported gas (Aguilers, 2010).

Increasing distances to the LNG reserves can cause locally higher gas pricing, for example Europe and Japan benefit large gas reserves close to them but USA can suffer significantly (Lochner and Bothe, 2009). On the other hand, current and upcoming increase in North America’s unconventional gas production, i.e. shale gas, can create even excess of gas in a short view (Aguilera, 2010). Also, it is possible that previously unavailable natural gas resources can be used due to higher prices or developing technology.

Estimated SNG production based on agricultural residuals could be about from $555 \cdot 10^8$ to $611 \cdot 10^8$ m$^3$ and it could cover about 30% of the demand growth that China faces until 2020 (Song, 2013). China has natural gas resources but it is rather poor if estimated by gas resources per-capita and due to the urbanization and economic growth China’s gas consumption growth is predicted to continue (Song, 2013). The situation is somewhat similar in all the economically growing countries where the great challenge is to provide energy for poor households. This will cause pressure for the growing use of gas in the future but strategically avoiding the countries growing dependence on imported gas the syntheticallying SNG directly from the carbon dioxide could achieve more interest. One strategically considered perspective is to diversify the energy production in the case of crisis and SNG could give interesting possibility for that. SNG could also be produced locally in remote locations without high transport costs.

### 3.5 PROS AND CONS AND SUSTAINABILITY

The large availability of CO$_2$ due to CSS in e.g. energy production and metallurgical industry can offer a cheap or even zero cost material for innovative fuels and chemicals production processes. CO$_2$ to SNG is one and very important option in this future scenario not only due to the cheap and abundant raw material but also due to the change of the societies to the bioeconomy and gas societies. Gaseous waste streams, i.e. CO$_2$ in flue and process gases and
their wise integration to the biomass streams can offer very innovative and novel concepts in the future in fuels and chemicals production.

Catalysts play a key role when utilizing waste CO\textsubscript{2} as a raw material. Lately many methods, e.g. adsorption and membranes, and catalysts have been developed to recover CO\textsubscript{2} and to use it to prepare fuels and added value chemicals and materials. High energy efficiencies, high reaction rates and valuable products have been achieved by current catalytic technologies. Nanostructured and functional materials are, however, needed to make CO\textsubscript{2} an important and sustainable raw material in the future chemical industry. Catalytic material development for CO\textsubscript{2} to SNG has to face also e.g. higher tolerance towards impurities in raw materials streams, i.e. CO\textsubscript{2} and biomass streams. CO\textsubscript{2} separation from flue and exhaust gases as well as its purification before the SNG production step needs to be solved technically and economically. There is the need to find the best possible technologies for different industries interested in using CCS and CCU concepts efficiently and to make new chemicals and fuels out of its waste streams. The role of hydrogen is also important and a question remains what will be the most optimal hydrogen source for these reactions and how to produce hydrogen economically and without increasing CO\textsubscript{2} emissions.

Sustainability of CO\textsubscript{2} to SNG needs to be assessed parallel to the process design and development of this concept. The sustainability assessment containing three (3) dimensional aspect evaluation, i.e. social, environmental and economic impacts (Manley et al., 2008, Huesemann, 2004, Saavalainen et al., 2013) is crucial to measure the benefits achieved by implementing new production methods for SNG. It allows assessing and comparing the processes utilizing different raw materials, e.g. fossil and renewable, natural resources and waste streams, reaction routes, unit operations, and catalysts to the process being developed. The amount of needed raw materials, resources and produced waste materials can be reduced by proper process development (Niemistö et al., 2013, Saavalainen et al., 2013). Thus, the comparison between conventional process alternatives with the new developed technology can show the potential for sustainability. The assessment will help in optimizing the use of resources and minimizing production costs and impacts on the environment and give competitive advantages in the early design phase of a new process. It can also offer data and thus convince researchers and companies to work more to solve the bottlenecks of the SNG production from CO\textsubscript{2} streams.

The sustainability assessment analysis of the CO\textsubscript{2} to SNG process is a complex issue and thus it is addressed in this section only briefly. In terms of economic impacts, the price of feedstock, i.e. separation and purification of CO\textsubscript{2}, production of H\textsubscript{2} using different raw materials and sources, and finally the costs of SNG production have important impacts. There may be great variations in the production costs of CO\textsubscript{2} and H\textsubscript{2} depending on the selection of raw materials, process technology, and the scale and capacity and finally the location of the plant. The aspect of generating regional added value is very important. The regional added value is defined to be the sum of all additional values originating in a region in a given time period (Heck, 2004). Nowadays, particularly social, ethical and environmental issues should be considered in addition to economic aspects, e.g. cost reduction, cost of power, tax revenues, and generation of jobs. The positive impacts by using waste streams, e.g. CO\textsubscript{2} and waste biomass lead to a reduced need of fossil fuels, GHG savings and better
carbon economy (Demirbas, 2009). In addition, the CO₂ utilizing SNG production process can have direct environmental impacts in terms of increased or reduced energy consumption and waste generation which need to be evaluated. Regarding social impacts, the use of CO₂ in SNG production can have enhanced energy security due to reduced dependency on imported crude oil, and increased employment and customer as well as society acceptance. The need for education and training for the new processes may also positively impact on the societal capital.

3.6 CONCLUDING REMARKS

The production of SNG from synthesis gas has been of considerable interest among chemical engineers because of the shortage of natural gas supplies and the increasing use of biomass.

There are several starting materials and reaction routes to produce SNG from fossil raw materials and also active research to utilize biomass and wastes in SNG production on its way. The utilization of CO₂ to produce synthetic natural gas is the newest trend among research groups in SNG production. Industry has also found and shown some interest to use this abundant and non-toxic molecule, i.e. CO₂ in SNG and further value added chemicals and fuels production.

This approach, if successful, could also offer us a possibility to considerably reduce anthropogenic CO₂ emissions. This area seems to be very appealing and it interests the research communities and young researchers in the field of chemistry, chemical and environmental engineering, even economists. However, technologies to put these ideas forward are needed to enable a highly efficient and environmentally benign conversion of CO₂ and hydrogen from biomass or even water into methane and SNG. Novel and innovative active, selective and stable catalysts are needed as well as new reactor technologies to enable CCU operation at a commercial scale. It is forecasted that costs for the new technology and its development can be reduced so much that in certain industries, e.g. CHP plants the CCU concept can be more attractive than the CCS approach.

There is also a need to convince company researchers and leaders as well as societies to strive towards this goal. The sustainability assessment of the CO₂-concept in SNG production needs to be done to the existing, e.g. fossils based concepts, and other concepts under research to gain the acceptance of the proposed technology from the economic, environmental and social points of view. The idea of combining gaseous waste compounds, i.e. CO₂ together with hydrogen from biomass or organic waste related streams to new and valuable products, i.e. chemicals and fuels can offer several advantages and can be a new step towards resources use optimization and waste minimization as well as diminishing green house gas emissions.
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4. **CO₂ UTILIZATION IN “POWER TO GAS”**

4.1 **STATE OF TECHNOLOGY**

All over the world, the amount of electricity being generated from wind and solar sources is increasing to shift towards carbon-free energy, which can be correlated with climate change policies and carbon resources depletion. One of the main characteristics of wind turbines and photovoltaic (PV) cells is to produce electricity at irregular intervals and energy output depending on wind speed and sun irradiation, respectively. The mismatch between production and use implies that these technologies can only be deployed on a large-scale if downstream processes are set to operate energy storage (Beaudin et al., 2010).

The surplus of conventional electricity supply from power plants is mainly achieved by converting electricity into potential, kinetic and chemical energy with systems such as compressed air, pumped hydro, kinetic hydro, flywheels, supercapacitors, latent heat and batteries (Sandia/DOE, 2012). The choice of the energy storage systems is driven by five main constraints, including location, capacity, duration, response, and cost. The DOE International Energy Storage Database provides free up-to-date information on grid-connected energy storage projects worldwide.

Energy storage issues, as a result of intermittent decentralized production, further leads to the development of the concept of dynamic storage through smart electric and gas grid to meeting reactive power needs and avoiding blackouts. The concept may be referred to as the battery of the future. Large-scale storage of energy would reliably secure the economics of renewable sources. Chemical energy storage concept can effectively store energy over long periods of time according to the capacities of the natural gas grids along with its utilization back to the energy sector and for making chemicals as shown in Scheme 4.1.

![Scheme 4.1](image)

**Scheme 4.1** “Power to Gas” scenario.

In this way, the natural gas network provides additional storage and transport capacities complementing those of the power grid. This chapter focuses on developmental routes to hydrogen and its subsequent utilization to hydrogenate CO₂ hydrogenation to methane.
4.2 CO₂ UTILIZATION IN “POWER TO GAS”

4.2.1 Electricity to H₂

The basics of the “Power to Gas” process is to convert electric energy into chemical energy by the electrolysis technique. The electrolyzer is, therefore, the heart of the system. The current preferred process is based on water electrolysis to produce H₂ and O₂. The hydrogen can then be injected into the existing natural gas or hydrogen pipelines. Alternatively, it can be stored in underground caverns (Forsberg, 2006), as hydrides (Graetz, 2009), or consumed in fuel cells to generate electricity for stationary and transport applications (Emonts et al., 2012), according to the available facilities.

4.2.1.1 Hydrogen usage and production

Hydrogen has been an energy carrier as well as an important feedstock in the chemical industry and in oil refining (Subramani et al., 2010). It has a very high gravimetric energy density of 142 MJ kg⁻¹ (39.4 kWh kg⁻¹) compared with those of natural gas and gasoline of 55.5 and 45.8 MJ kg⁻¹, respectively. The current worldwide H₂ production has been estimated to be about 3.4 trillion standard cubic meter per year. Most of this H₂ is consumed for the synthesis of ammonia and methanol, and used in oil refineries for hydrocracking and hydrotreating processes. At present, steam reforming of methane and coal gasification are the preferred technologies to H₂. However, the processes produce a mixture of CO and H₂ (syngas) which necessitates further downstream purification processes. Water electrolysis to H₂ is also practiced where high purity CO-free hydrogen is needed, but it accounts to roughly 4% of total H₂ production. The foreseen deployment of hydrogen-based fuel cells for integration into the cycle power-gas-power will foster the water electrolysis technology.

4.2.1.2 Hydrogen for energy storage

According to Müller and Arlt (2013), short-term energy storage (minutes to days) strongly depends on the kinetics of H₂ uptake and release. For very short periods (seconds to minutes) hydrogen is not suitable at all. Supercapacitors, flywheels, and batteries are more convenient technologies. To bridge the gap from minutes to hours, compressed or adsorbed H₂ might be the option due to fast uptake and release. From hours to days storage, hydrides as well as organic hydrogen carriers can be used, as their efficiency is high and dynamics are less crucial. For mobile applications the storage density is the primary criterion. Thus, conversion into carbon-based fuels is not only attractive because of the existing infrastructure but also because of the extremely high volumetric storage density of such fuels. Liquid fuels are especially well suited for large units, e.g., trucks, ships. Their usage in small cars for short distances might compete with other options such as batteries and fuel cells.
4.2.2 Electrolysis, Other routes

4.2.2.1 Electrolysis

An electrochemical cell is composed of two electrodes (anode and cathode) connected to external DC electric current. The electrodes are separated by an ion-conducting electrolyte which can be either an acidic or alkaline aqueous solution, a solid polymeric membrane exchanging protons (PEM), or a solid ceramic exchanging O$_2^-$ anions (SOEC). Electrolyzer technologies developed for Power to Gas are based on alkaline, PEM and SOEC water electrolysis cells as sketched in Scheme 4.2.2.

![Scheme 4.2.2: Principle of water electrolysis with (a) alkaline, (b) PEM, and (c) SOEC cells.](image)

Salt-free water is mandatory prior to electrolysis otherwise irreversible poisoning of the system does occur by sludge and chloride deposits. Purification is achieved by reverse osmosis and ion exchange resin to get a residual ionic conductivity value of few μS cm$^{-1}$.

Water dissociation to H$_2$ and O$_2$ is an endothermic process (equation (4.1)) and operates at theoretical potential of 1.481 V at 298 K.

$$
\text{H}_2\text{O}_{\text{liquid}} \rightarrow \text{H}_2 + 0.5 \text{O}_2 \quad \Delta H^0 = +286 \text{ kJ mol}^{-1}
$$

As shown in Figure 4.2.2.1a, 15% of the energy required for electrolyzing water comes from heat and 85% from electricity, at room temperature. At 1,000°C, one-third comes from heat and two-third from electricity. Hence, increasing temperature decreases the electric input, therefore the potential (Figure 4.2.2.1b), and pressure has the inverse effect (Figure 4.2.2.1c). This shows steam electrolysis to be of interest where high-temperature heat is available as it requires less electricity.
Figure 4.2.2.1  Thermodynamics of the water splitting process at 0.1 MPa: (a) energy with temperature, (b) cell voltage with temperature, and (c) cell voltage with pressure at three different temperatures (adapted from Millet, 2012).

The alkaline electrolyzer is commercial technology (Holladay et al., 2009; Gahleitner, 2013). Water is reduced to H₂. The by-species OH⁻ then migrates to the anode to liberate O₂ (Scheme 4.2.2a). The cathode is commonly made of nickel with a catalytic coating of platinum and the anode of nickel or copper. It can operate between 70 and 140°C at pressure ranging from 0.1 to 10 MPa, with efficiency between 50 and 60% producing up to 760 Nm³ h⁻¹ of hydrogen with nominal power up to 500 kW at typical current density of 100-300 mA cm⁻². It has years-lifetime but the main disadvantages are the corrosive caustic liquid electrolyte, H₂ production needs additional gas-liquid separation unit, and not well adapted to fluctuating power sources.

The PEM electrolyzer is simpler in design with the electrolyte being a solid organic membrane such as Nafion® (DuPont trade name for perfluorinated sulfonic-acid-type proton-exchange membranes). As shown in Scheme 4.2.2b, water is oxidized at the anode, then solvated protons migrate to the cathode to be reduced to hydrogen. The electrolysis temperature is maintained as low as possible, typically lower than 80°C to prevent membrane from drying and degradation. The electrodes are made of noble metals such as platinum for the cathode and iridium for the anode (Millet, 2012). Although, high efficiency (55-70%), high current density (>1500 mA cm⁻²) and fast load changes can be obtained (>65%), the technology is still at the demonstration stage due to the high cost of the membrane and electrodes. However, it is more adapted to fluctuating power sources than alkaline electrolysis.

As shown in Figure 4.2.2.1, performing water electrolysis at elevated temperatures (800-1,000°C) decreases the amount of electricity required for the process (equation 4.1) and favors kinetics. The corresponding SOEC process (Solid Oxide Electrochemical Cell), the reverse mode of SOFC for fuel cells, operates with steam that is reduced at the cathode, then O²⁻ migrates to the anode to be oxidized to O₂ (Scheme 4.2.2c). The electrolyte, cathode and anode are made, for example, of yttrium-stabilized zirconia (YSZ), Ni supported on YSZ, and lanthanum strontium manganite-based cermet (LSM-YSZ), respectively (Stempien et al., 2012). Total energy efficiency including heat and electricity is higher than 50% and can reach 90% if
internal waste heat is used to split water. Haldor Topsoe Fuel Cell company is partnering in the RelHy EU project to develop the SOEC technology.

4.2.2.2 Others

Making hydrogen through electrolysis consumes 286 kJ per mole of hydrogen formed (equation (4.1)). This is much more than producing one mole of hydrogen from methane by either steam reforming (4.2), CO₂ reforming (4.3), or dissociation (4.4).

\[
\text{CH}_4 + \text{H}_2\text{O}_{\text{steam}} \rightarrow \text{CO} + 3 \text{H}_2 \quad \Delta rH^0 = +206 \text{kJ mol}^{-1} \quad (4.2)
\]

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2 \quad \Delta rH^0 = +247 \text{kJ mol}^{-1} \quad (4.3)
\]

\[
\text{CH}_4 \rightarrow \text{C}_{\text{graphite}} + 2 \text{H}_2 \quad \Delta rH^0 = +75 \text{kJ mol}^{-1} \quad (4.4)
\]

Water thermolysis is conceptually simple, the need for a high-temperature heat source above 2200°C to achieve a reasonable degree of dissociation and the requirement for an effective technique to separate H₂ and O₂ at high temperatures to avoid explosive mixtures are major barriers to technical success. Thermochemical cycles avoid the separation problem and further allow operation at moderately high temperatures (Holladay et al., 2009). Solar thermochemical water splitting involving redox cycles is under development with solar concentrator devices (Roeb et al., 2012).

Water splitting can also be achieved by photo-electrochemical processes that may involve catalysts for enhancing the process rate through photo-electro-catalytic processes (Du and Eisenberg, 2012; Burschka et al., 2013). The electric current is provided by irradiation of coupled p- and n-type semiconductors which constitute the electrodes. Further research is being actively pursued in this areas for enhancing efficiency in the perspective of long-term development.

4.2.3 CO₂ Utilization in Gas

Captive hydrogen from water electrolysis may be reacted with carbon dioxide to produce methane through the Sabatier reaction (4.5), which is a catalytic process.

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H^0 = -253 \text{ kJ mol}^{-1} \quad (4.5)
\]

The process is exothermic forming water as by-product which means half of initial hydrogen is reoxidized to water. The process is thermodynamically favorable with \(\Delta G^0\) value of -131 kJ mol⁻¹. However, in order to achieve highest rate and selectivity a catalyst is necessary. The catalytic process operates in the temperature range of 300-400°C. Extensive studies have been reported on metal-based catalysts. They include Ni, Pt, Ru, and Rh supported on SiO₂, TiO₂, Al₂O₃, ZrO₂, and CeO₂ (Wang et al., 2011). Supported nickel catalysts have been the most widely studied because of their poor activity in carbon-carbon bond formation via the Fisher-Tropsch process. However, carbon monoxide has been evidenced along with methane formation.
depending on the nature of the support and the synthetic procedure. This observation has led to the proposal that CO₂ hydrogenation is better viewed as CO hydrogenation, CO being formed at first from CO₂. This is still a highly debated topic. A recent report on the process mechanism with Ni-CeO₂ points out CO is better formed by CO₂ activation on the support (Ussa Aldana et al., 2013). The main pathway to methane is the hydrogenation of CO₂. The process is at the research stage, contrasting with the hydrogenation of CO that is practiced on industrial scale for getting CO-free hydrogen from carbonaceous feedstocks.

4.2.4 Enabling Technologies

There is an increased number of international projects and demonstration plants focusing on Power to Gas technology for assessing the economic viability and other concerns such as public acceptance and safety (Gahleitner, 2013; Grond et al., 2013). A selection based on stationary and mobile applications is presented in the following sub-sections.

4.2.4.1 The first full-scale stand-alone wind-hydrogen project in the World

In 2004, Norsk Hydro and Enercon have installed a wind-hydrogen plant in Norwegian Utsira island (6.2 km², 235 inhabitants). Since 2006, it has been operated as an isolated power system with 90% availability (Korpaas and Greiner, 2008). It couples a 600 kW wind turbine with a 48 kW electrolyzer and a 10 kW fuel cell. Hydrogen is stored in a 12 m³ tank to power 10 houses for 2-3 days without wind. Grid stability and back-up are provided by a flywheel and a battery bank (Figure 4.2.4.1).

Figure 4.2.4.1 Utsira wind-hydrogen integrated system.
4.2.4.2 Residential H₂ to power in Denmark

Since 2007, a wind-hydrogen project named "Hydrogen Community Lolland" has been successfully producing hydrogen in Nakskov Industrial and Environmental Park on the island of Lolland, Denmark (Iskov, 2009). The hydrogen is used to power fuel cells for the waste water plant. The oxygen produced by water electrolysis is used to speed up the biological waste water cleaning process. High purity demineralized water is obtained by successive reverse osmosis and ion exchange purification processes (Silhorko Eurowater). There are two PEM electrolyzers of 4 kW each provided by Hydrogenics company, and a 25 m³ hydrogen storage tank under 6 bar from Linde. Downstream, two PEM fuel cells (9.5 kW, IRD Fuel Cell A/S) are installed to produce power and heat. The extension of the technology will include the installation in residential homes and small workshops for providing combined heat and power generation.

4.2.4.3 First sale of residential H₂ to power in Germany

Since 2013, ITM Power (www.itm-power.com) has been partnering with a Thüga Group (the largest network of energy companies in Germany with around 100 municipal utility members). The aim is to develop a 360 kW production unit based on PEM water electrolyzer. The unit will produce 125 kg per day of H₂ in Frankfurt. The technology is unique since it can respond in one second and is self-pressurizing up to 80 bar, permitting direct injection into the German gas grid.

4.2.4.4 Public transportation with H₂ fuel

HyFLEET:CUTE is a large program supported by the European Union which ran for 4 years from the beginning of 2006 to the end of 2009. Being the World's largest hydrogen powered bus project, it has involved the operation of 47 buses for regular public transportation in 10 cities in Europe, Australia and China (Figure 4.2.4.2). More than 8 million passengers have been transported, 2.5 million km travelled and 555 tons of H₂ dispensed.

![Figure 4.2.4.2 Cities involved in the HYFLEET:CUTE project, and bus fueling station in Berlin.](image)

The main challenges to be overcome for commercialization are the purchase price of the buses and hydrogen production which should be cheaper. In addition, hydrogen infrastructure must be
able to operate as reliably as the buses, especially the electrolyser, the hydrogen compressors and dispensing equipment.

4.2.4.5 Public transportation with Hythane<sup>®</sup> fuel

A five-year project was launched mid-2013. The GRHYD demonstration project, led by GDF Suez, will assess the technical, economic and environmental soundness of Hythane<sup>®</sup> fuel. A Hythane<sup>®</sup> bus fueling station in the Dunkirk urban community, France, will be made available at first with a mixture of 6% of hydrogen in natural gas, then up to 20%. In parallel, the injection of hydrogen into a natural gas distribution network will be realized to provide heat to around 200 homes. McPhy Energy will supply the GRHYD project with several solid H<sub>2</sub> storage units for a total close to 200 kg of H<sub>2</sub>.

Similar projects can be found worldwide in Belgium, Germany, Italy, Sweden, Japan, and USA (www.althytude.info/fr/tous-les-documents/).

4.2.4.6 H<sub>2</sub> storage for automobile fueling

Air Liquide in partnership with Daimler, Linde, OMV, Shell and Total is implementing hydrogen fueling station network in Germany. In 2012, the first hydrogen station was opened for the general public in Düsseldorf, Germany. By 2023, the current German network of 15 hydrogen filling stations will be expanded to about 400 hydrogen stations covering the whole country to support the mass production of fuel cell electric vehicles. The overall investment by all partners will be around €350 million. Air Liquide envisioned similar initiatives in Great Britain, France, the Netherlands, Denmark, Sweden, Switzerland as well as in Japan.

The California Energy Commission recently adopted the 2013-2014 Investment Plan Update to support the development of alternative fuels. A budget of $20 million is allocated to hydrogen fueling infrastructure. An estimated 68 stations are needed to support the anticipated rollout of these vehicles in 2015-2017. Roughly 24 stations are built or in development.

4.2.4.7 Solid H<sub>2</sub> storage

The world's first industrial system coupling electrolysis and solid hydrogen storage has been demonstrated in September 2013 by McPhy Energy company. The water electrolyzer is powered by 60 kW of electricity from local electrical grid for producing 12 m<sup>3</sup> of hydrogen per hour. Then, H<sub>2</sub> is stored as magnesium hydride with a storage capacity up to 500 kg (for an energy content of 16.5 MWh). It enables H<sub>2</sub> production at the point of use and aligned with demand.

4.2.4.8 The Audi e-gas for automobile fuel

The German project called Audi e-gas Plant is shown in Figure 4.2.4.3.
In Germany, it is already no longer possible to feed surplus renewable electricity into the grid. Between 2020 and 2030, surplus electric power in the gigawatt range can be expected during specific weather conditions. Since 2013, ETOGAS GmbH (formerly SolarFuel) has been constructing in Wertle (Lower Saxony) a 6-MW plant alkaline electrolyzer with a planned efficiency higher than 54% with the aim of attaining the industrial application stage on behalf of Audi AG automobile company. Electricity is coming from nearby wind turbines, and Clariant is supplying its proprietary methanation catalyst to produce around 1.4 million cubic meters of synthetic methane per year, chemically fixing some 2 800 metric tons of CO₂ from biogass. It will allow to run 1500 new Audi A3 Sportback g-tron vehicles with an annual mileage of 15 000 CO₂ neutral km.

4.3 COMMERCIAL/MARKET OPPORTUNITIES

4.3.1 Markets

The interest in H₂ for the Power to Gas market, combined with the usage in the fuel cell sector, will continue to grow because more projects and demonstration plants are on the track. They are sustained by the increasing availability of distributed electrolysis and low off-peak electricity prices. Moreover, Power to Gas technology addresses the issue of intermittent and variable energy output in offering a dynamic storage solution of the surplus which can be effective over long periods of time. The other advantage lies in the variety of downstream applications and, therefore, markets. Four of them can be easily identified like stationary delivery of power and heat, transport and chemical production. Overall, hydrogen from electrolysis is becoming an increasingly important commercial process. Navigant Research forecasts that global demand for hydrogen from the Power to Gas, Power to Transport, and Power to Power sectors will reach 3.5 billion kg annually by 2030. However, this amounts to roughly 1% of the current estimated production from carbon feedstocks (Subramani et al., 2010). Nonetheless, the shift to non
carbon-based hydrogen production for avoiding carbon dioxide emissions will favor water-based technologies thereby stimulating market introduction of clean technologies.

Scheme 4.3.1 shows the network that can be envisaged where the direct usage of hydrogen may be hampered by safety issues and capacities to be injected into the natural gas grids.

It is, therefore, worthwhile to consider that once formed at the electrolyzer hydrogen should be converted to methane, preferably by carbon dioxide hydrogenation. The methane markets are heat and power generation as well as the production of a mixture of carbon monoxide and hydrogen (syngas) by mature reforming and oxidation technologies. Syngas is already a commercial intermediate to liquid fuels and chemicals. The water electrolysis process co-produces oxygen which is marketable to oxidation technologies.

Scheme 4.3.1 Power and gas grid network for different markets.

4.3.2 Participants

The value chain of Power to Gas involves different industrial actors specialized in water purification, electrolyzer design, gas storage, mobility, catalyst manufacturers, engineering, power and gas providers along with governing bodies to encourage the commercialization of the different technologies. The industrial actors are small to medium enterprises applying their know-how to the business of Power to Gas as well as large companies with recognized expertise either in power, gas or mobility. The business of the large companies will probably be more diversified. As an example Audi AG company, which has a long-established experience in producing cars, is now engaged as electricity and fuel producer.

Table 4.3.2 provides a selection of the list published by Grond et al. (2013) for demonstration projects in Europe.
Table 4.3.2
Selection of Power to Gas Demonstration Projects in Europe (Grond et al., 2013)

<table>
<thead>
<tr>
<th>Project Description</th>
<th>Power installed</th>
<th>Electrolysis Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Werlte D) - Audi AG</td>
<td>6000</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Aragon (S) - IITHER</td>
<td>4000 &amp; 70</td>
<td>Alkaline &amp; PEM</td>
</tr>
<tr>
<td>Falkenhagen (D) - E.ON AG</td>
<td>2000</td>
<td>PEM</td>
</tr>
<tr>
<td>Puglia region (I) - INGRID project</td>
<td>1200</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Grapzow (D) - RH2 WIND project gruppe</td>
<td>1000</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Grabenn (D)</td>
<td>1000</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Hambourg (D) - Vattenfall</td>
<td>900</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Prenzlau (D) - Enetrag AG</td>
<td>500</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Frankfurt (D) - Thuga &amp; ITM Power</td>
<td>360</td>
<td>PEM</td>
</tr>
<tr>
<td>Foulum (DK) Electrochaea</td>
<td>250</td>
<td>PEM</td>
</tr>
<tr>
<td>Stuttgart (D) - Solar Fuel &amp; Fraunhofer IWES</td>
<td>250</td>
<td>PEM</td>
</tr>
<tr>
<td>Karlsruhe (D) - DVGW &amp; KIT</td>
<td>200</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Xermade (S) - Sotavento Project</td>
<td>200</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Herten (D) - Stadt Herten &amp; Evonic Industries</td>
<td>165</td>
<td>PEM</td>
</tr>
<tr>
<td>Leverkusen (D) - CO2RECT Project: Siemens &amp; RWE</td>
<td>100</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Schwandorf (D) - Eucolino: Schmack &amp; Viessmann</td>
<td>100</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Ibbenburen (D) - RWE, CERAM Hyd</td>
<td>100</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Utsira (N)</td>
<td>50</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Freiburg (D) - H2Move: Fraunhofer ISE</td>
<td>40</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Tahivilla (S) - Hidrolica Project</td>
<td>40</td>
<td>PEM</td>
</tr>
<tr>
<td>Stuttgart (D) - Solar Fuel &amp; Fraunhofer ZWS</td>
<td>25</td>
<td>PEM</td>
</tr>
<tr>
<td>SamsØ (DK) - SamsØ Energy Academy</td>
<td>20</td>
<td>undisclosed</td>
</tr>
<tr>
<td>Groningen (NL) - DNV KEMA</td>
<td>7</td>
<td>PEM</td>
</tr>
<tr>
<td>France - GDF Suez GRHYD project</td>
<td>new project</td>
<td></td>
</tr>
</tbody>
</table>

SolarFuel is now ETOGAS

4.4 TECHNICAL/ECONOMIC HURDLES

4.4.1 Cost-effective H₂ Generation, Energy Storage, Others

4.4.1.1 Cost effective H₂ generation

As mentioned above, pilot and demonstration plants are installed around the World aimed at stationary and mobile commercialization. According to the learning curve principle, the electrolysis process cost should drop with the deployment of the technology. Another criterion for cost effective H₂ generation is the price of water purification and its availability. Water consumption by electrolysis may also raise ethical issue where it could compete with its life usages. The price of electricity is also an important factor in cost evaluation. It may be highly variable with location, access or not to the grid, and with balance between surplus and shortage.
of renewable electricity production. Saur and Ramsden (2011) reported a cost analysis on wind-based water electrolysis process at a rate of 50 000 kg per day of hydrogen produced. They concluded that hydrogen price is correlated with wind turbine performances and cost. Hydrogen could be produced for less than $3/kg (2005$) at good wind sites. Therefore, the choice of the wind electrolysis site will dictate the final cost of hydrogen generation. The technical hurdles are access to water, and flexibility, reliability and ageing of the electrolysis process.

4.4.1.2 Energy storage

Hydrogen and methane storage include compression, delivery, cylinder and grid storage. There are some concerns with possible gas leakage, methane for greenhouse gas effect and hydrogen for safety reasons. However, methane storage is a mature technology. Adding hydrogen to natural gas grid may affect the integrity of the pipes depending on storage conditions, i.e. pressure and temperature. In August 2013, E.ON has demonstrated that 5% hydrogen can be stored in the gas pipeline system (Figure 4.4.1.1).

Figure 4.4.1.1 E.ON electrolysis hydrogen station for the injection of hydrogen into the gas grid at Falkenhagen, Germany, showing the 2 MW electrolyzers installed by Hydrogenics.

As recognized in the HYFLEET:CUTE project, hydrogen infrastructure must be able to operate as reliably as the buses, including but not limited to hydrogen compressors and dispensing equipment.

4.4.1.3 Others

Power to Gas technology may compete with Power to Power technology as the market for batteries is established for energy storage and delivery. Therefore, if each technology has its own specific characteristics then the Power to Gas may be faster developed, especially for mobility. Figure 4.4.1.2 shows the trends of several technologies.
According to Figure 4.4.1.2, H₂ and SNG have the highest storage capacities with a discharge time higher than one hour. Batteries have much lower discharge time but can store less. Grond et al. (2013) reviewed the technology of Power to Gas. Considering the storage issue of intermittent energy sources, they recommended that assessments be made of alkaline electrolysis, PEM electrolysis and methanation process against alternatives including batteries, CAES, PHS and SMES.

Public acceptance will have an important influence on the use of H₂ as a fuel and the broad marketing of hydrogen technologies. Public attitudes may lead to serious obstacles in the establishment of a mass market infrastructure. Therefore, synthetic natural gas scenario may has a better image as gas grid and utilization is already a reality.

4.5 CONCLUSIONS

Electrolysis of water to hydrogen and the subsequent catalytic hydrogenation of carbon dioxide to methane provide a chemical storage solution of electricity surplus from fluctuating renewable sources, i.e., the “Power to Gas” concept. Compared to other storage technologies, higher capacities for longer term can be achieved by injection into the natural gas grid. Technologies based on Power to Gas to Heat, Power to Gas to Power, and Power to Gas to Liquid fuels and chemicals are feasible and allow, therefore, high flexibility in applications. Overall, these technologies are centered on the transformation of H₂O/CO₂ mixture to heat, electricity, and chemicals energy vectors. The initial energy input into the system comes from electricity whereas Nature uses directly intermittent solar energy by the photosynthesis process. It is worth noting such scenarios do not rely on fossil fuel resources.

Considering the production technologies of hydrogen, electrolysis is much more energy-intensive than through thermal methane processes. Nonetheless, the major advantages lie in the
following: (1) water is abundant on Earth, (2) transport fuels and chemicals can be made from H₂ and CO₂, (3) electrolyzers are compact utilities to H₂ and O₂, two gases which are marketable, and (4) there are geographical regions where hydrocarbons are simply not available, H₂ from water is the only practical means of providing hydrogen.

Small-, medium- and large-scale delivery of H₂ in remote areas, at fueling stations, and integrated to the natural gas grid are possible. To enable a greater penetration of renewable energy resources, H₂ production from wind- or solar-based electrolysis must be cost competitive which is better achieve with low electricity price, even negative, where surplus production is occurring. Chemical storage by CO₂ hydrogenation to methane is attractive because methane has mature markets in the energy sector and in the chemical industry, and can be stored into the natural gas grid. The economics of the process relies upon the availability of inexpensive CO₂.

While resource consumption and availability define the boundaries of electric energy storage developments, growth rates for variable renewable electricity sources favor the development of several storage technologies. Electrolyzers coupled to power-generating facilities, including fuel cells, offer new markets related to distributed energy storage. The current cost of electrolyzers is an issue that may be overcome with the deployment of the technology.

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94 | CO₂ Utilization in “Power to Gas”


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