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

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/clean-up and 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 CO_2 capture/clean-up as well as its conversion into useful products which meaningfully address the challenges posed by CO_2 life-cycle and overall sustainability issues.

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CONVERSION OF CO$_2$ TO SYNGAS AND SYNTHETIC NATURAL GAS (SNG): TECHNOLOGIES AND MARKETS

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CONVERSION OF CO_2 TO SYNGAS AND SYNTHETIC NATURAL GAS (SNG): TECHNOLOGIES AND MARKETS

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.

PEER REVIEW
by
Dr. Joel Rosenthal

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 is 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.

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*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: CO$_2$ conversion to syngas
Part 3: CO$_2$ conversion to synthetic natural gas (SNG)
Part 4: CO$_2$ utilization in "power to gas"

The contributions in parts 2 and 3 are compact materials on conventional syngas production and conversion of CO$_2$ 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 CO$_2$ 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 CO$_2$-conversion to syngas.

The sets of key gasification reactions given are over determined: with 6 species C, CO, CO$_2$, H$_2$, H$_2$O CH$_4$, 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: CO$_2$-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 CO$_2$-conversion with mixtures of H$_2$O, CH4 and O$_2$ as well as electrochemical routes, CO$_2$-

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 CO_2 emissions via utilization of CO_2 as C_1-feedstock. Yet the production of organic fuels and chemicals from CO_2 does not reduce CO_2 emissions, since the carbon products are reoxidized to CO_2 after use with a delay of few years or decades. To maintain a huge CO_2-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 CO_2 is already available sustainably in the form of biomass in its most abundant type: lignocellulose like wood or straw.

Interestingly, CO_2-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 competiveness. 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 CO_2-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 CO_2 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 CO_2 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 CO_2-utilisation are described; the main CO_2-user is ca. 114 Mt/ a for urea production in ammonia plants.

The economics of SNG production via reduction of CO_2 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 CO_2 emissions.

For SNG production from CO_2 and H_2, 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 proc−ess parameters are quite different and longtime tests are not available.

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By the way, using H_2 from "power to gas" the carbon effectiveness for synthetic fuels can be increased (factor 2) because the H_2/ CO ratio can be increased from 1:1 to 2:1 and a WGSR for CO conversion to H_2 is no longer necessary and simultaneously lowers the plant investment costs.

The contribution in **part 4 CO_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_2-production via water electrolysis and the possible reactions with CO_2. The hurdles for using this process to decrease of CO_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_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, 'CO2-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 (CO_2). However, rather than simply capturing and sequestering such emissions, CO_2 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 (CO_2CC) Program** in 2013 provides:

- An analysis of the technology and economic potential of CO_2 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 CO_2 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 H_2 using excess electricity produced at power plants, and its potential storage through conversion with CO_2 to syngas or SNG.

CO_2 CONVERSION TO SYNGAS

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

- **Methane reforming** – Using steam or CO_2;
- **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 H_2/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, H_2, CO_2, and CH_4 from feedstocks such as coal, petroleum, and biomass. The disadvantage of gasification compared to SMR is that its outlet H_2/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 H_2/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% $Ni/\gamma-Al_2O_3$ 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 $MgAl_2O_4$ 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 Nm3h-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 H2O 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 (La1-xSrx)MnO3/YSZ composite anode. This type of electrolyzer reaches a CO_2 and H_2O 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 H_2/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 CO_2 and H_2O into CO and H_2 using concentrated solar power, and CO_2 dissociation by plasma through either thermal decomposition or energy transfer through the vibrational modes of the reactants.

CO_2 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 H_2O and CO_2 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 CO_2 to methane: catalytic conversion, photocatalytic conversion, and electrochemical conversion. In addition to these routes, there is also research into membrane assisted CO_2 conversion reactors, using materials such as microporous zeolite for selective H_2O removal or H_2 addition into the reactor. At the time of writing, the only SNG plant in production using CO_2 as feedstock employs catalytic conversion to produce SNG, while the other two technologies are still confined to laboratory-scale operations.

The methanation of CO_2 is a highly exothermic reaction that is thermodynamically favorable at low temperatures (i.e., 400oC). For catalytic conversion of CO_2 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 CO_2 are similar to those used for CO_2 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, CO_2 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 CO_2 to produce synthetic methane is a multistep process consisting of parallel and series reactions; CO_2 adsorbed on the photocatalyst's surface interacts with photogenerated electrons and hydrogen to yield an entire series of C_1 and C_2 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, CO_2 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 CO_2 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 CO_2 (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, CO_2 is reduced at the cathode to form CO_2-, while an O_2-/H+ evolution takes place at the anode with H_2O 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 CO_2 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 CO_2 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.

CO_2 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 CO_2 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 H_2 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 CO_2.

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 CO_2 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)

Project	Power installed	Electrolysis Technique
Werlte D) - Audi AG	6000	Alkaline
Aragon (S) - ITHER	4000 & 70	Alkaline & PEM
Falkenhagen (D) - E.ON AG	2000	PEM
Puglia region (I) -INGRID project	1200	Alkaline
Grapzow (D) - RH2 WIND project gruppe	1000	Alkaline
Grabenn (D)	1000	Alkaline
Hambourg (D) - Vattenfall	900	Alkaline
Prenzlau (D) - Enetrag AG	500	Alkaline
Frankfurt (D) - Thuga & ITM Power	360	PEM
Foulum (DK) Electrochaea	250	PEM
Stuttgart (D) – Solar Fuel & Fraunhofer IWES	250	PEM
Karlsruhe (D) - DVGW & KIT	200	undisclosed
Xermade (S) - Sotavento Project	200	Alkaline

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

Project	Power installed	Electrolysis Technique
Herten (D) - Stadt Herten & Evonic Industries	165	PEM
Leverkusen (D) - CO2RRECT Project: Siemens & RWE	100	undisclosed
Schwandorf (D) - Eucolino: Schmack & Viessmann	100	undisclosed
Ibbenburen (D) - RWE, CERAM Hyd	100	undisclosed
Utsira (N)	50	Alkaline
Freiburg (D) - H2Move: Fraunhofer ISE	40	undisclosed
Tahivilla (S) - Hidrolica Project	40	PEM
Stuttgart (D) - Solar Fuel & Fraunhofer ZWS	25	PEM
SamsØ (DK) - SamsØ Energy Academy	20	undisclosed
Groningen (NL) - DNV KEMA	7	PEM
France - GDF Suez GRHYD project	new project	

SolarFuel is now ETOGAS

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 CO_2. Dry reforming for syngas production and catalytic conversion of CO_2 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 CO_2 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 CO_2 as a chemical feedstock. The report goes beyond the earlier studies of 2010-2012, which presented predominantly techno-economic information and benchmarks on CO_2 capture/conversion, and instead addresses the important scientific and commercial developments in the conversion of CO_2 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 CO_2 capture/clean-up as well as its utilization/conversion in products which meaningfully address the challenges posed by CO_2 life-cycle and overall sustainability issues.

1.1   SCOPE AND OBJECTIVES

The objectives of this report are to comprehensively cover the technology and economic potential of CO_2 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 H_2, 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 CO_2 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 CO_2 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 CO_2 and steam for syngas production. The second main chapter on (SNG) investigates the catalytic, photocatalytic, and electrochemical conversion routes for conversion of CO_2. The report finishes with a chapter analyzing the potential for "power to gas" technologies that make use of excess electricity production to generate H_2, and discusses the potential ways to store this gas, including conversion syngas and SNG.

1.2   OVERVIEW OF CO_2 CONVERSION OPTIONS

The largest commercial use for CO_2 at present is in the production of urea (i.e. fertilizer), which accounts for over half of the estimated 200 million tonnes of CO_2 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 CO_2 utilization is split between production of tert butyl methyl ether (TBME), methanol, and other chemicals.

Virtually all CO_2 conversion processes currently in use are low energy, with only a few catalytic high energy CO_2 conversion facilities in operation. More importantly, use of these low energy CO_2 conversion processes will not substantially increase CO_2 consumption in the coming years due to limited demand for the end products. Thus, new strategies are required to promote CO_2 use for chemical and fuel production. There are two potential use cases with the greatest potential impact for using CO_2 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 CO_2 and H_2 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 CO_2-BASED SYNGAS AND SNG

The major drivers affecting market adoption of CO_2-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 CO_2 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 CO_2 emissions to reduce the effects of climate change. Of course, this awareness of the link between anthropogenic CO_2 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 CO_2 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 CO_2 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 competiveness of such renewable resources.

1.4   CHALLENGES TO USING CO_2 AS A FEEDSTOCK

The single biggest factor limiting use of CO_2 as a feedstock is the process costs associated with converting CO_2 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 CO_2 to SNG to make these technologies economically competitive. For this to happen, however, there must be sufficient political impetus regarding issues surrounding CO_2 "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 CO_2 conversion technologies. In order to successfully promote CO_2 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 CO_2 conversion technologies have the potential to limit CO_2 emissions, the sustainably of these processes must be verified to maintain the political and social support needed to develop CO_2 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 (CO_2CC) 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 CO_2-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 CO_2 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 CO_2 containing flue and process gases. His field of expertise covers thermodynamics, the technologies for CO_2 utilization, synthesis gas/hydrogen production (reforming, gasification and pyrolysis) and gas upgrading to valuable products. He has been involved in several CO_2 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 CO_2 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

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2. CO$_2$ CONVERSION TO SYNGAS

The term syngas (or synthesis gas) is herein used for gas mixtures consisting of CO and H$_2$ in various ratios suitable for the production of synthetic fuels and chemicals such as methanol, hydrocarbons, and higher aldehydes/alcohols. Basically, H$_2$/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 H$_2$/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 CO$_2$ 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.

2.1.1.1 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 oulet of the reformer is controlled by thermodynamics. In other words, maximum methane conversion achievable in the catalytic process is dictated by thermodynamics.

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2 \qquad \Delta_r H^0 = +206\ kJ\ mol^{-1} \qquad (2.1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta_r H^0 = -42\ kJ\ mol^{-1} \qquad (2.2)$$

$$CH_4 + CO_2 \rightleftharpoons 2\ CO + 2\ H_2 \qquad \Delta_r H^0 = +247\ kJ\ mol^{-1} \qquad (2.3)$$

$$CH_4 \rightleftharpoons C + 2\ H_2 \qquad \Delta_r H^0 = +75\ kJ\ mol^{-1} \qquad (2.4)$$

$$2\ CO \rightleftharpoons C + CO_2 \qquad \Delta_r H^0 = -173\ kJ\ mol^{-1} \qquad (2.5)$$
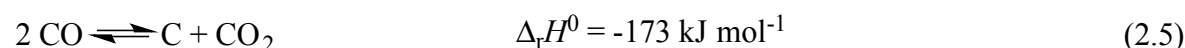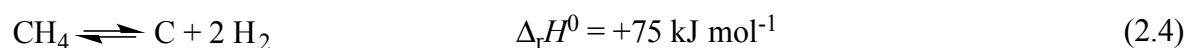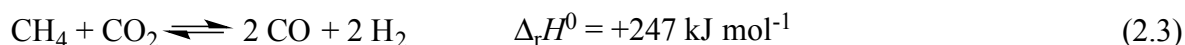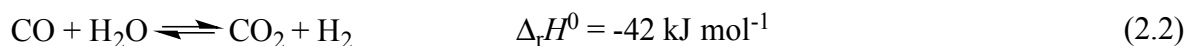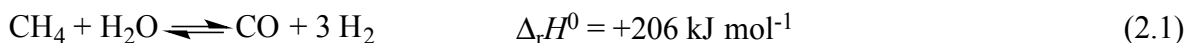
The given standard enthalpy values, $\Delta_r H^0$ ($T = 298$ K, $P = 0.1$ MPa), refer to gaseous CH_4, CO, H_2 and CO_2, vapor H_2O, and graphite C states.

Steam reforming itself, reaction (2.1), is endothermic. Hence, methane conversion at equilibrium increases with temperature. The coexistence of H_2O 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.
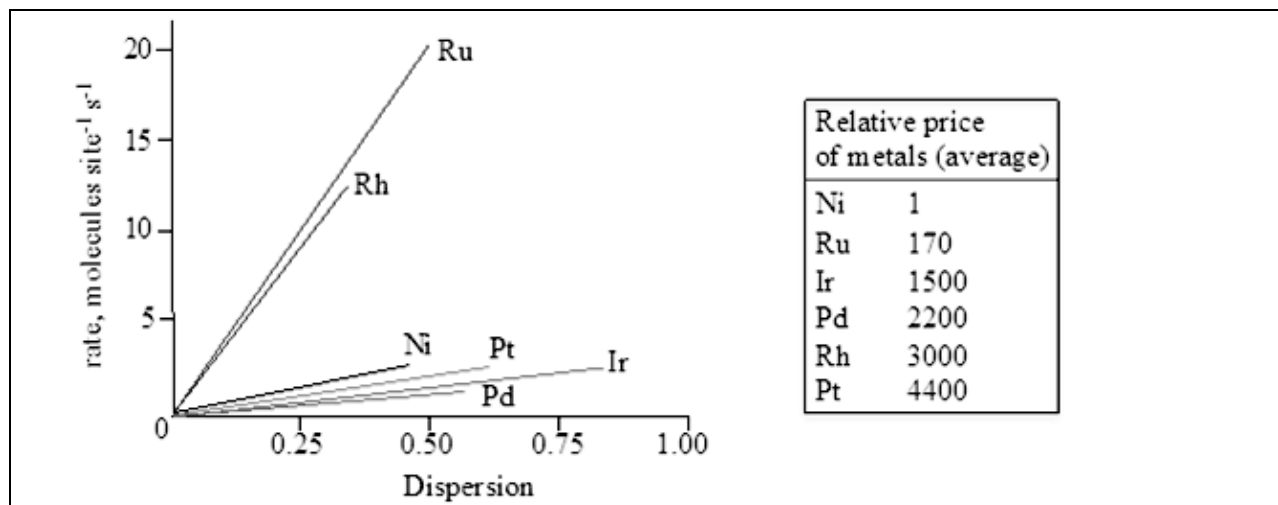
Figure 2.1.1.1 Reaction rate vs metal dispersion on ZrO2, Al2O3 and MgAl2O4 support at 500°C with steam/CH4 molar ratio of 4 (adapted from Jones et al., 2008).

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 Al_2O_3, $MgAl_2O_4$, MgO, ZrO_2 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/CH_4 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: H_2/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 CH_4-rich mixture of CH_4, H_2, CO_2, 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 H_2/CO molar ratio is >3, too high for most applications, and unconverted methane remains. Some CO_2 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, H_2, CO_2, and CH_4 from a wide range of feedstocks such as coal, petcoke, 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.

$$C + 0.5\, O_2 \longrightarrow CO \qquad\qquad \Delta_r H^0 = -111 \text{ kJ mol}^{-1} \qquad\qquad (2.6)$$

$$C + O_2 \longrightarrow CO_2 \qquad\qquad \Delta_r H^0 = -393 \text{ kJ mol}^{-1} \qquad\qquad (2.7)$$

$$CO + 0.5\, O_2 \longrightarrow CO_2 \qquad\qquad \Delta_r H^0 = -283 \text{ kJ mol}^{-1} \qquad\qquad (2.8)$$

$$C + CO_2 \rightleftharpoons 2\, CO \qquad\qquad \Delta_r H^0 = +173 \text{ kJ mol}^{-1} \qquad\qquad (2.9)$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad\qquad \Delta_r H^0 = +131 \text{ kJ mol}^{-1} \qquad\qquad (2.10)$$

$$2\, C + 2\, H_2O \rightleftharpoons CH_4 + CO_2 \qquad\qquad \Delta_r H^0 = +105 \text{ kJ mol}^{-1} \qquad\qquad (2.11)$$

$$C + 2\, H_2O \rightleftharpoons 2\, H_2 + CO_2 \qquad\qquad \Delta_r H^0 = +90 \text{ kJ mol}^{-1} \qquad\qquad (2.12)$$

$$C + 2\, H_2 \rightleftharpoons CH_4 \qquad\qquad \Delta_r H^0 = -75 \text{ kJ mol}^{-1} \qquad\qquad (2.13)$$
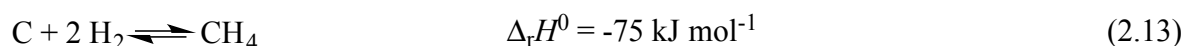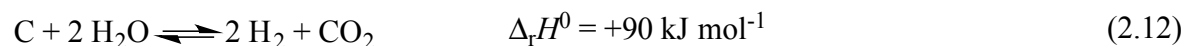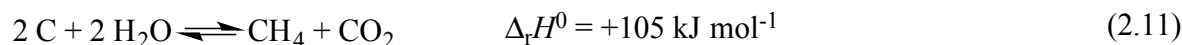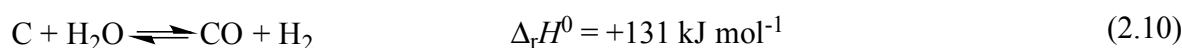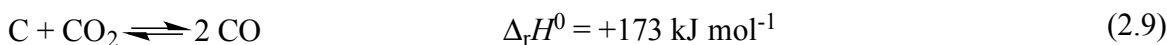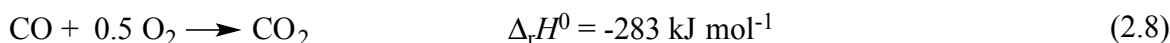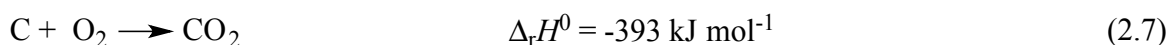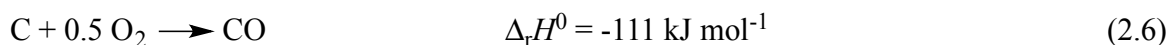
Reactions with oxygen are nearly complete under reaction conditions which means there are no thermodynamics restrictions. The other reactions are under thermodynamic control. The balance between partial oxidation, steam reforming and the hydrogen content of coal dictates the outlet H_2/CO ratio which 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 therefof 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

<1, WGSR (reaction (2.2)) is a critical downstream technology in gasification processes to enrich syngas mixture in hydrogen (Ratnasamy and Wagner, 2009).

Coal, biomass and waste gasification technologies and their recent developments concerning gasifiers, catalytic and plasma gasification have been very recently reviewed (Prins et al., 2007; Mondal et al., 2011; Bulushev and Ross, 2011; Taba et al., 2012; Fabry et al., 2013; Popa et al., 2013). They will not be herein discussed being out of scope of this report.

CO_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_2 promotes the formation of micropores in the carbon structure favoring, therefore, the kinetics of gasification (Butterman and Castaldi, 2009).

2.1.2.3 *Environmental benefits*

The increasing awareness of greenhouse gases (GHGs) issues and waste reduction bring gasification to the forefront of beneficial technologies for low- or negative-value carbonaceous feedstocks. Converting them to syngas avoids disposal of waste along with valorization into marketable products (Neste Oil, 2009). In addition, the gasification process separates the harmful substances before syngas transformation units. In comparison with incineration, gasification emissions are generally an order of magnitude lower (www.gasification.org).

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_2/CO molar ratio of about 2 that fits for methanol and long-chain Fischer−Tropsch products.

$$CH_4 + 0.5\ O_2 \longrightarrow CO + 2\ H_2 \qquad \Delta_r H^0 = \text{-36 kJ mol}^{-1} \qquad\qquad (2.13)$$

$$CH_4 + 1.5\ O_2 \longrightarrow CO + 2\ H_2O \qquad \Delta_r H^0 = \text{-520 kJ mol}^{-1} \qquad\qquad (2.14)$$
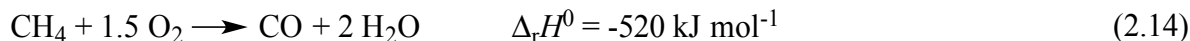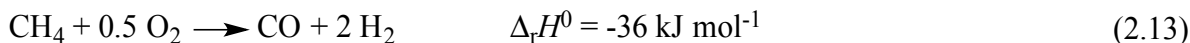
Most often, reaction (2.13) is accompanied by over oxidation reactions that are strongly exothermic. For example, reaction (2.14) corresponds to the oxidation of hydrogen into water leading to a decrease in H_2/CO molar ratio.

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 H_2/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.
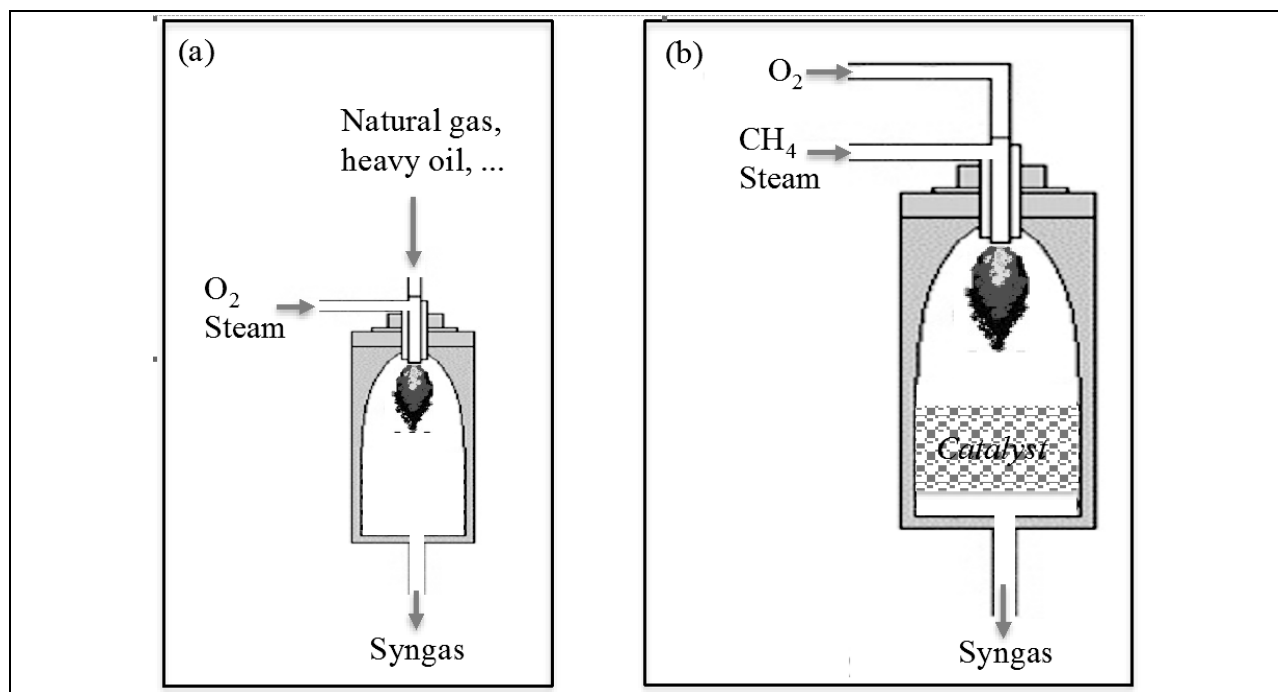
Figure 2.1.3.1 Basics of (a) multi-purpose gasification and (b) autothermal reforming reactors (adapted from Lurgi, 2003).

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, H_2/CO molar ratio is dictated by the feed composition that implies catalytic downstream technologies to be installed whenever H_2/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-Al_2O_3 and $MgAl_2O_4$ 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, CO_2 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.
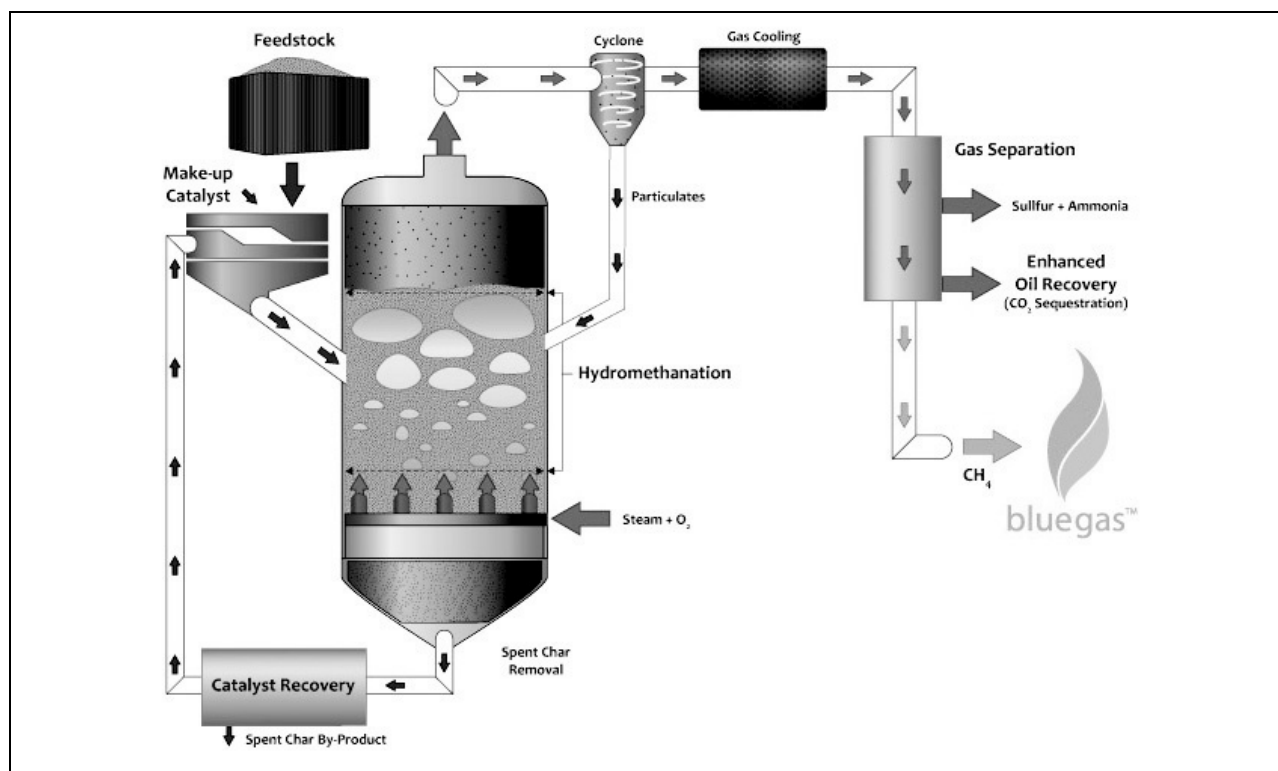
Figure 2.1.4.1   The hydromethanation process developed by GreatPoint Energy.

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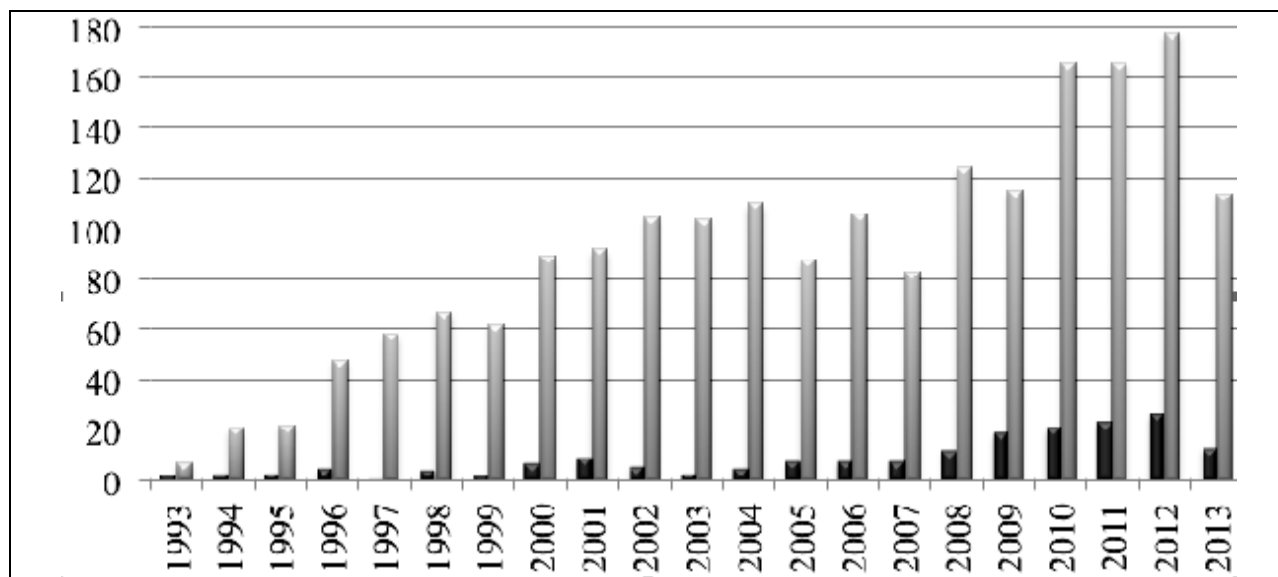
Figure 2.2.1   Number of publications (blue) and patents (red) published per year dealing with CO$_2$ reforming of methane or dry reforming. Source: SciFinder database, last accessed September 18, 2013).

2.2.1   Processes/ Catalysts/ Other Factors

2.2.1.1   Processes

CO_2 reforming of methane gives H_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 ($CO_2 + H_2 \rightarrow CO + H_2O$). Therefore, these three latter reactions constitute a loss of carbon and hydrogen with respect to CO and H_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_2 and CH_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_2/CH_4 ratios, whereas negligible amount is found at temperature over 900°C leading to H_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_2 and CH_4 conversions, and to H_2 and CO selectivity with H_2/CO close to unity. Another thermodynamic study shows complete conversion of the reactants above 1,000°C with 100% selectivity into H_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 worthnoting 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_x ($x = 0$-3) and H species on all catalysts. CO_2 activation and oxygen transfer to adsorbed CH_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_2 may react either directly in the gas phase with CH_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 .
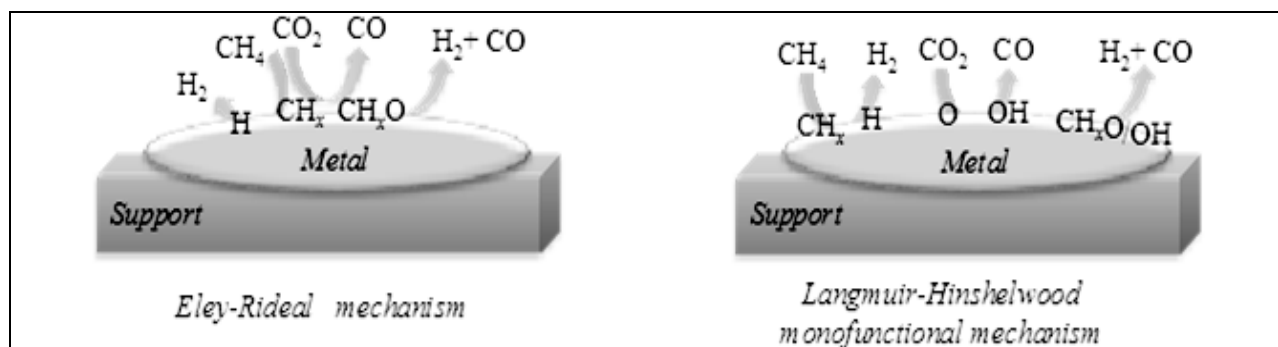
Scheme 2.2.1.1   Basics of Eley-Rideal and Langmuir-Hinshelwood mechanism in dry reforming.

Then, O_{ads} and/or OH species migrates towards CH_x ones to form CH_xO and/or CH_xOH 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_2O 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.
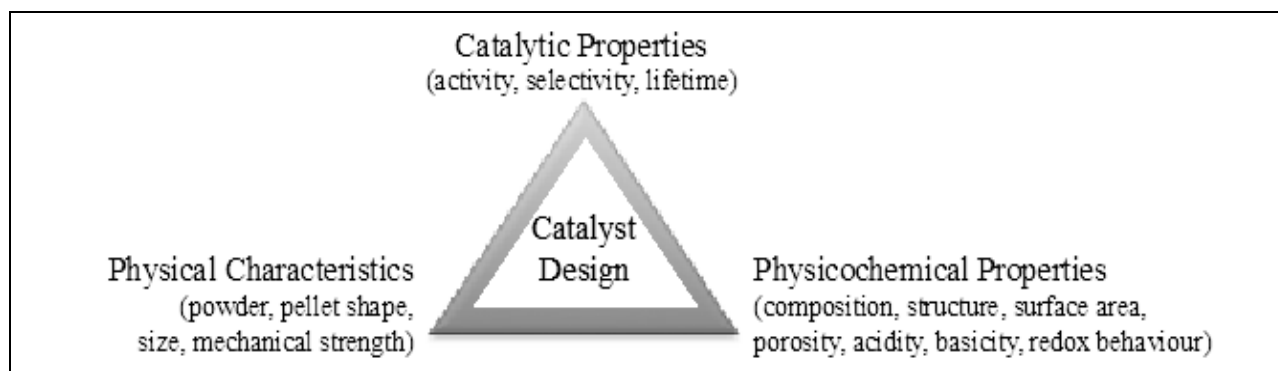
Scheme 2.2.1.2   Main approaches of catalyst design.

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 dissolved into nickel lattice leading then to nickel carbide and whiskers, as well as nickel encapsulation (Scheme 2.2.1.3).
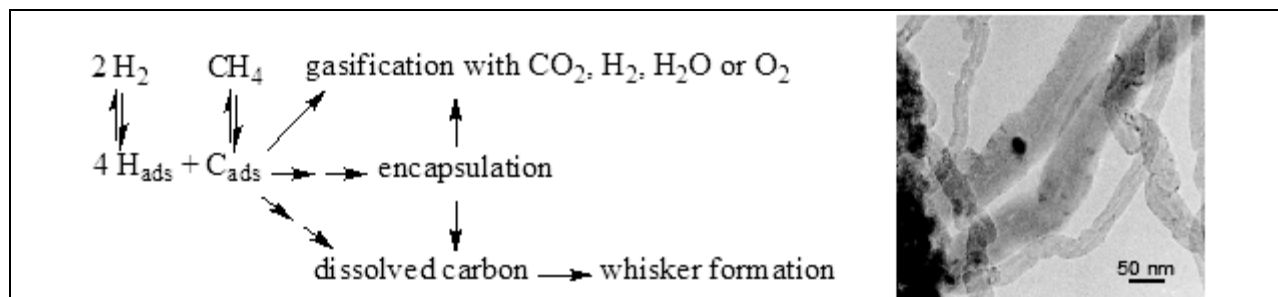
Scheme 2.2.1.3 Schematic reaction network of carbon formation and TEM image of encapsulated nickel catalyst into whisker (adapted from Trimm, 1997).

Dissolved carbon and whiskers formation are irreversible processes, whereas the other types can be gasified by CO_2 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 Al_2O_3, MgO, TiO_2, ZrO_2, CeO_2, La_2O_3, 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 carbonaceaous 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 $NiAl_2O_4$ 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 $CO_2/CH_4 = 1$, the conversion of CO_2 and CH_4 was 70 and 68%, respectively, and provided H_2/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).

$$CH_4 + Ni \rightarrow Ni\text{-}C + 2H_2 \qquad\qquad (2.15)$$

$$2\ CeO_2 + Ni\text{-}C \rightarrow Ce_2O_3 + Ni + CO \qquad\qquad (2.16)$$

$$Ce_2O_3 + CO_2 \rightarrow 2\ CeO_2 + CO \qquad\qquad (2.17)$$

The mechanism behind relies on the well-known redox process $Ce^{IV} \Leftrightarrow Ce^{III}$ 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_2O_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.
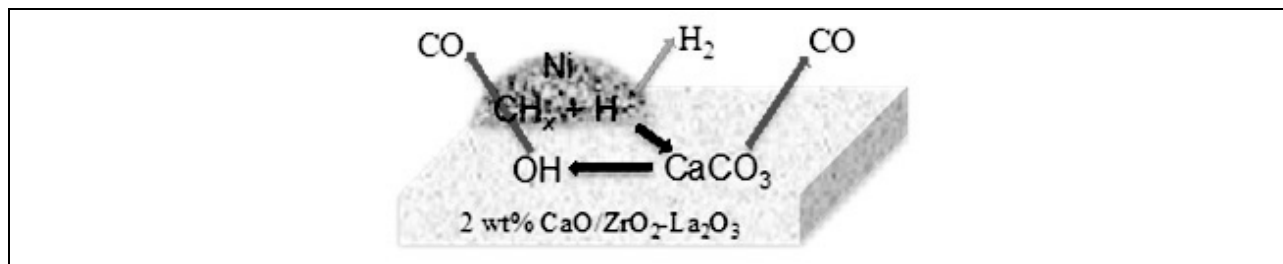
Figure 2.2.1.1 Schematic representation of bifunctional catalysis on basic support (adapted from Bachiller-Baeza et al. 2013).

The effect of additives such as K, Sn, Mn and Ca on Ni-Al_2O_3 catalyst have been reported to slightly decrease the activity compared to the original Ni-Al_2O_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_2O_3, CeO_2, La_2O_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_2O_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)
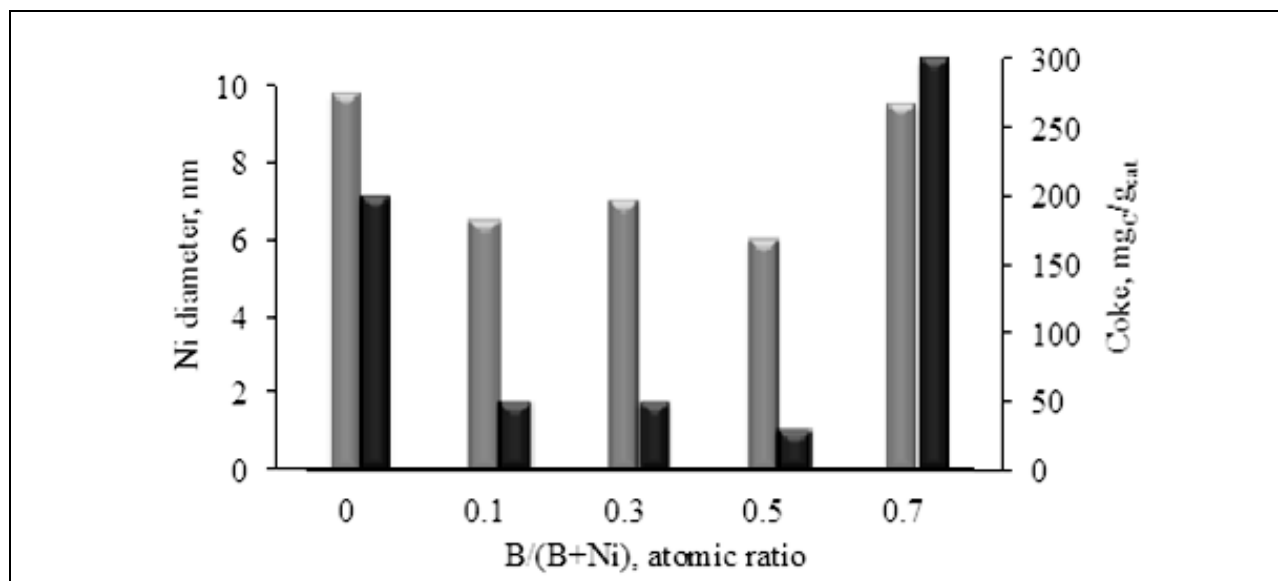
Figure 2.2.1.2   Ni particles diameter (blue) and amount of coke (red) on NiB_x/Al_2O_3 catalysts (adapted from Fouskas et al., 2013).

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 $MgAl_2O_4$ 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 $Ba_{0.75}Ni_{1.0}Al_{11.0}O_{19-\delta}$ leads to high CH_4 and CO_2 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 (ABO_3, A = lanthanide, B = transition metal) are also good catalyst precursors to getting high metallic dispersion after the H_2 reduction pretreatment preceding the reforming process. As an example, $LaNiO_3$ perovskite is transformed into supported Ni on $La_2O_2CO_3$ (Gallego et al., 2008). The catalytic activity has been correlated with the oxygen storage capacity of the support that provides oxygen to gasify CH_x 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-ZrO_2 (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 CO_2 and CH_4 (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 CH_4 and CO_2 is 97 and 90%, respectively, with $H_2/CO = 0.87$. In addition, the amount of carbon is reported to be very low.

An interesting system based on Ni-Co bimetallic catalyst, associated with MgO-Al_2O_3 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 CO_2 reforming of CH_4 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 CeO_2-ZrO_2 mixed oxide are not as good at the same reaction temperature (Djinović et al., 2012).

Monometallic Co-supported catalysts are active in CO_2 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 $NdCoO_3$ perovskite-type precursor to convert, at 850°C and 0.1MPa, around 92% of CH_4 and CO_2 from an undiluted equimolar mixture affording a selectivity of 96% for syngas with a H_2/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-Nd_2O_3 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 CO_2, 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 CO_2-rich sites, CO_2 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 CO_2 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 H_2/CO molar ratio of 0.42 and CH_4 content of 0.0005 v%. A schematic overview of the process is shown in Figure 2.2.2.1.
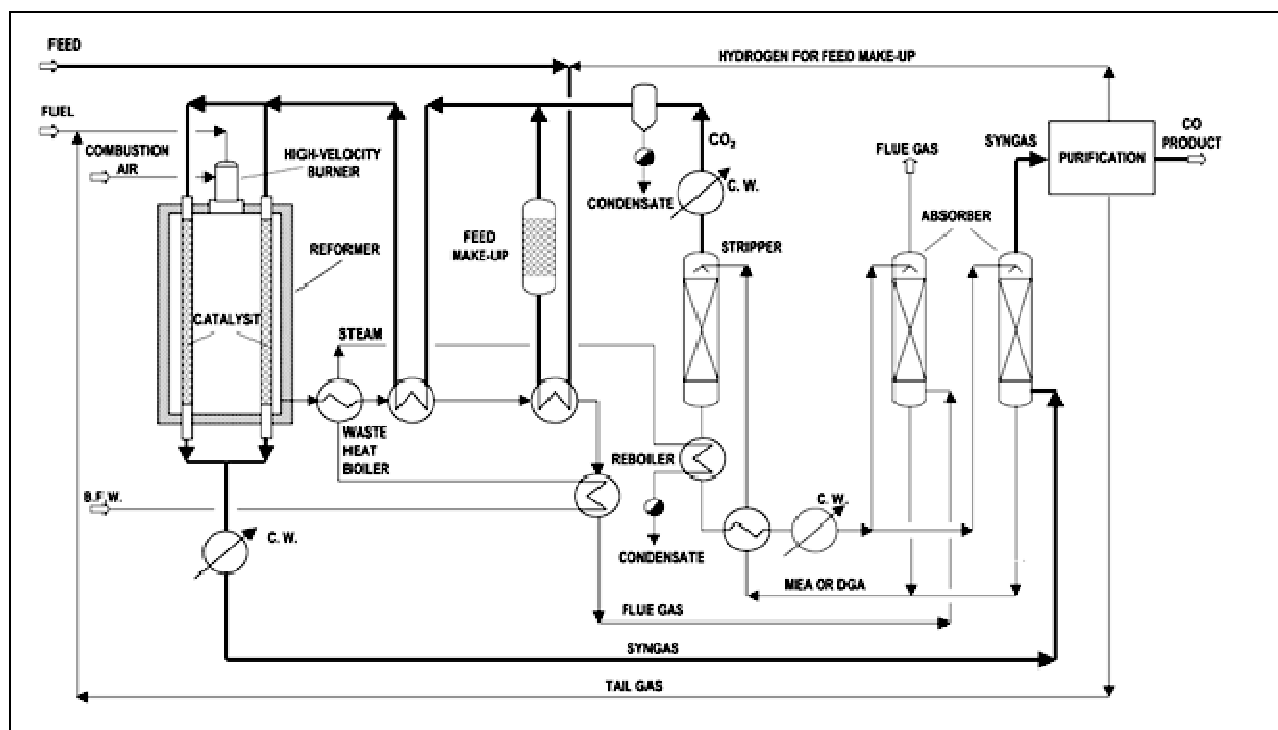
Figure 2.2.2.1   Schematic flow diagram for Calcor Standard process

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, H_2, H_2O, CO_2, and traces of CH_4. Cooling to ambient temperature allows CO_2 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 H_2 and remaining CO_2.

As shown in Table 2.2.1, the Calcor technology has operated worldwide since the end of the 1970s with productivity up to 850 Nm^3 h^{-1} per unit.

Table 2.2.1
Installed Calcor Technology Around the World
(adapted from www.caloric.com/en/produkte/co-plants/co-plants.html)

Country	Capacity (Nm^3 h^{-1})	Year delivered
Bulgaria	220	1990
Czech Republic	160	1998
Germany	40	1978
Germany	77	1978
Germany	250	1986
Germany	300	1991
India	450	1990
Japan	160	1984
Korea	330	1990
Korea	330	1996
Middle East	400	2001
Singapore	850	2006
Spain	40	2005
Spain	530	2008
Total Capacity	**4137**	

The final CO purity is between 99.25 and 99.98%. The H_2-rich tail gas stream obtained from the CO purification step is sold as technical grade hydrogen with a yield of 37 Nm^3 per 100 Nm^3 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, CO_2

emissions to the atmosphere are low, and have been estimated to be 15 kg of CO_2 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 CO_2 content. Small-scale units are targeted with production of liquid fuel amounting to 1,000 to 2,000 barrels per day. Hence, CO_2-rich small to medium size gas fields could be valorized. Noteworthy, they represent nearly 40% of worlwide 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 CO_2 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 CO_2 reforming of methane should be performed above 800°C to get reactants conversion and H_2/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 CH_4 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 H_2/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 $CH_4/CO_2/H_2O$ 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 2.2.2
Optimized $CH_4/CO_2/H_2O$ Feed Molar Ratio and Corresponding Parameters of Syngas
(Adapted from Demidov et al., 2011)

T °C	P MPa	$CH_4/CO_2/H_2O$ molar ratio	CO_2 %	CH_4 %	H_2/CO molar ratio	ΔH kJ mol^{-1}
800	0.1	1/0.31/0.83	1.68	1.46	2.18	220.7
	0.5	1/0.42/1.03	6.08	5.85	2.19	184.8
	2	1/0.58/1.30	13.96	14	2.19	131.6
900	0.1	1/0.27/0.78	0.46	0.53	2.18	229.6
	0.5	1/0.32/0.91	2.16	2.17	2.18	214.9
	2	1/0.43/1.22	6.51	6.35	2.18	181.3
1,000	0.1	1/0.26/0.76	0.15	0.2	2.18	232.3
	0.5	1/0.28/0.84	0.84	0.82	2.19	226.6
	2	1/0.34/1.07	2.93	2.75	2.18	209.7

Table 2.2.2 shows that the optimal CH_4/CO_2 and CH_4/H_2O 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 H_2/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 $CH_4/CO_2/H_2O$ mixtures decrease the upper temperature limit of coke formation by 150°C. In fact, the optimized values and the H_2/CO ratio are very close to the theoritical ones considering the overall reaction to syngas (2.18).

$$3\,CH_4 + 2\,H_2O + CO_2 \rightleftharpoons 8\,H_2 + 4\,CO \qquad\qquad (2.18)$$

Another thermodynamic study confirmed the same trends (Sun et al., 2011). Suppression of carbon deposits is thermodynamically possible at CH_4/CO_2 greater than 1.5 and $T \geq 800°C$. And carbon deposits are always in equilibrium with an equimolar amount of CH_4 and CO_2 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 H_2/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 CH_4 and CO_2 is about 71%.
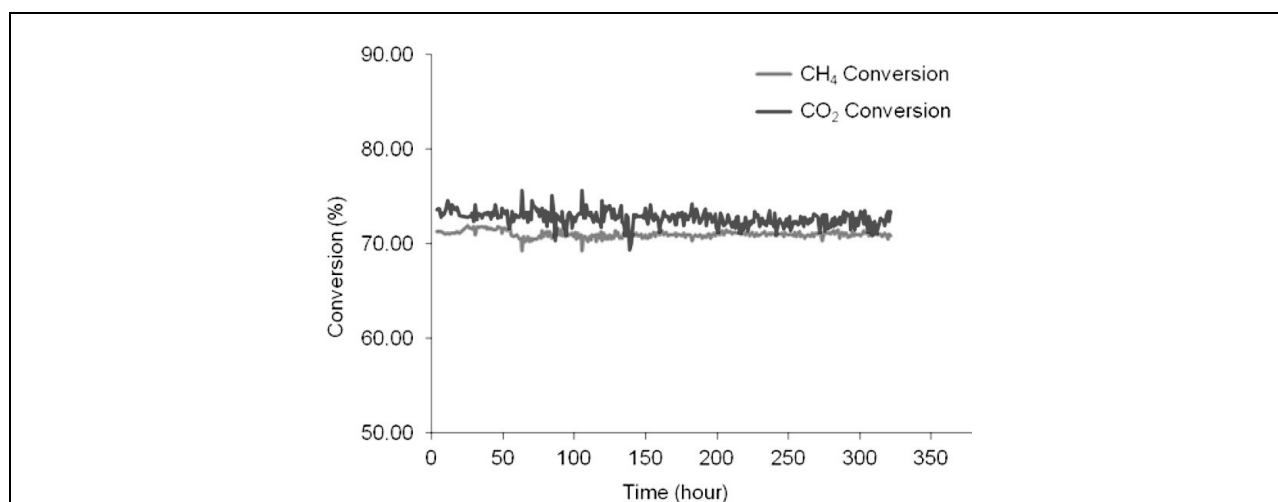
Figure 2.3.1.1 CO_2 and CH_4 conversion in bireforming of methane over 15 wt% Ni/MgO at 0.7 MPa and 830°C. 100 mL min^{-1} of $CH_4/CO_2/H_2O$ with a molar ratio of 3/1.2/2.4 and GHSV of $6\ 10^4$ mL h^{-1} g^{-1} catalyst. Reprint from permission of Olah et al., 2013 (American Chemical Society).

The obtained H_2/CO molar ratio amounted to two, and selectivity to H_2 and CO is 98 and 100%, respectively. Changing the initial relative CH_4/CO_2/H_2O feed ratio from 1/0.33/0.66 to feed 1/0.8/1.6, i.e doubling the amounts of CO_2 and H_2O, increased CH_4 conversion to 85%. The same catalyst was also evaluated for the bireforming of natural gas. Stable CO_2 and CH_4 conversion was again observed over a 160-h run with a natural gas conversion of 70%.

Other nickel-based catalysts such as Ni/Al_2O_3 and Ni/Al_2O_3-La_2O_3 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 CH_4/CO_2/O_2 molar ratio should be in the range of 1.0/0.5-1.0/0.2-0.4 for high CH_4 and CO_2 conversion, and high H_2 and CO yield, while minimizing H_2O 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, CH_x from methane and O_{ads} from either H_2O, CO_2 or O_2, are producing H_2 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.
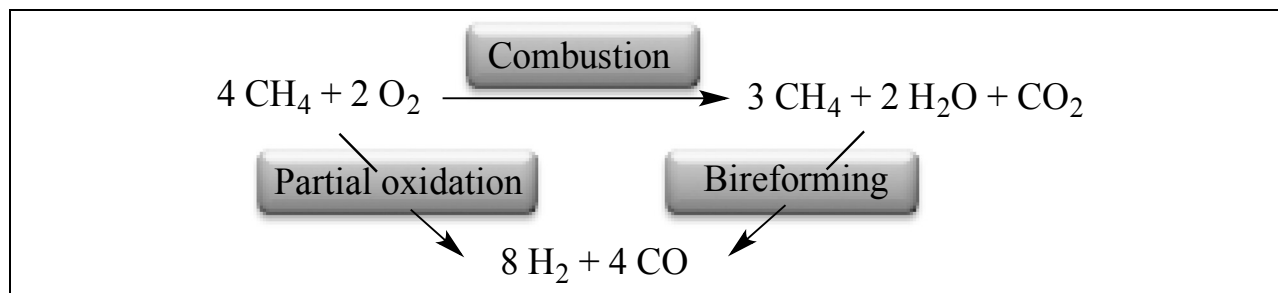
Scheme 2.3.2.1   Reaction pathways for methane partial oxidation to syngas.

The one-step partial oxidation corresponds to the direct pathway. The two-step process consists at first in CH_4 combustion providing CO_2 and H_2O and 75% of unreacted CH_4, then bireforming takes place. Hence, under oxidative CO_2 reforming bireforming may contribute to the overall process.

The net heat of the oxidative CO_2 reforming process can be estimated taking into account the co-feed $CH_4/CO_2/O_2$ relative ratio and the H_2/CO syngas ratio. On a Co/MgO-based catalyst with $CH_4/CO_2/O_2 = 1/0.2/0.4$, the H_2/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 CO_2 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 Al_2O_3-CeO_2 and Pt-Rh on CeO_2-ZrO_2 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 H_2.

Besides noble metals, molybdenum and tunsgsten 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. $BaMn_2Al_{10}O_{19}$, transferring maximum heat to the reforming catalyst such as $Co_{0.2}W_{0.8}C_x$ (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 H_2/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 $CO_2/H_2O/O_2$ mimicking flue gases composition. Although there is no need to separate and concentrate the individual feed components, SO_x, NO_x, 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.
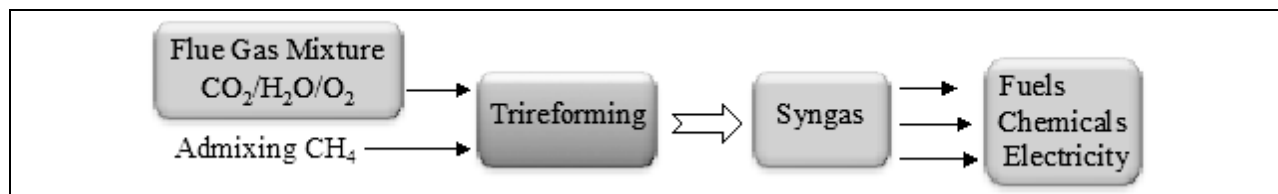
Scheme 2.3.3.1   Flue gases value chain by the trireforming process.

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% CO_2, 18-20% H_2O, 2-3% O_2, and 67-72% N_2, whereas from coal-fired plants a composition of 12-14% CO_2, 8-10% H_2O, 3-5% O_2, 72-77% N_2, 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 H_2, CO, CO_2, H_2O and CH_4 at equilibrium at different temperatures from an initial feed of 8.4v% CO_2, 12.9 v% H_2O, 5.8 v% O_2, and 60 v% N_2.
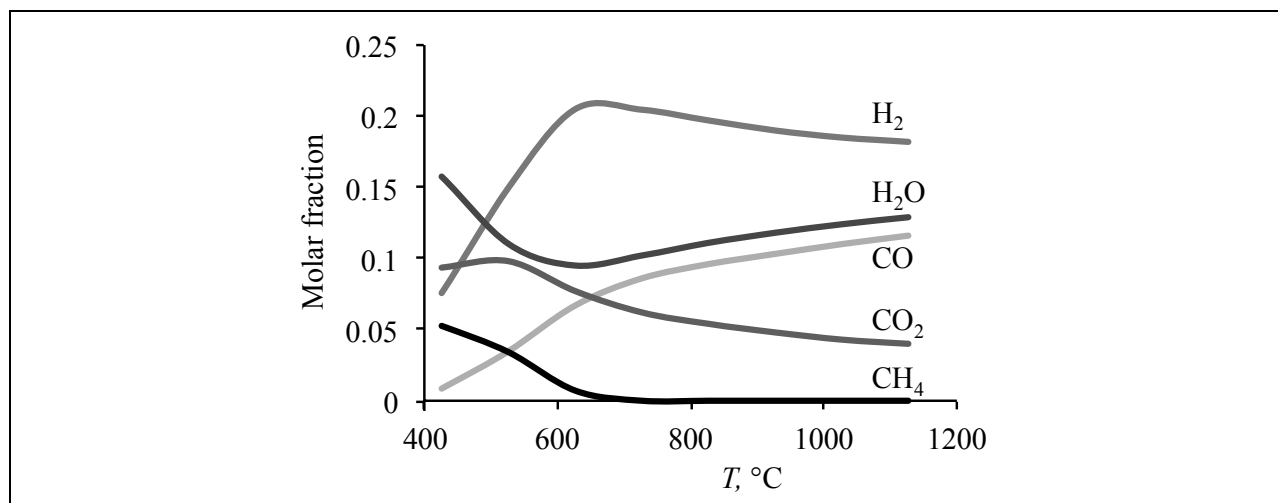
Figure 2.3.3.1   Thermodynamic equilibrium with temperature at 0.1 MPa from a feed of 8.4v% CO_2, 12.9v% H_2O, 5.8v% O_2, and 60v% N_2 (Halmann and Steinfeld, 2006).

As shown in Figure 2.3.3.1, the H_2/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 CO_2 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 CO_2 emissions. It is concluded that trireforming process does not decrease the power plant efficiency contrasting with the conventional CO_2 capture by the amine technology. Moreover, the reduction in CO_2 emissions is about 83%. Therefore, there is a clear advantage of the trireforming process over the amine one to capture CO_2 (Minutillo and Perna, 2009). In addition, trireforming is directly valorizing CO_2 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 $CH_4/CO_2/H_2O/O_2/N_2$ feed composition of 1/0.25/0.5/0.075/1.67. Under these conditions, CO_2 conversion of 99% and H_2/CO of 2 can be achieved. However, carbon and oxygen are found in trace amounts in the simulation.

Trireforming is not restricted to flue gases treatment. Biogas, the composition of which lies in the range of 50-75 v% CH_4, 25-45 v% CO_2, 2-7 v% H_2O, 2 v% N_2, has been reformed for fuel cell application. Upstream to solid oxide fuel cell (SOFC), biogas trireforming, after elimination of H_2 (<1%) and trace amounts of H_2S, O_2, NH_3, halides and siloxanes, allows to convert CH_4 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 $Ni_{0.15}Mg_{0.85}O$ 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 CH_4 conversion (≥ 97%) and high CO_2 conversion (around 80%) for producing syngas with H_2/CO ratio in the range of 1.5-2.0 could be obtained over supported nickel on MgO, ZrO_2, CeO_2 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 CO_2 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, β-SiC, for the reforming catalysts. The β-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/β-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_2O to H_2 followed by the reverse water gas shift reaction; (b) separate electroreduction of CO_2 to CO and H_2O to H_2; and (c) co-electroreduction of CO_2 and H_2O. Both electroreduction of H_2O 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.

$$CO_2 + H_2O \longrightarrow CO + H_2 + O_2 \tag{2.19}$$

$$CO_2 + 2\,H_2O \longrightarrow CO + 2\,H_2 + 1.5\,O_2 \tag{2.20}$$

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).
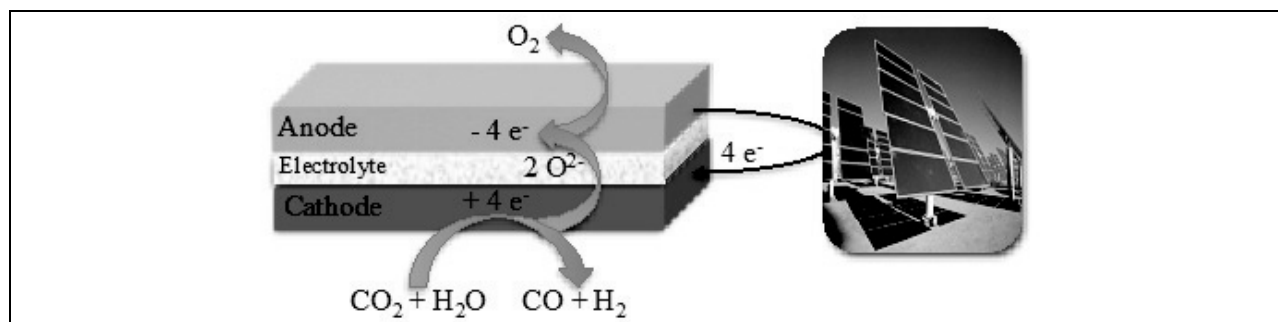
Scheme 2.3.4.1 Basic principle of SOEC for the co-electroreduction of CO_2 and steam.

As shown in Scheme 2.3.4.1, steam electrolysis involves the reductive dissociation of H_2O 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 electrolysis. In line with, it has been proposed that the predominant CO_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 $(La_{1-x}Sr_x)MnO_3$/YSZ composite for the anode.

2.3.4.2 Performances

Sulfur-free CO_2 and deionized H_2O should be used to keep the cathode efficiency. It should also be emphasized that electroreduction of CO_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^{2-} diffusion across the electrolyte. At the same time, thermal energy increases with temperature. Moreover, CO_2 and H_2O 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_2 and H_2O conversion and CO and H_2 yield increased with the applied current. Under a current of -25 A, CO_2 and H_2O conversion reached 93% and H_2/CO molar ratio was 2.1. High current density of -1.46 A cm^{-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_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^2. Co-electrolysis of CO_2 and steam was performed at 800°C and -0.75 A cm^{-2}, from a 1/1 mixture of CO_2 and H_2O. 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 1020 J h^{-1} and 4.7 1016 J h^{-1}, respectively, highlights unlimited amounts of energy that may be benifical to a variety of endothermic chemical transformations (Izumi Y, 2013). However, 1 kW m^{-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_2 reforming (Agrafiotis et al., 2014). Figure 2.3.5.1 shows the principle and a picture of solar power concentration.

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_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_2 and H_2O into CO and H_2 has emerged as a concept for fuel-free pathway to syngas.

The developed technology for solar thermal conversion of CO_2 and H_2O 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_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_2 redox cycle involves the endothermic reduction of CeO_2 followed by its exothermic oxidation by H_2O:

$$2\ CeO_2 \longrightarrow 2\ CeO_{2-x} + x\ O_2\ (g) \tag{2.21}$$

$$CeO_{2-x} + x\ H_2O \longrightarrow CeO_2 + x\ H_2\ (g) \tag{2.22}$$

$$CeO_{2-x} + x\ CO_2 \longrightarrow CeO_2 + x\ CO\ (g) \tag{2.23}$$

2.3.5.2   *Performances*

Le Gal et al. (2011) observed that upon CeO_2 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 H_2. However, the rate of reoxidation by CO_2 and H_2O was slower with $Zr_{0.25}Ce_{0.75}O_2$ with an optimum temperature at 1,100°C. This effect is consistent with the reoxidation of the surface of CeO_2, whereas with $Zr_{0.25}Ce_{0.75}O_2$ reoxidation of the bulk is operative.

Furler et al. (2012) reported on CeO_2 being reduced at 1,527°C to an oxygen deficient state. Re-oxidation at 827°C with a mixture of CO_2 and H_2O in the range of 0.8-7.7 produced syngas with H_2/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.
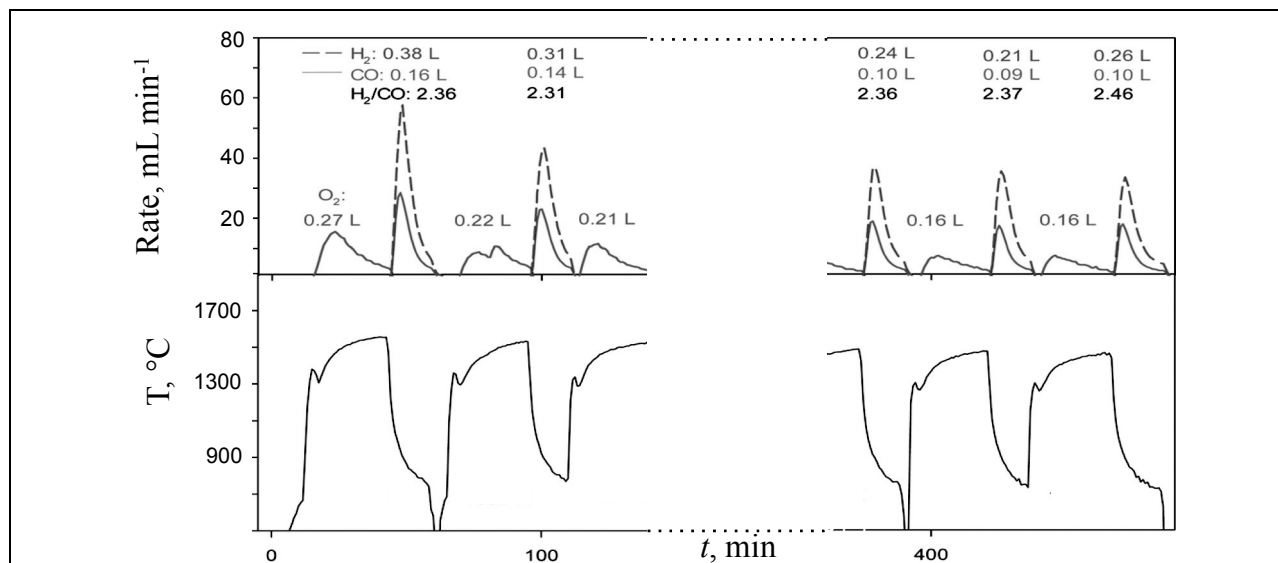
Figure 2.3.5.2 Ceria temperature profile, CO, H_2 and O_2 production rate, and H_2/CO molar ratio during ten consecutive splitting cycles. Experimental conditions: 3.6 and 0.7 kW radiation power input during reduction and oxidation steps, respectively; $H_2O/CO_2 = 6.7$; reduction and oxidation steps 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 CO_2 and H_2O 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", CO_2 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 predominent 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 CO_2 reforming processes and CO_2 dissociation into CO and O_2. Tao et al. (2011) recently reviewed the CO_2 reforming of methane assisted by different plasma technologies. The general trends are variable conversion in CO_2 and CH_4 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 CO_2 reforming (Mahammadunnisa et al., 2013). The schematic setup is shown in Figure 2.3.6.1
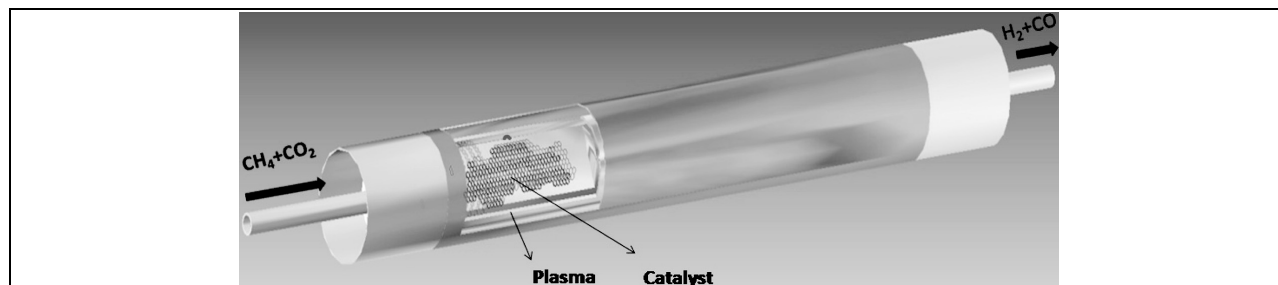
Figure 2.3.6.1 Schematic representation of the catalyst-packed dielectric barrier discharge reactor for dry reforming of methane. Reprint from permission of Mahammadunnisa et al., 2013 (American Chemical Society).

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).
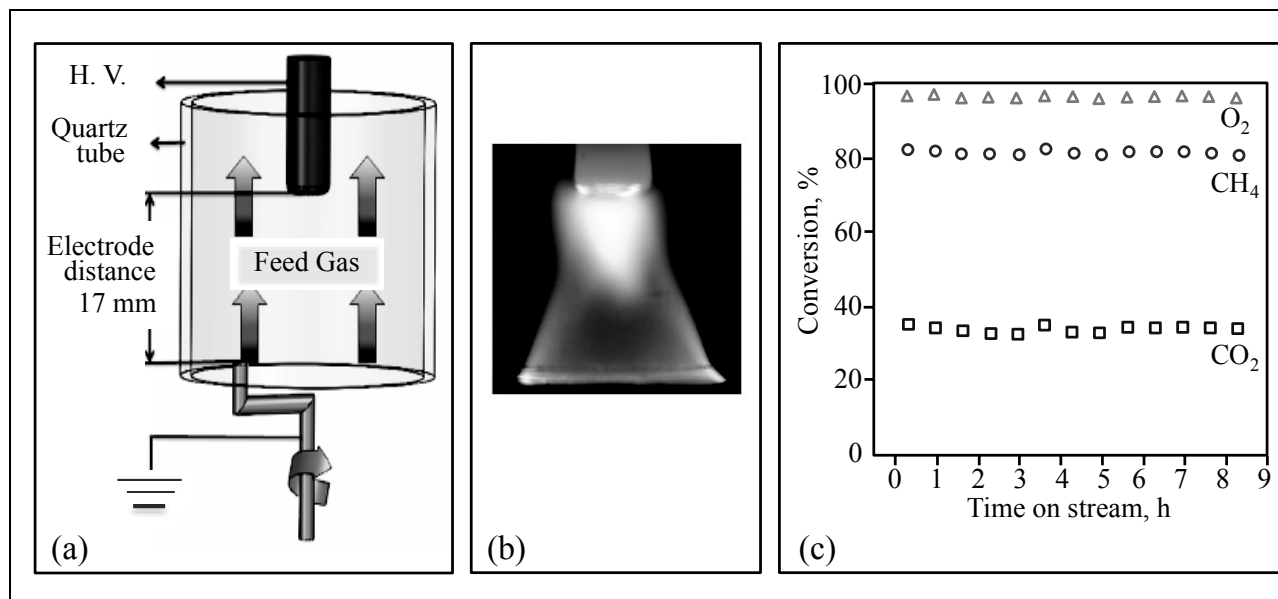
Figure 2.3.6.2   (a) Schematic representation of the shade reactor, $CH_4/CO_2/O_2$ fed at room temperature and atmospheric pressure from the bottom; (b) Picture of the 2.5 cm3 shade reactor at gas residence time of 0.1 s and SEI of 84 kJ mol-1; (c) CH_4, CO_2 and O_2 conversion with time on stream (Liu et al., 2013).

Selectivities to CO, H_2, and H_2O close to 92, 48 and 48%, respectively, have been calculated leading to H_2/CO ratio of 0.8. Hydrocarbons, i.e. C_2H_2, C_2H_4 and C_2H_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 PAssivated 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 H_2O /natural gas ($H_2O/C = 0.93$) and CO_2/natural gas ($CO_2/C = 0.65$) result in a H_2/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 CO_2 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 CO_2 reforming in a single reactor. Therefore, the reformer is similar to the ATR one, with a burner and H_2O and CO_2 as co-oxidants (Figure 2.3.7.2).
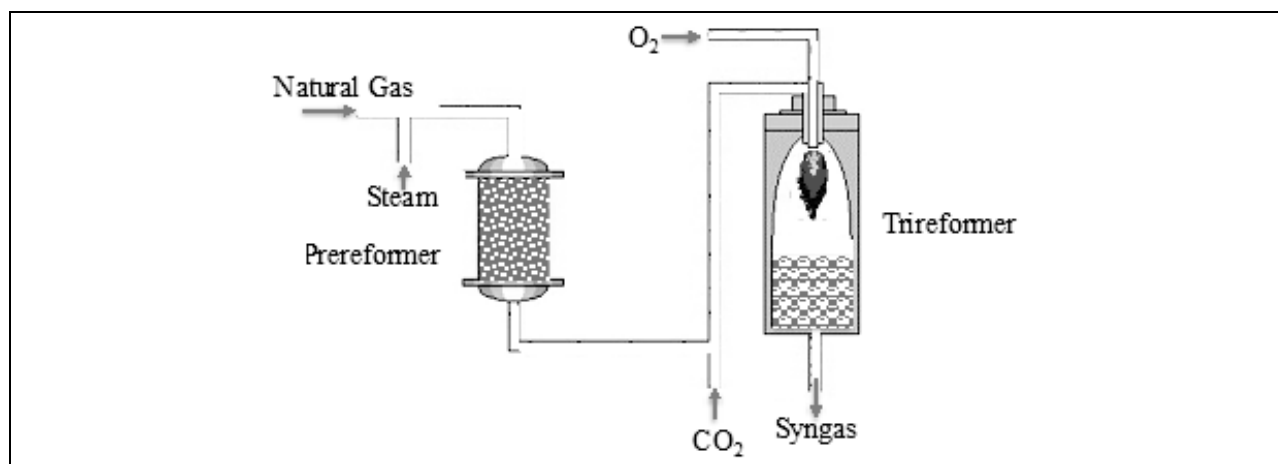
Figure 2.3.7.2   Schematic flow diagram of KOGAS trireforming process.

A prereformer is installed upstream for reforming, at 350°C and 3 MPa, C_2 and C_3 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 H_2/CO ratio lies in the range 1.2-1.5 and coke deposition is limited. The appropriate H_2/CO ratio for operating downstream dimethyl ether production avoids installing water gas shift technology and is therefore cost-effective. With Ni catalyst supported on Al_2O_3 promoted with CeO_2, ZrO_2 and MgO, reactor optimization led to methane conversion close to the equilibrium value with $H_2/CO_2 = 1.2$. 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 CO_2 to afford methanol. Named as the Carnol process, CO_2 mitigation could be effective if it can be recycled from power plant stack gas. It is woth noting that, when comparing the endothermal enthalpy for hydrogen production by methane deep cracking process with that for steam and CO_2 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 CO_2 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 CO_2 emissions by about 50%, and carbon black will be valorized by steel industry. In the second process which is catalytic, H_2 will be reacted with CO_2 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 CO_2 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. Concomitantly, H_2/CO ratio could be tuned at values equal or lower than 2. Flue gases can be directly processed to syngas avoiding energy-intensive CO_2 concentration. Alternative technologies that provide energy into the system to get syngas include electroreduction and solar thermochemistry of CO_2-H_2O mixtures bypassing hydrocarbon co-feed. Plasma-assisted processes have also been demonstrated but energy efficiency for the dissociation reaction is much higher for CH_4 than for CO_2. The enabling technologies are based on combined CO_2 reforming, CO_2-H_2O electroreduction, and CH_4 deep cracking to H_2 that is further processed with CO_2.

2.4   COMMERCIAL/MARKET SIZE(S) AND OPPORTUNITIES

2.4.1   Value chain of CO_2

The worlwide strong incentive to slow down CO_2 emissions from stationary and mobile energy production brings to the forefront the utilization of CO_2 as C_1 feedstock. Additionally, one may argue that nature solely uses CO_2 as carbon resource for biomass production. Hence, designing synthetic procedures to convert CO_2 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 CO_2, 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 CO_2 capture and storage from industry emitters. Therefore, its expansion will depend on the development of CO_2 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 CO_2 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 Winschel, 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 CO_2 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 CO_2 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 CO_2 cannot counterbalance its emissions, being less than 1%.
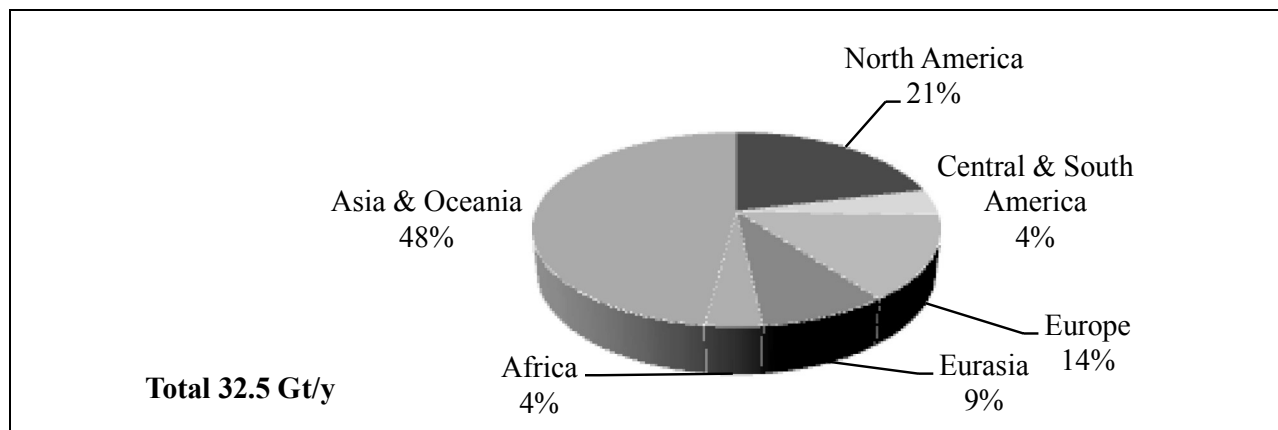
Figure 2.4.1.1 CO_2 emissions percentage by regions (EIA, 2011).

New concepts are, therefore, necessary to assess which technologies would have a stronger positive impact on CO_2 transformation. At a first glance, making chemicals for the energy sector should greatly improve CO_2 utilization. Syngas as intermediate represent a huge potential market as fossil fuels become further depleted, and syngas production from CO_2 may play a key role. More benefits could arise from avoiding CO_2 to be flared and from new opportunities in full use of CO_2-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 CO_2 into the processes tunes H_2/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 Nm^3/y. Additional 5 and 100 billions Nm^3/y are estimated for hydrogen and Fischer–Tropsch fuels, respectively. These figures correspond to around 10% of the 3,282 billions Nm^3/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.

2.4.3   Syngas production capacity

Syngas production capacity of a plant and the dowstream process to fuels or chemicals are interlinked as syngas continuously feeds the dowstream 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 CO_2 to syngas

Mature technologies in syngas synthesis and its purification for methanol production emits 1 ton of CO_2-eq per ton of methanol from natural gas, and twice more from coal (IEA, 2013). This example justifies the strong incentive for developing CO_2 to syngas routes for being implemented on an industrial scale to decrease net emissions. The sources of CO_2 vary from dilute stream, such as flue gases, to concentrated ones. The latter can originate from either capture/separation processes, oxy-combustion, or CO_2-rich natural gas fields. Developing CO_2 to syngas routes can be achieved through two strategies. The first one takes advantage of the mature technologies adapting them to CO_2 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 CO_2 in the co-feed provides a better adjusement of syngas composition suitable for a given downstream application. Derived-benchmark technologies are based on CO_2 reforming combined or not with steam reforming and/or partial oxidation. The contribution of CO_2 to syngas is there high. Nearly half of the co-feed may be made of CO_2. The processes, therefore, are of interest for CO_2-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 CO_2 reforming lies in the deployment of biogas which can be valorized one-step to syngas. Interestingly, operating CO_2 reforming with steam and oxygen allows the direct processing of flue gases. These alternatives will increase the CO_2 market to syngas as attested by on-stream technologies and demonstration units.

New concepts to convert CO_2 to syngas are best based on the use of renewable energies for providing electricity along with heat. In these cases, either CH_4 or H_2O is the hydrogen source. The processes converting CO_2 and H_2O into syngas do not anymore involve carbonaceous feedstocks and may open to new technologies free from constraints on carbon reserves and CO_2 emissions.

2.5   REMAINING HURDLES

The implementation of CO_2-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 H_2/CO ratio of unity is desired.

Gangadharan et al. (2012) evaluated the economic and environmental impact of combining CO_2 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 CO_2 emissions was calculated when comparing optimized combined reforming and steam reforming (Lim et al. 2012).

Zhang et al. (2013) compared bi- and trireforming economics for methanol production. The trireforming and bireforming processes require 19.0 kWh and 11.5 kWh per kg of CO_2 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 CO_2 utilization from flue gases in industrial scale.

Minutillo and Perna (2009) carried out an extensive investigation on the treatment of CO_2 from fossil-fuel-fired power plants, using the tri-reforming process integrated with electrical power co-generation. An impressive estimated reduction in CO_2 emissions close to 85% was calculated.

Fu et al. (2010) reported on the economics of high-temperature steam/CO_2 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 O_2, 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 CO_2 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 CO_2 dissociation to be a competitive technology.
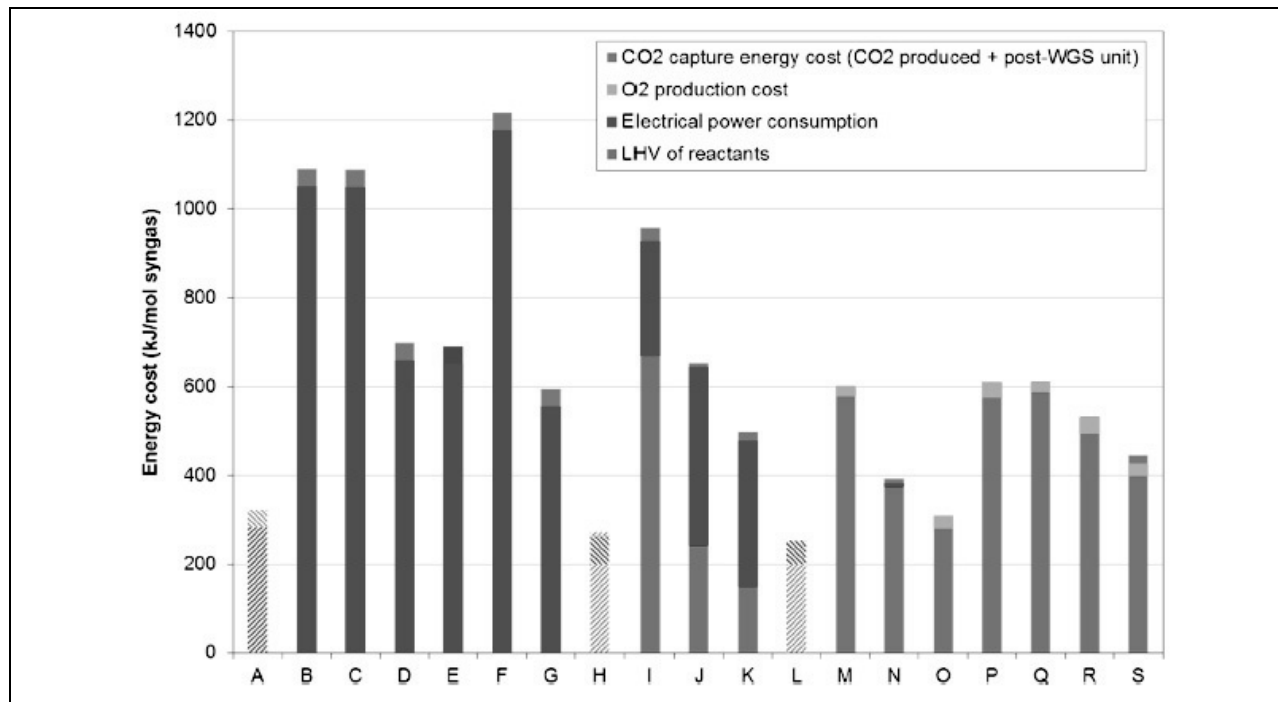
Figure 2.5.1   Energy cost for the production of 1 mol of syngas through different processes. (A) Perfect CO_2 dissociation-100% conversion, 100% chemical energy efficiency; (B) CO_2 dissociation by dielectric barrier discharge; (C) CO_2 dissociation by thermal plasma jet; (D) CO_2 dissociation by DC corona discharge; (E) CO_2 dissociation by gliding arc plasmatron; (F) CO_2 dissociation by dielectric barrier discharge with catalyst; (G) CO_2 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 plama-based technologies in the future. Globally, the usage of CO_2 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_2O 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_2O 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_2O for producing syngas and O_2 as by-product which can be sold birnging 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.
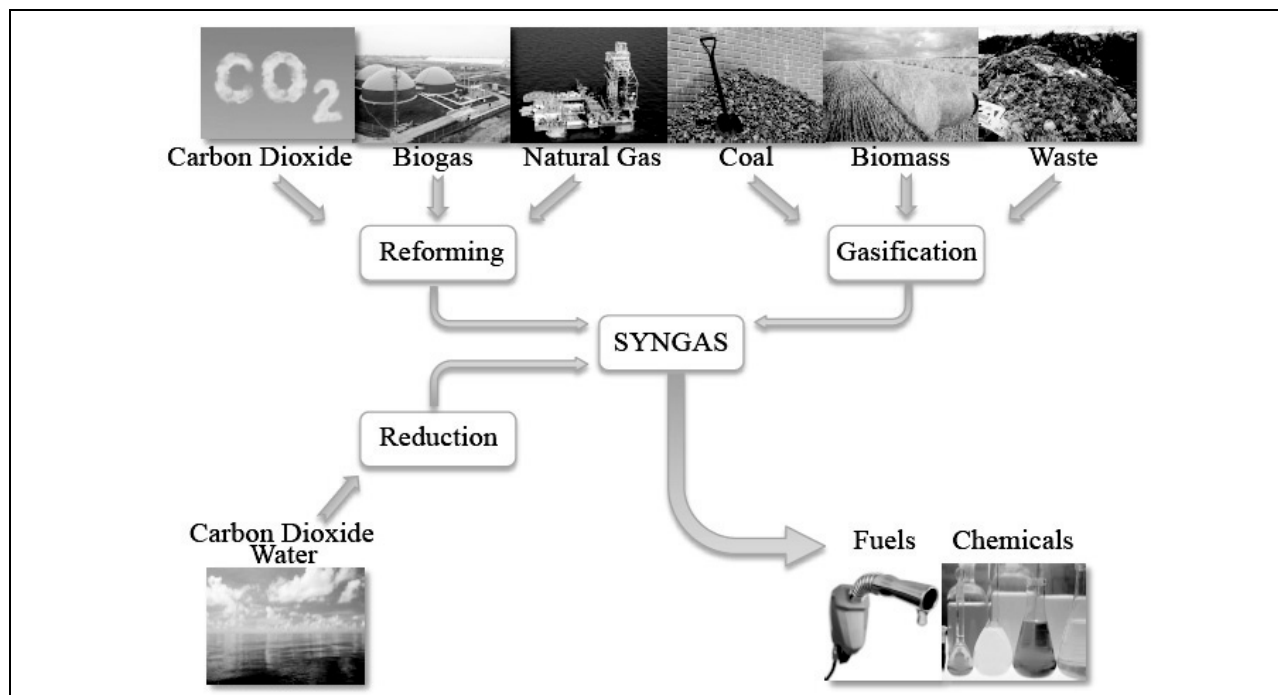
Scheme 2.6.1   Schematic representation of the network of processes to syngas.

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3. CO$_2$ 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 CO$_2$ 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 CO$_2$ emissions, CO$_2$ 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 CO$_2$ 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 CO$_2$. 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

al., 1995). 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 hydrogencarbonates, 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, H_2CO, CH_3OH, CH_4, 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 CO_2 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 CO_2 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 CH_4, 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
Present and Short Term Usage of CO_2 (modified from Aresta et al., 2013).

Compound	Production (Mt)	CO_2 used (Mt)	2016 forecast (Mt)	CO_2 required (Mt)
Urea	155	114	180	132
Methanol	50	8	60	10
Organic carbonates	0.2	0.005	>2	0.5
Polycarbonates	4	0.01	5	1
Carbamates	5.5	0	>6	1
Polyurethans	>8	0	10	0.5
Acrylates	2.5	0	3	1.5
Formic acid	0.6	0	1	0.9
Inorganic carbonates	200	~50	250	70
Technological fluids		28		80
DME	*11.4*	*3*	*>20*	*>5*
TBME	*30*	*1.5*	*40*	*3*
CH_2O	*21*	*3.5*	*25*	*5*
Higher alcohols				
Hydrocarbons				
Methane				
Total		200		~300

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

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 H_2, CO, CO_2, and H_2O but the producer gas also contains CH_4, 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).
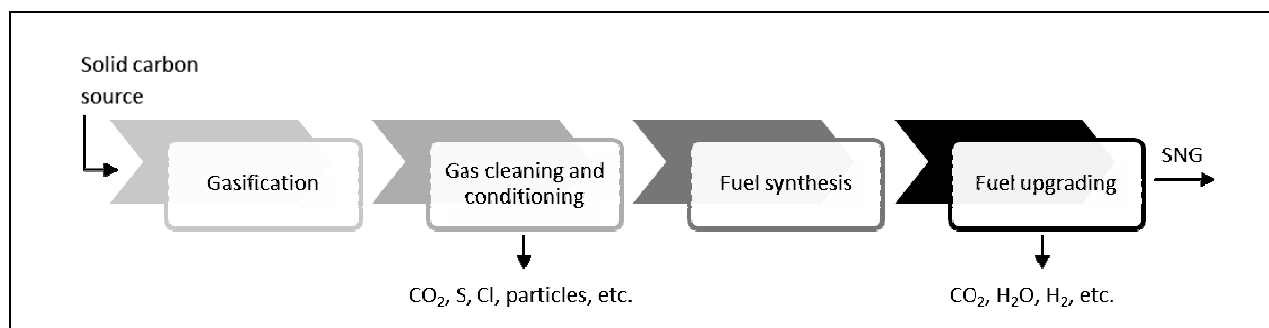
Figure 3.2.1   General scheme of the process chain from a solid carbon source to SNG (modified from Kopyscinski et al., 2010).

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 H_2/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_2O 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 kW$_{th}$ 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).
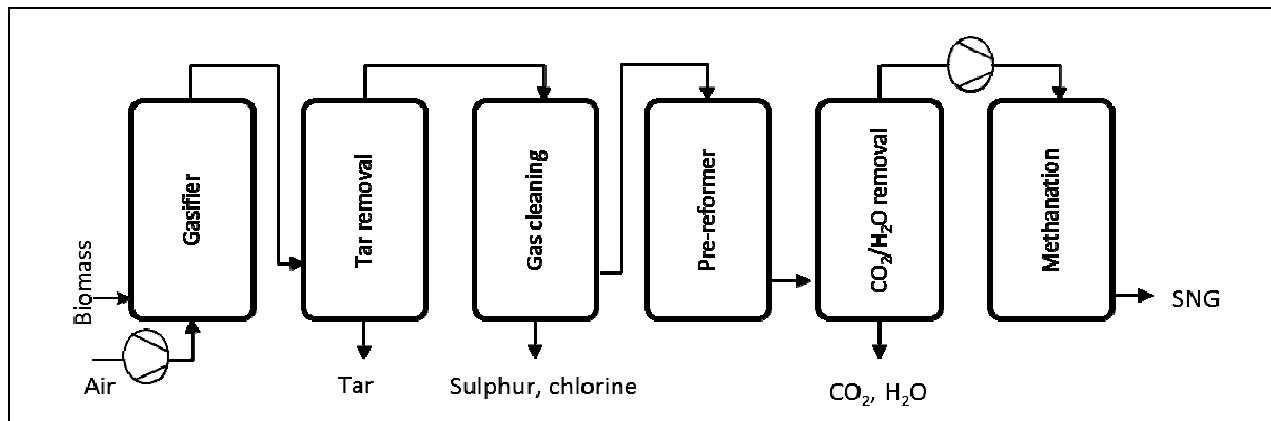
Figure 3.2.2   High-efficiency SNG production system (modified from Rabou & Bos, 2012).

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 m^3/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 CO_2 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 CO_2

The reaction of CO_2 methanation that is the hydrogenation of CO_2 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 CO_2 fixation technologies.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{3.1}$$

Carbon dioxide turns out to be an important C_1 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 CO_2 to fuels or raw materials which are easily transportable. However, there are not yet many commercial plants established using CO_2 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 m^3 of renewable synthetic methane per year (NGVA Europe, 2013; Clariant, 2013; Park and McFarland, 2009).

3.3.1   Catalytic CO_2 conversion

The methanation of carbon dioxide is thermodynamically favorable at low temperatures (ΔG_{298K} = -130 kJ/mol). Thus, the methanation process generally operates at around 670 K (Gao et al., 2009). The methanation reaction is highly exothermic (ΔH_{298K} = -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 CO_2 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 CO_2 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., Al_2O_3, SiO_2, TiO_2, ZrO_2 and CeO_2). The catalysts used have many similarities to those for CO_2 reforming (dry reforming). CO_2 hydrogenation has been studied and described recently by using various catalysts including Ni/γ-Al_2O_3 (Rahmani et al., 2013), Ni/SiO_2 (Chang et al., 2001), Ni/TiO_2 (Liu et al., 2013), Ni/ZrO_2 (Perkas et al., 2009), Ni/CeO_2 (Tada et al., 2012), Ni/La_2O_3 (Song et al., 2010), Ni-Mo/Al_2O_3 (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), $Ni/CeZrO_2$ (Ocampo et al., 2009), $Ni/ZrO_2-Al_2O_3$ (Mengdie et al., 2011), Raney nickel (Sane et al., 1984), Ni/zeolite (Jwa et al., 2013), NiHNaUSY zeolites (Graca et al., 2014), $LaNiO_3$ 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 CeO_2 (Sharma et al., 2011), Co/SiO_2 (Guilin et al., 2013), Co/KIT-6 (Guilin et al., 2013), $MoO_3/CeO_2-Al_2O_3$ (Jiang et al., 2013), Pd-MgO/SiO (Kim et al., 2010), Pd–Mg/SiO_2 (Park and McFarland, 2009), Pt/Tnt (Yu et al., 2008), Rh/γ-Al_2O_3 (Beuls et al., 2012), Rh/SiO_2 (Kusama et al., 2000), Rh/TiO_2 (Abe et al., 2009), Rh/Y zeolites (Bando et al., 2000), Ru/Al_2O_3 (Kusmierz, 2008), Ru and Pd doped MnNi/Al_2O_3 (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 CO_2 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 carbonyls 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 CO_2 methanation than nickel catalysts. However, noble metal catalysts are notably more expensive than nickel based catalysts limiting their use in the catalytic hydrogenation of CO_2. The Ru catalyst has an excellent low temperature CO_2 catalytic methanation activity compared to other studied precious metal catalysts,

exhibiting high CO_2 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 CO_2 methanation (Chang et al., 2003). Presently, various materials are used as the support for nickel catalysts such as γ-Al_2O_3, SiO_2 (amorphous and mesoporous silicas), ZrO_2, CeO_2 and zeolites. (Rahmani et al., 2013, Zhou et al., 2013, Tada et al., 2012, Wang and Gong 2011)

CeO_2 is generally used to improve the performance of alumina. CeO_2 can affect the thermal and structural stability of alumina, the degree of dispersion of active ingredients on the Al_2O_3 carrier, and the storage and release of oxygen by the catalyst. (Gao et al., 2009b) ZrO_2 is another support of interest due to its acidic/basic features and CO_2 adsorption ability. Ni/ZrO_2 catalysts with various amounts of ZrO_2 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, TiO_2, 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 CO_2 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 CO_2 methanation fall into two main categories. The first one involves the conversion of CO_2 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 CO_2 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).
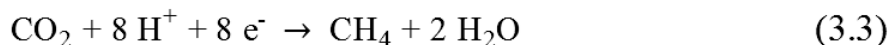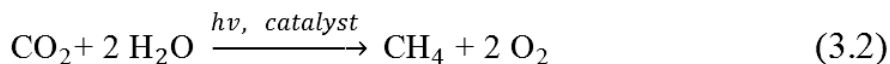
Since the 1970s a number of methanation processes have been developed, comprising both fixed bed and fluidized bed methanation (Kopyscinski, 2010). Most of the units for the catalytic methanation of CO_2 have been fixed-bed reactors. A number of current SNG plant designs are based on a series of adiabatic 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).
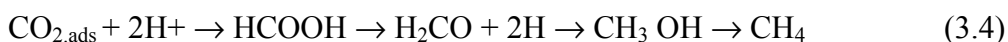
3.3.2   Photocatalytic CO_2 conversion

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_{redox}^0) 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):

$$CO_2 + 2\,H_2O \xrightarrow{\;hv,\;catalyst\;} CH_4 + 2\,O_2 \qquad\qquad (3.2)$$

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O \qquad\qquad (3.3)$$

Recently there are studies which have been concentrated to find out the detailed mechanistic steps to improve the efficiency of the CO_2 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 CO_2 via the Fischer−Tropsch sequence (Eq. 3.4):

$$CO_{2.ads} + 2H+ \rightarrow HCOOH \rightarrow H_2CO + 2H \rightarrow CH_3\,OH \rightarrow CH_4 \qquad\qquad (3.4)$$

The most crucial challenge to meet in the CO_2 conversion to methane and other C1 products is that CO_2 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 3.3.2.1
Some Photocatalysts Found Possible Especially for SNG Production
(Tahir and Amin, 2013a; Mao et al., 2013; Cybula et al., 2012; Wu et al., 2013;
Varghese et al., 2009, Zhai et al., 2013, Li et al., 2010, Corma and Garcia, 2013,
Mei et al., 2013, Li et al., 2012)

UV light	UV-C (<280 nm)	TiO_2, ZrO_2, Ag/TiO_2, TiO_2-P25, K/Y-zeolite, MgO, Zn/Ce-LDH, Zn/Ti-LDH
	UV-B (280−315 nm)	TiO_2, Cu/TiO_2, Ti-MCM-41, Ti-MCM-48, Ag/TiO_2, ZnS-MMT
	UV-A (315−380 nm)	TiO_2, ZrO_2, Ag/TiO_2, Pt/TiO_2, Nafion layer on Pd/TiO_2, Ru/TiO_2, Cu/SiC, Cu/TiO_2
	Wavelength of UV-irradiation not specified	TiO_2/SiO_2, Ti/Si-h-c, TiSBA-15, Ru-RuO/Ti-NPs, Li_2O/TiO_2 over MgO and/or Al_2O_3, Cu/ZnO, $TiO_2/Pd/Al_2O_3$, Au/Ti/SBA-15, Ti/SBA-15, KNb_3O_8, HNb_3O_8
Visible light		Ni-NiO/$InTaO_4$, $AgBr/TiO_2$, $CeSe/Pt/TiO_2$, $Cu/Pt/TiO_2$

LDH = layered double hydroxide, MMT = montmorillonite modified TiO_2, NP = nanoparticle

The studied materials for CO_2 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 CO_2. 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 CO_2 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 CO_2 (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 H_2 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).
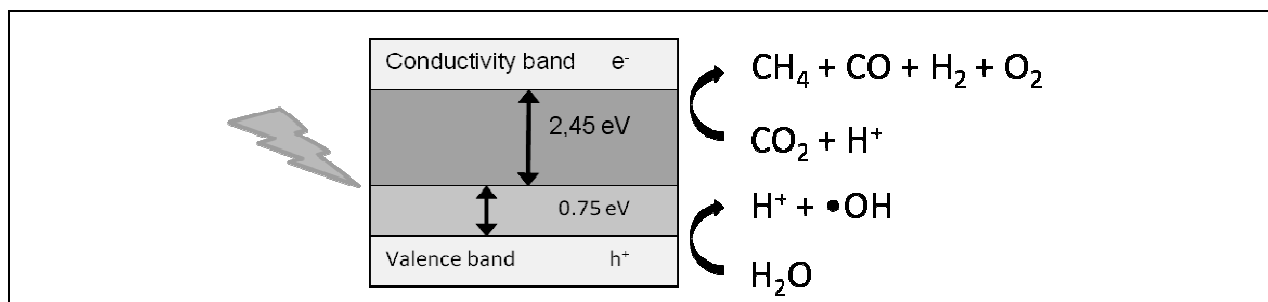
Figure 3.3.2.1   Carbon dioxide conversion to hydrocarbon fuels by sunlight-driven routes (based on Varghese et al., 2009).

The photoreduction of CO_2 and formation of hydrocarbons especially methane is still in the level of experiencing in the laboratory scale. The amounts of CH_4 (and other hydrocarbons) formed during the photocatalytic reactions are in many studies quite low, being from few (<1 $\mu mol\ g^{-1}h^{-1}$) up to around one hundred (100 $\mu mol\ g^{-1}h^{-1}$) 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 CH_4 has also been reported to be reached the formation level being at around 350 $\mu mol\ g^{-1}h^{-1}$ over the 20%MMT/TiO_2 catalyst (Tahir and Amin, 2013b).
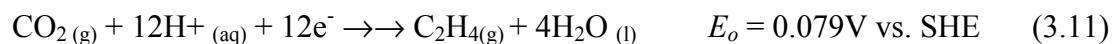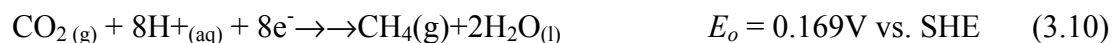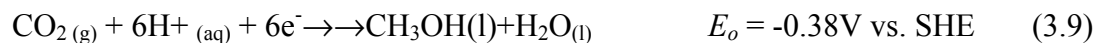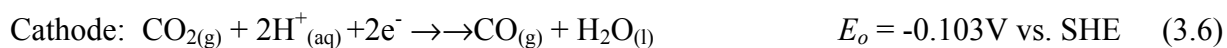
As a summary, the photocatalytic CO_2 reduction and conversion to SNG and higher hydrocarbons contains a series of reactions both parallel and in series. These reaction mechanisms are not yet fully understood and further research is still needed. Thus, efficient

materials and catalysts are needed to achieve the reasonable levels of the selectivity and the yield of the desired products.

3.3.3   Electrochemical CO_2 conversion

In CO_2 utilization one important conversion technology is the electrochemical reduction of CO_2 (ERC). Electrochemically CO_2 is converted into wide variety of products such as CO, $HCOO^-$, CH_4, C_2H_4, CH_3OH, etc. (Halmann and Steinberg, 1999) at different reaction conditions. The ERC is widely studied using different electrocatalysts, and operating conditions. The electroreduction of CO_2 generally takes place in aqueous, and non-aqueous solutions and also in metal mediated complexes (Aresta, 2010). In the ERC process, CO_2 is reduced at cathode electrode to form CO_2^- anion and the O_2^-/H^+ evolution (Equation 3.5) takes place at the anode by H_2O to form intermediates and products. The balanced reactions with standard potentials (E_o) versus standard hydrogen electrode (SHE) at anode and cathode are presented as follows.

Anode: $H_2O_{(l)} \rightarrow \rightarrow 2H^+_{(aq)} + 0.5O2_{(g)} + 2e^-$ $E_o = 0.0V$ vs. SHE   (3.5)

Cathode: $CO_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow \rightarrow CO_{(g)} + H_2O_{(l)}$ $E_o = -0.103V$ vs. SHE   (3.6)

$\quad\quad\quad\quad CO_{2\,(g)} + 2H^+_{(aq)} + 2e^- \rightarrow \rightarrow HCOOH_{(aq)}$ $E_o = 0.225V$ vs. SHE   (3.7)

$\quad\quad\quad\quad 2H^+_{(aq)} + 2e^- \rightarrow \rightarrow H2_{(g)}$ $E_o = 0.0V$ vs. SHE   (3.8)

$\quad\quad\quad\quad CO_{2\,(g)} + 6H+_{(aq)} + 6e^- \rightarrow \rightarrow CH_3OH(l) + H_2O_{(l)}$ $E_o = -0.38V$ vs. SHE   (3.9)

$\quad\quad\quad\quad CO_{2\,(g)} + 8H+_{(aq)} + 8e^- \rightarrow \rightarrow CH_4(g) + 2H_2O_{(l)}$ $E_o = 0.169V$ vs. SHE   (3.10)

$\quad\quad\quad\quad CO_{2\,(g)} + 12H+_{(aq)} + 12e^- \rightarrow \rightarrow C_2H_{4(g)} + 4H_2O_{(l)}$ $E_o = 0.079V$ 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_e), faradaic (η_e), and energetic (ε_e) efficiencies (Equations 3.12-3.14, respectively) (Jhong et al., 2013). The parameters are defined as follows (where, E_k^o is the equilibrium potential ($E^o_{cathode} - E^o_{anode}$) and η is the cell overpotentials (cathode + anode)).

Current density: $J_e = \dfrac{\text{Total current produced (A)}}{\text{Total electrode area (m}^2)}$ (3.12)

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

Energetic efficiency: $\varepsilon_e = \sum \dfrac{E_k^0\, \eta_e}{E_k^0 + \eta}$ (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

- CO_2 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.
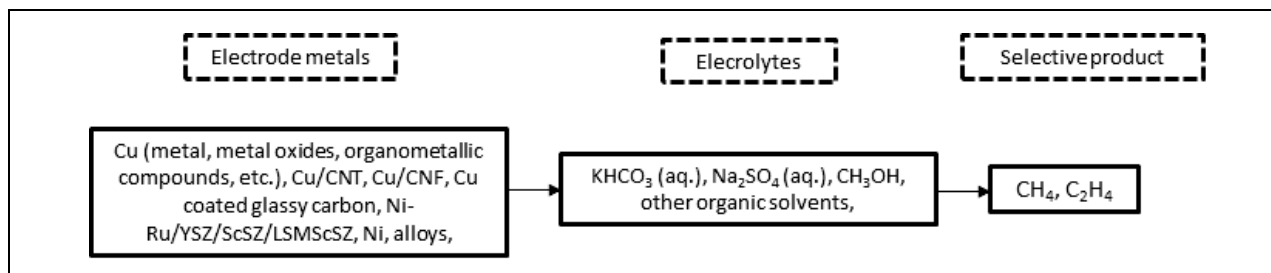
Figure 3.3.3.1   Electrochemical reduction of CO_2 to methane and ethylene on various studied electrodes, electrolyte solutions (aqueous and non-aqueous) (modified from Halmann and Steinberg, 1999; Jhong et al., 2013).

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/cm^2. 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 CO_2 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 CO_2 on the metal is needed in order to undergo the desired reaction path to form CH_4 species (Gattrell et al., 2006 and 2007). The solubility of CO_2 is a very crucial factor which determines the CO_{ads} 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 CO_2, deactivation, poor kinetics, by-products formation, and low tolerance to impurities (Li, 2010). In aprotic organic solvents (e.g., methanol) CO_2 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 CO_2 into hydrocarbons (i.e. CH_4, C_2H_4 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 CO_2 reduction on a Cu catalyst undergoes series of consecutive steps to form various products. First, CO_2 is adsorbed on the electrode to form an anion radical and then it is reduced to CO_{ads}. 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, H_2, CO and formate are formed with high current densities. The CO_{ads} 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 H_2 evolution is the crucial step to avoid. Recently Li et al. (2013) have reported CO_2-H_2O 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 CO_2 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 CO_2 but many technical challenges and economical constrains should be addressed before the process can be commercially applied.

3.3.4   Membrane assisted CO_2 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.
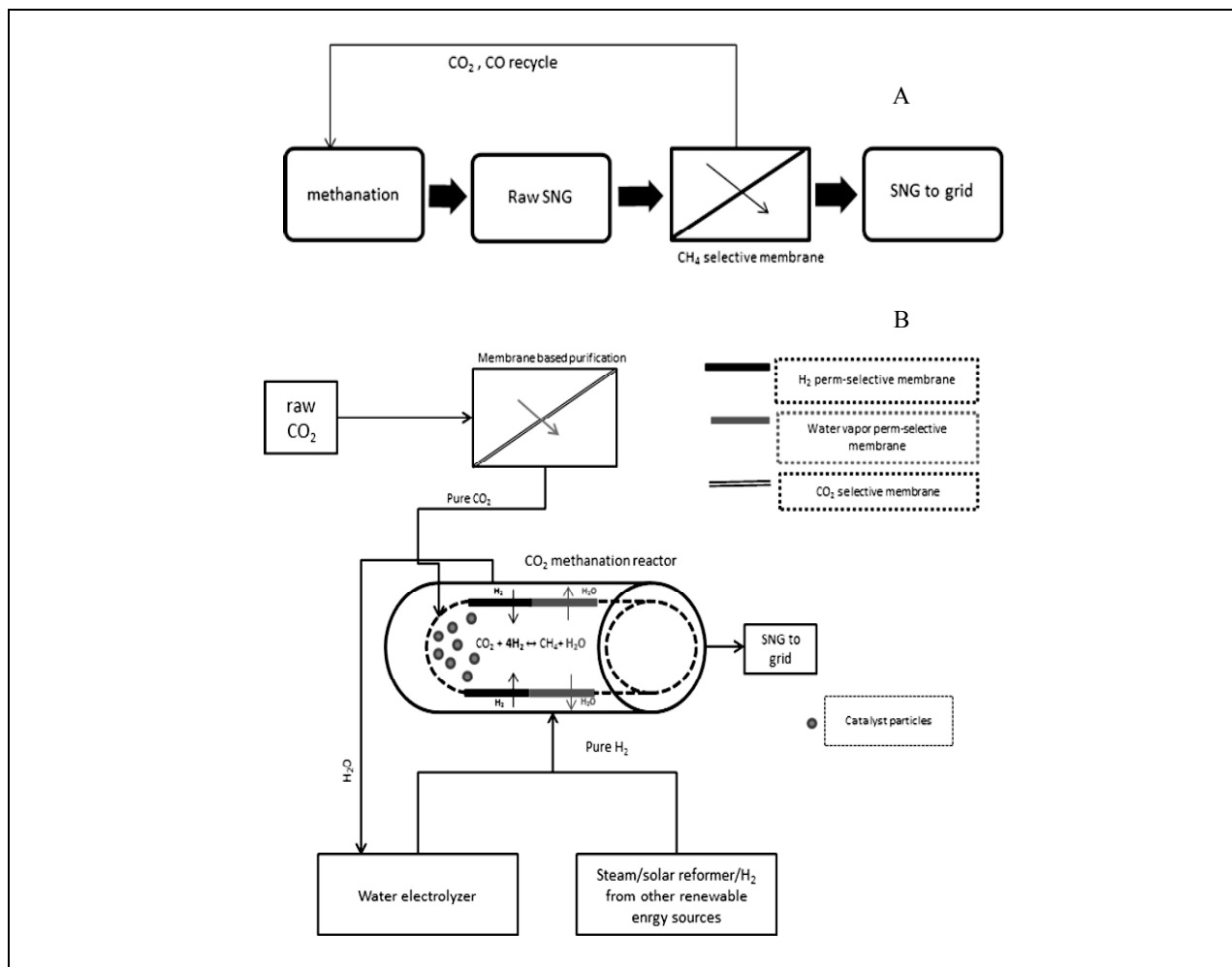
Figure 3.3.4.1   Possible configurations for the membrane applications in the framework of SNG production. A) Upgrading and purification of raw SNG via membrane system. B) Three potential options for membrane applications in CO_2 conversion to SNG, membranes for CCS to purify the raw CO_2 gas to high purity gas before feeding it into a methanation reactor, membrane assisted reactor for selective removal of by-product water-vapor and distribution of pure H_2 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 CO_2 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 H_2 (i.e. a distributor type MR) gas into the methanation reactor (H_2 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 H_2O 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 H_2O 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 CO_2 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 CO_2 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 liquour 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/CO_2 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 CO_2 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 CO_2 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 becouse it can be used in a remote natural gas fields for changing LNG to liquid fuel that can be tranported 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 CO_2 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 dependency 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 syntheticing 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_2 as a raw material. Lately many methods, e.g. adsorption and membranes, and catalysts have been developed to recover CO_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_2 an important and sustainable raw material in the future chemical industry. Catalytic material development for CO_2 to SNG has to face also e.g. higher tolerance towards impurities in raw materials streams, *i.e.* CO_2 and biomass streams. CO_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_2 emissions.

Sustainability of CO_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_2 streams.

The sustainability assessment analysis of the CO_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_2, production of H_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_2 and H_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_2 and waste biomass lead to a reduced need of fossil fuels, GHG savings and better

carbon economy (Demirbas, 2009). In addition, the CO_2 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 CO_2 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 CO_2 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. CO_2 in SNG and further value added chemicals and fuels production.

This approach, if successful, could also offer us a possibility to considerably reduce anthropogenic CO_2 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 CO_2 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 CO_2-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. CO_2 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. CO$_2$ 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.
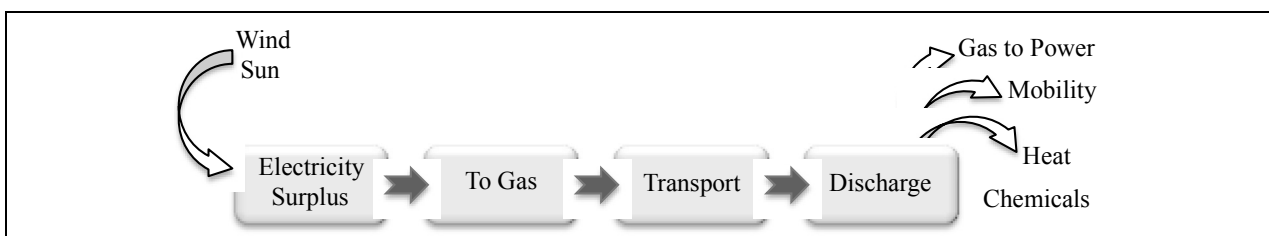
Scheme 4.1 "Power to Gas" scenario.

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 CO$_2$ hydrogenation to methane.

4.2   CO$_2$ UTILIZATION IN "POWER TO GAS"

4.2.1   Electricity to H$_2$

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 H$_2$ and O$_2$. 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 H$_2$ production has been estimated to be about 3.4 trillion standard cubic meter per year. Most of this H$_2$ 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 H$_2$. However, the processes produce a mixture of CO and H$_2$ (syngas) which necessitates further downstream purification processes. Water electrolysis to H$_2$ is also practiced where high purity CO-free hydrogen is needed, but it accounts to roughly 4% of total H$_2$ 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 H$_2$ 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 H$_2$ 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 exhanging 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.
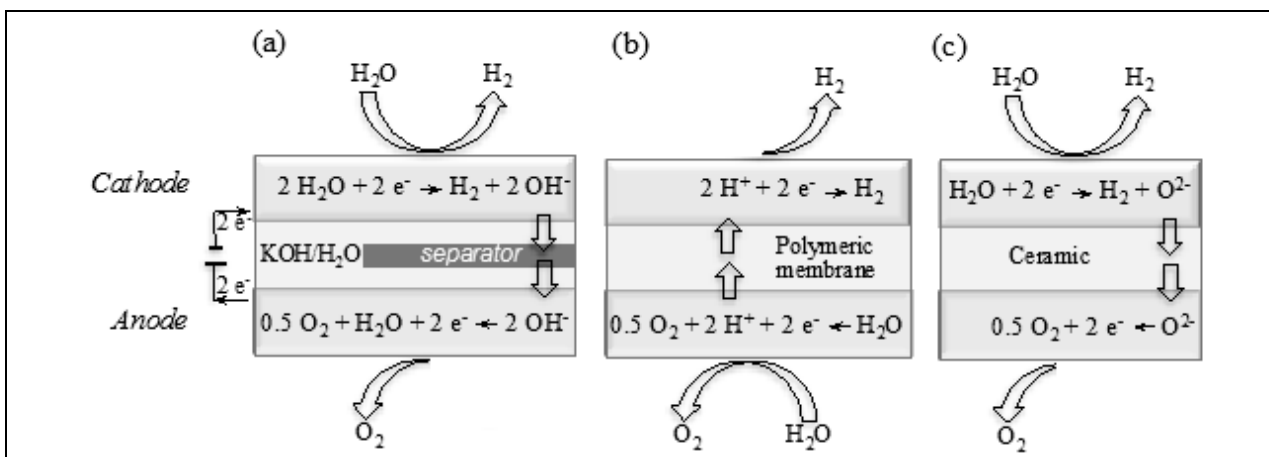
Scheme 4.2.2 Principle of water electrolysis with (a) alkaline, (b) PEM, and (c) SOEC cells.

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 $\mu S\ cm^{-1}$.

Water disssociation to H_2 and O_2 is an endothermic process (equation (4.1)) and operates at theoritical potential of 1.481 V at 298 K.

$$H_2O_{(liquid)} \longrightarrow H_2 + 0.5\ O_2 \qquad \Delta_r H^0 = +286\ kJ\ mol^{-1}$$

(4.1)

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.
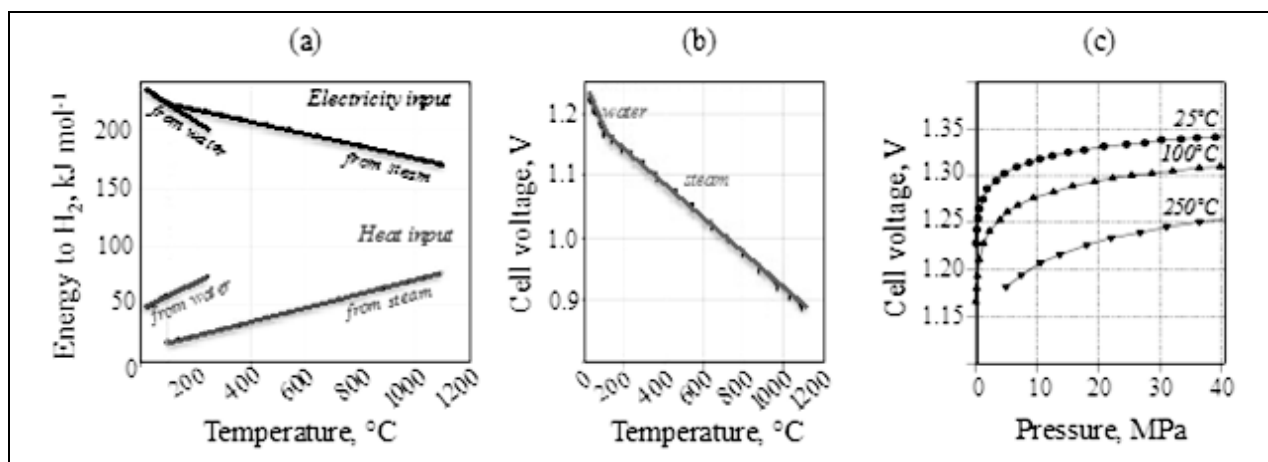
Figure 4.2.2.1 Thermodynamics of the water splitting process at 0.1 MPa: (a)energy with temperature, (b) cell voltage with temperature, and (c) cell voltage with pressure at three different temperatures (adapted from Millet, 2012).

The alkaline electrolyzer is commercial technology (Holladay et al., 2009; Gahleitner, 2013). Water is reduced to H_2. The by-species OH^- then migrates to the anode to liberate O_2 (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 $Nm^3\ h^{-1}$ 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 disavantages are the corrosive caustic liquid electrolyte, H_2 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 currrent 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 O^{2-} migrates to the anode to be oxidized to O_2 (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), CO_2 reforming (4.3), or dissociation (4.4).

$$CH_4 + H_2O \text{ (steam)} \rightarrow \quad CO + 3\,H_2 \qquad \Delta_r H^0 = +206 \text{kJ mol}^{-1} \qquad\qquad (4.2)$$

$$CH_4 + CO_2 \rightarrow \quad 2\,CO + 2\,H_2 \qquad \Delta_r H^0 = +247 \text{kJ mol}^{-1} \qquad\qquad (4.3)$$

$$CH_4 \rightarrow C \text{ (graphite)} + 2\,H_2 \qquad \Delta_r H^0 = +75 \text{kJ mol}^{-1} \qquad\qquad (4.4)$$

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 H_2 and O_2 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   CO$_2$ 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.

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O \qquad \Delta_r H^0 = -253 \text{ kJ mol}^{-1}$$
$$(4.5)$$

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 ΔG^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 SiO_2, TiO_2, Al_2O_3, ZrO_2, and CeO_2 (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 CO_2 hydrogenation is better viewed as CO hydrogenation, CO being formed at first from CO_2. This is still a highly debated topic. A recent report on the process mechanism with Ni-CeO$_2$ points out CO is better formed by CO_2 activation on the support (Ussa Aldana et al., 2013). The main pathway to methane is the hydrogenation of CO_2. 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 Norvegian Utsira island (6.2 km^2, 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 m^3 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).
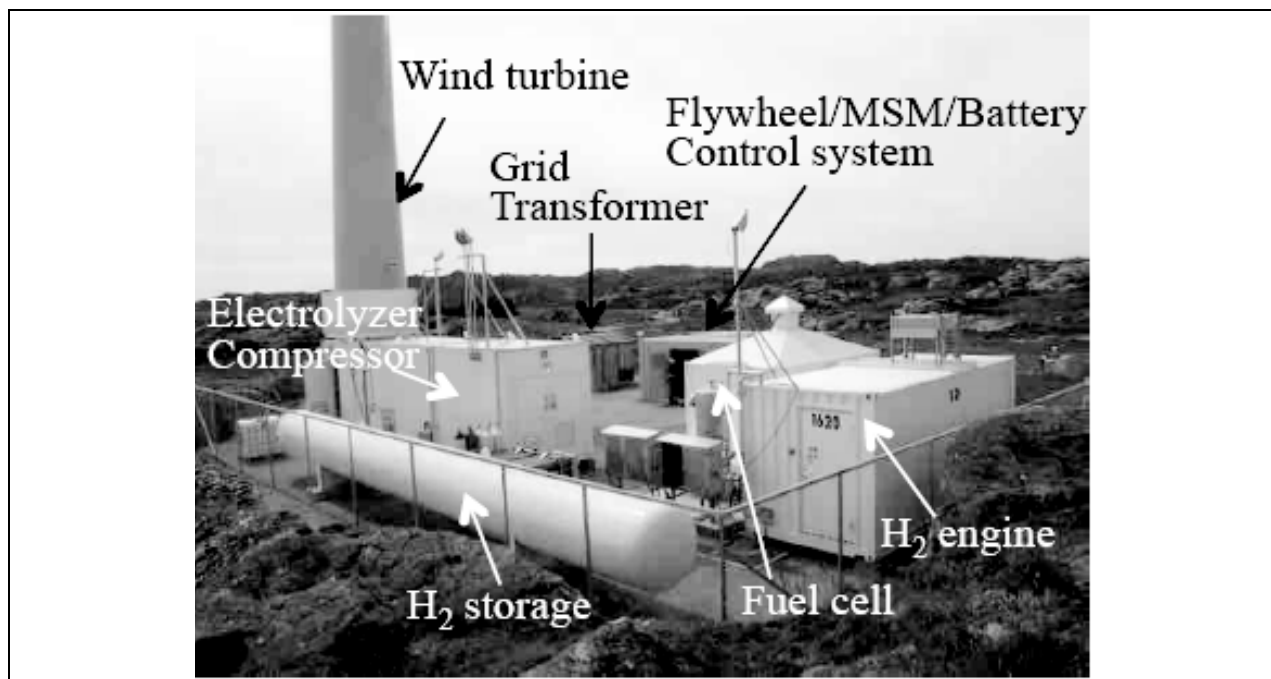
Figure 4.2.4.1   Utsira wind-hydrogen integrated system.

4.2.4.2   Residential H_2 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 m^3 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 H_2 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 H_2 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 H_2 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 H_2 dispensed.
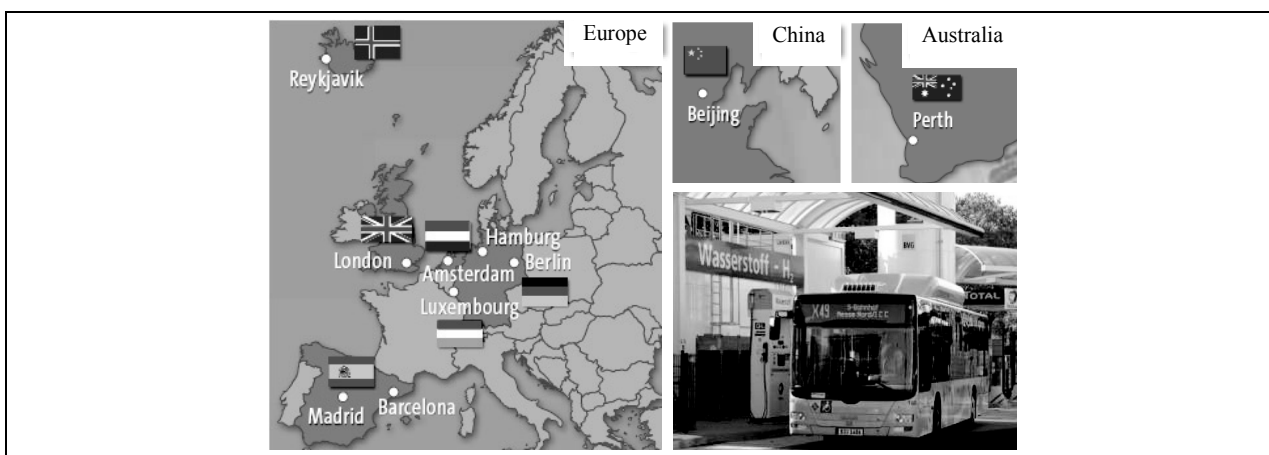
Figure 4.2.4.2   Cities involved in the HYFLEET:CUTE project, and bus fueling station in Berlin.

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® 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® fuel. A Hythane® 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_2 storage units for a total close to 200 kg of H_2.

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_2 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_2 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 m3 of hydrogen per hour. Then, H2 is stored as magnesium hydride with a storage capacity up to 500 kg (for an energy content of 16.5 MWh). It enables H2 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.
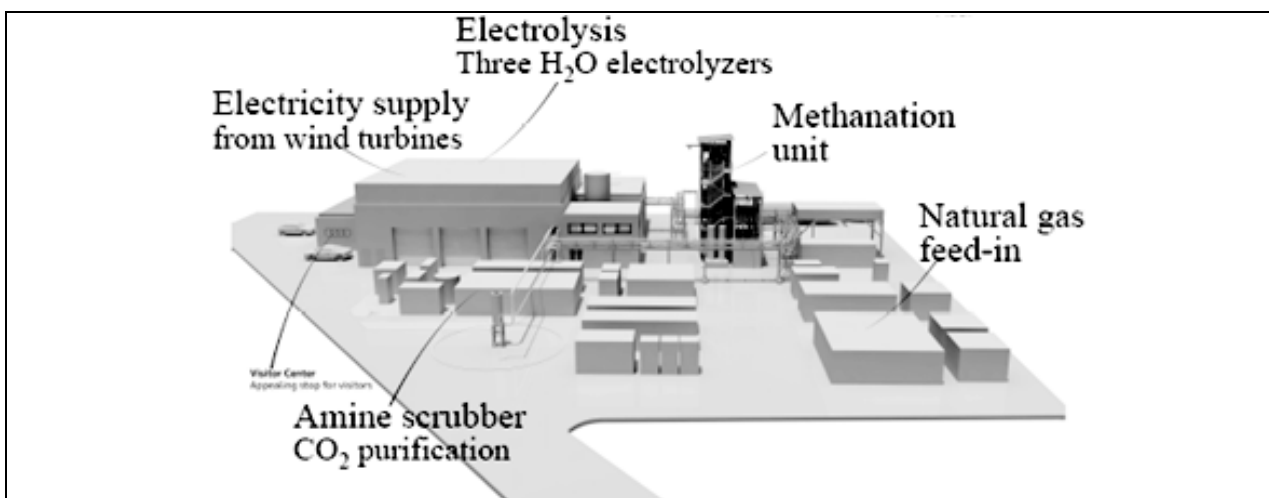
Figure 4.2.4.3   Audi e-gas plant maquette.

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 CO_2 from biogass. It will alllow to run 1500 new Audi A3 Sportback g-tron vehicles with an annual mileage of 15 000 CO_2 neutral km.

4.3   COMMERCIAL/MARKET OPPORTUNITIES

4.3.1   Markets

The interest in H_2 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.
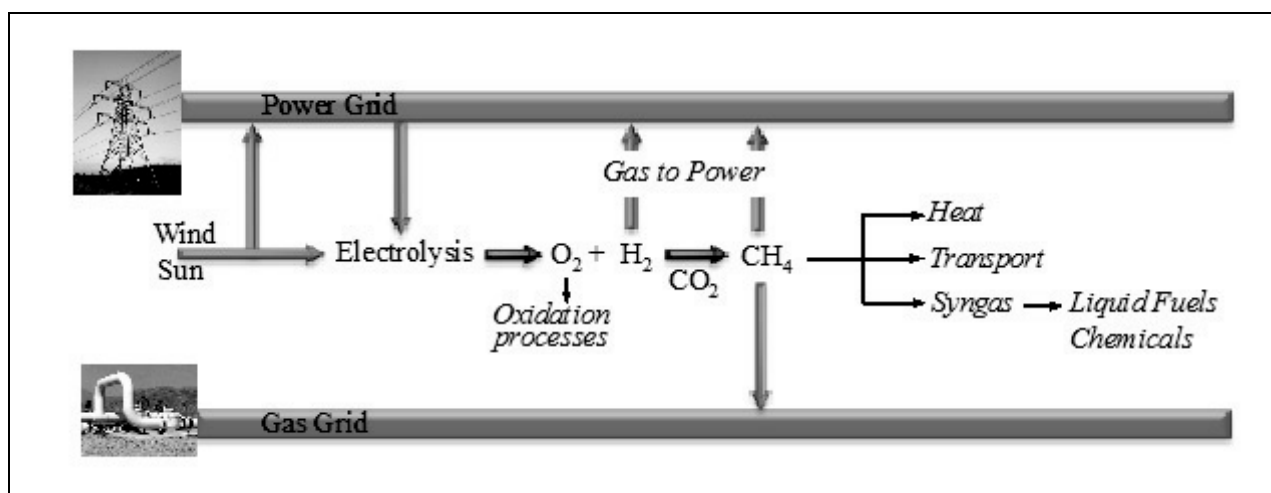
Scheme 4.3.1   Power and gas grid network for different markets.

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)

Project	Power installed	Electrolysis Technique
Werlte D) - Audi AG	6000	Alkaline
Aragon (S) - ITHER	4000 & 70	Alkaline & PEM
Falkenhagen (D) - E.ON AG	2000	PEM
Puglia region (I) -INGRID project	1200	Alkaline
Grapzow (D) - RH2 WIND project gruppe	1000	Alkaline
Grabenn (D)	1000	Alkaline
Hambourg (D) - Vattenfall	900	Alkaline
Prenzlau (D) - Enetrag AG	500	Alkaline
Frankfurt (D) - Thuga & ITM Power	360	PEM
Foulum (DK) Electrochaea	250	PEM
Stuttgart (D) – Solar Fuel & Fraunhofer IWES	250	PEM
Karlsruhe (D) - DVGW & KIT	200	undisclosed
Xermade (S) - Sotavento Project	200	Alkaline
Herten (D) - Stadt Herten & Evonic Industries	165	PEM
Leverkusen (D) - CO2RRECT Project: Siemens & RWE	100	undisclosed
Schwandorf (D) - Eucolino: Schmack & Viessmann	100	undisclosed
Ibbenburen (D) - RWE, CERAM Hyd	100	undisclosed
Utsira (N)	50	Alkaline
Freiburg (D) - H2Move: Fraunhofer ISE	40	undisclosed
Tahivilla (S) - Hidrolica Project	40	PEM
Stuttgart (D) - Solar Fuel & Fraunhofer ZWS	25	PEM
SamsØ (DK) - SamsØ Energy Academy	20	undisclosed
Groningen (NL) - DNV KEMA	7	PEM
France - GDF Suez GRHYD project	new project	

SolarFuel is now ETOGAS

4.4   TECHNICAL/ECONOMIC HURDLES

4.4.1   Cost-effective H_2 Generation, Energy Storage, Others

4.4.1.1   Cost effective H_2 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 H_2 generation is the price of water purification and its avaibility. 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.
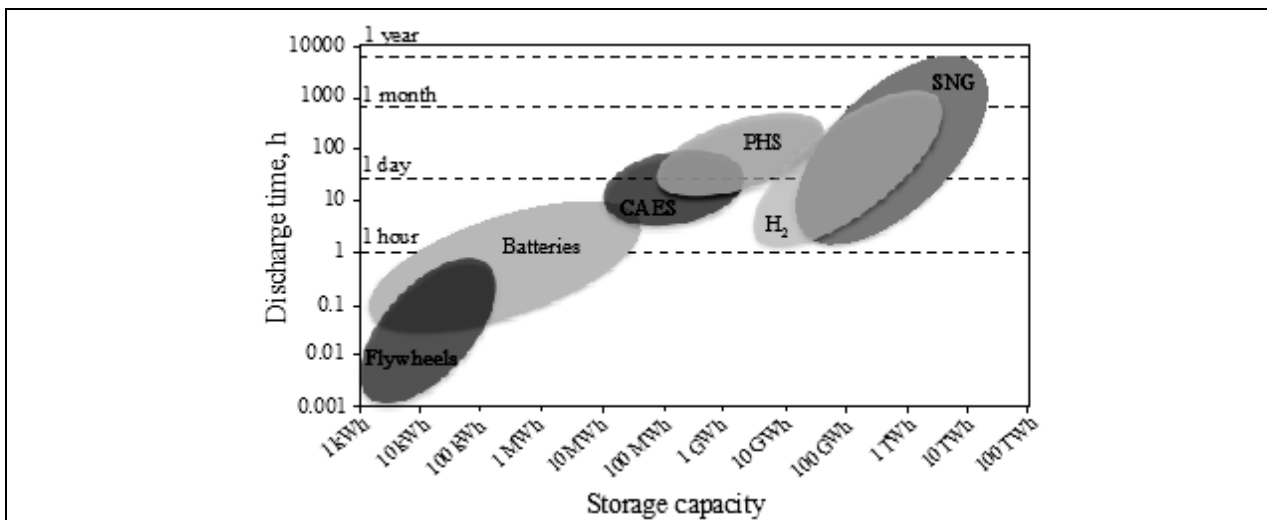
Figure 4.4.1.2   Discharge time vs storage capacity of flywheels, batteries, compressed airenergy storage (CAES), pumped hydro storage (PHS), hydrogen (H_2) and synthetic natural gas (SNG). Adapted from Specht et al. (2009).

According to Figure 4.4.1.2, H_2 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 H_2 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 H_2O/CO_2 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 H_2 and CO_2, (*3*) electrolyzers are compact utilities to H_2 and O_2, two gases which are marketable, and (*4*) there are geographical regions where hydrocarbons are simply not available, H_2 from water is the only practical means of providing hydrogen.

Small-, medium- and large-scale delivery of H_2 in remote areas, at fueling stations, and integrated to the natural gas grid are possible. To enable a greater penetration of renewable energy resources, H_2 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 CO_2 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 avaibility of inexpensive CO_2.

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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