

CO₂ Conversion to Synthetic Natural Gas (SNG)
Literature Review

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1. INTRODUCTION

Global warming-induced climate change is one of the significant threats to civilization of modern times. CO₂ is the main contributor to the greenhouse gases, so the efforts should be allocated to mitigate CO₂ emissions. The different proposed technologies follow one of two major approaches: to capture and geologically sequester CO₂, or to convert CO₂ into useful low-carbon fuels. In today's world of high-energy demands, CO₂ conversion and utilization seems to be a more attractive and promising solution.

The Power-to-Gas (PtG) process chain could play a significant role in the future energy system. By utilizing this Power-to-Gas pathway, electrical energy from renewable resources can be converted into storable chemical energy carriers (i.e. methane). In comparison to traditional methanation processes where hydrogen is supplied by a gasifier, in PtG the hydrogen comes from an electrolysis plant which uses excess electrical energy to split water into hydrogen and oxygen. Then, the hydrogen, together with CO₂, is fed into a methanation reactor. For the methanation process, several process concepts exist: chemical, photochemical, electrochemical and biological methanation.

CO₂ as a raw material has been a focus in the CO₂-reduction research area. Presently, the use of CO₂ as chemical feedstock is limited to a few industrial processes; synthesis of urea and its derivatives, salicylic acid, carbonates and methanol. The CO₂ hydrogenation to methane (CO₂ methanation) presents several advantages over other chemicals because it can be injected directly into already existing natural gas pipelines, and it can be used as a fuel or raw material for the production of chemicals. In addition, methane formation from CO₂ is a more simple reaction which can generate methane under atmospheric pressure. Furthermore, the formation of CH₄ from CO₂ at (low) room temperature has become an important breakthrough in the knowledge of the role and in the use of CO₂, although the conversion is still very low. Moreover, CO₂ methanation remains the most advantageous reaction with respect to thermodynamics, since the reaction is considerably faster than other reactions which form hydrocarbons or alcohols

2. METHANATION REACTIONS

The methanation reactions of carbon monoxide (1) and carbon dioxide (2) were discovered at the beginning of the 19th century (Sabatier and Senderens, 1902).



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. Methanation reactions have been widely used in ammonia synthesis plants to remove traces of carbon monoxide that acts as a catalyst poison for the ammonia synthesis catalyst (Appl, 1999). In addition, refineries and hydrogen plants make use of the methanation reactions for the purification of hydrogen by removing the carbon monoxide (Xu *et al.*, 2006). Originally considered as a pure gas cleaning technology, it is today viewed as a major chemical synthesis process. Another reason for the increasing importance of the methanation process is the need for storing excess electrical energy from renewable sources.

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 feedstock for synthesis gas production which can be further converted to SNG. Besides fossils limited reserves, also the need for decreasing the greenhouse gas emissions are the main motivations in increasing the usage of alternative feedstock such as renewable biomass and other feedstock such as CO₂. The production of synthetic natural gas (SNG) to replace the 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)

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 attempt is 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 1. The first step is the gasification to produce syngas or producer gas. Both consisting of H_2 , CO , CO_2 , and H_2O but the producer gas contains also CH_4 , and other hydrocarbons. The next step is the gas cleaning and conditioning step to remove impurities and catalysts 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 catalysed 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)

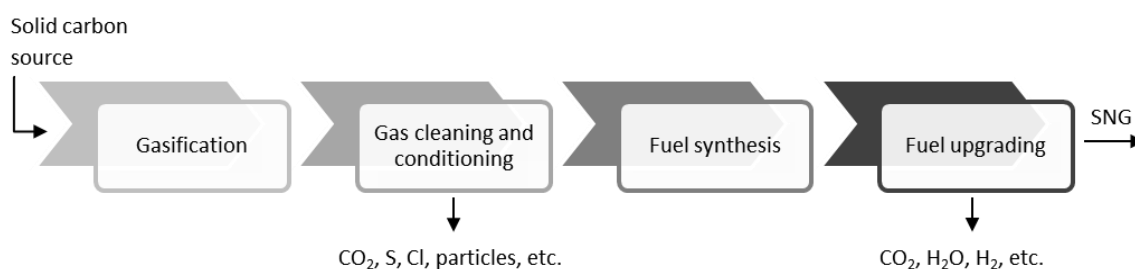


Figure 1. General scheme of the process chain from a solid carbon source to SNG (modified from Kopyscinski *et al.*, 2010).

3. REACTOR DESIGN

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)

There are basically two state-of-the-art reactor types that can be used for this process: two-phase fixed bed reactors and fluidized bed reactors. Whatever reactor design is selected, the generated heat of the methanation reaction has to be continuously removed from the reactor. An effective way to reduce temperatures in the reactor is the reduction of the reactive feed via a controlled dilution of the reactor inlet gas stream. This can be conducted by cooling down and recirculating a portion of the reactor's outlet gas stream. Cooling down the product gas, however, causes undesired energy losses. An alternative solution is the isothermal operation of the reactor. In this case, a cooled reactor is needed to transfer the reaction heat from the reaction zone to a cooling medium (Pedersen *et al.*, 1980). However, due to strong exothermic nature of the methanation reaction and the limited radial and axial heat transfer in a fixed bed reactor, it is difficult to operate a single fixed bed reactor under isothermal conditions. For a proper control of the reaction temperature in a fixed bed reactor, at least two adiabatic reactors have to be connected in series. Temperature control can be implemented by recirculation of the reactor outlet gas streams and by intermediate gas cooling steps (Pedersen *et al.*, 1980; Hedden, 1986; Kopyscinski, 2010).

As an alternative to the fixed bed reactors, also fluidized bed reactors can be used in the methanation reaction. In these reactors, the methanation reaction takes place within a fluidized bed of catalyst particles. Due to the very good mixing of gas and solid catalyst particles in the fluidized bed, high mass and heat transfer and almost isothermal conditions can be achieved. A further advantage of the fluidized bed reactors is the very good process control. However, abrasion and entrainment of catalyst particles in the gas flow are challenging issues. (Kopyscinski 2010; Kunii and Levenspiel, 1991). 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)

4. METHANATION PROCESSES

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 CO₂ 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.

Table 1 summarizes already realized reactor concepts for the methanation process along with some operational data (Graf, 2010; Kopyscinski, 2010; Rönsch and Ortwein 2011; Sudiro and Bertucco, 2010). All presented processes used coal or naphtha as a feedstock. Major developments in the field of SNG production from coal or naphtha date back to a time between the sixties and eighties.

Table 1. Fixed bed and fluidized methanation processes.

Process/Company	Reactor	Stages	Pres. (bar)	Temp. (°C)	Feed
TREMP/Haldoe Topsoe	Fixed bed	3	30	300-700	Coal, petr. coke, biomass
Hicom/British Gas Corp.	Fixed bed	4	25-70	230-640	Coal
RMP/Ralph Parson Co.	Fixed bed	4-6	1-70	315-780	Coal, heavy fuel
SuperMeth/Conoco	Fixed bed	4	80	n.s.	Coal
CRG/British Gas Corp.	Fixed bed	2	25	300	Naphtha
Hygas/Inst. of Gas Technol.	Fixed bed	2	70	280-480	Coal
Lurgi,Sasol/Lurgi GmbH	Fixed bed	2	18	450	Coal

ICI,Koppers/Imperial Chemical Industries	Fixed bed	3		400-700	Coal
Linde/Linde AG	Fixed bed	2	n.s.	n.s.	Coal
Bi-Gas/Bituminous Coal Res. Inc.	Fluid. bed	1	86	n.s.	Coal
Bureau of Mines/Us depart. of the interior	Fluid. bed	1	20	200-400	
Comflux/Thysengas Gmbh	Fluid. bed	1	20-60	400-500	Coal (biomass)

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 m³ SNG every year. The plant consists of 14 Lurgi Mark IV fixed bed gasifiers, shift conversion units, Rectisol scrubbers (CO₂ 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 H₂, CO, CO₂, H₂O and CH₄ (depending on the gasification temperature). Minor components such as sulphur compounds, ammonia, tars and dust loads must be removed from the gas.

An additional challenge in biomass based SNG production is the catalysts 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 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)

5. SNG PRODUCTION FROM CO₂

The reaction of CO₂ methanation that is the hydrogenation of CO₂ to methane (Eq.2) has been known for over a century as the Sabatier reaction but has received renewed interest recently for the development of new CO₂ fixation technologies. The methanation of carbon dioxide is thermodynamically favorable at low temperatures ($\Delta G_{298K} = -130$ kJ/mol). Thus, the methanation process generally operates at around 670 K (Gao et al., 2009). The methanation reaction is highly exothermic ($\Delta H_{298K} = -165$ kJ/mol). For the methanation of carbon dioxide (reaction Equation 1), an increase of the methane's molar gas fraction of about 1% in the product gas induces a temperature rise of about 60 K (Schaaf, 2014).



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

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

5.1 CO₂ methanation plants

ETOGAS has three plants in Germany. A 25 kW pilot plant was built in Bad Hersfeldt for testing of biogas upgrading. There is also a 250 kW installation in Stuttgart. In collaboration with Audi, ETOGAS has built a 6 MW plant in Werlte. The 6 MW plant in Werlte consists of three 2 MW units. A methanation reactor has a capacity to produce 300 Nm³ methane per hour.

ETOGAS's reactor in Bad Hersfeldt is an adiabatic reactor with catalysts (mainly nickel) placed in tubes. Besides using the pure gases hydrogen and CO₂, ETOGAS methanation reactors in particular allow the use of biogenic gas mixtures (raw biogas, sewage gas) as well as other CO₂ methane mixtures and other industrial CO₂ sources (e.g. steel, cement and lime production). (Benjaminsson *et al.* 2013). A comparison of ETOGAS's three plants is summarized in Table 2.

Table 2. ETOGAS's pilot and demonstration plants.

	Bad Hersfeldt	Stuttgart	Werlte
Power Input	25 kW	250 kW	6 MW
Production rate	Not in continuous operation	Not data available	25 GWh/year
Commissioning year	2009	2012	2013
Source of hydrogen	Electrolysis	Electrolysis	Electrolysis
Source of carbon dioxide	Non-upgraded biogas	Air	Separated from upgrading plant
Methane content	>96 %	>96 %	>96 %

Sunfire has developed a technique for efficient methane production. The gas is produced using carbon dioxide and water in combination with electrical energy from regenerative sources. Sunfire plans to produce hydrogen using efficient high-temperature steam electrolysis. The technique is still under development and Sunfire has not yet delivered any facility for catalytic methanation. (Benjaminsson *et al.* 2013)

Haldor Topsøe has a patented process for methanation of synthesis gas called TREMP (Topsøe Recycle Methanation Process). The process consists of three adiabatic fixed bed reactors. The process consists of three adiabatic fixed bed reactors. Haldor Topsøe uses home developed catalysts in the process. (Benjaminsson *et al.* 2013)

5.2 Catalytic conversion

CO₂ methanation remains an advantageous reaction with respect to thermodynamics, since the reaction is considerably faster than other reactions which form hydrocarbons or alcohols. 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). In recent years, CO₂ methanation via heterogeneous catalysts has recently attracted a considerable amount of attention.

Most of the methanation studies have been focused on metal-based catalytic systems. Both homogeneous and heterogeneous catalysts have been applied to CO₂ hydrogenation. Although homogeneous catalysts display suitable activity and selectivity, the regeneration of catalysts is not straightforward. In contrast, heterogeneous catalysts are preferred considering stability, separation, handling and reuse. (Jessop *et al.*, 2004, Centi and Perathoner, 2009) The methanation of CO₂ has been extensively studied and reviewed using numerous catalytic systems based on the group VIII B transition metals (e.g. Ni, Co, Pd, Pt, Ru and Rh) supported on various metal oxides (e.g., Al₂O₃, SiO₂, TiO₂, ZrO₂ and CeO₂). The catalysts used have many similarities to those for CO₂ reforming (dry reforming). CO₂ hydrogenation has been studied and described recently by using various catalysts including Ni/ γ -Al₂O₃ (Rahmani *et al.*, 2013), Ni/SiO₂ (Chang *et al.*, 2001), Ni/TiO₂ (Liu *et al.*, 2013), Ni/ZrO₂ (Perkas *et al.*, 2009), Ni/CeO₂ (Tada *et al.*, 2012), Ni/La₂O₃ (Song *et al.*, 2010), Ni-Mo/Al₂O₃ (Aksoylu *et al.*, 1999), Ni-Al alloys (Abello *et al.*, 2013, Lee *et al.*, 2005), Ni-Fe alloys (Sehested *et al.*, 2007), Ni-Zr alloys (Yamasaki *et al.*, 2006), Ni-Fe-Ru alloys (Hwang *et al.*, 2013), Ni/CeZrO₂ (Ocampo *et al.*, 2009), Ni/ZrO₂-Al₂O₃ (Mengdie *et al.*, 2011), Raney nickel (Sane *et al.*, 1984), Ni/zeolite (Jwa *et al.*, 2013), NiHNaUSY zeolites (Graca *et al.*, 2014), LaNiO₃ perovskites (Gao *et al.*, 2009), Ni/SiC (Zhang *et al.*, 2013), Ni/MCM-41 (Du *et al.*, 2007), Ni/MSN (Aziz *et al.*, 2014), Ni, Co, Pd, or Ru doped CeO₂ (Sharma *et al.*, 2011), Co/SiO₂ (Guilin *et al.*, 2013), Co/KIT-6 (Guilin *et al.*, 2013), MoO₃/CeO₂-Al₂O₃ (Jiang *et al.*, 2013), Pd-MgO/SiO (Kim *et al.*, 2010), Pd-Mg/SiO₂ (Park and McFarland, 2009), Pt/Tnt (Yu *et al.*, 2008), Rh/ γ -Al₂O₃ (Beuls *et al.*, 2012), Rh/SiO₂ (Kusama *et al.*, 2000), Rh/TiO₂ (Abe *et al.*, 2009), Rh/Y zeolites (Bando *et al.*, 2000), Ru/Al₂O₃ (Kusmierz, 2008), Ru and Pd doped MnNi/Al₂O₃ (Wan Abu Bakar *et al.*, 2013), Ru/C (Kowalczyk *et al.*, 2008), Ru/CNT (Jimenez *et al.*, 2010).

Supported nickel catalysts remain the most widely studied materials (Abello *et al.* 2013). Nickel based catalysts have been mostly used for methanation reaction because of their relatively low cost, high activity, and the best selectivity to methane as compared to other metals. All commercial methanation catalysts are Ni-based (Nguyen *et al.*, 2013). Nickel is not the most active methanation catalyst but provides the best methanation activity per unit cost while maintaining a high selectivity towards methane (Bligaard *et al.*, 2004). However, a high

activation temperature (above 620 K) is generally needed to achieve the maximum CO₂ conversion, which results in undesirable influences on the stability/lifetime of the catalysts as well as increased energy consumption (Park and McFarland, 2009, Chang *et al.*, 2003, Yamasaki *et al.*, 2006). Many studies have focused on improving the stability of nickel catalysts by varying support materials, promoters, and preparation methods (Liu *et al.*, 2011, Gao *et al.*, 2012, Yu *et al.*, 2011, Zhao *et al.*, 2012, Hu *et al.*, 2012, Bartholomew *et al.*, 1983). It has previously been shown that the methanation reactions are highly sensitive to the structure of the catalyst (Andersson *et al.*, 2008), and that methanation only occurs on Ni step sites, which account for only a small fraction of the total active Ni sites (Rostrup-Nielsen, 1975). The exact fraction varies greatly depending on the catalyst preparation method and characteristics, but an averaged level for a number of Ni catalysts is in the order of 5% (Rostrup-Nielsen, 1975).

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

One of major problems of Ni-based catalysts is the deactivation due to the interaction of the metal particles with CO and formation of mobile nickel 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 CO₂ methanation than nickel catalysts. However, noble metal catalysts are notably more expensive than nickel based catalysts limiting their use in the catalytic hydrogenation of CO₂. The Ru catalyst has an excellent low temperature CO₂ catalytic methanation activity compared to other studied precious metal catalysts, exhibiting high CO₂ conversion at 673 K (Lu *et al.*, 2005). It has been found that Ru and Rh are much more active hydrogenation catalysts as compared to Pt and Pd, which promote the undesired reverse water gas shift reaction. (Jimenez *et al.*, 2010)

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

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

Supports such as carbon nanofibers could be an alternative to the classical support materials (alumina, silica, TiO₂, etc.) widely studied on the literature due to their excellent characteristics such as the high purity of the material, high mechanical strength and mesopore nature which results in low internal mass-transfer resistances (Díaz-Taboada *et al.*, 2009). The co-precipitation method has been considered as the most conventional method for the preparation of mesoporous nickel–alumina catalysts due to its high reproducibility. The co-precipitation method has also advantages such as high metal loading and high metal dispersion compared to the impregnation method. (Lok, 2009)

5.2.1 Reaction mechanism

Although the methanation of CO₂ is a comparatively simple reaction, its reaction mechanism appears to be difficult to establish. There are different opinions on the nature of the intermediates and the methane formation process. Reaction mechanisms proposed for CO₂ methanation fall into two main categories. The first one involves the conversion of CO₂ to CO prior to methanation, and the subsequent reaction follows the same mechanism as CO

methanation (Beuls *et al.*, 2012, Eckle *et al.*, 2010, Fischer and Bell, 1996). The other one involves the direct hydrogenation of CO₂ to methane without forming CO as an intermediate.

5.2.2 Recent catalysts developed and studied in CO₂ methanation

Several heterogeneous catalysts have been tested in CO₂ methanation and most commonly used metal catalysts are from group VIII B (Ni and Ru are popular). Recent studies are focused on low temperature operation under ambient pressure (Tada *et al.* 2014, Zhang *et al.* 2013). A highly dispersed Ni nanoparticles (NPs) are immobilized on a TiO₂ supported was found to be very active at low temperature 260°C and able to achieve 96% CO₂ conversion with close to 99% methane selectivity (Liu *et al.* 2013). Surface dissociative adsorption of hydrogen and sequential hydrogenation of CO₂ over the surface of active metal is a critical step for overall reaction rate (Liu *et al.* 2013). A highly stable and active Co₄N/Al₂O₃ catalyst (Razzaq *et al.* 2015) was found to be highly durable for nearly 250 h stability test with high space velocity (GHSV: 10,000 h⁻¹) and over 98% CH₄ selectivity for CO/CO₂ methanation. A high dispersion, better adsorption capacity, and understanding level of support-metal interactions were crucial in preparing an active catalyst system. The effect of metal loading with respective active carrier oxides is very important in preparing robust catalysts. As reported by Karelavic and Ruiz 2013, an optimal metal loading and particle size is crucial to obtain high turnover frequencies of methane. Ni/Ce_{0.5}Zr_{0.5}O₂ catalysts in methanation have proved to be strongly dependent on method of catalyst preparation. The support materials pre-treatment and modification were also important in activity. By adding VO_x to Ni supported on acid-alkali treated bentonite resulted in activity improvement than raw bentonite (Lu *et al.* 2014) Moreover, higher Ni loading resulted in bigger cubic particle sizes produces higher CO intermediate and avoid carbon whiskers (Garbarino *et al.* 2014). Conventional catalyst preparation method still holds promising but new and modified techniques are needed to reduce the metal content as low as possible. For example nano based catalysts with minimal metal loading such as Ni immobilized on TiO₂. Over Ru/Mn/Ce/Al₂O₃, Ce loading had a significant effect on catalytic performance, over 65 wt.% of Ce loading, 98% CO₂ conversion with 91 % methane selectivity was achieved at 200 °C (Toemen *et al.* 2014). As reported in Pan *et al.* 2014, the reactive sites of Ni/Ce_{0.5}Zr_{0.5}O₂ catalysts were investigated; medium basic sites were responsible for the monodentate species formation which were quickly hydrogenated than bidentate.

A new hybrid carrier materials will be required in order to obtain desired physicochemical properties with high coking resistant, such zeolites with high surface area, thermal stability and high affinity towards CO₂ (Jwa *et al.* 2013). Combination of oxygen storage materials and high CO₂ adsorption and activation can be effective catalysts with high durability. The methanation of CO has been studied mainly over Ni- and Ru-based catalytic. In CM, performance of a slurry bubble column reactor (3-phase) was investigated and optimal process conditions were evaluated (Lefebvre *et al.* 2015). At elevated pressure, higher temperature and H₂/CO₂ were found to be advantageous to achieve high performance. Significant progress has been in done in process intensified reactors approach such as in membrane reactors and microreactors. CO₂ methanation was combined with hydrogen production by *in situ* H₂ selective separation through Pd membrane reactor (MR). Hydrogen is selectively permeated to the CO₂ methanation zone, thus enhance the CH₄ selectivity (Miyamoto *et al.* 2014). In recent times (Zhang *et al.* 2013), CM in a plasma-assisted activation in ambient conditions was shown promising results over Ni/SiO₂ compared to thermally operated conventional reactors.

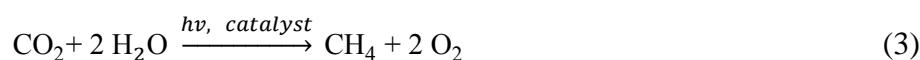
5.3 Photocatalytic CO₂ conversion

Photocatalytic conversion of CO₂ to synthetic methane has been studied since decades by several research groups, as the conversion of CO₂ to C1 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)

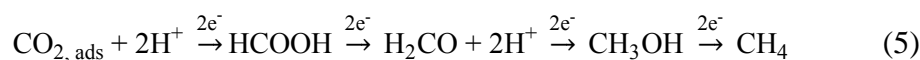
In the photocatalytic CO₂ reduction the catalysts have a significant role as several multistep reactions and processes are occurring at the same time on the catalyst surface. At the first step CO₂ adsorbed on a photocatalysts' surface, then interacts with photogenerated electrons and hydrogen, yielding finally a set of various products mainly C1 (such as CO, methane, methanol, formic acid, formaldehyde) but possibly also C2 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 CO₂. (Tahir and Amin, 2013a, Mao *et al.*, 2013)

The overall reaction for the photocatalysis of CO₂ with water (Eq. 3) or with protons (Eq. 4) is as follows. It has been noted that the methane formation reaction requires eight photons. The thermodynamic reduction potential (E_{redox}^0) of CO₂ to methane at pH 7 is determined to be -0.24 V vs. normal hydrogen electrode (NHE) (Tahir and Amin, 2013a, Hong *et al.*, 2013, Mao *et al.*, 2013, Varghese *et al.*, 2009):



Recently there are studies which have been concentrated to find out the detailed mechanistic steps to improve the efficiency of the CO₂ conversion. Some of the studies have utilised 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 one a bit more detailed reaction mechanism for methanation of CO₂ via the Fischer-Tropsch sequence (Eq. 5):



The most crucial challenge to meet in the CO₂ conversion to methane and other C1 products is that CO₂ is a very stable molecule which does not absorb visible or ultraviolet radiation. So, efficient photocatalysts are needed to be developed. Some of the developed and studied photocatalytic materials for SNG production are summarised in Table 3. The studied materials for CO₂ activation and conversion to fuels in general are e.g. semiconductors and metal complexes, such as various oxides (*e.g.*, Ti, Mg, Zr, Cu, In, W), sulphides (Cd, Bi) and halides (Br, Cl) both in powder and immobilized forms. In addition, decoration of active metals (Ag, Au, Cu, Ru, Pt, Rh, etc.) on the photocatalytic supports has been studied widely. Besides the materials, various irradiations from the UV-range (>254 nm) to visible (>420 nm) with Xe, W and Hg-lamps has been studied to activate CO₂. UV-C (250-350 nm) range is the most

energetic; however, the most suitable irradiation (i.e. UV-C, UV-B, UV-A, visible) is dependent on the catalytic material and reaction conditions used. It has also been noticed that the CO₂ reduction is accelerated in alkaline solutions. The hole scavenger formation is observed to be promoted in alkaline solutions, thus, increasing the rate of photoactivation on CO₂. (Mao *et al.*, 2013; Tahir and Amin, 2013a; Cybula *et al.*, 2012)

Table 3. 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 ₂ O/TiO ₂ over MgO and/or Al ₂ O ₃ , Cu/ZnO, TiO ₂ /Pd/Al ₂ O ₃ , Au/Ti/SBA-15, Ti/SBA-15, KNb ₃ O ₈ , HNb ₃ O 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 TiO₂, NP = nanoparticle

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

The most important phenomenon is the catalyst's ability to generate electron-hole pairs by adsorbed irradiation energy. Thus, there is also a need to develop catalytic materials which have the band gap (E_{bg}) between the conductivity and valence bands in a reasonable level to promote the electron-hole pairs formation and, at the same time, prevent the recombination of

these. An illustration of the possible reactions over the photocatalyst is presented in Figure 1 (Varghese *et al.*, 2009).

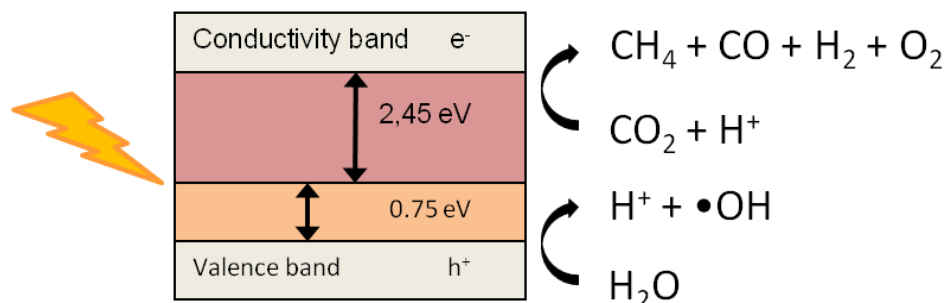


Figure 1. Carbon dioxide conversion to hydrocarbon fuels by sunlight-driven photocatalysis. (based on Varghese *et al.*, 2009).

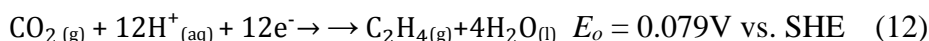
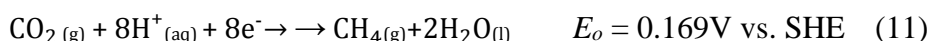
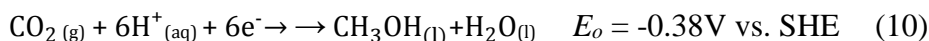
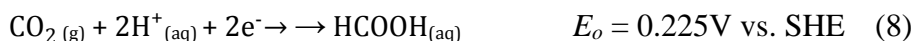
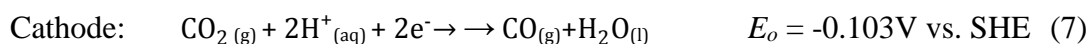
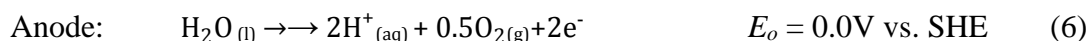
The photoreduction of CO_2 and formation of hydrocarbons especially methane is still in the level of experiencing in the laboratory scale. The amounts of CH_4 (and other hydrocarbons) formed during the photocatalytic reactions are in many studies quite low, being from few ($<1 \mu\text{mol g}^{-1}\text{h}^{-1}$) up to around one hundred ($100 \mu\text{mol g}^{-1}\text{h}^{-1}$) 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 $350 \mu\text{mol g}^{-1}\text{h}^{-1}$ 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.

5.4 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 CO₂ generally takes place in aqueous, and non-aqueous solutions and also in metal mediated complexes (Aresta, 2010). In the ERC process, CO₂ is reduced at cathode electrode to form CO₂⁻ anion and the O₂⁻/H⁺ evolution takes place at the anode by H₂O 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.



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).

An efficient ERC electrolyzer should have high current density, high energetic and faradaic efficiency (Jhong *et al.*, 2013). To obtain high efficiency many factors will influence such as: CO₂ purity, optimal electrodes composition, electrolyte solution, gas diffusion layers, optimal operating conditions and selectivity and stability.

The list of various metal electrodes, electrolytes, and selective product formation are presented in Figure 2 (with different efficiencies and current densities). In this section, the topic is restricted to ERC to methane (or SNG) formation.

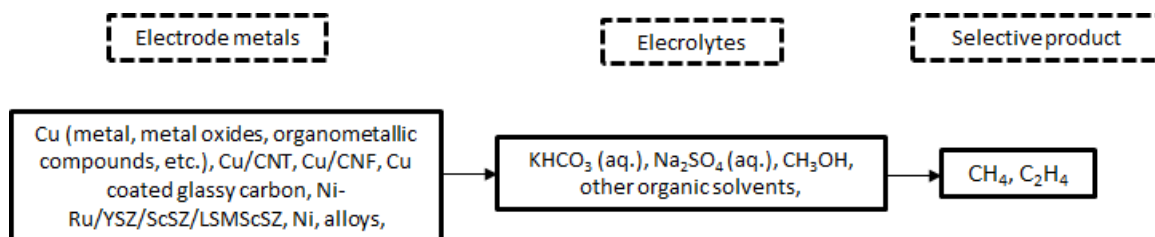


Figure 2. Electrochemical reduction of CO₂ to methane and ethylene on various studied electrodes, electrolyte solutions (aqueous and non-aqueous) (modified from Halmann and Steinberg, 1999; Jong *et al.*, 2013).

5.4.1 Electrodes for methane production via ERC

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

Copper catalyzes CO₂ into hydrocarbons (i.e. CH₄, C₂H₄ etc.) and this topic is well addressed in the scientific literature using different Cu materials (Peterson *et al.*, 2010). A comprehensive review on ERC to hydrocarbons at Cu electrodes was published in 2006 (Gattrell *et al.*, 2006; Kuhl *et al.*, 2012). The mechanism of CO₂ reduction on a Cu catalyst undergoes series of consecutive steps to form various products. First, CO₂ is adsorbed on the electrode to form an anion radical and then it is reduced to 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.* (2010) have studied ERC on transition metal catalysts, and found that the protonation of CO is the most critical step in operating at lower overpotentials. At low overpotentials, H₂, CO and formate are formed with high current densities. The 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 H₂ evolution is the crucial step to avoid. Recently Li *et al.* (2013) have reported CO₂-H₂O electrolysis in a solid oxide Ni-YSZ based cell operating at 550-750 °C. They found that, operating at higher voltage (> 2V, 750 °C), methane production was significantly increased and Ru promoted Ni-YSZ promoted hydrogenation of carbon to methane formation.

As proposed by Whipple *et al.* (2010) that the biggest challenge in ERC is to reduce the higher overpotentials which significantly effecting the efficiency and current density. In order to solve these problems, a new class of Cu based materials and hybrid materials should be designed and tested. It is important to understand the CO₂ interface with Cu electrode in atomic level and a better mechanistic approach is needed. Controlling and optimizing the conditions and improving the durability of Cu need also to be taken into consideration. ERC to methane is

foreseen as a promising way to utilize CO₂ but many technical challenges and economical constrains should be addressed before the process can be commercially applied.

5.5 Membrane assisted CO₂ conversion

One approach is to maximize the performance of CO₂ methanation can be done by shifting the thermodynamic equilibrium. Process intensified reactors such as membrane-assisted systems can be utilized to enhance the overall performance of the reaction. 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. There is a need to develop new membranes and membrane based reactor systems for the CO₂ methanation. As illustrated in Figure 3, a membrane-assisted reactor (MR) can be applied in two ways in a methanation reaction loop or a dual membrane mode can be introduced into the reactor system. In the dual mode module, one part will be an extractor type membrane for perm-selective water vapor removal and the second being the distribution and feeding of pure H₂ (i.e. a distributor type MR) gas into the methanation reactor (H₂ can be produced from renewable energy source). Henceforth, by applying a dual mode membrane type, the exothermic methanation reaction can be controlled and can be operated at low temperature. Furthermore, by continuous H₂O removal, the reaction will shift towards the product side (i.e. an extractor type MR), which also avoids the catalyst deactivation (Rohde *et al.*, 2008; Hwang, 2009). Hydrophilic membranes like microporous zeolite can be good materials for the perm-selective H₂O removal in the methanation membrane assisted reactor (Rohde *et al.*, 2008). In CO₂ methanation, H₂ is an important raw material and globally most of the H₂ is produced via steam reforming of natural gas, which is not an environmentally sustainable process, and moreover it is an highly energy intensive. The critical factor will be H₂ must be produced from renewable feedstocks in order to convert CO₂ to hydrogenated products sustainably.

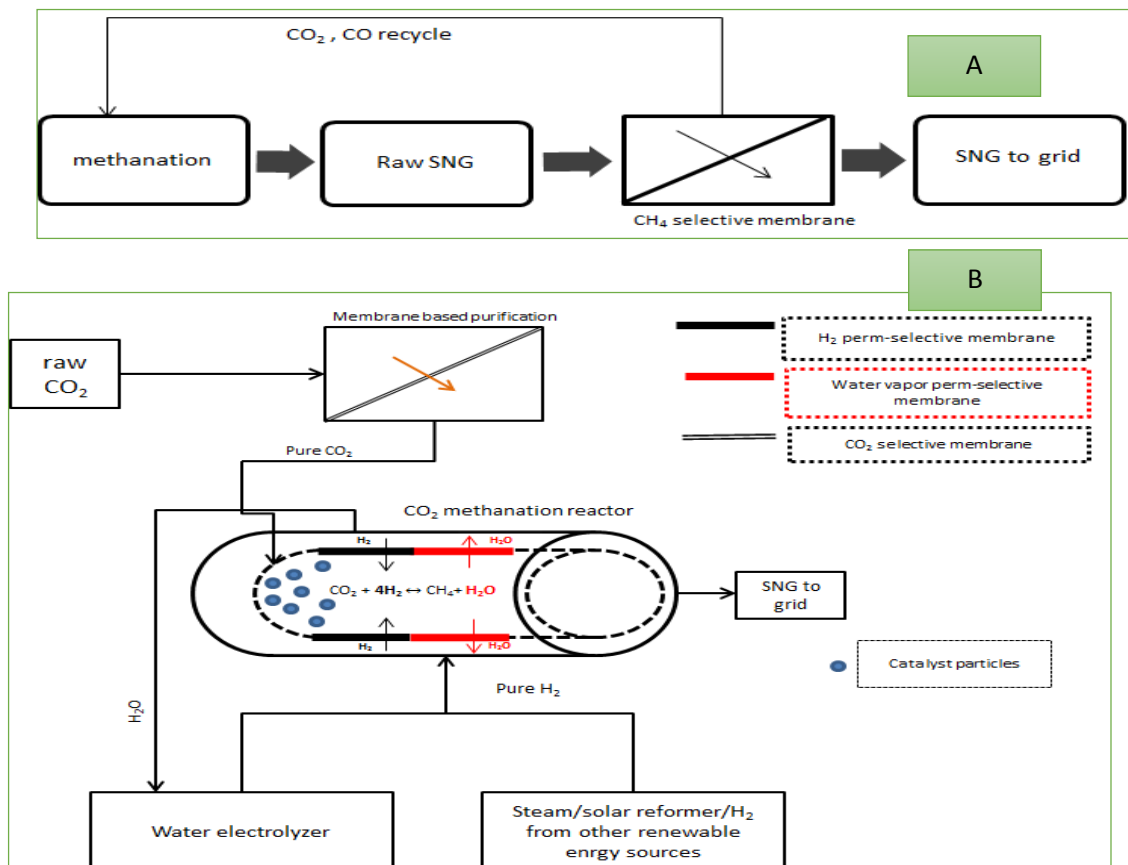


Figure 3. Possible configurations for the membrane applications in the framework of SNG production. A) Upgrading and purification of raw SNG via membrane system. B) Three potential options for membrane applications in CO₂ conversion to SNG, membranes for carbon capture and storage (CCS) to purify the raw CO₂ gas to high purity gas before feeding it into a methanation reactor, membrane assisted reactor for selective removal of by-product water-vapor and distribution of pure H₂ for example in a Pd-based membrane to control the reaction.

A new approach was reported on integration of CO₂ methanation and H₂ production via NH₃ decomposition in a membrane assisted reactor. Methanation consumes the *in situ* H₂ removal from the reaction to permeation zone via Pd membrane layer (Miyamoto et al. 2014).

6. COMMERCIALIZATION AND ECONOMICS

The methanation process is viable if the CO₂ and H₂ are generated from waste and renewable energy. For instance, CO₂ can be generated from local biomass or power plants and H₂ can be produced via water electrolysis using inexpensive renewable power sources. Renewable energy sources including wind, solar, hydro and geothermal as well nuclear energy that are bound to play an increasing role in the world's energy mix, produce primarily electricity.

In terms of the hydrogen production from renewable energy, the splitting of water would be the simplest way to produce synthetic hydrogen. The practical technology to split water into hydrogen today is electrolysis, but others such as photochemical and thermal splitting as well as high temperature chemical cycles are also under investigation. Electrolysis of water has been practised for more than 100 years and is efficient with overall system conversions higher than 75 to 80%, with further improvements possible. Water is concluded to be the only suitable CO₂ emission free source of hydrogen. While having these advantages of availability, flexibility and high purity, to achieve widespread application hydrogen production using water electrolysis still needs improvements in energy efficiency, safety, durability, operability and portability and, above all, reduction in costs of installation and operation. These open up many new opportunities for research and development leading to technological breakthroughs in water electrolysis. Furthermore, the economy will be significantly improved when novel cost- and energy-efficient technologies for providing large amounts of pure CO₂ are developed. Many industrial processes such as power generation, cement manufacture, refineries and iron and steel making produce CO₂ and can be fitted with CO₂ capture technologies. Currently, carbon capture and storage (CCS) offers one of the methods to reduce CO₂ emissions. The captured CO₂ can be pressurized to 100 bar (or more), prior to being transported to a storage site and further used in a methanation unit. After all, as a green carbon source and renewable feedstock, the methanation of CO₂ definitely has a promising future. (Aziz, 2015)

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).

Synthetic natural gas (SNG) production has the potential to reduce CO₂ emissions by replacing liquefied natural gas (LNG) consumption. Local SNG production can be also considered to increase national security and national economy. SNG has a great potential for fuel consumption in the transport sector and it can replace even about 72% of gasoline and about 40% of the total motor fuel consumption (Naqvi *et al.*, 2012). For example some LNG using

ships are already constructed for environmentally conscious sea transporting. Methane is an excellent fuel for Otto-engines (Johansson, 1999). The rapid growth in the number of vehicles in China has given more pressure for environmental protection and energy security due to the oil demand. This shows a great potential for the use of gas as an automotive fuel (Ma, 2013).

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

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

Using CO₂ from the atmosphere enables to decouple the methanation plant from a point source of CO₂, which increases the amount of suitable locations. However, this process has a low efficiency because the atmospheric CO₂ content is only about 390 parts per million. Experiments at the Fraunhofer ZWS institute showed that the absorption of CO₂ from the atmosphere is an energy efficient solution (Bandi *et al.*, 1995). This technique requires 8.2 GJ of electricity and 2,300,000 m³ of air from the atmosphere to produce 1 ton of CO₂ (Weimer, 1996; Sterner, 2009). With an electricity price of 0.05 €/kWh, this results in 0.20 €/Nm³ of CO₂ (and thus 0.20 €/Nm³ of methane produced in the Sabatier process for capturing CO₂) (Sterner, 2009). When obtaining the CO₂ from conventional power plants by scrubbing, about 2 – 4.8 GJ_e per ton of CO₂ is needed (Muller *et al.*, 2011), which is 0.05 – 0.13 €/Nm³ CO₂ (and thus 0.05 – 0.13 €/Nm³ of methane produced in the Sabatier process for capturing CO₂). However, American Physical Society (2011) estimates somewhat higher costs for CO₂ capture from the atmosphere, being in the range of 0.8 – 0.9 €/Nm³ CO₂. Sterner (2009) stresses that as long as

concentrated CO₂ sources are available, it is more energy and cost efficient to use them instead of using CO₂ from the atmosphere.

The estimated costs of methanation are presented in the picture below (Figure 4). The costs are based on plants with a capacity of < 10MW_{th} combined with a scale exponent. It must be remarked that the investment costs seems to be somewhat high but when the market for small scale methanation develops, it is expected that these units can be purchased for 300 – 500 €/kW. (DNV KEMA, 2013)

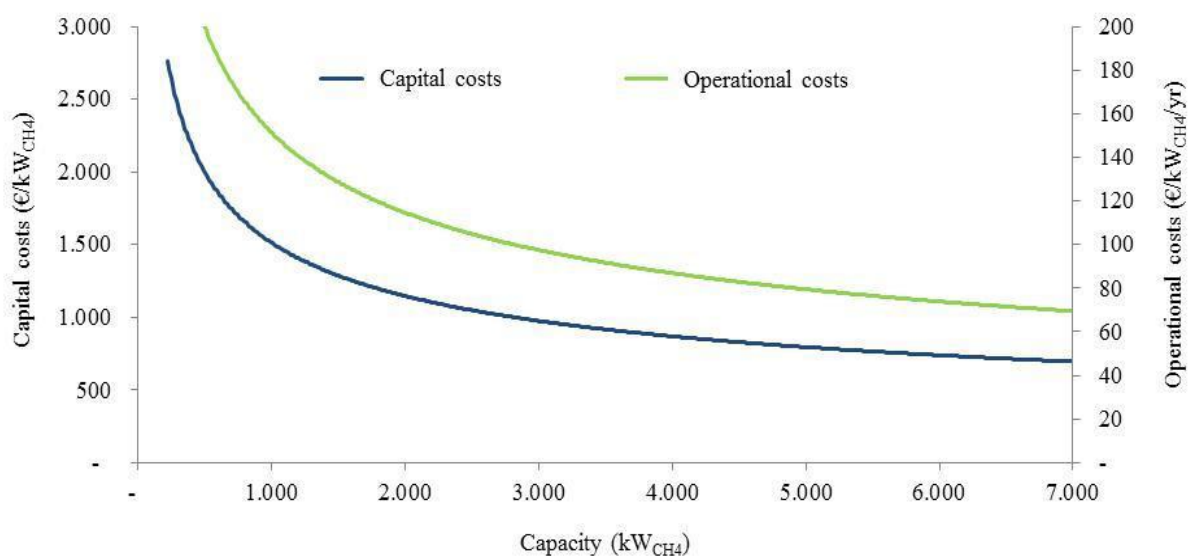


Figure 4. Capital and operational costs of chemical methanation plants (DNV KEMA, 2013).

6.1 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

mandating a minimum percentage of use, as EU has done. These can also create economically lucrative markets for CO₂ to SNG production.

The found and proven LNG reserves are over 56 years and its availability seems not 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 (Aguilera, 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 $611 \cdot 10^8 \text{ m}^3$ 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 synthesizing 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 the distant places without high transport costs.

7. SUSTAINABILITY

The large availability of CO_2 due to the 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 of course 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 to use

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 CO₂ emissions.

Sustainability of the CO₂ 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 to assess and to compare 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 bottle necks of the SNG production from CO₂ streams. Besides, the society can have data from the political decision making and new openings in the society.

The sustainability assessment analysis of the CO₂ to SNG process is of complex issue and thus it is touched in this section only briefly. In terms of economic impacts, the price of feedstock, i.e. separation and purification of CO₂, production of H₂ 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 CO₂ and H₂ 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. CO₂ and waste biomass lead to a reduced need of fossil fuels,

GHG savings and better carbon economy (Demirbas, 2009). In addition, the CO₂ utilizing SNG production process can have direct environmental impacts in terms of increased or reduced energy consumption and waste generation which need to be evaluated. Regarding social impacts, the use of CO₂ in SNG production can have enhanced energy security due to reduced dependency on imported crude oil, and increased employment and customer as well as society acceptance. The need for education and training for the new processes may also positively impact on the societal capital.

8. CONCLUDING REMARKS

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

There are several starting materials and reaction routes to produce SNG from fossil raw materials and also active research to utilize biomass and wastes in SNG production on its way.

The utilization of CO₂ to produce synthetic natural gas is the newest trend among research groups in SNG production. Industry has also found and shown some interest to use this abundant and non-toxic molecule, i.e. CO₂ in SNG and further value added chemicals and fuels production.

This approach if being successful could also offer us a possibility to considerably reduce anthropogenic CO₂ emissions. This area seems to be very appealing and it interests very much the research communities and researchers in the field of chemistry, chemical and environmental engineering, even economists. However, technologies to put these ideas forward are needed to enable a highly efficient and environmentally benign conversion of CO₂ and H₂ into SNG. Novel and innovative active, selective and stable catalysts are needed as well as new reactor technologies to enable the CCU option at a commercial scale. It is forecasted that costs for the new technology and its development can be reduced so much that in certain industries, e.g. CHP plants the CCU concept can be more attractive than the CCS approach.

There is also a need to convince company researchers and leaders as well as societies to strive towards this goal. The sustainability assessment of the CO₂-concept in SNG production needs to be done to the existing, e.g. fossils based concepts, and other concepts under research to gain the acceptance of the proposed technology from the economic, environmental and social

points of view. The idea to combine gaseous waste compounds, i.e. CO₂ together with hydrogen from biomass or organic waste related streams to new and valuable products, i.e. chemicals and fuels can offer several advantages and can be a new step towards resources use optimization and waste minimization as well as diminishing the greenhouse gas emissions, global warming, and climate change.

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