POLITECNICO DI TORINO

I Facoltà di Ingegneria
Corso di Laurea in Ingegneria Energetica e Nucleare

Master of Science Thesis

CARBON CAPTURE AND UTILIZATION - SYNTHETIC FUELS

Technical and Economical comparison between synthetic Methanol and Methane

Supervisor:

Prof. Massimo Santarelli

Advisors:

Dr. Emanuele Giglio
Dr. Alicia Soto

Candidate:

Davide Parigi

April 2018

Table of Contents

Abstract

The objective of this Thesis is to investigate several technologies in which the reuse of the carbon dioxide is possible. One of the most promising application of the carbon capture and utilization will prove to be the production of Synthetic Fuels from direct hydrogenation of the carbon dioxide.

To better understand all the possible obstacles that could rise while approaching this topic, a SWOT analysis has been performed by following the directives learned during the period spent at the Technical University of Eindhoven (TU/e).

The technical side of this Thesis is focused in the design and analysis of two different typologies of plant, aimed at the production of Methane and Methanol, through high-temperature electrolysis carried out by solid oxide electrolysers (SOEC).

The first plant provides the coupling of a steam electrolysis with two catalytic reactors: in these reactors enters a gaseous mixture composed of the cathodic exhaust of the electrolyser (water vapor and hydrogen) appropriately mixed with carbon dioxide. The resulting chemical reaction allows the production of a synthesis gas with a high methane content.

The second plant differs from the first one in the reactor section: the mixture of hydrogen, water vapour and carbon dioxide is sent in a high pressure catalytic reactor where methanol, water and carbon monoxide are formed. A subsequent distillation allows to separate the methanol from the other by-products.

The modelling of both plants was performed using the Aspen Plus® software.

Afterwards the designing part, a system analysis has been performed:

- A series of sensitivity analysis regarding the reactors sections to evaluate the trend of some parameters by varying the operational conditions to obtain the highest conversion efficiency of the reactants
- A thermal integration made according to the rules of "Pinch Analysis", in order to minimize the need for thermal energy from the outside and thus maximize the overall efficiency of the system
- An economic analysis to estimate the feasibility of both plants and compare the obtained cost of the products with those ones that are currently available in the market.

Furthermore, some conclusions on the competitiveness between methane and methanol produced from power (power-to gas vs power-to-liquids) are provided.

Introduction

According to the United Nations’ Intergovernmental Panel on Climate Change (IPCC), carbon dioxide (CO_2) emissions must be reduced by at least 50 % by 2050 compared to levels in 1990 if the expected temperature increase caused by the greenhouse effect is to be limited to around 2-3°C by the 2100. [1]

Carbon dioxide is a well-known gas and considered by many as un undesirable substance. However, it has to be recognized as a key solution for critical issues facing the world like the greenhouse problem and the energy storage.

In July 2009, the 17 partners of the Major Economies Forum (MEF) on Energy and Climate agreed that transition to a low-carbon economy “provides an opportunity to promote continued economic growth as part of a vigorous response to the dangers created by climate change.”

One priority action outlined in this Action Plan was to:

‘…encourage the use of captured carbon dioxide to generate revenue that can partially offset the cost of CO_2 capture, as a transitional measure to assist the accelerated uptake of carbon capture and sequestration (CCS).’ [2]

The possibility of yielding revenue from the utilization of CO_2 could motivate investors to commit capital for the development of more complex and expensive technologies.

This research has examined the numerous possibilities offered by the utilization of CO_2, starting from the broadest possible point of view, followed by a detailed analysis to finally comparing the technical and economic perspectives of the production of synthetic methanol and methane.

The gradual transition towards ever cleaner energy production has highlighted the necessity for systems that guarantee the storage of large amounts of energy over long periods of time. In this context, the application of solid-oxide electrolytic cells (SOECs) for the conversion of electrical energy into chemical form by electrolysis is generating great interest.

Electrolysis has always been used for hydrogen production from water. The combustion of hydrogen produces only pure water. However, despite some advantages, the very low power density of the hydrogen and the lack of infrastructure to distribute it, point out other more practical solutions for the transformation of electrical power.

Fuels like methane and methanol seem to be more appropriate for this purpose.

Methane is considered one of the cleanest fossil fuel currently available, despite being considered a greenhouse gas; the combustion process has the lower ratio of Carbon Dioxide produced per unit of thermal energy produced. Moreover, its combustion doesn’t generate pollutant in high quantity.

Methane is largely used in three key sectors: transportation, electricity production and civil heating sector. Furthermore, in the gradual outspread of a clean electricity policies, methane can play a fundamental role.

Instead, methanol is a fuel that due its good octane number it can be used directly as fuel in cars (including hybrid cars and plug-in models) using various types of internal combustion engines already in use. Under normal conditions, methanol is a liquid, that allows for easy storage, transportation and distribution, similar to what is done with petrol and diesel. Methanol can be considered a commodity chemical because it can be transformed into various products such as dimethyl ether (DME), a diesel substitute formed by a dehydration process. Also, it can be transformed in gasoline or olefin through the methanol-to-gasoline (MTG) process and the methanol-to-olefin (MTO) process.

Methanol can also be converted to ethylene and propylene, the two chemicals produced in large amounts by the petrochemical industry. These are important building blocks for the production of essential polymers (LDPE[i], HDPE[ii], PP[iii]) and like other chemical intermediates are currently produced mainly from petroleum feedstock. Their production from methanol could therefore reduce our dependency on petroleum.

It is important to stress that both methane than methanol can also be used in the fuel cells: the methane is directly used while the methanol can be used either directly, in the direct methanol fuel cells (DMFCs), or indirectly, after its transformation into hydrogen by reforming[iv].

This work is divided in four chapters:

Chapter one focuses on the carbon dioxide, considering how to collect it and the market forecasts for its utilisation. A SWOT analysis is also conducted to better understand the context of the production of synthetic fuels from carbon dioxide.

Chapter two presents a brief description of technologies involved in the methanation system and in the methanol production. A review of some technologies that can produce hydrogen from renewable sources is presented, focusing deeper in the high temperature electrolysis.

Chapter three present the modelling of two plants, one for methane and the other for methanol production from hydrogen and carbon dioxide, using the software Aspen Plus®.

Chapter four exposes some system analysis. First, a sensitivity analysis is conducted with the goal of evaluating the maximum efficiency working point of the systems by varying some operational parameters is realized. Then a thermal integration is performed to maximize the plant's efficiency. Finally, an economic analysis is completed to estimate the production cost of methane and methanol.

---

[i] Low-density polyethylene (LDPE) is a thermoplastic made from the monomer ethylene.

[ii] High-density polyethylene (HDPE) or polyethylene high-density (PEHD) is a polyethylene thermoplastic made from petroleum.

[iii] Polypropylene (PP), also known as polypropene, is a thermoplastic polymer made from the monomer propylene.

[iv] The reforming reaction (or steam reforming) is a chemical process for the production of a syngas (a H_2, CO_2, CO and sometimes CH_4) from hydrocarbons and water vapour under the action of a heterogeneous catalyst and through the contribution of thermal energy.

1 Situation Analysis in CCU

In this section the carbon dioxide is examined from different angles: firstly, is presented a chapter dedicated to the possible and most developed ways to capture it from industrial processes; afterwards an analysis of the market for a feasible use of the CO_2 has been conducted.

1.1 Carbon Capture Technologies

Carbon dioxide can be captured from CO_2 containing gases by using technologies, which are commercially available and established in chemical processing. The main challenges are the large flue gas flows, the chemical composition of flue gases, a high degree of CO_2 purity and the CO_2 capture rate. Worldwide, studies are focusing at present on identifying energy and cost-efficient capture solutions. The purity of the CO_2-stream after separation is the most influencing factor for how much energy is needed for the capture of CO_2 but also is a significant aspect for the transport, storage and exploitation of the carbon dioxide stream. With increasing requirements regarding the purity of the CO_2, its capture is more expensive and requires more energy. [3]

There are different commercial technologies to capture carbon dioxide from gases. Three technology routes are currently most intensively discussed:

- CO_2-capture from the flue gas stream after combustion (Post-combustion);
- Use of nearly pure oxygen for fuel combustion instead of air which increases the CO_2-concentration of the flue gas (Oxyfuel);
- CO_2-capture from the reformed synthesis gas of an upstream gasification unit (Pre-combustion).

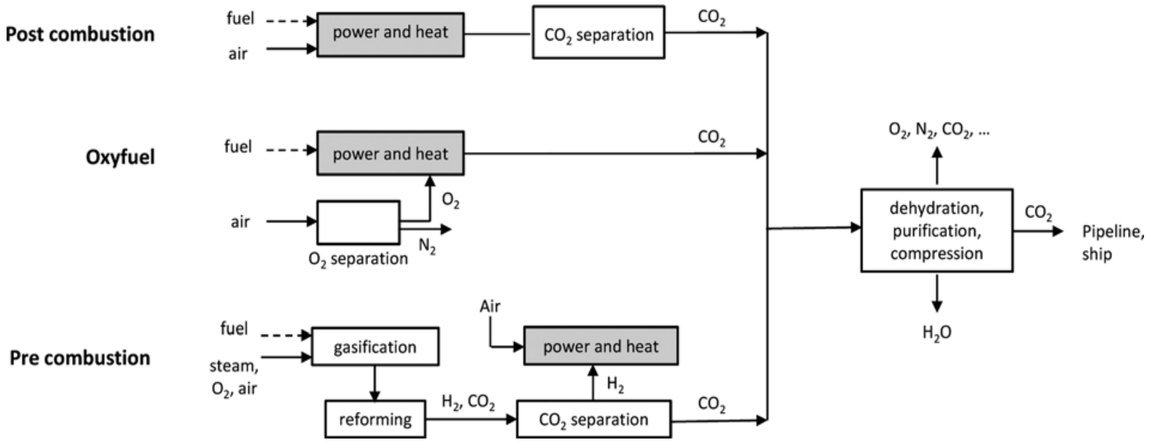


Figure 1 – Currently favoured CCS-process families [3]

1.1.1 CO_2-capture after combustion: post-combustion processes

When carbon dioxide is captured after the combustion process, including the subsequent flue gas cleaning (removal of dust, sulphur and nitrogen compounds), the process line is described as ‘post-combustion’. Nowadays, the most promising methods are the so-called ‘chemical absorption’ processes that are often denoted as chemical washes.

The absorption in liquid solvents is an industrially tested and widely applied CO_2-separation technique, with which high purities and high degrees of separation can be attained. Currently, the most developed technique is the amine-based separation method. In particular, monoethanolamine (MEA) and other amines have found widespread use.

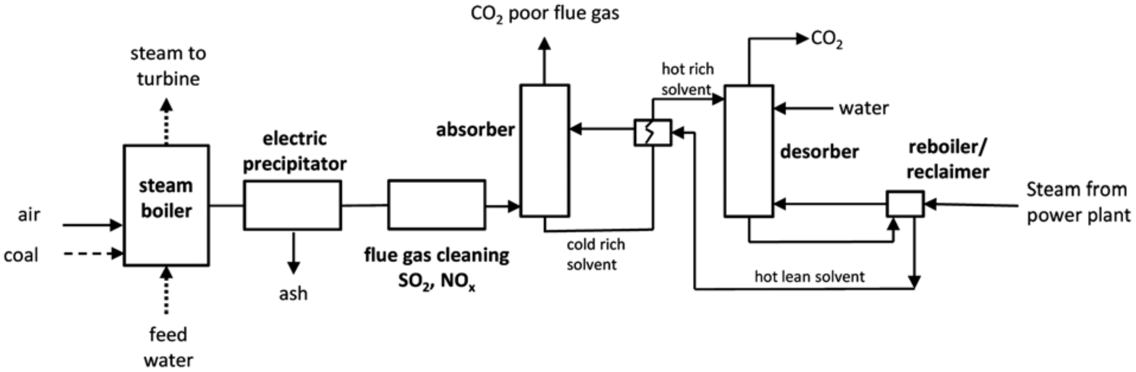


Figure 2 - Processing scheme of a CO_2-capture from the flue gas (post-combustion). **[3]**

A possible processing scheme of a plant for post-combustion capture of CO_2 is shown in the figure above. After the flue gas is cooled, the absorption takes place at a temperature of about 40°C to 60°. The CO_2-loaded liquid is then directed to a regenerator (stripper). The low-pressure steam for the necessary temperature change for the regeneration of the washing liquid is taken from the power plant process at a temperature of about 100-140°C. Since the steam is no longer available for electricity generation, this leads to considerable decrease in the efficiency of the power plant. [3]

1.1.2 Combustion in pure oxygen: Oxyfuel process

The term ''Oxyfuel process'' denotes the combustion of carbon containing fuels with pure oxygen. After the flue gas cleaning and washing, the flue gas essentially consists of a mixture of carbon dioxide and steam. Unlike conventional power plants, for which the CO_2-content in the flue gas ranges from 12-15 vol.%, the carbon dioxide content in Oxyfuel plants lies at about 89 vol.%. By condensing the steam, one obtains a pure CO_2 flue gas, which, after being first demoisturized, dried and compressed, can be transported to the storage site.

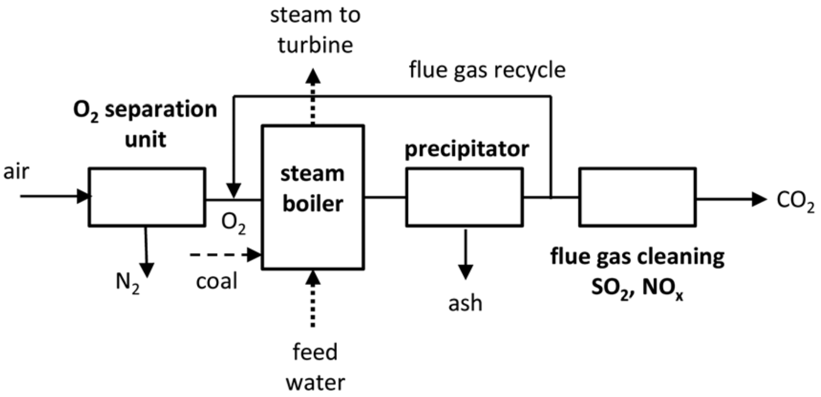


Figure 3 - Processing scheme of CO_2-capture (Oxyfuel). **[3]**

Nowadays, the oxygen for the combustion process is supplied by means of cryogenic air separation units, in which oxygen is separated from the air by condensation at low temperatures (less than 182°C). When fuel is burned with pure oxygen, the combustion temperature is higher than that in conventional combustion and requires, due to the different heat and flow specific limiting conditions, a modification of the steam generator as well as measures for limiting the combustion temperature, as the heat stability of the applied materials is limited. Thus, a large fraction of the CO_2-rich combustion gas (about two-thirds of the volume stream of the flue gas) is directed back into the combustion chamber. Furthermore, unreacted oxygen is recycled back into the oxidation process, thereby decreasing the residual oxygen content in the flue gas. [3]

1.1.3 Decarbonisation of the combustion gas: pre-combustion processes

The method for capturing CO_2 from the fuel gas exploits the combination of converting the fuel to a hydrogen-rich synthesis gas and capturing the resulting CO_2 from the fuel gas. The decarbonized fuel gas is then directed to a combined gas and steam turbine cycle process for generating electricity. The CO_2-capture takes place after the fuel gas production and the conversion of the carbon monoxide to CO_2 and H_2.

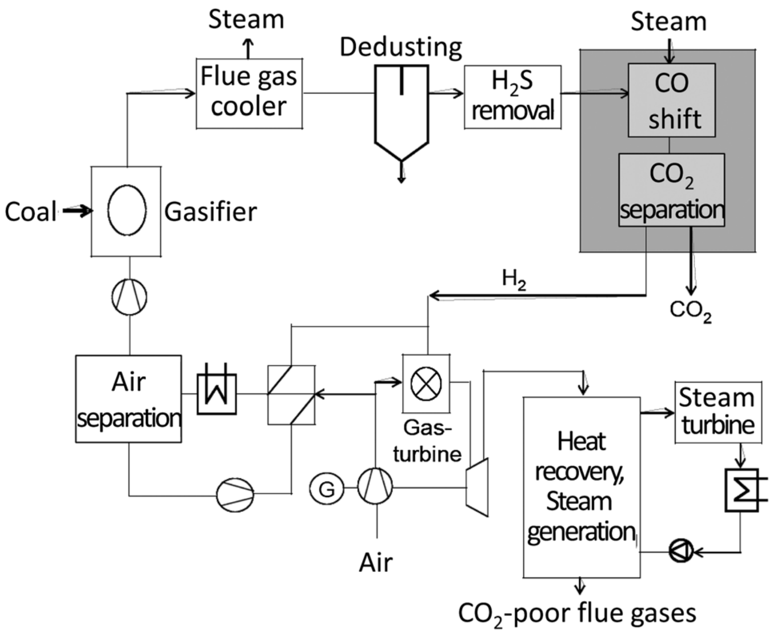


Figure 4 - Schematic representation of an IGCC[v]-plant with CO_2-capture. **[3]**

The conversion of fossil fuels to synthesis gas occurs by partial oxidation in a gasification process. The use of coal or heavy oil requires cleaning of the synthesis gas in order to remove ash particles, alkali and sulphur compounds as well as other impurities. By a subsequent catalytic conversion, the CO is reacted with steam as oxidant to form carbon dioxide and hydrogen (CO-shift reaction). Since the fuel gas is available after the CO-shift at high pressure and consists of

---

[v] An *integrated gasification combined cycle* (*IGCC*) is a technology that uses a high-pressure gasifier to turn coal and other carbon-based fuels into pressurized gas-synthesis gas (syngas).

high H_2-fractions, the CO_2-capture is advantageous by using physical solvents. This type of gas separation is marked by moderate reductions in efficiency and costs. It is being commercially used in some branches of the chemical industry and is, thus, state-of-the art technology. An air separation unit is placed before the gasification process in order to increase the yield in the gasification step, to keep atmospheric nitrogen out of the synthesis gas process, as well as to minimize the volume streams and, hence, the unit components. After the conversion of the CO, the fuel gas produced in this way consists almost exclusively of carbon dioxide and hydrogen. [3]

1.1.4 Comparative evaluation of the Carbon Capture technologies

In the following table are summarised the advantages and disadvantages of the three capturing technologies illustrated before.

	Post-combustion	**Oxyfuel**	**Pre-combustion**
ADVANTAGES	• Chemical absorption processes are well known • High optimization potential to reduce energy losses • Retrofitting of existing power plants is possible • No fundamental changes of the original power plant process are necessary • Highest purity of the CO_2 (>99.99%) of all carbon capture technology routes.	• Environmental impacts are low • Cryogenic air separation technology is well known • High potential to reduce energy losses	• High efficiency potential • Poly-generation of electricity and hydrogen gives flexibility
DISADVANTAGES	• High costs • Comparably large environmental impact • Flexible operation mode has yet to be demonstrated	• Modification of burners and boiler design are necessary • Probably no retrofitting option • High costs	• High investment costs • Lower availability and reliability so far • Less technology experience compared with conventional power plant technologies.

1.2 The CO_2 Market

Millions of tonnes of CO_2 are used in industry each year. The largest provision of this is Enhanced Oil Recovery (EOR), with some 70 Mt of CO_2 used annually. The future potential demand for CO_2 that could eventuate by 2020 is estimated to be 140 Mtpa[vi], taking into consideration the current development status of the reuse technologies. The current and future potential CO_2 demand are immaterial when compared to the total potential CO_2 supply from large point sources, which is estimated at 500 million tonnes annually for high-concentration sources, and 18 gigatonnes per annum (18000 Mtpa) of dilute CO_2 from power, steel and cement plants.

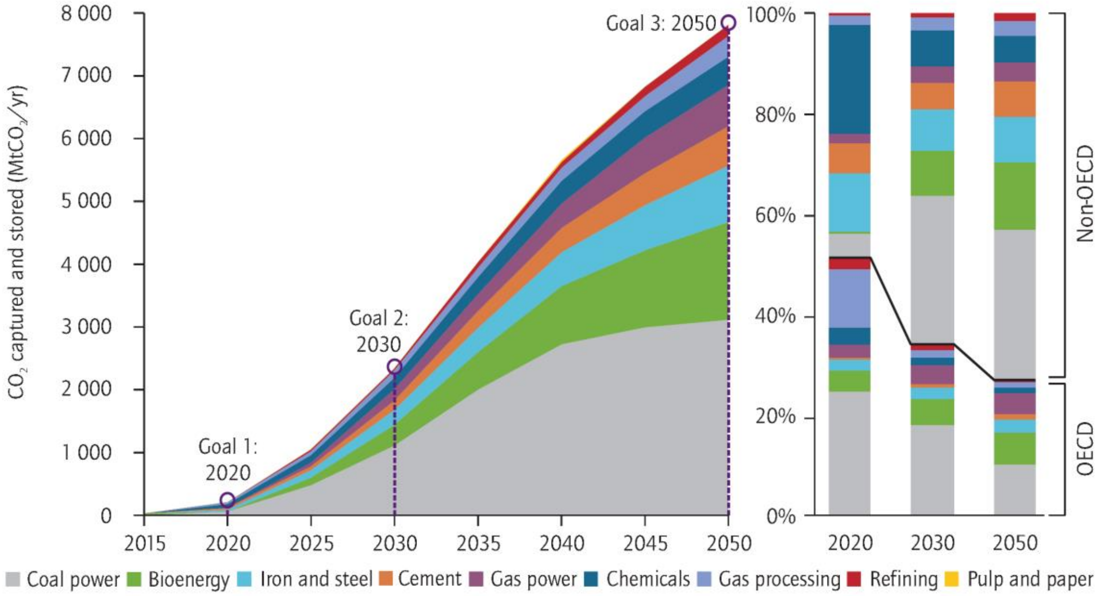


Figure 5 - CCS in the power and industrial sectors in the 2DS **[4]**

Due to this supply surplus, large scale facilities such as power, steel and cement plants that install CO_2 capture, and natural gas processing plants which produce CO_2 as a by-product of their operations, are likely to be price-takers in the market for CO_2, particularly under regimes that impose a carbon price penalty on emissions. The likelihood of a growing global CO_2 supply surplus is consistent with an expectation that bulk CO_2 market prices for reuse applications will be no higher than at present, and that they will be subject to future downward pressure that will strengthen with the adoption of regimes that impose a carbon price penalty on emissions. [2]

Although two-thirds of the quantities used are actually from natural CO_2 sources. In time this could be replaced with CO_2 captured from power and industrial facilities and, with appropriate site characterisation and monitoring, could provide a permanent storage solution. Other current large-scale uses (in the millions of tonnes per year) include urea yield boosting, carbonated drinks, water treatment and pharmaceutical processes. However, these uses are relatively limited when considered from the perspective of tackling climate change: for example, the

---

[vi] Millions of tonnes per annum

global beverage industry uses around 8 Mt CO_2 each year, which is approximately 0.5% of the CO_2 that would need to be captured and stored in the 2DS[vii] by 2030. Most of these alternative large-scale uses also do not offer a permanent storage solution.

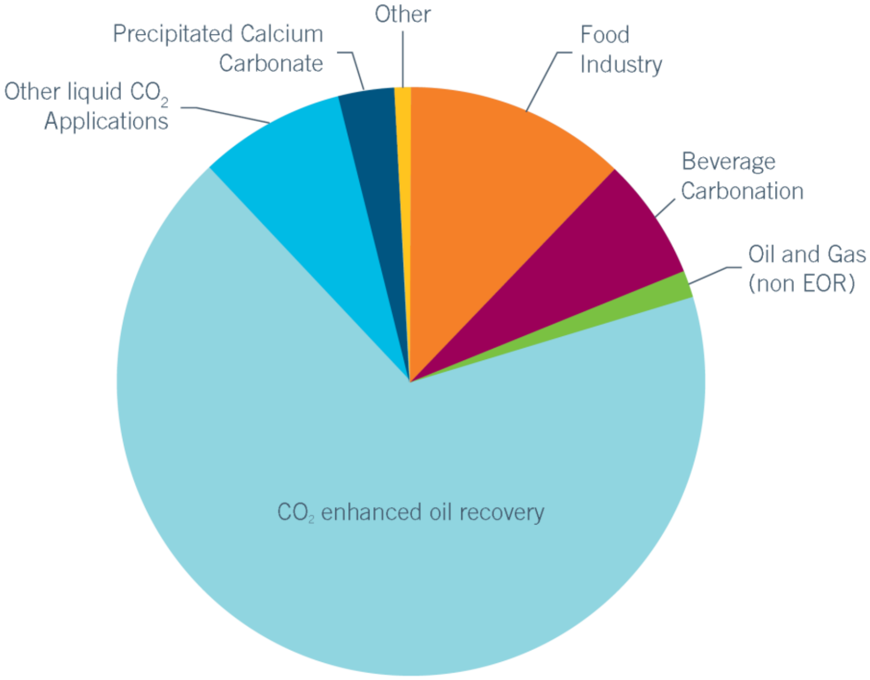


Figure 6 - Approximate proportion of current CO_2 demand by end use **[2]**

Emerging CO_2 utilisation opportunities such as mineral carbonation and CO_2 concrete curing have the potential to provide long-term storage in building materials, but again the potential contribution of these measures to climate change is likely to be limited as demand for these products becomes saturated. The proposed conversion of CO_2 to liquid fuels could potentially displace fossil fuel use (thereby reducing emissions) but requires extensive energy use and would not deliver the same net climate benefit as geological storage because in such conversion the CO_2 is ultimately re-released. [5]

Near-term CO_2 demand for use in EOR will help to support the development of initial CCS demonstration projects in favourable locations. However, for any CO_2 reuse technology to have the potential to materially accelerate CCS deployment in the longer term, it must have the potential to demand large quantities of CO_2, e.g. on a scale commensurate with capture from power generation and other large industrial sources.

The '*order of magnitude*' is very pertinent to the discussion on CO_2 reuse, as there is a significant discrepancy in scale between current industrial CO_2 consumption and CO_2 capture quantities from a commercial-scale CCS plant. For example, a single 300 MW (net) CCS demonstration

---

[vii] International Energy Agency (IEA) scenario that consider, thanks the contribution of Carbon Capture, a potentially critical option for limiting future temperature increases to 2°C or below.

project may capture approximately 2.5 Mtpa of CO_2. This single 300 MW (net) demonstration project represents a rate of CO_2 production that is greater than the current non-captive[viii] industrial consumption of Japan, South Korea and Australia combined. [2]

To permit a more comprehensive study on those technologies which have the most potential, have been considered only those that overcome a threshold of 5 Mtpa global CO_2 potential reuse. On this basis, the technologies considered are the following:

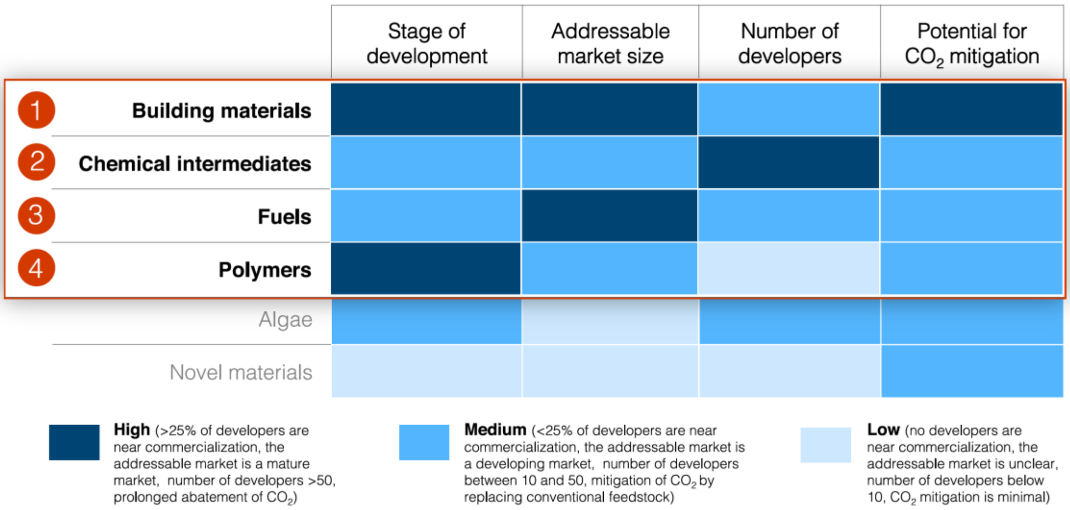
- CO_2 enhanced oil recovery;
- CO_2 as a feedstock for urea yield boosting;
- Enhanced geothermal systems (using CO_2 as a working fluid);
- CO_2 as a feedstock in polymer processing;
- Algae production;
- Mineralisation (including carbonate mineralisation / concrete curing / bauxite residue carbonation);
- Liquid fuels (including renewable methanol / formic acid);
- CO_2 enhanced coal bed methane (ECBM) recovery.

This study has the aim to identify the technologies for the utilisation un the carbon dioxide that could have a bigger footprint in the market. Therefore, will be considered only those technologies that implies the transformation of the CO_2. The Global CO_2 Initiative suggest eight product categories to pursue, based on maturity of their technology, market promise and potential impact on the mitigation of carbon emission. For each product or product category, was applied a Technology Readiness Level (TRL) of 1 (least) to 9 (most) to determine the relative stage of development and create a framework for expected time-to-market. Standardized rubrics was used to better quantify the mitigation potential and technology fit of each market. As a result, four markets were recommended for further analysis as shown in Figure 7. Algae and novel materials will not be part of the roadmap development as they will not significantly impact markets before 2030. [6]

The roadmap analysis focused on eight categories within these four markets:

1. Chemical Intermediates: Methanol
2. Chemical Intermediates: Syngas
3. Chemical Intermediates: Formic acid
4. Fuels: Methane
5. Fuels: Liquid fuels
6. Building materials: Concrete
7. Building materials: Aggregates
8. Polymers

[viii] Non-captive CO_2 use is where the CO_2 needs to be sourced external to the process.



	Stage of development	Addressable market size	Number of developers	Potential for CO_2 mitigation
① **Building materials**	■	■	▨	■
② **Chemical intermediates**	▨	▨	■	▨
③ **Fuels**	▨	■	▨	▨
④ **Polymers**	■	▨	□	▨
Algae	▨	□	▨	▨
Novel materials	□	□	□	▨

■ **High** (>25% of developers are near commercialization, the addressable market is a mature market, number of developers >50, prolonged abatement of CO_2)

▨ **Medium** (<25% of developers are near commercialization, the addressable market is a developing market, number of developers between 10 and 50, mitigation of CO_2 by replacing conventional feedstock)

□ **Low** (no developers are near commercialization, the addressable market is unclear, number of developers below 10, CO_2 mitigation is minimal)

Figure 7 -Markets that offer best opportunities for support and investment [6]

1.2.1 Building Materials

The two main CO_2 utilization technologies used in building materials are mineralization for carbonate aggregates and the use of CO_2 to cure concrete[ix]. It's thermodynamically favourable to make carbonates and requires less energy input to achieve. This makes this market attractive for developers because the technology is more readily scalable today.

Research Status

The study found that the use of CO_2 utilization in concrete curing represents an immediate opportunity. Moreover, with additional allocated resources, building materials can have a significant mitigation impact on CO_2 emissions.

Potential Market

Potential markets for products generated from mineralisation include:

- Mine reclamation
- Construction materials – aggregate
- Supplant portion of cement

The main markets for the use of carbonates are the cement and aggregates market as alternatives to traditionally materials.

Concrete curing is a technology used by manufacturers of precast concrete worldwide. The main potential for the CO_2 curing method would be through the displacement of the traditional

---

[ix] The concrete curing is the process in which is provided the adequate moisture, temperature and time to allow the concrete to achieve the desired properties for its intended use. During this process huge amounts of CO_2 can be stored.

methods by existing manufacturers. Since, the flue gas produced by the concrete production process itself is a suitable source of CO_2, countries in which there exists a carbon scheme hold the most potential.

Size of Markets

Calera[x] has estimated that the current global demand for building materials is 32 billion tonnes per year and is expected to see year on year growth. According to the International Energy Agency, cement production is projected to grow by 0.8 - 1.2 per cent per year until 2050. [2]

Barriers

The mass of natural silicate rocks (containing magnesium ore) to store CO_2 generated by coal combustion is calculated to be over eight times the mass of coal. Despite the large difference in mass, the mining operation is claimed to be of similar magnitude to that of coal. It is likely that the carbonation process would need to take place at the mine, adding geographical constraints to this technology, raising similar issues to geological storage.
The concrete sector operates within a highly competitive commodity market with limited capital to invest in new technologies.

1.2.2 Chemical Intermediates

Methanol, syngas and formic acid are the most widely developed. Most of them are also recognized as fuels, so the considerations are similar. Commodity chemicals are one of the CO_2-based products considered in the top categories to pursue because of the wide range of market opportunities, the possibility to scale up relatively mature technologies for commercial production in the medium-term, and the challenges in assessing the climate benefits of myriad production pathways and products. [7]

Potential Market

The most promising chemical intermediate is the methanol. The total methanol market size in 2015 is 60-70 million metric tons and is expected to grow to approximately 190 million metric tons by 2030, with a CAGR[xi] between 7 and 9 percent. The estimate assumes that the bio feed stock market share for methanol used as a fuel is 50 percent by 2030, and the overall market share of methanol used a fuel increases from 12 percent in 2015 to 30 percent in 2030. [6]

Barriers

Methanol from CO_2 conversion, usually produced by the electrolysis of water, requires cheap hydrogen and demands inexpensive/renewable sources of electricity.

---

[x] Calera is an organisation involved in developing the carbonate mineralization technology using industrial emission, that operates in California.

[xi] Compound Annual Growth Rate (CAGR) is a business and investing specific term for the geometric progression ratio that provides a constant rate of return over the time period.

1.2.3 Fuels

CO_2 as a feedstock for liquid fuel production is a broad category for CO_2 reuse, which includes conversion of CO_2 to a number of alternative fuel products, including formic acid, methanol, dimethyl ether, ethanol, and other petroleum equivalent products. In general, the primary energy input for these conversion technologies is renewable energy, with the current proponents focused on solar and geothermal energy. This is an important requirement for these technologies, as generally they have relatively low thermal efficiency (e.g. relatively small fraction of the energy input is converted to useful fuel). Consequently, the primary energy input needs to have a low CO_2 emissions intensity. If fossil-fuel based energy were used as the primary input into CO_2-based liquid fuel production, more CO_2 would be released than if the fossil fuel were used directly as a fuel.

Research Status

Considerable progress within the liquid fuels sub-category during the last five years shows that the technology is primed for production at scale.

In the following table are summarised the main technologies, the corporation involved and their readiness level into the market.

	Technology	Companies Involved	Maturity of Technology
Methanol	Electrolysis of water, catalytic conversion of H_2 and CO_2	Carbon Recycling International (Iceland)	The commercial deployment is almost reached
Formic acid	Electro-reduction of CO_2 to produce formic acid and O_2.	Mantra Venture Group (USA)	Formic acid from CO_2 cannot compete for another 10 years, perhaps 15
Methane	Electrolysis of water, catalytic conversion of H_2 and CO_2	ETOGAS (Germany), Electrochaea (Germany), Carbon Sciences (USA)	Stage of development went from pilot testing in the lab in 2011 to pilot testing at commercial scale in 2016

There has been a great increase in R&D for liquid fuels due to available government funding. The focus of developments has been on integrating CO_2 capture, renewable energy supply, hydrogen generation and CO_2 conversion in the case of methanol and on efficient (multi-step) conversion of CO_2 into fuels in the case of other liquid fuels. Europe is at the forefront of the CCU market because it has set some strict goals to create a low-carbon emission economy.

Potential Market

As a replacement for fossil fuels, the potential market for CO_2 derived fuels is large, and global. Consumption of fossil fuels for transport in 2007 was 2297 Mtoe (Million tonnes of oil equivalent). [2]

	Market share	Global Trends	Market Possibilities
Methanol	Production of formaldehyde, methyl tert-butyl ether, acetic acid and dimethyl ether; mostly used as a fuel blend	The total methanol market is expected to grow from 60 to approximately 190 million metric tons by 2030	High potential, the overall market share of methanol used a fuel increases from 12 percent in 2015 to 30 percent in 2030.
Formic acid	Production of adhesives, dimethylformamide (DMF), and other products. Because it's more reactive than methanol, formic acid is more suitable as a chemical intermediate. Formic acid also has been proposed as a fuel source for fuel cells. This application is still in a proof-of-concept phase.	The total formic acid market is expected to grow from 0.5 to approximately 1.0 million metric tons by 2030	Low potential. Global market of 1 billion dollars
Methane	The widest areas of market application are the automotive and the energy storage (power-to-gas).	The estimated total market size is 3-4 trillion cubic meters annually. The overall methane market is expected to grow to 4-5 trillion cubic meters by 2030	Very high potential. The market is estimated to be bigger than 100 billion dollars.

The main driver to support the commercialisation of the technology regarding liquid fuels is the potential to penetrate the transportation energy market which is expected to see significant growth in the forthcoming years.

By 2030, the CCU liquid fuels market is expected to grow to between 7 billion (pessimistic), 45 billion (optimistic) and 165 billion (best case) US gallons annually. [6]

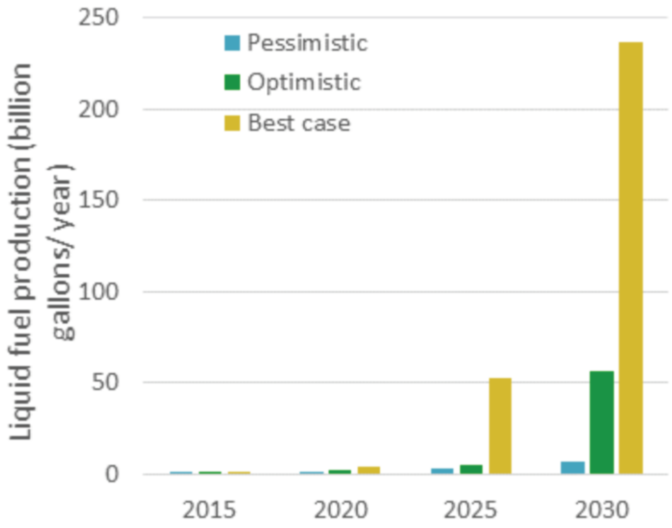


Figure 8 - Estimated growth of CO_2U liquid fuels market by 2030 **[6]**

Barriers

Some critical barriers include the low efficiency and high capital cost that is a characteristic of some of the CO_2-to-liquid fuel technologies. It is likely that some technologies will never overcome these cost barriers and will consequently not be commercial.

Another potential barrier is that alternative transport systems (such as electric vehicles with regenerative braking coupled to a renewable energy powered electricity grid) may be a more competitive solution, with significantly higher overall energy conversion efficiency.

	Barriers and competitors	Strategic Actions
Methanol	• Low efficiency process; requires renewable or low emissions energy to have net CO_2 abatement benefit • Needs low cost renewable hydrogen • Cost of purifying CO_2 • The competitor is the biofuels from bio-based feedstock	• Development of electrolysis and access to low-cost renewable energy • Further catalyst R&D • Implement carbon tax or replace bio-based feedstocks
Formic acid	• Inefficient process; requires renewable or low emissions energy to have net CO_2 abatement benefit • Chemistry needs to be perfected cost of purifying CO_2 • Lack of funding for programs to focus on formic acid from CO_2 • Lack of current demand for formic acid	• Research into improving catalyst selectivity and increasing catalyst life. This includes catalysts that would allow for contaminated CO_2 • Formic acid could be developed as an alternative `green' chemical intermediate or a fuel to fuel cells
Methane	• Requirement of process integration • Needs of low-cost and effective catalysts • the competitor is an alternative transport system (such as electric vehicles)	• Development of conversion technology and access to low-cost renewable energy, i.e. process integration of renewable energy or excess energy, carbon capture and conversion

1.2.4 Polymers

Currently, the most widely used feedstock in polymer production is petroleum derived, such as ethylene or propylene which, once reacted, make-up chains in polyethylene (PE) or polypropylene (PP), respectively. PE and PP represent the largest volume of polymers currently produced. PE is used to produce a range of items including plastic bags, milk bottles and film wrap. PP creates and forms parts of item such as automotive components, textiles and polymer banknotes. The polymers created by the new process are polypropylene carbonate (PPC) and polyethylene carbonate (PEC). Such polymers can contain up to 50 per cent carbon dioxide or carbon monoxide and therefore have a significantly reduced carbon and energy footprint compared to the materials they will replace. Therefore, this technology creates a useful demand for CO_2 as a product, which waste CO_2 sources could supply, while reducing demand for finite oil-based feedstocks. [2]

Research Status

The creation of polymers through CO_2 utilization is possible, but not yet economical. A limited number of developers are investing in it, but lack of incentives is inhibiting the entry of startups.

Potential Market

Polymers created in part from CO_2 could replace traditional petroleum based plastics such as polypropylene, polyethylene, polystyrene and polyvinyl chloride if the properties of PPC remain the same for application in a wide range of areas traditional plastics are employed.

Size of Markets

The global markets for polyethylene and polypropylene were approximately 80 Mt and 45 Mt respectively, representing the two largest polymer markets.

Barriers

The technology is still a relatively early stage and present a significant number of issues that need to be resolved:

- The source of CO_2 and the purity required could mean additional polishing at the point of source is required, increasing cost.
- CO_2 is a very stable molecule and takes significant energy to split and allow reaction. Therefore, this process was traditionally expensive and would contribute significant greenhouse gas emissions on a commercial scale of production through the energy demands (assuming fossil fuel generated power).
- The main market target is the packaging industry which is a low-end application so acceptance will be entirely driven by cost. PPC will have to compete with traditional polymers on a cost basis to win market share, otherwise it will be left to high end niche applications such as medical devices.

1.3 SWOT Analysis of CCU – Synthetic Fuels

The development of the technologies dealt with in this work, the production of synthetic fuels from hydrogen and CO_2, is strongly linked to the diffusion and regulation of carbon dioxide capture from industrial processes and, on the other hand, to the market trend of electrolysers. A SWOT analysis is proposed below, which will try to highlight the most crucial aspects of these systems, from a technical and economical point of view.
The SWOT is a situation analysis in which internal strengths and weaknesses of an organization or of a process, and external opportunities and threats faced by it are closely examined to chart a strategy. SWOT stands for strengths, weaknesses, opportunities, and threats.

1.3.1 Strengths

General benefits

In an ideal embodiment of the CO_2 to liquid and gaseous fuels concept, the CO_2 feedstock is converted into an energy carrier, but the energy input is renewable or has very low CO_2 emissions intensity. The ideal embodiment gives potential for a reduction in CO_2 emissions as compared to the combination of an uncaptured CO_2 and fossil-fuel based economy. Proponents argue that the ability to use existing petroleum-based infrastructure (transport, distribution, storage, engines, and vehicles) is a benefit of the CO_2-to-liquid or CO_2-to-gas fuels approach, assuming the liquid fuels produced are comparable to petroleum diesel or gasoline (which is not always the case).
The widespread use of this technology will help governments meet their targets for low and zero emission vehicles. [2]

Commercial viability

Since CO_2-recycled synthetic fuels are environmentally friendly (potentially more so than biofuels), they might go to market without the same level of taxation as gasoline in some countries. This would give these clean fuels an advantage as they would be competing against the post-tax price of gasoline rather than the wholesale price. A price on CO_2 emissions would likely further improve the economic competitiveness of CO_2-based synthetic fuels. Finally, the potentially greater sustainability of CO_2-recycled fuels over fossil or biomass derived fuels, as well as independence from the geographic and supply related issues of conventional fuels, could also give CO_2-recycled fuels a market advantage. [8]
As a replacement for fossil fuels, the potential market for CO_2 derived fuels is large, and global. The main driver to support the commercialisation of the technology is the potential to penetrate the transportation energy market which is expected to see significant growth in the forthcoming years.

Coal-dominated energy structure

Demand for electricity and power capacity is increasing with the rapid development of domestic economy. The thermal power installed capacity in a lot of countries still maintains growing. Coal-dominated energy structure externalities have negative impact on the environment. With the increasing environmental pressure, in order to complete the target while guaranteeing the power supply, to promote the widespread implementation of Carbon Capture, within developing clean coal technology and improving the efficiency of power generation, promoting the overall goal of energy conservation and emissions reduction.

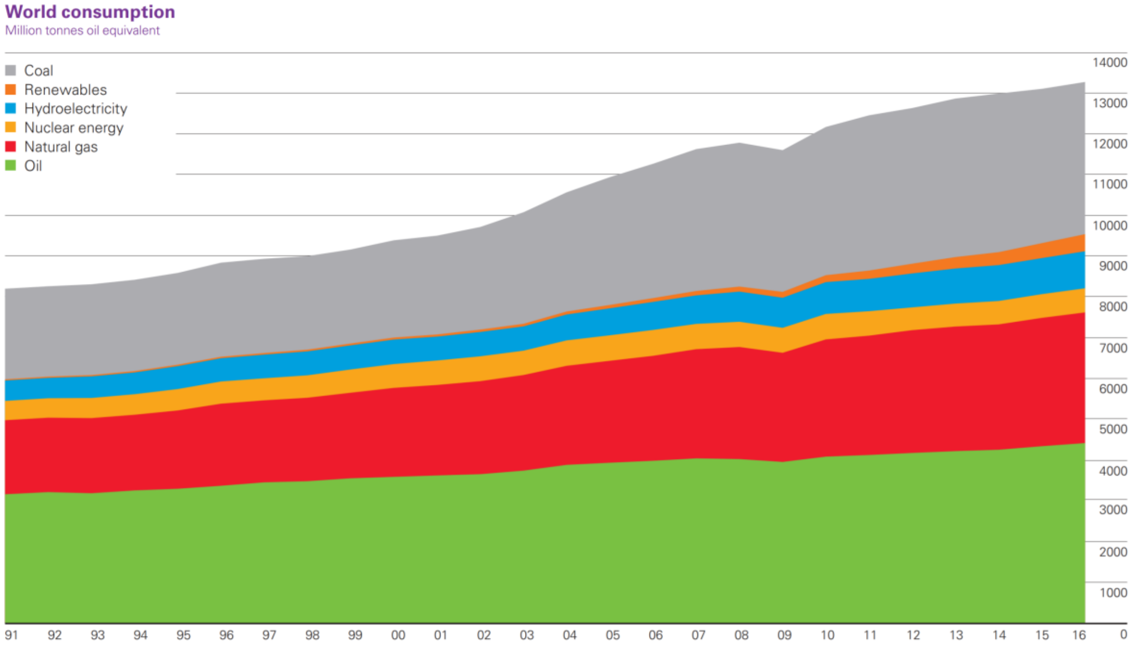


Figure 9 - World energy consumption divided by source [9]

1.3.2 Weaknesses

Poor economic feasibility

Carbon Capture is a high-cost abatement option and will remain so in the short-term and, unlike renewable energy and energy efficiency, it does not generate revenues if there is no carbon price or a commercial market for the captured CO_2. Current carbon prices are well below Carbon Capture costs. This is because current short-term emissions targets can be met without the use of capturing systems. [10]

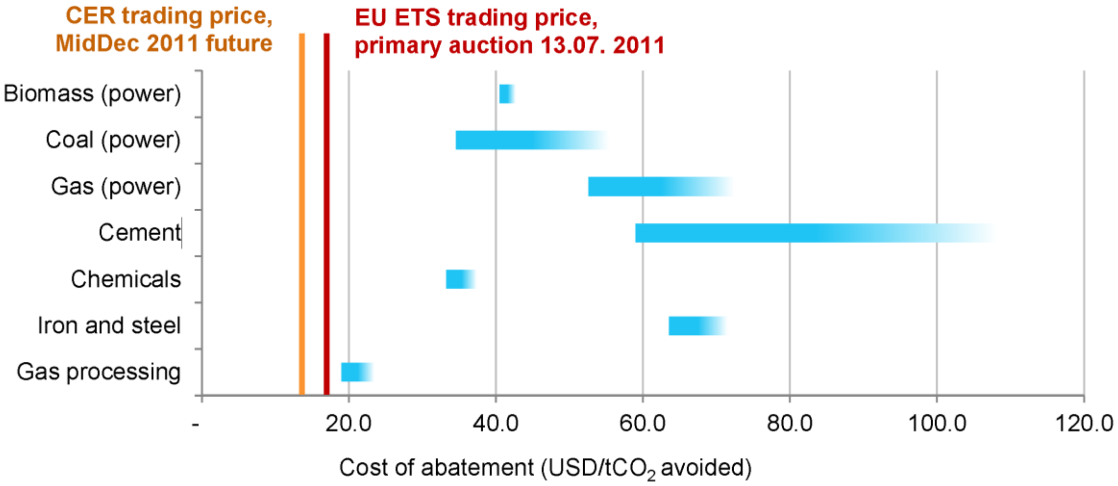


Figure 10 - Current carbon prices from the EU Emission Trading Scheme **[10]**

The utilization processes of the CO_2 dealt in this work, the methanation and the methanol production via direct hydrogenation of the CO_2, are also severely affected by the high cost of the SOEC system. Fuel cell markets worldwide are in an embryonic stage, as no fuel cell systems are cost-competitive yet (except in some niches). Moreover, reliability is still unproven for most systems. On the other hand, the utilities will only start investing in fuel cell systems for centralised power generation (where the investment costs are even higher) once the reliability and the possibility of cost reductions have been proven on small-scale applications. [11]

Lack of capital source

Clean development mechanism (CDM), is one of three kinds of flexible implementation mechanisms that the Kyoto protocol set, the core is developed countries buy certified emission reduction (CER) from developing countries in the project cooperation way, on the one hand to ensure that developed countries can perform their part of the emissions reduction obligations, on the other hand, to provide money and technology to developing countries, promoting the sustainable development of developing countries. However, CCS and accordingly CCU does not belong to the CDM projects at present, due to project boundary issues, persistent problem, leakage issues and sustainable development issues. Overall it is difficult for Carbon Capture to finance through CDM in the international category for financial support. [12]

Only few companies in the world are trying to invest money in large scale CCU project (as Carbon Recycle International for Methanol and Audi for Methane).

1.3.3 Opportunities

Reduction of greenhouse gases

Contrary to some CCU technologies that are considered as a permanent CO_2 storage solution such as concrete curing or mineral carbonation, synthetic liquids are a reuse technology which do not permanently store CO_2. However, the displacement of 10 per cent of the world's fossil petroleum consumption with renewable CO_2 derived fuels would represent in excess of 1 Gtpa CO_2 recycling.

Supporting the development of renewable energy

The better situation of renewable energy development is a double-edged sword for Carbon Capture technology. On the one hand, Carbon Capture technology and renewable energy technology are two alternative technologies. In the case that renewable energy development can alleviate environmental pressure and reduce carbon emissions, the importance of Carbon Capture technology is bound to decline and detrimental to the development. However, considering the small proportion of renewable energy in the overall energy consumption structure currently, the impact is relatively less. With the increase in the proportion of renewable energy, the importance of Carbon Capture technology will be subject to greater impact. On the other hand, renewable energy promotes the Carbon Capture. While renewable energy is clean and can be used as an additional energy generation for CCU equipment, and Carbon Capture could reduce carbon emissions of fossil fuels at the same time, so the collocation of them can result in the maximum reduction carbon emissions with no increasing consumption of additional fossil energy. Thus, the resistance to Carbon Capture technology development can be reduced, and public acceptance is improved. Overall, renewable energy still has an active role for CCU technology, providing opportunity to develop it. [12]

Storing surplus energy for later use

The progressively diffusion of the renewable energy bring some issues to the energy system management due to the natural intermittency of renewable energy sources (RES). This problem could be solved thanks to the power-to-gas and power-to-liquid technologies. Thanks to these procedures is possible to store directly in the existing infrastructure the synthetic fuels obtained avoiding the waste of RES or the phenomenon of curtailment[xii].

RES development also does not directly address non-electric energy needs such as fuels for transportation and industry feedstock, which are presently relying on fossil fuels. Therefore, the conversion of surplus renewable electricity into the more convenient form of a liquid or gas (power-to-liquid and power-to-gas) could help offset RES intermittency while providing a diverse mix of energy carriers. If recycled CO_2 is used in the fuel synthesis process, overall emissions can be greatly reduced. [13]

Yet, RES deployment at a significant scale faces a number of constraints or limiting factors. In particular, the natural intermittency of RES translates into a variable and not entirely predictable

---

[xii] Curtailment is a reduction in the output of a generator from what it could otherwise produce given available resources, typically on an involuntary basis.

power output, thereby creating system balancing and capacity adequacy issues that may hamper the viability of an energy supply configuration relying mostly on RES. For instance, the ability of wind power to ensure availability of sufficient power generation (capacity value) ranges from 5 % to 40 % of the nameplate capacity. Conversely, variable RES output can lead to periods when power generation far exceeds demand, thus straining the system's flexibility or resulting in an economic loss if plants are switched off. [13]

The energy from RES is expected to grow in the next years, highlighting the necessity of storages solution. Nowadays the most diffused energy carries that have the capacity to store energy are those shown in the following figure.

Most renewable energy is converted to electricity in a transportable form. However, electricity can only be stored directly to a limited extent (e.g. in capacitors). Electricity storage technologies therefore use the following forms of energy:

- Electric energy (supercapacitors)
- Potential energy (hydropower, pumped storage power plant)
- Mechanical energy (compressed air reservoirs, flywheel energy storage systems)
- Electrochemical energy (batteries)
- Chemical energy (fuels)

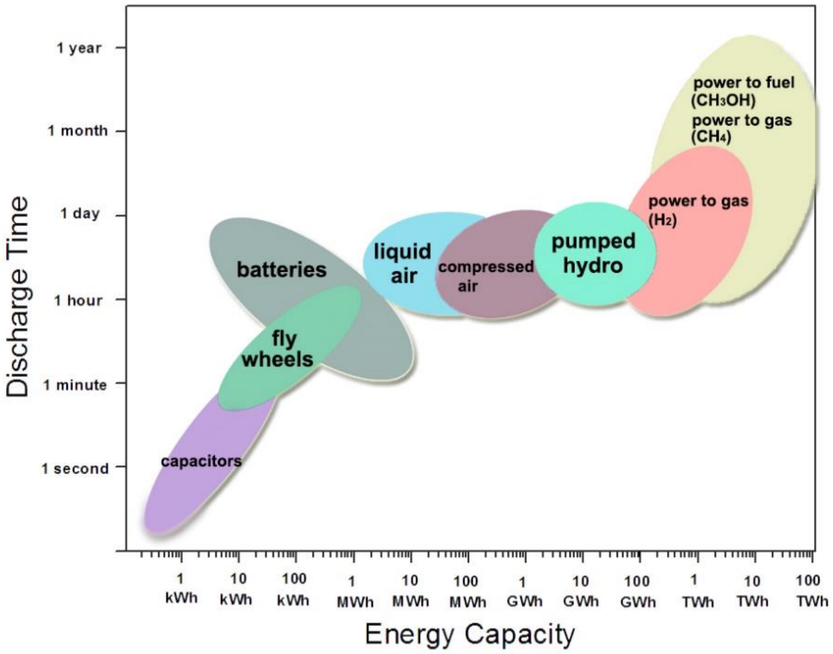


Figure 11 - Relationship between energy capacity and time for discharge for storage solutions **[14]**

Pumped storage power plants are generally used for storing electricity for periods ranging from several hours to several days. Their existing capacity and expansion potential are strictly limited by geographical factors and environmental conditions. Compressed air reservoirs operate with output ranges similar to those of pumped storage power plants. However, there are as yet only two systems in operation worldwide. Storage in flywheel energy storage systems or supercapacitors is limited, particularly with regard to duration and capacity. Therefore, they are primarily used for short-term (less than one hour) provision of power to compensate for

fluctuations. Stationary and mobile batteries represent a medium-term (under a day) power reserve, although their use is limited by their very low energy and power density and lifetime. For long-term storage and seasonal balancing of renewable energy sources, currently only chemical secondary energy carriers can be used, such as hydrogen and carbon-based fuels. [15]
In this context, synthetic fuels such as methanol (CH_3OH), dimethyl ether (DME), methane (CH_4) and other hydrocarbons are being promoted as storage media for surplus RES power that could easily substitute fossil fuels and their derived products in many sectors, including transportation. Transforming renewable energy (electricity and/or heat) into the more convenient form of liquid and gaseous energy carriers (power-to-liquid and power-to-gas) offers a way to buffer RES intermittency and thereby alleviate one of the main constraints to their large-scale deployment. All synthetic fuels could moreover be directly integrated into existing infrastructure (e.g. filling stations) without incurring excessive costs, technical barriers or change in habits. This has implications for the transport sector, but also for many other sectors of application where synthetic fuels could be used as final energy carriers and raw material: industry, electricity generation, heating, chemical feedstock, fuel cells.

Consequently, the combination of renewable inputs (RES power and captured CO_2) in the synthesis process could lead to a potentially carbon neutral fuel cycle, and truly sustainable synthetic fuels. Based on Power-to-liquid and Power-to-gas technologies, all components of the final energy mix – electricity, liquid and gaseous fuels, feedstocks – could therefore be successfully covered whilst greatly reducing CO_2 emissions.

1.3.4 Threats

Imperfect Policy and Laws

Perfect government's policy and legal framework for large-scale CCU projects implementation do important means, long-term stable and clear energy policy will bring CCU technology users and investors confidence, increasing the investment return. CCU projects are often difficult to promote only relying on their own strength because of costly CCU implementation and high risk. Thus the benefits of numerous CCU large-scale implementation involved several aspects, including international organizations, national, local governments, businesses, and the social public. It is significant to establish a legal and policy framework and effective running mechanism under the system which express and coordinate the demands of stakeholders. [12]

Uncertainties in Carbon Dioxide price

As said before, the technologies discussed in this work like renewable methane, methanol and other liquid fuels, do not store permanently the CO_2. This expose these reuse technologies to a greater risk due the uncertainty of the carbon price, so the resultant net cost will depend on:

- the structure of the emissions trading or taxation system that is in place
- the approach taken to carbon liabilities (e.g. whether the carbon price is passed on to the end product of CO_2 reuse or it remains with the original CO_2 source/emitter)
- whether the end use for the CO_2 remains competitive with non-carbon based alternative products. Competition may restrict the extent to which any carbon price can be borne by the end product of reuse.

With a high carbon price and surplus supply of CO_2, the key issue that control the uptake of these technologies is the extent to which they are accepted as having an abatement effect and are validated as an emissions offset. This suggests that with a weak bulk CO_2 market price for reuse, the prospects for reuse technologies that provide only temporary storage are very uncertain.

At face value reuse technologies with only temporary CO_2 storage characteristics have no real prospect of being credited with a CO_2 abatement effect. The only exception may be where it is accepted that anthropogenic CO_2 used in the reuse technology effectively replaces naturally occurring reservoir CO_2 in the process, or where the end product replaces a product which would otherwise be sourced from fossil fuels. This is a reversal of the logic which would potentially disadvantaging EOR for mitigation purposes because it increases fossil fuel production and consumption.

Overall there is very limited potential for reuse technologies where CO_2 storage is temporary in a strong carbon price environment – except in circumstances where regulators accept that the process either replaces natural reservoir CO_2 or the product replaces products derived from fossil fuels. [2]

1.4 Final Considerations and Recommendations

In the recent years CCU has received more attention than in the past but it is evident that these technologies need some coherent funding strategies from governments in order to scale up in the market.

The main limits to CCU are linked with:

- POLICY:
  - Currently CCU is not seen as a priority in government R&D strategies
- TECHNOLOGY:
  - Lack of funding strategies from governments to support CCU technologies
  - Lack of access to facilities and to feedstocks (hydrogen, CO_2 and renewable energy)
- MARKET:
  - Cost, CCU must compete with conventional feedstock and bio-based feedstocks, which are lower in cost
  - Access to a national CO_2 infrastructure
  - Lack of process integration of renewable energy and conversion processes (no robust value chain)

In the following image is presented the market forecast for synthetic fuels highlighting the difference between the cases in which strategic actions was implemented or not.

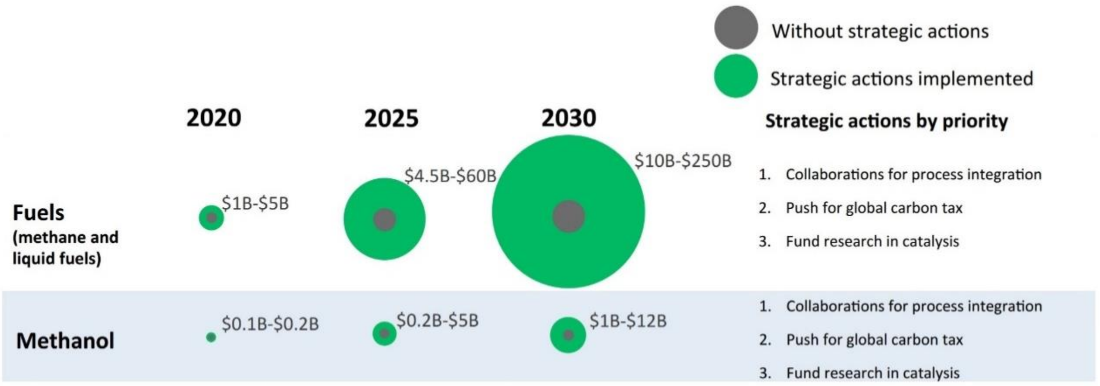


Figure 12 – Market size of fuels with and without strategic actions. **[16]**

The ICEF[xiii] roadmap suggests targeted R&D activities in the following areas would likely accelerate commercialization and improve performance for CO_2 conversion to synthetic fuels:

- Better catalysts would be inherently more efficient, and would reduce energy costs, improve yields, and improve emissions footprint.
- With the costs reduction of the renewable energy and the providing of a larger share of the grid electricity mix, electrochemical pathways become more attractive for the upgrading of CO_2. Modelling of CO_2 activation on metal surfaces for electrochemistry,

---

[xiii] Innovation for Cool Earth Forum

innovations to improve electrode stability, and development of new cell designs are important targets for R&D.

- Advances in the fundamental understanding of high-temperature electrolysis (e.g. SOEC[xiv]) are required, along with advances in materials to allow more reliability and operation durability of the SOEC cells.
- The combination of commercially available thermo-catalytic pathways with emerging electro or biochemical processes to create hybrid systems appears to be a promising strategy to advance CO_2 conversions and modelling to evaluate the technical, economic and environmental performance is needed to drive innovation in this area. The combination of separations with reactions, long a goal for chemical engineering research, would be particularly helpful to improve yields in all pathways.
- Innovative approaches are needed to advance photocatalysis and investments should focus on long-term R&D. In addition, practitioners should aim to make studies more consistent and comparable both in experimental design (e.g. light sources), but also in presentation of results (e.g. by providing better information on quantum yield or efficiency).
- There are few examples of life-cycle assessments for commodity chemicals and synthetic fuels today, and those that exist are difficult to compare. Additional studies are required to better define the potential climate (and environmental) benefit of the wide range of conversion pathways and products, and these studies should follow a consistent approach that improves their comparability.

Much remains to be understood regarding the chemical conversion approaches and life-cycle implications for a CO_2-to-fuels enterprise. While some processes are near commercial, the possibilities to improve cost, performance, and emissions footprint are real. A coordinated innovation agenda in this space is a priority since many technical advances are new, many opportunities exist to improve, the technical readiness range is large, and the potential for climate benefits is high. [7]

[xiv] Solid Oxide Electrolyser Cell (see section 2.3.1)

2 Synthetic Fuels Production

Hydrocarbon fuels provide the majority of all transportation energy, and petroleum is the dominant feedstock from which transportation fuels are produced. Hydrocarbons produced from other feedstocks (fossil and biomass), as well as carbon-free energy carriers (such as hydrogen, batteries and ultracapacitors), are potentially more sustainable alternatives. The benefits of hydrocarbons over carbon-free energy carriers include higher energy density and use of existing infrastructure (fuel distribution and vehicles). While increased use of electric propulsion will likely reduce liquid fuel demand, hydrocarbons will continue to be needed especially as fuels in aircraft, sea vessels, and haulage vehicles, and they also provide the chemical building blocks for much of the chemical industry. Their widespread use calls for means to produce them sustainably. As a direct replacement for petroleum-based hydrocarbons, biofuels and fossil carbon derived synthetic fuels (e.g. coal derived liquid fuels) are receiving the most attention.

The concept and technology behind synthetic hydrocarbon fuels are not new. The predominant process for synfuel production is called the Fischer-Tropsch[xv] process, which was invented during the Second World War. Currently, the crude oil supply is still plentiful and thus the price of synfuels, which is high due to the cost of initial implementation of infrastructure, is not competitive in the market.

Similar hydrocarbons can also be produced without using fossil fuels or biomass. Using renewable and/or nuclear energy (in the form of heat, electricity, and/or sunlight), carbon dioxide and water can be recycled into hydrocarbon fuels in a non-biological process. [8]

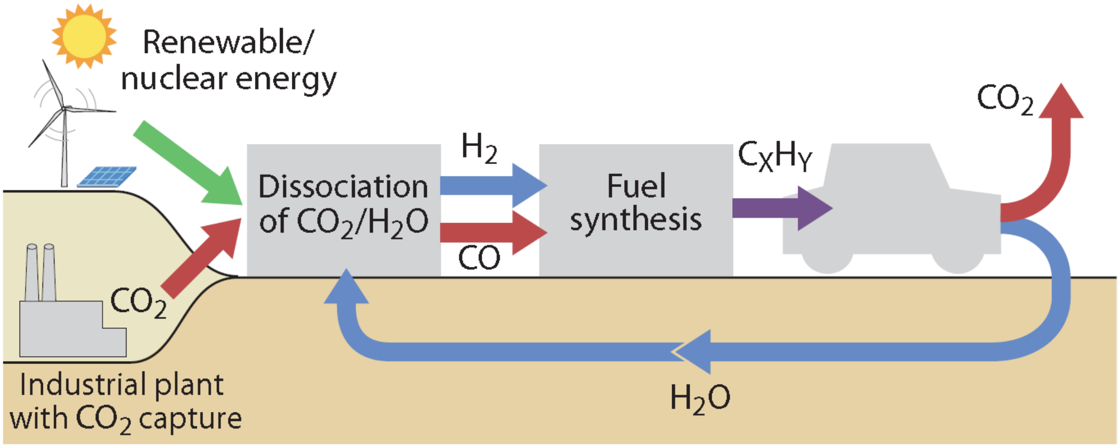


Figure 13 - CO_2-recycled synthetic fuel cycles **[8]**

[xv] From the name of the two chemist Franz Fischer and Hans Tropsch, researcher in the Kaiser Wilhelm Institute. They patented the process in the 1925

2.1 Methane: process of production

Research into catalytic methanation processes focuses on two options, CO methanation and CO_2 methanation.

- CO methanation is an exothermic process using carbon monoxide and hydrogen as educts for the catalytic production of methane and water. Educt gases mainly come from coal or biomass gasification at synthetic fuel production plants.

$$CO_{(g)} + 3H_{2(g)} \leftrightarrow CH_4 + H_2O_{(g)} \qquad \Delta H = -206\frac{kJ}{mol}(298\ K)$$

- CO_2 methanation processes use carbon dioxide and hydrogen as educts. The methanation of carbon dioxide is an exothermic as well as exergonic reaction with volume contraction.

$$CO2_{(g)} + 4H_{2(g)} \leftrightarrow CH_4 + 2H_2O_{(g)} \qquad \Delta H = -164\frac{kJ}{mol}(298\ K)$$

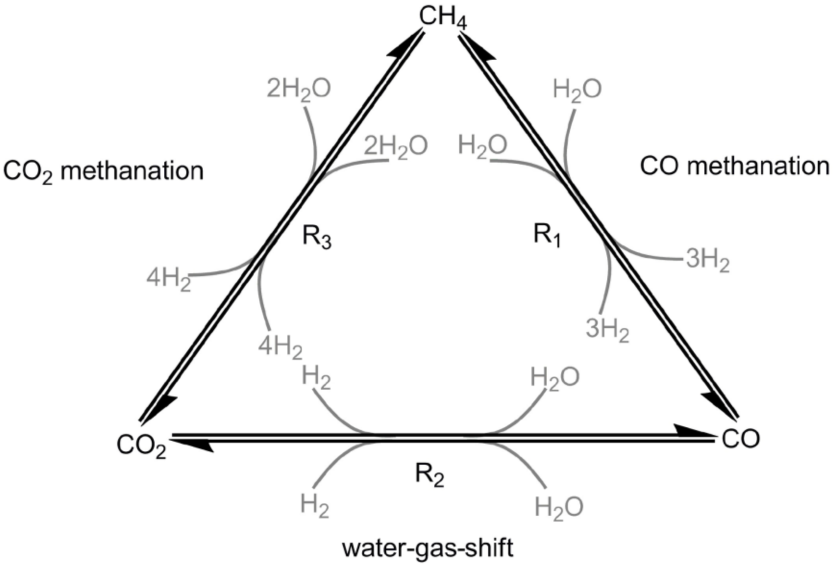


Figure 14 - Reaction scheme according to Xu and Froment **[17]**

The equilibrium of both reactions is influenced by pressure and temperature: In thermodynamic equilibrium, high pressures favour the production of methane. High temperatures, by contrast, limit methane formation.

CO and CO_2 methanation processes were first discovered by Sabatier and Senderens in 1902 and have now been investigated and developed for more than 100 years. CO methanation gained importance for the production of SNG during the oil crisis in the late 1970s. The aim was to produce a natural gas substitute using syngas from coal gasification. At that time, several methanation concepts were developed.

CO_2 methanation process developments primarily rely on CO methanation research, but they were driven by the wish of using alternative educt gases. Basic studies covering CO_2 methanation processes were performed in the 1980s. [18]

The methane synthesis from CO_2, which is the topic on which this thesis will focus, is composed by three main steps:

1. H_2 production (water electrolysis unit)
2. Methanation reaction
3. Methane cleaning and correction

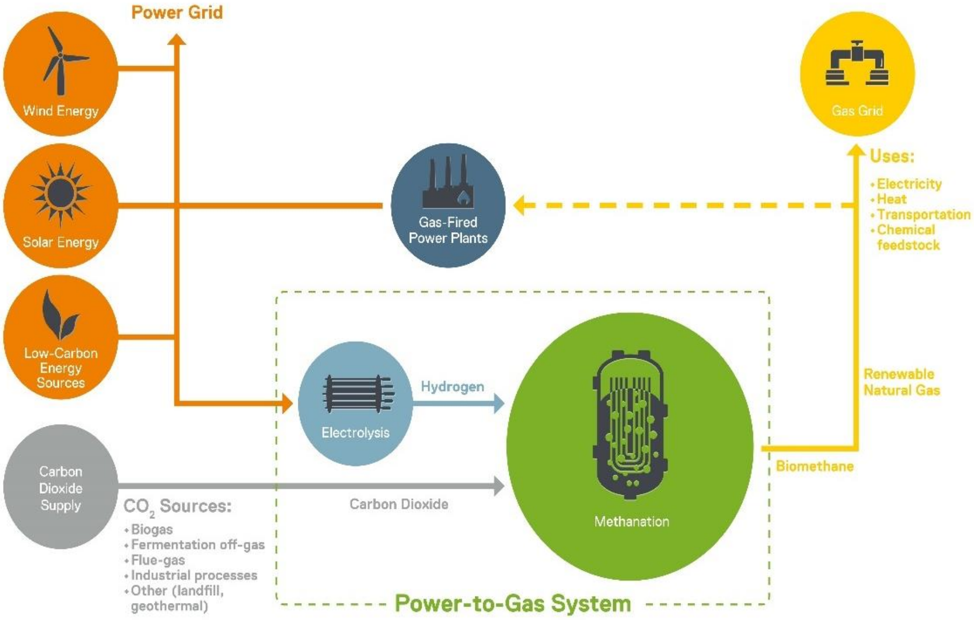


Figure 6 - Synthetic methane production overview **[19]**

Catalytic methanation reactors are typically operated at temperatures between 200°C and 550°C and at pressures ranging from 1 to 100 bar. Several metals such as Ni, Ru, Rh, and Co may be used as the catalyst for the methanation reaction. However, most often Ni is considered to be the optimum catalyst choice due to its relatively high activity, good CH_4 selectivity, and low raw material price. As already said, the methanation reaction is highly exothermic, as a consequence, a significant issue in a methanation reactor is to realise good temperature control in the reactor in order to prevent thermodynamic limitation and catalyst sintering. [20]

In large-scale industrial applications and for continuous operations, the temperature control is achieved with a series of adiabatic fixed-bed reactors and intercooling of the stream between each reactor. However, power-to-gas processes are implemented at smaller scales, with intermittent operations, for which adiabatic reactors are not suitable. In this context, isothermal reactors where a cooling fluid directly cools the reactor are usually preferred. Other types of reactors such as fluidized bed reactors, three-phase reactors or structured reactors are also researched but are not mature today. [21]

The methane synthesis process considered in this work is the "isothermal operation". By increasing the allowable temperatures for methanation catalysts, methane synthesis can be performed by a once-through method in quasi-isothermal reactors cooled by evaporating water which generates saturated steam. Under favourable conditions, such systems produce specification grade SNG in only one catalytic step. [22]

2.2 Methanol: process of production

Methanol can be produced from CO_2 in two different ways: in one step or in two steps. The one step conversion is the direct hydrogenation of CO_2 to methanol. In two steps conversion, CO_2 is first converted into CO through the Reverse Water Gas Shift (RWGS) reaction and then hydrogenated to methanol. In this work, the conversion of CO_2 in one step was employed. Some routes of conversion of CO_2 to produce fuels are shown in the following figure.

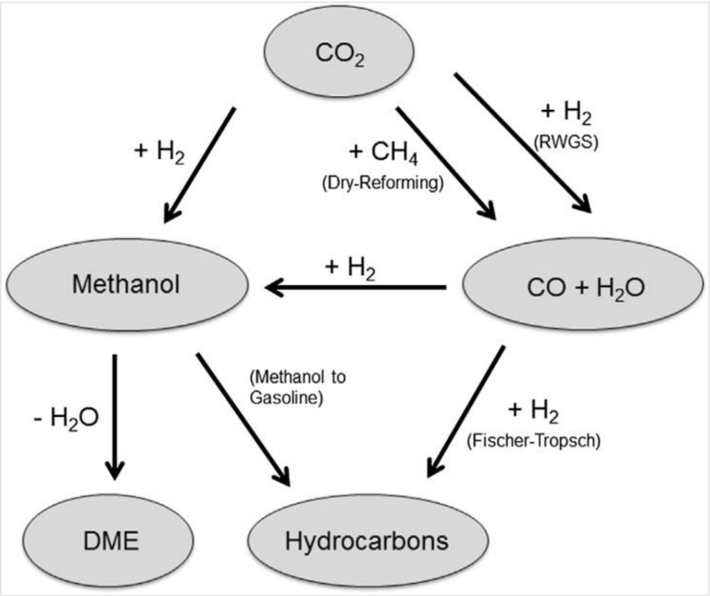


Figure 15 - CO_2 utilization diagram **[23]**

Exothermic reactions (the first and the second one) produce methanol. The RWGS reaction (the last one) occurs in parallel.

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} \qquad \Delta H = -128\frac{kJ}{mol}(298\ K)$$

$$CO_{2(g)} + 3H_{2(g)} \leftrightarrow CH_3OH_{(l)} \qquad \Delta H = -87\frac{kJ}{mol}(298\ K)$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)} \qquad \Delta H = +41\frac{kJ}{mol}(298\ K)$$

RWGS and one of the two hydrogenation reactions are enough to completely describe the system. Methanol synthesis is exothermic and involves a decreasing number of moles, thus it is favoured by relatively low temperature and high pressure (according to Le Chatelier’s principle) [24].

The process depends on availability of waste heat in the power plant to provide thermal energy to the process in order to have a significant abate of CO_2. In the absence of these thermal sources, CO_2 abatement is almost null. [23]

The methanol synthesis is composed by four main steps:

1. H_2 production (water electrolysis unit)
2. Syngas compression
3. Methanol formation reaction
4. Methanol distillation

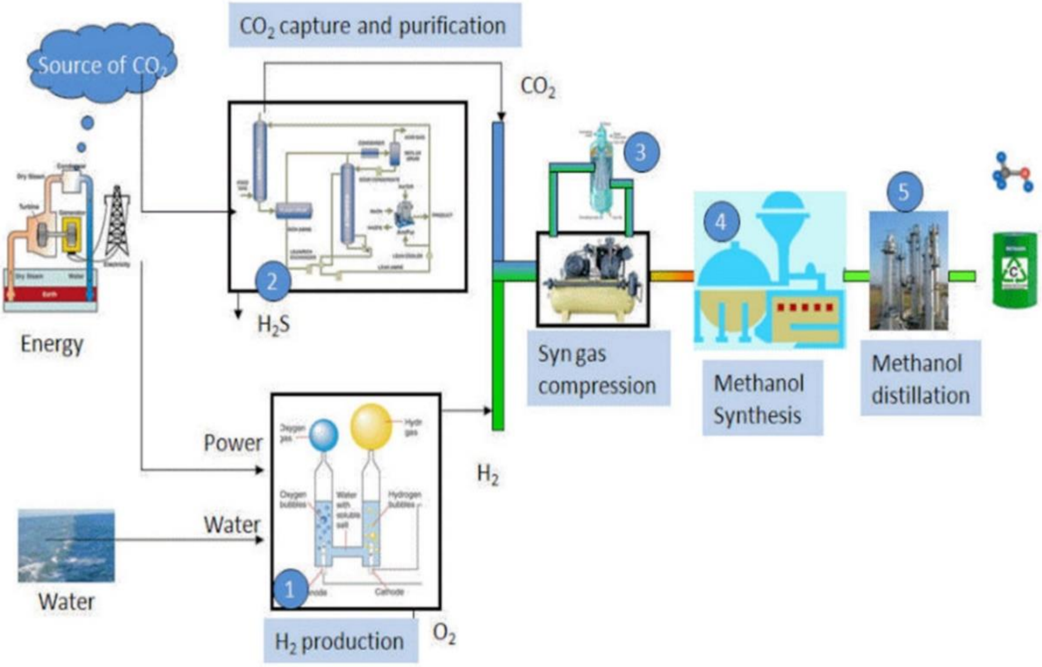


Figure 7 - Synthetic Methanol production overview **[25]**

In the methanol production the conversion rates are dependent on temperature, thus the key challenge in the design of reactor systems lies in the way in which exothermic heat of reaction is removed in an efficient and economic manner in order to follow as close as possible the highest rate as the reaction advances. A significant number of designs are commercially available today with more or less sophisticated internals in order to achieve low catalyst volume, low outlet temperature (high conversion), heat recovery at high temperature (good energy efficiency) and low by-product formation.

One of the existing design represents a boiling water reactor. In this typology the catalyst is loaded into tubes immersed in boiling water which is the cooling means. The temperature is controlled by controlling the pressure of the boiling water. In other configurations it is possible to find spiral-shaped tubes or the combination with gas-gas heat exchangers. This kind of reactors well approach the best rate trajectory and are very easy to control. On the other hand, they present a mechanically expensive design and constraints on the maximum size making it necessary to adopt more reactors working in parallel in larger plants. This constraint makes it impossible to take advantage of scale economy. As the maximum single-line capacity is 1800 [t/day], in this study it is possible to use this kind of reactor. [26]

2.3 Hydrogen Production from RES

Water splitting can be divided into three categories: electrolysis, thermolysis, and photoelectrolysis.

2.3.1 Electrolysis

The principle of water electrolysis is to pass a direct current between two electrodes immersed in an electrolyte. Hydrogen is formed at the cathode and oxygen at the anode (positive terminal). The production of hydrogen is directly proportional to the current passing through the electrodes. More commonly, Michael Faraday's laws of electrolysis state that:

1. The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred.
2. For a given quantity of electric charge, the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight. The equivalent weight of a substance is equal to its molar mass divided by the change in oxidation state it undergoes upon electrolysis.

The electrodes should be resistant to corrosion, have a good electric conductivity, exhibit good catalytic properties and show a suitable structural integrity. Furthermore, the electrodes should not react with the electrolyte. The overall chemical reaction of water electrolysis without required thermodynamic energy values can be written as:

$$H_2O_{(l)} \rightarrow \ H_{2(g)} + \frac{1}{2}O_{2(g)}$$

Implementation of a diaphragm or separator is required to avoid recombination of the hydrogen and oxygen to preserve efficiency and safety. The electrodes, the separator, and the electrolyte form the electrolytic cell. Water electrolysers and fuel cells use similar technology, and the process in fuel cells is the reverse; hydrogen is converted into electricity and heat. [27]

Electrolysis technologies are usually grouped in two big categories depending on operation temperature:

1. Low temperature electrolysis
    - Alkaline Electrolysis
    - Proton Exchange Membrane (PEM) Electrolysis
2. High temperature electrolysis
    - Molten Carbonate Electrolysis
    - Solid Oxide Electrolysis

Alkaline Electrolysis

Alkaline water electrolysers account for the majority of the installed water electrolysis capacity worldwide. Commercial alkaline electrolysis system sizes range from 1.8 to 5300 kW.

The operating principle of an alkaline electrolysis cell is described in the following figure.

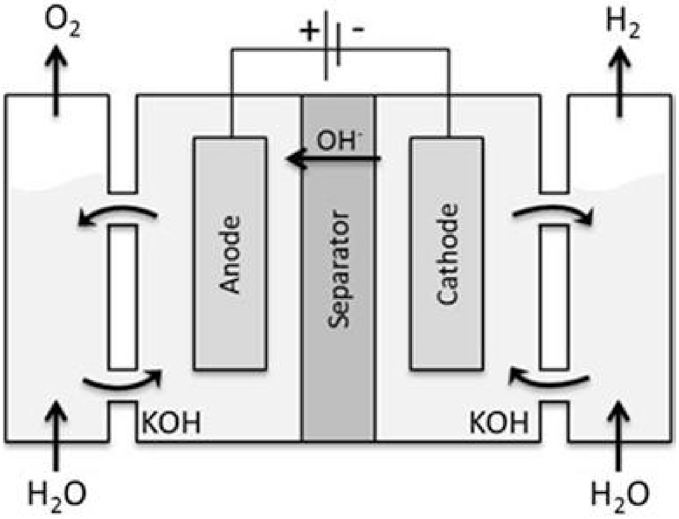


Figure 16 - The operating principle of an alkaline electrolysis cell **[28]**

Applied DC voltage decomposes water molecules and the diaphragm passes hydroxide ions from the cathode to the anode. Hydrogen is formed at the cathode and oxygen at the anode.

Chemical reactions taking place in alkaline electrolysis at the cathode and the anode, respectively, are as follows:

$$2H_2O_{(l)} + 2e^- \rightarrow \ H_{2(g)} + 2OH^-{}_{(aq)}$$

$$2OH^-{}_{(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)} + 2e^-$$

In an alkaline electrolysis cell, which is typically housed in a steel compartment, the two electrodes are separated by a gas-tight diaphragm submerged in a liquid electrolyte. To improve the ionic conductivity of the electrolyte, the electrolyte is usually a 20 - 40 wt % aqueous solution of potassium hydroxide (KOH), which is preferred over sodium hydroxide (NaOH) due to its higher conductivity. Neglecting physical losses, the liquid electrolyte is not consumed. Since water is consumed in water electrolysis, it has to be supplied continuously. The electrodes are usually made of nickel or nickel-plated steel. The diaphragms have previously been made of asbestos, but nowadays they are mainly based on sulphonated polymers, polyphenylene sulphides, polybenzimides, and composite materials. The diaphragm must keep the product gasses apart to maintain efficiency and safety. The diaphragm also has to be permeable to the hydroxide ions and water molecules. The electrical resistance of the diaphragm is frequently three to five times that of the electrolyte.

The typical operating temperatures and pressures of these electrolysers are 70–100°C and 1–30 bar, respectively.

Physically an electrolyser stack consists of several cells linked in series. Two distinct cell designs exist: monopolar and bipolar. In the monopolar design the electrodes are either negative or positive with parallel electrical connection of the individual cells, while in the bipolar design the individual cells are linked in series electrically and geometrically. One advantage of the bipolar

electrolyser stacks is that they are more compact than monopolar systems. The advantage of the compactness of the bipolar cell design is that it gives shorter current paths in the electrical wires and electrodes. This reduces the losses due to internal ohmic resistance of the electrolyte, and therefore increases the electrolyser efficiency. However, there are also some disadvantages with bipolar cells. One example is the parasitic currents that can cause corrosion problems. Furthermore, the compactness and high pressures of the bipolar electrolysers require relatively sophisticated and complex system designs, and consequently increases the manufacturing costs. The relatively simple and sturdy monopolar electrolysers systems are in comparison less costly to manufacture. Nevertheless, most commercial alkaline electrolysers manufactured today are bipolar. pressures of the bipolar electrolysers require relatively sophisticated and complex system designs, and consequently increases the manufacturing costs. The relatively simple and sturdy monopolar electrolysers systems are in comparison less costly to manufacture. Nevertheless, most commercial alkaline electrolysers manufactured today are bipolar. [29]
Three improvements can be implemented in the design of advanced alkaline electrolysers:

1. new cell configurations to reduce the surface-specific cell resistance despite increased current
2. higher process temperatures (up to 160°C) to reduce the electric cell resistance in order to increase the electric conductivity of the electrolyte
3. new electrocatalysts to reduce anodic and cathodic overpotentials (e.g., mixed-metal coating containing cobalt oxide at anode and Raney-nickel coatings at cathode).

Proton Exchange Membrane (PEM) Electrolysis

A PEM electrolyser uses an ionically conductive solid polymer. When potential difference (voltage) is applied between the two electrodes, negatively charged Oxygen in the water molecules give up their electron at the anode to make protons, electrons, and O_2 at the anode. The H+ ions travel through the proton conducting polymer towards the cathode where they take an electron and become neutral H atoms which combine to make H_2 at the cathode. The electrolyte and two electrodes are sandwiched between two bipolar plates. The role of bipolar plate is to transport water to the plates, transport product gases away from the cell, conduct electricity, and circulate a coolant fluid to cool down the process.

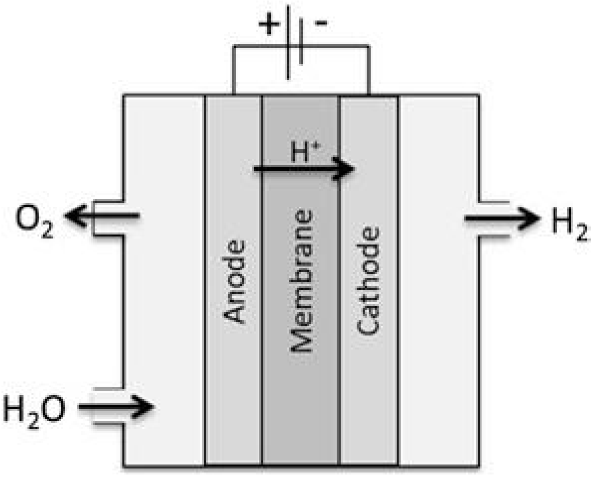


Figure 17 - The operating principle of PEM electrolysers **[28]**

Chemical reactions taking place in PEM electrolysis at anode and cathode, respectively, are as follows:

$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$$

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)}$$

The polymer electrolyte membranes have a strongly acid character and are mechanically strong. Common theme is to use sulphonated fluoropolymers, usually fluoroethylene. The most established one of these is Nafion™. The basic polymer, polyethylene, is modified by substituting fluorine for the hydrogen and this chemical compound is further sulphonated by adding a side chain ending with sulphonic acid HSO3. Thus, a polymeric electrolyte is formed. The added HSO3 group is ionically bonded and due to the ionic bonding there's a strong mutual attraction between H+ and SO3 from each molecule. An essential property of sulphonic acid is that it attracts water, and the conductivity of the polymer electrolyte membrane is dependent on hydration, decreasing water content decreases conductivity. Mixing of water and the ionic bonding of the sulphonic acid group enable the H+ protons to move through the molecule structure.

The water-assisted proton conduction of PEM electrolysers limits the operation temperature below 80°C. Additionally, the solid polymer membrane enables the electrolyser to respond more quickly to fluctuations in the input power. Thus, PEM electrolysers can be operated in a much more dynamic fashion than alkaline electrolysers. Due to the lack of liquid electrolyte and the associated equipment (pumps, gas separators), PEM electrolysers allow a more compact system design. The compact character of electrolysis modules and the structural properties of the membrane electrode assemblies (MEA), allow high operating pressures. [27]

Molten Carbonate Electrolysis

The electrolysis of water takes place at the Ni electrode (cathode) according to

$$H_2O_{(g)} + CO_{2\,(g)} + 2e^- \rightarrow H_2 + CO_3^{2-}$$

Unlike other electrolysis cells, carbon dioxide as well as water must be present in the inlet gas, since CO_2 is a reactant when producing carbonate ions. The electrochemical reaction on the NiO electrode, anode in the MCEC, is the electrolysis of carbonate ions producing oxygen and carbon dioxide.

$$CO_3^{2-} \rightarrow \frac{1}{2}O_{2\,(g)} + CO_{2\,(g)} + 2e^-$$

Due to the presence of carbon dioxide in the inlet fuel gas, direct CO_2 electrolysis generating CO may take place at the Ni electrode through the following reaction

$$2CO_{2\,(g)} + 2e^- \rightarrow CO_{\,(g)} + CO_3^{2-}$$

However, it has been reported that the kinetics of this reaction is much slower compared to water electrolysis on nickel-based electrodes.

The MCFC technology has already reached a level of maturity enough for commercialization. Thus, the operation of the electrolysis cell in the commercial fuel cell set-up is of great interest and will provide new opportunities. [30]

Solid Oxide Electrolysis

Solid oxide electrolyte (SOE) electrolysis is the third main water electrolysis technology besides alkaline and PEM technologies. SOE electrolysis is the least mature of the three main electrolysis technologies, still being in R&D stage. The SOE technology is not new, since pioneering work was done in the late 1960s. SOE technology is gaining growing interest due to its potential to increase the efficiency of water electrolysis by using high operating temperatures, typically 700–1000 °C. Therefore, SOE is actually steam electrolysis. However, such high temperatures cause severely fast degradation of the cell components, and thus keep SOE electrolysis in the R&D stage. To gain thermal stability of the materials, research efforts are focusing on SOE systems operated at 500–700 °C. For the same reason, current densities are kept in the range of 0.3–0.6 A/cm2. The corresponding cell voltages are around 1.2–1.3 V, which result in low electrical energy consumptions. Taking the energy demands for electricity and heat into account, the system efficiencies are typically over 90 %. [27]

A schematic diagram of a SOEC cell is depicted in the following figure. In SOEC cells a thin, dense solid oxide layer, which becomes conductive for (commonly oxygen) ions at elevated temperatures, is used as the electrolyte. At both sides of such an electrolyte, porous electrode layers adjoined by current collectors are directly attached. Water (vapor) is usually fed at the cathode side, where the reduction reaction takes place.

$$H_2O_{(g)} + 2e^- \rightarrow H_2 + O^{2-}$$

The generated oxygen ions migrate to the anode side, where elemental oxygen evolves according to half-cell reaction. [28]

$$O^{2-} \rightarrow \frac{1}{2}O_{2\,(g)} + 2e^-$$

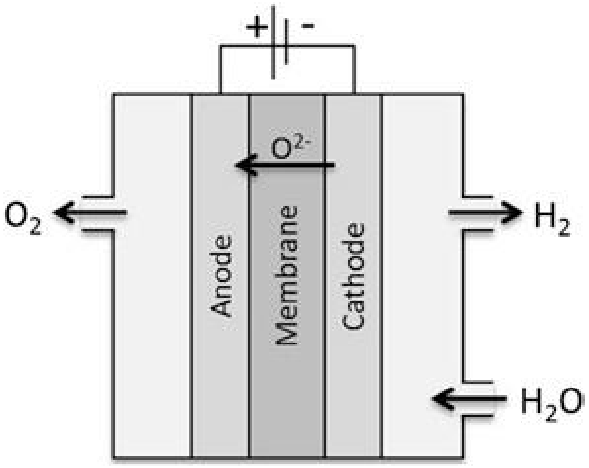


Figure 18 - Figure 12 - The operating principle of SOEC cell **[28]**

The thickness of each layer mainly depends on its intrinsic conductivity and if it has to provide mechanical support to the cell. Supporting layers are usually the thicker ones used with typical thicknesses in the range of a few 100 µm, where the remaining layers are around 10–30 µm thick.

The single cells can have fairly different geometries and can be carried out either in planar or tubular configuration. Tubular based systems exhibit higher mechanical strength and shorter start-up respectively shut-down times compared to planar ones. Anyhow, planar configurations are currently more widespread due to higher electrochemical performance and better manufacturability.

To summarize, alkaline and PEM are the two main water electrolysis technologies, which are commercially available. Alkaline water electrolysis is the more matured and widespread of the two technologies. The high cost of components and scale-up procedures in PEM electrolysis have limited the number of PEM electrolyser manufacturers. Furthermore, alkaline electrolyser cells typically have longer lifetimes than PEM electrolyser cells. However, PEM technology has various advantages over alkaline systems, such as compact system design, lack of liquid electrolyte, wide partial load range, and high flexibility in modes of operation. The high temperature electrolysis technology (SOEC), has the highest efficiency potential. It is currently the least developed technology and suffers from severe material degradation issues. A lot of fundamental research has to be carried out to overcome those limitations. [28]
In the following table is presented a synthetic comparison between alkaline, PEM and SOEC electrolysis systems. [31]

ALKALINE	**PEM**	**SOEC**
Advantages		
Well estabilished technology	High current densities	Efficiency in the range of 90+%
Non-noble catalyst	High voltage efficiency	High pressure operation
Long-term stability	Good partial load range	Non-noble catalyst
Relative low cost	Rapid system response	Reversible fuel cells
Stack in the MW range	Compact system design	Co-electrolysis process
Cost effective	High gas purity	
	Dynamic operation	
Disadvantages		
Low current densities	High cost of components	Laboratory stage
Crossover gases	Acidic corrosive environment	Durability (brittle ceramics)
Low partial load range	Possibily low durability	Non dependable cost information
Low dynamics	Commercialization	
Low operational pressures	Stack below MW range	
Corrosive liquid electrolyte		

2.3.2 Thermolysis

In thermochemical water splitting, also called thermolysis, heat alone is used to decompose water to hydrogen and oxygen. It is believed that overall efficiencies of close to 50% are achievable using these processes. It is well known that water will decompose above 2500 °C, but materials stable at this temperature and also sustainable heat sources are not easily available. Hydrogen may be produced from a two-step cycle. In the thermal reduction step, a metal oxide, MO_x, is reduced to a lower oxidation state, $MO_{x-\delta}$, with the release of oxygen. The thermal reduction step is highly endothermic and requires high temperatures, which may be obtained by concentrated solar power. In the gas splitting step $MO_{x-\delta}$ is reoxidized by water at a lower temperature accompanied by the release of H_2. [32]

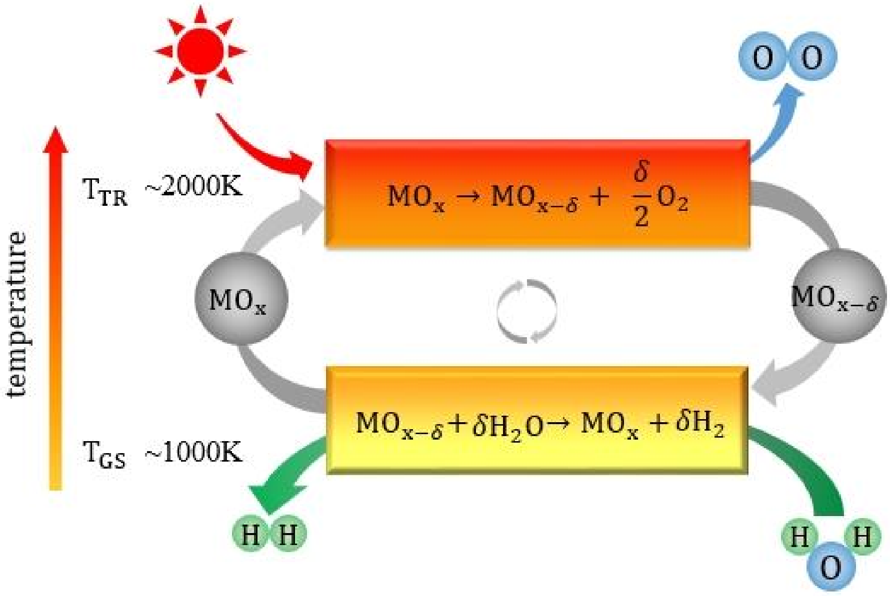


Figure 19 - Generic thermochemical looping process [33]

At the heart of the thermochemical cycle is a metal oxide that changes oxidation states during the cycles. Several binary metal oxides have been tested. The ZnO system has been studied as a promising metal oxide for practical applications. However, the O_2-releasing reaction in the ZnO system requires a high temperature of around 2000 K.

$$ZnO_{(s)} \leftrightarrow Zn_{(g)} + \frac{1}{2}O_{2(g)} \quad 1600-2000\,°C$$
$$Zn_{(s)} + H_2O_{(l)} \leftrightarrow ZnO_{(s)} + H_{2(g)} \quad 300-400\,°C$$

A similar process could be done with a hybrid cycles that has three or more steps. Typically, direct cycles are less complex with fewer steps, but they require higher operating temperatures compared with the more complicated hybrid cycles.

Challenges remain, however, in the research, development, and demonstration of commercially viable thermochemical cycles and reactors:

- The efficiency and durability of reactant materials for thermochemical cycling need to be improved.
- Efficient and robust reactor designs compatible with high temperatures and heat cycling need to be developed.
- For solar thermochemical systems, the cost of the concentrating mirror systems needs to be reduced.

2.3.3 Photoelectrolysis

Photoelectrolysis describes electrolysis by the direct use of light; that is to say, the conversion of light into electrical current and then the transformation of a chemical entity (H_2O, H_2S, etc.) into useful chemical energy (such as H_2) using that current. A photoelectrochemical cell is used to carry out the various photoelectrolytic reactions, being comprised of a semiconductor device that absorbs solar energy and generates the necessary voltage to split water molecules.

In such devices sunlight produce electron-hole pairs in the semiconductor in contact with an aqueous electrolyte. The electrons combine with protons and produce hydrogen at the counter electrode while the holes oxidize water to oxygen at the semiconductor electrode. Although many semiconductor materials have shown photocatalytic activity, most of them suffer from limitations including photo-corrosion, poor solar spectrum absorption and the need of external bias. In practice, several characteristics of the photo-electrode must be satisfied simultaneously: the electronic band gap of the photo-electrode must be low enough for efficient photon collecting from the solar spectrum (<2.2 eV) and high enough such that the excited electrons have enough energy to split water (>1.23 eV or typically at least 1.6–1.7 eV for sufficient rates). These constraints rule out most inexpensive, conventional PV, yet the photo-electrode should also have similar photo-conversion efficiency as conventional PV to give this option an advantage over a PV plus electrolysis system made of separate units. Indeed, TiO_2 is one of the most studied oxide semiconductor materials in this regard because of its stability in aqueous electrolytes. However, the band gap of TiO_2 (3.2 eV) limits the absorption of sunlight to the high-energy portion (UV) of the solar spectrum. It has been reported earlier that attempts have been made to improve the absorption of visible light of TiO_2 by incorporation of substitutional atoms into the lattice. Although the incorporation of transition metals improves the visible light absorption in TiO_2 electrodes, they have not yet been shown to have proper band gap and band positioning to be suitable for efficient water splitting reactions.

The technique of photoelectrolysis is still far from commercialization due to the high cost, low efficiency and low stability of the semiconductor electrodes. To be able to commercialize a photoelectrolysis system it needs at least a 10% conversion efficiency. Recently 12% efficiency has been reported for a photoelectrolysis system. [34]

2.3.4 Thermodynamics of a SOEC

Thermodynamics provides a framework for describing reaction equilibrium and thermal effects in electrochemical reactors. It also gives a basis for the definition of the driving forces for transport phenomena in electrolytes and leads to the description of the properties of the electrolyte solutions. Below is a brief description of the theoretical background of electrochemical devices under the hypothesis of constant temperature and stationary conditions.

An electrochemical cell is composed by three main components:

- Anode: is the electrode where the oxidation reaction take place (the reactant loses electrons).
- Cathode: is the electrode where the reduction take place.
- Electrolyte: is a porous medium which separates the two electrodes and allows the ionic conduction. For this reason, it must be a very good ionic conductor (it contains ions in the structure of its lattice) and a poor electrical conductor (electrons must flow in the external circuit connected with the device).

Nernst Equation

Considering a generic control volume with an exchange of heat and electrical power, and with inlet and outlet material flows, is possible to express the First and Second Law of Thermodynamics for open systems: [35]

$$\Phi - W_{el}^{rev} = \sum_{p}^{N_p} \dot{n}_p \cdot \bar{h}_p - \sum_{r}^{M_r} \dot{n}_r \cdot \bar{h}_r$$

$$\frac{\Phi}{\mathrm{T}} + \Delta S_{\mathrm{irr}} = \sum_{p}^{N_p} \dot{n}_p \cdot \bar{s}_p - \sum_{r}^{M_r} \dot{n}_r \cdot \bar{s}_r$$

Where:

- Φ $[W]$ exchanged heat power, it is considered with positive sign if entering the cell and vice versa if leaving it;
- W_{el}^{rev} $[W]$ exchanged electrical work, it is assumed with positive sign if produced by the cell (Galvanic Cell) and with negative sign if supplied to the cell (Electrolytic Cell);
- $\dot{n}_p$ $[\frac{mol}{s}]$ and $\dot{n}_r$ $[\frac{mol}{s}]$ respectively molar flow of products and reactants;
- $\bar{h}_p$ $[\frac{J}{mol}]$ and $\bar{h}_r$ $[\frac{J}{mol}]$ respectively molar enthalpy of products and reactants;
- $\bar{s}_p$ $[\frac{J}{mol\ K}]$ and $\bar{s}_r$ $[\frac{J}{mol\ K}]$ respectively molar entropy of products and reactants;
- ΔS_{irr} entropy generated due to irreversibility of the process (it is equal to zero in the considered reversible condition);

This is true under isothermal condition and steady state assumption.

Dividing by what is called the “fuel of the process”, or rather the fuel molar flow, the following relations are obtained:

$$\mathrm{q} - l_{el}^{rev} = \sum_{p}^{N_p} \nu_p \cdot \bar{h}_p - \sum_{r}^{M_r} \nu_r \cdot \bar{h}_r = \Delta\bar{h}_{react}$$

$$\frac{q}{\mathrm{T}} + \Delta S_{\mathrm{irr}} = \sum_{p}^{N_p} \nu_p \cdot \bar{s}_p - \sum_{r}^{M_r} \nu_r \cdot \bar{s}_r = \Delta \bar{s}_{react}$$

Stoichiometric coefficient $\nu_p = \frac{n_i}{n_{inlet}}$ expresses the ratio between a generic i-th mole flow and the total inlet mole flow.
Combining first and second principle in reversible condition ($\Delta S_{\mathrm{irr}} = 0$), is possible to obtain:

$$-\, l_{el}^{rev} = \Delta \bar{h}_{react} - T \cdot \Delta \bar{s}_{react} = \Delta \bar{g}_{react}$$

Where:

- l_{el}^{rev} $[\frac{J}{mol}]$ the reversible electric molar work;
- $\Delta \bar{h}_{react}$ $[\frac{J}{mol}]$ molar enthalpy variation occurring in the reaction;
- $\Delta \bar{s}_{react}$ $[\frac{J}{mol\,K}]$ molar entropy variation occurring in the reaction;
- $\Delta \bar{g}_{react}$ $[\frac{J}{mol}]$ molar free Gibbs energy variation;

Before continuing, is useful to consider the Faraday's Law of Electrolysis, which express that reactant consumption in an electrochemical cell is related to the current flowing through the device. This formula is very general and can be applied both to cathode and anode side, because the number of electrons generated at one electrode is recombined at the other.

$$\dot{n}_r = \frac{I}{z_F \cdot F} = \frac{j \cdot A}{z_F \cdot F}$$

Where:

- $\dot{n}_r$ $\left[\frac{mol}{s}\right]$ is the fraction of reactant mole flow which effectively reacts;
- $I[A]$ is the Faradic Current;
- A $[cm^2]$ is the Active Area of the cell;
- j $[\frac{A}{cm^2}]$ is the current density;
- F is the Faraday constant, that has the value 96487 $\frac{C}{mol}$
- z_F is the charge number of the molecules of the reactant, or the number of the electrons in the orbital that participate to the reaction.

It is possible to link electric parameters to the previous results:

$$l_{el}^{rev} = \frac{W_{el}^{rev}}{\dot{n}_{fuel}} = \frac{OCV \cdot I}{\frac{I}{z_F \cdot F}} = z_F \cdot F \cdot OCV = -\Delta \bar{g}_{react}$$

Working with reversible electric power means that no irreversibility occurs, and this happens only at open circuit operation; OCV $[V]$ is then the open circuit voltage.
Making then substitutions and simplifications and supposing to focus on cathode, the following relation can be inferred, that is the Nernst equation in a generic case:

$$OCV = -\frac{\Delta \bar{g}_{react}}{z_F \cdot F}$$

Gibbs free energy of a reaction indicates the spontaneity of a reaction, in particular a spontaneous reaction always moves towards the minimum of Gibbs free energy. [26]
When $\Delta \bar{g}_{react} = 0$ the reaction is in equilibrium. Is possible to separate two operational conditions for an electrochemical device:

- Galvanic Cell (Δg < 0 thus OCV > 0) the process is spontaneous,
- Electrolytic Cell (Δg > 0 thus OCV < 0) the process must be forced in order to proceed.

The Gibbs free energy is a thermodynamic function which takes into account the variation of other functions of the system, is dependent on pressure and temperature:

$$\Delta\bar{g}_{react}(T,p) = \Delta\bar{h}_{react}(T) - T \cdot \Delta\bar{s}_{react}(T,p)$$

In general, values of $\bar{g}$, $\bar{h}$ and $\bar{s}$ are referred to reference values $T_0 = 25\ [°C]$ and $p_0 = 1\ [bar]$. Under the hypothesis of ideal gas, it is possible to develop the Nernst Equation as follows:

$$OCV = -\frac{\Delta\bar{g}_{react}(T,p_0)}{z_F \cdot F} + \frac{T \cdot \bar{R}}{z_F \cdot F}\ln\frac{\prod_i \left(\frac{p_{Ri}}{p_0}\right)^{\nu_{Ri}}}{\prod_j \left(\frac{p_{Pj}}{p_0}\right)^{\nu_{Pj}}}$$

Where p_{Ri} and p_{Pj} are partial pressures of reactants and products.

As can be noticed, Nernst potential is influenced by operating conditions (temperature of the cell and partial pressure of reactants and products). Increasing temperature causes a decrease of Nernst Voltage: this is a potential disadvantage for a galvanic cell (which target is to maximize the electrical output). On the contrary is a potential advantage foe an electrolysis cell (which target is to minimize the electrical input) [36]

Electrochemical Model

The electrical behaviour of an electrochemical cell is generally described by the Polarisation Curve which relates the cell voltage to the cell current. At open circuit the operative Voltage coincides with reversible potential but "closing" the circuit the presence of three transport mechanism determines the generation of irreversibility and so a modification of the cell voltage:

$$V_C(j) = OCV(T,p) \pm \sum_{i}^{3} \eta_i(j)$$

The three transport mechanisms considered are:

- Charge transfer that causes and activation overvoltage (η_{act})
- Charge conduction (or migration) that causes an ohmic overvoltage (η_{ohm})
- Mass transport that causes the diffusion (or concentration) overvoltage (η_{diff})

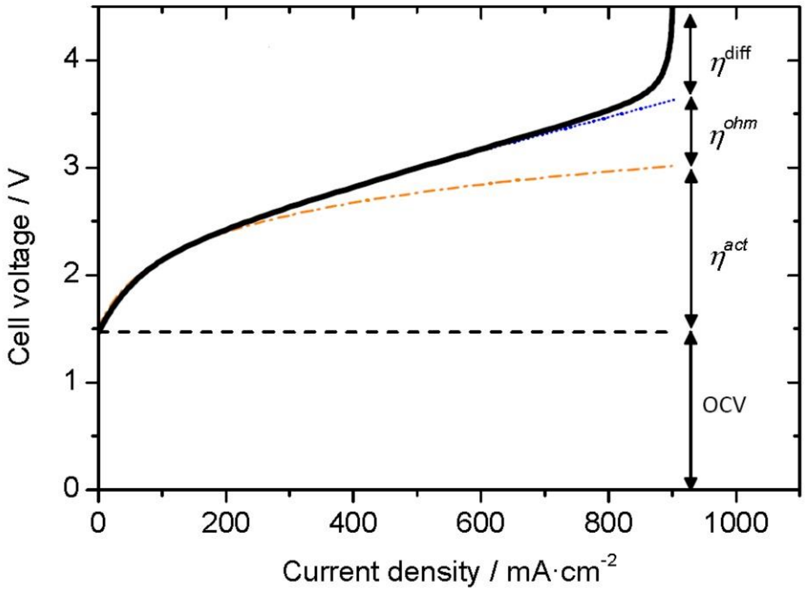


Figure 20 - Polarization Curve of a generic Electrolyser **[37]**

Activation Overvoltage

The first overvoltage to be encountered is the *activation overvoltage*. It is connected to charge transfer reaction from electrode to a molecule or vice versa from an ion to the electrode. It is explained by the Butler-Volmer equation, that relates the current density with the overvoltage:

$$j = i_0 \left[e^{(\frac{\alpha_1 F}{RT}\eta)} - e^{(\frac{\alpha_2 F}{RT}\eta)} \right]$$

Where i_0 is the exchange current density, α_1 and α_2 are the charge transfer coefficients defined as follows:

$$\alpha_1 = \beta \cdot n_{RDS}$$
$$\alpha_2 = (1 - \beta) \cdot n_{RDS}$$

Where:

- β representing the symmetry factor usually set as 0.5 with the following result $\alpha_1 = \alpha_2$
- n_{RDS} is the number of electrons transferred in the rate determining step[xvi].

Butler-Volmer equation is applied both at cathode and anode. The exchange current density is a parameter which express the “ability” of an electrode to realise the charge transfer. It depends on operative temperature and on type and quantity of catalyst present on the electrode.

The resulting overvoltage as function of current density is described as follows:

$$\eta_{act}(i) = \eta_{act,an}(i) + \eta_{act,cat}(i) = \frac{R\,T}{\alpha_{an} F} sinh^{-1}\left(\frac{i}{2 i_{0,an}}\right) + \frac{R\,T}{\alpha_{cat} F} sinh^{-1}\left(\frac{i}{2 i_{0,cat}}\right)$$

[xvi] A chemical reaction is usually split in many sub-reaction, each one of them characterized by a reaction rate. The slowest rate has the largest influence on the global reaction rate, thus it is said that the sub-reaction with the slowest kinetic determines the kinetic of the global sub-reaction.

Ohmic Overvoltage

The second overpotential affecting the cell is the *ohmic overvoltage*. It is assumed to follow a linear behavior because of the resistance offered by the SOEC conductors and thus described by the Ohm's law and resistivity:

$$\eta_{ohm}(i) = ASR \cdot i$$

The ASR (Area Specific Resistance) is described by the product of the resistivity and the thickness of the electrolyte layer, so depends from the temperature, the material and the geometry of the cell (the resistivity decrease with the increasing of the temperature).

The main contribution comes from the electrolyte ionic resistivity which is $10^5 \div 10^7$ times larger than the electronic resistivity.

Diffusion Overvoltage

The third loss is the *diffusion overvoltage*. It appears in correspondence of high reactant utilization such that the diffusive mechanism of gases through the porous medium is not fast enough to compensate the reactant consumption, and causes a phenomenon called "starvation". It can be expressed in the following form:

$$\eta_{diff}(i) = \left|\frac{\bar{R} \cdot T}{z_F \cdot F} \ln(1 - \frac{j}{j_{lim,an}})\right| + \left|\frac{\bar{R} \cdot T}{z_F \cdot F} \ln(1 - \frac{j}{j_{lim,cat}})\right|$$

$j_{lim,an}$ and $j_{lim,cat}$ are two parameters called limit current densities respectively at cathode and anode. They represent the maximum current density passing through an electrode.

Thermal behaviour of a SOEC

Operation of a solid-oxide stack in the electrolysis mode is fundamentally different than operation in the fuel-cell mode for several reasons, aside from the obvious change in the direction of the electrochemical reaction. From the standpoint of heat transfer, operation in the fuel-cell mode typically necessitates the use of significant excess air flow in order to prevent overheating of the stack. [36] The potential for overheating arises from two sources:

- The exothermic nature of the fuel oxidation reaction
- A series of transport mechanism that generate heating associated with the electrolyte ionic resistance and other loss mechanisms. Conversely, in the electrolysis mode, the steam and/or carbon dioxide reduction reaction is endothermic. Therefore, depending on the operating voltage, the net heat generation in the stack may be negative, zero, or positive.

The heat connected to the redox reaction is given by:

$$\Phi_R = T \cdot \Delta s_r \cdot \dot{n}_f = \frac{T \cdot \Delta s_r}{z_F \cdot F} \cdot I$$

Where:

- $\dot{n}_f \ [\frac{mol}{s}]$ represent the molar flow of the fuel.

Instead, the heat connected to transport phenomena is described as follow:

$$\Phi_{IRR} = I \cdot \sum_{i}^{3} \eta_i(j)$$

Doing a balance between the two heats flux of the cell is possible to obtain:

$$\Phi_{CELL} = \Phi_R - \Phi_{IRR} = \left(\frac{T \cdot \Delta s_r}{z_F \cdot F} - \sum_{i}^{3} \eta_i(j)\right) I = \left[\frac{\Delta h_r}{z_F \cdot F} - \left(\frac{\Delta g_r}{z_F \cdot F} + \sum_{i}^{3} \eta_i(j)\right)\right] I$$

Or better:

$$\Phi_{CELL} = \left[\frac{\Delta h_r}{z_F \cdot F} - V_c\right] I$$

In the electrolysis mode, the net heat flux is negative for low operating voltages, increases to zero at a voltage called “Thermal-Neutral Voltage” (or “Thermoneutral Voltage”), and is positive at higher voltages and current densities. The thermal-neutral voltage can be predicted from direct application of the rate-based First Law to the isothermal system, when the global heat flux of the cell is null:

$$V_{tn} = \frac{\Delta h_r}{z_F \cdot F}$$

There are also implications related to ASR: if the ASR increases the current of thermoneutrality becomes lower at fixed voltage. It means lower ASR values allow stack operation at lower voltages and correspondingly higher efficiencies. The challenge is to develop electrolysis stacks with low ASR such that a reasonable current density will be achievable at lower operating voltages.

2.4 Existing projects

In this section are presented two examples of power-to-fuel plants, one involving methanation process and the other one the production of methanol.

2.4.1 Audi e-gas - ETOGAS

The first power-to-gas plant of industrial scale was inaugurated in Werlte, Lower Saxony, in the 2013. The plant manufacturer ETOGAS GmbH (formerly SolarFuel) has timely developed and built the world's largest power-to-gas plant. Customer and operator is the Audi AG.

The plant produces synthetic methane called Audi e-gas. The plant uses three electrolysers with total power input of 6.3 MW to produce hydrogen from intermittent wind power. The hydrogen is reacted with carbon dioxide in a chemical-catalytic process under high pressure and temperature. The CO_2 is extracted from a nearby biogas plant and the end-product is synthetic methane which is injected to the natural gas transmission network. With its annual e-gas production of about 1000 metric tons, the plant can supply a fleet of 1500 Audi A3 gas vehicles with an annual mileage of 15 000 km annually. The conversion efficiency from electricity to gas is around 54 %, but the total efficiency of the plant is higher since the waste heat is recycled in the processes and utilized also in the adjoining biogas plant. The plant recycles around 2 800 tons of CO_2 annually. [38]

2.4.2 Vulcanol – Carbon Recycling International

Carbon Recycling International (CRI) was founded in 2006 in Reykjavik, Iceland, to develop and market a process for producing fuel from industrial carbon dioxide emissions. CRI produces renewable methanol under the registered brand name Vulcanol™ on a commercial scale at its production facility in Grindavik.

Vulcanol™ is produced from carbon dioxide and hydrogen from renewable sources of electricity (hydro, geothermal, wind and solar). In their first commercial scale production plant they obtain carbon dioxide by processing of gas emissions from a geothermal power plant and obtain hydrogen by electrolysis of water using renewable sources of energy from the Icelandic power grid (from hydro, geothermal and wind sources). This is the world's first production of a liquid renewable transport fuel from non-biological sources of energy. Currently they have a 4000-metric ton/year production capacity.

Chemically, Vulcanol™ is fuel grade methanol, a clean burning, high octane fuel that can be blended with gasoline for automobiles and used in the production of biodiesel or fuel ethers (DME[xvii], MTBE[xviii], OME[xix] etc.). Renewable methanol is also a low-carbon feedstock for production of synthetic materials. Among uses for Vulcanol™ is gasoline blending, biodiesel production and production of synthetic materials. The CRI declares that Vulcanol™ from their current production plant reduces carbon emissions by more than 90% compared to fossil fuels, in the complete product life-cycle, from extraction, production to end use.

Biofuels, such as ethanol and biodiesel, are produced using fossil fuel inputs and scarce agricultural resources. The production of Vulcanol requires no arable land, produces no direct emissions of greenhouse gas in the production process and uses energy from renewable sources with known cost and minimal environmental impact. [39].

[xvii] Dimethyl ether (DME), also known as methoxymethane, is the organic compound with the formula CH3OCH3, simplified to C2H6O.

[xviii] Methyl tert-butyl ether (also known as MTBE and tert-butyl methyl ether) is an organic compound with a structural formula (CH3)3COCH3

[xix] Polyoxymethylene dimethyl ethers - abbreviated OME, PODE or POMDME - are a class of DME derivatives that include several oxymethylene ($-O-CH_2-$) groups in the molecule, with a chemical formula $CH_3(-O-CH_2)_n-O-CH_3$

3 Plants Design

In this section two models to simulate operation of plants for SNG production and for methanol production are proposed. Both systems start from water and carbon dioxide as raw materials.
The first model has the purpose of simulating a system based on high temperature Steam Electrolysis and Methanation, the second provides a simulation of high temperature Steam Electrolysis and direct hydrogenation of CO_2 in order to produce liquid methanol.
Both models were built using the software Aspen Plus®.
For all simulations the chosen thermodynamic model is “Peng-Robinson Model”, because using Ideal gas model could lead to considerable errors related to high pressures involved.

3.1 Steam Electrolysis and Methanation

In the process flowsheet presented in this section is described the steam electrolysis coupled with the methanation section composed by two isothermal reactors. The final cleaning section allows to have a product with high purity. In this model the ratio between the two inlet gases has been imposed following the stoichiometric condition ($\frac{CO_2}{H_2} = 0.25$).

3.1.1 Electrolysis Section

In the following figure an image representing model of the Steam Electrolysis section is provided:

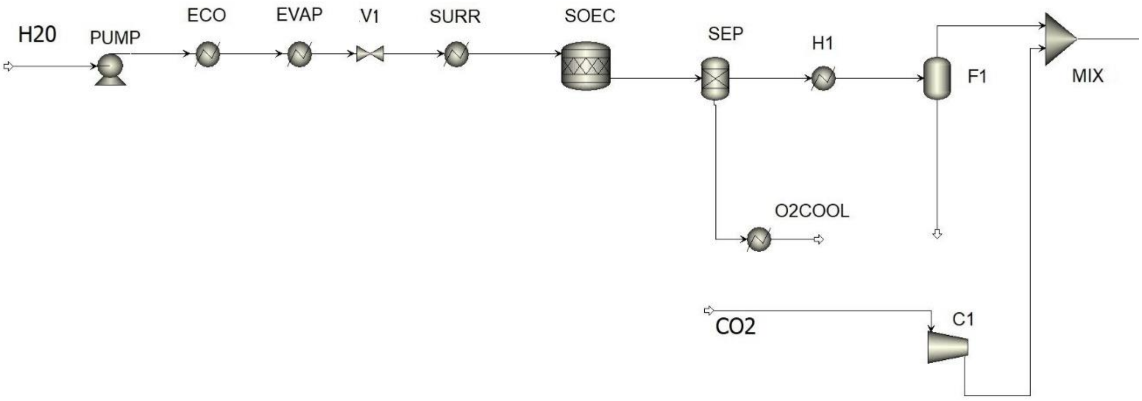


Figure 21 - Steam Electrolysis Model on Aspen Plus®

Following the previous image is now provided a briefly description of the blocks involved in the process.
PUMP is the block in which water pressure is increased for two reasons: to compensate pressure drop during the following evaporation and because of the fact that electrolyser, in this model, works in pressure. The pressure generated by the PUMP is slightly higher also to manage the thermal integration of the system: is possible to utilise the heat of the methanation reaction to evaporate the water stream. This will be discussed later.

The high-pressure operation of the electrolyser maybe is not necessary an advantage from an electrochemical point of view; but making electrolysis at a pressure similar to that required by methanation section, will avoid further post-compression of the syngas produced at cathode side.

ECO, EVAP and SURR are three heaters in which pre-heating, evaporation and superheating of water are realized. These three phases have been separated for practical reasons related (as will be discussed) to thermal integration of the plant.

V1 is a valve that allows a pressure drop in order to achieve the operating pressure of the electrolyser, that in this case is 15 bars.

SOEC is a stoichiometric reactor, used to simulate steam reduction. This reactor requires the knowledge about reactant, products and fractional conversion.

The information about products and reactants are introduced putting in the model the water reduction reaction:

$$2H_2O \rightarrow 2H_2 + O_2$$

This is not exactly what happens into an electrolysis cell but is the only way to simulate an electrochemical device with Aspen Plus. No electrons are involved, and so in model results what that in a real device is an electrical input, in this model will be expressed as Heat Duty.

Stoichiometric reactor requires also the specification of fractional conversion of a key reactant (steam in this case). This value coincides with the Reactant Utilization (RU) mentioned in previous sections. RU was chosen equal to 80% (0.8).

SEP is a separator which realizes effectively the physical separation between anode and cathode side. In component specifications is supposed that oxygen is mechanically separated from other substances, to simulate the fact that at anode side only oxygen production takes place.

H1 is a heater for cooling after electrolysis: cooling down the stream is possible to partially condensate in the block F1 (that represents a Flash Drum Separator) the water that is still present at the SOEC outlet, in this way, eliminating the water the equilibrium of the methanation reaction (see section 3.2) is pushed towards the products, according to Le Chatelier's principle.

O2COOL is the oxygen cooler, outlet temperature is 35°C and pressure drop was set to 0.7 bar.

C1 represent CO_2 compression section: the heat produced during the compression helps to reach the required temperature of the methanation process, increasing the temperature of the mixture of CO_2 and H_2 (also a little traces of steam) obtained after the union of the two streams in the block MIX, that acts for a mixer.

Stack Power

The size of the plant must be fixed in order to perform a system comparison between Methanol and Methane production. The common parameter between the two processes showed in this work which has been chosen is the power of the electrolysis section: for both the system treated the size of 10 MW was modelled.

The power is calculated according the following equation:

$$W_{el} = \sum \dot{n}_{out} . h_{out} - \sum \dot{n}_{in} . h_{in} = \dot{n}_{out,cat} . h_{out,cat} + \dot{n}_{out,an} . h_{out,an} - \dot{n}_{in} . h_{in}$$

With a tool called “Design Specification” is possible to force in Aspen Plus® the electrical input of SOEC. A design specification sets the value of a variable that Aspen Plus® would otherwise calculate. For each design specification, a block input variable, process feed stream variable or other simulation input to be manipulated (adjusted) to meet the specification are identified. Design specifications create loops that must be solved iteratively.

For Electric Power, a target value of 10 MW was obtained by varying water mole flow in input.

3.1.2 Methanation Reactors

In the following figure is shown the model corresponding the “methanation section”:

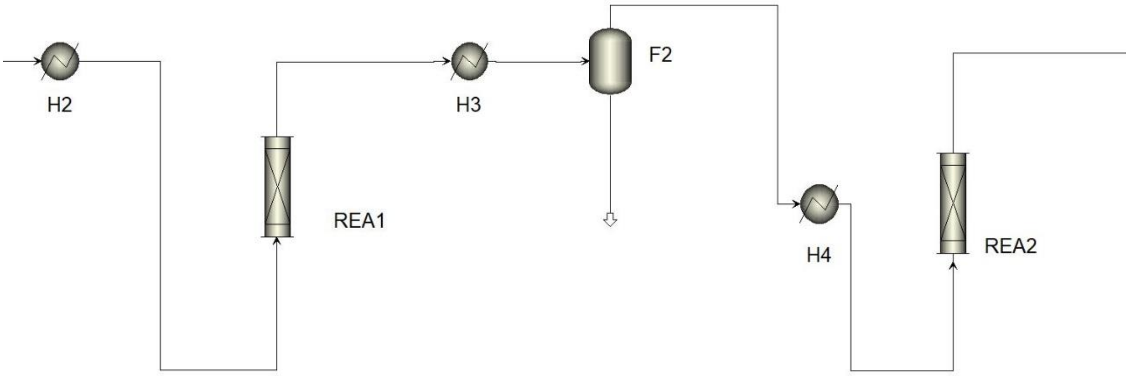


Figure 22 - Methanation Section on Aspen Plus®

The two heaters H2 and H4 have the aim to control the temperature of the feed of the two reactors that is fixed ad 300°C.

The heat exchanger H3 cool down the stream in order to partially condensate the steam produced in the first reactor: the water is separated in the Flash Drum Separator F1. This allows to push faster the reaction towards the product, as already said.

The reactors REA1 and REA2 considered for the two-step methane synthesis are a BWR (boiling water reactor), fixed bed isothermal reactors where boiling water on the shell side is used to remove the process heat. Operating temperature is controlled by controlling the pressure of the boiling water.

The model used to describe this reactor was a PFR (Plug Flow Reactor) with the following assumptions:

- one-dimensional heterogeneous model;
- no mass and heat transfer limitation in catalyst pellets;
- negligible radial temperature gradient and axial dispersion in the reactor tube;
- insignificant radial temperature gradient in catalyst pellets (high conductivity);
- dynamics of catalyst deactivation ignored;

With a PFR reactor is possible to describe a kinetic model for a catalyst system: in Aspen Plus® is possible to configure the kinetic of the reaction through a Langmuir-Hinshelwood-Hougen-Watson (LHHW) equation. Rate expressions for methanol synthesis in a Nickel based catalyst (Ni/Al2O3) are here presented: [40]

$$r = \frac{k \cdot p_{H_2}^{0.5} p_{CO_2}^{0.5} \left(1 - \frac{p_{CH_4} p_{H_2O}^{2}}{p_{CO_2} p_{H_2}^{4} K_{eq}}\right)}{\left(1 + K_{OH} \frac{p_{H_2O}}{p_{H_2}^{0.5}} + K_{H_2} p_{H_2}^{0.5} + K_{mix} p_{CO_2}^{0.5}\right)^{2}}$$

The general LHHW kinetic expression consists of a kinetic factor, a driving force expression, and an adsorption term. All reactions are occurring in the vapour phase and the reaction rate is based on catalyst weight. The concentration basis for the driving force is partial pressure powered by the concentration exponents for forward and backward reactions.

All rate and adsorption constants are treated as Arrhenius-type, all adsorption constants as Van't Hoff-type:

$$K_x = K_{x,0} \cdot exp\left(-\frac{E_A}{RT}\right) \quad and \quad k_x = k_{x,0} \cdot exp\left(-\frac{\Delta H_X}{RT}\right)$$

Where E_A and ΔH_X represent, respectively, the activation energy and the adsorption enthalpy.

To use these expression of the LHHW equation in Aspen Plus® is necessary to insert the values A_i, B_i, C_i, D_i linked to each temperature dependent expression k_i in the following way:

$$ln(k_i) = A_i + \frac{B_i}{T} + C_i ln(T) + D_i T$$

Equilibrium constants for the methanation reaction is [40]:

$$K_{eq} = 137 \cdot T^{-3.998} \cdot exp\left(-\frac{158.7\ {}^{kJ}/_{mol}}{RT}\right)$$

In the following table are showed the parameter estimation for the LHHW equation with a reference temperature of 555 K.

$k_{0,555K}$	$3.46e-4 \pm 4.1e-5$	$mol\ bar^{-1}\ s^{-1} g_{cat}^{-1}$
E_A	77.5 ± 6.9	$kJ\ mol^{-1}$
$A_{OH,555K}$	0.5 ± 0.05	$bar^{-0.5}$
ΔH_{OH}	22.4 ± 6.4	$kJ\ mol^{-1}$
$A_{H2,555K}$	0.44 ± 0.08	$bar^{-0.5}$
ΔH_{H2}	-6.2 ± 10	$kJ\ mol^{-1}$
$A_{mix,555K}$	0.88 ± 0.10	$bar^{-0.5}$
ΔH_{mix}	-10.0 ± 5.7	$kJ\ mol^{-1}$

Some further consideration was done to consider the effects of the porosity of the catalyst inside the reactor, in the case of interaction of solid and gaseous phase between catalyst and reacting gases. [41]

A single spherical particle of catalyst, being considered as a porous medium, it is filled in cavities by gases, so is possible to define an internal porosity of the particle as:

$$\varepsilon_i = \frac{Volume\ filled\ by\ gases}{Total\ Volume\ of\ the\ particle}$$

Considering the sphere as pseudo-homogeneous, that is, constituted by only gas, we can define an effective diffusivity:

$$D_e = \frac{D_A \cdot \varepsilon_i}{\tau_i}$$

Where D_A is the gas diffusivity and τ_i is the tortuosity coefficient, that takes into account the effective path of the gas molecules into the porous catalyst.

To consider the transport effects inside the catalyst particle is defined now a parameter that is useful for the reactor design called *effectiveness*:

$$\eta = \frac{3}{\varphi^2}\left(\frac{\varphi}{\tanh \varphi} - 1\right)$$

It shows the ratio between the moles of the reactant actually converted and the moles that would react if the concentration and the temperature inside were actually constant.

The parameter φ is the Thiele Module defined as:

$$\varphi = \frac{D_p}{2}\sqrt{\frac{k'}{D_e}}$$

Where D_p is the diameter of the catalyst particle and k' is the ratio between the rate constant calculated with the LHHW expression and the concentration of the reactant in the catalyst volume. The following table summarise the values considered to calculate the effectiveness factor. [42]

ρ catalyst [kg /m^3] density	ϕ [-] bed voidage	D_p [m]	$D_{e\ CO2}$ [m^2/s]
2000	0.5	4e-3	3,40e-07

With these data the effectiveness factors calculated is 0.35÷0.4 different for the two reactors because the CO_2 concentration is not the same. Multiplying the kinetic factor of the LHHW expression by the effectiveness factor is possible to take into account the effect of the CO_2 diffusion inside the pores of the catalyst.

With all these considerations are now summarised the geometrical characteristics obtained for the two reactors:

	Tubes diam. [m]	Tubes Number	Reactor Length [m]
REACTOR 1	0.075	20	0.9 (fixed)
REACTOR 2	0.075	20	0.95 (calculated by design spec.)

The length of the second reactor has been calculated by a design specification of Aspen Plus® where has been imposed the molar fraction of the CH_4 at the end of the two reactors as 0.95. More detailed consideration about the reactors length will be discussed later (see section 4.1.1).

The pressure drops inside the two reactors have been calculated with the already implemented Ergun equation in Aspen Plus®.

3.1.3 Cleaning Section

In the following image is showed the final cleaning section of the methanation process.

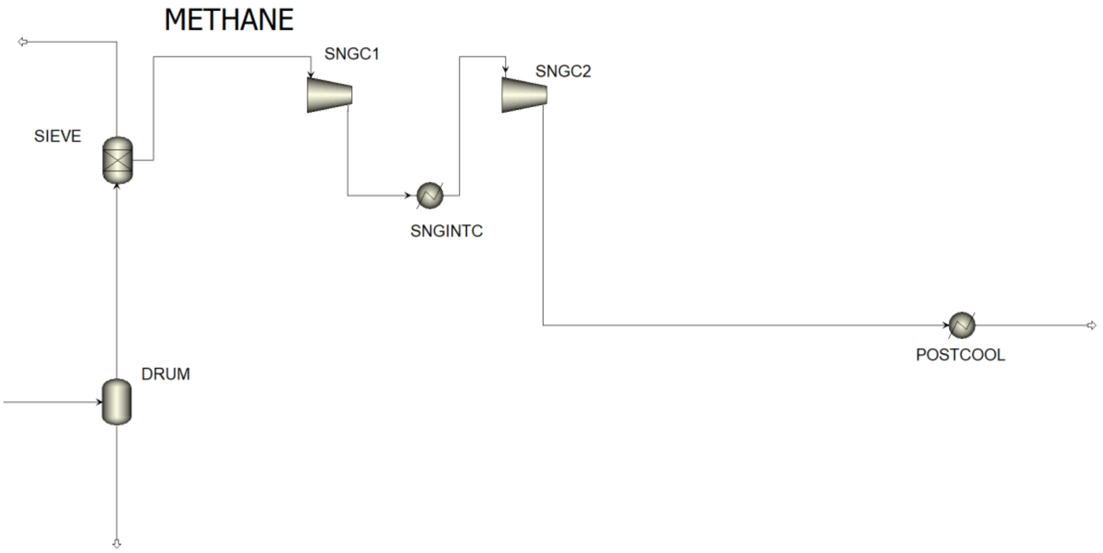


Figure 23 - Cleaning and Compression Section on Aspen Plus®

DRUM is a Flash separator which allows thermodynamic equilibrium between liquid phase and gaseous phase. This component allows separating from the syngas a huge fraction of water (which is a product of both methanation reactions and is present in high concentration).
SIEVE is a molecular sieve which retains substances as water and carbon dioxide (in particular water is not desirable in high concentration into a gas pipeline).
SNGC1, SNGC2 and SNGINTC are components of natural gas compression section, bringing gas pressure to a value of 60 bar, which is a typical value of natural gas pipelines pressure. [36]

3.2 Steam Electrolysis and Methanol production

The process flowsheet presented here is based over the process published by Van-Dal and Bouallou. [23]
The description is divide in the three main constituents section: electrolysis, the reactor section and the distillation.

3.2.1 Electrolysis Section

The electrolysis section of the methanol plant has been designed with the same criterion used in the methane plant (section 4.1.1): the only differences are the splitting of the evaporating flow before the electrolyser and the multistage compression of CO_2 flow and of the cathodic outlet.
The water flow after the heater ECO has been separated for practical reasons related (as will be discussed) to thermal integration of the plant.

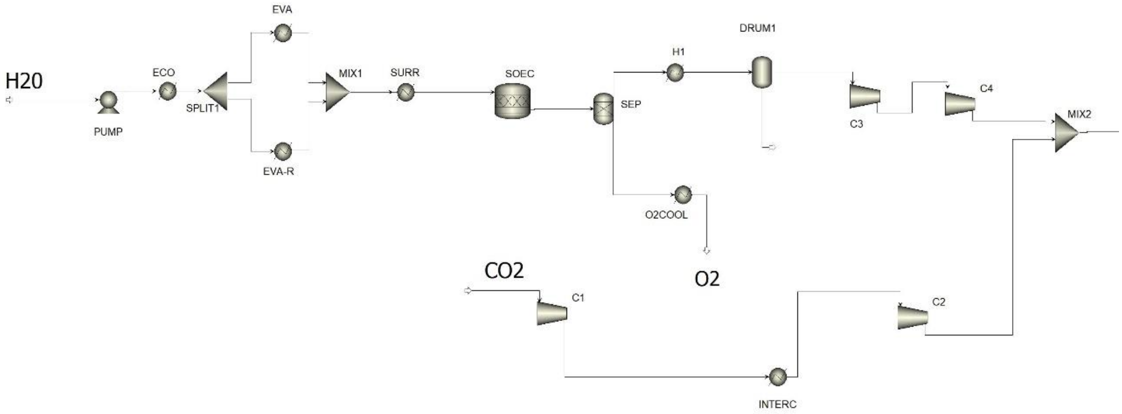


Figure 24 - Steam Electrolysis Model on Aspen Plus®

In the multistage compression of CO_2 and of the cathodic outlet, the pressure ratio β of each compression stage was calculated assuming that pressure ratios of stage 1 and 2 are equal ($\beta_1 = \beta_2$), so results that $\beta_1 = \beta_2 = \sqrt{\beta_{TOT}}$, where β_{TOT} is ratio between outlet and inlet pressure. Inlet pressure was set to 1 atm (1, 01325 bar). Outlet pressure is the sum of inlet pressure at the methanol reactor section (set to 75 bar according to [23]) and pressure drop in the following heaters.
INTERC simulates intercooling between stage 1 and stage 2, the pressure drop in the intercooling section was set as 0.3 bar according to [23].
In the mixer MIX2 the two gases are mixed.

3.2.2 Methanol Reactor and Recycling

The gases coming from the previous section are re-mixed in the MIX3 with the recycle stream composed by the non-reacted gases in the reactor. This recirculation allows to reach higher conversion of the reactant.

The stream is then heated (H2) to 210°C and injected into the fixed bed isothermal reactor. Water and methanol, which were condensed in exchanger H3, are separated from the non-reacted gases in a knock-out drum (DRUM2). Some of the non-reacted gases (5%) are purged to minimise the accumulation of by-products in the reaction loop.

The liquid stream leaving the knock-out drum (DRUM2), called crude methanol, is composed of methanol, water and residual dissolved gases. The crude methanol is expanded to 1.2 bar in two valves (V1 and V2).

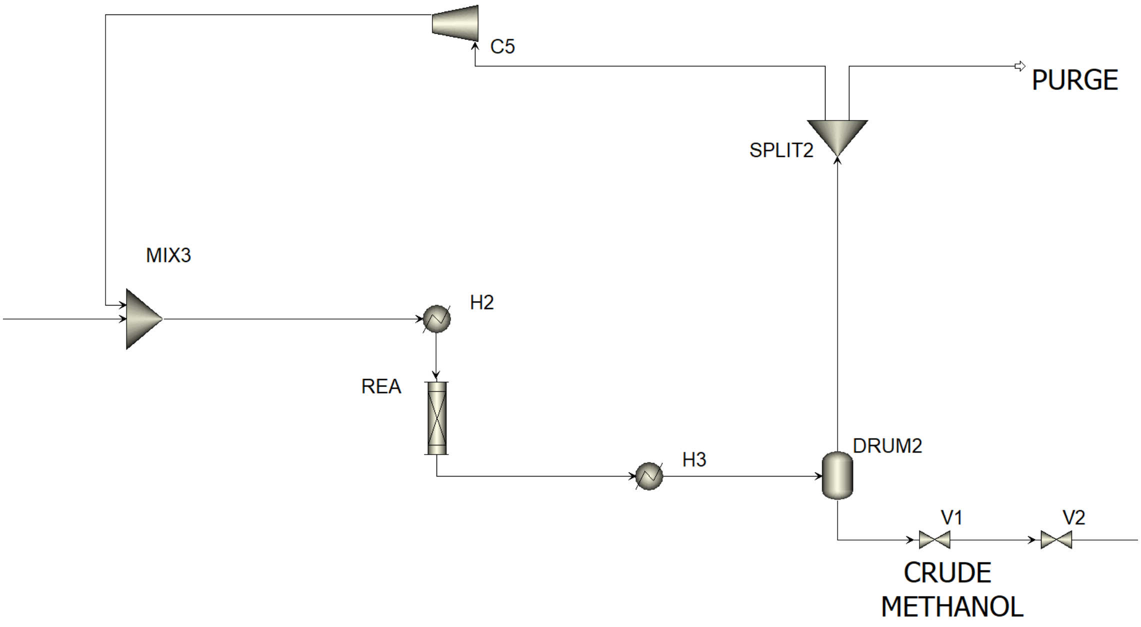


Figure 25 -Methanol synthesis unit on Aspen Plus®

The REA is an isothermal reactor modelled in Aspen Plus® as a Plug Flow Reactor (PFR).

The reactor is packed with a fixed bed of Cu/ZnO/Al2O3 commercial catalyst. For this catalyst, the model proposed by Vanden Bussche and Froment (1996) is able to describe with good precision the reactions of methanol production and the RWGS reaction. The model assumes that the CO_2 is the main source of carbon for the synthesis of. In addition, the model considers the inhibitory effect of water formed by the RWGS reaction. The activation energies of reactions were readjusted by Mignard and Pritchard (2008) to better represent the experimental data, which also expanded the application range of the model up to 75 bar.

The kinetic model used in this paper is that of Vanden Bussche and Froment (1996) [24] with readjusted parameters of Mignard and Pritchard (2008) [43], in which pressures are expressed in bar and temperatures in K. [23]

$$r_{CH3OH} = \frac{k_1\left(p_{H_2} \cdot p_{CO_2}\right)\left[1 - \frac{1}{K_{eq1}} \frac{p_{CH_3OH} \cdot p_{H_2O}}{p_{CO_2} \cdot {p_{H_2}}^3}\right]}{\left(1 + k_2 \frac{p_{H_2O}}{p_{H_2}} + k_3 \cdot {p_{H_2}}^{0.5} + k_4 \cdot p_{H_2O}\right)^3}$$

$$r_{RWGS} = \frac{k_5\, p_{CO_2}\left[1-\left(K_{eq2}\right)\dfrac{p_{CO}\cdot p_{H_2O}}{p_{CO_2}\cdot p_{H_2}}\right]}{1+k_2\dfrac{p_{H_2O}}{p_{H_2}}+k_3\cdot {p_{H_2}}^{0.5}+k_4\cdot p_{H_2O}}$$

The kinetic constants follow the Arrhenius law, its parameters are shown in the following table.

$$k_i = A_i \cdot exp\left(\frac{B_i}{RT}\right)$$

	A		**B**	
k_1	1.07	$mol\ bar^{-2}\ s^{-1} kg_{cat}^{-1}$	36696	$J\ mol^{-1}$
k_2	3453.38		-	
k_3	0.499	$bar^{-0.5}$	17197	$J\ mol^{-1}$
k_4	$6.62e-11$	bar^{-1}	124119	$J\ mol^{-1}$
k_5	$1.22e+10$	$mol\ bar^{-2}\ s^{-1} kg_{cat}^{-1}$	-98084	$J\ mol^{-1}$

The thermodynamic equilibrium constants are given by Graaf et al. (1986). [44]

$$\log_{10} \mathrm{K_{eq1}} = \frac{3066}{\mathrm{T}} - 10.592$$

$$\log_{10}\left(\frac{1}{\mathrm{K_{eq2}}}\right) = -\frac{2073}{\mathrm{T}} + 2.029$$

In the following table are summarised all the characteristics used to model the reactor in Aspen Plus®.

Tubes diam. [m]	Tubes Number	Reactor Length [m]	ρ catalyst [kg /m^3] density	ϕ [-] bed voidage	D_p [m]
0.085	30	1.5 (fixed)	2000	0.5	0.005

With these data is possible to reach a CO_2 conversion of 55%, but further discussion about the reactor length will be presented later.

The pressure drop in the fixed bed is calculated by the Ergun equation, already implemented in Aspen Plus®.

3.2.3 Distillation

The residual gases in the flow that comes from the previous section are almost completely removed in a flash tank (DRUM3). The remaining stream is heated to 80°C in exchanger H4, and then sent to a distillation column (DIST). The column was simulated with the rigorous model RadFrac in Equilibrium mode of Aspen Plus®. The water comes out of the bottom of the column at 102°C containing also a very small amount of methanol and purge gases. Methanol comes out of the top at 1 bar and 64°C, in gaseous form, containing also water in small part and some non-reacted gases. Methanol is then compressed (C6) and cooled (H5) to 40°C. In a knock-out drum (DRUM4), nonreacted gases come out of the top, and methanol product comes out of the bottom in liquid form.

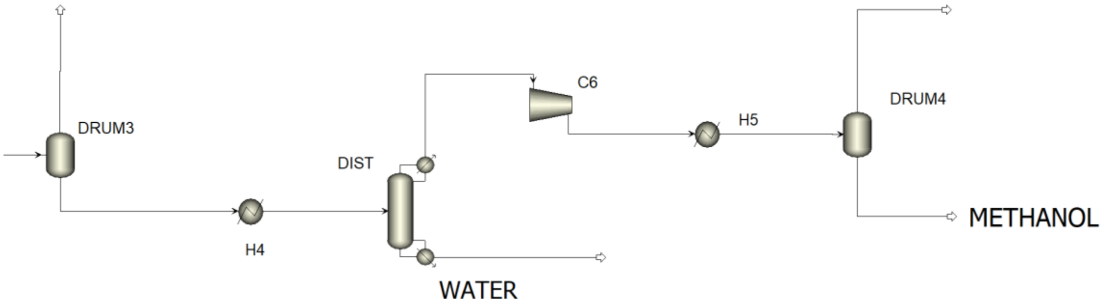


Figure 26 – Distillation unit on Aspen Plus®

4 System Analysis

In this chapter some analyses will be performed with the aim to characterize systems performances and find the way to optimise the models, in order to obtain higher systems efficiencies.

At first, “sensitivity analysis” aims to evaluate trend of certain physical parameters by varying some others. Sensitivity analyses has been focused especially in the reactors of the two models and has been realized using Aspen Plus®. In Aspen Plus® Sensitivity analysis is a tool for determining how a process reacts to varying key operating and design variables. It can be used to vary one or more flowsheet variables and study the effect of that variation on other flowsheet variables. The variables that are varied must be inputs to the flowsheet. They can’t be variables that are calculated during the simulation. Sensitivity analysis can be used to verify if the solution to a design specification lies within the range of the manipulated variable, or to perform simple process optimization. [45]

The second step of this chapter will be to manage the thermal integration of the two systems: with the use of the “Design Specification” tool of Aspen Plus® and with the realization of a “Pinch Analysis” the external heat requirement of both the systems has been minimized.

At last an economic analysis is performed in order to estimate final costs of products under certain economic hypothesis.

4.1 Sensitivity

As mentioned before, the sensitivity analysis allows to vary some variables, keeping as constant some constrains, in order to understand the point where the system works at higher efficiency. In the following some analysis are presented, regarding parameters linked with the reactions of formation of the two systems analysed. For better understanding the results showed is necessary to define three terms that define the system efficiency:

- Conversion (X) is the ratio between the number of moles of a reactant converted and all the moles introduced in the system

$$X_i = \frac{\dot{n}_{reactant,in} - \dot{n}_{reactant,out}}{\dot{n}_{reactant,in}}$$

- Selectivity (S) that define the rate of generation of a desired product relative to the generation of some undesired product, or better the ratio between the moles of the desired product formed and the moles of the reactant that actually react

$$S_i = \frac{\dot{n}_{prod,out} - \dot{n}_{prod,in}}{\dot{n}_{reactant,in} - \dot{n}_{reactant,out}}$$

- Yield (Y) that shows the real efficiency of the system being the ratio between moles of product formed and the moles of reactant present in the reactor. It can be seen also as the product of selectivity and conversion

$$Y_i = X_i \cdot S_i = \frac{\dot{n}_{prod,out} - \dot{n}_{prod,in}}{\dot{n}_{reactant,in}}$$

4.1.1 Methane Reactors Length

This study in the methanation process has the aim to find an optimum point in the economy of the system: has been studied the correlation between the two reactors to find the situation where the minimum total length of the reactors occurs.

With a design specification in Aspen Plus® is imposed to achieve at the end of the two reactors a molar fraction of CH_4 equal to 0.95 that correspond to a conversion of the CO_2 (X_{CO2}) equal to 98,953%. At the same time the length of the first reactor has been varied between 0.5 and 2 meters. This allows to change the "geometry" of the system maintaining constant the overall efficiency.

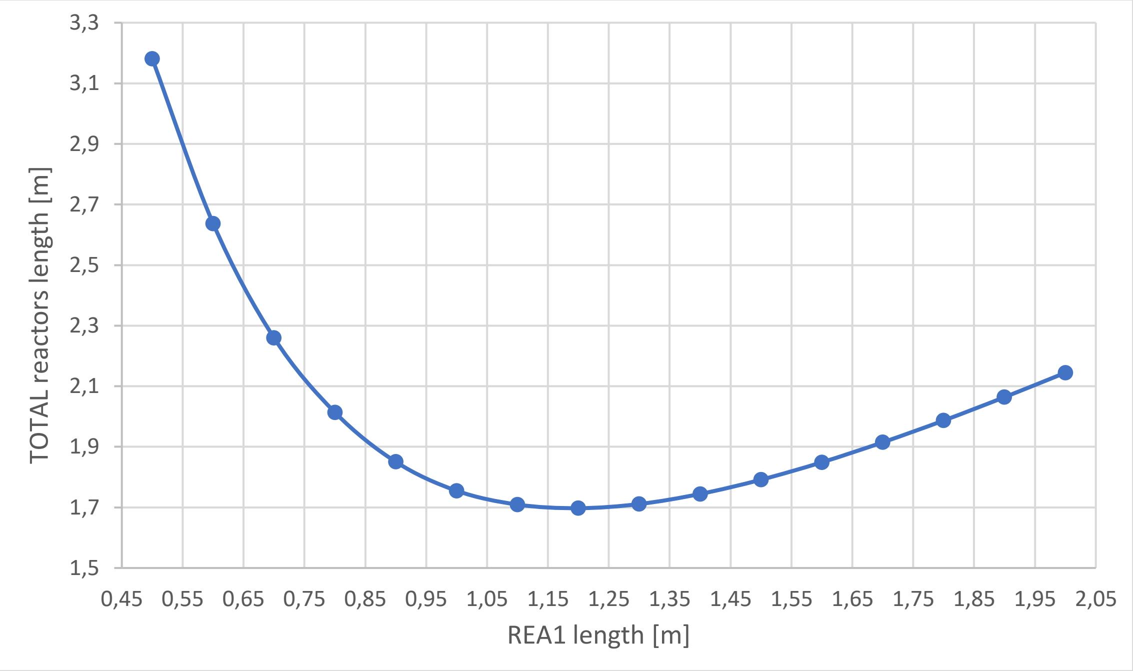


Figure 27 - Total reactors length by varying the length of the first reactor

The graph shows that for the value of the length of the first reactor equal to 1.2 meters a minimum is reached. This result has a fundamental importance in the following evaluation of the cost of the methanation system: the bare cost of the reactors and the cost of the catalyst inside the tubes of the reactors are minimised.

4.1.2 Methanol Feed Composition

As seen before (section 2.2), three reactions occur in parallel in the methanol production, the methanol formation from CO and CO_2 and the reverse water gas shift. Due to the equilibrium between the reactions and due to the recirculation of the non-reacted gases in the production line is necessary a sensitivity analysis in order to find the ratio between the reactants that allows the highest methanol production rate. Of course, is the kinetic of the reactions that strongly influence the conversion rate and furthermore, the kinetic depends on temperature.

In the design of the methanol production plant the size of the electrolysis system has been fixed to correctly compare the methane and methanol plant. This cause a fixed production of hydrogen: consequently, to change the CO_2/H_2 ratio in the reactor is necessary to vary the CO_2 feed.

The following graph highlights the point where the maximum production of methanol is achieved.

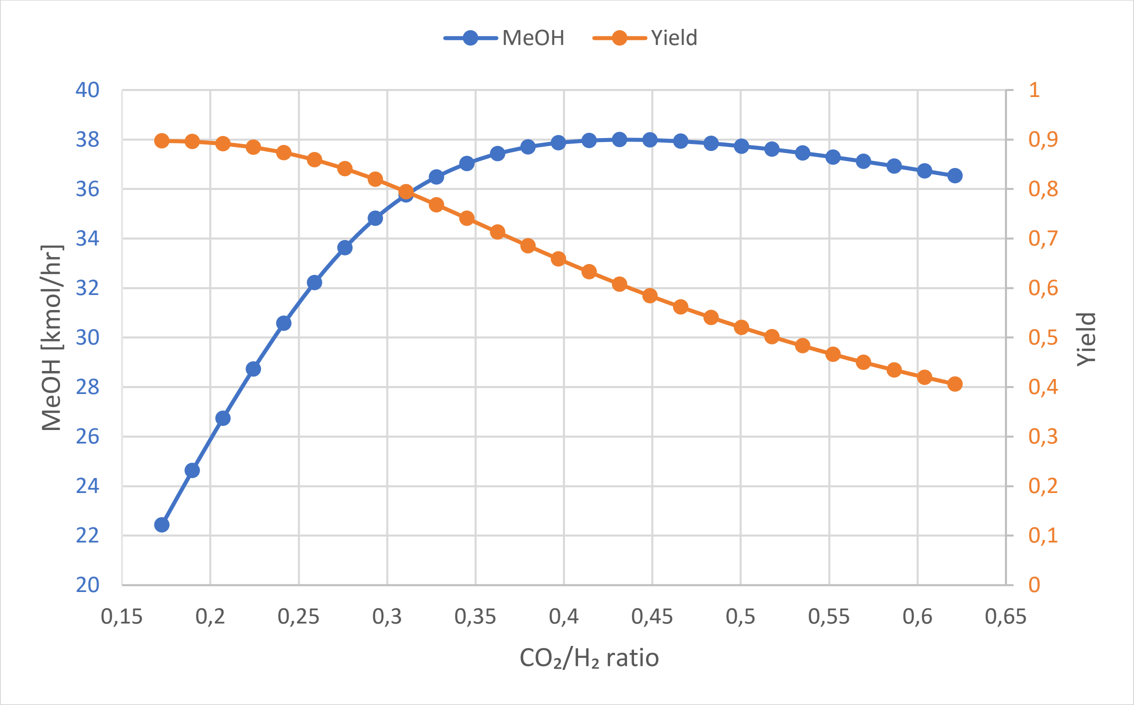


Figure 28 - Reaction Yield and Methanol outlet by varying the CO_2/H_2 ratio

Is important to notice by these results that the yield of the reaction decrease with the rising of the CO_2 flow: with a low amount of carbon dioxide in the reactor, almost everything reacts forming methanol but increasing the CO_2 feed also some by-products are produced like the CO. The optimal point for the methanol production in achieved with a ratio between the CO_2 and H_2 mole flow of 0.43.

This analysis has been executed with at constant temperature and length of the reactor.

4.1.3 Methanol Reactor Temperature

The sensitivity tool has been used to vary the temperature in which the reaction occurs inside the isothermal Plug flow reactor in the Aspen Plus® model. In this analysis the reactor length and the composition of the inlet flow have been fixed. The maximum methanol yield is achieved at the temperature of 270°C, is also important to observe that the heat produced by the exothermic reaction also grows with the temperature, this lets possible to increase the portion of the inlet water at the electrolyser that is evaporated thanks to the available heat at the reactor.

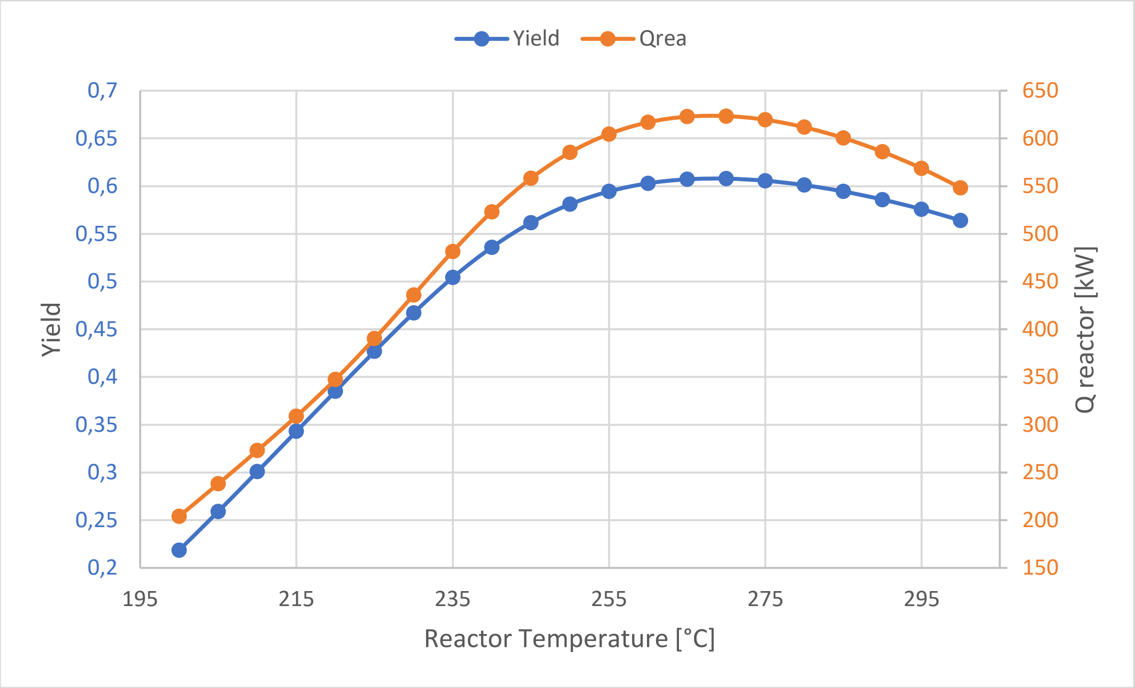


Figure 29 - Reaction Yield and thermal power of the reactor as function of the reactor's temperature

4.1.4 Methanol Reactor Length

The last analysis has been done in order to set the reactor length in the design of the methanol plant. Once fixed the parameters following the results of the previous sensitivity analysis $\left({CO_2}/{H_2}\ \text{ratio as } 0.43,\ T_{reactor} = 270°\text{C}\right)$, the reactor length has been changed to obtain different values of methanol yield. In this case, as also in the previous analysis, the CO_2 mole flow at the inlet is fixed, so the path of the methanol yield corresponds to the path of the methanol production.

Is possible to notice that after 1,5 m, a further the increase of the length of the reactor, does not correspond to the same growth of the yield. A target value of 2 m has been chosen also to not encounter the problem of an excessive pressure drop in the reactor.

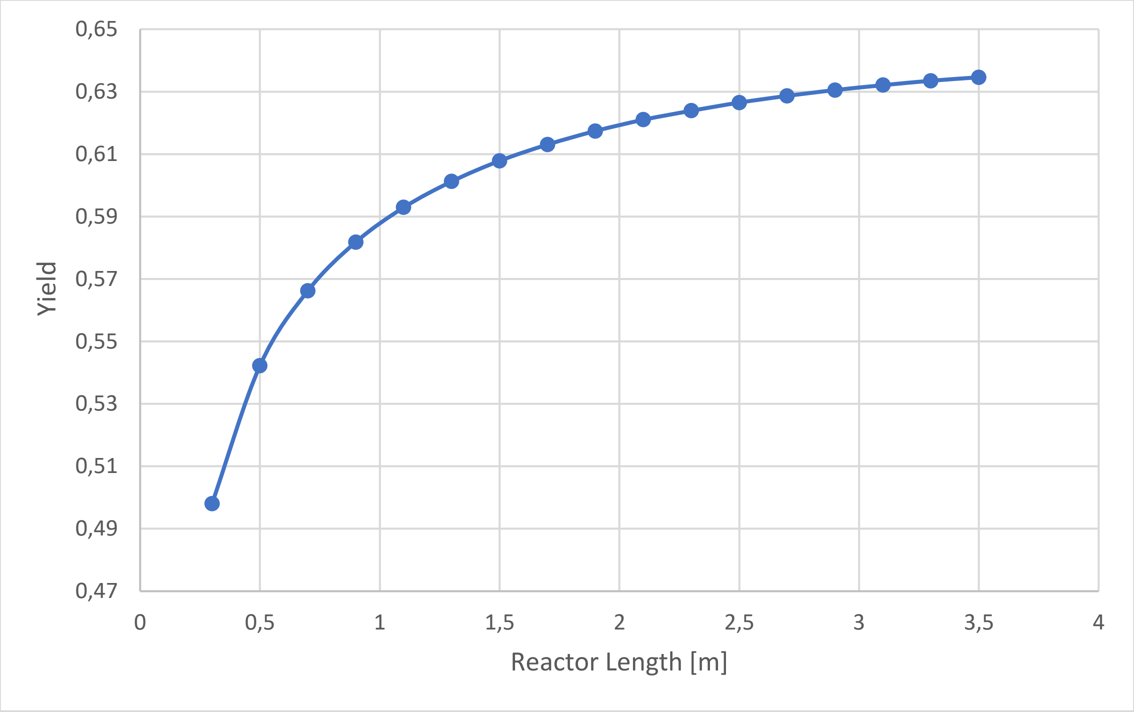


Figure 30 - Reaction Yield as function of the reactor's length

4.2 Thermal Integration

Pinch Analysis is used to design energy systems characterized by a heat exchangers network. In these systems there are constraints which have to be satisfied like the temperature of involved fluids during the process. These temperatures are fixed and must be constant for the correct working of the system.

The aim of this network is to reduce the needs of external heating: is possible to design the network of heat exchangers in order to obtain other objectives like the minimum heat exchange area, that afflicts the cost of the exchangers, but, in this work, has been studied the thermodynamic optimal. [46]

Another constrain that must be respected is the minimum temperature difference between the hot and cold fluids of the system: it has been chosen $\Delta T_{min} = 20°C$.

The Pinch Analysis is based on found the so called "*Pinch Point*": this is a specific point where there's the minimum value of temperature difference between a hot and cold fluids in the entire system. The Pinch point allows to divide the system in two distinct parts:

- Above pinch point: system requires a heat input and is therefore a net heat sink
- Below pinch point: system rejects heat and so is a net heat source

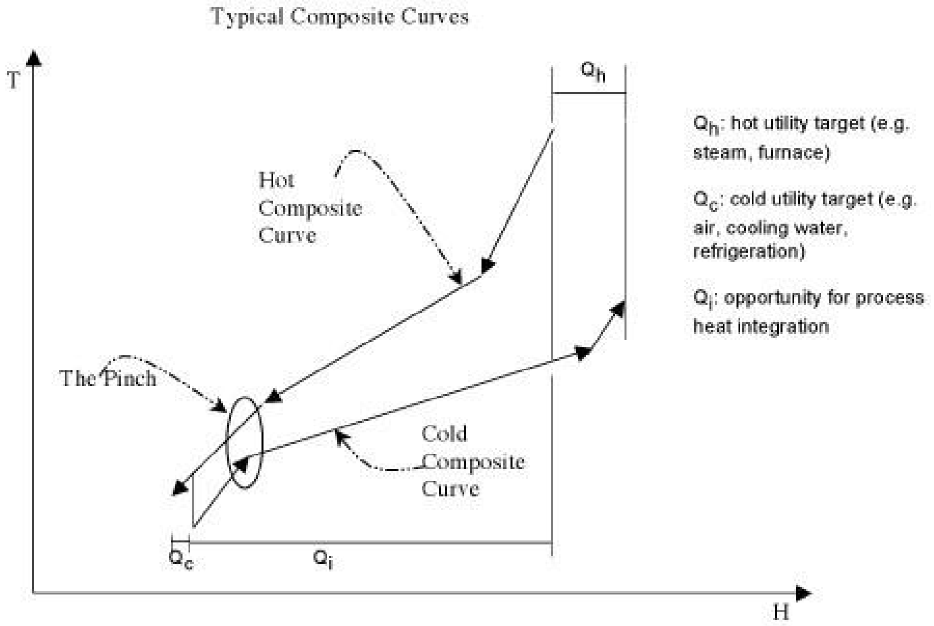


Figure 31 - Composite curve and Pinch Point

"Above" the pinch (i.e. in the region to the right) the hot composite transfers all its heat into the cold composite, leaving utility heating only required. The region above the pinch is therefore a net heat sink, with heat flowing into it but no heat flowing out. It involves heat exchange and hot utility, but no cold utility. Conversely below the pinch cooling only is required and the region is therefore a net heat source, requiring heat exchange and cold utility but no hot utility. The problem therefore falls into two thermodynamically distinct regions, as indicated by the enthalpy balance envelopes in the last figure. Heat $Q_h$flows into the problem above the pinch and Q_c out of the problem below, but the heat flow across the pinch is zero. [47]

To achieve the minimum energy targets for a process is necessary to follow three rules:

- Heat must not be transferred across the pinch
- There must be no external cooling above the pinch
- There must be no external heating below the pinch

Violating any of these rules will lead to cross-pinch heat transfer resulting in an increase in the energy requirement beyond the target. The design procedure for heat exchanger networks ensures that there is no cross pinch heat transfer.

Calculation Procedures

The algebraic procedure starts with definition of temperature intervals. The bounds of these intervals are "fictitious temperatures" (T^*) defined as follows: inlet and outlet temperature of each cold fluid are increased of $\frac{1}{2}\Delta T_{min}$; inlet and outlet temperature of each hot fluid are decreased of $\frac{1}{2}\Delta T_{min}$.

All these temperatures T^* are sorted from largest to smallest, defining a certain number of intervals.

For each interval so defined, the global heat flux required is calculated:

$$\Phi_i = (T_i^* - T_{i+1}^*) \cdot \left(\sum G \cdot c_{cold} - \sum G \cdot c_{hot}\right)$$

Where G is mass flow and c is specific heat. If is positive, this implies a deficit of thermal flux in the corresponding interval (otherwise there's a surplus).

Is now possible to cumulate the Φ_i of each interval, starting from the assumption that there's not external input in the first interval. Negative values of the cumulate are not acceptable, then the external heat is increased until each value of the cumulate will be higher than zero.

The interval that has a value of the cumulate equal to zero is the pinch point (T_{PP}^*). This means that pinch point temperature for hot fluids is $T_{PP,hot}^* = T_{PP}^* + \frac{1}{2}\Delta T_{min}$., and pinch point temperature for cold fluids is $T_{PP,cold}^* = T_{PP}^* - \frac{1}{2}\Delta T_{min}$.

Are now presented the rules used to design the heat exchangers network in order to obtain the minimum energy requirement: [47]

- Above pinch point $G \cdot c_{hot} \leq G \cdot c_{cold}$
- Below pinch point $G \cdot c_{cold} \leq G \cdot c_{hot}$

These rules must be respected near the pinch point, if you are far from that are allowed exceptions but, in every case, the ΔT_{min} has to be guaranteed all along the heat exchange.

Other additional rules are the followings:

- Above pinch point $N_{hot} \leq N_{cold}$
- Below pinch point $N_{cold} \leq N_{hot}$

These rules can be respected splitting hot or cold fluids into two or more flows.

Furthermore, when there's a phase change of a pure substance (i.e. at constant temperature), an important device consists in a variation in outlet temperature of a little quantity (e.g. 1°C) to allow pinch analysis calculation.

Composite Curves

To handle multiple streams, we add together the heat loads or heat capacity flowrates of all streams existing over any given temperature range. Thus, a single composite of all hot streams and a single composite of all cold streams can be produced in the *T/Φ* diagram.

For each temperature interval the angular coefficient represents the heat flux globally exchanged in the interval.

If the composite curves are re-plotted on axes of shifted temperature, we obtain the *shifted composite curves,* in which the minimum temperature difference between two points with the same abscissa is equal to the ΔT_{min}.

The point in which there's the minimum temperature difference between the two composite curves is the Pinch point.

Hence, knowing the shifted composite curves, we can find the minimum amount of heating or cooling that needs to be supplied at any given temperature: the horizontal difference between the two curves at right side represents the minimum energy requirement from external sources, whereas the horizontal difference at left side is the cooling power required.

It's also possible to build the *Grand Composite Curve*, it represents the difference between the heat available from the hot streams and the heat required by the cold streams, relative to the pinch, at a given shifted temperature. Thus, the Grand Composite Curve is a plot of the net heat flow against the shifted (interval) temperature. In particular, the point in which the grand Composite Curve reaches a value of *Φ=0* is the Pinch Point (according to the definition provided before).

4.2.1 Steam Electrolysis and Methanation

In the methanation process, the exothermic reaction that happens inside the two reactors gives available heat that could be used to evaporate the flow of water that is entering in the electrolysis section. In the following table is summarised the available thermal power that must be removed from each reactor to maintain the isothermal condition.

Q_{rea} Reactor 1 [kW]	1478,3
Q_{rea} Reactor 2 [kW]	298,4

The water in the evaporator needs a slightly higher amount of heat to complete the evaporation, with respect to the total heat made available by the two reactors: is possible, with a Design Specification in Aspen Plus®, to make the it coincides. This is thanks to the property of the water, increasing the pressure, the latent heat of evaporation is lower: is possible to easily observe this in the Temperature – Entropy (T-s) diagram for the water.

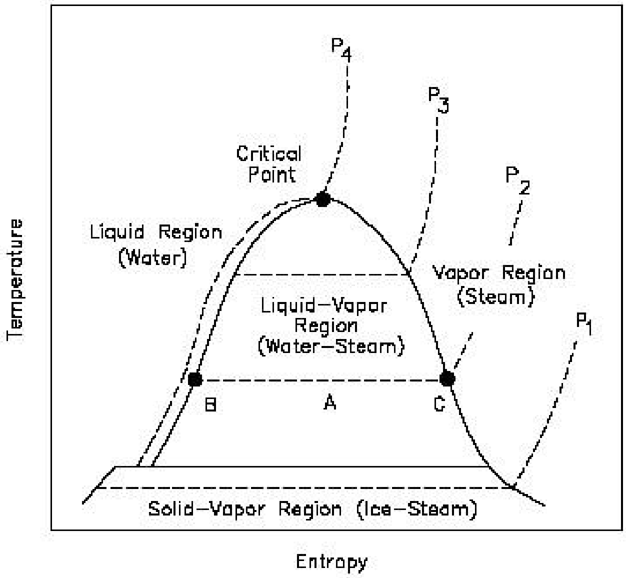


Figure 32 - Temperature – Entropy (T-s) diagram for water

The Design Specification impose the outlet pressure of the Pump, that results near 20 bar against the 15 bar needed in the electrolyser, to make coincide the latent heat of evaporation of the water with the available heat at the two reactors. The following lamination in the valve allows to have the correct pressure in the SOEC.

For this reason, in the following Pinch Analysis calculations the heat needed at the evaporating stream (block EVA) is no more considered.
The fluids involved in the analysis are now reported: to identify each fluid has been used the name of the model's block that the fluid flows through.

	Fluid Type	G*c [kW/K]	Tin [°C]	Tout [°C]	Φ [kW]
ECO	cold	4,28	21,2	212,4	817,30
SURR	cold	1,99	205,2	800,0	1182,11
O2COOL	hot	0,66	800,0	35,0	-505,09
H1	hot	2,16	800,0	35,0	-1649,83
H2	cold	1,63	106,9	300,0	315,19
H3	hot	4,05	300,0	35,0	-1073,93
H4	cold	0,65	35,0	300,0	171,99
H5	hot	1,14	300,0	35,0	-302,78
SNGINTC	hot	0,40	107,5	35,0	-28,86
POSTCOOL	hot	0,43	108,0	35,0	-31,13

As mentioned before, all the temperatures T^* are sorted from largest to smallest, defining some number of intervals $(T_i^* - T_{i+1}^*)$. For each interval the global heat flux required has been calculated.

T* [°C]	Φ [kW]	Cumulate [kW]	Cumulate with external Φ [kW]
810,0		0	39,75
790,0	-39,75	-39,75	0
310,0	398,16	358,42	398,16
290,0	-29,03	329,39	369,13
222,4	253,10	582,49	622,24
215,2	-3,83	578,66	618,41
116,9	143,12	721,78	761,53
98,0	58,22	780,01	819,76
97,5	1,84	781,84	821,59
45,0	205,33	987,18	1026,93
31,2	62,82	1050,00	1089,75
25,0	55,02	1105,02	1144,77

Is possible to observe that in the second interval is present a negative value for the cumulative: it means that an energy external input slightly lower of 40 kW is necessary.
Results show also that $T^*_{PP} = 790°C$. So, according to before-mentioned theory of pinch analysis, it's possible to calculate pinch point temperatures for hot and cold fluids, which are reported in following table.

$T^*_{PP,hot}$ [°C]	800
$T^*_{PP,cold}$ [°C]	780
$\Phi_{heat,min}$ [kW]	39.75
$\Phi_{cold,min}$ [kW]	1144.77

In the table is also shown the minimum external requirement of heat and cold.

Heat Exchanger Network Configuration

Is now possible to provide the heat exchanger network, dividing between the two regions above and below the pinch point.
Above the pinch the situation is simple thanks to the thermal integration done during the design of the model: just an external electric heater is needed to provide the thermal power (that coincide with the $\Phi_{heat,min}$) to overheat the steam stream that flows towards the electrolyser.

Heat exchanger	HOT Fluid	COLD Fluid	G*c hot [kW/K]	G*c cold [kW/K]	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]
HEAT 1		SURR		1,99			780	800	39,75

Instead the design of the heat exchanger network is quite different below the pinch point: to observe the prescriptions given before is necessary to split the stream that flows in the economiser (ECO block).

C1, C2, C3, C4, C5 and C6 are coolers which receive heat from hot fluids which still must be cooled.

In the following table network configuration below the pinch point is shown.

Note that Sum of cooling power is equal to the value of $\Phi_{cold,min}$ [kW].

Heat exchanger	HOT Fluid	COLD Fluid	G*c hot [kW/K]	G*c cold [kW/K]	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]
1	H2	SURR	2,16	1,99	800,0	270,3	205,2	780,0	1142,37
2	O2COOL	H3	0,66	1,63	800,0	676,4	250,0	300,0	81,60
3	O2COOL	H5	0,66	0,65	676,4	415,9	35,0	300,0	171,99
4	H2	H3	2,16	1,63	270,3	162,0	106,9	250,0	233,59
5	H4	ECO - A	4,05	3,00	300,0	158,5	21,2	212,4	573,49
6	O2COOL	ECO - B	0,66	1,28	415,9	46,7	21,2	212,4	243,80
C1	O2COOL		0,66		46,7	35,0			7,70
C2	H2		2,16		162,0	35,0			273,87
C3	H4		4,05		158,5	35,0			500,43
C4	H6		1,14		300,0	35,0			302,78
C5	SNGINTC		0,40		107,5	35,0			28,86
C6	POSTCOOL		0,43		108,0	35,0			31,13

Composite Curves

The composite curves are now presented: is possible to observe that these curves don't present the "classical" horizontal line in correspondence of the pinch point due to the fact that the latent heat of evaporation of the water is completely managed by the available heat of the two reactors, as already said before.

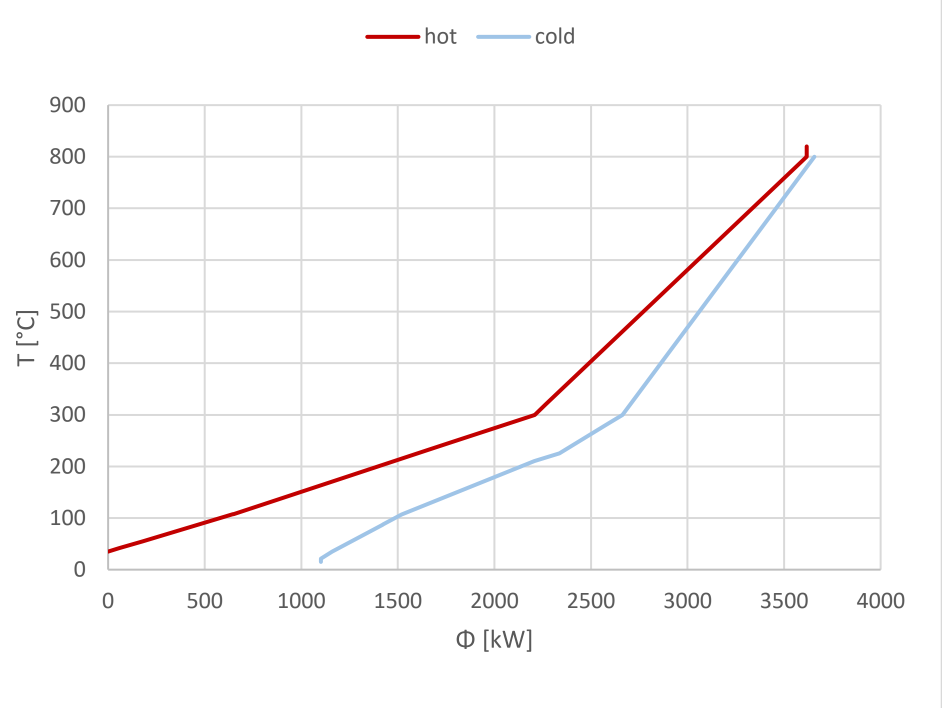


Figure 33 - Shifted Composite Curve for Steam Electrolysis and Methanation

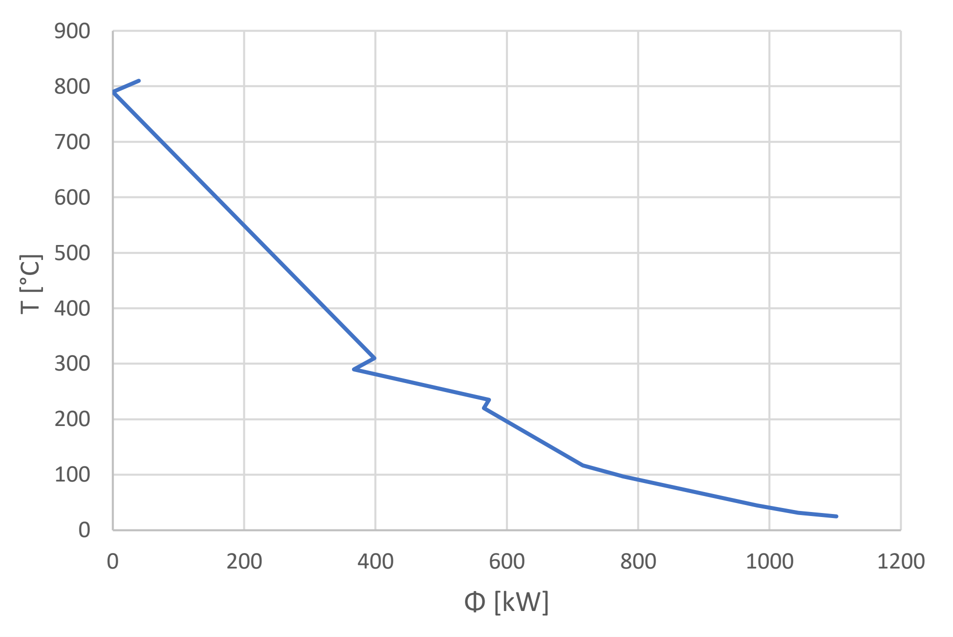


Figure 34 - Grand Composite Curve for Steam Electrolysis and Methanation

4.2.2 Steam Electrolysis and Methanol production

The reactor in the methanol plant works in isothermal condition, to provide the correct working is necessary to take away the heat produced by the reactions. The reactions that occur in the reactor are less exothermic as compared to the methanation reaction, indeed, the heat available at the reactor (Q_{rea} = 145.2 kW) is not sufficient to cover the thermal power needed at the evaporator (Q_{eva} = 436.6 kW) as happened in the previous case.

With a Design Specification in Aspen Plus® the evaporating stream before the electrolyser has been separated: in this way about the 33% of the heat of evaporation is given by the thermal power that must be removed from the reactor. Is possible to see the splitting of the evaporating water in the description of the methanol plant (section 4.2.1), where the block EVA-R indicates that part of the evaporating flow of water managed by the reactor's thermal power.

For this reason, in the following Pinch Analysis calculations the heat needed in the block EVA-R is no more considered.

The fluids involved in the analysis are now reported: to identify each fluid has been used the name of the model's block that the fluid flows through.

	Fluid type	G*c [kW/K]	Tin [°C]	Tout [°C]	Φ [kW]
ECO	cold	4,25	21,0	199,2	756,55
EVA	cold	3891,20	199,2	198,8	1203,50
SURR	cold	1,99	198,8	800,0	1194,18
O2COOL	hot	0,66	800,0	35,0	-505,09
INTERC	hot	0,75	244,5	38,0	-153,88
H1	hot	2,16	800,0	35,0	-1649,79
H2	cold	11,41	83,4	270,0	2129,08
H3	hot	14,73	270,0	35,0	-3460,83
H4	cold	8,49	22,0	80,0	492,20
H5	hot	10,80	78,4	40,0	-414,64

As before, all the temperatures T^* are sorted from largest to smallest, defining some number of intervals ($T_i^* - T_{i+1}^*$). For each interval the global heat flux required has been calculated.

T* [°C]	Φ [kW]	Cumulate [kW]	Cumulate with external Φ [kW]
810,0		0	801,59
790,0	-39,73	-39,73	761,86
280,0	423,47	383,74	1185,34
260,0	-211,64	172,10	973,70
234,5	105,76	277,87	1079,46
209,2	123,84	401,71	1203,30
208,8	-1203,30	-801,59	0
93,4	303,63	-497,97	303,63
90,0	48,32	-449,65	351,94
68,4	119,98	-329,67	471,93
32,0	595,38	265,71	1067,31
31,0	25,61	291,32	1092,92
30,0	28,18	319,50	1121,10
28,0	36,58	356,08	1157,67
25,0	52,63	408,71	1210,31

As for the methane's pinch analysis is possible to observe in the previous table the minimum heat and cold requirement and, also, the pinch point temperature that is $T^*_{PP} = 208.8°C.$ So, according to before-mentioned theory of pinch analysis, the pinch point temperatures for hot and cold fluids has been calculated and reported in following table.

$T^*_{PP,hot}$ [$°C$]	218.8
$T^*_{PP,cold}$ [$°C$]	198.8
$\Phi_{heat,min}$ [kW]	801.59
$\Phi_{cold,min}$ [kW]	1210.31

Heat Exchanger Network Configuration

The following table shows the configuration of the heat exchangers network above the pinch point.

The exchanger HEAT1 gives the external thermal power to complete the necessary overheating of the water steam, is possible to mark that it power is equal to external heat calculated through cumulative value.

Heat exchanger	HOT Fluid	COLD Fluid	G*c hot [kW/K]	G*c cold [kW/K]	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]
1	H3	EVA	14,73	3891,20	270,0	218,8	198,8	199,0	753,29
2	H1	EVA	2,16	3891,20	427,6	218,8	199,0	199,2	450,21
3	INTERC	ECO	0,75	4,25	220,6	218,8	198,8	199,2	1,31
4	O2COOL	SURR	0,66	1,99	800,0	218,8	198,8	392,0	383,70
5	INTERC	H2	0,75	11,41	244,5	220,6	198,8	200,4	17,79
6	H1	H2	2,16	11,41	795,9	427,6	200,4	270,0	794,20
7	H1	SURR	2,16	1,99	800,0	795,9	392,0	396,5	8,89
HEAT 1		SURR		1,99			396,5	800,0	801,59

Below the pinch point is necessary to split some streams in order to follow the rules on the pinch analysis. The sum of the power of the six coolers necessary to the system correspond to the minimum cold requirement, calculated before through the cumulative.

Heat exchanger	HOT Fluid	COLD Fluid	G*c hot [kW/K]	G*c cold [kW/K]	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]
8	H3 - A	H2	12,00	11,41	218,8	109,1	83,4	198,8	1317,09
9	H3 - B	ECO - A	2,73	2,20	218,8	75,3	21,0	198,8	391,34
10	H1	ECO - B	2,16	2,05	218,8	50,1	21,0	198,8	363,90
11	O2COOL	H4	0,66	8,49	218,8	90,0	70,0	80,0	85,09
12	INTERC	H4	0,75	8,49	218,8	77,6	57,6	70,0	105,29
13	H5	H4	11,18	8,49	78,4	51,4	22,0	57,6	301,82
C1	O2COOL		0,66		90,0	35,0			36,30
C2	INTERC		0,75		77,6	38,0			29,49
C3	H1		2,16		50,1	35,0			32,59
C4	H5		11,18		51,4	40,0			127,44
C5	H3 - A		12,00		109,1	35,0			889,11
C6	H3 - B		2,73		75,3	35,0			110,01

Composite Curves

The composite curves for the Methanol plant are here provided.

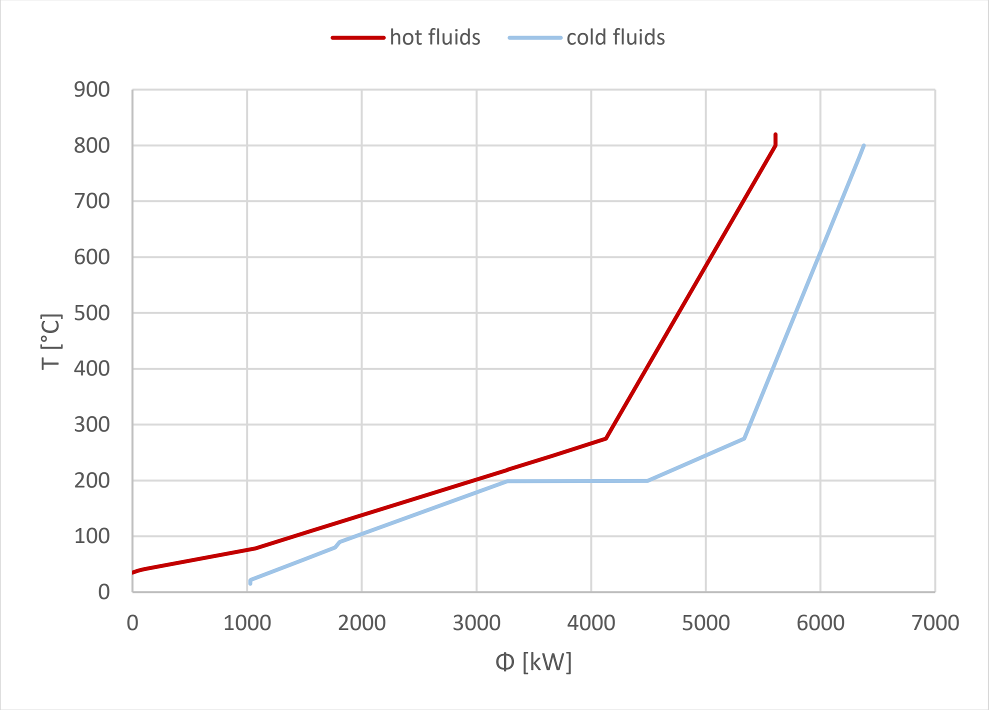


Figure 35 - Shifted Composite Curve for Steam Electrolysis and Methanol production plant

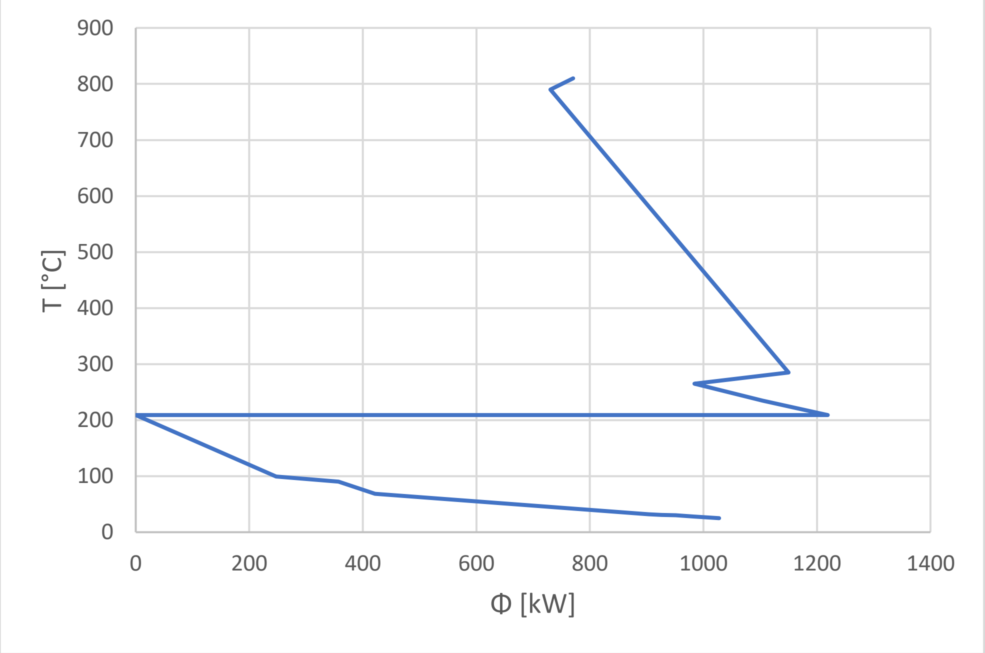


Figure 36 - Grand Composite Curve for Steam Electrolysis and Methanol production plant

4.3 Plants Performances

In this section have been calculated the global energy requirement of the systems, knowing the external energy demand, in order to evaluate the efficiency of the plants.

The efficiency will be calculated as the ratio between the chemical power of the products (methane and methanol) and the total electric input.

The electrical input is composed by:

- Electrical input in Alternate Current (AC) into the stacks of the SOEC
- Electricity for the compressors and pumps
- Electricity for the electric heaters needed to provide the external thermal energy

The following hypotheses for the efficiencies of the components of the models have been considered:

- $\eta_{is,c}\ compressors = 0.75$
- $\eta_{is,c}\ pumps = 0.8$
- $\eta_{el}\ compressors = 0.95$
- $\eta_{el}\ pumps = 0.9$
- $\eta_{AC/DC}\ rectifier = 0.98$

Efficiency can be can be expressed through the following formula:

$$\eta = \frac{Power_{product}}{W_{el}} = \frac{LHV_{product} \cdot m_{product}}{W_{el}}$$

	Steam Electrolysis + Methanation	Steam Electrolysis + Methanol Production
$W_{in,SOEC}\ [kW]$	10000	10000
$W_{compr,\mathrm{CO_2}}\ [kW]$	117,48	318,99
$W_{compr,plant}\ [kW]$	51,90	383,47
$W_{pump}\ [kW]$	5,85	4,38
$W_{external\ heating}\ [kW]$	39,75	801,59
$W_{el\ input,TOT}\ [kW]$	10419,06	11712,52
$LHV\ product\ \left[{}^{MJ}/_{kg}\right]$	50,17	19,93
$product\ mass\ flow\ \left[{}^{kg}/_{s}\right]$	0,16	0,35
$Chemical\ power\ [kW]$	8034,39	6883,13
$Energy\ requirement\ \left[{}^{kWh_{el}}/_{kg}\right]$	18,07	9,42
$EFFICIENCY\ [\%]$	77,11	58,77

Is possible to denote from the table that the electric requirement for the methanol plant is higher: this is due to the higher work needed for the compression of the reactant and also to the amount of external energy demand.

In particular, the electric power for carbon dioxide compression is higher for the methanol plant because of the pressure, but also due to the fact that the molar flow in the case of the methanol is nearly the double that in the methane plant $\left(\frac{CO_2}{H_2}_{CH4} = 0.25,\ \frac{CO_2}{H_2}_{CH3OH} = 0.43\right)$.

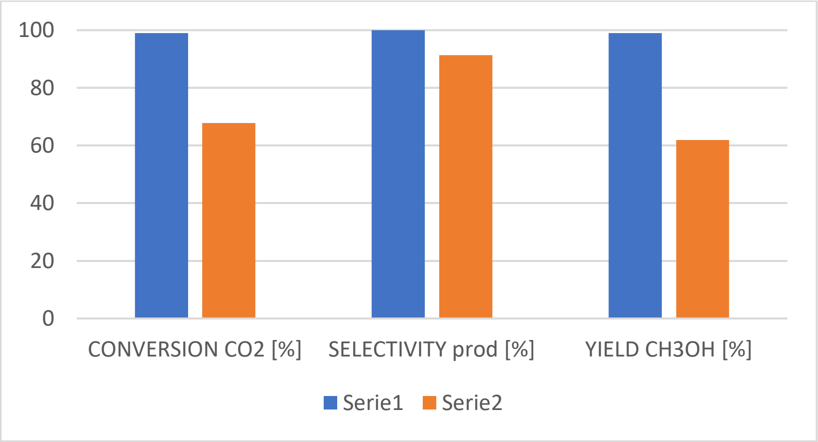
Moreover, the methane formation reaction is more exothermic, this allows to have a higher amount of heat that must be removed from the reactor: the external thermal power demand for the methanol plant is almost null if compared to the total energy needing (0.38%).

4.3.1 CO_2 Balance

In the following table are shown the results of the reactors section both for the methane and for the methanol plants as CO_2 conversion, selectivity and yield of the two desired products.

	Steam Electrolysis + Methanation	Steam Electrolysis + Methanol Production
CO_2 $CONVERSION$ [%]	98,953	67,811
$SELECTIVITY$ [%]	99,999	91,322
$YIELD$ [%]	98,953	61,926

Is evident that the efficiency of the systems is also correlated with the specific yields of the plants: in the methanol production is not possible to have high values of yield due to the reactions that they develop in the reactor, i.e. the formation of carbon monoxide. Instead, in the methanation, almost all the CO_2 is converted into the desired product.



2

Figure 37 - Comparison between methane and methanol production

Are now measured the CO_2 balances of the two plants, firstly to calculate the net CO_2 abatement in a scenario where the electricity is generated from renewable sources (RES).
Moreover, different energy sources from RES have been considered, i.e. electric energy from coal and synthetic natural gas (SNG) plants: imposing the CO_2 abatement as null, the percentage of the electrical energy that can be produced with fossil fuels, to have globally a zero-emission condition, has been calculated.
Furthermore, the carbon credits[xx] generated by the sale of by-product oxygen have been calculated.
Some hypothesises have been considered:

- The CO_2 emission from a coal plant is fixed at 0.723 $\frac{kg_{CO2}}{kWh_{el}}$ [48]
- The CO_2 emission from a SNG plant is fixed at 0.365 $\frac{kg_{CO2}}{kWh_{el}}$ [48]
- The O_2 production with the common technique of cryogenic air distillation and the following compression consumes 0.4 $\frac{kWh_{el}}{kg_{O2}}$ [23]

	Steam Electrolysis + Methanation	Steam Electrolysis + Methanol Production
$CO_2\ fed\ \left[{kg}/{h}\right]$	1593,7	2750,6
$CO_2\ rejected\ \left[{kg}/{h}\right]$	16,7	885,4
$Thermal\ energy\ consumption\ [kW]$	39,8	801,6
$Electricity\ consumption\ [kW]$	10379,3	10911,0
$O_2\ production\ \left[{kg}/{h}\right]$	2317,5	2317,5
$CO_2\ abatement\ (100\%\ RES)\ \left[{kg}/{h}\right]$	-1577,1	-1865,2
$COAL\ SOURCE\ (CO_2\ abatement = 0)$	20,9 %	22,0 %
$COAL\ SOURCE\ (CO_2\ abatement = 0)\ with\ O_2\ sale$	23,0 %	23,9 %
$SNG\ SOURCE\ (CO_2\ abatement = 0)$	41,5 %	43,6 %
$SNG\ SOURCE\ (CO_2\ abatement = 0)\ with\ O_2\ sale$	45,5 %	47,4 %

[xx] A carbon credit is a generic term for any tradable certificate or permit representing the right to emit one tonne of carbon dioxide or the mass of another greenhouse gas with a carbon dioxide equivalent (tCO_2e) equivalent to one tonne of carbon dioxide.

4.4 Economic Analysis

The objective of this section is to determine a comparison between the methanol and the methane from an economic perspective, understanding how these technologies can place in the actual market of the fuels.

4.4.1 Cost Estimation Methodology

The calculation procedure adopted in this work follows the guidelines for the energy system studies given by the National Energy Technology Laboratory (NETL) of the US Energy Department. [49]

Levels of Capital Costs

This methodology proposed to divide the capital cost in five levels: BEC, EPCC, TPC, TOC and TASC. BEC, EPCC, TPC and TOC are "overnight" costs and are expressed in "base-year" dollars. The overnight construction cost does not take into account financing costs or escalation. The base year is the first year of capital expenditure. TASC is expressed in mixed, current-year dollars over the entire capital expenditure period, which is assumed in most NETL studies to last five years for coal plants and three years for natural gas plants.

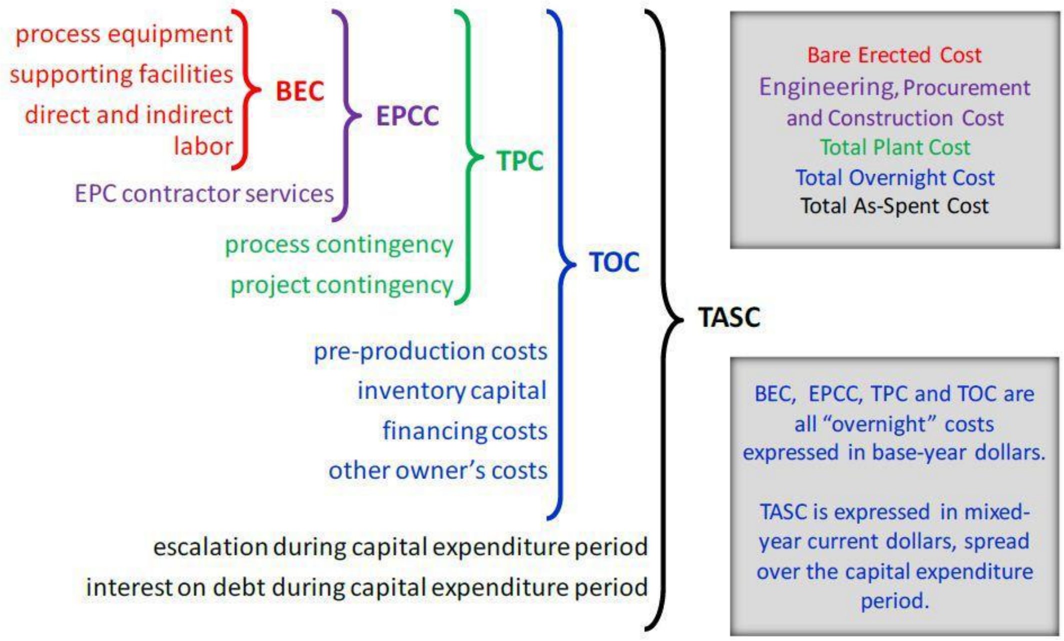


Figure 38 - Capital cost levels and their elements **[49]**

The Bare Erected Cost (BEC) is an overnight cost expressed in base-year dollars that comprises the cost of process equipment, on-site facilities and infrastructure that support the plant (e.g., shops, offices, labs, road), and the direct and indirect labour required for its construction and/or installation.

The Engineering, Procurement and Construction Cost (EPCC) comprises the BEC plus the cost of services provided by the engineering, procurement and construction (EPC) contractor. EPC services include: detailed design, contractor permitting and project/construction management costs.

The Total Plant Cost (TPC) comprises the EPCC plus project and process contingencies.

The Total Overnight Capital (TOC) comprises the TPC plus all other overnight costs, including owner’s costs. TOC, like EPCC and TPC costs, is an “overnight” cost, expressed in base-year dollars and as such does not include escalation during construction or interest during construction.

The Total As-Spent Capital (TASC) is the sum of all capital expenditures as they are incurred during the capital expenditure period including their escalation. TASC also includes interest during construction. Accordingly, TASC is expressed in mixed, current-year dollars over the capital expenditure period.

Contracting Strategy and EPC Contractor Services

The cost estimates are based on an engineering, procurement and construction management (EPCM) contracting strategy utilizing multiple subcontracts. With this approach is guaranteed to the Owner grater control of the project, minimizing most of the risk premiums typically included in a EPC contract price.

EPCM contractor services are usually estimated at 8 to 10% of BEC, in this work an intermediate value of 9% has been assumed. These costs consist of all home office engineering and procurement services as well as field construction management costs. Site staffing generally includes a construction manager, resident engineer, scheduler, and personnel for project controls, document control, materials management, site safety, and field inspection.

Estimation of Capital Cost Contingencies

Process and project contingencies are included in estimates to account for unknown costs that are omitted or unforeseen due to a lack of complete project definition and engineering. Contingencies are added because experience has shown that such costs are likely, and expected, to be incurred even though they cannot be explicitly determined at the time the estimate is prepared.

Capital cost contingencies do not cover uncertainties or risks associated with:

- scope changes
- changes in labour availability or productivity
- delays in equipment deliveries
- changes in regulatory requirements
- unexpected cost escalation
- performance of the plant after start-up (e.g., availability, efficiency)

Process Contingency

Process contingency is considered to compensate the uncertainty in the estimation of costs caused by unpredictability associated with the development status of a technology and are applied to each plant section based on its current technology status.

For a small pilot plant, and those considered in this work can belong to this category, the process contingency is estimated at 25% of BEC.

Project Contingency

Project Contingency is evaluated at 20% of the sum of EPCC and Process Contingency.

Estimation of Owner's Costs

Owner's costs are composed by several addends:

- Inventory Capital: calculated as 0,5% of TPC for spare parts
- Land's Cost: a price of 3000 $/acre and a needed surface of 2o acres were hypothesised.
- Financing Cost: it covers the cost of securing financing, including fees and closing costs but not including interest during construction. Estimated as 2,7% of TPC
- Other Owner's cost, calculated as 15% of TPC, include:
    - Preliminary feasibility studies, including a Front-End Engineering Design (FEED) study
    - Economic development (costs for incentivizing local collaboration and support)
    - Construction and/or improvement of roads and/or railroad spurs outside of site boundary
    - Legal fees
    - Permitting costs
    - Owner's engineering (staff paid by owner to give third-party advice and to help the owner oversee/evaluate the work of the EPC contractor and other contractors)
    - Owner's contingency; sometimes called "management reserve", these are funds to cover costs relating to delayed start-up, fluctuations in equipment costs, unplanned labour incentives in excess of a five-day/ten-hour-per-day work week. Owner's contingency is NOT a part of project contingency

Cost of the product

Starting from knowing the Total Overnight Cost of a plant, is possible to calculate the cost of the products through the NPV analysis.

Net present value (NPV) is determined by calculating the costs (negative cash flows) and benefits (positive cash flows) for each period of an investment that is typically one year. After the cash flow for each period is calculated, the present value of each one is achieved by discounting its future value at a periodic rate of return dictated by the market. NPV is the sum of all the discounted future cash flows. Because of its simplicity, NPV is a useful tool to determine whether a project or investment will result in a net profit or a loss. A positive NPV results in profit, while a negative NPV results in a loss.

The Net Present Value can be calculated as:

$$NPV = -TOC + \sum_{n=1}^{LT} \frac{CF_n}{(1+i)^n}$$

The summation of all the cash flows (CF) considered in the analysis has been made up to the useful life of the plant, which in this work has been estimated at 30 years.

The shown formula allows to calculate the future value of the money through the discount rate i: this term defines the values of the future cash flows as "how much money would have to be invested currently, at a given rate of return, to yield the cash flow in future".

The Cash Flow has been calculated as the balance between the operating revenues, expenses and taxes:

$$CF_n = Rev_n - Exp_n - Tx_n$$

In detail:

$$Rev_n = UF \cdot \left(C_{prod} \cdot E_{prod} + C_{O_2} \cdot M_{O_2}\right)$$

Where UF stands for Utilization Factor that represent the ratio between the yearly operating hours of the plants and the total hours in a year. The revenues are given by the sale of the desired product (methane or methanol) and by the oxygen by-product.

The Expenses are composed by the Operation and Maintenance (O&M) costs and by the costs of the external flows needed from the plants (i.e. electrical energy, carbon dioxide and water).

$$Exp_n = FIXOM + UF \cdot \left(VAROM + C_{CO_2} \cdot M_{CO_2} + C_{el} \cdot E_{el} + C_{H_2O} \cdot M_{H_2O}\right)$$

The O&M are divided in two components, one that is depending from the operating hours of the plant (VAROM) and the other that is constant (FIXOM).

Yearly income taxes are calculated as the product between taxable income and tax rate. Taxable income is obtained by subtracting to operating revenues the operating expenses and the depreciation.

$$Tx_n = r_t \cdot (Rev_n - Exp_n - Dep_n)$$

The depreciation is a technical-accounting procedure for the distribution of a multi-year cost over the estimated years of life of the plant: it is constant and can be obtained dividing TOC over the amortization period, considered as the lifetime of the plant.

The final cost of the product (C_{prod} expressed in $\$/kWh$) has been calculated imposing to zero the NPV at the end of the operating life of the plant. It means calculate the price at which is possible to sell the product to have, at the end of the lifetime of the plant, no economic losses.

4.4.2 Calculation Assumption

Estimation of BEC ("Bare Erected Cost")

In this section the estimation of the Bare Erected Cost of the components of both plant treated was analysed, considering the crucial components described in the previous Design Section.
To obtain the purchasing cost of the equipment is possible to use mathematical expressions that correlate the equipment cost to an attribute of the component. The general formula (valid for various type of components) is the following:

$$\log_{10} C_p^0 = k_1 + k_2 \cdot \log_{10}(A) + k_3 \cdot \left[\log_{10}(A)\right]^2$$

Where A is the capacity or size parameter for the equipment and k1, k2 and k3 are constant values depending on the specific equipment type. The previous formula provides the purchasing equipment cost for components operating at base conditions (C_p^0), which are identified by atmospheric operating pressure and a defined temperature level. In [50] (Turton et al.) the methodology to obtain the bare erected cost for actual operating condition starting from base conditions is provided for some equipment. Operating conditions affect design and also the materials used. Pressure effects are taken into account through a pressure factor (F_p). The equation to calculate F_p is the following:

$$\log_{10} F_p = C_1 + C_2 \cdot \log_{10}(P) + C_3 \cdot \left[\log_{10}(P)\right]^2$$

where C1, C2 and C3 are constant values depending on the equipment type and p is pressure expressed in barg. Temperature effect, and consequently the material choice, is represented by a material factor (F_M), which is provided through tables and diagrams. The bare erected cost for the section is then calculable as:

$$C_{BM} = C_p^0\left(B_1 + B_2 \cdot F_M \cdot F_p\right)$$

The value of the constants B1 and B2 is given for different components. Both F_p and F_M are greater than one.

Compressors and Pumps

The size parameters for compressors and pumps for the estimation of the purchasing equipment cost are, respectively, the fluid power and the shaft power both calculated in the Aspen Plus® models. Pressure factor F_p is present only for pumps while material factors F_M have been chosen considering the maximum temperature reached.

Heat Exchangers

Cost estimation for heat exchangers is provided as function of the Heat Exchange Area. Starting from the Pinch Point Analysis realised in the previous section is possible to calculate the Areas of the Exchangers with the following equation:

$$\Phi = U \cdot A \cdot \Delta T_{ml}$$

Where Φ is the heat flus expressed in kW, U is the global heat exchange coefficient in kW/m^2K and A is the heat exchange area in m^2. For a classical counter-current heat exchanger the logarithmic mean temperature difference ΔT_{ml} is calculated as:

$$\Delta T_{ml} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

$$\Delta T_1 = T_{in,hot\ fluid} - T_{out,cold\ fluid}$$

$$\Delta T_1 = T_{out,hot\ fluid} - T_{in,cold\ fluid}$$

As coolant, water at 15°C has been considered, respecting the minimum temperature difference between inlet and outlet considered in the Pinch Analysis ($\Delta T_{min} = 20°C$).

The global heat exchange coefficient U depends on some parameters as the physical state of the streams involved in the heat transfer and also temperature and pressure. The values obtained was taken from literature. [51]

In the following tables are presented the operative parameters of heat exchangers, firstly for the methanation plant and then relatively to the methanol production plant.

Heat exchanger are identified by the nomenclature chosen in the section 4.2.

Heat exchanger	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]	ΔT_{ml} [°C]	U [kW/m²K]	A [m²]
1	800	270,3	205,2	780	1142,4	38,2	0,35	85,4
2	800	676,4	250	300	81,6	462,2	0,2	0,9
3	676,4	415,9	35	300	172,0	378,6	0,2	2,3
4	270,3	162	106,9	250	233,6	34,9	0,3	22,3
5	300	158,5	21,2	212,4	573,5	110,6	0,27	19,2
6	415,9	46,7	21,2	212,4	243,8	85,7	0,3	9,5
C1	46,7	35	15	20	7,7	23,2	0,25	1,3
C2	162	35	15	20	273,9	62,2	0,27	16,3
C3	158,5	35	15	20	500,4	61,2	0,31	26,4
C4	300	35	15	20	302,8	98,5	0,7	4,4
C5	107,5	35	15	20	28,9	45,7	0,8	0,8
C6	108	35	15	20	31,1	45,9	0,8	0,8

Heat exchanger	Tin hot [°C]	Tout hot [°C]	Tin cold [°C]	Tout cold [°C]	Φ [kW]	ΔT_{ml} [°C]	U [kW/m^{2}K]	A [m^2]
1	270	218,8	198,8	199	753,3	40,3	0,45	41,6
2	427,6	218,8	199	199,2	450,2	85,3	0,4	13,2
3	220,6	218,8	198,8	199,2	1,3	20,7	0,2	0,3
4	800	218,8	198,8	392	383,7	128,7	0,3	9,9
5	244,5	220,6	198,8	200,4	17,8	31,7	0,16	3,5
6	795,9	427,6	200,4	270	794,2	355,9	0,27	8,3
7	800	795,9	392	396,5	8,9	403,7	0,3	0,1
8	218,8	109,1	83,4	198,8	1317,1	22,7	0,26	222,9
9	218,8	75,3	21	198,8	391,3	34,3	0,41	27,8
10	218,8	50,1	21	198,8	363,9	24,3	0,3	50,0
11	218,8	90	70	80	85,1	61,3	0,35	4,0
12	218,8	77,6	57,6	70	105,3	64,2	0,3	5,5
13	78,4	51,4	22	57,6	301,8	24,9	0,65	18,7
C1	90	35	15	20	36,3	39,9	0,27	3,4
C2	77,6	38	15	20	29,5	37,7	0,2	3,9
C3	50,1	35	15	20	32,6	24,7	0,3	4,4
C4	51,4	40	15	20	127,4	28,1	0,43	10,6
C5	109,1	35	15	20	889,1	46,3	0,95	20,2
C6	75,3	35	15	20	110,0	34,7	0,95	3,3

Pressure factor F_p and material factor F_M have been used to calculate the purchasing cost of the equipment: for very high-temperature operating exchangers a Ni-alloy was considered.

Reactors

In the Aspen Plus® models the reactors have been designed considering the number of tubes, the diameter of the tubes and the length of the reactor. The reactors considered consist in a structure similar to a heat exchanger, in which inside the tubes filled by the catalyst flow the reacting gases and outside the coolant (water) has the aim to remove the formed heat.

For the economic evaluation the equation regarding shell and tube exchanger has been considered, in which the sizing parameters is the heat exchanging area, that corresponds to the external surface of the tubes.

Moreover, the catalyst mass inside each reactor has been calculated: due to the inevitable catalyst deactivation it has to be substituted to maintain the activity of the reactions at desired values. The catalyst cost and substitution will be discussed later.

The following tables summarise the values considered for the economic evaluation of the methane reactors first and subsequently for the methanol.

	Length [m]	Tubes Diameter [m]	# Tubes	Area [m2]	Catalyst Vol. [m^3]
REACTOR 1	1,20	0,075	20	5,65	0,053
REACTOR 2	0,50	0,075	20	2,34	0,022

	Length [m]	Tubes Diameter [m]	# Tubes	Area [m²]	Catalyst mass [kg]
REACTOR 1	2	0,085	30	16,02	340,5

Like for heat exchangers, Pressure factor F_p and material factor F_M have been used to correctly calculate the purchasing cost of the equipment: the methanol reactor works at high pressure (75.7 barg) so this will greatly affect the cost.

Distillation Column

To a good estimation of the cost of the distillation section in the methanol plant a reference founded in literature has been used. [52]

However, as usually happens in these cases, the price is available for a different size than what needed. In order to correctly scale the equipment price according to it size, the following relationship between BEC and size was used [50]:

$$C = C_0 \cdot \left(\frac{S}{S_0}\right)^f$$

where S is the equipment cost attribute (representing size or capacity) and f is a cost scaling factor (smaller than one). Subscripts 0 refers to equipment with the base (i.e. available) attribute. S depends on the considered component, in this case it corresponds to the methanol flow rate.

The scaling factor (sometime also defined cost exponent) generally depends on the specific equipment type. It is set to a default value of 0,6 (giving the “six-tenths-rule” [50]) when better estimations are not available.

SOEC Electrolysers

The estimation of SOEC cost, that is the component that has a higher impact on the plant cost, has been done following information found in literature. [53]

The economic analysis was conducted considering the expert’s market perspective on the SOEC cost, that depends on several factors, like the presence of Research and Development (R&D) funding to support the innovations in materials and technology and the increasing in the production that strongly break down the prices (sometimes this is called RD&D that stands for Research, Development and Deployment)

The cost impact of production scale-up at current funding (RD&D, 1x) ranges from 17 to 30% by 2020 and 23-27% by 2030 and is higher than increasing R&D funding only (R&D, 2x and 10x): 6-18% by 2020 and 0-24% by 2030. This aligns with studies which find that cost reductions for solar PV modules should mainly be attributed to economies of scale as opposed to technology advances.

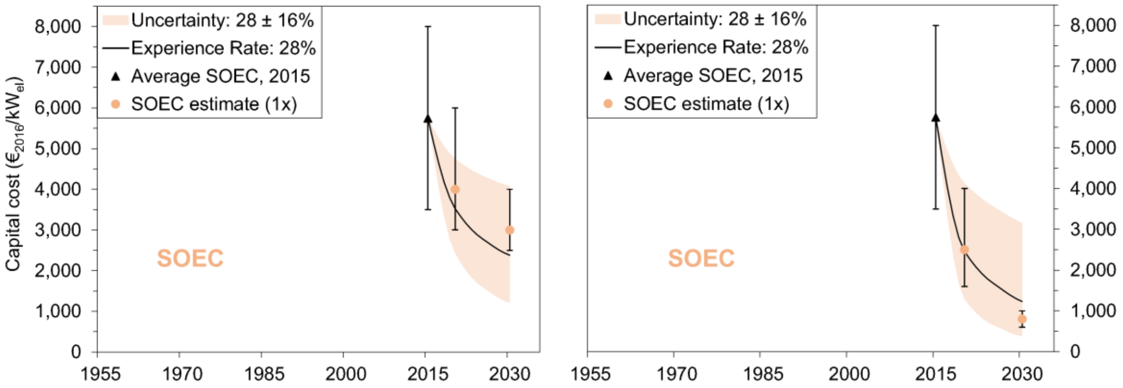


Figure 39 - Comparison of expert estimates on capital costs to capital cost projections based on experience rates for SOEC at current R&D funding (1x) without (left) and with production scale-up (right). **[53]**

Four different cases were taken into account:

- CASE 1 (2020 R&D 1x, 10th)
  The capital cost of a SOEC at current R&D funding (1x) without a production scale-up is estimating to be by the 2020, with a high uncertainty range (10th percentile [xxi] estimation), to 2500 €/kWh (about 3080 $/kWh).
- CASE 2 (2030 R&D 1x, 50th)
  The capital cost of a SOEC at current R&D funding (1x) without a production scale-up is estimating to be by the 2030, with a low uncertainty range (50th percentile estimation), to 1050 €/kWh (about 1294 $/kWh).
- CASE 3 (2030 R&D 1x, 10th)
  The capital cost of a SOEC at current R&D funding (1x) without a production scale-up is estimating to be by the 2030, with a high uncertainty range (10th percentile estimation), to 750 €/kWh (about 924 $/kWh).
- CASE 4 (2030 RD&D 1x, 10th)
  The capital cost of a SOEC at current Research and Development funding (1x) with a production scale-up (RD&D) is estimating to be by the 2030, with a high uncertainty range (10th percentile estimation), to 450 €/kWh (about 555 $/kWh).

Total Plant Cost (TPC)

The before calculated purchasing equipment cost for all the components of both plants need to be escalated from the available year to the chosen base year. To do this the following scaling relationship must be applied:

$$C = C_0 \cdot \frac{CI}{CI_0}$$

Where CI is a time-dependent cost index, while the subscript 0 refers to the time when the cost is known or calculated. In this work, the chemical engineering plant cost index (CEPCI) is the chosen cost index used to escalate costs. The base year to which all cost estimations refer to is 2017. In the following tables main assumptions useful for capital cost estimation are

---

[xxi] A percentile is a measure used in statistics indicating the value below which a given percentage of observations in a group of observations fall.

summarized, the first one is for methanation plant, the second regards methanol production plant.

Section	Reference Year	Cost in Reference year [$]	BEC [$]	TPC [$]
Compressor	2006	762203,67	1025221,9	1630102,8
Pump	2002	1800	3057,634	4861,6
Heat Exchanger	2008	1343134,9	1334003,3	2121065,2
Reactors	2008	164654,21	163679,92	260251,1
SOEC	2017			12940000
			TOTAL	16956281

Section	Reference Year	Cost in Reference year [$]	BEC [$]	TPC [$]
Compressor	2006	3162988	4254459	6764590
Pump	2002	1800	3057,634	4861,6
Heat Exchanger	2008	2626813	2608954	4148237
Reactors	2008	111546,8	110886,7	176309,9
Distillation Column	2016	164081,4	172150,9	273720
SOEC	2017			12940000
			TOTAL	24307718

For the SOEC component EPC, Project and Process Contingencies costs were not calculated because it can be considered like a “closed box” and the relative cost is already considered in the price provided by the manufacturer. The base cases for the economic analysis of both plants have been done considering a possible, near-term scenario in the SOEC price (2030 R&D 1x, 50th).

O&M Cost

The Operation and Maintenance (O&M) costs involved in the calculation have been divided in FIXOM and VAROM.

FIXOM

The FIXOM costs do not depend in the effective operating hours of the plant. The following voices have been taken into account:

- Yearly Catalyst replacement for methanation section. Data regarding the specific replacement cost (15538,5 $/m³) are provided. [54]
- Yearly Catalyst replacement for methanol plant. Data the specific replacement cost (117,7 $/kg) are provided. [55]
- Labour Cost: an average yearly cost of 75000 $ per worker is considered, a single operator is considered as a highly automated plant is assumed. [56]
- Ordinary Maintenance: considered as 0.5 % of TOC
- Stack Replacement: Replacement is related to the limited life of cells, which must be periodically replaced. Usually the lifetime of a stack is set to a value of 5 years, but in

this work the replacement cost is spread during the whole lifetime of the plant, considering it as the 2.5% of the TOC.

VAROM

The VAROM costs depend on the hours per year that the plant actually works, so they depend on the Utilization Factor (UF).

The costs considered are:

- Carbon Dioxide Cost: a reference value of 9 $/t has been considered for the base cases, but it will be varied between 3-26 $/t according to literature. [2]
- Water Cost: it was set to 1$/t according to literature. [8]
- Electricity Cost: it will be varied between 0-20 $/kWh to consider various scenarios. For the base cases it has been set to 0.3$/kWh that is an optimistic evaluation (actual market price are around 0.118 $/kWh [52]) but it can be a probable value for a power-to-fuel scenario.

The O&M variables are summarised in the following table.

	Steam Electrolysis + Methanation	Steam Electrolysis + Methanol Production
Catalyst replacement [$/year]	1165,2	40084,5
CO_2 involved [kg/h]	1593,7	2750,6
H_20 involved [kg/h]	3261,9	3261,9
EE involved [kWh]	10419,1	11712,5
O_2 production [kg/h]	2317,5	2317,5

Global Assumption

Oxygen price

The oxygen produced in the electrolysis section is a by-product that can be sold as a source of further gain. In the base cases of the economic analysis its price has been considered as 79 $/t according to literature [57]. It will be varied between 56-90 $/t to consider various scenarios.

Tax rate

In a tax system, the tax rate is the ratio at which a business is taxed. The tax calculation has already been explicated previously. The tax rate in the base case is considered as 20 %of the taxable income but it has been varied between 0 and 30% to consider different possibility.

Discount rate

The discount rate i is a powerful tool for valuing businesses or other investments with predictable profits and cash flow.

As time passes, the value of money tends to decrease; therefore, the purchasing power of income at a time in the future is worth less right now. The time value of money and uncertainty risk combine themselves to form the theoretical basis for the discount rate. A higher discount rate implies greater uncertainty, the lower the present value of our future cash flow.
In the economic analysis it was varied between 6-10%. In the base cases it has been considered as 6%.

NG market price
The price of energy in the EU depends on a range of different supply and demand conditions, including the geopolitical situation, the national energy mix, import diversification, network costs, environmental protection costs, severe weather conditions, or levels of excise and taxation.
The Natural Gas (methane) price is several affected by the final user, so two different prices have been considered:

- NG household price, set to 0.065 €/kWh (about 0,037 $/kWh)
- NG industrial price, set to 0.030 €/kWh (about 0,080 $/kWh)

Note that prices presented include taxes, levies and VAT[xxii] for household consumers but exclude refundable taxes, levies and VAT for industrial consumers. [58]

Methanol market price
The Methanol market price has an important volatility connected with the variation of the price of the crude oil. For this reason, an upper and a lower bound condition are considered: [59]

- MeOH low price, set to 380 $/t (about 0,069 $/kWh considering the LHV)
- MeOH high price, set to 496 $/t (about 0,090 $/kWh considering the LHV

[xxii] A value-added tax (VAT) is a type of consumption tax that is placed on a product whenever value is added at a stage of production and at the point of retail sale. The amount of VAT that the user pays is on the cost of the product, less any of the costs of materials used in the product that have already been taxed.

4.4.3 Economic Results

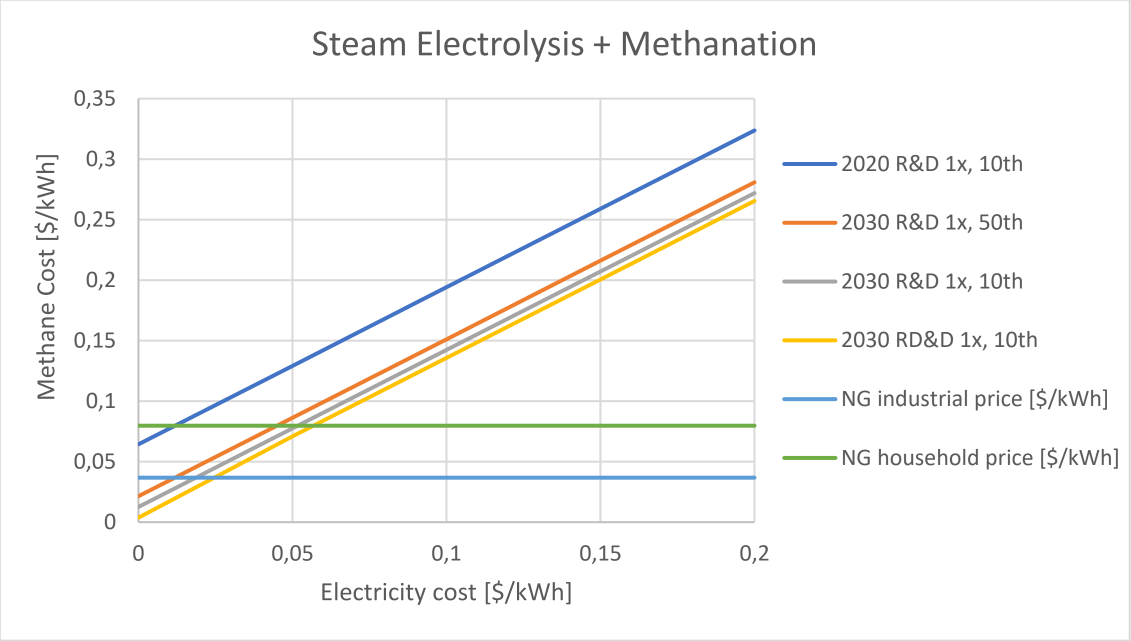
In the following table the main economic results for both plants are summarised, these values are obtained considering the base case condition:

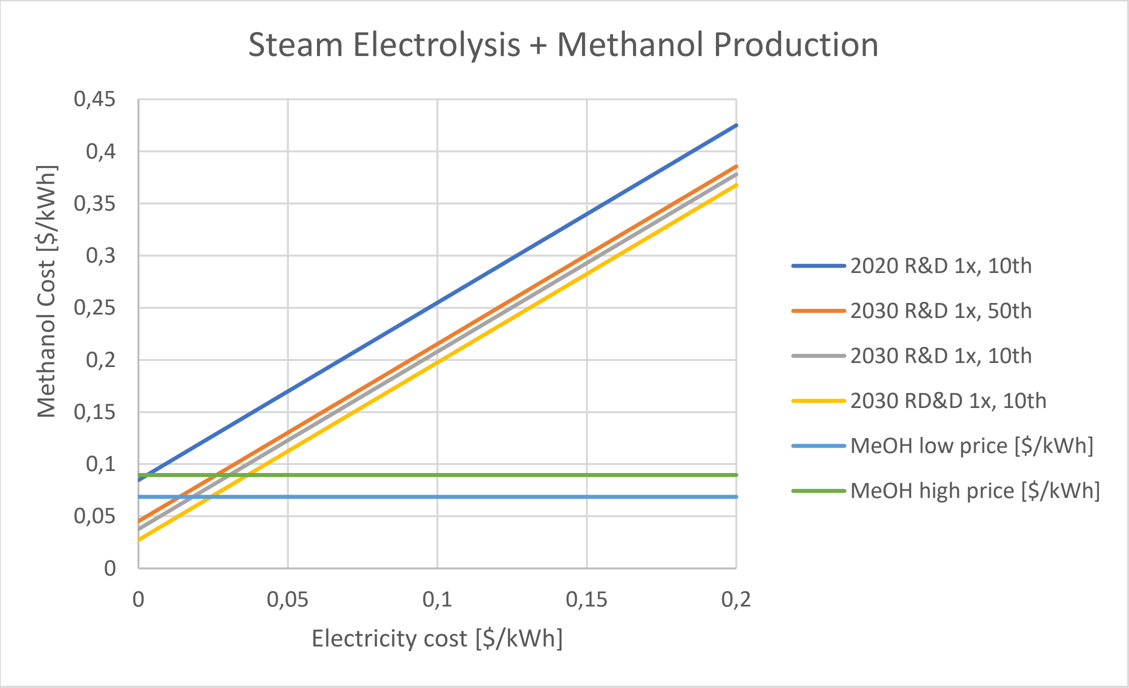
Utilization Factor	0.8
Oxygen price	79 \$/t
Carbon Dioxide Cost	9 \$/t
Electricity cost	0.03 \$/kWh

	Steam Electrolysis + Methanation	Steam Electrolysis + Methanol Production
TPC [\$]	16956281	24307718
TOC [\$]	20387450	29223877
TASC [\$]	21916508	31415668
O&M [\$/year]	687788,7	858378,8
CO_2 cost [\$/year]	100517,8	173486,7
H_20 cost [\$/year]	22859,6	22859,7
EE cost [\$/year]	2190503,8	2462440,2
O_2 revenue [\$/year]	1283067,3	1283067,3
Yearly Product Energy [MWh/year]	56305,0	48237,0

With reference to the previous table, it appears that the methanol plant is more expensive especially from the point of view of the capital costs, O&M costs and electricity. Is also evident that the Energy yearly stored in chemical form is lower for the methanol plant. Despite that, as will clarified in the next graphs, the two technologies are not so different in terms of economy return due to the very competitive price of the methane in the actual market.

Cost of the Products varying Electricity Price and SOEC scenario

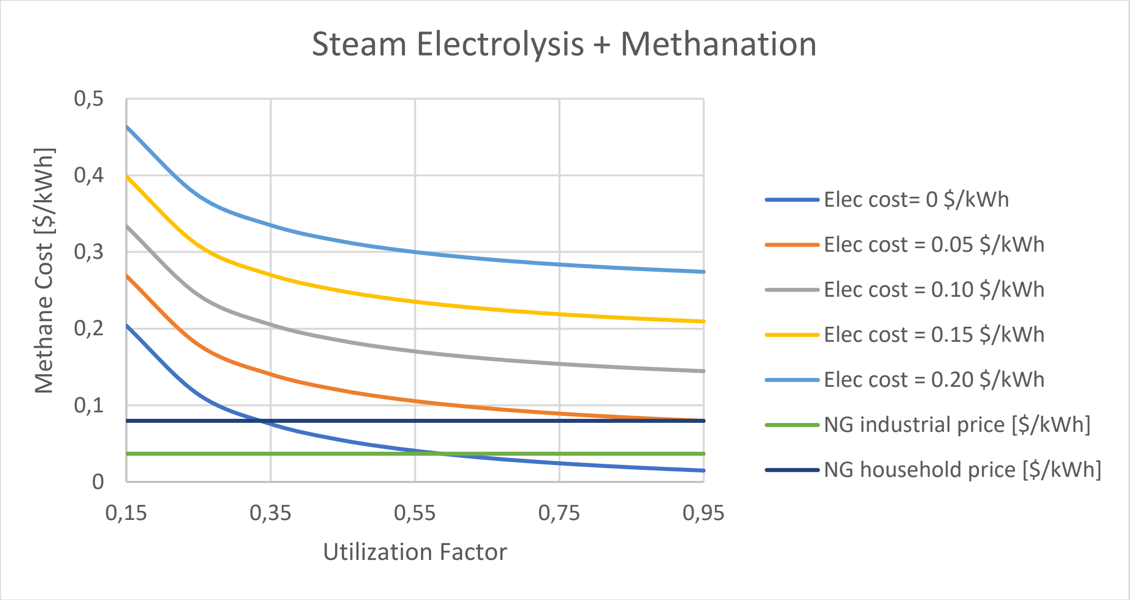


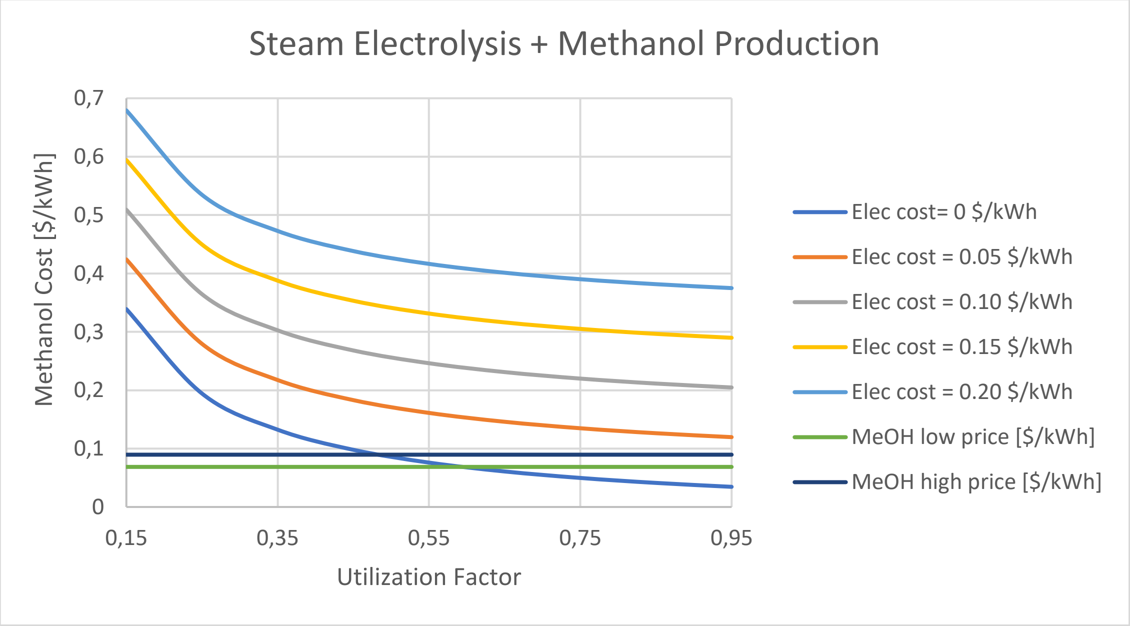


These charts describe the variation of the cost of the products as function of the electricity cost and for different scenario of the SOECs cost. In the case named “2020 R&D 1x, 10th” that shows the actual situation in the SOECs prices, the breakeven point is reached only if the electricity consumed is nearly free. With the more optimistic scenarios of the future cost of the SOECs the breakeven point is at higher electricity prices.

Considering the NG household price, the situation for the methanation seems to be better with respect to the methanol production, but is important to remember that the NG household price include taxes, levies and VAT.

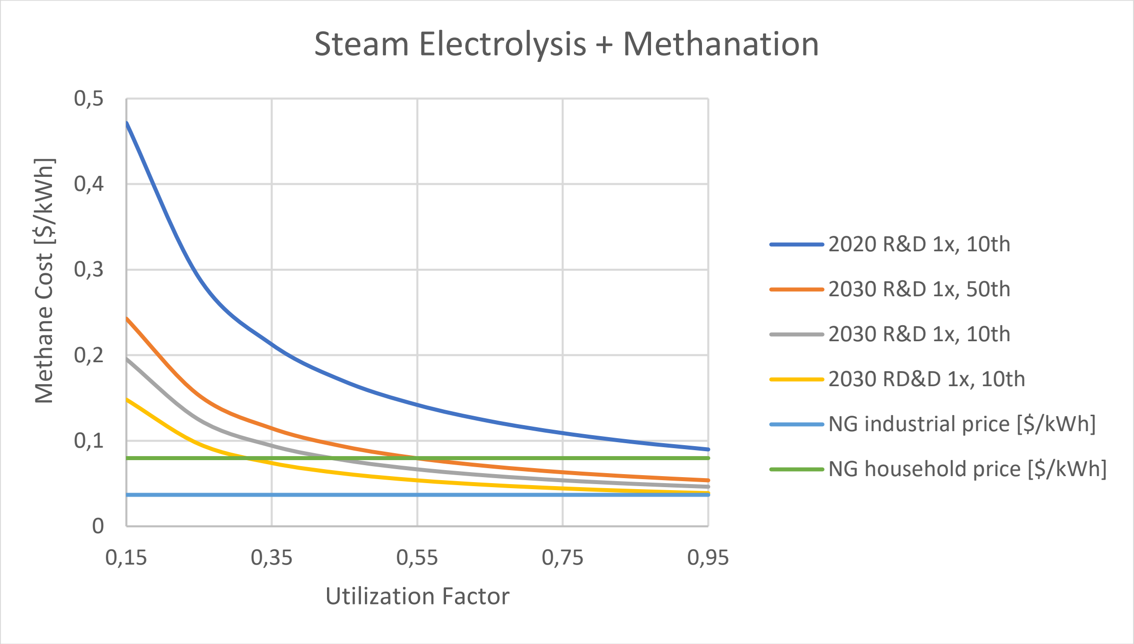
Cost of the Products varying Electricity Price and Utilization Factor

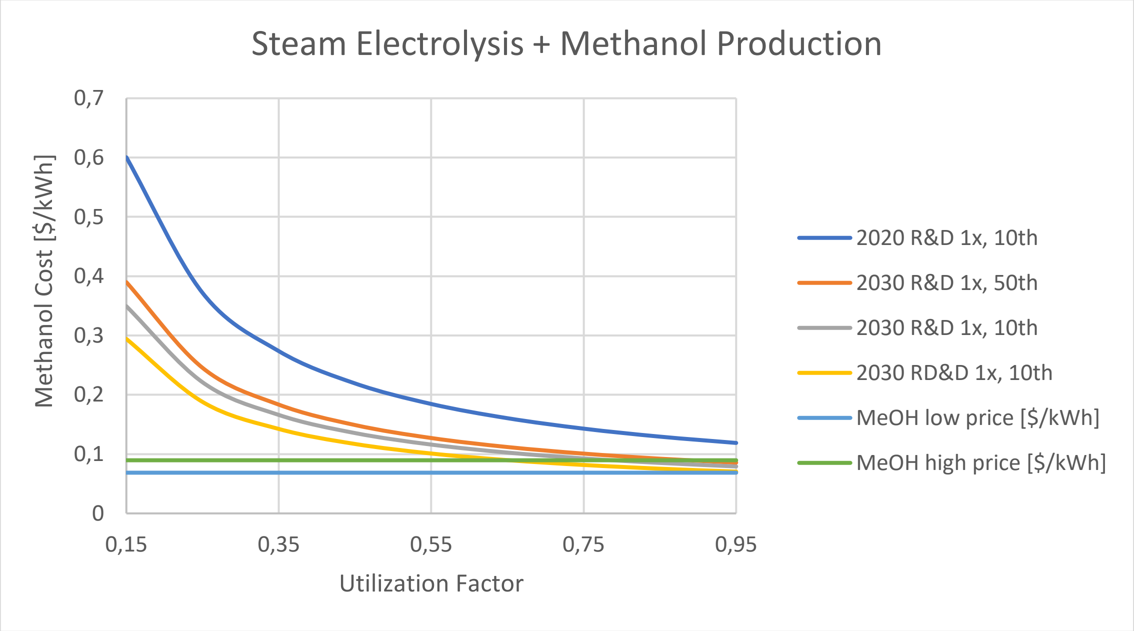

Steam Electrolysis + Methanation


Steam Electrolysis + Methanol Production

In both charts outcome that increasing the Utilization Factor, and accordingly the operational hours, leads to positive effects on the cost of the products. Indeed, the investment costs are fixed and independent by plant functioning hours, but obviously, the revenues increase with a growth of yearly hours. For similar reasons increasing hours have benefits on O&M costs, which are formed by a variable term (unaffected by operation hours) and by a fix term, for which are valid the same considerations made for capital costs. Considering the lowest prices in the market (NG industrial price and MeOH low price) the breakeven point in the case of free electrical energy is reached in both plants with a UF slightly higher than 55%.

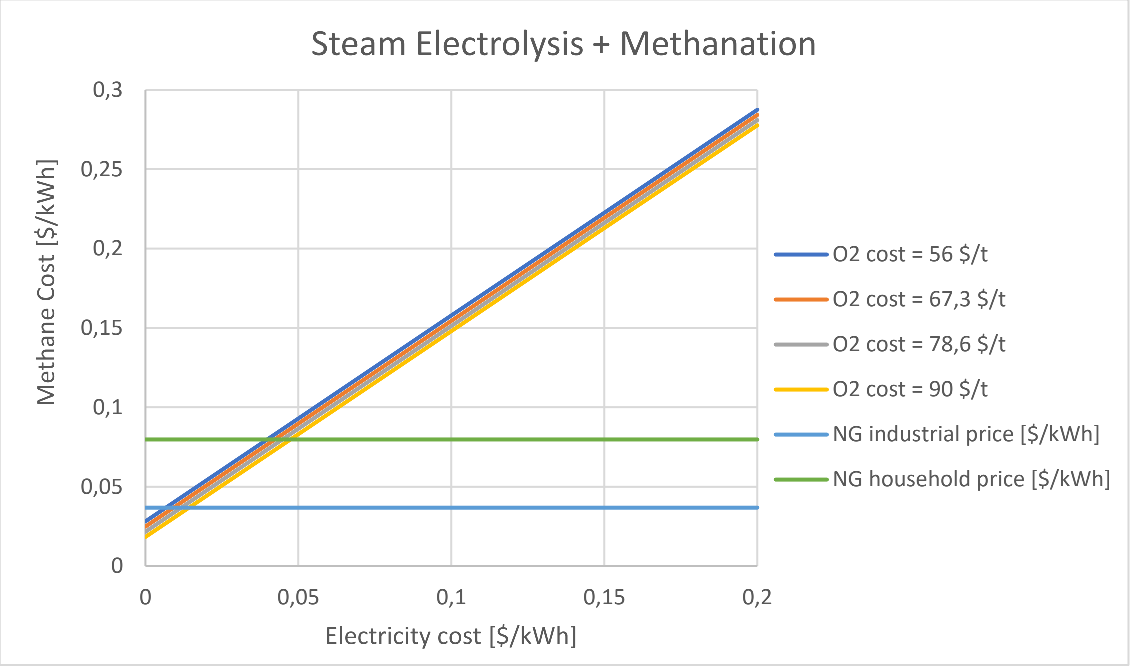
Cost of the Products varying Utilization Factor and SOEC scenario

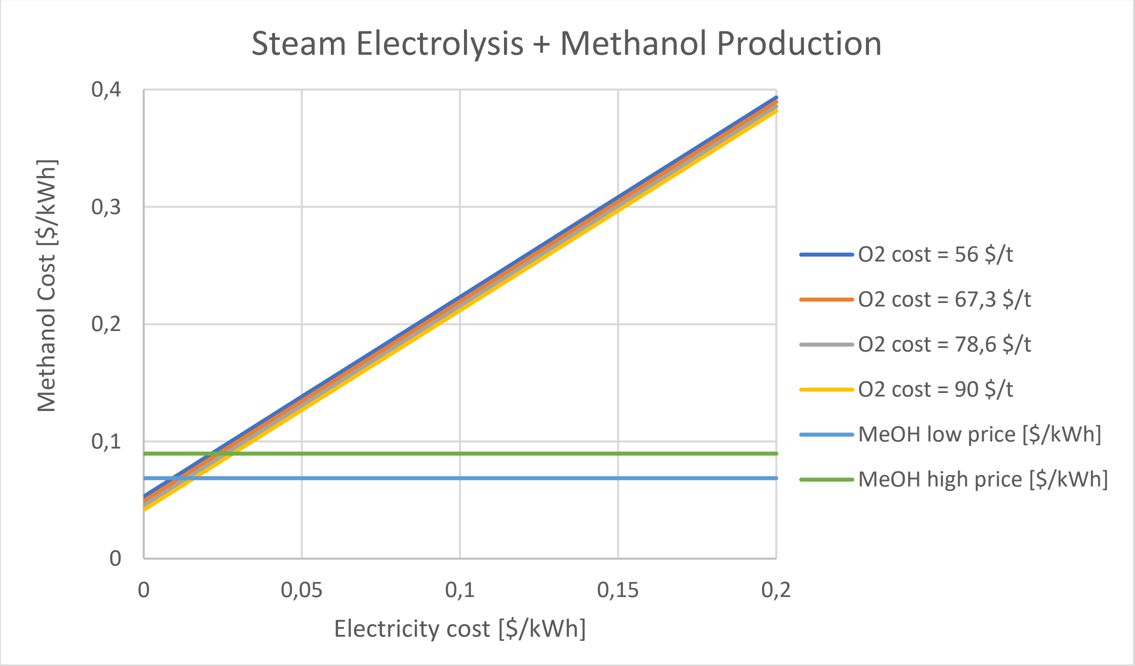




At fixed electricity price, set to 3c$/kWh, the breakeven point is not reached for both plants considering the higher (actual) price for SOEC system. These graphs underline that increasing the Utilization Factor the incidence of the capital investment is lower.

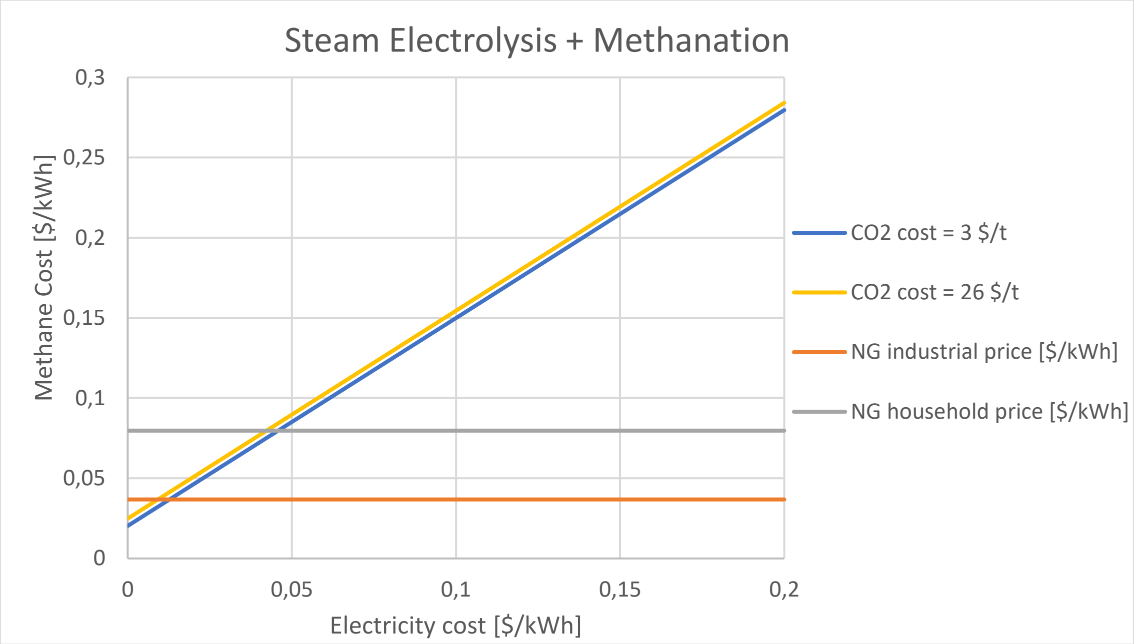
Cost of the Products varying Electricity and O_2 price

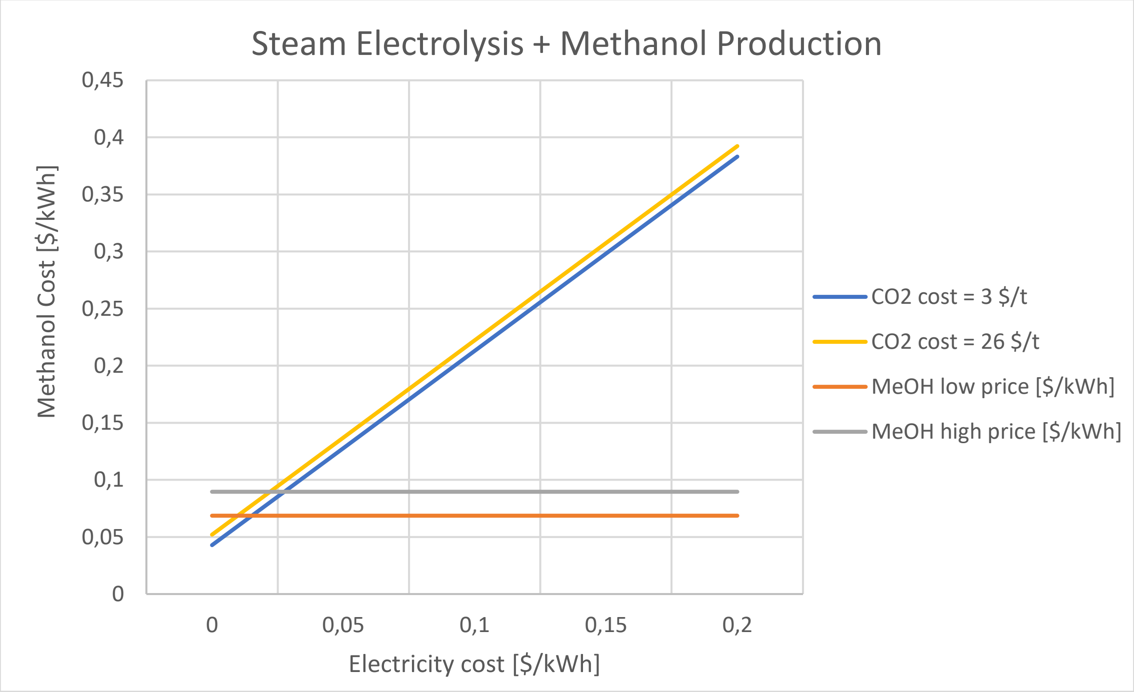




By varying the cost of selling oxygen, the price at which products must be sold increases linearly with the decrease in the cost of oxygen. This result was expected, as the higher the selling price of the oxygen will be the greater the revenues that will directly affect the cost of production of methane and methanol.

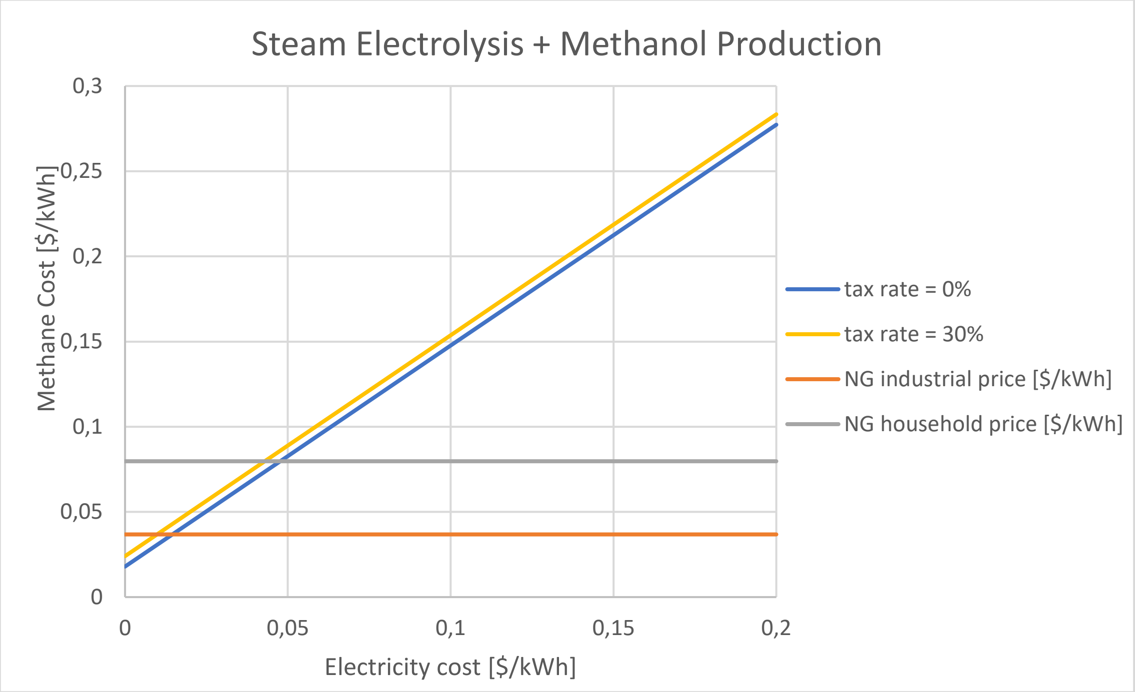
Cost of the Products varying Electricity and CO_2 price

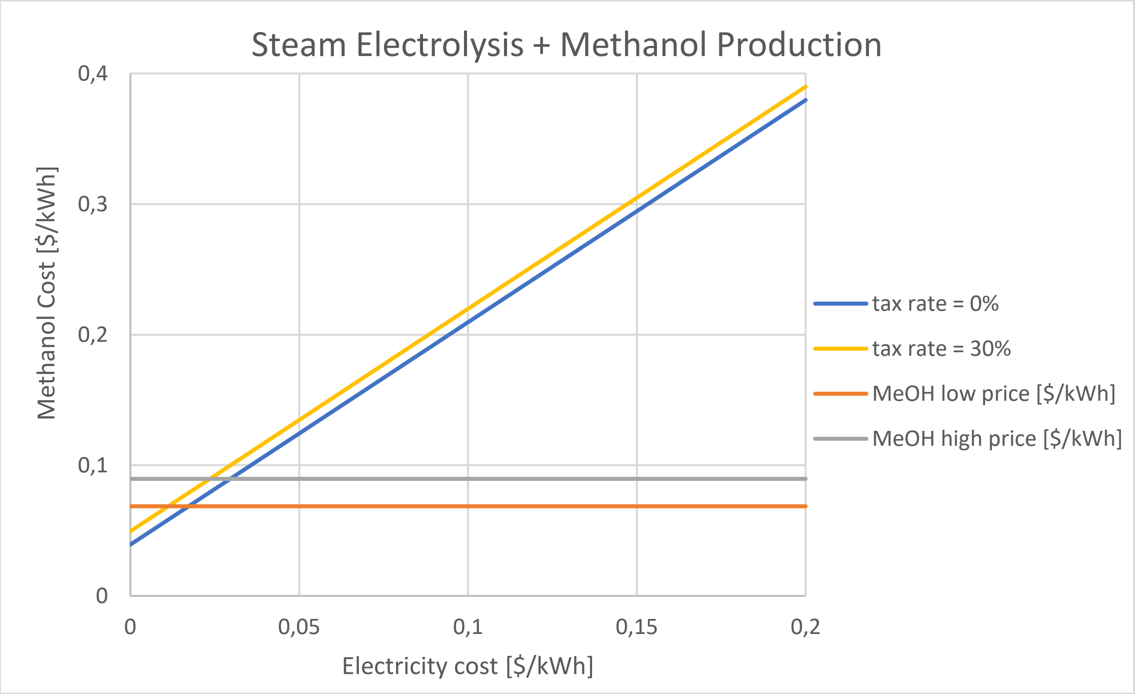




The opposite consideration to oxygen can be made for carbon dioxide: the higher the cost of carbon dioxide, the higher the selling price of the products. It can be observed that the graph shows that the increase in the price of carbon dioxide has a greater influence on the costs of methanol, as more CO_2 is consumed in the respective system.

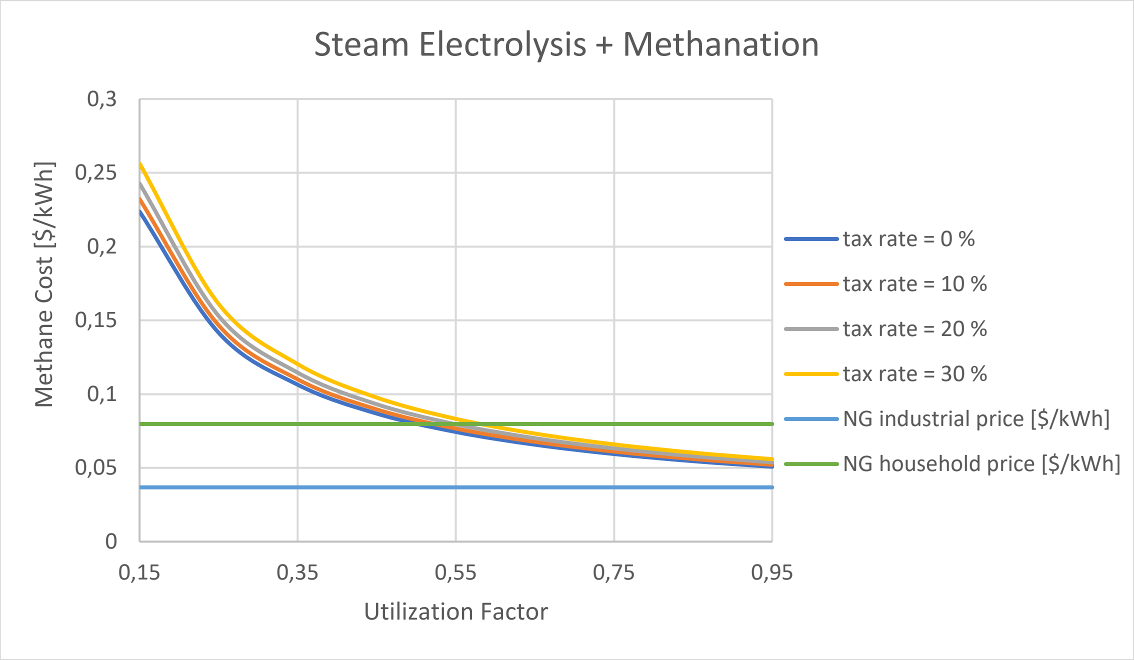
Cost of the Products varying Electricity price and Tax Rate

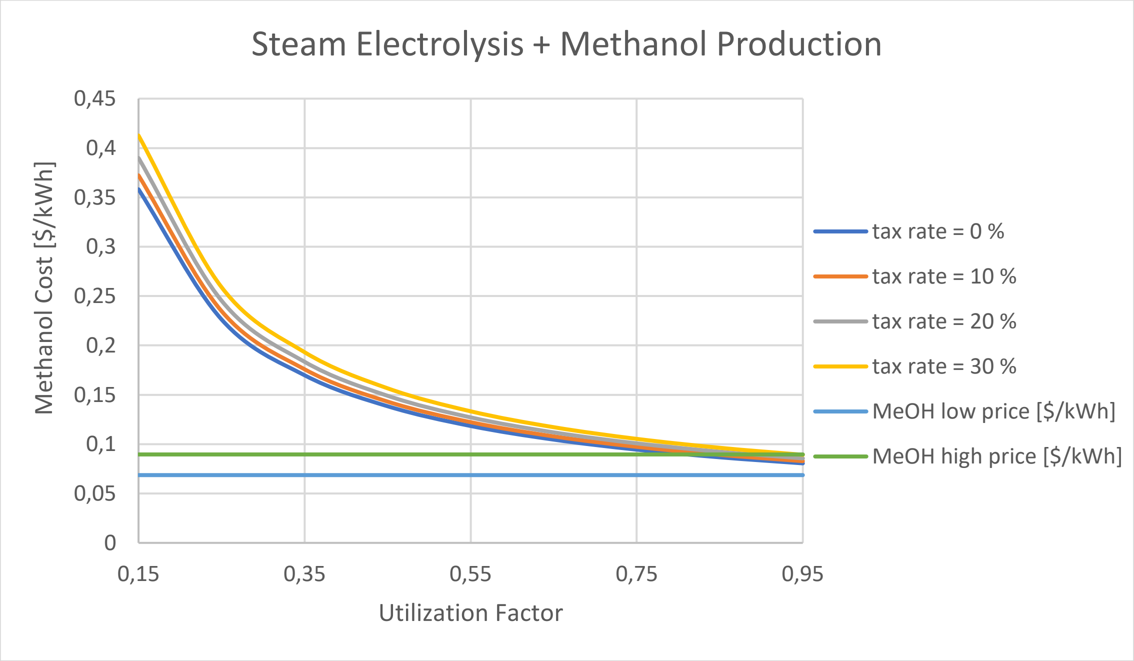




As expected, the increase in the tax rate directly affects product costs. It can be observed that, since methanol is sold at higher methane prices, revenues will be higher over the years and more taxes will be levied on them.

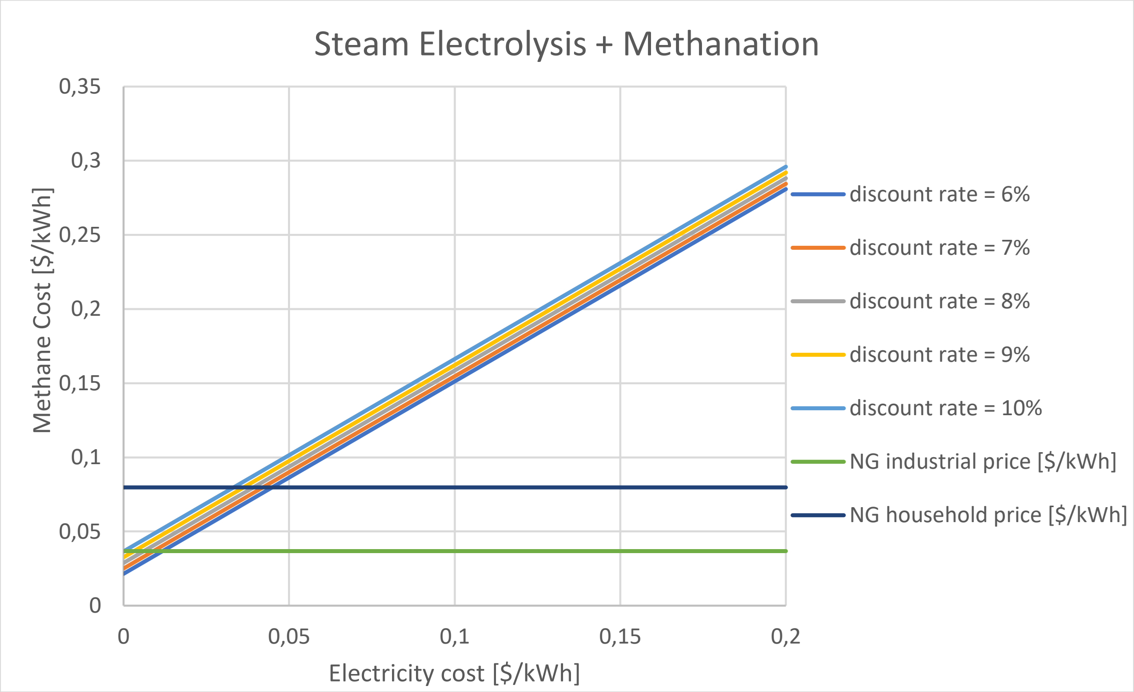
Cost of the Products varying Utilization Factor and Tax Rate

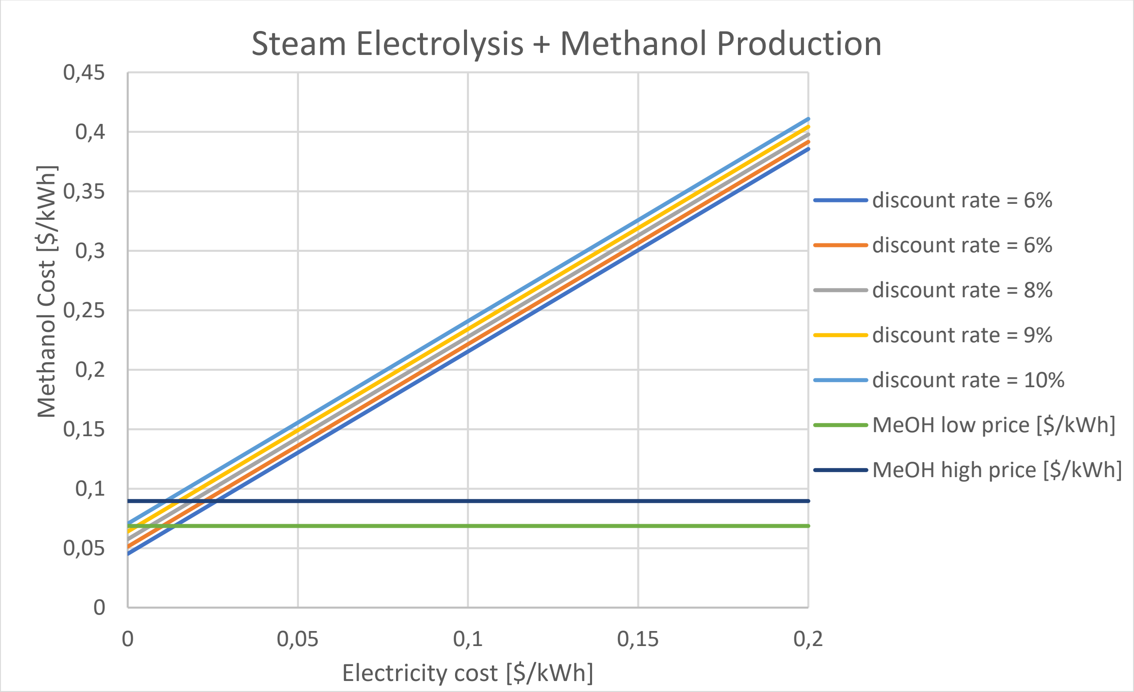




In this case the tax rate and also the utilization factor are changed: the influence of the taxes is greater with the increase in the annual operating hours as revenues are also a function of them.

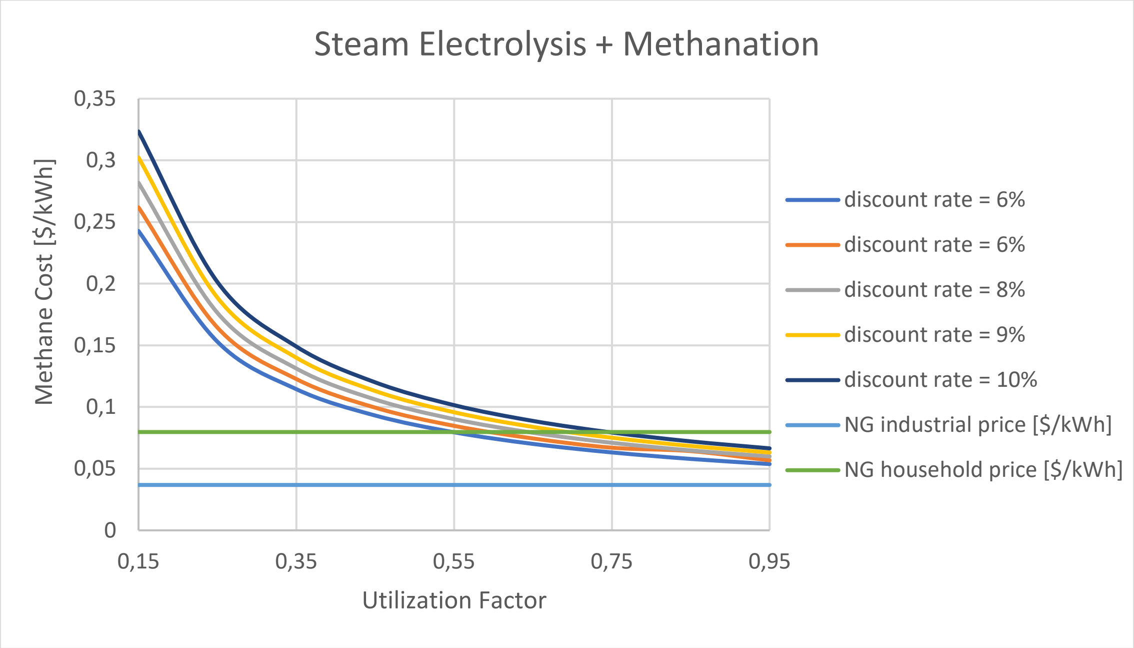
Cost of the Products varying Electricity price and Discount Rate

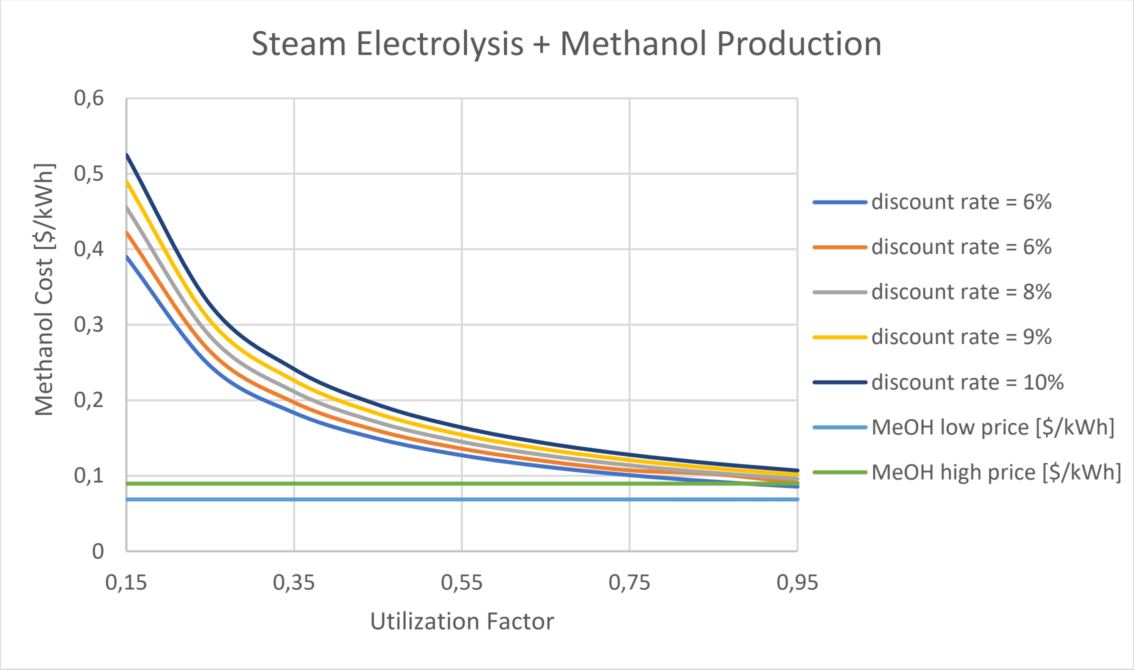




As for the tax rate, the discount rate also directly affects the selling price of the products. However, it can be observed that a greater discount rate significantly changes the conditions for both methane and methanol.

Cost of the Products varying Utilization Factor and Discount Rate



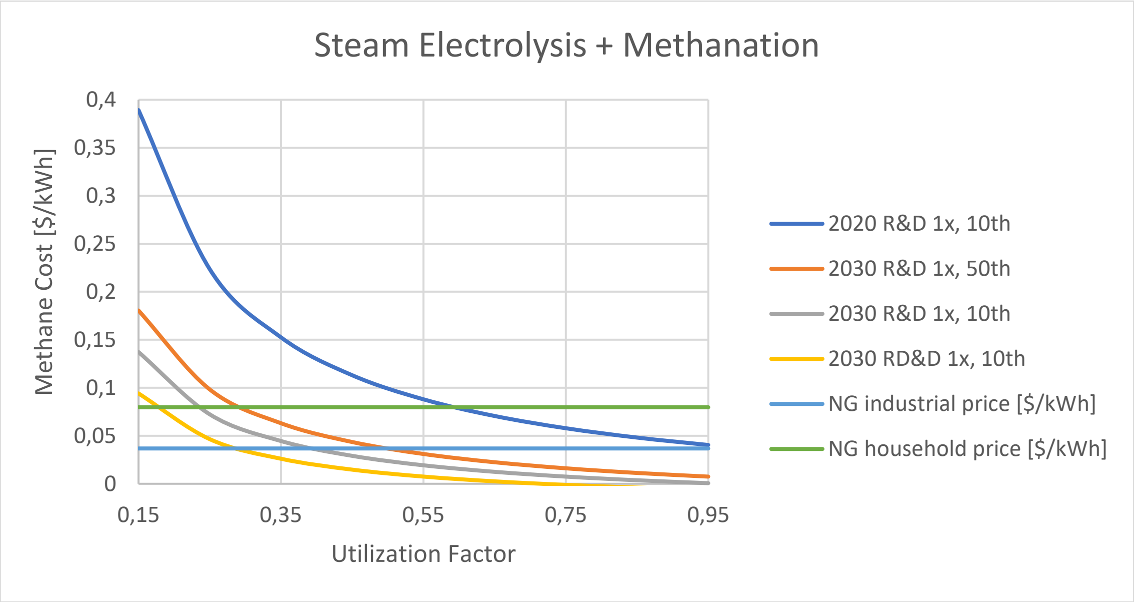


The effect of considering an higher tax rate is more evident, like for tax rate, at lower yearly operating hours.

Power-To-Gas and Power-to-Liquid: an optimistic case

In the last case considered, some optimistic assumptions have been done to simulate a possible power-to-fuel contest:

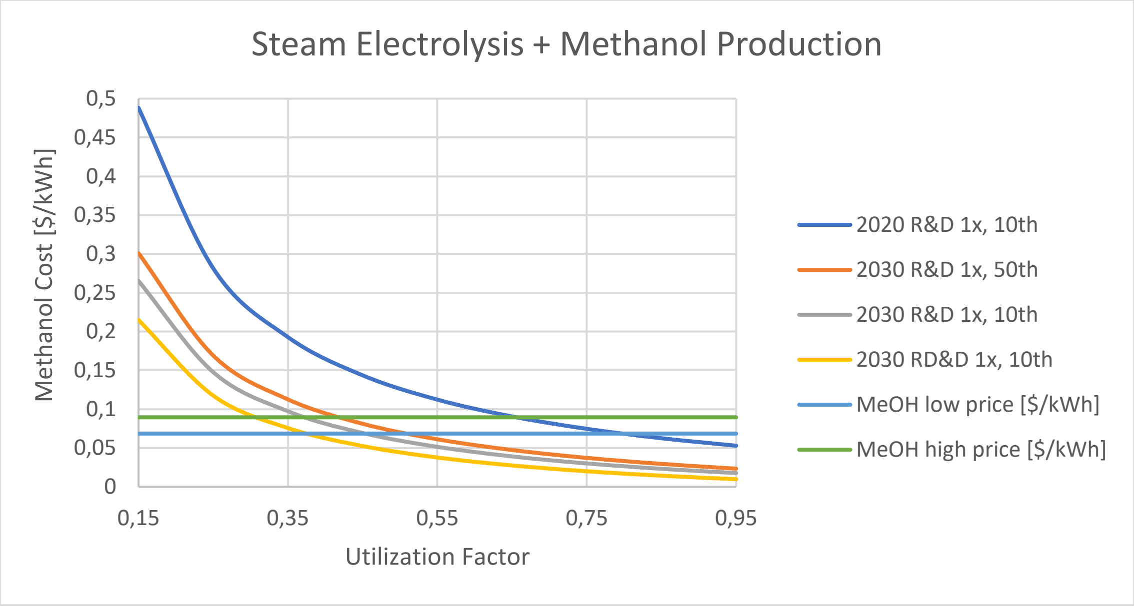
- The electrical energy cost has been set to zero considering that power-to-fuel plants use surplus energy from the network that can be provided free of charge
- The CO_2 cost has been fixed to 3 $/t, using the threshold value considered in the previous cases, considering that a future development of CO_2 capture techniques may affect the lowering of costs.
- The tax rate has been set to zero, implying with this an incentive from government agencies to environmental-friendly technologies.



Considering the current price of the SOECs systems, the breakeven point is reached at UF=60% for the NG household price, but to compete with the actual market price for industrial consumers is necessary to have a plant that is never shut down (unrealistic situation for power-to-fuel plant in which a low UF and very low electricity costs are more common).

With the “2030 R&D 1x, 50^{th}” scenario, that considers a cost of SOEC of 1050 € / kWh, the situation changes considerably: the breakeven point is get with a UF=50% (that implies near 4380 yearly operative hours) competing with the NG industrial price.

Even better situations, with very low UF, can be achieved in more optimistic evaluation of SOECs prices.



The situation is slightly different for methanol, as with the current costs of SOEC a competitive price with the market can be reached with UF between 65% and 80%.

In the scenario “2030 R&D 1x, 50th”, on the other hand, with a UF between 42% and 50% it is possible to compete with fossil-based methanol.

Conclusions

In this work, two different plants for synthetic production of fuel from hydrogen and carbon dioxide have been analysed: some considerations can be made from a technical and economic point of view.

For the methane production plant, the great exothermicity of the reaction allows a perfect thermal integration, minimizing and making almost zero the requirement of thermal energy from the outside. This factor, linked to a high conversion yield in the reactor leads to a system with high efficiencies, of about 77%.

On the other hand, for the production of methanol higher pressures are required, this fact, combined with a lower availability of heat from the reactor, means that the demand for external energy is greater, effectively reducing the efficiency of the system.

From a carbon dioxide conversion point of view, the methanol production plant contributes much more than the methanation system.

The need of higher pressure for methanol production means that the initial investment costs are larger, as the O&M costs will be higher due to a greater demand for external energy needs.

Despite this, the sensitivity on the economic analysis highlighted the fact that the two products do not behave very far from an economic point of view, unlike expectations due to the difference between the efficiency of the plants.

The very low cost on the methane market for industrial use (which corresponds to less than half the price paid for domestic consumption due to excise duties and other costs) means that it is very difficult to compete for synthetic natural gas. The production of methanol, on the other hand, compensates for the need for greater investments and costs thanks to a higher market price than that of methane.

More generally, the modelling shows that economic viability of power-to-gas for grid injection requires to reduce capital cost and to benefit from very low electricity prices. Gains on investment cost are possible with R&D efforts on electrolysis and methanation and with project costs optimisation (e.g. mutualisation of infrastructures, standardization of procedures and equipment). The purchase of electricity at a price sufficiently low (i.e. 0.03 $/kWh for 6500 hours/year) requires an electric mix with very high shares of wind and solar power and exemption of the power-to-gas plant from paying for the fixed cost of such renewable mix. This could be achieved whether through tax exemption or in specific project configurations (power-to-gas plant located at an industrial site already exempted from the tax for instance, or at a baseload production plant depending on the regulation framework).

As a result from the economic analysis of methanol plant, it is likely that in the medium to long term, gains on plant cost achieved with R&D efforts on electrolysis and scale effect on the SOEC system and on the methanol plant will be sufficient for power-to-methanol to become economically viable if the fuels produced are not taxed (i.e. competing with prices of taxed-gasoline).

References

[1] W. Kuckshinrichs, Carbon Capture, Storage and Use: Technical, Economic, Environmental and Societal Perspectives, Springer.

[2] Global CCS institute, “Accelerating the Uptake of CCS: Industrial use of Captured Carbon Dioxide,” 2011.

[3] P. Markewitz, “Worldwide innovations in the development of carbon capture technologies and the utilization of CO2,” *Energy & Environmental Science,* 2011.

[4] International Energy Agency, “CCS in the power and industrial sectors in the 2DS – “Technology Roadmap: Carbon Capture and Sequestration”,” 2013.

[5] International Energy Agency, “20 Years of Carbon Capture and Storage: Accelerating Future Deployment,” 2016.

[6] The Global CO2 Initiative, “Carbon dioxide Utilization (CO2U) – ICEF Roadmap 1.0,” 2016.

[7] Innovation for Cool Earth Forum (ICEF), Carbon Dioxide Utilization (CO2U) ICEF Roadmap 2.0., 2017.

[8] C. Graves, “Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy,” *Renewable and Sustainable Energy Reviews,* 2010.

[9] British Petroleum, “BP Statistical Review,” 2017.

[10] International Energy Agency, “A policy strategy for Carbon Capture and Storage,” 2012.

[11] European Commission Community Research, “Strengths, Weaknesses, Opportunities and Threats in Energy Research,” 2005.

[12] Renewable and Sustainable Energy Reviews, “CCS technology development in China: Status, problems and countermeasures - Based on SWOT analysis,” *Elsevier,* 2014.

[13] A. Varone, “Power to liquid and power to gas: An option for the German Energiewende,” *Renewable and Sustainable Energy Reviews,* 2015.

[14] Advanced Science News, [Online]. Available: http://www.advancedsciencenews.com/climate-busters.

[15] M. Specht, “Storing bioenergy and renewable electricity in the natural gas grid,” *FVEE AEE Topics,* 2009.

[16] The Global CO2 Initiative, “Draft Roadmap for Implementation of Carbon Dioxide Utilization Technologies,” 2016.

[17] D. Schlereth, “Kinetic and Reactor Modeling for the Methanation of Carbon Dioxide,” 2015.

[18] S. Rönsch, “Review on methanation: From fundamentals to current projects,” *Fuel,* 2015.

[19] Electrochaea, [Online]. Available: http://www.electrochaea.com/.

[20] M. Gotz, “Renewable Power-to-Gas: A technological and economic review,” *Renewable Energy,* 2015.

[21] Enea Consulting, “The potential of Power-to-gas: Technology review and economic potential assessment,” Paris, 2016.

[22] A. Bertucco, “Synthetic Natural Gas (SNG) from coal and biomass: a survey of existing process technologies, open issues and perspectives,” DIPIC - University of Padova..

[23] S. Van-Dal, “Design and simulation of a methanol production plant from CO2 hydrogenation,” *Journal of Cleaner Production,* 2013.

[24] K. M. VandenBussche and G. F. Froment, “A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst,” *Journal of catalyst,* no. 161, p. 1–10, 1996.

[25] “Askja Energy,” [Online]. Available: https://askjaenergy.com/.

[26] M. Pozzo, *Master Thesis.*

[27] J. Koponen, “Review of water electrolysis technologies and design of renewable hydrogen production systems,” 2015.

[28] M. Lehner, Power-to-Gas: Technology and Business Models, Springer, 2014.

[29] O. Ulleberg, “Modelling of advanced alkaline electrolysers: a system simulation approach,” *International Journal of Hydrogen Energy,* 2003.

[30] L. Hu, “Molten Carbonate Fuel Cells for Electrolysis,” 2016.

[31] M. Carmo, “A comprehensive review on PEM water electrolysis,” *International journal of Hydrogen Energy,* 2013.

[32] J. Holladay, “An overview of hydrogen production technologies,” *Catalysis Today,* 2008.

[33] “Wolverton Research Group,” [Online]. Available: http://wolverton.northwestern.edu/.

[34] W. Siripala, “Hydrogen Energy and Photoelectrolysis of Water,” *Research Gate,* 2004.

[35] M. Santarelli, “Course of Polygeneration and Advanced Energy Systems,” Torino, 2017.

[36] E. Giglio, *Master Thesis.*

[37] Royal Society of Chemistry, “Towards sustainable fuels and chemicals through the electrochemical reduction of CO2: lessons from water electrolysis,” *Green Chemistry,* 2015.

[38] V. Vartiainen, “Screening of power to gas projects”.

[39] Carbon Recycling international , [Online]. Available: http://carbonrecycling.is/.

[40] F. Koschany, “On the kinetics of the methanation of carbon dioxide oncoprecipitated NiAl(O)xFranz,” *Applied Catalysis B: Environmental,* 2015.

[41] Sicardi, “Corso di Reattori Chimici,” Politecnico di Torino, 2011.

[42] H. Teshima, “Determination of Effective Diffusion Coeficient of Carbon Dioxide in Porous Catalyst by the Isotropic Exchange Reaction,” Department of Chemical Engineering, Nagoya University, Nagoya, Japan, 1973.

[43] D. Mignard, “Methanol synthesis from flue-gas CO2 and renewable electricity: a feasibility study,” *International Journal of Hydrogen Energy,* 2003.

[44] G. Graaf, P. Sijtsema, E. Stamhuis and G. Joosten, “Chemical equilibria in methanol synthesis,” *Chemical Engeneering Science,* vol. 41, no. 11, pp. 2883-2890, 1986.

[45] Aspen Plus®, “Aspen Plus User Guide,” Aspen Technology, Inc., 2000.

[46] V. Verda, Metodi Termodinamici per l'uso efficiente delle Risorse Energetiche, Esculapio, 2015.

[47] I. C. Kemp, Pinch Analysis and Process Integration: A User Guide on Process Integration for the Efficient Use of Energy, Elsevier Ltd, 2007.

[48] Parliamentary Office of Science and Technology, “Carbon Footprint of Electricity Generation,” London, 2011.

[49] National Energy Technology Laboratory, “Quality Guidelines For Energy Dystem Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance,” U.S. Department of Energy, 2011.

[50] R. Turton, Analysis, Synthesis and Design of Chemical Processes, Pearson Education, 2008.

[51] C. Bonacina, Trasmissione del Calore, CLEUP, 1989.

[52] Joint Research Centre of the the European Commission, Institute for Energy and Transport, “Techno-economic and environmental evaluation of CO2 utilisation for fuel production: Synthesis of methanol and formic acid,” 2016.

[53] O. Schmidt, “Future cost and performance of water electrolysis: An expert elicitation study,” *International Journal of Hydrogen Energy,* 2017.

[54] DOE/NETL, “Cost and Performance Baseline for Fossil Energy Plants Vo.2: Coal to synthetic natural gas and ammonia,” National Energy Technology Laboratory, 2011.

[55] M. Pérez-Fortes, “Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment,” Applied Energy, 2015.

[56] E. Giglio, “Synthetic natural gas via integrated high-temperature electrolysis and methanation,” *Journal of Energy Storage,* 2015.

[57] M. Gassner, “Thermo-economic optimisation of the integration of electrolysis in synthetic natural gas production from wood,” *Energy Journal,* 2007.

[58] Eurostat, “Eurostat,” [Online]. Available: http://ec.europa.eu/eurostat.

[59] Metanex, “Metanex,” [Online]. Available: https://www.methanex.com/.

Acknowledgments - Ringraziamenti

Vorrei ringraziare il Prof. Massimo Santarelli per avermi affidato una tematica alla quale ero molto interessato, che ho potuto approfondire durante lo svolgimento di questa Tesi ed inoltre per avermi dato la possibilità di fare una positiva esperienza all'estero.

Ringrazio vivamente l'ing. Emanuele Giglio per il grandissimo aiuto fornitomi in questo periodo, posso dire di aver molto appreso grazie alla sua disponibilità e alla sua ineccepibile conoscenza dei temi trattati.

Many thanks to Dr. Annelies Bobelyn for the hospitality showed during my stay at the Eindhoven University of Technology and for the help that I received in dealing with totally new issues for me, despite all the difficulties that have arisen.

A special thanks to Dr. Alicia Soto, both for the help given in this period and above all for having always believed in my abilities.

Ovviamente non possono mancare i ringraziamenti per i miei più vecchi amici Maurizio, Nicolò, Marco, Simone e Alessandro con i quali ho condiviso le esperienze più importanti della mia vita.

Ringrazio Marco e Caterina, per essere sempre presenti dai tempi del liceo, per le infinite chiacchierate e per i bei ricordi che ci legano.

Un doveroso ringraziamento va ai miei cari amici della pizzeria, che fin dall'inizio hanno seguito e sostenuto il mio periodo universitario, tra tutti Massimo, Paola, Maurizio e Giusy.

Vanno ringraziati tutti i compagni del Politecnico che con me hanno condiviso momenti felici ed altri meno, ma grazie ai quali posso dire di aver concluso un'avventura, in particolare Alessandro e Danilo, Francesca, Stefano, Alessandro e Lorenzo.

Voglio ringraziare coloro che, chi da più tempo e chi da meno, sono usciti dalla mia vita quotidiana ma che sempre ricorderò con affetto e spero che in questo giorno speciale possiate essere orgogliosi di me.

Ringrazio mia sorella Silvia, per la sua perenne disponibilità e il suo affetto, per aver sempre capito le mie difficoltà ed aiutato a superarle. Un ringraziamento va a mia nonna Anna, per avermi seguito e supportato in tutti questi anni.

Dedico questo traguardo ai miei genitori, perché più di tutti sapete quanta fatica e quanti sacrifici è costato a me e a voi, per avermi sostenuto nei momenti più difficili, per avermi ascoltato con pazienza nei momenti di euforia ma soprattutto per aver sempre creduto in me.