Thermodynamic and economic analysis of a plant for the CO_2 hydrogenation for methanol production

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Abstract. A major goal of politics, society, and industry is the reduction of carbon dioxide (CO_2) emissions in order to prevent anthropogenic climate change and an increase in earth's temperature. In addition, the expansion of renewable energies and the use of nuclear power, CO_2 capturing (e.g. from exhaust gases), is regarded as a promising strategy to reduce global CO_2 emissions. In this context, the Power-to-X technologies can provide an innovative energy storage concept by combining the main trends of energy systems aiming at high shares of renewable energies, reduction of CO_2 emissions and sector coupling. A promising approach is the production of methanol as a chemical raw material or fuel. The goal of this paper is to present (i) an extensive thermodynamic analysis for the methanol production from carbon dioxide and hydrogen and (ii) an economic analysis for the process based on the thermodynamic studies. The thermodynamic analysis was carried out in the simulation tool Aspen Plus™ in order to investigate the impact of the operating temperature and pressure on the performance of the synthesis unit. Based on the thermodynamic results, an economic analysis has been performed in order to define the most feasible solution. For a defined optimal operating temperature, the fixed and operating costs and the methanol production cost were evaluated for different operating pressures. Finally, a sensitivity analysis has been performed in order to define the minimum methanol selling price that allows for a payback period of 10 years for different values of the electrical energy purchasing price.

Nomeclature
CCU: Carbon Capture Unit
MPC: Methanol Production Cost
PEC: Purchase Equipment Cost
PEMEL: Proton Exchange Membrane Electrolyser
PFR: Plug Flow Reactor
PtF: Power to Fuel
TCI: Total Capital Investment
WACC: Weighted Average Cost of Capital

1 Introduction

A major goal of politics, society, and industry is the reduction of carbon dioxide (CO_2) emissions in order to prevent anthropogenic climate change and an increase in earth's temperature. Besides the expansion of renewable energies and the use of nuclear power, CO_2 capturing from exhaust gases is regarded as a promising strategy to reduce global CO_2 emissions.

In this context there are two main technologies discussed today in research and application; Carbon Capturing and Storage (CCS) and Carbon Capturing and Utilization (CCU) [1, 2]. Considering CCU, the Power-to-X technologies provide an innovative energy storage concept by combining the renewable energies, and the CO2 coming from the industrial or agriculture sector, to produce innovative chemicals (such as methanol) with low environmental impact that can be used for different purposes (as fuel or as chemical feedstock in substitution of the fossil-based products)

A promising approach is the production of methanol as a chemical raw material or fuel [19]. The global demand for methanol is growing steadily and it is expected to be about 118 million tons per year by 2020 [3]. Today the methanol production is mostly based on steam reforming of natural gas. But recent studies demonstrated that it is possible to produce methanol directly from carbon dioxide and hydrogen (e.g. from electrolysis) [4] [5].

The goal of this paper is to present (i) an extensive sensitivity analysis for the methanol production from carbon dioxide and hydrogen and (ii) an economic analysis for the process based on the sensitivity studies.

1.1 Process description

The plant layout for the CO_2-based methanol production is shown in figure 1. It is composed by (i) a pressurised PEM water electrolyser at 30 bar for the hydrogen production, (the co-produced oxygen is assumed to be sold to the market); (ii) an amine-based CO_2 capture unit where the required amount of CO_2 is separated from exhaust gases of a coal fired power plant and stored into a tank; (iii) a CO_2 compressor to bring the CO_2 pressure from 1 bar (at the outlet of the tank) up to the hydrogen pressure (30 bar) and mix them together; (iv) a mix compressor to bring the H_2/CO_2 mixture pressure at the operating pressure and mix it with the with the recirculated stream; (v) an heat exchanger that recovers the thermal energy from the gas at the outlet of the reactor to preheat the fresh inlet; (vi) a methanol reactor for the methanol synthesis;

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(vii) a separation section where the water and methanol are condensed and the unreacted gases are separated; (viii) a recirculation compressor to recirculate the unreacted gas at the outlet of the reactor. A constant pressure drop of 3.5 bar is assumed over the recirculation cycle, with a pressure drop of 1.5 bar over the reactor.

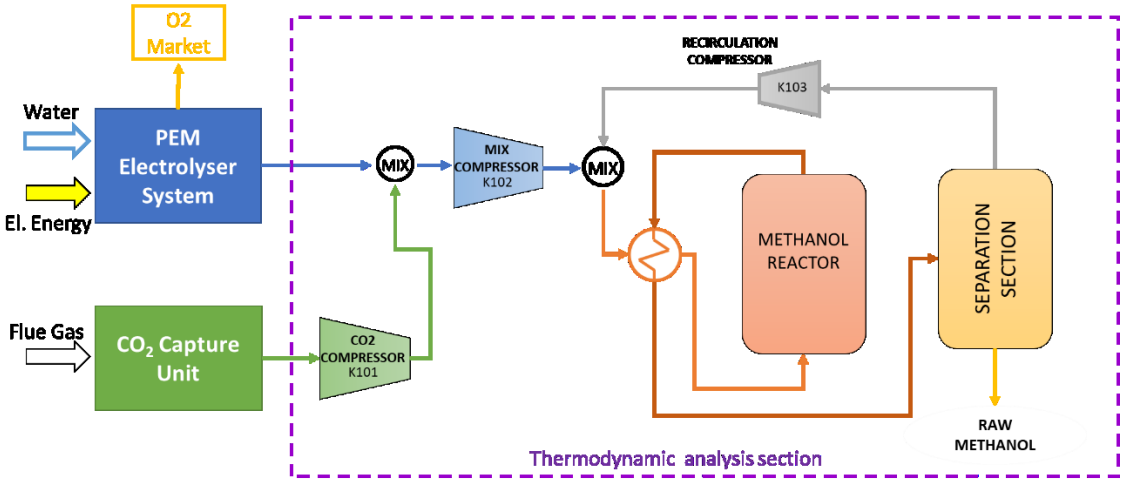

Fig. 1. Flowsheet of CO_2-based methanol synthesis

In Table 1, the technical assumptions of the main components are reported.

Table 1. Technical data [8, 9, 10].

PEM Electrolyser		**Methanol Reactor**	
Electrical consumption	4.7 kWh/Nm^3 H_2	Reactor type	PFR
Operating Pressure	30 bar	Length	12.2 m
PEMEL efficiency	75% (HHV based)	Number of tubes	8000
PEM availability	95%	Tube diameter	0.03675 m
Carbon Capture Unit		Pressure drop	1.5 bar
Treatment kind	Amines (MEA) (30%)	Catalyst mass	104 t
Flue gases inlet T and p	40°C, 2 bar	**Compressors**	
CO_2 capture rate	90%	Efficiency	0.9

There are three overall reactions taking place in the reactor. The hydrogenation of CO_2 (1), the hydrogenation of CO (2) and the reverse water gas shift reaction (3).

$$CO_{2(g)} + 3H_{2(g)} \rightleftharpoons CH_3OH_{(g)} + H_2O_{(g)} \qquad \Delta H^O(298\ K) = -49\ \text{kJ mol}^{-1} \tag{1}$$

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \qquad \Delta H^O(298\ K) = -91\ \text{kJ mol}^{-1} \tag{2}$$

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \qquad \Delta H^O(298\ K) = +42\ \text{kJ mol}^{-1} \tag{3}$$

For the modelling of the reactions inside the reactor the kinetic reaction parameters at a copper-based catalyst from Graaf et. al. [6, 7] are used. The formation of methanol is exothermal and leads to a reduction in the number of moles. For this reason, according to the principle of Le Chatelier, low temperatures and high pressures are advantageous for the methanol synthesis. An optimal conversion in the reactor should be achieved by isothermal operation at low temperatures and high pressures.

The process control is subject to two conditions. First, the mole flow through the reactor is held constant at 10,000 kmol/h. This is achieved by adjusting the mole flow of the hydrogen and carbon dioxide inlet streams of the methanol synthesis. The second condition is the stoichiometric number in front of the reactor which is defined as

$$SN = \frac{(nH_2 - nCO_2)}{(nCO + nCO_2)}. \tag{1}$$

An SN equal to 2 corresponds to the stoichiometric ratio, higher numbers indicate over-stoichiometric conditions and lower numbers indicate under-stoichiometric conditions. Therefore, higher numbers increase conversion but also increase recirculation due to the excess H_2 at the reactor outlet. Lower numbers result in a decrease of conversion since the reaction is limited by educts. For controlling both inlet streams are adjusted to keep a constant SN of 2 in front of the reactor, to minimize recirculation and prevent limited conversion by lack of educts.

1.2 Simulation results for the thermodynamic analysis

For the analysis, the process temperature is varied between 190°C and 300°C in steps of 10°C and the process pressure is varied between 30 bar and 100 bar in steps of 10 bar. The results at 210°C and different pressures are shown in figure 2. The methanol yield is an indicator of the performance of the reactor and is defined as follows:

$$Y = \frac{(n_{CH_3OH,out} - n_{CH_3OH,in})}{(n_{CO_2,in} + n_{CO,in})} \quad (2)$$

The methanol yield increases with increasing pressure, as described by the principle of Le Chatelier. An increase of 131% can be noted by changing the pressure from 30 bar to 100 bar. The feed to the process increases due to the implemented control, which keeps the mole flow through the reactor constant. If the methanol yield increases, the recirculation decreases, and more feed must be fed into the process to keep the mole flow through the reactor constant. The increase in feed results in an increase of the compressor work by 329% from 30 bar to 100 bar, but the specific compressor work per ton of methanol produced only increases by 87%.

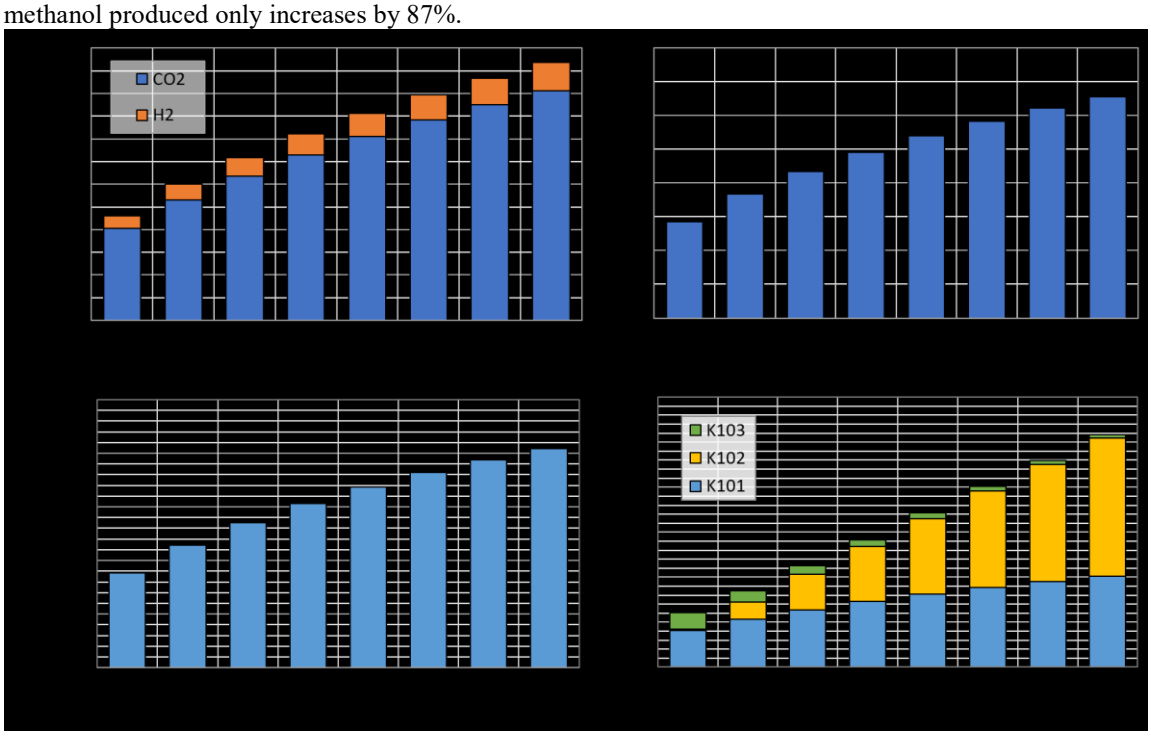

Fig. 2. Plots of the methanol yield, total methanol production, total feed consumed for H_2 and CO_2 and total compressor work.

2 Economic analysis

Based on the thermodynamic results, an economic analysis is performed in order to evaluate the impact of the operating pressure on the installation and operating cost of the plant for the methanol production and to define the best solution that minimises the methanol production cost (MPC). Moreover, the option to sell the oxygen co-produced by the water electrolyser is considered and its impact on the potential reduction in the MPC is estimated. In the following section, the main assumptions used to perform the economic analysis are reported

2.1 Assumptions

It is assumed that the plant runs for 8500 h per year and the electrical energy required is purchased from the grid at 50 €/MWh (that is the average market price in Germany in 2018 [9]). The size of the electrolyser depends on the operating pressure: as the methanol reactor size is fixed, increasing the operating pressure, the amount of H_2 at the inlet of the reactor increases and the PEMEL size as well.

The fixed and variable costs are evaluated in reference to the economic assumptions reported in Tab 2. The capital cost of the plant components is estimated using cost functions that correlate the component cost to the size using a specific scale factor and to the operating pressure. In particular, the methanol units cost function comprises the reactor, the separation unit, the thermal exchangers and the function that expresses the effect of the operating pressure takes into account the increasing cost for both the material and the safety issue management.

Table 2. Economic assumptions [9-17]

Plant lifetime:	20 years	OPEX of PEMEL	45 €/kW
Equivalent operating hours:	8500 h	OPEX of CCU	7 €/tCO_2
WACC	5%	OPEX of Methanol Unit	25 €/tCH_3OH
O_2 selling price	150 €/ton	TCI factor	2.2
El. Energy cost	50 €/MWh		
Catalyst cost	160 €/kg		

Catalyst replacement	3 years
Cost functions	
PEM electrolyser	$C_{PEM} = 1.2 * 10^6 * (P_{inst})^{0.85}$
CO_2 Capture Unit	$C_{CCU} = 2.4 * 10^3 * (M_{in})^{0.65}$
CO_2 compressor	$C_{compressor,CO_2} = 2.651 * 10^3 * \left(M_{CO_2} * ln\beta\right)^{0.65}$
Mix compressor	$C_{compressor,mix} = 36.858 * 10^3 * (M_{Mix} * ln\beta)^{0.65}$
Recirculation compressor	$C_{compressor,recic} = C_{compressor,CO_2}$
MeOH synthesis unit	$C_{MeOH\ Unit} = (7493.6 * 10^3 * (Q_{in})^{0.65}) * (7 * 10^{-6} * p^2 + 0.0016 * p + 1)$
P_{inst} [MW], M [kg/h], Q [m3/h], p [bar]	

The MPC with and without the O_2 selling options is calculated as follows:

$$MPC = \frac{Total\ annual\ costs}{Annual\ methanol\ production} \tag{4}$$

$$MPC_{O_2} = \frac{Total\ annual\ costs - O_2 annual\ sales}{Annual\ methanol\ production} \tag{5}$$

The total annual cost is the sum of the fixed costs (the annual rate of the TCI calculated using a WACC of 6%) and the variable cost (made of the annual cost of the electrical energy purchasing, the OPEX of PEM and the methanol Unit) The annual methanol production and the total annual costs depend on the operating pressure as reported in the previous section.

2.2 Results

In Fig. 4 and 5 show the Purchased Equipment Cost (PEC), and fixed and variable annual costs at the different operating pressures, respectively.

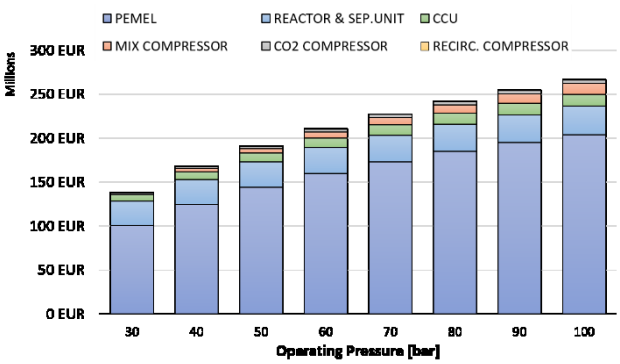

Fig. 4. Purchased equipment cost breakdown for different operating pressure

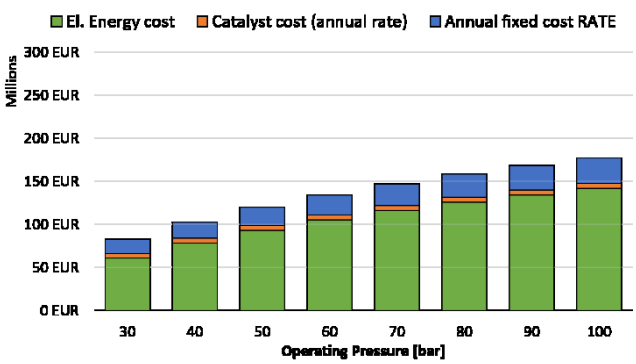

Fig. 5. Fixed and Variable annual cost breakdown for different operating pressure

The total equipment purchasing cost grows as the operating pressure increases due to the increase in the technical and safety requirements, and above all, the increase in the PEMEL size which represents the major cost (>70%). With regard to the fixed and variable annual costs, the major expense is the electrical energy purchase (>50%, mostly due to the PEMEL consumption), followed by the annual fixed cost rate and the OPEX of PEMEL.
In Fig. 6 the MPC and the MPC_{O2} are reported as a function of the operating pressure.

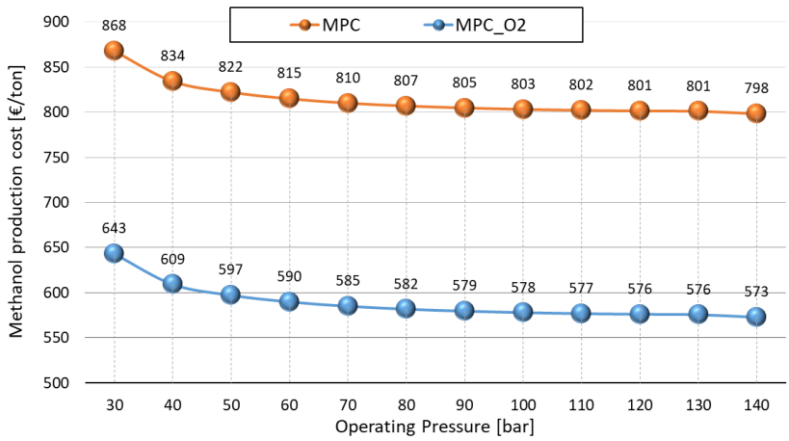

Fig. 6. The MPC and MPC$_{O2selling\ option}$ as function of the operating pressure

The methanol production cost decreases as the operating pressure increases: from 30 bar to 80 bar the decrease is significant (around 60 €/ton); at operating pressures higher than 80 – 90 bar, the MPC reduction is not high enough to compensate for the increasing technical complexity and safety issues due to the high pressure. Therefore, the operating pressure, that reasonably minimises the MPC, is around 80 – 90 bar. Taking into account the revenues from the sale of oxygen, co-produced by the PEMEL, the MPC is reduced by about 30%.

In the end, a sensitivity analysis was carried out to investigate the impact of the main affecting parameters (such as electrical energy purchasing price, methanol selling price, oxygen selling price and capital cost of the PEM electrolyser) on plant feasibility. Moreover, the minimal methanol price for a PBP of 10 years (the defined target for a plant lifetime of 20 years) could be determined.

The referring plant operates at 80 bar. In Table 3 the range of variation of each parameter is reported.

Table 3. Economic assumptions

Parameter	Range
Electrical energy cost	20 - 100 €/MWh
Methanol selling price	400 – 1200 €/ton
Oxygen selling price	100 – 200 €/ton
PEMEL capita cost reduction	0% – 50%

In Figure 7 the influence of the parameter variation on the PBP is shown.

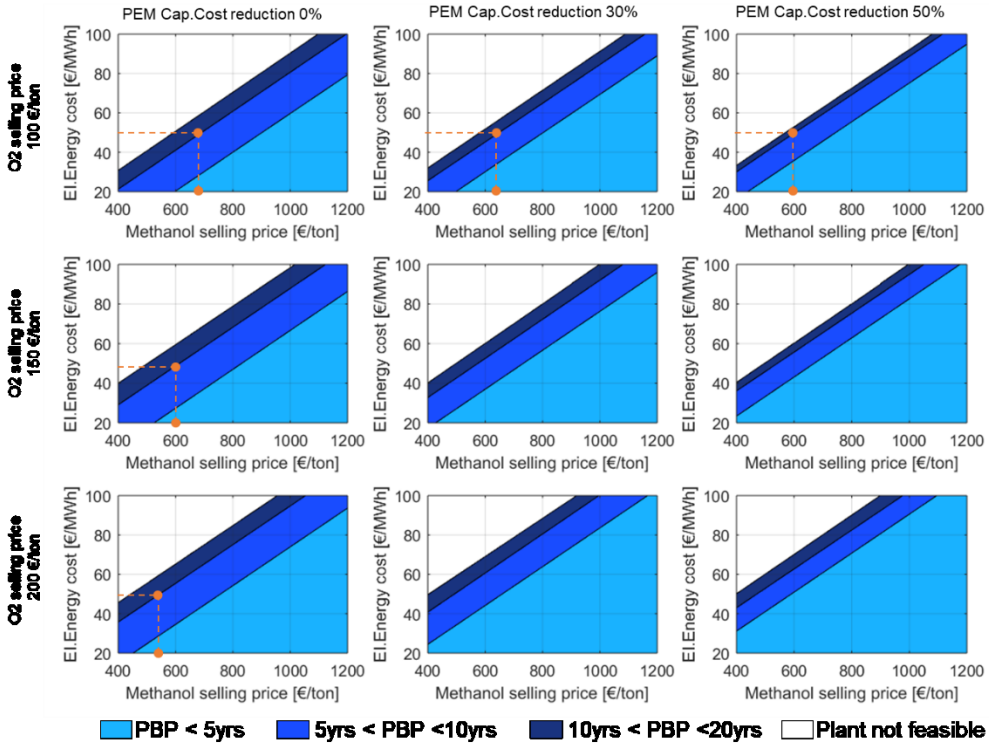

Fig. 7. PBP sensitivity analysis results

Considering an electrical energy cost of 50 €/MWh and an O_2 selling price of 100 €/ton, it is possible to note how the methanol selling price for a fixed PBP of 10 years decreases from around 685 €/ton to around 600 €/ton (-12.4%), when the capital cost of the PEMEL is reduced by 50%.
In the same way, not considering a capital cost reduction of PEMEL but increasing the oxygen selling price by 50% to 150 €/ton, the minimum methanol price decreases of about 11% to 609 €/ton.
Furthermore, an increase of the electrical energy cost of 50% (to 75 €/MWh) results in an increase in the methanol selling price of about 40% (up to 980 €/ton) at an O_2 selling price of 100 €/ton and no PEMEL capital cost reduction.

3 Conclusion

In the present work, thermodynamic and economic analyses of a large electrolyser-based methanol plant were performed in order to investigate the impact of the operating pressure on the plant feasibility and define the value that minimises the methanol production cost. Moreover, a sensitivity analysis was carried out to evaluate the correlation between the methanol selling price, the electrical energy cost, the oxygen selling price and the capital cost of the PEM electrolyser on the PBP of the whole system.

Form the obtained results, the following conclusions can be drawn:

- The thermodynamic analyses have shown that high pressures lead to a strong improvement in the methanol yield (131%). At the same time, higher pressures lead to higher energy consumption for the compressors (329%).
- In addition, the implemented control leads to a larger educts input when the pressure is increased and consequently to a larger electrolyser to be installed.
- From the economic point of view, the electrolyser turned out to be the most critical component representing more than 70% of the fixed costs and the biggest share of the variable costs due to its high energy consumption and maintaining cost
- Even if at increasing pressure the annual fixed and variable costs increase, the annual methanol production is higher, resulting in a decreasing specific methanol production cost. The most significant decrement is observed from 30 bar to 80 bar, resulting in the best operating pressure.
- Considering the actual market values, the methanol production cost at 80 bar was found to be around 800 €/ton is almost twice the actual market price [17]. In this sense, the sale of the oxygen co-produced by the electrolyser is crucial for the economic viability of the plant, as it could potentially reduce the methanol costs by about 30%.
- The sensitivity analysis showed that with the same percentage variation, the most affecting parameter is the electrical energy cost, followed by the PEMEL capital costs and the oxygen price.

In conclusion, the present analysis showed that the methanol production form H_2 produced by water electrolyser and CO_2 sequestrated from flue gases is not economically competitive compared to the traditional natural gas-based production method. Nevertheless, some important aspects need to be highlighted:

- It is very likely to suppose a cost reduction of the water electrolyser in the next future due to the technology improvements and the market growth;
- The methanol so produced allows to recycle more than 380000 ton/yr of CO_2 (at 80 bar), and it is a good reason to believe that government incentives will be created for the production and commercialisation of such methanol
- Compared to the traditional natural gas-based production chain, this PtF concept allows for saving about 340 Mm^3 of NG and avoiding the related emission of about 660 kton/yr of CO_2 [18]

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