

Conceptual Design, Performance and Economic Evaluation of Carbon Dioxide Methanation Plant

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In the present study, a possible pathway of converting renewable electricity into synthetic natural gas via carbon dioxide methanation is presented. This pathway, discussed nowadays as Power-to-Gas approach, represents an innovative concept that is able to access the tremendous storage and transport capacities of the gas grid to store renewable electricity. Carbon dioxide methanation is the main conversion step in this process. The simulation models were developed in Aspen Plus software using literature design parameters. Two conceptual designs were suggested and evaluated by rigorous Aspen Plus simulations in order to assess the current economic feasibility of the methanation process.

Keywords: renewable methane, energy storage; renewable energy integration, design and simulation, Power-to-Gas

Nowadays, the major part of the worldwide natural gas (methane), one important backbone for the energy supply, is provided by fossil sources [1]. In order to reduce the greenhouse gases (GHG) emissions caused by excessive use of fossil fuels, it is imperative to develop and promote new ways to produce methane using as much as possible what nature can offer: biomass residue and carbon dioxide emissions [2,3]. During the last years, new initiatives addressing climate change objectives were adopted at European Union level by imposing drastic reductions of CO₂ emissions. Thus, there is a lot of interest in developing new cleaner hydrocarbon methane with the goal of valorisation of CO₂ emissions linked with renewable energy integration [4].

In this context, high concentrations CO₂ gas, captured from industrial emitters such as power plants, cement, steel industry or refineries [5] is combined with hydrogen delivered by the electrolysis process using excess electricity produced from renewable energy, to obtain SNG (synthetic natural gas or substitute natural gas) through methanation reaction [6-8]. This pathway discussed nowadays as Power-to-Gas concept represents a major

challenge in order to successfully make the transition towards a sustainable low carbon economy. The result of this process is a synthetic gas compatible with the natural gas network [9]. This hydrocarbon fuel is considered to be a promising renewable energy storage gaseous medium; it can be easily stored, transported and used using the existing infrastructure without additional modifications to the end user appliances [10]. Two main steps are required in the Power-to-Gas concept to produce SNG: the water electrolysis to produce hydrogen using the surplus electric energy from fluctuating renewable energy sources and the methanation reaction which uses carbon dioxide from different capture processes (fig. 1).

Chemical reactions

The CO₂ methanation process converts carbon dioxide to methane. The process is based on the Sabatier reaction discovered in 1902 by Sabatier and Senderens. The methanation reaction is catalysed by Ni on various oxide supports [11-13] in a broad temperature (250 – 650 °C) and pressure (1 – 80 bar) range [3].

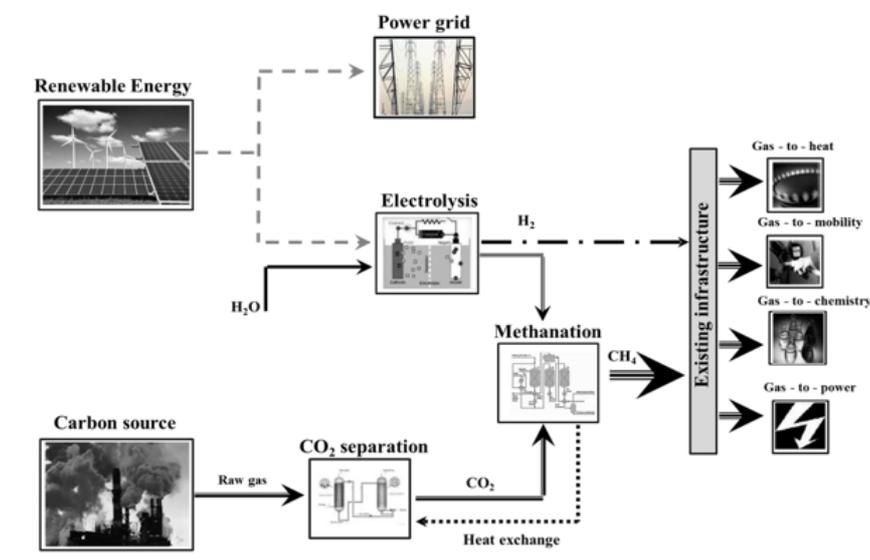
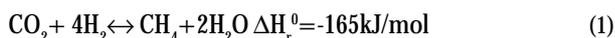


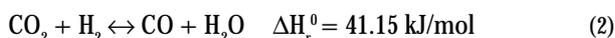
Fig. 1. Power-to-Gas concept

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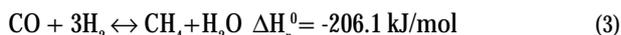
Carbon dioxide and hydrogen react in the presence of catalysts to form methane and water (Sabatier reaction). The stoichiometric ratio is $\text{CO}_2:\text{H}_2 = 1:4$ eq. (1) and the reaction is highly exothermic:



The Reverse Water Gas Shift reaction (RWGS) occurs simultaneously whenever active catalysts are used, eq. (2):



The RWGS reaction is endothermic and favoured by high temperature. However, the formed CO is quickly converted to methane eq. (3):



Many research efforts dealing with the synthesis of methane from carbon dioxide and hydrogen are reported in the literature. However, the design and economic evaluation of the entire chemical plant is missing.

The goal of this paper is to fill this gap by presenting an integrated design study and economic evaluation of two technical pathways of the methanation process, both cases involving an internal recycle loop to lower the temperature in the first reactor. Moreover, the operating conditions were determined in such way to maximize the methane selectivity and to ensure that maximum temperature allowed by the catalyst is not exceeded during adiabatic reactor operation.

Two conceptual designs were suggested and evaluated by rigorous Aspen Plus [14] simulations in order to predict the effect of the key design parameters on the reaction temperature and purity of the synthetic natural gas product and to assess the current economic feasibility of the methanation process.

Methanation process modeling

The simplified process flowsheet for carbon dioxide methanation depicted in figure 2 includes one, two or more catalytic reactors, operated adiabatically, in which

reactions described in eq. (1-3) take place. The number of reactors depends on the required methane yield. In each reactor, the process approaches the equilibrium conditions. As the process is exothermic, the reaction mixture is cooled after each reactor in order to allow further conversion increase. The stoichiometric ratio is $\text{CO}_2:\text{H}_2 = 1:4$ eq. (1), but the reaction can be performed with an excess of either reactant.

The adiabatic reactors were simulated using Aspen Plus by means of the GIBBS model, which calculate the chemical equilibrium through minimization of the Gibbs free energy of the mixture.

Due to the highly exothermic reactions, the first reactor has a special design: a part of the reactor effluent is recycled back to the reactor inlet, mixed with the reactants (fresh and recycled) and cooled to a suitable temperature (sufficiently high to initiate the reaction). Thus, this dilution effect leads to a lower temperature increase along the reactor bed. The two most important design parameters are the ratio between reactants at the inlet of the first reactor, $F_{1,\text{CO}_2} / F_{1,\text{H}_2}$ and the fraction of the reactor effluent that is recycled - R , where F_{1,CO_2} and F_{1,H_2} represents molar flow rates of CO_2 and H_2 , kmol/h. The recycle ratio - R is defined as molar flow ratio between the recycled gas and the stream leaving the reactor bed.

For the present case, the plant inlet H_2 fresh flow was specified as 54 kmol/h H_2 at 30 bar and 303 K, corresponding to the nominal production of a 10 MW electrolyser. In order to achieve flowsheet convergence a DESIGN SPECIFICATION block was used to adjust the fresh CO_2 flow rate necessary to maintain the desired CO_2 / H_2 flow ratio at the inlet of the first reactor. As expected, the corresponding flow rate of fresh carbon dioxide (obtained as a result of simulation), 13 kmol/h at 30 bar and 303 K, was very close the stoichiometric value. The ASPEN PLUS simulation ends with a sensitivity analysis that uses the reactor model to understand the effect of the reaction temperature, the reactants concentration and the recycle ratio on the maximum reactor temperature.

The sensitivity analysis shows that the increase in the recycle ratio R leads to a decrease of the maximum temperature. Figure 3 presents the maximum temperature

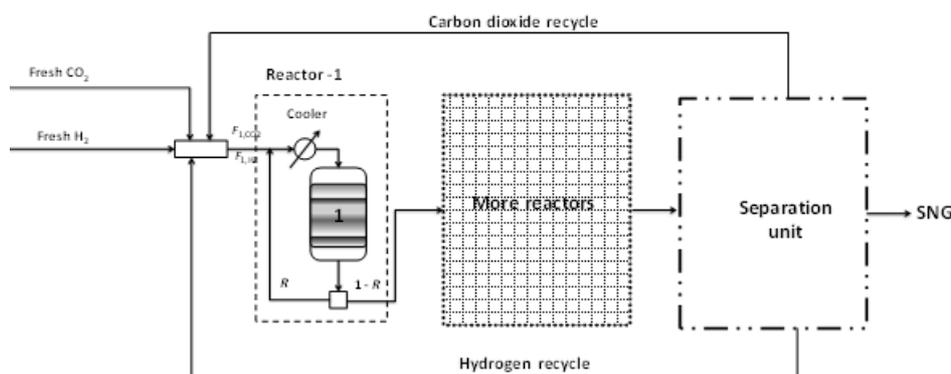


Fig 2. Schematic representation of carbon dioxide methanation process

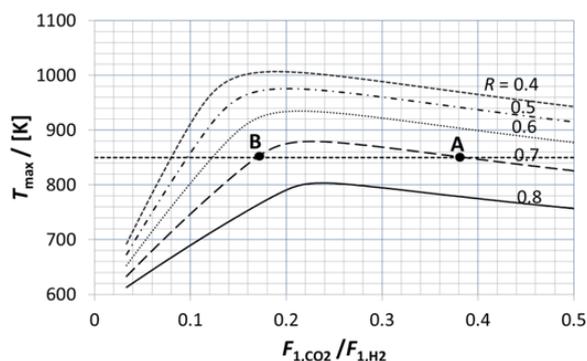


Fig 3 - Maximum temperature of the first reactor bed versus the reactants ratio $F_{1,\text{CO}_2} / F_{1,\text{H}_2}$ at various values of the recycle fraction R . Bed-inlet temperature and pressure are 573 K and to 30 bar, respectively

Table 1
EFFECT OF THE RECYCLE RATIO ON THE GAS COMPOSITION AND OPERATING CONDITIONS AT THE OUTLET OF THE FIRST METHANATION REACTOR AND ON THE SNG COMPOSITION

Stream	Recycle ratio				
	0.4	0.5	0.6	0.7	0.8
REACTOR-1 OUTLET					
Total molar flow (kmol/h)	102.067	119.744	145.827	171.106	277.041
Total mass flow (kg/h)	2160.25	2592.41	3240.33	3421.914	6480.63
Temperature (K)	943	915	877	850	756
Pressure (bar)	30	30	30	30	30
Composition (mole%)					
CO ₂	22.212	23.159	24.110	16.311	25.196
H ₂	18.019	15.437	12.230	12.154	4.777
CH ₄	16.080	17.593	19.374	22.911	23.033
H ₂ O	37.923	39.498	41.517	47.222	46.531
CO	5.763	4.311	2.767	1.402	0.460
SNG PRODUCT					
Total molar flow (kmol/h)	14.123	13.957	13.836	13.848	13.728
Total mass flow (kg/h)	215.9	216.0	216.2	216.3	216.3
Temperature (K)	298	298	298	298	298
Pressure (bar)	30	30	30	30	30
Composition (mole%)					
CO ₂	0	0	0	0	0
H ₂	5.565	4.128	3.045	2.342	2.058
CH ₄	94.064	95.582	96.710	97.340	97.729
H ₂ O	0.180	0.181	0.182	0.286	0.182
CO	0.190	0.108	0.061	0.032	0.029

in the first reactor bed versus the reactants ratio $F_{1,CO_2} / F_{1,H_2}$, calculated for an inlet temperature of 573 K and various values of the recycle fraction R . The reaction pressure was set to 30 bar. According to the literature, high temperatures affect the catalyst stability. As expected, the sensitivity analysis (fig. 3) shows that the increase in the recycle ratio leads to a decrease of the maximum temperature. In order to fulfil the technological constraint of maximum temperature below 850 K, large excess of one reactant (either CO₂ or H₂) should be used, which imply an increase of the separation costs. On the other hand, higher recycle leads to higher costs (large reactor, recycle compressor). Therefore, the first-reactor recycle ratio, R , and the reactants ratio, $F_{1,CO_2} / F_{1,H_2}$, are important design decisions.

Moreover, figure 3 shows that there are two different operating conditions which lead to the same maximum temperature within the first reactor bed. This two operating points, denoted by A and B (for $R=0.7$, at 850K) were considered for further investigation:

Case A: involves a high conversion of hydrogen followed by carbon dioxide separation and recycle (excess of CO₂ - relatively to the stoichiometric ratio $CO_2/H_2 = 0.25$), (fig. 4).

Case B: involves a high conversion of carbon dioxide followed by hydrogen separation and recycle (excess of

H₂ - relatively to the stoichiometric ratio $CO_2/H_2 = 0.25$), (fig.5).

Thus, both cases were designed and rigorous simulations were performed. Table 1 presents simulation results obtained for reactants ratio $F_{1,CO_2} / F_{1,H_2} = 0.386$. At $R = 0.7$, the outlet temperature of the first reactor is 850K. Below this value of R the high temperature could destroy the catalyst.

Conceptual design

Two conceptual designs are presented and evaluated by rigorous Aspen Plus simulation. Working at (or close to) the stoichiometric ratio does not ensure high conversion of both reactants, therefore, two separation units are needed (one for H₂ and one for CO₂). Thus, designing the plant for an excess of one of the reactants is preferable, as this implies almost complete conversion of the other reactant, with the results of only one separation unit and only one recycle. Both cases imply a recycling loop after the first reactor, to lower the temperature in the first reactor. After the first reactor, the reaction mixture is cooled before being sent to the second reactor (case A and B). The cooling - reaction sequence is repeated at the third reactor (which is only necessary in case A). Finally, the reaction mixture is cooled to a temperature that is low enough to allow water

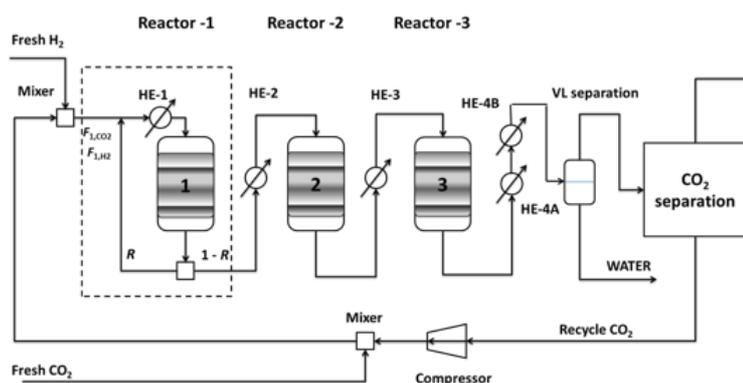


Fig. 4. Flowsheet of CO₂ methanation process Design A (CO₂ separation - recycle)

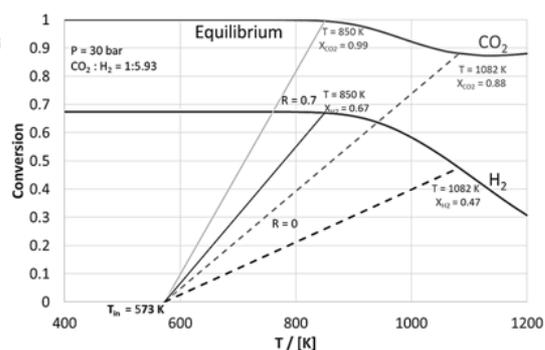


Fig. 5. CO₂ and H₂ conversion - temperature profile at equilibrium for CO₂:H₂ = 1:2.59

Table 2
STREAM RESULTS FOR THE REACTION SECTION FOR CASE A

Property	CASE A						
	Reactor-1 IN	Reactor-1 OUT	Reactor-2 IN	Reactor-2 OUT	Reactor-3 IN	Reactor-3 OUT	SNG
Temperature [K]	573	850	573	697	573	599	298
Pressure [bar]	30	30	30	30	30	30	30
Total molar flow [kmol/h]	194.627	171.106	51.331	48.650	48.650	48.067	13.848
Total mass flow [kg/h]	3421.9	3421.9	1026.5	1026.5	1026.5	1026.5	216.3
Composition [mole%]							
CO ₂	20.752	16.311	16.311	15.831	15.831	15.509	0.000
H ₂	35.225	12.154	12.154	3.176	3.176	0.884	2.342
CH ₄	14.099	22.911	22.911	26.930	26.930	27.862	97.340
H ₂ O	29.061	47.222	47.222	53.961	53.961	55.734	0.286
CO	0.863	1.402	1.402	0.102	0.102	0.009	0.032

condensation and therefore vapour – liquid separation (VL separation). The liquid phase collects water, as well as dissolved gases. The water produced in the process can be collected and reused. The heat exchangers HE provide steam at different pressure levels. The heat-exchangers were modelled as HEATER units, which allow estimation of the heat duty. Finally, the compressor model offered the energy required for CO₂ and H₂ pressure increase and recycle.

Figure 4 presents the Aspen Plus flowsheet for CO₂ methanation performed with CO₂ excess, separation and recycle. In this case, three catalytic reactors were used in order to achieve almost complete H₂ conversion. The CO₂ separation was accomplished by absorption / desorption using ethanol amine. The excess carbon dioxide is recycled to the first reactor via a compressor. Following the CO₂ separation the SNG product is obtained. Figure 5 presents

the CO₂ and H₂ conversion – temperature profile at equilibrium for CO₂:H₂ = 1:2.59, for a gas composition leaving the methanation unit of: 97.340 mole% CH₄, 2.342 mole% H₂, 0.286 mole% H₂O and 0.032 mole% CO, a composition which is compliant with the natural gas injection standards.

Table 2 shows the Aspen Plus detailed simulation results for the reactor inlet and outlet streams for case A.

Figure 6 presents the Aspen Plus flowsheet for CO₂ methanation performed with excess, separation and recycle of hydrogen. In this case, for the almost complete CO₂ conversion only one catalytic reactor is needed. The unconverted H₂ is removed from the plant using palladium-based membranes, then compressed and recycled to the reactor, after being mixed with fresh reactants. Following the H₂ separation the SNG product is obtained. Note that the final cooling is achieved in a sequence of 3 heat exchangers (HE-2A, HE-2B and HE-2C) which generate

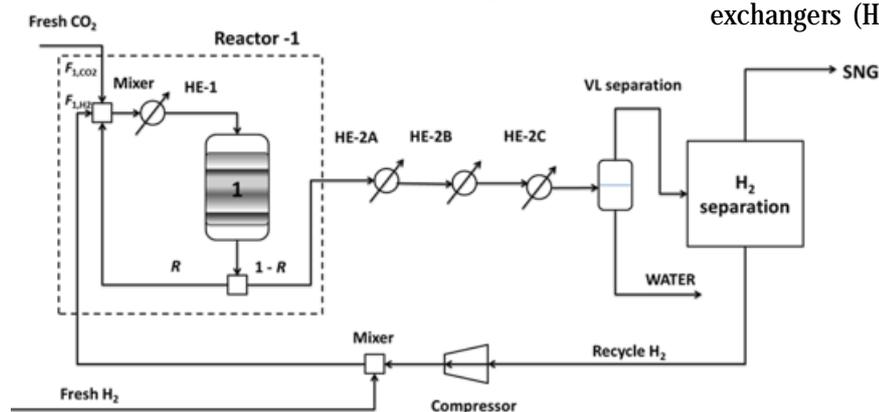


Fig. 6. Flowsheet of CO₂ methanation process Design B (H₂ separation – recycle)

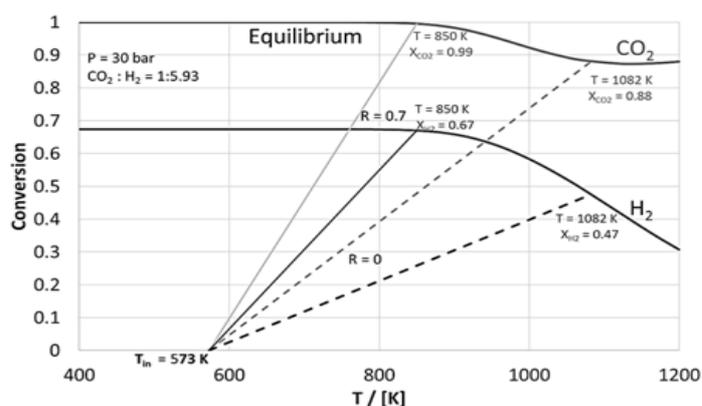


Fig. 7. CO₂ and H₂ conversion – temperature profile at equilibrium for CO₂:H₂ = 1:5.93

Property	CASE B		
	Reactor-1 IN	Reactor-1 OUT	SNG
Temperature [K]	573	850	298
Pressure [bar]	30	30	30
Total molar flow [kmol/h]	249.494	222.659	13.540
Total mass flow [kg/h]	2518.8	2518.8	219.2
Composition [mole%]			
CO ₂	5.469	0.093	0.459
H ₂	56.848	39.586	0.000
CH ₄	12.548	20.086	99.088
H ₂ O	25.115	40.203	0.302
CO	0.002	0.032	0.151

Table 3
STREAM RESULTS
FOR THE
REACTION
SECTION FOR
CASE B

steam at different pressure levels. Figure 7 presents the CO₂ and H₂ conversion – temperature profile at equilibrium for CO₂:H₂ = 1:5.93, for a gas composition leaving the methanation unit of: 99.088 mole% CH₄, 0.459 mole% CO₂, 0.302 mole% H₂O and 0.151 mole% CO.

Table 3 shows the Aspen Plus detailed simulation results for the reactor inlet and outlet streams for case B.

Economic evaluation

An economic evaluation of the process was performed. A payback period of 3 years was considered, and it was assumed that the plant is running 8000 h/year. The total annual cost of the plant (TAC) was calculated as following:

$$TAC = \frac{\text{capital cost}}{\text{payback period}} + \text{operating cost} \quad (4)$$

The capital cost, including the costs of mixers, reactors, heat exchangers, gas compressors, turbo blowers and separation columns was calculated using well-known relationships. The operating cost includes the costs of cooling water (0.72 US\$/GJ) and electricity (16.8 US\$/GJ).

The installed costs for the reactor, distillation columns and vessels were calculated by the following relationships [15]:

$$\text{Installed Cost (US\$)} = (\text{M\&S index} / 280) \cdot (957.9 \cdot D^{1.066} \cdot H^{0.82}) \cdot (2.18 + F_c) \quad (5)$$

where *M&S index* = 1536.5, year 2011, [16]; D is the diameter and H is the height, expressed in meter; $F_c = F_m + F_p$ is a factor that takes into account the material (F_m) and the pressure (F_p).

The material factor (F_m) was taken as 1, while the pressure factor (F_p) is correlated by the expression (with P in bar):

$$F_p = 1 + 0.0074 \cdot (P - 3.48) + 0.00023 \cdot (P - 3.48)^2 \quad (6)$$

The installed cost of heat exchangers is calculated by equation:

$$\text{Installed Cost (US\$)} = (\text{M\&S index} / 280) \cdot (474.7 \cdot A^{0.65}) \cdot (2.29 + F_c) \quad (7)$$

where A is the heat exchange area, in m², and 20 < A < 500 m²/shell. $F_c = F_m \cdot F_d \cdot F_p$, F_m , F_d and F_p are correction factors for material, design type and design pressure. The following values were used: $F_m = 1$ (carbon steel), $F_d = 1.35$ (for reboilers), $F_d = 0.8$ (for fixed-tube), $F_p = 0.25$ (30 bar).

The purchased cost of gas compressors is calculated by equation:

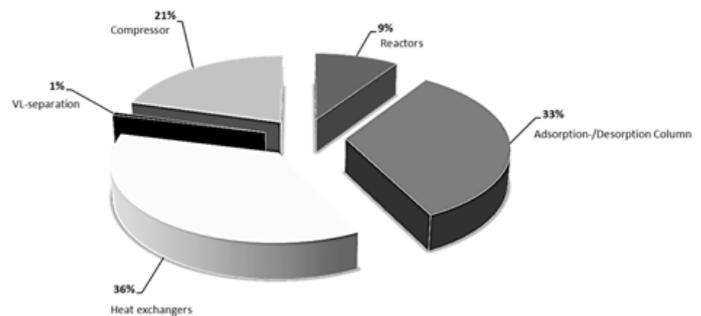


Fig. 8. Economic evaluation for case A

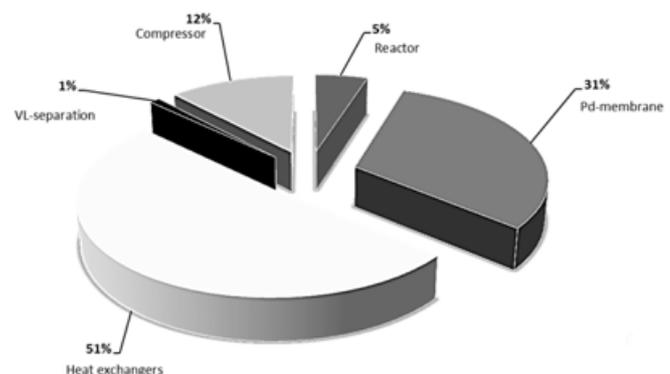


Fig. 9. Economic evaluation for case B

$$\text{Purchased cost (US\$)} = (\text{M\&S index} / 280) \cdot (664.1 \cdot P^{0.82} \cdot F_c) \quad (8)$$

where P is the brake power in kW, with 25 < P < 750 kW. The correction factor F_c was taken as 1.

The purchased cost of turbo blowers is calculated by equation:

$$\text{Purchased cost (US\$)} = (\text{M\&S index} / 280) \cdot CQ^m \quad (9)$$

where:

Q is the capacity and is expressed in m³/s. Constant C and exponent m depend on the maximum discharge pressure drop.

The results of the economic evaluation are presented in figure 8 and 9.

Conclusions

Following an initial stage of sizing the carbon dioxide methanation unit using hydrogen produced from renewable energy sources, a preliminary study on the industrial methane production process configuration was

carried out in order to assess the current economic feasibility of the methanation process for further parametric sensitivity study. The end product of both pathways consists in SNG compliant with the natural gas injection standards. The steady state results of the simulation are in agreement with the experimental observations available in literature. The total annual cost of the plant for case A (CO₂ excess, separation and recycle) is higher than the total annual cost of the plant for case B (H₂ excess, separation and recycle). The approach used for the performance and economic evaluation of the of carbon dioxide methanation plant in the described context proved to be efficient and flexible in terms of understanding the influence that various parameters have on the viability of the process.

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