

**Process simulation and economic feasibility assessment of the
methanol production via tri-reforming using experimental
kinetic equations**

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Abstract

The purpose of this paper is to assess via techno-economic metrics the feasibility of a tri-reforming coupled methanol process. The simulation of the tri-reforming reactor considered empiric kinetic equations, developed by our group in previous studies. The flue gas coming from the furnace that provides the energy required by the reforming reactor was also used as feed, thus avoiding CO₂ emissions. A sensitivity analysis was carried out to select the best feed composition for the tri-reforming process, studying H₂O/CH₄ and O₂/CH₄ ratios (0.5-1.5 and 0.35-0.40, respectively), and temperature (850-1050 °C). The methanol plant was also simulated, and an economical study was carried out to know if the proposed process would be economically feasible. The most relevant economic parameters (including the Net Present Value, the Internal Rate of Return, the Payback Period and the break-even) were calculated, showing a quite robust process from an economical point of view.

Keywords: Tri-reforming; Methanol synthesis; Kinetic-based simulation; Economic analysis.

1. Introduction

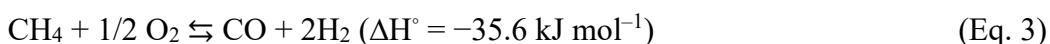
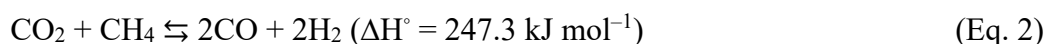
The production of chemical compounds, specially commodities, from a renewable and environmentally friendly source is one of the main challenges of the chemical industry nowadays. Environmental awareness of societies and governments keeps growing and more strict regulations regarding pollutants emissions are released each year, what leads the industry to the search of new process and raw materials. In this sense, the obtention of synthesis gas from natural gas or biogas attracts great attention as a key step in the production of many important chemical compounds, like methanol [1].

Methanol is one of the most consumed chemicals in the world, due to its role as intermediate in the synthesis of many valuable chemicals, like dimethyl ether, formaldehyde, light olefins and acetic acid [2,3]. The several number of applications of this molecule has led to the defense by some authors of the concept “Methanol economy”[4,5], a proposal where methanol is the base of the storage, transport and use of energy instead the traditional fossil fuels. Currently, the annual production of methanol is about 70 million tons per year and it continues growing about 4 % per year [6], with China as the mayor producer with about 40 million tons per year. Most of this methanol comes from fossil fuels through conversion to syngas by reforming. However, methanol can be essentially produced from any carbon source including biomass and CO₂ [7].

Steam reforming is the main reforming process currently carried out in the chemical industry. Approximately 95% of industrial hydrogen in the United States is currently produced through natural gas reforming [8]. However, steam reforming of hydrocarbons yield not only hydrogen but a mixture of mainly H₂ and CO, known as syngas, which is a versatile and useful feedstock to produce a number of industrially relevant chemical commodities such as methanol, dimethyl ether [9], and Fischer-Tropsch products [10,11], as previously commented. Apart from steam reforming, there are other common reforming processes in which the hydrocarbon reacts with CO₂ (dry reforming, DR), O₂ (partial oxidation, PO) or a mixture of H₂O and O₂ (autothermal reforming, AR). The influence of the co-reactant is very important as it affects the H₂/CO molar ratio of the syngas produced, which is a key factor for the determination of the possible applications of the syngas obtained. All of these reforming reactions offer some serious drawbacks. For instance, high energy requirements (SR and DR), high deactivation of the catalyst due to coke formation (DR), or high risk of explosion due to the presence of pure oxygen

and hydrocarbons (PO). These disadvantages make interesting the search of alternative processes.

In order to avoid some of these problems the tri-reforming process was proposed by professor Song in 2001 [12]. Tri-reforming of methane combines SR (Eq. 1), DR (Eq. 2) and PO (Eq. 3) in a single process. This combination has some advantages when compared with the single reforming reactions, as the possibility to tune the H₂/CO molar ratio by shifting the proportion of each one of the co-reactants; a lower energy consumption compared with SR due to the presence of exothermic reactions (PO); and a higher stability of the catalyst due to a lower formation of coke due to the presence of strong oxidants like H₂O and O₂.



Due to these properties, the tri-reforming process has attracted a great attention in the scientific community and many works have been published about this topic in the last years. In this sense our group has a wide experience in the tri-reforming process [13,14], analysing the influence of different catalytic parameters over the tri-reforming process. In addition, we also studied the kinetic of the tri-reforming process [15]. In that work, a kinetic model for the tri-reforming process was developed in order to represent the experimental catalytic results. Single reaction equations for SR, DR and water gas shift (WGS) were considered. It was assumed that PO was close to the full conversion whenever oxygen was not practically detected in the effluent gas. The set of equations was based on the mechanism proposed by Wei and Iglesia [16] for the steam and dry reforming reactions, whereas the kinetic equation for WGS was taken from the work by De la Osa et al. [17].

The study of the tri-reforming has also been carried out from the point of view of the chemical process simulators by different authors. In a previous work [18], we reported energetic and exergetic analyses that were applied to the methane tri-reforming process in order to assess the suitability of this reaction for the production of syngas. It was observed that the reactor was the component where most of the exergy was destroyed. This is mostly due to the high irreversibility of the chemical reactions. A. Dwivedi et al.

[19] reported the simulation of a chemical plant for the production of methanol from CO₂ and CH₄ by generation of syngas using the tri-reforming process. A number of process simulations were carried out in that paper to demonstrate the advantage of utilizing a steam input combined with a water separation step onto the tri-reforming coupled methanol production process (especially when the tri-reformer is operated at higher pressures). This process was also simulated by Y. Zhang et al [20], where they optimized the unit operating conditions for maximum production rate. In addition, they carried out a thermodynamic analysis in order to identify the factors that have influence on the syngas composition. However, both studies employed equilibrium conditions for the simulation of the tri-reforming process, without taking into account the kinetic of the process.

In the present work, we report a simulation of the methanol production via tri-reforming using natural gas as raw material. In order to get results closer to the reality, we have simulated the tri-reforming process with the kinetic equations obtained in our previous work [15]. In addition, due to the high energetic requirements of the tri-reforming process, we have integrated a furnace for the obtention of the heat needed in the tri-reforming reactor (as it is done in the typical industrial plants for the SR of natural gas). The combustion products obtained in this furnace (mainly CO₂ and H₂O) were also used as raw materials, as they are co-reactants in the tri-reforming process, what is also very important from an environmental point of view in order to avoid greenhouse gases emissions. Besides, the operating conditions were optimized considering the effect of four variables of the tri-reforming reaction: temperature, water to methane molar ratio and oxygen to methane molar ratio; and observing the effect on the syngas product characteristics and reactor volume. Finally, the economic assessment of the process in the selected conditions was carried out in order to evaluate its economic feasibility and robustness.

2. Methodology

For the simulation, the whole process was divided into two sections: the first one corresponds to the tri-reforming process (Figure 1) and the second one to the methanol production (Figure 2). The chemical process simulator selected was Aspen HYSYS[®] V11, licensed by Aspen Technology. All the feed streams entered at 1.013 bar and 25 °C.

2.1. Tri-reforming process simulation

Following the scheme of a real natural gas reforming industrial plant, in the tri-reforming section we can find two main reactors (“Pre-reactor” and “TRM reactor”) and a furnace. Three streams were mixed prior to the pre-reactor: “Feed O₂”, which simulates the addition of oxygen; stream “Nat gas”, which simulates the addition of natural gas (molar composition of 0.8261 CH₄, 0.077 C₂H₆, 0.03 C₃H₈, 0.065 N₂ and 0.0019 CO₂); and stream “water”, which was evaporated before being mixed with the others in the block called “Heater 1”, using the energy obtained in the cooler “Cooler 1” in order to fix the temperature of the stream “Feed mix” at 100 °C. This stream enters the “Heat Exchanger” where increase its temperature up to 520 °C thanks to the stream “Furnace out”, which is the stream that corresponds to the exhaust gases from the furnace used to supply heat to the tri-reforming reactor. The furnace is fed by the streams “Nat gas 2”, which has the same composition than “Nat gas”; and “Feed O₂-2”, which simulates the flow of oxygen necessary for the combustion in the furnace. Molar ratio between “Nat gas 2” and “Feed O₂-2” was fixed by using the manipulator “SET-2” in order to have a molar ratio “Feed O₂-2”/ “Nat gas 2” of 2.225. The molar flow of “Nat gas 2” was determined by the manipulator “ADJ-2” in order to fix the temperature of the feed stream entering the tri-reforming reactor at 800 °C. The “Pre-Reactor” converts ethane and propane into syngas by the combination of the steam reforming and partial oxidation reactions. The temperature of the stream “to mixer 2” was fixed at 465 °C thanks to the manipulator “ADJ-3”, which modifies the flow of the stream “Feed O₂”, affecting therefore the global enthalpy of the process that takes place in the “Pre-Reactor”, as it is a combination of the exothermic partial oxidation and the endothermic steam reforming. Gases leaving the “Pre-reactor” are mixed with the exhaust gases from the “Furnace” and another stream of oxygen (“Feed O₂-3”) in “Mix 2”, yielding the stream “To Reactor”. The main properties of the feed streams can be observed in Table 1.

Table 1. Feed streams properties in the tri-reforming section.

Variable	Feed O2	Nat Gas	water	Nat Gas 2	Feed O2-2	Feed O2-3
Mass Flow (kg/h)	5517.8	39810	12391	3680.2	13941	23044
Temperature (°C)	25	25	25	25	25	25
Pressure (bar)	1.013	1.013	1.013	1.013	1.013	1.013
O ₂ (mole fraction)	1	0	0	0	1	1
H ₂ O (mole fraction)	0	0	1	0	0	0
CH ₄ (mole fraction)	0	0.8261	0	0.8261	0	0
C ₂ H ₆ (mole fraction)	0	0.077	0	0.077	0	0
C ₃ H ₈ (mole fraction)	0	0.03	0	0.03	0	0
N ₂ (mole fraction)	0	0.065	0	0.065	0	0
CO ₂ (mole fraction)	0	0.0019	0	0.0019	0	0

The gas entering the tri-reforming reactor, the one called “to Reactor” in the flow diagram, is a combination of methane, water, carbon dioxide and oxygen, the main raw materials for the tri-reforming process; plus a small quantity of hydrogen, carbon monoxide and nitrogen (see Table 2). The reactor was modelled using a Plug Flow Reactor with the kinetic expressions and parameters obtained experimentally in a previous study by our group [15], as explained in the Introduction section. The kinetic expressions and the parameters obtained are listed in Table 3. The reactions that were considered to make a contribution to the global kinetic of the tri-reforming process were SR, DR and the WGS (Eq. 4). It was assumed that the partial oxidation was close to full conversion. Most of the methane is converted in the tri-reforming reactor, yielding synthesis gas, as can be observed in Table 2 for the stream “to Cooler 1”, which is the one going out from the tri-reforming reactor.

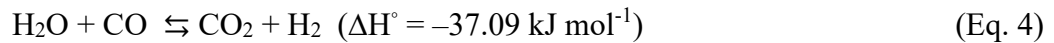


Table 2. Key streams properties in the tri-reforming section.

Variable	to Furnace	To Pre-Reactor	to Reactor	to Cooler 1	RAW SYNGAS
Mass Flow (kg/h)	17621	57719	98383	98383	85481
Temperature (°C)	25	520	800	850	45
Pressure (bar)	1.013	1.013	1.013	1.013	1.013
O ₂ (mole fraction)	0.6899	0.0579	0.1441	0	0
H ₂ O (mole fraction)	0	0.2309	0.1745	0.0918	0
CH ₄ (mole fraction)	0.2561	0.5875	0.3362	0.0095	0.0105
C ₂ H ₆ (mole fraction)	0.0239	0.0548	0	0	0
C ₃ H ₈ (mole fraction)	0.0093	0.0213	0	0	0
N ₂ (mole fraction)	0.0202	0.0462	0.0289	0.0193	0.0212
CO ₂ (mole fraction)	0.0006	0.0014	0.0411	0.0295	0.0325
CO (mole fraction)	0	0	0.0993	0.2787	0.3069
H ₂ (mole fraction)	0	0	0.1759	0.5712	0.6289

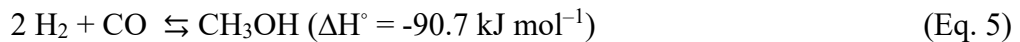
After three consecutive cooling steps in “Cooler 1”, “Vap 1” and “Cooler 2” the gas flow reaches a temperature of 45 °C and enters into an adsorber, where the remaining water is removed. As commented previously, the energy obtained in “Cooler 1” is used in “Heater 1” to evaporate the flow “water”. In addition, the energy obtained in “Vap 1” is used for the generation of steam at 4 bar, which could be used to heat other streams if needed or for the generation of electricity in a turbine. The stream leaving the adsorber is called “RAW SYNGAS” and will be used as feed stream for the methanol production section. Its composition can be observed in Table 2.

Table 3. Kinetic expressions and parameters used in the tri-reforming reactor.

Reaction	Kinetic expressions	Parameters
SR $\text{H}_2\text{O} + \text{CH}_4 \rightleftharpoons \text{CO} + 3\text{H}_2$	$r_{SR} = K_1 \cdot P_{\text{CH}_4} \cdot \left(1 - \frac{P_{\text{CO}} \cdot P_{\text{H}_2}^3}{P_{\text{CH}_4} \cdot P_{\text{CO}_2} \cdot K_{SR}} \right)$ $K_{SR} = 1,198E17 \cdot e^{\left(\frac{-26830}{T}\right)}$ $k_1 = k_1^0 \cdot e^{\left(\frac{-E_{a1}}{R \cdot T}\right)}$	$k_1^0 = 85.77 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$ $E_{a1} = 74.72 \text{ kJ} \cdot \text{mol}^{-1}$
DR $\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	$r_{DR} = K_2 \cdot P_{\text{CH}_4} \cdot \left(1 - \frac{P_{\text{CO}}^2 \cdot P_{\text{H}_2}^2}{P_{\text{CH}_4} \cdot P_{\text{CO}_2} \cdot K_{DR}} \right)$ $K_{DR} = 6,78E18 \cdot e^{\left(\frac{-31230}{T}\right)}$ $k_2 = k_2^0 \cdot e^{\left(\frac{-E_{a2}}{R \cdot T}\right)}$	$k_2^0 = 70.99 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$ $E_{a2} = 77.82 \text{ kJ} \cdot \text{mol}^{-1}$
WGS $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$	$r_{WGS} = K_3 \cdot \left(\frac{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} - \frac{P_{\text{CO}_2}}{k_{eqWGS}} \right)$ $k_{eqWGS} = 10^{\left(\frac{2073}{T} - 2,2029\right)}$ $k_3 = k_3^0 \cdot e^{\left(\frac{-E_{a3}}{R \cdot T}\right)}$	$k_3^0 = 149.92 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$ $E_{a3} = 54.26 \text{ kJ} \cdot \text{mol}^{-1}$

2.2. Methanol production simulation

The synthesis gas produced in the previous section was conditioned before entering the methanol production reactor. Three compressors were used in order to increase the pressure up to 50 bar, with cooling steps after each compressor in order to keep the gas at reasonable conditions. In this way, the stream “to MeOH reactor” enters the “MeOH Reactor” at 50 bar and 120.7 °C. This stream is a combination of the gas coming from “RAW SYNGAS” and the gas recycled after “Flash 1”. The “MeOH Reactor” is considered to work close to equilibrium conditions at 220 °C, with two ways to obtain methanol: from the reaction of H₂ and CO (Eq. 5) and from the reaction of H₂ and CO₂ (Eq. 6). The main properties of the effluent gas coming out from this reactor (“to Vap 4”) and the stream used as feed (“to MeOH Reactor”) appear in Table 4.



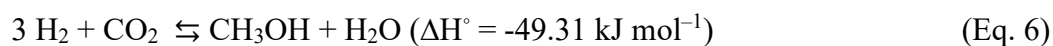


Table 4. Key streams properties in the methanol section.

Variable	to MeOH Reactor	to Vap 4	to Flash 1	Purge to mix	to Flash 2	Pure MeOH
Mass Flow (kg/h)	247384	247384	247384	161904	75801	68117
Temperature (°C)	120.7	220	12	14.22	6.87	-1.68
Pressure (bar)	50	49	49	50	1	1
O ₂ (mole fraction)	0	0	0	0	0	0
H ₂ O (mole fraction)	0	0.0019	0.0019	0	0.0087	0
CH ₄ (mole fraction)	0.0049	0.0069	0.0069	0	0.0005	0
C ₂ H ₆ (mole fraction)	0	0	0	0	0	0
C ₃ H ₈ (mole fraction)	0	0	0	0	0	0
N ₂ (mole fraction)	0.1797	0.2507	0.2507	0.3204	0.0070	0
CO ₂ (mole fraction)	0.0942	0.1295	0.1295	0.1489	0.0635	0
CO (mole fraction)	0.2180	0.1084	0.1084	0.1390	0.0012	0
H ₂ (mole fraction)	0.5020	0.3033	0.3033	0.3893	0.0019	0
CH ₃ OH (mole fraction)	0.0013	0.1994	0.1994	0.0024	0.9171	1

The product gas is cooled in three different steps (“Vap 4”, “Cooler5” and “Vap NH3”). In the first one, a steam at 4 bar is obtained, while in the last one liquid NH₃ is used as refrigeration, and vapor NH₃ is obtained. Once cooled, the gases enter “Flash 1” where the gas and liquid phases are separated. 5% of the gas effluent is purged (stream “vent”) and the rest is recirculated to the feed stream of the MeOH reactor after increasing its pressure to 50 bar and removing methane in the adsorber “Adsorber 3”. The liquid stream from “Flash 1” is conducted to a valve where the pressure is decreased to 1 bar. After that, it enters into “Flash 2”. The liquid stream from this block, rich in methanol, is finally conducted to “Adsorber 2”, where methanol is separated from the rest of the components, yielding the final product in the stream called “Pure MeOH”. The properties of this stream, “to Flash 1”, “Purge to mix” and “to Flash 2” can be observed in Table 4.

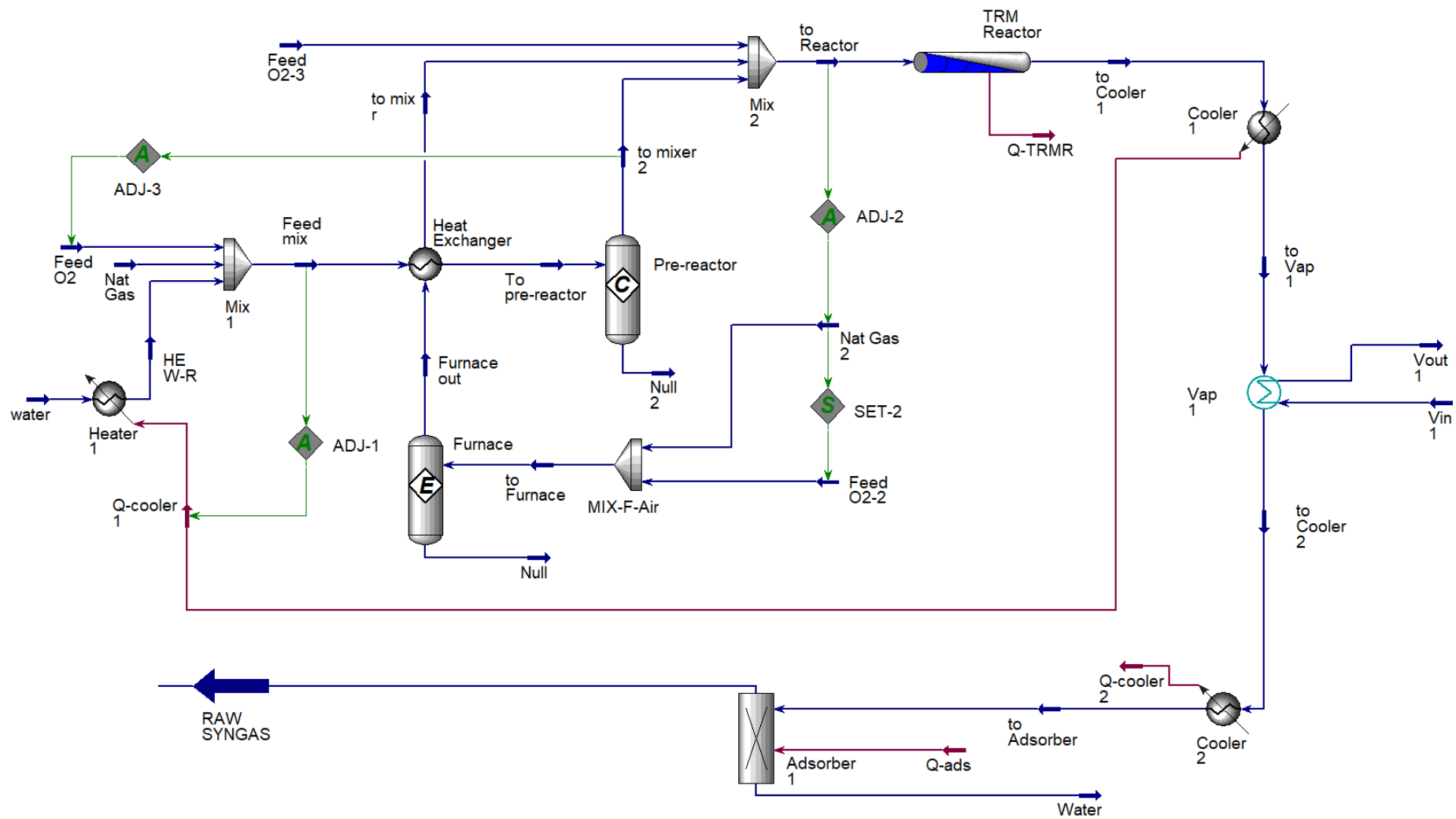


Figure 1. Tri-reforming process flow diagram.

3. Results and discussion

3.1. Validation of the Simulation Process

The suitability of the developed simulation using kinetic equations and plug flow reactors to reproduce a real tri-reforming process was verified by comparing the simulation results with those reported by Zhang et al. [20] for a similar process. The main process streams of the tri-reforming section are those related to the tri-reforming reactor where the syngas is produced. Besides, the key parameter of this section is the H₂/CO ratio in the syngas stream, in order to optimize the further methanol production. Thus, Table 5 compares the composition of the feed and syngas streams of the tri-reforming reactor and the H₂/CO ratio in the syngas stream. It is also shown the standard deviation (SD).

Table 5. Composition of the feed and syngas streams of the tri-reforming reactor from the developed simulation and from the work by Zhang et al. [20].

	Feed to Reactor			Syngas		
	Simulation	Zhang et al. [20]	SD	Simulation	Zhang et al. [20]	SD
CH₄	0.3362	0.29	0.0327	0.0105	0.02	0.0067
CO₂	0.0411	0.07	0.0204	0.0325	0.00	0.0230
CO	0.0993	0.00	0.0702	0.3069	0.22	0.0614
H₂	0.1759	0.00	0.1244	0.6289	0.44	0.1336
O₂	0.1441	0.02	0.0878	0.00	0.00	0.00
H₂O	0.1745	0.14	0.0244	0.00	0.00	0.00
N₂	0.0289	0.48	0.3190	0.0212	0.32	0.2113
H₂/CO Molar Ratio				2.049	2.000	0.0348

The main deviations are due to the use of an oxygen stream as raw material instead of only air, as in the case of the work by Zhang et al. [20]. Apart from the nitrogen molar composition, the rest of molar fractions presented standard deviations lower than a 15 % for the hydrogen and lower than a 10% in all the rest. Regarding the H₂/CO₂ molar ratio, the deviation is very low and both values are in the proper range to be used for methanol production [21]. Thus, it is demonstrated the suitability of using kinetic equations and plug flow reactors to simulate the tri-reforming process.

The methanol production section was also validated by comparing the results with those reported by Zhang et al. [20]. In this case, the same operating conditions of the reactor

were used (220 °C and 50 bar), but we have just considered the methanol production reactions (Eq. 5 and 6), while Zhang [20] considered also the side reaction of WGS (Eq. 4).

The compared streams were the liquid streams from the flash separators (“to valve” from “Flash 1” and “MeOH” from “Flash 2”) and the final process stream (“Pure MeOH”). The final process stream just contains methanol with a 100% of purity in both works. The compositions of the liquid flash streams composition are shown in Table 6.

Table 6. Composition of the main methanol production streams from the developed simulation and the work by Zhang et al. [20]

	Liquid Stream from first flash			Liquid Stream from second flash		
	Simulation	Zhang et al. [20]	SD	Simulation	Zhang et al. [20]	SD
CH₄	0.0005	0.0003	0.0001	0.0000	0.0000	0.0000
CO₂	0.0635	0.0130	0.0357	0.0090	0.0068	0.0016
CO	0.0012	0.0001	0.0008	0.0000	0.0000	0.0000
H₂	0.0019	0.0035	0.0011	0.0000	0.0000	0.0000
O₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H₂O	0.0087	0.0706	0.0438	0.0094	0.0420	0.0231
CH₃OH	0.9171	0.9095	0.0054	0.9815	0.9500	0.0223
N₂	0.0070	0.0000	0.0050	0.0000	0.0000	0.0000
C₂H₆	0.0000	0.0000	0.0000	0.0000	0.0004	0.0003

The low deviation between the proposed simulation and the literature results (always below 5 %) allowed to conclude that the developed simulation is valid for the methanol production simulation.

3.2.Sensitivity analysis

Different sensitivity analyses were performed in order to optimize the temperature of the tri-reforming reactor and the influence of the molar ratios water to methane (H₂O/CH₄) and oxygen to methane (O₂/CH₄) on the syngas product. It should be remarked that the CO₂/CH₄ molar ratio is not a degree of freedom: once the reactor temperature is established, the feed for the furnace is determined by the corresponding energetic requirements, and consequently the CO₂ obtained after the combustion is also established. On the other hand, a pressure of 1.013 bar was selected for the tri-reforming process.

Even though a higher pressure would reduce the reactor volume (and consequently its cost), it has serious drawbacks: first, the equilibrium of the reforming reactions is shifted to the left, and therefore lower methane conversion and syngas production are obtained; and second (and likely more important from a practical point of view), the coke generation is strongly enhanced [22,23], which would cause critical catalysts deactivation problems even under the oxidizing conditions of the tri-reforming process. Anyway, to minimize the impact of a low pressure on the reactor volume, oxygen was not fed using an air stream, but a pure component. In this regard, it should be remarked that preliminary simulations (not shown in this paper) indicated that the combination of using pure oxygen and low pressure was better than the option air plus high pressure.

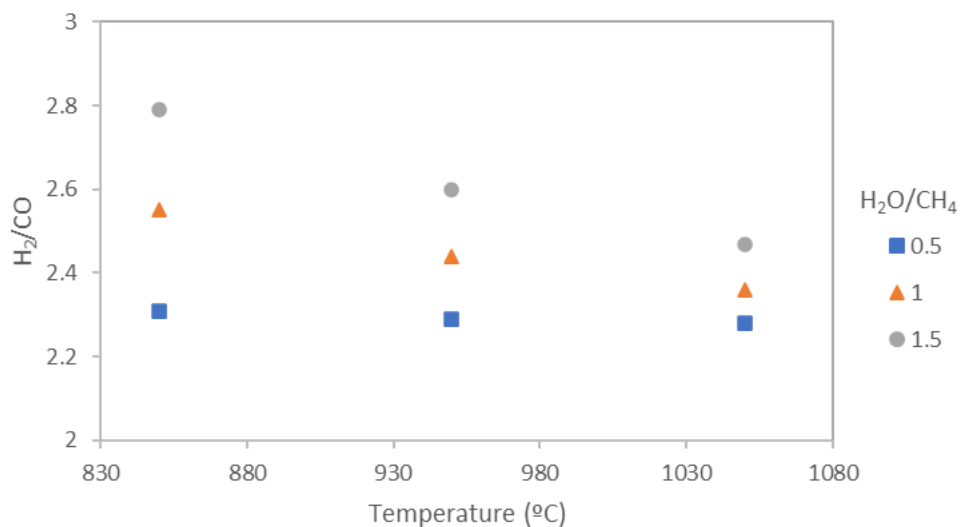
A H_2/CO between 2.1 and 2.3 and a methane conversion of 95.0 % were established as targets for these analyses. The steps followed were:

1. The O_2/CH_4 was fixed at 0.25 and the H_2O/CH_4 was modified with the values 0.5, 1.0 and 1.5. For each case, it was studied the influence of the operating temperature (with values of 850 °C, 950 °C and 1050 °C) on the volume reactor and on the H_2/CO . The operating pressure was fixed at 1.013 bar. From these results, the H_2O/CH_4 that required lower temperature to achieve the targets was selected. If there were two ratios with the same temperature, it would be chosen that one involving a smaller reactor volume.
2. With the selected H_2O/CH_4 , the O_2/CH_4 was varied to 0.35 and 0.4, testing also the effect of temperature with the same values (850 °C, 950 °C and 1050 °C). The same criteria than in the first step were considered for the O_2/CH_4 selection.
3. Finally, the influence of the operating pressure on the volume reactor and on the H_2/CO was analysed, again for the syngas temperatures of 850 °C, 950 °C and 1050 °C.

The tool ADJUST from Aspen HYSYS[®] allowed to calculate the reactor volume required for the target methanol conversion, as well as the molar flows of water and oxygen for the corresponding H_2O/CH_4 and O_2/CH_4 ratios.

The results of the first step of the sensitivity analysis are shown in Figure 3.

a)



b)

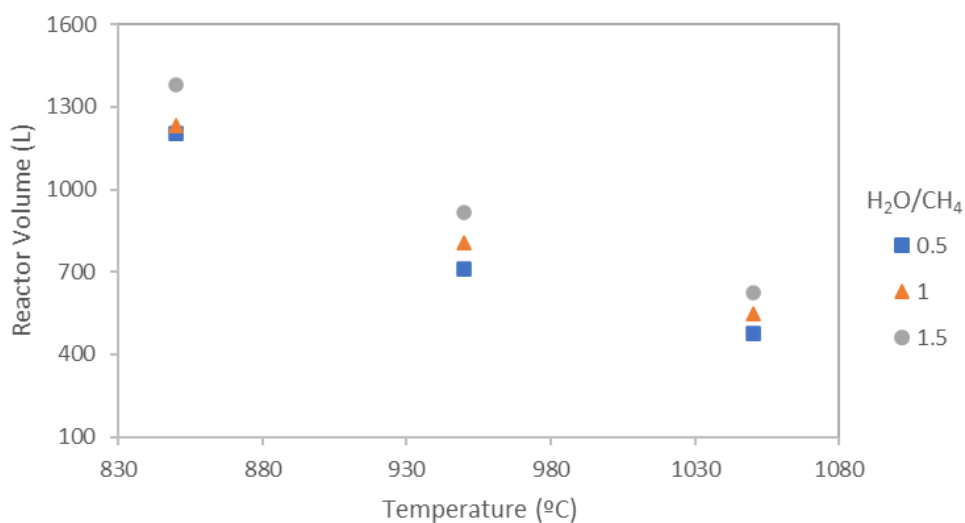


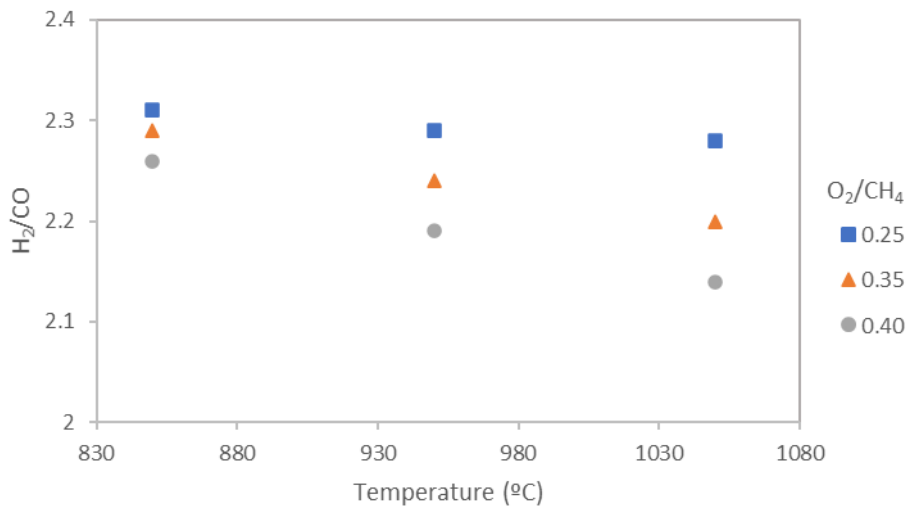
Figure 3. Influence of the H₂O/CH₄ (a) and reaction temperature (b) on the syngas H₂/CO ratio and the reactor volume.

As can be seen in Figure 3a, the higher the H₂O/CH₄ ratio, the higher the H₂/CO molar ratio, since the steam reforming reaction (Eq. 1) is favoured and thus, the generation of H₂. On the other hand, according to Figure 3b, the increase in the reactor temperature promotes a decrease of the H₂/CO, as previously reported in literature [24]. Moreover, the temperature increase benefits the reaction kinetic, decreasing the reactor volume required for a methane conversion of 95 %. The influence of the temperature is very

precise thanks to the implementation of all the kinetic equations of the tri-reforming process in the reforming reactor. Considering these results, a $\text{H}_2\text{O}/\text{CH}_4$ ratio of 0.5 was chosen as the best value for the reforming process.

As commented before, once selected the $\text{H}_2\text{O}/\text{CH}_4$ ratio, different values of the O_2/CH_4 were assayed. The obtained results are shown in Figure 4.

a)



b)

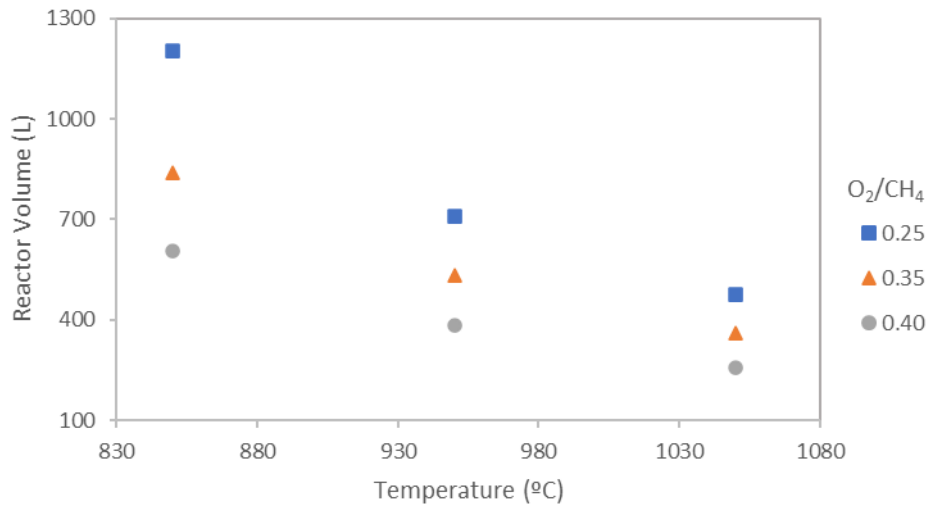


Figure 4. Influence of the O_2/CH_4 (a) and reaction temperature (b) on the syngas H_2/CO ratio and the reactor volume.

It can be observed that the increase of the O_2/CH_4 reduces the H_2/CO ratio, since the partial oxidation of methane is favoured [25]. The optimal value for the studied O_2/CH_4

ratios was 0.4, since allowed to achieve a 95% conversion of methane with a H₂/CO ratio of 2.26 and the smallest reactor volume for a temperature of 850 °C.

The optimal conditions found for the tri-reforming process are summarized in Table 7.

Table 7. Optimal conditions for the tri-reforming process

Operating parameter	Value
H₂O/CH₄ molar ratio	0.5
O₂/CH₄ molar ratio	0.4
Temperature (°C)	850

3.3. Economic Assessment

As commented in the methodology section, one of the main differences with other works regarding tri-reforming simulation [19,20,26] is the implementation of a furnace to provide the energy for the reactors, which also generates CO₂ and water for the process. In this section, the economic feasibility of the proposed process under the selected condition after the sensitivity analyses will be checked.

The production was defined considering the methanol consumption of three different industrial plants located in Tarragona (Spain) which is about $1.2 \cdot 10^6$ t/year [27]. Operating the proposed plant for 8000 h/year, the production would be of $4.3 \cdot 10^5$ t/year, covering a 36% of the demand.

The first step for the economic assessment will be the equipment cost estimation, based on their main dimensions or characteristic parameters (Table 8). Most of the equipment costs have been estimated by means of the Economic Analyzer tool from Aspen Hysys[®], but some of them were obtained from the webpage www.matche.com or calculated by the method described by Cabra et al. [28]. If the costs are calculated with any of these last two alternatives, it is indicated in the table.

Table 8. Main equipment and their individual costs.

Equipment	C₂₀₁₉ (€)	Description
Comp syngas 1	39,821,213	Compressor to increase the furnace gases pressure
Comp syngas 2	6,642,000	Second compression step of the syngas for methanol reactor
Comp syngas 3	3,862,202	Third compression step of the syngas for methanol reactor
Comp Rec	869,140	Compressor for the recirculation in the methanol section
Cooler 1	137,621	Heat Exchanger
Cooler 2	24,257	Heat Exchanger
Cooler 3	73,232	Heat exchanger
Cooler 4	55,774	Heat exchanger
Cooler 5	583,194	Heat exchanger
Flash 1	68,822	
Flash 2	33,079	MeOH product separator
Heat Exchanger [29]	34,248	Heat exchanger
Heater 1 [29]	1,016,860	Heat exchanger for steam generation as feed to the TRM Reactor
Vap 1	407,050	Heat exchanger with generation of steam
Vap 2	85,269	Heat exchanger with generation of steam
Vap 3	24,258	Heat exchanger with generation of steam
Vap 4	87,750	Heat exchanger with generation of steam
Vap NH₃	39,143	Heat exchanger with generation of NH ₃ vapour
PFR-100 TRM Reactor	58,487	Tri-reforming plug Flow reactor
Furnace	436,791	Furnace for the production of the CO ₂ from natural gas
Pre-reactor	1,375,240	Pre-reactor for syngas production
MeOH reactor	301,661	Reactor for MeOH production
Adsorber 1	900,000	Absorber for water removal from syngas
Adsorber 2	850,000	Absorber for MeOH purification
Adsorber 3	900,000	Absorber for methane removal
TOTAL	58,687,291	

Once the main equipment costs are known, the fixed capital was calculated by means of the percentage method [28], with a value of 163,544,306 €. The summary of the percentage method is shown in Table 9.

Table 9. Percentage method results.

Item	Percentage (%)	Costs (€)
Main equipment costs (E)		58,687,291
Installation costs (M)	60% E	35,212,375
Buildings	28%	9,859,465
Piping	45%	15,845,569
Instrumentation and control	10%	3,521,237
Electricity	10%	3,521,237
Insulation	5%	1,760,619
Painting	2%	704,247
Detail engineering	15% (E+M)	14,084,950
Process engineering, licensing	20% (E+M)	18,779,933
Construction	50% (E+M)	46,949,833
Construction supervision	10% (E+M)	9,389,967
Total area of process. Inside battery limit (ISBL)		184,104,348
Auxiliary services	4% ISBL	7,364,174
Construction expenses	8% ISBL	14,728,348
Contractor's fee	3,5% ISBL	6,443,652
Contingency	15% ISBL	27,615,652
TOTAL CAPITAL INVESTMENT		240,256,174

The working capital value for chemical industries is commonly between 10 % and 30 % of the capital investment. In this case, an average value of 20 % has been selected. It has been also assumed that it is recovered at the end of the project and that the total production was sold. For the sales and costs, the only sold product is the obtained methanol. Costs are considered the raw materials and auxiliary services (direct costs) and the indirect labour, maintenance, insurances, operating supplies, laboratory, payroll charges and taxes (indirect costs). Considering the previous work by Lázaro [30], the indirect labour, the payroll charges and the laboratory were considered as 30 %, 25 % and 20 % of the direct labour, respectively. On the other hand, the maintenance and insurances, the operating supplies and taxes, were estimated as a 3%, 5% and 3% of the fixed capital, respectively.

The total methanol production, its price and the benefits obtained from the sales are shown in Table 10, whereas the different costs are summarized in Table 11.

Table 10. Methanol sales per year

Mass Flow (kg/h)	Mass Flow (kg/year)	Methanol Price (€/kg)	Total Sales (€/year)
68,120	544,960,000	0.35 [31]	190,736,000

Table 11. Operation costs.

RAW MATERIALS			
Natural Gas	Price (€/kg)	Consumption (kg/h)	Cost (€/year)
	0.05 [32]	43,490	17,396,000
Water	Price (€/m³)	Consumption (m³/h)	Cost (€/year)
	0.43 [33]	12.39	125,763
Oxygen	Price (€/kg)	Consumption (kg/h)	Cost (€/year)
	0.4 [34]	19,458	62,265,600
AUXILIARY SERVICES			
Electricity	Price (€/kWh)	Consumption (kW)	Cost (€/year)
	0.07015 [35]	90,037	50,548,968
Cooling water	Price (€/m³)	Consumption (m³/h)	Cost (€/year)
	1.2688 [33]	62.0	899,071,680
DIRECT LABOR			
	Cost/unit (€)	Units	Total Cost (€/year)
Control Operator	30,000	5	150,000
Plant Operator	25,000	10	250,000
TOTAL DIRECT LABOR (€)			400,000
Indirect labor			120,000
Maintenance			7,207,685
Operating supplies			12,012,809
Laboratory			80,000
Payroll charges			100,000
Tax			7,207,685
TOTAL MANUFACTURING COSTS (€)			126,346,751

Finally, the economic feasibility of the process was analysed by comparing the most relevant economic parameters, including the Net Present Value (NPV), the Internal Rate of Return (IRR), the Payback Period (PBP) and the break-even.

For this economic analyse, the considered time for the start-up of the plant was 2 years and the period of use for the project was 15 years due to the capacity of the plant. The investment curve is based on 100 % in the start-up period (50 % each year) and the amortization is considered linear during the whole time of the process. Besides, the discount rate was 3.0 %, corresponding to the legal rate of interest applied in Spain in 2019 [36]; the estimated inflation rate for the whole period was 1.52 %, corresponding to the value of April 2019 [37], and a tax rate of 35.0 %. Considering all this data, the cash flow was calculated (Figure 5).

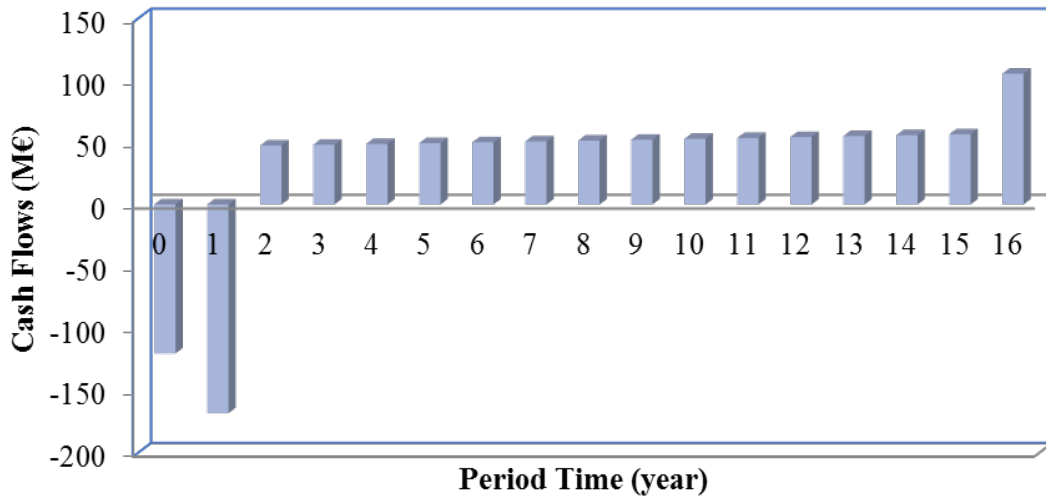


Figure 5. Temporary evolution of the cash flow.

Then, the NPV and IRR can be estimated by Eq. 7 and 8:

$$NPV = \sum_{t=0}^T \frac{F_t}{(1+r)^t} \quad (\text{Eq. 7})$$

$$\sum_{t=0}^T \frac{F_t}{(1+IRR)^t} = 0 \quad (\text{Eq. 8})$$

where F_t is the net cash inflow during the considered period t , r is the discount rate (2.7 %) and T is the time interval considered for the whole investment.

Concerning the payback period, it is the period of time required to recover the total investment, and thus, the period of time for the project to start being profitable. It was calculated from the cumulative cash flows for all preceding years and the current

year. The first year where the cumulative cash flow is positive will indicate the payback period. Finally, the break-even can be defined as the number of sold units that allows to cover the total costs, without suffering no financial losses [38]. Therefore, the break-even is the number of units that makes the NPV of all cash flows equal to zero. The most relevant economic parameters are gathered in Table 12.

Table 12. Relevant economic parameters.

<i>NPV</i> (M€)	<i>IRR</i> (%)	<i>PBP</i> (year)	<i>Break-even</i> (kg/h)
347.62	14.72	7	53,200

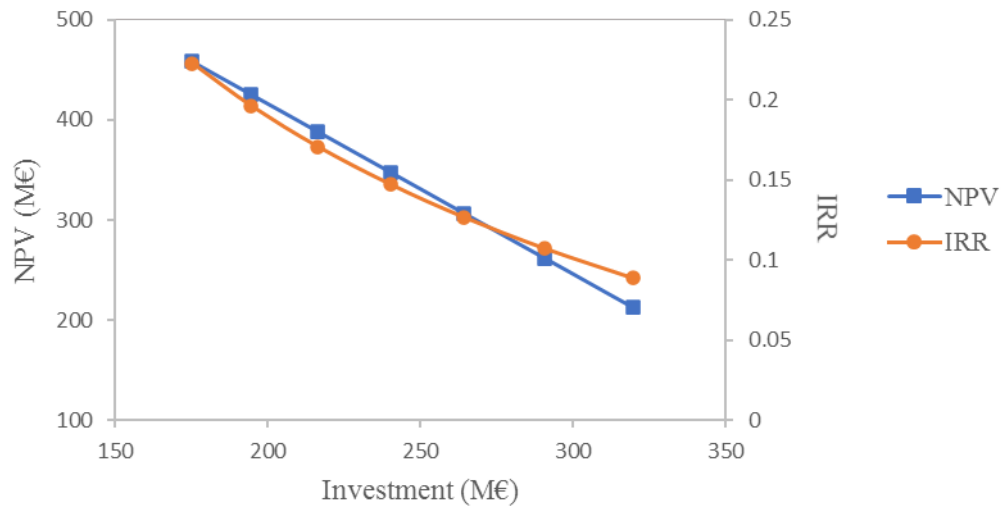
All the economic parameters indicated a good profitability of the process. Besides, this analysis allows to know that the investment could be recovered in 7 years and that the process would be profitable even with a reduction of the methanol production of about a 22 %. This means that the optimal conditions found in the previous sections for the syngas and methanol production allow to achieve a robust process from an economical point of view. Moreover, the utilization of the CO₂ coming from the natural gas combustion in the furnace is also a good alternative, not only from an environmental point of view, but also from an economic perspective.

Finally, in order to check the influence of more variables on the economic robustness of the process, sensitivity analyses were carried out considering the methanol price and the variation in the final plant capital cost.

3.4. Economic sensitivity analyses.

As commented before, the only product to be commercialized is methanol. Thus, the profitability of the process is quite dependent on its price. On the other hand, many assumptions have been considered in the investment estimation. Thus, the influence of a variation of ± 30 % of these two parameters, the investment and the methanol price, on the final profitability of the process was analysed by studying the NPV and IRR values for these variations (Figure 6).

a)



b)

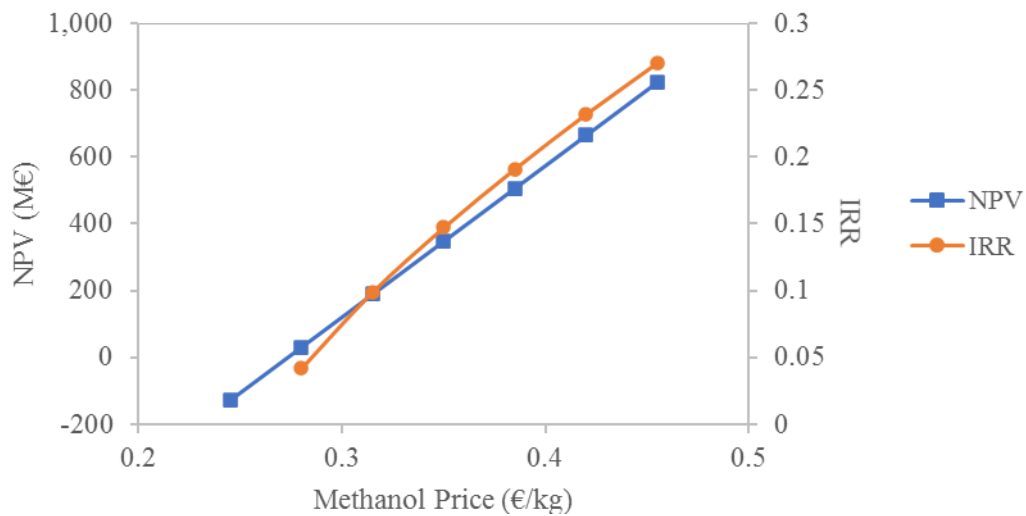


Figure 6. Sensitivity analyses of the investment (a) and the methanol price (b).

As can be observed in Figure 6, the process showed good profitability in the whole studied investment range. The methanol price presented higher influence since the slopes of the NPV and IRR variations are higher. According to Figure 6, the project would be profitable from a methanol price of 0.28 €/kg. For lower prices, negative values of NPV are obtained. This agrees with the break-even result and indicates a quite economically robust process.

4. Conclusions

Methanol production via tri-reforming using natural gas as raw material was simulated using kinetic equations and plug flow reactors. In addition, the flue gas from furnace was used as feed in the tri-reforming process to reduce greenhouse emissions. The effect of operating conditions ($\text{H}_2\text{O}/\text{CH}_4$ and O_2/CH_4 ratios and temperature) on the tri-reforming process were analyzed. $\text{H}_2\text{O}/\text{CH}_4$ ratio of 0.5, O_2/CH_4 ratio of 0.4 and 850 °C were the parameters selected to achieve a 95% conversion of methane with a H_2/CO ratio of 2.26. Finally, the profitability of the process was evaluated considering a variation of the investment and the methanol price. It was observed that the process is profitable for the whole studied investment range and the methanol price have to be higher than 0.28 €/kg.

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