Multi-objective Optimization of a New Sustainable Methanol Plant with Cogenerated Energy

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Abstract

Contemplating the situation of biofuels, the objective of this work is to investigate the techno-economic feasibility of methanol synthesis using carbon dioxide captured as an output of fermentation process in bioethanol production distilleries, carrying out an integrated analysis of the overall system. Up to now, studies limited to evaluate the methanol production hydrogenating CO_2 from fossil sources. Systems assessed in this perspective usually are not economically viable due to the high cost associated to obtain hydrogen. In this work, we designed a new sustainable methanol production process from a renewable source. Aiming to promote the advancement and applicability of carbon capture processes, an industrial methanol plant was modeled in Aspen Plus®. The hydrogen required was produced electrolyzing treated water of the distilleries, producing oxygen as a valuable byproduct. Design parameters were manipulated taking into account the associated capital costs and applying factorial design and sensitivity analysis techniques. The response surfaces were obtained according to the amount of bagasse used to cogenerate energy, which has a direct relation with the objective function, attempting to minimize the total annualized costs and the CO_2 Net of the scenario. The results show that the problem of high-energy consumption for the production of hydrogen via electrolysis was bypassed using co-generated energy, being possible and viable to synthesize this process in distilleries able to emit more than 350,000 ton/year of CO_2 with enough cogeneration plants installed. The gross profits obtained by this process are derived from the methanol and oxygen produced being significantly superior by a factor of 4.5 compared to sale of electricity and 8.0 for sale of pure hydrogen. The designed plant led us to conclude that this improved process can be implemented and is an innovative option for carbon mitigation, contributing to the sustainable production of methanol.

Keywords: Ethanol distillery, Optimization, Methanol synthesis, Cogeneration; Hybrid models.

1. Introduction

Warming of the climate is undeniable. The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, sea level has risen, and the concentrations of greenhouse gases (GHG) have increased. Among the GHG, carbon dioxide contributes to the atmosphere warming, as a result of emissions directly related to human activities, with 64.3% of the total gases emitted. Carbon dioxide concentrations have increased by 40% since pre-industrial times, primarily from fossil fuel emissions and secondarily from net land use change emissions (IPCC, 2013).

In order to reduce CO_2 emissions from power plants, CO_2 capture appears as a promising option. However, the costs of capture are still high and the energy required to operate CO_2 capture systems might reduce the overall efficiency of power generation or other processes, leading to increased fuel requirements, solid wastes and environmental impacts related (Harkin *et al.*, 2012). Therefore, if the captured CO_2 were used as raw material in the production of a marketable product, its capture and sale might become not only economically viable but also a profitable business, besides the advantage to replace fossil fuels by renewable ones (Van-Dal and Bouallou, 2013). Captured CO_2 can be used in different industrial sectors, including the food and beverage as well as pharmaceutical industry. It can also be converted into high demanded products such as urea, methanol, and biofuels (Cuéllar-Franca and Azapagic, 2015). Among various possible fuel products, methanol is of particular interest because it can be used for gasoline blending or direct methanol fuel cell. Moreover, methanol can be used to produce other valuable chemical derivatives, such as formaldehyde, acetic acid, methyl methacrylate, etc... Methanol also is a clean-burning, biodegradable fuel. Increasingly, methanol's environmental and economic advantages are making it an attractive alternative fuel for powering vehicles and ships, cooking food and heating homes (Goeppert *et al.*, 2014).

The works presented in the literature for the design of methanol from CO_2 hydrogenation processes have one main limitation (Bhandari *et al.*, 2016): they rarely approach the economic performance or points as infeasible other aspects of the problem (i.*e.*, hydrogen cost). In this study, a novel sustainable scenario for methanol production is proposed, capturing CO_2 released from an ethanol industrial unit, specifically from the fermentation system. This new scenario might result in a practical advance for the methanol production market and other products derived from CO_2 and H_2 combination. The case study initially considers a methanol plant annexed to a hypothetic autonomous distillery based on a Brazilian case, which crushes 7,000,000 t/y of sugarcane and cogenerates a boiler steam production of 935 t/h and supplying 71.2 MWh of electricity (Renó *et al.*, 2011). In this process the main part of the cogenerated energy is used to operate the electrolyzers, being a possible surplus directed to the distillery and the methanol plant, which supplies part of the electricity and thermal demand of the plant. The scheme of is shown in Fig. 1.

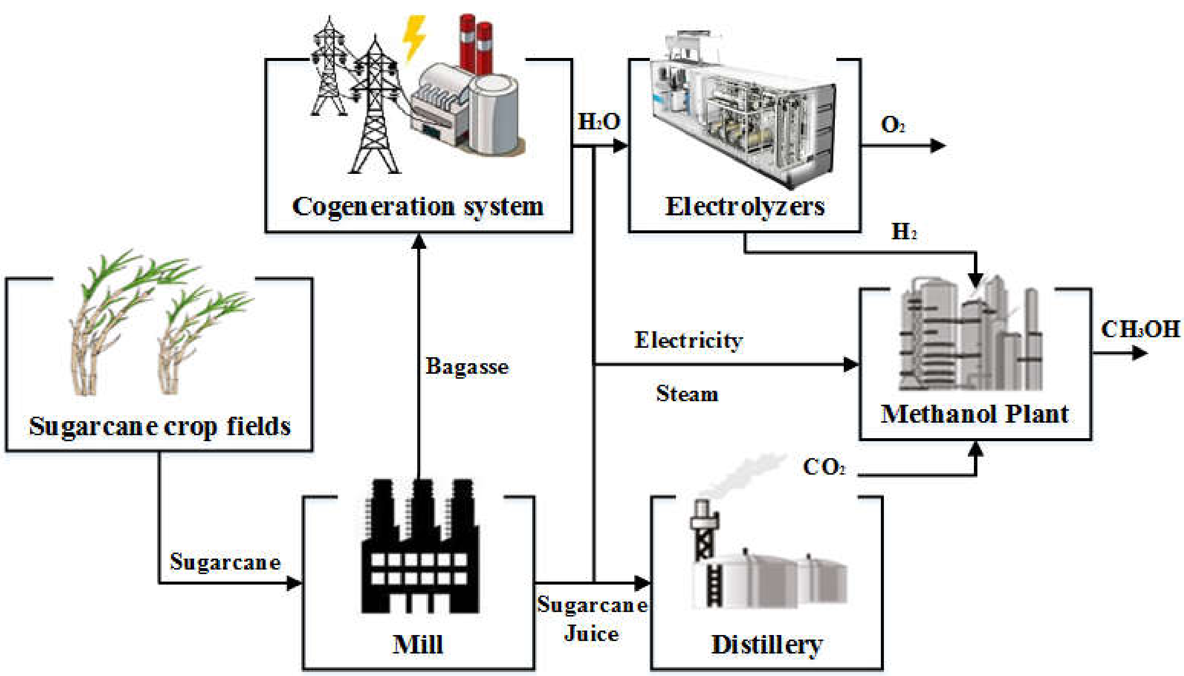

Fig. 1. Partial view of the supply chain of the case-study.

2. Methods

2.1 Problem statement

In this paper we approach and design a new scenario of methanol synthesis coupled to an autonomous ethanol distillery by hydrogenating CO_2 to methanol using cogenerated energy. Moreover, a systematic methodology for optimization of chemical processes that relies on the combined use of simulation and optimization techniques is applied. The design task is solved by a hybrid simulation-optimization method presented by Brunet *et al.* (2014) that exploits the complementary strengths of optimization tools (*i.e.*, NLP) and commercial process simulators (*e.g.*, Aspen Plus). The highlights of the process simulation are described hereafter using the nomenclature presented in Table 1.

Table 1. Nomenclature.

Abbreviation		*Parameters*	
NLP	Non Linear Programming	$\sum_{streams} CO_{2,out}$	CO_2 in output streams
GWP	Global warming potential	$\sum_{Utilities} CO_{2,prod}$	CO_2 producer by required utilities
moMINLP	Multi-objective Mixed Integer Non Linear Programming	$\sum_{streams} CO_{2,in}$	CO_2 fed in the process
Functions		OPEX	Annualized operational expenditure
U	Multi-objective function	CAPEX	Annualized capital expenditure
TAC	Economic function	P	Pressure
$CO_2\ Net$	Environmental function	x	Mass fraction

2.2 Water electrolysis unit

Hydrogen can be produced by electrolysis according to:

$$H_2O_{(l)} \rightarrow H_{2(g)} + ½O_{2(g)}$$
(1)

The water electrolysis unit considered uses electrolyzer modules with an energy consumption of 51.2 kWh_{el}/kg H_2 (E4TECH). The hydrogen leaves the electrolyser at 1 bar and 298 K and is directed to the methanol plant. A large amount of valuable oxygen is generated as by-product (Eq. 1).

2.3 CO_2 source

The presented scenario uses CO_2 as raw material to produce methanol. In the ethanol distillery, the juice extracted from the sugarcane is concentrated in a serie of evaporators and then sent to the fermentation system. This system is composed of fermenters that convert sucrose to ethanol and carbon dioxide (Eq. 2) and an absorption column that recovers some of the ethanol present in the gaseous stream, releasing CO_2 to the atmosphere with more than 99% of purity (detailed process can be found in Silva *et al.*, 2015).

$$C_{12}H_{22}O_{11(l)} + H_2O_{(l)} \rightarrow 4C_2H_5OH_{(l)} + 4CO_{2(g)} \quad (2)$$

2.4 Methanol process description

The methanol industrial plant is designed based on Van-Dal and Bouallou (2013). Two models are employed to determine the thermodynamic properties: Redlich-Kwong-Soave with Huron-Vidal mixing rules for streams at high pressure (>10 bar), and NRTL-RK for streams at low pressure (<10 bar). Mass and energy balances are solved using Aspen Plus v8.8 (Fig. 2).

Compression and preheating: Gases are fed in the process at 298 K and 1 bar, passing through a series of compressors with intercooling, up to the pressure of 50 bar. The pressurized streams are mixed and enters into a heat exchanger that raises the reactor feed stream to 523 K.

Methanol synthesis reactor: The production of methanol using CO_2 occurs through two possible ways: direct hydrogenation of CO_2 (Eq. 3), or the conversion of CO_2 to CO (through the reverse water gas shift reaction, Eq. 4) and then hydrogenated to methanol (Eq. 5).

$$CO_{2(g)} + 3H_{2(g)} \leftrightarrow CH_3OH_{(l)} + H_2O_{(g)} \quad (3)$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)} \quad (4)$$

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} \quad (5)$$

The reactor is simulated as isothermally, with 810 tubes of 12 m of length and 0.06 m of diameter each, and packed with a load of 865 kg of Cu/Zn/Al/Zr catalyst, with a bed voidage of 0.98. Pressure drop is evaluated using Ergun's correlation. These conditions are taken from Kiss *et al.* (2016) who described a Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model for the methanol synthesis. The reactor effluent, at 523 K, is then divided into two streams: 80% of the stream proceeds to heating the reactor feed stream (HX4) while the other 20% is used to heat the reboiler of the distillation column. The streams are mixed again posteriorly (MIX3).

Distillation and purification: The crude methanol that leaves the reactor is a mixture of methanol, water and residual gases (*i.e.*, H_2 and CO and CO_2). To remove recycle the non-reacted gases, the stream is expanded to 1 bar using valves, and then separated in a flash tank. The remaining liquid is heated to 344 K and fed into the distillation column with a reflux ratio of 1.2. The bottom product of the distillation column corresponds to the water produced and might be re-used in the absorption column of the ethanol distillery, while the top product is mostly methanol with some unreacted gases. Methanol is then compressed to 1.2 bar and cooled to 313 K proceeding to another flash that separates the gases (top outlet) from the methanol product with 99% w/w in the bottom stream.

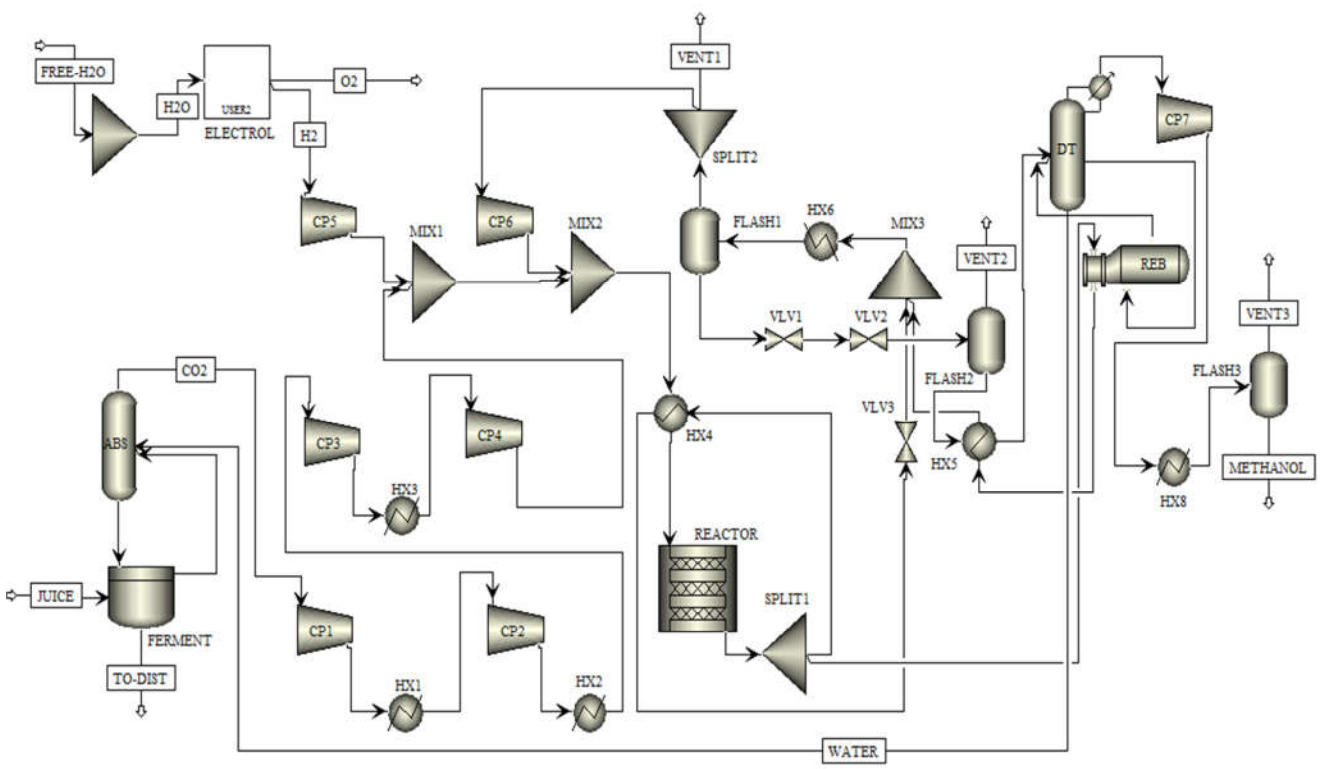

Fig. 2. Process flowsheet of the case study modelled in Aspen Plus v8.8.

3. Calculation

Once the base case of the process is obtained, the next step is to optimize it, including equipment sizes and operating conditions that simultaneously minimizes the total annualized cost (*TAC*) and the environmental impact ($CO_2\ Net$), measured according to LCA principles. The optimization problem of the methanol production process can be formally stated as follows.

3.1 Modelling

The purposed model seeks to optimize simultaneously *TAC* and $CO_2\ Net$. Details on the calculation of each objective function and the constraints are provided hereafter. Fig. 3 outlines the methodology containing the hybrid algorithm that combines mathematical programming and process simulators. One of the main advantages of the approach adopted is that it has benefits from the unit operation, thermodynamic models and physical propertymodels already implemented in the process simulator. To solve the moMINLP problem, the design variables are fixed to the optimal values obtained in the latest NLP solved at iteration k of the algorithm.

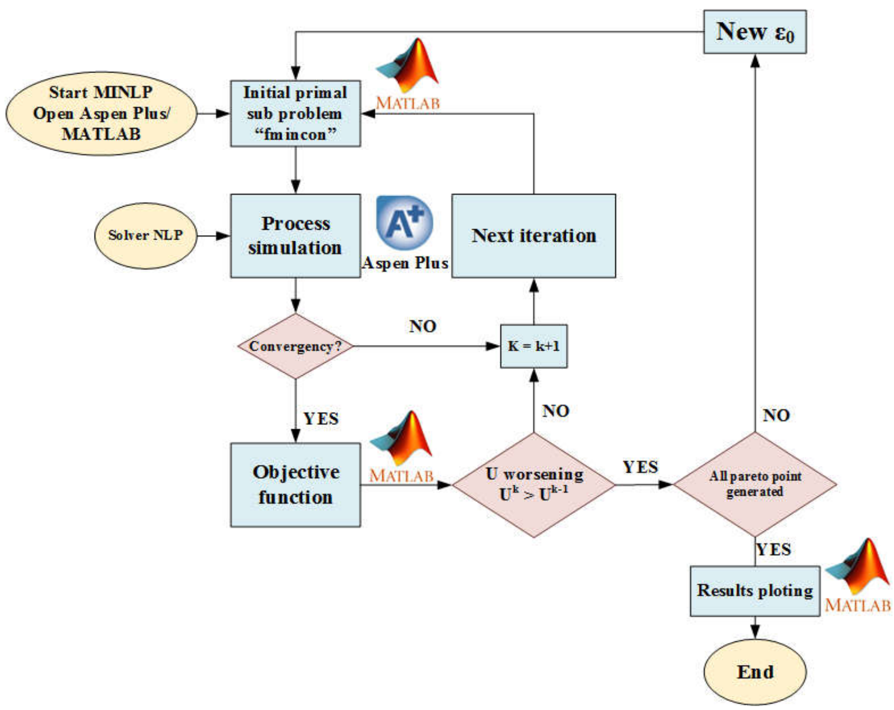

Fig. 3. Algorithm of the proposed methodology.

The optimization methodology is performed only for the configuration that presented the best results for the process after the factorial design followed. An external NLP solver in Matlab is employed to explore the design and operating variables that minimize the total cost and the environmental impacts of the process (Torres *et al.*, 2013; Galán-Martín *et al.*, 2017). As NLP solver, we use the "*fmincon*", as it is able to cope with an objective function that includes constraints. Since Matlab minimizes just *one* objective function, we must change the objective function to pose the problem as a moMINLP one.

3.2 Pareto frontier

Pareto curves show trade-off relationships between different objectives. In this work, we use the ε-constraint method to optimize one of the objective functions using the other objective functions as an additional constraint with the epsilon value as a bound. Therefore, the modified NLP takes the form presented next (Eq. 6).

$$
\begin{aligned}
J = f_1(x,u,x_D,y) + \prod(s_1+s_2+s_3+s_4) \\
s.t. \quad & f_0(x,u,x_D,y) \le \epsilon_o + s_1 \qquad o = 2, \dots, n \\
& \underbrace{\epsilon_o} \le \epsilon_o \le \overbrace{\epsilon_o} \qquad o = 2, \dots, n \\
& h_I(x,u,x_D) = 0 \\
& h_E(x,u,x_D) + s_1 - s_2 = 0 \\
& g_E(x,u,x_D) \le s_3 \\
& s_1; s_2; s_3; s_4 \ge 0
\end{aligned} \qquad (6)
$$

In model (M), f_1 is the optimized objective function with continuous variables and $\prod$ is a penalty parameter vector, and s_1, s_2, s_3 and s_4 are vectors of positive slack variables. Functions h_I are implicit equations solved by the process simulator, whereas h_E and g_E are explicit external equality and inequality constraints. As observed, f_0 is the objective function taken as a constraint by ϵ_o.

The independent variables in the process are operating reactor pressure and temperature, number of tubes inside the reactor, length of tubes, outlet pressure of flash tanks, reflux ratio and feed stage of the distillation column.

3.3 Objective functions: TAC and CO_2 Net

The economic indicator to evaluate the profitability of the process alternatives is the total annualized cost (*TAC*) that accounts for the annualized capital (*CAPEX*) and operational (*OPEX*) expenditures.

$$TAC = CAPEX + OPEX \qquad (7)$$

As the goal of this study is the design of a more sustainable CO_2 utilization process, the Net CO_2 emission of the process is the primary criterion following the LCA methodology for climate change analysis (Roh *et al.*, 2016). The Net CO_2 balance is defined following the Equation 8:

$$CO_2\ Net = \sum_{streams} CO_{2,out} + \sum_{Utilities} CO_{2,prod} - \sum_{streams} CO_{2,in} \qquad (8)$$

When the right hand side of Eq. (8) is negative, the amount of CO_2 that is utilized by the process is greater than the amount that is generated making it a CO_2 reducing process. However, when the net CO_2 emission for is positive, it should be compared with existing conventional processes. The contribution of all material streams and utilities entering and leaving the process are analyzed.

3.4 Process constraints

To accomplish the optimization problem, it is necessary to obtain gradient information about the objective function and constraints. Additional constraints also should be respected: positive variable (Eq. 9); maximum pressure rate in the compressors (Eq. 10); output methanol mass fraction greater than 99% (Eq. 11); CO_2 conversion in the reactor (Eq. 12); methanol losses in Vent outputs (Eq. 13) and CO_2 net for the environmental objective function (Eq. 14).

All variables ≥ 0 (9)

$$\frac{P_{out}}{P_{in}} \le 3 \qquad (10)$$

$$x_{CH3OH}^{product} \ge 0{,}99 \qquad (11)$$

$$\frac{\left(CO_{2_{in}}^{reactor} - CO_{2_{out}}^{reactor}\right)}{CO_{2_{in}}^{reactor}} \ge 20\% \qquad (12)$$

$$x_{CH3OH}^{vent} \le 0{,}02 \qquad (13)$$

$$CO_2Net\left({}^{t_{CO2}}/_{year}\right) \le 0 \qquad (14)$$

4. Results and discussion

Our results highlight the methanol production in ethanol distilleries as a suspicious market to countries ascending in the energy cogeneration scenario with deficits in the electricity market.

4.1 Process evaluation

In this work, a plant capacity of approximately 60 kton/year of methanol is modeled. Table 2 provides mass and energy balances for the main streams of the process with their conditions.

Table 2. Mass balance of the process.

Stream parameter	CO_2	H_2	RX-IN	RX-OUT	WATER	METHANOL
Temperature (K)	298.15	298.15	497.15	523.15	372.78	312.15
Pressure (bar)	1.00	1.00	50.00	47.00	1.00	1.00
Vapor Fraction	1.00	1.00	1.00	1.00	0.00	0.00
Mole Flow (kmol/h)	1,205.21	52,360.27	512,141.76	59,821.20	3,006.23	1,896.54
Mass Flow (kg/h)	52,740.00	105,552.00	1,245,028.72	1,245,028.72	54,158.00	37,760.26
Mass frac CO_2	0.99	0.00	0.05	0.01	0.00	0.00
Mass frac H_2	0.00	1.00	0.85	0.83	0.00	0.00
Mass frac H_2O	0.00	0.00	0.01	0.03	1.00	0.01
Mass frac CO	0.01	0.00	0.01	0.01	0.00	0.00
Mass frac CH_3OH	0.00	0.00	0.08	0.12	0.00	0.99

4.2 Sensitivity analyses

To better understand the process applicability, a factorial design is performed to purpose alternatives that compare the methanol production with other scenarios, as the common electricity production and the simple hydrogen production. Factors and levels used as performance indicators for the case study are indicated in Table 3. The electricity price is taken from Aspen Plus and the products prices are obtained from Roh *et al.* (2016).

Table 3. Factors and levels adopted for the factorial design.

Factor	Initial level	Case of Study	Final level	Step
Sugarcane processed (ton/year)	6,000,000	7,000,000	8,000,000	100,000
Electricity price (US$/MWh)	92.00	177.00	262.00	8.5
Hydrogen price (US$/ton)	1,280.00	2,710.00	4,140.00	143
Methanol price (US$/ton)	452.97	766.28	1,079.59	31.33
Oxygen price (US$/ton)	244.00	251.50	259.00	0.75

According to the factorial design, Table 4 presents the results of the simulated process for the edges of the distillery size in the sensitivity analyses.

Table 4. Results of the sensitivity analyses.

Response	Initial level	Case of study	Final level
CO_2 emission (ton/year)	396,216.00	462,252.00	528,288.00
Cogenerated energy (MWh)	58.17	67.86	77.56
Hydrogen production (ton/year)	1,136.13	1,325.49	1,514.84
Oxygen production (ton/year)	9,089.05	10,603.89	12,118.74
Methanol production (ton/year)	94,926.75	110,747.88	126,569.00

It is possible to observe in Table 4 that the amount of sugarcane processed influence directly in the emissions of CO_2 and the cogenerated energy to produce the desired products.

4.3 Economic assessment

The response surfaces for the products prices are obtained according to the amount of sugarcane processed in the cogeneration. Then, three scenarios are compared (Figure 4): a scenario that sales the produced electricity, other which stops in the hydrogen production by electrolyzers and a third one with the methanol plant.

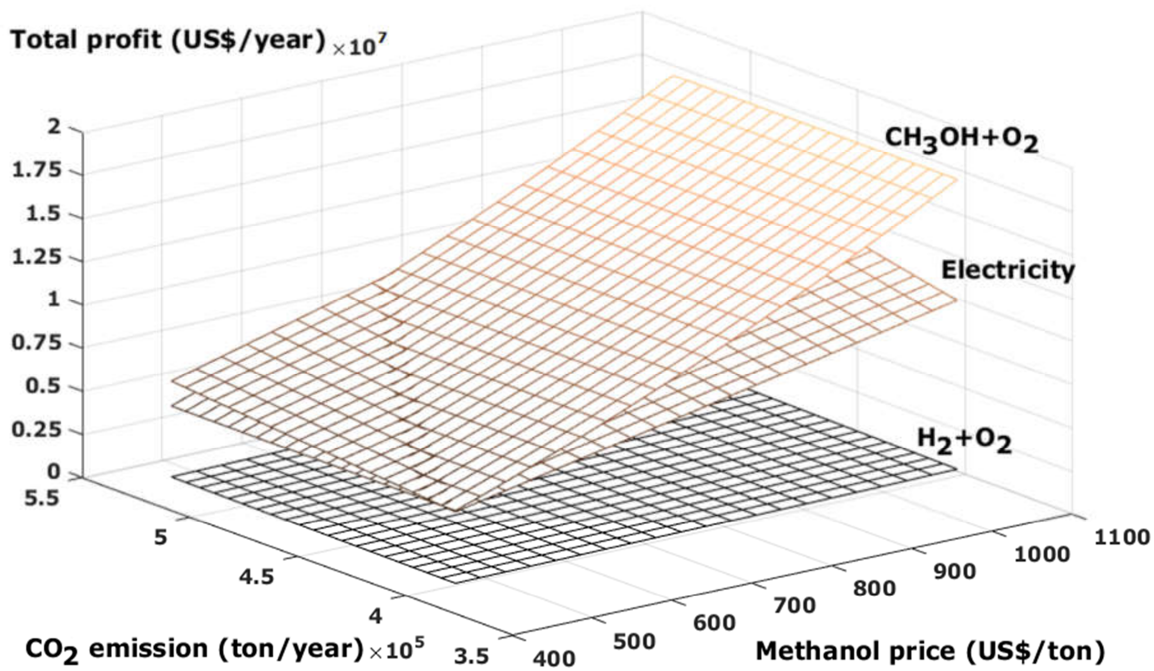

Fig. 4. Response surface of the total profit obtained in the alternatives.

The profit obtained in each alternative are derived from the methanol and oxygen produced being significantly superior by a factor of 4.5 to those compared to sale of electricity and 8.0 for sales of hydrogen and oxygen in the extreme scenarios. In Figure 4 can be noted that the methanol's price must be over than 700 US$ to be considered more attractive than electricity production, what requires a market study to implement the process in the distillery region. For a lifeplant of 20 years operating 8600 h/year and an interest rate of 10%, the period of payback is 3.2 years approximately. The period is determined taking into account the total profit and the annualized total cost presented in Table 5.

4.4 Environmental assessment

In relation to environmental impacts, the results showed that the process has a negative CO_2 Net balance (quantities presented in Figure 5 and Table 5). It is important to note that methanol synthesis has additional emissions of pollutants (ash, tar, particulates, carbon monoxide, and others), which have additional contributions to some environmental impacts, such as global warming and must be quantified with specific studies.

4.5 Pareto frontier

The multi-objective optimization is applied to the designed process, which presented the best results for both economic and environmental assessment. These conditions are presented in the Pareto curve with the important points represented in Figure 5.

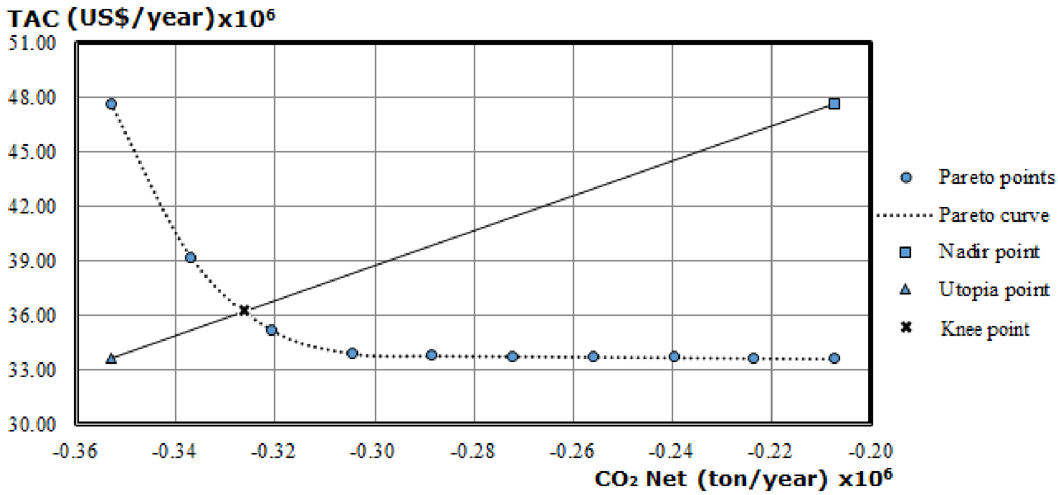

Fig. 5. Pareto set of solutions for the studied scenario.

As observed in the Pareto curve, both the cost and environmental impact can be improved. It seems that the most interesting operation is around the so-called "*knee point*", which is located at the intersection of the two sections of the Pareto frontier. The set of points $f^{Knee} = [-0.325; 36.6x10^6]$ represents the better process design. Table 5 shows the key performance indicators of the best alternatives and it is possible to observe that the *knee point* has intermediary conditions between the optimum solutions.

Table 5. Comparison of key performance indicators for the best alternatives.

Key performance indicators	Minimum *CO_2 Net*	Minimum *TAC*	*Knee point*
CO_2 conversion per pass (%)	20.9	21.51	21.4
CO_2 conversion overall (%)	90.18	95.38	93.18
Electricity usage (kWh/ton CH_3OH)	4,831.58	3,126.21	4,023.89
Steam usage (ton steam/ton CH_3OH)	8.66	7.52	7.72
CO_2 use per unit of methanol product (kg/kg)	2.47	1.41	2.34
H_2 usage per unit of methanol product (kg/kg)	0.97	0.89	0.90

5. Conclusion

The designed plant led us to conclude that this scenario can be implemented being an innovative option for carbon mitigation and contributing to the sustainable production of methanol. The proposed process allows assessing the process economic performance of different systems under consideration. The scenario of methanol production has been shown The designed plant led us to conclude that this scenario can be implemented being an innovative option for carbon mitigation and contributing to the sustainable production of methanol more attractive than the other alternatives (electricity and hydrogen production), because CO_2 adds value to the product without including any raw material costs allowing a much larger production. The results show that the methanol produced cooperate with the global warming issue pulling out carbon dioxide of the atmosphere and emerging as an alternative sustainable process compared with the usual petrochemical process. The problem of high-energy consumption for the production of hydrogen via electrolysis was bypassed using co-generation, being possible and viable to synthesize this process in distilleries able to emit more than 350,000 ton/year of CO_2 with enough cogeneration capacity installed. The methanol production from sugarcane bagasse is a promising alternative for the substitution of significant amount of methanol obtained from natural gas and can also improve the output/input ratio of others biofuel productions that uses methanol as raw material, such as the biodiesel.

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