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

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Academic Work

INTRODUCTION

- **Global warming**
- **CO_2 capture systems**
- **CO_2 reuse**
- **Methanol production**
- **Challenges:**

INTRODUCTION

Main goal:

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 for the methanol production market derived from CO_2 and H_2 combination.

CASE OF STUDY

Initially, is considered 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).

CASE OF STUDY

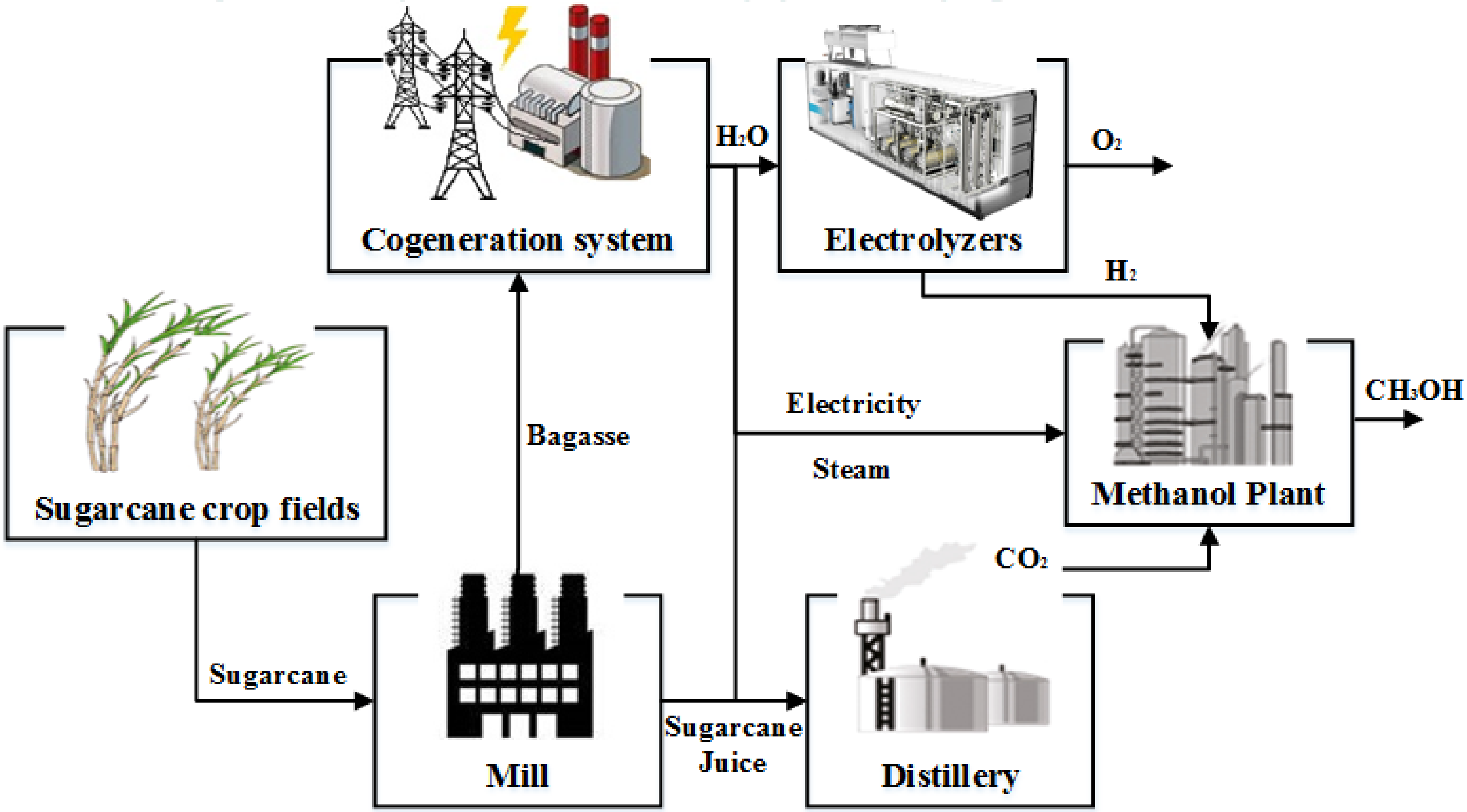

Fig. 1. Partial view of the supply chain of the case-study.

METHODOLOGY

- ***Problem statement***
- ***Water electrolysis unit***

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

Modules with an energy consumption of 51.2 $kWh_{el}/kg\ H_2$ (E4TECH).

By-product: O_2

METHODOLOGY

- ***CO_2 source***

The presented scenario uses CO_2 releasing to the atmosphere with more than 99% of purity (detailed process can be found in Silva et al., 2015).

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

METHODOLOGY

Methanol process description:

- **Compression and preheating**
- **Methanol synthesis reactor**

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

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

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

- **Distillation and purification**

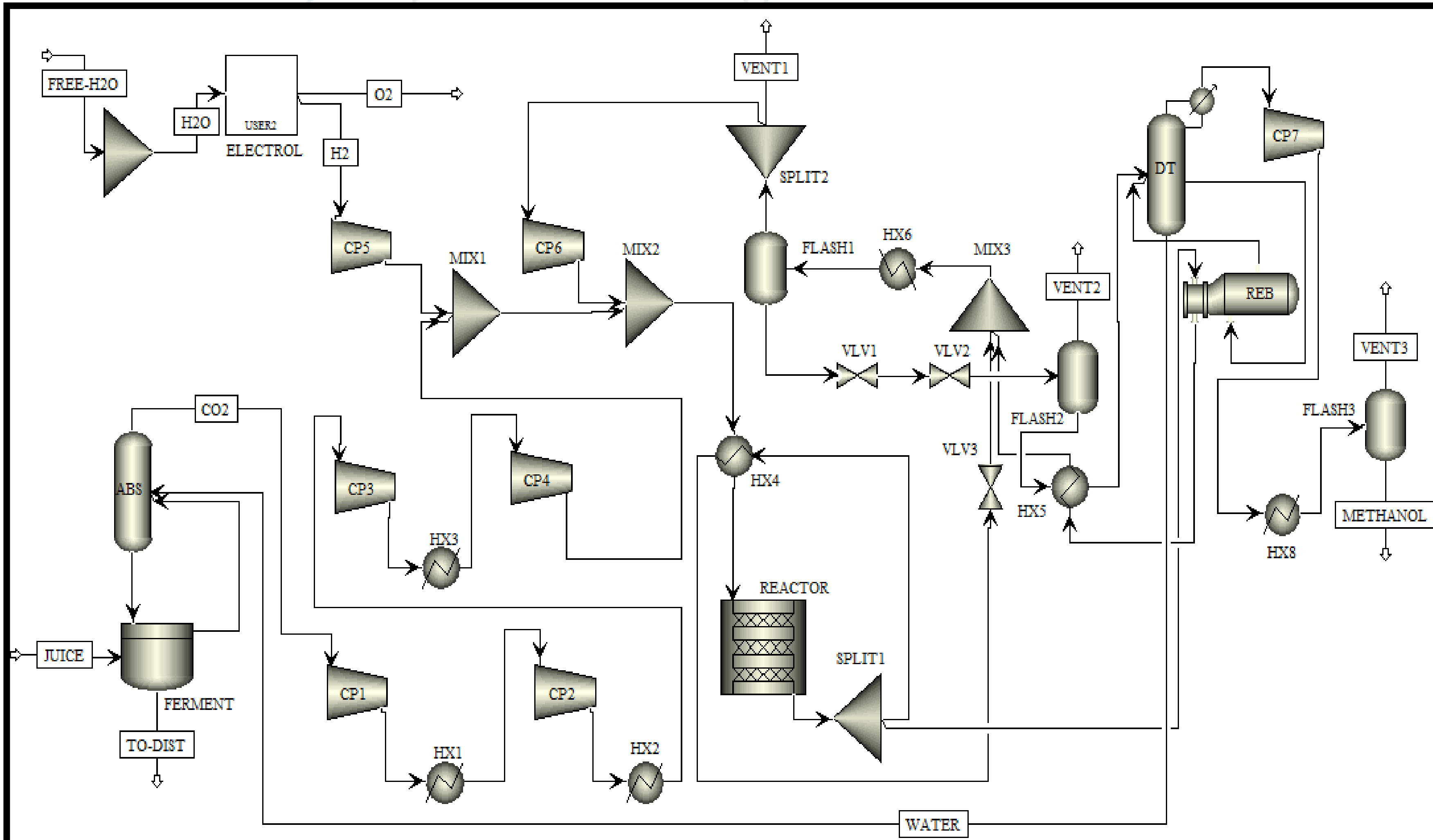

Fig. 2. Process flowsheet of the case study modelled in Aspen Plus v8.8.

CALCULATION

- ***Sensitivity analyses***

Table 1. Factors and levels adopted for the factorial design.

Factor	Initial level	Case of Study	Final level	Step	Reference
Sugarcane processed (ton/year)	6,000,000	7,000,000	8,000,000	100,000	Renó et al. (2011)
Electricity price (US$/MWh)	92.00	177.00	262.00	8.5	UNICA (2016)
Hydrogen price (US$/ton)	1,280.00	2,710.00	4,140.00	143	Roh et al. (2016)
Methanol price (US$/ton)	452.97	766.28	1,079.59	31.33	METHANEX (2016)
Oxygen price (US$/ton)	244.00	251.50	259.00	0.75	Roh et al. (2016)

CALCULATION

- ***Multi-objective Optimization:***
  Pareto frontier with ε-constraint method
- ***Modelling :***

$$(M)\ \min_{x_D} \quad U = f_1(x,u,x_D,y) + \prod(s_1 + s_2 + s_3 + s_4)$$

$$s.t. \qquad f_0(x,u,x_D,y) \le \epsilon_o + s_1 \qquad o = 2\,, \dots, n$$

$$\underbrace{\epsilon_o} \le \epsilon_o \le \overbrace{\epsilon_o} \qquad o = 2\,, \dots, n$$

$$h_I(x,u,x_D) = 0$$

$$h_E(x,u,x_D) + s_1 - s_2 = 0$$

$$g_E(x,u,x_D) \le s_3$$

$$s_1; s_2; s_3; s_4 \ge 0$$

CALCULATION

Objective functions: *TAC* and *CO_2 Net*

- $f_1(x,u,x_D,y)$: $$TAC = CAPEX + OPEX$$
- $f_2(x,u,x_D,y)$:

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

CALCULATION

- **Main constraints:**

All variables ≥ 0

$$\frac{P_{out}}{P_{in}} \leq 3$$

$$x_{CH3OH}^{product} \geq 0,99$$

$$\frac{\left(CO_2{}_{in}^{reactor} - CO_2{}_{out}^{reactor}\right)}{CO_2{}_{in}^{reactor}} \geq 20\%$$

$$x_{CH3OH}^{vent} \leq 0,02$$

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

CALCULATION

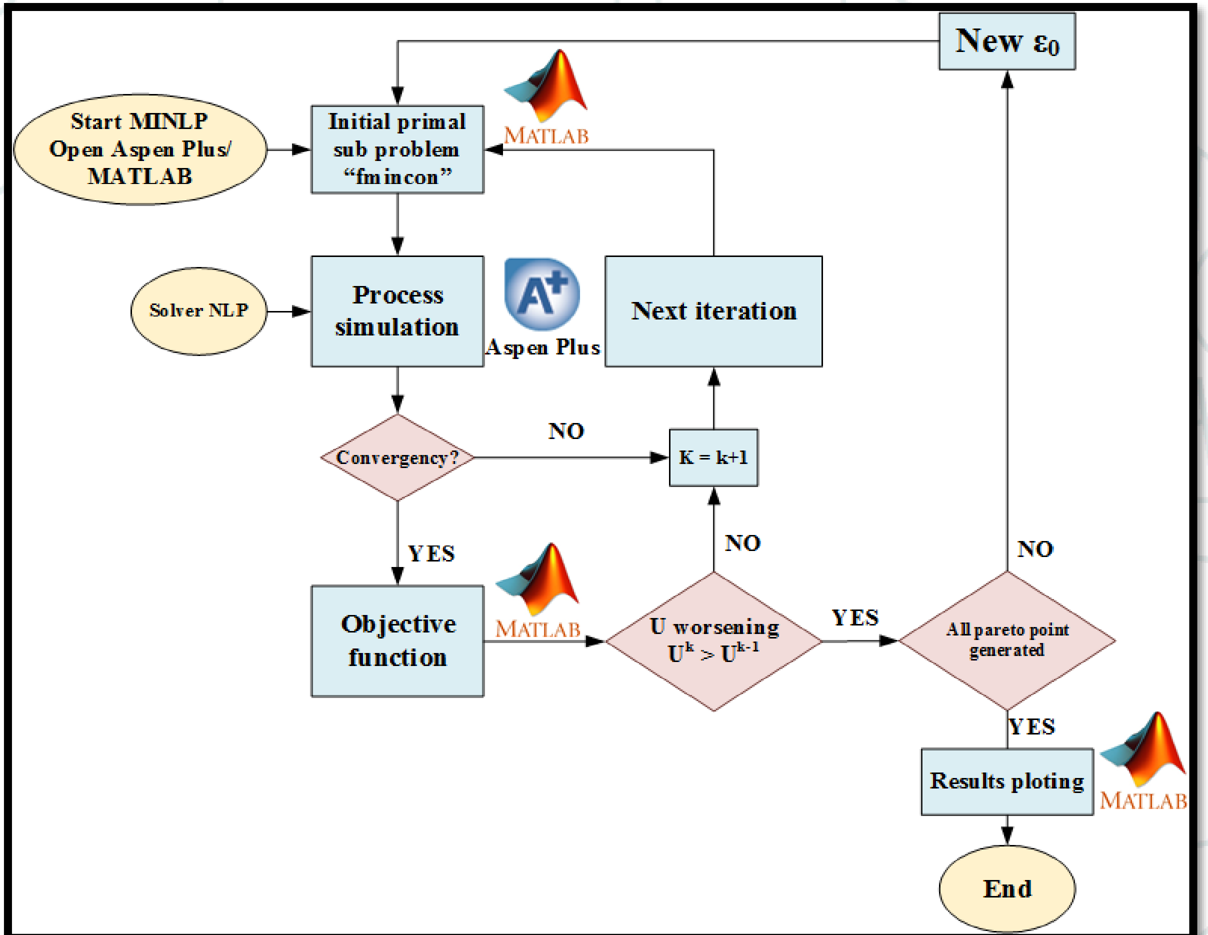

Fig. 3. Algorithm of the proposed methodology.

RESULTS AND DISCUSSION

- **Process evaluation**

Table 2. Mass balance of mains streams of the process in Aspen Plus®.

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

RESULTS AND DISCUSSION

- **Response parameters**

Table 3. 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

RESULTS AND DISCUSSION

- **Economic assessment**

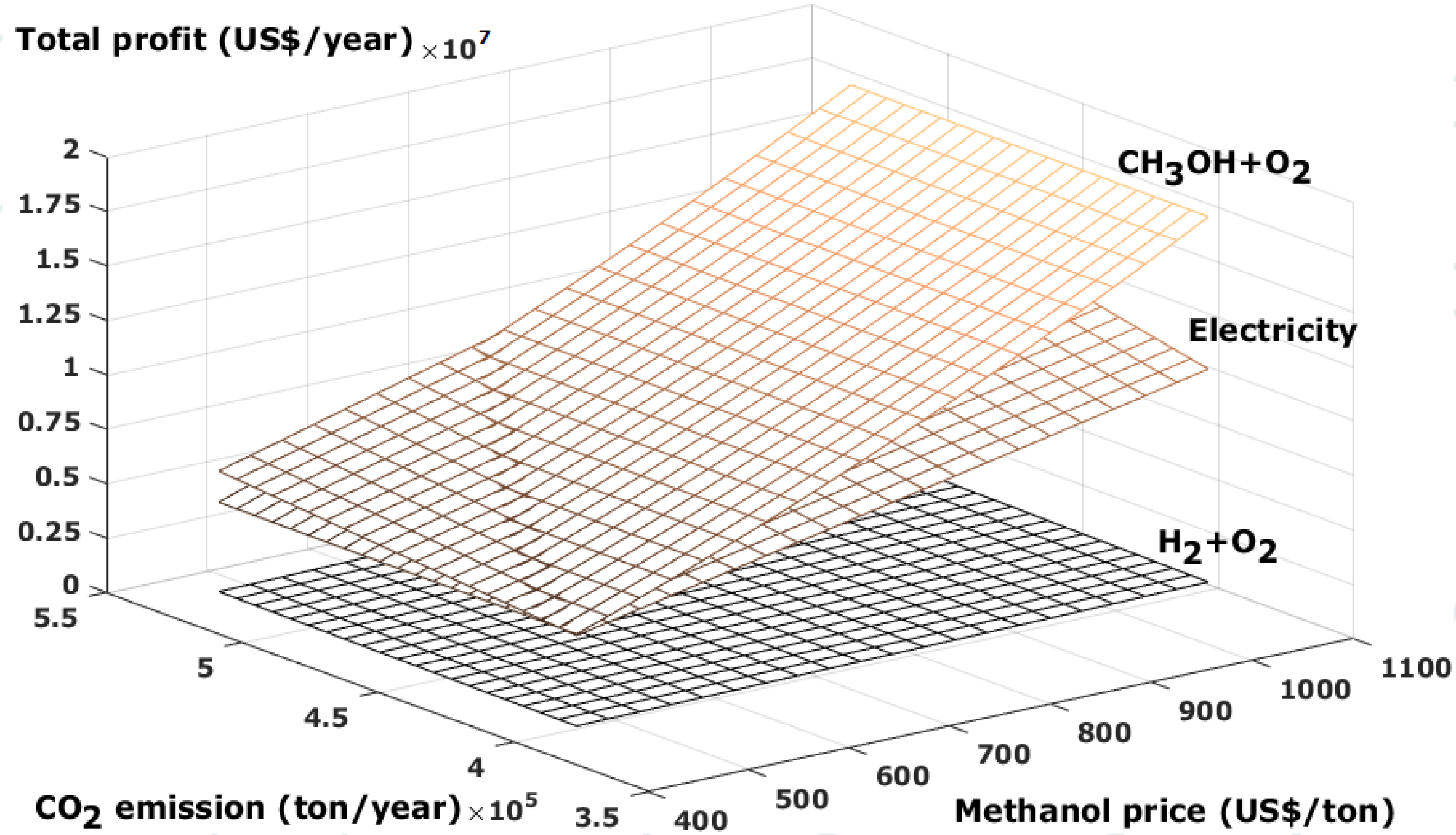

Fig. 4. Response surface of the total profit obtained in the alternatives.

RESULTS AND DISCUSSION

- **Environmental assessment and Pareto frontier**

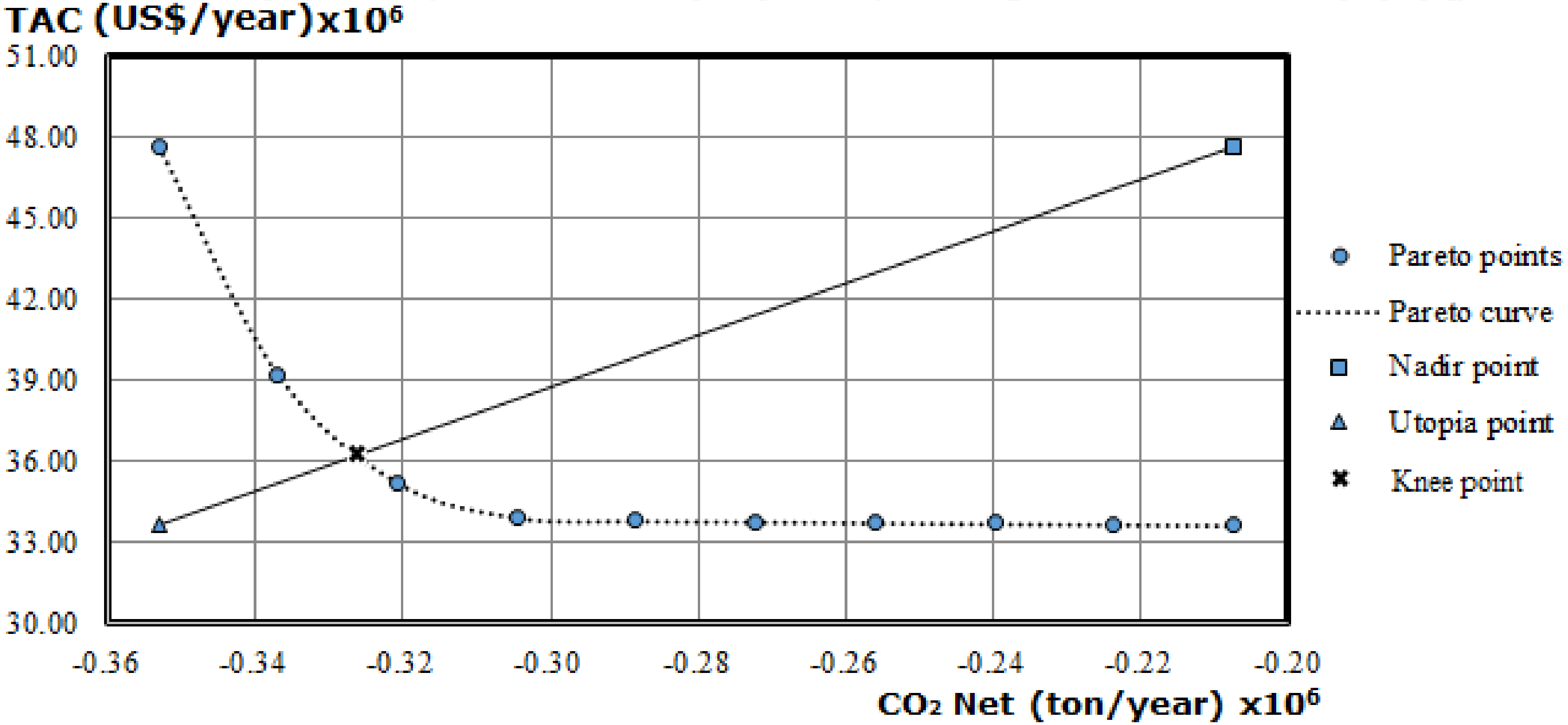

Fig. 5. Pareto set of solutions for the studied scenario.

RESULTS AND DISCUSSION

- **Performance indicators**

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

CONCLUSIONS

- **The scenario is an appropriate option for carbon reuse contributing to the cleaner production of chemicals.**
- **This route is a promising alternative for the substitution of significant amount of methanol obtained from syngas and can also improve other biofuel productions that uses methanol as raw material (biodiesel).**
- **Sustainable production of methanol is more attractive than the other alternatives (electricity and only hydrogen production).**
- **The problem of high-energy consumption for the production of hydrogen via electrolysis was bypassed with cogenerated energy.**

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CAPES

PEQ

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