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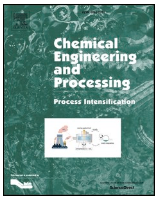

Optimization and sensitivity analysis of a multi-product solar grade silicon refinery: Considering environmental and economic metrics

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ABSTRACT

Today, one of the main lines of solar energy development is the creation of environmentally friendly, waste-free and inexpensive solar grade silicon production technologies. Presently, the main solar grade silicon production technologies are based on the reduction of silicon hydrogen chloride compounds (trichlorosilane, tetrachlorosilane and silane). This paper will examine the results of the optimization of a multi-product silicon refinery, where the objective functions are Profit and Eco-indicator99. Seven scenarios are considered for the work. The best scenario (S4) showed a tendency to maintain a balance between Profit (98.66 M$/y) and the environmental indicator Eco99 (6.04 MP/y). Similarly, a sensitivity analysis was carried out by varying the market prices of each of the products obtained (solar grade silicon, TEOS at different purities, and chlorosilanes) with an increase of 10% and a decrease of 10%, resulting in multiple production scenarios depending on what the market dictates. By increasing the cost of solar grade silicon by 10%, the multi-product refinery achieves the highest profit (151.84 [M$/y] with an environmental impact of 9.8 [MP/y]), and by decreasing the cost of the same silicon by 10%, the lowest environmental impact is achieved (36 [M$/y] with an environmental impact of 3 [MP/y]).

1. Introduction

Pollution problems and global warming are today's challenging issues. It is because of these issues that the development of renewable energy sources is of great importance. Within the variety of renewable energies, photovoltaic (PV) power generation is considered the most promising, due to its large installation capacity and its enormous potential to reduce energy consumption which does not generate large amounts of pollutants [1]. The PV industry has been growing steadily since the end of the 20th century [2]. Global market demand, the Asian market growth, each country's own regulations and international energy policies have triggered an exponential growth of the PV industry [3]. According to IRENA, China's installed solar energy capacity in 2021 was 254,355 MWp, which represents 35.6% of the world's total, making it the largest market in the world [4]. The rapid growth of the PV industry and the market is giving rise to key technologies in the energy sector [5], and the ratio of energy production and consumption per kilogram of solar grade silicon (Si_{SG}) has been reduced significantly, as well as the costs per PV module [6].

However, there is a controversy about the generation of energy produced by PV since solar cells are not able to compensate for the energy consumption in their production, compared to the energy consumption they provide in their lifetime. With the most advanced processes and starting from sand, the total electricity consumption to produce 1 kg of purified polysilicon feedstock amounts to about 60 kWh (11 kWh kg^{-1} to produce metallurgical-grade silicon, 49 kWh for polysilicon purification and production) [7]. Furthermore, power generation per photovoltaic module is approximately 120 kWhel/year (considering a new PV module) [8]. Another debate states that PV energy is not green nor a clean energy source due to the high energy consumption in the manufacture of each component of solar modules, especially in the production of solar-grade silicon, and also due to the large amount of pollutants produced during the manufacture of silicon (tetrachlorosilane, dichlorosilane, etc.) [9]. The truth is that PV system operation is almost maintenance-free and completely clean, and the problem most likely lies in the fact that the processes for obtaining solar-grade silicon are designed without taking into account the

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Nomenclature

\$/kg	dollars per kilogram.
C_{Elec}	cost of the electricity.
C_{RM}	cost of raw material.
C_{SP}	price of the high added-value products.
C_{ref}	cost of the refrigerant.
C_{vap}	cost of the steam.
H_{Elect}	amount of electrical energy.
H_{Ref}	amount of the electrical energy used for the refrigeration.
H_{steam}	vapor amount (i).
P_{SiSG}	price of solar grade silicon.
$\alpha_{b,k}$	damage caused in category *k* per unit of chemical product *b* released to the environment.
β_b	represents the total amount of chemical product b released per unit of reference flow due to direct emissions.
δ_d	normalization factor for damage of category *d*.
ω_d	weighting factor for the damage of category *d*.
b	unit cost of each raw material.
c	cost of each utility *E*.
C1	column 1.
C2	column 2.
Col RD	reactive distillation Column.
DFR	distillate to feed ratio.
E	utility.
FR	feed ratio.
Hy	hydrochlorination reactor.
kg/h	kilogram per hour.
kg/year	kilogram per year.
M\$/y	millions of dollars per year.
N/A	not apply.
NLP	nonlinear programming.
P	pressure.
Pt/kg	eco-points per kilogram of steam.
RM	raw material.
RR	reflux ratio.
SiH_2Cl_2	dichlorosilane.
SiH_3Cl	monochlorosilane.
SiH_4	silane.
Si_{SG}	solar grade silicon.
T	temperature.
T_{Ca}	thermal carboreduction.
TEOS	tetraethoxysilane.
ε	epsilon-constraint.
EI_{Elect}	value of the eco-indicator99 for each damage category (*j*).
EI_{Ref}	value of the eco-indicator99 for each damage category (*j*) used for electricity.
EI_{steam}	value of the eco-indicator99 for each energy category (*j*).

environmental impact that this process could represent and only considering the economic aspect of the factory. When thinking about the environmental impact of PV power generation, one must consider quartz extraction, metallurgical silicon production, solar-grade silicon production, energy consumption, and pollutant emissions [10]. It is, therefore, a priority to quantify the energy consumption and environmental impact of PV power generation to define whether PV technology is an environmentally friendly renewable energy.

Some studies have evaluated the environmental impact of PV energy. Peng et al. [11] examined the sustainability and environmental impact of PV-based electricity generation systems through a comprehensive review of life cycle assessment (LCA) studies of common PV systems. Peng & Yang estimated that the environmental impact of PV technologies continues to improve in the near future. Fthenakis and Kim [12] analyzed the life-cycle environmental metrics of a PV system and evaluated some life-cycle risk indicators for photovoltaics, i.e., fatalities, injuries, and peak consequences in a comparative context with other electricity generation pathways. However, these studies neither examined the environmental impact in the production of solar grade silicon nor examined the design stage of a silicon refinery. Ramírez-Márquez et al. [13] presented a preliminary stage of the integration of environmental metrics in the optimization of the design of a solar grade silicon plant. The limitation of the work that they presented refers to the reaction equipment, which is practically fixed at one conversion.

Kannan et al. [14] perform a life cycle assessment of solar photovoltaic systems. They reveal that the greenhouse gas emissions from solar photovoltaic system electricity generation are less than a quarter of those of an oil-fired steam turbine plant, and half of those are from a gas-fired combined cycle plant. However, the electricity cost is five to seven times that of an oil or gas-fired power plant. Environmental uncertainties of the solar PV system are also critically reviewed and presented. Dones and Frischknecht [15] discuss life cycle assessment on current and future energy systems. They also analyze polycrystalline silicon technologies used in current panels. They present environmental inventories of solar panels and compare greenhouse gas emissions of current and future power systems. Peng et al. [16] examine the sustainability and environmental performance of PV-based electricity generation systems by conducting a comprehensive review of life cycle assessment studies. The results reveal that, among the five PV systems studied, the monocrystalline silicon PV system is the worst performer due to its high energy intensity during the solar cell production process. Alsema and De Wild [17] compile a series of life cycle inventory data that represent the current state of the art in silicon module production technology. The data covers all processes, from silicon feedstock production to cell and module manufacturing. They state that life cycle CO_2 emissions are in the range of 30–46 g/kWh.

The aforementioned literature reviews show limited results in the design of solar-grade silicon production plants. Few works examine the environmental impact of solar-grade silicon production issues [11–13]. The novelty of this work is to present the integration of environmental metrics (Eco-indicator99) in the design, and optimization, not only of a single-product solar-grade silicon plant, but also in a multi-product solar-grade silicon refinery. The best scenario of the multi-product refinery that not only meets the best profit, but also balances the environmental impact derived from producing each of the products of the refinery (solar-grade silicon, TEOS 99.5, TEOS 99, TEOS 98.5, silane, dichlorosilane, and monochlorosilane) will be suggested. The sensitivity analysis was performed by varying the market prices of each product, increasing and decreasing its cost by 10%. A percentage of 10% upward and downward was decided, due to the variations of the real market in the last decade [18]. There are no works in the literature that show a sensitivity analysis in this type of multi-product plant or in a silicon refinery. In other words, the main contribution of this work is to show the design of a multiproduct silicon refinery with the optimum operating conditions to be economically profitable and to guarantee a minimum environmental impact. It should be remembered that solar-grade silicon production requires enormous amounts of raw material and energy, in addition to the fact that it generates toxic waste. Therefore, in view of the climate crisis that the planet is facing, the production of solar-grade silicon and other high value-added products (TEOS and chlorosilanes) should be promoted in the cleanest way possible and in a way that does not reduce the profitability of the process. This was done to promote economically viable and environmentally friendly designs. The sensitivity analysis will aid in the understanding of market projections in the face of cost oscillations and will also help select the best plant design scenario. The following sections will show the methodology and an in-depth analysis of the results in the selection of the best design.

2. Methodology

2.1. Case study

The present work was applied to a case study of a refinery in the production of solar grade silicon by a hybrid process studied, designed and modeled in the General Algebraic Modeling System (GAMS) by Ramírez-Márquez et al. [19] An average production capacity of 15,000 t per year of polycrystalline silicon was considered [20]. In the Supporting Information section, the surrogated models of each of the refinery sections are presented. It is substantial to mention that the modeling approach of each unit is highly dependent on the type of experimental studies available in the literature and that its main limitation is in the use of any modeling technique. Regarding accuracy, each model was validated against the original data in order to reproduce the data under the same operating conditions. This hybrid process takes the better part of two processes in the obtainment of solar grade silicon: The Siemens Process and the FBR Union Carbide process, as shown in Fig. 1.

The hybrid process requires a higher energy demand in the production of 1 kg of solar grade silicon for use in PV applications than the traditional Siemens process, and a reduction of energy consumption of the process is needed. It is essential to maintain a sustainable energy consumption in the processes so that current generations can meet their daily needs without compromising future generations. As is known, high energy consumption generates damaging effects, such as greenhouse gasses, water/land/atmosphere contamination, and global warming, in our environment.

To evaluate and make decisions about the optimal production of the main product (Si_{SG}) and other byproducts of higher added value to the refinery, we will take into account two indexes (the economic profit and the Eco-Indicator99 (Eco99)) that will help us analyze the economic and environmental aspects of the process. The importance of the evaluation of these criteria is to make a reflective analysis about the profitability for the existence of the refinery and the process design involved. Both of these indexes are used not only for their importance but also because they are accessible when measuring and quantifying the economic and the environmental impact respectively.

In the next section, these indexes will be defined using the environmental and economic aspects and their objective function respectively, to implement the multi-objective optimization problem.

2.1.1. Objective function for the economic aspect (Profit)

This represents the economic profit of the process; the proposed objective function represents the profit of selling the solar grade silicon and the high valuable byproducts as TEOS 98.5, TEOS 99, TEOS 99.5, silane (SiH_4), dichlorosilane (SiH_2Cl_2), monochlorosilane (SiH_3Cl), where the production costs and the obtention of raw materials are taken into account.

The objective function for the economic profit is defined by the next equation:

$$maxProfit = P_{SiSG} + C_{SP} - C_{RM} - C_{Elec} - C_{Vap} - C_{Ref} \tag{1}$$

Where P_{SiSG} is the price of solar grade silicon, C_{SP} is the price of the high added value products, C_{RM} is the cost of raw material and the variables C_{Elec}, C_{vap}, C_{ref} represent the cost of the electricity, steam and refrigerant used in the process for the production of Si_{SG} respectively, and in different energy requirements to satisfy the quantity of yielded products. Each price shown in the objective function considers the mass quantity obtained of the product in a working year multiplied by the cost in the market.

2.1.2. Objective function for the environmental impact (Eco-Indicator99)

For the environmental impact analysis, it will be quantified using an Eco-Indicator. This indicator represents a measure of the environmental impact of a process, a material, or a simple activity through the life cycle analysis techniques; here, the Eco-Indicator99 methodology of Goedkoop and Spriensma will be used [21]. This methodology takes into account three categories of environmental damage that are caused when an activity, a process or usage of a material is being carried out. These categories are: damage to ecosystem quality, damage to human health and damage to natural resources. All of these categories affect the environment. The extent to which an effect contributes to a category of

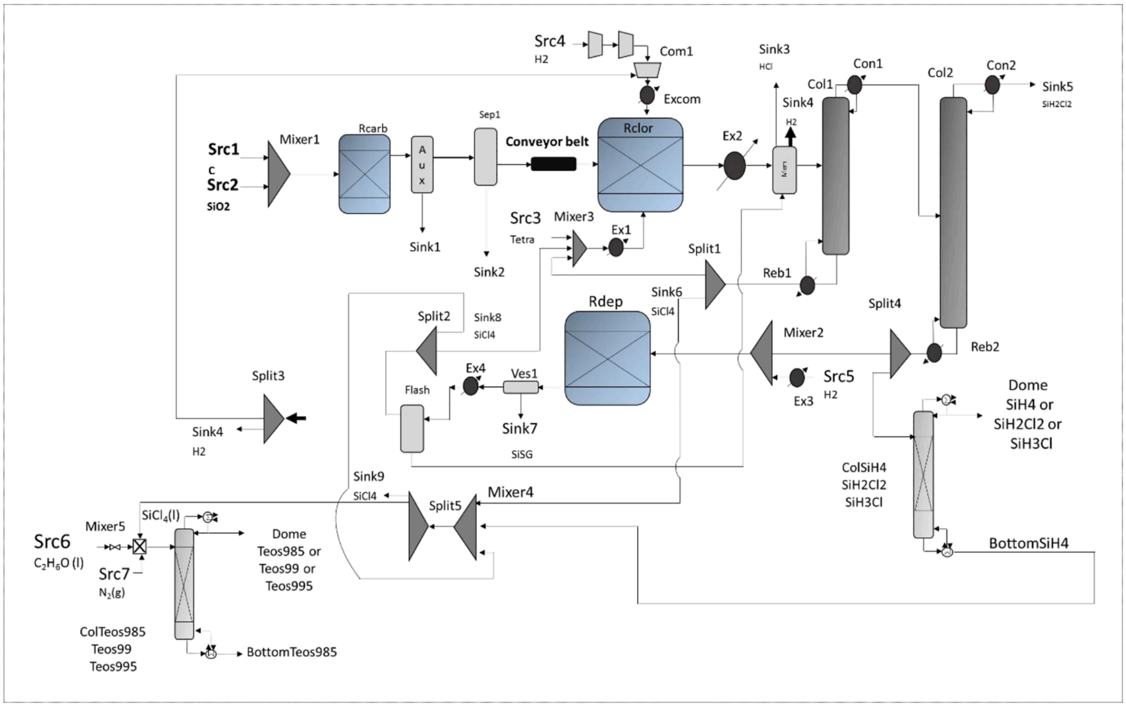

Fig. 1. Process diagram of the solar grade silicon multiproduct refinery.

damage is classified from 1 to 11 and a score is assigned to each one. The damages to the environment categories are shown in Table S1 in the Supplementary Information section (with a respective score assigned for the steam used in heating and the electricity consumed in refrigeration). The score of this eco-indicator is known as the Eco-Indicator Point (Pt) or Eco-Point; the scale of these points is chosen in such a way that the value of 1 Pt is representative for one thousandth of the yearly environmental load of one average European inhabitant.

The EI99 is defined in the following equation:

$$EI99 = \sum_{b}\sum_{d}\sum_{k\in K}\delta_d\omega_d\beta_b\alpha_{b,k} \tag{2}$$

where, δ_d is the normalization factor for damage of category d, ω_d is the weighting factor for the damage of category d, β_b represents the total amount of chemical product b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical product b released to the environment.

For the objective function of the environmental impact, following the Eco-Indicator99 methodology, where only the energy consumption in the hybrid process of the refinery for solar grade silicon is taken into account, is as follows:

$$\left\{\begin{array}{c} Electity \\ Steam \\ Refrigeration \end{array}\right\} Energy\ consumptions \tag{3}$$

Within the electricity consumption, according to the model of the designed process by Ramírez-Márquez et al. [13] the amounts of the electrical energy that require the following process units were taken into account. These are considered the carboreduction and deposition reactors since these reactors require large amounts of electrical energy for their operation.

For the steam consumption, the following process units were included: the conventional distillation columns and the reactive distillation columns. These were included in the operation of their reboilers and the heat exchangers since these process units have a high energy consumption. Refrigeration consumption occurs in the heat exchangers and condensers of the distillation columns.

The objective function of the Eco-Indicator99 that measures the environmental impact is defined by:

$$\begin{aligned} minEco99 = {} & \sum_{i}\sum_{j}H_{steam,i}\ EI_{steam,j} + \sum_{i}\sum_{j}H_{Elect,i}\ EI_{Elect,j} \\ & + \sum_{i}\sum_{j}H_{Ref,i}\ EI_{Ref,j} \end{aligned} \tag{4}$$

Where H_{steam} is the vapor amount used for the process units aforesaid (i) that require steam used for heating [kg/year], EI_{steam} is the value of the Eco-Indicator99 for each energy category taken in this study (j), by Eco-Points per kilogram of steam [Pt/kg] as shown in Table S1 (**S**upplementary Information) for the specific case of the steam. H_{Elect} represents the amount of electrical energy used in the different process units (i) in [kW/year], whereas EI_{Elect} is the value of the Eco-Indicator99 for each damage category (j) in Eco-Points per kilowatt [Pt/kW], as shown in Table S1 (Supplementary Information). The term for the refrigeration energy consumption, H_{Ref}, represents the amount of the electrical energy used for the refrigeration (taking into account that the energy efficiency of a refrigeration system is about 70% of the process units that are required for a refrigeration utility (i) in Eco-Points per kilowatt [Pt/kW]). The term EI_{Ref}, represents the value of the Eco-Indicator99 for each damage category (*j*) used for electricity. The optimization aims to minimize the objective function for the environmental impact [Pt/year].

It can be observed that the Eco-Indicator99 methodology is an integral approach since it takes into account eleven damage categories. This is of great importance to the chemical industry as it will aid us in the evaluation and analysis of environmental impacts caused by a process. Carbon footprint is another method that can be used to evaluate an environmental impact. The main advantage of the Eco-Indicator99 over other methodologies is that it estimates a single environmental impact score. This, alongside the scores for both the perspective-specified and perspective-averaged options. All within the egalitarian, hierarchical, and individualistic perspectives.

2.2. Multiobjective optimization

The optimization problem was formulated as a mathematical problem that seeks to maximize the annual economic profit and simultaneously minimize the environmental impact. In the Supporting Information section, the subrogated models of each of the refinery sections, optimization variables, parameters, and constraints inherent to the silicon refinery are presented. Among the most important optimization variables are: thermal carboreduction temperature (in the range of 2600–3100 K); temperature (373–873 K), pressure (1–20 atm), and $H_2/SiCl_4$ molar feeding ratio (1–5) for the hydrochlorination reactor; reflux ratio and feeding molar ratio for separation and purification (range depending on the distillation column); molar flow of each product, condenser heat duty and reboiler heat duty, for the reactive distillation columns (range depending on the column); and temperature for the Siemens reactor. The reliability and accuracy of surrogate models can be assessed a posteriori by associating an independent set of objective function data with the values taken from the surrogate at the points corresponding to the variables for which the independent objective function values are calculated. Each unit, such as tanks, reactors, compressors, separation columns, reactive distillation columns, etc., is sequentially fed. So the choice of how much of any high value-added product to feed is subject to the preset objective function. That is, which products provide the greatest economic benefit to the refinery and the least environmental impact? It is also important to mention that we took care in detail that the conditions between the equipment were adequate for them to be really operable. The aforesaid makes a multiobjective problem. This problem will be solved applying the epsilon-constraint method, based on solving the original problem and taking one of the two objective functions as the main objective function, which is subject to different lower limit values for the other objective functions. In this case study, the objective function for the economic profit of the process (1) was taken as the main objective function subject to the environmental impact objective function, whereas the last objective function will be assigned with different lower limit values (δ) for each optimal scenario where the profit will be maximized to obtain the Pareto front with their optimal solutions. The multiobjective optimization formulation is defined by:

$$Objective\ function:\ \ Max\ \left(P_{SiSG} + C_{SP} - C_{RM} - C_{Elec} - C_{Vap} - C_{Ref}\right)$$

$$Subject\ to:$$

$$\sum_{i}\sum_{j}H_{steam,i}\ EI_{steam,j} + \sum_{i}\sum_{j}H_{Elect,i}\ EI_{Elect,j} + \sum_{i}\sum_{j}H_{Ref,i}\ EI_{Ref,j} \leq \delta \tag{5}$$

For the epsilon-constraint (ε) method, the extreme points will be first defined. The first point is the minimizing of the Eco-indicator99 function (2) without considering the economic profit, in contrast, the opposite extreme point is to maximize the profit (1) without taking into account the environmental impact. With the data obtained, the Pareto front has the upper and lower limits. It is worth noting that the underlying problem of the chemical industries lies in their pursuit to maximize their economic profit without taking into account the environmental impact and the effects that their actions can create.

The next step is to solve the optimization approach and to obtain a maximum profit taking into account an Eco-Indicator99 limit value, here, five limit values δ were established with different intervals and each optimization generates a different scenario to build the Pareto front. It is important to mention that once the range of each objective function is determined, in the conventional approach of the epsilon-constraint (ε) method, the optimization of a single objective can lead to an inefficient solution. That is why lexicographic optimization is used to avoid this problem, i.e. only efficient solutions were included. For lexicographic optimization, the first objective function is first optimized and then, from the set of possible optimal solutions, the second objective function is optimized as well. Subsequently, the range of all objective functions (p) is found by dividing it into n equal intervals. The minimum and maximum values of each interval are considered, and ($n_i + 1$) grid points are generated for each objective function. So ($n_2 + 1$) ($n_3 + 1$) . . . . ($n_p + 1$) optimization sub-problems are solved to find the Pareto optimal solutions. By doing so, it is found that the ability to control the density of Pareto solutions by appropriate interval selection is one of the most substantial advantages of the epsilon-constraint (ε) method.

2.3. Methodology for sensitivity analysis

For the sensitivity analysis, we will consider the variation of the Si_{SG} and optimal byproduct prices (see Table 1), within a 10% increase and 10% decrease interval. Taking this into account will help us make decisions, and to have a future projection in the different cases that the prices of the products offered by the refinery under study increase or decrease. Decisions could be based on increasing the manufacturing of any of the high value-added products according to the oscillation of market prices, ensuring a good profit and a low environmental impact.

Thus, for each one of the upper and lower limits (10% increase, 10% decrease) of the optimal byproduct prices, and taking into account the variance of the prices, a new Pareto front will be built, with seven optimal scenarios, one minimizing the Eco-Indicator99, one maximizing the profit and the others subject to a different limit value for the Eco-indicator99. Therefore, for one value of the Eco-Indicator99, there will be several profit values. In this study, a mean profit will be calculated, and the models will be compared to reach a conclusion. A percentage of 10% upward and downward was decided, due to the variations of the real market in the last decade [18].

A tool that will allow us to make a test of this sensitivity analysis is the calculation of the standard deviation for each one of the optimal scenarios shown in the Pareto front. Moreover, the epsilon-constraint method tells us that, of the different optimal solutions, the one closest to the utopian point should be the best one. It is at this point that a balance is struck between environmental impact and economic benefit.

For each upper and lower limit (10% up, 10% down) of the prices of the optimal products of the refinery, a Pareto front will be made with seven different scenarios, the first one where Eco-Indicator99 is minimized, the second one where profit is maximized and the remaining scenarios will be subject to different Eco-Indicator99 limit values, so there will be a different Pareto front for the different optimal products and their price variations, but by having a variety of Pareto fronts and looking for the behavior of the analyzed variables under sensitivity analysis it is necessary to obtain an average value, this to establish a deep and clearer analysis, since for a fixed value of Eco-Indicator99 there will be different profit values due to the analysis of the variation of the products, an average of those values will be obtained and compared with the Pareto front of the original scenarios to be able to obtain conclusions. To obtain the mean of the different profits, Eco-Indicator99 values were established in a range of 3–11 MP/y, with a step size of 0.5 MP/y, in which, for each value, its corresponding profit value was noted in the different variations of each optimum product, these obtained values were added and an average was obtained, this result corresponds to its corresponding Eco-Indicator99 value, and so on, the obtained values were plotted to build the Pareto front of the average profit values where the sensitivity analysis is already contemplated and to contrast it with the original curve.

Table 1
Price of each Product.

	Original	10% up	10% down
Price of Polycrystalline Silicon [$/kg]	6.86 [22]	7.54	6.17
Price of TEOS 99.5 [$/kg]	3.75 [23]	4.12	3.37
Price of TEOS 99.0 [$/kg]	2.50 [24]	2.75	2.25
Price of TEOS 98.5 [$/kg]	1.50 [25]	1.65	1.35
Price of SiH_4 [$/kg]	88.44 [26]	97.28	79.59
Price of SiH_2Cl_2 [$/kg]	3.67 [27]	4.03	3.30
Price of SiH_3Cl [$/kg]	3.0 [28]	3.30	2.70

3. Results and discussion

3.1. Pareto front

As mentioned above, the Pareto front for the proposed optimization model was obtained where the optimization of the economic profit for different limit values of the Eco-Indicator99 was optimized on the GAMS software. The code that contains the model of the refinery for the production of solar grade silicon has around 2789 equations and 3743 variables, and it is solved with the solver CONOPT. The CONOPT solver is chosen because it is well suited for models with highly nonlinear constraints. Unlike other solvers, such as MINOS or KNITRO, which have problems maintaining feasibility during optimization. All the trials to carry out the optimization were performed, and each one of the trials takes a computing time to obtain the optimal solutions, which is around 1200 s (20 min) using a computer with an AMD ryzen 7 CPU at 2.3 GHz and 8.00 GB RAM.

In this work, we will call a scenario to each of the optimizations performed. To delimit the scenario with the larger profit, the optimization was carried out maximizing profit and leaving the environmental impact free of restrictions. Moreover, the scenario with the lowest environmental impact was carried out with the optimization under the objective function of minimizing Eco-indicator99. For the other scenarios, the epsilon-constraint (ε) method was used as explained in Section 2.2. Seven were the total scenarios for the optimization process. This can be observed at each point in Fig. 2, i.e. each scenario S corresponds to the points within the graph and together they form the Pareto front. Table 2 shows the results of the values for the Eco-Indicator99 (millions of Eco-Points per year) and the profit (millions of dollars per year) for each one of the proposed scenarios.

Taking the data obtained from Table 2, the Pareto front was built as it is shown in Fig. 2. It is important to note the structure of the Pareto front performed for this study. Scenario 1 (S1) represents the minimum value of the environmental impact of the process, on the contrary, Scenario 7 (S7) represents the maximum economic profit, and the other scenarios between S1 and S7 correspond to different optimal scenarios. This means that the Pareto front contains an optimal solution for the process, subject to a different limit, and an attractive solution as well.

The area below the curve represents suboptimal solutions, while the area above the curve represents infeasible solutions. The work seeks to

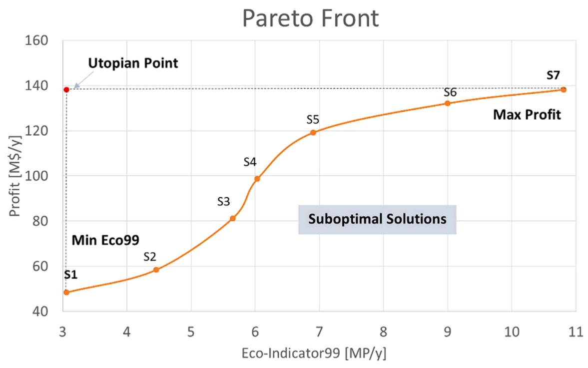

Fig. 2. Pareto front for the environmental and economic aspects.

Table 2
Optimal solutions obtained taking into count the environmental and the economic objective functions.

Escenario	Eco99 [MP/y]	Profit [M$/y]
Minimum Eco99: S1	3.06	48.4
S2	4.4557	58.39
S3	5.6486	81.19
S4	6.0355	98.66
S5	6.9055	119.18
S6	9	132.1
Maximum Profit: S7	10.81	138.18

find scenarios that strike a balance between profit and environmental impact. In the Pareto front, we found the utopian point which can be used as a standard idea for the criterion values to find the best solution from the Pareto front optimal set. The minimum environmental impact has an Eco-Indicator99 value of 3.06 MP/y, whereas the maximum economic profit has a value of 138.18 M$/y.

To carry out the discussion of the different solutions obtained from the optimization of the model, the balance between the economic and environmental aspects must be taken into account. For this purpose, the Pareto front criterion will be considered, where the best scenario is the one that is closest to the utopian point. And from the above, better decisions about the refinery's production can be made.

It can be observed in Fig. 2 that the profit in each one of the scenarios is increasing at an interval of 20 M$/y approximately. In the regions that include S5, S6, and S7, there is a significant increase in terms of environmental impact. Since there is no significant increase in the economic profit among these scenarios, a choice for the best solution among these three scenarios cannot be made, as these have 10% standard deviation among them in terms of the economic profit. On the contrary, among scenarios S2, S3, S4 and S5, a significant increase in the function of profit among them can be observed, so the choice for the best solution can be discussed as there is not a great difference among them in the value of the environmental impact function, which is about 20–30% of deviation among these scenarios.

A tool that will allow us to make a deep analysis in the decision-making of this study is the percentage of deviation for each one of the optimal solutions shown in the Pareto front concerning the utopian point, as is shown in Table 3. Here, it is established how far each scenario is concerning the utopian point. In other words, how far each optimal solution is to the minimum environmental impact as well as to the maximum economic profit. Out of all these optimal scenarios, the one that most compensates the environmental and economic aspects is Scenario 4 (S4), with an Eco-Indicator99 value of 6.0355 MP/y and a profit value of 98.66 M$/y. Scenario (S4) is the closest to the utopian point and it is chosen as the optimal solution.

An optimal amount of Si_{SG} production is determined through the optimization of each scenario. The optimal production of the byproducts of high added value that are considered in the refinery is also calculated. All the products taken into account are: Solar grade silicon (Si_{SG}), TEOS at 98.5, 99 and 99.5% purity, silane, monochlorosilane and dichlorosilane. For each one of the scenarios, there is an amount of production of these lists of products (see Fig. 3). It was observed in different scenarios, like the production of a certain amount of any product in the refinery, for example, that the process will stop producing others, and the energy demand for steam, refrigeration and electricity for the different scenarios will vary depending on the products to be produced. Since different amounts of energy will be required for different scenarios, thus, the energy requirements will change and the operating conditions of the processes will change as well.

Table 3
Percentage of deviation between the different scenarios and the utopian point.

Optimal scenario	% Deviation Min Eco99	% Deviation Max Profit
S2	31.32%	136.65%
S3	45.83%	70.19%
S4	49.30%	40.06%
S5	55.69%	15.94%
S6	66.00%	4.60%

The highest profit has the highest amount of solar grade silicon production, the highest amount of dichlorosilane production, and a small amount of TEOS 99% purity and monochlorosilane to cause the minimum environmental impact. It is the refinery that tends to produce around 5000 ton/y of Si_{SG} and 8000 ton/y of dichlorosilane. For this reason, other byproducts, like the ones mentioned above, would stop being produced.

It is important to note that in all the proposed scenarios, the production of dichlorosilane and Si_{SG} is active. This is evident since the Si_{SG} guarantees the profitability of the refinery. In this study, the minimum environmental impact is not a zero in the Eco-Indicator99 because the model optimized was always pursuing an optimal profit in the production of the Si_{SG} and dichlorosilane. If we desire to obtain a zero environmental impact, then nothing would be produced, which means that refineries would not exist.

An attractive option as the best solution is Scenario 5 (S5). It is important to note that S5 has a disadvantage since this scenario produces higher amounts of TEOS in its different purities (98.5, 99 and 99,5). This implies a higher energy consumption that translates to a higher value of environmental impact. However, this aspect is still an attractive solution since this scenario has a deviation of 15% concerning the maximum economic benefit that can be obtained in the process.

With regards to the scenario chosen as the best solution (S4), there is a good and balanced production between the different byproducts, which guarantees the profitability of the process. The selection of the optimal sequence of non-dominated points set was carried out by selecting a point in the inflection zone where the values of the objectives meet a minimum value without compromising the other. Wang and Rangaiah [29] show the methodology for choosing the optimal point. They exhibit the same zone of choice of the utopian point with the optimal point selected for this work. So it turns out to be a good indicator of the choice made. Here, only the production of TEOS 99.5% purity is excluded. In other words, the higher the required purity, the higher the environmental impact of the refinery is. This scenario has a deviation of 49.3% concerning the minimum Eco-Indicator99 that the process may have. It also has a deviation of 40% from the maximum economic benefit that can be obtained. A midpoint or a trade-off between the economic and environmental aspects can be observed. In this scenario, the production of solar grade silicon is about 10,880 ton/year, 149 ton/year of TEOS 98.5, 15 ton/year of TEOS 99, 0.5 ton/year of silane, 1382 ton/year of dichlorosilane and 16 ton/year of monochlorosilane.

It is interesting to note that the higher the purity requirement is, the larger the energy consumption in the process equipment is too, such as in the conventional and reactive distillation columns. This can be observed in Fig. 4. For a higher reboiler duty, the environmental impact value will be greater in the graphs, as it must meet a higher energy demand for the global process. This is because the distillation operation also involves considerable cooling and energy needs. Therefore, by reducing byproducts of high added value, utility consumption will be reduced as well.

Fig. 4 describes the contribution of the three different utilities (electricity, steam and refrigerant) to the total environmental impact quantified on each scenario. It is important to note that the energy used for refrigeration has a greater impact on the environment than the other two. Used steam does not significantly impact the environment as it would be expected due to the higher temperatures of the process. The energy consumption of the scenarios with minimum Eco-Indicator99 values (S1, S2, S3) is lower and their use of electrical energy is higher which represents 20–30% of the total environmental impact of each scenario. In the scenarios where the Eco-Indicator99 value is given greater flexibility, more refrigerant is commonly used, which means that

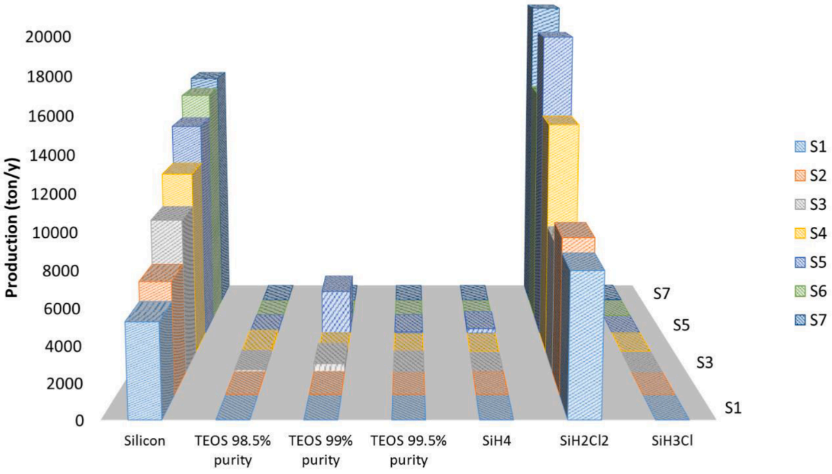

Fig. 3. Production of silicon and products of high added value in ecah scenario.

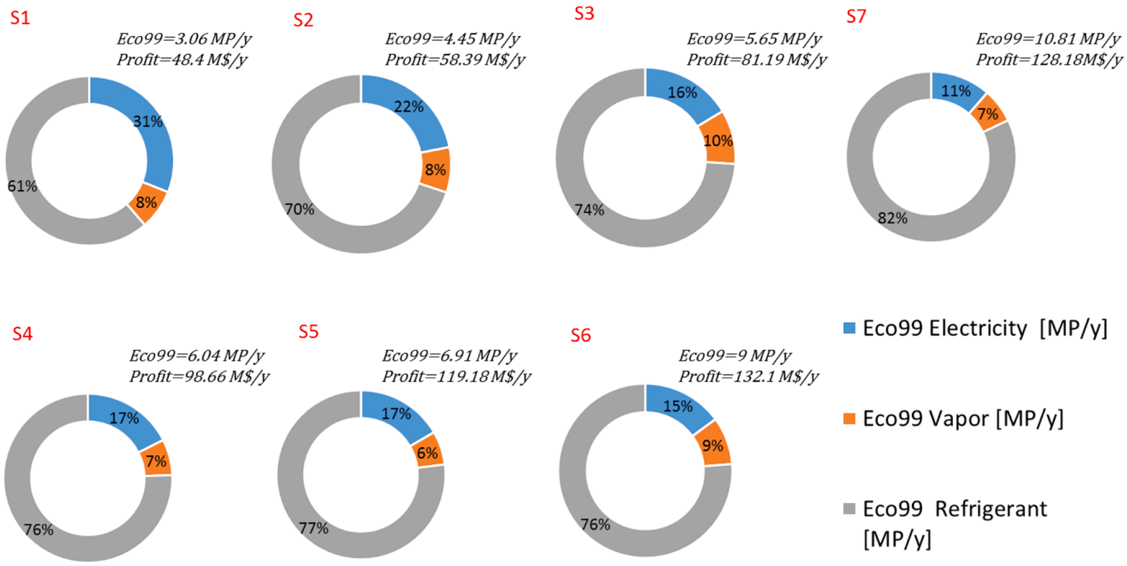

Fig. 4. Influence to the Eco-Indicator99 of the energy consumption in each scenario.

most of its negative environmental impact is caused by the use of refrigeration in the process.

From the analysis of the design and operating conditions presented in Table 4, it is apparent that each operating unit requires different conditions to meet production, profit and environmental care requirements. Depending on the production demand, the equipment will require a greater or lesser amount of energy. The more energy that is used, the greater the environmental impact will be. In S4, Table 3 shows an increase in both the carboreduction reactor temperature (2676 K) and in the deposition (1434 K), combined with a low value of $H_2/SiCl_4$ (1.54). This combination of operating conditions generates a medium production scenario of both trichlorosilane and tetrachlorosilane, which is mandatory since the system is forced to produce a considerable amount of solar grade silicon and a large amount of TEOS 99, TEOS 98.5, silane, dichlorosilane, and monochlorosilane, in order to obtain the highest possible profit. The results show that it is the process with the highest production of TEOS 98.5 (149.21 ton/y), which is reflected in high profit and low environmental impact.

The profit, environmental impact, operating conditions, and large-scale resource requirements of a solar-grade silicon refinery are analyzed. Solar-grade silicon production technology is being adopted in energy plans around the world to reduce growing CO_2 emissions. The average lifetime of a solar-grade silicon panel is between 20 and 30 years, and it is necessary to make its production processes economically and environmentally profitable, and also to consider generating responsible end-of-life treatment of these panels to minimize the environmental burden. Wong et al. [30] agree that improvements in conversion efficiency decrease the environmental impact in the generation of silicon-based PV cell precursors. Therefore, improving conversion efficiency is key to improving the environmental and economic profile of silicon production processes. Cucchiella & D'Adamo [31] agree that photovoltaic systems based on silicon technologies require the highest cost in silicon production and that optimizing the operating variables could reduce both the total cost of the photovoltaic cell and the environmental impact, as demonstrated by a life cycle analysis.

3.2. *Sensitivity analysis results*

If we asked the question, what would happen if the selling prices of the solar grade silicon and the products of high added value increased or decreased by 10%? An answer could be given or explained by the sensitivity analysis. It is important to mention that, as with the optimization results shown above, for the sensitivity analysis of the sale prices of each high value-added product, seven scenarios were considered in

Table 4
Operating conditions of each scenario.

	TCa	Hy			Separation				Col RD TEOS						Col RD SiH_4 – SiH_2Cl_2- SiH_3Cl						Siemens
					C1		C2		98.5		99.0		99.5		SiH_4		SiH_2Cl_2		SiH_3Cl		
	T [K]	T [K]	P [kPa]	$H_2/SiCl_4$	FR	RR	FR	RR	RR	P [kPa]	RR	P [kPa]	RR	P [kPa]	DFR	RR	DFR	RR	DFR	RR	T [K]
S1	2600	515.2	2026.5	1.45	2.17	14.94	7.24	59.99	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1372
S2	2608	552.2	2002.9	1.68	2.16	31.81	7.11	66.26	1.90	101.32	1.37	101.32	1.21	101.32	0.25	61.2	0.50	25.8	N/A	N/A	1497
S3	2600	373.2	2026.5	1.04	2.17	46.01	7.55	73.17	1.90	101.32	1.37	101.32	1.21	101.32	N/A	N/A	0.50	25.8	0.33	24.3	1491
S4	2676	373.1	2026.5	1.54	2.17	46.01	7.55	73.17	1.90	101.32	1.37	101.32	N/A	N/A	0.25	61.2	0.50	25.8	0.33	24.3	1434
S5	2701	573.1	1736.3	5.00	2.09	14.66	5.74	73.75	1.90	101.32	1.37	101.32	1.21	101.32	0.25	61.2	0.50	25.8	0.33	24.3	1494
S6	2998	373.1	2026.5	1.04	2.17	74.18	7.55	90.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1500
S7	2780	373.1	2026.5	2.28	2.12	80.00	7.30	59.99	N/A	N/A	1.37	101.32	N/A	N/A	N/A	N/A	N/A	N/A	0.33	24.3	1500

*TCa = Thermal Carboreduction; Hy = Hydrochlorination Reactor; C1 = Column 1; C2 = Column 2; Col RD = Reactive distillation Column; *T* = Temperature; *P* = Pressure; FR = Feed Ratio; RR = Reflux Ratio; DFR = Distillate to feed ratio; N/A = Not apply.

each analysis. Fig. 5 shows a comparison between the Pareto front of the original model and the Pareto front under each sensitivity analysis of the sale prices of the products. Fig. 5 shows how Profit and Eco-indicator99 move depending on the demand of the product to be manufactured. It is evident that by increasing prices by 10%, the model tends to produce the component of interest. However, this has an impact on Eco-indicator99, an example is given in high purity products such as TEOS 99.5. When they require a high reboiler duty, Eco-indicator99 shoots up. A similar phenomenon happens when reducing prices by 10%, the model tends to the production of other components of interest to raise the profit, compromising the environmental impact. However, there are also balanced solutions to obtain an adequate profit without compromising the environment.

Multiple situations can be inferred from Fig. 5. The first and most important is the large influence of the price of solar grade silicon. By increasing its price by 10%, the profit rises by 54.91% (higher profit case) with respect to the original Pareto scenario S4. At the same time, decreasing the price of silicon by 10% in the lower environmental impact scenario reduces it by 49.75% with respect to the original Pareto S4. This means that the price of silicon in the multi-product refinery has the greatest impact on both economic and environmental metrics. Among the other products, there are two that have a favorable trend in terms of price variation. Such is the case of monochlorosilane and TEOS 99.0, both with a 10% price increase. The effect of both products is seen in their proximity to the utopian point. In this scenario, the multiproduct refinery gives a profit of 101.66 [M$/y] and an environmental impact of 4.77 [MP/y] with the sensitivity analysis of TEOS 99. And with the sensitivity analysis in monochlorosilane the refinery gives a scenario with a profit of 81.19 [M$/y] and an environmental impact of 3.51 [MP/y]. All this means that the multi-product refinery design can have variants as the market dictates. This is not convenient in terms of design, so it is important to visualize the behavior of the multi-product refinery by having an "average" Pareto front of the variations presented.

Fig. 6 shows a plot of the mean values obtained from the sensitivity analysis plots. Considering the variation of the prices, the values of the objective functions show a better estimate for case studies in the future and decision making becomes a trade-off between an increase and a decrease in prices since an average economic benefit is being considered.

It is important to note that the original model fits great with the model under sensitivity analysis. It can be observed that the solar grade silicon production governs the model under sensitivity analysis. This means that in order to have the minimum environmental impact, only solar grade silicon and dichlorosilane should be produced, (because they are the main contributors to economic profit) but this, by itself, would not be profitable. The greater the number of byproducts of higher added value that are produced, the greater the environmental impact of the refinery will be. The higher the purity of the byproducts is, the greater the energy demand is as well.

For Eco-Indicator99 values from 4 to 6 MP/y, it is observed that in the model under sensitivity analysis, the economic profit increases significantly over the original Pareto front because in these scenarios the production of the different high added value byproducts predominates, while, in other values of environmental impact and economic profit, the scenario does not change significantly from the original model.

4. Conclusion

To reduce emissions and move towards a complete economy with a low environmental impact, green technologies must be promoted. However, many critical elements are needed to manufacture green technologies and, as discussed in the article, the availability of optimizing a design under environmental and economic metrics can produce constraints and bottlenecks that must be avoided. Knowing what to produce and how much of it to produce combined with the best design of a green multiproduct silicon refinery can be critical from a supply-

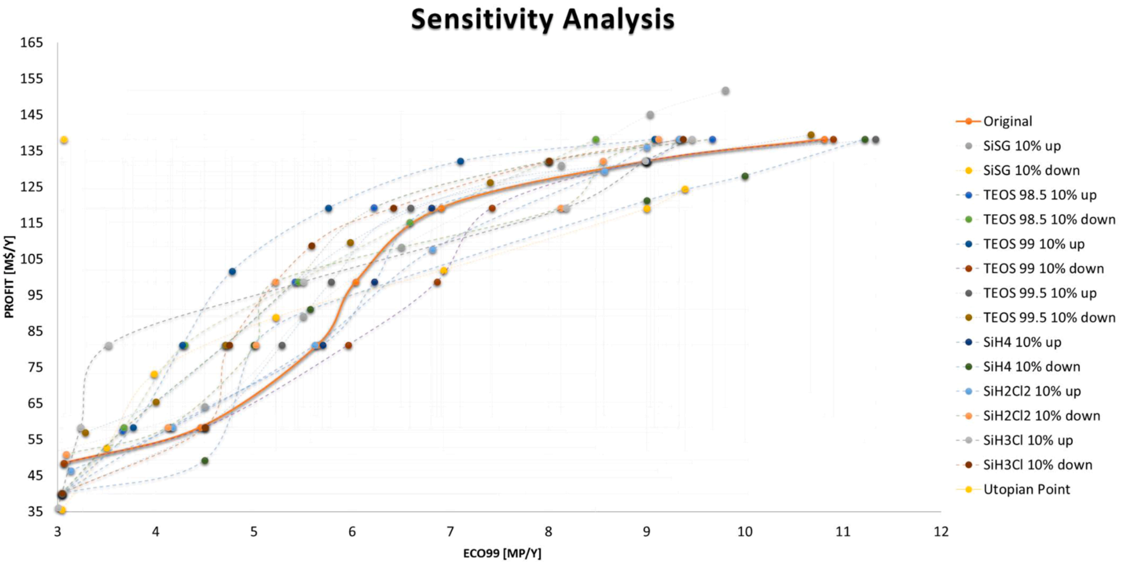

Fig. 5. Pareto front of each model in the face of sensitivity analysis in selling prices by 10% upward and 10% downward.

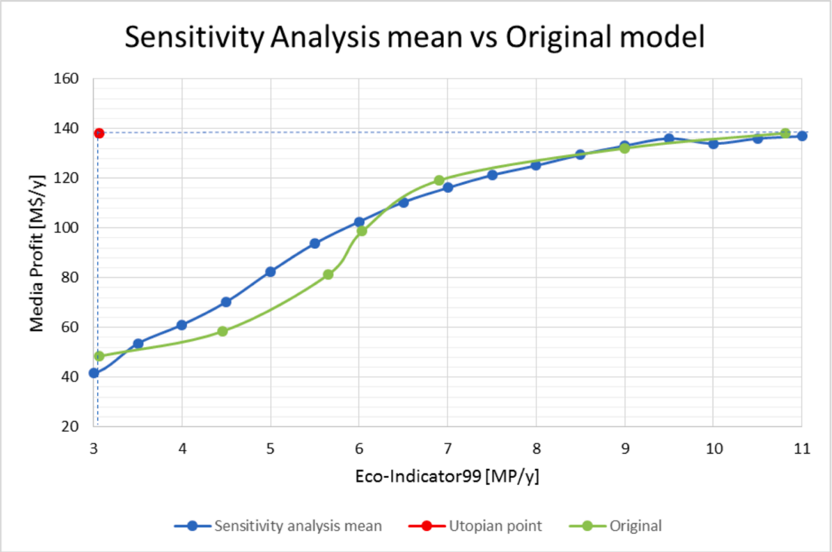

Fig. 6. Pareto front of the original model and the model under sensitivity analysis.

demand point of view and can favor the promotion of policies related to equipment design, substitution and efficiency, capable of avoiding these bottlenecks. In the scenario analysis of the selected multi-product solar grade silicon refineries, different constraints in terms of product demand, profit, and environmental impact have been identified.

The main conclusions are as follows:

(1) The best scenario (S4) showed a tendency to maintain a balance between Profit (98.66 M$/y) and the environmental Eco-indicator99 (6.04 MP/y).
(2) It should be noted that not all commercially available products have the same impact on the environment. For example, TEOS 99.5, the permanent energy demand is higher than in the case of TEOS 99 or TEOS 98.5. This issue must be analyzed in-depth in order to define adequate design strategies to avoid the non-production of any component that the market demands.
(3) The optimization and design methodology under economic and environmental impact metrics shown in this work are so useful, and could become generalized methodologies for other types of multi-product industrial factories.
(4) In combination, the sensitivity analysis study helped to envision the possible scenarios of profit and environmental impact of the multi-product solar grade silicon refinery designs, under the perspective of current market oscillation.
(5) Among all the sensitivity analysis scenarios presented, the case of a 10% increase and decrease in the price of solar grade silicon is the most significant, predicting a 54.91% increase in profit in the best scenario and a 49.75% decrease in environmental impact in the lowest impact scenario.

In the future, the proposed framework for multi-product silicon refinery can be developed in the following directions:

The accumulation of photovoltaic waste is considered one of the main obstacles to the sustainable development of solar-grade silicon refineries. The first step in addressing this challenge is to estimate the production of such waste, which requires a projection model. The projection model can incorporate artificial intelligence to perform an analysis that considers prediction and planning aspects. In addition, it is intended to incorporate this methodology for an economic-environmental study of the production process of other raw materials for the manufacture of solar panels.

CRediT authorship contribution statement

César Eduardo Cortés-Estrada: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **César Ramírez-Márquez:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **José María Ponce-Ortega:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Juan Gabriel Segovia-Hernández:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Mariano Martín:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Supplementary materials

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