

Safety, Economic, and Environmental Optimization Applied to Three Processes for the Production of Solar-Grade Silicon

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Supporting Information

ABSTRACT: In this work, we present the multiobjective optimization of the Siemens Process, the Intensified FBR Union Carbide Process, and the Hybrid Process (the three processes to obtain solar-grade silicon), including considerations of safety, economic, and environmental impact at the design stage of the process. Safety is considered through the individual risk index, the economy through the return on investment, and the environmental impact using the eco-indicator 99. The design of the Siemens Process turned out to be the one that showed the best safety, profitability, and environmental indexes, despite having the lowest solar-grade silicon production capacity, a fourth of that of the Hybrid Process. The results showed similar profitability values for the Hybrid and Siemens processes. In general, because of the high demand of the product of interest and under the premise of a safe process, the Hybrid Process can be chosen as a promising option for its industrial implementation.

KEYWORDS: solar-grade silicon, inherent safety, multiobjective optimization



INTRODUCTION

There is a growing awareness of the importance of including safety and environmental impact issues as design criteria for the industrial process.¹ This trend is due to the fact that the greatest challenges that society faces today are related to pollution issues, scarcity of resources, and global warming.² Consequently, the safety risks, as well as the environmental impact associated with processes, becomes a focal point to the industrial development in the long term. In past decade, significant advances have been achieved in identification and understanding of the problems related to the safety and environmental impact in industries. Chemical engineers and chemists are involved in and responsible for the life of a product from the discovery stage to manufacturing, safety, market introduction, and end of life.³ Nowadays, many products and processes are already designed considering safety and environmental issues. Nevertheless, there is still much to be done in novel processes and products, since the safe and clean engineering practice has shown its potential for being applied more broadly, deeper and in a more systematic way.²

One of the main reasons to incorporate safety, environmental, and profitability as design criteria of any process, is closing the gap between research and technological development, and consequently developing sustainable processes. This ideas follow the OECD definition of sustainable chemistry that presents the need for a life-cycle perspective by saying that sustainable chemistry “encompasses the design, manufacture and use of efficient, effective, safe and more environmentally

benign chemical products and processes”.⁴ At present, this appreciation of the importance of safety and environmental issues has broadened into the more holistic concept of sustainability, and increasingly, many companies embrace the concept of sustainability into their company’s culture.⁵ A research key area is the energy industry and the challenges that it presents. The production and use of energy are responsible for most of the safety problems and environmental issues. The reason can be found in the extreme operating conditions of the processes, the raw materials themselves, and the resulting greenhouse gas emissions.¹ Therefore, one of the ways to limit and prevent the serious environmental, safety, and economic consequences, which is related to increased risks, and climate change, among others, is to find more efficient energy resources.

The increase of the global energy demand and the issues previously presented have served as a driver to find alternative and renewable energy sources. An adequate solution to supply the world with electricity is through renewable energy sources such as solar energy, which is ready to accelerate the transition to a low-carbon economy, limiting the use of fossil fuels and their harmful effects on the environment. Currently, one of the most consolidated and used forms of solar energy in the world is by means of crystalline silicon photovoltaic (PV) cells. The

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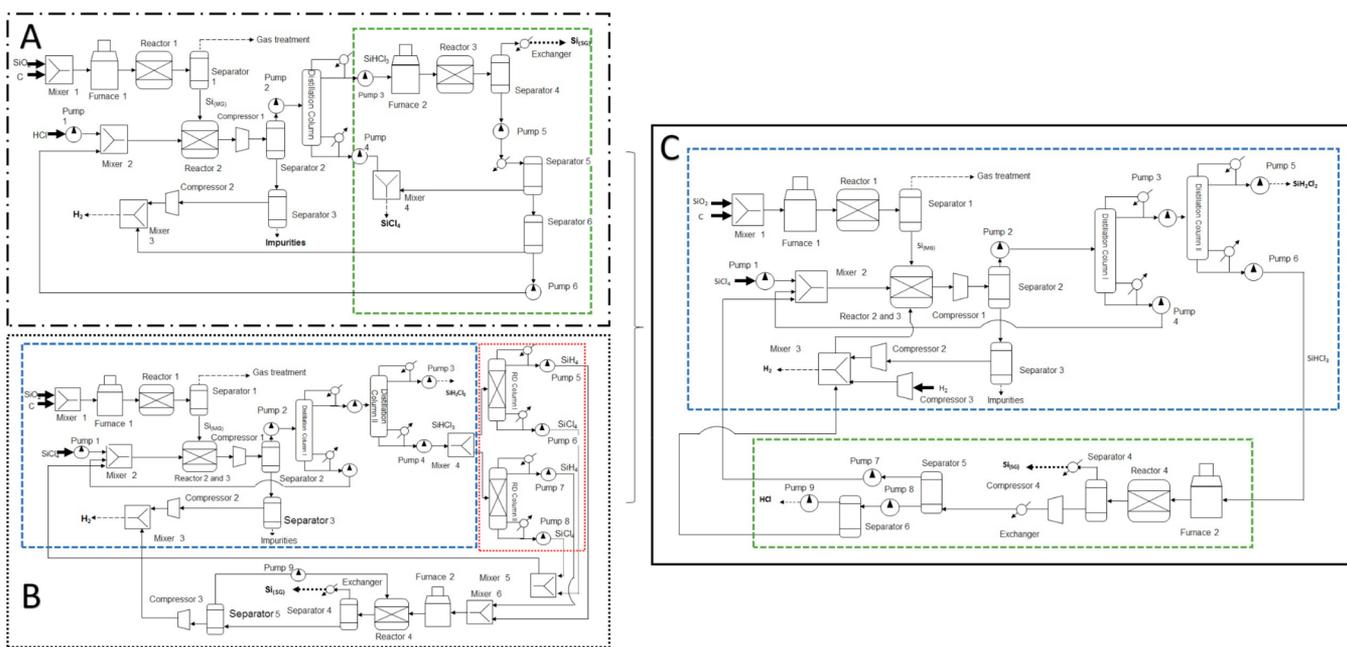


Figure 1. (A) Flowcharts of Siemens Process, (B) Intensified FRB Union Carbide Process, and (C) Hybrid Process.

solar silicon production is a key step in the PV industry. The solar-grade silicon (Si_{SG}) production should consider, besides the economic aspect, both the process safety and the environmental aspects. The Si_{SG} production can be carried out mainly following two routes. The first route consists of following a metallurgical approach, which combines a series of refining stages, as well as a solidification stage.⁶ This approach involves several stages in batch, which causes difficulties in the operation, the process dynamics, the reduction of energy costs, and also several issues with the environmental regulations. The second route is the solar-grade silicon production following chemical methods, which have the advantage of producing better quality solar-grade silicon.⁷ The chemical methods essentially involve two known paths. The Siemens Process, where the metallurgical silicon is first treated with hydrogen chloride (HCl) to produce trichlorosilane (SiHCl_3). Then a hydrogenated reduction produces solar-grade silicon. Similarly, the Union Carbide Process consists of the production of the metallurgical silicon. The next stage produces silicon tetrachloride (SiCl_4) as an intermediate to trichlorosilane, which by a series of redistribution reactions produce silane (SiH_4). The silane is fed to a vapor deposition reactor where it decomposes to produce solar-grade silicon.⁸

In the production of high-quality silicon, the chemical routes are mostly used worldwide because of the operational advantages.⁹ However, these routes are subjected to several safety and environmental issues. The main problems of the chemical routes are the high consumption of energy, the safety risks due to the species involved, and the extreme operating conditions. In general, production of chlorosilanes presents an environmental hazard. In addition to this, the species involved are toxic and corrosive, therefore presenting safety and environmental problems.⁷ In particular, silane gas (SiH_4) represents a significant risk in solar-grade silicon production via the Union Carbide Process because it is extremely explosive and it is dangerous to workers and communities. It is known that accidental releases of silane explode spontaneously. The semiconductor industry reports several silane incidents every

year.¹⁰ Another substances that represent a risk are silicon tetrachloride (SiCl_4) and hydrogen chloride (HCl), as they are extremely toxic, corrosive, and the first one reacts violently with water. Nevertheless, the HCl can be easily recovered and reused as input for the silane production, to mitigate safety and environmental concerns. The Washington Post reported in 2008 that silicon manufacturing is increasing rapidly in China, but the infrastructure to recycle the silicon tetrachloride and other toxic products does not follow.¹⁰

Therefore, inherent safe process design has become a valuable concept over the last years, since it provides the necessary information to avoid, mitigate, and prevent possible incidents.¹¹ Building on the description above, it is extremely important to consider environmental and safety issues in the design of the solar-grade silicon production plants. In this work, the inherent safety, the environmental impact, and the economic aspect are a fundamental part to select a design. The main contribution of the presented work is optimization of the design of solar-grade silicon based on the multiobjective optimization including economic, environmental and safety concerns (profitability (ROI), environmental (EI99), and safety (IR)), to provide the guideless for the design of the equipment, of the processes and of the operating conditions toward an inherently safe and sustainable process design.

In this methodology, safety, profitability, and environmental metrics are conflicting factors that must be either maximized, safety and profitability, and minimized, environmental impact. The rest of the paper is organized as follows: The next section presents the methodology. Then, the results of the three processes are shown. Finally, some conclusions are drawn.

METHODOLOGY

The present section depicts the multiobjective optimization methodology. First, the processes are described, and then the objective functions and the optimization methodology are presented.

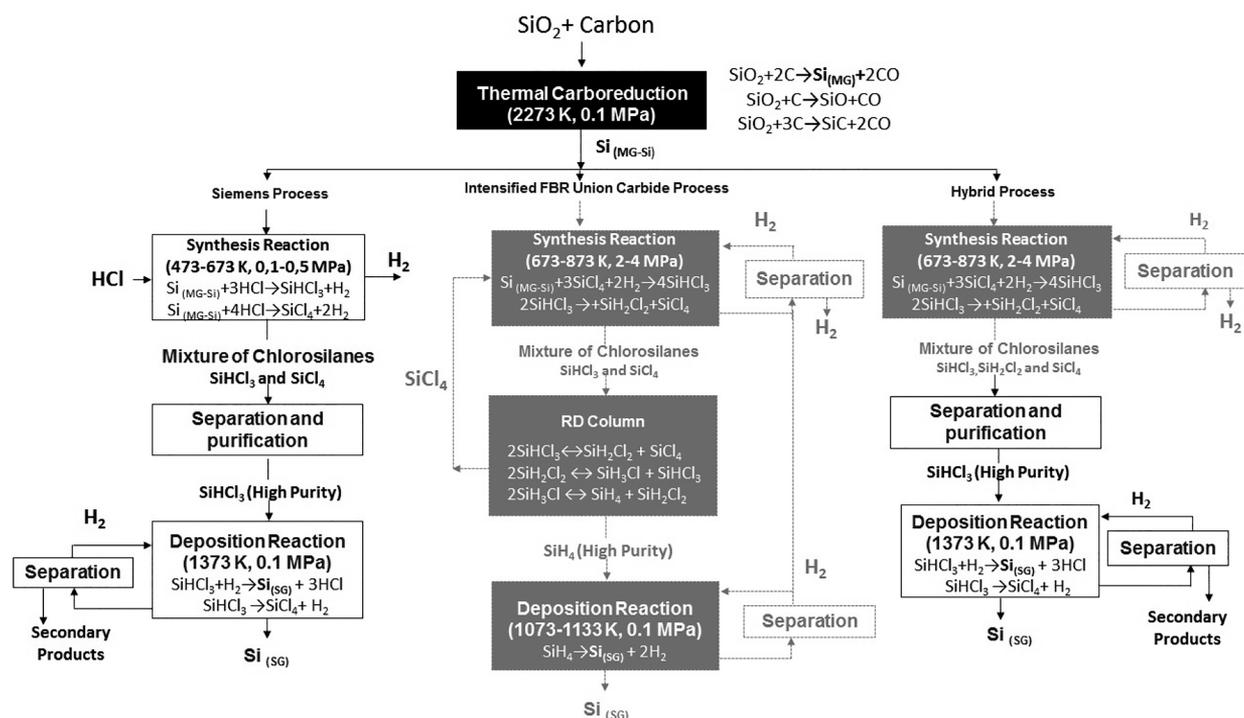


Figure 2. Siemens Process, Intensified FRB Union Carbide Process, and Hybrid Process.

Processes for the Production of Solar-Grade Silicon.

Three processes are evaluated in this work (see Figures 1 and 2). The procedure to elaborate process diagrams was described in Ramirez-Márquez et al.⁸ They are modeled in Aspen Plus V8.4, but several additional considerations are presented to include the features that cannot be directly simulated using Aspen modules as well as the considerations used to assemble each one and the modeling of special units.

Siemens Process. This process uses SiO_2 as raw material. The first stage is to produce metallurgic silicon via SiO_2 reduction with coal. An electric arc furnace is the unit used for this transformation.¹² The purity achieved for metallurgic-grade silicon, Si_{MG} , is around 98–99%. The Si_{MG} , H_2 , and HCl are fed to a fluidized bed reactor for the production of chlorosilanes. The exit stream is fractionated. The hydrogen (H_2) and hydrogen chloride (HCl) are removed when chlorosilanes condense. Then, a distillation column is used to split the liquid stream of SiHCl_3 and SiCl_4 . The bottoms, mostly SiCl_4 , are a byproduct of the process while from the top a stream of 99.99% SiHCl_3 is obtained.¹³ This purity is good enough to feed the stream to the chemical vapor deposition reactor (CVD) of the Siemens Process. U shape bars of ultrapure silicon are used as seed. These bars are heated up using electric current. After silicon deposition, byproducts of HCl , H_2 , and SiCl_4 are obtained. The silicon is cooled down to ambient temperature and the gases are separated by a set of equipment, to be recycled to the process (see Figure 1A).

Intensified FBR Union Carbide Process. The stage to obtain the Si_{MG} is the same as for the Siemens Process. Next, the Si_{MG} is hydrogenated together with SiCl_4 in a fluidized bed reactor. The stream of products is separated using a flash module to recover the chlorosilanes. Afterward, the stream consisting mainly of trichlorosilane and tetrachlorosilane is fed to a system of two distillation columns. We obtain a high-purity stream of SiCl_4 from the bottoms of the first column, which is recycled. From the other column a high purity

trichlorosilane stream is obtained from the bottoms that will be fed to the reactive distillation column. Next, trichlorosilane disproportionation reactions are carried out in a reactive distillation column. The column produces high-purity silane over the top that is fed to the chemical vapor deposition reactor to produce high-purity silicon and hydrogen.¹⁴ The CVD reactor is modeled using a stoichiometric reactor module where the silane conversion reaches 80%.¹⁵ The product stream is separated to isolate the polysilicon from the gases. Polysilicon is solidified while the gases, mainly H_2 and HCl , are recycled (see Figure 1B).

Hybrid Process. The production of Si_{MG} is carried out as in previous cases, by means of the carboreduction of SiO_2 . Then, an FBR is used for the hydrogenation of Si_{MG} and SiCl_4 to obtain a mixture of di, tri, and tetrachlorosilane. Next, two distillation columns are used to separate the mixture of chlorosilanes. From the top of the first column we obtain di and trichloro silane, while from the bottoms, tetrachlorosilane with traces of SiHCl_3 . The SiHCl_3 is removed, and the tetrachlorosilane is recycled to the process. The second column, separates the mixture of SiHCl_2 and SiHCl_3 , obtaining a stream of SiHCl_3 of high purity from the bottom. After that, the SiHCl_3 is used as feed for the chemical Siemens vapor deposition reactor. After the deposition, HCl and hydrogen are separated from the Si_{SG} . Both streams are cooled down (see Figure 1C).

Optimization. The processes described above are optimized by an hybrid algorithm called differential evolution with Taboo List (DETL). Generally, to evaluate a process, the main indicator is the economy. However, in recent years, there has been an effort to incorporate environmental impact and safety indicators as criteria for process design, increasing the depth of the analyzes. In particular, the silicon photovoltaic industry needs to be evaluated in the three criteria to continue growing and to be considered a sustainable system. In other words,

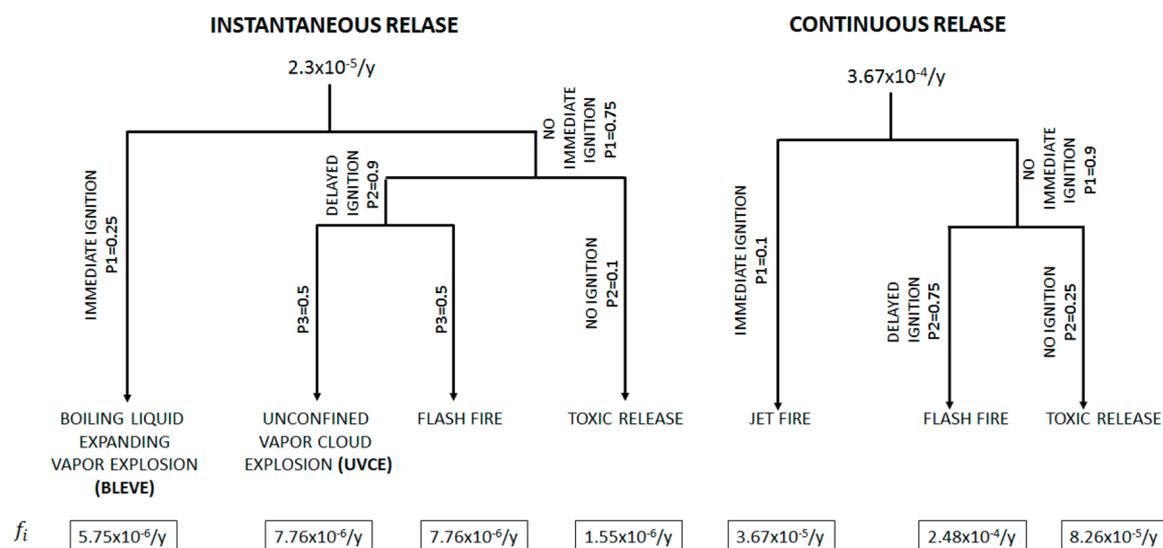


Figure 3. Possible accidents and frequencies that can happen in a process.²¹

objective functions including economics, environmental, and safety are required for the photovoltaic industry development.

Unlike the economic aspect, the environmental and safety indicators are hindered due to problems related with the lack of availability and reliability of data. The objective functions chosen are ROI, Eco-indicator 99, and IR, because they result in suitable and reliable indicators for the three aspects analysis.

This optimization methodology allows incorporating conflicting objective functions, aiming at a more robust design that accounts for probability, respects the environment, and yields an inherently safe design.

The optimization indexes are described below, and then the multiobjective optimization problem is defined. The adequate conditions obtained in each process optimization must consider several aspects such as profitability, environmental impact, and safety factors, which entail an important optimization issue.

Return on Investment (ROI). The use of the return on investment (ROI) as economic objective allows evaluating the economic performance of the process. ROI deals with the money you invest in the company and the return achieved on that money based on the net profit of the business. A simple definition of ROI is the following:

$$ROI = \frac{\sum_{i=1}^N CF_i/N}{I} \quad (1)$$

where CF_i is the after-taxes cash flow, I is the capital investment, and N is the number of years of the project; overall, the calculated value is used as an average value of the after-taxes revenues.¹⁶

Environmental Index. In this work, eco-indicator 99 (EI99) was used to evaluate the environmental impact. The EI99 is a methodology based on the life cycle assessment (LCA). The EI99 makes possible the environmental burden evaluation associated with a process, a product, or an activity, by analyzing and quantifying the material and the energy used. This methodology has been used by many authors in recent years.^{17,18} One point on the EI99 scale represents 1000th part of the annual environmental loads of an average European citizen.¹⁹

The EI99 methodology considers three main categories of impact: (1) human health, (2) ecosystem quality, and (3) resources depletion. The following elements are selected to compute EI99: steel to build equipment and important accessories, the steam used to produce heat and electricity. The associated data with these activities were taken from the standard databases.¹⁹

The EI99 is defined in the following equation:

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (2)$$

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.

Safety Index. In this work, the individual risk (IR) index was used to quantify the process safety. The IR defines the risk that a person experiences depending on their position, taking into account the frequency of occurrence and a probability of death or injuries that could be caused by an accident. The IR is defined as follows:

$$IR = \sum f_i P_{x,y} \quad (3)$$

where f_i is the frequency of a possible accident; and $P_{x,y}$ is the event probability in a specific area.

The use of a qualitative risk analysis (QRA) allows identifying the event frequency and probability of the potential incidents and accidents, as well as possible consequences that may have. The first step of the QRA methodology is to identify the incidents. Incident is defined as any material or energy release in the process.²⁰ Figure 3 displays the possible accidents and the frequencies that can happen in a process.²¹ Once the possible accidents are identified, we proceed to the identification of variables that causes them. According to Kumar,²⁰ the BLEVE, Jet Fire, and Flash Fire, have as causative variable the thermal radiation (E_r). For UVCE, the overpressure (P_o) is the reason; and finally for the Toxic Release the release concentration de la is the cause. The probable

Table 1. Decision Variables Used in the Optimization of Process Routes for Si₅G Production

decision variables	Siemens Process		Intensified FBR Union Carbide Process		Hybrid Process	
	continuous	discrete	continuous	discrete	continuous	discrete
number of stages COLCONV1	N/A	X	N/A	X	N/A	X
number of stages COLCONV2	N/A	N/A	N/A	X	N/A	X
number of stages RDC 1	N/A	N/A	N/A	X	N/A	N/A
number of stages RDC 2	N/A	N/A	N/A	X	N/A	N/A
feed stages COLCONV1	N/A	X	N/A	X	N/A	X
feed stages COLCONV2	N/A	N/A	N/A	X	N/A	X
feed stages RDC 1	N/A	N/A	N/A	X	N/A	N/A
feed stages RDC 2	N/A	N/A	N/A	X	N/A	N/A
reflux ratio COLCONV1	X	N/A	X	N/A	X	N/A
reflux ratio COLCONV2	N/A	N/A	X	N/A	X	N/A
reflux ratio RDC 1	N/A	N/A	X	N/A	N/A	N/A
reflux ratio RDC 2	N/A	N/A	X	N/A	N/A	N/A
distillate rate COLCONV1	X	N/A	X	N/A	X	N/A
distillate rate COLCONV2	N/A	N/A	X	N/A	X	N/A
distillate rate RDC 1	N/A	N/A	X	N/A		N/A
distillate rate RDC 2	N/A	N/A	X	N/A		N/A
diameter COLCONV1	X	N/A	X	N/A	X	N/A
diameter COLCONV2	N/A	N/A	X	N/A	X	N/A
diameter RDC 1	N/A	N/A	X	N/A	X	N/A
diameter RDC 2	N/A	N/A	X	N/A	X	N/A
top pressure COLCONV1	X	N/A	X	N/A	N/A	N/A
top pressure COLCONV2	N/A	N/A	X	N/A	N/A	N/A
top pressure RDC 1	N/A	N/A	X	N/A	N/A	N/A
top pressure RDC 2	N/A	N/A	X	N/A	N/A	N/A
feed SiCl ₄	N/A	N/A	X	N/A	X	N/A
feed HCl	X	N/A	N/A	N/A	N/A	N/A
reactive distillation stages RC1	N/A	N/A	N/A	X	N/A	N/A
reactive distillation stages RC2	N/A	N/A	N/A	X	N/A	N/A
holdup 1	N/A	N/A	X	N/A	N/A	N/A
holdup 2	N/A	N/A	X	N/A	N/A	N/A
total		7		29		13

accidents and causative variables calculations of each accident are shown in the [Supporting Information](#).

Multiojective Function. Taking into account the profitability, environmental, and safety indexes described above, the objective function can be written as follows:

$$\begin{aligned} \min (-ROI, EI99, IR) &= f(N_{tn}, N_{fn}, R_m, F_m, D_{cn}, P_{tn}, R_{tn}^*, H_R^*) \\ \text{subject to } x_m^{\rightarrow} &> y_m^{\rightarrow} \end{aligned} \quad (4)$$

where N_{tn} are total column stages, N_{fn} is the feed stages in column, R_m is the reflux ratio, F_m is the distillate fluxes, D_{cn} is the column diameter, P_{tn} is the top pressure, R_{tn} are the reactive stages, H_R is the holdup (these last two in the case of reactive distillation), y_m^{\rightarrow} and x_m^{\rightarrow} are vectors of obtained and required purities for the m components, respectively. The results must satisfy each restriction of purity of at least 99.999% of each output component. All design variables for the cases of study are described in [Table 1](#). The optimization infers the manipulation of continuous and discrete variables for each route process: 7 decision variables for Siemens Process, 29 variables for Intensified FBR Union Carbide Process, and 13 continuous and discrete variables for Hybrid Process. These variables correspond to all the existing variables in the conventional and reactive distillation columns, and also in the feed of SiCl₄ and HCl, because they represent the variables with the largest impact in the dimensioning of the processes, as

well as in all aspects economic, environmental, and safety issues that they represent. From Górak and Olujić,²² it can be observed the boundaries of the values of the design variables in the optimization for the distillation columns and the reactive distillation columns, the number of stages and their heights are consistent with the mechanical considerations in the design of distillation columns built so far.

Methodology for Global Optimization. All the processes were optimized individually using the stochastic hybrid optimization method called Differential Evolution with Tabu List (DETL). The stochastic methods are attractive for the optimization of complex, high nonlinear and potentially nonconvex problems.⁸ In particular, for complex problems DETL algorithm is appropriate, as shown in previous works.^{18,23,24}

The optimization with the DETL method was carried out by means of a hybrid platform that includes Microsoft Excel and Aspen Plus. Where basically the vector of decision variables is sent from Microsoft Excel to Aspen Plus through DDE (Dynamic Data Exchange) through COM technology. There the values are assigned to the process variables in Aspen Plus Modeler, to perform the simulation. Once the simulation is done, Aspen Plus returns the exit values to Microsoft Excel in the form of a result vector that contains the exit data. Finally, Microsoft Excel analyzes the objective function values and

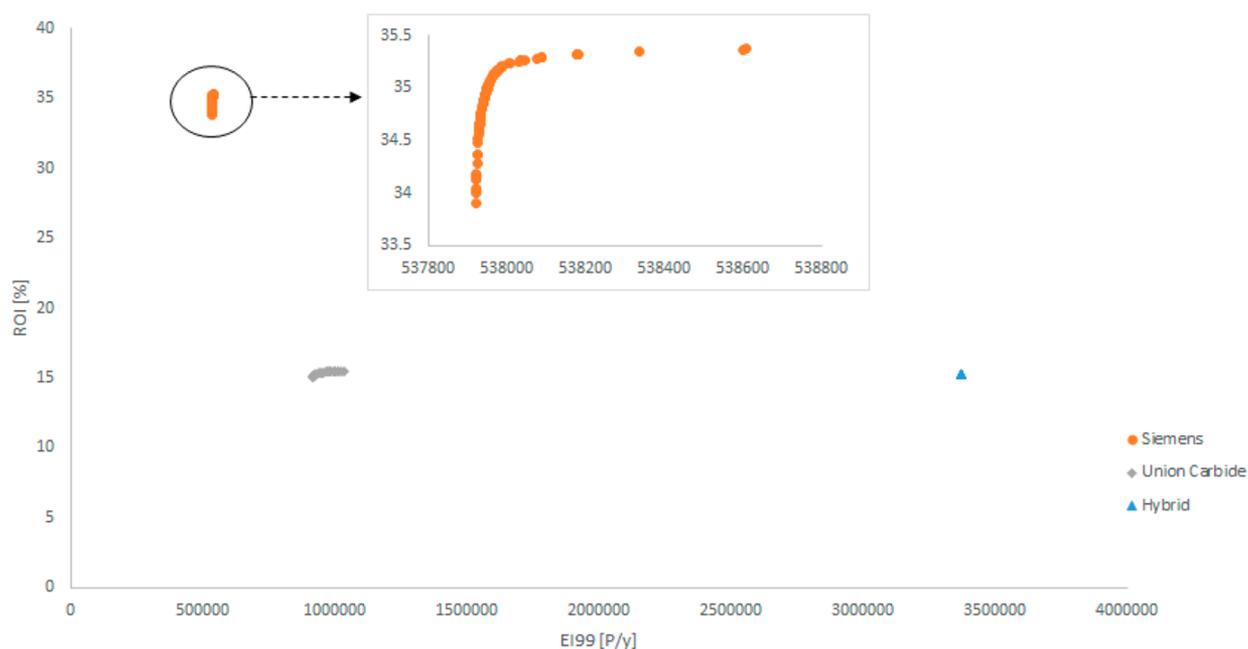


Figure 4. Pareto front between ROI and EI99 for the three processes.

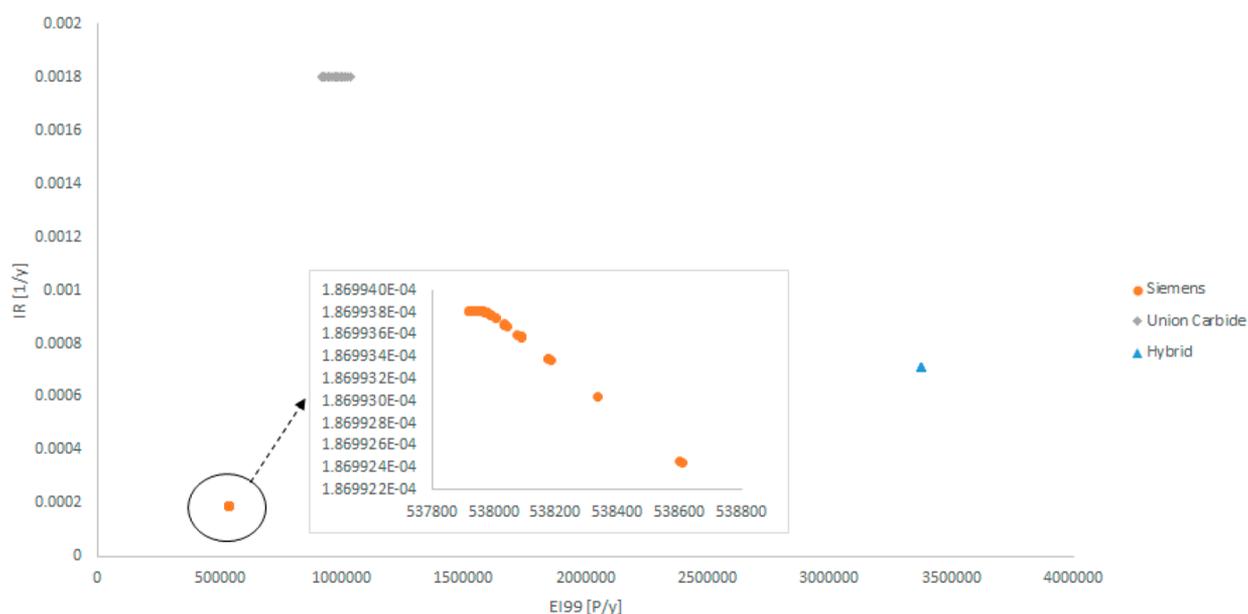


Figure 5. Pareto front between IR and EI99 for the three processes.

proposes new values of variables of decision according to DETL methodology.

For this study, the following parameters have been used for the DETL method: 834 generations, 120 individuals, a Tabu list size of 60 individuals, a Tabu radius of 0.01, Crossover fractions (Cr): 0.8, Mutation fractions (F): 0.3, respectively. The parameters were obtained via preliminary calculations, as shown in the methodology of Srinivas and Rangaiah.²⁵

In each of the iterations, the three indexes are calculated for each of the units involved the processes such as the reactor vessel, furnaces, separators, mixers, heat exchangers, pumps, and compressors. The unit's indexes depends of their size, operating conditions, and operating cost.

RESULTS

This section shows the results of the multiobjective optimization of the three processes described above. The Pareto fronts were obtained after 100 080 evaluations, observing that there are no significant improvements after this number of evaluations. The optimization executions were carried out in a computer with the following specifications: AMD Ryzen™ 5–1600 @3.2 GHz, and 16GB of RAM. The computing time for obtaining the optimal solutions was different according to the complexity of each process: The Siemens Process required 168 h, the FBR Union Carbide Process required 432 h, and the Hybrid Process required 260 h. That corresponds to approximately 20 h per decision variable.

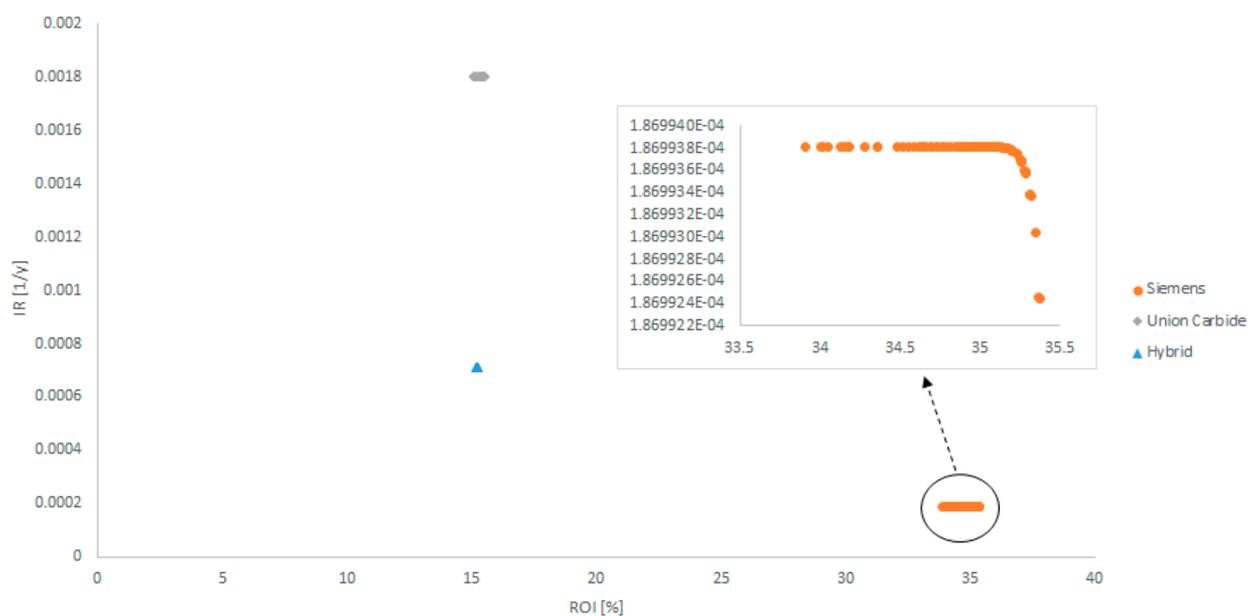


Figure 6. Pareto front between IR and ROI for the three processes.

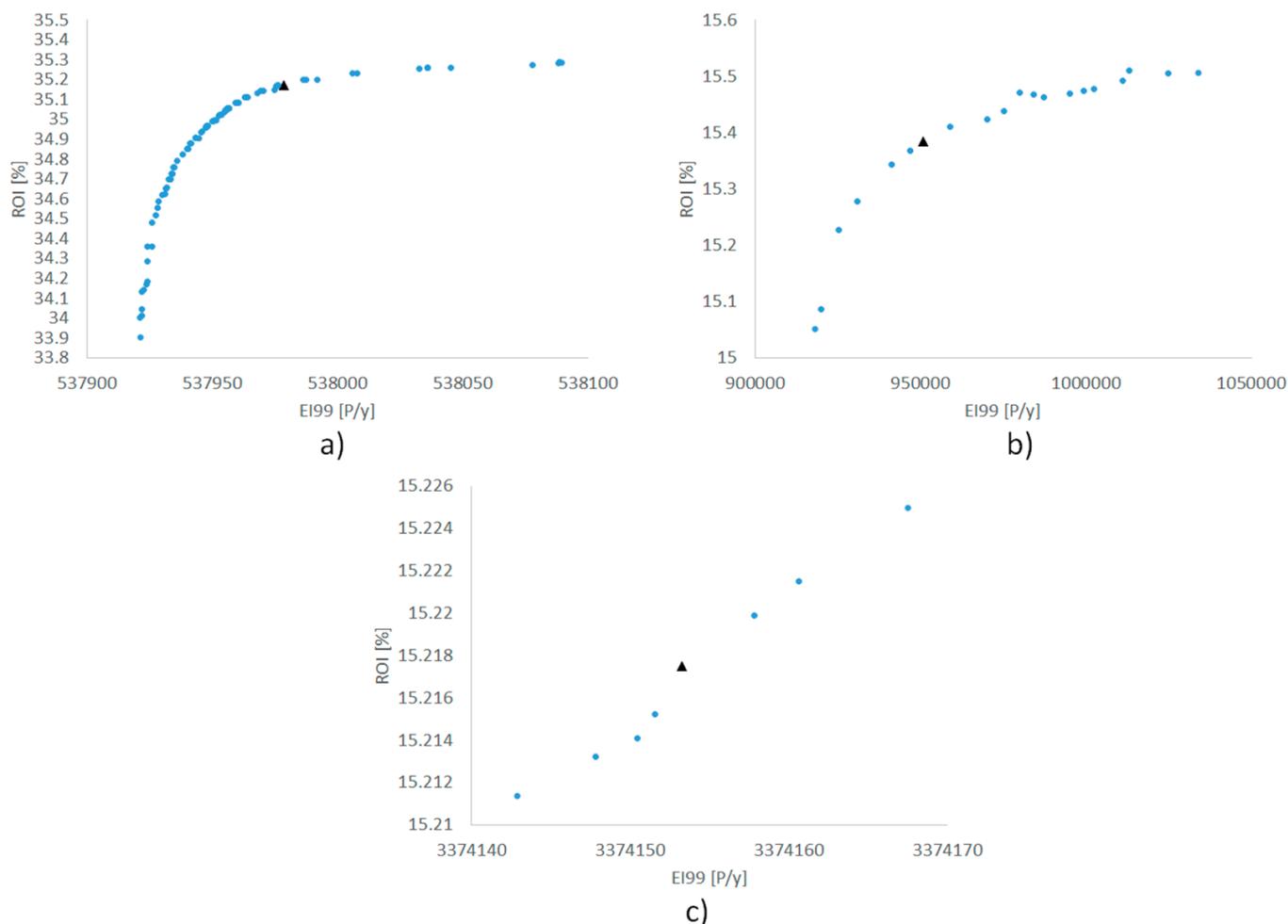


Figure 7. Pareto front between ROI and EI99 for (a) Siemens Process, (b) Intensified FRB Union Carbide Process, and (c) Hybrid Process.

In the case of the Siemens configuration, the performance of the optimization can be summarized in the following results. While the initial configuration has a ROI of 12.49%, EI99 of 0.539 [MP/y], and IR of 1.870×10^{-4} [1/y], ending with a

ROI of 35.17%, EI99 of 0.538 [MP/y], and IR of 1.870×10^{-4} [1/y]. Representing an increase of a profitability of 64.49%, a reduction in the EI99 of 0.12% in EI99, and with no change in the IR. For the Intensified FBR Union Carbide Process, where

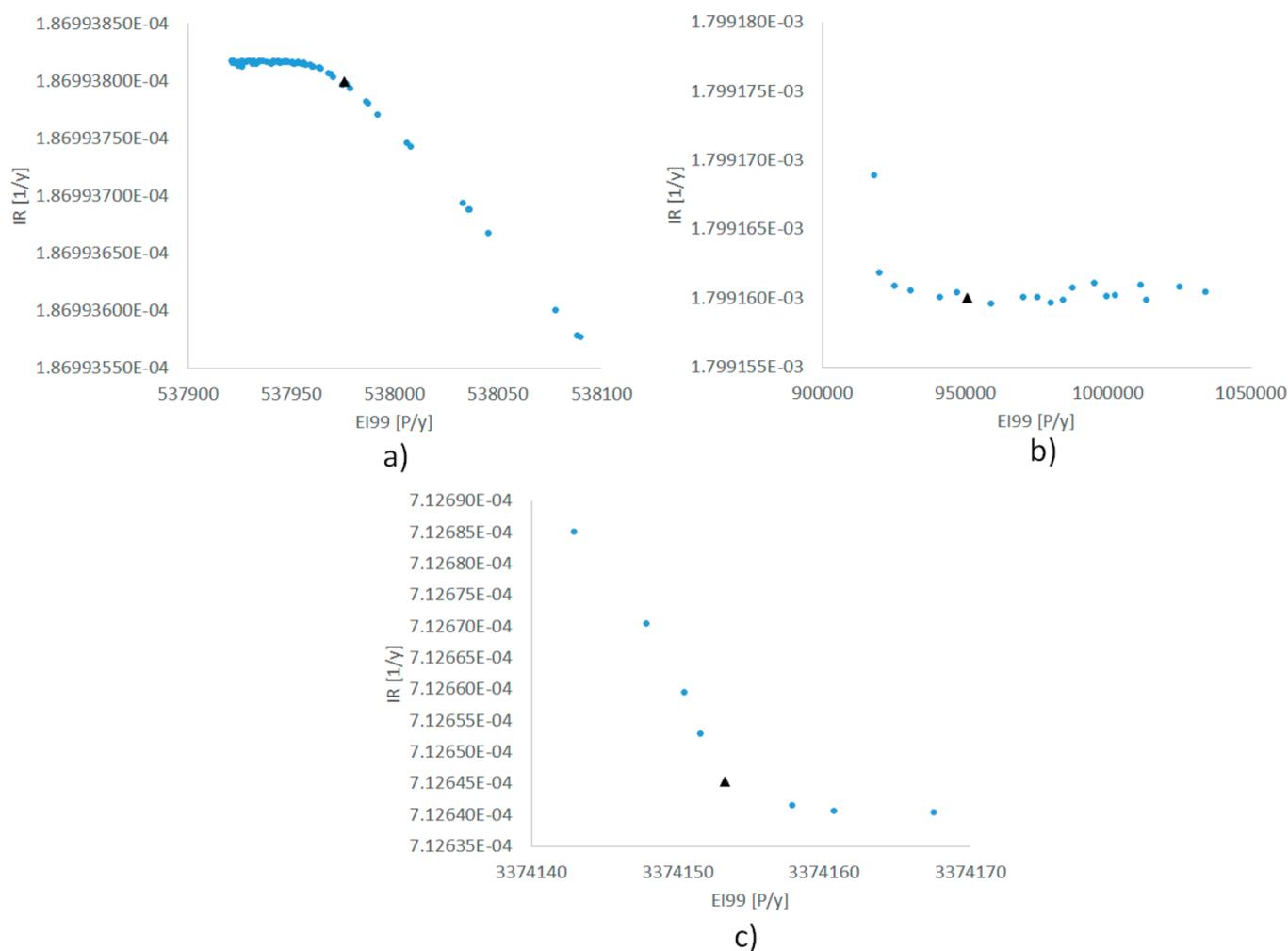


Figure 8. Pareto front between IR and EI99 for (a) Siemens Process, (b) Intensified FRB Union Carbide Process, and (c) Hybrid Process.

the initial configuration presented a ROI of 13.75%, an EI99 of 0.928 [MP/y] and IR of 1.801×10^{-3} [1/y], ending with a ROI of 15.38%, EI99 of 0.951 [MP/y] and IR of 1.799×10^{-3} [1/y] representing a 10.61% improvement in the profitability, a reduction of the EI99 by 2.35%, and a small decrease of the IR, by only 0.075% in IR, which in terms of safety represents a substantial reduction. Finally the Hybrid Process, where the initial configuration showed a ROI of 9.13%, an EI99 of 3.377 [MP/y], and IR of 7.207×10^{-4} [1/y], ending with a ROI of 15.21%, EI99 of 3.374 [MP/y], and IR of 7.126×10^{-4} [1/y], resulting in an increase of a profitability of 39.97%, a reduction of 0.09% in EI99, and a decrease of 1.13% in IR.

In Figure 4, the three processes can be compared in terms of the profitability (ROI) and the environmental impact (EI99). For the case of the Siemens Process, it can be observed that the higher the profitability, the lower the environmental impact. In the other two processes, the Intensified FRB Union Carbide and the Hybrid, it can be seen that even though the ROI is similar, the EI99 increases considerably for the hybrid process case. It can also be observed that the Hybrid Process presents less environmental impact than the FRB Union Carbide Process due to the smaller number of pieces of equipment required. However, the Hybrid Process has more EI99 points, due to the amount of byproducts (SiCl_4 and HCl) that are generated in the final reactor, affecting the human health and ecosystem quality factors in the calculation of EI99.

Figure 5 shows the Pareto between IR and EI99 objectives. Similarly, the Siemens Process shows a desirable behavior. It presents a better safety index and lower environmental risk. For the Intensified FRB Union Carbide Process, the behavior is different. In this case, a high safety index is presented, and there is an intermediate environmental impact between the other two processes. The increase in the IR index in the FRB Union Carbide Process is due to the addition of SiH_4 , which increases the frequency and the event probability of some accidents in the process. The reason is that it is a gas that ignites spontaneously in air and that in case of blow up, the fire cannot be extinguished according to the data of the safety sheet. A different behavior can be observed for the Hybrid Process. Since while it presents the worst environmental index, it is the second best process in safety terms. The value of the EI99 of the Hybrid process is due to the need for a large amount of steel to build it, and the electricity consumption for pumping the high flows of raw material to obtain the product Si_{SG} . The Hybrid Process has a good safety index, due to the avoidance of the use of SiH_4 in the production of Si_{SG} , since this turns out to be a dangerous and toxic material which, together with the reactive distillation processes, increases the risk of the Intensified FRB Union Carbide Process.

In Figure 6 it can be observed the Pareto Front of IR versus the ROI. As in previous results, the Siemens Process shows a desirable behavior. The process has larger profitability and less

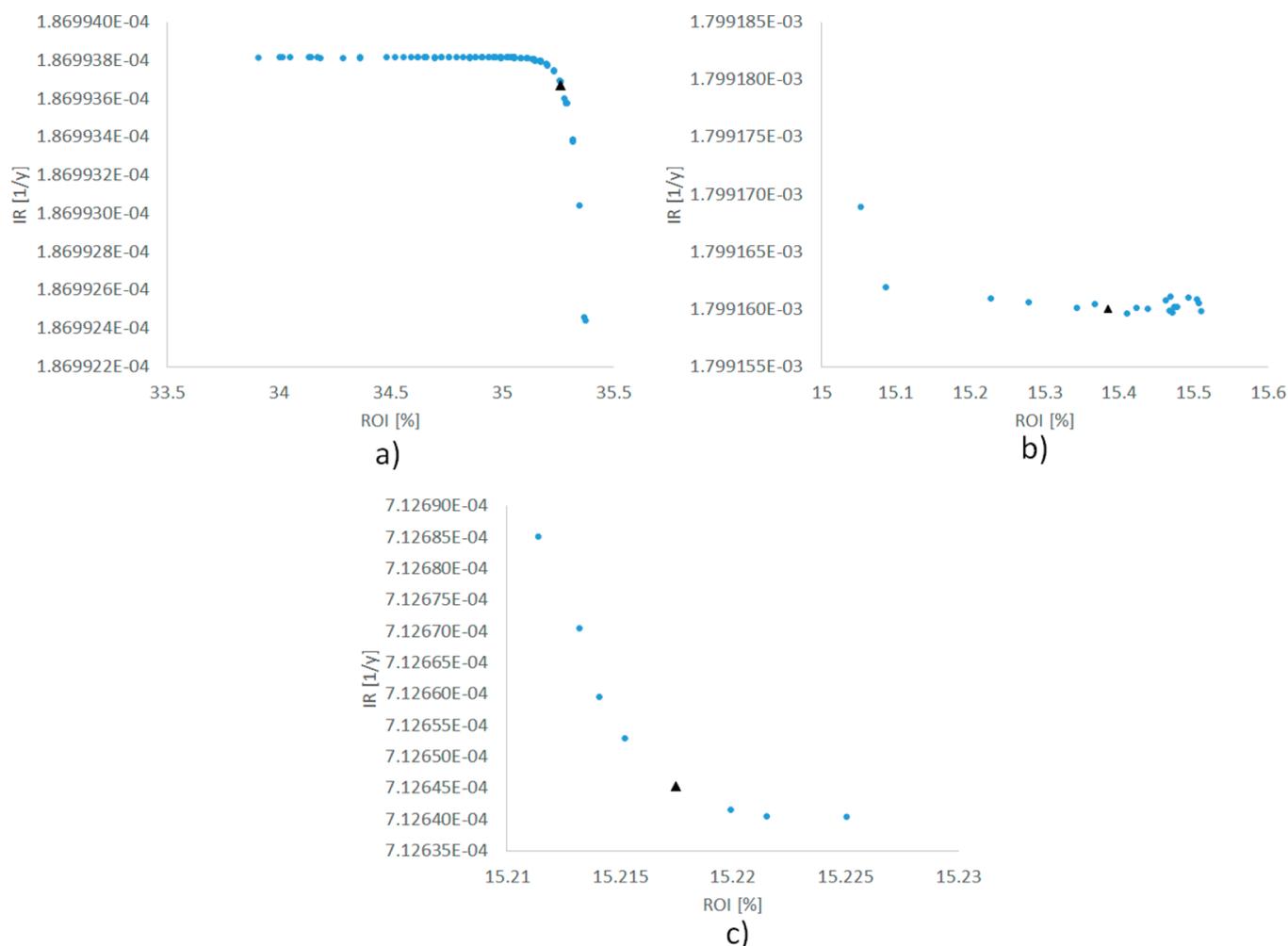


Figure 9. Pareto front between IR and ROI for (a) Siemens Process, (b) Intensified FRB Union Carbide Process, and (c) Hybrid Process.

danger associated with its operation. The Hybrid and Intensified FRB Union Carbide processes practically present the same ROI with a considerable difference in safety. The IR for the Intensified FRB Union Carbide Process is twice as high as that of the Hybrid Process. A dangerous species such as the SiH_4 , increases greatly the frequency and the event probability of some accidents in the process. This species is considered highly hazardous by the OSHA Hazard Communication Standard.²⁶

Figures 7–9 present more clearly each one of the Pareto Fronts for each process. It is important to note that each process has an optimal operating condition, and in this case, it is marked with a triangle. The choice of optimal sequence of nondominated points set was carried out selecting one point of the inflection area where the objectives values find a minimum value without compromising the other one. There are several methodologies for the utopian point choice as it is shown in Wang and Pandu²⁷ work, where 10 methodologies are presented. All of them show the same election area for the utopian point with the optimal point selected for this work, so it turns out to be a good indicator of the choice made. For these cases, Tables S2–S7 (Supporting Information) provide the optimal obtained parameters of each case.

The results shown in Figures 4–6 provide a brief overview of the performance of the processes with respect to the three objectives. However, to evaluate the processes, a more detailed

study is needed. The ROI for the Siemens Process is more than twice as large as the Intensified FRB Union Carbide and Hybrid processes, and it would turn out to be the most profitable process. Nevertheless, it is the one with the smaller production of Si_{SG} , see Tables S2, S4, and S6 (Supporting Information) (55.25 kg/h, 183.26 kg/h y 219.80 kg/h, respectively). It is assumed that the high profitability of 35.17%, the low environmental factor given by an environmental index of 0.53 (MP/y) and better safety index of 1.86×10^{-4} (1/y) of the Siemens Process is given by the small number of pieces of equipment and small amount of material required in comparison to the other processes, and that in the case of the profitability index, ROI is not enough to notice the improvement in Si_{SG} production and others byproduct that are sell.

The Intensified FRB Union Carbide and Hybrid processes exhibit practically the same profitability 15.39% vs 15.22%, respectively. It can be seen a notorious difference in the case of EI99, in favor of the Intensified FRB Union Carbide Process that shows an index of 0.95 (MP/y) compared to 3.37 (MP/y) of the Hybrid Process. In addition, we can also see a large difference in the IR in favor to the Hybrid Process with 7.13×10^{-4} (1/y), being an order of magnitude smaller than Intensified FBR Union Carbide Process, for the reasons explained above. It can be said that the three processes are profitable, although with a significant difference in the others

indexes (EI99 and IR), all the results can be observed in Table 2.

Table 2. Results of ROI, Eco 99, and IR for All the Processes

	ROI [%]	Eco-99[MP/y]	IR [1/y]
Siemens Process	35.17123	0.53797	1.86993 x10 ⁻⁴
Intensified FBR Union Carbide Process	15.38502	0.95079	1.79916 x10 ⁻³
Hybrid Process	15.21748	3.37415	7.12645 x10 ⁻⁴

The work by Ramírez-Márquez et al.,⁸ presented the Hybrid Process as an attractive alternative due to the larger production capacity. The results obtained in this work shows that it also presents the second best safety index with respect to the other two processes. However, it shows the worst EI99 index.

A comparison between the design provided by the optimization of the TAC⁸ and that resulting from the multiobjective optimization presented in this work is shown. Substantial changes can be observed in the parameters of each process, as is the case of the number of stages in the distillation columns, the feed stage, the reflux ratio, and so on. The parameter of greatest change in the Siemens Process is the reboiler heat duty where, when the three objectives are optimized (ROI, EI99, and IR; see Tables S2 and S3, Supporting Information), the value is brought down to 410.82 kW (representing 25.19% lower value). Additionally, the change in the number of stages of 43 for the TAC optimization to 40 for the optimization of the three objectives decreases the column height. We can also observe a change in the diameter of the column going from 1 m (TAC

optimization) to 0.3646 m. The temperatures and pressures remain almost the same in both designs.

In the Intensified FRB Union Carbide Process there are structural modifications in the distillation columns such as the number of stages, the reboiler heat duty and the diameter of all the columns. More important are the changes in the second conventional column which happens to have 40 stages when the TAC alone is optimized,⁸ while the number of stages increases to 93 for the multiobjective optimization and a diameter almost 3 times larger for the multiobjective case (see Tables S4 and S5, Supporting Information).

The Hybrid Process also presents important changes in its design parameters. The reboiler heat duty of the first column is the most significant one. Going from 2141.79 kW for TAC optimization to 1674.72 kW for the multiobjective optimization, see Tables S6 and S7 (Supporting Information). As well as the columns diameters that are a third and one-half of the presented diameters in the TAC optimization.

In general terms, there is a certain convenience to use in the Hybrid Process election based on the production capacity and process safety. A relevant factor to design a process is based on avoiding highly toxic and flammable substances. However, for small production capacities of Si_{SG}, the Siemens Process shows clear advantage in economic, environmental, and safety terms.

Likewise, as it can be inferred from the present work, the IR value reduction for any process can be explained mainly in two ways. The process size reduction will result in a reduction in the IR, while the presence of toxic and dangerous substances through it will increase the IR values. For EI99, the steel used for building equipment and accessories, the utilized steam to produce heat and electricity increases the index value considerably. Finally, the ROI allows to visualize generally



Figure 10. Normalization of safety and environmental indexes.

the process profitability, but can leave aside aspects that determine the production capacity of any process.

As previously mentioned, the results of the safety and the environment indexes are independent of the amount of Si_{SG} obtained. The optimization was based on facilities that processed the same amount of raw material. Therefore, in a further comparison, the results were normalized by the amount of Si_{SG} obtained in each of the processes instead of by the feed of raw material. Figure 10a,c shows the results of the environmental and the safety indexes with the techniques described in Methodology, and discussion of those results are described above. Figure 10b,d presents the results of the normalized environmental and safety indexes by the production of Si_{SG} . The important part to observe in Figure 10b) is that the Eco-indicator 99 is now better for the Intensified FBR Union Carbide Process, while the Hybrid process shows and ECO 99 index of the same order as that of the Siemens process. Likewise, in Figure 10d) the best safety index is in the Hybrid Process. This analysis helps to reaffirm that the Hybrid Process is a good economic, environmental, and safety option due to the amount of Si_{SG} obtained.

CONCLUSIONS

The work presents the evaluation of three processes to produce Si_{SG} , according to safety, profitability, and environmental impact. The optimal parameters of each process were obtained by means of a multiobjective optimization using the DETL method. Through the Pareto Fronts, the solutions with the best values of each objective function were found. The addition of safety principles in the design of the three processes allows considering one of the main issues that must be taken into account in the design of any process. The results show that the Siemens Process is the best process in terms of the three objectives. However, note that Si_{SG} production is very low (25% of that obtained from the Hybrid Process) and that current markets demand higher production, so the choice of ROI as an economic index did not turn out to be the adequate, the other indexes were unable to capture the actual yield of the processes. Taking into account the production capacity and considering that the Hybrid Process shows a safety index very similar to that of the Siemens Process, it can be the best option for its industrial implementation. The Intensified FBR Union Carbide Process proved to be the least safe process of the three, although it shows better performance in environmental terms than the Hybrid Process. It was concluded that one of the factors that affect the safety in the Intensified FBR Union Carbide Process is the inclusion of SiH_4 in the production of Si_{SG} , that increases greatly the frequency and the event probability of some accident in the process. By normalizing the safety and environmental indexes, it is reaffirmed that the Hybrid Process can be a good option for the implementation. The approach presented here is an effort to include safety as part of process design, and in particular, it can be extended to other systems that also present substances that represent a hazard.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b06375.

Causative variable, with equations for quantification of material released; probable accidents, and causative variables, with the methodology of equations resolution for the: BLEVE's, UVCE's JET FIRE's, calculation of continuous flash fire and toxic release, and calculation of instantaneous flash fire and toxic release, for the causative variables calculation; consequences analysis with the probit parameters; and the results of the optimization of ROI, Eco 99, and IR for the all processes (PDF)

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Notes

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ABBREVIATIONS

Si_{MG}	metallurgical-grade silicon
Si_{SG}	solar-grade silicon
SiHCl_3	trichlorosilane
SiCl_4	silicon tetrachloride
SiH_4	silane
ROI	return on investment
EI99	eco-indicator 99
IR	individual risk
LCA	life-cycle assessment
QRA	quantitative risk analysis
TAC	total annual cost
BLEVE	boiling liquid expanding vapor explosion
UVECE	unconfined vapor cloud explosion
LC50	lethal concentration
DETL	differential evolution with tabu list
DE	differential evolution
TL	tabu list
DDE	dynamic data exchange

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