



Process design and intensification for the production of solar grade silicon



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ABSTRACT

Solar grade silicon (Si_{SG}) is typically used in photovoltaic applications, and it is commercially manufactured via the Siemens process. Despite the fact that current levels of demand are satisfied, there may be a shortage of Si_{SG} in the near future. To improve the low yield of the Siemens process, two alternative types of Si_{SG} production processes have been developed and analyzed using a stochastic optimization scheme within ASPEN PLUS. The first one is an intensified Fluidized Bed Reactor (FBR) process using a reactive distillation column. The second one is a hybrid process combining both the Siemens and the conventional FBR processes. In addition to supplying future demand, these processes are intended to reduce the use of raw materials. The results show the great value of optimizing the processes, since it achieves savings in the TAC of 53.28%, 67.65% and 62.58% (Siemens, Intensified FBR and Hybrid process), respectively. Siemens process shows the lowest TAC (\$0.50 M/y), but this does not mean that it is the process with the highest potential, since it has the lowest silicon production rate, 0.47 kt/y. The Intensified FBR Union Carbide Process turns out to be the most expensive of the three (\$2.57 M/y), with a large production of Si_{SG} , 1.49 kt/y. However, it is the hybrid process which shows the larger yield by far, with a production of 1.89 kt/y of Si_{SG} and TAC of \$1.95 M/y, showing the highest profit from sales, \$40.47 M/y. However, from the environmental point of view, the Siemens process shows the lowest environmental impact based on the eco-indicator 99, while the Hybrid process is the second best.

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1. Introduction

Solar photovoltaics, PV solar, is gaining attention as a technology to make use of the largest energy source available, up to 162,000 TW that the Earth's receives annually (Bououdina, 2014). Its market share among renewable energy increases and currently it is the most newly installed renewable source of power (Solar Market Insight Report, 2016), in the race to replace fossil based power and fuel sources. Furthermore, current volatility in crude prices is another driver towards the goal of self sufficient supply of energy (Ginley et al., 2008). However, renewable technologies are not yet competitive with their fossil based counterparts. Therefore, there is a research opportunity to improve their yields and

efficiencies. In particular, PV panels have improved their performance reducing the cost. For instance, in the southwest of the United States, in order to meet the cost goal of \$0.33/W or \$0.05–0.06/kWh for utility-scale production, these modules with 15% efficiency, needed to be manufactured at a cost of \$50/m² or less (Ginley et al., 2008). Further penetration of this technology into the market will make possible to reduce costs even further. So far, the basic raw material for the production of these panels is polysilicon.

For years, microelectronic industry has been an important source of polysilicon. In that industry, ultrapure Si, 9N or Si_{EG} , is required. The waste of Si remaining in the melting units as well as the pieces of waffles that do not reach the proper purity are typical sources of solar grade Si (Braga et al., 2008). However, the development of the solar sector has increased the demand for solar grade Silicon and the scraps from microelectronic industry are no longer enough to meet the needs as raw material. Therefore, there is a

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need to improve the production processes from polysilicon to reduce their cost. The cost shares per Watt Peak of polysilicon solar systems are roughly as follows: Solar grade silicon ($\text{Si}_{(\text{SG})}$): 20%; ingot and wafer production: 28%; solar cell processing: 13%; solar module processing: 9%; installation of the PV-system including converter costs: 30% (Sadique, 2010). There are two main possibilities to achieve the cost reduction since approximately half of the costs are caused by feedstock, bulk silicon production and wafer manufacturing (Müller et al., 2006). Thus, the development of optimized processes for production of cheap $\text{Si}_{(\text{SG})}$ feedstock material can allow better competitiveness.

Solar grade silicon can be produced from quartz following a two-stage process consisting of the production of metallurgical silicon and its further purification up to solar grade quality. The two most used processes are Siemens and Fluidized Bed Reactor, FBR, from Union Carbide. Siemens process was patented by Siemens Corporation in the 1950's. Its main feature is the Siemens or Bell reactor where 6N silicon is produced by Si deposition on a silicon pole (Payo, 2009). However, this alternative shows a large energy consumption and a number of waste streams. On the other hand, Union Carbide's process uses Silane as a raw material for the production of Si. It was developed in the 1970–1980 (Erickson and Wagner, 1952). Even though the yield of this alternative is larger than the one provided by Siemens process, the conversion from silane is larger than that from trichlorosilane and the operating conditions are more difficult to achieve.

Due to the high production cost of PV panels, the aim of this work is to reduce the production costs of $\text{Si}_{(\text{SG})}$ by developing more efficient processes. In particular two novel processes have been proposed in this paper. The first one corresponds with an intensified FBR's process by substituting the conventional reactors and separation zone with a reactive distillation column. In this case, a reactive distillation column (RD) is used to overcome the traditional process since fewer distillation columns and no reactors are required. Essentially, the idea of employing a reactive distillation column is to improve the chemical conversion, because products alone are withdrawn from the reactive zone while reactants remain inside for further reaction. This reactive distillation process is reported previously in the work of Ramírez-Márquez et al. (2016). The second alternative process is a novel process that is based on both, the Siemens and the FBR attempting to reduce the use of raw material (Vidal and Martín, 2014).

It is important to note that the three simulated processes were optimized to make a comparison in their Total Annual Cost (TAC) and in their production of solar grade silicon. Since scale is an advantage for any of these processes we target an annual production similar to the ones reported by major competitors (Nitol Chem Group [1,500 t/y], PV Crystalox [2,250 t/y], SolarWorld [3,200 t/y] (SOLAR PV INVESTOR) (List of World's Polysilicon Producers According to Country for Last 3, 2013)).

The rest of the work is organized as follows. Section two presents the description of each one of the three alternatives compared, Siemens as a base case, intensified FBR and hybrid process, discussing the modelling effort and the assumptions. The section ends with the description of the optimization method used, an evolutionary hybrid method based on tabu list using the total annualized cost as objective function. Section three presents the results comparing the operation and the economics of the three processes. Finally we draw some conclusions in section four.

2. Methodology

We first simulate the all three processes rigorously in Aspen Plus V8.4. To predict the thermodynamics of the system, we used the

thermodynamic package Peng-Robinson, and 'Solids' property method for solids components. All the sequences presented were obtained considering the complete set of mass and energy balances, equilibrium relationships, and summation constraints along with the phase equilibrium calculations. Over sections 2.1–2.3 all three alternatives are described in terms of the chemical reactions and separations taking place and the assumptions to model the various units in Aspen Plus. The production capacity selected, 2000 t/y is based on the average production of major companies (List of World's Polysilicon Producers According to Country for Last 3, 2013). The standard feed can be seen in Table 1. Next, we perform a stochastic based optimization to decide on the column design and the operating conditions for each process.

Furthermore in this work we have added the calculation of the environmental impact which is measured through the Eco-indicator 99, a cradle to gate methodology, which reflects the advances in the damage-oriented method recently developed for Life Cycle Impact Assessment, as show Guillen-Gosalbez et al. (2008). With regards to the environmental impact, three damage categories are considered: human health, ecosystem quality, and resources. The process data are used to compute the environmental performance information. The human health damages are quantified in terms of disability adjusted life years (DALYs). The ecosystem quality damages are defined in terms of possible disappearance of species m^2/y . Finally, regarding the damages to resources, these are specified in terms of megajoules (MJ) of surplus energy (Guillen-Gosalbez et al., 2008). The data associated with the three categories above mentioned, will be taken from standard databases, i.e. TEAM and DEAM (1998). Finally, the damages of each category are normalized and aggregated into a single impact factor (Eco-indicator 99). By normalizing categories with different units as described above, a single unit of P/y is given, where one point per year is the one-thousandth of the impact of one European citizen per year.

2.1. Siemens Process

This process uses quartz as raw material. It is cheap and readily available, as it can be seen in Figs. 1 and 2. The first stage is to produce metallurgical silicon via quartz reduction with coal. An electric arc furnace is the unit used for this transformation (Ranjan et al., 2011). The purity obtained for metallurgical grade silicon, $\text{Si}_{(\text{MG})}$ is around 98–99%. The typical impurities remaining are Fe, Al, Ti, P and B (Søiland, 2005). In this work it is considered a base feed of pure SiO_2 . This furnace transforms high voltage and low intensity current into high intensity and low voltage to make use of Joule's heating effect to melt the feed. The unit consists of a crucible of 10 m diameter and three electrodes where the feed is loaded. Tri-phasic current is made through the feed to carry on the reaction. Large amount of energy is required to melt silicon, which takes place at 1986 K. The furnace performance must be in the order of 45–50% so that the energy consumption matches the experimental results from Brage (2003). Thus, we model this unit in Aspen Plus 8.4v using a mixer module (Mixers/Splitters-Mixer) to feed coal and Si, a furnace (Exchangers-Heater-Furnace module) to heat up the mixture from standard conditions, 298 K and 1 bar up to 2273 K and 1 bar. We use a stoichiometric reactor (Reactors-RStoic module) to

Table 1
Feeding of processes.

Component	kg/h
SiO_2	532,32
C	369,84

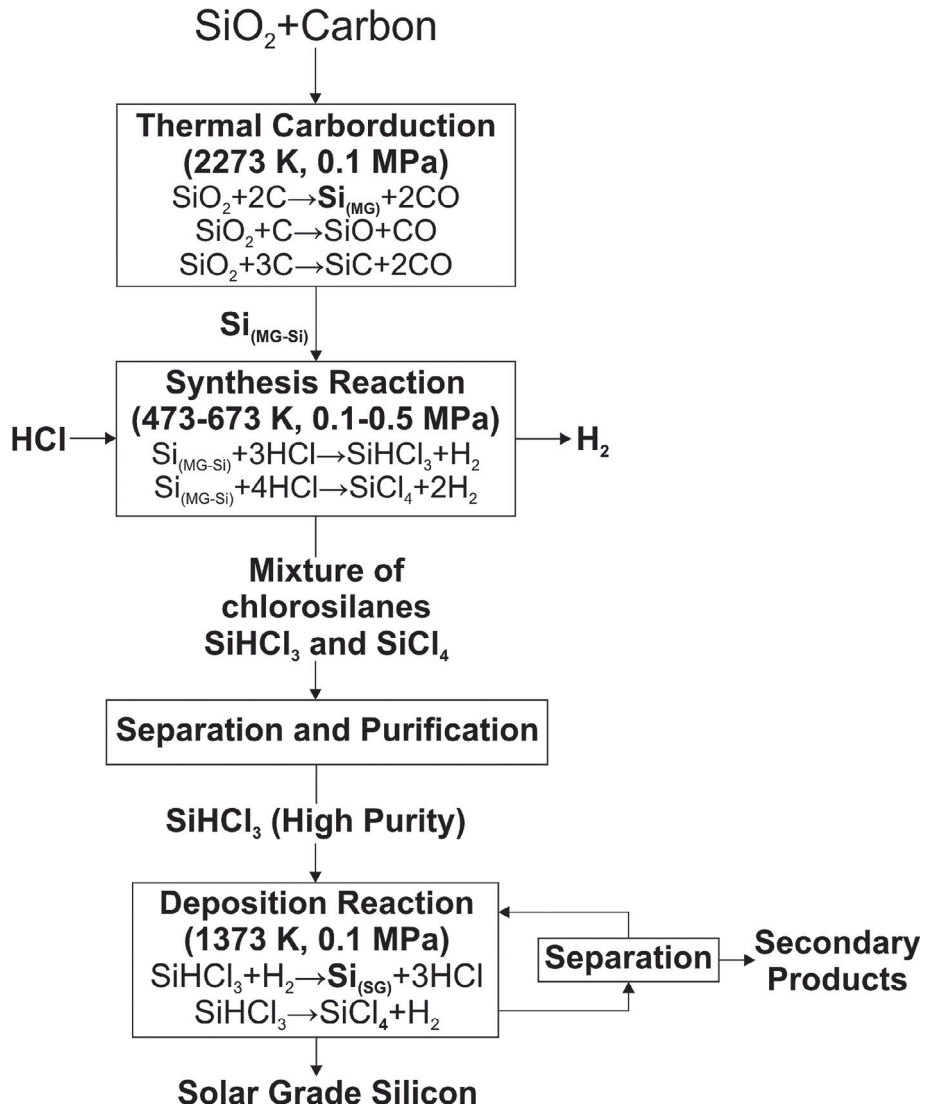


Fig. 1. Siemens process.

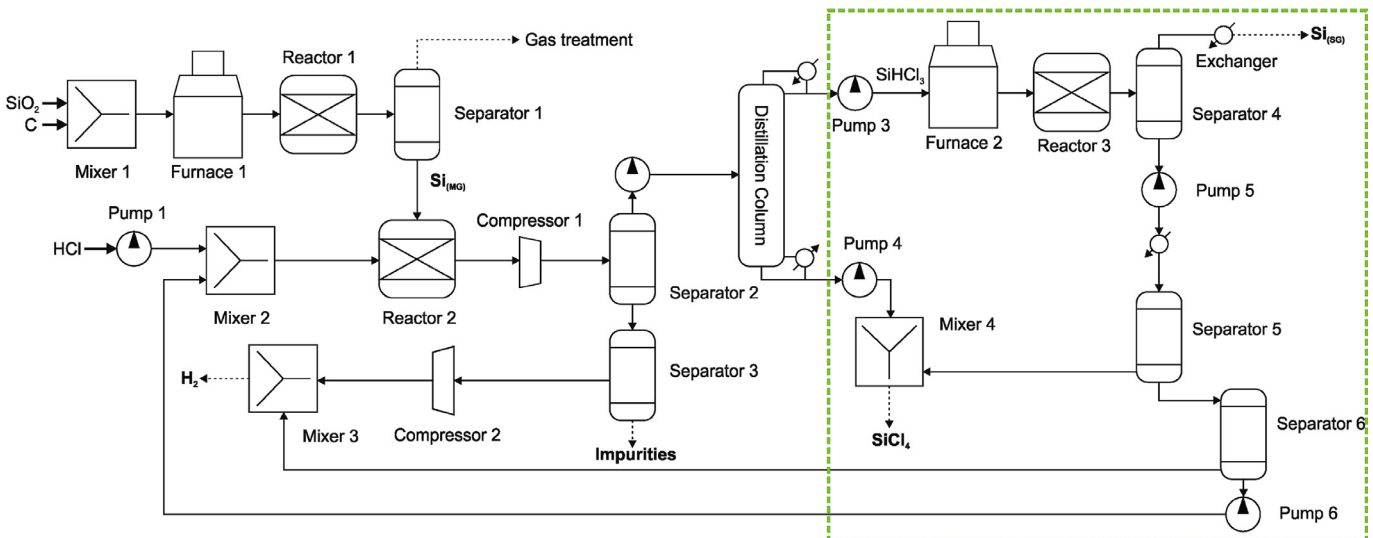


Fig. 2. Flowsheet siemens process.

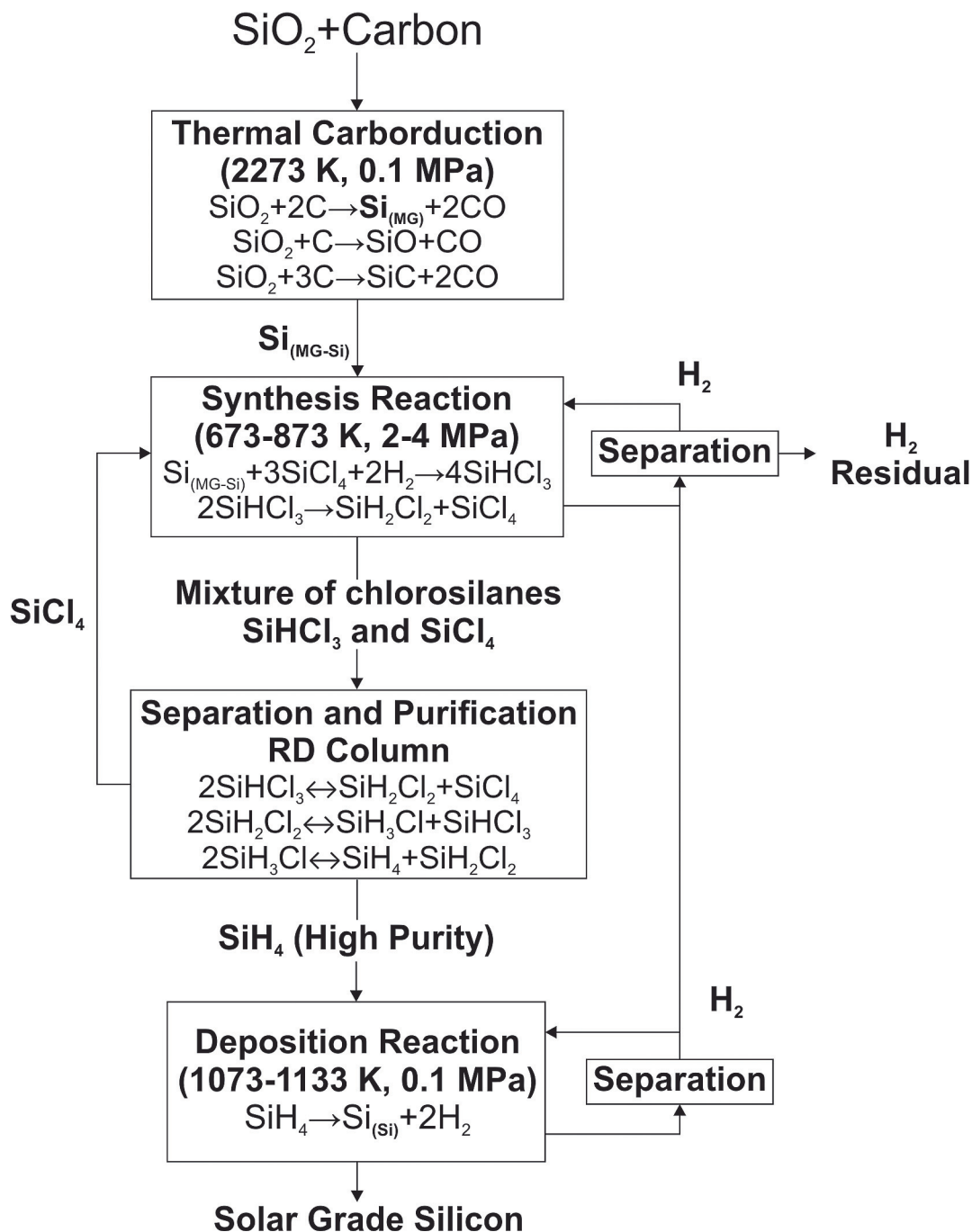
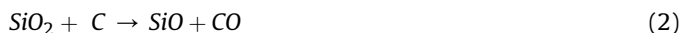


Fig. 3. FBR Union Carbide with RD column process.

evaluate the product of the reactions taking place in equations (1)–(3) (Schei et al., 1998).



The conversion of silicon dioxide (SiO₂) to metallurgical grade silicon (Si_(MG)) is 85%. The rest is slag. To compute the slag, we assume that the rest of the SiO₂ reacts equally through each of the

reactions (2) and (3). Since the stoichiometric reactor (Reactor-RStoic module) in Aspen only has one exit stream, we use a component separator (Separator-Sep module) so that we separate the slag and gases from the Si_(MG) (Barbouche et al., 2016). Gas processing is out of the scope of this work.

The Si_(MG) is fed to the fluidized bed for the production of chlorosilanes. The target is trichlorosilane (Payo, 2009). It operates at 273–673 K and 1.5 bar. In the reactor the following reactions take place:



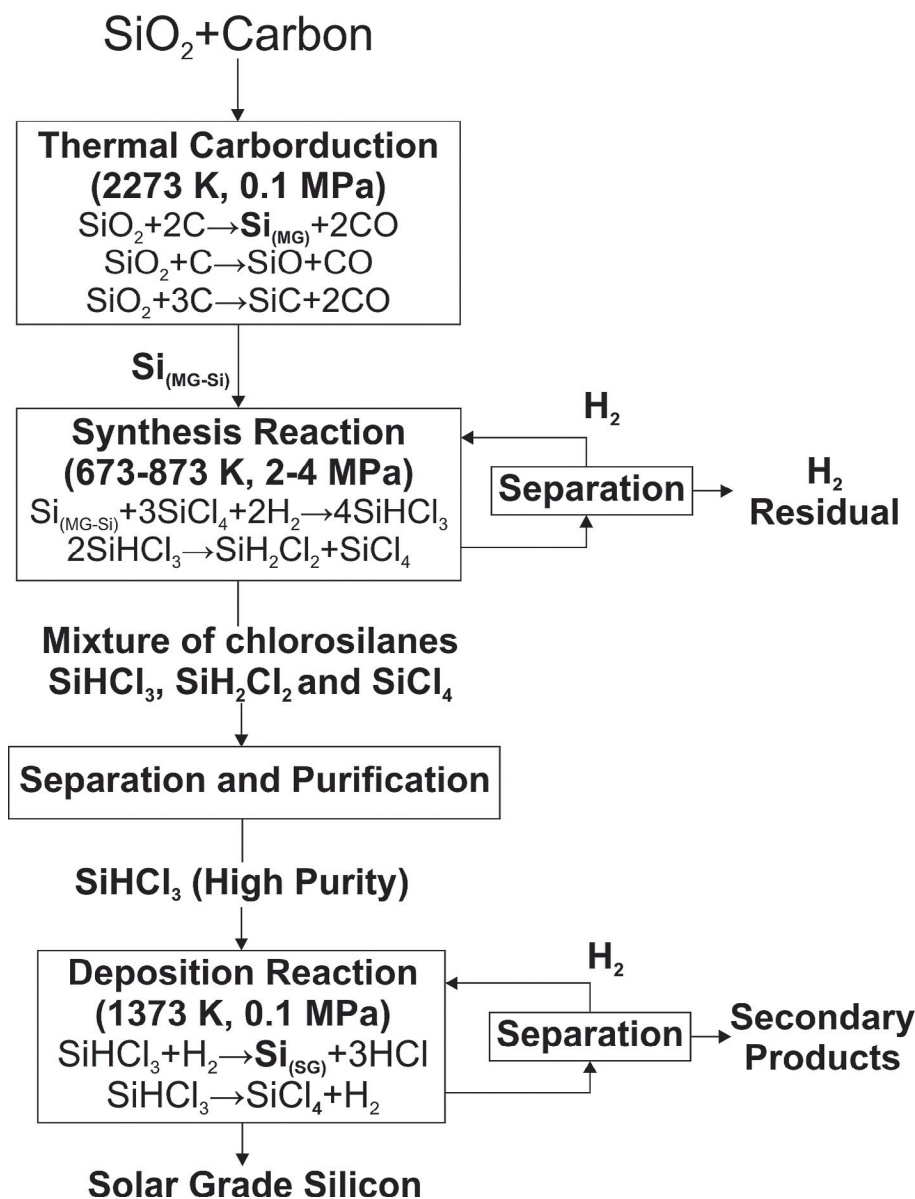
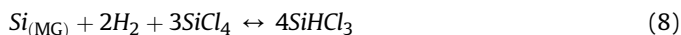


Fig. 5. Hybrid process FBR Union Carbide with Siemens.

Si_(MG), with Siemens process. From that point on Si_(MG) is hydrogenated together with SiCl₄ in a fluidized bed reactor at 774 K and 36 bar (Erickson and Wagner, 1952). This reactor is modelled as a stoichiometric one (Reactors-RStoic module) where the following reactions take place:



The yield of the first reaction reaches 25%. Typically, redistribution reaction may also take place (see equation (9)). The conversion from SiHCl₃ to SiH₂Cl₂ is 10.5% (Pazzaglia et al., 2011). The stream of products is processed by a flash module (Separators-Flash2) to separate the chlorosilanes and others gases, such as hydrogen. Now the other gases pass through a separator (Separators-Sep module) to obtain pure hydrogen, that is transported by a compressor (Pressure Changers-Comp-Icon2 module) and stored as a by-product.

Next, the stream consisting mainly of trichlorosilane and tetrachlorosilane, is fed to a regular system of two distillation columns modelled using “RadFrac” module (Columns-RadFrac-Fract1). From the bottoms of the first column we obtain a high purity SiCl₄ stream that is recycled. In the last column we obtain high purity trichlorosilane bottom product that will be fed to the reactive distillation column. Auxiliary equipment is required, such as pumps (Pressure Changers-Pump module) to give the necessary force to transport the liquid from the dome liquid streams and bottom of the column. However, trichlorosilane disproportion reactions (see equations (10)–(12)) are carried out in a reactive distillation column. Thus, SiCl₄ is fed to the reactor with a 10% excess (Yaws et al., 1986)

High purity trichlorosilane is fed to the new intensified process, the reactive distillation system, that it was previously reported by Ramírez-Márquez et al. (2016). The reaction takes place following a three step mechanism, eqs. 10–12. Apart from silane, intermediates such as dichlorosilane (SiH₂Cl₂) and monochlorosilane (SiH₃Cl) are produced together with SiCl₄ (Ramírez-Márquez et al., 2016).

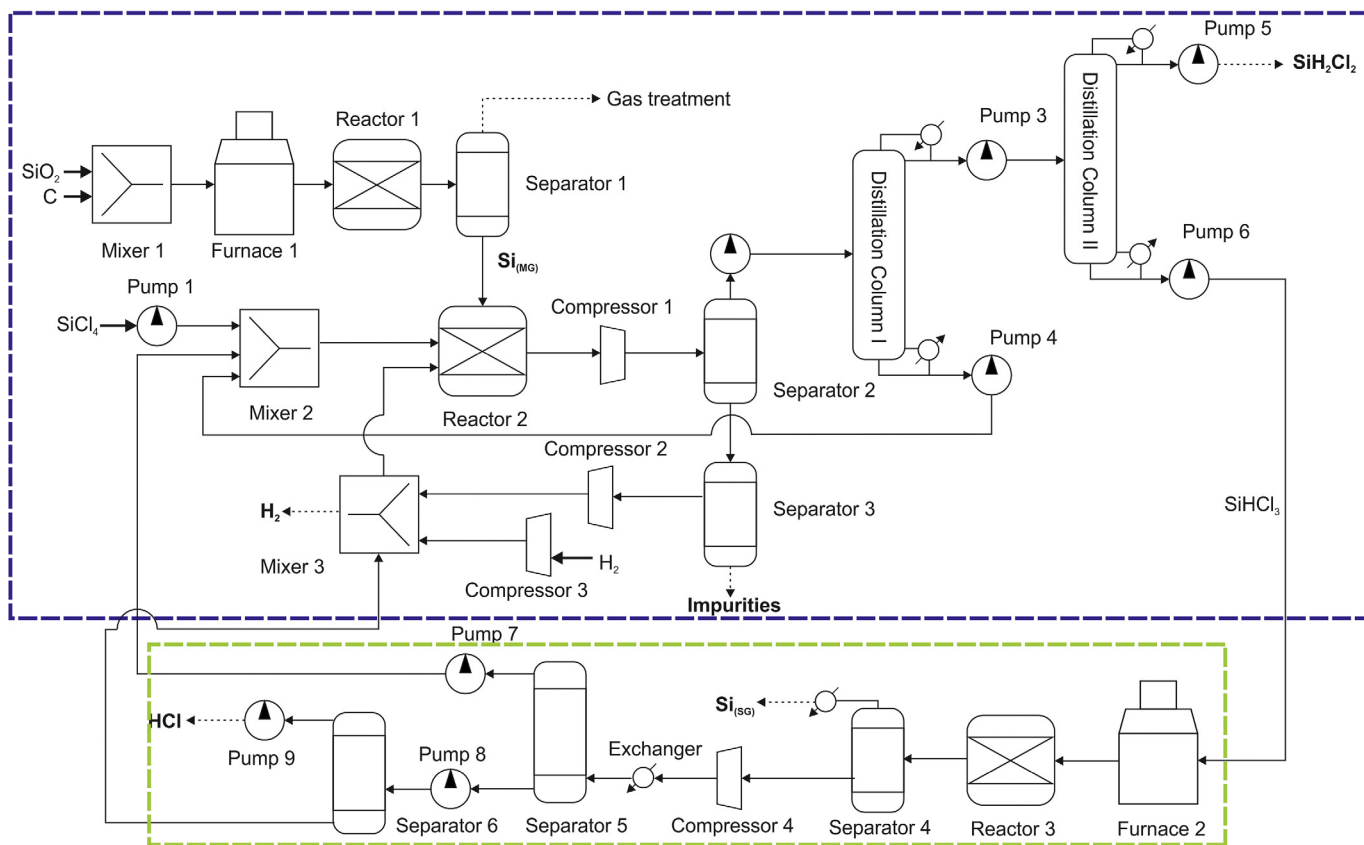


Fig. 6. Flowsheet hybrid process FBR Union Carbide with Siemens.



The catalyst selected for the reaction is “Amberlyst” (A-21) that shows good reaction rates from 30 to 80 °C and it is resistant up to 100 °C. The temperature profile of the reaction zone shows that the maximum temperature achieved at the catalyst was 71.80 °C, and the pressure reached is 2.54 atm. Table 2 shows the kinetic parameters (Ramírez-Márquez et al., 2016). The reactive distillation

column was modelled using the “RadFrac” module (Columns-RadFrac-Frac1). 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 at 973 K, see eq. (13) (Farrow, 1974). The dome and bottom streams are carried by pumps (Pressure Changers-Pump module). We model this reactor as a furnace (Exchangers-Heater-Furnace module) and a stoichiometric reactor (Reactors-RStoic module). Where the following reaction takes place:



Silane conversion reaches 80% (Tejero-Ezpeleta et al., 2004). The product stream is separated to isolate the polysilicon from the

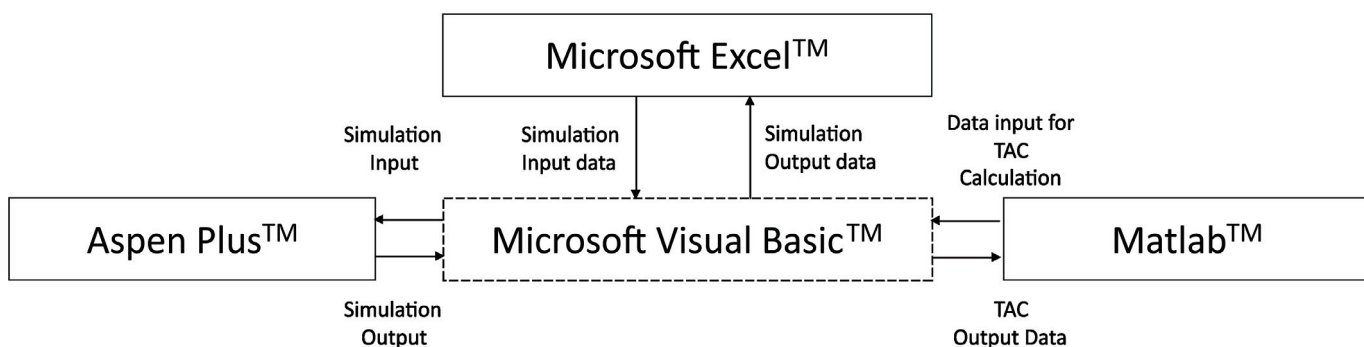


Fig. 7. Hybrid platform to implement optimization.

Table 3
Decision variables used in the global optimization of process routes for Si_{SC} 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	

gases. Both streams are cooled down in two different heat exchangers (Exchangers-Heater-Furnace module). Polysilicon is solidified while the gases, mainly H₂ and HCl, are recycled. Fig. 3 shows a scheme of the process and Fig. 4 for the complete flowsheet.

2.3. Hybrid process

This process, see Fig. 5 for a scheme, aims at combining Siemens and FBR processes to make the most of the advantages of both. In Fig. 6, a blue dashed line box is identified; this box refers to the FBR Union Carbide Process area, and a dotted green line box surrounds the Siemens section. The whole of the two zones is what generates the process so called hybrid.

The flowsheet, see Fig. 6, is based on the work presented in a previous papers by Vidal and Martín (2014). The production of Si_(MG) is carried out as in previous cases, by means of the carbor-education of SiO₂. Next, an FBR is used for the hydrogenation of Si_(MG) and SiCl₄ operating at 773 K and 36 bar. The process initially requires a fresh feed of SiCl₄ for its operation. As the process reaches steady state this compound is obtained as a secondary product and is recirculated to this stage (Erickson and Wagner, 1952). The reactions taking place are those given by equations (8) and (9).

The exit stream contains solids, non-condensables and a mixture of di, tri and tetrachlorosilane. Solids and non-condensable gases are separated and the chlorosilane mixture is condensed. Two regular distillation columns are used to separate the mixture of chlorosilanes. We model the columns using the module “RadFrac”

(Columns-RadFrac-Fract1). From the top of the first column we obtain di and trichloro silane while from the bottoms we use tetrachlorosilane with traces of SiHCl₃ that will be removed. It is better to remove SiCl₄ by the bottoms of the first column, because of the large amount of this compound in the mixture, so that it is recycled to the process. The second column, separates the mixture of SiHCl₂ and SiHCl₃ obtaining from the top a high purity stream of SiHCl₂ and from the bottom SiHCl₃ of high purity. This stream is mixed with the traces separated from the SiCl₄ stream in a flash unit. Support equipment is required, such as pumps (Pressure Changers-Pump module) to give the necessary force to transport the liquid from the dome liquid streams and bottom of the column.

The next step uses SiHCl₃ as feed for the chemical vapor deposition reactor. SiHCl₃ is fed together with hydrogen as in equations (6) and (7). This reactor is similar to the one in the Siemens process and therefore, the same assumptions are made to model it. After the deposition, HCl and hydrogen are separated from the Si_(SC). We use a separator to simulate this operation (Separators-Sep module). Both streams are cooled down. The gas stream is purified using a membrane assumed to have 100% recovery to recycle hydrogen to the process, see Fig. 6.

2.4. Optimization problem

Each process is optimized separately. Note that the design and the optimization of the processes are highly nonlinear problems involving continuous and discrete design variables. Within the simulation and optimization of each process, a solution is given to

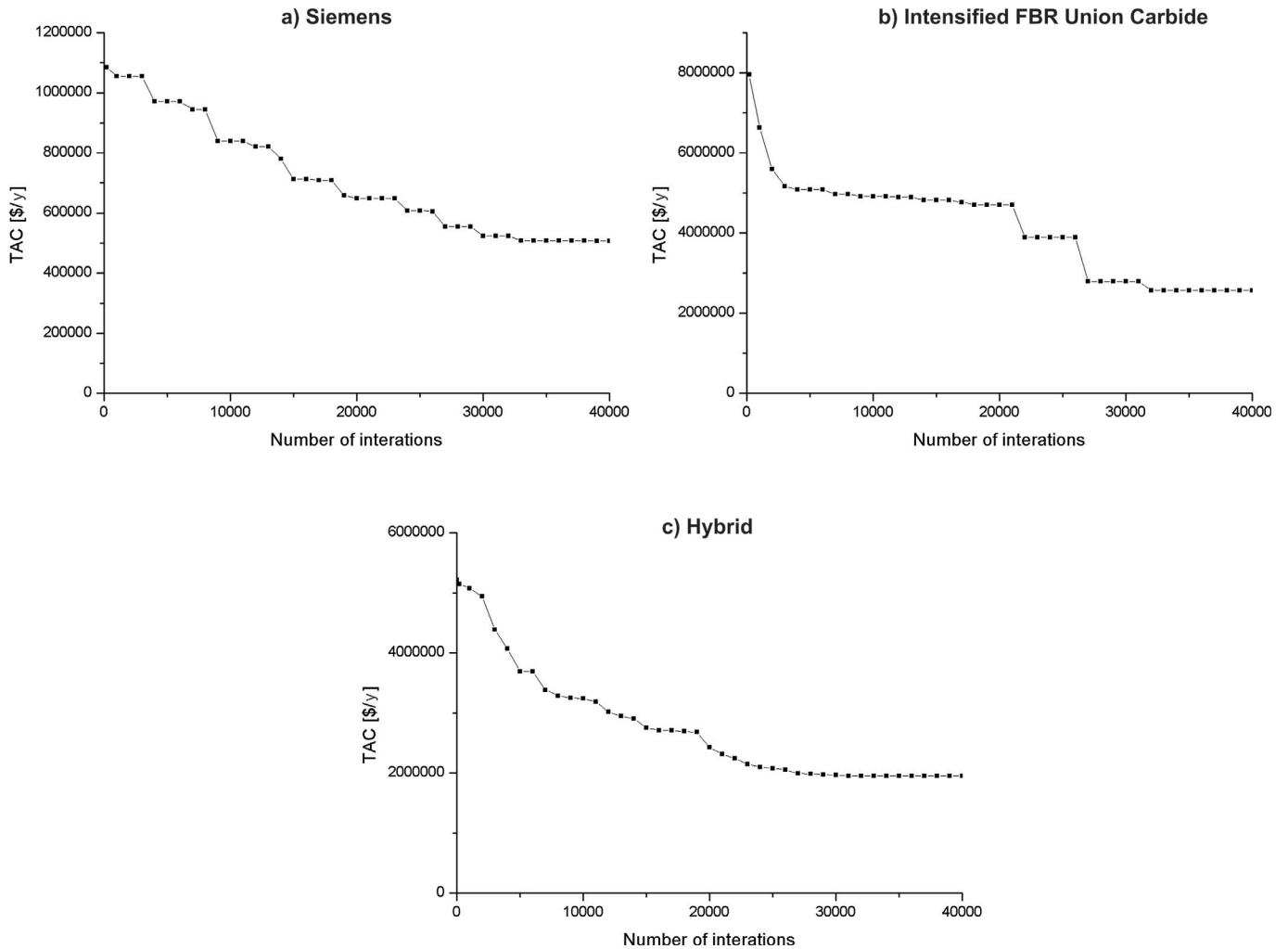


Fig. 8. Optimization results of process sequences a) Siemens, b) Intensified FBR Union Carbide and c) Hybrid process.

the set of equations “MESH”, which are described in [Appendix A](#). Furthermore, the objective function is potentially non-convex, with the possibility of finding local optimum and being subject to constraints.

In order to optimize the three processes, we used a stochastic hybrid optimization method, called differential evolution with tabu list (DETL) ([Srinivas and Rangaiah, 2007a](#)). This method is based on the theory of natural selection proposed by Darwin ([Srinivas and Rangaiah, 2007a](#)). It is very similar to the methods of genetic optimization, although with some differences in its coding. The description of the DETL algorithm can be reviewed in the work by [Srinivas and Rangaiah \(2007a\)](#). That work shows that using the tabu list helps improve the performance of the evolutionary differential algorithm. In general, the DETL hybrid method, which contains parts of the evolutionary differential method and parts of the tabu list. The tabu list is used to follow up the evaluated points, helping to not to be subjects of search in the optimization again.

[Srinivas and Rangaiah \(2007b\)](#) compared the performance of various algorithms using two types of problems, moderate and difficult ones and classifying the response into two categories: reliability and computational efficiency. The results of [Srinivas and Rangaiah \(2007b\)](#), showed that the number of function evaluations of DETL is fewer for both moderate and difficult functions compared to differential evolution algorithm, tabu search algorithm, and modified differential evolution algorithm. Furthermore

they also showed that on average, DETL took less CPU time compared to the others methods for the parameter estimation problems due to the computationally intensive objective function. With the significant reductions in the number of function evaluations, it was shown that DETL is attractive for engineering applications where the objective function evaluation requires considerable computational time, as is the case of this work.

The implementation of this optimization approach was made using a hybrid platform including Microsoft Excel, Aspen Plus and Matlab. The vector of decision variables (i.e., the design variables) are sent to Microsoft Excel to Aspen Plus using DDE (Dynamic Data Exchange) through COM technology. In Microsoft Excel, these values are attributed to the process variables that Aspen Plus needs. After the simulation, Aspen Plus returns to Microsoft Excel the resulting vector. Those values are sent from Microsoft Excel to Matlab where the objective functions are calculated. Finally Microsoft Excel suggests new values of decision variables according to the used stochastic optimization method. [Fig. 7](#) illustrates the optimization process involving the software aforementioned.

For this study, the following parameters have been used for DETL method: 200 generations, 200 individuals, a tabu list size of 100 individuals, a tabu radius of 2.5×10^{-6} , Crossover fractions (Cr): 0.8, Mutation fractions (F): 0.6, respectively. The parameters were obtained via preliminary calculations, as shown in the methodology of [Srinivas and Rangaiah \(2007a\)](#).

The objective function for this work is the total annual cost (TAC), based on Guthrie's, (1969) method modified by Ulrich (1984). The objective function estimates the lowest annual cost of the process, considering both the units and the plant's utilities. For the estimating the cost of the units, the correlations published by Turton et al., (2009) are used. The objective function used is shown in equation (14).

$$TAC = \frac{\text{Capital Cost}}{\text{Payback time}} + \text{Operating cost} \quad (14)$$

The payback time of the plant is considered to be five years, and 8400 h of yearly operation for each process are assumed. The design variables are presented in Table 3.

In each of the iterations we calculate the TAC of units such as the vessel of the reactor, furnaces, separators, mixers, heat exchangers, pumps and compressors. The units cost depend on their size and operating cost.

2.4.1. Optimization of the Siemens Process

The Siemens process is optimized using as objective function, the TAC which is directly proportional to the heat duty of the units (reactors, columns, and separators), services, and size of the units. The minimization of this objective is subject to the required recoveries and purities in each product stream, as shown in equation (15).

$$(\text{Min})TAC = f(N_{tn,i}, N_{fn,i}, R_{m,i}, F_{tn,i}, D_{tn,i}, P_{tn,i}) \text{ Subject to } \vec{y}_m \geq \vec{x}_m \quad (15)$$

where $N_{tn,i}$ are total stages of column i , $N_{fn,i}$ is the feed stages in column i , $R_{m,i}$ is the reflux ratio of column i , $F_{tn,i}$ is the distillate fluxes of each of the columns, $D_{cn,i}$ is the column diameter, $P_{tn,i}$ is the top pressure, y_m and x_m are vectors of obtained and required purities for the m components, respectively. The results must satisfy each restriction of purity, $\text{Si}_{(\text{SG})}$ 99.999% (wt %), SiCl_4 99.999%

(wt %), SiHCl_3 99.99% (wt %), HCl 99.99% (wt %), and H_2 99.9999% (wt %) for Siemens Process.

The minimization manipulates 7 decision variables among continuous and discrete variables for each route process, where 6 variables are used for the design of the column.

2.4.2. Optimization of the intensified FBR Union Carbide Process

The objective function for the intensified process is again the minimization of TAC. The minimization of this objective is shown in equation (16). The major difference is the inclusion of the reactive distillation column, which has an additional constraint, the reactive zone should not exceed 100 °C so that the catalyst does not deactivate, as described in section 2.2.

$$(\text{Min}) TAC = f(N_{tn}, N_{fn}, R_{m}, F_{tn}, D_{tn}, P_{tn}, R_{tn}, H_R) \text{ subject to } \vec{y}_m \geq \vec{x}_m \quad (16)$$

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, y_m and x_m are vectors of obtained and required purities for the m components, respectively. The results must satisfy each restriction of purity $\text{Si}_{(\text{SG})}$ 99.999% (wt %), SiH_2Cl_2 99.999% (wt %), SiH_2Cl_2 99.99% (wt %), SiHCl_3 99.99% (wt %), SiH_4 99.999% (wt %) and H_2 99.9999% (wt %) for Intensified FBR Union Carbide Process.

The minimization manipulates 29 variables among continuous and discrete variables for each route process, where 6 variables are used for the design of each conventional column and 8 variables are used for the design of each reactive distillation column. The design variables can be seen in Table 3.

2.4.3. Optimization of hybrid process

The hybrid process is a combination of the two processes described before. As in the Intensified FBR Union Carbide Process, it

Table 4
Results of the optimization of TAC for the siemens process.

	COLCONV1	REACTOR 1	REACTOR 2	REACTOR 3
Feed Stream flow (kg/h)	123.805 (SiCl ₄) 888.34 (SiHCl ₃) 0.0006 (SiH ₂ Cl ₂)	369.84 (C) 532.32 (SiO ₂)	204.66 (Si _(SG)) 887.92 (HCl)	888.24 (SiHCl ₃)
Feed Stream temperature (K)	323.15	298.15	491.79	350.44
Output stream (kg/h)	Top 8.60e-6 (SiCl ₄) 888.24 (SiHCl ₃) 0.0006 (SiH ₂ Cl ₂) Bottom 123.805 (SiCl ₄) 0.09 (SiHCl ₃) 4.32 e-11 (SiH ₂ Cl ₂)	204.66 (Si _(SG)) 76.23 (CO)	16.16 (H ₂) 123.81 (SiCl ₄) 888.34 (SiHCl ₃) 0.0006 (SiH ₂ Cl ₂) 64.28 (HCl)	55.25 (Si _(SG)) 5.29 (H ₂) 779.886 (SiCl ₄) 47.82(HCl)
Output Stream temperature (K)	N/A	2273	533	1373
Number of stages	43	N/A	N/A	N/A
Feed stage	33	N/A	N/A	N/A
Reflux ratio	39.69	N/A	N/A	N/A
Distillate rate (kmol/h)	6.55	N/A	N/A	N/A
Reboiler heat duty (kW)	1630.76	N/A	N/A	N/A
Condenser heat duty (kW)	-1709.59	N/A	N/A	N/A
Diameter (m)	1.00	N/A	N/A	N/A
Top pressure (atm)	3.88	N/A	N/A	N/A
Bottom pressure (atm)	4.58	N/A	N/A	N/A
Top temperature (K)	350.44	N/A	N/A	N/A
Bottom temperature (K)	386.62	N/A	N/A	N/A
Fresh feed				
HCl (kg/h)	840.103			

includes a reactive distillation column for the disproportion of trichlorosilane. Therefore, the equation that governs this optimization is (17).

$$\begin{aligned} (\text{Min})TAC &= f(N_{tn,i}, N_{fn,i}, R_{rn,i}, F_{tn,i}, D_{tn,i}, P_{tn,i}) \\ &\text{subject to } \vec{y}_m \geq \vec{x}_m \end{aligned} \quad (17)$$

The minimization manipulates 13 continuous and discrete variables for each route process, where 6 variables are used for the design of each column. All design variables for the cases of study are described in Table 3. The results must satisfy each restriction of purity Si_(SG) 99.999% (wt %), SiH₂Cl₂ 99.999% (wt %), SiHCl₃ 99.99% (wt %), SiCl₄ 99.999% (wt %), HCl 99.99% (wt %), and H₂ 99.9999% (wt %).

The sequences shown in Figs. 2, 4 and 6 are the initial designs, these comply with the above-mentioned purities and will be sought to reduce their TAC.

3. Results

In this section we present the results of the optimization of each of the processes including the iteration results to show that a plateau is reached and the operating and design variables.

In order to illustrate the progress of the optimization, the graphs of the iterations vs the TAC are presented (See Fig. 8). We can see

that the TAC decreases over the iterations and a good value is achieved for 40,000 iterations. This is taken to be a valid solution since there is not a significant decrease in the last evaluations. This demonstrates the robustness of DETL method, showing the convergence and results corresponding to good solutions.

All the runs to carry out the optimization were performed on an Intel (R) Core™ i7-4790 CPU @ 3.6 GHz, 16 GB computer, the computing time for obtaining the optimal solutions was different according to the complexity of each process: The Siemens process required 28.2 h, the FBR Union Carbide Process required 125.6 h, and the Hybrid process required 127.2 h. Tables 4–6 show the optimized variables for the units.

In the case of the Siemens configuration, it is possible to observe that only the optimization of a single conventional column and the fresh feed of HCl to initiate the reaction of the reactor producing the silanes are performed. These parameters represent substantial economic savings in the process, since the separation section always constitutes a high cost in any chemical process, and that the right amount of reactant represents large savings in the actual operation of the process. This can be seen in Fig. 8a, where the initial configuration has a TAC of \$1.08 M/y, ending with a TAC of \$0.50 \$/y, representing a saving of 53.28%.

The Intensified FBR Union Carbide Process has the highest number of decision variables to optimize. The optimization was carried out in two conventional columns, two reactive distillation

Table 5
Results of the optimization of TAC for the intensified FBR union carbide process.

	COLCONV1	COLCONV2	RDC1	RDC2	REACTOR 1	REACTOR 2	REACTOR 3	REACTOR 4
Feed Stream flow (kg/h)	12,672.1 (SiCl ₄) 3533.64 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂)	0.0054 (SiCl ₄) 3533.63 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂)	1766.75 (SiHCl ₃)	1766.75 (SiHCl ₃)	369.84 (C) 532.32 (SiO ₂)	204.66 (Si _{MC}) 16,126.3 (SiCl ₄)	151.27 (H ₂) 12,412.1 (SiCl ₄) 3948.2 (SiHCl ₃)	200.53 (SiH ₄)
Feed Stream temperature (K)	323.15	335.29	323.15	323.15	298.15	491.79	773	333
Output stream (kg/h)	Top 0.0054 (SiCl ₄) 3533.63 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂) Bottom 12,672 (SiCl ₄) 0.01 (SiHCl ₃) 7.99e-6 (SiH ₂ Cl ₂)	Top 1.14e-3 (SiHCl ₃) 154.56 (SiH ₂ Cl ₂) Bottom 0.0054 (SiCl ₄) 3533.49 (SiHCl ₃) 0.01 (SiH ₂ Cl ₂)	Top 100.26 (SiH ₄) Bottom 1674.45.1 (SiCl ₄)	Top 100.27 (SiH ₄) Bottom 1765.8.(SiCl ₄)	204.66 (Si _{MC}) 76.23 (CO)	151.27 (H ₂) 12,412.1 (SiCl ₄) 3948.2 (SiHCl ₃)	151.27 (H ₂) 12,672.1 (SiCl ₄) 3533.64 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂)	173.15 (Si _{SG}) 24.86 (H ₂) 49.50 (SiH ₄)
Output Stream temperature (K)	N/A	N/A	N/A	N/A	2273	773	773	1273
Number of stages	41	40	63	62	N/A	N/A	N/A	N/A
Feed stage	21	27	49	50	N/A	N/A	N/A	N/A
Reflux ratio	12.82	47.73	85.56	86.23	N/A	N/A	N/A	N/A
Distillate rate (kmol/h)	29.63	1.42	3.125	3.125	N/A	N/A	N/A	N/A
Reboiler heat duty (kW)	950.77	241.69	949.42	951.34	N/A	N/A	N/A	N/A
Condenser heat duty (kW)	-2751.04	-396.59	-928.23	-925.78	N/A	N/A	N/A	N/A
Diameter (m)	1.02	1.06	1.00	1.00	N/A	N/A	N/A	N/A
Top pressure (atm)	2.63	4.86	2.33	2.34	N/A	N/A	N/A	N/A
Bottom pressure (atm)	3.32	5.55	2.65	2.65	N/A	N/A	N/A	N/A
Top temperature (K)	335.29	332.22	177.84	177.65	N/A	N/A	N/A	N/A
Bottom temperature (K)	372.85	365.04	364.56	363.59	N/A	N/A	N/A	N/A
Reactive Stages	N/A	N/A	21–48	21–49	N/A	N/A	N/A	N/A
Holdup (cum)	N/A	N/A	0.13	0.14	N/A	N/A	N/A	N/A
Fresh feed								
SiCl ₄ (kg/h)	1123							

Table 6
Results of the optimization of TAC for the hybrid process.

	COLCONV1	COLCONV2	REACTOR 1	REACTOR 2	REACTOR 3	REACTOR 4
Feed Stream flow (kg/h)	31,549.2 (SiCl ₄) 3533.64 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂)	3.53 e−3 (SiCl ₄) 3532.65 (SiHCl ₃) 154.57 (SiH ₂ Cl ₂)	369.84 (C) 532.32 (SiO ₂)	204.66 (Si _{MC}) 35,004.3(SiCl ₄)	151.27 (H ₂) 31,289.3 (SiCl ₄) 3948.2 (SiHCl ₃)	3533.43 (SiHCl ₃)
Feed Stream temperature (K)	323.15	357.23	298.15	491.79	773	359.93
Output stream (kg/h)	Top 3.53 e−3(SiCl ₄) 3532.65(SiHCl ₃) 154.57 (SiH ₂ Cl ₂) Bottom 31,289 (SiCl ₄) 0.95 (SiHCl ₃) 4.79 e−6 (SiH ₂ Cl ₂)	Top 0.2 (SiHCl ₃) 154.52 (SiH ₂ Cl ₂) Bottom 3533.43 (SiHCl ₃) 0.5 (SiH ₂ Cl ₂)	204.66 (Si _{MC}) 76.23 (CO)	151.27 (H ₂) 31,289.3 (SiCl ₄) 3948.2 (SiHCl ₃)	151.27 (H ₂) 31,549.2 (SiCl ₄) 154.57 (SiH ₂ Cl ₂) 3533.64 (SiHCl ₃)	219.79 (Si _{SC}) 21.03 (H ₂) 3102.38 (SiCl ₄) 190.23 (HCl)
Output Stream temperature (K)	N/A	N/A	2273	773	773	1373
Number of stages	42	81	N/A	N/A	N/A	N/A
Feed stage	16	41	N/A	N/A	N/A	N/A
Reflux ratio	27.69	55.70	N/A	N/A	N/A	N/A
Reboiler heat duty (kW)	2141.79	335.21	N/A	N/A	N/A	N/A
Distillate rate (kmol/h)	31.24	1.53	N/A	N/A	N/A	N/A
Condenser heat duty (kW)	−5750.24	−505.63	N/A	N/A	N/A	N/A
Diameter (m)	1.02	1.00	N/A	N/A	N/A	N/A
Top pressure (atm)	4.49	4.21	N/A	N/A	N/A	N/A
Bottom pressure (atm)	5.18	4.90	N/A	N/A	N/A	N/A
Top temperature (K)	357.23	326.72	N/A	N/A	N/A	N/A
Bottom temperature (K)	392.25	359.93	N/A	N/A	N/A	N/A
Fresh feed						
SiCl ₄ (kg/h)	994.445					

columns, and the fresh feed stream of SiCl₄. In Fig. 8b it can be seen that the TAC of the initial configuration is \$7.95 M/y and ending with \$2.57 M/y, saving 67.65%. The Hybrid Process shows the optimization of two conventional columns, and the fresh SiCl₄ feed. The initial configuration has a TAC of \$5.21 M/y, ending with \$1.95 M/y, saving 62.58% (see Fig. 8c).

Since all three sequences are optimized, and with the same feed as mentioned in Table 1, a comparison can be made to find the best sequence for the production of Si_(SG). Table 7 shows, for all sequences, the capital cost, the TAC, the energy required and the products. Note the comparison between the TAC and the amount of products, mainly with the produced Si_(SG).

It can be observed that the optimized designs for the distillation columns and the reactive distillation columns, the number of stages and their heights are in concordance with the mechanical considerations in the design of distillation columns built so far (Górák and

Olujic, 2014).

The least expensive process is the Siemens process. However, it also shows the minimum annual production of Si_(SG) of 0.47 kt/y. The Intensified FBR Union Carbide process turns out to be the most expensive of the three proposed, with a large production of Si_(SG) of 1.49 kt/y, but it is not the best in this way. The Hybrid Process shows the highest production of Si_(SG) of 1.89 kt/y, at a higher cost compared to the Siemens process, but lower than the Intensified FBR Union Carbide process. The final column of Table 8 shows the annual profits that are obtained by selling all products from each process, these benefits were considered before taxes. In this table we can see the profitability of the Hybrid Process, providing the largest benefits of all three processes. It is necessary to take into account that the Hybrid Process is the one that obtains larger amount of byproducts, which makes it to have larger profits. Fig. 9 is very illustrative, it shows the potential of the hybrid process with

Table 7
Comparative results for all process.

	Capital Cost [\$]	TAC [\$y]	Q [kW]	Products				
				SiS-G [ton/y]	H ₂ [ton/y]	SiH ₂ Cl ₂ [ton/y]	SiCl ₄ [ton/y]	HCl [ton/y]
Siemens	2,025,253.25	506,790.12	58,963.48	477.36	185.24	N/A	7807.88	N/A
FBR Union Carbide	11,992,503.8	2,573,400.30	63,042.65	1495.93	221.01	1237.16	N/A	N/A
Hybrid	9,741,229.2	1,951,075.43	64,344.18	1899.02	260.15	1335.13	5762.88	1643.50

Table 8
Prices of annualized products ^(a)Sun&Wind Energy, 2017; ^(b)Product Listing Policy a, 2017; ^(c)Yaws et al., 1979; ^(d)Product Listing Policy b, 2017; ^(e)Product Listing Policy c, 2017).

	(a) Si(SG) [\$y]	(b) H ₂ [\$y]	(c) SiH ₂ Cl ₂ [\$y]	(d) SiCl ₄ [\$y]	(e) HCl [\$y]	Profit per sale [\$y]
Siemens	6,172,264.80	2,060,511.68	N/A	19,519,704.00	N/A	27,245,690.36
FBR Union Carbide	19,342,369.73	2,458,398.22	184.71	N/A	N/A	19,227,552.36
Hybrid	24,554,330.67	2,893,770.85	199.342	14,407,200.00	575,225.00	40,479,650.43

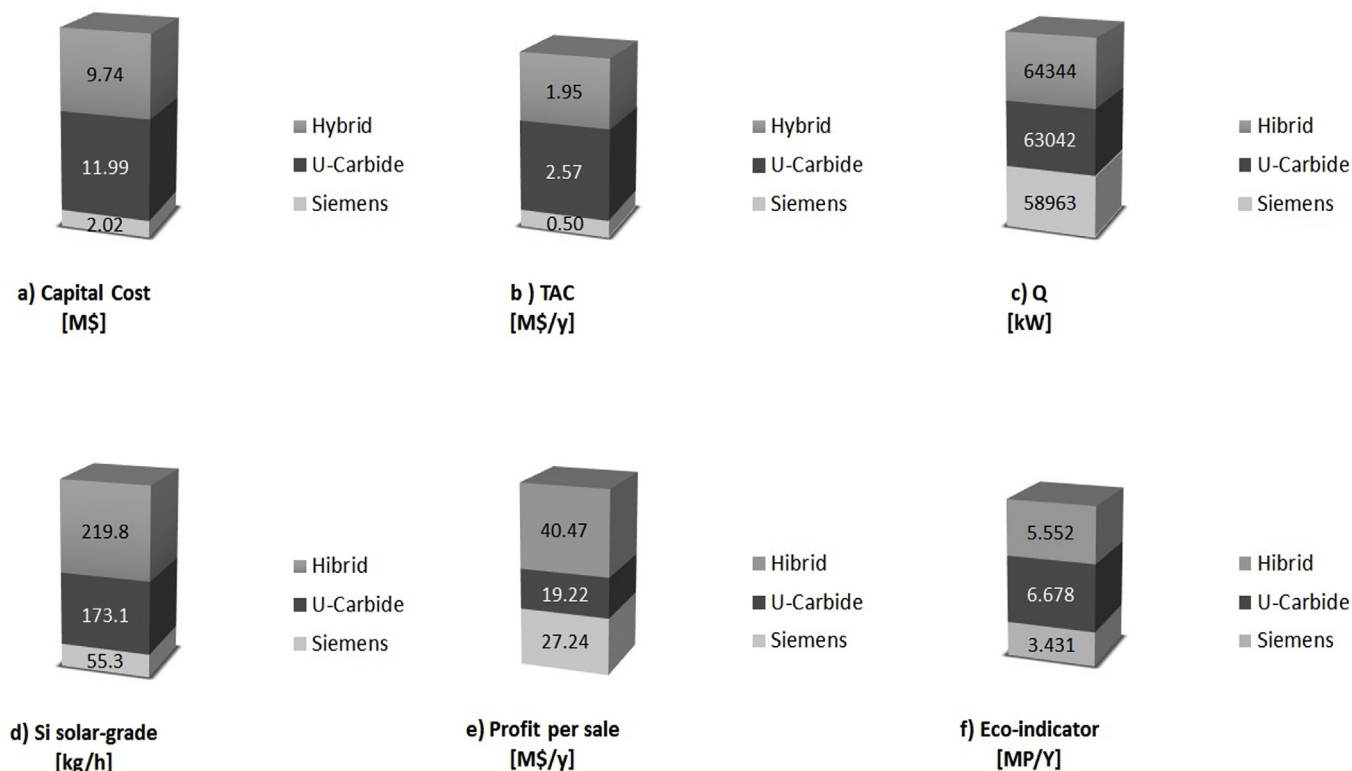


Fig. 9. Results of capital cost, TAC, energy required, solar grade silicon, profit per sale, and Eco-Indicator of all configurations.

the most important items.

Performing the analysis of the results the potential of the Hybrid Process could be observed, which could represent an incentive for the silicon industry. It is known that the processes Siemens and FBR Union Carbide, are technologies that have matured over time and are the ones usually used in the production of $\text{Si}_{(\text{SG})}$, but the $\text{Si}_{(\text{SG})}$ industry could benefit from novel alternatives such as the Hybrid Process.

Considering the environmental impact measured by the Eco-Indicator 99, Siemens process showed the lowest impact, 3.43 [MP/y], followed by the Hybrid process, 5.55 [MP/y]. Finally the intensified process shows an impact almost twice that of the Siemens process, see Fig. 9. The reason for the difference in the environmental impact among the processes is due to the number of units, in particular, the difference in the number of distillation columns. The index is directly related to the amount of steel required in construction. Thus, the smaller the number of units the less the steel used. Furthermore, distillation also involves large cooling and energy needs. Therefore, reducing the distillation columns, we reduce utilities consumption too.

4. Conclusions

In this work, we used a stochastic global optimization for the design of processes for $\text{Si}_{(\text{SG})}$ production to improve and compare their cost. The Siemens process is the base case, but it has been optimized, and two novel processes have been developed and optimized, an intensified process based on the one Union Carbide is using, where we substitute the distillation columns by a reaction distillation column and a Hybrid one combining Siemens and Union Carbide processes.

The results showed that the Siemens process presented the smallest TAC, but with the lowest production of $\text{Si}_{(\text{SG})}$. The

Intensified FBR Union Carbide Process, showed the largest TAC due to the capital cost of the equipment and the heat duty for $\text{Si}_{(\text{SG})}$ purification. Finally the Hybrid Process exhibited a large production of $\text{Si}_{(\text{SG})}$, with a TAC between the one of the Siemens process and that of the Intensified FBR Union Carbide. Evaluating the TAC vs production of $\text{Si}_{(\text{SG})}$, it turned out that the Hybrid Process was the best of the three from the economic point of view. The Hybrid Process shows the largest profit from the sale of the multiple products resulting, with earnings of \$40.47 M/y. However, the environmental impact measured by the Eco-Indicator 99 showed that the Siemens process is the one with the lowest impact. The Hybrid process is the second best. It is expected that with this type of research can be made more competitive the technology based on $\text{Si}_{(\text{SG})}$, lowering the costs of the process and generating new research routes to be carried out for the industry of solar panels.

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Appendix A

The reactive distillation MESH equations are very similar to conventional distillation MESH equations. The main difference is the addition of the reaction rate term in the total material balance and component material balance as well as the addition of the heat of reaction to total heat balance (Al-Arfaj, 1999). The reactive MESH equation are:

Total material balance

Total condenser

$$V_{NT} = D(1 + RR) \quad (18)$$

Tray j

$$V_{j-1} + L_{j+1} + F_j + \sum_i r_{i,j} = (L_j + U_j) + (V_j + W_j) \quad (19)$$

Reboiler

$$L_1 = B + V_B \quad (20)$$

Component material balance (Component i)

Total condenser

$$V_{NT}y_{i,NT} = D(1 + RR)x_{i,D} \quad (21)$$

Tray j

$$V_{j-1}y_{i,j-1} + L_{j+1}x_{i,j+1} + F_{i,j} + r_{i,j} = (L_j + U_j)x_{i,j} + (V_j + W_j)y_{i,j} \quad (22)$$

Reboiler

$$L_1x_{i,1} = Bx_{i,B} + V_By_{i,B} \quad (23)$$

Total energy balance

Total condenser

$$V_{NT}H_{NT} = D(1 + RR)h_D + Q_D \quad (24)$$

Tray j

$$V_{j-1}H_{j-1} + L_{j+1}h_{j+1} + F_{i,j}H_j^F + Q_j + \sum_i r_{i,j}H_j^R = (L_j + U_j)h_j + (V_j + W_j)H \quad (25)$$

Reboiler

$$L_1h_1 + Q_B = Bh_B + V_BH_B \quad (26)$$

Vapor Liquid Equilibrium equation

$$y_{i,j} = K_{i,j}x_{i,j} = \frac{\gamma_{i,j}P_{i,j}^{vap}}{P}x_{i,j} \quad (27)$$

Summation equation

$$\sum_i y_{i,j} = 1 \quad (28)$$

$$\sum_i x_{i,j} = 1 \quad (29)$$

where.

 L_j = liquid flowrate of tray j V_j = vapor flowrate of tray j F_j = feed flowrate to tray j U_j = liquid side stream flowrate of tray j W_j = vapor side stream flow rate of tray j $x_{i,j}$ = liquid mole fraction of component i in tray j $y_{i,j}$ = vapor mole fraction of component i in tray j $x_{F,i}$ = feed mole fraction of component i in tray j h_j = liquid enthalpy of tray j H_j = vapor enthalpy of tray j H^F = feed enthalpy Q_j = side heating or cooling rate of tray j $\gamma_{i,j}$ = activity coefficient of component i in tray j $P_{i,j}^{vap}$ = vapor pressure of component, i in tray j P = total pressure $r_{i,j}$ = reaction rate of component i in tray j H_j^R = heat of reaction in tray j.

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