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Alternative processes for obtaining solar grade silicon

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Abstract

In this work we have developed and analyzed two alternative $Si_{(SG)}$ production processes 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 process is a hybrid process combining both the Siemens and the conventional FBR processes. The base case is the optimized Siemens process. The optimized processes show savings in the TAC of 53.28%, 67.65% and 62.58% for Siemens, Intensified FBR and Hybrid process, respectively. Siemens process is the one with the lowest TAC. However, 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, but 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$/y, showing the highest profit from sales of the three, 40.47 M$/y. 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.

Keywords: Silicon, Alternative processes, Optimization, TAC

1. Introduction

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 of PV industry. Therefore, there is a 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 ($Si_{(SG)}$): 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 opportunities to reduce the panels cost since approximately half ot it is due to the materials, bulk silicon production and wafer manufacturing (Müller et al., 2006). Thus, the development of optimized processes for production of cheap $Si_{(SG)}$ feedstock material can help reduce PV power production costs

Solar grade silicon can be produced from quartz following a two-stage process consisting of the production of metallurgic 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 1970s (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 $Si_{(SG)}$ by developing more efficient processes. In particular two novel processes have been developed in this paper. The first one corresponds with an intensified FBR's process by substituting the conventional reactors and separation stage with a reactive distillation column (RD) intensifying the process.. Furthermore, this configuration improves the yield, because products alone are withdrawn from the reactive zone while reactants remain inside the reactive zone for further reaction. This reactive distillation section has been 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). The three simulated processes were optimized for a consistent comparison of their in their Total Annual Cost (TAC) and in their production capacity of solar grade silicon.

2. Methodology

We first simulate the all three processes rigorously in Aspen Plus V8.4. To predict the thermodynamic of the system, we used the thermodynamic package Peng-Robinson, and 'Solids' property method for solids components. To meet the typical production capacity of around 2000 t/y, the processes are fed with the components and quantities with 532.32 kg/h of SiO_2 and 369.84 kg/h of Carbon. The simulation was carried out through the use of various Aspen modules. In the case of reactors, the stoichiometric module was mainly used, in the chlorosilanes synthesis reactors, the combination of two reactors had to be considered, because the software did not allow the sequential reaction of the components in a single reactor. Something similar happened with the carboreduction and deposition of silicon, where the reactor is essentially an oven, where the reactor was used with an oven to achieve the simulation The 'RadFac' module was used for rigorous conventional distillation columns and for reactive distillation. A conventional set of modules was also used to implement the separators, pumps, compressors and exchangers, always trying to take care of each of the processes. Note that implementing solid compounds in Aspen is an arduous task. 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 (LCA), as show Guillén-Gosálbez et al., (2008). The Eco-indicator 99 was chosen, since it is one of the most widely used impact assessment methods in LCA, and for the purposes of this work it is indicated, because allows the environmental load of a product to be expressed in a single score. Three different processes are proposed for obtaining the $Si_{(SG)}$, such is the case of the a) Siemens Process, b) the Enhanced FRB Process and c) the Hybrid Process (See Figure 1).

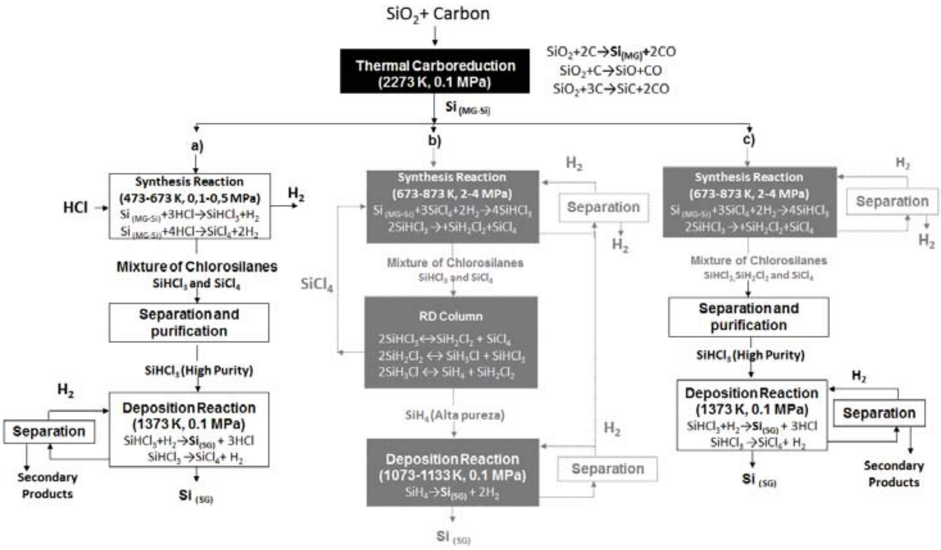

Figure 1. Scheme of the Si(SG) production processes. a) Siemens process, b) FBR Union Carbide with RD column process, c) Hybrid process.

The first case is the Siemens Process, which consists of a carboreduction section, followed by a chlorosilanes synthesis reactor using HCl as a precursor. Next, the mixture is separated in a conventional distillation column, to finish with the Siemens deposition reaction to produce solar grade silicon. The second process called intensified FRB, begins also with quartz carboreduction. Next, chlorosilanes are produced using $SiCl_4$ as a precursor. Subsequently, the separation process consists of two conventional separation columns, and two reactive distillation columns to obtain silane before moving on to the silicon deposition reaction. The last process is the one named as the Hybrid Process. It consists basically of the combination of the two previous ones. The first part of the process, until the separation, corresponds to the FRB Process. Then in the separation, two conventional columns are used, and the part of the deposition reaction, similar to the Siemens Process. 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. 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 due to the model is highly non-linear, potentially non-convex and with a large amount of local minimums, also the model is not explicitly stated. The use of stochastic optimization methods is a good alternative; several reports have proved the successful application in cases of study with those already mentioned characteristics. The stochastic hybrid optimization is called differential evolution with tabu list (DETL) (Srinivas and Rangaiah, 2007). 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 a 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.

For this study, the following parameters have been used for the DETL method: 200 generations, 200 individuals, a tabu list size of 100 individuals, a tabu radius of $2.5 \cdot 10^{-6}$, 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 used is shown in equation (1).

$$TAC = \frac{Capital\ Cost}{Payback\ time} + Operating\ cost \tag{1}$$

The payback time of the plant is considered to be five years, and 8400 hours of annual operation for each process are assumed. 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.

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. Thus, we first show a Figure of the iterations vs TAC obtained for each case will be shown. 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 the 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 TM 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 hours, the FBR Union Carbide Process required 125.6 hours, and the Hybrid process required 127.2 hours. 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 represents a high cost in any chemical process, and that the right amount of reactant represent large savings in the actual operation of the process. In the optimization of the Siemens Process, the initial configuration has a TAC of 1.08 M$/y, ending with a TAC of 0.50 M$/y, representing savings of 53.28%.

The Intensified FBR Union Carbide Process has the highest number of decision variables to optimize. For the Siemens Process infers the manipulation of 7 decision variables among continuous and discrete variables for each route process. The Intensified FBR Union Carbide Process implies the manipulation of 29 variables among continuous and discrete variables for each route process. And for the Hybrid Process infers the manipulation of 13 continuous and discrete variables for each route process. The optimization was carried out in two conventional columns, two reactive distillation columns, and the fresh feed stream of $SiCl_4$. The TAC of the initial configuration of the Intensified FBR Union Carbide 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 $SiCl_4$ feed. The initial configuration has a TAC of 5.21 M$/y, ending with 1.95 M$/y, saving 62.58%. Table 1 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 $Si_{(SG)}$.

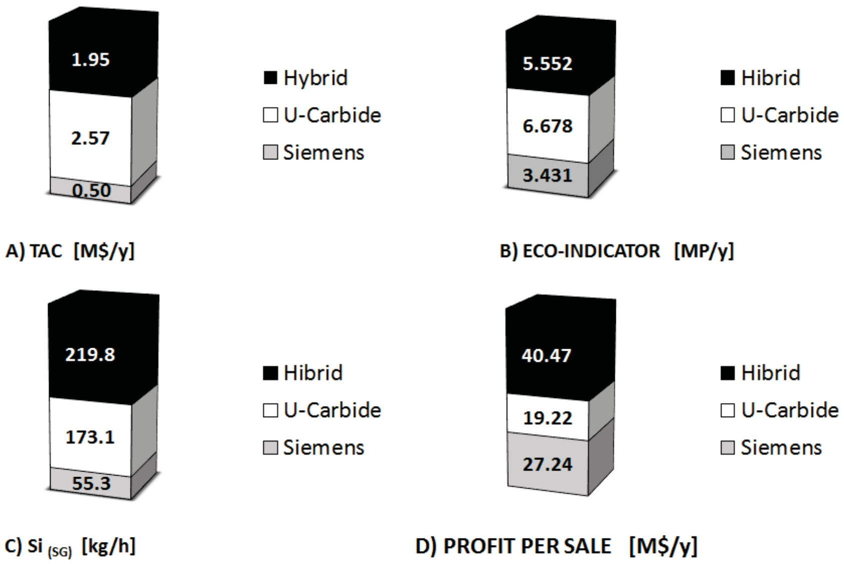

Figure 2. Results of TAC, ECO-99, amount of solar grade silicon, and profit per sale of all configurations.

Table 1. Comparative results for all process.

	Q [kW]	TAC [$/y]	Si_{S-G} [ton/y]	H_2 [ton/y]	SiH_2Cl_2 [ton/y]	$SiCl_4$ [ton/y]	HCl [ton/y]
Siemens	58,963	506,790	477.4	185.2	N/A	7807.9	N/A
FBR	63,042	2,573,400	1,495.9	221.0	1,237.2	N/A	N/A
Hybrid	64,344	1,951,075	1,899.0	260.1	1,335.1	5762.9	1643.5

The least expensive process is the Siemens one. However, it also shows the minimum annual production of $Si_{(SG)}$. The Intensified FBR Union Carbide Process turns out to be the most expensive of the three proposed, with a large production of $Si_{(SG)}$, but it is not the best in this way. The Hybrid Process shows the highest production of $Si_{(SG)}$, at a higher cost compared to the Siemens process, but lower than the Intensified FBR Union Carbide process. Figure 2 shows the potential of the hybrid process with 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 $Si_{(SG)}$, but the $Si_{(SG)}$ industry could benefit from novel alternatives such as the Hybrid Process.

4. Conclusions

In this work, we have developed intensified and optimized processes for the production of $Si_{(SG)}$. The results show than the Siemens process presented the smallest TAC, but with the lowest production of $Si_{(SG)}$. The Intensified FBR Union Carbide Process, showed the largest TAC due to the capital cost of the equipment and the heat duty for $Si_{(SG)}$ purification. Finally, the Hybrid Process exhibited a large production of $Si_{(SG)}$, with a TAC between the one of the Siemens process and that of the Intensified FBR Union Carbide. However, evaluating the TAC vs production of $Si_{(SG)}$, it turned out that the Hybrid Process was the best of the three. In addition to the above, the Hybrid Process shows the largest gains from the sale of the multiple products resulting, with earnings of 40.47 M$/y. It is expected that with this type of research can be made more competitive the technology based on $Si_{(SG)}$, lowering the costs for the industry of solar panels.

5. References

M. Bououdina, 2014. Handbook of research on nanoscience, nanotechnology, and advanced materials. IGI Global, 119-126.

A. F. B. Braga, S. P. Moreira, P. R. Zampieri, J. M. G. Bacchin, P. R. Mei, 2008. New processes for the production of solar-grade polycrystalline silicon: A review. Sol. Energ. Mat. Sol. C, 92(4), 418-424.

C. E. Erickson, and G. H. Wagner, 1952. U.S. Patent No. 2,595,620. Washington, DC: U.S. Patent and Trademark Office.

G. Guillen-Gosalbez, J. A. Caballero, L. Jimenez, 2008. Application of life cycle assessment to the structural optimization of process flowsheets. Industrial & Engineering Chemistry Research, 47(3), 777-789.

A. Müller, M. Ghosh, R. Sonnenschein, P. Woditsch, 2006. Silicon for photovoltaic applications. Mat. Sci. Eng. B, 134(2), 257-262.

M. J. R. Payo, 2009. Purificación de triclorosilano por destilación en el proceso de obtención de silicio de grado solar. PhD Thesis. Universidad Complutense de Madrid.

C. Ramírez-Márquez, E. Sánchez-Ramírez, J.J. Quiroz-Ramírez, F.I. Gómez-Castro, N. Ramírez-Corona, J.A. Cervantes-Jauregui, J.G. Segovia-Hernández, 2016. Dynamic behavior of a multi-tasking reactive distillation column for production of silane, dichlorosilane and monochlorosilane. Chem. Eng. Process., 108, 125-138.

S. E. Sadique, 2010. Production and Purification of Silicon by Magnesiothermic Reduction of Silica Fume. MSc Thesis. University of Toronto.

Solar Market Insight Report, 2016. http://www.seia.org/research-resources/solar-market-insight-report-2016-q2.

M. Srinivas, G.P. Rangaiah, 2007. Differential Evolution with Tabu List for Solving Nonlinear and Mixed-Integer Nonlinear Programming Problems. Ind. Eng. Chem. Res., 46, 7126−7135.

M. Vidal, M. Martín, 2014. Planta de producción de silicio para módulos fotovoltaicos. Era Solar. Fototérmica y Fotovoltaica. 180, Año XXXII. 24-35.