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Optimal Design of a Multi-Product Polycrystalline Silicon Facility

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Abstract

The silicon industry is a source of different types of products, including materials for the implementation of renewable energy systems, with a comparatively lower environmental impact than conventional fossil energy sources, and high added value by-products. In this context, the exploitation of the different by-products generated in the production of polycrystalline silicon (polysilicon) offers opportunities to increase the economic efficiency of the polycrystalline silicon production processes. In this work, a silicon based refinery is conceptually designed, estimating the optimal operating conditions by using surrogate models for the major units involved. Although the main product is polysilicon, there are different products that could be generated in the process increasing its profitability, such as tetraethoxysilane (at different purities). Likewise, series of chlorosilanes with high added value, including SiH_4, SiH_2Cl_2, and SiH_3Cl, can also be produced. Additionally, an economic evaluation of the facility is carried out to determine its economic feasibility. The results show that the refinery produces tetraethoxysilane and chlorosilanes in addition to the production of polysilicon. The proposed design reduces the cost for polycrystalline silicon to 6.86 $/kg, below the commercial price estimated at 10 $/kg. Therefore, the refinery is not only capable to meet the market share requirements but that the generation of different high added value by-products increases the plant profit compared with the net income earned by a traditional polysilicon mono-product plants.

Keywords: Multi-Product, Polycrystalline Silicon, Economic Evaluation.

1. Introduction

In recent years, the polycrystalline silicon photovoltaic (PV) industry has grown vividly, developing a truly global supply chain. In the past 10 years, polycrystalline silicon based solar panels represent more than 90% of photovoltaic production, accounting more than 95% of production in 2018 (Mints, 2018). This development has been induced by the increase in the demand of photovoltaic (PV) energy, as well as by the technical progress in the performance of PV cells, and the improvement in the manufacturing processes of polycrystalline silicon, allowing drastic cost reductions in PV modules cost. However, the polysilicon production costs can be further improved valorizing the by-products generated in the process, which otherwise would be considered as waste.

In the case of the polycrystalline silicon industry, the main by-product of polycrystalline silicon manufacturing is tetrachlorosilane, which currently is fed back into the production cycle. Tetrachlorosilane can also be extracted and post-processed to obtain added value products. However, the processing tetrachlorosilane to obtain high added value by-products can be integrated with the main polycrystalline silicon production process, avoiding the need to dispose of waste streams and increasing the economic and environmental efficiencies of the process.

The statement above has been demonstrated by the polycrystalline silicon company Wacker™, who integrated the production of pyrogenic silica from tetrachlorosilane to the polycrystalline silicon process in different facilities, such as Charleston in the USA, and Burghausen and Nuenchritz in Germany (Rubber & Plastics News Report, 2016). Pyrogenic silica is a valuable product used as a filler in silicone elastomers and as an archeology control additive in paints, adhesives, and unsaturated polyester resins (Rubber & Plastics News Report, 2016). However, pyrogenic silica is not the only product that can be generated from tetrachlorosilane.

In the present work develops a superstructure for the selection of the portfolio of products from quartz including the production tetraethoxysilane (TEOS), which is the most prominent derivative of the family of silicon compounds. Tetraethoxysilane is mainly used in the manufacture of chemical and heat resistant coatings, organic silicon solvents, and precision casting adhesives. Additionally, the production of a series of chlorosilanes with high added value (silane, dichlorosilane and monochlorosilane) is also considered from trichlorosilane.

2. Methodology

To design a polycrystalline silicon process with an analogous production capacity to current polycrystalline silicon production companies as Wacker Co., an average production capacity of the plant of 15,000 annual metric tons of polycrystalline silicon is considered (Rubber & Plastics News Report, 2016). The polycrystalline silicon production process expand the one proposed by Ramírez-Márquez et al., (2019). In this work, the conceptual design of the process, named as Hybrid Process, is presented. The Hybrid Process is the result of a strategic combination of the stages of the Siemens and the Union Carbide process. The Hybrid Process is extended using a couple of reactive distillation columns for the production of high added value products such as: TEOS 98.5, TEOS 99.0, TEOS 99.5, silane, dichlorosilane and monochlorosilane. The process diagram for Multi-Product Polycrystalline Silicon Facility that was used in the present work is showed in Figure 1.

2.1 Modelling approach

The model for the superstructure is developed based on mass and energy balances, thermodynamics, experimental data and rules of thumb for basic units and surrogate models for major ones such as reactors and distillation columns. The process starts with the carboreduction process of quartz. The raw materials used are silica in form of quartz (SiO_2) and carbon (C). These raw materials are stored in storage tanks, to be further blended in a mixer, and fed into the carboreduction reactor. The storage tanks and mixers have been modeled through material balances. The model for the carboreduction reactor is based on the work reported by Wai and Hutchison (1989), computing the products distribution for a C/SiO_2 feeding molar ratio of 2:1, a total pressure of 1 atm, and a temperature range of 2500-3500 K. To achieve the production capacity of typical industrial plants, in the present work a feed of 150 kmol/h of SiO_2 and 300 kmol/h of C is considered. Based on that work, correlations are developed to estimate the distribution of the products obtained at the reactor (mol fraction) as a function of the reaction temperature (K).

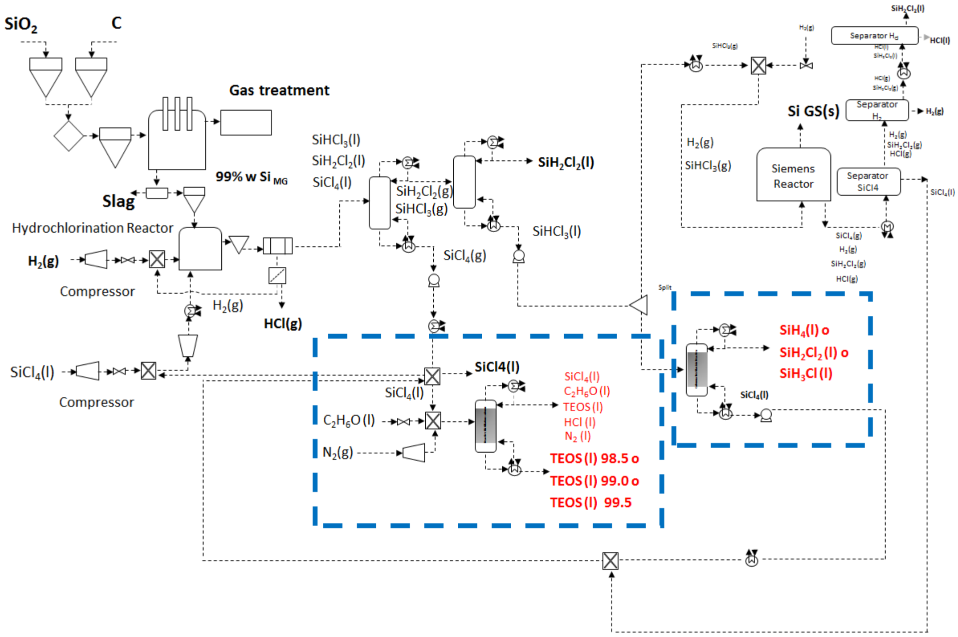

Figure 1. Flowsheet of the Multi-Product Polycrystalline Silicon Facility.

In the hydrochlorination reactor, $SiCl_4$ is hydrogenated in the presence of Si_{MG}. To model this equipment, the minimization for the Gibbs free energy for the system $SiCl_4-H_2-Si_{MG}$ is used, based on the work by Ding, et al., (2014). For convenience, the reaction system $SiCl_4-H_2-Si_{MG}$ was treated as ideal, and the following variables ranges were studied: temperature (T), 573−873 K; pressure (P), 1−20 atm; y molar feeding ratio (Rel) $H_2/SiCl_4$, 1-5 evaluating the yield to each product as a function of them. Then the surrogate models are developed to estimate the composition as a function of the operating conditions.

The condensation step was modelled based on material and energy balances considering complete separation of the effluent in a gas phase stream and the liquid phase stream. For the separation of the chlorosilanes two convectional distillation columns are used. The rigorous modeling and sizing of the columns was performed using the Aspen Plus software, based on a previous work (Ramírez-Márquez et al., 2019). By varying the feeding and the degrees of freedom as the reflux ratio, surfaces of response are obtained to estimate the energy involved in the reboiler, at the condense and their operating temperatures. The variables evaluated were the feeding molar ratio $SiCl_4$-(SiH_2Cl_2-$SiHCl_3$), within the range from 1 to 2.1698 for the first column; the SiH_2Cl_2-$SiHCl_3$ molar ratio, for a range from 2.99 to 7.5678 for the second column; and reflux ratio from 10 to 80 for the first column and from 60 to 90 for the second column.

For waste streams of $SiCl_4$, remnants of the first column at the bottom, process intensification adding a reactive distillation (RD) column is suggested to produce TEOS (at different purities 98.5-99.0 or 99.5). Sánchez-Ramírez et al. (2018) showed that the reactive distillation has a better performance than the conventional system regarding TAC values. The variables were evaluated in the following ranges: feeding molar ratio $SiCl_4$- C_2H_5OH values from 1 to 100 for the TEOS reactive column. Also, in the second distillation column at the bottom, a stream of pure trichlorosilane is obtained. That stream is divided into a splitter to feed the Siemens reactors or the reactive distillation columns for the disproportion of trichlorosilane to obtain silane, dichlorosilane or monochlorosilane (each one at 99.0 purity), as proposed by Ramírez Márquez et al. (2016). The trichlorosilane feed was varied in a range of 1 to 10 kmol/h.

The deposition of polycrystalline silicon was modeled according to the work presented by Del Coso and Luque, (2008). In this work, the kinetics of the deposition for polycrystalline silicon in the traditional Siemens reactor are provided. They present analytic solutions for the deposition process, based on the approach of splitting the second-order reaction rate into two systems of first-order reaction rate. The growth rate, deposition efficiency, and power-loss dependence on the gas velocity, the mixture of gas composition, the reactor pressure, and the surface temperature have been analyzed, providing information regarding the deposition velocity and the polycrystalline silicon production rate. The variables analyzed were the polysilicon growth rate, the deposition efficiency and the system temperature. The model defined was solved with the data reported by Del Coso and Luque, (2008) for a temperature range from 1372 to 1500 K.

2.2 Solution procedure

The process was formulated as a nonlinear programming (NLP) problem. The model consists of 3,014 equations and 3,716 variables, which are solved to optimize the operating conditions of the Multi-Product Polycrystalline Silicon facility, using a profit objective function, Eq. 1. Hence, the main variables of decision are: the temperature of the thermal carboreduction reactor; the temperature, pressure, and $H_2/SiCl_4$ feeding molar ratio of the hydrochlorination reactor, the feeding ratio and the reflux ratio of each distillation column, for the reactive columns the feeding ratio, and the operating temperature of the Siemens Reactor.

The objective function, Eq. 1, aims to maximize the process total profit, considering not only the production of the main product (polysilicon), but also the income from by-products (chlorosilanes), deducting the manufacturing cost.

$$\text{OF)}\ \max z = S_{polycrystalline\ silico} + p\,SP - b\,RM - c\,E \tag{1}$$

where, *b* is the unit cost of each raw material *RM*; c is the cost of each utility *E*; *d MO* is the labour cost; *p* is the price of each by-product *SP*, and $S_{polycrystalline\ silicon}$ is profit from the sale of the polycrystalline silicon.

Also, a detailed economic evaluation based on the procedure proposed by Turton et al. (2012) has been carried out, estimating the equipment cost, production cost, maintenance, administration and manpower. The NLP problem was solved using a multistart initialization approach with CONOPT as the preferred solver.

3. Results

The results shown in Table 1 summarize the economic parameters of the process. It can be seen how with an adequate arrangement of the operation conditions of each unit, the production of tetraethoxysilane and chlorosilanes, the raw material consumption, and the services consumption, it is possible to reduce the cost for polycrystalline silicon to 6.86 $/kg, below the commercial price estimated at 10 $/kg. Besides, the comparison was made with the model without the addition of high value-added products, and the price of polycrystalline silicon in this context is 8.93 \$/kg (higher than the price by adding high value-added products). Also, the byproducts cost are: 1.5 \$/kg for TEOS 98.5; 2.5 \$/kg for TEOS 99.0; 3.75 \$/kg for TEOS 99.5; 88.44 \$/kg for SiH_4; 3.0 \$/kg for SiH_3Cl; and 3.67 \$/kg for SiH_2Cl_2. Despite being able to choose from a wide range of high value-added products such as: TEOS 98.5, TEOS 99.0, TEOS 99.5, silane, dichlorosilane and monochlorosilane, in the optimization it can be seen that solution choose the components of greater economic value for its production, as is the case of polycrystalline silicon, silane and TEOS 99.5. The objective function maximizes the profit of the Multi-Product Polycrystalline Silicon Facility, giving a maximum profit in the process of 113.57 M\$/y, and presents some particularities. For example, for a large production of silicon, the hydrochlorination reactor temperature is 573 K using a $H_2/SiCl_4$ molar ratio of 2.17. However, despite the low energy requirement of the reactor, high production costs of $SiHCl_3$ are obtained due to the use of considerable amounts of $SiCl_4$. It should be also noted that the process requires a high energy consumption in the distillation columns due to the high values of the reflux ratios. This guarantees a high polycrystalline silicon production capacity although the operating cost is high it also respects an adequate production of high value-added products such as TEOS and chlorosilanes, which makes the process of production of polycrystalline silicon much more profitable. The investment cost of the Multi-Product Polycrystalline Silicon Facility results in 85.93 \$M. It can be seen that the distillation columns (conventional or reactive) are the most expensive units, followed by the Siemens reactor and the thermal carboreduction reactor. Only these equipment represent more than 75% of the total cost of the process. Figure 2 shows the consumption of each one of the utilities and raw materials for the objective function evaluated, showing that the maximum profit in a Multi-Product Polycrystalline Silicon Facility.

Table 1. Profit [M\$/y], Operating costs [M\$/y], kg of polycrystalline silicon/h, kg of TEOS, and kg of silane of the objective function.

Profit [M\$/y]	113.57
Operating costs [M\$/y]	10.10
kg of polycrystalline silicon/h	1800.50
kg of TEOS (99.5 of purity)/h	632.84
kg of SiH_4/h	42.68
Price of Polycrystalline Silicon \$/kg	6.86
Price of TEOS 99.5 \$/kg	3.75
Price of SiH_4 \$/kg	88.44

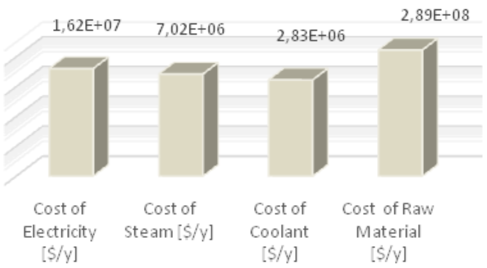

Figure 2. Utilities and raw materials for the Multi-Product Polycrystalline Silicon Facility.

4. Conclusions

In this work a superstructure optimization approach is used for the selection of the portfolio of products within a Multi-Product Polycrystalline Silicon Facility. Surrogate models for major units allow selecting the yield and operating conditions. The proposed process is able to meet the same production of polysilicon than current tradition polysilicon facilities at a lower production cost since the benefits obtained from selling the high added value by-products obtained increase the profit of the facility. The complete process, and therefore the operating conditions of each unit of the process were optimized under the objective of the maximization profit of the process. The optimal operating conditions of the facility that guarantee a lower energetic consumption, meeting with the required production of polycrystalline silicon require the production of high valuable by-products (TEOS 98.5, TEOS 99.0, TEOS 99.5, SiH_4, SiH_3Cl and SiH_2Cl_2), which aid in the economic sustainability of the process. The results after operating expenses, and considering the sale of polycrystalline silicon and the byproducts of the process, are an operational cost of 10 M$/y. The investment for the process is 85.93M$. Obtaining a competitive production cost for polycrystalline silicon of 6.86 $/kg, below the commercial price estimated at 10 $/kg, and the byproducts cost are: 1.5 $/kg for TEOS 98.5; 2.5 $/kg for TEOS 99.0; 3.75 $/kg for TEOS 99.5; 88.44 $/kg for SiH_4; 3.0 $/kg for SiH_3Cl; and 3.67 $/kg for SiH_2Cl_2.

References

E. Sánchez-Ramírez, C. Ramírez-Márquez, J. J. Quiroz-Ramírez, G. Contreras-Zarazúa, J. G. Segovia-Hernández, & J. A. Cervantes-Jauregui, 2018. Reactive Distillation Column Design for Tetraethoxysilane (TEOS) Production: Economic and Environmental Aspects. Industrial & Engineering Chemistry Research, 57(14), 5024-5034.

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. Chemical Engineering and Processing: Process Intensification, 108, 125-138.

Rubber & Plastics News Report, 2016. Wacker to build silica plant in Tenn. https://www.rubbernews.com/article/20161214/NEWS/161219980/wacker-to-build-silica-plant-intenn.

C. Ramírez-Márquez, G. Contreras-Zarazúa, M. Martín, & J. G. Segovia-Hernández, 2019. Safety, Economic, and Environmental Optimization Applied to Three Processes for the Production of Solar-Grade Silicon. ACS Sustainable Chemistry & Engineering, 7(5), 5355-5366.

G. Del Coso, C. Del Canizo, & A. Luque, 2008. Chemical vapor deposition model of polysilicon in a trichlorosilane and hydrogen system. Journal of the Electrochemical Society, 155(6).

W. J. Ding, J. M. Yan, & W. D. Xiao, 2014. Hydrogenation of silicon tetrachloride in the presence of silicon: thermodynamic and experimental investigation. Industrial & Engineering Chemistry Research, 53(27).

C. M. Wai & S. G. Hutchison, 1989. Free energy minimization calculation of complex chemical equilibria: Reduction of silicon dioxide with carbon at high temperature. Journal of Chemical Education, 66 (7), 546.

P. Mints, 2018. Photovoltaic Manufacturer Capacity, Shipments, Price & Revenues 2017/2018. SPV Market Research.