Optimal design of a multi-product reactive distillation system for silanes production

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A B S T R A C T

Silane has found recent applications in the manufacture of solar photovoltaic cells, which provide solar power economically. One method for the production of silane takes trichlorosilane as a starting molecule, with a reaction mechanism that involves two other intermediate valuable products, dichlorosilane and monochlorosilane. The production system involves a series of reactors and separation steps that can be intensified via reactive distillation. In this work, optimal designs of reactive distillation systems for the production of trichlorosilane, dichlorosilane and silane are developed. Furthermore, a multi-product reactive distillation system for the production of any of these types of silane products is designed. It is shown that an intensified design can be obtained for the production of the three silane products using the same column. The operating conditions at which the columns should be adjusted for the production of each product are reported.

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1. Introduction

The quest for new sustainable fuels has become an important effort because of fossil fuels depletion and its negative impact on the environment. As part of that search, solar energy has received significant attention recently. For instance, solar cells or photovoltaic cells have been manufactured in the last decades at increasing rates. Single crystal silicon is the most important material for modern solar and semiconductor industries. Ultra-high purity of polysilicon is achieved first by the preparation of a volatile silicon hydride, i.e. silane, and its purification, generally using fractional distillation. This is followed by the decomposition of this hydride to hyper-pure elemental silicon by reductive pyrolysis or chemical vapor deposition. The preparation of the volatile silicon (Si) compound involves external reactants and its decomposition generates by-products, mainly silicon tetrachloride and other chlorosilanes; such by-products are typically recycled to improve the process efficiency, although market conditions could promote their sales for applications in the manufacture of optical fibers.

Three processes can be mentioned as the commonly used routes to produce polysilicon. The most popular process, developed in the late 1950s, is based on the thermal decomposition of trichlorosilane (TCS) on a heated silicon rod or filament placed inside a deposition chamber. This process is commonly referred to as the Siemens process, is energy intensive, and a major part of the energy is disseminated and lost. In 2001 processes based on this technology still accounted for at least 60% of the worldwide production of polysilicon (Ceccaroli and Lohne, 2010). The by-product SiCl₄ (STC) is a low-value waste product that cannot be used efficiently for polysilicon growth. However, STC can be used for its reconversion to the valuable starting material SiHCl₃ to form a closed-loop production process (Sarma and Rice, 1982).

The second process came from an improvement of the Siemens process developed by Union Carbide corporation (Luque and Hegedus, 2011). Fig. 1 presents the flowsheet for such a process for the production of polysilicon from mineral grade silicon. The trichlorosilane was replaced by monosilane SiH₄, with the same principle of decomposition on a heated silicon rod inside a closed deposition chamber. In this process silicon STC is converted to TCS via a hydrogenation reaction, after which TCS is converted to dichlorosilane (DCS) and then to monosilane through redistribu-
tion reactions. This process has found significant market acceptance over the last 30 years.

The other commonly used process, developed in the 1980s–1990s, is the Ethyl Corporation process (Luque and Hegedus, 2011). It also makes use of monosilane, for which the heated silicon rod in the closed reaction chamber is replaced by a fluidized bed of heated silicon particles, which act as seeds for the continuous decomposition of SiH₄ into larger granules of hyperpure silicon. As opposed to the previous two technologies, this process operates on a continuous basis.

Dichlorosilane and monochlorosilane are intermediate compounds in the production of silane that are typically recycled, but they also have other important applications. Some of them are described below.

Robinson and Goldsmith (1975) studied silicon epitaxial growth using dichlorosilane. They found that dichlorosilane is a suitable material for the deposition of high quality epitaxial layers of silicon. A process developed by Hemlock Semiconductor Corporation showed the feasibility of using dichlorosilane instead of trichlorosilane for the production of polycrystalline silicon (McCormick et al., 1989). They reported a faster deposition rate and lower power consumption when dichlorosilane was used instead of trichlorosilane. Dichlorosilane (DCS) is mainly used for the preparation of semiconducting epitaxial silicon layers of very high purity, as required for their application in the microelectronics industry (Marin and Lefort, 1977). Among the chlorosilane products, dichlorosilane has been found to be the best material for epitaxial growth of integrated circuits (Chowdhury et al., 2011). DCS has also been used for the production of silicon nitride, a material in microelectronic and optoelectronic industries; the conversion is based on chemical vapor deposition or plasma-enhanced chemical vapor deposition (Santana et al., 2005). Among the routes to obtain dichlorosilane, the one based on trichlorosilane disproportionation is the most widely used. Li and Huang (1988) investigated the redistribution reaction of trichlorosilane to dichlorosilane in a fixed bed reactor using different types of ionic-exchange resin catalysts, and proposed a reaction mechanism to explain the redistribution reaction.

The other silane product of interest in this work, monochlorosilane (MCS), was investigated as a precursor for the vapor phase epitaxy of silicon. Tomasinis and Weeks (2011) found that MCS is an equally effective Si precursor in comparison to SiH₄ and DCS. Monochlorosilane can also be used as reagent to produce chemicals such as trisilylamine (Hoppe et al., 2014), which is used as precursor for the deposition of high purity silicon oxide films for gap fill applications in the semiconductor industry. Additional applications of chlorosilanes have been developed (Bailey and York, 1959; Seyferth et al., 1984).

Given the importance of the three types of silanes mentioned above, this work focuses on the analysis, design and optimization of a reactive distillation system that has the flexibility to shift the production of silane, monochlorosilane and dichlorosilane as a function of the market demand for each product. The system is to be operated to produce one product at a time. For the sake of this paper, the problem is simply defined as the design of a multiproduct reactive distillation column. Structurally, the problem can be viewed as the substitution of the highlighted section of Fig. 1, which includes two reactors and four distillation columns, into a single piece of equipment, i.e. a reactive distillation column.

This work is organized in the following way. The design strategy and the equations for the chemical kinetic reactions for silanes production are presented. The design of reactive distillation columns for each silane product is then carried out. From these results, a base design is developed for the production of any of the three products with a single unit, which is then subject to an optimization task to find the best structure and operating conditions for each product. Given the importance of the temperature of the reactive zone due to catalyst restrictions, an initial dynamic analysis is then reported on the changes of the hottest stage against feed disturbances. The last section gives the relevant conclusions from this work.

2. Design of the silanes process

A single reactive distillation unit is to be designed for the production of silane, monochlorosilane and dichlorosilane with high purities. The reaction step starts with the disproportionation of trichlorosilane, which produces the three silane products as part of the following reaction mechanism involving five chemical species and three reversible reactions,

\[
\begin{align*}
2\text{SiHCl}_3 & \leftrightarrow \text{SiCl}_4 + \text{SiH}_2\text{Cl}_2 \\
2\text{SiH}_2\text{Cl}_2 & \leftrightarrow \text{SiHCl}_3 + \text{SiH}_3\text{Cl} \\
2\text{SiH}_3\text{Cl} & \leftrightarrow \text{SiH}_2\text{Cl}_2 + \text{SiH}_4
\end{align*}
\]
The first two reactions are slightly endothermic, while the last one is exothermic. According to the reaction mechanism, dichlorosilane can be produced if only the first reaction is carried out. Similarly, monochlorosilane is produced if only the first two reactions take place, while the production of silane requires all three reactions to occur. Therefore, for the production of the silane product of interest, the operating conditions must be set accordingly so as to favor the reaction(s) of interest.

For this mechanism, the following reaction rate equations have been reported by Huang et al. (2013)

\[ \begin{align*} 
    r_1 &= k_1 \left( x_1^2 - x_0 x_3 / K_1 \right) \\
    r_2 &= k_2 \left( x_2^2 - x_1 x_3 / K_2 \right) \\
    r_3 &= k_3 \left( x_3^2 - x_2 x_4 / K_3 \right) 
\end{align*} \tag{2} \]

where \( x_0, x_1, x_2, x_3, \) and \( x_4 \) correspond to the liquid mole fraction of silicon tetrachloride, trichlorosilane, dichlorosilane, monochlorosilane and silane respectively; \( r_1, r_2, \) and \( r_3 \) are the reaction rates of trichlorosilane, dichlorosilane, and monochlorosilane disproportionation; \( k \) is the forward rate constant and \( K \) the chemical equilibrium constant, for which the following relationships apply:

\[ \begin{align*} 
    k_1 &= 7.35 \times 10^{-5} \text{e}^{-30045 / R T}, \quad K_1 = 0.1856 \text{e}^{-640 / R T} \\
    k_2 &= 9.49 \times 10^4 \text{e}^{-309 / R T}, \quad K_2 = 0.7669 \text{e}^{-7226 / R T} \\
    k_3 &= 11.76 \text{e}^{-26320 / R T}, \quad K_3 = 0.689 \text{e}^{548 / R T} 
\end{align*} \]

where \( k \) is obtained in \( \text{s}^{-1} \).

### 3. Initial design and search variables for each product

The main goal of this work is the design of a multi-product reactive distillation (RD) system. The first step we follow is the development of individually intensified processes via reactive distillation systems for the production of each silane product. The design of reactive distillation systems involves the detection of rectifying, reactive and stripping sections; a conceptual structure of this system is shown in Fig. 2. Subawailla and Fair (1999) report some guidelines for several design variables such as the location of the reactive zone, feed location, number of stages, pressure, and reflux ratio. Initial interest in the reactive distillation process for silane production is reflected in the patent by Bakay (1976) and the work by Müller et al. (2002). A relevant aspect for silane production is the need for refrigeration utilities at the top of the column. Also, it is important to avoid thermal decomposition of the catalyst in the reactive trays, which restricts the use of high pressure operation. In this work, the design reported by Huang et al. (2013) for the production of silane with a purity of 99.3% was taken as a basis. The analysis will serve to establish conditions that promote the production of each of the three silane products, which will then be subjected to the optimization procedure. The RD column consists of 60 stages, out of which 29 are reactive; the reactive zone starts at stage 16, with a residence time per stage of 2.5 s. The feed stage is located at stage 46, just below reactive zone, and the feed flowrate is 10 kmol/h of TCS. The operating specifications include a reflux ratio of 63 and a feed to distillate ratio of 0.25. The pressure on the top of the column is 5 atm, with a pressure drop of 0.5 kPa per stage. The design was validated in ASPEN Plus using a RADFRAC block.

In order to identify the conditions under which the production of each silane product would be favored, a sensitivity analysis was conducted through variations on the design pressure and the distillate to feed ratio (D/F). The results are shown in Fig. 3. From this analysis, one can identify that with distillate to feed ratios of 0.25, 0.35, and 0.5 the corresponding distillate compositions of silane, monochlorosilane and dichlorosilane are favored. When the pressure was varied, values of 5, 1.5 and 1 atm increased the distillate composition of silane, monochlorosilane and dichlorosilane, respectively. One can also observe in Fig. 3 how those D/F ratios and pressure values generate the highest amount of the silane compound of interest. Such values were then used as starting points for the optimization step for the production of the individual products. It should be noted that the reflux ratio was not analyzed since one degree of freedom is lost due to the purity specification.

#### 3.1. Individual designs for the production of each silane product

The three individual designs for reactive distillation columns, one for the production of each silane product, were then carried out. The optimization procedure was based on the minimization of the total annual cost (TAC), which includes a total investment cost (TIC), the total energy cost (TEC), and the total catalyst cost (TCC). The optimization variables are the number of stages, feed stage, number of stages for the reactive zone and their location, total liquid holdup of reactive zone, and column pressure. The number of stages in the reactive zone and liquid holdup are associated to the amount of catalyst needed annually \( m_{\text{catalyst}} \). The optimization model is written as,

\[ \text{MinTAC} = \text{TIC} + \text{TEC} + \text{TCC} \]

s.t. \[ \text{TIC} = \frac{\text{Cost}_{\text{boiler}} + \text{Cost}_{\text{condenser}} + \text{Cost}_{\text{reboiler}}}{\text{payback period}} \]

\[ \text{TEC} = \pi_{\text{utility}} * Q_{\text{condenser}} + P_{\text{pump}} * Q_{\text{reboiler}} \]

\[ \text{TCC} = P_{\text{catalyst}} * m_{\text{catalyst}} \]

The costing equations for the distillation system were taken from Kiss (2013) and are reported in Table 1. The price of Amberlyst catalyst \( P_{\text{catalyst}} \) was fixed at $330/kg. Three months of catalyst life and a volume of 50% of the liquid holdup of reactive zone were...
assumed. A product purity specification of 99.5% was used for each silane product. The top temperature in the column affects the type of refrigeration utility needed for the condenser. The utilities considered in this work, along with their prices, are given in Table 2.

The optimization of reactive distillation processes presents major challenges, particularly when use of gradient methods is considered. The problem involves simultaneous reaction-separation operations, which drives a highly nonlinear model with heavy interactions among design variables. To tackle this problem, derivative-free optimization methods, such as the use of genetic algorithms (GAs), provide a suitable approach. This technique has shown its effectiveness in several design applications, for instance in the optimization of heat transfer processes (Ponce-Ortega et al., 2009) and the design of complex separation systems (Gutiérrez-Antonio and Briones-Ramírez, 2009; Vázquez-Ojeda et al., 2013).

The optimization approach was implemented in a similar way as in Medina-Herrera et al. (2014) for the optimal design of extractive distillation systems. The GA method available in the MATLAB environment was used, and a link between MATLAB and ASPEN Plus was created so that each search point was provided from rigorous simulations as part of the automated procedure. The general approach, shown schematically in Fig. 4, was as follows. An initial point for the optimization variables was provided, along with bounds on the search variables and the GA parameters. The GA sent the values of the optimization variables to ASPEN Plus, in which the rigorous simulations were performed using RADFRAC blocks. The simulations proved to be straightforward, with no convergence issues for any of the runs that were required. The results from the simulation were then sent back to MATLAB, where the genetic algorithm calculated the objective function (total annual cost).

The steps of the genetic algorithm are described briefly. First, an initial population (i.e. a set of RD designs) is created randomly. Then a sequence of new populations is created, with each population based on the best individuals of the current generation. There are six steps to create the next population. (1) Each individual of the current population is evaluated and its corresponding objective function is computed. (2) An escalation based on objective function values is carried out so that more suitable or promising ranges of the search variable are obtained. (3) The best individuals (i.e. the best designs) are selected as parents for the next generation. (4) Some of the individuals of the current population with the best objective function (lower total annual costs) are chosen as elite and pass directly to the next generation (elite count). (5) Children are created based on random changes to a single parent (mutation) or a combination of two parents (crossover). (6) The next generation is formed with the children of the current population. The algorithm finishes when a given stopping criterion such as a maximum number of iterations (generations) is reached. The GA parameters used in this work were 50 generations, a population size of 250 individuals, and a parent selection option of “stochastic uniform”. For children creation, a cross over fraction of 0.8, a mutation fraction of 0.2 and elite count of 2 were used.

The base case and the optimal designs obtained for silane, monochlorosilane and dichlorosilane individual products are given in Table 3, where a comparison to the design reported by Huang et al. (2013) for silane production is included. The optimization task...
took 8, 5 and 5 h for silane, monochlorosilane and dichlorosilane designs, respectively. One can observe that the design obtained in this work for silane requires a higher number of stages than the one by Huang et al. (2013), mostly due to the number of stages for the reactive zone (67 vs. 30). However, the design obtained here provides savings in total annual cost of 45%, driven by energy savings of 56% and investment savings of 24%. The investment savings were obtained because of a smaller column diameter and smaller areas for the condenser and the reboiler. The feed is placed in stage 17, within the reactive zone, which differs from the one reported by Huang et al. (2013) in which the feed stream is located in stage 46, just below the reactive zone. It should be noticed that the silane optimized design requires 1.7 times more catalyst than the design of Huang et al. (2013) Nonetheless, the energy and investment savings observed for the design obtained here provide a more economical design.

When comparing the designs for the three products, one can see that the silane reactive distillation column requires the highest

<table>
<thead>
<tr>
<th>Utility ID</th>
<th>Inlet temperature, C</th>
<th>Outlet temperature, C</th>
<th>Utility price Putility ($/MWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>−88</td>
<td>−88</td>
<td>151.94</td>
</tr>
<tr>
<td>R2</td>
<td>−30</td>
<td>−30</td>
<td>34.67</td>
</tr>
<tr>
<td>R3</td>
<td>−20</td>
<td>−20</td>
<td>28.4</td>
</tr>
<tr>
<td>CHW</td>
<td>5</td>
<td>15</td>
<td>15.95</td>
</tr>
<tr>
<td>CW</td>
<td>30</td>
<td>40</td>
<td>1.274</td>
</tr>
<tr>
<td>LPS</td>
<td>160</td>
<td>160</td>
<td>50.58</td>
</tr>
</tbody>
</table>

Table 2
Refrigeration and heating utilities.
number of stages (91) with respect to those needed for monochloro and dichlorosilane of 72 and 71 trays. Dichlorosilane requires the lowest number of stages for the reactive zone (35) but the highest for the separation (36). The feed stage is located inside the reactive zone for all designs, a different feature with respect to the initial design taken from Huang et al. (2013) in agreement with the constraint imposed for the reactive zone, the maximum temperature is below the thermal decomposition of the Amberlyst catalyst of 100 °C; the highest temperature in the reactive zone for silane and monochlorosilane column was the same, 97 °C, while that for dichlorosilane was quite lower, 65.1 °C. Although the energy consumption required by the silane design is the lowest, the energy cost is the highest because of the low temperature of the distillate product (-78.9 °C), compared to temperatures of -5.1 °C and 5.7 °C required at the top of the column for monochlorosilane and dichlorosilane. As a result, the production of silane requires the most expensive type of refrigerant. In terms of the total annual cost, monochlorosilane would require the most expensive process, while the one for dichlorosilane would be the most economical.

The composition and temperature profiles for each design are presented in Fig. 5 (the reactive zones are highlighted). For silane production the stages of the reactive zone account for 74% of the total stages, while the rectifying section has only 6 stages. On the other hand, for dichlorosilane column, the reactive zone comprises 49% of its design, while the rectifying zone accounts for 42%. These observations serve as a basis to develop an initial design for the optimization of a multi-product reactive distillation system.

### 3.2. Design of a multi-product reactive distillation column

For the silanes multi-product design, an initial structure of the column was built taking into account the highest number of trays observed in the previous designs for the reaction and for the separation tasks, which means that basically it is a combination of the silane and dichlorosilane designs. As a result, the initial design has 115 total stages, feed stage is located at stage 42, and the reactive zone has 67 stages starting at stage 30, with a liquid holdup of 0.16 m³. This structure provides an overdesign that ensures feasibility for the production of any silane product, and serves as an initial point for the optimization procedure. The design was complemented with the biggest column diameter and the largest heat exchanger areas observed for the previous individual designs. This initial design is then revised and adjusted as part of the optimization task, from which the best values for the remaining variables such as pressure, reflux ratio, heat duties and distillate to feed ratio are also obtained; such variables are dependent on the particular product of interest, i.e., we will detect one set of variables for each silane product.

The design of the multi-product reactive distillation system will depend on the demand levels for each of the three silane products. For this analysis, we use an assumption of an equal production requirement for each of the three silanes; the procedure can be readily adjusted to any different type of market requirements. The same unit is to be used for the production of each product, one at a time, and no distinction is made at this point in time as to the order in which each product would be produced. Under the assumed production scenario, the optimization model is written as follows,

\[
\text{MinTAC} = \text{TIC} + \text{TEC} + \text{TCC}
\]

\[
s.t. \quad \text{TIC} = \frac{1}{2} \times \text{TIC}_{\text{SiH4}} + \frac{2}{3} \times \text{TIC}_{\text{SiH2Cl}} + \frac{1}{3} \times \text{TIC}_{\text{SiH2Cl2}}
\]

\[
\text{TEC} = \max \left( \frac{\text{TEC}_{\text{SiH4 reboiler}} \times \text{TEC}_{\text{SiH2Cl reboiler}} \times \text{TEC}_{\text{SiH2Cl2 reboiler}}}{\text{payback period}} \right)
\]

\[
\text{max} \left( \frac{\text{TEC}_{\text{SiH4 condenser}} \times \text{TEC}_{\text{SiH2Cl condenser}} \times \text{TEC}_{\text{SiH2Cl2 condenser}}}{\text{payback period}} \right)
\]

\[
\text{TCC} = \text{P}_{\text{catalyst}} \times m_{\text{catalyst}}
\]

\[
\text{max} \times \text{reactivezone < thermalresistance catalyst}
\]
The optimization task took close to 10 h to find the optimal design. The results of the multi-product optimization design are given in Table 4. The column characteristics for the intensified process consist of 89 stages (compared to 115 for the initial design), with the feed stream located at stage 42, and the reactive zone going from stages 29–72 (compared to 30–97 for the initial design). The liquid holdup is 0.068 m³ and the diameter 0.73 m, lower values than those for the base design of 0.16 m³ and 0.82 m. In terms of the operating conditions for each product, the results indicate that the column should be operated at a pressure of 4.9 atm if the production of silane is desired, 2.3 atm for monochlorosilane and 1 atm for dichlorosilane. Reflux ratio should be 34.9 for silane production, or 38.9 for monochlorosilane, or 11.3 when dichlorosilane is the product of interest. The values of distillate to feed ratio obtained from the optimization procedure are 0.25 for silane, 0.33 for monochlorosilane, and 0.5 for dichlorosilane. For the temperature of the reactive zone, the operating conditions for silane production ensure a maximum value of 97 °C, and for monochlorosilane of 92 °C. The production of dichlorosilane is less critical in this regard, since a maximum temperature of 51.4 °C would be observed, a trend consistent with the results for the individual designs.

As far as energy requirements, the production of silane is by nature the most expensive because of the distillate temperature required for its high purity of ~79 °C, even when heat loads of 292 kW in the condenser and 333 kW in the reboiler are the lowest from the three products. When the production of dichlorosilane is under consideration, the energy cost is the lowest, due to a slightly higher load than the one required for silane but with a cheaper refrigerant in the condenser. For the operation of the multi-product column under the production scheme assumed here, the total annual energy cost amounts to 4.35 × 10⁵ $/year, which reflects a reduction of 2.7% with respect to the base design. The catalyst cost also drops from the base design as a result of the optimization procedure by 57%.

The minimum TAC for the optimum design was $8.78 × 10⁵/yr, which represents a reduction of 14.1% with respect to the initial point established for the optimization procedure. It should be noted that the design involves the use of two different cooling services (R1 and R3) that are needed for different products. When silane is produced, R1 is needed as cooling utility, but when the column operates to produce monochloro or dichlorosilane, R3 can be used as cooling utility. Using both R1 and R3 at different production times may probably translate into a more expensive utility plant. However, the selected use of two cooling utilities provides 47.4% energy cost savings ($3.9 × 10⁵/yr) in comparison with using only R1, which may compensate for the possible cost increase of the utility plant. Also, it is worth of mention that the condenser of the RD column has been designed to meet any of these needs, and the only thing to adjust is the refrigerant fluid needed for each product.

Another relevant observation is that the multi-product design requires two fewer stages than those obtained for the production of silane. This is the result of the search for the optimum condition considering the production of three components. In other words, the search for the optimum design is not driven towards the production of any individual product, but to provide the best compromise for the production of the three components at different times using the same equipment. Thus, energy duties for monochloro and dichlorosilane production are lower than from their individual designs, while silane duties increased from 228 MW to 292 MW in the condenser and 269 MW to 333 MW in reboiler. These changes reflect the tradeoff between fixed costs and energy costs for the design of the column.

Fig. 6 shows the composition and temperature profiles for the multi-product design. One can see that the production of silane generates the most extreme values of temperature in the column, with a temperature at the top of the reactive zone of 38.4 °C, and reaching quickly the high value of 97 °C before getting into the stripping section. The temperature profile for the production of dichlorosilane shows a flat temperature profile in most of the reactive zone,
Fig. 6. Temperature and composition profiles for the production of each silane product.

Fig. 7. Dynamic response of the reactive distillation column against 10% feed flowrate and −10% composition disturbances.
Table 4
Design of the multi-product silane reactive distillation system.

<table>
<thead>
<tr>
<th></th>
<th>Base Design</th>
<th>Optimized Multi-product for Silane</th>
<th>Optimized Multi-product for Monochloro-Silane</th>
<th>Optimized Multi-product for Dichloro-Silane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of stages</td>
<td>115</td>
<td>89</td>
<td>89</td>
<td>89</td>
</tr>
<tr>
<td>Feed stage</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>Feed flowrate of SiH₄Cl₄ (kmol/h)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Reactive Zone (Stage to Stage)</td>
<td>30–97</td>
<td>29–72</td>
<td>29–72</td>
<td>29–72</td>
</tr>
<tr>
<td>Liquid Holdup (m³)</td>
<td>0.1600</td>
<td>0.068</td>
<td>0.068</td>
<td>0.068</td>
</tr>
<tr>
<td>Purity of product in D1 (mol%)</td>
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<td>99.5</td>
<td>99.5</td>
<td>99.5</td>
</tr>
<tr>
<td>Purity of SiCl₄ in B1 (mol%)</td>
<td>99.8/100/100</td>
<td>99.8</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Distillate to feed ratio</td>
<td>0.25/0.333/0.5</td>
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<td>0.333</td>
<td>0.5</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>26.7/50/11.45</td>
<td>34.9</td>
<td>38.9</td>
<td>11.3</td>
</tr>
<tr>
<td>Operating pressure (atm)</td>
<td>4.9/2.7/1</td>
<td>4.9</td>
<td>2.3</td>
<td>1</td>
</tr>
<tr>
<td>Pressure drop per stage (kPa)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Column diameter (m)</td>
<td>0.82</td>
<td>0.73</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>Maximum temperature in the reactive zone, (°C)</td>
<td>98.1/98.7/69.7</td>
<td>97</td>
<td>91.5</td>
<td>51.4</td>
</tr>
<tr>
<td>Top Temperature (°C)</td>
<td>–78.9/–5.5/5.7</td>
<td>–78.7</td>
<td>–9.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Cooling utilities</td>
<td>R1/R3/R3</td>
<td>R1</td>
<td>R3</td>
<td>R3</td>
</tr>
<tr>
<td>Qc (kW)</td>
<td>228/918/383</td>
<td>292</td>
<td>712</td>
<td>375</td>
</tr>
<tr>
<td>Qc (kW)</td>
<td>270/947/395</td>
<td>333</td>
<td>739</td>
<td>387</td>
</tr>
</tbody>
</table>

below 50 °C, exits the zone at 51.4 °C and keeps a flat temperature profile in the stripping section as well.

The design of the multi–product reactive distillation system has been shown to be an effective way to produce the three silane products at high purities with the same equipment by adjusting the operating conditions of the column.

3.2.1. Dynamic analysis for the maximum temperature of the reactive zone

The maximum temperature observed in the reactive zone of the multi–product column was 97 °C, meeting the constraint of the maximum temperature of 100 °C stated for proper operation of the catalyst A-21. A natural concern is whether this value is susceptible to exceed the maximum catalyst temperature of 100 °C in the reactive zone during plant operation. Although a formal study is needed, we conducted a preliminary assessment on this issue via Aspen Dynamics by considering the closed-loop dynamic response of the system under disturbances of ±10% in feed flowrate and –10% in feed composition. The analysis includes the consideration of impurities of SiCl₄ in the feed.

Following the approach described by Luyben (2006), we carried out a sensitivity analysis as a first step for the implementation of a temperature control strategy, taking the operation for silane production as a basis, we found that stage 3 was the most sensitive tray to changes in reflux ratio, while stage 78 showed the highest sensitivity against changes in reboiler duty. Control loops based on these stages were then implemented. The temperature of stage 3 was controlled by manipulating the reflux to feed ratio (R/F), while that of stage 78 was controlled with the reboiler duty to feed ratio (QR/F). Tyreus-Luyben tuning rules were used to tune the PI controllers. Inventory and pressure controllers were also included (Tyreus and Luyben 1992).

Fig. 7 shows the dynamic responses of the reactive distillation column in the face of the implemented feed disturbances. First of all, one can observe that a good control behavior was obtained for the silane product composition. Then, the major aspect dealing with the temperature profile was analyzed, and it was observed that the temperature in the hottest stage (stage 72) in the reactive zone suffered a minor deviation of 0.5 K when the maximum temperature was recorded. The analysis was also carried out for the reactive column under monochlorosilane and dichlorosilane production with similar results. These results seem to indicate that a safe operation on the catalyst performance, regardless of the silane compound of interest, could then be expected.

Some of the operational issues that need to be addressed in future research include the startup and shutdown strategies for each product, or in general the analysis of dynamic aspects related to the transition times between two given products. The order in which each product should be produced has not been explored here either. This novel design therefore poses an interesting problem for a formal study dealing with proper control/scheduling strategies for the operation of the multi-product reactive distillation system.

4. Concluding remarks

An intensified design of a multi-product reactive distillation column for the production of three silane products has been developed. The system was modeled by combining the results of the reactive distillation systems for the individual production of silane, monochlorosilane and dichlorosilane, and formulating an optimization problem to find the best common structure of the system, as well as the operating conditions related to each product. The use of genetic algorithms as the optimization tool proved to be an effective approach given the complexity of the optimization problem, in which the major characteristics of the column structure (number of trays for each section and feed location) as well as the operating conditions (pressure, reflux ratio, distillate to feed ratio) related to each product were required. An initial dynamic analysis of the design obtained with this procedure was conducted to see if the maximum temperature of the reactive zone would meet the constraint for proper operation of the catalyst under feed flow and composition disturbances. The results showed only a minor effect
on the steady state values of maximum temperatures for the production of the three silane products. A formal dynamic and control analysis should be conducted to complement these initial findings for the multi-product reactive distillation system.

References


