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Dynamic behavior of a multi-tasking reactive distillation column for production of silane, dichlorosilane and monochlorosilane

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ABSTRACT

Solar cell manufacturing is based on solar grade silicon which can be obtained using silane as precursor. Silane is produced by redistribution reactions of trichlorosilane. The aim of the present work is to study the control properties of a multitasking reactive distillation column to produce silane, dichlorosilane and monochlorosilane. Control adjustment was defined in such way that the column may work in multitasking mode producing the three interest components in high purity. Several control strategies were studied to define the best dynamic performance which allow to produce those three components within the same column. In order to observe the dynamic behavior of the multitasking reactive distillation column, this system was tested under various control strategies: temperature, composition and cascade (temperature/composition), having as target to keep silanes purity in 99.5%mol. The results indicated that is possible to obtain a conceptual design of a single reactive distillation column which would be able to produce all products. The proposed multitasking column avoids all hurdles involved in the traditional way to produce and purify all those three components. It was observed those evaluated control structures can stabilize the system against tested disturbances, even the simplest temperature control structure.

1. Introduction

Globally, since reserves of crude oil are continuously decreasing there is an increasing interest of having other kind of energy sources, mainly renewable, clean and environmental friendly. Currently, several research groups are focus on finding a competitive energy source in comparison with fossil fuels. Solar photovoltaic energy as well as other renewable energy sources are attempting to diminish the energetic dependence of fossil fuels. Moreover, wind, hydroelectric and solar energies have been recently relevant. Particularly, solar energy has been exploiting in many ways, the most known method is to use solar cells based in silicon, which transform solar light into electricity through the photovoltaic effect (PV).

The growing interest to obtain silicon as raw material for solar cells has evolved significantly in recent decades [1]. It is expected a growing demand of 30% per year for the next 10 years [2]. A more detailed analysis indicates that photovoltaic market has increased an average rate of 45% per year over the past decade showing a major demand between 2007 and 2011, up to 70% per year; with a decrease of 15% in 2012 because some european countries reduced the incentives for its implementation. Although several reports indicate continuous growing in this sector, the entire capacity installed in 2011 was 27 GW which only represents 1% of the total energy production considering all available sources [3].

Even when silicon solar cells are competing with other kind of cells made of advanced material, it has predicted that silicon solar cells will continue making an important contribution to the market depending on the maturity of the technology, its availability and especially its cost [4]. For such reasons, the assessment of new alternatives for its production with competitive costs constitutes an area of opportunity for research in solar technology [3,4]

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Silicon cells are made from silicon raw materials. Those materials can be found as polycrystalline, monocrystalline and amorphous silicon. Polycrystalline silicon is the most used. However, it is important to note that the high cost of polycrystalline silicon is due to both the process to obtain it and the raw materials in production such as silane (SiH_4) [5].

One of the processes developed long time ago but currently working for silane production involves the disproportionation of trichlorosilane (obtained from the reaction between metallurgical grade silicon and hydrogen chloride) and the metallurgical silicon [6]. According to different reports, about 40% of the energy required to produce a solar panel is consumed in the precursor production. Therefore, a reduction of the energy consumed during the silane production is crucial to minimize the return of the investment and thus the cost of the technology [7].

All reactions involved in silane production are quite complex, so very few studies have approached the Siemens process in a thermodynamic rigorous way [8]. Further, the traditional process to produce silane involves the use of two reactors, a first reactor performs the first redistribution reaction from trichlorosilane to dichlorosilane and a second reactor blends both flows to continue with the redistribution reactions. On the other hand, four conventional distillations columns are used to separate and purify those products and all remaining reactants are then recycled. The necessity of this reactant recycle appears because unfavourable chemical equilibrium, however all this material recycled implies both equipment and high energy costs [9]. An alternative of the conventional process to produce silanes is the reactive distillation process (DR) which overcome the traditional process since fewer distillation columns and no reactors are required. Basically, the idea of reactive distillation column is to improve the chemical conversion, moreover only products are withdrawn from the reactive zone while reactants remain inside the reactive zone for further reaction. Also all material recycles can be eluded and consequently both energy and equipment costs are diminished. Additionally since several degrees of freedom are found in a reactive distillation column, such as reflux ratio, total stages, reactive stages and so on, is highly possible to find a single reactive distillation column which may produces all the other silanes involved in the silane redistribution only varying those degrees of freedom. The application of RD columns requires a proper understanding of their dynamic behavior and control properties. The RD column design offers the convenience that one reactive column makes the job of four columns and two reactors. Due to this simple configuration, RD structures were originally assumed to be easy controlled. Indeed, they have shown to provide suitable control properties [10]. It can be drawn from those studies that control properties of RD column should be examined to determine the control properties of those particular systems [10].

In this manner, the aim of this work is to propose a conceptual design and evaluate its control properties of a single reactive distillation column to produce high purity silane, dichlorosilane and monochlorosilane respectively. It has been reported that it is possible to obtain silane with the redistribution reaction from trichlorosilane in a RD column [11], the relevance of this work is to show the feasibility to produce pure monochlorosilane and dichlorosilane in the same RD column just varying the operative variables. First, it is important to note that there is no large-scale industrial processes to generate dichlorosilane which is further used as starting material for semiconducting silicon layers found in microelectronics. Particularly, it was object of this study to provide a process to produce monochlorosilane, due to its requirement on industrial scale, in pure form and in substantial quantities to be used as raw material. The process for making monochlorosilane should also be economical. A further target was to provide a cheaper design to carry out the process. A particular advantage of the monochlorosilane obtained in process is the low exposure to chloride for later deposition of silicon. The column design considers the advantages of the intensification process, having as target, besides the recovery of the three products, the diminishment of the environmental impact. The control structures for the RD column are explored to maintain product quality. Composition, temperature and cascading control structures are also developed on this work.

2. Model development

2.1. Chemical reactions

The reaction system consists in three simultaneous reactions. In the first one, trichlorosilane ($SiHCl_3$) reacts to dichlorosilane (SiH_2Cl_2) and tetrachlorosilane ($SiCl_4$). Subsequently, dichlorosilane reacts to monochlorosilane (SiH_3Cl) and trichlorosilane. Finally, monochlorosilane is converted to silane (SiH_4) and dichlorosilane. The three reaction steps are shown in Eqs. (1)–(3) [11].

$$2SiHCl_3 \overset{cat}{\leftrightarrow} SiCl_4 + SiH_2Cl_2 \tag{1}$$

$$2SiH_2Cl_2 \overset{cat}{\leftrightarrow} SiHCl_3 + SiH_3Cl \tag{2}$$

$$2SiH_3Cl \overset{cat}{\leftrightarrow} SiH_2Cl_2 + SiH_4 \tag{3}$$

The kinetic data of each reaction has been described as follows [11].

$$r_1 = k_1(x_1^2 - x_0x_2/K_1) \tag{4}$$

$$r_2 = k_1(x_2^2 - x_1x_3/K_2) \tag{5}$$

$$r_3 = k_3(x_3^2 - x_2x_4/K_3) \tag{6}$$

Where x_0, x_1, x_2, x_3 y x_4 are the molar fraction of tetrachlorosilane, trichlorosilane, dichlorosilane, monochlorosilane and silane respectively; r_1, r_2 and r_3 are reaction rates of trichlorosilane, dichlorosilane and monochlorosilane respectively; k's and K's are reactions constants and chemical equilibrium constants respectively (See Table 1) [11]. Since the mixture studied is not polar, the thermodynamic method Peng-Robinson has been selected [11].

2.2. Description of reactive distillation column

For a catalytic heterogeneous reaction, commonly is included a solid reactive zone in the distillation column where several mass transfer phenomena are carried out. This make possible the integration among reaction and separation at the same time. The typical distillation column is shown in Fig. 1, this columns includes three zones: rectifying zone, reactive zone and stripping zone placed at the high zone, middle zone and inferior zone respectively. The reaction occurs using as catalyst an ionic exchange polymeric

Table 1
Kinetic parameters for disproportionation of trichlorosilane in the liquid phase.

	k_0 (s^{-1})	E (J/mol)	K_0	ΔH (J/mol)
r_1	73.5	30045	0.1856	6402
r_2	949466.4	51083	0.7669	2226
r_3	1176.9	26320	0.6890	−2548

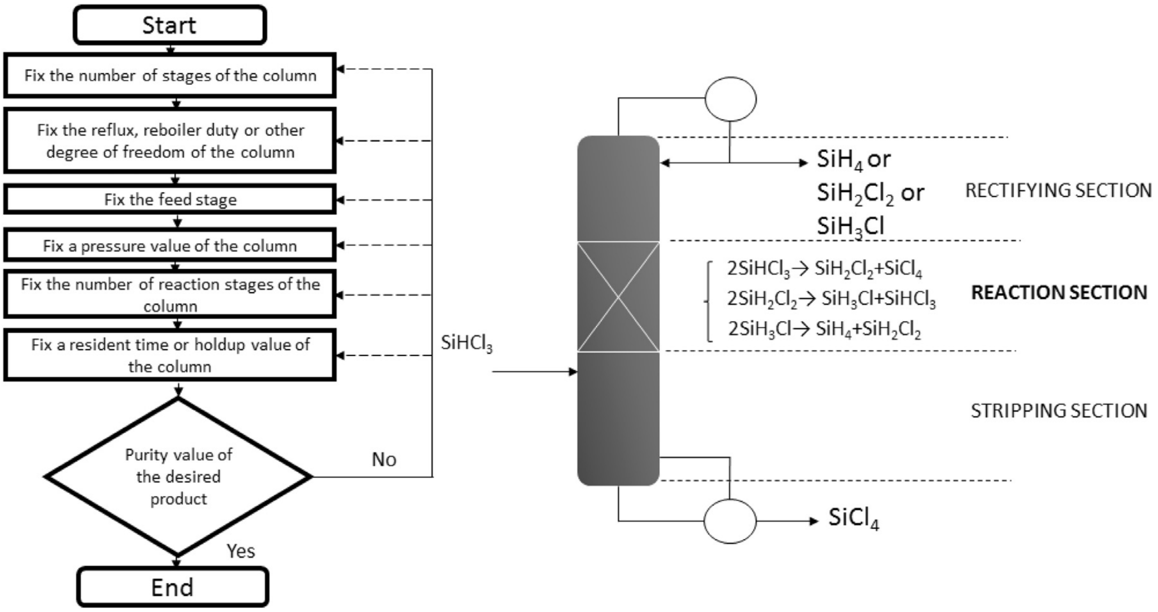

Fig. 1. Methodology of multitasking reactive distillation column, and scheme of multitasking reactive distillation column for purifying silane, dichlorosilane and monochlorosilane.

resin pearls with a size of 0.3–1.2 mm. The pearls are supported and fixed in an iron wire mesh to avoid high drop pressure issues [11].

In accord to the proposed conceptual design, the distillation reactive column is operating in the following way: Initially trichlorosilane is fed in the lower part of reactive zone. After that, the disproportion is carried out in the reactive zone in order to generate the different products (trichlorosilane, dichlorosilane, monochlorosilane and silane). Those main products are mixed in vapor phase after reaction and all of them rise to the rectifying zone while the heavy component (tetrachlorosilane) descend to the stripping zone.

This operative mode is quite effective since all reactions are performed entirely, and the main interest components can be recovered at top of the column while byproducts can be removed at bottom of the column [11]. In the industrial practice, tetrachlorosilane is recycled to the hydrochlorination reactor upstream in order to regenerate the trichlorosilane.

3. Methodology

Commonly the multitasking columns are batch columns, however in this case we present a RD continuous column because the demand of solar grade silicon in the PV is growing in recent years [1]. It is important to note that for designing RD columns does not exist a well-kwon methodology as for conventional distillation columns.

Please note, the main goal of this proposal is not only to produce silane at the top of the column otherwise to produce also dichlorosilane and monochlorosilane just varying the operative conditions. Initially, we took as reference point, the design proposed by Xun Huang et al. [11] which is only to produce silane. Further, a sensibility analysis study was performed (see Table 2 and Fig. 2) to find those design variables to reach a purity of 99.5% (%mol). After that, several study similar to the first sensibility analysis was carried out. Those studies had as objective both, to guarantee the lower energetic consumption and to find all appropriate parameters such as: total stages, reactive stages, feed stage, hold up, operative pressure, reflux ratio, reboiler heat duty and son, to produce dichlorosilane and monochlorosilane with 99.5%(%mol) of purity (see Table 2 and Fig. 2).

Once it was possible to design every single column separately, the consequently goal was to design a single column which let us to manufacturing our three interest components just varying the operative conditions (reflux ratio, reboiler heat duty, pressure and so on). Note, the general methodology was to compare those variables values among three designs and to keep the highest value, in other words we kept the highest amount of total stages (selected form the dichlorosilane design), the highest value of hold up (selected from the monochlorosilane design) and so on. For the heat duty was varied considering two constrains, the first one related to supply the necessary energy to promote all reactions, and the second one to guarantee that reactive zone temperature does not exceed the thermal resistance of the catalyst (100 °C) [11]. Under this perspective Fig. 3 shows the temperature along RD column, seeing that the temperature profile does not exceed 100 °C in the reaction zone. The parameters that were obtained are considered suitable for the RD column. This heat duty ensures enough energy for all reactions. In the three production cases, the same reaction stages were necessary.

Evidently, this multitasking column is over designed and consequently it is not possible to guarantee the lower heat duty consumption when we produce two of the three desired components. However note this is a preliminary proposal whose goal is to show the feasibility of a single column producing different components just varying the operative conditions.

Table 3 shows the adequate parameters to design a single column which produce our three interest components, we call it the multitasking reactive distillation column.

The entire design of the multitasking reactive distillation column was performed using the Aspen Plus process simulator. The RadFrac module was chosen to consider the complete set of MESH equations. Also, a set of chemical reaction were considered to describe all the reactions. Besides, the Peng-Robinson method was chosen as thermodynamic method to modeling the interaction among all compounds [11]. Fig. 1 shows a complete flowchart to design the reactive distillation column.

Once the multitasking reactive column is designed, three possible operative variables (degrees of freedom) were identified, all variables set to ensure the production of the three interest products in a single reactive distillation column. To understand the

Table 2
Data for the independent design reactive distillation column for the production of silane, dichlorosilane and monochlorosilane.

Silane				
Stages	62			
Feed stage	51			
Condenser	Total			
Convergence	Standard			
Reflux ratio	Mole	63		
Distillate to feed ratio	Mole	0.25		
Pressure		5	atm	
Pressure drop per stage		500	N/sqm	
Reaction				
Start stage	Final stage			ID Reaction
21	42			R-1
Holdup				
Start stage	Final stage			Vol [cum]
21	42			0.09
Dichlorosilane				
Stages	65			
Feed stage	51			
Condenser	Total			
Convergence	Standard			
Reflux ratio	Mole	30		
Distillate to feed ratio	Mole	0.50		
Pressure		1.0	atm	
Pressure drop per stage		500	N/sqm	
Reaction				
Start stage	Final stage			ID Reaction
21	50			R-1
Holdup				
Start stage	Final stage			Vol [cum]
21	50			0.10
Monochlorosilane				
Stages	63			
Feed stage	51			
Condenser	Total			
Convergence	Standard			
Reflux ratio	Mole	68		
Distillate to feed ratio	Mole	0.3335		
Pressure		1.5	atm	
Pressure drop per stage		500	N/sqm	
Reaction				
Start stage	Final stage			ID Reaction
21	50			R-1
Holdup				
Start stage	Final stage			Vol [cum]
21	50			0.15

role of those three degrees of freedom, a parametric study was performed getting as result that the column pressure does not affect as much as the other variables, however it was possible to find a wide range of column pressure values. Furthermore, to delimitate and set a single column pressure value some calculation was performed, the total annual cost [12], the green-house gas emission [13] and a preliminary qualitative control study such the singular value decomposition (SVD) respectively.

In order to calculate the total annual cost (TAC), we used the method published by Guthrie [12]. It performs cost estimation of an industrial plant separated in units, we carried out a cost approximation of the process using Equation (7), i.e.:

$$TAC = \frac{\sum_{i=1}^{n} C_{TM,i}}{n} + \sum_{j=1}^{n} C_{ut,j} \tag{7}$$

Where TAC is the total annual cost, C_{TM} is the capital cost of the plant, n is the total number of individual units and C_{ut} is the cost of services, respectively.

To calculate the green-house gas emission, the CO_2 produced by combustion in a stoichiometric equation is described as follow:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \tag{8}$$

where x and y denote the amount of carbon, C, and hydrogen, H, present in the fuel compositions. A complete oxidation of carbon is assumed.

In the combustion of fuels, air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed. CO_2 emissions (ton/y), are related to the amount of fuel burnt, QFuel (kW), in a heating device is calculated as follow:

$$[CO_2]_{Emiss} = \left(\frac{Q_{Fuel}}{NHV}\right)\left(\frac{C\%}{100}\right) \propto \tag{9}$$

where α(=3.67) is the ratio of molar masses of CO_2 and C, while NHV (kJ/kg) represents the net heating value of a fuel with a carbon content of C% (–) [13].

The singular value decomposition technique (SVD) is an open-loop control methodology where the natural dynamic of any process is observed. The initial target is to obtain the open-loop response after disturbance of those analyzed process. The responses were obtained through the use of Aspen Dynamics. The transfer function matrices (G) were then collected for each case, and they were subjected to singular value decomposition (SVD):

$$G = V\Sigma W^H \tag{10}$$

where $\Sigma = \text{diag}\ (\sigma_{1,} \cdots, \sigma_n)$, σ_ι = singular value of $G = \lambda_i^{1/2}\ (GG^H)$; $V = (v_1,\ v_2, \ldots.)$ matrix of left singular vectors, and $W = (w_1,\ w_{2,} \ldots.)$ matrix of right singular vectors. Two parameters of interest are the minimum singular value, σ^*, and the ratio maximum to minimum singular values, or condition number:

$$\gamma^* = \sigma^{*}/\sigma^* \tag{11}$$

The minimum singular value is a measure of the invertibility of the system and represents a measure of potential problems in the system under feedback control. The condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control [14].

Once the TAC, green-house emission and SVD calculation were performed, the column pressure was selected such that a good balance among economic, environmental and preliminary dynamic results was obtained. Then, several comparative studies of the control properties in multitasking reactive column were developed. The control strategies considered are described in the next section.

3.1. Setting-up the temperature, composition and cascade controllers

In order to establish if the column can be effectively controlled during operation is necessary to carry out a control analysis and three different control methodologies were analyzed: temperature, composition and cascade (control/composition) [15]. Those three methodologies were applied to the multitasking reactive distillation column during the production of each component ensuring the operability of the column.

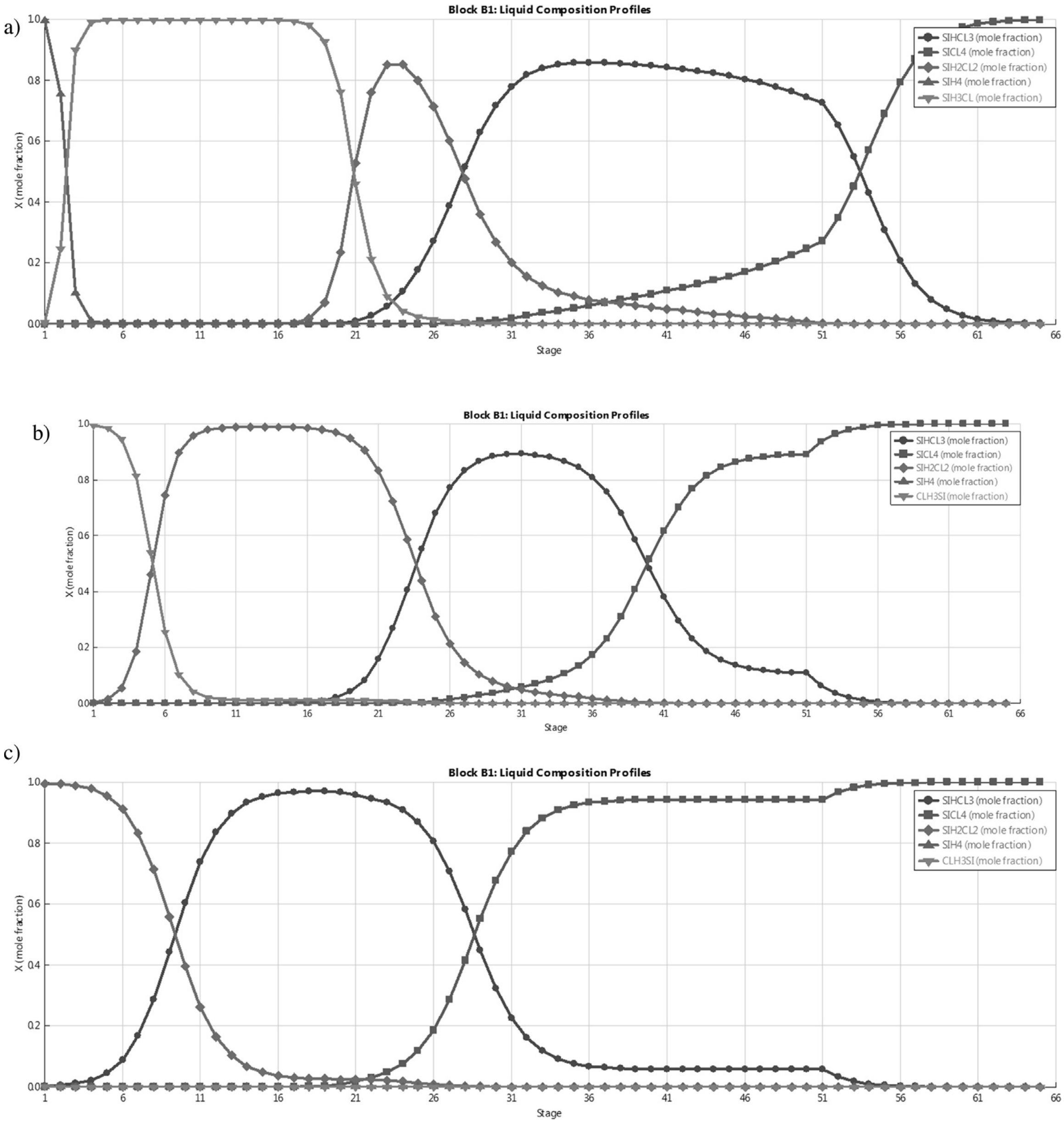

Fig. 2. Compositions profiles: a) silane, b) monochlorosilane and c) dichlorosilane.

3.1.1. Temperature controller

All control studies were performed in Aspen Plus Dynamics. In this case the initial step to design the temperature control is to find the proper tray where the controller must be placed [15]. The controller location is possible if the analyzed scheme is subject to a disturbance in the manipulated variable. The disturbance will produce a ΔT on each stage considering as initial temperature these before the disturbance. Once all ΔT are known, the controller is set where the biggest ΔT is located [16].

Once the location of the highest ΔT is done, a death time module followed by a PI controller are placed selecting the temperature as process variable. The controller action must be specified as reverse. Moreover, it must be placed a level controller on each reboiler/condenser, a pressure controller on condenser and a feed controller at entrance of the column (See Fig. 4).

After that, a positive/negative disturbance of 10% in column feed is done, later in order to evaluate the effect of impurities in the feed stream, a disturbance of −5% is applied to the component obtained as distillate flowrate. Finally, all those controllers are tuned up considering the technique proposed by Tyreus-Luyben [17].

3.1.2. Composition controller

Using a composition controller usually the measurements has bigger dead times than temperature controllers [15]. In this case, a 3 min delay on composition measurement was considered.

Initially a dead time module followed by a PI controller is set (See Fig. 5). In order to control the distillate and bottoms output composition a structure based on energy balance considerations is used, this structure yields to the called LV control structure, which use the reflux flowrate L and the vapor boilup rate V [18]. As initial step a disturbance of 10% in column feed is done, later in order to evaluate the effect of impurities in the feed stream, a disturbance of −5% is applied to the component obtained as distillate flowrate.

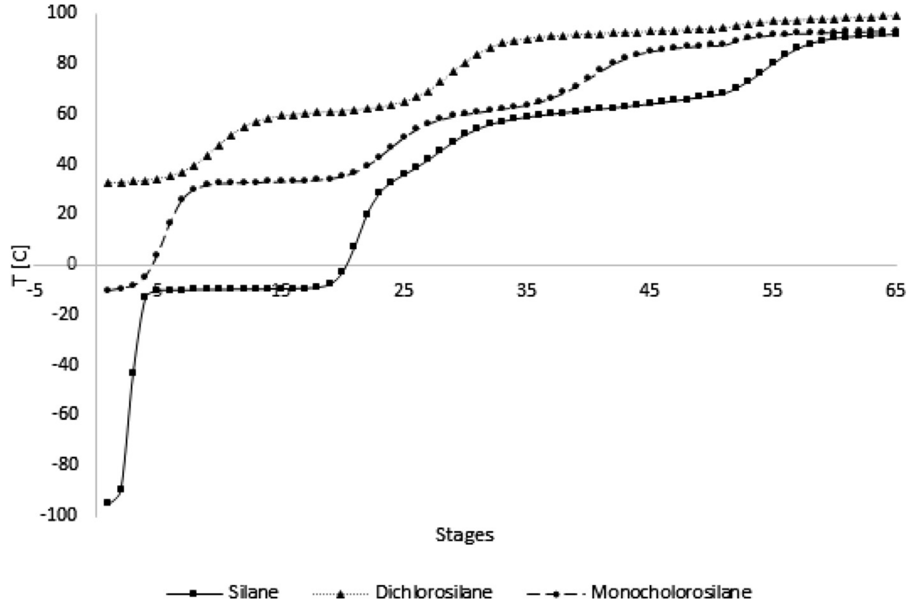

Fig. 3. Temperature profiles (silane, monochlorosilane and dichlorosilane).

Finally, all those controllers are tuned up considering the technique proposed by Tyreus-Luyben [17].

3.1.3. Cascade control

In the cascade control strategy a composition and temperature controller are used. The composition controller is considered as primary, and the temperatures is considered as secondary [15]. The temperature controller is placed following the methodology described in temperature controller section, however now the new set point is the output signal of composition controller (See Fig. 6).

The temperature controller is tuned up as has been described in composition controller section. The composition controller is retuned up from its output signal, which is now the new temperature set point. In this manner the temperature control is set automatically and the feedback control is carried out in the composition controller. All those controllers are tuned up considering the methodology proposed by Tyreus-Luyben [17].

3.2. Methodology to switch products in the RD column multitasking

A fundamental part of this study is to have a manual operation to switch from one component to other without affecting their control properties.

The control temperature strategy is chosen to perform the shift in components since this strategy is the simplest one, as it provides degrees of freedom in the output of the current distillate flow rate. This scenario is quite different than the other two strategies as well as less equipment is required for industrial operation, in example only two thermocouples in the right position and the controller in that column are needed. It is also important to note that the change among components begins with the conditions to produce dichlorosilane, since this variable values are the biggest regarding to distillate flow rate and reboiler heat duty.

The change was made by connecting a multiply between the output at top of the column and the feed flow rate, providing the proper distillate to feed ratio to produce each component

Table 3
Data for the reactive distillation column for the production of silane, dichlorosilane and monochlorosilane.

Silane					Dichlorosilane	Monochlorosilane
Stages	65					
Feed stage	51					
Condenser	Total					
Convergence	Standard					
Design specifications						
Reflux ratio	Mole	63			30	68
Distillate to feed ratio	Mole	0.25			0.50	0.3335
Pressure		2.3	atm			
Pressure drop						
Pressure drop per stage		500	N/sqm			
Reaction						
Start stage	Final stage			ID Reaction		
21	50			R-1		
			Holdup			
Start stage	Final stage			Vol cum		
21	50			0.15		

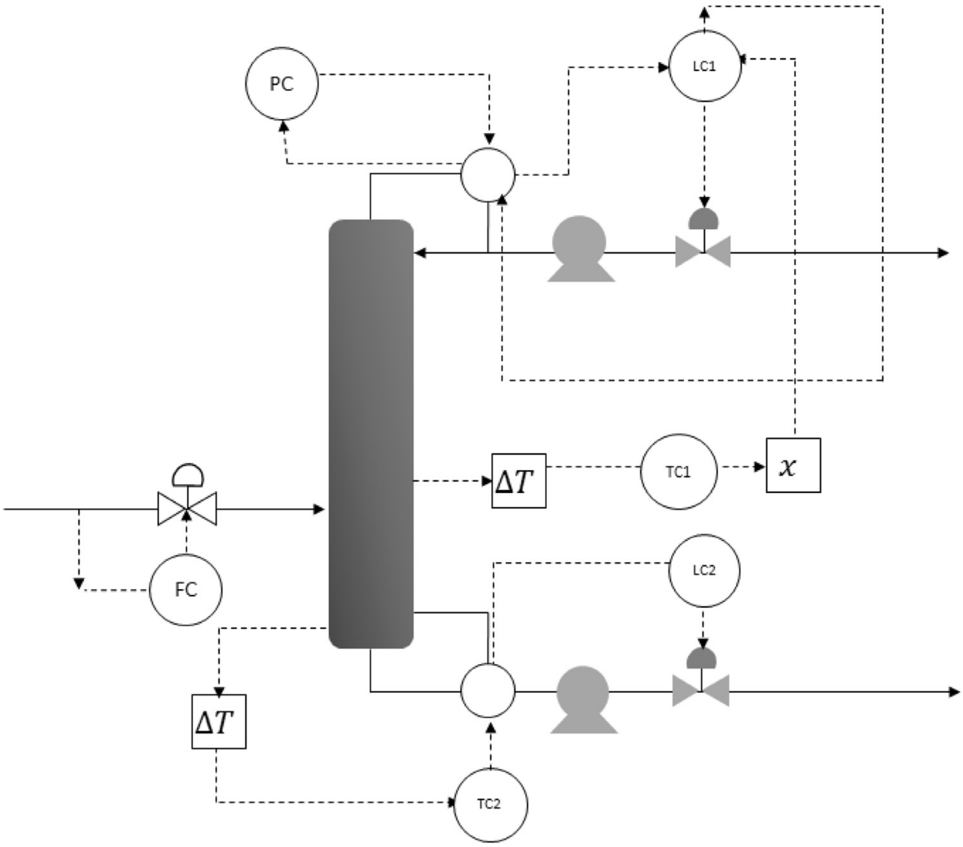

Fig. 4. Temperature controller scheme.

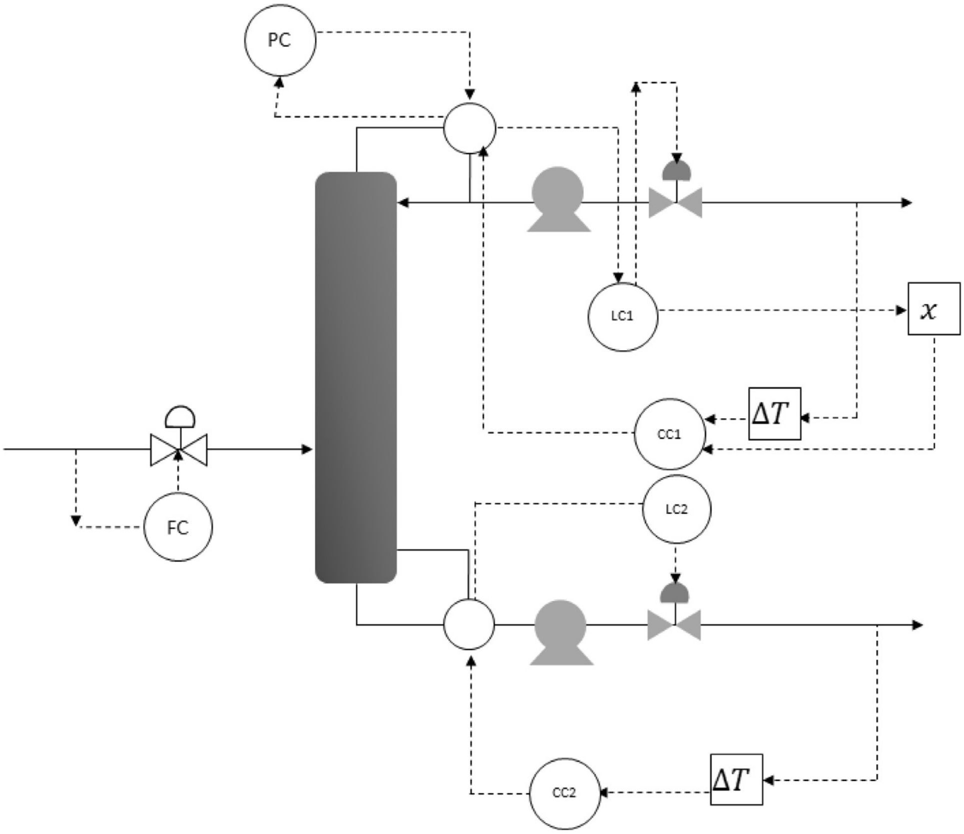

Fig. 5. Composition controller scheme.

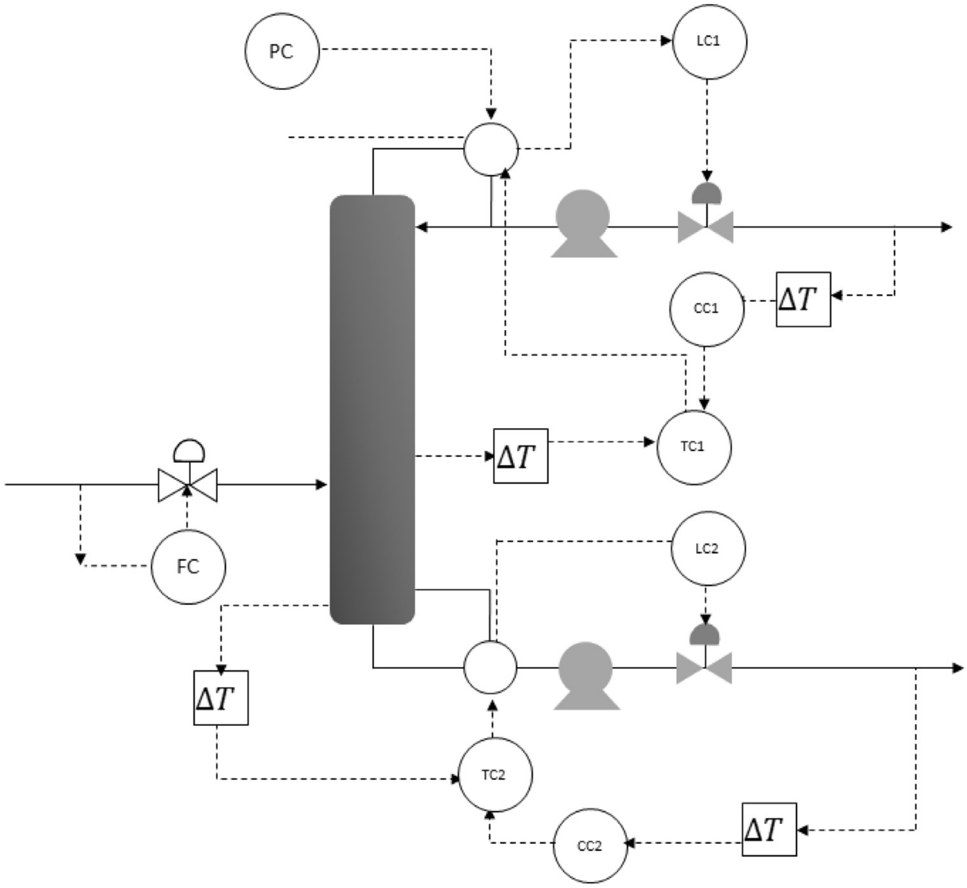

Fig. 6. Cascade controller scheme.

(Distillate to feed = 3 when dichlorosilane pass to monochlorosilane and Distillate to feed = 4 when silane pass to monochlorosilane). Once the multiply is connected, the temperature of the controlled tray is varied gradually, until obtain the necessary tray temperature to produce each desired component.

4. Results

According to the methodology section, initially three different schemes were consider to produce one single interest product in a separately way. Table 2 shows all variable values such as theoretical stages, reactive stages, reflux ratio, feed stage and column pressure of each design. Please note that in order to design a single RD column to produce the three interest component, some variables values were kept in the higher obtained values. I.e., the design to produce dichlorosilane has the highest amount of stages, so this design is considered as the reference in number of stages. It happens the same in hold up values, the biggest value in hold up was kept to design a single multitasking reactive column (See Table 3). The remaining degrees of freedom were used to define the operating conditions for obtaining each product of interest in the same column. As described above, the column pressure in a multitasking reactive distillation column would cover an operative window wherein the three components can be produced under a range of 1.7 and 2.6 atm. To facilitate the column operation in multitask mode the pressure column must be adjusted in the same value for all products. Such selection cannot be done based only on the energy requirements but also on their dynamic characteristics.

The results obtained from the TAC, green-house emission and SVD calculation will be presented in section 4.1. Note that all those analysis were very useful to set the operation variables values such as pressure in the design a single multitasking reactive distillation column which can be able to produce independently silane, monochlorosilane and dichlorosilane.

4.1. Preliminary analysis

It is well known that distillation columns have a high energy consumption. Under this perspective, energy studies were made to produce a single interest component. The data suggested that operating at 2 atm forwards generate a diminishment in TAC values and heat duty consumption when silane and monochlorosilane are produced.

Other important aspect which must be considered jointly with economic aspects is the green-house emissions produced by burning fuel to produce heat enough in a distillation column. Table 4 shows the results of the green-house emissions. It is clear that the green-house emissions are not determinant to fix the column pressure. However the best values are obtained in a range among 2 and 2.5 atm.

When the SVD analysis is made, despite this analysis was performed in a wide pressure range, is quite clear that the column pressure which produce a better dynamic behavior to produce silane, monochlorosilane and dichlorosilane is 2, 1 and 0.5 atm respectively. In distillation, pressure is commonly controlled by adjusting the condenser duty, such that the operating pressure also defines the size of the heat exchanger and cooling requirements. In order to guarantee the proper operation of the multitask column, it should be fixed in the upper value, obtained for the silane production. In this way, the column pressure could be fixed as 2 atm. However, the SVD results showed are not conclusive to fix a

Table 4
Result of CO_2 emissions for the production of silane, dichlorosilane and monochlorosilane.

Pressure (atm)	Silane CO_2 (ton/h)	Pressure (atm)	Monochlorosilane CO_2 (ton/h)	Pressure (atm)	Dichlorosilane CO_2 (ton/h)
1.70	4.92747	1.20	5.07306	0.50	3.16067
2.00	3.55637	1.50	4.07404	1.00	4.27660
2.50	2.81488	2.00	4.16240	1.50	5.47618
3.00	2.56178	2.50	4.42536	2.00	6.74180
3.50	2.45115	3.00	4.76929	2.50	8.10976
4.00	2.40081	3.20	4.92136		
4.50	2.38322				

Table 5
Operating conditions for multitasking DR column for production of silane, monochlorosilane and dichlorosilane.

Pressure (atm)	Silane		Monochlorosilane		Dichlorosilane	
	Reflux	Reboiler Duty (kW)	Reflux	Reboiler Duty (kW)	Reflux	Reboiler Duty (kW)
1.60	–	–	42.66	813.4	35.01	1146.6
1.70	106.81	987.2	42.89	815.5	36.72	1196.6
1.80	93.53	866.5	43.26	820.0	38.46	1247.3
1.90	83.68	777.1	43.72	826.3	40.23	1298.7
2.00	76.58	712.5	44.26	834.0	42.04	1350.8
2.10	71.40	665.3	44.86	842.7	43.88	1403.7
2.20	67.52	629.9	45.52	852.5	45.76	1457.5
2.30	64.56	602.7	46.23	863.2	47.67	1512.2
2.40	62.24	581.2	46.98	874.5	49.63	1568.0
2.50	60.39	564.0	47.78	886.6	51.64	1624.8
2.60	58.89	549.9	48.61	899.4	53.69	1682.9
2.70	57.65	538.1	49.48	912.7	–	–

single column pressure value since the operative range is located in a range among 0.5 and 4.5 atm.

All the results obtained in section 4.1 leaded us to set the column pressure in an average pressure values, 2.3 atm. Consequently only the reflux ratio and reboiler heat duty are left as degrees of freedom to obtain in a single multitasking reactive column all the desired products. Once the pressure column is set, varying a range of values in reboiler heat duty and reflux ratio was possible to find some values which may produce all our interest products.

Fig. 3 describes the multitasking reactive distillation column. The parameters to design this columns are shown in Table 5, as well the operation variables to produce each interest component with a purity of 99.5% (%mol). The dash cells dash [-] where found as non-feasible operation points.

4.2. Dynamic simulation

With a fixed pressure column, three control structures (Temperature, composition and cascade strategy) were analyzed separately and applied to the multitasking reactive distillation column during the production of each component. In all control structures the target was to keep the product purity at top in 99.5% (%mol) of silane, monochlorosilane and dichlorosilane. All those controllers are tuned up considering the technique proposed by Tyreus-Luyben and the results are showed in Table 6. The results of each control tests will be described below.

4.2.1. Temperature control scheme

In accord to the methodology section, where the highest ΔT on each stage was found, in such stage the controller was located. In Fig. 7 the most sensitive stages are shown. In the case of silane production, the controllers was located at stage 3 and 54. When dichlorosilane was produced the controllers was located at stage 9 and 30, and finally for monochlorosilane production the controllers was located at stage 5 and 41. Fig. 4 shows the entire control structure.

When a positive/negative disturbance of 10% was applied in the feed flow stream, the responses obtained are shown in Fig. 8. Fig. 8 shows that in despite of those disturbances, the purity in product stream was keep it in the target value. In the case of silane and tetrachlorosilane, the observed settling time was near 5 h in both cases and the settling time of temperature process was less than 5 h in both components. Moreover, Fig. 9 shows the response of product composition after the contamination in feed stream. Note that after disturbance, the composition returned to its nominal value at both top and bottom of the column.

In the case of dichlorosilane production, the temperature control strategy could keep the purity in the target value after disturbance with only a slight offset of 0.0005% mol. The observed settling time for dichlorosilane was around 4 h. Furthermore, the tetrachlorosilane purity was not affected by disturbance. However, in this case after disturbance, the composition did not return to its nominal value at the top of the column. At the bottom of the column no changes in purity were observed.

Table 6
Results of Tyreus-Luyben tuning.

Temperature				
K [%%]/T_i [min]	TC1		TC2	
Silane	5.73/19.79		2.12/9.24	
Dichlorosilane	39.51/13.20		1.07/7.92	
Monochlorosilane	1.52/19.80		2.06/7.92	
Composition				
K [%%]/T_i [min]	CC1		CC2	
Silane	6.83/15.84		134.57/9.26	
Dichlorosilane	26.91/37.68		10.02/20.05	
Monochlorosilane	4.85/58.08		471.13/100.32	
Cascade				
K [%%]/T_i [min]	TC1	TC2	CC1	CC2
Silane	0.13/9.24	2.29/7.92	6.83/15.84	37.33/21.12
Dichlorosilane	0.49/11.88	1.21/10.56	69.92/15.84	11.71/23.69
Monochlorosilane	0.03/10.56	3.82/6.60	351.37/34.32	2.76/19.58

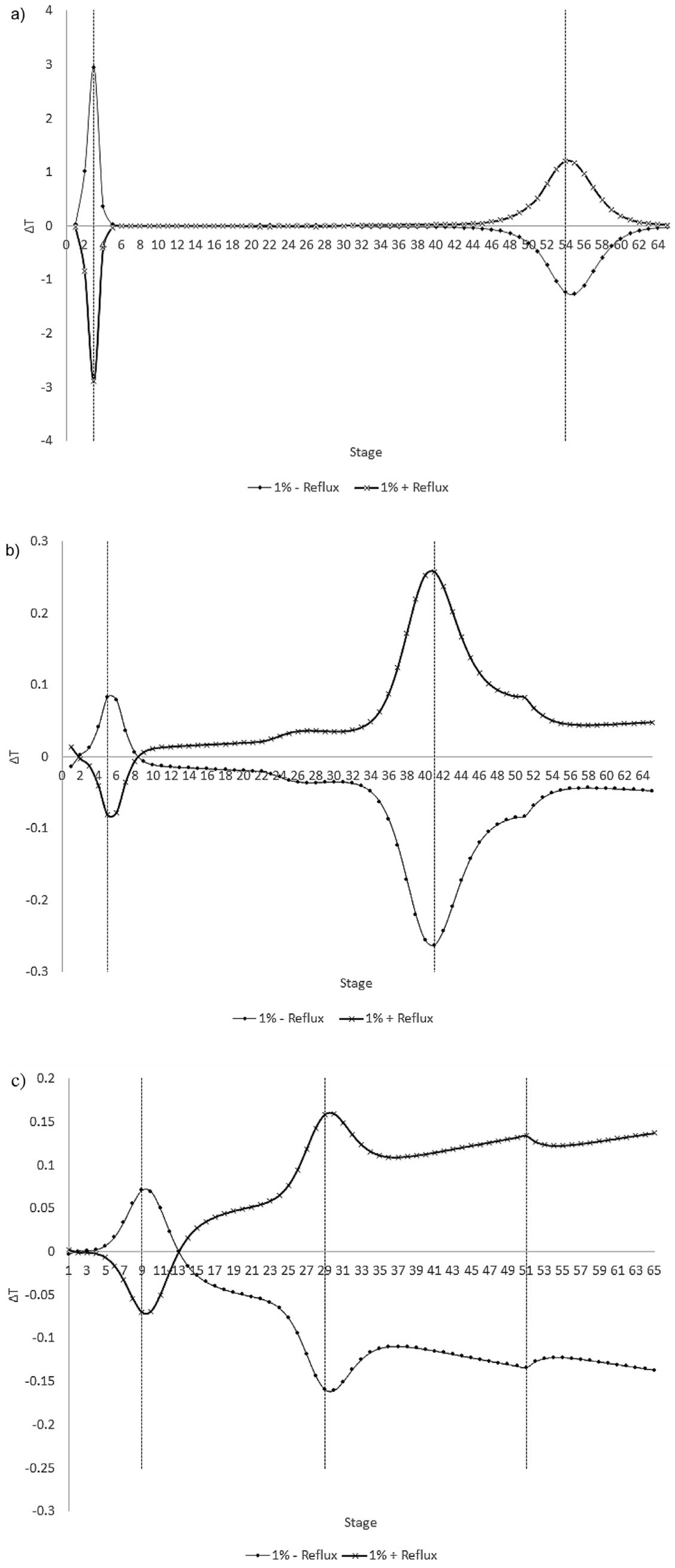

Fig. 7. Sensitivity analysis ΔT for: a) silane, b) monochlorosilane and c) dichlorosilane.

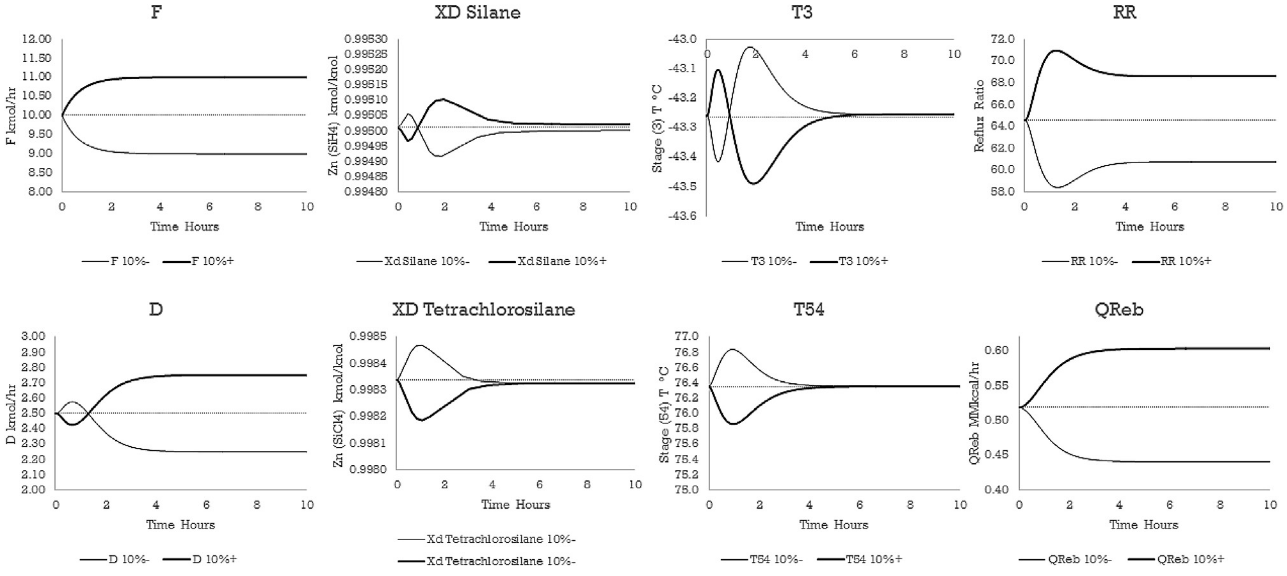

Fig. 8. Disturbance in feed flow stream (± 10% F) for silane [temperature].

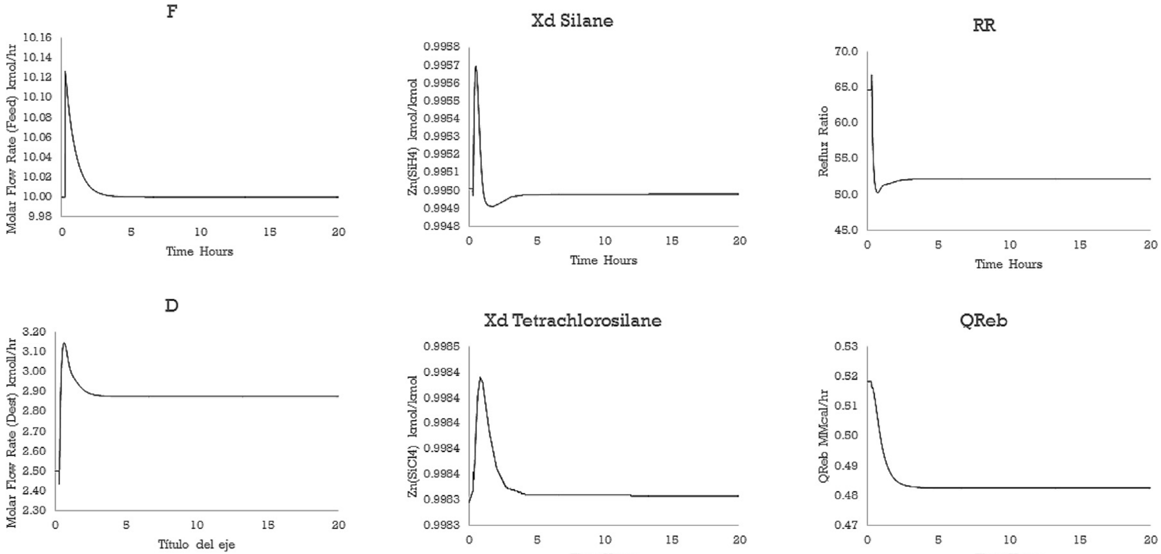

Fig. 9. Composition of feed which has an impurity of silane (SiH_4 0.05, 0.95 $SiHCl_3$) [temperature].

When monochlorosilane is produced, the temperature control strategy was capable to keep the purity in the target value after disturbance. However a similar scenario was observed in dichlorosilane production in terms of a little offset of 0.0005% mol. The settling time of monochlorosilane response was near 3 h and the tetrachlorosilane purity was not affected by disturbance. In the same way the dichlorosilane feed flow stream was subject to contamination. However, it was not feasible to return the purity to its nominal value. At the bottom of the column the tetrachlorosilane purity did not show any change.

Very important to notice that the temperature control strategy resulted to be a feasible alternative to perform a switch among desired components since it was possible to stabilize all components temperature.

4.2.2. Composition control scheme

As in temperature control study the multitasking column was subjected to a positive/negative disturbance of 10% in feed flow stream. Fig. 10 shows that is totally possible to control both silane and tetrachlorosilane purities in stream products despite big disturbances. The settling time in both cases are around 4 h. However under this strategy a higher overshot in dynamic response is observed in comparison with temperature control strategy. Moreover, Fig. 11 shows the response of product composition after the contamination in feed stream. It is clear that after disturbance, the composition returned to its nominal value at both top and bottom of the column.

Analyzing under this strategy the dichlorosilane production, the dynamic responses after disturbance, in this case the settling times observed were near 2 h. The tetrachlorosilane did not show any change on composition. When the feed flowrate was contaminated with both components, dichlorosilane and silicon tetrachloride returned to its nominal purity values.

Furthermore, when monochlorosilane is produced, this control strategy as well as with other components the purity response was controlled with settling times near 5 h in both components

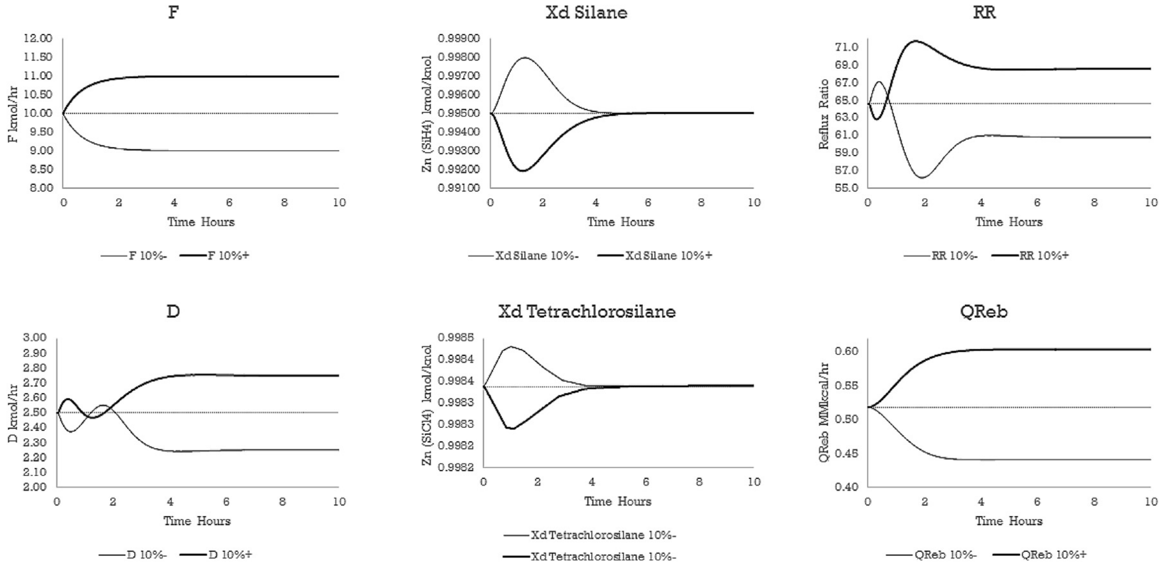

Fig. 10. Disturbance in feed flow stream (± 10% F) for silane [composition].

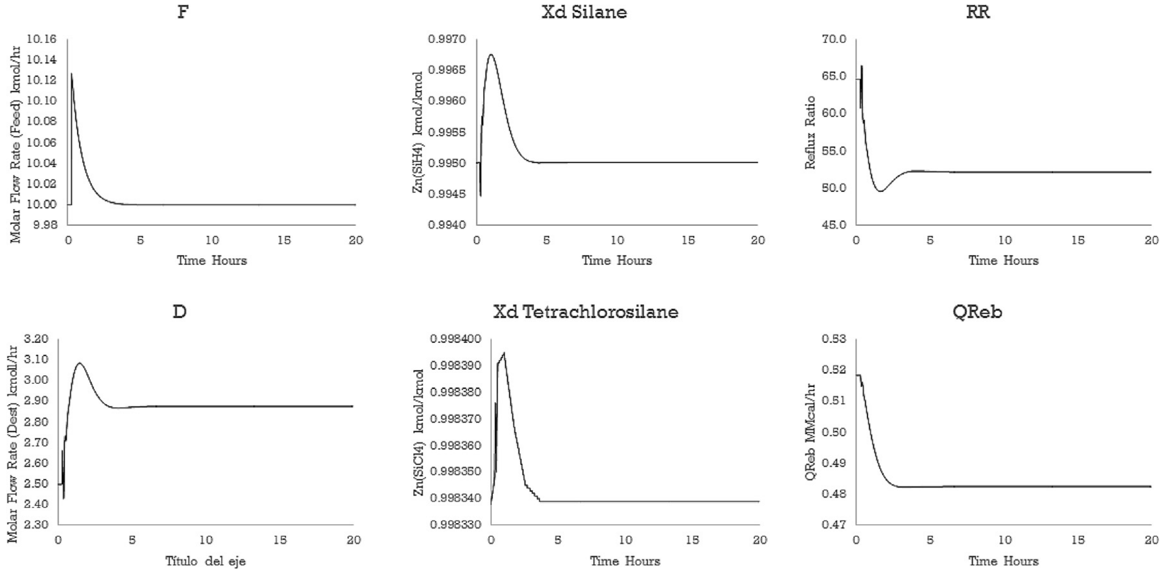

Fig. 11. Composition of feed which has an impurity of silane (SiH_4 0.05, 0.95 $SiHCl_3$) [composition].

monochlorosilane and tetrachlorosilane. After feed flowrate contamination the purity returned to the nominal purity in both top and bottom of the column. Under this strategy was possible to stabilize all composition at top and bottom when all silanes of interest are produced.

4.2.3. Cascade control strategy

In order to keep the product purity under a stricter scenario, a cascade control (temperature/composition) strategy was used. Fig. 7 show the most sensitive stages as has been described in temperature control strategy. Fig. 6 shows the complete cascade control structure.

As in previous situations, a positive/negative disturbance in 10% in the feed flow rate was considered. Fig. 12 show how all responses returned to their nominal values despite those big disturbances. Moreover, Fig. 12 shows the response at top and bottom of silane and tetrachlorosilane, both responses obtained after a disturbance in feed stream. In silane production the settling time was around 7 h, much longer in comparison with temperature and composition control strategies. The settling time observed in tetrachlorosilane response was near 6 h, however less overshot was observed in comparison with other strategies. On the other hand, Fig. 13 shows the responses after contamination in feed flowrate and it can be seen that silane purity response returned to its nominal point at top of the column. In tetrachlorosilane purity, no changes were observed.

As in the other case, it was possible to stabilize the dichlorosilane production with settling times near 10 h. In tetrachlorosilane production, no changes were observed in purity response. The responses after contamination in feed flowrate and dichlorosilane purity response returned to its nominal point at top of the column.

When monochlorosilane production was evaluated, it was observed settling time after disturbances near 10 h. In tetrachlorosilane production, no changes in purities after disturbance were observed. In the same way, after contamination in feed flowrate, it

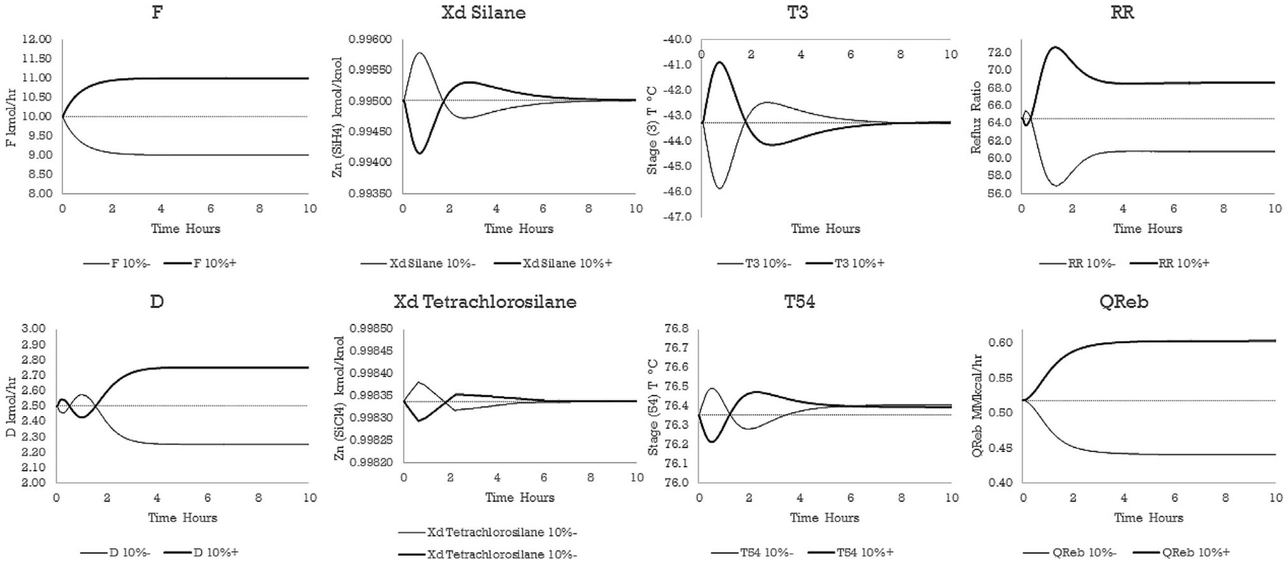

Fig. 12. Disturbance in feed flow stream (± 10% F) for silane [cascade].

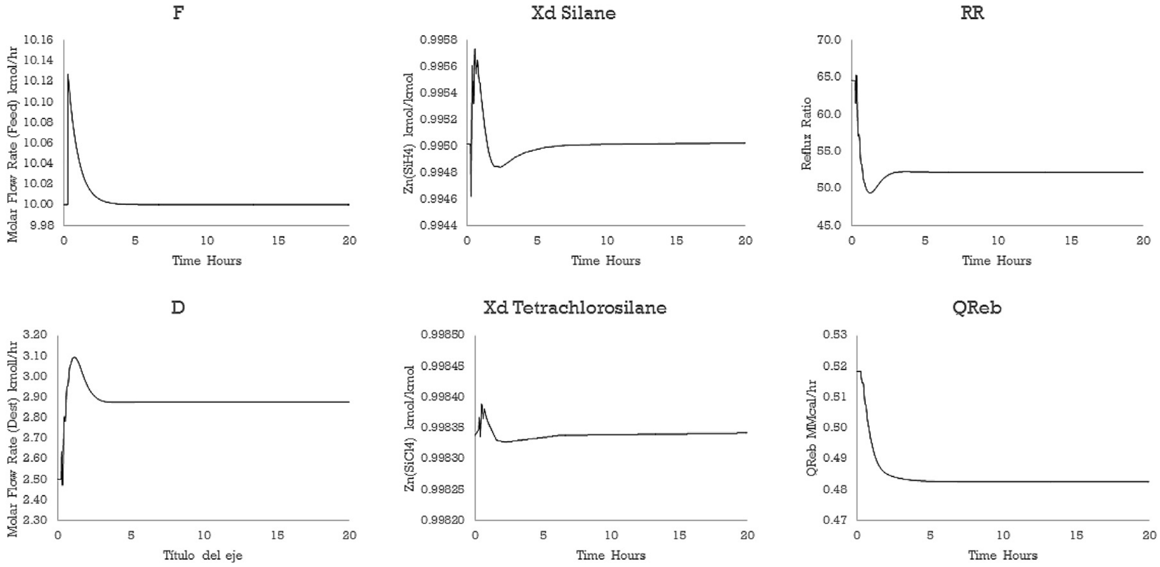

Fig. 13. Composition of feed which has an impurity of silane (SiH_4 0.05, 0.95 $SiHCl_3$) [cascade].

was possible return the composition to its nominal purity value for both products.

As general analysis, the temperature control strategy resulted to be the simplest control strategy, which is also the most used in industry since only thermocouples are required in the column controlled. Further, it was possible to control the temperature on each stage selected.

Despite a good dynamic behavior observed during composition control strategy, in industrial practice is not a good alternative since an online chromatograph is required to measure the purity of each component. However, it was possible to stabilize the composition of each silane of interest.

In cascade control case, the dynamic response and purity regulation was fast enough in comparison with other strategies. Moreover, this strategy showed the advantage of eliminate the offset among nominal values and responses after disturbances. However, this control strategy is quite complex and consequently all degrees of freedom are specified in a more rigorous way, which is not suitable to switch the production from one silane to the other.

4.3. Switch products in the RD column multitasking

Fig. 14 shows that it is possible to change the production of any component to other in the column and this took place under the strategy of temperature control. The switch of components was considered under this control strategy since this control structure is the most simple control methodology, beside industrial instrumentation requires devices relatively easy to operate, and with good dynamic performance.

We can see that it is possible to switch from one component to another with the required purity, by variation in temperature and food/distillate ratio.

It is evident from the temperatures of the stages that there is only one route by which can carry out the change component:

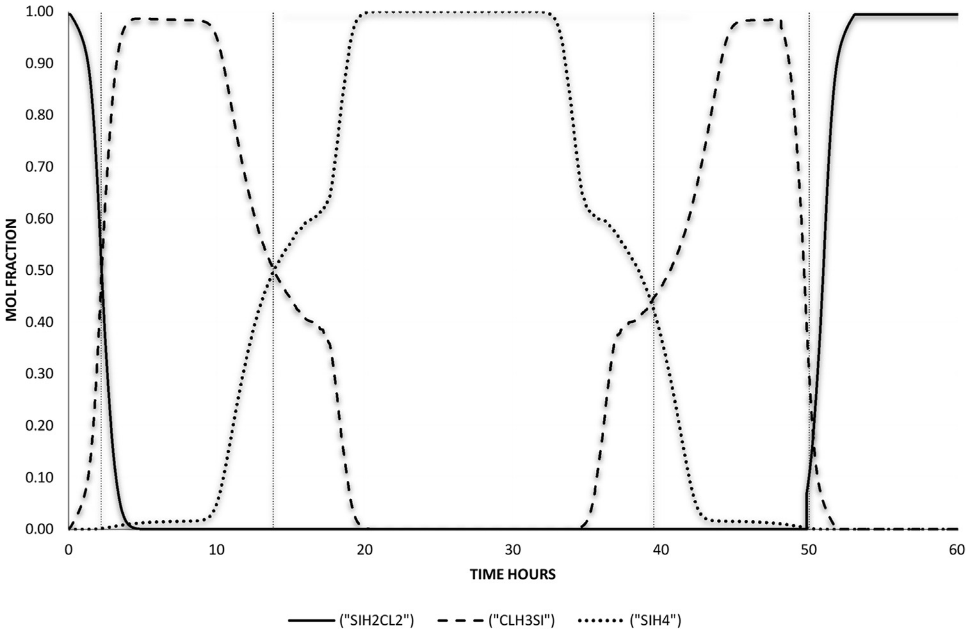

Fig. 14. Graphic switch of components in the DR column multitasking.

dichlorosilane-monochlorosilane-silane- and silane-monochlorosilane dichlorosilane, closing the cycle. The controller does not support such drastic temperature changes, so changes must be applied gradually.

5. Conclusions

In this study is showed the feasibility to produce three components (silane, dichlorosilane and monochlorosilane) using a single multitasking reactive distillation column, taking trichlorosilane as raw material. This column overcomes the traditional process since only one single unit performs the production and purification instead of two reactors and four distillation columns, also all material recycles are avoided diminishing the energy and equipment requirements. In this single unit all components were obtained with high purity, having an entire conversion of the trichlorosilane to silane and so on. This process showed an economical advantage in comparison with the conventional process where production and purification are separated operations. In this proposed design, it was possible to switch from a product to other changing only the operating variables such as column pressure, reboiler heat duty and reflux ratio. We must consider the values of the parameters in the design of the multitasking RD column do not guarantee the lower energy and the lowest operating cost for all products. To ensure it, a rigorous optimization study is necessary. After several tests the column pressure was fixed at 2.3 atm since this condition produced the best transient response for all products. Moreover, three control strategies were evaluated and the results obtained suggest that the three strategies are able to stabilize the process with similar dynamic performance. Although more complex control strategies lead to better dynamic responses, the simplest temperature control strategy, which is widely implemented in industry, guarantees the proper operation of the systems. Moreover using this strategy the multitasking scheme remains keeping some degrees of freedom for the operation of the multitasking column. Furthermore, the temperature controlling strategy was chosen to make the switch from a product to other because it is simpler since requires less expensive equipment and the structure is less complex than the composition and cascade control strategies.

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