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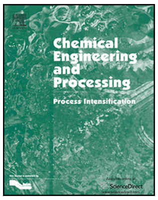

Dynamic behavior of a multi-tasking reactive distillation column for production of silane, dichlorosilane and monochlorosilane

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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