

DEVELOPMENT AND ECONOMIC EVALUATION OF A REACTIVE DISTILLATION PROCESS FOR SILANE PRODUCTION

Dirk Müller, Georg Ronge, Johannes-Peter Schäfer, Hans-Joachim Leimkühler

Bayer AG, D-51368 Leverkusen

Abstract

The growing importance of photovoltaic applications leads to an increasing demand for silane as an intermediate product for the synthesis of high purity, solar grade silicon. One important method to produce silane is the redistribution of trichlorosilane via dichlorosilane and monochlorosilane to silane and silicon tetrachloride. Conventional redistribution processes, however, require high energy costs as well as high investment costs. The reason is, that extremely high recycle rates are necessary due to equilibrium limitations of the redistribution reactions. In this paper a reactive distillation process for silane production is considered. All redistribution reactions are carried out in one single reactive distillation column replacing 2 reactors and multiple columns as in conventional processes. In this way the estimated overall production costs are reduced by approximately 46 %.

Keywords: Reactive Distillation; Trichlorosilane; Silane; Silicon; Redistribution; Dismutation

INTRODUCTION

The growing importance of photovoltaic applications leads to an increasing demand for solar grade silicon. It is expected that the photovoltaic industry grows more than 15 % per year [1].

Today, the photovoltaic industry mainly uses silicon provided by the electronic industry. In particular, off spec silicon not matching the electronic grade specifications is used. Assuming that the amount of available off spec silicon will approximately remain constant there will be an increasing demand for additional pure silicon. Figure 1 shows that the expected additional demand will approach 5000 t in 2010 and 7500 t in 2015 [1]. These figures motivate the development of economically attractive processes for the production of solar grade silicon. Please note, that these figures already include the growing importance of the thin film technology for the production of solar cells. It is assumed that the importance of thin film technology will approach 10 % of the market in 2010 and 30 % of the market in 2015.

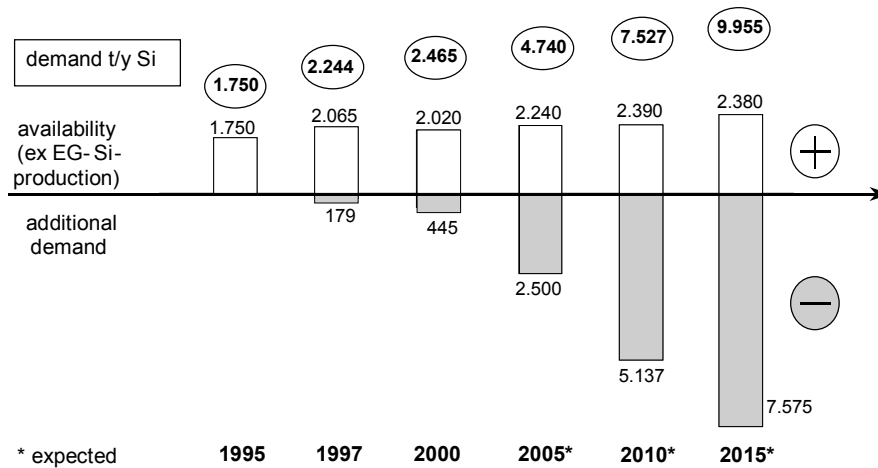
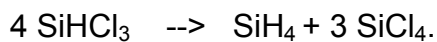


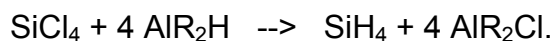
Fig. 1: Solar grade silicon: availability and demand 1995 – 2015 [1].

For the production of pure silicon a number of different processes has been proposed. In general, these processes include the production of silane which is then decomposed to silicon and hydrogen. For the synthesis of silane different routes are used, for example:

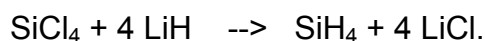
- Trichlorosilane is converted to silane and silicon tetrachloride [2]:



- Silicon tetrachloride or another polyhalosilane is reduced with an alkyl aluminum hydride, e.g. dimethyl aluminum hydride or diethyl aluminum hydride [3]:



- Lithium hydride is treated with silicon tetrachloride, the reaction medium being molten lithium chloride and potassium chloride [4, 5, 6]:



In this paper, silane synthesis via the first reaction, i.e. redistribution of trichlorosilane is considered because trichlorosilane is the most important precursor to produce pure silicon. It is obtained from metallurgical-grade silicon or another silicon solid. Figure 2 shows the corresponding overall structure of the whole silicon process from metallurgical-grade silicon to solar-grade silicon [1]. The process includes four major steps: In the first step metallurgical silicon, recycled silicon tetrachloride and hydrogen are used to produce trichlorosilane. In the second step trichlorosilane is converted to silane and silicon tetrachloride by redistribution reactions. In the third step silane is purified, and finally silane is decomposed to silicon and hydrogen. In the following the paper focuses on the second step of the process, i.e. the redistribution of trichlorosilane to silane and silicon tetrachloride. This reaction comprises three redistribution steps.

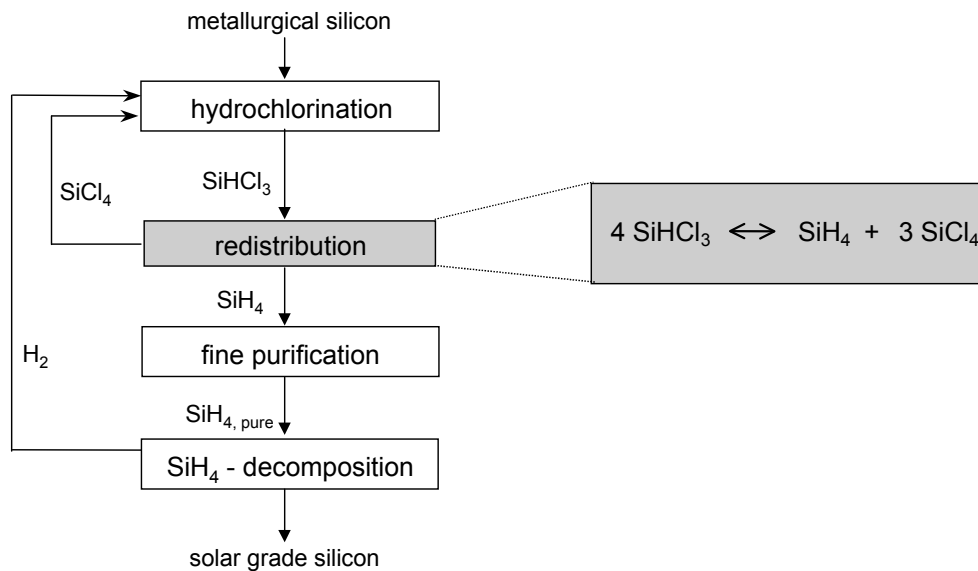
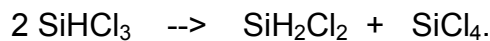


Fig. 2: Structure of the silicon process via trichlorosilane redistribution.

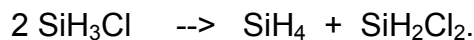
First, trichlorosilane is converted to dichlorosilane and silicon tetrachloride:



Second, dichlorosilane is converted to monochlorosilane and trichlorosilane:



Third, monochlorosilane is converted to silane and dichlorosilane:



CONVENTIONAL SILANE PRODUCTION

Conventional silane processes consist of two reactors and multiple distillation columns [7, 8, 9]. Figure 3 shows a typical process which may serve as an improvable base case. Here, a first reactor is used for the first redistribution reaction from trichlorosilane to dichlorosilane and a second reactor combines both following redistribution reactions. Furthermore, four distillations columns are used to separate the products from reactants, which are then recycled.

Such conventional processes have the disadvantage that extremely high recycle rates are necessary. For example, in a silicon process with a silicon capacity of 5000 t/y a recycle rate of 94 t/h trichlorosilane is required. Such recycle rates cause high equipment and high energy costs.

The necessity for high recycle rates in conventional silane processes arises from unfavourable chemical equilibria. Figure 4 shows the equilibrium conversions for all

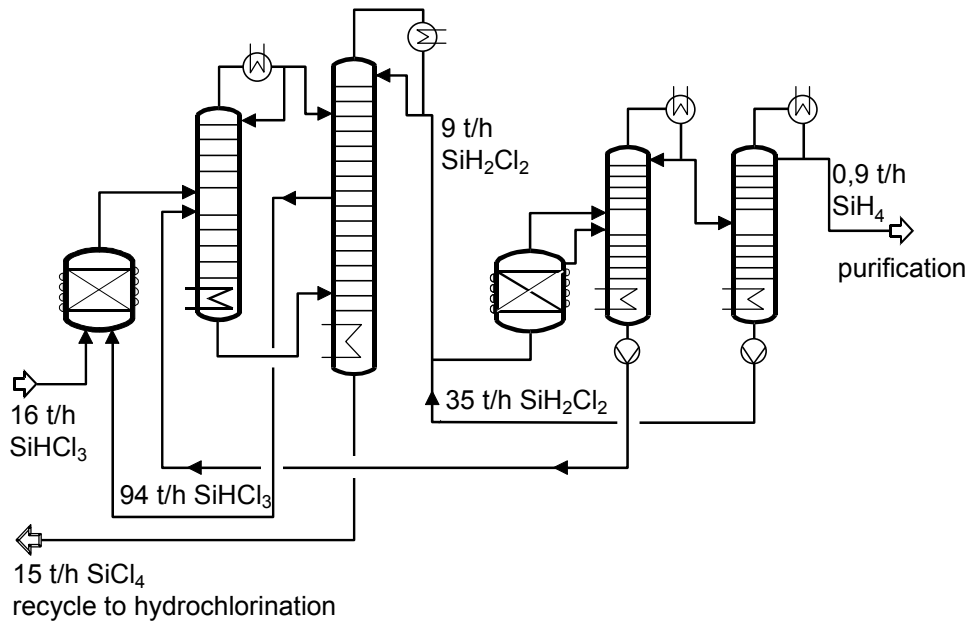
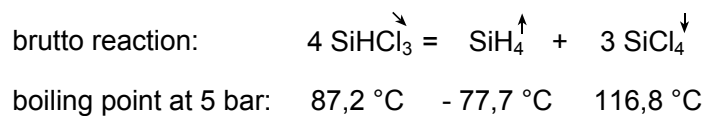


Fig. 3: Conventional process for silane production.



chemical equilibria at 80 °C

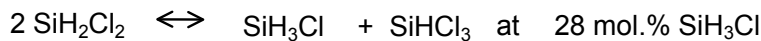
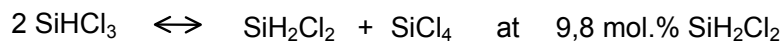


Fig. 4: Chemical equilibria of chlorosilane redistribution reactions.

redistribution reactions. The equilibrium of the first reaction is at about 10 mol-% dichlorosilane, the equilibrium of the second reaction is at about 28 mol-% monochlorosilane, and the third reaction yields about 36 mol-% silane. These equilibrium conversions are unfavourable. Large amounts of reactants remain in the product streams leaving the reactor. They are therefore the reason for high recycle rates necessary in conventional silane processes.

REACTIVE DISTILLATION FOR SILANE PRODUCTION

Reactive distillation is a technology particularly attractive for equilibrium limited reactions like trichlorosilane redistribution. The basic idea is to combine reaction and distillation in one column. The integration has a number of general advantages [10]:

- higher conversion for reactions limited by chemical equilibrium,
- improved selectivity for systems with side reactions,
- the possibility to circumvent azeotropes by chemical conversion,
- the use of heat from exothermic reactions directly for separation,
- avoidance of hot spots by the vaporization of liquid.

Due to these general advantages a high economic benefit is expected for many reactive distillation applications. An impressive example of the benefits of reactive distillation is the production of methyl acetate [11, 12]. Concerning silane production a high benefit can be expected from the first point, i.e. from a significant improvement of the chemical conversions. Here, the idea is to apply reactive distillation in a way that only products are removed from the reactive zone whereas reactants remain within the reactive zone for further reaction. In this way high recycle rates of unreacted reactants can be avoided. Consequently, equipment and energy costs can be reduced. Therefore, reactive distillation should be an attractive process for chlorosilane redistribution reactions.

However, against these advantages of reactive distillation there are a number of possible constraints and difficulties [10]. General limitations and their consequences for silane production are the following:

- First, the relative volatility of the components must be checked. The reactants and products must have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone. In figure 4 the boiling points of silane, trichlorosilane and silicon tetrachloride are given for a pressure of 5 bar. The boiling point differences are very large. Therefore, separation by distillation is in these cases very simple. Thus, the relative volatility is favourable for applying reactive distillation.
- Further, it is important that high reaction rates can be obtained at distillation conditions. Here it is important to note, that the redistribution reactions must be carried out in a small temperature range. If the temperature is too low, then the reactions are slow and high residence times are required. Too high temperatures cause undesired catalyst deactivation rates. The optimum temperature range depends on the catalyst. Experimental data [7, 13] show that reasonable reaction rates are achieved at temperatures between 30 °C and 80 °C, which can easily be established in distillation columns operated between 1 and 10 bars.
- Then, there are residence time constraints: If the residence time for the reaction is long, a large column size and large hold-ups will be needed and it may be more economic to use a conventional reactor-separator arrangement. From available experimental data [7, 13] it is expected that it is possible to establish the required residence time by using suitable column internals. However, a detailed column design requires kinetic data and thus a kinetic study for the chosen catalyst at distillation conditions.
- A final constraint may result from a quick catalyst deactivation. The use of some column internals for reactive distillation such as catalytic packings with no possibility to replace the catalyst may not be economical.

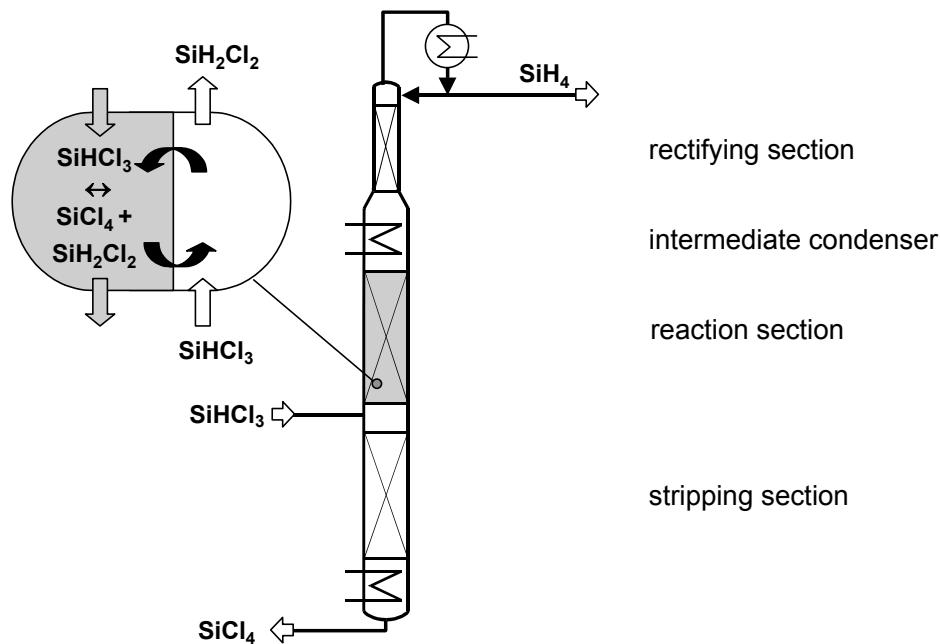


Fig. 5: Reactive distillation process for silane production.

Considering all these points reactive distillation is a technically possible and attractive process for silane production. A first reactive distillation process for chlorosilane redistribution reactions in a bed of a solid ion exchange resin has been proposed by Bakay [2]. Yamada et al. [14] proposed a process using dimethylamine or diethylamine as homogeneous catalysts, which are middle boiling components and thus remaining inside the column. Inoue [15] developed a reactive distillation process for dichlorosilane redistribution to silane, trichlorosilane and silicon tetrachloride. Matthes et al. [16] and Frings [17] published a distillation process with a coupled reactor for trichlorosilane redistribution to dichlorosilane and silicon tetrachloride.

In the following a reactive distillation process combining all three redistribution reactions in one single column with an intermediate condenser is presented. Figure 5 shows a simplified flowsheet of the reaction column including three sections: one reaction sections in the middle of the column and two separation sections below and above. Trichlorosilane is supplied to the reaction section where the first redistribution reaction is carried out. The products are dichlorosilane and silicon tetrachloride. Silicon tetrachloride - the high boiling component – is purified in the stripping section below and taken off as bottoms product. Dichlorosilane is further converted within the upper part of the reaction section, first to monochlorosilane and then to silane. Finally the desired product silane – which is the lowest boiling component of the system – is purified in the rectifying section and taken off as distillate.

An important point of the process is the use of an intermediate condenser. The intermediate condenser already takes off most of the heat of condensation – compared to the column top temperatures at a significant higher temperature level. This is possible as within the rectifying section only a small reflux is necessary. Furthermore, it is also possible to install the intermediate condenser between two reaction zones so that trichlorosilane redistribution is performed in a lower reaction zone whereas dichlorosilane and monochlorosilane redistribution are performed in an

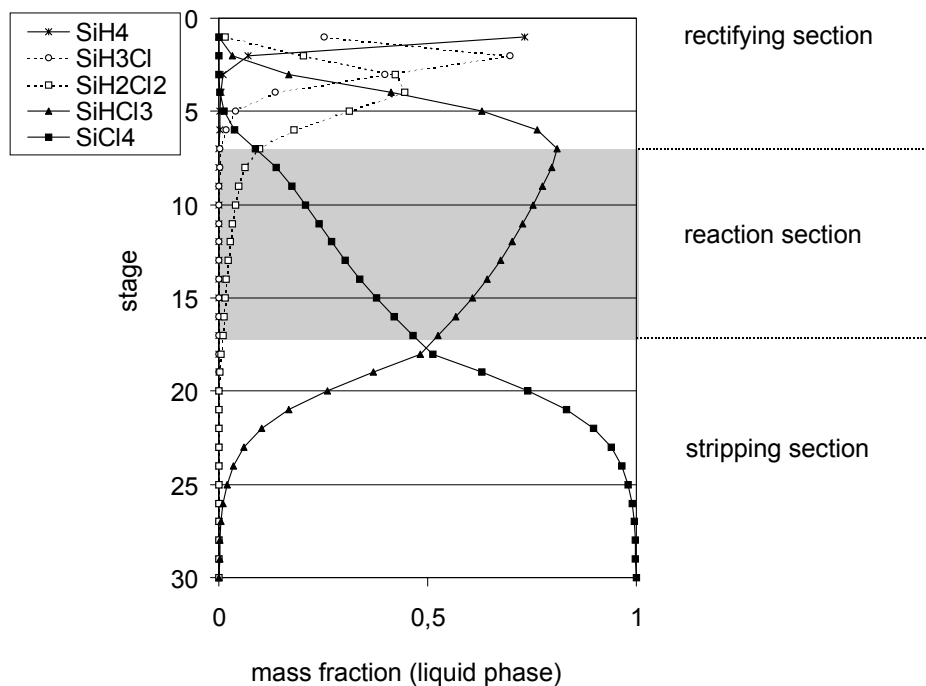


Fig. 6: Calculated composition profile of the reactive distillation column.

upper reaction zone. In any case, the use of an intermediate condenser has a significant influence on the process economics.

In figure 6 a calculated composition profile of the liquid phase within the reaction column is presented. The simulation results are based on an equilibrium stage model neglecting reaction kinetics. The figure shows the purification of the product silane at the top of the column as well as the purification of silicon tetrachloride at the bottom of the column. The figure further shows that all intermediate boiling components – i.e. trichlorosilane, dichlorosilane and monochlorosilane - reach high concentrations at different heights of the column. The intermediate condenser on stage 6 has a significant effect on the profiles as trichlorosilane is kept away from the rectifying section.

The simulation presented in figure 6 has been carried out for a bottoms product purity of 99 weight % silicon tetrachloride and a distillate purity of 75 weight % silane. Please note, that these simulations do not consider reactions kinetics. In general, kinetic data for chlorosilane redistribution as reported in [7, 13] confirm the feasibility of the reactive distillation process presented here. But more detailed simulation studies with a kinetic model are necessary to determine the amount of intermediates within the column such as monochlorosilane. If more monochlorosilane is formed as found within the simulation studies presented here then a higher demand is necessary for the purification of the product silane. For this purpose, the general reactive distillation concept presented above can be extended by a coupled silane purification column as shown in figure 7. Here, a second column is used to separate the product silane from monochlorosilane and dichlorosilane, which are then recycled

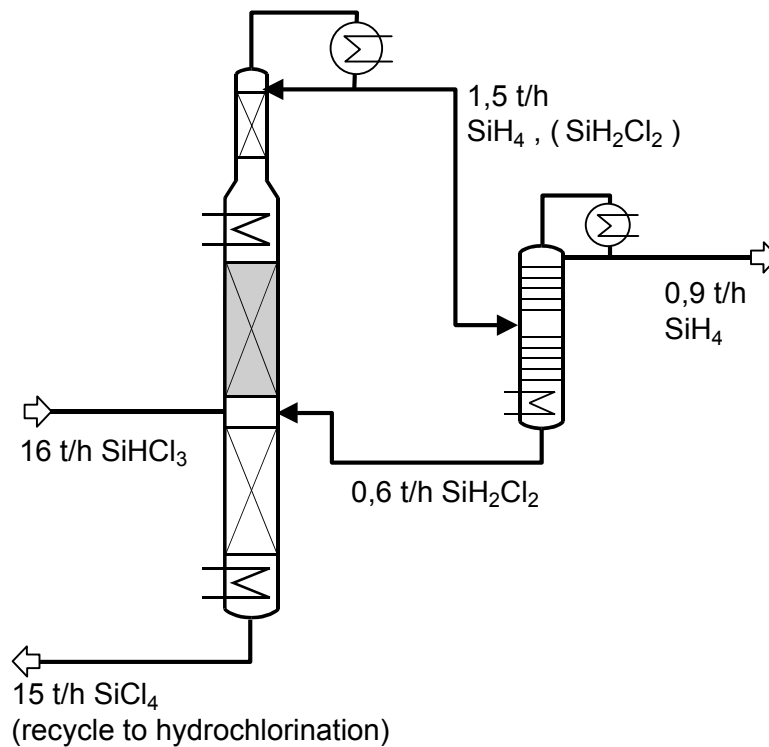


Fig. 7: Extended reactive distillation process with a coupled silane purification column.

to the reaction column. By using the second column more flexibility for additional separation is achieved.

The reactive distillation concept as a technical plant for silane production requires suitable column internals. As the chlorosilane redistribution reactions are heterogeneously catalyzed, packings may be used where catalyst particles are enclosed in wire gauze envelopes (e.g. Montz MULTIPAK, Sulzer KATAPAK SP) or sandwiched between corrugated sheets of wire gauze (Sulzer KATAPAK S, Koch-Glitch KATAMAX). The most important design data concerning fluid dynamics and mass transfer can be taken from the literature [18, 19]. However, catalytic packings have the disadvantage, that it is difficult to remove and replace a deactivated catalyst. Tray concepts with catalyst envelopes, packed catalyst sections or downcomers holding catalyst particles [20, 21] should be considered as an alternative. Then standard tray design procedures [22] can be used if residence time requirements within the catalytic zones are taken into account.

The final choice of the right column internals should not only consider mass transfer and residence time requirements but also take into account catalyst deactivation rates.

ECONOMIC POTENTIAL

Figure 8 shows the estimated production costs for the reactive distillation process based on a column design for a catalytic packing. The cost data are shown in comparison with the corresponding cost data for the conventional silane process shown in figure 3. Basis is a capacity of 5000 t/y pure silicon.

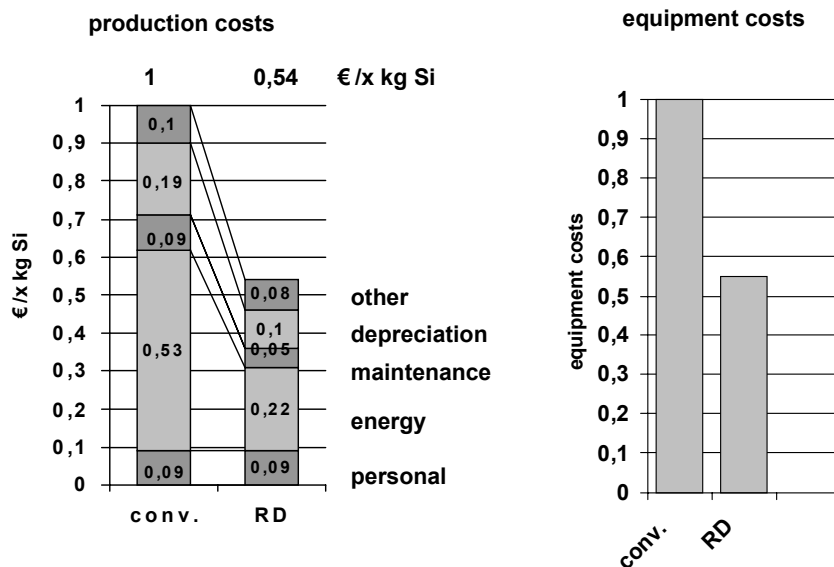


Fig. 8: Economic comparison of the reactive distillation process (Fig. 7) and the conventional process (Fig. 3) for silane production: estimated production and equipment costs.

The comparison shows that a significant cost reduction can be achieved by applying reactive distillation. There are two reasons for this cost reduction:

- The first point is, that equipment costs are reduced by 45 %. Consequently also depreciation and maintenance costs are reduced by approximately 45 %.
- The second point is, that energy costs can be reduced by 60 %.

Altogether, the cost reduction for the redistribution process is about 46 %.

CONCLUSIONS

For silane production a significant economic benefit can be derived by applying reactive distillation: 2 reactors and 4 columns can be replaced by one single reactive distillation column, if necessary coupled with one further distillation column. The estimated overall production costs of silane are reduced by approximately 46 %.

Concerning the benefit of reactive distillation technology silane production is a good example fulfilling the expectations currently expressed in many scientific papers. Therefore, this example may serve as a motivation for future research activities in the field of reactive distillation. Nevertheless, it should be noted that reactive distillation is not a technology which is optimum for all kind of chemical processes. This is indicated by the small number of industrial applications. In many cases there are significant constraints of reactive distillation. Conventional process structures are then more economic. But also in these cases economically interesting process structures are often found by considering reaction and separation simultaneously. Therefore, an integrated process development considering both reaction and separation is in many cases a key to success.

Acknowledgements

We would like to thank to H.-D. Block, S. Klein, G. Olf, U. Strauß (Bayer AG), T. Frey, N. Poth, J. Stichlmair (Technical University of München), S. Petkov, G. Brunner (Technical University of Hamburg-Harburg) and G. Schembecker (GHN Dortmund) for their significant contributions concerning this work. We are further grateful to the „Bundesministerium für Bildung und Forschung“ for partially sponsoring this work.

References

1. H.-D. Block and G. Wagner (2000). The Bayer route to low cost solar grade silicon. Proceedings of: Silicon for the Chemical Industry V, Tromsø, May 29 – June 2, 2000.
2. C. J. Bakay (1976). Process for making silane. US 3,968,199 (Union Carbide Corporation).
3. T. Iwao, Y. Toyoda, K. Wakimura, N. Kitano and M. Tanaka (1983). Process for preparing silanes. European Patent 0128962 (Mitsui Toatsu Chemicals, Inc.).
4. W. Sundermeyer (1960). Verfahren und Vorrichtung zum Hydrieren von Halogenverbindungen der Elemente der Gruppen III und IV des Periodischen Systems. DP 1080077.
5. L. M. Litz and S. A. Ring (1964). Hydrogenation of groups III, IV and V elements. US 3,163,590 (Union Carbide Corporation).
6. H.-J. Klockner and M. Eschwey (1988). High-purity monosilane for the electronics industry – Synthesis, purification, characterization. Chem. Ing. Tech. 60, 11, 815-821.
7. JPL (1979). NASA, Jet Propulsion Laboratory, NASA Contract Report NASA-CR-173762, Phase III, JPL-Publication 79-81.
8. L. Coleman (1982). Process for the production of ultrahigh purity silane with recycle from separation columns. US 4,340,574 (Union Carbide Corporation).
9. W. Breneman (1983). Process for making high purity silane. DE 33 11 650 (Union Carbide Corporation).
10. R. Taylor and R. Krishna (2000). Modelling reactive distillation. Chemical Engineering Science 55, 5183-5229.
11. V. H. Agreda and L. R. Partin (1984). Reactive distillation process for the production of methyl acetate. US 4,435,595 (Eastman Kodak Company).
12. J. J. Siirola (1995). An industrial perspective on process synthesis. A.I.Ch.E. Symposium Series No. 304, 91, 222-233.

13. K. Y. Li and C. D. Huang (1988). Redistribution reaction of trichlorosilane in a fixed-bed reactor. *Ind. Eng. Chem. Res.*, 27, 1600-1606.
14. M. Yamada, S. Ishii and T. Nakajima (1984). Method for continuous production of silanes. JP 121110 (Denki Kagaku Kogyo Kabushiki Kaisha).
15. K. Inoue (1988). A simple process for the production of monosilane. JP 01317114 (Mitsui Toatsu Chemicals, Inc.).
16. R. Matthes, R. Schork, H.-J. Vahlensieck (1988). Method for the preparation of Dichlorosilane. EP 0474265 (Hüls AG).
17. A. J. Frings (2000). Continuous catalytic process for the production of dichlorosilane. *Proceedings of: Silicon for the Chemical Industry V*, Tromsø, May 29 – June 2, 2000.
18. J. Ellenberger and R. Krishna (1999). Counter-current operation of structured catalytically packed distillation columns: pressure drop, holdup and mixing. *Chem. Eng. Sci.*, 54, 1339.
19. P. Moritz and H. Hasse (1999). Fluid dynamics in reactive distillation packing KATAPAK S. *Chem. Eng. Sci.* 54, 1367-1374.
20. J.-L. Nocca, J. Leonard, J.-F. Gaillard and P. Amigues (1991). Apparatus for reactive distillation. US 5,013,407 (IFP).
21. L. S. Gordeew, M. B. Glebow and N. K. Georgiew (1997). RU 2081694.
22. J. G. Stichlmair and J. R. Fair (1998). *Distillation principles and practice*, Wiley-VCH, New York.