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A Reactive Distillation Process for Ultrapure Silane Production from Trichlorosilane

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Highlights

- Reactive distillation is particularly suited to the TCS disproportionation system.
- Pursuing a silane purity over 99% at RD overhead was uneconomical.
- The optimal RD column configuration was to insert a single intermediate condenser.
- The optimal overhead and intermediate condensing temperatures were determined.

1. Introduction

Silane is an excellent starting material for manufacturing electronic-grade (EG) and solar-grade (SoG) polysilicon, and also a kind of electronic specialty gas itself that is configured for specific manufacturing processed of integrated circuits (IC) and other semiconductor devices. The increasingly growing market demand calls for efficient and low-cost solutions to ultrapure silane over 99.9999%.

The silane can be formed according to the following reactions:

$Si+H_2+3SiCl_4=4HSiCl_3$ (1); $4HSiCl_3=3SiCl_4+SiH_4$ (2), and,

The second reaction is the overall of the consecutive three reactions:

$2HSiCl_3=SiCl_4+H_2SiCl_2$ (2-1), $2H_2SiCl_2=HSiCl_3+H_3SiCl$ (2-2), and $2H_3SiCl=H_2SiCl_2+SiH_4$ (2-3).

These reactions are characterized by the conversion limit in thermodynamics, with the final equilibrium conversion of Eq.(2) is less than 0.2%, which would present no practical significance. In spite of this, the species among the reaction system show big difference in their boiling points, which make the distillation reactor or reactive distillation column useful.

We have been working on this topic for 10 years from the metallurgical silicon (MG-Si) to ultrapure silane. In an early phase, experimental investigations were carried out concerning the chemical kinetics and reaction mechanisms of the co-hydrogenation of silicon tetrachloride and MG-Si, and the catalytic disproportionation of trichlorosilane ($SiHCl_3$, TCS). We developed a novel scheme facilitated by reactive distillation (RD) technology (FIG. 1) to overcome the thermodynamic limit by continuous removal of products from the reaction zone, achieving nearly complete conversion of TCS [1–3]. On the basis of laboratory experiments, we conducted a pilot test with silane production capacity of 600 tons per year. This test achieved success after its initial commissioning, and the purity of final product reached 99.99999% with a TCS conversion above 98%. Recently, we are carrying out further optimization of the process with an extended simulation scheme. The most economical purity of crude silane at the RD column overhead and the optimal intermediate condensing conditions were determined via comparative simulations and economic analysis in greater detail [4].

2. Methods

Due to the lack of space, only process simulation study was included below, which was conducted using Aspen Plus. Utility cost was estimated based on a two-factor equation proposed by Ulrich and Vasudevan [5]. We would like to make a general introduction of our work at the congress covering both experiments and calculations.

3. Results and discussion

The cost for the heating steam of RD reboiler accounts for an overwhelming proportion of total operating cost (COP), and shows a slight decline with lowering the overhead condensing temperature, while the cost for crude silane purification unit never reaches a dominating level. Attributing to deeper refrigeration requirement, rising cost for RD overhead refrigerant is evident, which is responsible for the COP increase. With increasing the overhead condensing temperature, the cost for the intermediate condenser shows gradual increase which results in a reversal of COP above -40 °C. Further simulation cases were also conducted to determine the appropriate number of intermediate condensers and the optimal condensing temperature. Analysis of the fluid flowrates and reaction efficiency well explicated the cost dependency on the RD column configuration.

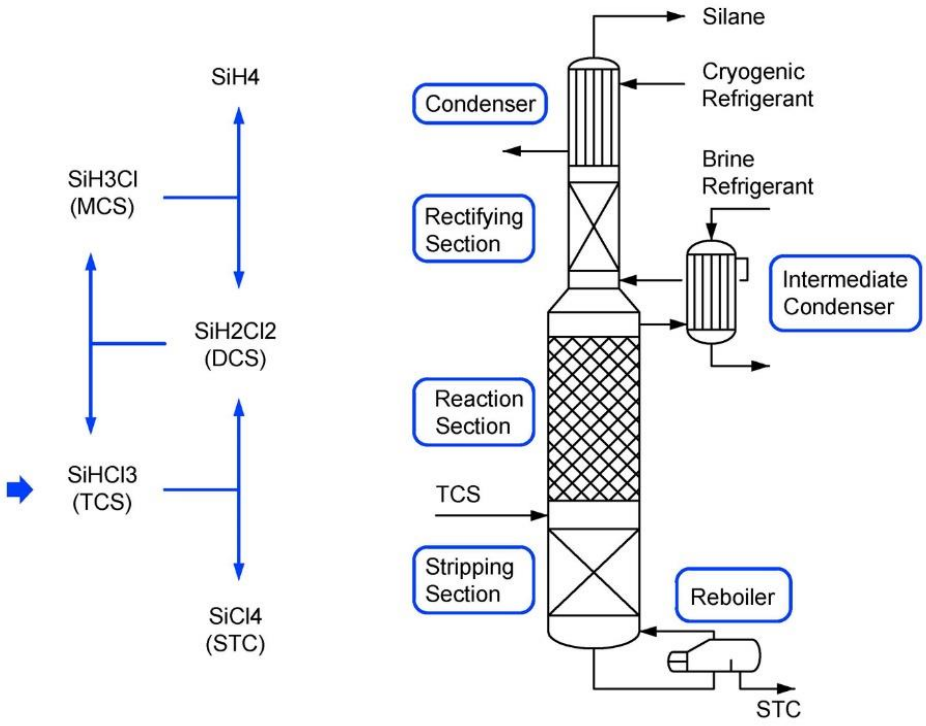

Figure 1. RD aided TCS disproportionation. Left: Basic chemistry; Right: RD column.

4. Conclusions

Inserting two intermediate condensers was also unnecessary because it would interfere the reaction and eventually increase the overall operation cost. The optimal configuration was to insert a single intermediate condenser in between the reaction and rectifying sections, with an overhead silane content in the order of 82% at an overhead condensing temperature about –40 °C and an intermediate condensing temperature in the range of 7–10 °C.

References

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Keywords
Silane; Reactive distillation; Trichlorosilane disproportionation; Aspen Plus.