CHLOROSILANE DISPROPORTIONATION: MODELING A DENAL-TYPE REACTOR

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Abstract

Content

This document follows a previous note on the modeling of a mono-chamber disproportionation reactor of uniform temperature (ALL R1710). This work reviews previous results, and extends the modeling to an actual distillative multi-plateau disproportionation reactor (Denal-type reactor).

Context

This is documented as a R&D support to silane production activities, and firstly targets the acquisition of chlorosilane disproportionation know-how. This work helps to understand the physical reasons that have led to Denal technological choices, and offers the basic understanding that is necessary to set the operating parameters of the future R&D set-up(s).

Summary

The chemical concentration within a disproportionation reactor can be estimated from the minimization of Gibbs free energy. We previously presented how-to for a simple one-pot reactor (report ALL R1710). Here, we first compare previous results to available experimental data to show the consistency. Then we extend the model to a multi-plateau disproportionation reactor such as the Denal reactor. We find that the results are consistent with a numerical modeling done at ALEJ. Thanks to this analytical approach, we demonstrate that the Denal design imposes a trade-off relation between the distillation efficiency and the catalyst amount in the reactor. In particular, we believe this is why Denal plant operates away from optimal catalyst concentration (7% instead of 20%).

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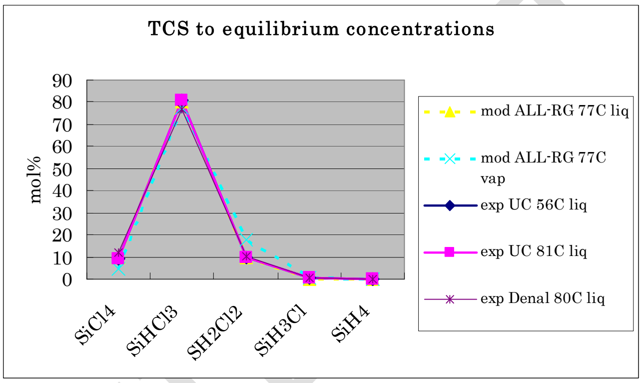
1. INTRODUCTION

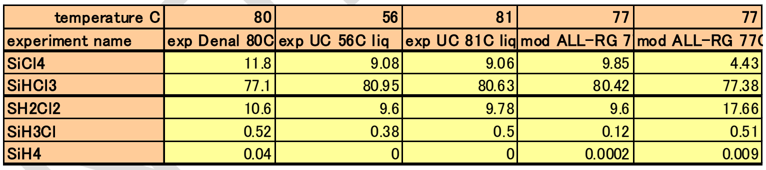
In previous notes, we presented how to modelize equilibrium concentrations in both liquid and vapour phases for a uniform disproportionation reactor (mono-chamber modeling). For this, we assumed the knowledge of:

- Temperature
- Elemental stoichiometry Si-H-Cl-catalyst

The model was based on the minimization of Gibbs free energy, which could be minimized in liquid phase, vapour phase, or in both phases (in the most practical case of a liquid catalyst, the minimization should be led in the liquid phase only).

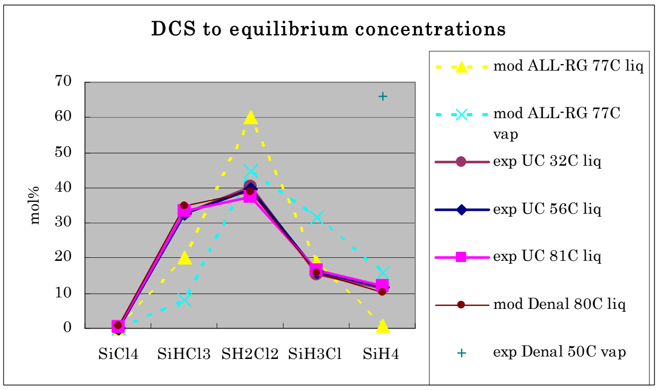
The pressure was also determined by the model, and was related to the amount of liquid catalyst (see annex 2).





temperature C	80	56	81	77	77
experiment name	exp Denal 80C	exp UC 56C liq	exp UC 81C liq	mod ALL-RG 7	mod ALL-RG 77
SiCl4	11.8	9.08	9.06	9.85	4.43
SiHCl3	77.1	80.95	80.63	80.42	77.38
SH2Cl2	10.6	9.6	9.78	9.6	17.66
SiH3Cl	0.52	0.38	0.5	0.12	0.51
SiH4	0.04	0	0	0.0002	0.009

Fig 1 ALL modeling and comparable experimental results from Union Carbide and Denal (TCS input). The estimation was led at 77C, with TCS stoichiometry (no catalyst), and minimizing Gibbs free energy in liquid phase only. The model gives all chemical concentrations both in liquid and vapour phases.



temperature C	80	32	56	81	77	77	50
experiment name	mod Denal 8	exp UC 32C li	exp UC 56C	exp UC 81C	mod ALL-RG	mod ALL-RG	exp Denal 50C
SiCl4	0.65	0.13	0.1	0.54	0.1	0.018	
SiHCl3	34.7	32.62	32.69	33.36	20.26	7.9179	
SH2Cl2	38.8	40.22	39.53	37.46	60.06	44.84	
SiH3Cl	15.6	15.5	16.1	16.66	18.66	31.58	
SiH4	10.2	11.5	11.59	11.98	0.901	15.63	66

Fig 2 ALL modeling and comparable experimental results from Union Carbide and Denal (DCS input). The estimation was led at 77C, with DCS stoichiometry (no catalyst), and minimizing Gibbs free energy in liquid phase only. The model gives all chemical concentrations both in liquid and vapour phases.

Starting from TCS (H=1 Si=1 Cl=3 stiochiometry,), ALL model was very consistent with experimental data from UC (obtained for a solid catalyst reactor) and of Denal.

Starting from DCS, ALL model was somehow different from experimental data of UC and Denal (fig. 2). The most probable reason is a difficulty with measuring chemical concentrations around 10 bar, the vapour pressure of DCS (see annex 3). On the other hand, we ruled out a calculation error (the result was double checked), or a convergence error (we have the same convergence when starting from UC experimental values).

In any case, the accuracy of the model enables us to extend it to a multi-plateau modeling such as that of Denal.

2. MODEL OF DENAL OPERATIVE CONDITIONS

The reactive distillation reactor is a pile of plateaus, and hence it can be described as a pile of mono-chamber reactors connected to each others through up-going vapour and down-going liquid.

Assuming that we have the stoichiometry at one plateau, and an inter-plateau relation for stoichiometry (see the estimation of the inter-plateau relations, annex 1), we can estimate stoichiometry on neighboring plateaus. By iteration we may deduce the chemical composition on each plateau.

One important source of difficulty for the Denal apparatus is the flowing catalyst. Catalyst flows by gravity down column, and this flow is commensurate both with the interplateau flow (liquid or vapour), and with the output flow down column. This imposes a low reflux (= ratio of interplateau flow to output flow) situation for

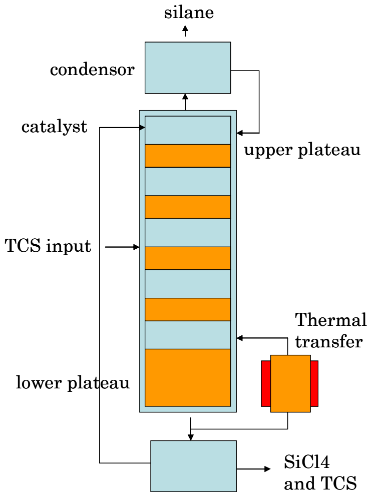


Fig. 3 Denal plant diagram

the distillation.

With a Denal type column, there are two inter-plateau relations, one above TCS input, and one below. These inter-plateau relations are not simple neighboring relations, but they actually depend on conditions up and down column (stoichiometries at upper and lower plateaus, and output flows). Fortunately, this data is available from Denal documents. We have the detailed liquid concentrations at lower plateau (extracted down column), the gas concentration on upper plateau (exhausted up column), and the flows of chemical at up and down outputs.

For the model, the column was divided in 18 plateau, with linear temperature profile between 55C (plateau 1, up) to 104C (plateau 18, down). The TCS input was placed on plateau 9.

Pressure was not fixed within the column, however, we assumed a uniform total liquid flow along column (approximation). Consequently this imposes a uniform total vapour flow up column, and a uniform catalyst concentration.

The catalyst concentration was set so that the concentrations down column at the end of the modeling, was equal to the actual Denal values (catalyst concentration could also be deduced from input flows on upper plateau. In this case the value is +8%).

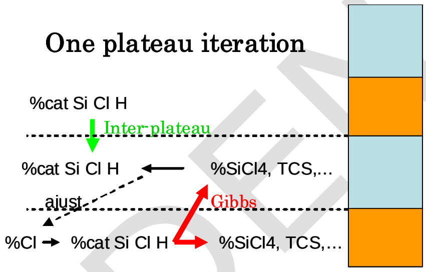


Fig. 4 One plateau iteration

The iteration was led downward starting from the upper plateau. Practically one iteration was led as follows:

1. we started from the elemental concentrations in liquid above plateau
2. we deduced elemental concentration in vapour at plateau below, using the interplateau relation
3. we set an arbitrary elemental concentration for Cl in liquid phase below, knowing that other concentrations can be deduced mechanically.
4. we ran the minimization of Gibbs free energy to deduce chemical concentrations in both liquid and vapour (same routine as the one-pot model)
5. we deduced a new elemental concentrations in vapour, and we checked that it is same as that of 2. If not, we iterated with a new Cl value.

3. RESULTS

The convergence of the model was successful. The hydrogen-chloride ratio (elemental) gives the profile of the separation.

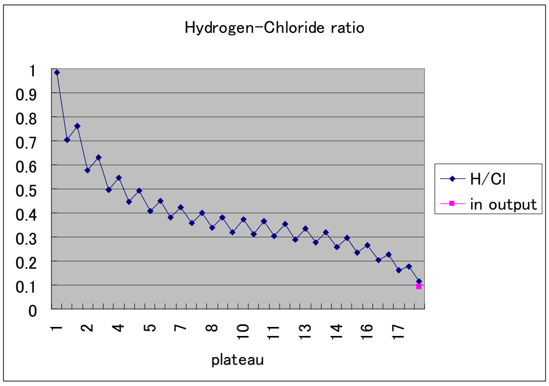


Fig. 5 Results of our model. Elemental separation in liquid and vapour at each plateau.

The dented profile shows an alternation between the intra-plateau separation (favorable to distillation) and the inter-plateau separation (unfavorable to distillation). The unfavorable inter-plateau separation is imposed by the low reflux situation (high Rn value in the inter-plateau relation, see annex 1), which in terms is imposed by the concentration of the catalyst.

This result illustrates that using a liquid catalyst imposes to operate the distillation under low reflux, which in terms is detrimental to the separation efficiency. This also explains why a relatively low concentration of catalyst (hence low catalyst flow) is used (around 7%) rather than the value of optimal reaction rate (around 20%).

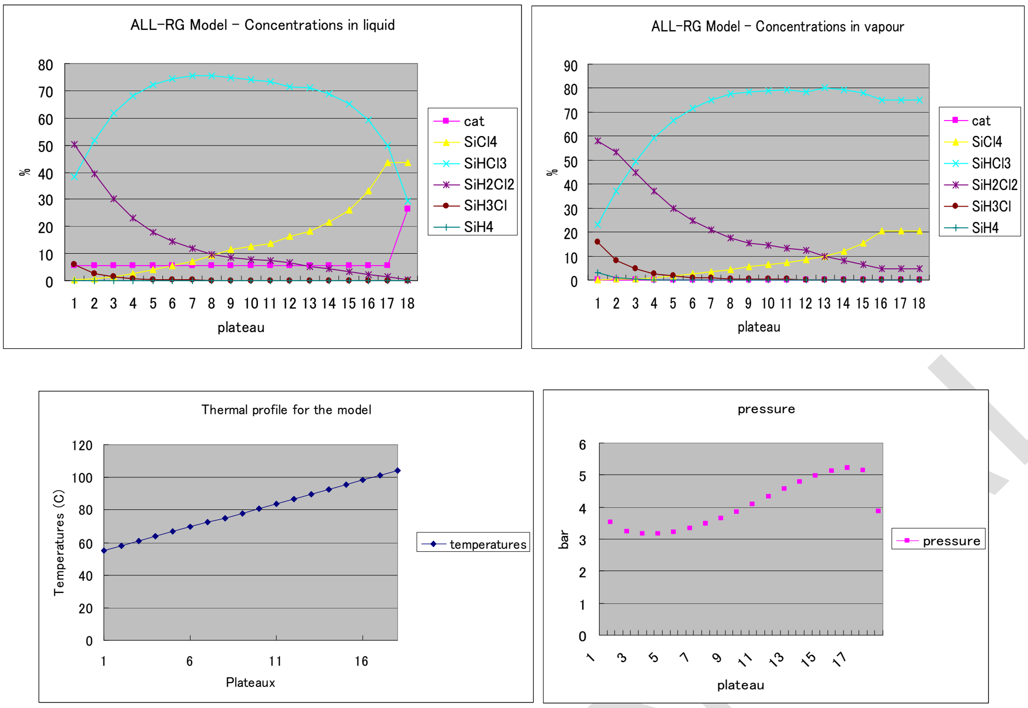


Fig. 6 Results of our model. Chemical concentrations in liquid and vapour at each plateau. Temperature and pressure profiles.

For comparison, ALEJ-Harima has obtained comparable result with a fully numeric simulation using a commercial software (Hysis). The results are consistent.

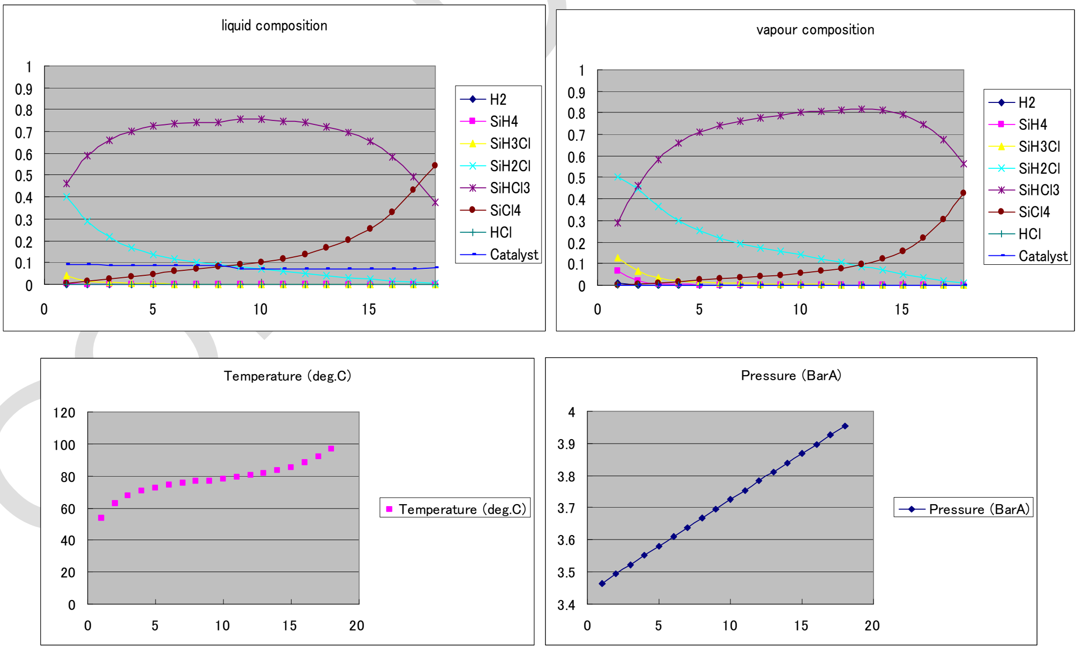
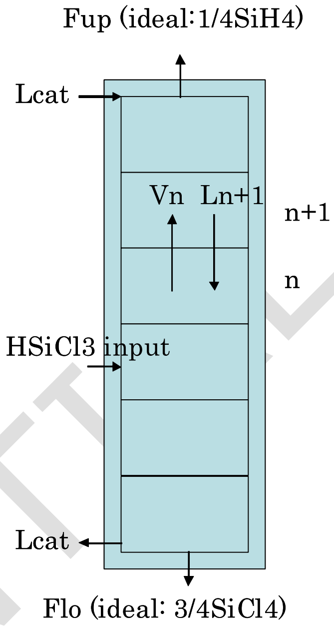


Fig. 7 Numeric (Hysis) ALEJ results for concentration and flows in a multiplateau reactor of Denal type (I.Abe and K.Hirose).

4. CONCLUSIONS

- We have revisited the previous results for a one-pot reactor. We have shown that the results fit the available experimental data very well, if we consider a TCS input. When considering a DCS input, we found some discrepancy, but we tentatively attribute this to a measurement issue.
- We discussed the various aspects of modeling a multi-plateau disproportionation reactor
- We applied this model to the Denal reactor with available operative parameters. We have noted that the Denal design imposes a trade off relation between the distillation efficiency and catalyst amount in the reactor. This causes a relatively poor separation efficiency (additional separation means are needed) and operation away from optimal catalyst concentration.

ANNEX 1: THE INTER-PLATEAU RELATION FOR STOICHIOMETRY



n = plateau number

up = upper plateau

lo = lower plateau

i = element/atom (Si Cl or H)

x atomic concentration in liquid

x' atomic concentration in vapour

Vn total vapour atomic flow at n (all atoms included)

Ln total liquid atomic flow at n (all atoms included)

F_{up} total atomic output up

F_{lo} total atomic output down, after catalyst separation

Lcat liquid catalyst flow

note: F_{up} *and* $x_{up}^{i}{}'$ correspond to the extraction after the recycle loop (hence almost pure silane), they do not correspond to gas concentration at upper plateau.

For a liquid catalyst flowing down column, we have:

$$(1)\quad L_n = \frac{L_{cat}}{x_n^{cat}}$$

For plateaux located over TCS input, total flow relation is:

$$(2)\quad V_n = L_{n+1} + F_{up} - L_{cat}$$

The same flow relation, but for each H, Cl, and Si (as i index) is:

$$(3)\quad V_n x_n^i{}' = L_{n+1} x_{n+1}^i + F_{up} x_{up}^i{}'$$

dividing (3) by (2) and using (1), leads to:

$$(4)\begin{cases} x_n^i{}' = (x_{n+1}^i + R_{n+1}^{up} x_{up}^i{}')/(1 + R_{n+1}^{up} - x_{n+1}^{cat}) \\ with \quad R_{n+1}^{up} = \dfrac{F_{up}}{L_{n+1}} \end{cases}$$

For plateaux located below TCS input,total flow relation is:

$$(5)\quad V_n = L_{n+1} - F_{lo} - L_{cat}$$

For each H, Cl, and Si:

$$(6)\quad V_n x_n^i{}' = L_{n+1} x_{n+1}^i - F_{lo} \frac{x_{lo}^i}{1 - x_{lo}^{cat}}$$

dividing (6) by (5) and using (1) leads to:

$$(7)\begin{cases} x_n^i{}' = (x_{n+1}^i - R_{n+1}^{lo}\dfrac{x_{lo}^i}{1-x_{lo}^{cat}})/(1-R_{n+1}^{lo}-x_{n+1}^{cat}) \\ with \quad R_{n+1}^{lo} = \dfrac{F_{lo}}{L_{n+1}} \end{cases}$$

(4) and (7) are the inter-plateau relations. Physically, Rn (up or lo) corresponds to the ratio of the output to the inter-plateau liquid flow (“reflux”).

Liquid catalyst case（Denal case)

If catalyst and tetrachlorosilane are extracted together down column, we have:

$$(8) \quad L_{cat} = \frac{x_{lo}^{cat}}{1-x_{lo}^{cat}} F_{lo}$$

For plateaus located over TCS input, this leads to:

$$(9) \quad R_{n+1}^{up} = (1-x_{lo}^{cat})\frac{x_{n+1}^{cat}}{x_{lo}^{cat}}\frac{F_{up}}{F_{lo}}$$

For plateaus located below TCS input, this leads to:

$$(10) \quad R_{n+1}^{lo} = (1-x_{lo}^{cat})\frac{x_{n+1}^{cat}}{x_{lo}^{cat}}$$

The value of the Rn are different from zero, and inter-plateau relation depend on concentration at upper and lower plateaus.

Hypothesis of “total reflux” (not Denal case)

If the interflow is large compared to the output $L_n >> F_{lo}$ and $L_n >> F_{up}$. We have $R_n \sim 0$. The interplateau relation (4) and (7) simplify to:

$$(11) \quad x_n^i{}' = x_{n+1}^i/(1-x_{n+1}^{cat})$$

This situation is simple because the inter-plateau relation does not depend on concentrations at upper or lower plateaus.

ANNEX 2: HOW WE MODELIZE THE VAPOUR-LIQUID EQUILIBRIUM (VLE)

In order to modelize the single-level reactor, it was necessary to assume a relation for the vapour-liquid equilibrium (VLE) of each chemical. Practically, we used the most simple expression for each chemical, namely:

$$x' P = x \, VP \, (T)$$

with x concentration in liquid, x' concentration in vapour, *VP(T)* = vapour pressure at T. Strictly speaking, this expression is incorrect because:

1. For very volatile chemicals, and silane in particular, there is no value of vapour pressure above the critical temperature (-3.5C for silane), and hence VP can not be used. One would typically use the Henry's constant instead, which corresponds to the solubility of the gas in the liquid. Unfortunately this data is not available for silane today. This is why we used an extrapolation of the VP values instead. This is incorrect, but as long as the silane amount is small, this does not influence the concentrations of other chemicals than silane.
2. Activity coefficient should be inserted to take into account the interactions between each chemical. These activity coefficients are available for TCS-DCS interaction and $SiCl_4$-TCS interaction (UC data). However, similar coefficients are not available for the interaction between the catalyst and other chemicals (because UC did not consider the case of a liquid catalyst).

In any-case, as long as we consider minimization in the liquid phase only (hence as long as most chemical are in the liquid phase), the VLE modeling will only affect vapour concentrations, but not liquid concentrations.

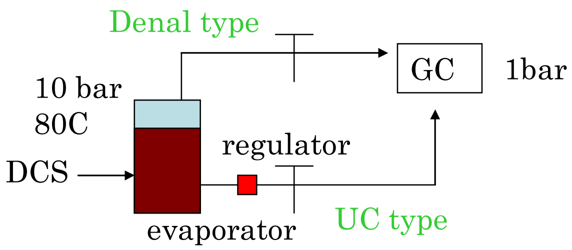
Relation between catalyst concentration and pressure

Assuming that the catalyst is perfectly soluble in trichlorosilanes, and knowing that catalyst has negligible volatility at temperatures of the reactor, we have:

$$P = (1 - x^{cat}) P_0$$

P_0 is the pressure of a mixture without catalyst. Catalyst concentration directly relates to pressure, and pressure is set by the concentration of the liquid catalyst. Hence pressure can be any value below P_0.

ANNEX 3: DIFFICULTY WITH MEASURING CHEMICAL CONCENTRATIONS



Two ways to measure the concentrations in the liquid phase of the reactor

The measurement of concentrations during disproportionation is difficult, because the reactor is pressurized (~3 bar for TCS, ~10 bar for DCS) and warm (50-100C). In order to measure concentrations with a GC or another analytical tool, it is necessary to consider chemical transfer properly.

The measurement of concentrations has been led in different ways at UC and Denal. For UC, the chemicals are continuously extracted from the reactor and mostly liquid. This liquid is vapourised by an evaporator, and then decompressed to 1 bar for measurement. For Denal, a small amount of vapour is exhausted from reactor top, and then decompressed to 1 bar, the concentration in liquid phase being deduced later numerically from vapour concentration.

3 problems may occur:

- If temperature is not maintained sufficiently high along the pipe, non-volatile chemicals deposit in the pipe, resulting in an increase of volatile chemical in the measurement (silane in particular).
- If the reaction continues to proceed, in the pipe within the vapour phase (non-catalysed reaction), the concentrations change. This can be modelized: with DCS stoichiometry, a reaction in the vapour phase leads to almost equal among of $HSiCl_3$ and H_2SiCl_2, which is similar to figure 2 experiments.
- Vapour to liquid conversion may be faulty

Note: If a measurement is at fault in fig. 2, it may be wondered why UC and Denal have the similar results. However, it may be argued also that Denal data is possibly a empirical “model” based on UC results. In anycase, it should be possible to redo those measurements in ALL when a setup is available.

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