

# Computers and Chemical Engineering

## Letter to the Editor

--Manuscript Draft--

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To the Editor:

There are no highlights for this Letter to the Editor.

Regards,

Dr. Aaron Drews

4 Nov 2024

To the Editor:

“Control structure design for the ammonia synthesis process” by Araújo and Skogestad<sup>1</sup> discussed application of plantwide control design for an ammonia synthesis process. The rate constants in the corresponding Aspen model were entered incorrectly, being too large by a factor of about 2950. This significantly affected reactor performance.

The gas-phase ammonia production reaction  $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$  was modeled within a series of adiabatic, packed bed reactors assumed to follow Temkin-Pyzhev kinetics with the net rate of reaction  $r$  as

$$r = \frac{r_{\text{NH}_3}}{2} = \frac{f}{\rho_{\text{bulk}}} \left( k_1 \frac{p_{\text{N}_2} p_{\text{H}_2}^{1.5}}{p_{\text{NH}_3}} - k_{-1} \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{1.5}} \right) \quad (\text{kmol kg}_{\text{cat}}^{-1} \text{h}^{-1}) \quad (2)$$

with  $f = 4.75$ ,  $\rho_{\text{bulk}} = (1 - \varphi)\rho_{\text{part}} = (1 - 0.33)2200 = 1474 \text{ kg m}^{-3}$ ,  $k_1 = 1.79 \times 10^4 e^{-87090/RT}$ , and  $k_{-1} = 2.57 \times 10^{16} e^{-198464/RT}$ .<sup>2</sup> Catalyst mass (weight) was selected in Aspen as the rate basis.

Aspen’s POWERLAW kinetic sheet required the net rate  $r$  to be separated into irreversible forward ( $f$ ) and reverse ( $r$ ) reactions such that  $r = r_f - r_r$  where

$$r_f = k_f \exp \left[ \frac{-87090}{RT} \right] \frac{p'_{\text{N}_2} (p'_{\text{H}_2})^{1.5}}{p'_{\text{NH}_3}} \quad (\text{kmol kg}_{\text{cat}}^{-1} \text{s}^{-1}) \quad (2a)$$

$$r_r = k_r \exp \left[ \frac{-198464}{RT} \right] \frac{p'_{\text{NH}_3}}{(p'_{\text{H}_2})^{1.5}} \quad (\text{kmol kg}_{\text{cat}}^{-1} \text{s}^{-1}) \quad (2b)$$

In the formulations of Equations (2a) and (2b) the partial pressure  $p'_i$  of species  $i$  must be in Pa. Comparing Equation (2) to Equations (2a) and (2b) implies

$$\begin{aligned} k_f &= (1.79 \times 10^4) \frac{f (10^{-5})^{1.5}}{3600 \rho_{\text{bulk}}} = 5.067 \times 10^{-10} \text{ kmol kg}_{\text{cat}}^{-1} \text{ s}^{-1} \text{ Pa}^{-1.5} \\ k_r &= (2.57 \times 10^{16}) \frac{f}{3600 \rho_{\text{bulk}} (10^{-5})^{0.5}} = 7.275 \times 10^{12} \text{ kmol kg}_{\text{cat}}^{-1} \text{ s}^{-1} \text{ Pa}^{0.5} \end{aligned}$$

However the publication’s Aspen model used  $k_f = 1.4915 \times 10^{-6}$  and  $k_r = 2.147 \times 10^{16}$ , values each approximately 2950 (or  $2\rho_{\text{bulk}}$ ) times larger than the correct values. All three beds in the simulation relied on the same incorrectly entered rate expression.

These errors significantly impacted reactor performance. For example, the nominally optimal model (see

<sup>1</sup>Araújo, A. and Skogestad, S. Control structure design for the ammonia synthesis process. *Comp. Chem. Eng.* 32 (2008) 2920-2932.

<sup>2</sup>A minor typo in the publication showed the pre-exponential factor for  $k_{-1}$  as 2.75 rather than the 2.57 found in the associated reference to Froment & Bischoff.

Table 1 in publication) implied an  $N_2$  conversion in Bed 1 of about 25.2%, with net  $NH_3$  production of about 2740  $kmol\ h^{-1}$ . Notably, the majority of reaction progress occurred in the first 0.03 m of the 2.13 m bed; no appreciable conversion occurred in the remaining 98% of the reactor length. Assuming for illustration stream 10 as a fixed input to Bed 1 (*i.e.*, ignoring recycle effects) then  $N_2$  conversion across the entire bed should be closer to about 0.3% with net  $NH_3$  production of just 31  $kmol\ h^{-1}$  if the correct coefficients were used.

The publication's stated intent was to apply a control design procedure "in order to illustrate its applicability to actual industrial plants." Given the flaws noted above and the central role of the reactors in the ammonia synthesis process, such applicability cannot be assumed.

Regards,

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