

CHEMICAL REACTOR DESIGN FOR PROCESS PLANTS

Volume Two: Case Studies and Design Data

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CASE STUDY 109

Ammonia Oxidation

THIS STUDY illustrates design aspects of a shallow-bed adiabatic reactor involving a very rapid reaction, which is diffusion controlled. The design of the bed, composed of a small number of catalyst screens, is normally based on past experience, scale-up on the basis of equal velocity, and careful planning for good distribution. A design model can be useful in economic or operating studies.

Problem Statement

Design a reactor for producing sufficient nitric oxide by partial oxidation of ammonia to supply a nitric acid plant having a capacity of 245 tons of nitric acid per day. Catalyst: 90% Pt + 10% Rh alloy as fine-mesh screen (p. 531¹). Its average life is 3–9 mo. Depending on raw material, operating and catalyst costs, operating cycles vary from 30–90 days. After each cycle, one or more gauzes at the top is removed for reclaiming. The remaining gauzes are made the top portion and new gauzes added at the bottom of the stack.

Process Description

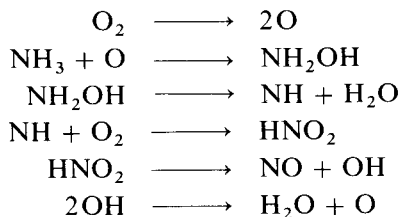
The direct oxidation of ammonia to nitric oxide (NO) over platinum catalyst is one of the major steps in the production of nitric acid. Subsequent steps include oxidation of NO to NO₂ and absorption of NO₂ in water to form HNO₃ (1,2). The direct oxidation step occurs in the range of 930°C and 100–125 psig. At this temperature platinum oxides are formed on the surface and a portion of these vaporize and are carried away in the gas stream (3).

The typical loss in a well-operated plant is 0.01–0.012 Troy oz/ton of nitric acid produced (3).

Operating conditions will, of course, alter these values. Poor distribution of gases that can induce localized hot spots in this exothermic system can materially increase the platinum loss. High platinum costs give top priority to designs and operating procedures which minimize losses. Even though filter equipment for recovering platinum from the exit gases is normally specified, it is not 100% efficient. Between 30% and 50% of that volatilized is recoverable from the filter elements and by cleaning downstream equipment. To alleviate this problem further, a Pd/Au getter directly below the catalyst mesh is used (see Fig. 11.14, p. 531¹) to capture volatilized platinum by alloying with it.

Chemistry

This very rapid reaction has been difficult to study mechanistically. The overall stoichiometric reaction ($4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$) occurs by some complex mechanism. The following has been suggested.



Typical of oxidation catalysts, it is thought that oxygen is chemisorbed on the catalyst. This chemisorbed oxygen then reacts with ammonia, producing a chemisorbed imide radical that is proposed here to react with molecular oxygen to yield finally nitric oxide.

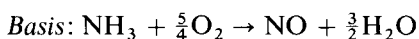
Thermodynamics

The reaction is highly exothermic and not equilibrium limited. The following relations have been reported for this reaction system in the limited temperature range of interest (4–6).

$$(-\Delta H) = 54,250 - 0.4(T - 298) \text{ cal/g mole of NH}_3 \text{ reacted} \quad (\text{CS-9.1})$$

where $T = ^\circ\text{K}$

$$K = 2.11 \times 10^{19} @ 700^\circ\text{K}$$



$$c_{pm} = 6.45 + T(1.52 + 4.08y_A)10^{-3} \quad (\text{CS-9.2})$$

where y_A is the mole fraction of ammonia in feed. This heat capacity equation applies in the region of $T = 600\text{--}1100^\circ\text{K}$ and $y_A = 0.09\text{--}0.12$.

Referring to Table 6.4 the adiabatic factor of 633 is large, but the heat generation potential is low because of the dilute system and the mass-transfer control.

For convenience the equations for viscosity and thermal conductivity of the mixture in the same temperature regions will also be given at this point (6).

$$\lambda_t = (3.31 + 12.77 \times 10^{-3}T)10^{-6} \frac{\text{k cal}}{\text{m sec}} ^\circ\text{C} \quad (\text{CS-9.3})$$

$$\mu_t = (12.5 + 29.20 \times 10^{-3}T)10^{-5} \text{ g/cm sec} \quad (\text{CS-9.4})$$

where $T = ^\circ\text{K}$.

Kinetics

Early experimental work on this process demonstrated that under normal operating conditions the physical transport of ammonia to the catalyst surface is the rate determining step (7). At low temperatures or with deactivated catalyst the chemical rate can become limiting or partially limiting. With active catalyst, however, it is clear that high temperatures and high velocities will produce essentially total conversion of ammonia. The maximum temperature is limited by the aforementioned catalyst loss that becomes excessive much above 900°C . The loss per unit surface area is apparently a direct function of gauze temperature, mass flow rate, and ammonia-to-oxygen ratio in the feed. The temperature dependency in the region 825 to 900°C is steep and expressed (4) approximately as $10^{-20000/T}$.

On the basis of mass-transfer control the rate of ammonia oxidation may be written in terms of a mass-transfer coefficient with the ammonia partial pressure at the catalyst surface assumed to be zero for this rapid reaction.

$$(-r_A) = k_{gA}^s a_{WR} P_A \quad (\text{CS-9.5})$$

where P_A is the partial pressure of ammonia in bulk fluid and a_{WR} is the surface area per unit volume of screen. For shallow beds of the type shown on p. 531¹, axial diffusion must surely be important, but the very high flow rates encountered in commercial equipment cause it to be less important than the problem of equal flow distribution across the gauzes. By including a gas distributor below the catalyst pad, as described on p. 531¹, this problem is

greatly alleviated, and as a first approximation a model is developed based on plug flow.

$$\frac{-G}{M_F} dy_A = (-r_A) dZ \quad (\text{CS-9.6})$$

where $(-r_A)$ is the g-moles of NH_3 converted/ cm^3sec .

For this rapid reaction assume that partial pressure of ammonia on the catalytic surface is zero. Then the rate of transfer of ammonia becomes (6)

$$(-r_A) dZ = k_{gA}^s a_{WR} y_A P dZ = k_{gA}^s y_A P f_w dn_s \quad (\text{CS-9.7})$$

where n_s is the number of gauzes and f_w is the wire area per gauze cross-sectional area for one gauze.

$$\frac{-G}{M_F} dy_A = k_{gA}^s y_A P f_w dn_s \quad (\text{CS-9.8})$$

or integrating and simplifying by assuming constant number of moles

$$k_{gA}^s P n_s f_w = \frac{G}{M_F} \ln \frac{y_{A1}}{y_{A2}} = \frac{G}{M_F} \ln \frac{y_{A1}}{y_{A1}(1 - X_A)} = \frac{G}{M_F} \ln \frac{1}{1 - X_A}$$

or

$$\ln(1 - X_A) = -k_{gA}^s P n_s f_w \frac{M_F}{G} \quad (\text{CS-9.9})$$

The following substitutions, which conveniently eliminate some variables follow the procedure of Ref. 6, except more recent mass-transfer data are used (8). From p. 532¹,

$$k_{gA}^s = \frac{0.865 N_{\text{Re}}^{-0.648} G}{P N_{\text{Sc}}^{\frac{2}{3}} M_m \epsilon_w}$$

where M_m is the molecular weight of mixture.

$$\begin{aligned} \ln(1 - X_A) &= \frac{-0.865 n_s f_w M_F N_{\text{Re}}^{-0.648}}{\epsilon_w M_m N_{\text{Sc}}^{\frac{2}{3}}} \\ &= \frac{-0.865 n_s f_w \epsilon_w^{0.648} \mu_f^{0.648} \mathcal{D}^{\frac{2}{3}} \rho_f^{\frac{2}{3}}}{\epsilon_w \mu_f^{\frac{2}{3}} d_w^{0.648} G^{0.648}} \quad (\text{CS-9.10}) \end{aligned}$$

where d_w is the diameter of wire. M_F/M_m is approximately unity.

$$\ln(1 - X_A) = - \frac{(0.865) n_s f_w \mathcal{D}^{\frac{2}{3}} \rho_f^{\frac{2}{3}}}{\epsilon_w^{0.352} d_w^{0.648} G^{0.648} \mu_f^{0.019}} \quad (\text{CS-9.11})$$

Using

$$\mathcal{D} = 0.227 \left(\frac{T}{293} \right)^{\frac{3}{2}} \left(\frac{1}{P} \right)^* \text{ cm}^2/\text{sec}$$

$$\rho_f = \frac{MP}{RT} \text{ and } \mu_f \text{ from Eq. CS-9.4}$$

$$\begin{aligned} M = M_F &= (32)(0.21)(1 - y_A)_0 + (28.01)(0.79)(1 - y_A)_0 + 17.03y_{A_0} \\ &= 28.85 + 11.82y_{A_0} \end{aligned}$$

$$\ln(1 - X_A) = - \frac{5.81761 \times 10^{-5} n_s f_w T_i^{0.333} (28.85 + 11.82y_{A_0})^{0.667}}{\varepsilon_w^{0.352} d_w^{0.648} G^{0.648} \mu_f^{0.019}} \quad (\text{CS-9.12})$$

Since \mathcal{D} has been introduced as cm^2/sec and R as $\text{cm}^3 \text{ atm}/\text{g-moles } ^\circ\text{K}$, $d_w = \text{cm}$, $G = \text{g}/\text{cm}^2\text{sec}$, and $\mu_f = \text{g}/\text{cm sec}$. T_i is the mean film temperature.

The temperature dependency in Eq. CS-9.12 is relatively minor. Heat-transfer calculations based on assuming a constant gauze temperature corresponding approximately to the outlet gas temperature indicate a mean film temperature of 50° less than the exit temperature. Thus it is within the present accuracy of transport properties to simply use the exit gas temperature as the film temperature (12). This is the commonly measured temperature in commercial units. The inlet gas temperature may be calculated from an adiabatic heat balance with an exit gas temperature 20°C less than theoretical to account for incomplete combustion and radiation losses (4).

When these equations are applied to conditions for which experimental data are known, the calculated conversions are higher than the experimental values. It has been shown recently that in high-pressure plants with up to 50 gauze pads only the upper $\frac{2}{3}$'s of the bed appears to be active as a catalyst, and the lower $\frac{1}{3}$ is not (3). But when the extra screens are removed, the conversion declines because the reduced ΔP causes uneven distribution and bypassing of portions of the catalyst. Thus Eq. CS-9.12 must be multiplied by a correction factor (6). Experimental data involving small numbers of screens (≈ 3) agree when the right-hand side of Eq. CS-9.12 is multiplied by two-thirds (6), which fortuitously corresponds to the aforementioned $\frac{2}{3}$'s of the bed (3).

Design

This reaction system is another example of an old process for which catalyst suppliers provide special catalyst and are helpful in recommending the

* $\mathcal{D} = 0.227 \text{ cm}^2/\text{sec}$ @ 293°K for NH_3 in air at 1 atm (9).

configuration and amount of catalyst based on knowledge of many operating plants. In such cases a model for the reactor is not as important in initial design as it is in subsequent studies concerning economics associated with catalyst replacement, operating strategy and yield.

Typical reported requirements at 900°C gauze temperature and 100 psig are a quantity of 80 mesh gauze with wire of 0.003 in. in diameter equivalent to 2 Troy oz/ton of acid produced and a cross-sectional area of 2.7547 sq ft/100 daily tons of HNO_3 produced (3). A conversion of 96% would be expected at the outset (3). The ammonia would be adjusted to be 10% of the total feed. The explosive limit is reported to be 13% (4) and the usual operating range is between 8 and 11.5%.

Equal performance is obtained with 40–45% of this amount of catalyst if a gas distributor is used, as described on p. 513¹ (3). Thus the desired 245-ton plant for this alternate would be specified to have 0.8–0.9 Troy oz of Pt-Rh/100 ton acid, two to four sheets of Degussa getter for Pt recovery, and the aforementioned gas distributor. The cross-sectional area and mass velocity for this 245-ton plant are:

Cross Sectional Area

$$2.7547 \text{ sq ft/100 tons HNO}_3$$

$$(2.7547)(2.45) = 6.749 \text{ sq ft or 33.5 in.}$$

$$\text{hexagonal gauze (19.34 in. side)}$$

Weight of 80 mesh Pt-Rh gauze = 1.71 Troy oz/ft². Use 2 Troy oz/ton HNO_3 .
 \therefore Number of gauzes = $[(2)(245)]/[(6.749)(1.71)] = 42.46$ or 43 gauzes.
 Alternatively, a gas distributor and Degussa getter would improve distribution and reduce the number of gauzes. Use the higher value 0.9 Troy oz/ton as conservative value.

$$\left(\frac{0.9}{2}\right)(42.46) = 19.1 \text{ gauzes}$$

Inlet and outlet distributions, as shown in Fig. 11.14, should be designed in accordance with the criteria set forth on p. 309¹ in order to maximize pressure recovery and assure good distribution. A magnetic separator should be located in the liquid ammonia stream to remove iron oxide, which accelerates gauze deterioration (10).

Ideally if an elbow must be used, it should be at least 10 diameters upstream from the diffuser. If less, circular arc vanes must be installed in the elbow, as discussed on p. 309¹. To minimize diffuser cost, it may be necessary to use larger angles than indicated on p. 309¹. In such cases multiple screen distributors should be installed downstream of the throat. Alternatively,

extrapolating Fig. 7.3, a 30° diffuser may be selected with a 12-in. diameter inlet pipe. The outlet diffuser would be similar. It is most important in this case to avoid a close elbow. Many units have been carefully designed at the diffuser and then installed immediately after the elbow thereby negating the effect of the diffuser. Further experimental work should be done on the optimum arrangement for such short-bed reactors.

Design with Model

It is now instructive to determine the usefulness of the proposed model by comparing predicted performance with the specification of 19 gauzes when a gas distributor is used.

Basis: 100 psig and 900°C gauze temperature; 10% NH₃ in feed. Gauze mesh size 80 in.⁻¹ and diameter 0.003 in. From Ref. 28, Chapter 7 and based on plain square weave with a thickness of $2d_w$, the surface area per unit volume, a_{WR} , for the gauze and other properties are:

$$a_{WR} = \pi l_w n_w^2$$

$$\text{where } l_w = [(1/n_w)^2 + d_w^2]^{0.5}$$

$$\begin{aligned} a_{WR} &= \pi n_w^2 \sqrt{\left(\frac{1}{n_w}\right)^2 + d_w^2} = \pi(80)^2 \sqrt{\frac{1}{(80)^2} + 0.003^2} \\ &= 258 \text{ in.}^{-1} \text{ or } 101.7 \text{ cm}^{-1} \end{aligned}$$

where n_w is the mesh size and d_w is the wire diameter.

$$f_w = a_{WR} 2d_w = (258)(2)(0.003) = 1.55$$

$$\epsilon_w = 1 - \frac{\pi l_w n_w^2 d_w}{4} = 1 - \frac{a_{WR} d_w}{4} = 0.806$$

Mass Velocity

$$G = \frac{(1)(2000)(30.03/63)}{(24)(3600)(0.96)(0.1)(0.027547)} = 4.17 \text{ lb/ft}^2 \text{ sec or } 2.04 \text{ g/cm}^2 \text{ sec}$$

This corresponds to a superficial velocity based on outlet conditions of

$$u_s = (2.04) \frac{1}{\rho_f} = (2.04) \frac{(82.06)(1203)}{(115/14.7)(30.03)} = 857 \text{ cm/sec or } 28 \text{ ft/sec}$$

Thus $u_s \approx 28 \text{ ft/sec}$ constitutes a more general criterion based on these reported data.

Equation CS-9.12 provides a means for estimating the number of gauzes when perfect plug flow is assumed which is approached in the unit with a special gas distributor.

$$n_s = \frac{-\ln(1 - X_A) \epsilon^{0.352} d_w^{0.648} G^{0.648} \mu_f^{0.019}}{(5.81761 \times 10^{-5}) f_w T_i^{0.333} (28.85 + 11.82 y_{A0})^{0.667}}$$

$$n_s = \frac{(-\ln 0.04)(0.806)^{0.352} (0.0076)^{0.648} (2.04)^{0.648} (41.99 \times 10^{-5})^{0.019}}{(5.81761 \times 10^{-5})(1.55)(1173)^{0.333} (30.03)^{0.667}}$$

$$= 18.8$$

Since the predicted mass-transfer coefficient has a mean deviation of $\pm 12\%$, the number of gauzes is well within experimental error. A more useful model would include the decline in conversion with time which is caused by deactivation. The apparent mass-transfer coefficient is reduced by this phenomenon as the resistance caused by the chemical reaction becomes finite. If this effect can be correlated with temperature and time, various operating strategies can be studied. Higher temperatures will increase yield but also platinum losses. A complete economic assessment would be possible if such predictive tools were known.

Equation CS-9.11 can be useful in comparing various gauze configurations with performance using efficiency factors observed for operating plants. More recent mass-transfer data have been reported (11) and when substituted into Eq. CS-9.9, approximately the same result is obtained (see also Ref. 12).

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