

# CHEMICAL REACTOR DESIGN FOR PROCESS PLANTS

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## Volume Two: Case Studies and Design Data

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# CASE STUDY 106

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## Ammonia Synthesis

THIS STUDY illustrates the design of multistage, fixed-bed reactors with direct-contact quench between stages. The optimum approach to equilibrium is sought, and convenient graphical procedures that aid in selecting operating conditions are illustrated. This reactor is in the synthesis portion of the total ammonia plant as shown in Fig. CS-5.1 (p. 45).

### Problem Statement

Design the converter for an ammonia plant capable of producing 1000 tons/day of liquid ammonia delivered at the battery limits at  $-28^{\circ}\text{F}$ .

### Feed

Synthesis gas from the methanator is delivered to the converter at  $100^{\circ}\text{F}$  and 335 psig (see Fig. CS-5.1).

Component	Mole %
$\text{H}_2$	74.03
$\text{N}_2$	24.68
$\text{CH}_4$	0.95
Ar	0.34
	<hr/> 100.00

### Catalyst

A triply promoted ( $\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$ ) iron-oxide catalyst will be used. The iron oxide ( $\text{Fe}_2\text{O}_3-\text{FeO}$ ) is in the form of nonstoichiometric magnetite.

It is made by fusing the magnetite with the promoters. The catalyst is reduced in situ, and the removal of oxygen yields a highly porous structure of iron with promoters present as interphases between the iron crystals and as porous clusters along the pore walls (1). The pores range from 50°A to 100°A, and intraparticle diffusion is thought to occur by the bulk mechanism.

Alumina prevents sintering and corresponding loss of surface area and also bonds the  $K_2O$ , preventing its loss during use (1). The  $K_2O$  and  $CaO$  neutralize the acid character of  $Al_2O_3$ . Both  $K_2O$  and  $CaO$  decrease the electron work function of iron and increase its ability to chemisorb nitrogen by charge transfer to the nitrogen (1).

### ***Properties***

*Particle Size.* Granules, in size range 6–10 mm.

*Bulk Density.* 165 lb/cu ft (2.65 kg/liter).

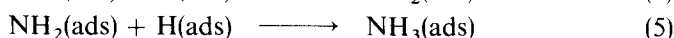
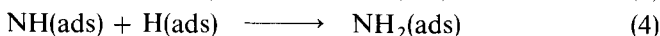
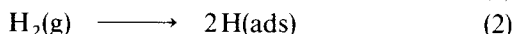
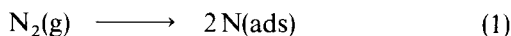
*Particle Density.* 305 lb/cu ft (4.9 g/cm<sup>3</sup>)

*Activity loss in service.* 30–50% in 3 yr depending on severity of operating conditions and presence of poisons. Catalyst is slowly deactivated at operating temperatures above 985°F (530°C).

*Catalyst Poisons.* In addition to poisons shown in Table 2.13, hydrocarbons such as lubricating oils and olefins can crack and plug pores. Sulfur, phosphorous, and arsenic compounds are permanent poisons. Oxygen and listed oxygen compounds should not exceed 15 ppm. Though temporary poisons, they cause crystal growth and attendant area decline. Chlorine compounds form volatile alkylchlorides with promoters (1).

### **Chemistry and Kinetics**

The overall stoichiometric equation is:  $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$ . Extensive studies of ammonia synthesis on iron catalysts suggest that the reaction occurs through surface imine radicals and the following elementary steps (1,2).



A rate equation based on nitrogen adsorption as the slow step and the Temkin isotherm is the most commonly used although other forms have been developed that also correlate the data.

Since the effectiveness factor of ammonia catalyst is less than unity in commercial size pellets, it is desirable to develop a rate equation from laboratory data on finely ground catalyst and employ an effectiveness factor correction for other sizes. Ammonia synthesis is another example of an old reaction with sufficient data existent to make this procedure feasible. The following equations in terms of activity have been recommended (3).

#### *Rate on Fine Catalyst*

$$2(-r_N) = r_A = 2k\psi \left[ K^2 \left( \frac{a_N a_H^{\frac{3}{2}}}{a_A} \right) - \left( \frac{a_A}{a_H^{\frac{3}{2}}} \right) \right] \frac{\text{kg moles NH}_3}{(\text{m}^3 \text{cat.})(\text{hr})} \quad (\text{CS-6.1})^*$$

where subscripts A, H, and N refer to ammonia, hydrogen, and nitrogen, respectively,  $K$  is the equilibrium constant and  $\psi$  is the activity factor to account for effect of particle size on the ultimate surface area after reduction.

The original data are based on reduced particles of 3–6 mm size (4.6 mm effective diameter and 8.6 m<sup>2</sup>/g). We will use 6–10 mm (5.8 mm effective diameter) for which the area can be estimated from Ref. 15 as 7.5 m<sup>2</sup>/g. Thus  $\psi = 7.5/8.6 = 0.87$ .

$$2k = 1.7698 \times 10^{15} \exp(-40,765/R'T) \quad (\text{CS-6.2})$$

$$\begin{aligned} \log_{10} K = & -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T \\ & + 1.848863 \times 10^{-7} T^2 + \frac{2001.6}{T} + 2.6899 \end{aligned} \quad (\text{CS-6.3})(5)$$

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

Equation CS-6.1 is based on the most complete data on an industrial-type catalyst formulation (4) and predicts ammonia mole fraction with a nominal maximum deviation of 10–20% in the usual pressure range of interest, 150–300 atm. Thus a pressure correction, as suggested on p. 41<sup>1</sup>, is included in the value of  $k$  as a nominal value.

An effectiveness factor equation developed for the indicated kinetics, rather than pseudo-first-order kinetics, yields a complex expression which

\* This unusual arrangement results from using the reverse rate constant (ammonia dissociation constant) as the rate constant  $k$ .

was solved for a number of values of  $P$  and  $T$  for a catalyst charge composed of 6–10 mm particles. The values were then summarized in a simple form (3).

$$\eta = b_0 + b_1 T + b_2 X + b_3 T^2 + b_4 X^2 + b_5 T^3 + b_6 X^3 \quad (\text{CS-6.4})$$

Values of the constants at 150, 225, and 300 atm are given in Ref. 3.

Since  $\mathbf{a}_j = f_j/f_j^\circ$  and  $f_j^\circ = 1$  atm for gases,  $\mathbf{a}_j = f_j = y_j v_j P$ , where  $v_j$  is the fugacity coefficient for component  $j$  for which the following equations may be used (6–8) with  $T$  in  $^\circ\text{K}$  and  $P$  in atm.

$$v_H = \exp \{ e^{(-3.8402T^{0.125} + 0.541)} P - e^{(-0.1263T^{0.5} - 15.980)} P^2 + 300[e^{(-0.011901T - 5.941)}](e^{-P/300} - 1) \} \quad (\text{CS-6.5})$$

$$v_N = 0.93431737 + 0.3101804 \times 10^{-3} T + 0.295896 \times 10^{-3} P - 0.2707279 \times 10^{-6} T^2 + 0.4775207 \times 10^{-6} P^2 \quad (\text{CS-6.6})$$

$$v_A = 0.1438996 + 0.2028538 \times 10^{-2} T - 0.4487672 \times 10^{-3} P - 0.1142945 \times 10^{-5} T^2 + 0.2761216 \times 10^{-6} P^2 \quad (\text{CS-6.7})$$

Thus Eq. CS-6.1 for the industrial catalyst becomes in kg moles/(m<sup>3</sup>cat.) (hr),

$$r_A = \eta 1.7698 \times 10^{15} \exp \left( -\frac{40,765}{RT} \right) \left[ K^2 P^{\frac{2}{3}} \left( \frac{v_N y_N v_H^{\frac{2}{3}} y_H^{\frac{2}{3}}}{v_A y_A} \right) - \frac{1}{P} \left( \frac{v_A y_A}{v_H^{\frac{2}{3}} y_H^{\frac{2}{3}}} \right) \right] \quad (\text{CS-6.8})$$

This can be converted to lb moles/(lb cat.) (hr) by multiplying by the factor  $3.7836 \times 10^{-4}$ .

### Thermodynamics

For a single reaction, such as ammonia synthesis, the entire message of thermodynamics is conveniently presented on an equilibrium conversion and adiabatic reaction-temperature plot such as shown in Fig. CS-6.1. It is quite clear from this figure that adiabatic beds in series with intermediate cooling will be necessary to attain a conversion in the 15% or over level, as discussed on p. 513<sup>1</sup>. Various strategies can be planned by using an equilibrium approach for this process of 40–50°F; or, more conveniently, rate plots as shown in the next section can be employed.

Direct-contact quench, which is most attractive for a high-pressure system, in contrast to expensive exchangers, will be used. Design strategies can be rapidly developed by graphical constructions using adiabatic lines and quench lines in accordance with the procedure given on p. 530<sup>1</sup>. Alternatively, and perhaps more precisely, such paths may be considered on rate plots, as described on p. 526<sup>1</sup> and shown on p. 69.

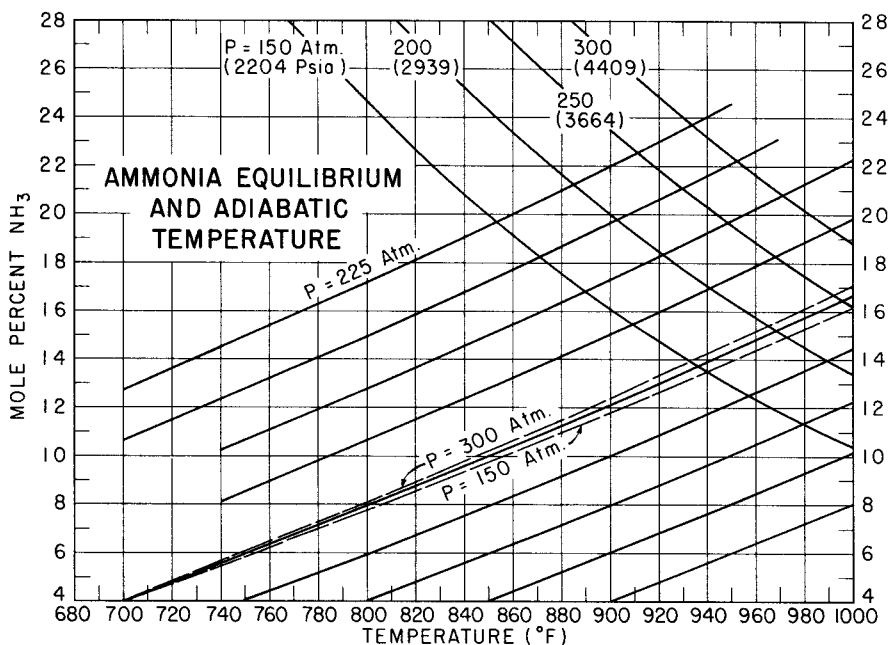


Fig. CS-6.1 Ammonia equilibrium and adiabatic temperature.

## Design Equations

### Component Balance

Since the feed quantities vary with each bed in a quench reactor, it is convenient to base the component balance on the feed to the first bed.

### Mole Balance

Basis: feed to first bed

$$\Delta W \hat{r}_A = \Delta n_{AF} F_I \quad (\text{CS-6.9})$$

or

$$\frac{\Delta W}{F_I} = \frac{\Delta n_{AF}}{r_A} \quad (\text{CS-6.10})$$

$$\Delta n_{AF} = -\frac{3}{2} \Delta n_{\text{HF}} = -\frac{1}{2} \Delta n_{\text{NF}} \quad (\text{CS-6.11})$$

where  $F_j$  is the feed to first bed and  $n_{AF}$  is the moles of ammonia per mole of feed to first bed.

As quench is added between beds, the value of  $n$  for each component changes depending on the amount of quench.

*Basis:* per mole of feed to first bed

$$\begin{aligned}(n_{AF})_c^I &= (n_{AF})_0^I + \Delta n_{AF} \\ (n_{AF})_0^{II} &= (n_{AF})_c^I + \gamma_{II}(n_{AF})_0^I\end{aligned}\quad (\text{CS-6.12})$$

where  $\gamma_{II}$  is the fraction of feed to first bed for quench between first and second bed,  $(n_{AF})_0$  is the inlet ammonia per mole of feed to first bed for numbered bed, and  $(n_{AF})_c$  is the outlet ammonia per mole of feed to first bed from numbered bed. For  $n$ th bed

$$(n_{AF})_0^n = (n_{AF})_c^{n-1} + \gamma_{n-1}(n_{AF})_0^{n-1} \quad (\text{CS-6.13})$$

Similar equations for other components based on Eq. CS-6.11 are apparent.

### *Heat Balance (between $i$ and $i + 1$ positions)*

*Basis:* per mole of feed to first bed

$$\begin{aligned}(\sum n_{jF} H_{f_j})_i + \sum \left[ (n_{jF})_i \int_{298}^{T_i} c_{p_j} dT \right] \\ = (\sum n_{jF} H_{f_j})_{i+1} + \sum \left[ (n_{jF})_{i+1} \int_{298}^{T_{i+1}} c_{p_j} dT \right]\end{aligned}\quad (\text{CS-6.14})$$

or in terms of heat of reaction

$$\sum \left[ (n_{jF})_{i+1} \int_{T_i}^{T_{i+1}} c_{p_j} dT \right] = \Delta n_{AF} (-\Delta H_A)_{T_i, P} \quad (\text{CS-6.15})$$

It is sufficient to consider the pure component enthalpies of the various gases additive. In this system ideal-gas heat capacity equations apply to all but ammonia, for which the following was used in cgs units (11).

$$\begin{aligned}c_{pA} &= 6.5846 - 0.61251 \times 10^{-2}T + 0.23663 \times 10^{-5}T^2 \\ &\quad - 1.5981 \times 10^{-9}T^3 + 96.1678 - 0.067571P + (-0.2225 \\ &\quad + 1.6847 \times 10^{-4}P)T + (1.289 \times 10^{-4} - 1.0095 \times 10^{-7}P)T^2\end{aligned}$$

where  $T = ^\circ\text{K}$  and  $P$  is in atm.

Other  $c_p$  equations are the same as used for Case Study 105. The expression for the heat of reaction based on this equation and the other ideal heat capacities is (11):

$$\begin{aligned}
 (\Delta H_A)_{T,P} = & -9184.0 - 7.2949T + 0.34996 \times 10^{-2}T^2 + 0.03356 \\
 & \times 10^{-5}T^3 - 0.11625 \times 10^{-9}T^4 - (6329.3 - 3.1619P) \\
 & + (14.3595 + 4.4552 \times 10^{-3}P)T - T^2(8.3395 \times 10^{-3} \\
 & + 1.928 \times 10^{-6}P) - 51.21 + 0.14215P, \text{ cal/g mole NH}_3
 \end{aligned}
 \tag{CS-6.16}$$

### *Establishing Purge, Recycle, and Total Feed*

Referring to Fig. CS-6.2, the following mole balances may be formulated.

#### *Inert Balance*

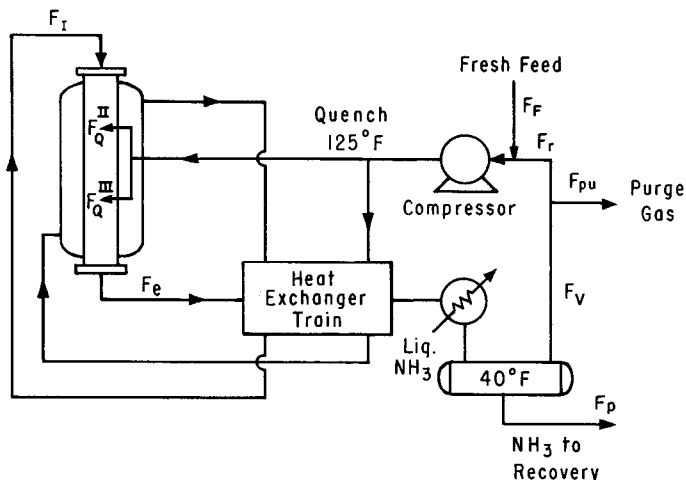
$$(y_I)_F F_F = (y_I)_{PU} F_{PU} \tag{CS-6.17}$$

#### *N<sub>2</sub> + H<sub>2</sub> Balance*

$$(y_{N_2+H_2})_F F_F = (y_{N_2+H_2} + 2y_A)_{PU} F_{PU} + 2F_P \tag{CS-6.18}$$

$$[(y)_{N_2+H_2} + y_I + y_A]_{PU} = 1 \tag{CS-6.19}$$

where F refers to fresh feed, P to product, and PU to purge;  $y_I$  is mole fraction inerts.



**Fig. CS-6.2** Converter and recycle system.



Based on phase equilibrium at the separator,

$$(f_A)_{\text{LIQ}} = (v_A)_{\text{LIQ}}(P_A)_{\text{VP}} = (f_A)_g \quad (\text{CS-6.20})$$

where  $(P_A)_{\text{VP}}$  is the vapor pressure of ammonia at temperature and pressure of the system and  $(f_A)_g$  is the ammonia fugacity in the vapor phase.

The fugacity of ammonia in the vapor phase can be calculated using the Redlich-Kwong equation of state (9,10).

$$\ln \frac{(f_A)_g}{P y_A} = (z_m - 1) \frac{B_A}{B} - \ln(z_m - BP) - \frac{A^2}{B} \left( \frac{2A_A}{A} - \frac{B_A}{B} \right) \ln \left( 1 + \frac{BP}{Z} \right) \quad (\text{CS-6.21})$$

where  $A = \sum A_j y_j$ ,  $B = \sum B_j y_j$ ,  $A_j = 0.6541/T_{rj}^{1.25} P_{crj}^{0.5}$ , and  $B_j = 0.0867/T_{rj} P_{crj}$ .

$$z_m = \frac{1}{1-h} - \frac{A^2}{B} \frac{h}{1+h} \quad (\text{CS-6.22})$$

where  $h = BP/z_m$ ,  $z_m$  is the compressibility factor,  $P_{cr}$  is the critical pressure, and  $T_r$  is the reduced temperature.

This requires trial-and-error since  $z_m$  and  $f_A$  depend on composition. At a set inerts composition and  $\text{H}_2/\text{N}_2$  ratio, an ammonia mole fraction in the vapor phase is assumed. Then Eqs. CS-6.20 and CS-6.21 are applied with acceptable convergence defined as

$$\frac{(f_A)_g - (f_A)_{\text{LIQ}}}{(f_A)_g} \leq 10^{-3}$$

### Design Studies—Rapid Overview

The large number of interrelated variables involving inerts, recycle, separator, and reactor conditions and number of beds makes it necessary to limit or set some of these consistent with good practice. Any attempt to search the entire universe of values is not rational particularly when low sensitivity of results to many changes and accuracy of the rate data are considered. Because composition of inerts affects reactor performance, recycle, and separator equilibrium, it is convenient to base cases for study on inerts composition. The inerts composition of the total feed to the converter (fresh feed plus recycle) can be specified at various values in a range known to be consistent with good practice (8–15%). One might, for example, select an intermediate value of 12% for the purpose of studying various operating pressures. Product recovery and quench temperatures can also be set as well

as ammonia production rate, number of beds, and inlet and outlet temperature of each bed. These latter temperatures are most conveniently selected by generating a rate plot, such as presented in Fig. CS-6.3. Graphical constructions are made using the adiabatic line and quench slopes, as discussed on p. 530<sup>1</sup>. Since the feed and quench composition depend somewhat on recycle rates, the first approximations must be made on the basis of a guess for this value (3–4%). The first run of the computer program on a case will establish not only this composition but also the slopes of the quench and adiabatic lines with greater precision so that other cases of bed temperatures may be considered. It will become apparent that catalyst is minimized by avoiding too close an approach to equilibrium and by selecting as the inlet temperature of the next bed a point along the quench line where the adiabatic temperature line just becomes parallel with a constant rate line. Usually this occurs over a range. In graphically determining bed temperature strategies

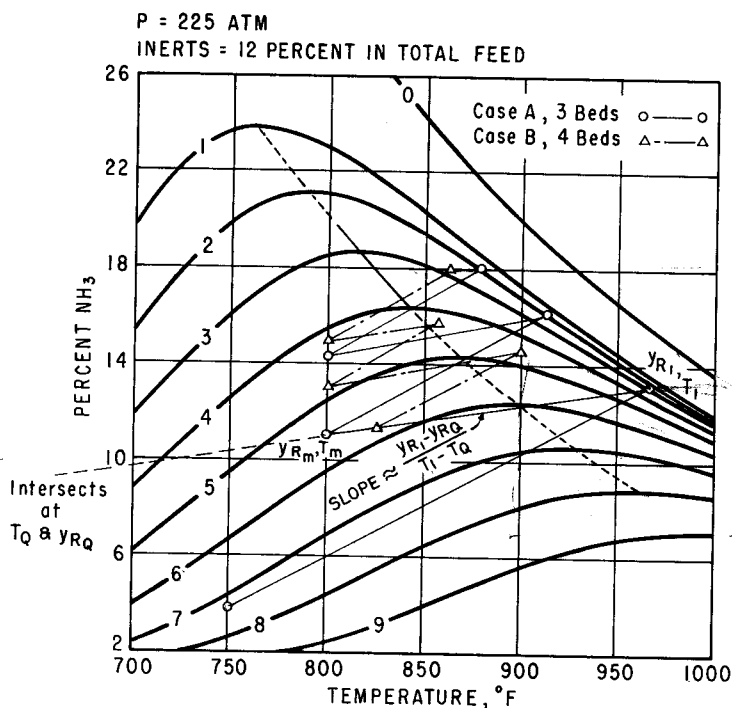


Fig. CS-6.3 Graphical solutions on computer-generated rate plot. ( $r \times 10^4 = 50$  lb-moles/(lb cat.) (hr) for contour 1, 71 for 2, 100 for 3, 141 for 4, 200 for 5, 282 for 6, 398 for 7, 562 for 8, and 795 for 9. These rates for 3–6 mm catalyst. Multiply by 0.87 for 6–10 mm catalyst.)

for trial, it is most convenient at a given pressure to select a reasonable low rate as the closest approach (e.g., line 2 on Fig. CS-6.3 for 225 atm) and a corresponding outlet percentage  $\text{NH}_3$  at a reasonable outlet temperature (e.g., 18% at 225 atm and 875°F). In this manner the reaction paths straddle the locus of maximum rates. Various cases in these general regions may then be calculated and compared. Referring to Fig. CS-6.3, a graphical procedure involving beginning at the set outlet conversion is followed, and one proceeds backward through the reactor. The adiabatic line *A* is followed until the rate begins to decrease and then the quench line is drawn and the process repeated. Two such cases are sketched. The inlet and outlet temperatures approximated from these constructions are then used to provide cases for computer calculations.

Alternatively, a computer routine can be devised to search for the minimum catalyst requirement by changing bed inlet and outlet temperatures systematically. The graphical selection of reasonable cases, however, is so rapid and efficient that the effort in developing this additional subroutine may not be warranted.

### Design Algorithm

Input data are: number of beds, pressure at reactor inlet (*P*) and at separator ( $\approx 0.92P$ ), product-recovery separator temperature, ammonia product rate, percent inerts in converter inlet, temperature of quench, and inlet and outlet temperature of each bed.

1. Select and set as independent variable the percentage inerts in purge.
2. At set inerts in purge determine  $y_{\text{H}_2}$ ,  $y_{\text{N}_2}$ , and  $y_{\text{A}}$  from equilibrium at separator.
3. Determine purge flow rate and fresh feed using Eqs. CS-6.17–CS-6.19 to solve for  $F_{\text{PU}}$  and  $F_{\text{F}}$ .
4. Determine recycle ( $F_{\text{r}}$ ) from inerts balance on reactor total feed ( $F_{\text{T}}$ ), fresh feed ( $F_{\text{F}}$ ) and recycle

$$(y_{\text{I}})_{\text{T}} F_{\text{T}} = (y_{\text{I}})_{\text{F}} F_{\text{F}} + (y_{\text{I}})_{\text{r}} F_{\text{r}} \quad (\text{CS-6.23})$$

$$(y_{\text{I}})_{\text{r}} = (y_{\text{I}})_{\text{PU}} \quad (\text{CS-6.24})$$

$$F_{\text{T}} = F_{\text{F}} + F_{\text{r}} \quad (\text{CS-6.25})$$

where *y* is the mole fraction inerts. Sub F indicates fresh feed.

5. Calculate first bed at point *i* in reactor.
  - (a) Calculate rate,  $\hat{r}_{\text{A}_i} = f(P, T_i, y_i)$  (pressure drop will be minimized and average *P* for bed is used).
  - (b) Calculate average rate for increment by linear extrapolation

$$\bar{\hat{r}}_{\text{A}_i} = \hat{r}_{\text{A}_i} + \frac{1}{2}(\hat{r}_{\text{A}_i} - \hat{r}_{\text{A}_{i-1}}) \quad (\text{CS-6.26})$$

- (c) Calculate  $\Delta n_{A_F}$ ,  $\Delta n_{H_F}$  and  $\Delta n_{N_F}$  for increment  $\Delta W/F_I$  using Eqs. CS-6.9–CS-6.11, where  $F_I$  is feed to first bed.
  - (d) Calculate  $(-\Delta H)_A$  at  $P$ ,  $T_i$  (Eq. CS-6.16 and  $C_{p_i} = f(T_i, P)$ ).
  - (e) Calculate  $T_{i+1}$  from heat balance over increment using Eq. CS-6.15.
  - (f) Go to step 5(a).
6. Calculate fraction quench required to produce temperature at inlet to bed no.  $II$  ( $T_0''$ )

Basis:  $T_0''$  and 1 mole feed to first bed

$$\sum [(n_j)_e^I c_{p_j}(T_e^I - T_0'')] + \sum_i [\gamma_{II}(n_j)_o^I c_{p_j}(T_Q'' - T_0'')] = 0$$

where  $T_Q$  is the quench temperature and  $n_j$  is the moles of component  $j$  per mole of feed to first bed.

$$\gamma_{II} = \frac{\sum [(n_j)_e^I c_{p_j}(T_e^I - T_0'')] }{\sum [(n_j)_o^I c_{p_j}(T_0'' - T_Q'')] } \quad (\text{CS-6.27})$$

7. Calculate composition and mole fractions of inlet to bed  $II$

$$(n_j)_o'' = (n_j)_e^I + \gamma_{II}(n_j)_o^I$$

$$y_j'' = \frac{(n_j)_o''}{\sum (n_j)_o''}$$

8. Proceed as in item 5 through bed  $II$ , etc.
9. At outlet of last bed calculate ratio  $F_I/F_T$  where  $F_T$  is the total feed.

$$F_T = F_I(1 + \gamma_{II} + \gamma_{III} + \cdots + \gamma_n)$$

$$\frac{F_I}{F_T} = \frac{1}{1 + \gamma_{II} + \gamma_{III} + \cdots + \gamma_n} \quad (\text{CS-6.28})$$

where  $\gamma$  is the fraction of feed to first bed as quench at entrance to indicated bed.

10. Calculate flow rates  $F_I$ ,  $F_Q''$ ,  $F_Q'''$ , etc.  $F_e$ , and  $F_v$  where  $F_e$  is the outlet flow in moles/time from reactor.  $F_T$  is known from Item 4. From CS-6.28

$$F_I = \left( \frac{1}{1 + \gamma_{II} + \gamma_{III} + \cdots + \gamma_n} \right) F_T \quad (\text{CS-6.29})$$

$$F_e = \sum (n_j)_e F \quad (\text{CS-6.30})$$

$$F_Q'' = \gamma_{II} F_I, F_Q''' = \gamma_{III} F_I, \text{ etc.} \quad (\text{CS-6.31})$$

$$F_v = F_e - F_P \quad (\text{CS-6.32})$$

11. Calculate vapor composition from separator for all components except  $\text{NH}_3$

$$F_v(y_j)_v = (y_j)_e F_e P \quad (\text{CS-6.33})$$

$$(y_A)_v = 1 - (y_N + y_H + y_A + y_M)_v \quad (\text{CS-6.34})$$

where  $y_M$  is the mole fraction of methane.

12. Compare with vapor compositions originally calculated. Seek the minimum of

$$f(x) = \sum [y_{j_v} F_v - y_{j_r} (F_{PU} + F_r)]^2 \quad (\text{CS-6.35})$$

13. Calculate function given by Eq. CS-6.35 and select new value of percent inerts in purge and return to item 1. The selection of a new value is guided by a unidimensional search subroutine.
14. Convergence Criterion

$$\frac{(y_I)_{\text{new}} - (y_I)_{\text{old}}}{(y_I)_{\text{old}}} < 10^{-2} \quad (\text{CS-6.36})$$

15. Calculate  $W$  for each bed

$$W_n = \left( \frac{W}{F_I} \right)_n F_I \quad (\text{CS-6.37})$$

This describes one case as set by input variables.

### Design Cases

Three pressures (150, 225, and 300 atm) will be studied at 12% inerts in the total feed and 40°F separator temperature. For each the catalyst will be minimized and a maximum allowable temperature of 970°F used as a safe distance from the maximum catalyst-use temperature. Since the rate data will be considered to represent lined-out activity after the early high activity, the amounts of catalyst determined for each case will be increased by the factor 1/0.70 to allow for full production at end-of-run conditions. The cost differentials between the several pressures will be determined and the final design pressure selected.

With converter bed sizes and number fixed, an operating study at various temperatures, purge rates, inert contents, and catalyst activity factor can be conducted. A program in which catalyst quantities are set and operating conditions varied is used. In this manner the affect of operating variables on product rate can be determined, and the flexibility of the proposed design assessed.

*Required Production*

Basis: 1000 tons/day

$$\frac{(1000)(2000)}{(24)(17)} = 4902 \text{ lb moles/hr}$$

Assume 99% recovery

$$\frac{4902}{0.99} = 4952 \text{ lb moles/hr}$$

*Recycle Loop  $\Delta P$  and Separator Pressure*

The recycle is handled in one wheel and modern compressors can be designed for a head of 15,000 ft  $\text{lb}_f/\text{lb}_m$  per stage (wheel). It is possible, however, to design the stage for the recycle to operate at a minimum of 50% of this value. The values given below are based on this assumption, and the corresponding separator pressures are calculated using a 1%  $\Delta P$  between the separator and the compressor.

Pressure, atm.	Loop $\Delta P$ , atm.	Separator Press., atm.	Nominal value, atm.
150	13.8	137.5	138
225	20	207.3	207
300	25.4	277.6	278

**Results**

The results for the cases selected for the three pressures are given in Tables CS-6.1–CS-6.3, and temperatures in the associated heat exchanger train were determined by heat and material balances.

*Vessel Diameter and Bed Lengths*

Calculate lengths and diameter on the basis of catalyst amounts shown in Tables CS-6.1–CS-6.3 increased by 1/0.7 to satisfy end of run conditions. For this study a bed  $\Delta P \approx 0.02P$  will be used. Other values could be studied in a similar manner. Pressure drop in the compressor loop, of which the converter is a part, sets a portion of the power requirements and various  $\Delta P$ 's must be considered. Higher values reduce vessel and catalyst costs but increase power consumption. Excessively low values cause maldistribution and temperature gradients between the catalyst and bulk fluid.

Table CS-6.1 Ammonia Synthesis Converter<sup>a</sup> (150 atm)

Stream	Total Flow	Material Balance									
		Hydrogen		Nitrogen		Ammonia		Methane		Argon	
		Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow
Fresh feed	10948.7	0.740300	8105.3	0.246800	2702.1	0.000000	0.0	0.009500	104.0	0.003400	37.2
Recycle	49382.0	0.594743	29369.6	0.198248	9789.9	0.063264	3124.1	0.105859	5227.5	0.037886	1870.9
In	60330.7	0.621158	37474.9	0.207059	12492.0	0.051783	3124.1	0.088372	5331.5	0.031628	1908.1
Outlet	55311.3	0.541405	29945.9	0.180475	9982.3	0.147230	8143.5	0.096392	5331.5	0.034498	1908.1
Sep. Vapor	50359.3	0.594644	29945.9	0.198222	9982.3	0.063374	3191.5	0.105870	5331.5	0.037890	1908.1
Purge	982.6	0.594743	584.4	0.198248	194.8	0.063264	62.2	0.105859	104.0	0.037886	37.2

## Reactor Summary

Quench Temperature = 125.00°F

Bed	Lb Cat.	Temp. In	Temp Out	Mole Fraction		Frac. Feed	Total Feed into Bed	Flow out of Bed	Quench at Bed Outlet
				NH <sub>3</sub> In	NH <sub>3</sub> Out				
1	110481.5	812.00	942.02	0.051783	0.103940	0.735448	44370.1	42273.8	
2	179476.9	800.00	888.04	0.094680	0.131748	0.151265	51399.7	49716.2	9125.9
3	190791.3	800.00	858.01	0.122083	0.147230	0.113287	56550.9	55311.3	6834.7
Total Catalyst = 480749.7 lb									

<sup>a</sup> Reactor pressure = 150.00 atm.

Fraction inerts in reactor inlet = 0.12.

Ammonia recovered at 138.000 atm and 40.00°F at a rate of 4952.0 lb moles/hr.

Flows given in lb moles/hr and temperature in °F.

Design catalyst loadings are  $\frac{1}{0.70}$  (total shown).

**Table CS-6.2 Ammonia Synthesis Converter<sup>a</sup> (225 atm)**

Stream	Total Flow	Material Balance									
		Hydrogen		Nitrogen		Ammonia		Methane		Argon	
		Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow
Fresh feed	10836.9	0.740300	8022.6	0.246800	2674.6	0.000000	0.0	0.009500	103.0	0.003400	36.8
Recycle	30852.1	0.592868	18291.2	0.197623	6097.1	0.051891	1600.9	0.116076	3581.1	0.041543	1281.7
In	41689.0	0.631192	26313.8	0.210406	8771.6	0.038402	1600.9	0.088372	3684.1	0.031628	1318.5
Outlet	36691.6	0.512859	18817.6	0.170963	6272.9	0.179834	6598.4	0.100409	3684.1	0.035036	1318.5
Sep. Vapor	31739.6	0.592875	18817.6	0.197636	6272.9	0.051872	1646.4	0.116074	3684.1	0.041542	1318.5
Purge	886.9	0.592868	525.8	0.197623	175.3	0.051891	46.0	0.116076	103.0	0.041543	36.8

**Reactor Summary**

Quench Temperature = 125.00°F

Bed	Lb Cat.	Temp. In	Temp Out	Mole Fraction			Total Feed into Bed	Flow out of Bed	Quench at Bed Outlet
				NH <sub>3</sub> In	NH <sub>3</sub> Out	Frac. Feed			
1	70887.1	750.00	970.07	0.038402	0.130499	0.684257	28526.0	26202.1	
2	89001.2	800.00	913.01	0.110693	0.161874	0.172195	33380.7	31910.3	7178.6
3	101695.2	800.00	880.02	0.142375	0.179834	0.143549	37894.7	36691.6	5984.4
Total Catalyst = 261583.5 lb									

<sup>a</sup> Reactor pressure = 225.00 atm.

Fraction inerts in reactor inlet = 0.12.

Ammonia recovered at 207.00 atm and 40.00°F at a rate of 4952.0 lb moles/hr.

Flows given in lb moles/hr and temperature in °F.

Design catalyst loadings are  $\frac{1}{0.70}$  (total shown).



Table CS-6.3 Ammonia Synthesis Converter<sup>a</sup> (300 atm)

Material Balance											
Stream	Total Flow	Hydrogen		Nitrogen		Ammonia		Methane		Argon	
		Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow	Frac.	Flow
Fresh feed	10743.5	0.740300	7953.4	0.246800	2651.5	0.000000	0.0	0.009500	102.1	0.003400	36.5
Recycle	21728.1	0.584507	12700.2	0.194836	4233.4	0.047701	1036.5	0.127371	2767.5	0.045585	990.5
In	32471.6	0.636053	20653.7	0.212029	6884.9	0.031919	1036.5	0.088372	2869.6	0.031628	1027.0
Outlet	27481.4	0.479171	13168.3	0.159737	4389.8	0.219302	6026.7	0.104419	2869.6	0.037371	1027.0
Sep. Vapor	22529.4	0.584493	13168.3	0.194847	4389.8	0.047704	1074.7	0.127371	2869.6	0.045585	1027.0
Purge	801.3	0.584507	468.4	0.194836	156.1	0.047701	38.2	0.127371	102.1	0.045585	36.5

## Reactor Summary

Quench Temperature = 125.00°F.

Bed	Lb Cat.	Temp. In	Temp. Out	Mole Fraction		Frac. Feed	Total Feed into Bed	Flow out of Bed	Quench at Bed Outlet
				NH <sub>3</sub> In	NH <sub>3</sub> Out				
1	41409.0	700.00	970.08	0.031919	0.149635	0.580973	18865.1	16933.4	
2	72347.9	750.00	915.02	0.116166	0.195490	0.207172	23660.6	22090.7	6727.2
3	103286.8	750.00	875.02	0.156648	0.219302	0.211854	28969.9	27481.4	6879.2
Total Catalyst = 217043.7 lb									

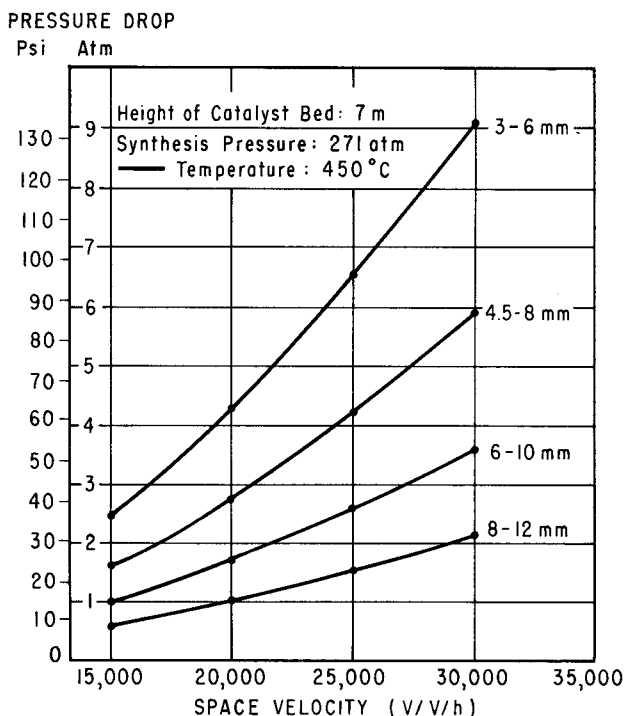
<sup>a</sup> Reactor pressure = 300.00 atm.

Fraction inerts in reactor inlet = 0.12

Ammonia recovered at 278.00 atm and 40.00°F at a rate 4952.0 lb moles/hr.

Flows given in lb moles/hr and temperature in F.

Design catalyst loadings are  $\frac{1}{0.70}$  (total shown).



**Fig. CS-6.4** Pressure-drop data for granular ammonia catalyst (multiply by 1.9 to obtain  $\Delta P$  for dense-packed arrangement for design). [For other conditions:

$$\frac{\Delta P_2}{\Delta P_1} = \left( \frac{Z_2}{Z_1} \right)^{2.85} \left[ \frac{(SV)_2}{(SV)_1} \right]^{1.85} \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right) \left( \frac{M_2}{M_1} \right)^{0.85}$$

(SV) is the space velocity  $V/V/h$  measured at 0°C and 1 atm,  $M_2$  and  $M_1$  are the molecular weights of mixture]. Reproduced by permission: Haldor Topsoe A/S, Copenhagen, Denmark, A. Nielsen, *An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia*, 3rd ed., Gjellerups, Copenhagen, 1968.

Set the diameter using bed II as representing an average condition. Pressure-drop data obtained for the particular granular catalyst are given in Fig. CS-6.4.

*Example Case 2:* (avg. flow = 32646 lb moles/hr,  $\rho_b = 165$ ,  $T = 856^\circ\text{F}$  (731°K),  $P = 225$  atm

$$(SV)_2 = \frac{(32640)(359)}{89001/(0.7)(165)} = 15206 \text{ V/V/hr}$$

From Fig. CS-6.4 @ (SV) = 15206 and catalyst 6–10 mm

$$\Delta P_1 = (1.9)(1.02) = 1.94 \text{ atm}$$

Let

$$\Delta P_2 = (225)(0.02) \left( \frac{89001}{261584} \right) = 1.53 \text{ atm}$$

$$\frac{1.53}{1.94} = \left[ \frac{Z_2}{(7)(3.28)} \right]^{2.85} \left( \frac{271}{225} \right) \left( \frac{731}{723} \right)$$

$$Z_2 = 19.72 \text{ ft}$$

$$D = \left[ \frac{(89001)(4)}{(0.7)(165)(\pi)(19.72)} \right]^{\frac{1}{2}} = 7.05 \text{ ft}$$

$\Delta P$  and lengths for beds *I* and *III* are 15.7 ft and 0.9 atm and 22.56 ft and 2.2 atm, respectively.

Check  $\Delta T$  between bulk fluid and catalyst to see if mass velocity is adequate. The pressure drop data in Fig. CS-6.4 was plotted as  $\Delta P/Lu_s$  versus  $G$ .

$G = \frac{(SV)(M_m)}{2.24 \times 10^4} L$ g/cm <sup>2</sup> sec	$u_s = \frac{G}{\rho}$ cm/sec	$\frac{\Delta P}{Lu_s}, \frac{\text{dynes sec}}{\text{cm}^4}$
1.125	28.5	50.8
1.50	38.0	66.6
1.88	47.6	82.2
2.25	57.0	94.0

A plot of  $\Delta P/(Lu_s)$  versus  $G$  yields the slope  $b$  in the expression,  $\Delta P/(Lu_s) = a + bG$ , as described on p. 113<sup>1</sup>.

$$b = 37.7, \varepsilon = 1 - \frac{\rho_b}{\rho_p} = 1 - \frac{165}{305} = 0.459$$

$$a_s = \frac{b\varepsilon^3}{(\beta/8)(1 - \varepsilon)} = \frac{(37.7)(0.179)}{0.48} = 14.1 \text{ cm}^{-1}$$

$$a_m = a_s/\rho_p = (14.1)(2.54)(12)/305 = 1.41 \text{ ft}^2/\text{lb}$$

$$D_p = \frac{6}{0.41} = 0.43 \text{ cm or } 4.3 \text{ mm}$$

$$d_p \approx (1.35)(0.43) = 0.58 \text{ cm or } 0.019 \text{ ft}$$

Mixture Properties at inlet to case 2, bed I:

$$\mu = 0.026 \text{ cp} \quad (\text{API Data Book, Proc. 71 B2.1})$$

$$c_p = 7.7 \text{ BTU/lb mole } ^\circ\text{F}, M = 10.57 \quad (14)$$

$$\lambda_f = 0.132 \text{ BTU/hr ft}^\circ\text{F} \quad (\text{API Data Book, Proc. 12B2.1})$$

Rate at inlet from Fig. CS-6.3 is 0.0394 lb mole/(lb cat.) (hr):

$$\left(\frac{c_p \mu}{\lambda_f}\right)^{\frac{1}{3}} = \left[\frac{(7.7)(0.026)(2.42)}{(10.57)(0.132)}\right]^{\frac{1}{3}} = 0.494$$

From Fig. 11.5

$$R_m = \frac{(-r_N)M_m}{a_m G} = \frac{(0.0394)}{(1.41)(28526/39)} = 3.82 \times 10^{-5}$$

$$q_m = \frac{R_m(-\Delta H)}{c_{pm}} = \frac{(3.82 \times 10^{-5})(22000)(1.8)}{7.7} = 0.197$$

$$N_{Re} = \frac{0.019[(28526)(10.57)/39]}{(0.026)(2.42)} = 2335$$

$$\Delta T = 4\left(\frac{0.46}{0.4}\right)(0.5) = 2.3^\circ\text{F within accuracy of data.}$$

$\therefore$   $G$  adequate and diameter selected OK.

### Vessel Design

High pressure vessels require the attention of experts in design and fabrication. Ammonia converters in particular, with the many internals and high pressure, present complex mechanical design problems that are wisely assigned to firms specializing in these units. Our focus in this study will be confined only to estimating a vessel weight so that approximate vessel cost can be determined based on data from fabricators on previously built converters of similar size. To reduce vessel thickness a cooling jacket will be used through which will be passed cool synthesis gas that has been only partially exchanged in the heat recovery train. The temperature rise will be about  $25^\circ\text{F}$  and the corresponding heat removed only 3% of that generated in the reactor. The adiabatic assumption in the original calculations remains justifiable although it is possible to add a loss term to the model if accuracy of rate data being used should justify such action. The style vessel will be similar to that shown in Fig. 11.10, and cost will be based on 70¢/lb of vessel including internals and nozzles (1972 costs). The inner shell will be constructed of stainless steel (SA 240 type 316) and the outer shell of carbon steel (SA 204 grade A).

Since the cooling stream (Fig. CS-6.2) is at a higher pressure than the reacting gases inside the shell, this thickness must be calculated using Fig. UHA 28.2 of the ASME Code for vessels under external pressure. Final design would include a shell of increasing thickness toward the bottom, but for estimating purpose we will determine a single thickness based on maximum design pressure.

The results of calculations on both inner and outer shells are summarized in Table CS-6.4, together with estimated costs. Refer to Appendix B and the ASME Code for design procedures.

### *Compressor Costing and Selection*

The crucial nature and high cost of the synthesis and recycle compressor chain demands serious study by a team of experts including compressor manufacturer's representatives. The latter can often suggest even modest changes in design conditions which are perfectly acceptable that will fit better into a given compressor design and save much capital and operating cost.

Higher pressure systems require three barrel casings (frames) on a single drive shaft, and lower pressure, two. Obviously, the fewer casings the lower the capital, and maintenance cost. The trend in compressor development is toward more horsepower per wheel. For purposes of cost estimating, we will employ 2 casings for 150 atm and 3 casings for 225 atm and 300 atm, realizing that it may be possible to include the 225 atm in two casings as well and reduce its cost.

The results of these calculations, which were made in accordance with the procedures outlined in Appendix C, are given in Table CS-6.5.

Higher pressures reduce the refrigeration requirements for ammonia recovery; and refrigeration compression costs, as summarized in Table CS-6.6, must also be included.

### *Selecting Operating Pressure*

The major equipment and operating costs for which significant cost differences exist are summarized in Table CS-6.7. A 3-yr basis or payout was selected which corresponds to the assumed life of the catalyst.

As has been shown previously on a slightly different basis (13), there is little difference between the three cases. The 150 atm and 225 atm cases are essentially the same, but the higher energy requirements for the 225 atm case, provide ominous warnings in an era of constantly rising fuel costs. It seems preferable, therefore, to select the lower pressure case (150 atm), for

**Table CS-6.4 Converter Summary (1972 Costs)**

Case	Nominal Pressure atm	ID Inner Shell, ft	Total Bed Height, ft	Total Bed $\Delta P$ , atm	Inner Shell <sup>a</sup>		Outer Shell <sup>b</sup>			Total Weight lb	Vessel Cost \$ <sup>c</sup>
					Height ft	Weight lb	ID ft	Height ft	Weight lb		
1	150	10.4	49	3	55	135,147	10.7	56	944,307	$1.08 \times 10^6$	756,000
2	225	7.05	58	4.6	64	100,958	7.45	65	794,448	$0.895 \times 10^6$	626,500
3	300	5.6	76.3	6.1	82	105,799	6.1	83	924,911	$1.031 \times 10^6$	721,700

<sup>a</sup> Design for 1020° F and 2 (bed  $\Delta P$ ) to allow for partial plugging. Use Fig. UHA 28.2 in ASME Code for vessels with exterior pressure. Use ASTM A240 Type 316. See Appendix B for costing technique.

<sup>b</sup> Design for 600° F and 1.1 (nominal pressure). Use a 0.5 Mo steel (see Fig. B.1 in Appendix), ASTM A204 grade A (avoid prolonged exposure above 875° F. See Appendix B for discussion on vessel costing.

<sup>c</sup> \$0.7 lb of vessel weight without nozzles and other internals.

Table CS-6.5 Synthesis and Recycle Compressor Summary (1972 Costs)

Nominal Pressure Atm	No. Comp. Casings	Total HP	Compressor Cost, \$	Turbine Cost, \$	Total \$	Energy Consumption Equivalent Fuel, BTU/hr
150	2	17,370	339,500	403,700	743,200	$9.71 \times 10^7$
225	3	21,460	428,500	446,000	874,500	$12.10 \times 10^7$
300	3	22,240	443,800	452,400	896,200	$12.50 \times 10^7$

## Notes:

1. Fresh feed compressed from 365 psia and 100°F to 945 psia in first casing, 150-atm alternate, and 888 psia and 853 psia for 225-atm and 300-atm alternates, respectively.
2. Recycle enters last casing at 40°F and 2120, 3180, and 4230 psia, respectively for the three alternates.
3. Discharge pressure of last casings are 2260, 3380, and 4500 psia, respectively.
4. Intercooling is at 40°F between casings.
5. Isentropic work was determined using an HTS diagram prepared from literature data for 3:1 H<sub>2</sub>-N<sub>2</sub> (12) that were found satisfactory and most convenient for this purpose. Actual horsepower was determined based on polytropic efficiency of 74% corrected to an isentropic efficiency, as described in Appendix C.
6. Steam turbine estimates are based on dual-turbine drives, 70% of power in 1500 psig steam @ 900°F to 600 psig and 30% in 600 psig @ 695°F to 4 in. Hg absolute. Efficiency assumed to be 75%.
7. Energy consumption based on 85% efficiency at boiler plant. No credit for excess 600 psig steam made in first turbine.

it will become even more attractive as fuel costs inevitably rise. Obviously, longer catalyst life and higher activity should be important goals in this business. Higher conversions reduce power requirements by lowering the amount of recycle. A catalyst active at a lower temperature would be most attractive for this exothermic reaction.

Earlier studies (13) indicated that higher pressures are required for plants operating at 1500 tons per day capacity. This was necessitated by the impractical converter sizes encountered for this larger capacity at 150 atm. Again, however, escalating fuel costs suggest reevaluation of this conclusion. It is possible that the new horizontal converters (see p. 518<sup>1</sup>) could be specified at lower pressures without encountering impractical configurations.

Although the operating pressure was based on a particular inert level, quench temperature, and approach to equilibrium, other conditions do not substantially alter the conclusions. The next step in design would be a study of other operating conditions at the selected pressure.

Table CS-6.6 Refrigeration Compression Costs (1972 Costs)

Nominal Converter Pressure, Atm	Total Refrigeration HP	Compressor Cost	Turbine Cost	Total \$	Energy Consumption Equiv. Fuel, BTU/hr
150	7300	209,200	152,500	361,700	$5.05 \times 10^7$
225	5199	191,200	118,900	310,100	$3.96 \times 10^7$
300	4154	184,200	102,100	286,300	$3.17 \times 10^7$

By lowering the separator temperature, for example, the inlet  $\text{NH}_3$  in the recycle will be reduced. The outlet concentration of ammonia can be reduced accordingly while maintaining the same conversion level. The net result will be a smaller catalyst charge because the average rate will be higher. There may be merit in limiting the maximum operating temperature and thus design temperatures so that the vessel walls may be made slightly less thick. Alternatively, the Nuclear Section of the ASME Code may be used to effect possible savings. These and similar points need to be carefully studied along with studies of the operating flexibility of the final design.

Table CS-6.7 Cost Comparison (1972 Costs)

Basis: 3 yr	150 Atm	225 Atm	300 Atm
Converter	\$756,000	\$626,500	\$721,700
Fresh feed and recycle compressors and turbines	743,200	874,500	896,200
Refrigeration compressors and turbines	361,700	310,100	286,300
Catalyst cost <sup>a</sup>	228,700	124,440	103,250
Sub-total	2,089,600	1,935,540	2,007,450
Misc. equip cost difference (piping, etc.) <sup>b</sup>	—	25,000	32,000
Fuel cost difference <sup>c</sup>	—	—	—
(Basis: 3 years, 40¢/MM BTU)	—	133,923	93,746
Net difference	—	4,863	43,596

<sup>a</sup> \$0.333/lb.

<sup>b</sup> Incremental increase due to higher pressure for piping, heat exchangers, drums, etc.

<sup>c</sup> From Tables CS-6.5 and CS-6.6. Operating factor = 0.98.



### Operating Flexibility

A designer can be much more confident in the operability of his selected design by using the "what if" approach, discussed on p. 264<sup>1</sup>. For example, if the catalyst activity factor,  $\psi$ , in the first bed should decline to 0.5 and in the other beds to 0.8 how should production be maintained.

Questions such as this are answered using a revised design program which can be called an operating program. Briefly, now the inputs become catalyst quantities (1.429 times amounts shown in Table CS-6.1), inlet temperatures, feed composition, and pressure. We desire an output ammonia production and bed outlet temperatures. To simplify the program, the separator loop is eliminated and the inert level in the recycle fixed at an average value. This does not affect the outcomes greatly and enables the simplified program to be incorporated into an optimization routine if desired.

The answer to the question is given in Table CS-6.8 which indicates that the unit as designed has good flexibility. Other similar concerns can be resolved in this manner with assurance that the conclusions are reasonably correct.

**Table CS-6.8 Results of Operating Study (150 Atm)**

Bed No.	Temp. In °F	Temp. Out °F	NH <sub>3</sub> In %	NH <sub>3</sub> Out %
1	850	959	5.18	9.54
2	750	853	8.43	12.69
3	750	814	11.58	14.29
Outlet flow, moles/hr				62,882.5
Ammonia production, tons/day				1114 <sup>a</sup>

<sup>a</sup> The design production can clearly be exceeded even with deactivated catalyst, but the total flow must be increased which means higher recycle compressor costs.

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