

## Nomenclature

$A$  = cross-sectional area of bed,  $\text{cm}^2$   
 $B_i$  = Langmuir constant,  $\text{atm}^{-1}$  or  $\text{psi}^{-1}$   
 $C_p$  = heat capacity of gas,  $\text{cal/mol/K}$   
 $C_p^a$  = heat capacity of adsorbed phase,  $\text{cal/mol/K}$   
 $C_p^s$  = heat capacity of solid carbon,  $\text{cal/mol/K}$   
 $d$  = diameter of the tube,  $\text{cm}$   
 $d_p$  = diameter of particle,  $\text{cm}$   
 $h$  = overall heat-transfer coefficient,  $\text{cal/cm}^2/\text{K/s}$   
 $L$  = length of bed,  $\text{cm}$   
 $n$  = constant  
 $p$  = pressure,  $\text{atm}$   
 $q$  = amount adsorbed,  $\text{L STP/g}$   
 $q_m$  = monolayer amount adsorbed,  $\text{L STP/g}$   
 $R$  = gas constant  
 $t$  = time,  $\text{s}$   
 $T$  = temperature,  $\text{K}$   
 $T_0$  = ambient temperature ( $= 20^\circ\text{C}$ )  
 $u$  = gas velocity,  $\text{mol/s}$   
 $V_m$  = molar volume at STP ( $= 22.4 \text{ L/mol}$ )  
 $z$  = height of bed ( $= 0$  at the feed end),  $\text{cm}$

## Greek Symbols

$\epsilon$  = fractional void in bed  
 $\rho$  = bed density,  $\text{g/cm}^3$  bed

## Subscripts

$f$  = feed  
 $i$  = component  $i$   
 $0$  = initial  
 $1$  = bed 1  
 $2$  = bed 2

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# Optimal Temperature Profile for an Ammonia Reactor

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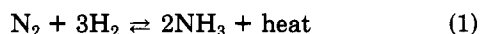
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A model of the industrially important catalyzed ammonia synthesis reaction,  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ , in a continuous-flow reactor is analyzed. Optimal control theory, with the reaction temperature as the control variable, is applied to the model in order to maximize the molar fraction of ammonia at the end point of the reactor for a given constant mass flow and given inlet conditions. The optimal temperature profile along the reactor along with the associated heat production rate and its exergy equivalent is calculated and the performance compared with that of conventional operation of ammonia synthesis reactors. The kinetics are assumed to obey a Temkin-Pyzhev-type rate equation, and the properties of the gaseous mixture are represented throughout by the equation of state formulated by Beattie and Bridgeman. The numerical calculations are carried out for operating conditions representative of a commercial prereduced promoted iron catalyst. Substantial room for improvement of efficiency seems to exist compared to conventional adiabatic reactors.

## I. Introduction

Since it is one of the most important industrial chemical reactions, synthesis of ammonia has been treated extensively in the literature (see, e.g. Vancini (1971), Strelzoff (1981), or the books edited by Slack and James (1973, 1974, 1977, 1979)) from technical as well as economical points of view, and the production has reached a remarkable degree of efficiency. The technical investigations can generally be divided into the following three categories: (i) analyses of the energetics and equilibrium behavior of the reaction



at a wide range of temperatures and pressures by traditional (reversible) thermodynamics, in many cases empirically describing the nonidealities of the gas mixture

through fugacities; (ii) studies of the kinetics of reaction 1 in the presence of catalysts, either empirically or involving the expected detailed reaction mechanism on a catalytic surface (Nielsen, 1968); and (iii) attempts to optimize the performance of an entire ammonia production plant, or major parts thereof, by adjusting flows between the different subsystems and scaling component sizes appropriately.

Working in an academic environment, we leave problems in the last category to practicing engineers. The two former problems, which contain more of the basic science, unfortunately seem to be almost mutually exclusive since reversible thermodynamic theory describes a static, equilibrium situation. Traditionally, this theory admits constraints on state variables, such as constancy of temperature, pressure, or volume, or constraints on process

variables, such as adiabaticity, but not constraints on time or rate. This makes such analyses rather unrealistic, since nobody is willing to wait—or pay—for the reversible operation of a plant. It is therefore necessary to analyze industrial processes by using other methods. The standard way is to optimize the yield of a process by varying its operating conditions, using the state and rate equations as constraints. Such optimizations may be limited to key parameters (e.g., inlet temperature and flow, selected quench flows, and the like) assuming a given behavior of the stage (isothermal, adiabatic, etc.), or they may be unrestricted. In either case, they are rather cumbersome, and simpler, approximate methods are required. One such new method is finite-time thermodynamics (for an overview, see Andresen et al. (1984a,b)) which extends reversible thermodynamic theory to allow constraints involving time or rate, e.g., in the form of chemical or thermal rate equations, thus taking into account the most important irreversibilities associated with the process considered. Until now, finite-time thermodynamics has primarily been applied to various heat engines and combinations of these (Salamon et al., 1977, 1980; Andresen et al., 1983) and to simplified chemical systems with work output (Ondrechen et al., 1980a,b), but the methodology is equally applicable to synthetic reactions.

We here present a detailed and self-consistent traditional optimization of such a reactor model which is close to real conditions by incorporating empirical state and rate equations. In a forthcoming publication, we will use these results as a benchmark for finite-time thermodynamic analyses of the same reaction. For this reason, the calculation must be fully self-consistent. In addition, this is the first published completely unrestricted optimization of an exothermic reaction in a realistic formulation and as such has value as the ultimate goal for improvement of reactors. The ammonia synthesis process was chosen because it has a long history of research and improvements so that there are large amounts of empirical data and experience of optimization available.

We have chosen our assumptions regarding reactor geometry, kinetics, etc., in the present model of the ammonia synthesis reaction to be a good compromise between simplicity and realism and at the same time similar to those of earlier optimization efforts (Aris, 1961a,b; Horn, 1961; Amundson and Bilous, 1956; Annable, 1952; Murase et al., 1979). Using the methods of optimal control theory, we calculate that temperature profile in the gas along the reactor which yields the highest content of ammonia in the product stream and derive from that the corresponding energy and exergy flows. We have tried to describe the steps of the present analysis so clearly and detailed that it will be simple to transfer the procedures presented here to other industrial processes. We pay particular attention to the possibilities of improvement compared to an idealized contemporary industrial reactor when all external processes are treated as reversible. We also study the effects of varying several controllable parameters, e.g., pressure and stoichiometry of the synthesis gas. We have taken special care to use a consistent set of data throughout the analysis.

## II. Reactor

The model reactor is tubular of length  $L$  and constant cross-sectional area  $B$ . These are effective measures in the sense that they take into account that the reactor is filled with catalyst pellets which occupy part of the actual volume of the reactor vessel. We assume that the flow occurs under ideal displacement conditions, i.e., with no longitudinal mixing and with flat radial velocity, concen-

tration, and temperature profiles. The feed rate and the composition of the feed mixture are constant and known. The pressure drop, which in modern reactors can be made quite small, is here neglected entirely, so that the process is treated as isobaric. The difference in temperature between the bulk gas and the catalyst pellets as well as inside the pellets is also neglected (Vancini, 1971).

The gas temperature  $T$  is allowed to vary with the coordinate  $l$  along the reactor in order to achieve optimization. To maintain this temperature profile  $T(l)$ , a heat flow  $q$  (W/m) through the walls per unit length of the reactor is needed. The conditions in the reactor are assumed to be stationary, so that the mass flow rate  $G$  (kg/(m<sup>2</sup> s)) is constant along the reactor. (The flow rate in units of mol/(m<sup>2</sup> s) will vary since reaction 1 results in a decrease in the number of moles.) The feed consists of a mixture of hydrogen, nitrogen, ammonia, and inert gases, primarily methane and argon. Although the inerts do not participate in the reaction, they dilute the active components and may influence their fugacities as well as increase the heat capacity of the mixture and the workload on the circulation compressors.

## III. Equation of State

In the present investigation, we emphasize the self-consistency of the data representing the thermodynamic properties of the synthesis gas; i.e., given a certain equation of state which describes the  $P$ - $V$ - $T$  relationship in the gas mixture, other thermodynamic variables such as heat capacity and heat of reaction should be chosen with empirical constants calculated on the basis of this equation. We use one form of the equation of state given by Beattie and Bridgeman (1927, 1928). This equation has been superseded by other expressions (e.g., based upon Lee and Kesler (1975) or Redlich and Kwong (1949)) in contemporary industrial calculations, but no complete self-consistent data set encompassing all the other empirical quantities is available for these later and presumably more accurate expressions. Our results depend primarily on the expressions for the reaction rate, equilibrium constant, and heat of reaction. These quantities are interrelated through the equation of state, and we therefore use only data derived from experiments by way of the same expressions as we use here and performed in appropriate pressure, temperature, and composition ranges. It is straightforward to apply the procedure developed here to other equations of state, provided a consistent set of empirical constants is available.

The equation was originally formulated in the form  $P(n_i, V, T) = 0$ , but the form  $V(n_i, P, T) = 0$  is better suited in our context, since the pressure is constant. Following Beattie (1930), we expand the equation in powers of  $1/P$  and keep only terms up to first order. For  $n$  moles of a gas mixture,  $n = \sum_i n_i$ , this yields the expression ( $m = \text{mixture}$ )

$$V = \frac{nRT}{P} + \frac{n}{RT}\beta_m \quad (2)$$

where

$$\beta_m = RTB_m - A_m - RC_m/T^2 \quad (3)$$

The mixture parameters are determined by

$$A_m = (\sum_i x_i A_i^{1/2})^2 \quad (4a)$$

$$B_m = \sum_i \sum_j x_i x_j (B_i^{1/3} + B_j^{1/3})^3 \quad (4b)$$

$$C_m = (\sum_i x_i C_i^{1/2})^2 \quad (4c)$$

**Table I. Constants in the Beattie-Bridgeman Equation of State (Beattie and Bridgeman, 1927, 1928) Eq 4, and in the Heat Capacity Expression (Beattie, 1929; Gillespie and Beattie, 1930) Eq 48**

|                 | <i>i</i> | $10^{-3} A_i / \text{m}^3 / \text{mol}^2$ | $10^{-6} B_i / \text{m}^3 / \text{mol}$ | $C_i / \text{K}^3 \text{m}^3 / \text{mol}$ | $A_i^* / \text{J} / (\text{mol K})$ | $10^{-3} B_i^* / \text{J} / (\text{mol K}^2)$ | $10^{-6} C_i^* / \text{J} / (\text{mol K}^3)$ |
|-----------------|----------|---|---|--|-------------------------------------|---|---|
| H <sub>2</sub>  | H        | 20.01                                     | 20.96                                   | 0.504                                      | 27.810                              | 2.9288  | 0.0   |
| N <sub>2</sub>  | N        | 136.23                                    | 50.46                                   | 42.0                                       | 28.480                              | 1.3807  | 0.2092  |
| NH <sub>3</sub> | Z        | 242.47                                    | 34.15                                   | 4768.7                                     | 33.584                              | 2.9706  | 21.338  |
| Ar              | A        | 130.78                                    | 39.31                                   | 59.9                                       | 20.79                               | 0.0   | 0.0   |
| CH <sub>4</sub> | M        | 230.70                                    | 55.87                                   | 128.3                                      | 23.64                               | 47.86   | 0.0   |

where  $x_i$  is the mole fraction of substance  $i$ , and  $A_i$ ,  $B_i$ , and  $C_i$  are the corresponding pure gas equation-of-state coefficients listed in Table I.

#### IV. Rate Equation

The ammonia synthesis reaction 1 proceeds through a number of (partly undetermined) steps on the catalytic surface with the overall production rate  $r$  (mol NH<sub>3</sub>/(m<sup>3</sup> s)), i.e., the difference between formation and decomposition rates, fairly well described by the Temkin-Pyzhev rate equation (Temkin and Pyzhev, 1939),

$$r = k_1 p_N (p_H^3 / p_Z^2)^\alpha - k_2 (p_Z^2 / p_H^3)^{1-\alpha} \quad (5)$$

$k_1$  and  $k_2$  are the forward and backward rate constants, and  $\alpha$  is a constant,  $0 < \alpha < 1$  connected to the dissociation state of nitrogen on the catalyst. Normally  $\alpha$  is set equal to 0.5, but values in the range 0.5–0.75 have also been reported (Nielsen, 1968). The partial pressures are denoted by  $p_i$  with  $i = \text{H}$  (hydrogen),  $\text{N}$  (nitrogen),  $\text{Z}$  (ammonia), and  $\text{I}$  (inerts); when appropriate, we specify  $\text{A}$  (argon) and  $\text{M}$  (methane) instead of  $\text{I}$ . The rate constants in eq 5 depend on both temperature and pressure in the ranges of industrial importance, but the pressure dependence can be removed if activities (fugacities) are used instead of partial pressures. A drawback of eq 5 is that it obviously is not valid for very low ammonia concentrations since the first term diverges, a fact which must be borne in mind when selecting inlet conditions for our analysis.

Introducing the equilibrium constant  $K_a$ , and assuming that the absorption of nitrogen on the surface of the catalyst is the rate-determining step, Nielsen et al. (1964) and Nielsen (1968) derived an equation of the form

$$r = \frac{K_b (K_a^2 a_N - a_Z^2 / a_H^3)}{(1 + K_c a_Z / a_H^w)^{2\alpha}} \quad (6)$$

in terms of the activities  $a_i$ .  $K_b$  and  $K_c$  are temperature-dependent coefficients and  $\alpha$  and  $w$  are empirically determined constants. These authors found that their experimental results (using a prerduced promoted iron catalyst and steady-state conditions at 450 °C and 300 atm) are best represented by eq 6 with  $w = 1.50$  and that the number 1 in the denominator is negligible compared to the other term. Then, eq 6 reduces to

$$r = \frac{K_b}{K_c^{2\alpha}} [K_a^2 a_N (a_H^3 / a_Z^2)^\alpha - (a_Z^2 / a_H^3)^{1-\alpha}] \quad (7)$$

which is the original Temkin-Pyzhev equation (5) with activities instead of partial pressures. They also found the best value of  $\alpha$  to be 0.75. Ferraris et al. (1974) generated 23 different models for describing the rate of ammonia formation, of which 21 fit the data almost equally well. Their "best" equation is very similar to eq 6. We will regard the activity of the catalyst as constant, and set the effectiveness factor (Nielsen, 1968) equal to one. Equation 7 has been tested for temperatures in the range 550–1100 K and pressures between 100 and 1000 atm, but the actual range of applicability is difficult to determine.

**Table II. Three Possible Sets of Values for the Constants in the Rate Equation 7 and Equations 10 and 11 (From Nielsen et al. (1964) and Nielsen (1968))**

|  | set 1                 | set 2                 | set 3                 |
|--|-----------------------|-----------------------|-----------------------|
| $K_{b0}$ , mol of NH <sub>3</sub> atm/(m <sup>3</sup> s) | $5.89 \times 10^{12}$ | $2.19 \times 10^{10}$ | $1.28 \times 10^8$    |
| $E_b$ , kJ/mol   | 72.189                | 46.752                | 20.315                |
| $K_{c0}$ , atm <sup>1/2</sup>                            | $3.07 \times 10^{-2}$ | $2.94 \times 10^{-4}$ | $2.96 \times 10^{-6}$ |
| $E_c$ , kJ/mol   | -81.028               | -100.66               | -122.38               |

To be consistent with our choice of the equation of state, eq 2–4, we use the following expression (Gillespie and Beattie, 1930) for the equilibrium constant  $K_a$ :

$$\log (K_a / K_a^*) = [0.119 184 9 T^{-1} + 25 122 730 T^{-4} + 38.768 16 T^{-2} \sum_i \bar{x}_i A_i^{1/2} + 64.494 29 T^{-2} (\sum_i \bar{x}_i A_i^{1/2})^2] P \quad (8)$$

$$\log K_a^* = -2.691 122 \log T - 5.519 265 \times 10^{-5} T + 2.6899 + 1.848 863 \times 10^{-7} T^2 + 2001.6 T^{-1} \quad (9)$$

where in eq 8 the total pressure  $P$  is in atmospheres, and  $\bar{x}_i$  is the mole fraction of gas  $i$  in the equilibrium mixture.  $K_a^*$  is the equilibrium constant at zero pressure. The factors  $K_b$  and  $K_c$ , being essentially rate constants, may be expressed as (Nielsen et al., 1964)

$$K_b(T) = K_{b0} \exp(-E_b/RT) \quad (10)$$

$$K_c(T) = K_{c0} \exp(-E_c/RT) \quad (11)$$

with three empirically determined sets of interdependent values for the constants in eq 10 and 11 shown in Table II.

#### V. Activities

The activity coefficients  $\gamma_i$  are introduced by

$$a_i = \gamma_i x_i P \quad (12)$$

After extensive manipulation using the general expression

$$RT \ln \gamma_i = \int_0^P \left[ \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_{j \neq i}} - \frac{RT}{P} \right] dp \quad (13)$$

one may arrive at (for details, see Beattie and Bridgeman (1927, 1928) and Beattie (1949))

$$RT \ln \gamma_i = (\beta_i + D_i) P / RT \quad (14)$$

with (c.f. eq 3)

$$\beta_i = RT B_i - A_i - RC_i / T^2 \quad (15)$$

and

$$D_i = (A_i^{1/2} - \sum_j x_j A_j^{1/2})^2 + (C_i^{1/2} - \sum_j x_j C_j^{1/2})^2 R / T^2 - \frac{3}{4} RT (B_i^{1/3} - \sum_j x_j B_j^{1/3}) (B_i^{2/3} - \sum_j x_j B_j^{2/3}) \quad (16)$$

A comparison with eq 55 in Nielsen (1968) shows that the last two terms in eq 16 have been neglected there which is not always justifiable. Combining eq 14 and 12, we finally arrive at the equation

$$a_i = x_i P \exp[(\beta_i + D_i) P / (RT)^2] \quad (17)$$

for the activities as functions of pressure, temperature, and mole fractions.

## VI. Fractional Conversion and Reaction Rate

Next, we use the fact that in a system with a single reaction such as this, all mole fractions can be expressed in terms of a single variable, which we choose to be related to the mole fraction of ammonia. We define this variable  $\varphi$ , the fractional conversion, as the ratio of the number of moles of  $H_2$  and  $N_2$  that are converted into  $NH_3$  to the total number of moles of gas in the completely unreacted mixture, i.e., when N and H atoms in ammonia are counted as the corresponding number of  $N_2$  and  $H_2$  molecules:

$$\varphi \equiv \frac{2n_Z}{n_I + n_H + n_N + 2n_Z} = \frac{2n_Z}{n + n_Z} = \frac{2x_Z}{1 + x_Z} \quad (18)$$

Note that the denominator in the first two expressions is a constant. If we denote the conditions at the inlet by  $x_i^\circ$ ,  $\varphi^\circ$ ,  $T^\circ$ , etc., and introduce the parameter  $\epsilon$  to indicate the deviation from stoichiometry by

$$x_{H^\circ} = 3(1 + \epsilon)x_{N^\circ} \quad (19)$$

then all mole fractions can be expressed in terms of  $\varphi$  (and the constant  $\epsilon$ ) as

$$x_H = \frac{3[(1 + \epsilon)(2 - \sigma) - \varphi(2 + 3\epsilon/2) - \epsilon\varphi^\circ/2]}{(4 + 3\epsilon)(2 - \varphi)} \quad (20)$$

$$x_N = \frac{2(1 - \varphi) - \sigma - (3\epsilon/2)(\varphi - \varphi^\circ)}{(4 + 3\epsilon)(2 - \varphi)} \quad (21)$$

$$x_Z = \varphi/(2 - \varphi) \quad (22)$$

where

$$\sigma = (2 - \varphi^\circ)x_{I^\circ} \quad (23)$$

measures the inert content. Furthermore

$$x_A = \kappa\sigma/(1 + \kappa)(2 - \varphi) \quad (24)$$

$$x_M = \sigma/(1 + \kappa)(2 - \varphi) \quad (25)$$

when we define  $\kappa \equiv x_{A^\circ}/x_{M^\circ}$  to describe the composition of the inert component.

The next step is to connect the time derivative of the fractional conversion  $\varphi$  with the reaction rate. As pointed out earlier, we must take into account that the number of molecules decreases in reaction 1. We consider a thin slice of reaction mixture, originally consisting of  $\{n_i^\circ\}$  moles, as it flows through the reactor, and let  $\{n_i(l)\}$  denote the numbers of moles in the slice at  $l$ ,  $V(l)$  the corresponding volume of the slice, and  $T(l)$  the temperature. Then, in the absence of longitudinal mixing as assumed in section II,

$$n + n_Z = n^\circ + n_Z^\circ \equiv C^\circ \quad (26)$$

is a constant, and

$$\varphi = 2n_Z/C^\circ \quad (27)$$

$$n_Z(l + dl) = n_Z(l) + rV(l) \frac{dl}{v(l)} \quad (28)$$

where  $v(l)$  is the velocity of the slice. We can write the constant mass flow rate  $G$  as

$$G = \rho(l)v(l) \quad (29)$$

where  $\rho(l)$ , the mass density, can be expressed in terms of the molecular weights  $M_i$  of the constituents,

$$\rho(l) = \sum_i M_i n_i(l) / V(l) \quad (30)$$

Combining eq 27-30 yields

$$\frac{d\varphi}{dl} = \frac{2r}{G(1 + x_Z)} \sum_i x_i M_i \quad (31)$$

## VII. Formulation of the Optimization Problem

Our optimization problem is a maximization of the end-point value of a state variable with a differential equation as a constraint and a given initial state, explicitly maximize  $\varphi(L)$  subject to

$$\frac{d\varphi}{dl} = \frac{2r(T, \varphi)}{G(1 + x_Z(\varphi))} \sum_i M_i x_i(\varphi) \equiv \varphi', \varphi(0) = \varphi^\circ \quad (32)$$

This is an example of a common type of optimal control problem (sometimes called the Mayer problem, see e.g., Cesari (1983)) which is solved by introducing the Hamiltonian

$$\mathcal{H} = \lambda(l)\varphi'(T(l), \varphi(l)) \quad (33)$$

with a multiplier  $\lambda$ . The necessary (and in this case sufficient) conditions for an optimum are

$$\frac{\partial \mathcal{H}}{\partial T} = 0 \quad (34)$$

$$\frac{\partial \mathcal{H}}{\partial \varphi} = -\frac{d\lambda}{dl} \quad (35)$$

$$\lambda(L) = 1 \quad (36)$$

In this system, as in all systems with only one chemical reaction, eq 35 is redundant. In the multireaction case, eq 35 is a set of differential equations for multipliers  $\lambda_i(l)$ , with  $\lambda_i(L)$  given for all  $i$  through the objective function. Equation 34 can be solved (numerically) for  $T$  for every  $\varphi$ , and this  $T(\varphi)$  can then be substituted into eq 31 to give  $d\varphi/dl$ . Thus, we can, through eq 31 and 34, find the optimal concentration profile in the reactor, and by using eq 34 again we find the optimal temperature profile. Explicitly, the two governing equations are

$$\left( \frac{E_b - 2\alpha E_c}{RT^2} \right) [K_a^2 a_N (a_H^3/a_Z^2)^\alpha - (a_Z^2/a_H^3)^{1-\alpha}] + \frac{\partial}{\partial T} [K_a^2 a_N (a_H^3/a_Z^2)^\alpha - (a_Z^2/a_H^3)^{1-\alpha}] = 0 \quad (37)$$

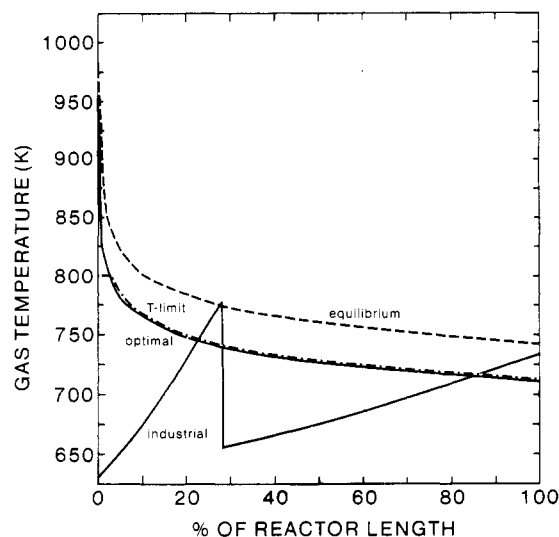
$$\frac{d\varphi}{dl} =$$

$$\frac{2}{G(1 + x_Z)} \frac{K_b}{K_c^{2\alpha}} [K_a^2 a_N (a_H^3/a_Z^2)^\alpha - (a_Z^2/a_H^3)^{1-\alpha}] \sum_i x_i M_i \quad (38)$$

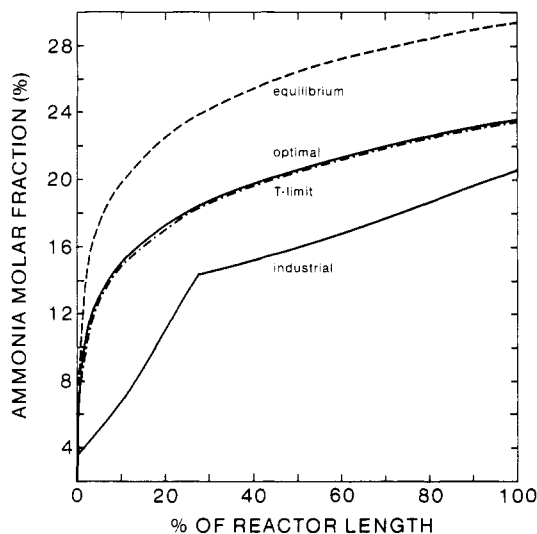
The rate equation 7 is, of course, not valid for the full range of temperatures that this optimization scheme can yield. The practical temperature is also constrained by the properties of the catalyst, since high temperature increases its decay. This means that the temperature in the reactor has an upper safe bound which is below the maximum allowed in eq 7. The optimization scheme is not changed in any substantial way by this. If we denote the maximum allowed temperature by  $\hat{T}$ , we just set

$$T = \hat{T} \quad \text{if} \quad \varphi < \hat{\varphi} \quad (39)$$

where  $\hat{\varphi}$  is found by inserting  $\hat{T}$  in eq 34; i.e., the optimal temperature is constant until the fractional conversion reaches the optimal profile given by eq 37 and 38, and thereafter it follows this profile. The practical lower temperature bound is set by economic considerations with a finite reactor (catalyst) volume rather than the lower limit of applicability of eq 7.



**Figure 1.** Temperature profiles as functions of reactor length (percent of the industrial reactor length). "optimal": optimal profile generating the largest concentration of  $\text{NH}_3$  at the exit. "T-limit": optimal profile with the temperature limited to 800 K. "equilibrium": the temperature at which the optimal reaction mixture would be in equilibrium. "industrial": temperature profile of the industrial reactor model.



**Figure 2.** Concentration profiles of  $\text{NH}_3$  (mol %) as functions of length. Same labels as Figure 1, except for "equilibrium": the ammonia content which would be in equilibrium at the optimal temperature.

### VIII. Optimal Temperature and Concentration Profiles

The expressions in the previous section (eq 37 and 38) have been applied to generate the optimal gas temperature and ammonia concentration profiles of Figures 1 and 2, respectively, for an inlet mixture described by  $\epsilon = 0$ ,  $x_2^0 = 0.036$ ,  $x_1^0 = 0.12$ , and  $\kappa = 0.5$ . The flow rate ( $G = 50$  kg/s) corresponds to a 1000 tons/day ammonia production. The chosen values for the pressure (262 atm), catalyst properties ( $\alpha = 0.75$  and the second set of constants in Table II were used), and other parameters correspond to the Topsøe S-200 reactor (Topsøe, 1979). These conditions were chosen simply to have empirical data representative of a modern industrial reactor.

The optimal curves are labeled "optimal" and the curves with data from the industrial reactor "industrial". The optimal temperature is initially quite high to get a high reaction rate while the ammonia concentration is low, and it decreases thereafter to maintain a suitable distance to

the equilibrium temperature profile. This is illustrated by the curves marked "equilibrium" which in Figure 1 is the temperature at which the optimal reaction mixture would be in equilibrium and in Figure 2 is the ammonia content which would make the mixture an equilibrium mixture at the optimal temperature. Thus, the fairly constant (35 K or 5.5 mol %  $\text{NH}_3$ ) difference between the optimal and equilibrium curves is the driving force of the reaction.

By contrast, a typical industrial process (described further in section IX), being adiabatic in each of its two catalyst beds, has a counterproductive temperature profile with a small reaction rate at the initial low temperature and the equilibrium point displaced toward lower  $\text{NH}_3$  concentration at the exit. (A reactor with more beds and intermediate heat exchangers would of course be able to come closer to the optimal profile.) The potential gain in ammonia production by operating the same catalyst at the optimal temperature profile is obvious from Figure 2. Either the same amount of catalyst can produce 3 percentage points more  $\text{NH}_3$  in the output stream, a relative increase of 15%, or the present level of conversion can be achieved with half the amount of catalyst. Indeed half of the conversion takes place in the initial 5% of the reactor. If it is necessary to limit the temperature of the catalyst to say 800 K to decrease decay, the curves labeled "T-limit" result. This only degrades the conversion rate of the reactor slightly at the beginning and is hardly noticeable at the exit.

Since the ammonia reaction is exothermic, the optimal temperature profile may be attained simply by regulating the flow of heat out of the flow reactor, either in a countercurrent fashion, to the incoming fresh synthesis gas, or to an external cooling medium which in turn may be used in power production. In the former case, the most obvious means of regulation is a heat-transfer coefficient between the two flows which varies appropriately along the reactor. In the latter case, varying the temperature of the cooling medium while maintaining maximum heat contact keeps dissipation at a minimum.

In the present study, we consider only ammonia mole fraction in the exit stream as the objective function, but the whole procedure could just as easily be repeated with any economic objective function. Our conclusions would remain qualitatively the same.

The differential equations 37 and 38 are well-behaved and stable as is the subroutine we used to solve them, so computational errors should be minimal. It is considerably harder to estimate the sensitivity of our results to the approximations made. But during trial runs, we changed the empirical parameters by more than an order of magnitude with a resulting change in ammonia yield of less than 1%. Even removing all nonidealities affected the result by only 3%. This is in agreement with Schneiderman and Brasil (1976) which also find nonidealities to have minor, but consistent, effects in a related study.

The idea of optimizing the temperature profile in an ammonia reactor is not new, but the previous studies have been either purely abstract (Katz, 1960) or qualitative (Gmelin, 1936) with suggested temperature ranges significantly different from the optimal ones we find. Subsequent theoretical elaborations on Fauser's idea (Gmelin, 1936) for ideal gases (Temkin and Pyzhev, 1940; Denbigh, 1944) have gone largely unnoticed, maybe because of their oversimplification and lack of indication of the potential gain. The closest available approximation to the optimal profiles is provided by the Fauser-Montecatini reactor (see Strelzoff (1981)) with the largest deviation occurring in the

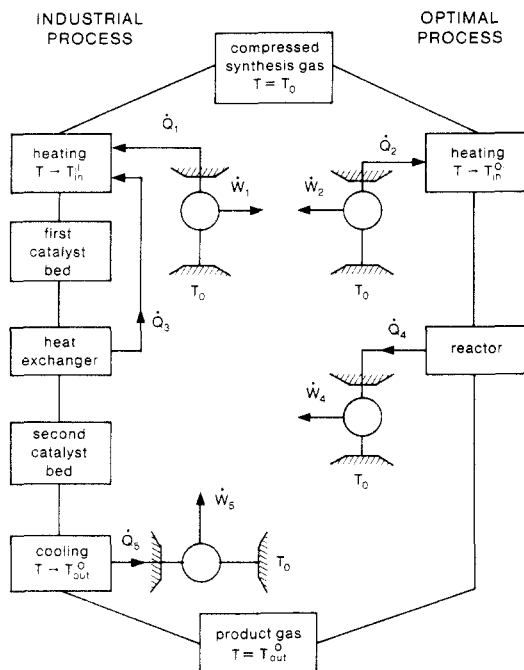


Figure 3. Energy ( $\dot{Q}$ ) and exergy ( $\dot{W}$ ) flows of the industrial and optimal processes.  $T_0$  is the environment temperature.

first of its six adiabatic beds.

The most recent optimization analysis we are aware of (Murase et al., 1970) treats a countercurrent ammonia reactor where the heat-transfer coefficient between the two streams is varied so as to generate that reaction temperature profile which produces a given ammonia content in the exit stream with the shortest reactor. That study uses a simplified Temkin-Pyzhev rate equation and ideal gas equilibrium constant, fugacities, heat capacities, etc., to arrive at an approximate temperature profile and corresponding heat conductance function. Since their reference reactor is different from ours (which is based upon Topsøe (1979)), the improvements cannot be compared directly, but the fact that their optimal exit ammonia mole fraction is 2.5 percentage points less than ours indicates further room for improvement. Their variable heat conductance between the counterflowing streams yields the best temperature profile obtainable by passive means, but the important initial segment of the reactor is still too cold and reaction therefore too slow. It is actually conceivable that decreasing the flow through the reactor would result in a sufficiently higher maximum temperature that the total amount of ammonia produced would increase.

### IX. Energy and Exergy Flows

We will compare the energy and exergy flows of our optimized reactor (O) with those of a model of a typical contemporary industrial reactor (I). This model reactor (see e.g. Topsøe (1979)) has two adiabatic catalyst beds with an intermediate heat exchanger, where the ingoing synthesis gas is heated to the inlet temperature of the first bed while the gas from the first bed is cooled to the inlet temperature of the second bed. This heat exchange occurs inside the reactor vessel, which does not exchange heat with the environment except through the in- and out-flowing gases. The comparison is made with the same initial and final temperatures and compositions, as indicated on Figure 3. The initial state is the compressed synthesis gas at the temperature of the environment  $T_0$  (here 298.15 K).

Assuming that the heat capacities are additive, we find the total rate of exergy production of the industrial reactor to be, except for  $PV$  work,

$$\dot{W}^I = \dot{W}_5 - \dot{W}_1 = \dot{n}(\text{out}) \sum_i \left[ x_i(\text{out}) \int_{T_0}^{T_{\text{out}}^{(i)}} \left( 1 - \frac{T_0}{T} \right) C_{pi}(T) dT \right] - \dot{n}(\text{in}) \sum_i \left[ x_i(\text{in}) \int_{T_0}^{T^*} \left( 1 - \frac{T_0}{T} \right) C_{pi}(T) dT \right] \quad (40)$$

where  $T^*$  is the temperature at which the further addition of  $Q_3$  brings the inflowing gas up to  $T_{\text{in}}^{(i)}$ . The molar heat capacity  $C_{pi}$  for each component gas ( $P$  in atm) is given by (Gillespie and Beattie, 1930; Beattie, 1929)

$$C_{pi}(T) = A_i^* + B_i^*T + C_i^*T^2 + \left[ \frac{2A_i}{RT^2} + \frac{12C_i}{T^4} \right] P \quad (41)$$

where  $A_i^*$ ,  $B_i^*$ , and  $C_i^*$  are the ideal gas (zero pressure) coefficients listed in Table I. (We thus neglect the heat of mixing. See Nielsen (1968), p 23, and Strelzoff (1981), pp 83-84, for a discussion of this approximation.)

The optimized process has a similar heating term,

$$\dot{W}_2 = \dot{n}(\text{in}) \sum_i \left[ x_i(\text{in}) \int_{T_0}^{T_{\text{in}}^{(i)}} \left( 1 - \frac{T_0}{T} \right) C_{pi}(T) dT \right] \quad (42)$$

but since the reactor gives off heat (to maintain the optimal temperature profile), we get a cooling term composed of two parts, one due to the heat of reaction and one due to the temperature decrease along the reactor

$$\dot{W}_4 = - \int_0^L \left( 1 - \frac{T_0}{T(l)} \right) [\Delta H(T(l)) r(l) + \dot{n}(l) (dT/dl) \sum_i x_i(l) C_{pi}(T(l))] dl \quad (43)$$

where the heat of the reaction is given by (Nielsen (1968),  $P$  in atm)

$$\Delta H(T) = -(2.2823 + 3.5186 \times 10^3/T + 1.9244 \times 10^9/T^3)P - 22.381T - 1.0569 \times 10^{-3}T^2 + 7.0810 \times 10^{-6}T^3 - 38329.7 \text{ (J/mol)} \quad (44)$$

Since this comparison is made with the same initial and final states for the two reactors, their heat flows must necessarily be the same,  $\dot{Q}_5 - \dot{Q}_1 = \dot{Q}_4 - \dot{Q}_2$ . However, more importantly, most of the heat of reaction in the optimized reactor is produced at the high initial temperatures, since most of the reaction occurs there, and can thus be converted to work with high efficiency.

We do not include either the compression work or the possible work yield of the cooling and condensation of the product gas, so both  $\dot{W}^{(I)}$  and  $\dot{W}^{(O)}$  turn out to be negative, but the improvement in exergy balance due to optimal operation,  $\dot{W}^{(O)} - \dot{W}^{(I)}$  is 9.0 MW. Although the optimized reactor needs a much hotter inlet gas, this is more than compensated for by the higher temperature of reaction. (Note that since the outlet ammonia content is the same, the volume  $V^*$  of the optimized reactor is less than half of the volume of the industrial reactor. If we let the catalyst volume be the same in the two cases,  $\dot{W}^{(O)} > 0$ , although the outlet compositions then differ.)

Even though the losses in the ammonia reactor unit itself decrease by more than 60%, from approximately 1300 kJ/kg of  $\text{NH}_3$  to approximately 500 kJ/kg, if the reactor vessel is replaced with an optimized vessel of the same volume, a comparison with the exergy analyses of Cremer (1980) and Hedman (1981) shows that the exergy losses in a complete 1000 tons/day plant decrease by only 6% since the synthesis gas unit accounts for more than 50%

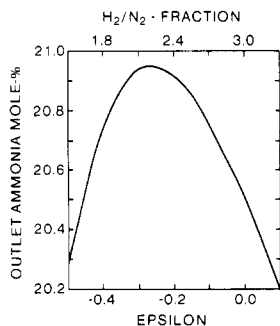


Figure 4. Optimal exit  $\text{NH}_3$  molar fraction for varying  $\text{H}_2/\text{N}_2$  ratio in feed gas.

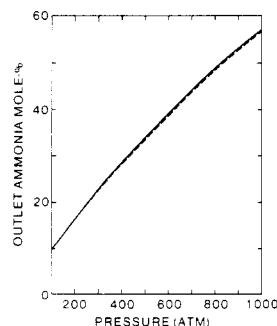


Figure 5. Optimal exit  $\text{NH}_3$  molar fraction as a function of reactor pressure: (—) unconstrained temperature; (---) temperature limited to 800 K.

of the exergy losses in an ammonia plant.

#### X. Variation of Parameter Values

A few authors (Strelzoff, 1981; Reddy and Husain, 1982) have suggested using a nonstoichiometric feed gas with excess nitrogen. This is intuitively obvious, since the rate-determining step is the dissociation of  $\text{N}_2$  on the catalyst surface (Nielsen et al., 1964; Nielsen, 1968), and our calculations (with reactor volume =  $V^*$ ) indicate an optimal nitrogen excess of 35% ( $\epsilon = -0.26$ ) (see Figure 4), somewhat more than the previous studies.

Reactor pressure has a strong influence on the reactor conversion, as shown in Figure 5, only slightly offset by limiting the catalyst temperature. It is also exergetically favorable to increase the pressure, since the associated higher optimal temperature increases the Carnot efficiency of the heat produced. The extra work required to compress the synthesis gas may be partly recovered during expansion of the product gas. In addition, condensing the produced ammonia is easier at higher pressure, and refrigeration may conceivably be avoided. The optimal pressure is however determined by the cost of high pressure shells and available compressors, not by thermodynamics.

The main detrimental effect of inerts in the synthesis gas is to reduce the effective pressure of the reactants and thus the conversion rate. (The conversion increases by 20% when there are no inert gases.) The increases in heat capacity of the mixture and of mass to be circulated are only secondary. Of even less influence is the distribution of inerts between argon and methane (high argon/methane ratio is favorable) which shows up mainly in their different heat capacities and different effects on fugacities; for ideal gases there would, of course, be no difference.

Since the conversion rate, eq 31, is inversely proportional to the flow rate, one will achieve the same overall rate of production of ammonia with a given quantity of catalyst arranged in a wide and short reactor as in a narrow and long one; the residence time is the same. However, the resistance to gas flow is much less in the former case, which will reduce the recirculation pumping work.

## XI. Summary

We have carried out a full optimization of the gas temperature profile in a tubular ammonia reactor, using accurate empirical expressions for the equation of state, rate constant, and activities. We find that the same conversion can be achieved with less than half the amount of catalyst compared to a two-bed adiabatic reactor with intermediate heat exchange. At the same time, the exergy balance of the reactor is considerably improved. The synthesis gas should have a 2.25:1 hydrogen/nitrogen ratio; the inert gas content should be as low as possible, and the pressure as high as practical.

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