Optimal Thermal Design of an Autothermal Ammonia Synthesis Reactor

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The following optimization problem is considered: To maximize profit by optimal choice of heat transfer coefficient as a function of reactor length, feed gas temperature, and reactor length, subject to the physical laws governing the behavior of an autothermal ammonia synthesis reactor and upper and lower bounds on the heat transfer coefficients. Assumptions are made about the economics that reduce the profit objective to a weighted sum of reactor length and ammonia yield. The results are presented graphically in parametric form to permit application with little additional computation. The effect of a variable heat transfer coefficient is considerable. For a reactor 5.18 meters long increase in ammonia yield is 5.4%; at constant yield the reactor can be shortened by 17%. The assumptions about the economics are then relaxed. Economic groups are defined which characterize the profit objective. The optimal design is insensitive to some groups over the range of interest, so that valid simplifications of the objective function can be made.

The treatment of variational problems has received considerable attention in the chemical engineering literature in the past decade. These can be classified as control or design problems. In chemical engineering, one would expect the most useful results to come from the solution of the design rather than the control problems, because in controlling a process one can, through feedback, correct and control by specifying the control algorithm (the functional relationship between corrective action and error) and not the control action function—e.g., valve stem position vs. time. The solution to the variational control problem would yield the control action function, and while there are cases—e.g., batch processes—in which this would be useful, in most process control problems we are free to exert corrective action after the process has started and error has been measured. This is obviously not true in design problems; the configuration is first set and then the process is operated. This situation is more compatible to the nature of variational problem solutions. Thus it was decided to study variational problems that arise in design.

Beginning with Temkin and Pyzhev (1960) and Denbigh (1944), there has developed a considerable literature (Aris, 1961) on the processing conditions under which a chemical reaction should be carried out in order to obtain maximum yield or selectivity. Although this work is of great value, there are two shortcomings: The process variables such as temperature, pressure, and concentration are not under direct control of the designer—for example, the designer can affect the temperature profile only indirectly through the mechanical design of the heat transfer system—and the process-variable-based objectives do not always correspond to economic objectives. McEwan and Beveridge (1965) offer an exception. Hence, it was decided to formulate the problem in terms of design variables and economic objectives.

Annable (1952) compared the performance of an autothermal ammonia synthesis reactor (Figure 1) with the maximum yield that could be obtained if one had direct control of the temperature profile. He found that
conversion could be increased by 14%. Obviously, one does not have direct control of the temperature profile, but it could be affected by the configuration of the heat transfer surface—e.g., added insulation and/or fins. Indeed, Dyson (1965) considered the general problem of determining the heat transfer coefficient as a length function that would maximize the yield in an autothermal reactor.

In this paper, the Maximum Principle is applied to the design of a variable heat transfer coefficient, ammonia synthesis reactor. Economic factors are included in the analysis. A simplified computational procedure is developed and results are presented in graphical form to permit design of reactors of this class with little additional computation. It was found that the yield could have been increased by 5.4%, had the TVA reactor, as described by Baddour et al., (1965) and Eymery (1964), been designed with a variable heat transfer coefficient.

In addition to being a contribution to the specific field of ammonia synthesis reactor design, it is hoped that the paper contributes to the more general field of economic autothermal reactor design.

**Simulation**

**Process Description.** The Haber process is operated at high pressure and produces ammonia from the following catalyzed reaction:

\[ \text{N}_2 + 3 \text{H}_2 = 2 \text{NH}_3 \]

A schematic diagram of the TVA reactor (Eymery, 1964) is presented in Figure 1. The reaction zone (shaded) contains the catalyst. A number of cooling tubes are inserted vertically through the reaction zone. The feed gas comes in from the lower part of the reactor and flows up through the heat exchanger and cooling tubes to the top of the reactor. Then, changing direction, it flows down through the reaction zone and heat exchanger to the outlet.

As with all reversible exothermic reactions, the temperature at which the reaction rate is maximum decreases as the conversion increases. The relationship between this "ideal" temperature and the conversion is presented in Figure 2. Even though one would like to maximize the reaction rate at each instant, it is impossible to obtain this "ideal" temperature profile by control of the available design variables. The countercurrent flow does, however, cause the temperature to decrease in the bottom part of the reactor because of heat transfer between the reacting and feed gases. It is possible to enhance this effect by causing the heat transfer coefficient to vary along the feed gas tube. It is this enhancement that is considered in this paper.

**Assumptions.** The following assumptions are used:

- The Temkin-Pyzhev (1960) equation for the rate expression is valid.
- The model is one-dimensional—i.e., the temperature and concentration gradients in the radial direction are neglected.
- Heat and mass diffusion in the longitudinal direction are negligible.
- The temperature of the gas flowing through the catalyst zone is equal to the temperature of the catalyst particles.
- The heat capacities of the reacting gas and the feed gas are constant.
- The catalyst activity is uniform along the reactor and equal to unity.

**Pressure drop across the reactor is negligible compared to the total pressure of the system.**

**Energy Balances.** Feed Gas. Referring to Figure 3, an energy balance on the feed stream yields the following equation:

\[
\frac{dT_f}{dx} = -\frac{u \cdot S_i}{W \cdot C_{st}} (T_f - T_i) \tag{1}
\]

where

- \( u \) = over-all heat transfer coefficient, kcal/(m²·hr·°C)
- \( S_i \) = surface area of cooling tubes per unit length of reactor, meters
- \( T_r \) = temperature of reacting gas, °C
- \( T_i \) = temperature of feed gas, °C
- \( W \) = total mass flow rate, kg/hr
- \( C_{st} \) = specific heat of feed gas, kcal/kg · °C
- \( x \) = distance along axis

Reacting Gas. Similarly, for the reacting gas,

\[
\frac{dT_r}{dx} = -\frac{u \cdot S_i}{W \cdot C_{st}} (T_r - T_i) + \frac{(-\Delta H) S_i}{W \cdot C_{st}} R \tag{2}
\]

**Figure 2.** Schematic of temperature profiles and NH₃ mole fraction in TVA NH₃ synthesis reactor

**Figure 3.** Heat flow from reacting gas to feed gas
where

\[ -\Delta H = \text{heat of reaction, kcal/kg mole of } N_2 \]
\[ S_z = \text{cross-sectional area of catalyst zone, m}^2 \]
\[ R = \text{reaction rate, kg moles of } N_2/(\text{hr} \text{ m}^2) \]
\[ C_{tJ} = \text{heat capacity of reacting gas} \]

**Material Balance.** Referring to Figure 3, consider the incremental distance in the catalyst zone. Performing a \( N_z \) material balance yields

\[ \frac{dN_N}{dx} = -R \quad (3) \]

where \( N_N \) = mass flow of nitrogen per unit area of catalyst zone, kg moles/(m\(^2\)-hr).

On a semiempirical basis, the Temkin-Pyzhev (1960) equation for the ammonia synthesis is given as

\[ R = f \left\{ K_1 \frac{P_{N_2} \cdot P_{H_2}^{1.5}}{P_{NH_3}} - K_2 \frac{P_{NH_3}}{P_{H_2}^{1.5}} \right\} \quad (4) \]

where

\[ f = \text{catalyst activity} \]
\[ P_{H_2}, P_{N_2} = \text{partial pressures of } H_2, N_2, \text{ and NH}_3 \]
\[ K_1, K_2 = \text{rate constants; } K = f \exp (-E_/RT) \]

**Reduction of Differential Equations to Dimensionless Form.** Using the dimensionless groups

\[ X_0 = N_N/G \]
\[ X_1 = T_0/T_r \]
\[ X_2 = T_1/T_r \]
\[ X_3 = x/L \quad (5) \]

where

\[ G = \text{total flow at top of reactor, kg moles/m}^2 \text{ hr} \]
\[ T_r = \text{reference temperature} \]
\[ L = \text{reference length} \]

The system equations can be written as

\[ \frac{dX_0}{ds} = -K_0 R \quad (6) \]
\[ \frac{dX_1}{ds} = -K_1 (X_1 - X_2)u + K_2 R \quad (7) \]
\[ \frac{dX_2}{ds} = -K_1 (X_1 - X_2)u \quad (8) \]
\[ \frac{dX_3}{ds} = 1 \quad (9) \]

where the variable, \( s \), is to be viewed as a general “distance along the path” or “extent” of the phenomena (In this particular problem it is identified, as shown in Equation 9, with the dimensionless reactor length) and where

\[ K_0 = L/G \]
\[ K_1 = S_1 L/W \cdot C_{pf} \]
\[ K_2 = S_2 L/W \cdot C_{pf} \]
\[ K_1 = (-\Delta H \cdot S_2)/(C \cdot C_{pf} \cdot L \cdot T_r) \]

**Results.** The temperature profile computed is compared with the measured plant profile in Figure 4. The data used in the simulation are presented in Appendix A.

**Design Problem**

**Objective Function.** Let:

\[ V_1(X_0, X_1) = \text{value of the product, considered to be a function of the composition, } X_0, \text{ and the temperature, } X_1, \text{ only, the pressure being regarded as fixed} \]
\[ V_2(X_2) = \text{value of the feed gas, considered to be a function of the temperature, } X_2, \text{ only, the pressure and composition being regarded as fixed} \]
\[ C(X_3) = \text{annual cost of the reactor, considered to be a function of the length, } X_3, \text{ only, the pressure being regarded as fixed} \]

The following objective function is used in this study.

**Figure 4. Comparison of temperature profiles**

where $n$ is a normalization constant to be evaluated at a later step.

**Formal Statement.** MAXIMIZE $J = [V_1 - V_2 - C_L]/n$

By optimal choice of

$u(s) = \text{heat transfer coefficient as a function of axial position}$

$X_1(S) = \text{inlet feed gas temperature}$

$X_2(S) = \text{reactor length}$

Subject to Equations 6 through 9

$0 \leq u(s) \leq u^*$

$X_1(0) = X_1(0)$; feed and reacting gas temperatures must be equal at top

$X_1(0)$ given

$X_1(S) = k_1X_2(S) + k_2[X_3(0) - X_2(S)]$;

over-all enthalpy balance

where

\[
K_1 = \frac{C_p f}{C_p \gamma}
\]

\[
K_2 = \frac{-\Delta H G S_2}{T_2 C_p \gamma W}
\]

**Adjoint System and General Design Policy**

For convenience we define the so-called adjoint variables,

\[
Z_i = \frac{\partial J}{\partial X_i}, \quad i = 0, 1, \ldots, 3
\]

and the Hamiltonian

\[
H = \sum_{i=0}^3 Z_i G_i = 0
\]

It can be shown (Equations 9 and 10) that

\[
dx_i = -\frac{\partial H}{\partial X_i}, \quad i = 0, 1, \ldots, 3
\]

From Equations 6 to 9 and 11,

\[
H = -[Z_1 K_1 + Z_2 K_2] \frac{\partial R}{\partial X_1}[X_1 - X_2]u - [Z_1 K_0 - Z_2 K_1] R + Z_3
\]

From Equations 12 and 13,

\[
Z_0 = \text{unit value of feed gas flow}
\]

\[
dx_0 = -\frac{\partial H}{\partial X_0} Z_0 - \frac{\partial R}{\partial X_0} Z_3
\]

\[
Z_3 = \text{unit value of reactor length}
\]

\[
dx_3 = -\frac{\partial H}{\partial X_3} Z_3 - \frac{\partial R}{\partial X_3} Z_1
\]

According to the Maximum Principle (Rozonoer, 1969), if $J$ is to be maximized, $H(s)$ must be extremized with respect to $u(s)$ at each point, $0 \leq s \leq S$.

For convenience we define

\[
K_H = [Z_1 K_1 + Z_2 K_2]
\]

From Equation 13 $H$ is linear in $u$ and the coefficient of $u$ is $K_H(X_1 - X_2)$.

Since $(X_1 - X_2) > 0$, $0 \leq s \leq S$, the general design policy is as follows:

If $K_H < 0$, then $u_{opt} = u^*$

$K_H > 0$, then $u_{opt} = 0$

$K_H = 0$, then $u_{opt}$ is not specified by the maximum principle—i.e., extremization of $H$.

This last case, in which $K_H = 0$, is known as the singular case. It is of interest only if it persists. $Z_1 = Z_2 = 0$ is sufficient to cause $K_H = 0$. For this condition to persist, it is sufficient to have $\frac{dX_1}{ds} = \frac{dX_2}{ds} = 0$. From Equation 14, $\frac{dR}{dX_1} = 0$ is sufficient. This is a particularly interesting condition, since it defines the ideal temperature discussed above. This condition allows one to evaluate $u_{opt}$ when $K_H = 0$.

The corresponding solutions to Equations 6 to 9 and 14 must satisfy the eight boundary conditions. Three of these are imposed on the state variables:

$X_a(0) = a_0$, a known value

$X_b(0) = X_b(0)$, continuity

$X_c(0) = 0$, reactor length measured from the top

We now derive the remaining five boundary conditions on the adjoint variables. The boundary conditions on the adjoint variables are obtained from the following definition:

\[
Z_i(s) = \frac{\partial J_{\max}}{\partial X_i(s)}, \quad \forall i
\]

where $J_{\max}$ is the maximum value of $J$.

Now, at $s = 0$ the above constraints apply. Treating these constraints by the method of Lagrange multipliers (Converse, 1970) we form the Lagrangian

\[
L = J_{\max} [X(0)] - \lambda_1 [X_a(0) - a_0] - \lambda_2 [X_b(0) - X_c(0) - X_b(0)]
\]

\[
\frac{\partial L}{\partial X_a} = \frac{\partial J_{\max}}{\partial X_a} - \lambda_1 = 0
\]

or $Z_a(0) = \lambda_1$—i.e., is unknown.

\[
\frac{\partial L}{\partial X_b} = \frac{\partial J_{\max}}{\partial X_b} - \lambda_2 = 0
\]

or $Z_b(0) = \lambda_2$—i.e., is unknown.
\[ \frac{\partial L}{\partial X_i} = \frac{\partial J_{\text{max}}}{\partial X_i} + \lambda_2 = 0 \]

or

\[ Z_i(0) = -\lambda_2 = -Z(0) \] i.e., \( Z_i(0) \) is set by \( Z(0) \) \hspace{1cm} (17)

\[ \frac{\partial L}{\partial X_i} = \frac{\partial J_{\text{max}}}{\partial X_i} - \lambda_1 = 0 \]

or \( Z_i(0) = \lambda_1 \) i.e., is unknown.

At \( s = S \) there are no explicit state constraints. The over-all enthalpy balance does apply, but this is taken into account through the integration of the state equations.

Hence

\[ n Z_i(S) = \frac{\partial V_i}{\partial X_i} \] \( n Z_i(S) = - \frac{\partial V_i}{\partial X_i} \)

\[ n Z_i(S) = \frac{\partial V_i}{\partial X_i} \] \( n Z_i(S) = - \frac{\partial V_i}{\partial X_i} \)

The above four equations plus Equation 17 constitute the five boundary conditions on the adjoint equations.

The normalization constant, \( n \), is chosen to make

\[ Z_i(S) = 1 \] \hspace{1cm} (18)

This yields

\[ Z_i(S) = \left( \frac{\partial V_i}{\partial X_i} \right) / \left( \frac{\partial V_i}{\partial X_i} \right) \] \hspace{1cm} (19)

\[ Z_i(S) = - \frac{\partial V_i}{\partial X_i} \] \hspace{1cm} (20)

\[ Z_i(S) = - \frac{\partial V_i}{\partial X_i} \] \hspace{1cm} (21)

It is important to recognize the role played by the adjoint variables. They really are evaluators and the external economics influence the design through the boundary conditions of the adjoint variables. The above partial derivatives are unit prices i.e., interstage transfer prices.

The economic analysis presented in Appendix B indicates that \( Z_i(0) \approx 0 \) and \( Z_i(0) \approx 0 \). The effect of this approximation was studied by Roberts (1969) and found to be negligible. From Equation 14d, \( Z_i(s) \) is constant. In determining the optimal \( u(s) \) we are therefore free to select \( Z_i(S) \) to be any value, since it merely changes the value of \( H \) by a constant value and therefore does not affect the design policy i.e., \( u(s) \). In computing the optimal length of the reactor, \( \frac{\partial C_i}{\partial X_i} \) is important and the optimal length could be determined from Equations 11 and 21, recognizing that \( \frac{\partial C_i}{\partial X_i} \) is a function of \( X_i \).

Although the adjoint boundary conditions are known at \( s = S \), three of the four state boundary conditions are known at \( s = S \). Formally, one could guess three of the state variables at \( s = S \) (setting the fourth in accord with Equation 10d), and integrate the state and adjoint equations to \( s = 0 \), iteratively guessing the values until the boundary conditions at \( s = S \) are met. Such mixed boundary value problems are difficult to solve numerically, and we therefore seek to limit the number of boundary conditions to be matched.

Since \( X_i \) is absent from all \( C_i \), its absolute value is important. The length of the reactor is given by \( X_i(S) \) = \( X_i(0) \) and the value of \( X_i(S) \) can be chosen to be any value. If one guesses a value for \( X_i(S) \) and assumes that the singular case will persist for a finite region connected to \( s = S \), say \( s_i \leq s \leq S \), then \( X_i(S) \) can be evaluated from \( \partial R \partial X_i = 0 \). The following algorithm can now be followed:

1. Guess \( s_i \).
2. Guess \( X_i(0) \).
3. Integrate the state and adjoint equations until \( X_i = X_i(0) \), which is fixed. This identifies the top of the reactor. During this integration \( u(s) \) is chosen so that \( \partial R \partial X_i = 0 \) in the region \( s_i \leq s \leq S \). For \( s \geq s_i \), it is set equal \( u^* \) or \( -u^* \), depending on the sign of \( K_i \).
4. Integrate from \( X_i(0) = X_i(0) ? \)
   Yes: \( X_i(S) \) is satisfactory.
   No: Reset \( X_i(S) \) and return to step 3.
5. Iterate on \( s_i \) until \( J \) is maximum.

Murase (1968) found that because of instability in the numerical integration of the adjoint equations, the iteration on \( s_i \) did not converge; the following general design policy seemed to apply.

For \( s_i \leq s \leq S \), choose \( u(s) \) so that \( \partial R \partial X_i = 0 \).

For \( s \leq s \leq s_i \), set \( u(s) = u^* \).

For \( 0 \leq s \leq s_i \), set \( u(s) = 0 \).

Intuitively, this is a satisfying policy. At the top, the heat transfer coefficient is set at its lowest value in order to increase the reacting gas temperature. This is followed by a section in which the coefficient is large, in order to bring the reacting gas temperature back down to the ideal temperature. At this point, the coefficient is set in a variable manner, so that the ideal temperature profile is followed in the rest of the reactor. This has intuitive appeal when one is trying to maximize the yield. When one is trying to maximize economic return as in this case, this policy is correct only because \( Z_i(S) \approx Z_i(S) \approx 0 \); else the singular policy at the bottom of the reactor would be incorrect.

Results

Murase (1968) used the above design policy to solve problems in which the conversion is fixed and the reactor length is to be minimized.

The state equations were integrated from \( s = 0 \) to \( s = S \) in accord with the following algorithm.

1. Set \( X_i(0) \) and \( X_i(0) \) to known values.
2. Guess \( X_i(0) \).
3. Set \( X_i(0) = X_i(0) \).
4. Guess \( s_i \).
5. Integrate over \( 0 \leq s \leq s_i \) with \( u(s) = 0 \).
6. Integrate from \( s = s_i \) with \( u(s) = u^* \) until an ideal temperature is reached i.e., the temperature at which \( \partial R \partial X_i = 0 \). Call this point \( s_i \).
7. Integrate from \( s_i \) until \( X_i = \) known final value, with \( u(s) = u^* \) so as to cause \( \partial R \partial X_i = 0 \).
8. Iterate on \( s_i \) until reactor length is minimum.
9. Iterate on \( X_i(0) \) until reactor length is minimum.

Murase (1968) carried out these calculations for \( 0.10 \leq X_i(S) \leq 0.22 \). The results for \( X_i(S) = 0.20 \) (the value obtained from the simulation of the TVA reactor) are shown in Figure 5. The loci of \( s_i \), \( s_i \), and \( X_i(S) \) are shown as a function of the top temperature. From this figure the optimal conditions are: top temperature \( 451^\circ \), \( s_i = 0 \), \( s_i = 2.17 \) meters, and minimum length \( 4.29 \) meters. The corresponding bottom temperatures were found to be \( 474^\circ \) and \( 249^\circ \) for the reacting and
feed gas streams, respectively. As presented in Figure 7, this composition with the simulated, constant-heat-transfer-coefficient, TVA reactor indicates that the reactor could have been shortened by 17% in order to obtain the same yield, or the yield increased by 5.4% with the same length. The corresponding temperature and heat transfer coefficient profiles are presented in Figures 6 and 8.

The calculations are greatly simplified by the fact that the design policy displayed in Figure 8 is not affected by the outlet ammonia conversion. Hence, one could solve the economic problem by choosing the reactor length so that Equation 17 is satisfied, or what is easier, so that \( J \) is maximum. This can be done with use of Figures 7 and 9. Figure 7 presents the relationship between optimal ammonia mole fraction and reactor length. Figure 9 presents the corresponding values of feed and reacting gas temperatures, thus permitting evaluation of \( J \) as a function of reactor length. The corresponding hot spot locations and temperatures are presented in Figure 10. A logical extension of this work would be the case in which this temperature is constrained to be less than, say, 500°C, in order to prevent catalyst deactivation. These results are all for an ammonia concentration in the feed gas of 0.05 mole fraction. Murase (1968) carried out similar calculations for a value of 0.01. Proceeding in this manner, one could optimize the entire process recycle loop.

**Extension of Range of Application**

The results thus far have been restricted to the given gas flow rate and reactor geometry. To remove these restrictions, the state equations are transformed as follows: Let

\[
t = sL/G
\]

\[
u_1 = uS_1/M_{Si}
\]

where \( M_i \) = molecular weight of the feed.

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**Figure 5.** Top temperature vs. minimum reactor length and locations of first and second switching points

\( s = s_1, s = s_2 \). Given \( N_{opt}(s) = 2.0 \), bottom temperature of reacting gas = 473.7°C, of feed gas, 249°C

**Figure 6.** Temperature profiles of optimal trajectory and plant case

If \( Y_0 = X_0, Y_1 = T_1, Y_2 = T_2 \), then from Equations 5 through 8

\[
\frac{dY_0}{dt} = -R
\]

\[
\frac{dY_1}{dt} = -\frac{1}{C_{p,\gamma}} [Y_1 - Y_2]u_1 + \frac{1}{C_{p,\gamma}} \left[ -\frac{\Delta H}{M_f} \right] R
\]

\[
\frac{dY_2}{dt} = -\frac{1}{C_{p,\gamma}} [Y_1 - Y_2]u_1
\]

By definition,

\[
\frac{dY_3}{dt} = 1
\]

The \( Y_i \) obey the same boundary conditions as the \( X_i \); hence the solutions are similar. Murase (1968) solved this problem in the same manner as the previous one. From

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**Figure 7.** Ammonia mole fraction profile
the resulting relationship between $u_1$ and $t$ (see Figure 11), one can obtain $u(s)$ for any known $W$, $S_1$, $S_2$, and $D_i$. The lower limit of $u_1$ is the same as $u$—namely, zero. As can be seen from Equation 23, the upper limit of $u_1$ depends on $S_1$, $D_i$, and $S_2$ as well as the upper limit on $u$. For this reason the following range of values for the upper limit on $u$ was investigated: $u_1^* = 350$, 613.2 (corresponds to the case reported above), 1000, 1500, and 2000, referred to as cases A through E, respectively. The resulting design relationships are presented in Figures 11 through 15.

Conclusions

If the ideal trajectory were followed along the whole length of the reactor, the exit ammonia mole fraction would be 0.218 for a reactor length of 5.18 meters. This represents an improvement of 8.32% of the conversion achieved in the plant (0.20) and is the upper limit of the improvement which can in practice be obtained.

This upper limit is displayed in Figure 16, together with the percentage improvement obtained by the optimal trajectory for various values of $u^*$. The value of high $u^*$ is apparent.

In terms of the general problem, this means that a large value of $u_1$ is desirable above the switch point;

Figure 8. Ammonia mole fraction vs. reactor length and optimal heat transfer coefficient vs. reactor length

Figure 9. Ammonia mole fraction vs. optimal temperatures of reacting gas at bottom

Figure 10. Ammonia mole fraction vs. maximum temperature and its location
this can be achieved in a number of ways (Equation 22).

I. Increase \( u \) above the switch point.
II. Increase \( S_1 \) above the switch point.
III. Decrease \( S_2 \) above the switch point.

II and III can be achieved by increasing the number of cooling tubes above the switch point, whereas in our initial problem only I was considered.

Consideration of an economic objective function indicates approximately the same general design policy as a minimum length objective function subject to fixed conversion. The solutions to this problem are presented graphically, permitting design without numerical integration of the state differential equations. The procedures whereby the results of this latter problem can be used to solve the original economic problem are described above.
Appendix A. Data Used in Simulation

Eymery (1964) presented plant dimensions and operating conditions in an actual plant. The same conditions are used here.

**Reactor Dimensions.**

Catalyst Zone

- Total volume: 4.07 m³
- Reactor length: 5.18 m
- Reactor basket diameter, $D_0$: 1.1 m
- Reactor basket cross-section area, $S_0$: 0.95 m²
- Catalyst zone cross-section area, $S_2$: 0.78 m²

Cooling Tubes

- Number of tubes: 84
- Tube outside diameter, $D_2$: 50.8 mm
- Tube inside diameter, $D_1$: 38.1 mm
- Tube heat exchange area (outer): 69.4 m²
- Tube heat exchange area (inner), $S_1$: 52.0 m²

**Heat Transfer Coefficient, $u$.** Baddour (1965) gave the heat transfer conductance ($US$) = 57.300 Btu/hr °F for

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Figure 14. Ammonia mole fraction vs. optimal temperature of feed gas at bottom

Figure 15. Ammonia mole fraction vs. maximum temperature of reacting gas and its location

Figure 16. Ammonia production increase vs. maximum limit for $U^*$

On basis of plant case
this reactor. On the basis of the cooling tube inside diameter,

\[
\frac{u}{S} = \frac{57,300 \times 4.882 \times 0.092903}{51,918.5} = 500.564 \frac{\text{kcal}}{\text{hr} \cdot \text{m}^2 \cdot ^\circ \text{C}} \quad (A1)
\]

\[
u = 500 \text{ is used in this paper}
\]

**Operating Conditions.**

<table>
<thead>
<tr>
<th>Feed Compositions, Mole Fraction</th>
<th>H₂</th>
<th>N₂</th>
<th>NH₃</th>
<th>CH₄</th>
<th>A₅</th>
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</thead>
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<td>0.2175</td>
<td>0.6525</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Plant data</td>
<td>0.219</td>
<td>0.65</td>
<td>0.052</td>
<td>0.79</td>
<td></td>
</tr>
</tbody>
</table>

Pressure, \( P = 286 \text{ atm} \)

Top temperature, \( T_{in} = T_{out} = 421 \pm 1 \text{ C} \)

Mass flow rate, \( W = 26,400 \text{ kg/hr} \)

(Space velocity, \( V_s = 13,800 \text{ hr}^{-1} \))

Density of the feed gas, \( D = 10.5 \text{ kg/kg-mole} \)

Exit ammonia concentration (mole fraction) = 0.200728

**Properties of Reaction System.**

**Heat Capacity**

Reacting gas \( C_p = 0.719 \text{ kcal/kg} \cdot ^\circ \text{C} \)

Feed gas \( C_{p, f} = 0.707 \text{ kcal/kg} \cdot ^\circ \text{C} \)

**Reaction Kinetics**

\( E_1 = 20,800 \text{ kcal/kmole of N₂} \)

\( E_2 = 47,400 \text{ kcal/kmole of N₂} \)

\( f_1 = 1.78954 \times 10^8 \)

\( f_2 = 2.5714 \times 10^{11} \)

\( -\Delta H = 26,600 \text{ kcal/kg mole of N₂} \)

\( f = 1 \)

**Appendix B. Determination of Economic Objective Function and Partial Derivatives**

**Value of Product Gas.** By assumption, the value of the product gas is dependent on its temperature and ammonia content—i.e., first-order approximations are used: \( C_H \), cost of heating, and \( C_A \), cost of ammonia, are considered fixed, whereas in fact they vary with temperature and ammonia concentration, respectively.

\[
V_J = V_J(X_0, X_i)
\]

By assertion,

\[
V_J = C_{p, J} \cdot T_{in} \cdot [X_J(S) - X_J^s] \cdot W \cdot N_1 \cdot C_H
\]

(Enthalpy, kcal/kg) (kg/hr) (hr/yr) ($/kcal)

Heating value, $/yr

\[
+ \frac{\rho_{NH_3}(0) + 2[X_a(0) - X_a(S)]}{W} \cdot N_1 \cdot C_A
\]

Dimensionless ammonia flow, kg NH₃/kg hr/yr $/kg NH₃$

Sale value, $/year

**Value of Feed Gas.** The feed gas composition is considered fixed; hence, its value is considered to be a function of temperature only—i.e.,

\[
V_I = V_I(X_I)
\]

By assertion,

\[
V_I = C_{p, I} \cdot T_{in} \cdot [X_I(S) - X_I^s] \cdot W \cdot N_1 \cdot C_H
\]

Heating value

**Reactor Cost.** Data published in 1956 were used as a guide to reactor cost. Costs were obtained by extrapolating data for 1500-psi steel pressure vessels to 4500 psi (Aries and Newton, 1955). For the reactor under consideration with cross-sectional area of 0.95 sq meter, the costs are given in Table I as a function of reactor length.

<table>
<thead>
<tr>
<th>Reactor Length, Meters</th>
<th>Cost, $ \times 10^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.398</td>
<td>72.879</td>
</tr>
<tr>
<td>1.591</td>
<td>141.471</td>
</tr>
<tr>
<td>3.985</td>
<td>235.785</td>
</tr>
<tr>
<td>7.970</td>
<td>330.099</td>
</tr>
</tbody>
</table>

**Table I. Costs**
where
\[ K_i = -GS_iC_i\gamma_{NH}(0)N_i + C_{pi}T_iW_iC_iF \]
\[ K_i = C_{pi}T_iW_iC_iF \]
\[ C_i(S) = AD + [K_s + K_sX_i(S)]^2 \quad (B7) \]

where
\[ K_s = BD^2 \]
\[ K_i = CD_i^2 \]

Then from Equation 3 and above
\[ J = |K_i + K_i| - K_sX_i(S) + K_sX_i(S) - K_iX_i(S) - [K_s + K_sX_i(S)]^1 \quad (B8) \]

ECONOMIC DERIVATIVES
From Equation B5,
\[ \frac{\partial V_i}{\partial X_i} = -K_i; \quad \frac{\partial V_i}{\partial X_i} = K_i \]

From Equation B6,
\[ \frac{\partial V_2}{\partial X_2} = -K_s \]

From Equation B7,
\[ \frac{\partial C}{\partial X_i} = \frac{1}{2} [K_s + K_sX_i(S)]^{-1} K_s \]

From Equations 19 and 20, together with the above equations,
\[ Z_1(S) = - \frac{K_i}{K_i} = 0.0054 \]
\[ Z_2(S) = \frac{K_i}{K_i} = 0.0054 \]

Cost Data. Cost of Heat. Based on the cost of heating oil, the cost of heat is taken to be
\[ C_{oil} = 4.453 \times 10^{-6} \text{ per kcal} \]

Cost of Ammonia. Gaseous industrial ammonia is sold for $70 per ton (Axton Cross Corp., 1968), so that
\[ C_4 = 81.3147 \text{ per kg-mole} \]

N. is taken to be 8330 hours per year.

Cost of Heat Exchange. The annual cost of heat exchange equipment has been assumed proportional to the heat exchange duty. A rough calibration for the case \( T_i(S) = 127^\circ C \) gave the capital cost of the heat exchanger, adjusted according to Marshall and Stevens process industries indices to be $4850 (Chilton, 1960). Amortization at 10% for 10 years gives an annual cost of $790. Comparing this figure with the total cost of heating in Equation B2 gives
\[ F = 1.01 \]

All other values in the cost equations are the same as those used by Roberts (1969). Substituting values into Equation B6,
\[ K_i + K_s = 11.9877 \]
\[ K_s = 55.063 \]
\[ K_s = 0.2964 \]
\[ K_i = 0.2944 \]
\[ K_2 = 3.475 \times 10^{-3} \]
\[ K_3 = 1.987 \times 10^{-3} \]

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