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## PROCESS DESIGN AND CONTROL

## Minimizing the Entropy Production Rate of an Exothermic Reactor with a Constant Heat-Transfer Coefficient: The Ammonia Reaction

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We use the ammonia reactor to develop further a method that minimizes the entropy production rate of a reactor with one chemical reaction. The method presented here determines operating conditions that are compatible with minimum lost exergy, i.e., the minimum total entropy production rate in the system. The entropy produced in the system by the chemical reaction and the heat transfer from the reaction mixture to the cooling medium is expressed by irreversible thermodynamics. The total entropy production rate is minimized subject to a fixed ammonia production. The mole and energy balances of the system must also be fulfilled. The results give inlet conditions compatible with the minimum entropy production rate. The results suggest that the reactor can be shortened or more high-quality heat can be taken out from the process. The nature of the solution, or the optimal temperature and concentration profiles in the reactor and the chemical and thermal driving forces, is presented and discussed.

## 1. Introduction

It has been known for a long time that the total entropy production rate or exergy loss in chemical reactors is large.<sup>1</sup> Some authors consider this to be unavoidable.<sup>2</sup> We have over the past few years studied a possible reduction of these second law losses using irreversible thermodynamics. Conversion and temperature profiles have first been found by solving the conservation equations for a given reactor (a reference system).<sup>3</sup> Next, we have looked for how boundary conditions should be changed in order to produce the same amount of chemical product but at a minimum total entropy production rate. The problem includes derivatives of functionals and has so far not been solved properly. We have, for instance, not yet been able to formulate the restrictions imposed on the minimization problem by the energy and mole balance(s). This shall be done in the present work.

We have approached the problem by analyzing the different parts of the reactor system separately. We have studied the lower bound of the entropy production rate in a heat exchanger for a given duty.<sup>4,5</sup> The sulfur dioxide oxidation,<sup>3</sup> the ammonia reaction,<sup>6</sup> and the methanol reaction in the presence of the reverse water-gas shift reaction<sup>7</sup> have also been studied with a restriction on the chemical production only. In this work we report efforts to minimize the total entropy production rate in a reactor with an exothermic reaction and an adjacent cooling system combined. We shall also use, as a restriction, the energy and the mole balances of the system. As in our previous work, we use a one-dimensional plug-flow reactor (PFR) model to keep

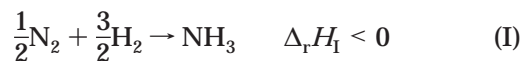
things simple. A more complex reactor model will not further the physical understanding of the solution of the minimization problem.

Ammonia is widely used in the industry as an important starting material in the production of fertilizer and synthetic fibers.<sup>1</sup> The ammonia synthesis is dominated by one exothermic reaction. Several technologies exist for excess heat removal, among them cocurrent cooling. These characteristics make the synthesis a convenient target for a case study and for method development. The same reactor was used earlier in an analysis of the chemical reaction alone.<sup>6</sup>

Only one set of the possible variables (one set of degrees of freedom) shall be studied in the present case, namely, the temperature profile of the coolant and the inlet composition and temperature of the reaction mixture. The coolant temperature profile is a realistic first target for a possible change in operating conditions. It may not be realistic to set both the inlet composition and temperature free. Also, one may question the assumption of constant pressure. These issues shall be pursued in the future. The primary result of the minimization is, therefore, a temperature profile of the coolant which, along with the inlet conditions, gives the corresponding temperature and conversion profiles in the reactor. Thermodynamic driving forces and equilibrium data shall be calculated from the primary result to help elucidate the nature of the solution of the minimization problem.

## 2. The System

Ammonia is produced by the following chemical reaction:



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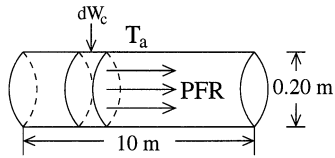


Figure 1. System sketch.

Its corresponding reaction rate (the rate of formation of ammonia),  $r_i$ , is<sup>8,9</sup>

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

where the subscripts N, H, and Z are abbreviations for  $N_2$ ,  $H_2$ , and  $NH_3$ , respectively. The chemical activities of the components are  $a_N$ ,  $a_H$ , and  $a_Z$ , respectively,  $K_a$  is the equilibrium constant of the reaction, and  $K_b$  and  $K_c$  are rate constants. Nielsen has found that the reaction rate model gives the best results when the model parameter  $\alpha$  is 0.75.<sup>8</sup>

In addition to the three components participating in the chemical reaction, the reaction mixture contains the two inerts methane and argon. The abbreviations that will be used for them are A (Ar) and M ( $CH_4$ ).

The system to be optimized, or our reference system, consisted of a catalyst-filled tubular reactor (fixed bed) which gives off heat to a coolant surrounding the reactor. The coolant can, for example, be a boiling liquid. In the industry, the ammonia production process is more complex.<sup>1</sup> The reactor and its dimensions are illustrated in Figure 1. The cooling system was not shown.

We assume the flow to be perfectly mixed over the cross section of the reactor and that the flow is one-dimensional along the reactor tube. We also assume that there is no mixing, diffusion, or thermal conduction along the reactor tube. These assumptions define the one-dimensional PFR. The pressure drop (frictional loss) in the reactor was neglected. The accumulated catalyst weight,  $W_c$ , was taken as a measure of the distance from the inlet of the reactor. Using  $W_c$  as a position variable is equivalent to using the  $z$  coordinate when the catalyst is homogeneously distributed in the reactor.

Different designs exist for reactor cooling. For the reference system, we chose to cool the reaction mixture with a boiling liquid at constant temperature. The direction of heat transfer was perpendicular to the reactor wall. As inlet conditions to our reference system, we used values from ref 9. We chose values for the coolant temperature, overall heat-transfer coefficient, catalyst density, and catalyst porosity that gave profiles that resembled profiles in real reactors. The parameters of the reference system are given in Table 1. Three different values of the overall heat-transfer coefficient were studied.

The overall heat-transfer coefficient was taken to be constant through the reactor in order to simplify and speed up the calculations. In a real system, the value depends somewhat on the local temperature and flows.

### 3. Reactor Modeling

This section contains the equations needed to calculate the temperature and conversion profiles in the reference system. All thermodynamic and kinetic data are taken from the literature.<sup>9</sup>

Before we set up the energy and mole balances for the reactor, we introduce two useful dimensionless

Table 1. Reactor Parameters

parameter	symbol	value
inlet reaction mixture temperature	$T_{in}$	650 K
coolant temperature	$T_a$	630 K
overall heat-transfer coefficient	$U$	case 1: 100 J/K·m <sup>2</sup> ·s case 2: 200 J/K·m <sup>2</sup> ·s case 3: 400 J/K·m <sup>2</sup> ·s
total pressure	$P_{Tot}$	262 atm
superficial mass velocity	$G$	50 kg/m <sup>2</sup> ·s
catalyst density	$\rho_c$	2600 kg/m <sup>3</sup>
catalyst void fraction	$\epsilon$	0.65
total catalyst weight	$W_{c,Tot}$	290 kg
inlet hydrogen mole fraction	$y_{H0}$	0.633
inlet nitrogen mole fraction	$y_{N0}$	0.211
inlet ammonia mole fraction	$y_{Z0}$	0.036
inlet argon mole fraction	$y_{A0}$	0.040
inlet methane mole fraction	$y_{M0}$	0.080

Table 2. Component Molar Flow Rates as Functions of  $\xi_H$

species	abbrev	initial	change	remaining
$H_2$	H	$F_{H0}$	$-F_{H0}\xi_H$	$F_H = F_{H0}(1 - \xi_H)$
$N_2$	N	$F_{N0} = \Theta_N F_{H0}$	$-(1/3)F_{H0}\xi_H$	$F_N = F_{H0}[\Theta_N - (1/3)\xi_H]$
$NH_3$	Z	$F_{Z0} = \Theta_Z F_{H0}$	$+(2/3)F_{H0}\xi_H$	$F_Z = F_{H0}[\Theta_Z + (2/3)\xi_H]$
Ar	A	$F_{A0} = \Theta_A F_{H0}$	0 (inert)	$F_A = \Theta_A F_{H0}$
$CH_4$	M	$F_{M0} = \Theta_M F_{H0}$	0 (inert)	$F_M = \Theta_M F_{H0}$

parameters. Given reaction (I) and the set of inlet molar flow rates for all five components in the reaction mixture, the component flows/compositions at any position in the reactor can be expressed in terms of the conversion of a chosen reference component and the inlet molar flow rates.<sup>10</sup> We have chosen hydrogen as the reference component. Thus, the conversion of hydrogen is defined as

$$\chi = \frac{F_{H0} - F_H}{F_{H0}} \quad (2)$$

where  $F_{H0}$  is the inlet flow rate of hydrogen and  $F_H$  is the flow rate of hydrogen at position  $W_c$ . The ratio between the inlet flow rate of component  $k$  and of hydrogen is expressed as

$$\Theta = F_{k0}/F_{H0} \quad (3)$$

where  $F_{k0}$  is the inlet flow rate of component  $k$ . Component molar flow rates are given as functions of the hydrogen conversion and the inlet flow rates in Table 2.

**3.1. Energy Balance.** The energy balance in differential form for the reactor is<sup>10</sup>

$$\frac{dT}{dW_c} = \frac{1}{(1 - \epsilon)\rho_c} \frac{\frac{4}{d_{ti}} U(T_a - T) - r_i \Delta_r H_i}{F_{H0} \left[ \sum_k \Theta_k C_{p,k} + \frac{2}{3} \xi_H \Delta C_{p,I} \right]} \quad (4)$$

where  $d_{ti}$  is the tube diameter,  $T$  and  $T_a$  are the temperatures of the reaction mixture and the coolant, respectively,  $U$  is the overall heat-transfer coefficient,  $C_{p,k}$  is the heat capacity of component  $k$ , and  $\Delta_r H_i$  and  $\Delta C_{p,I}$  are the reaction enthalpy and the difference between the heat capacities of the products and the reactants of reaction (I). The catalyst density is  $\rho_c$ , and  $\epsilon$  is the void fraction of the catalyst bed.

The overall heat-transfer coefficient has contributions from the convective heat transfer between the reaction mixture and the reactor wall, through the reactor wall, and between the reactor wall and the coolant. The energy balance shall be used as a restriction in the minimization problem.

**3.2. Mole Balance.** The mole balance in differential form for the reactor is<sup>10</sup>

$$\frac{d\xi_H}{dW_c} = \frac{1}{(1-\epsilon)\rho_c} \frac{3}{2} \frac{r_I}{F_{H_2O}} \quad (5)$$

where  $r_I$  is the rate of formation of ammonia. While the total mass of the reaction mixture is conserved, the total number of moles is not. The mole balance shall be used as a restriction in the minimization problem.

#### 4. Minimization Problem

The aim of this work is to minimize the entropy production rate of the exothermic ammonia reactor with a surrounding heat exchanger. As the reference reactor, we have used a system with a constant boiling liquid as the coolant. In the minimization, we shall ask the following questions: Given that the production of ammonia is maintained, what is the temperature profile of the coolant that gives minimum entropy production rate for the reaction plus heat exchange processes and what are the inlet conditions for the reactants? The purpose of the minimization is to recover more high-temperature heat, or heat at a higher temperature than that in the reference system. We shall see that this is indeed the outcome of the minimization.

**4.1. Object Function.** The object function in the minimization problem is the total entropy production rate<sup>11</sup> of the reactor system illustrated in Figure 1. It contains the entropy produced by the chemical reaction and by the heat exchange process between the reaction mixture and the coolant that surrounds the reactor:

$$\begin{aligned} \frac{dS_{\text{irr}}}{dt} &= \int_0^{W_{c,\text{Tot}}} \sigma dW_c \\ &= \int_0^{W_{c,\text{Tot}}} \frac{1}{(1-\epsilon)\rho_c} \left[ -r_I \frac{\Delta_r G_I}{T} + \frac{4}{d_{ti}} J_q \Delta\left(\frac{1}{T}\right) \right] dW_c \quad (6) \end{aligned}$$

where  $\sigma$  is the local entropy production rate,  $W_{c,\text{Tot}}$  is the total catalyst weight,  $\Delta_r G_I$  is the change in Gibbs energy of reaction (I), and  $-J_q$  is the heat flux from the reaction mixture to the coolant. It is defined as

$$J_q = \bar{l}_{qq} \Delta\left(\frac{1}{T}\right) = U(T_a - T) \quad (7)$$

The first equality gives the heat flux in the context of irreversible thermodynamics, with  $\bar{l}_{qq}$  as the overall heat-transfer coefficient. The second equality gives the heat flux by the integrated Fourier law, with  $U$  as the overall heat-transfer coefficient. The heat flux is defined as positive when heat is added to the system.

The total entropy production rate (eq 6) is a product sum of fluxes and driving forces. The reaction rate (a scalar "flux"),  $r_I$ , is multiplied by its conjugate thermodynamic driving force (the chemical driving force)

$$\frac{-\Delta G_I}{T} = -R \ln \frac{a_Z}{a_N^{1/2} a_H^{3/2} K_a} \quad (8)$$

where  $R$  is the universal gas constant. Similarly, the heat flux,  $J_q$ , is multiplied by its conjugate thermodynamic driving force (the thermal driving force)

$$\Delta\left(\frac{1}{T}\right) = \frac{1}{T} - \frac{1}{T_a} \quad (9)$$

The object function is a functional (see, e.g., ref 12) depending on the temperature profile of the reaction mixture, the conversion profile of hydrogen, and the temperature profile of the coolant:

$$\frac{dS_{\text{irr}}}{dt} = \int_0^{W_{c,\text{Tot}}} \sigma(\mathbf{x}, \mathbf{u}) dW_c = \frac{dS_{\text{irr}}}{dt}(\mathbf{x}, \mathbf{u}) \quad (10)$$

where  $\mathbf{u}$  is the degree of freedom or the control and  $\mathbf{x}$ , governed by the conservation equations, contains the state variables describing the reactor system

$$\mathbf{x} \equiv [T(W_c) \ \xi_H(W_c)] \quad \mathbf{u} \equiv [T_a(W_c)] \quad (11)$$

Constant parameters are left out of the variable list of the functional.

**4.2. Constraints.** The trivial solution to the problem of finding the minimum entropy production rate of any system is the solution for which the entropy production rate is zero everywhere. This is a reactor in local chemical equilibrium (with  $\Delta G = 0$  everywhere), with the coolant temperature being equal to the reactor temperature. This solution is not of any practical interest. The interesting minimization problems are constrained ones: problems with a given production of chemicals and heat to be exchanged (duty), governed by the systems' conservation equations. The object function shall, therefore, be minimized subject to one or more constraints.

The constraints imposed on the optimization can be divided into two classes. The first class contains constraints such as production, duty, and/or upper/lower boundaries on one or more of the variables used in the optimization. In the current treatment of the ammonia reactor, there is one constraint in this class, namely, the production constraint: We require that the total production of ammonia is unchanged in the minimization. The production of chemicals in the optimal reactor is, therefore, equal to the production in the chosen reference case.

The ammonia production in our reactor is

$$J_Z = \int_0^{W_{c,\text{Tot}}} \frac{1}{(1-\epsilon)\rho_c} r_I dW_c \quad (12)$$

This production in the reference reactor can also be expressed in terms of its average reaction rate:

$$J_{Z,\text{ref}} = \int_0^{W_{c,\text{Tot}}} \frac{1}{(1-\epsilon)\rho_c} \bar{r}_{I,\text{ref}} dW_c \quad (13)$$

where the subscript ref indicates the reference reactor and

$$\bar{r}_{I,\text{ref}} = \frac{1}{W_{c,\text{Tot}}} \int_0^{W_{c,\text{Tot}}} r_{I,\text{ref}} dW_c \quad (14)$$

We require that the ammonia production in the entropy-minimized reactor is equal to the production in the reference reactor, so eqs 12 and 13 are equal:



$$\int_0^{W_{c,Tot}} \frac{1}{(1-\epsilon)\rho_c} \bar{r}_{l,ref} dW_c = \int_0^{W_{c,Tot}} \frac{1}{(1-\epsilon)\rho_c} r_l dW_c \quad (15)$$

The form that uses the average rate is better suited for the numerical solution procedure.

In our previous work on chemical reactors,<sup>6,7</sup> we used only a production constraint in the formulation of the entropy production minimization problem. We did not take into account the fact that the composition and temperature of a reaction mixture at one location in the reactor depend on the history up until that particular position. With the present formulation of the problem, we have introduced constraints which regulate the developments along the reactor coordinate according to a given energy balance and certain mole balances.

Thus, not surprisingly, the second class of constraints are the conservation equations of the system. In general, this class should at least contain a system's energy and mole balances. Other conservation equations can, for example, be the momentum balance, like the Ergun equation. In the current treatment, the pressure drop in the reactor is neglected. Hence, the constraints in the second class for the reactor considered in this work are the energy and mole/mass balances given in eqs 4 and 5.

**4.3. Euler–Lagrange Functional.** The Euler–Lagrange method was used to solve the minimization problem described in sections 4.1 and 4.2. The method consists of writing the Euler–Lagrange functional and minimizing it. The functional takes the object function, eq 6, as well as all of the constraints, eqs 4, 5, and 15, into account:

$$\begin{aligned} \mathcal{L} = \int_0^{W_{c,Tot}} & \left\{ \sigma(\mathbf{x}, \mathbf{u}) + \lambda_z \frac{1}{(1-\epsilon)\rho_c} [\bar{r}_{l,ref} - r_l] + \lambda_q(W_c) \times \right. \\ & \left[ \frac{dT}{dW_c} - \frac{1}{(1-\epsilon)\rho_c} \frac{\frac{4}{d_{ti}} U(T_a - T) - r_l \Delta_r H_l}{F_{H0} \left[ \sum_k \Theta_k C_{p,k} + \frac{2}{3} \xi_H \Delta C_{p,l} \right]} \right] + \\ & \left. \lambda_{\xi_H}(W_c) \left[ \frac{d\xi_H}{dW_c} - \frac{1}{(1-\epsilon)\rho_c} \frac{3}{2} \frac{r_l}{F_{H0}} \right] \right\} dW_c \quad (16) \end{aligned}$$

where  $\lambda_z$  is a scalar Lagrange multiplier related to the total production of ammonia in the reactor. The Lagrange multiplier functions  $\lambda_q(W_c)$  and  $\lambda_{\xi_H}(W_c)$  are related to the energy and mole balances, respectively. The Euler–Lagrange functional depends on the control variables,  $\mathbf{x}$ , the state variables,  $\mathbf{u}$ , and the Lagrange multipliers:

$$\mathcal{L} = \mathcal{L}(\mathbf{x}, \mathbf{u}, \lambda, \lambda_z) \quad (17)$$

where

$$\lambda \equiv [\lambda_q(W_c) \lambda_{\xi_H}(W_c)] \quad (18)$$

Minimizing the above Euler–Lagrange functional is analogous to minimizing the total entropy production rate of the reactor subject to the production and conservation constraints.

The full solution to the minimization of the Euler–Lagrange functional consists, in addition to the temperature and composition profiles, also of the Lagrange

multipliers. An analytical solution to the minimization of eq 16 has not been sought. Instead, we will minimize eq 16 numerically. The necessary changes to the formulation of the minimization problem are given in the next section.

As a start, we have chosen to set the compositions at the inlet and outlet, as well as the outlet temperatures free in the minimization (because the pressure was chosen to be constant). This choice can be changed later.

## 5. Minimization Problem in Discrete Form

The minimization problem must be discretized in order to solve it numerically. The reactor was discretized into  $j = 1, \dots, n - 1$  cylindrical control volumes (see Figure 1). This means that the continuous profiles  $T(W_c)$ ,  $T_a(W_c)$ , and  $\xi_H(W_c)$  became discrete and were written in vectorial form. The vectors  $\mathbf{W}_c$ ,  $\mathbf{T}$ ,  $\mathbf{T}_a$ , and  $\xi_H$  all have  $n$  elements each.

The total entropy production rate, eq 6, was discretized into

$$\frac{dS_{irr}}{dt} = \sum_{j=1}^{n-1} \left\{ \frac{1}{(1-\epsilon)\rho_c} \left[ r_l \frac{-\Delta_r G_l}{T} + \frac{4}{d_{ti}} J_q \Delta \left( \frac{1}{T} \right) \right] \right\}_m \times (W_{c,j+1} - W_{c,j}) \quad (19)$$

where  $m = (2j + 1)/2$  is the center of control volume  $j$ , i.e., the average between two steps.

The production constraint, eq 15, was discretized into

$$\sum_{j=1}^{n-1} [\bar{r}_{l,ref}]_m (W_{c,j+1} - W_{c,j}) = \sum_{j=1}^{n-1} [r_l]_m (W_{c,j+1} - W_{c,j}) \quad (20)$$

The discretization of the second class of constraints containing the energy and the mole balance, eqs 4 and 5, gave

$$\frac{T_{j+1} - T_j}{W_{c,j+1} - W_{c,j}} = \left\{ \left[ \frac{\frac{4}{d_{ti}} U(T_a - T) - r_l \Delta_r H_l}{(1-\epsilon)\rho_c F_{H0} \left[ \sum_k \Theta_k C_{p,k} + \frac{2}{3} \xi_H \Delta C_{p,l} \right]} \right] \right\}_m \quad (21)$$

$$\frac{\xi_{H,j+1} - \xi_{H,j}}{W_{c,j+1} - W_{c,j}} = \left[ \frac{1}{(1-\epsilon)\rho_c} \frac{3}{2} \frac{r_l}{F_{H0}} \right]_m \quad (22)$$

where  $j = 1, \dots, n - 1$ .

The discrete form of the Euler–Lagrange functional was generated by the numerical solver from the discrete forms of the object function and the constraints.

## 6. Calculations

Three hundred control volumes ( $n = 301$ ) were used in all calculations. Lower numbers of  $n$  than 301 gave slightly different profiles, while increasing  $n$  to 401 gave no significant difference in the results. Three different reactor systems were optimized. The only parameter that differed between them was the overall heat-transfer coefficient. The system parameters were taken from Figure 1 and Table 1.

A numerical integration of the energy and mole balance, eqs 4 and 5, over the total catalyst weight, gave

**Table 3. Total Entropy Production Rate [J/K·s] in Three Cases of Different Heat-Transfer Coefficients**

$dS_{irr}/dt$	$U = 100$ J/K·m <sup>2</sup> ·s		$U = 200$ J/K·m <sup>2</sup> ·s		$U = 400$ J/K·m <sup>2</sup> ·s	
	ref.	min.	ref.	min.	ref.	min.
reaction	208	218	213	225	226	220
heat transfer	24.1	5.81	44	13.8	71.8	30.5
total	232	223	258	239	298	250
total / $J_Z$	15.4	14.8	16.3	15.1	18.0	15.1
% reduction		3.9		7.4		16

the discrete temperature and conversion profiles of the systems that were to be optimized (the reference systems).

The ammonia production of the three systems was first calculated using eq 13. The total entropy production rate, reaction rate, chemical and thermal forces, and local entropy production rate profiles were calculated next. These results serve as benchmarks for the results from the numerical entropy production minimization. The profiles from the reference system calculations are labeled "ref." in the figures.

The entropy production minimization consisted of minimizing the total entropy production rate of the system, eq 19, subject to the three constraints in eqs 20–22, by varying  $T_a$  (the coolant temperature profile),  $T$  (the reaction temperature profile),  $\xi_H$  (the hydrogen conversion profile), the inlet/outlet composition, and the inlet/outlet temperature.

This constrained numerical minimization was carried out using the Matlab 5.3.1 (R11.1) Optimization Toolbox function `fmincon`<sup>13</sup> with the profiles of the reference system as starting values. `fmincon` uses a sequential quadratic programming (SQP) method. In this method, a quadratic programming (QP) subproblem is solved at each iteration. An estimate of the Hessian of the Lagrangian is updated at each iteration using the BFGS formula. See, e.g., ref 14 for details on numerical optimization. Other starting values were also used to see if the solver was able to find more than one stable minimum. Only one minimum was found. The set of profiles from the entropy production minimization is called the minimized or optimized system and is labeled "min." in the figures.

The results obtained in the entropy production minimization were tested for consistency. By solving the mole and energy balance, using the calculated optimal coolant temperature profile and the optimal inlet values as boundary conditions, we regained the optimal temperature and conversion profiles. This showed that the method fulfills the mole and energy balance, as required.

## 7. Results and Discussion

The ammonia production in the three reference systems was 15.1, 15.8, and 16.6 mol/s, respectively. We thus found that the production increased with an increasing value of the overall heat-transfer coefficient.

The total entropy production rates of the three reference systems and their corresponding minimized systems are given in Table 3. Savings of 3.9, 7.4, and 16% were obtained by the entropy production minimization procedure of the three reference systems, respectively. Because the ammonia production varied between the cases, we calculated the ratio of the total entropy

production rate of each reactor to its ammonia production to make the results comparable. The table row containing those numbers is labeled "total/ $J_Z$ ".

Table 3 shows that an increasing value of  $U$  increases the entropy production in the reference systems, both because of heat transfer and because of chemical reaction. The numbers suggest that the potential for savings in the total entropy production rate for the current reactor setup increases as the overall heat-transfer coefficient increases. The total entropy produced per mole of ammonia is almost constant for the minimized systems, while it increases with increasing  $U$  for the reference systems.

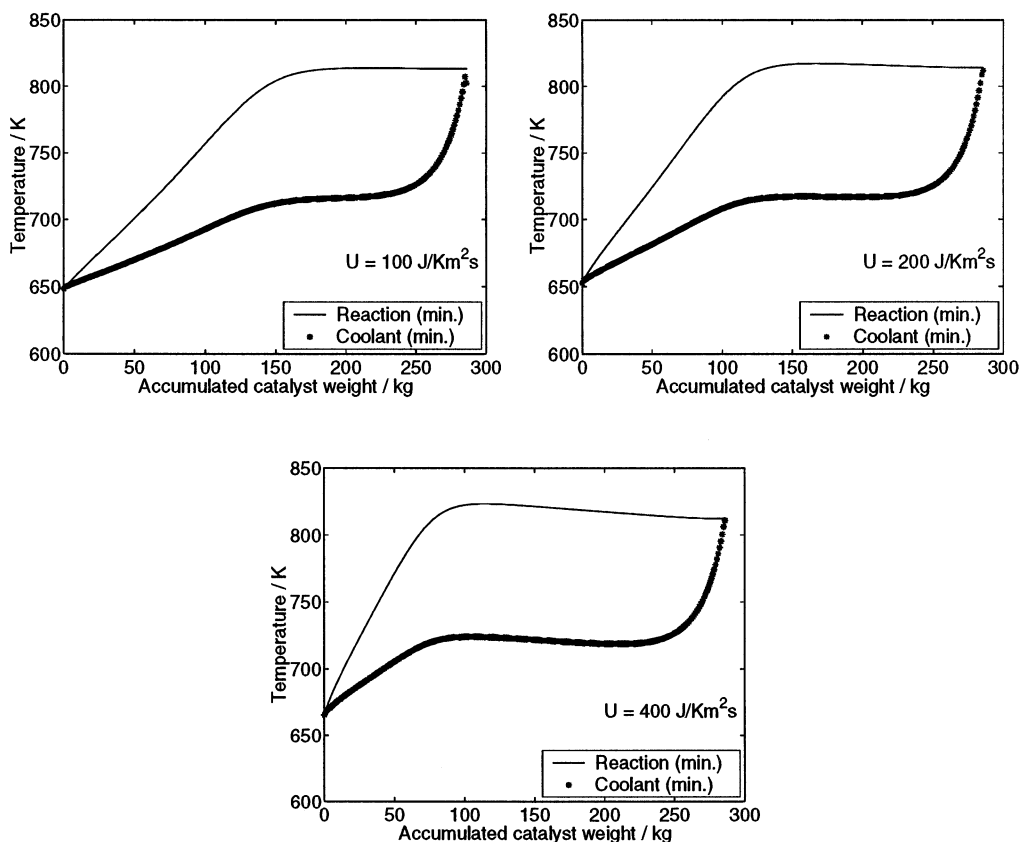
The last variation can be explained by the better reactor cooling for larger values of  $U$ . Better cooling in the beginning of an exothermic reactor gives a higher reaction rate down to a certain temperature, the temperature of the maximum reaction rate. When the cooling as well as the reaction rate increase, their respective terms in the total entropy production rate increase (see eq 6). So, by increasing  $U$  for the current reference reactor setup, we are creating a reactor that is less and less optimal with respect to the second law of thermodynamics. This is not true for the minimized cases. A larger value of  $U$  does not alter the entropy produced per unit of ammonia produced. So, the potential for saving is larger, the larger  $U$  becomes. This result follows from the choice of the coolant temperature as the control variable. The chemical reaction is controlled by  $T_a$  only, while the entropy production in the reaction and the heat exchange process are being weighed. We shall see in the following that the reactor works mostly as a heat exchanger in the end parts. It follows that the end part of the reactor has a minor function in the present context.

The main results from the minimization of the total entropy production rate of the three systems are illustrated in Figures 2–10. All variables presented in these figures are given as functions of the accumulated catalyst weight,  $W_c$ . They will be presented and discussed consecutively. The nature of the entropy production minimized systems is characterized by all of the curves in Figures 2–10. The figures present different aspects of the same solution.

**7.1. Temperature Profiles in the Optimal and Reference Reactors.** Figure 2 presents the coolant temperature profiles and the reaction mixture temperature profiles for the three values of  $U$  after the minimization procedure has been carried out. While the coolant temperature in the reference systems was constant (630 K), we see from Figure 2 that the temperature varies along the reactor in the minimized systems.

The main gain of the entropy production minimization procedure can be read directly from Figure 2 as an increase in the coolant temperature. This increase in temperature means more high-quality heat to be used elsewhere in the process. The temperature of the coolant rises from a constant 630 K in the reference system to a value between 650 K at the inlet of the reactor or just above 800 K at the outlet.

The temperature profiles in Figure 2 can be compared to previous results.<sup>6,7</sup> The inlet temperature of the reactants is much lower compared to these results. This is due to the fact that we are using the full object function in this work. By including the entropy produced by the cooling process, it is impossible to obtain such



**Figure 2.** Reaction mixture and coolant temperature profiles in the minimized reactors for different values of  $U$ .

high inlet temperatures as those presented before because they give a high penalty in the entropy produced by the cooling process. This penalty comes from the heat exchange needed to both cool the reaction mixture to keep it at a distance from the equilibrium temperature (to produce ammonia) and simultaneously remove the heat dissipated in the reaction.

The temperature profiles in Figure 2 do, of course, depend on all variables and boundary conditions that are used in the calculations. When one of them is changed, the temperature profiles will change. In particular, when the overall heat-transfer coefficient is changed, the distance between the profiles will become smaller, but their shape will remain essentially the same.<sup>15</sup> The profiles depend highly on the value of  $U$ . Thus, it is important that  $U$  is predicted as well as possible; a temperature-dependent model of the overall heat-transfer coefficient should be included in calculations of real systems.

It is interesting that the coolant and reaction mixture temperatures become identical at the reactor inlet and outlet. This observation is independent of the value of  $U$  and can be explained from a formulation of the problem using control theory.<sup>16</sup> The higher the overall heat-transfer coefficient becomes, the more the coolant/reaction mixture temperature profiles resemble a symmetrical object. At the outlet, the steep slope of the coolant temperature combined with an almost constant temperature inside the reactor suggests that the mixture leaves the reactor close to equilibrium. This is confirmed numerically by the reaction rate being close to zero there (see Figure 7).

It is also interesting to see that the temperature difference becomes very close to constant in the middle

of the reactors. The range of constancy is larger, the larger the overall heat-transfer coefficient. A constant temperature difference means that the heat exchange process is optimal.<sup>4,5</sup> Also, there is, in general, a bend in the minimized temperature profiles that shifts toward lower  $W_c$  with increasing  $U$ . The bend coincides with the start of the region where the temperature difference is close to constant.

The reaction mixture temperature profiles of the three cases are shown in Figure 3. The figure shows how the reaction temperature changes by the minimization procedure for increasing values of  $U$ . The higher the overall heat-transfer coefficient becomes, the higher is the temperature rise in the beginning of the reactor. The reaction is shifted toward the beginning of the reactor. The larger potential for saving in the entropy production rate at high values of  $U$  (cf. Table 3) is reflected in Figure 3. The higher the value of  $U$ , the more the minimized reactor differs from the reference. The same can also be read from the hydrogen conversion profiles (see Figure 4).

**7.2. Hydrogen Conversion Profiles.** The hydrogen conversion profiles in both the reference reactors (ref.) and the minimized reactors (min.) are plotted in Figure 4.

The inlet composition, shown in Table 1, represents  $\xi_H = 0$ . A negative conversion at the inlet ( $\xi_{H0} < 0$ ), as suggested by the minimized profiles, means that the components' compositions at the inlet should be changed as if reaction (I) was shifted to the left compared to the reference reactor. That means no change in the contents of inerts, a slight increase in the nitrogen and hydrogen contents, and finally a decrease in the ammonia content. The absolute value of the conversion at the outlet is,

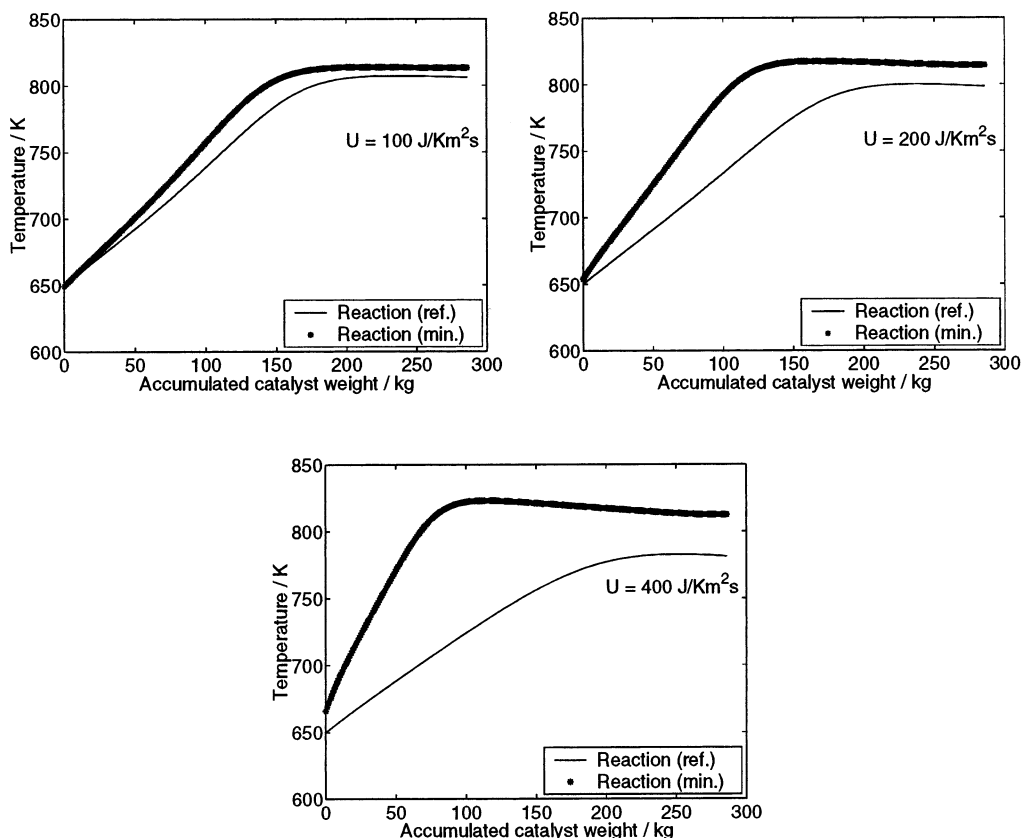


Figure 3. Reaction mixture temperature profiles in the reference (ref.) and minimized (min.) reactors.

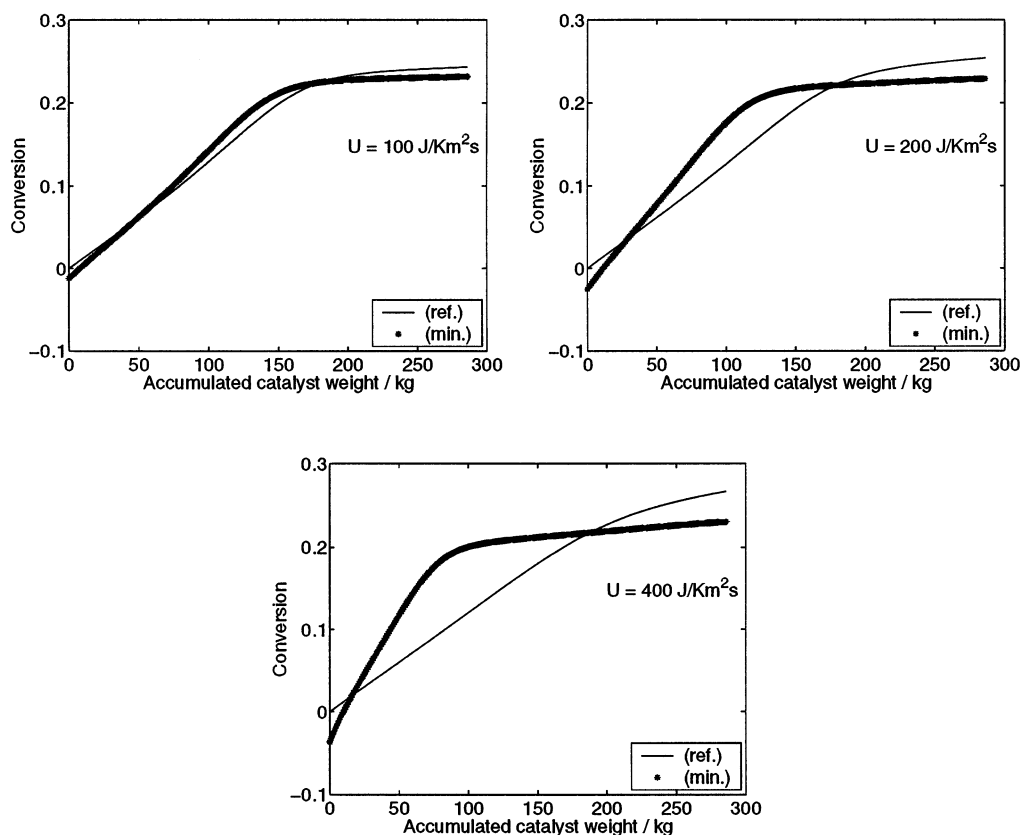


Figure 4. Hydrogen conversions in the reference (ref.) and minimized (min.) reactors.

therefore, lower because the ammonia production in the minimized reactors is the same as that in their corresponding reference reactors.

**7.3. Driving Forces.** The chemical and thermal driving forces, eqs 8 and 9, in the minimized reactors are shown in Figures 5 and 6. Both forces are large in



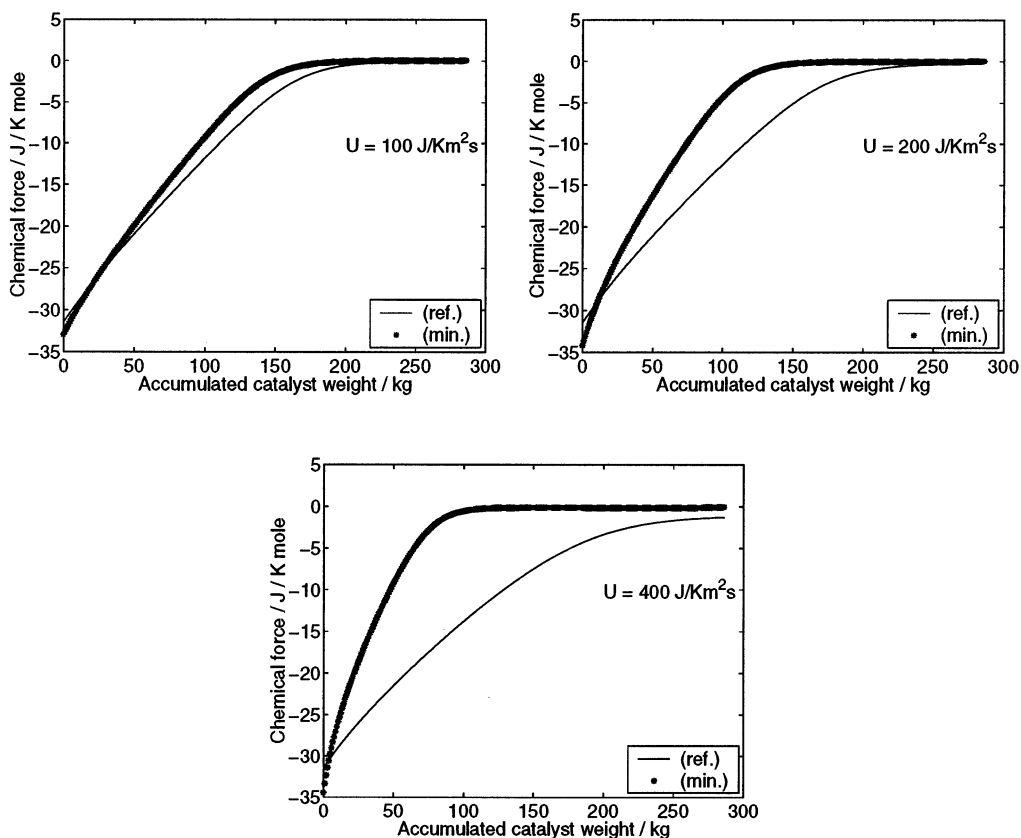


Figure 5. Chemical driving forces, eq 8, in the reference (ref.) and minimized (min.) reactors.

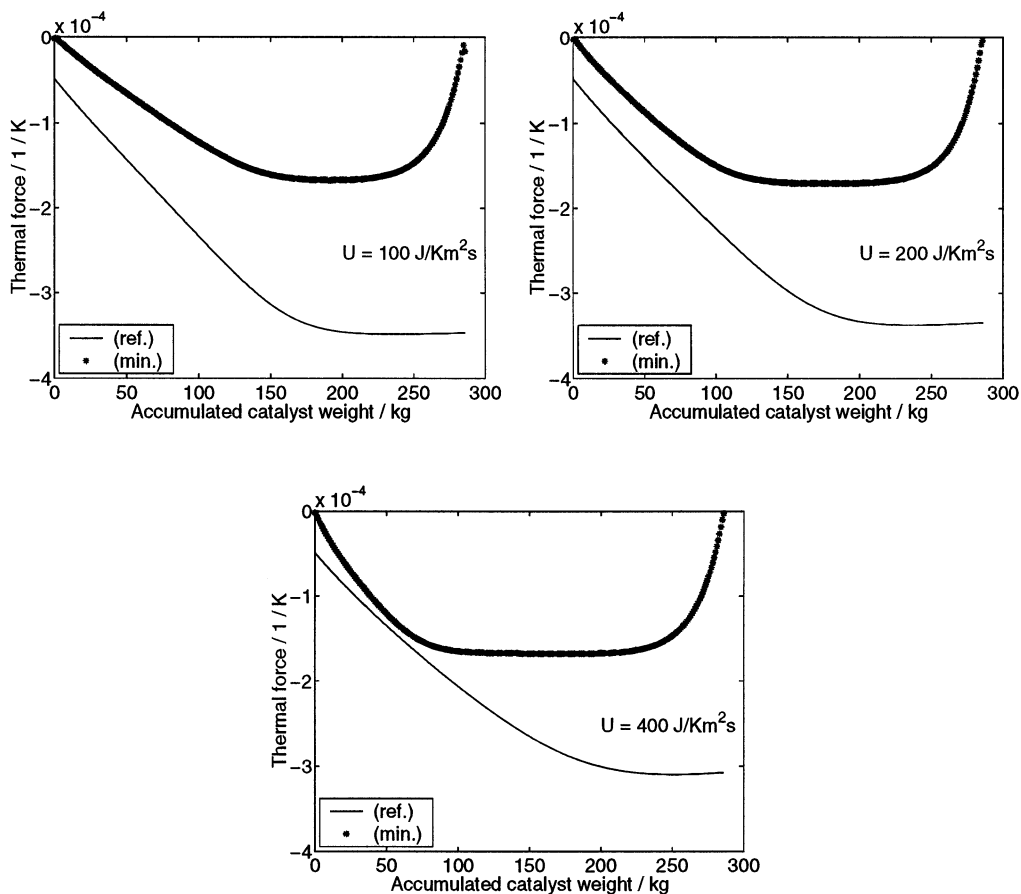
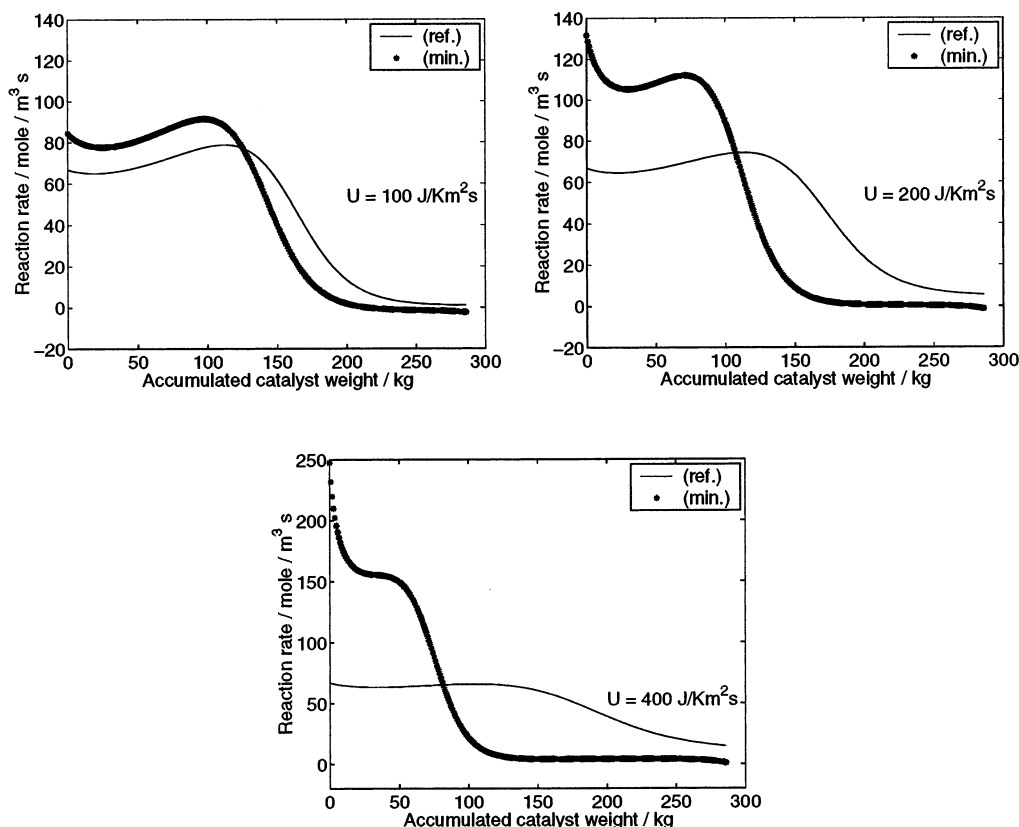


Figure 6. Thermal driving forces, eq 9, in the reference (ref.) and minimized (min.) reactors.

significant parts of the reactors. The chemical force being close to zero in the last half of the reactor suggests

a shorter reactor. A lower value for  $U$  is not interesting because it will give a smaller ammonia production.



**Figure 7.** Reaction rate distribution in the reference (ref.) and minimized (min.) reactors.

The thermal force is constant in the middle of the reactor and goes toward zero at the beginning and at the end. In Figure 6 we also see the emerging symmetry (increasing with an increasing overall heat-transfer coefficient) that was observed in Figure 2.

The driving forces are far from constant throughout the reactor. They are, however, both constant in parts of the reactor; the higher the value of the overall heat-transfer coefficient, the larger is this part. The constant level of the thermal force might be explained by earlier work,<sup>4,5</sup> with the heat exchange as the dominating process in the reactor at those positions. From Figures 6 and 7, this seems indeed to be the case: The thermal force becomes constant just before the point where the reaction rate and thus the chemical force approach zero.

**7.4. Reaction Rate Distribution.** Figure 7 illustrates how the chemical production is distributed in both the reference and the minimized reactors.

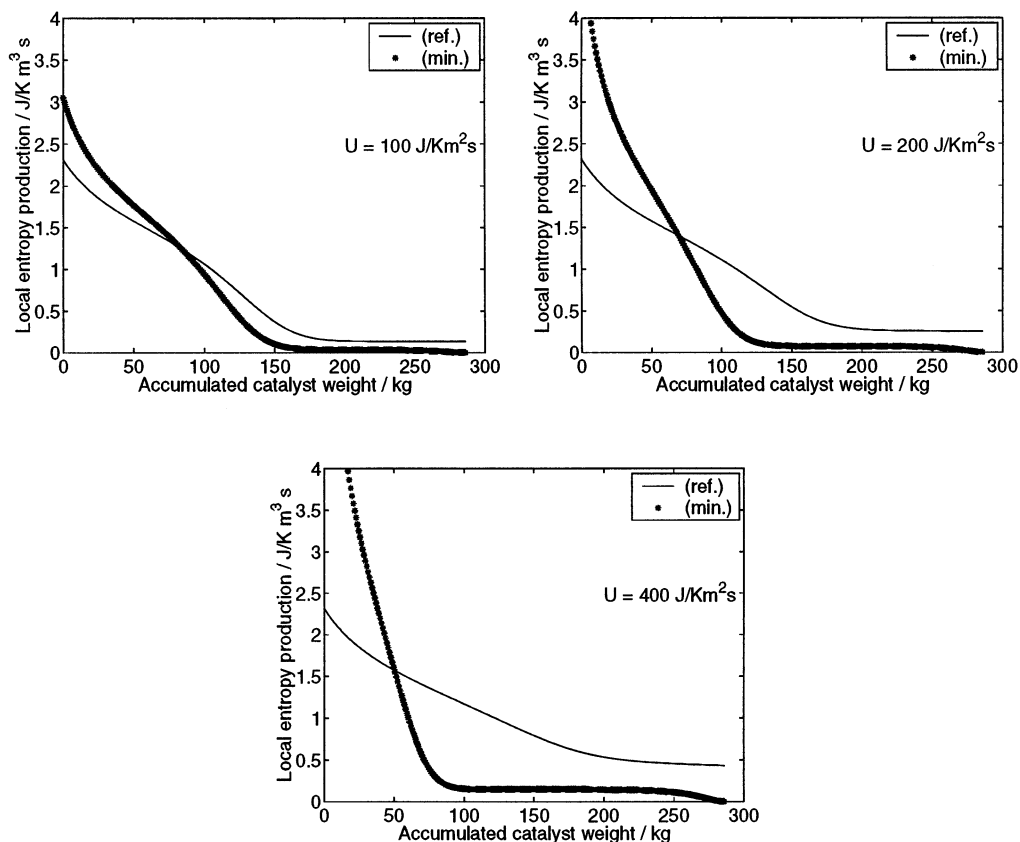
For the minimized systems, this figure clearly shows where the main part of the chemical reaction takes place: in the beginning of the reactor. These results can also be taken as a suggestion that a shorter reactor may do (almost) the same job. It is more homogeneously distributed in the reference than in the minimized reactor. In our earlier work, when we only included the entropy production rate due to the chemical reaction in our object function,<sup>7</sup> we observed the opposite behavior.

**7.5. Entropy Production Rate and the Distance to Equilibrium.** In Figure 8, we have plotted the local entropy production rate in both the reference and the minimized reactors. These profiles show the same behavior as the reaction rate profiles in Figure 7: The entropy production rate is more homogeneous along the reactor in the reference systems than in the minimized systems.

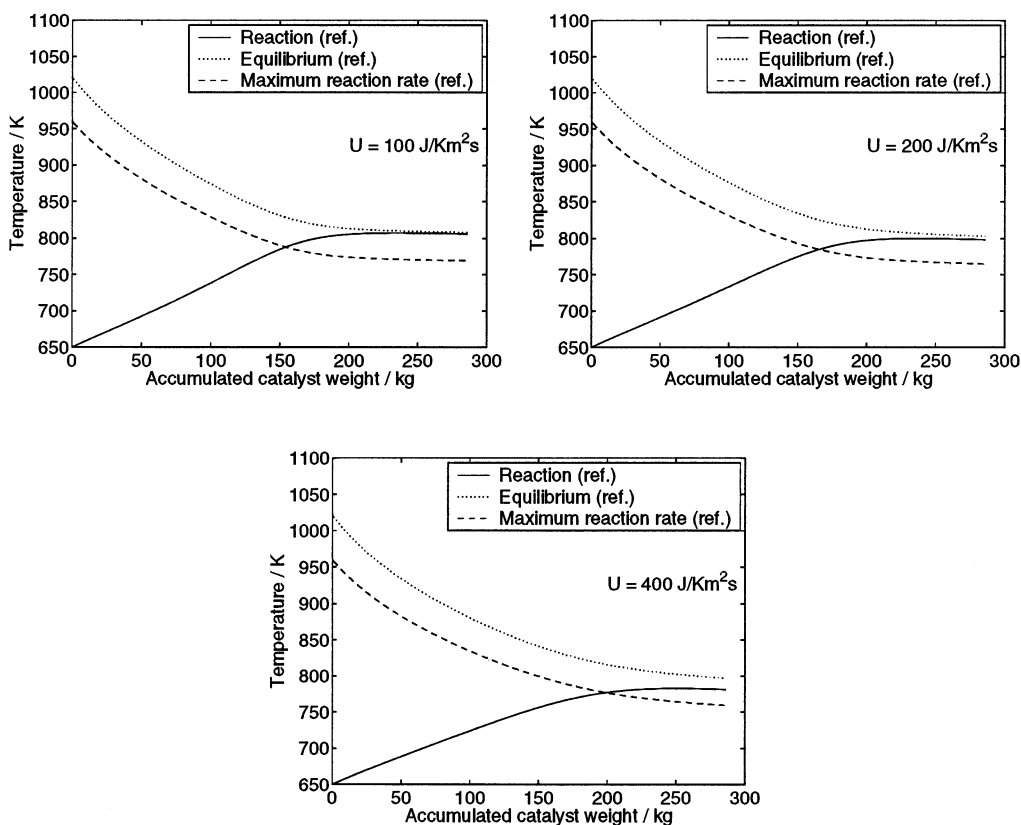
At any state in the reactor, defined by temperature and conversion, one can find the temperature that the mixture would have in equilibrium and the temperature where the mixture has its maximum reaction rate. At a given composition, the equilibrium temperature of a reaction mixture is the temperature at which it would be in equilibrium, i.e.,  $r_1 = 0$ . Similarly, the maximum reaction rate temperature is the temperature at which the same reaction mixture would have its maximum reaction rate, i.e.,  $dr_1/d\xi_H = 0$  and  $d^2r_1/d\xi_H^2 < 0$ . Figures 9 and 10 give these temperature profiles for both the reference and the minimized systems. The equilibrium and maximum reaction rate temperatures in the reference systems are given in Figure 9.

It is known that the equilibrium temperature and the temperature of the maximum reaction rate vary in a parallel fashion through the reactor.<sup>17</sup> The distance to the maximum reaction rate is an important variable that can be related to reactor volume and production per unit of volume.

From Figures 9 and 10, we see that the reaction mixture temperature in the minimized systems approaches its corresponding equilibrium temperature earlier than that in the reference systems. In the minimized systems, the two temperatures coincide from approximately the middle of the reactor and out, i.e., when we have local chemical equilibrium (compare also Figure 7). In the reference systems, the two temperatures are at a distance apart throughout the whole reactor at high overall heat-transfer coefficients. The discontinuities in the equilibrium temperatures at the inlet of the minimized systems with  $U = 200$  and  $400$  stems from numerical instabilities in the reaction rate model (eq 1) at very high temperatures.



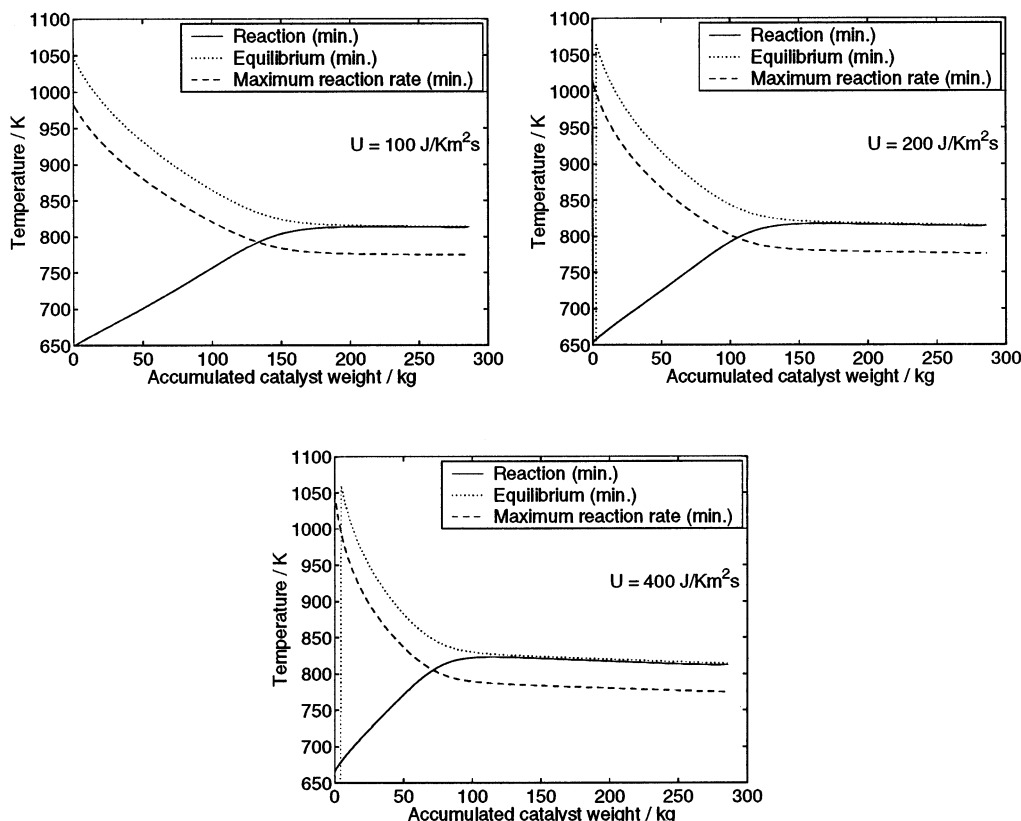
**Figure 8.** Local entropy production rate distribution in the reference (ref.) and minimized (min.) reactors.



**Figure 9.** Equilibrium and maximum reaction rate temperature profiles in the reference systems.

The outcome of the optimization could not be predicted in an intuitive manner. Previous work,<sup>6,9</sup> which only took the chemical reaction into account, showed results at variance with the present ones: It was earlier

found that the reaction mixture temperature should be parallel to its equilibrium and to the maximum reaction rate temperatures. However, common to all of Figures 2–10 is that the optimal profiles seem to have two



**Figure 10.** Equilibrium and maximum reaction rate temperature profiles in the minimized systems.

phases: one initial phase with a relatively rapid rise in variables and one phase where the variables turn almost constant. Whether this two-phase behavior is characteristic for the optimal solution may deserve further attention. These results do also suggest a shorter reactor. Such a possible change must, of course, be traded off with, e.g., the need for excess catalyst in the reactor because of catalyst decay.

**7.6. Optimization Method.** A numerical method for the minimization of the total entropy production rate of a reactor system has been presented, where the contributions from the chemical reaction plus the heat exchange with the coolant are taken into account. The total entropy production rate is minimized subject to a constant ammonia production, ensuring that the energy and mole balances are fulfilled. An exothermic ammonia reaction has been studied in a tubular fixed-bed reactor. The method can, however, also be used on endothermic reactors because the nature of the optimization equations (eqs 4–6 and 15) are the same for endothermic and exothermic reactors; the difference between the reactor systems will enter in the choice of constraints, in rate expressions, and through physical properties.

The optimization method presented here improves our previous efforts<sup>6,7</sup> with two new and important features. First, the entropy produced by the heat exchange from the reaction mixture to the coolant has now been included in the object function. Second, we impose both the energy and mole balance as constraints in the problem formulation. This means that we *require* that the mole and energy balances are fulfilled. Now that we have included both the heat transfer and the chemical reaction in the object function, the object function becomes more realistic. This is an important step in the model development. The second improve-

ment is most important, however, because any real system *has* to fulfill its energy and mole balance(s).

We have chosen to use the coolant temperature profile as well as the inlet temperature and conversion as degrees of freedom or control in our optimization efforts so far. The coolant temperature was chosen because it is the function or vector that directly controls both the temperature of the reaction mixture and the chemical conversion through the energy and mole balance, given that the reactor only has one feeding point. The inlet temperature and conversion can be set or allowed to vary freely in the calculations depending on the purpose of the minimization. Here, we have chosen to let them vary freely to try to find the true minimum in produced entropy. This might not be possible in the optimization of an existing process. The inlet stream parameters may then be fixed. Similarly, the outlet composition/temperature may be fixed by a downstream process.

In addition to adding or removing constraints (flow-rate limits, temperature limits, etc.), it is also possible to use more or different degrees of freedom, like the pressure and catalyst distribution/density, in the model. Future developments of the optimization method should include different reactions, in particular endothermic ones, more realistic operating conditions (two-dimensional reactor models and controllability), and several process units combined.

In the current formulation of the minimization method, the component mole balances are represented by one expression: eq 5. Given the hydrogen conversion at one point in the reactor, one can calculate all of the flow rates/mole fractions at that position using the expressions in Table 2. However, the mole balance formulation limits the freedom of the numerical optimizer in the sense that it can only vary the composition in a pattern

compatible with the stoichiometry of reaction (I). Thus, at points where the mole balance is not fulfilled, i.e., at the inlet or at additional feed points (if such points exist), the optimizer cannot choose truly free flow rates. To avoid this limitation, we will have to impose all of the component mole balances, instead of the current mole balance, as constraints to the minimization problem. This also requires that the component molar flow rates must be included as variables in the model and the conversion be removed.

All of our reactor calculations have been obtained using a PFR model. This is a choice we have made to keep the reactor model simple while our main focus is on developing the entropy production minimization model. The PFR model should at least be kept until phenomena such as pressure drop have been included.

**7.7. Technical Perspectives.** This paper has presented a method for entropy production minimization. The method was applied to an industrial example but cannot be seen as a real case of minimization yet.

The savings that is reported here must be seen on the background of the assumptions and conditions that are used. We believe that the plug-flow model captures the essence of the behavior, even if it does not give correct numbers. Before an application, the numbers may have to be verified by more elaborate computer fluid dynamics models of the optimal and reference reactor.

In the minimization of a real process, one may have to introduce technical constraints that are not used here. For instance, the catalyst has a normal window for thermoresistance<sup>8</sup> between 480 and 550 °C, and one may want to implement such a restriction in the minimization procedure. There is most likely a tradeoff between the reactor system and other processes in the plant (i.e., compressors). We have only optimized the reactor and its utility. More units may have to be included to find realistic total minima. The choice of degrees of freedom in the inlet–outlet conditions is also affected by this.

Several technologies exist for excess heat removal in the ammonia plant, among them cocurrent internal cooling at the same pressure as the synthesis.<sup>1</sup> A technical implementation of the results for realistic boundary conditions and operating constraints seems, therefore, feasible in the future.

We have mentioned in the Introduction other important types of reactor optimizations. This work does not replace these. It should be seen as a step in a direction to systematically analyze chemical processes also from the perspective of their second law efficiency.

## 8. Conclusion

We have presented a numerical method for the minimization of the total entropy production rate of a chemical reactor system, where both the entropy produced by the chemical reaction and the cooling of the reaction mixture are taken into account. Application of the method gives operating conditions compatible with minimum lost exergy. The method was applied on the exothermic ammonia reaction in a tubular fixed-bed reactor with external cooling. Reductions in the total entropy production rate, ranging from 3.9% to 16% depending on the value of the overall heat-transfer coefficient, were obtained by changing the inlet conditions and coolant temperature profile. The gain may be taken out as the temperature of the coolant increased.

The results also suggest that a shorter reactor may do the same job. Our earlier results for reaction optimal reactors (i.e., reactor systems where we only considered the chemical reaction) were very different from the results obtained here. The nature of the present solution depends largely on the overall heat-transfer coefficient. While the method itself has a potential for further development, it should also be possible to apply it in its present stage to obtain further information for reactor design.

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## Nomenclature

$a_k$  = activity of component  $k$  [atm]  
 $C_{p,k}$  = heat capacity of component  $k$  [J/K·mol]  
 $\Delta C_{p,I} = \sum_{\text{products}} \nu_k C_{p,k} - \sum_{\text{reactants}} \nu_k C_{p,k}$  [J/K·mol]  
 $d_{ti}$  = inner tube diameter of the reactor [m]  
 $\Delta_r H_i$  = enthalpy of the ammonia reaction [J/mol]  
 $F_k$  = molar flow rate of component  $k$  [mol/s]  
 $F_{k0}$  = entering molar flow rate of component  $k$  [mol/s]  
 $G$  = superficial mass velocity [kg/m<sup>2</sup>·s]  
 $\Delta_r G_i$  = change in the Gibbs energy of reaction (I) [J/mol]  
 $J_q$  = measurable heat flux [J/m<sup>2</sup>·s]  
 $J_Z$  = ammonia production [mol/s]  
 $j$  = control volume index  
 $K_a$  = equilibrium constant [1/atm]  
 $K_b$  = rate constant [mol·atm/m<sup>3</sup>·s]  
 $K_c$  = rate constant [atm<sup>1/2</sup>]  
 $k$  = component index  
 $\mathcal{L}$  = Euler–Lagrange functional  
 $\bar{l}_{qq}$  = average phenom heat-transfer coefficient [J/K·m<sup>2</sup>·s]  
 $n$  = number of steps in the optimization  
 $P_{\text{Tot}}$  = total pressure [atm]  
 $R$  = universal gas constant [J/K·mol]  
 $r_I$  = ammonia formation rate [mol/m<sup>3</sup>·s]  
 $dS_{\text{irr}}/dt$  = total entropy production rate [J/K·s]  
 $T$  = temperature of the reaction mixture [K]  
 $T_a$  = coolant temperature [K]  
 $T_{\text{in}}$  = entering reaction mixture temperature [K]  
 $\Delta(1/T)$  = thermal force [1/K]  
 $U$  = overall heat-transfer coefficient [J/K·m<sup>2</sup>·s]  
 $\mathbf{u}$  = vector containing process control variables  
 $W_c$  = accumulated catalyst weight [kg]  
 $W_{c,\text{Tot}}$  = total catalyst weight [kg]  
 $\mathbf{x}$  = vector containing process state variables  
 $y_{k0}$  = inlet mole fraction of component  $k$

## Greek Symbols

$\alpha$  = kinetic model parameter  
 $\epsilon$  = catalyst void fraction  
 $\lambda$  = Lagrange multiplier  
 $\boldsymbol{\lambda}$  = vector containing Lagrange multipliers  
 $\nu_k$  = stoichiometric coefficient  
 $\rho_c$  = catalyst density [kg/m<sup>3</sup>]  
 $\sigma$  = local entropy production rate [J/K·m<sup>3</sup>·s]  
 $\Theta_k$  = molar flow rate ratio  
 $\xi_H$  = hydrogen conversion

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