Dynamic Model of an Industrial Steam Reformer and Its Use for Multiobjective Optimization

Anjana D. Nandasana,1 Ajay K. Ray,1 and Santosh K. Gupta*,†

Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, India, and Department of Chemical and Environmental Engineering, National University of Singapore, 10, Kent Ridge Crescent, Singapore 119260

An industrial side-fired steam reformer in a hydrogen plant is simulated under dynamic conditions. A rigorous model with verified reaction kinetics is used. This model incorporates aspects of heat transfer in the furnace and diffusion inside the catalyst pellet. The dynamic model is used to study the effects of a few (planned) disturbances that reduce the production of both hydrogen and steam and adversely influence the safety of the plant if corrective control action is not taken in time. The operation of the steam reformer is simulated in the presence of three idealized disturbances in (1) the inlet feed temperature, (2) the inlet feed rate of natural gas, and (3) the furnace gas temperature. The model is then used to obtain optimal operating conditions required to negate the effects of two disturbances using several control or decision variables. Two objective functions are minimized simultaneously: the cumulative (integrated over time) deviation of the flow rate of hydrogen and the cumulative deviation of the steam flow rate. The elitist nondominated sorting genetic algorithm NSGA-II is used to obtain solutions of this multiobjective optimization problem. Nondominating Pareto-optimal solutions are obtained.

Introduction

Steam reforming of hydrocarbons is an economical method of producing synthesis gas and generating hydrogen. The former is the feedstock for the synthesis of ammonia, methanol, etc., and the latter is an environmentally clean fuel.1 Steam reforming plants also produce considerable amounts of exportable steam. The process flow sheet of a typical plant is shown in Figure 1. A hydrocarbon stream, assumed to be essentially methane (with CO2 and N2 impurities) in this study, is desulfurized and preheated. This stream is mixed with appropriate quantities of steam and recycled hydrogen (both from the plant) and fed to the first reactor (called the reformer). The following catalytic reactions take place in this reactor

Reforming: \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \) \( \Delta H = 8.623 \times 10^5 \text{kJ/kmol} \) (1)

Shift: \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) \( \Delta H = -1.7196 \times 10^5 \text{kJ/kmol} \) (2)

Reforming: \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \) \( \Delta H = 6.904 \times 10^5 \text{kJ/kmol} \) (3)

The gas exiting the reformer, rich in CO and H2, exchanges heat with the boiler feedwater to generate very high pressure (VHP) steam. The cooled process gas is then fed to a two-stage adiabatic shift converter, where CO is converted into CO2 and additional hydrogen. Hydrogen is separated from the exit gas in a pressure-swing adsorption (PSA) unit. The reforming reactions (eqs 1 and 3) are strongly endothermic in nature and require large energy inputs. Increasing energy costs and competition require that reforming plants be operated optimally, both under steady-state conditions and in the presence of unplanned disturbances. The effects of these disturbances need to be negated by advanced model-based process control strategies. A good dynamic model is a prerequisite for this. The development and application of such a model-based control strategy is the main focus of the present study.

Several studies2–6 have been reported in the open literature on the steady-state modeling, simulation, kinetics, optimization, and control of steam reformers. These have been reviewed by Elnashaie and Elshishini2 and Rajesh et al.6 Elnashaie and Elshishini7 also presented an elaborate study on the dynamic modeling of gas–solid catalytic reactors in general but did not study industrial reformers in detail. Alatiqi and co-workers8–12 reported some work on the dynamic modeling and simulation of industrial steam reformers under load disturbances and validated their simulation results with actual plant data. However, they did not provide complete information on their approach for proprietary reasons. They used different control methods to minimize the effects of disturbances. Their dynamic model uses a simplified overall reaction rate expression rather than eqs 1–3. In addition, the reaction-oust-diffusion of the several molecular species present inside the porous catalyst is not considered separately. Kvamsdal et al.13 also carried out the dynamic simulation of industrial steam reformers in the presence of sudden stoppages (tripping) of the feed gas flow and of the steam supply. They used the pseudo-homogeneous kinetic model of Xu and Froment.3 Again, these workers did not provide complete details on the reactor. There is, thus, a definite need for the development of a dynamic model based on first principles, with complete...
details provided. Such fundamental models can also be used for off-line optimization purposes to obtain optimal control strategies required to negate the effects of a number of idealized disturbances. A file of such strategies (a few of which are obtained here) would be of immense use for the optimal operation of these plants. It should be mentioned here that the detailed model developed here for the steam reformer is somewhat similar to that for packed-bed adsorbers, in which no reactions take place.

**Formulation**

The steady-state model of the reformer is modified in this study to apply to transient conditions. The concentrations, $C_i(Z,t)$, and the temperature, $T(Z,t)$, of the gas phase (outside the solid) are functions of both the axial location, $Z$, and the time, $t$. It is assumed that there are no radial gradients in the gas phase. The equation for $C_i(Z,t)$ can be written, for a semidifferential control volume of length $\delta Z$, as

$$\frac{\partial}{\partial Z}(v_i C_i) = \frac{\partial C_i}{\partial t} + \rho_b \eta_i R_i,$$

where $v_i$ is the superficial velocity of the gas; $\rho_b$ is the volume fraction of the pores inside the solid; and $R_i$ is the net rate of consumption of the $i$th species because of the three reactions, which is related to $r_i$, the (net) forward rate of the $i$th reaction (eqs 1–3). At the solid boundary, this equation15 would make the problem computationally intense. We can then write the simplified energy balance equation for the semidifferential control volume (gas plus solid) of length $\delta Z$ as

$$\frac{\partial}{\partial Z}(GC_{p,g} A T) = \pi d_i U (T_{w,i} - T) - [C_{p,g} \rho_b + (1 - \rho_b) \kappa_g C_{p,g} A_i] \frac{\partial T}{\partial t} + \sum_{i=1}^{\infty} (-AH_i) \eta_i r_i \rho_b$$

In eq 5, $G (\equiv \rho_0 V)$ is the mass velocity of the gas; $\rho_0$ is the volume fraction of the voids in the catalytic bed (outside the porous solids); $\rho_b$ is the volume fraction of the pores inside the catalytic bed (including the void in the bed and the pores in the catalyst); $R_i$ is the net rate of consumption of the $i$th species because of the three reactions, which is related to $r_i$, the (net) forward rate of the $i$th reaction (eqs 1–3), at the conditions just outside the catalyst particle, through the stoichiometric coefficients $a_{i,k}$, and $\eta_i$ is the effectiveness factor for the $i$th reaction. No accumulation term corresponding to the solid is necessary in this equation, as the balance is on the gas alone.

The most general form of the energy balance equation would make the problem computationally intense and would require separate equations for the gas and solid phases. In such a model, the temperature of the solid phase, $T_s(Z,t)$, would depend on $Z$ and $t$ as well as the internal location, $l$. At the solid boundary, this temperature would be related to the local gas-phase temperature, $T(Z,t)$, through the gas–film resistance model. Simplifying assumptions are needed to obtain a model that is useful for optimization and control. It is known that the thermal conductivity of the catalyst pellet is quite high (low Prater number). Also, the resistance of the gas film surrounding the catalyst particles is small. Under these conditions, we can assume that the entire catalyst particle attains the temperature, $T(Z,t)$, of the gas phase (at axial position $Z$ and time $t$) instantly. Villadsen and Michelsen and Elnashai and Elshishini mention that this is a reasonable approximation to make. We can then write the simplified energy balance equation for the semidifferential control volume (gas plus solid) of length $\delta Z$ as

$$\frac{\partial}{\partial Z}(GC_{p,g} A T) = \pi d_i U (T_{w,i} - T) - [C_{p,g} \rho_b + (1 - \rho_b) \kappa_g C_{p,g} A_i] \frac{\partial T}{\partial t} + \sum_{i=1}^{\infty} (-AH_i) \eta_i r_i \rho_b$$

In eq 5, $G (\equiv \rho_0 V)$ is the mass velocity of the gas; $\rho_0$ is the volume fraction of the voids in the catalytic bed (outside the porous solids); $\rho_b$ is the volume fraction of the pores inside the catalyst particle, $\rho_s$ and $\rho_p$ are the densities of the porous catalyst (kilograms of solid per cubic meter of porous catalyst particles) and of the pure gas, respectively; $U$ is the film heat-transfer coefficient on the inside of the tube surface (sum of the effects of heat transfer to the gas and to the solid); $C_{p,g}$ and $C_{p,s}$ are the heat capacities of the pure gas mixture (in the voids) and of the solid catalyst (without pores), respectively; $T_{w,i}$ is the temperature at the inner tube wall; and $AH_i$ is the heat of reaction of the $i$th reaction. Equation 5 can easily be deduced from eqs e and f (page 492) of Froment and Bischoff, using these assumptions. It would be interesting to compare the results obtained from the simplified model developed here with those obtained using a more rigorous model for $T_s(Z,t)$, when the latter becomes available (work is in progress along these lines).

The following initial conditions (ICs) can be used with eqs 4 and 5:

$$C_i(Z,t=0) = C_i^{SS}(Z), \quad 0 \leq Z \leq L \quad (6a)$$

$$T(Z,t=0) = T_i^{SS}(Z), \quad 0 \leq Z \leq L \quad (6b)$$

**Figure 1.** Process flow diagram of the steam reforming plant using natural gas feed.
In the above equations, \( N_i \) with the following boundary conditions (BCs) at \( l = 0 \) and \( l = l_c \):

\[
C_i(l=0; t) = C_i(Z; t), \quad i = CH_4, H_2O, CO, CO_2, H_2
\]

\[
N_i(l=l_c; t) = 0, \quad i = CH_4, H_2O, CO, CO_2, H_2
\]  

In the above equations, \( N_i \) is the molar flux of component \( i \) at any location \( l \) (0 \( \leq l \leq l_c \)) inside the catalyst slab, and \( D_i^{\text{eff}} \) is the effective diffusivity of component \( i \) in the catalyst. \( r_k \) is the net forward rate of the \( k \)th reaction (\( k = \text{I} - \text{III} \)) for eqs 1–3, respectively) at any \( l \) and \( t \), and \( \alpha_{i,k} \) is the stoichiometric coefficient of the \( i \)th component participating in the \( k \)th reaction. The concentrations of CO, CO\(_2\), and H\(_2\) (and N\(_2\)) inside the catalyst at any location \( l \) and time \( t \) are evaluated using stoichiometry. The complete set of model equations is given in the appendix. The list of model parameters used, as well as the details of the industrial reformer and the initial operating conditions, are given in Table 2.4,6,17,18 The correlations for the effective diffusivity are taken from Elnashaie and Elshishini,2,6 and the correlations for the specific heat, viscosity, and thermal conductivity are taken from\(^6\) the HYSYS Process (version 1.5) code.

---

**Table 1. Model Parameters for the Industrial Steam Reformer\(^2,4,6,17,18\)**

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Value/Specification</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heated length of reformer tube, L</td>
<td>11.95 m</td>
<td>2</td>
</tr>
<tr>
<td>Inside diameter of reformer tubes, ( d )</td>
<td>0.0795 m</td>
<td>2</td>
</tr>
<tr>
<td>Outside diameter of reformer tubes, ( d_o )</td>
<td>0.102 m</td>
<td>2</td>
</tr>
<tr>
<td>Ratio of reformer tube pitch to diameter</td>
<td>2.4</td>
<td>2</td>
</tr>
<tr>
<td>Number of tubes</td>
<td>176</td>
<td>2</td>
</tr>
<tr>
<td>Refractor surface area, ( A_{\text{crt}} )</td>
<td>1164 m(^2)</td>
<td>2</td>
</tr>
<tr>
<td>Number of burners, ( N_b )</td>
<td>112</td>
<td>2</td>
</tr>
<tr>
<td>Flame surface area, ( A_{\text{f}} )</td>
<td>0.01 m(^2)</td>
<td>6</td>
</tr>
<tr>
<td>Catalyst shape</td>
<td>Raschig ring</td>
<td>2</td>
</tr>
<tr>
<td>Catalyst pellet dimension</td>
<td>16 ( \times ) 6 ( \times ) 16 mm</td>
<td>2</td>
</tr>
<tr>
<td>Pellet porosity, ( \phi )</td>
<td>0.53963</td>
<td>2</td>
</tr>
<tr>
<td>Pellet equivalent diameter, ( D_{\text{p}} )</td>
<td>17.4131 mm</td>
<td>2</td>
</tr>
<tr>
<td>Pellet tortuosity, ( \tau )</td>
<td>2.74</td>
<td>2</td>
</tr>
<tr>
<td>Solid catalyst density, ( \rho )</td>
<td>2396.965 kg/m(^3)</td>
<td>(\text{calc from refs 2, 4})</td>
</tr>
<tr>
<td>Mean pore radius, ( d_p )</td>
<td>80.0 Å</td>
<td>2</td>
</tr>
<tr>
<td>Pellet characteristic length, ( l_c )</td>
<td>1.948 mm</td>
<td>2</td>
</tr>
<tr>
<td>Catalyst bed density, ( \rho_b )</td>
<td>946.8 kg/m(^3)</td>
<td>2</td>
</tr>
<tr>
<td>Catalyst bed void fraction, ( \epsilon_0 )</td>
<td>0.605</td>
<td>17</td>
</tr>
<tr>
<td>Carbon dioxide-to-methane ratio, D/C</td>
<td>0.091</td>
<td>2</td>
</tr>
<tr>
<td>Nitrogen-to-methane ratio, N/C</td>
<td>0.021</td>
<td>2</td>
</tr>
<tr>
<td>Emissivity of flames, ( \varepsilon_f )</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Emissivity of furnace gases, ( \varepsilon_g )</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Emissivity of reformer tubes, ( \varepsilon_{\text{r}} )</td>
<td>0.95</td>
<td>18</td>
</tr>
<tr>
<td>Adiabatic flame temperature, ( T_f )</td>
<td>2200 K</td>
<td>6</td>
</tr>
<tr>
<td>Tube thermal conductivity, ( k_w )</td>
<td>10.738 ( + \frac{0.0242 T_w}{W/(mK)} )</td>
<td>18</td>
</tr>
<tr>
<td>No. of collocation points, ( M + 2 )</td>
<td>10</td>
<td>(\text{this work})</td>
</tr>
<tr>
<td>Active fraction, ( a )</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>( k_i, K_i, K_{\text{II}}, K_{\text{III}}, K_{\text{IV}}, \text{AH} )</td>
<td>(\text{-} )</td>
<td>(6)</td>
</tr>
<tr>
<td>Other properties</td>
<td>(\text{-} )</td>
<td>(6)</td>
</tr>
</tbody>
</table>

Operating conditions at S51:

\[
F_{\text{CH}_{4\text{in}}} = 593.564 \text{ kmol/h} \quad 6
\]

\[
T_g = 1625 \text{ K} \quad 6
\]

\[
S/C = 4.8 \quad 6
\]

\[
H/C = 0.34 \quad 6
\]

\[
P_{\text{in}} = 2548.8 \text{ kPa} \quad 6
\]

\[
T_{\text{in}} = 841.7 \text{ K} \quad 6
\]
The profiles, $c(l, Z, t)$, and the effectiveness factors, $\eta_l$, are evaluated using the method of orthogonal collocation on finite elements (OCFE). The region $0 \leq l \leq l_c$ is divided into two finite elements extending over $0 \leq v \leq 0.2$ (outer region) and $0.2 \leq v \leq 1$ (inner region), where $v = l/l_c$. It is assumed that all fluxes are zero at
v = 0.2. This implies that, in the inner region of the catalyst slab, the reactions are at (instantaneous local) equilibrium. There are a total of 10 orthogonal collocation (OC) points (including two at the boundaries of the element) in the outer finite element, where most of the concentration changes take place.
The PDEs characterizing the gas phase are converted into ODEs using the finite difference method (the method of lines) with unequal spacing of the grid points [the finite difference equations used are accurate to O(\(Z^2\))]. The region \(0 \leq Z \leq 0.5\) m, which encompasses sharp changes in the variables, is divided into six equally spaced grid points (two at \(Z = 0\) and 0.5 m). The remaining 11.45 m of the reactor is divided into 10 equally spaced grid points. The first point in \(0 \leq Z \leq 11.95\) m is the same as the last point in \(0 \leq Z \leq 0.5\) m. The resulting set of ODEs (in \(t\)) is solved with the code D02EJF from the NAG library for the integration of stiff ordinary differential equations using Gear's technique. We use the C05NCF subroutine of the NAG library to solve the nonlinear algebraic collocation equations for \(c_i(v,Z,t)\) and \(T(Z,t)\) in the gas phase. These solutions are used to evaluate the effectiveness factors (eqs A21 and A22, Appendix) using appropriate Gauss–Legendre quadratures. The pressure at axial location \(Z\) and time \(t\) is computed from a fluid-mechanics-based equation (eq A4b) by the Euler technique.

Results and Discussion

A Fortran 90 program was written to solve the equations for different idealized disturbances. The CPU time required for solving a typical dynamic simulation is 2 h on a Pentium 4 computer (1.7 GHz). The code was tested by starting from one steady state, SS1 (generated using an SS code, as given in Table 1), providing a step change (at \(t = 0\)) in one of the operating variables, and solving until the final SS is attained. The results obtained at large values of \(t\) from the dynamic code, matched the final SS profiles generated directly. The model is then used to solve two sample multiobjective optimization problems under dynamic optimal control.

Dynamic Simulation. The first problem studied involves a step increase of 100 K in the feed temperature. Nonlinear effects of the model are exhibited under such large disturbances. The axial profiles of several important variables are shown in Figure 3a–h, both at the initial and the final steady states, as well as their variations with time (in terms of deviations from the initial SS). The final SS values of the temperature (Figure 3a), are observed to be higher than the initial SS values. There is an undesirable increase (Figure 3c,d) in the outer wall temperature, \(T_{w,o}\) (even small increases in \(T_{w,o}\) beyond 1200 K lead to a significant reduction in the life of the reformer tubes). Higher process-gas temperatures, however, lead to higher conversions of methane (Figure 3e,f) and higher productions of CO (Figure 3g,h) and steam. The mole fraction of CO\(_2\) increases from its initial SS value in the early part of the reformer, but falls beyond some axial location. This is because of the inhibiting effect of the endothermic reaction (eq 2) at higher process-gas temperatures. Plots of both the conversion of methane and the mole fraction of CO\(_2\) are not shown here, but can be supplied on request.

The second dynamic simulation studied here involves a step decrease of 30 kmol/h in the inlet flow rate of methane in the natural gas feed (the corresponding flow rates of the accompanying CO\(_2\) and N\(_2\) are also de-
creased), while the flow rates of recycle steam and hydrogen are maintained at their original values. The superficial velocity of the process gas at the feed end decreases (from 3.24 to 3.21 m/s) immediately upon the introduction of this step disturbance, and a wave front (with a lower superficial gas velocity upstream and a higher value downstream) travels through the reformer. Because of viscous effects, this front does not actually remain sharp, so one should really solve the equations of motion (eq A4b should be replaced by the highly nonlinear PDEs of fluid mechanics) simultaneously with the reaction equations. This would make the dynamic model almost intractable. Three simpler, though empirical, approaches were explored to model this phenomenon, while still using eq A4b and keeping the CPU time reasonable. In the first approach (approach 1), we use the lower mass velocity $G_{\text{new},\text{in}}$, at all locations and times. In approach 2, the original (higher) mass velocity is used throughout, even after the disturbance. In approach 3, which is slightly more realistic, we assume that the wave front is sharp and is traveling through the reformer tube at a constant velocity of $u_{\text{new}} (= G_{\text{new},\text{in}}/\rho_{\text{in}} = 3.21 \text{ m/s})$. The value of $t^* (= Z_{\text{new},\text{in}})$ is computed at each finite-difference grid point. This is the time at which the wave front passes the particular grid point. The new mass velocity is used at any grid point if $t \geq t^*$; otherwise, the original mass velocity is used. Figure 4a–c shows the results. These results do not differ much even at $t = 3.6 \text{ s}$, and in fact, all three approaches give identical results (not shown) for higher values of $t$. Hence, one can use any one of these three approaches. Figure 4a shows some oscillations in the flow rates of $H_2$ at low values of $t$. Such behavior is characteristic of the numerical solution of problems with sharp moving fronts and can be minimized by using moving finite-element techniques, as for the far simpler “color” equation. Figure 4d–g shows the profiles of several variables at different times.

Because of the decrease in the inlet feed rate of natural gas, the concentration of methane in the process gas decreases. This reduces the extent of the endothermic reactions (referred to as the concentration effect) and reduces the flow rates of both $H_2$ and CO (and steam; see Figure 4f,g). However, the higher temperatures of the process gas tend to increase the conversion to hydrogen and carbon monoxide by the endothermic reactions. This can be referred to as the temperature effect. Figure 4f and g indicates that the latter effect dominates. The complex interplay of several opposing physical phenomena is exhibited here quite well. Again, there is an increase in the outer wall temperature.

In the third dynamic simulation problem studied, a step decrease of 200 K is introduced in the furnace gas temperature. Such a disturbance can arise in industry through burner failure or a change in the feed rate of the fuel. No changes in the mass velocity are involved. Because less heat is transferred from the furnace after the disturbance, the process-gas temperature, as well as $T_{w,o}$, decreases with time to new SS values (Figure 5a,b). This leads to a simultaneous reduction in the production of $H_2$ and CO (and thus also steam; see Figure 5c,d). Obviously, the negative effect of such a failure on the production of desired chemicals needs to be compensated by appropriate control action, e.g., an increase in the feed temperature.

**Optimization.** We now study two sample optimization problems (referred to as problems 1 and 2) to illustrate the use of our dynamic model. A step pulse ($0 \leq t \leq t_r$, $t_r = 0.0245 \text{ h}$) of $-20 \text{ kmol/h}$ in the inlet flow rate of methane is taken as the disturbance

$$F_{\text{CH}_4,\text{in}} = F_{\text{CH}_4,\text{in,SS}} (= 593.564 \text{ kmol/h, SS1}),$$

$$t \leq 0 \text{ or } t \geq t_r$$

$$F_{\text{CH}_4,\text{in}} = F_{\text{CH}_4,\text{in,SS}} = 20 \text{ kmol/h, } 0 \leq t \leq t_r$$

There is a corresponding reduction in the flows of $CO_2$ and $N_2$ (in the natural gas) as well. If the input flow rates of (recycle) hydrogen and steam remained unchanged, there would be a decrease in the inlet concentration of methane. Such a decrease would lead to a decrease in the outlet conversions associated with the reforming reactions and to a decrease in the heat consumed by these endothermic reactions. If, in addition, the supply of heat from the furnace is unchanged, this would lead to an increase in the temperature, $T_{w,o}$, of the outer wall of the reformer tube. Indeed, Kvamsdal et al. have shown that a decrease in the flow rate of methane could lead to thermal runaways in the reformer. This can reduce the life of the reformer tubes or cause their rupture. To counter the ill effects of this disturbance, we use the following general control action (pulse over $0 \leq t \leq t_r$)
Problem 1

The constraint on \( T_g \) increases in the flow rates above the steady-state of the integrands in eqs 11a and b, because any short-reformer. It can be noted that we do not use the squares of H\(_2\) and CO, respectively, in the syngas exiting the

Two objective functions are minimized simultaneously. They are the total (cumulative over \( t \)) deviations\(^{22}\) of the production of (a) hydrogen and (b) steam, from their SS1 values, integrated over an appropriately long time span, \( 0 \leq t \leq t_f \) (\( t_f = 0.05 \) h), so that their rates of production reattain their initial steady-state values. The flow rate of steam is related to that of CO, and we can minimize the cumulative deviation of the production of CO.\(^6\) The final optimization problem (referred to as problem 1) is written mathematically (along with the constraints and bounds) as

Problem 1

\[
\begin{align*}
\text{min } & f_1[\Delta T_g, \Delta(S/C), \Delta(H/C)] = \int_0^{t_r} [F_{H_2,SS,out} - F_{H_2,\text{out}}(t)] \, dt \\
\text{min } & f_2[\Delta T_g, \Delta(S/C), \Delta(H/C)] = \int_0^{t_r} [F_{CO,SS,out} - F_{CO,\text{out}}(t)] \, dt
\end{align*}
\]

subject to (s.t.) the constraint

\[ T_{w,0} \leq 1200 \text{ K} \]  
and the bounds

\[ -25 \leq \Delta T_g \leq 5 \]  
\[ -0.4 \leq \Delta(S/C) \leq 0.3 \]  
\[ -0.02 \leq \Delta(H/C) \leq 0.02 \]

In eqs 11, \( F_{H_2,\text{out}}(t) \) and \( F_{CO,\text{out}}(t) \) are the mass flow rates of H\(_2\) and CO, respectively, in the syngas exiting the reformer. It can be noted that we do not use the squares of the integrands in eqs 11a and b, because any short-term increases in the flow rates above the steady-state values need not be penalized because they are beneficial. The constraint on \( T_{w,0} \) is that used by Rajesh et al.\(^6\) In these equations, the bounds on \( \Delta(S/C) \) and \( \Delta(H/C) \) are taken to be about 5% of the SS values and are of the same order as the deviation in the methane flow rate.

The following penalty\(^{23}\) is added to both objective functions

\[ P \equiv 10^4[(T_{w,0} - 1200) + \text{abs}(T_{w,0} - 1200)] \]  

\( T_g = T_{g,SS} (= 1625 \text{ K}) \), \( t \leq 0, t \geq t_f \)  
\( T_g = T_{g,SS} - \Delta T_g, 0 \leq t \leq t_f \)  
\( S/C = (S/C)_{SS} (= 4.8^6), t \leq 0, t \geq t_f \)  
\( S/C = (S/C)_{SS} + \Delta(S/C), 0 \leq t \leq t_f \)  
\( H/C = (H/C)_{SS} (= 0.34^6), t \leq 0, t \geq t_f \)  
\( H/C = (H/C)_{SS} + \Delta(H/C), 0 \leq t \leq t_f \)

The second multiobjective optimization problem (problem 2) involves a pulse decrease in the feed temperature

\[ T_{in} = T_{in,SS} (= 841.7 \text{ K}) \], \( t \leq 0, t \geq t_f \)  
\[ T_{in} = T_{in,SS} - 50 \text{ K}, 0 \leq t \leq t_f \]

with \( t_f \) taken as 0.023 h (slightly different than for problem 1). Because of the decrease in the inlet feed temperature, the outlet temperature of the syngas and the conversion of methane decrease. This results in a decrease in the production of both hydrogen and steam. The effects of this disturbance are negated once again using step changes in the furnace gas temperature, \( T_g \), the steam-to-methane ratio, \( S/C \); and the hydrogen-to-methane ratio, \( H/C \), as follows

\[ T_g = T_{g,SS} (= 1625 \text{ K}) \], \( t \leq t_1 \) or \( t \geq t_2 \)  
\[ T_g = T_{g,SS} + \Delta T_g, t_1 \leq t \leq t_2 \]  
\[ S/C = (S/C)_{SS} (= 4.8^6), t \leq t_1 \) or \( t \geq t_2 \)  
\[ S/C = (S/C)_{SS} + \Delta(S/C), t_1 \leq t \leq t_2 \]  
\[ H/C = (H/C)_{SS} (= 0.34^6), t \leq t_1 \) or \( t \geq t_2 \)  
\[ H/C = (H/C)_{SS} + \Delta(H/C), t_1 \leq t \leq t_2 \]

\( t_1 \) and \( t_2 \) are additional decision variables used to make the problem general. An increase in the temperature of the furnace gas increases the heat content of the reformer gases and helps compensate for the effect of the decrease in the inlet feed temperature. Higher steam-to-methane ratios help to increase the hydrogen production, while higher hydrogen-to-methane ratios increase the carbon monoxide (and, therefore, also the steam) production. Problem 2 can thus, be written as

Problem 2

\[
\begin{align*}
\text{min } & f_1[\Delta T_g, \Delta(S/C), \Delta(H/C), t_1, t_2] = \int_0^{t_f} [F_{H_2,SS,out} - F_{H_2,\text{out}}(t)] \, dt \\
\text{min } & f_2[\Delta T_g, \Delta(S/C), \Delta(H/C), t_1, t_2] = \int_0^{t_f} [F_{CO,SS,out} - F_{CO,\text{out}}(t)] \, dt
\end{align*}
\]

subject to (s.t.)

\[ T_{w,0} \leq 1200 \text{ K} \]  
\[ -15 \leq \Delta T_g \leq 25 \text{ K} \]  
\[ -0.4 \leq \Delta(S/C) \leq 0.3 \]  
\[ -0.03 \leq \Delta(H/C) \leq 0.03 \]  
\[ 0 \leq t_1 \leq 0.023 \text{ h} \]  
\[ 0.023 \leq t_2 \leq 0.058 \text{ h} \]

with \( t_f = 0.058 \) h. The lower bound on \( \Delta T_g \) is relatively unimportant because, intuitively, it is expected that \( \Delta T_g \) will be positive. The upper bound on \( \Delta T_g \) was determined on the basis of the normal operating conditions possible in industrial reformers. The ranges of \( \Delta(S/C) \)
and \( \Delta (H/C) \) were determined on the basis of the magnitude of the disturbance. The lower bound on \( t_1 \) is the time at which the disturbance is introduced (\( t = 0 \)), while the upper bound (and the lower bound on \( t_2 \)) is set at a conservatively high value of \( t_f \), the time at which the input disturbance ceases (higher values of \( t_f \) are nonoptimal). The upper bound on \( t_2 \) is the time corresponding to the final steady state, \( t_f \). The value of \( t_f \) is selected on the basis of experience with simulation runs.

The recently developed robust and efficient technique called the elitist nondominated sorting genetic algorithm (NSGA-II)\(^\text{23-24} \) is used to solve these problems. The parameters associated with NSGA-II for problems 1 and 2 are given in Table 2. The CPU times required to solve problems 1 (9 generations) and 2 (18 generations) on a Silicon Graphics server (SGI origin 270, 400 MHz) are 110 and 144 h, respectively. The highly computationally intensive nature of these problems puts constraints on the number of runs (or the size of populations or the number of generations), and we have to be content with the reasonable Pareto solutions obtained. Because the main focus in this paper was not optimization, we did not explore other techniques (e.g., using parallel computing platforms or developing empirical and faster model equations) to improve the solutions. Several checks were made on our code, as discussed by Kasat et al.,\(^\text{26} \) to ensure that the solutions obtained were correct. In addition, we used the \( \varepsilon \)-constraint technique\(^\text{27} \) (in which one objective function is taken as a constant, \( \varepsilon \), to form an additional constraint and the resulting single-objective function optimization problem is solved using a different code) and found that the solutions matched those obtained using NSGA-II, confirming that we did, indeed, attain optimal solutions.

The results for problem 1 are shown in Figure 6. If we go from any one point (say, 1) to another (say, 2) in Figure 6a, we find that \( f_1 \) improves (decreases) whereas \( f_2 \) worsens (increases). This plot, therefore, represents a Pareto set.\(^\text{23-25} \) Clearly, the control action taken to negate the effect of this disturbance is unable to increase the rates of production of both hydrogen and steam. A decision maker would have to decide on the preferred solution (operating point) from among these several, equally good, Pareto points. Figure 6b–d shows the corresponding decision variables (actual values). High values of \( T_g \) and the \( S/C \) ratio are associated with lower \( f_1 \) values (larger hydrogen production) and higher \( f_2 \) values (lower CO or steam production) under optimal conditions. The optimal values of \( H/C \) do not appear to exhibit any definite trend, and we believe that there is some scatter in these data. Such scatter in one or more decision variables seems to be the norm rather than an exception for most real-life problems\(^\text{29} \) and to reflect the relative insensitivity of the objective functions to variations in these decision variables. As mentioned before, the results could be improved but at the cost of excessive computational effort. A study of several members of the initial (nonoptimal) solutions reveals that chromosomes having high values of \( T_g \) and relatively low values of \( S/C \) violate the constraint on the outer wall temperature, \( T_{w,or} \), and are "killed" over the generations. Table 3 reports the values of the decision variables for three different chromosomes, 1–3 (in Figure 6a), in the Pareto set.

The variation of several important variables over time, both in the absence (broken curves) and in the presence (continuous curves) of optimal control action for chromosome 1, are shown in Figure 6e–h. It is observed that the outer tube-wall temperature at the exit (the highest value in the reformer) under optimal conditions hovers around its bound of 1200 K (see Figure 6g). If control action were not used, the tube-wall temperature would violate this constraint. This simultaneously leads to the gas temperature at the exit of the reformer lying near its steady-state value of 1076 K. The lower process-gas temperatures in the presence of optimal control lead to lower conversions of methane and lower productions of both hydrogen and carbon monoxide/steam. Figure 6i and j shows the variations of the exit flow rates of both hydrogen and carbon monoxide for chromosomes 1–3. Chromosomes having high values of \( S/C \) (e.g., chromosome 3) are associated with a lower cumulative deviation in the flow rate of hydrogen but a higher deviation in the flow rate of carbon monoxide.

Figure 7a shows the Pareto set at the 18th generation for problem 2. It can be noted that negative values (high total production of hydrogen under dynamic control) of \( f_1 \) are obtained here. This, of course, occurs with a worsening of \( f_2 \). Figure 7b–f shows the corresponding decision variables. It is observed that the furnace gas temperature, \( T_g \), remains at slightly higher values (than the SS value) for all of the Pareto points. In contrast, \( S/C \) and \( t_2 \) decrease as the optimal value of \( f_2 \) increases. The optimal values of \( t_2 \) remain near their lower bounds. Figure 7g–j shows the variations of some important variables over time for chromosome 2 of the Pareto set. The high value of \( S/C \) used for this chromosome increases the production of hydrogen (to even better values than in the absence of the disturbance; see Figure 7f) and reduces the production of carbon monoxide and steam. Figure 7k and l shows the variations of the exit flow rates of both hydrogen and carbon monoxide with time for chromosomes 1–3 in Figure 7a. It can be observed from these diagrams that chromosomes having higher \( S/C \) values have lower deviations in the exit flow rate of hydrogen and higher deviations in the exit flow rate of carbon monoxide. High values of \( T_g \) improve both objective functions. Table 4 provides values of the decision variables for the three different chromosomes, 1–3, shown in Figure 7a.

**Conclusions**

A dynamic model for the first reactor, the reformer, in a steam reformer plant is presented. The effects of a

**Table 2. GA Parameters Used for Optimization**

<table>
<thead>
<tr>
<th>parameter</th>
<th>problem 1</th>
<th>problem 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>total chromosome length (( N_{ch} ))</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>population size (( N_p ))</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>number of generations (( N_g ))</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>crossover probability (( p_c ))</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>mutation probability (( p_m ))</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>random seed number</td>
<td>0.888 76</td>
<td>0.888 76</td>
</tr>
</tbody>
</table>

**Table 3. Decision Variables (in Nondeviation Form) and Objective Functions for Three Chromosomes in Figure 6a**

<table>
<thead>
<tr>
<th>decision variable</th>
<th>chromosome 1</th>
<th>chromosome 2</th>
<th>chromosome 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g )</td>
<td>1609.8</td>
<td>1619.2</td>
<td>1620.4</td>
</tr>
<tr>
<td>( S/C )</td>
<td>4.63</td>
<td>5.01</td>
<td>5.09</td>
</tr>
<tr>
<td>( H/C )</td>
<td>0.326</td>
<td>0.358</td>
<td>0.359</td>
</tr>
<tr>
<td>( f_1 )</td>
<td>3.12</td>
<td>1.50</td>
<td>0.645</td>
</tr>
<tr>
<td>( f_2 )</td>
<td>7.84</td>
<td>6.69</td>
<td>8.92</td>
</tr>
</tbody>
</table>
few idealized disturbances are studied. The model is then used to study two sample multiobjective optimization problems for this reactor, and Pareto-optimal solutions are obtained. An extensive file of similar optimal control actions under a variety of disturbances can be generated for later use.

Acknowledgment

Partial financial support from the Department of Science and Technology, Government of India, New Delhi, India [through grant III-5(13)/2001-ET] is gratefully acknowledged.

Nomenclature

\( a \) = fractional length of the half-catalyst slab in which the concentration varies

\( A_c \) = inside cross-sectional area of the reformer tube, m²

\( A_p \) = cross-sectional area of the catalyst slab, m²

\( A_{nr} \) = surface area of the refra ractor, m²

\( A_{t,i} \) = total internal surface area of reformer tubes, m²

\( c_i \) = concentration of species \( i \) in the catalyst slab, kmol m⁻³

\( C_{p,g} \) = specific heat of the process gas, kJ kmol⁻¹ K⁻¹

\( C_{p,s} \) = specific heat of the solid (catalyst), kJ kmol⁻¹ K⁻¹

\( C_{p,t} \) = specific heat of the bed, kJ kmol⁻¹ K⁻¹

\( C_t \) = molar concentration of the gas mixture (\( P/RT \)), kmol m⁻³

\( d_i, d_o \) = inner and outer diameters, respectively, of the reformer tube, m

\( D_i^e \) = effective diffusivity of species \( i \) in the catalyst at axial location \( Z \) and time \( t \), m² h⁻¹

\( D_p \) = equivalent diameter of the catalyst pellet (Raschig ring), m

\( D/C \) = ratio of carbon dioxide to methane in feed, (kmol/h of CO₂) /[kmol/h of methane fed (F\text{CH}_4\text{in})]

\( E \) = quantity defined in eq A11

\( f_i \) = objective function, \( i = 1, 2 \)

\( F \) = total feed rate, kmol h⁻¹

\( F_{CH_4} \) = flow rate of methane, kg h⁻¹

\( F_{CO} \) = flow rate of CO, kg h⁻¹

\( F_{H_2} \) = flow rate of H₂, kg h⁻¹

\( G \) = mass velocity of the process gas in the reformer, kg m⁻² h⁻¹

\( H/C \) = ratio of hydrogen to methane in feed, (kmol/h of hydrogen recycled) /[kmol/h of methane fed (F\text{CH}_4\text{in})]
Greek Symbols

\( \Delta H_i \) = enthalpy of the \( i \)th reaction, kJ kmol\(^{-1} \)

\( k_p \) = thermal conductivity of the process gas, kJ h\(^{-1} \) m\(^{-1} \) K\(^{-1} \)

\( k_w \) = thermal conductivity of the tube-wall material, kJ h\(^{-1} \) m\(^{-1} \) K\(^{-1} \)

\( k_t \) = rate constant of the \( i \)th (\( i = I-III \)) reaction, kmol kPa\(^{0.5} \)

\( k_{cat} \) = rate constant or kmol kPa\(^{-1} \) kgcat\(^{-1} \) h\(^{-1} \)

\( K_i \), \( K_{II} \), \( K_{III} \) = equilibrium constants of reactions I–III, respectively

\( K_f \) = equilibrium adsorption constant for species \( i \) (\( i = CH_4, H_2, CO, H_2O \)), kPa\(^{-1} \)

\( I \) = axial location in the catalyst slab, m

\( l_c \) = thickness of the wall of the Raschig ring, m

\( l_p \) = length of the Raschig ring, m

\( L \) = total length of the reactor, m

\( M \) = number of internal collocation points

\( N/C \) = ratio of carbon dioxide to methane in feed, (kmol/h of nitrogen)/(kmol/h of methane fed (\( F_{CH_4,in} \))

\( N_b \) = number of burners in the reformer furnace

\( N_{ch} \) = total chromosome length for NSGA-II

\( N_{gs} \) = number of generations for NSGA-II

\( N_i \) = flux of species \( i \) at any axial location \( I \) inside the catalyst slab, kmol m\(^{-2} \) h\(^{-1} \)

\( N_p \) = population size for NSGA-II

\( p_c \) = probability of crossover

\( p_m \) = probability of mutation

\( P \) = operating pressure at axial location \( Z \) and time \( t \), kPa

\( q_{rad} \) = radiative heat flux based on the average surface area of the tube, kJ m\(^{-2} \) h\(^{-1} \)

\( q_{conv} \) = convective heat flux based on the outer surface area of the tube, kJ m\(^{-2} \) h\(^{-1} \)

\( q_{convec} \) = convective heat flux based on the inner surface area of the tube, kJ m\(^{-2} \) h\(^{-1} \)

\( r_i \) = radial position, m

\( r_{i} \) = rate of the \( i \)th reaction (\( i = I-III \)) corresponding to conditions at the catalyst surface at axial location \( Z \) and time \( t \), kmol h\(^{-1} \) kgcat\(^{-1} \)

\( R \) = sum of feed molar ratios

\( R_{b} \) = rate of production of the \( ith \) component at the catalyst surface at any axial location \( Z \) and time \( t \), kmol h\(^{-1} \) kgcat\(^{-1} \)

\( R_{in} \) = rate of production of the \( ith \) component at the \( n \)th collocation point inside the catalyst slab at axial location \( Z \) and time \( t \), kmol h\(^{-1} \) kgcat\(^{-1} \)

\( S/C \) = ratio of carbon dioxide to methane in feed, (kmol/h of steam recycled)/(kmol/h of methane fed (\( F_{CH_4,in} \))

\( S \) = operating pressure at axial location \( Z \) and time \( t \), kPa

\( T \) = process-gas temperature at axial location \( Z \) and time \( t \), K

\( T_0 \) = adiabatic flame temperature at any axial location in the reactor, K

\( T_g \) = temperature of the furnace gas, K

\( T_w \) = tube-wall temperature, K

\( U \) = film heat-transfer coefficient on the inside of the tube (to gas + catalyst), kJ h\(^{-1} \) m\(^{-2} \) K\(^{-1} \)

\( v \) = dimensionless distance within the catalyst slab (\( v = 1/l_c \))

\( v_i \) = superficial velocity of gas in the reformer, m h\(^{-1} \)

\( y_{i} \) = mole fraction of species \( i \) in the gas phase at axial location \( Z \) and time \( t \)

\( y_{in} \) = mole fraction of component \( i \) at the \( n \)th collocation point inside the catalyst slab at axial location \( Z \) and time \( t \)

\( Z \) = axial location, m

Subscripts/Superscripts

\( i, 1 \) = inner or initial

\( in \) = inlet of the reformer

\( a, 2 \) = outer

\( out \) = outlet of the reformer

\( SS \) = stable state

\( SS1 \) = initial steady state

\( w \) = wall

Appendix

Model Equations

\( F_{CH_4,in} = 16R \)

\( F_{H_2,in} = 28C_{CO,out}(v_{i,out}A_{c}) \)

\( F_{CO,out} = 28C_{CO,out}(v_{i,out}A_{c}) \)

(a) Gas Phase

\( \frac{\partial C_i}{\partial t} = \frac{1}{\epsilon_b} \left[ \frac{\partial (\epsilon_b C_i)}{\partial Z} - \rho_b \eta_i R_i \right] \)

\( C_i(Z,t=0) = C_i^{SS}(Z), \quad 0 \leq Z \leq L; \ i = CH_4, H_2O, CO, CO_2, H_2 \ (A4a) \)

\( \frac{\partial P}{\partial Z} = \frac{1.75G^2(1 - \epsilon_b)}{\phi_3 D \rho_b^3} \rho g \)

\( \frac{\partial T}{\partial t} = \frac{1}{C_{p,t}} \left[ 4U(T_{w,i} - T) - \rho_b C_{p,g} \frac{\partial T}{\partial Z} + \rho_b \sum_{i-1}^{III} (\Delta H_i) \eta_i \frac{R_i}{\rho_b} \right] \)

\( C_{p,t} = \rho_b C_{p,s} + [\epsilon_b + (1 - \epsilon_b) \epsilon_{ch} g] \rho C_{p,g} \)

Initial Conditions
The inner tube wall temperature, $T_{w,i}$, is obtained by equating the heat fluxes due to (i) radiative transfer from the furnace gases to the outer surface of the tubes

$$q_{rad} = a' \frac{(A_{t,o} + A_{ref}) \xi g_t \xi (T_{w,i}^4 - T_{w,o}^4) + \frac{N_b A_{t,o} \xi g_t \xi (1 - \xi g_t)}{A_{t,o} T_{w,i}^4}}{\ln(d_j/d_i)}$$

(ii) conductive transfer through the tube material

$$q_{cond} = \frac{2k_w(T_{w,o} - T_{w,i})}{\ln(d_j/d_i)}$$

and (iii) convective transfer to the gas mixture and catalyst bed from the inner surface of the tubes

$$q_{conv} = \frac{U(T_{w,i} - T)}{d_i}$$

(b) Solid (Catalyst) Phase. The intraparticle mole fraction, $y_i(t)$, of species $i$ at the $n$th orthogonal collocation point for a catalyst slab at axial location $Z$ and time $t$ is obtained by solving the coupled set of 5M equations ($n = 1$ is the first collocation point at $v = 0$; $n = M + 2$ is the last collocation point at $v = 0.2$; $n = 2, 3, ..., M + 1$ are the internal collocation points in $0 \leq v \leq 0.2$): 3M algebraic and 2M differential equations (which are transformed into algebraic equations by the method of orthogonal collocation on finite elements)

$$\frac{d^2 y_{CH_4,n}}{dv^2} = a_1 \lambda_c \left[ \frac{\rho_d (r_1 + r_2 + r_{III})}{(P/RT)} \left( \frac{P}{D_{CH_4}^e} \right) \right] R_{CH_4,n}$$

$$\frac{d^2 y_{H_2,n}}{dv^2} = a_1 \lambda_c \left[ \frac{\rho_d (r_1 + r_2 + 2r_{III})}{(P/RT)} \left( \frac{P}{D_{H_2}^e} \right) \right] R_{H_2,n}$$

$$y_{CO,n} = y_{CO} - \frac{1}{D_{CO}^e} [2D_{CH_4}(y_{CH_4,n} - y_{CH_4}) - D_{CH_4}(y_{H_2,n} - y_{H_2,n})]$$

$$y_{CO_2,n} = y_{CO_2} + \frac{1}{D_{CO_2}^e} [D_{CH_4}(y_{CH_4,n} - y_{CH_4}) - D_{H_2O}(y_{H_2O,n} - y_{H_2O})]$$

$$y_{H_2,n} = y_{H_2} - \frac{1}{D_{H_2}^e} [2D_{CH_4}(y_{CH_4,n} - y_{CH_4}) + D_{H_2O}(y_{H_2O,n} - y_{H_2O})]$$

Boundary Conditions

(i) at Axial Location $Z$ and Time $t$

$$\frac{d y_{i,1}}{dt} = y_i(Z,t), \quad i = CH_4, H_2O, CO, CO_2, H_2$$

$$\frac{dy_{i,M+2}}{dv} = 0, \quad i = CH_4, H_2O, CO, CO_2, H_2$$

$$\eta_k = \frac{f_{v=a} y_k(T, P) dv}{r_k(y_k, T, P)|_{c}}, \quad k = I, II, III$$

Effectiveness factors for the components are evaluated from those for the reactions through the equation

$$\sum_{k=1}^{III} \sigma_{ik} \eta_k f_k$$

$$\eta_i = \frac{\sum_{k=1}^{III} \sigma_{ik} f_k}{\sum_{k=1}^{III} \sigma_{ik} f_k}, \quad i = CH_4, H_2O, CO, CO_2, H_2$$

(b) Solid (Catalyst) Phase. The intraparticle mole fraction, $y_i(t)$, of species $i$ at the $n$th orthogonal collocation point for a catalyst slab at axial location $Z$ and time $t$ is obtained by solving the coupled set of 5M equations ($n = 1$ is the first collocation point at $v = 0$; $n = M + 2$ is the last collocation point at $v = 0.2$; $n = 2, 3, ..., M + 1$ are the internal collocation points in $0 \leq v \leq 0.2$): 3M algebraic and 2M differential equations (which are transformed into algebraic equations by the method of orthogonal collocation on finite elements)

$$\frac{d^2 y_{CH_4,n}}{dv^2} = a_1 \lambda_c \left[ \frac{\rho_d (r_1 + r_2 + r_{III})}{(P/RT)} \left( \frac{P}{D_{CH_4}^e} \right) \right] R_{CH_4,n}$$

$$\frac{d^2 y_{H_2,n}}{dv^2} = a_1 \lambda_c \left[ \frac{\rho_d (r_1 + r_2 + 2r_{III})}{(P/RT)} \left( \frac{P}{D_{H_2}^e} \right) \right] R_{H_2,n}$$

$$y_{CO,n} = y_{CO} - \frac{1}{D_{CO}^e} [2D_{CH_4}(y_{CH_4,n} - y_{CH_4}) - D_{CH_4}(y_{H_2,n} - y_{H_2,n})]$$

$$y_{CO_2,n} = y_{CO_2} + \frac{1}{D_{CO_2}^e} [D_{CH_4}(y_{CH_4,n} - y_{CH_4}) - D_{H_2O}(y_{H_2O,n} - y_{H_2O})]$$

$$y_{H_2,n} = y_{H_2} - \frac{1}{D_{H_2}^e} [2D_{CH_4}(y_{CH_4,n} - y_{CH_4}) + D_{H_2O}(y_{H_2O,n} - y_{H_2O})]$$

Boundary Conditions

(i) at Axial Location $Z$ and Time $t$

$$\frac{d y_{i,1}}{dt} = y_i(Z,t), \quad i = CH_4, H_2O, CO, CO_2, H_2$$

$$\frac{dy_{i,M+2}}{dv} = 0, \quad i = CH_4, H_2O, CO, CO_2, H_2$$

$$\eta_k = \frac{f_{v=a} y_k(T, P) dv}{r_k(y_k, T, P)|_{c}}, \quad k = I, II, III$$

Effectiveness factors for the components are evaluated from those for the reactions through the equation

$$\sum_{k=1}^{III} \sigma_{ik} \eta_k f_k$$

$$\eta_i = \frac{\sum_{k=1}^{III} \sigma_{ik} f_k}{\sum_{k=1}^{III} \sigma_{ik} f_k}, \quad i = CH_4, H_2O, CO, CO_2, H_2$$


Received for review December 3, 2002
Revised manuscript received April 15, 2003
Accepted June 14, 2003

IE0209576