Minimization of the Entropy Production in the Primary Steam Reformer

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Abstract
We have developed further a numerical method that minimizes the total entropy production rate of a chemical reactor. The method can now be used on reactors with more than one chemical reaction. The method was used on one tube in a primary steam reformer. The total entropy production rate is minimized subject to a given entering total molar flow rate, and a given production of hydrogen. The degrees of freedom used in the minimization, are the inlet temperatures and molar flow rates, and the temperature profile of the furnace gases. The total entropy production rate in the optimal unit was 70% lower than in the reference system. Optimal reaction mixture temperature and molar flow rate profiles are obtained.

1. Introduction
The primary steam reformer is widely used in the industry as the first of two steps that convert natural gas (mostly methane) into synthesis gas, Rostrup-Nielsen (1983). The synthesis gas obtained in the steam reforming reactions is the starting point in many chemical processes, e.g. the methanol synthesis and the ammonia synthesis. Due to their highly endothermic nature, the chemical reactions in the primary steam reformer require a substantial amount of added heat. Heat is added by placing several reactor tubes inside a furnace. In this work, we minimize the entropy production rate of a typical steam reformer tube surrounded by a furnace. The purpose is to produce the same amount of product in a more energy efficient way. Possible energy savings might appear in the form of reduced temperature in the furnace or higher output temperature of the product. There are at least three reactions that should be considered. Thus, we have extended and reformulated the model presented earlier, Nummedal et al. (2001), to make it independent of the number of chemical reactions occurring in the reactor. As free variables we have chosen the temperature profile of the furnace chamber surrounding the tube and the inlet flow rates. Both the entropy produced by the steam reforming reactions and the heat transfer between the furnace and the reaction mixture, are included in the model. The entropy produced by the pressure drop and the furnace gas combustion process are not yet taken into account.
2. The system

The chemical reactions taking place on the Ni/Al₂O₃ catalyst in the primary steam reformer, are Xu and Froment (1989b)

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 & \Delta_r H_1 & > 0, \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 & \Delta_r H_{II} & < 0, \\
\text{CH}_4 + 2\text{H}_2\text{O} & = \text{CO}_2 + 4\text{H}_2 & \Delta_r H_{III} & > 0.
\end{align*}
\]

Nitrogen is also present in the reactor as an inert. All components are in their gaseous states. Coke formation and dusting are not included in the model. Expression for the rate of these three reactions, \(r_1\), \(r_{II}\) and \(r_{III}\), are taken from Xu and Froment (1989b).

The primary steam reformer often consists of a set of vertical catalyst filled tubes (fixed bed reactors) placed inside a large furnace to heat the endothermic reaction mixture, Rostrup-Nielson (1983). We study one such tube with dimensions and parameters taken from Xu and Froment (1989a). Furthermore, we assume a plug flow reactor (PFR) model which means that there are no gradients in the radial direction. The heat transfer is perpendicular to the reactor wall with an overall heat transfer coefficient, \(U\), constant equal to 100 J/K m² s.

In order to have something to compare our entropy minimized reactor with, we calculate a model of a reactor with a linear furnace gas temperature from 990 K (inlet) to 1160 K (outlet). This model is referred to as the reference reactor. The reactor geometry and the catalyst properties are kept constant in the optimization.

3. The optimization problem

We shall minimize the total entropy production rate, \(\frac{dS_{TT}}{dt}\), of the chemical reactions in the primary steam reformer, and the heat exchange process between the furnace gases and the reaction mixture:

\[
\frac{dS_{TT}}{dt} = \int_0^{W_{C,\text{Tot}}} \left( \sum_{i=1}^{3} \left[ r_i \frac{-\Delta_r G_i}{T} \right] + \frac{1}{\rho_{c,\text{eff}}} \frac{4}{d_i} U (T_a - T) \left( \frac{1}{T} - \frac{1}{T_a} \right) \right) dW_c, \quad (1)
\]

where \(W_c\) is the mass of catalyst from inlet to the current position in the reactor. \(T\) is the reaction mixture temperature, \(T_a\) is the furnace temperature and \(\Delta_r G_i\) is the Gibbs reaction energy of reaction \(i\), all at position \(W_c\). \(\rho_{c,\text{eff}}\) and \(d_i\) are the effective catalyst density and inner tube diameter, respectively.

The system is constrained by a given hydrogen production, equal to the production
in the reference reactor. The production of hydrogen is:

$$J_H = \int_0^{W_{c,T=0}} [3r_I + r_{II} + 4r_{III}] \, dW_c \equiv \int_0^{W_{c,T=0}} r_H \, dW_c, \quad (2)$$

where \( r_H \) is the rate of formation of hydrogen. However, to avoid certain numerical problems, we also want the total inlet flow rate to be the same as in the reference reactor:

$$F_{T0} = F_{T0,ref} \quad (3)$$

Both in the modeling and optimizing, the energy, momentum and component balances must be fulfilled. They are all given as differential equations, describing a control volume of infinitesimal thickness in the axial direction. The energy balance is:

$$\frac{dT}{dW_c} = \frac{1}{\rho c_v} \left( \frac{4}{\rho c_v} U (T_a - T) - \sum_i \frac{r_i \Delta_h i}{\sum_k F_k C_{p,k}} \right), \quad (4)$$

where \( C_{p,k} \) and \( F_k \) is the heat capacity and molar flow of component \( k \), respectively.

The momentum balance (pressure drop equation) is described by Erguns equation. Assuming ideal gases, the Ergun equation was rewritten as:

$$\frac{dP}{dW_c} = \left( \frac{150 \mu (1 - e)}{D_p^2} + 1.75 \frac{1}{D_p^2 A_c \rho c} \right) \frac{1}{D_p^3 A_c \rho c} v_0 F_T \frac{P_0 - T_0}{F_{T0} P_0 - T_0}, \quad (5)$$

where \( D_p \) is the catalyst ring diameter, \( G \) is the superficial mass velocity, \( A_c \) is the cross sectional area of the reactor tube, \( v_0 \) is the entering superficial volumetric velocity, and \( F_T \) and \( P \) are the total molar flow rate and the total pressure at position \( W_{c} \), respectively. Subscript 0 indicates properties at the inlet \( (W_c=0) \).

The component mole balances of all chemical components in the reaction mixture are:

$$\frac{dF_k}{dW_c} = \sum_i \nu_{ki} r_i, \quad (6)$$

where \( \nu_{ki} \) is the stoichiometric coefficient of component \( k \) in reaction \( i \).

### 4. Calculations

As free variables in the minimization, we use the temperature profile of the furnace gases, the inlet composition and the inlet temperature of the reaction mixture. From these variables, all other variables can be calculated through the energy, momentum and component balances, Eqs (4)- (6).
To provide a more stable solution algorithm, the energy, momentum and component balances were used as constraints, rather than directly in the objective function. This does not change the properties of the minimum state. The objective function, Eq. (1), and the constraints, Eqs. (4)-(6), were discretized to solve the optimization problem numerically. In this process, the functions for the profiles used in the previous section, e.g. $T_a(W_c)$ and $F_M(W_c)$, were converted into vectors $T_a$ and $F_M$ of $n$ elements, giving $n - 1$ control volumes.

Temperature and molar flow rate profiles of the reference reactor were calculated. They are labeled ref. in subsequent figures.

The numerical minimization of the total entropy production rate, was carried out using the Matlab$^\text{®} 6.0.0$ (R12) Optimization Toolbox function fmincon with the profiles of the reference system as initial guess. 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, Gill et al. (1981).

5. Results and discussion

We have developed a numerical method to minimize the total entropy production rate of a chemical reactor with $i$ reactions and external heating or cooling. The work presented here, is an extension of the method presented in previous work, Nummedal et al. (2001). The current method reproduced our earlier findings.

The hydrogen production in both the reference and the minimized system was $J_H = 1.277$ mole/s. The total pressure drops almost linearly from 29 bar at the inlet to 27.4 bar at the outlet. The entropy produced by both the chemical reaction and the heat transfer from the furnace gases to the reaction mixture, for both the reference and the minimized system, are presented in Table 1. We see that the entropy production minimized system has an amazing 76.7% lower total entropy production rate than the reference system. Most of this reduction comes from the heat transfer part of the objective function. The reaction mixture and

<table>
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<th>$dS_{rev}/dt$</th>
<th>ref.</th>
<th>min.</th>
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<tbody>
<tr>
<td>Reaction</td>
<td>11.48</td>
<td>7.165</td>
<td></td>
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<tr>
<td>Heat transfer</td>
<td>25.95</td>
<td>1.539</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>37.43</td>
<td>8.704</td>
<td></td>
</tr>
<tr>
<td>% reduction</td>
<td>-</td>
<td>76.7</td>
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Table 1: Total entropy production rate [J/Ks] in the reference and minimized system.
furnace gas temperatures in both the reference (ref.) and minimized (min.) system, as functions of the accumulated catalyst weight, $W_c$, are shown in Fig. 1. We see that the inlet values of both temperatures have been raised significantly in the reactor with minimum entropy production rate compared to the reference system. Thus, the pre-heating requirement of the reactants will be substantially increased. The temperature difference between the furnace gases and the reaction mixture has been more equipartitioned and significantly decreased, suggesting a lower chemical production towards the end of the reactor. The heat transfer from the furnace to the reaction mixture is the dominating process in those parts of the reactor. This complies with earlier findings, Nummedal et al. (2001).

An increased inlet temperature would require some pre-heating of the feed, which would increase the overall energy consumption of the system. In other words, the entropy minimized reactor seems to consume more energy than the reference reactor. However, the output temperature of the reaction mixture is much higher in the optimized reactor than in the reference reactor. This means that this stream can do more useful work. Also, the optimized reactor requires less heating than the reference reactor. This can be seen by considering the area between the $T$- and $T_A$-profiles, which is proportional to the heat added to the reactor. The reason for this seemingly increasing energy requirement is that the reactor is optimized as a single unit, not part of a larger process. Given the phenomena included in the optimization problem, this is a second law optimal unit. The distinction between unit and process is very important in the interpretation of these results. The entropy production minimized unit might not contribute to a second law optimal process. In process optimization, there will in general be more constraints than we have used here. Those constraints will come from the operation of other process units. We also want to emphasize that a second law optimal system not necessarily
is equivalent with an economical optimal system.

We have succeeded in modeling both the entropy production rate from the chemical reaction and the heat transfer between the reaction mixture and the external heating or cooling medium. By expanding the reactor model to e.g. a two-dimensional pseudohomogeneous one, we can take the resistance to heat and mass transfer in the radial direction into account. In e.g. the primary steam reformer, the resistance to heat transfer in the radial direction inside the reactor is a very important factor, Rostrup-Nielsen (1983). Using a heterogeneous model will allow us to study the effects of the temperature gradients inside the catalyst particle, or across the catalyst particle surface. Coke formation and dusting should also be included in the model to help in verifying the possibility of using suggested designs.

The increased furnace gas temperature will probably contribute the entropy production rate in the furnace. The entropy produced by the furnace flames, Stanciu et al. (2001), should be included in the model to account for this.

6. Conclusions

A new numerical method for the minimization of the total entropy production rate of a reactor system with one or more chemical reactions has been presented. The entropy produced by chemical reactions and the heating/cooling process of the reaction mixture were taken into account. For a chosen reference system, a possible reduction in the total entropy production rate of the primary steam reformer of over 70% was found.

References


