Analysis and Optimization of a CSTR by Direct Entropy Minimization

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  Determination of optimal operating conditions of chemical processes is difficult. Minimization of entropy generation is a simpler option for standard, either numerical or analytical, optimization techniques. This paper illustrates how entropy generation minimization can simplify the analysis and optimization of the operation of a CSTR. A typical irreversible, exothermic, first order chemical reaction taken from the literature has been considered. For this system, the entropy generation rate has been derived based on mass, energy and entropy balances. Using analytical derivatives it was found that entropy generation can be minimized if the inlet stream temperature is the same as the operating temperature of the reactor. Additionally, it was easy to draw from the analysis the operating temperature that achieved maximum conversion. Finally, the procedure proposed was compared with an indirect entropy minimization method, and shown to be simpler and clearer.

Introduction

Optimizations of industrial processes usually consider a heuristic cost-benefit function, plus environmental and process constraints. Nowadays, with the availability of high-speed computers, these problems can be tackled using well-established numerical methods, or in simple cases using analytical techniques. However, in practice, the implementation of such optimization strategies is still challenging. Besides, it is not always obvious how to define a proper cost function to optimize.

Using entropy together with other thermodynamic functions is an alternative and convenient form to establish optimal operating conditions for industrial processes. For instance, an increase in the production of by-products or the self-degradation of the main product in a given chemical reaction can be related to the entropy generation rate. If the concept of energy alone is used to optimize such a process, the additional energy required for separation, treatment and disposal will not be accounted for. Furthermore, the use of entropy generation minimization can establish a reduction in the dimension of the optimization problem, as well as ensuring the global minimum.

Notable contributions on minimum entropy generation have been made by Bejan (1982, 1988) and Schön and Andresen (1996). Sauar *et al*. (1996, 1997) have presented a process design method based on the principle of equipartition of forces, which uses the idea of minimum entropy generation. Recently, this method

was applied to establish an optimum temperature profile for a plug flow reactor (Johannessen and Kjelstrup, 2004).

In this paper, a direct and explicitly entropy minimization procedure is applied in order to find optimal operating conditions for an ideal CSTR, a problem that has not been tackled before using entropy. A first order, irreversible and exothermic reaction is assumed, where physical and chemical properties have been taken from the literature (Kurtz and Henson, 1997). Additionally, the results have been compared with those found using the indirect entropy minimization technique based on the work of Johannessen and Kjelstrup (2004).

1. The CSTR model

The **Figure 1** represents a CSTR where an irreversible, exothermic, first order chemical reaction ($A \rightarrow B$) occurs:
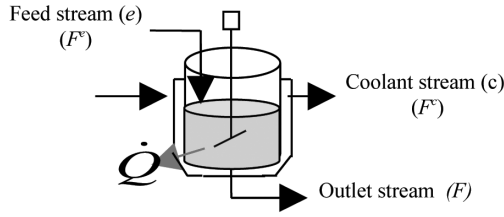
The standard mathematical model for such a process is given by the following equations:

$$\frac{dC_A}{dt} = \frac{F^e}{V}\left(C_A^e - C_A\right) - k_0 \exp\left(-\frac{E}{RT}\right)C_A \qquad (1)$$

$$\frac{dT}{dt} = \frac{F^e}{V}\left(T^e - T\right) + \left(\frac{-\Delta H}{\rho c_p}\right)k_0 \exp\left(-\frac{E}{RT}\right)C_A - \frac{\dot{Q}}{\rho c_p V} \qquad (2)$$

where V, C_A, F^e, T, T^c, ρ, c_p and $\dot{Q} = UA(T - T^c)$ denote the reactor volume, the concentration of the species A,

Fig. 1 Diagram of a jacketed CSTR

the feed stream, reactor temperature, cooling temperature, specific gravity, specific heat and the transferred heat, respectively. UA indicates the heat transfer rate.

In addition, ΔH is the heat of reaction, E the activation energy of reaction, R the gas constant, k_0 the kinetic constant and superscript e denotes the inlet variables.

The entropy balance in the model has also to be included:

$$\frac{dS}{dt} = -\frac{\dot{Q}}{T} + F^e \rho^e s^e(T^e) - F \rho s(T) + \dot{\sigma} \tag{3}$$

where S is the entropy of the system, s the specific entropy and $\dot{\sigma}$ represents the entropy generation rate.

Nominal reactor operating conditions, model parameters and thermodynamic properties were taken from Kurtz and Henson (1997) and Zhorov (1987), which are summarized in **Table 1**.

2. Direct Entropy Minimization

Since entropy is a function of temperature (T) and the number of moles (n) of each chemical species in the system and considering the definition of total differential of S, then:

$$S(T, n_A, n_B) \Rightarrow \frac{dS}{dt} = \frac{\partial S}{\partial T}\frac{dT}{dt} + \frac{\partial S}{\partial n_A}\frac{dn_A}{dt} + \frac{\partial S}{\partial n_B}\frac{dn_B}{dt} \tag{4}$$

Hence, substituting Eq. (3) into Eq. (4), results in

$$\dot{\sigma} = \frac{\partial S}{\partial T}\frac{dT}{dt} + \frac{\partial S}{\partial n_A}\frac{dn_A}{dt} + \frac{\partial S}{\partial n_B}\frac{dn_B}{dt} + \frac{\dot{Q}}{T} - F^e \rho^e s^e(T^e) + F \rho s(T) \tag{5}$$

Taking into account that,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{\rho V c_p}{T} \tag{6}$$

the following equation can be obtained

$$\dot{\sigma} = \rho V \frac{c_p}{T}\frac{dT}{dt} + \frac{\partial S}{\partial n_A}\frac{dn_A}{dt} + \frac{\partial S}{\partial n_B}\frac{dn_B}{dt} + \frac{\dot{Q}}{T} - F^e \rho^e \left[s^e(T) + c_p \ln\left(\frac{T^e}{T}\right)\right] + F \rho s(T) \tag{7}$$

or even

$$\dot{\sigma} = \rho V \frac{c_p}{T}\frac{dT}{dt} + \frac{\partial S}{\partial n_A}\frac{dn_A}{dt} + \frac{\partial S}{\partial n_B}\frac{dn_B}{dt} + \frac{\dot{Q}}{T} - F^e \rho^e \left[s^e(T) + c_p \ln\left(\frac{T^e}{T}\right)\right] + F\left[C_A \frac{\partial S}{\partial n_A} + C_B \frac{\partial S}{\partial n_B}\right] \tag{8}$$

Since

$$F^e \rho^e s^e(T) = F^e C_A^e \frac{\partial S}{\partial n_A} \tag{9}$$

and including the mass balances of components A and B into Eq. (8), then

$$\dot{\sigma} = \rho V \frac{c_p}{T}\frac{dT}{dt} + r V(\Delta S_R) + \frac{\dot{Q}}{T} - F^e \rho^e c_p \ln\left(\frac{T^e}{T}\right) \tag{10}$$

where $r = k_0 \exp(-E/RT)C_A$, ΔS_R denotes the entropy change of the reactive system and the subscript R refers to the reaction.

Substituting Eq. (2) into Eq. (10) and considering ΔG_R as the Gibbs free energy change of the reaction, as well as $\rho = \rho^c$, it is easy to show that,

$$\dot{\sigma} = F^e \rho c_p \left[\frac{(T^e - T)}{T} - \ln\left(\frac{T^e}{T}\right)\right] + r V \frac{(-\Delta G_R)}{T} \tag{11}$$

This equation describes the entropy production rate for the CSTR model above. For a more complex reactive system, it must be emphasized that the entropy production equation is still given by Eq. (11).

The so-called driving force $\Delta G_R/T$ presented in the Eq. (11) can be estimated by the classical Gibbs-Helmholtz relationship:

$$\left[\frac{\partial(\Delta G_R/T)}{\partial T}\right]_P = \frac{-\Delta H_R}{T^2} \tag{12}$$

3. Indirect Entropy Minimization

On the other hand, chemical or physical process rates cannot be obtained from equilibrium thermodynamics alone. In systems involving flow, rates depend on a driving potential and a resistance. Driving forces are defined by equilibrium thermodynamics, while resistances are not. Therefore, the following approach based on developments due to Sauar *et al.* (1996) provides an indirect entropy minimization approach to process design and analysis. It is well-known that

$$J = X/R \tag{13}$$

where J represents flow, X driving force and R resistance. Since conductance (L) is defined as the reciprocal of resistance, then:

$$J = L \cdot X \tag{14}$$

Then, according to De Groot and Mazur (1984), the specific entropy production rate may be written as,

$$\dot{\sigma} = J X \quad \text{or} \quad \dot{\sigma} = L X^2 \tag{15}$$

Since, $\dot{\sigma} \geq 0$, then Eq. (15) reveals that the conductance L is positive. Comparing Eq. (15) and Eq. (11) regarding the chemical reaction contribution to entropy, it is easy to see that if X denotes the driving force $\Delta G_R/T$, then the flow J per unit volume corresponds to the reaction conversion rate r. By minimizing the driving force X, Eq. (15) provides an indirect method for minimizing entropy.

4. Results and Discussion

4.1 The indirect approach

The indirect approach is based on the formulation developed above, together with the graphical analysis of the response surface of entropy production rate, which is a function of the concentration of A and the temperature of the reaction.

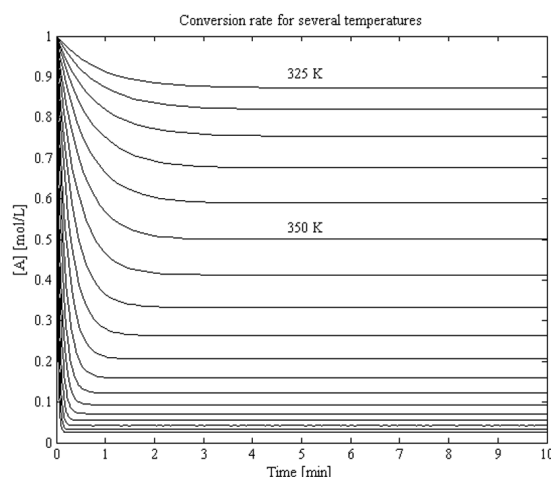**Figure 2** shows the dynamic behavior of the concentration of species A for several temperatures from

Fig. 2 Dynamic behavior of the concentration of *A*, when the temperature varies from 325 to 410 K
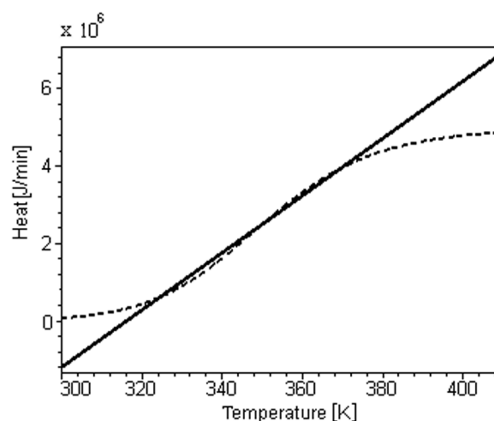

Fig. 3 Heat generated (dash line) and heat removed (solid line) when temperature in the inlet stream is 350 K

325 K increasing gradually by 5° to 410 K. It should be noted that the steady state or reversibility is reached quickly, as well as there being a significant difference over the conversion, which confirms the classical results. Since the reaction conversion rate is given by $r = -dC_A/dt$ meaning the slope of the straight line between $C_A = 1$ to C_A in the equilibrium, it can be verified from Figure 2 that the slopes of the straight lines around 400 K are very close to each other, indicating that the conversion rate remains approximately constant.

Figure 3 shows the equilibrium points of the reactor obtained from Eqs. (1) and (2), using the nominal operating conditions (Table 1). It can be easily verified that the points $C_A = 0.88$ mol/L and $C_A = 0.21$ corresponding to $T = 325$ and $T = 370$ are stable.

When the analytical approach is considered, it is important to investigate the behavior of entropy generation as functions of temperatures and concentrations.
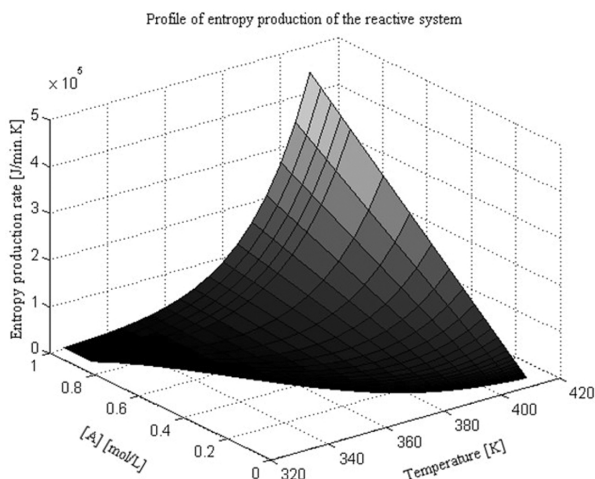
Fig. 4 Response surface of entropy production rate as a function of the concentration of *A*, and temperature when the temperature in the inlet stream is 350 K

Figure 4 shows the profile of the reactive system taking into account the conditions mentioned in Table 1.

A significant reduction in entropy production can be verified in Figure 4, mainly for the highest temperatures and conversion rates, and also a profile of entropy production rate in its minimum values can be observed.

Observations taken from Eq. (14) indicate that the constant value of *J* can be kept in the transformation by decreasing *X* when *L* increases. Once *X* decreases, the strategy leads to a decrease in the entropy production rate, Eq. (15), since the product *L•X*, that is, the flow *J*, given by the reaction conversion rate *r*, remains constant (Sauer *et al.*, 1996). From the second law of thermodynamics, it is well known that if the entropy production rate tends towards a minimum, then the process approaches reversibility. Therefore, from the practical point of view, it is straightforward to verify from Figure 4 that the lower profile corresponds to reversibility, and that the conversion rate remains constant when the temperature reaches values around 400 K, indicating that this is the boundary of the optimal limit for using the minimum profile of the entropy production rate in order to determine the optimal conditions for the process. This result can be also observed in Figure 2.

From Figure 4, it must be noted that the last points are nearly in a straight line, meaning an approximately constant conversion rate. What can also be verified is a break of values between the middle points and the last remaining points. This break is sometimes called an elbow and indicates from where the reaction rate starts to be considered constant. Since it can be found without difficulty, the projection of this point on the concentration and temperature axes determines graphically the maximum conversion and temperature of the reaction.

4.2 The direct approach

Sufficient and useful information can be extracted from Table 1 regarding, for instance, the solution of the Gibbs–Helmholtz equation and consequently the solution of Eq. (11). For the range of temperature normally used in practice, the heat of reaction may be considered constant. However, this is not the case for the ΔG_R. Since T_0 is the temperature of reference equal to 300 K and $\Delta T = T - T_0$, the driving force can be performed by the following equation:

$$\frac{\Delta G}{T} = \frac{\Delta G_0}{T_0} - \Delta H_0 \frac{\Delta T}{TT_0} \tag{16}$$

Then, $\dot{\sigma}$ can be expressed by

$$\dot{\sigma} = F^e \rho c_p \left[\frac{(T^e - T)}{T} - \ln\left(\frac{T^e}{T}\right) \right]$$
$$+ \left[k_0 \exp\left(-\frac{E}{RT}\right) \frac{F^e C_A^e}{k_0 \exp\left(-\frac{E}{RT}\right)V + F^e} V\left(\frac{-\Delta G_0}{T_0} + \Delta H_0 \frac{\Delta T}{TT_0}\right) \right] \tag{17}$$

The condition for minimum entropy generation requires the first derivative of Eq. (17). Therefore, based on the steady state of Eq. (1), on Eq. (17) and taking into account that it is differentiable, it is straightforward to derive from the classical procedure to find extrema that the minimum value for $\dot{\sigma}$ is obtained only when

$$T^e = T - \frac{k_0 C_A^e V}{\rho c_p}$$
$$\left\{ \Delta H_0 \left[\frac{\exp(-E/RT)\left[(E/RT)F^e - k_0 \exp(-E/RT)V - F^e\right]}{\left[k_0 \exp(-E/RT)V + F^e\right]^2} \right] \right.$$
$$\left. - T^2 \left[\left(\frac{-\Delta G_0}{T_0}\right) + \left(\frac{\Delta H}{T_0}\right) \right]\left[\frac{\exp(-E/RT)(E/RT^2)F^e}{\left[k_0 \exp(-E/RT)V + F^e\right]^2} \right] \right\} \tag{18}$$

When the data provided by Table 1 are considered, Eq. (18) can be lightly modified in order to express how the temperature difference $(T^e - T)$ varies as a function of temperature (T), which can be depicted as in **Figure 5**.

It can be observed from Figure 5 that the temperature difference $(T^e - T)$ is always positive for a given range of temperatures, resulting $T^e > T$. However, since the reaction is exothermic, this result becomes itself unsustainable and makes no sense. Furthermore, the point of intersection of the $(T^e - T)$ line and the Temperature axis yields the solution of Eq. (18).
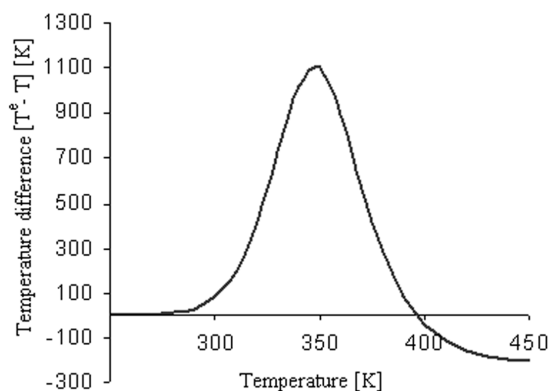
Fig. 5 Temperature difference ($T^{\,e} - T$) as a function of temperature
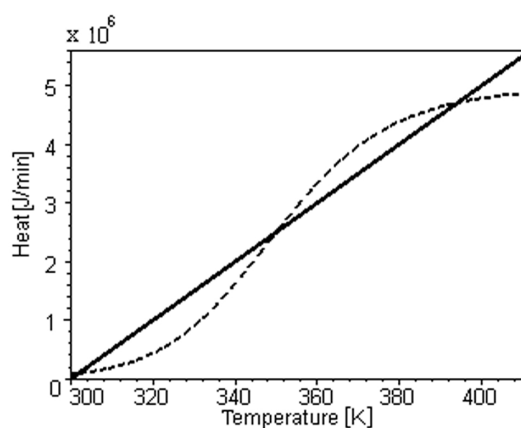

Fig. 6 Heat generated (dash line) and heat removed (solid line) when the reaction temperature has the same value as the inlet stream temperature

Therefore, this indicates that the optimal condition is given by $T^{\,e} = T$ for the global range of temperature, which is approximately 395 K for the case under study.

To confirm such a result, the system of equations consisting of Eqs. (1) and (2) for the steady state under the condition of $T^{\,e} = T$ was solved, and the results obtained can be viewed in **Figure 6**, which describes the behavior of the system when the heat generated and the heat removed are considered.

From Figure 6, all three steady states can be identified as the points of intersection of the heat generated and heat removed curves and the points mentioned can be determined approximately, resulting in ($C_A = 0.98$ mol/L, $T = 302$ K); ($C_A = 0.5$ mol/L, $T = 350$ K); ($C_A = 0.06$ mol/L, $T = 394.32$ K). It can be easily shown using the set of differential equations consisting of (1) and (2) and taking into account the condition of $T^{\,e} = T$ that the lower and upper steady states are stable while the intermediate one is unstable. These results indicate that the process can work in the upper steady state with the highest conversion rate as this is strongly de-
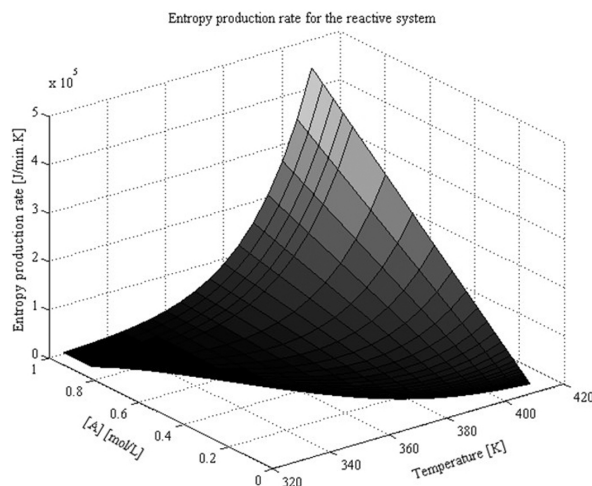

Fig. 7 Entropy production rate as a function of the concentration of A, and temperature when the feed inlet temperature is the same as the temperature of reaction (394.32 K)

sirable, and submitted to the necessary condition of minimum entropy production.

Comparing **Figure**s 4 and **7**, it should be noted that the systems have the similar behavior related to reactor temperature during entropy production for different Te conditions and that applying the procedure already mentioned, based on the Sauar *et al.* (1996) development, in order to optimize the system, values can be found, graphically, of the concentration and temperature of the reactor under the conditions of minimum entropy production rate, which are the same as those obtained by the methodology developed in this paper, though with a reduced accuracy.

It can also be verified that the graphical method does not have sufficient ability to show explicitly the relationships among other variables, for example $T^{\,e}$ as a function of T and other parameters, compared to that presented in the direct minimization procedure. The poor ability to extract more information can be evidenced by the similar behavior of the response surfaces for different $T^{\,e}$. This reveals a clear disadvantage.

On comparing the results from the optimization strategies taking into consideration the operating condition normally established for such a reaction, a considerable difference in the temperature of the reactor from 370 to 394.32 K is clearly verified.

Conclusions

In this paper, a model for the entropy production rate in a CSTR was developed based on mass, enthalpy and entropy balances for a reactive system, in which a $A \rightarrow B$ reaction occurs. Several operating conditions have been taken into account in order to describe the

system, particularly for analysis of the behavior of the entropy of the system. Two strategies were presented to deal with the minimum entropy generation. A minimum profile for the rate of entropy production was performed, indicating the feasibility of the use of a graphic methodology, denoted as an indirect method, in order to determine the optimal operating conditions. The so-called direct minimization of entropy generation based on the classical procedure of optimization with the analytical derivatives was also applied to minimize the entropy production rate equation, revealing that the system will reach its minimum value when the inlet temperature is equal to the temperature of reaction. The results indicate a new optimal operating condition for the system subject to the minimum entropy production rate maintaining a high conversion rate. Finally, the procedure proposed reveals itself to be simpler, clearer and more accurate when compared with the indirect method.

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