FP14 - 4:20

STABILITY OF CHEMICAL REACTIONS IN A CSTR
WITH DELAYED RECYCLE STREAM

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Abstract

This paper shows how recycling delays affect the dynamics of certain types of exothermic reactions in continuous stirred tank reactors.

I. INTRODUCTION

In the last forty years, there has been a great deal of literature published discussing the dynamics of continuous stirred tank reactors (CSTR) [1–7]. The breakthrough work by Bilous and Admundson [1] developed methods of calculating criteria for stability and instability of exothermic reactions. Several of these papers also include the effects of a recycle stream on the reactors dynamic response.

In order to implement a recycle stream for a CSTR, the output stream of the reactor is sent through a separation process (perhaps a centrifuge which spins the output chemicals so quick that they segregate by mass). Then the unreacted reagents are returned into the CSTR by travelling through pipes (see Figure 1).. Because recycling reduces waste of reagents, and hence the cost of reaction, its use is widespread in industry. For example, recycling is almost always used in the manufacturing of nylon 66 or in the oxidation of cyclohexene to KA (a mixture of ketone and alcohol of cyclohexene), among many other reactions.

A difficulty with much of the literature on recycling is that the model almost always assumes no time delay in the recycle line [1,6,7], i.e. the separation process and the return time is assumed instantaneous. While this assumption may make theoretical analysis simpler, it is highly unrealistic. In order to recycle, the output must be separated from the input, then travel through pipes after separation. This process requires a finite amount of time and will introduce a delay into the model since both the concentration of the reagents and the temperature in the reactor depend on some time in the past.

In practice (industry), it is quite common to ignore the recycle delay, and to use the standard ordinary differential equation models [1,6,7]. Clearly, if this is being done, then the recycle delay can often have negligible effects on the dynamics of the reaction. However, there has been no documented literature that explains analytically why this is the case. In this particular problem, the theory lags behind the known applications. In some sense, the problem has already been solved: process control engineers understand that the delays due to recycle can, at times, be neglected, but there has never been a theoretical explanation as to why this is true. It is the purpose of this paper to bridge the gap from practice to theory (not from theory to practice, as is usually the case), and give a partial explanation as to why the delay due to recycle can at times be ignored. Section II briefly describes the model to be discussed, while Section III discusses the dynamics of the system. Conclusions are given in Section IV

II. MODEL

Qualitatively, the material balance on any reactant species in a CSTR can be given as

Change of moles = Moles entering − Moles leaving − Moles
within CSTR   CSTR   CSTR   reacting

Likewise, the energy balance equations are given as

Change of heat = Heat entering + Heat generated − Heat removed
within CSTR   CSTR   by reaction   from CSTR.

In the case of recycle, the moles (heat) entering the CSTR depends on the number of moles (amount of heat) at some time in the past, due to the delay in the recycle stream.

In this paper, we will only consider a special type of recycle — that in which all chemical specie at the output are recycled at and identical rate. This is the most basic type of recycling strategy [1,6,7] and can be found in most undergraduate chemical reactor/kinetic texts [7]. In this case, for a CSTR with *instantaneous* recycle flow rate of $(1-\lambda)F$, the above concepts yield the following differential equations [3,7] for a single chemical reaction involving n chemical specie:

$$\frac{dc_j}{dt} = \frac{F\lambda}{V}c_{jf} + \frac{F(1-\lambda)}{V}c_j(t) - \frac{F}{V}c_j(t)$$
$$- a_j R\{c_1(t), \ldots, c_n(t), T(t)\}$$

$$\frac{dT}{dt} = \frac{F}{V\rho C_p}\left[\lambda T_f + (1-\lambda)T(t) - T(t)\right]$$
$$+ \frac{(-\Delta H)}{\rho C_p} R\{c_1(t), \ldots, c_n(t), T(t)\} - \frac{U}{V\rho C_p}(T(t) - T_c)$$
$$j = 1, 2, \ldots, n \qquad (1)$$

where $c_j(t)$ corresponds to the concentration of the jth species, $T(t)$ is the temperature of the reaction, and a_j is the stoichiometric coefficient of the jth species and is positive for reactants and negative for product. The coefficient λ is the recirculation coefficient, $0 \leq \lambda \leq 1$, where $\lambda = 0$ corresponds to total recycle and $\lambda = 1$ corresponds to no recycle. Reference [1] defines the remaining constants.

Suppose that the total time to recycle is equal to r and time, t, is the instant in which the output exits the CSTR (before entering the separator). Then a more accurate material and energy balance equation should be

$$\frac{dc_j}{dt} = \frac{F\lambda}{V}c_{jf} + \frac{F(1-\lambda)}{V}c_j(t-r) - \frac{F}{V}c_j(t)$$
$$- a_j R\{c_1(t), \ldots, c_n(t), T(t)\}$$

$$\frac{dT}{dt} = \frac{F}{V\rho C_p}\left[\lambda T_f + (1-\lambda)T(t-r) - T(t)\right] +$$
$$\frac{(-\Delta H)}{\rho C_p} R\{c_1(t), \ldots, c_n(t), T(t)\} - \frac{U}{V\rho C_p}(T(t) - T_c)$$

$$j = 1, 2, \ldots, n \qquad (2)$$

In the special case when $r = 0$, (2) reduces to (1). It is understandable as to why most discussions on recycle [1,6,7] do not include the effects of the delay: the nonlinear ordinary differential equation (1) now becomes infinite dimensional. However, as this paper shows, because of the special form of the system, analysis of (2) is not too difficult.
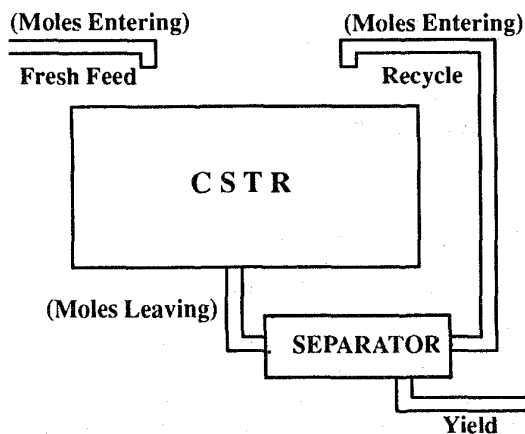
Figure 1. CSTR with recycle stream.

Figure 2. Intersection of the curves $y = \sigma - \alpha$ and
$y = \dfrac{F(1 - \lambda)}{V}(e^{-\sigma r} - 1)$ for different values of delay when $\alpha < 0$.

III. LOCAL STABILITY AND TRANSIENT BEHAVIOR

While there are several techniques that are used to analyze the stability properties of (1), the simplest and the most common technique is to examine the linear variational equation (the linearization) of (1) about a steady state. It turns out that this is also the simplest method in determining the stability properties of (2). The remaining part of this section will explain three statements which begin to give insights on the dynamics of (2).

1. The steady states of (1) are the same as the steady states of (2).

This statement is the easiest to understand. In order to determine the steady states of (1), the left hand side of (1) is set equal to zero, and variables $c_j(t)$ and $T(t)$ are set equal to constants c_{js} and T_s, respectively. Then $n+1$ nonlinear algebraic equations are obtained with a corresponding $n+1$ unknowns. (It is permissible that there exist multiple solutions to these $n+1$ equations.)

In order to determine the steady states of (2), almost the same procedure is used: the left hand side of (2) is set equal to zero, and $n+1$ nonlinear algebraic equations are obtained by setting $T(t) = T(t-r) = T_s$ as well as setting $c_j(t) = c_j(t-r) = c_{js}$. Since $T(t-r) = T_s$ and $c_j(t-r) = c_{js}$, the set of equations needed to solve for the steady states of (2) are the same as those needed to solve for (1). Hence, the steady states of (1) and (2) are the same.

2. Suppose that by examining the linearization of (1) about a steady state $x_s = [c_{1s}, c_{2s}, \ldots, c_{ns}, T_s]^T$, it is determined that x_s is locally asymptotically stable, i.e. the linearization of (1) about x_s, which is in the form of $\delta\dot{x}(t) = A\,\delta x(t)$, has matrix A such that all the eigenvalues of A have negative real parts. Then x_s is also a locally asymptotically stable steady state of (2), no matter how large the delay, r, is.

Theoretically, this is a surprising result, since delays are often thought of as destabilizing. However, for a CSTR with (identically) delayed recycle, the size of the delay does not affect the local stability properties of its steady states. This begins to explain what process control engineers have known for quite some time — recycling delays often do not cause instability. Of course, the delay may still cause increased oscillation in the transient response and perhaps a slower response time. This issue is addressed in statement 3, below. In general, though, steady state operation for chemical reactors is more important than transient analysis. So, even though solutions
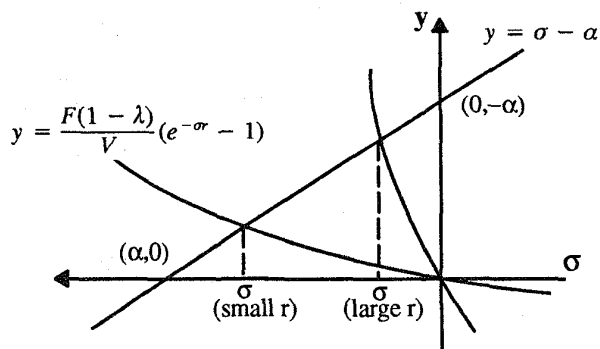
decay slower due to the recycle delay, once the system settles, operation of the CSTR runs smoothly.

3. Suppose that x_s is a locally asymptotically stable steady state and assume that solutions of (2) approach x_s as $t \to \infty$. Then, as the delay in (2) increases, the decay rate of the solutions will decrease. In particular, as r increases, the dominant eigenvalue of the linearization of (2) approaches the imaginary axis.

Suppose that the linear variational equation of (1) about x_s is given by $\delta\dot{x}(t) = A\,\delta x(t)$. Suppose further that the dominant eigenvalue of matrix A is given by $s = a \pm iw$, where $i = \sqrt{-1}$ and $\alpha < 0$. Then the dominant eigenvalue of the linearization of (2) about the same steady state is given by $s = \sigma \pm iw$ where w is the same as before and σ is given by the relation $\sigma = a + \dfrac{F(1 - \lambda)}{V}(e^{-\sigma r} - 1)$. As Figure 2 shows, the solution to this equation is the intersection of the line $y = \sigma - \alpha$ and the curve $y = \dfrac{F(1 - \lambda)}{V}(e^{-\sigma r} - 1)$. As r becomes larger, σ approaches zero. Hence, the real part of the dominant eigenvalue of the linearized system approaches the imaginary axis and the rise time of the system will decrease.

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