EXOTHERMIC CSTRs
Just How Stable Are The Multiple Steady States?

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This paper was prompted by a discussion with a colleague who has been teaching chemical reaction engineering for many years. During the discussion, mention was made of the fact that when there are three steady states in an exothermic continuous stirred tank reactor (CSTR), the upper one can be unstable. The colleague said that this is impossible, and he based his disbelief on the classic plot of the multiple steady states, shown in Figure 1. This particular plot was taken from Stephanopolous[1] but it appears in practically all the reaction engineering textbooks, probably starting with the book by Levenspiel.[2]

This plot shows the curve of heat generated (A) and the line of heat removed (B) versus the temperature in an exothermic CSTR. The three steady states are the points of intersection (P_1, P_2, and P_3, Figure 1) of curve A and line B. Let's assume that the reactor is started at temperature T_2'. At this point the heat generated by the reaction (Q_2') is greater than the heat removed (Q_2''). This will cause the temperature in the reactor to rise, and the rise will continue until the upper steady state, P_3, is reached. It is easy to show, using similar arguments, that P_1 and P_3 are stable steady states and that P_2 is an unstable one. There is really no indication from this plot that P_3 could also be unstable.

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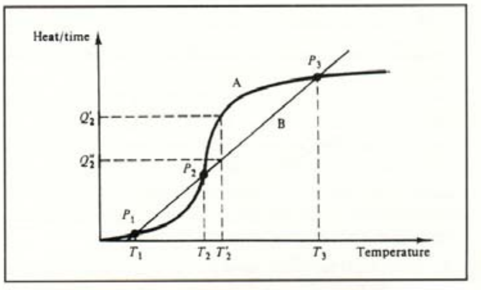

Figure 1. *Three steady states of an exothermic CSTR (adapted from [1]).*

We can conclude that the use of a plot such as the one in Figure 1 may lead to the misconception that the upper steady state in an exothermic CSTR is always stable, but the roots of this misconception are actually much deeper. They stem from the mistaken belief that *one can rely solely on results of a steady state model to predict dynamic behavior.* The steady state model can certainly provide some guidelines, but a dynamic model is needed to predict dynamic behavior.

It should be mentioned that there are textbooks (*i.e.*, Westerterp, *et al.*,[3] pg. 339) where dynamic analysis is discussed in detail, based mainly on the pioneering work of Aris and Amundson.[4] But in most reaction engineering courses, only plots such as the one in Figure 1 are mentioned

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as a practical means for analyzing CSTRs behavior. This should not be the case any longer. The introduction of user-friendly, interactive simulation packages which can solve nonlinear algebraic or ordinary differential equations (ODEs) has not only made the solution of dynamic nonlinear models possible but has even made it easy.

In this paper we will demonstrate the use of one such simulation package (POLYMATH) for analysis of the behavior of an exothermic CSTR. The POLYMATH package is a numerical simulation package to be used with IBM and compatible computers, and the current version (2.1.1 PC) is distributed by the CACHE (Computer Aids for Chemical Engineering Education) Corporation, a non-profit organization for disseminating educational computer programs among chemical engineering departments.*

POLYMATH has been used for almost a decade, and its structure and possible applications have been described in several publications.[5-7] From among the programs included in the package, the algebraic and ODE solver programs are the most useful for exothermic CSTR analysis. (The algebraic equation solver was described in detail in reference 5.)

The main advantage of the POLYMATH ODE solver over similar programs is that equations are typed in their mathematical form, and the user has to provide only information regarding the mathematical model (equations, initial, and final values). No technical information, such as integration method and step size, graph scaling, etc., has to be provided. After the equations have been entered, the computer time for solving even the most complicated problems is only a few seconds.

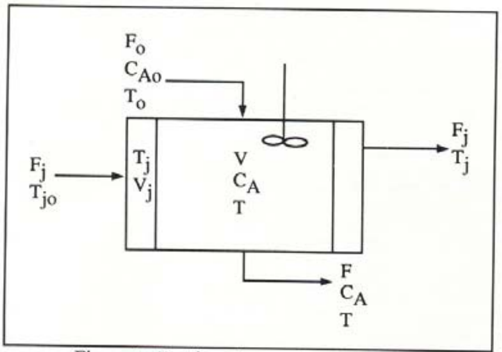

Figure 2. *Exothermic reaction in a CSTR.*

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For non-stiff equations, POLYMATH uses either an explicit Euler's method or the fourth-order Runge-Kutta method for integration. Euler's method is implemented when the estimated integration error is less than 0.1 times the error tolerance. For stiff equations the implicit Euler method is used.

The structure of the rest of this paper is as follows:

- *In the next section we introduce an example problem. It is essentially the same problem as Luyben presented.[8] The problem definition is reproduced for the reader's convenience.*
- *In the third section, different combinations of multiple steady states are demonstrated using a steady state model, while the fourth section deals with the analysis of the stability at different steady states, using the dynamic model.*
- *The model equations used for the reactor analysis are given in the Appendices, in a form suitable for use with the POLYMATH package.*

EXAMPLE PROBLEM

The typical CSTR problems, in which a first order, exothermic reaction is being carried out is presented in many textbooks. We used a slightly modified form of an example presented by Luyben.[8]

An irreversible exothermic reaction $A \xrightarrow{k} B$ is carried out in a perfectly mixed CSTR as shown in Figure 2. The reaction is first order in reactant A and has a heat of reaction λ(BTU/mole A reacted). Negligible heat losses and constant densities can be assumed. A cooling jacket surrounds the reactor to remove the heat of reaction. Cooling water is added to the jacket at a rate of F_j(ft^3/sec) and an inlet temperature T_{jo}(°R). The volume of the reactor, V, and the volume of water in the jacket, V_j(ft^3) are constant.

The reaction rate coefficient changes as function of the temperature according to the equation

$$k = \alpha \exp(-E / RT) \qquad (1)$$

The feed flow rate (F) and the cooling water flow rate (F_j) are constant. The jacket water is assumed to be perfectly mixed. Heat transferred from the reactor to the jacket can be calculated from

$$Q = UA\left(T - T_j\right) \tag{2}$$

where

Q heat transfer rate in BTU/hr

U overall heat transfer coefficient in BTU/(sec)(ft²)(°R)

A heat transfer area

The parameter values for the process[8] are shown in Table 1.

Taking into account that the inlet flow rate F_o is equal to the outlet flow rate F, we see that dV/dt = 0, and the mole and energy balances on the reactor and cooling jacket yield:

$$V\frac{dC_A}{dt} = F_o(C_{AO} - C_A) - VkC_A \tag{3}$$

$$\rho C_p V\frac{dT}{dt} = \rho C_p F_o(T_o - T) - \lambda VkC_A - UA\left(T - T_j\right) \tag{4}$$

$$\rho_j C_j V_j \frac{dT_j}{dt} = \rho_j C_j F_j\left(T_{jo} - T_j\right) + UA\left(T - T_j\right) \tag{5}$$

At steady state these equations become

$$F_o(C_{AO} - C_A) - VkC_A = 0 \tag{6}$$

$$\rho C_p F_o(T_o - T) - \lambda VkC_A - UA\left(T - T_j\right) = 0 \tag{7}$$

$$\rho_j C_j F_j\left(T_{jo} - T_j\right) + UA\left(T - T_j\right) = 0 \tag{8}$$

In the third and fourth sections we will discuss the number of steady state solutions of these equation sets for the parameter values of Table 1.

SOLVING THE CSTR STEADY STATE MODEL

There are several ways to solve the steady state equations of the CSTR (Eqs. 6-8). The most obvious way is to solve the three equations simultaneously, but this option has the disadvantage that most solution algorithms will find only one of the solutions. If there are several steady states, some trial and error involving the initial estimates will be required in order to find all the solutions.

Another option, one which will indicate all the steady states, involves the preparation of plots similar to the one in Figure 1. To accomplish this, we first must solve Eq. (6) for C_A and Eq. (8) for T_j. This gives us

$$C_A = \frac{F_o C_{AO}}{F_o + Vk} \tag{9}$$

$$T_j = \frac{T_{jo} + \beta T}{1 + \beta} \tag{10}$$

where $\beta = UA/(\rho_j C_j F_j)$.

Next, we define heat generated (Q_G) and the negative of heat removed ($-Q_R$) as

$$Q_G = -\lambda VkC_A \tag{11}$$

$$-Q_R = -\left[\rho C_p F_o(T - T_o) - UA\left(T - T_j\right)\right] \tag{12}$$

In order to change the temperature in the reactor continuously, a dummy differential equation

$$\frac{dT}{dt} = 1 \tag{13}$$

can be specified.

The set of equations consisting of Eq. (1) and Eqs. (9) to (13) can be typed into the POLYMATH ODE simulator. The form in which these equations are entered into POLYMATH is shown in Appendix A. (Note that in the appendix the notation "tr" is used for the temperature inside the reactor and "tin" for the feed inlet temperature.) The numerical values of the constants from Table 1 have already been introduced into these equations.

The plot obtained by using the numerical values from Table 1 is shown in Figure 3, above, which is very similar to Figure 1. The three steady states can be clearly identified as the points of intersections of the Q_R and Q_G curves, and the approximate temperatures at these points can be determined.

TABLE 1
CSTR Parameter Values

F_o	= 40 ft³/hr	U	= 150 BTU/hr-ft²-°R
F	= 40 ft³/hr	A	= 250 ft²
C_{AO}	= 0.50 mol/ft³	T_{jo}	= 530 °R
V	= 48 ft³	T_o	= 530 °R
F_j	= 49.9 ft³/hr	λ	= -30,000 BTU/mol
V_j	= 3.85 ft³	C_p	= 0.75 BTU/lbm-°R
α	= 7.08 x 10¹⁰ hr⁻¹	C_j	= 1.0 BTU/lbm-°R
E	= 30,000 BTU/mol	ρ	= 50 lbm/ft³
R	= 1.99 BTU/mol °R	ρ_j	= 62.3 lbm/ft³

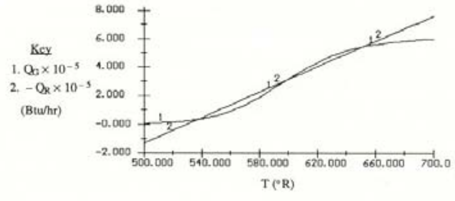

***Figure 3.** Heat removed (1) and heat generated (2) as functions of temperatures when T_o = 530 °R.*

The conditions can now be easily changed so as to get different combinations of steady states. By changing the reactor inlet temperature T_o, the heat removal line moves parallel to itself and one or two steady state conditions can be generated, as shown in Figure 4.

This is not the best way, however, to find the exact values of the variables at the various steady states. To do that we can rewrite Eq. (7) as a single nonlinear algebraic equation

$$f(T) = Q_G - Q_R \tag{14}$$

This equation, together with Eq. (1) and Eqs. (9) to (12) can be entered into the POLYMATH nonlinear algebraic equations' solver program (as described in Appendix A). The results for all three steady states for $T_o = 530$ °R are summarized in Table 2.

STABILITY ANALYSIS AND DYNAMIC SIMULATION OF THE CSTR

Once the steady states have been found, the most important factor is how stable they are. We usually prefer to operate the reactor at some particular steady state (most often at the one with the highest conversion), but instability at this steady state may cause many undesirable effects, such as highly oscillatory response to small disturbances, or drift to a different, less desirable steady state.

TABLE 2

Steady State	T(°R)	T_j(°R)	C_A(mole/ft^3)
1. Lower	537.16	536.62	0.4739
2. Intermediate	599.99	594.63	0.2451
3. Upper	651.06	641.79	0.0591

Stability at the different steady states can be determined by calculating the eigenvalues of the state matrix of the linearized model of the reactor. This method is widely taught in process dynamics and control courses, but is not mentioned in any of the reaction engineering textbooks. Using this method, the system of Equations (Eqs. 3,4,5) is linearized at the vicinity of a steady state. Once the state matrix which contains the multipliers of the state variables is constructed and its eigenvalues are calculated, the stability of a steady state solution is determined by the sign of the real part of the eigenvalues of the state matrix. If the real part is positive, the steady state is unstable; a negative real part indicates a stable steady state.

We have carried out such an analysis for the CSTR example which was discussed earlier. We used two different formulations of the problem. In the first formulation, we assumed pseudo steady state with regard to the cooling water temperature. That means that the differential equation, Eq. (5), was replaced by the algebraic equation, Eq. (10). The jacket's time constant is relatively small because of its small volume, with the result that steady state assumption reduces the stiffness of the problem and changes the result very little. We will henceforth refer to this formulation as the *modified model.*

In the second formulation, we used the basic set of equations, Eqs. (3), (4), and (5), and from this point on we will refer to it as the *basic model.* The calculated eigenvalues are shown in Tables 3 and 4.

For both formulations there is a positive real eigenvalue for the intermediate steady state, indicating that this steady

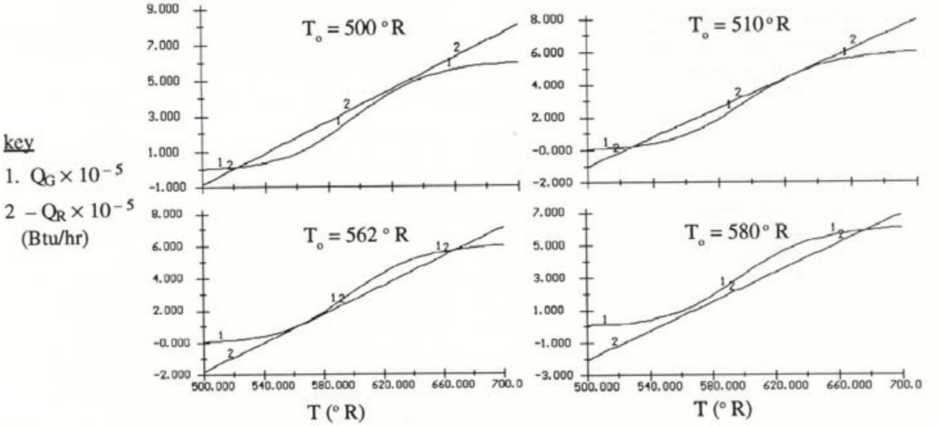

***Figure 4.** Heat generated (1) and heat removed (2) as functions of temperature for various T_o values.*

state is unstable. There is also a positive eigenvalue for the upper steady state. In this case the absolute value of the positive eigenvalue is much larger in the modified model than in the basic model. That indicates that the upper steady state will be unstable when using both formulations, but the oscillations in the basic model will grow much slower than in the modified model.

These results can be verified by simulation. The equations that have to be typed into the POLYMATH ODE simulation program are shown in Appendix B for both the modified and the basic model.

Figure 5 shows the change of temperature inside the reactor when it is started up at the three different steady states. These plots were obtained using the modified model and show that the reactor operation is as expected from the theoretical analysis. The lower steady state is stable and the intermediate state is very unstable, meaning that the temperature starts to go down after about one hour and stabilizes at the lower steady state after about five hours. In the upper steady state the temperature first starts oscillating and finally goes down toward the lower steady state.

The upper steady state can be further analyzed by looking at the plot of heat generated versus temperature, shown in Figure 6. It can be seen that for both the basic and the modified formulation the heat generated creates a spiral form where the growth rate of the spiral is much smaller in the basic model. This is what is expected from the state matrix eigenvalue analysis, but this plot is completely different from the one in Figure 3 which was generated using the steady state model.

It is interesting to note that when it is integrated for a long enough time, the basic model will produce a limit cycle.[9]

TABLE 3
Eigenvalue of the State Matrix Using the Modified Model

Steady State	1st	2nd
1. Lower	-1.446, 0	-0.953, 0
2. Intermediate	-0.515, 0	3.504, 0
3. Upper	0.486, -2.86	0.486, 2.86

TABLE 4
Eigenvalues of the State Matrix Using the Basic Model

Steady State	1st	2nd	3rd
1. Lower	-188.7, 0	-1.267, 0	-0.976, 0
2. Intermediate	-188.1, 0	-0.532, 0	3.049, 0
3. Upper	-187.7, 0	0.00746, -2.754	0.00746, 2.754

This requires programs, however, that are "tuned" for integration of stiff equations for long time intervals with high accuracy, and POLYMATH is not adequate.

The conclusion from these results is clear: using a steady state model for predicting CSTR behavior at the upper steady state can lead to wrong conclusions.

Several additional questions can be asked. First, is the state matrix eigenvalue analysis really needed in order to investigate the stability at different steady states? The an-

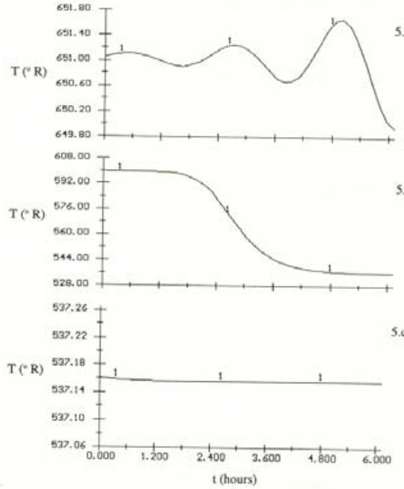

***Figure 5.** Temperature changes inside the reactor when started at different steady states, using the modified model.*

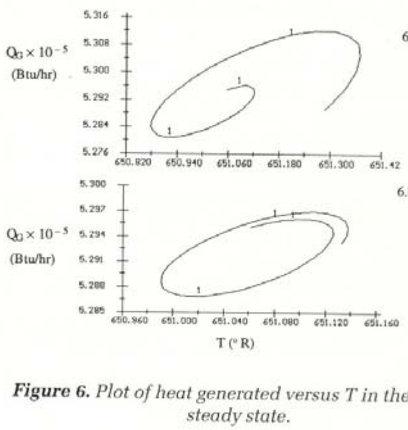

***Figure 6.** Plot of heat generated versus T in the upper steady state.*

swer in most cases will be *no.* Dynamic simulation can be much easier and faster, and the real physical behavior of the system can be observed, as opposed to observing indirect indicators such as the eigenvalues.

Can the conditions in the CSTR be changed so that the upper steady state is stable in the three steady state regions? The reader can verify that such conditions exist by multiplying the feed flow rate (F_o) by three and repeating the simulation using the equations in Appendices A and B.

Is the instability of the upper steady state a result of the varying cooling water temperature, and could it be prevented if there were only two variables (T and C_A)? The reader can verify that this assumption is not true by fixing the cooling water temperature at $T_j = 530°R$ and using the parameter values

$$F_o = 40 \times 10 \text{ ft}^3\text{/hr} \quad \text{and} \quad \alpha = 2 \times 7.08 \times 10^{11} \text{ hr}^{-1}$$

instead of the values shown in Table 1. This set of parameters gives three steady states, with the upper one being unstable.

CONCLUSIONS

In this paper, we have demonstrated the applications of an interactive numerical simulation package for location and analysis of the steady states in an exothermic CSTR. We showed that the use of a plot of heat generated and removed versus temperature as the only means for analyzing the stability at the steady states may lead to wrong conclusions. Also, that using this type of analysis sends the wrong message to students, implying that they can rely solely on the results of steady state models to predict dynamic behavior.

We have also shown that dynamic simulation is preferred over other methods (such as state matrix eigenvalue analysis) for testing stability at the steady states because it is easy, it is fast, and the test is based on the real physical behavior and not on indirect numerical indicators.

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APPENDIX A

Steady State Model

Plotting Heat Generated and Heat Released versus Temperature and Finding the Steady State Solutions.

```
(1) d(tr)/d(t)=1
(2) k=7.08*10**10*exp(-30000/1.99/tr)
(3) beta=150*250/(62.3*1.0*49.9)
(4) tj=(530+beta*tr)/(1+beta)
(5) ca=0.5/(1+48*k/40)
(6) qg=30000*k*ca*48
(7) tin=530
(8) rhocp=50*0.75
(9) qr=-(rhocp*40*(tin-tr)-150*250*(tr-tj))
     t(0)=     0, tr(0)=     500
     t(f)=   200
 - To change feed temperature change tin value in
   equation (7)
 - To find the steady state solutions change Eqn
   (1) to:
(1) f(tr) = qg-qr
    and use the algebraic equation solver program
 - To change feed flow rate change the number 40 in
   equations (5) and (9) to the desired value
 - To fix the cooling water temperature at Tj=530
   change equation (4) to: tj=530.
```

APPENDIX B

Dynamic Simulation of the CSTR—Modified and Basic Models

```
(1) d(ca)/d(t)=40*(0.5-ca)/48-k*ca
(2) d(tr)/d(t)=(qg-qr)/(rhocp*48)
(3) beta=150*250/(62.3*1.0*49.9)
(4) tj=(530+beta*tr)/(1+beta)
(5) k=7.08*10**10*exp(-30000/1.99/tr)
(6) rhocp=50*0.75
(7) qg=30000*k*ca*48
(8) qr=-(rhocp*40*(530-tr)-150*250*(tr-tj))
  t(0)=     0, ca(0)=     0.0581, tr(0)=     651.06
  t(f)=     3
 - The initial values shown are close to the upper
   steady state. To check additional steady states
   use the values shown in Table 2 as initial
   values.
 - To change the feed flow rate change the number
   40 in equations (1) and (8) to the desired
   value.
 - To fix the cooling water temperature at tj=530
   change equation (4) to: tj=530.
 - To change from modified to basic model replace
   Eqn (4) by the following equation:
(4) d(tj)/d(t)=49.9*((530-tj)+beta*(tr-tj))/3.85
```

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