THE DYNAMICS OF CHEMICAL REACTORS WITH HEAT INTEGRATION

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Abstract

In 1991, an industrial ammonia synthesis reactor in Germany became unstable, such that the temperatures oscillated with large amplitudes (limit cycles). A mathematical model of the reactor with its preheating system reproduces the phenomenon. The reactor with its preheater may be viewed as a positive feedback system, and for such systems it is usually assumed in chemical engineering that the response becomes slower as the feedback gain is increased, and that instability corresponds to a pole crossing through the origin. However, the onset of the instability can be explained by a linear analysis, and it is shown that it corresponds to a Hopf bifurcation where the system starts oscillating when instability occurs. The reason for this is the presence of an inverse response for the temperature response through the reactor. By using a simple controller, the possibility of limit cycles in a reactor may be eliminated. The effect of heat integration on the dynamics and control of plants in general is briefly discussed.

2 An industrial case: Temperature oscillations in an ammonia synthesis reactor

In 1991, a fixed bed ammonia synthesis reactor in Germany—operated without feedback control—suddenly became unstable, such that the recorded temperatures in the reactor started oscillating with a period of about 7 minutes, and a maximum amplitude of about 160 °C (Naess et al., 1993). As such oscillations may be damaging to the reactor, a study was initiated in order to explain and to be able to predict their occurrence.

1 Introduction

Although reactor stability and control has been an active area of research for at least 40 years, incidents such as reactor instability happen frequently in commercial plants. Plants may exhibit dynamic behavior totally unexpected to plant personnel, even though the general phenomena usually have been described in the literature. It is important to be able to predict such phenomena, as they may be fatal to a plant, and hazardous to the plant personnel.

General work on reactor stability, modeling and control is abundant. Crider and Foss (1968) refer to Nusselt (1927) and independently Schuman (1929) as the first to present a thermal analysis of packed beds. Van Heerden (1953) and Aris and Amundson (1958) analyzed the stability of the steady states of autothermal reactors.
2.1 A simple model of the reactor

Models for fixed beds are abundant in the literature (see e.g. Eigenberger, 1976). As the main purpose of the modeling was to give a qualitative understanding of the observed reactor behavior, the model was simplified as much as possible. Fig. 1 indicates the simplified system, consisting of three beds in series with quench using fresh feed between the beds and preheating of the feed with the effluent. A material and energy balance yields two partial differential equations:

\[
\frac{\partial c}{\partial z} = \frac{C_p}{C_p c} r(T, c) 
\]

\[
\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial z} = -\frac{\Delta H_{rx}}{C_p c} r(T, c) + \frac{\partial^2 T}{\partial z^2}
\]

where:

- \( t \) Time [sec.]
- \( z \) Position in reactor [-]
- \( T \) Particle temperature [K]
- \( c \) Ammonia concentration [kg NH3/kg gas]
- \( u \) Migration velocity of temperature wave [1/sec.]
- \( -\Delta H_{rx} \) Heat of reaction [J/kg.NH3]
- \( C_{pc} \) Heat capacity of catalyst and gas [J/kg cat.K]
- \( C_p \) Heat capacity of gas [J/kg.K]
- \( r(T, c) \) Reaction rate [kg NH3/kg cat.sec.]
- \( \gamma \) Dispersion coefficient due to finite heat transfer [1/sec.]

The heat exchanger was modeled with an \( \epsilon - NTU \) model (without dynamics for simplicity), which yields a relationship of the form:

\[
T_i = \epsilon T_o + (1-\epsilon) T_f
\]

where \( T_i \) is the reactor inlet temperature and \( T_o \) the reactor outlet temperature (see Fig. 1) and the heat exchanger efficiency \( \epsilon \in [0 \ 1] \) is a constant independent of temperature.

The model was discretized using a finite difference method, and integrated using a standard Runge-Kutta method.

2.2 Linearized model

For later analysis, the model of the reactor (without the heat exchanger) was linearized numerically about an operating point (feed temperature 240 °C), yielding a standard linear state space model with 30 states on the form:

\[
\frac{dx}{dt} = Ax + Bu, \quad y = Cx
\]

where the state vector \( x \) consists of temperatures along the bed; \( u \) is the inlet temperature to the first bed, \( T_i \) (before the quench; quench temperature \( T_f \) was assumed constant); and \( y \) is the outlet temperature of the third bed. The transfer function \( g(s) \) for the reactor is then \( g(s) = C(sI - A)^{-1}B \). The model was analyzed using MATLAB.

2.3 Simulations of limit cycle behavior

Simulations using the model reproduce the observed temperature oscillations in the industrial plant and confirm that the oscillations originates in the reactor/preheating system.

A typical simulation is shown in Figure 2, where the feed temperature to the reactor, \( T_f \), is reduced by steps of 10 °C every 4000 seconds. For a sufficiently high feed temperature, the system is stable. When the feed temperature falls below some critical value, the system becomes unstable and exhibit limit cycle behavior (oscillations), as shown in Figure 3.

To understand qualitatively what happens, consider Figures 4a to 4f which show the calculated profiles of the reactor temperature for different times during one period of the sustained oscillations. On the horizontal axis, \( x = 0 \) corresponds to the inlet of the first bed and \( x = 1 \) to the outlet of the last bed. The discontinuities

\[
\frac{\partial c}{\partial z} = \frac{C_p}{C_p c} r(T, c)
\]

\[
\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial z} = -\frac{\Delta H_{rx}}{C_p c} r(T, c) + \frac{\partial^2 T}{\partial z^2}
\]
in the figures are due to the quenching. On the vertical axis is the reactor temperature (range 250 °C-550 °C).

One should note the wavelike bump to the left in Figure 4a. 70 seconds later, see Figure 4b, the bump has moved a little to the right, growing in size. The wave may be traced through Figures 4c-f, where it induces a new wave by heat exchange with the reactor feed, resulting in the sustained temperature oscillations shown in Figure 3.

### 3 Analysis

The objective of this section is to explain the above results. We first start with a simple steady-state analysis which proves to be inadequate. We then perform a conventional linear stability analysis which is found to be consistent with the nonlinear simulations. Finally, we explain why the initial steady-state analysis was inadequate in this case.

#### 3.1 Simplified steady-state analysis

We first perform a simplified analysis based on steady-state information, similar to that of van Heerden (1953). Consider figure 5, where the steady state characteristics of the reactor and heat exchanger are shown. The plot shows the relationship between \( T_s \) versus \( T_i \) (see Figure 1) for the reactor (S-shaped curve) and the heat exchanger (straight line). It is implicitly assumed that other quantities are held constant (Flow rates, feed temperature etc.).

The heat exchanger characteristic gives the relation between \( T_s \), which is considered an input to the exchanger, and \( T_i \), which is considered an output. Similarly, the reactor characteristic gives the relation between reactor inlet temperature, \( T_i \), and reactor outlet temperature, \( T_o \).

The plot is very similar to the classical van Heerden plot (van Heerden, 1953), and the reason for giving it in terms of inlet temperature vs. outlet temperature of the units is that this simplifies the discussion later in this paper.

The steady state operating points are points where the two curves intersect. For the conditions given in Figure 5 there are three possible steady state solutions, and the desired one, in which we operate, is the upper one with the highest temperature. Van Heerden (1953) showed that steady states solutions where the reactor characteristic is steeper than the heat exchanger characteristic are always unstable; thus the middle solution in Figure 5 is unstable (Note that with control, it is possible to stabilize any operating point).

Now consider the stability of the upper (desired) operating point. Van Heerden (1953) claimed that points where the heat exchanger characteristic is steeper than the reactor characteristic are stable. To induce instability one may reduce the feed temperature as done in the previous section, which corresponds closely to translating the the two characteristics in Figure 5 in such a way as to bring the two curves closer to tangency (such that the middle and upper solutions coincide). From the interpretation of van Heerden (1953) one would expect instability to occur exactly when the two curves touch each other. However, the simulations indicate that the oscillatory behavior begins just before the curves become tangents to each other. At first this was believed to be caused by nonlinearity or numerical errors, but as we show below a more careful analysis shows that the simulations are indeed correct, and that the upper solution may be unstable, demonstrating that a steady-state analysis is insufficient (Aris and Anundson, 1958).
3.2 Linear stability analysis

Close to an operating point, the dynamics of a system is well described by its linearized model. The reactor system in Fig. 1 may hence be represented by the block diagram with positive feedback shown in Figure 6, where \( k = \varepsilon \) is the steady state gain of the heat exchanger and \( g(s) \) the transfer function of the reactor. A linear stability analysis based on computing the eigenvalues (given by the zeros of \( 1 - g(s)k = 0 \)) confirmed that the instability occurred at the point found in the nonlinear simulations. Below we consider a root locus analysis and the Nyquist plot to understand what happens.

3.2.1 Analysis of reactor model

An analysis of the transfer function of \( g(s) \) shows that it has several RHP (right half plane) zeros. Such RHP-zeros generally correspond to inverse responses, and this is confirmed by Figure 7 which shows the outlet temperature, \( T_o \), in response to a step increase in the inlet temperature, \( T_i \). The above response is for the linear model, and similar responses were found for the nonlinear model.

3.2.2 Root locus analysis

![Root locus plot of system](image)

To see how these zeros affect the system stability, assume that \( k \) is varied, corresponding to changing the heat transfer area in the heat exchanger. This yields the root locus plot shown in Figure 8. When \( k = 0 \), the poles of the system are equal to the poles of the system without the heat exchanger (marked with 'X' on the figure). As \( k \) is increased towards infinity (corresponding to increased heat transfer area), the poles which stay finite approach the zeros of \( g(s) \) (marked with 'O'). As \( k \) is increased, a pair of complex poles of the system cross the imaginary axis, and the system goes unstable.

3.2.3 Nyquist plot analysis

![Nyquist plot of g(s)](image)

The stability of the system may be analyzed using the standard Nyquist criterion: For positive feedback with a stable \( g(s) \), the system is unstable if and only if a plot of the loop transfer function \( g(j\omega)k \) encircles the \( 1 + j0 \) point (not -1 point) in the complex plane as the frequency \( \omega \) is varied from \(-\infty \) to \(+\infty \).

Consider first the stability of the middle operating point in Fig. 5. The reactor steady state gain, \( g(0) \), is the slope of the reactor characteristic, and the heat exchanger gain, \( k \), is the inverse of the slope of the heat
exchanger characteristic. It then follows that the steady state loop gain $g(0)k$ is the ratio of the two slopes, which is larger than one at this operating point since the reactor characteristic is steeper than the heat exchanger characteristic. Since $g(j\omega)k = 0$ at $\omega = \pm \infty$, encirclement of the $1 + j0$ point is unavoidable, and the system is therefore unstable at the middle operating point.

Normally, one will with positive feedback expect that the closed-loop system is stable when $g(0)k$ is less than one. The reason is that the gain $g(j\omega)k$ normally decreases with frequency, such that $g(j\omega)k$ never cross the real axis to the right of $g(0)k$ and hence never to the right of $1 + j0$. This implies no encirclement, and thus stability. However, in our case there are right half plane zeros in $g(s)$ which increase the loop gain and at the same time yield a negative phase shift, and make this assumption invalid. This is seen from the Nyquist plot of $g(j\omega)$ in Figure 9. There is a point of $g(j\omega)$ crossing the real axis to the right of $g(0)$ at some frequency $\omega_{36}$. As stated above, the Nyquist stability condition tells that the system will be unstable if this curve encircles the point $1/k$. The system is stable for small values of $k$ (corresponding to little heat integration), and is unstable if $k > k^*$, where the critical gain $k^*$ is given by $1/k^* = g(j\omega_{36})$. As can be seen, this gain, $k^*$, is a little lower than the one corresponding to the instability of the steady state, $1/k = g(0)$, i.e. the instability will occur when the heat exchanger characteristic in fig 5 is a little steeper than the reactor characteristic. The fact that the instability occurs at a nonzero frequency, also shows that the onset of the instability corresponds to a Hopf bifurcation, which is consistent with the observed limit cycles in the nonlinear simulations.

4 Discussion

4.1 ”Positive feedback yields slow responses”

For most chemical engineering systems, there is no point of $g(j\omega)$ crossing the real axis to the right of $g(0)$. When $k$ is increased, the instability will then occur as a pole moves through the origin. This has made many authors make statements like: ”Positive feedback in a plant make the response of the plant slow, and the sensitivity to slow disturbances high”. Since there are systems where this is not the case, as demonstrated above, such statements should be used with care.

4.2 Physical explanation for the inverse response

Consider a fixed bed where an exothermic reaction is taking place, and suppose we make a sudden decrease in the inlet temperature (step change). This will affect the bed outlet by two mechanisms: by the migration of temperature waves in the bed, which is a slow process; and by changes in the concentration of chemical species, which is a relatively fast process. Now, the initial effect of the decrease in inlet temperature is normally a decrease in the conversion in the first part of the bed. Since the temperature waves are slow, the initial effect on the last part of the bed is only to make the reactant concentration higher, such that the outlet temperature increases. Eventually, there is a loss of conversion in the whole reactor and the outlet temperature decreases. Such inverse response characteristics are well known (Silverstein, 1982), and indicate right half plane zeros in the linearized transfer function of the bed. Right half plane zeros are of fundamental importance when discussing control, as they limit the achievable control performance of any control system.

4.3 Control of reactors with heat integration

Although there has been a lot of work on the control of fixed bed reactors, many reactors in the industry are left uncontrolled. When a processing unit can be operated safely without control, this is to be preferred, as it is wanted to keep the complexity of a plant to a minimum.

Two important issues which have to be considered for the ammonia synthesis reactor in question are extinction and limit cycle behavior. Extinction of the reactor means plant shutdown and lost production. Limit cycle behavior may lead to material damage in the reactor, as well as deterioration of the catalyst.

To be accepted in a conservative community, a control system must be simple to understand. It should be easily tunable, and preferably be hierarchical, such that it may be turned on or off in a gradual manner. Behavior which may damage the reactor, such as large temperature oscillations, must be avoided.

Even a very simple controller will get rid of the possibility of the limit cycle behavior caused by preheating the reactor feed by the effluent. Consider e.g. controlling the temperature at the inlet of the first bed of the ammonia synthesis reactor using the quench valve before the first bed. This may be done by e.g. a simple PI-controller. Note that there is no RHP-zero for this control loop, and the controller may be made quite fast (compared to the overall response time of about 7 min.). Thus, the feedback path through the controller will dominate compared with the positive recycle through the heat exchanger, and thus the reactor with controller will behave approximately as a reactor without feed preheating. This controller will of course not eliminate the possibility of reactor extinction, which may or may not be a problem.

To avoid extinction, one may make sure that the setpoint of the controller is high enough, e.g. with a safety margin of $10^\circ C$ or so. Alternatively, one might specify that the quench valves should have a specified margin from fully closed or fully open, and cascade a (relatively slow) controller on top which sets the safety margin of the simple PI-controller according to this. It is important that this controller is not too fast, as the reactor transfer function has inverse response behavior.
One may ask whether the observed RHP-zeros will limit the performance of the reactor. The answer is that this will only be the case if one wants to control the reactor outlet temperature $T_o$ (or some other internal temperature in the reactor) using a quench further upstream in the reactor (and thus adjusting the inlet temperature to an upstream bed). Probably, it is not critical that the outlet temperature is tightly controlled, and the RHP-zero will not present a serious limitation. Also, as already noted, there is no RHP-zero when controlling the inlet temperature using the inlet quench, so stabilization is not limited by RHP-zeros.

4.4 Effect of plant integration on the dynamics of plants

From a general point of view, introducing heat integration in a plant may be thought of as moving the poles and zeros of the plant. Generally, the introduction of feedback paths moves poles, parallel paths move zeros. Feedback paths introduced by heat integration may therefore destabilize an otherwise stable plant.

For control, the zero locations of a plant may be more important than the pole locations. A controller may be considered to be an approximate inverse of the plant. Right half plane zeros of the plant will therefore limit the bandwidth of the control system, since they will end up as unstable poles in the controller if the bandwidth is too high. Parallel paths introduced by heat integration may move plant zeros into the right half plane, and hence introduce fundamental limitations in achievable control performance. However, as noted above the RHP-zero may not affect stabilization if there are measurements available for which the RHP-zero does not appear.

Positive feedback paths in plants will often make a pole go through the origin as the loop gain of the feedback path is increased towards 1. This will make the response of the plant slow, and the sensitivity to slow disturbances high. For fixed bed reactors, this is not what is happening.

5 Conclusion/Summary

An industrial case has been analyzed. A fixed bed autothermal ammonia synthesis reactor became unstable, such that the recorded temperatures in the reactor oscillated heavily. Such oscillations may damage the reactor.

A mathematical model of the reactor reproduces the phenomenon. The oscillatory behavior (limit cycles) occurs in the simulations when the reactor feed temperature or the operating pressure is too low. The phenomenon is best described as a temperature wave migrating through the reactor, being fed back through the heat exchanger.

A linear analysis close to the steady state operating point shows that for given operating conditions in the reactor, the phenomenon occurs when the heat exchanger area becomes sufficiently high. From a linear point of view, the phenomenon may be explained using root locus techniques. Right half plane zeros in the reactor bed transfer functions attract poles as the "gain" of the heat exchanger is increased. The instability occurs as a pair of complex conjugate poles cross the imaginary axis in the complex plane.

Even a simple controller may eliminate the possibility of limit cycle behavior. E.g. fixing the temperature at the entrance of the first bed using a PI-controller will do this. To avoid extinction, one could e.g. cascade a slow controller on top.

References