

## APPLICATION TO UNSTEADY STATE

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### 10.1 INTRODUCTION

While most process engineering courses deal with design and operations at steady state conditions, and most process operators target to achieve steady state, industrial processes operate at constantly changing conditions. The differences between steady and dynamic conditions can frequently be ignored. However, an approach to considering unsteady operations will be of value to every problem solver. There are multiple instances where unsteady state operations must be considered. Startups are never steady state; this is probably the most challenging phase of problem solving. This is often an area where the intuition of an experienced operator or engineer is more valuable than a detailed problem-solving activity. However, there are examples where a frequently encountered startup activity that involves a problem (reactor startup, for example) can be approached using some of the principles outlined in this book.

Batch operations are always dynamic. If problems are uncovered during a batch operation, typical process engineering calculations based on steady state operations will rarely be of any value. Thus the industrial problem solver needs to have tools to allow him to approach these dynamic operations. Problem 10.1 is a typical example of a problem within a batch operation.

Unsteady state upsets can often provide valuable information. For example, short term upsets caused by feed impurities can be extrapolated to steady state values using techniques that relate the time of the upset to the actual reactor

residence time. This will allow the problem solver to determine the steady state impact of these impurities. This is the impact on the process that would occur if the short term impurity concentration in the feed were at the upset level consistently. This information can be used to determine the specification of the impurity in the feed.

## 10.2 APPROACH TO UNSTEADY STATE PROBLEM SOLVING

The most difficult aspect of solving unsteady state problems in an industrial environment is the balance between formulating technically correct hypotheses and the need for expediency. This was referred to in Chapter 3 as optimum technical depth. Because of the difficulty of determining this balance, one of two extremes is often present. In one of these extremes, the problem solver begins developing a highly sophisticated dynamic model that requires a powerful computer to solve the differential equations. As the work slowly progresses, management becomes impatient and cancels the project. At the other extreme, the problem solver often gives up and uses intuitive methods, rather than developing a simplified dynamic model. Optimum technical depth is the approach used to achieve a balance between these two extremes. This balance will be a strong function of the environment surrounding the problem. For example, during a startup, a balance slanted toward intuition is likely the best approach. On the other hand, a chronic problem which does not have any apparent answer will require a more sophisticated approach. The following paragraphs present guidelines for approaching unsteady state problems.

If the problem requires an immediate recommendation, such as during a startup, the best approach will be to rely on the instinct of an operator or experienced startup engineer. Medical research has shown that our minds work by both instinct and logical reasoning; obviously, instinct is faster than development of a detailed logical path. Minds conditioned by years of experience with unsteady state operations such as a startup will react instinctively to provide an immediate response, as opposed to having to think about the situation.

The basic concept used when considering unsteady state operations is equation (10-1) shown below:

$$AD = I - O - RD \quad (10-1)$$

where

$AD$  = rate of accumulation (this could be accumulation of anything: level, heat, or reactant)

$I$  = inflow of material or heat

$O$  = outflow of material or heat

$RD$  = removal/addition of heat, or formation/destruction of material by reaction

This relationship can be used to as a building block for all unsteady state considerations from something as simple as the change of level in an accumulator to the development of complicated dynamic models. The main goal of this chapter is the development of simple but accurate dynamic models.

If it is considered desirable to build a dynamic model of the unsteady state process, all physical components of the system must be considered. For example, with steady state, the heat capacity of the process vessel is correctly never considered. This is because the vessel wall and the vessel content temperatures remain essentially constant. However, for unsteady state heat balances, the heat capacity of the vessel (both the walls and contents) must be considered. The heat capacity of the vessel walls will often be a moderating influence. This moderating influence will cause the rate of temperature change to be less than that calculated if the complete heat capacity of the vessel is ignored. The dynamic model should be kept simple by use of idealized mixing patterns, use of lumped parameter constants (such as overall heat transfer coefficients), and an assumption of uniform metal temperature. The two idealized mixing patterns are either a perfectly mixed vessel or “plug flow.” Plug flow involves an assumption that every particle has exactly the same residence time in the vessel. An example of a plug flow mixing pattern is a fixed bed dryer or reactor where the velocity is so low that a streamline flow pattern is developed. In this case, the residence time for every element is the vessel fluid holdup divided by the volumetric flow rate. The opposite mixing pattern is the perfectly mixed vessel. In a perfectly mixed vessel, the contents of the vessel are at the concentration of the outlet fluid. An example of a perfectly mixed vessel is a reactor used to produce polypropylene from propylene. The pure propylene enters the reactor, where about 50% is converted to polymer. The outlet concentration is 50% by weight polypropylene. Since the reactor is a perfectly mixed vessel, the polypropylene concentration at any point in the vessel is also 50% by weight.

If reaction is involved, it should be recognized that there are two models that can be used to simulate an unsteady state reaction. Traditional process engineering indicates that the reaction rate is proportional to the concentration of the reactant. That is, the rate of reaction will increase as the concentration of the reactant in the vessel increases. This has been referred to as the “slow response model.” For some reactants, such as impurities in a polymerization reactor, the impurity reacts as soon as it enters the reactor. This “fast response model” is easier to develop because it allows an engineer to assume that the concentration of the impurity in the reactor approximates zero. In order to determine whether the traditional model or the “fast response model” should be used, the problem solver must understand the technology. As a general rule, the “fast response model” will apply only to reaction impurities in a polymerization reaction. Most other reaction modeling will be more accurate if the traditional process engineering approach is utilized. Regardless which model is used, short term upsets and fundamental models of stirred tank or plug flow reactors can be used to estimate the full impact of an impurity.

### 10.3 EXAMPLE PROBLEMS

The problem-solving techniques associated with unsteady state operations are illustrated by the actual case histories described in the following paragraphs. Example Problem 10-1 illustrates the use of these techniques for solving a problem associated with a batch reactor which experienced a temperature “runaway” (such a rapid temperature increase that the emergency devices were activated). Problem 10-2 illustrates the use of these techniques to extrapolate short term reaction upsets caused by an impurity to steady state conditions.

#### EXAMPLE PROBLEM 10-1

A batch reaction was carried out in a reaction vessel with a cooling water jacket. The reaction was initiated when the primary reactant was added to the reaction vessel. The primary reactant was dissolved in hot hexane in a small vessel and then pressured into the reaction vessel with nitrogen as fast as possible. While the technology had been developed in the research facility of a major petrochemical company, the actual manufacturing of the material was being done by a contract manufacturer. His operation was designed and operated on an exceptionally low budget. There were no flow instruments to measure and control the rate of addition of the reactant. The average rate of reactant addition was obtained knowing the amount of material in the small vessel and the time that it took to add it to the reaction vessel.

The exothermic (heat generated) reaction had been conducted successfully many times. However, during a recent batch a rapid increase in temperature was experienced as the primary reactant was added to the reactor. The rapid temperature increase was so fast and of such a magnitude that the safety release system on the reactor was activated. The actual manufacturing location was located several hundred miles away from the technology center. Operations personnel decided to solve the temperature runaway problem without asking for help from the technology center. In order to eliminate the rapid increase in temperature, operations personnel decided to add the reactant at a very slow rate. The next batch was produced without a temperature runaway. However, the product produced in this fashion did not meet the product morphology specifications. Morphology includes such physical attributes as particle diameter, porosity, and surface area.

After this batch failed to meet the morphology specifications, the operations personnel requested help from the technology center. The problem solver was charged with the responsibility of determining how to conduct this reaction with an 80 to 90% probability that a second temperature runaway would not occur and so that the product morphology would be satisfactory.

The problem solver began accumulating technology information. It was known that the primary reactant reacted instantly when it entered the reactor

(fast response model). It was desirable to add the reactant as fast as possible for two reasons. As indicated earlier, the morphology of the product was adversely impacted by a slow addition rate of the reactant. In addition, the heat of reaction provided heat input to raise the reactor temperature rapidly from 149°F to 185°F.

The heat of reaction was unknown. It was not determined in the laboratory during the development part of the project. Actually, the laboratory chemists believed that there was no heat of reaction. The small scale reactor had an inherently high heat transfer area-to-volume ratio. Laboratory reactors will almost always have a higher heat transfer area-to-volume ratio than commercial size reactors. This always creates a potential problem in scaleup to a commercial-size process. In addition, this laboratory scale reactor was surrounded by a constant temperature sand bath. This combination essentially eliminated the chance to observe any heat of reaction in the laboratory. The nature of the reaction was such that the heat of reaction could not be determined by classic literature-based approaches. In addition, time and financial constraints did not allow determination of this variable from laboratory data.

The problem solver began using the five-step problem-solving approach described earlier, as is shown below:

### **Step 1: Verify that the problem actually occurred.**

Verification of this problem was easy since the hexane vapor from the safety release system on the reactor (a rupture disc) condensed in the air and “rained” on a local Veteran’s Day parade. There were no injuries, but several uniforms and band instruments required cleaning and reconditioning. In addition, a review of the reactor temperature and pressure data indicated that the rupture disc did not release prematurely. That is, the pressure and temperature had really gotten out of control.

### **Step 2: Write out an accurate statement of what problem you are trying to solve.**

The problem statement developed by the problem solver was as follows:

An exothermic reaction conducted in a batch reactor had a temperature runaway even though the same reaction had been conducted many times previously with no temperature runaway. In a subsequent batch it was demonstrated that the temperature could be controlled by a slow rate of addition of the primary reactant. However, it is necessary to add the primary reactant at a rapid rate in order to obtain the desired product morphology. Determine what caused the batch reactor to have a temperature runaway. In addition, develop procedures that ensure that there is at least an 80 to 90% confidence level that this temperature runaway will not reoccur when producing a product that meets the morphology specifications.

**Step 3: Develop a theoretically sound working hypothesis that explains as many specifications of the problem as possible.**

Table 10-1 shows the questions from Chapter 6 along with appropriate comments.

A review of the comments associated with these questions and a review of all previous runs indicated several points of interest that would require additional considerations. These were as follows:

- While the batch size was the same, the rate of reactant addition varied greatly from run to run. As indicated earlier, this rate of addition was only determined after completion of the addition since there were not flow meters on the transfer line. There were no procedures given for the rate of reactant addition. Some operations personnel pressured the drum used to mix the reactant and hexane with nitrogen prior to opening the

**Table 10-1 Questions/comments for Problem 10-1**

Question	Comment
Are all operating directives and procedures being followed?	For the batch that had a temperature runaway, all appeared to have been followed. However, there were no guidelines given for how fast to add the primary reactant.
Are all instruments correct?	The instruments had allegedly been calibrated.
Are laboratory results correct?	The product morphology on the second batch was confirmed by two independent techniques.
Were there any errors made in the original design?	Yes. The laboratory chemists indicated that there was essentially no heat of reaction based on their studies. In hindsight, this was obviously an error.
Were there changes in operating conditions?	Yes. Rate of addition of reactant was highly variable even though batch sizes were the same.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain problem?	This is possible, but it would cause the heat removal capability to decrease. This was not occurring based on measured coolant flows and temperatures.
Is the reaction rate as anticipated?	Reaction rate highly dependent on reactant rate of addition.
Are there adverse reactions occurring?	Adverse reactions were likely the cause of poor morphology. However, this is exceptionally complicated chemistry. Thus solving the morphology problem while maintaining slow addition of reagents is unlikely.
Were there errors made in the construction?	Not applicable. Some batches worked fine.

transfer valve. Others simply started the nitrogen flow to pressurize the drum and then opened the transfer valve. There were times when the mixing drum was hotter than it was at other times, which impacted the solution viscosity and would affect the rate of reactant transfer.

- While the laboratory chemists reported that the heat of reaction was insignificant, there had to be a significant heat of reaction to cause the vessel contents to increase from 149°F to 185°F in a short period of time. If the heat of reaction was known or could be determined, it would be possible to estimate the rate of temperature increase for any batch size and/or rate of reactant flow.
- In addition to the problem batch, there were several other runs where the temperature increased almost as rapidly, although the reactor temperature did not become unstable. The only difference in these runs was the rate of reactant addition.

While it could be theorized at this point that the temperature runaway was due to the rate of reactant addition, this theory would only allow one to specify that an addition rate equivalent to that of the first failed batch would cause a temperature runaway. It would not allow determination of the maximum rate of reactant addition. A more fundamental approach was required to allow specification of the target reactant addition rate.

The problem solver decided to approach the problem using a fundamental approach. He felt that if he could express the factors involved in the temperature runaway mathematically, he could understand better how to prevent it. A temperature runaway occurs when the rate of heat generated is greater than the maximum rate that heat can be removed. This can be expressed mathematically as follows in equations (10-2) through (10-4):

$$Q_g > (Q_r)_{\max} \quad (10-2)$$

where

$$Q_g = \text{rate of heat generation, BTU/hr}$$

$$(Q_r)_{\max} = \text{maximum rate of heat removal, BTU/hr}$$

$$Q_g = \Delta H_R \times R \quad (10-3)$$

$$(Q_r)_{\max} = U \times A \times (T_R - T_C) \quad (10-4)$$

where

$$\Delta H_R = \text{heat of reaction, BTU/lb}$$

$$R = \text{rate of reaction (for the case of an instantaneous reaction, it is the rate of reactant addition, lb/hr)}$$

$$U = \text{heat transfer coefficient, BTU/hr-°F-ft}^2$$

$$A = \text{heat transfer area, ft}^2$$

$T_R$  = temperature of the reactor, °F

$T_C$  = minimum temperature of the coolant, °F

Note that equation (10-4) has been simplified from the traditional heat transfer equation that involves use of a logarithmic relationship. This is valid for this particular case since the coolant is flowing through the reactor with a minimal increase in temperature. The temperature to be used is the minimum coolant temperature that can be obtained. It is assumed that the control system will react to provide the minimum coolant temperature possible. In addition, because the reactor vessel is well mixed, the reactor temperature throughout the vessel is constant at any point in time.

For a batch reactor, equations (10-3) and (10-4) can be combined and a heat accumulation term can be added to take into account the unsteady state nature. The amount of heat accumulated in the vessel will equal the heat of reaction minus the heat removed. Any heat accumulation will cause an increase in the temperature of the reactor. The increase in temperature will depend on the heat capacity of the vessel contents and on the vessel itself. Heat capacity is basically the weight of material multiplied by its specific heat. The equations below were developed to represent this situation.

$$AC = Q_g - (Q_r)_{\max} \quad (10-5)$$

$$AC = \Delta H_R \times R - U \times A \times (T_R - T_C) \quad (10-6)$$

$$AC = W \times C_p \times dT/dt \quad (10-7)$$

where

$AC$  = heat accumulation, BTU/hr

$W$  = weight of material (metal, water, reactants), lb

$C_p$  = average specific heat of material, BTU/lb-°F

$dT/dt$  = rate of temperature rise, °F/hr

Since the reaction of the reactant being pressured into the reactor is instantaneous, the heat generated ( $\Delta H_R \times R$ ) depends only on the rate of reactant addition. Thus equations (10-6) and (10-7) can be combined and modified to simplify solving for the heat of reaction.

$$\Delta H_R = (W \times C_p \times dT/dt + U \times A \times (T_R - T_C))/R \quad (10-8)$$

In the above equation,  $U$  and  $A$  can be estimated from physical dimensions and typical vessel heat transfer coefficients. Since all previous batches and future plans called for use of the same vessel, obtaining exact values of  $U$  and  $A$  was not important. The product of  $UA$  was considered a "lumped parameter constant."



Equation (10-8) was used to determine the heat of reaction for all previous runs. Since a reasonably constant heat of reaction was calculated over a wide range of reactant addition rates ( $R$ ), this approach seemed valid. After determining the heat of reaction using data from the batch runs, calculations were done to determine the maximum rate of reactant addition. Referring back to equation (10-2), a typical approach is to provide a 10% safety factor, so that the maximum rate of heat removal is 10% greater than the maximum rate of heat generated. Thus equation (10-2) can be modified as follows:

$$1.1 \times Q_g < Q_{r \max} \quad (10-9)$$

In order to estimate the maximum rate of reactant addition, equation (10-9), along with equation (10-10), shown below (which is rearrangement of equation (10-8)), were used.

$$dT/dt = (R \times \Delta H_R - U \times A \times (T_R - T_C)) / (W \times C_P) \quad (10-10)$$

Equation (10-10) was used to estimate the maximum rate of reactant addition ( $R$ ) that would allow the temperature to rise from 149°F to 185°F without causing a temperature runaway. This maximum rate of addition was determined using an iterative procedure along with a spread sheet. The calculated relationship between the reaction temperature and time for the maximum rate of addition is shown in Figure 10-1. After the maximum rate was determined, it was reduced by 10% to be consistent with the requirements shown in equation (10-9).

Using this approach, it was estimated that the maximum rate of reactant addition was 25% less than that which was utilized in the batch on which a

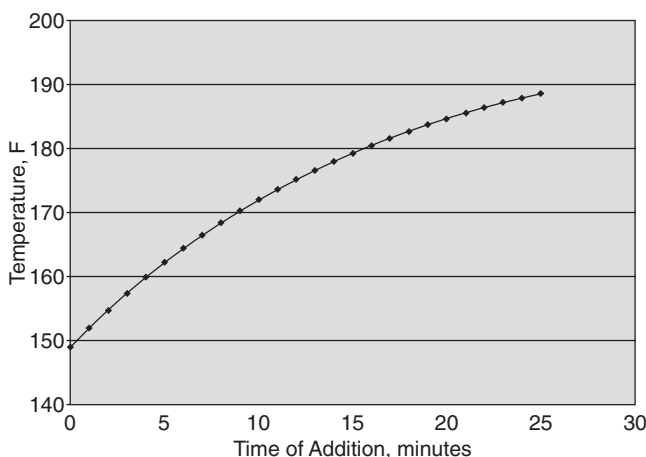


Figure 10-1 Reactor temperature vs. time.

temperature runaway occurred. The problem solver developed the following working hypothesis:

It is theorized that the temperature runaway was caused by the rapid addition of the primary reactant. This addition rate was so high that the temperature could not be controlled, even when the coolant was at the maximum rate. Calculations indicate that if the primary reactant rate addition was reduced by 25%, the reaction could be controlled.

#### **Step 4: Provide a mechanism to test the hypothesis.**

Developing a mechanism to test the hypothesis was easy from an engineering standpoint. As described above, the maximum rate of reactant addition to achieve a peak temperature of 185°F was easily estimated. However, convincing the operations personnel to add the reactant at this rate was difficult since they had recently had good success controlling the temperature while adding the reactant at a much lower rate and allowing the reactor to slowly heat up. As indicated earlier, this resulted in a product with poor morphology. In order to convince them to test the hypothesis, it was necessary to give them a complete explanation of the importance of the morphology of the product and to stand by the reactor when the reactant was added at a rapid rate. The problem solver had estimated the nitrogen pressure that would be required to transfer the reactant to the drum at the desired rate. He had also calculated the rate of level change in the reactant storage drum that would result if the reactant were added at the correct rate. The test was successful in producing a product with good morphology and the temperature rose, as predicted, without a temperature runaway.

#### **Step 5: Recommend remedial action to eliminate the problem without creating another problem.**

The hypothesis test (step 4) proved that the reactant could be added at a high rate. In order to prevent another temperature runaway, additional controls were considered to assure that the target reactant addition rate was maintained. Since, as indicated earlier, the only means used by operations personnel for knowing the addition rate was the amount of time that it took to add the reactant, a more specific technique was mandatory. The project did not have funds for the installation of a flow meter, nor was the required shutdown time immediately available. Three approaches were used to ensure that the reactant was being added at the correct rate. The pressure to be reached and maintained on the reactant storage drum was specified in the operating procedures. In addition, the rate of level change that would be anticipated was specified. As a final check, the curve shown in Figure 10-1 was provided and was to be used to monitor the rate of temperature rise in the first few minutes. For example, if the initial temperature increase was too fast, it would indicate that,

in spite of the other techniques, the rate of addition was too fast. The rate of addition would then be reduced.

**Lessons Learned** Although it has nothing directly to do with problem solving, one of the lessons learned was that it is very difficult to determine heat of reaction from laboratory experiments that are not specifically designed to obtain this variable. A typical laboratory experiment will be designed to obtain reaction rate variables or product quality attributes. The best way to do this will be at a constant temperature. This is usually done by utilizing small equipment which has a high area to volume ratio and is surrounded by a constant temperature bath. Within this facility, it will be impossible to determine the heat of reaction or even to notice whether there is a heat of reaction or not.

The utilization of the unsteady state relationship, equation (10-1), for heat accumulation proved to be a reliable tool for determining the heat of reaction. As indicated, the key to being able to successfully use this equation is the full inclusion of all of the heat content (vessel and reactants) of the process under consideration. The qualification that time and money were not available to determine the heat of reaction in the laboratory is often the case in industrial problem solving. In order to obtain the heat of reaction in the laboratory, it would have taken time and funds to build a laboratory reactor specifically designed to obtain heat of reaction data.

In problem solving, the engineering calculations are often the easiest part of the job. Convincing either operations management or the hourly work force of operators and mechanics that the recommended solution is correct is often more difficult. The process of convincing the operations organization to adopt the answer will be easier if they are convinced that the problem solver is there with them to assist them if something was wrong with the calculations. Thus in this example problem, the problem solver was present when the operator added the reactant at the calculated rate. While things went as planned, the operator felt much more comfortable in setting the pressure to give the high rate of flow since the problem solver was present with him.

## EXAMPLE PROBLEM 10-2

A continuous stirred tank reactor (CSTR) in a polymerization plant was plagued by short term “loss of reaction” events. While these events were small in magnitude, they created product quality upsets as well as a loss of catalyst efficiency. This type of reactor is highly agitated and can be treated for all practical purposes as a perfectly mixed vessel.

These loss of reaction upsets appeared to be associated with spikes of carbon dioxide ( $\text{CO}_2$ ) in the monomer feed. The reactor residence time was approximately 3 hr. The short-term spikes of  $\text{CO}_2$  lasted for only 30 to 60 min.

Some batch data was available from the laboratory indicating that the CO<sub>2</sub> specification of the monomer feed currently at 10ppm needed to be reduced. However, management would like to be convinced that the laboratory data was consistent with the plant experience. Management also believed that there was probably another impurity that was not being analyzed that was causing the problem. This belief was based on previous experience in another plant that utilized a similar, but not identical, catalyst system. Management was also concerned that a project to reduce the CO<sub>2</sub> specification and eliminate spikes would take several months to implement and require significant investment. Thus they did not want to proceed with the project unless there was a high probability of success.

The problem solver was asked to determine if these upsets were really caused by feed impurities, what the likely feed impurity was, and the impurity's real impact on the process. It was believed that this approach would lead to determining and setting realistic impurity specifications on the feed monomer.

The problem solver approached the problem using the 5-step problem-solving technique as shown in the following paragraphs.

### **Step 1: Verify that the problem actually occurred.**

Verification of this problem was done through the use of two different techniques. The polymer was analyzed to determine the concentration of catalyst in the polymer leaving the reactor. From this result, the catalyst efficiency was calculated and it was clear that, during CO<sub>2</sub> spikes, the catalyst efficiency did decrease. However, this approach only gave an average catalyst efficiency at any point in time. Since the reactor had a 3-hr residence time and the impurity spikes lasted only 30–60min, this average represented 2–2.5hr of normal operation and 0.5–1hr of upset operations. In addition to this analytical approach, the calculated production rate (as determined by the process control computer using a heat balance) was used to determine the instantaneous production rate. Both of these techniques confirmed the loss of reaction that occurred about the same time that the CO<sub>2</sub> content of the feed increased.

### **Step 2: Write out an accurate statement of what problem you are trying to solve.**

The statement written by the problem solver was as follows:

Frequent loss-of-reaction episodes are occurring in a polymer plant. These episodes cause a decrease in average catalyst efficiency as well as inconsistent product quality. These episodes appear to occur at the same time as short term spikes of CO<sub>2</sub> concentration in the monomer feed. Determine the cause of the frequent “loss of reaction” episodes. Any conclusions based on plant data must be consistent with available laboratory data on the impact of CO<sub>2</sub> on the polymerization reaction. This evaluation should also indicate whether or not there is

any indication that another impurity besides  $\text{CO}_2$  is present. Based on this data, the monomer feed specification should be reviewed.

**Step 3: Develop a theoretically sound working hypothesis that explains as many specifications of the problem as possible.**

In order to fully assess the possible causes of the upsets, the questions shown in Chapter 6 were utilized and Table 10-2 was developed.

The above comments tended to confirm the suspicion that the upsets were caused by the presence of  $\text{CO}_2$ . However, there was still a residual suspicion that there was another impurity that was causing the problem. The problem solver determined that if the batch laboratory data could be shown to be consistent with plant data, this suspicion would be removed. The batch laboratory

**Table 10-2 Questions/comments for Problem 10-2**

Question	Comment
Are all operating directives and procedures being followed?	All appeared to be correct and being followed.
Are all instruments correct?	The instruments had allegedly been calibrated. In addition, the heat balance was checked by manual calculations.
Are laboratory results correct?	Yes. The x-ray machine used to determine the catalyst concentration was cross checked with another machine. No other impurities besides $\text{CO}_2$ were observed on continuous analyzers during upsets. In addition, samples of the feed taken during upsets and analyzed in the laboratory confirmed the presence of $\text{CO}_2$ .
Were there any errors made in the original design?	No.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	The potential for reaction quench fluids leaking into the reactor was checked and it was concluded that they were not leaking into the reactor.
Has there been mechanical wear that would explain problem?	No.
Is the reaction rate as anticipated?	Yes, except during upsets.
Are there adverse reactions occurring?	Yes. During upsets the product quality attributes decreased.
Were there errors made in the construction?	Not applicable.

data was developed by blending  $\text{CO}_2$  into the monomer to the desired experimental level and then conducting a polymerization. In order to develop a comparison between laboratory data and commercial data, a technique was required to allow extrapolation of short term plant upset data to steady state operations. The steady state operation values would allow comparison to the batch laboratory data. After some literature research, the problem solver developed the four important concepts described in the next few paragraphs.

In most polymerization reactions, highly reactive impurities such as  $\text{CO}_2$  react immediately upon entering the reactor. That is, the rate of catalyst deactivation is not dependent on the concentration of the impurity in the reactor, but depends on the concentration of the impurity in the feed. As discussed earlier, this is known as the "fast response model." This is the first important concept.

The second concept is that for industrial problem solving, the polymerization reaction can be represented by simple first order kinetics with respect to the catalyst and monomer concentration. The equation shown below was utilized to approximate the polymerization kinetics in a reactor with a fixed volume.

$$R = k \times C \times M \quad (10-11)$$

where

$R$  = polymerization rate or monomer consumption rate, lb/hr

$k$  = kinetic rate constant including reactor volume,  $\text{ft}^6/\text{hr}\cdot\text{lb}$

$C$  = catalyst concentration in the reactor,  $\text{lb}/\text{ft}^3$

$M$  = monomer concentration in the reactor,  $\text{lb}/\text{ft}^3$

Note that the units of the kinetic constant ( $\text{ft}^6/\text{hr}\cdot\text{lb}$ ) include a fixed reactor volume. The absolute value of the kinetic constant is not important since, as will be shown later, all that is considered is the relative change in this constant.

The third concept involves the modification of equation (10-1) to include a catalyst deactivation term and development of an expression for catalyst concentration in the reactor. The rate of accumulation of catalyst in the reactor can be expressed as shown in equation (10-12), below:

$$A_C = I_C - O_C - D_C \quad (10-12)$$

where

$A_C$  = rate of accumulation of catalyst in the reactor, lb/hr

$I_C$  = inflow of catalyst, lb/hr

$O_C$  = outflow of catalyst, lb/hr

$D_C$  = deactivation of catalyst, lb/hr

Based on the “fast response model,” any  $\text{CO}_2$  entering the reactor will immediately deactivate some of the catalyst. This relationship can be expressed as follows:

$$D_C = Z \times B \quad (10-13)$$

where

$Z$  = ratio of catalyst deactivated to  $\text{CO}_2$ , lb/lb

$B$  = rate of  $\text{CO}_2$  entering reactor, lb/hr

Equation (10-12) then becomes:

$$A_C = I_C - O_C - Z \times B \quad (10-14)$$

If the flow of  $\text{CO}_2$  continues for an extended period, a steady state will be reached. At steady state, by definition, there is no accumulation of catalyst. Therefore

$$A_C = 0 \quad (10-15)$$

$$O_C = I_C - Z \times B \quad (10-16)$$

This steady state value will be the full impact of the particular rate of  $\text{CO}_2$  entering the reactor. While the deactivation ratio ( $Z$ ) is of theoretical interest, it can be eliminated from pragmatic considerations, as described later.

As indicated in equation (10-11), the important variable is the catalyst concentration in the reactor. Equation (10-14) can be transformed into equation (10-17) that uses the catalyst concentration by the appropriate substitutions.

$$dC/dt = (I_C - O_C - Z \times B)/V \quad (10-17)$$

where

$dC/dt$  = rate of catalyst concentration change in lb/ft<sup>3</sup>-hr

$V$  = volume of the reactor, ft<sup>3</sup>

Since the rate of catalyst concentration change in the reactor can be determined from equation (10-17), equation (10-18), shown below, can be used to determine the catalyst concentration at any point in time.

$$C_i = C_0 - (dC/dt) \times t \quad (10-18)$$

where

$C_i$  = catalyst concentration in the reactor at any point in time, lb/ft<sup>3</sup>

$C_o$  = initial catalyst concentration in the reactor, lb/ft<sup>3</sup>

$t$  = elapsed time from the start of the upset to the time of interest

The fourth concept involves developing a relationship between the concentration of active catalyst in the reactor at any point in time, the initial concentration, and the final concentration. This relationship assumes that a step change is made to an equilibrium condition and that the step change is continued until steady state is reached.

This relationship will allow translation of upset data into steady state for comparison to the batch laboratory data. For a perfectly mixed CSTR, the concentration of a component at any point in time after a step change is made can be expressed as shown in equation (10-19). In the specific case under consideration, the component is the catalyst and the step change is an increase in the CO<sub>2</sub> concentration in the feed.

$$(C_i - C_o)/(C_f - C_o) = 1 - e^{-T} \quad (10-19)$$

where

$C_i$  = concentration of catalyst in the reactor at any point in time

$C_o$  = concentration of catalyst in the reactor at time = 0

$C_f$  = concentration of catalyst in the reactor after an infinite amount of time

$T$  = number of reactor displacements; this is simply the time after a step change divided by the average residence time

An examination of equation (10-19) will show that after three reactor displacements, or 9 hr if the residence is 3 hr, that 95% of the final change has been achieved. That is,  $(C_i - C_o)/(C_f - C_o) = 0.95$ .

As indicated in equation (10-13), the amount of catalyst deactivated by each pound of CO<sub>2</sub> is not known and was set equal to  $Z$ . However, the instantaneous reaction rate is directionally proportional to the catalyst concentration in the reactor (assuming a constant monomer concentration) regardless of the value of  $Z$ . Thus the reaction rate can be substituted for the  $C$  values in equation (10-19). Equation (10-19) then becomes:

$$(R_i - R_o)/(R_f - R_o) = 1 - e^{-T} \quad (10-20)$$

where

$R_i$  = reactor production at any point in time

$R_o$  = reactor production at time = 0

$R_f$  = reactor production after an infinite amount of time

$T$  = number of reactor displacements at any point in time



Thus if reactor production at time = 0 ( $R_o$ ), the reactor production at any point in time ( $R_i$ ), and the number of reactor displacements at any point in time ( $T$ ) are known, the steady state impact ( $R_f$ ) of a step change in impurity level can be estimated. The number of reactor displacements is the time, since the step change in impurity level occurred divided by the reactor residence time. The use of equation (10-20) also eliminates some of the concerns associated with theoretically imperfect derivation of equations (10-17) and (10-18).

Unfortunately, the impurity upsets observed by the problem solver did not occur as step changes. He simulated the approximate sinusoidal curve of concentration versus time that often occurred during upsets as a step change. A typical impurity curve, along with the technique used to simulate a step change, is shown in Figure 10-2. The problem solver recognized that selecting the magnitude of the upset level to use was somewhat subjective. He tried to select it so that the areas below and above the increasing part of the actual curve were equal. He also used the peak in the concentration versus time curve as the termination point of the upset ( $R_i$  or  $C_i$ ).

The problem solver used this four-concept technique because it provides a consistent method for evaluating upsets of varying magnitudes and durations. For example, an upset where the  $\text{CO}_2$  concentration rose from 0 to 25 ppm and lasted for 15 min might have less actual impact than an upset where the  $\text{CO}_2$  concentration rose from 0 to 5 ppm and lasted for 45 min. However, the projected steady state impact of the first upset was greater. It was obvious that a steady state concentration of 25 ppm of  $\text{CO}_2$  in the monomer feed would have a much larger impact than 5 ppm. However, the exact magnitude of this difference could not be known without using the techniques described earlier.

In order to completely formulate the working hypothesis, several reaction upsets apparently caused by  $\text{CO}_2$  impurities of varying severity and duration were followed and the techniques discussed above were used to extrapolate to the steady state effect. These data, along with the batch laboratory data, are

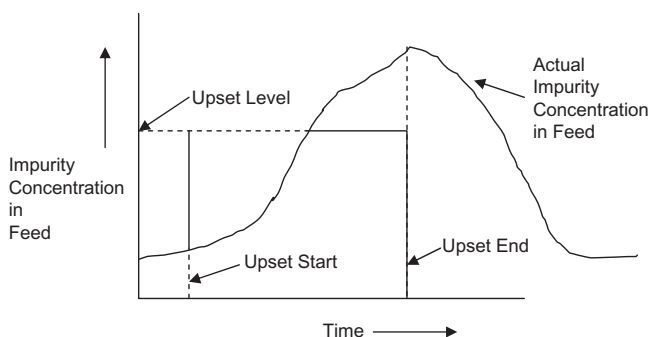
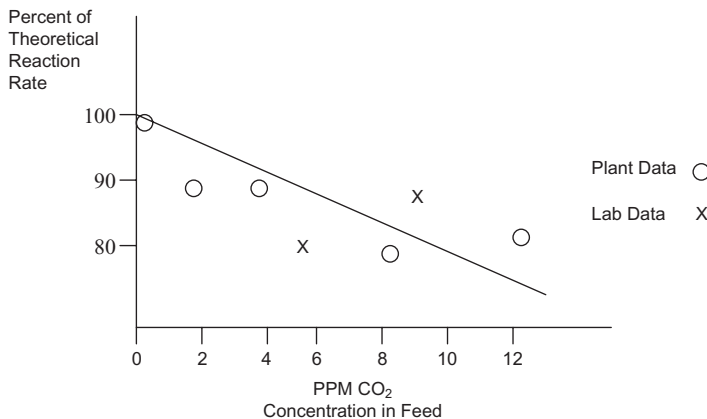


Figure 10-2 Simulation of actual change.



**Figure 10-3** Projected steady state reaction rate vs. CO<sub>2</sub> concentration.

shown in Figure 10-3. The problem solver then developed the following working hypothesis based on the data shown above:

It is theorized that the short term reaction upsets are due to the presence of CO<sub>2</sub> in the reactor feed. The plant data is consistent with laboratory data that indicates that CO<sub>2</sub> is a potent reactor impurity. The reaction upsets are likely to cause product quality upsets due to the unsteady nature of the reactor during these transients. In addition, the presence of a potent reactor impurity is anticipated to affect polymer quality attributes. There were no indications of any other impurities in any of the upsets that were followed.

#### **Step 4: Provide a mechanism to test the hypothesis.**

In order to test this hypothesis, a technique had to be developed to ensure that the reactor feed was free of CO<sub>2</sub> for an extended period of time. If no reaction upsets occurred during this time period, agreement was reached that this would be considered a successful test and proof of the hypothesis. While it would involve additional operating cost, it was agreed to operate the monomer production facilities in a fashion that would limit the probability of CO<sub>2</sub> upsets. While this additional operating cost was not acceptable in the long range, it was acceptable for a one-month trial. During this one month period there was no measurable CO<sub>2</sub> present in the monomer feed, nor were there any reaction upsets. Thus this appeared to be a successful test and the working hypothesis was proven.

#### **Step 5: Recommend remedial action to eliminate the problem without creating another problem.**

Based on the successful test that proved the hypothesis, the following remedial actions were taken:

- An evaluation was made to determine if the specification should be reduced from the existing 10 ppm to a lower level. Because of the high cost of the catalyst and the fact that operating at 10 ppm would cause the reaction rate to decrease from 100% of theoretical to about 80% of theoretical (see Fig. 10-3), it was concluded that the specification should be reduced to 1 ppm.
- Additional facilities were installed to allow reduction of the specification from 10 ppm to 1 ppm and to eliminate the occurrences of impurity upsets.
- A new, highly accurate continuous analyzer to monitor the reactor feed for CO<sub>2</sub> was installed.
- Contingency plans were developed for the possibility of a CO<sub>2</sub> upset. These plans included shutting down the reactor if the concentration reached such a high level that serious product quality problems would be encountered.

**Lessons Learned** While this problem might be considered an isolated example that has minimal application to the industrial world, it should be recognized that upsets do occur on a frequent basis. These upsets are often ignored because they are only short term. When they are considered, it is often with a minimal amount of data analysis and wrong conclusions are often reached.

In the real example problem, pursuing the presence of another impurity besides CO<sub>2</sub> would have been an easy trap to fall into because of the presence of previous experience and the persuasiveness of the proponent of the idea. However, it would have been the wrong route to pursue. It was only when data was developed and analyzed that it became obvious that the impurity upsets were associated with CO<sub>2</sub>. The problem also illustrates the value of quantitative data. The relationship between the concentration and reaction kinetics (Fig. 10-3) allowed determination of the optimum monomer impurity specification.

The problem illustrates the types of short cuts that can be taken in an industrial environment. While, theoretically, polymerization reaction kinetics involve several steps such as catalyst activation, polymerization initiation, polymerization propagation, and polymerization termination, there is no need to include all of these reactions. Essentially, all polymerization reactions can be modeled by simple first order kinetics with respect to the catalyst and monomer concentration. In addition, since in this specific problem the reactor volume is fixed, there is minimal need to include it in the kinetic relationship. What is important is the model to be used for the reaction of the impurity (fast response or slow response) and the reactor fluid flow (CSTR or plug flow). In this case, the problem description includes the idea that the impurity CO<sub>2</sub> reacts immediately as it enters the reactor and thus can be simulated with a fast response model. The problem description also indicated that the reactor was a CSTR.

The fact that the impurity concentration versus time relationship was simulated as a step change was a decision made by the problem solver. It would have been possible to simulate this as a sinusoidal relationship. However, it is doubtful that this would have improved the accuracy of the solution and it would have increased the complexity of the approach significantly.

## 10.4 FINAL WORDS

The primary purpose of this chapter is to illustrate the need to both have and apply techniques for the unsteady state. While it may be unlikely that the problem solver will have problems identical to the examples provided, it is a certainty that he will encounter problems that involve unsteady state. The engineering concept given in equation (10-1) is simple.

$$AD = I - O - RD \quad (10-1)$$

The techniques required to apply the equation are more complex. However, the problem solver must not be overcome by the complexity. Like all problems and/or projects, the complexity must be approached one step at a time. For example, questions must be asked such as what is the input; what is the output; and how can the reaction, addition, or removal of heat be estimated. The benefit of doing the work required to utilize the techniques described is that quantitative problem solutions are possible. For example, in Example Problem 10-1, it was possible to specify the rate of reactant addition based on the data analysis.

The two example problems are actual problems. The time pressures to develop solutions rapidly were present. But there was also a need to work the problem right the first time as opposed to using multiple “trial and error” attempts often characterized by the phrase “We have got to try something.”

## NOMENCLATURE

$A$	Heat transfer area, $\text{ft}^2$
$A_C$	Rate of accumulation of catalyst in the reactor, $\text{lb/hr}$
$AC$	Heat accumulation, $\text{BTU/hr}$
$AD$	Rate of accumulation. This could be accumulation of anything: level, heat, or reactant
$B$	Rate of $\text{CO}_2$ entering reactor, $\text{lb/hr}$
$C$	Catalyst concentration in the reactor, $\text{lb/ft}^3$
$C_f$	Concentration of catalyst in the reactor after an infinite amount of time, $\text{lb/ft}^3$
$C_i$	Catalyst concentration in the reactor at any point in time, $\text{lb/ft}^3$
$C_0$	Original catalyst concentration in the reactor, $\text{lb/ft}^3$

$C_p$	Average specific heat of material, BTU/lb-°F
$D_C$	Deactivation of catalyst, lb/hr
$dC/dt$	Rate of catalyst concentration change in lb/ft <sup>3</sup> -hr
$dT/dt$	Rate of temperature rise, °F/hr
$I$	Inflow of material or heat
$I_C$	Inflow of catalyst, lb/h
$k$	Polymerization kinetic rate constant including reactor volume, ft <sup>6</sup> /hr-lb
$M$	Monomer concentration in the reactor, lb/ft <sup>3</sup>
$O$	Outflow of material or heat
$O_C$	Outflow of catalyst, lb/hr
$R$	Rate of reaction. For the case of an instantaneous reaction, it is the rate of reactant addition, lb/hr. For a polymerization reactor it is the polymerization rate or monomer consumption rate, lb/hr.
$R_f$	Reactor production after an infinite amount of time
$R_i$	Reactor production at any point in time
$R_o$	Reactor production at time = 0
$RD$	Removal/addition of heat, or formation/destruction of material by reaction
$T$	The number of reactor displacements. This is simply the time after a step change divided by the average residence time.
$T_R$	Temperature of the reactor, °F
$T_C$	Minimum temperature of the coolant, °F
$t$	Elapsed time from the start of the upset to $C_i$
$U$	Heat transfer coefficient, BTU/hr-°F-ft <sup>2</sup>
$V$	Volume of the reactor, ft <sup>3</sup>
$W$	Weight of material (metal, water, reactants), lb
$Z$	Ratio of catalyst deactivated to CO <sub>2</sub> , lb/lb
$\Delta H_R$	Heat of reaction, BTU/lb