

APPLICATION TO KINETICALLY LIMITED PROCESSES

9.1 INTRODUCTION

A kinetically limited process is a process that does not go to completion because it is limited by the speed of mass or heat transfer. Completion can be defined as equilibrium or a state that would be reached if an infinite amount of time were available. Examples of this process are heat exchange, reaction, and diffusion-limited operations. Diffusion-limited processes are those that do not reach equilibrium because the material of interest cannot easily flow through a membrane or from the inner part of a particle to the surface.

The purpose of this chapter is to illustrate how the five-step approach to problem solving can be used to solve problems in this type of process. The chapter shows how a generalized approach can be used to develop theoretically sound working hypotheses for any kinetically limited process. The emphasis is on utilizing this approach in an industrial setting. Thus the more theoretical approach of using multiple constants has been replaced with an empirical “lumped parameter” approach. A specific example of this that most process engineers and operators are familiar with is the use of an overall heat transfer coefficient rather than individual film coefficients. In theory, the overall heat transfer coefficient can be derived from individual film coefficients. These

individual film coefficients are the coefficients for transferring heat from the fluid inside the tube to the tube wall, the coefficient for transferring heat across the thickness of the tube wall, and the coefficient for transferring heat from the outside tube wall to the process fluid flowing outside the tubes. The overall heat transfer coefficient can be calculated from these individual film coefficients. However, it can also be determined from vendor specification sheets or from plant test data when the exchanger is known to be clean. The overall coefficient determined in this fashion can be considered a “lumped parameter constant.”

9.2 KINETICALLY LIMITED MODELS

Any kinetically limited process can be described by the generalized equation shown below:

$$R = C \times DF \quad (9-1)$$

where

R = rate of change with time of the variable under study

C = a constant referred to as the “lumped parameter constant”

DF = driving force, or incentive for mass/heat transfer to occur

For a kinetically limited process, the lumped parameter constant C can be used for problem solving in multiple ways. The value of C can be determined on an hourly or daily basis and can be monitored as part of a daily monitoring system. Changes in C will be trigger points to start active problem solving. In addition, based on an estimated value of C , studies can be conducted to estimate the way changes in the driving force will impact the rate. This may allow process conditions to be modified to compensate for changes in C .

As indicated earlier, the heat transfer relationship shown below is the best known example of equation (9-1).

$$Q = U \times A \times \ln \Delta T \quad (9-2)$$

where

$Q = R$ = rate of heat transfer

$U \times A = C$ = lumped parameter or, for heat transfer, the heat transfer coefficient multiplied by the area

$\ln \Delta T = DF$ = driving force or, for heat transfer, the log mean temperature difference

The log mean temperature difference ($\ln \Delta T$) is an engineering relationship between the temperatures in a heat exchanger. It can be calculated using equation (9-3), shown below:

$$\ln \Delta T = (\Delta t_1 - \Delta t_2) / \ln(\Delta t_1 / \Delta t_2) \quad (9-3)$$

where

Δt_1 = temperature difference between the hot fluid and cold fluid on the inlet side of the heat exchanger

Δt_2 = temperature difference between the hot fluid and cold fluid on the outlet side of the heat exchanger

\ln = natural log

The driving force can also be approximated by the difference between the average of the hot side and cold side temperatures.

A more complicated form of equation (9-1) is encountered for reaction and diffusion-limited drying. The driving force in these cases is often related to the concentration of a molecule or the difference between the concentration and equilibrium concentration. For example, for diffusion-limited drying, equation (9-1) becomes:

$$dX/dt = K \times (X - X_e) \quad (9-4)$$

where

dX/dt = rate of removal of solvent from a polymer

K = lumped parameter constant which is somewhat related to diffusion (since it deals with mass transfer, it is also referenced in this chapter as a mass transfer coefficient)

$X - X_e$ = driving force

X = actual concentration of solvent in a polymer

X_e = concentration of solvent in the polymer in equilibrium with the vapor (at the same point in time as X)

Chemical reactions are generally "first order." This means that the reaction rate is proportional to the concentration of the reactants. For a simple reaction between two components where the reaction rate is first order, equation (9-1) becomes:

$$dX/dt = C_R \times X \times Y \quad (9-5)$$

where

dX/dt = rate of disappearance of component X

C_R = lumped parameter constant (reaction rate constant)

X = concentration of component X

Y = concentration of component Y

Relationships for other kinetically limited processes can be developed starting with equation (9-1). The key to using this equation for developing theoretically sound working hypotheses is the correct selection of the driving force and use of the “lumped parameter” constant.

The need to select the correct driving force can be illustrated by equation (9-4). The correct driving force is the difference between the actual and equilibrium concentration. If the equilibrium concentration is ignored, the constant determined from plant operating data will be lower than the actual amount. Another example where the use of the incorrect driving force will give improper constants is estimation of heat transfer constants in a fuel-fired furnace. Heat transfer from the flames and refractory surfaces to the metal tubes (primarily radiant heat) depends on the driving force for radiant heat transfer rather than convective heat transfer. Whereas the driving force for convective heat transfer is simply the log temperature difference, the driving force for radiant heat transfer is expressed as shown below:

$$DF_R = T_G^4 - T_M^4 \quad (9-6)$$

where

DF_R = driving force for radiant heat transfer

T_G = absolute temperature of gas, °R

T_M = absolute temperature of tube metal, °R

Lumped constant parameters that are developed from plant data are unreliable when used in large extrapolations. A lumped parameter constant that can be developed from fundamentals will always have a broader range of applicability. These constants that are developed from fundamentals can be used regardless of how close the operating conditions approach those under which the constant was determined.

However, some constants can be determined from fundamentals only by such an elaborate procedure that it becomes impractical for plant problem-solving activities. For example, in diffusion-related drying (equation 9-4), the lumped parameter constant or mass transfer coefficient depends on the diffusion rate through the polymer, the effective length of the flow path through the polymer particle, the actual particle surface area, and the mass transfer coefficients from the polymer surface to the bulk of the gas. Most polymer particles are irregularly shaped and have a large number of internal pores. This makes determination of items such as particle surface area and flow path through the particle difficult, if not impossible, to determine. If only one of these individual variables is not available and cannot be developed or deter-

mined, then utilizing a lumped parameter empirical constant (overall mass transfer coefficient) provides the only means to evaluate diffusion-related drying. This overall mass transfer coefficient can be determined from plant data, from pilot plant tests, or from bench scale tests.

9.3 LIMITATIONS TO THE LUMPED PARAMETER APPROACH

The lumped parameter approach has sometimes been referred to as a “black box” approach. This implies that the person using this approach does not understand the details of what is occurring inside the “black box.” For example, the use of an overall heat transfer coefficient does not take into account the individual film side coefficients, metal resistance, and fouling factors. However, in most process plant problem-solving activities, the significant observation is the change in the overall heat transfer coefficient. Whether the decrease of heat transfer coefficient is due to the tube- or shell-side film coefficient decrease can usually be determined based on experience. For example, the decrease in overall heat transfer coefficient for a fractionating tower overhead condenser that utilizes cooling tower water is almost always due to fouling on the cooling water side. Similar logic would apply to the use of the lumped parameter approach for problem solving with other kinetically limited processes.

The limitation of this approach is more severe when designing new facilities based on a lumped parameter coefficient determined from an operating plant. If a more fundamental analysis is not done, the lumped parameter approach can lead to design errors. An example of this is the design of a specialized vertical condenser for a new plant, based on a condenser in identical service in an existing plant. The condensation in this vertical condenser took place on the shell side and cooling water was utilized in the tubes. The new plant had a slightly higher capacity. To evaluate the overall heat transfer coefficient from pure fundamentals would have required an elaborate model that involved condensate thickness at various points in the vertical exchanger as well as the traditional resistances such as water side coefficient, condensing side coefficient, and metal resistance. Rather than do this highly theoretical analysis, however, the design team chose to utilize the overall heat transfer coefficient experienced in the existing plant. Based on the desire to minimize the overall height of the structure in the new plant, the height to diameter (H/D) ratio of the vertical condenser was reduced. In order to compensate for this reduced H/D ratio, the tube diameter and exchanger shell diameter were increased. No consideration was given to the effect of these increased diameters on the overall heat transfer coefficient. When the unit was started up, however, it was noticed that the heat transfer coefficient was 20% below anticipated values. This underscores the need for geometric similarity when basing a design on empirically developed constants.

In spite of the limitations, when considering plant-related problem solving, the utilization of an empirically derived lumped parameter constant along with

a theoretically correct driving force is almost always adequate, for the three reasons given below:

1. Daily monitoring of the process requires only an empirical constant.
2. Time is always critical. Laboratory or elaborate investigations to develop fundamental data are rarely appropriate.
3. If it is desirable to make operating changes, the new conditions are generally not extraordinarily different from current conditions. Thus there is minimal danger of extrapolation.

9.4 GUIDELINES FOR UTILIZATION OF THIS APPROACH FOR PLANT PROBLEM SOLVING

The “lumped parameter constant” approach for monitoring and solving plant problems is a powerful tool. However, like all tools, it must be used in an appropriate fashion. Some guidelines for using this tool are as follows:

1. Develop a meaningful driving force that is theoretically correct. It should be noted that there is often a difference between a driving force that appears logical and one that is theoretically correct. Logic cannot be substituted for the utilization of sound engineering fundamental knowledge. Without a meaningful driving force, the empirically developed lumped parameter constant will not be valid over any range of data.
2. Monitor this lumped parameter constant on a daily basis and over as wide a variety of conditions as possible. If the constant varies, look for correlations between the constant and independent variables that make theoretical sense. For example, a correlation between the lumped parameter constant in a diffusion-limited drying process and gas rates makes theoretical sense. The increased gas rate should increase the rate of mass transfer. If a lumped parameter constant varies with no process changes, it is an indication that an extraneous factor has caused a process deviation. If this extraneous factor can be eliminated, then the constant should return to normal. If this factor cannot be discovered or eliminated, then process changes will be required.
3. If it appears necessary to recommend a change in the driving force to increase the kinetically limited rate, minimize the length of the extrapolation that uses an empirically developed lumped parameter constant. That is, increasing a variable by 20–50% will likely be acceptable. But increasing the variable by 100% may make the approach based on the empirically developed lumped parameter constant invalid.

EXAMPLE PROBLEM 9-1

A polymer plant was experiencing problems in stripping the residual solvent from the polymer product. A counter flow agitated dryer with pure nitrogen sweep gas was utilized to strip the solvent. All operating conditions appeared to be normal. In addition, all instruments were checked and appeared to be accurate. A timeline indicated that the problem seemed have begun when a new catalyst was introduced into the process for a plant test. Even though the utilization of the new catalyst was considered a test, it was mandatory that the plant be switched to this new catalyst as soon as possible. One of the key advantages of the new catalyst was the higher bulk density product that could be produced with the catalyst. This had been well demonstrated in pilot plant studies. No drying studies had been conducted in the pilot plant. Drying capability was thought to be associated with sweep gas rate, residence time, and temperatures, all of which were not changed when the plant was switched to the new catalyst.

The problem solver was asked to determine what could be done to reduce the solvent levels to the previous concentrations while continuing to operate with the new catalyst. Operating conditions were as in Table 9-1.

In addition to the plant data shown above, laboratory results indicated that the equilibrium relationships for polymers produced with the old and new catalysts were identical and could be expressed as shown below:

$$X_E = 295,000 \times (Y \times \pi / VP)^{1.5} \quad (9-7)$$

where

X_E = equilibrium concentration of solvent in polymer

Y = concentration of the solvent in the vapor phase

Π = total pressure on the system

VP = vapor pressure of the solvent at the dryer temperature

Table 9-1 Operating conditions with old and new catalyst

	Old Catalyst	New Catalyst
Polymer rate, lb/hr	20,000	20,000
Polymer density, lb/ft ³	25	28
Pure nitrogen sweep gas rate, lb/hr	1000	1000
Dryer temperature (isothermal), °F	200	200
Hexane vapor pressure, psia	28.7	28.7
Dryer pressure, psia	15	15
Inlet hexane content, ppm	1000	1000
Outlet hexane content, ppm	25	75

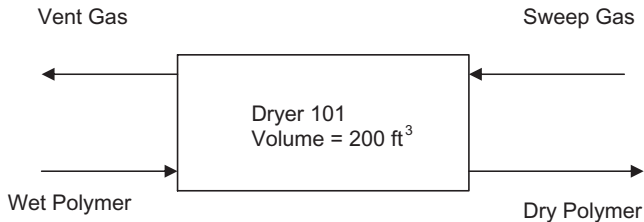


Figure 9-1 Schematic sketch of dryer.

A schematic sketch of the dryer is shown in Figure 9-1.

The problem solver began working on the problem using the five-step problem-solving approach. There was minimal need to verify that the problem had actually occurred. However, he did not skip this step.

Step 1: Verify that the problem actually occurred.

The problem solver confirmed that all of the meters were correct and that the hexane content was indeed three times the normal levels.

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

He wrote out the following problem statement.

The polymer leaving Dryer 101 contains excessive amounts of solvent. This condition started soon after the introduction of a new catalyst to the polymerization reactors. All operating conditions are normal and the instrumentation is correct. It is desirable to use the catalyst throughout the plant as soon as possible. Determine what operating condition changes or what new equipment is required to achieve 25 ppm hexane in the final product at the normal polymer production rate.

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

Referring back to the list of questions given in Chapter 6 was helpful in formulating possible hypotheses. The problem solver reviewed these questions and formulated appropriate comments for this example problem, as shown in Table 9-2.

As might be expected, these questions pointed strongly to the idea that the problem began when the new catalyst was introduced to the process. They also provided some possible explanation for why the new catalyst would cause a

Table 9-2 Questions/comments for Problem 9-1

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.
Are laboratory results correct?	Yes.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	New catalyst was started.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain problem?	Not applicable.
Is the reaction rate as anticipated?	The new catalyst might cause the polymer particles to be less porous. This would cause a lower than anticipated "mass transfer coefficient."
Are there adverse reactions occurring?	See above.
Were there errors made in the construction?	Not applicable.

drying problem to occur. It was theorized that the new catalyst created a less porous particle. The lower porosity would slow the diffusion of the solvent through the particle. This less porous particle would also have a higher particle density, which would explain the higher bulk density. It should be noted that if this list of questions were not utilized, the change in catalyst would have been pinpointed as the cause, but the explanation of the formation of a less porous polymer particle might have been missed.

As indicated in equation (9-4), the relationship between rate of drying and driving force for a diffusion-limited drying process can be expressed as follows:

$$dX/dt = K \times (X - X_c) \quad (9-4)$$

Since the problem statement indicates that all operating conditions were normal and laboratory results indicated that the equilibrium relationship for both catalysts was the same, there must be a difference in the K values between the two catalysts.

While a working hypothesis that the K value has changed is a perfectly valid hypothesis, it does not help determine what the next step should be because it does not specify the magnitude of the change. If the magnitude of the change is not known, it will be impossible to determine if operational changes or addition of new equipment will be required to allow operation with the new

catalyst. Thus the theoretically sound working hypothesis must include an estimate of the magnitude of the change in the mass transfer coefficient (K value).

While it is beyond the scope of this book to discuss integral calculus, the value of K can be estimated by simple integration using the rules of integral calculus, if X_e (the equilibrium concentration of solvent in the polymer) is equal to zero. In this special case, integration yields the following:

$$X_t/X_o = e^{-Kt} \quad (9-8)$$

where

- X_t = concentration of solvent in the outlet polymer
- X_o = concentration of solvent in the inlet polymer
- K = rate constant or mass transfer coefficient, 1/min
- t = amount of time in the dryer, min

For the general case where X_e is not equal to zero, numerical integration must be used to determine the unknown variable. Numerical integration is a mathematical technique that involves calculating a variable over a small segment of a fixed size piece of equipment. The values for each of the small segments can then be added to give the final answer.

This numerical integration can be used to determine the mass transfer coefficient (K) or the outlet concentration of solvent in the polymer (X_t). This numerical integration can be developed by visualizing a dryer segment as shown in Figure 9-2. The equilibrium concentration in Figure 9-2 can be determined by a Henry's Law-type relationship, as shown below:

$$X_e = C_E \times Y \quad (9-9)$$

where

- C_E = a constant determined from experimental data or application of theoretical principles
- Y = vapor phase composition at any point in the dryer

For the example problem, the equilibrium relationship shown in equation (9-7) can be utilized in place of that shown in equation (9-9) to determine the equilibrium concentration based on the vapor phase concentration.

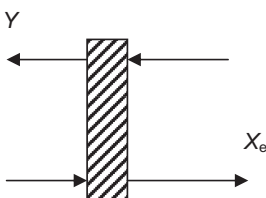


Figure 9-2 Dryer calculation segment.

In order to use numerical integration, equation (9-4) must be transformed as shown below. This will be the technique used when X_e is not equal to zero.

$$dX/dt = K \times (X - X_e) \quad (9-4)$$

$$dX/(X - X_e) = K \times dt \quad (9-10)$$

By integral calculus:

$$\int dX/(X - X_e) = Kt \quad (9-11)$$

For this problem, it is desired to obtain the K value for each catalyst system. The term $\int dX/(X - X_e)$ must be developed by splitting the dryer into several small sections as described in Figure 9-2 and determining the value of $dX/(X - X_e)$ for each segment. The value of the left hand side of equation (9-11) will then be the sum of the values for each segment. To determine the K value from this relationship using numerical integration requires the following steps using the data given above and a spread sheet:

1. Use values of the polymer and gas rates along with the inlet and outlet hexane concentrations in the polymer to determine the concentration of hexane in the outlet gas. Note that the data indicated that pure nitrogen was used as the sweep gas. The material balance concepts discussed in Chapter 5 will be used in this step.
2. Calculate the total residence time in the dryer assuming no "back-mixing" takes place. The assumption of no back mixing is equivalent to assuming that each polymer particle has the exact same residence time in the dryer. While this is highly idealistic, the K value will take the presence of back mixing into account. The residence time can be calculated by dividing the polymer holdup in the dryer by the polymer rate. The polymer holdup in the dryer is often specified by the dryer vendor or can be calculated if the polymer level in the dryer is known.
3. Split the dryer into several segments (100 to 500) and calculate the dX for each segment. The change in the volatiles concentration (dX) will simply be the total change in volatiles concentration divided by the number of dryer segments. The time increment (dt) can be determined in a similar fashion.
4. From the relationship given in equation (9-7) and the outlet vapor composition, calculate the X_e of the polymer leaving the first segment.
5. Since this segment represents only an exceptionally small part of the dryer, the actual solvent concentration (X) can be considered constant throughout this segment. For this small segment:

$$(Kdt)_i = dX/(X - X_e) \quad (9-12)$$

In equation (9-12), the term $(Kdt)_i$ is simply the product of the lumped parameter drying constant (mass transfer coefficient) and the residence time

in the small segment. The lumped parameter drying constant is assumed to be the same in all segments.

6. Using dx , the gas and polymer rates, and the gas concentration leaving the first segment, calculate the gas concentration entering the segment by a material balance around the segment. This will be the gas concentration leaving the next segment.
7. Continue this process until the same calculations have been made for each segment. Then K can be calculated as follows:

$$K = \xi (Kt)_i / t \quad (9-13)$$

That is, the overall K can be determined by summing up the Kt term from each segment as calculated from equation (9-12) and dividing the sum by the total residence time.

When the problem solver performed these calculations for the two cases described earlier, the following values of K were obtained as shown in Table 9-3. Extensive data was available from computer archives so that the value of K over the period of interest could be evaluated. When this was done, Figure 9-3 clearly showed that the mass transfer coefficient decreased when the new catalyst was introduced into the system.

Table 9-3 Results of numerical integration

Catalyst	K value, 1/min
Old	0.25
New	0.16

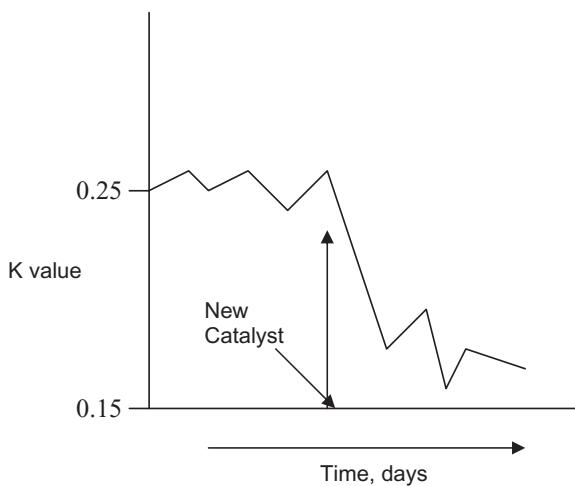


Figure 9-3 K value vs. time.

A theoretically sound working hypothesis that fits the data would be:

The recent loss of drying capability is associated with a decrease in the mass transfer coefficient (K) that occurred when the change to the new catalyst occurred. It is believed that this change is due to the lower porosity of the polymer particle produced with this catalyst. Evidence that supports this is the 35% lower K value and the higher bulk density.

Step 4: Provide a mechanism to test the hypothesis.

At this point, the problem solver gave consideration to the question of “optimum technical depth.” Several alternatives were available to test the hypothesis. The optimum alternative depended on the cost of the solution, the confidence level required and the cost of continuing poor drying performance. In this polymer process, the customer specifications and/or needs were considered more important than operating at full capacity. Thus, in this case, the cost of the poor drying performance was the lost profits associated with operating at lower than design production rates. Alternatives for testing the hypothesis that were considered were:

- Conducting a test run using the old catalyst to confirm that the old catalyst really had a K value higher than the new catalyst.
- Using the K value for the new catalyst to estimate what changes in operating conditions would be required to reduce the hexane concentration from 75 ppm to 25 ppm.
- Modifying the new catalyst so that it produced a polymer similar to that produced by the old catalyst.

In order to determine if operating conditions could be modified to reduce the amount of hexane to 25 ppm, the problem solver made calculations using the approach described earlier. However, in these calculations, the K value was known to be 0.161/min. The value to be estimated was the outlet solvent concentration. The same spread sheet and approach was used. The problem solver changed the operating variables as desired and then varied the outlet solvent concentration in the polymer until the calculations based on the spread sheet indicated a K value of 0.161/min. Based on the calculations, he concluded that increasing the sweep gas by a factor of 10 (1000 lb/hr to 10,000 lb/hr) would reduce the hexane content from 75 to 65 ppm. This was obviously not a valid approach. The calculations also indicated that if the residence time in the dryer were increased from 17 min to 24 min, the hexane concentration would be reduced to 25 ppm. This could be accomplished in a plant test by reducing the polymer production rate to 14,000 lb/hr. The volumetric holdup in the dryer was constant, so the only way to increase residence time was to reduce the production rate. The calculations also indicated that the approach of increasing the dryer temperature was not a fruitful route to improved

performance. They showed that if the dryer temperature were increased from 200°F to 225°F, at the same residence time and sweep gas rate, the hexane concentration would decrease from 75 to 65 ppm.

From these calculations, it was obvious that the only valid test of plant operating conditions was to reduce the polymer production rate from 20,000 to 14,000 lb/hr. The plant test of operating at reduced rates was the preferred test compared to a plant test of using the old catalyst, since it would be quicker. Introducing the old catalyst into the reactors would require significant residence time to completely displace the new catalyst from the entire system prior to the dryer. In addition, it was mandatory to continue to use the new catalyst. The plant test of returning to the old catalyst just confirms that the new catalyst is responsible for the problem. A plant test of increasing the dryer residence time by reducing the production to 14,000 lb/hr was successful at reducing the hexane content from 75 ppm to 25 ppm. The K value did not change as the residence time was increased.

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

Since the plant test of operating at reduced rates was successful and a study of changing the catalyst to produce a more porous structure indicated that other desirable catalyst attributes would be lost if the porosity was changed, it was decided to add an additional dryer. This additional dryer would provide the necessary residence time. Since the dryer addition would take several months, it was decided to return to using the old catalyst in the interim. When use of the old catalyst resumed, the mass transfer coefficient increased from 0.16 1/min to the previous value of 0.25 1/min.

Lessons Learned If daily monitoring of the K value had been done, it would have been possible to determine immediately that there was likely a drying problem associated with the new catalyst. As often happens in a plant test, there is only a minimal potential problem analysis conducted prior to the test. This often leads to a panicky approach to problem solving. Chapter 12 discusses approaches for conducting successful plant tests.

If drying problems had been anticipated prior to the plant test of the new catalyst, it would have been possible to use laboratory techniques to determine the magnitude of the difference in mass transfer coefficients. An apparatus such as a thermal gravimetric analyzer (TGA) could have been used to determine the mass transfer coefficient for polymer produced with both catalyst systems. While the exact absolute values of the mass transfer coefficient determined in this fashion may not have been the same as those in the plant, the relative values would have been accurate. That is, the TGA would have predicted that the mass transfer coefficient (K) would have been 35% lower with the new catalyst.

The model of the dryer that was developed is a good example of a simple but valuable tool for doing process analysis work. The driving force of the actual concentration less the equilibrium concentration ($X - X_e$) is theoretically correct and easy to determine. Experimental relationships such as equation (9-7) may not be available. However, there are calculation methods available to approximate the relationship between the vapor phase concentration of the solvent and the concentration of solvent in the solid. One of these techniques is discussed in Chapter 13. The mass transfer coefficient can be determined from plant data. It is subject to error if there is a significant change in the polymer morphology. For example, when the catalyst was changed, the mass transfer coefficient changed. However, it did not change when the production rate was reduced.

The calculations that were done to estimate the impact of changing plant operating conditions were performed very quickly once the spreadsheet described above was completed. The more expensive alternative of running multiple plant trials to test any reasonable hypothesis would have taken much more time and been much more expensive.

EXAMPLE PROBLEM 9-2

Several of the tube metal temperature indicators in an operating furnace were indicating considerably higher temperatures than anticipated when compared to historical values. Operations personnel were not concerned since this furnace was operating at normal heat duties and normal process fluid temperatures, and the furnace had never shown any tendency to foul. Fouling often occurs inside the tubes of an operating furnace as the high temperature of the tubes causes the material in the tubes to decompose and deposit a thin layer of fouling material on the tube surface. This reduces the heat transfer coefficient and results in the tube temperatures becoming even hotter. The operators concluded that the tube metal temperature indicators must have failed due to the harsh furnace environment. The problem solver did not believe that all of the tube metal indicators could have failed. A schematic diagram of this problem is shown in Figure 9-4.

The current operating data and the historical operating data are shown in Table 9-4. There was no other data available in the computer archives. Even though this problem was discovered by the problem solver rather than being delivered to him by a request from operations management, it is still a valid problem that can be approached using the five-step procedure. Because of the belief of operations personnel that there was not really any problem, step 1 had to be approached in a different fashion than it has been in problems described previously.

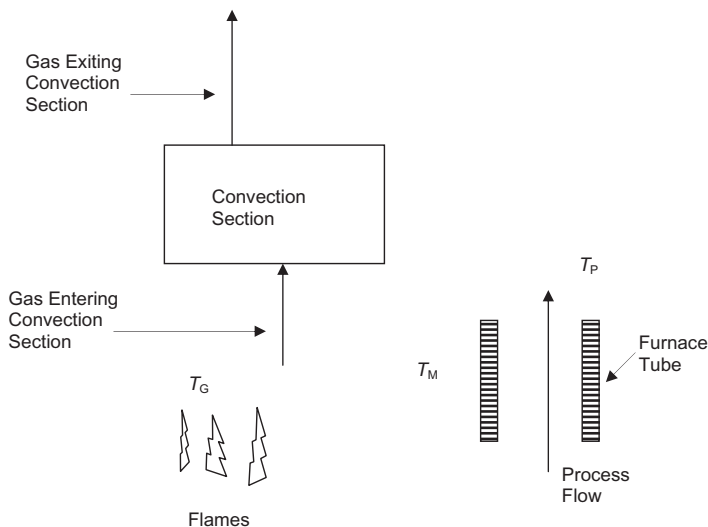


Figure 9-4 Furnace schematic. T_G , gas temperature; T_M , tube metal temperature; T_P , process temperature.

Table 9-4 Furnace data

	Historical	Current
Tube metal temperature, °F	600 to 650	750 to 900
Gas temperatures		
Entering convection section, °F	1200	1300
Leaving convection section, °F	650	700
Excess oxygen, %	15	15
Heat absorbed, MBTU/hr	80	80
Circulation to furnace k-lb/hr	700	700

Step 1: Verify that the problem actually occurred.

Step 1 required that careful examination be given to operation management's contention that there was really no problem with the indicated high tube metal temperatures. It was important that the problem solver convince himself as well as the operations personnel that there was a problem. If operations personnel were going to be expected to cooperate on any plant tests, they needed to be convinced that there was a problem. One of the first things that the problem solver had to do was understand how the tube metal temperature indicators were designed and installed. These thermocouples are different from normal ones in that they must measure the temperature of the furnace tube without being impacted by the radiant heat from the furnace flames. The problem solver obtained information from both instrument technicians and instrument engineers to make sure that he understood the technology of tube

metal temperature indicators. Once he understood this technology, he recognized that while tube metal temperature indicators do fail, they almost always fail in such a fashion that the failure is obvious. That is, they read ridiculously high or low temperatures. Failed tube metal temperature indicators will normally have “up scale burnout,” that is, they will read ridiculously high. He also recognized that if fouling had occurred on the inside of the tube, there would be other indications of fouling besides elevated tube metal temperatures. The problem solver decided to investigate whether there were other indications of fouling. He used the basic equation shown below to describe the radiant heat transfer that is occurring in the furnace:

$$Q = C_1 \times (T_G^4 - T_M^4) = C_2 \times (T_M - T_P) \quad (9-14)$$

where

Q = heat transferred to the process (this is equal to the heat transferred from the gas flame by radiation. In addition, it must also be equal to the heat transferred through the tube to the process fluid)

T_G = absolute temperature of the gas in the radiant section of the furnace

T_M = absolute temperature of the tube metal

T_P = absolute temperature of the process fluid in the tubes

C_1 = a constant that is related to the type of flame (should not change unless the type of fuel changes)

C_2 = product of the heat transfer coefficient and the area of the tubes (will only change if the heat transfer coefficient changes)

In equation (9-14), two different kinds of heat transfer are represented. Radiant heat transfer is the type of heat that is transferred through any type of fluid. It does not depend on the two bodies touching each other (conductive heat transfer) or on flow patterns (convective heat transfer). It is proportional to the difference in the absolute temperature of the hot source and the cold receiver, each raised to the fourth power. The warming impact of sunlight is an example of radiant heat transfer. Convection and conduction depend on the difference in temperature in either absolute or conventional units. As shown in this equation, the radiant heat transferred from the flame to the tube must equal the convective heat transferred from the tube to the process fluid.

From equation (9-14), the problem solver noted that if the tube metal temperature (T_M) increases at constant heat duty (Q), it must be due to a decrease in the convective heat transfer coefficient, since the area of the tubes will not change. This decrease in heat transfer coefficient could be caused by a change in fluid circulation rate or tube fouling. Since the process flow rate to the furnace is constant, the decrease in heat transfer coefficient is likely due to tube fouling. In order to achieve the same heat duty at the higher tube metal temperature, the gas temperature (T_G) must also increase so that the radiant heat transferred equals the convective heat transferred. Thus the increased gas

temperature shown in Table 9-4 was confirmation that the tube metal temperature had increased. A secondary confirmation was the higher-than-normal gas temperature leaving the convection section, also shown in Table 9-4. The higher-temperature gas entering the convection from the radiant section would not be cooled to as low a temperature as historical data would indicate since the heat transfer area in the convection section was fixed. Using this logic, the problem solver convinced the operations management that there might be a fouling problem in the furnace tubes.

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

An accurate statement of the furnace problem is as follows:

Tube metal temperatures on the process furnace indicate that the tubes are partially fouled with deposits. Since a furnace shutdown to inspect and possibly replace the tubes will require a plant shutdown, a detailed investigation was undertaken to confirm that the tube metal temperatures are higher than normal. This investigation indicated that the tubes are very likely fouled. There is no archived data to indicate when the fouling began or if it was a gradual fouling or a one-time event. While there is strong evidence that the furnace tubes are partially fouled, it is desirable to provide operations management with further evidence that the furnace is fouling and determine what steps should be taken to avoid a tube failure with a subsequent furnace fire. In addition, it will be necessary to determine why the tubes in this furnace are fouling when, based on operation personnel's memory, this has never happened in the past.

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

In this example problem, step 3 is different than it has been in previous problems. The gist is to convince operations that a problem exists with the furnace. As discussed earlier, the logic path that was developed was partially successful in convincing operations management that there really was a fouling problem. In addition to this, consideration was given to alternative means to measure the tube metal temperatures. One possibility was to use infra-red temperature measurements through a furnace peephole. Besides confirming the tube metal temperature measurements, this would also allow determination of where the hottest points were. The measurements based on tube metal temperature indicators are only single points in a few tubes; a much hotter point might exist in another location. An infra-red scan was conducted on the furnace tubes. The thermocouples were verified and even higher temperatures were discovered at spots where no tube metal indicators existed.

The furnace history was considered by asking such questions as:

- When did the fouling begin?
- Did it coincide with an upset of a magnitude never before experienced?

Table 9-5 Questions/comments for Problem 9-2

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.
Are laboratory results correct?	Not applicable.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	No.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain problem?	Fouling of tubes.
Is the reaction rate as anticipated?	Not applicable .
Are there adverse reactions occurring?	Fouling is caused by reaction to produce coke. This reaction might be catalyzed by material present in the process. The fouling rate seems much higher than it was in previous experience.
Were there errors made in the construction?	Not applicable. It had been 36 months since mechanical work was done on furnace.

- Has the furnace been operating for a longer continuous period than it was in previous experience?

In addition to these questions, the questions from Chapter 6 were used to help develop a working hypothesis.

The following was developed as a working hypothesis:

The higher-than-normal tube metal temperatures in the furnace appear to be correct based on both gas temperatures and an examination of the instrument specifications which indicates that the thermocouples are ‘up-scale burnout’ (if they fail their readings will be ridiculously high). In addition, an infra-red scan indicates that these thermocouple measurements are correct and that there are even higher temperatures on other tubes. A review of the furnace history indicates that the current run (36 months without water washing the tubes) is nearly twice the length of previous periods of operation. Historically, the furnace tubes were water washed at every 18 month furnace inspection downtime. However, they were not water washed at the last downtime because it was expedient to get the furnace back in service. It is believed that this water washing removes the fouling material before it becomes thick enough to impact the furnace operation. The fouling is believed to be initiated by process catalyst residue that is entrained during process upsets.

Step 4: Provide a mechanism to test the hypothesis.

In this case, because of the risk of a tube failure, the only mechanism was to shutdown the furnace and water wash and inspect the tubes. The downtime was timed to coincide with a period of reduced product demand so that the lost revenue was minimized. An inspection of the tubes indicated that many were approaching the point of incipient failure. If the tube metal temperatures had been ignored (as proposed by operating personnel), it is highly likely that a furnace fire would have occurred. This not only would have caused serious damage to the furnace, but is likely to have occurred at a time when full production rate was required.

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

Three remedial actions were recommended. The first was to carefully monitor the tube metal temperatures during the interim period between the discovery of the problem and the furnace shutdown. This allowed for a controlled plant shutdown to replace furnace tubes rather than an emergency shutdown during a period of high product demand. The second was to water wash the furnace tubes every 18 months. The third recommendation was to monitor the C_2 value as determined from equation (9-14) on a daily basis. This would provide information on how the fouling occurred. It could have been a one-time event that caused a sudden decrease in the value, or a slow continuous decrease.

Lessons Learned This problem illustrates the value of a careful analysis of all operating data as opposed to only working on problems that operations or mechanical personnel consider to be important. The initial reaction of operations personnel to ignore the high tube metal temperature indicators was carefully considered as part of step 1. In addition, the actions of the problem solver to understand the technology of tube metal thermocouples was consistent with the principle of knowing the technology before trying to solve problems.

This problem also illustrates the fact that historical data is of great value in solving problems. However, conclusions (e.g., the furnace tubes never foul) based on historical data or memories that are not well supported are counter-productive. In this case, all of the current data indicated that the furnace tubes were indeed fouled. Thus it was apparent that the conclusion based on memories and/or historical data that indicated the tubes could not be fouled was in error. It is also likely that the tubes had been fouling in the past, but because the C_2 value was not being monitored, the fouling went undetected. The fouling material was likely removed every 18 months when the tubes were water washed.

If the problem solver had not been aggressive to the point of creating tension, it is likely that a furnace tube failure with a subsequent furnace fire would have occurred.

EXAMPLE PROBLEM 9-3

A plant that produced and shipped a polyolefin polymer in railroad hopper cars was contacted by a TV station with a video of one of their hopper cars on fire. These hopper cars were loaded at the manufacturing plant by discharging pellet storage bins directly into the closed hopper cars. While the hopper cars were closed to protect the product from the elements (rain, sunshine, wind, debris, etc.) there were vents in the front and back of the each car. Thus the vapor space in the hopper car was essentially air at the ambient conditions plus any hydrocarbon that evolved from the polymer.

When the company public relations contact appeared on the TV station to discuss the hopper car fire, he indicated that the particular polymer was not flammable and that could not have possibly caught on fire without some external source such as sabotage or excessive heat generated by a mechanical failure or malfunctioning of the hopper car equipment.

Unfortunately, shortly after this occasion, several other hopper cars arrived at different customers with blackened vapor vents and some charred polymer, indicating that there had been a fire of a limited magnitude during transportation. The material that was being shipped in the hopper cars was in the form of small pellets that had been extruded after being produced in the polymerization section. The polymerization section stripped the solvent and unreacted monomer from the polymer at a temperature of 220°F and a dryer residence time of 30 min. In addition, during the extrusion operation, the polymer was heated in the extruder to 550°F before being pelletized and cooled in a water bath. It seemed very unlikely that there could be sufficient residual monomer or solvent that would create a fire. In addition, operations personnel knew that when the hopper cars were loaded, they could see a great deal of static electricity being discharged inside the hopper car. They reasoned that if there was an explosive atmosphere inside the hopper car, it would be ignited during the loading operation. They believed that the maximum concentration of hydrocarbons in the vapor space would occur during loading, and during transit the vents would create a sweep of air through the vapor space, reducing the concentration of hydrocarbons.

However, because of the multiple indications of fires in the hopper cars transporting the polymer, the operations personnel requested that a technical evaluation be made of what was causing the hopper car fires.

The problem solver used the five-step procedure to methodically develop a problem solution as described in the following paragraphs.

Step 1: Verify that the problem actually occurred.

There was no doubt that something unusual had happened. The problem solver decided that he needed to know what product had been loaded into the hopper cars that experienced the major fire and evidence of minor fires. When he investigated the loading records, he found that all of the unusual incidents

had occurred when a specific product (experimental product X3) was being produced and loaded into the hopper cars. However, not all hopper cars loaded with this product showed evidence of flash fires. He recognized that this product was one that had to be produced at reduced rates to ensure that the volatiles (unreacted monomer and solvent) were adequately stripped. He knew that rates had recently been increased by modifications to the operating procedures and directives.

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

The problem solver wrote out the following problem statement:

There are indications that flash fires are occurring in some of the railroad hopper cars loaded with experimental product X3. The evidence of these flash fires was noticed after the recently instituted operating procedures and directives were put into use. While the actual damage was minimal, there was a great deal of customer dissatisfaction. Determine the cause of the flash fires. This analysis should include the observation that not all hopper cars loaded with this product showed signs of a fire. Once the cause has been determined, provide recommendations for eliminating the flash fires. In addition, any recommendations should provide for shipping a product that meets Department of Transportation (DOT) regulations.

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

In addition to the observations described above, the questions from Chapter 6 were used to help develop a working hypothesis. These questions are shown in Table 9-6.

After reviewing the data and the questions, three possible hypotheses were developed as follows:

1. The new operating directives and procedures were causing excess quantities of unreacted monomer or solvent to be left in the polymer, which then accumulated in the hopper car and formed an explosive mixture. This mixture could then be ignited by an undefined ignition source.
2. There were changes in the catalyst which now resulted in a less porous polymer particle. Thus the temperature and residence time that were previously used successfully in a plant test to demonstrate the new procedures for X3 were no longer adequate. Again, if this happened, it was theorized that the excessive quantities of solvent and unreacted monomer accumulated in the hopper car and formed an explosive mixture.

Table 9-6 Questions/comments for Problem 9-3

Question	Comment
Are all operating directives and procedures correct and being followed?	All were being followed. However, there had been recent changes to the directives and procedures. Some of these appeared highly questionable.
Are all instruments correct?	The instruments used to monitor the stripping operation were calibrated weekly.
Are laboratory results correct?	The volatiles results were not routinely measured. It was believed that maintaining adequate temperature was all that was required to maintain volatiles control.
Were there any errors made in the original design?	Not applicable.
Were there changes in operating conditions?	Yes. See above.
Is fluid leakage occurring?	Not applicable.
Has there been mechanical wear that would explain problem?	Not applicable.
Is the reaction rate as anticipated?	Not applicable
Are there adverse reactions occurring?	Unknown changes in the catalyst might create a polymer with a less porous structure that would make volatiles removal more difficult. This could be detected by bulk density measurements. In addition, the polymer might be decomposing in the extruder forming volatile materials.
Were there errors made in the construction?	Not applicable.

- There was a change in the adequacy of stabilization so that the polymer decomposed in the extruder. This decomposition resulted in the formation of volatile materials which then did not vent out of the extruder because of the short residence time. They were trapped in the pellet and were carried into the hopper car where they evolved from the pellet and accumulated and formed an explosive mixture.

It was clear, after considering these three hypotheses, that all of them had a common thread. The common thread was twofold. In the first place, the hydrocarbons (solvent and unreacted monomer) had to build up to the point of forming an explosive mixture. The second aspect of this hypothesis was that the explosive mixture was ignited by an ignition source. This ignition source

could have been something dramatic, like a lightning strike, or something as common place as static electricity. The movement of pellets in the hopper car while it was in transit could generate sufficient static electricity to create an ignition source. This would be particularly true if the relative humidity of the air in the vapor space was very low. The problem solver used the traditional process engineering safety assumption: When dealing with an explosive mixture, an ignition source will always be found if the mixture is in the explosive range for a sufficient amount of time. Thus he only considered which hypothesis should be investigated for how an explosive mixture formed. All of the three hypotheses required that the gases accumulate in the vapor space to form an explosive mixture. The first question that the problem solver had to answer was “How much hydrocarbon had to be left in the polymer for an explosive mixture to form in the vapor space of the hopper car?”

It was necessary to develop some basic data before the problem solver could begin to assess this question. The data that he developed is shown in Table 9-7.

In order to test the hydrocarbon accumulation hypothesis, the following calculations were done to determine how much hydrocarbon would be left in the polymer entering the hopper car for an explosive mixture to accumulate in the hopper car vapor space. These calculations assumed that the polymer had been in the hopper car for such an extended period of time that equilibrium between the vapor space and the polymer was reached. The calculations also ignore the purging of the vapor space that might occur as the hopper car traveled to the customer. As such, they represent the worst case scenario. However, the case might occur if the hopper car sat stationary on the railroad track for an extended period of time with a minimal amount of wind. It was

Table 9-7 Data for evaluation

Item	Value
Hopper car capacity, lb of polymer	180000
Hopper car fill volume, %	70
Bulk density of the polymer, lb/ft ³	25
Skeletal ^a density of the polymer, lb/ft ³	56
Vapor pressure of monomer at 100°F, psia	220
Molecular weight of monomer	42
Explosive range of monomer, ^b volume %	
Lower (LEL)	2
Upper (UEL)	11

^aSkeletal density is the density of the polymer if the particle had no voids.

^bSince essentially the entire hydrocarbon was unreacted monomer, no consideration was given to the solvent. In addition, it should be noted that, for gases, the volume % and mol % are identical.

assumed that the equilibrium relationship given in equation (9-7), below, was applicable for this polymer. In addition to the equilibrium relationship, material balance relationships are given in equations (9-15) to (9-18). These relationships can be used to determine the residual pounds of monomer that would be required for the vapor space to be at the lower explosive limit of 2%.

$$X_E = 295,000 \times (Y \times \pi / VP)^{1.5} \tag{9-7}$$

$$F = V + S \tag{9-15}$$

where

F = total monomer in the hopper car, lb

V = monomer in vapor space, lb

S = monomer remaining in polymer at 100°F, lb

$$\begin{aligned} T &= Ca \times 100 / (BD \times FV) \\ &= 180,000 \times 100 / (25 \times 70) = 10285 \text{ ft}^3 \end{aligned} \tag{9-16}$$

$$\begin{aligned} VT &= T - Ca / SD \\ &= 10285 - 180,000 / 56 = 7070 \text{ ft}^3 \end{aligned} \tag{9-17}$$

where

T = total volume of hopper car, ft³

Ca = polymer capacity of hopper car, lb

BD = bulk density of polymer, lb/ft³

FV = volume of hopper car filled with polymer, %

VT = vapor volume of hopper car, ft³

SD = skeletal density of polymer, lb/ft³

Note that *VT* includes the volume associated with the pores in the polymer.

$$\begin{aligned} D &= MWM \times 520 / (379 \times (460 + 100)) \\ &= 42 \times 520 / (379 \times 560) = 0.1029 \text{ lb/ft}^3 \end{aligned} \tag{9-18}$$

where

D = density of monomer gas, lb/ft³

MWM = molecular weight of the monomer

$$\begin{aligned} V &= LEL \times D \times VT / 100 \\ &= 2 \times 0.1029 \times 7070 / 100 = 14.55 \text{ lb} \end{aligned}$$

$$\begin{aligned} X_E &= 295,000 \times (Y \times \pi / VP)^{1.5} \\ &= 295,000 \times (0.02 \times 14.7 / 220)^{1.5} = 14.4 \text{ ppm} \end{aligned} \tag{9-7}$$

$$\begin{aligned}
 F &= V + S \\
 &= 14.55 + 14.4 \times 180000 / 1,000,000 = 17.14 \text{ lb} \\
 &= 17.14 \times 1,000,000 / 180,000 = 95 \text{ ppm of monomer in the incoming polymer} \\
 &\hspace{15em} (9-15)
 \end{aligned}$$

Thus if the polymer going to the hopper contained more than 95 ppm of monomer, the vapor space could well be equal to or above the lower explosive limit (LEL).

The problem solver investigated the current operating directives and procedures and their bases. When he did this investigation, he found that the approach to setting the new directives and procedures had been strictly empirical with no consideration to the theory and time elements of diffusion. A test run had been conducted by establishing the new conditions and rates in the polymerization and extrusion sections. When the conditions were well established, samples downstream of the extrusion and pelletizing operations were collected in an open mouth container. A conventional gas explosivity analyzer was inserted into the container immediately after the sample was collected and the percentage LEL was measured. The explosivity analyzer gives a reading of the percentage LEL. For example, if the vapor space was at the LEL, the analyzer would read 100%. Thus percentage LEL is a measure of the approach to the lower explosion limit.

In this test of X3, it was believed that measuring the vapor space immediately would give the highest value, since the monomer in the vapor phase of the open container would not have time to diffuse into the surrounding air. A single measurement was made and since the percentage LEL was less than 100%, it was concluded that the new conditions and rates would produce a product that would satisfy the DOT regulations. These regulations stated that the vapor space of products shipped in hopper cars should be below the LEL. Obviously, if the vapor space in the hopper car was below the LEL, it would not ignite.

In addition, the problem solver reviewed the bulk density measurements. The experimental polymer (X3) actually had a slightly lower bulk density than the normal polyolefin products. Thus it appeared that the product would be more porous than the conventional product. He also reviewed the current stabilizer and found that it was the same that had been in use for several years. This cursory review did not mean that he had ruled out hypotheses 2 and 3 conclusively. But it did indicate that these were unlikely to be the simplest root cause. Following the concept of taking the simplest route whether it is the root cause or a calculation technique, the problem solver developed the following theoretically correct working hypothesis.

“It is believed that the hopper car fires and product charring that occurred when shipping X3 are associated with the residual monomer that remained with the polymer when the new rates and operating conditions were used. While the vapor space above the pellets was not in the explosive range immediately after they were loaded into the hopper car, the evolution of vapors

from the polymer over time allowed an explosive concentration to build up in the hopper car vapor space. While it is uncertain what the source of ignition was, it is known that static electricity is almost always present due to the movement of the polymer particles. Whether this explosive mixture ignited and to what degree a fire occurred depended on three factors:

1. "The movement of the hopper car. If the hopper car was continuously in motion, there was a high probability that some of the vapors would be replaced by air and the vapor phase concentration might be reduced to a level below the lower explosive limit.
2. "The humidity of the ambient air. If the humidity was high in the hopper car, it is unlikely that a static discharge would occur.
3. "The temperature. If the temperature of the polymer in the hopper car was elevated (due to the ambient temperature), then there is a higher probability of a major fire occurring, rather than a flash fire that chars some of the polymer on the top of the hopper car.

"In order to eliminate this problem, the production rates of X3 should be reduced to the previous levels. In addition, the new operating directives and procedures should be abandoned."

Step 4: Provide a mechanism to test the hypothesis.

Two mechanisms were provided to test the hypothesis. On the next X3 run, the rates were reduced to the previous levels. The percentage LEL was measured in the vapor space of each hopper car after 24 hr and prior to shipping. In each case, the LEL was well below 100%. There were no reports of charred polymer or fires even though the customers had been alerted to watch for such events. In addition, during the run, samples were taken of the product leaving the pelletizing section in the same fashion as discussed earlier. The percentage LEL was determined as a function of time and Figure 9-5 was used to illustrate

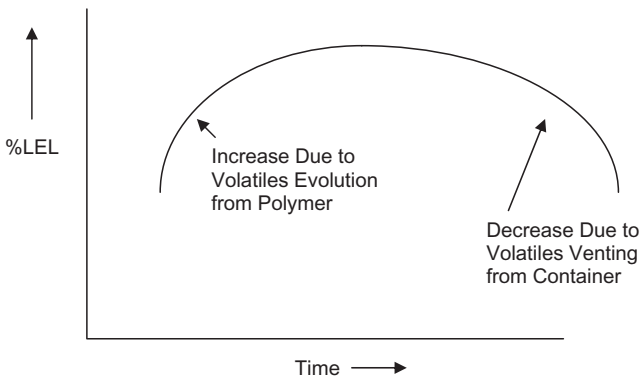


Figure 9-5 Percentage LEL vs. time.

the buildup of the percentage LEL as a function of time. Thus it was concluded that reducing the production rates was a successful test of the hypothesis.

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

The recommendation to operate at reduced rates could only be considered an interim recommendation. The problem solver used some of the techniques described in Example Problem 9-1 and concluded that the only way to operate at full rates while producing this polymer was to add additional dryer residence time. He recommended that a study be initiated to determine whether the economics of producing X3 could justify either operating at reduced rates or adding a larger dryer.

Lessons Learned There were pressures to increase the production rates of X3. It was obvious, in hindsight, that these pressures caused a blatantly flawed empirical test to be developed. The conclusion that rates could be increased was based completely on this flawed test with no theoretical calculations. This empirical test overlooked the obvious: that vapor evolution from the polymer that occurred over time might cause a maximum in the relationship between percentage LEL and time. This maximum could well be above the LEL. The risk of this approach could have been discovered if theoretical calculations had been done to determine what the maximum equilibrium concentration of monomer in the vapor phase of the sample container would be. This calculation would require that the concentration of the monomer in the polymer leaving the pelletizing section be known. The concentration of monomer in the vapor phase could then be calculated using the techniques described earlier and with the assumption that none of the monomer dispersed into the atmosphere from the container.

There are times when theoretical calculations are more accurate than laboratory results. In this case, if the concentration of monomer in the polymer could be analyzed and the equilibrium relationship was available (e.g., equation (9-7)), then the maximum equilibrium vapor phase concentration and the percentage LEL could be determined easily. This would be more accurate than the maximum percentage LEL determined by the explosivity meter. This is because the explosivity meter only measures the percentage LEL at a point in time which is not likely to be the maximum concentration.

The failure to do a detailed theoretical analysis of the proposal to increase rates by modified operating directives and procedures was costly. It gave the company adverse public publicity and adverse relationships with their customers. Their customers had never seen charred polyolefin products from this company or any other company from which they purchased material. The approach also cost problem-solving time. Instead of starting to understand the monomer removal limitation when X3 was first discovered to have a limitation, the empirical approach caused the start of problem-solving

activities to be delayed. In addition, problem-solving activities were diverted to understanding the hopper car fires as opposed to eliminating the drying limitation.

The approach of asking customers to be on the watch for charred polymer might seem to be “asking for trouble.” However, it was mandatory to confirm that the plant test of operating at reduced rates was truly successful. The failure to get this information would have likely resulted in a failed test, since not enough data would be present to prove or disprove the hypothesis.

NOMENCLATURE

BD	Bulk density of polymer, lb/ft ³
C	A constant referred to as the “lumped parameter constant.” If it is related to heat transfer, the constant is generally taken as $U \times A$. If reaction is involved, it is simply set equal to C_R in this chapter. If drying or stripping is involved, the value K is used in this chapter.
C_R	Lumped parameter constant for reaction (reaction rate constant)
C_E	A constant that relates equilibrium of solvent in polymer to the vapor phase composition. It can be determined from experimental data or approximated by application of theoretical relationships.
C_1	A constant that is related to the type of furnace flame. It should not change unless the type of fuel changes.
C_2	Product of the heat transfer coefficient and the area of the tubes. It will only change if the heat transfer coefficient changes
Ca	Polymer capacity of the hopper car, lb
DF	Driving force or incentive for mass or heat transfer to occur
DF_R	Driving force for radiant heat transfer
dX/dt	Rate of disappearance of component X by reaction or stripping
F	Total monomer in the hopper car, lb
FV	Volume of the hopper car filled with polymer, %
K	Lumped parameter constant for drying or stripping. It is somewhat related to diffusion. Since it deals with mass transfer, it is also referenced in this chapter as a mass transfer coefficient.
LEL	Lower explosive limit, volume or mol %
$\ln T$	Log mean temperature difference or the driving force for heat transfer
P	Partial pressure of the solvent in the vapor phase

Q	Rate of heat transfer
R	Rate of change with time of the variable under study. It could be heat transfer, reaction rate, or volatile stripping
S	Monomer remaining in polymer at 100°F, lb
SD	Skeletal density of polymer, lb/ft ³
T	Total volume of the hopper car, ft ³
t	Amount of time in the dryer, min
T_P	Absolute temperature of the process fluid in the tubes
T_G	Absolute temperature of the gas
T_M	Absolute temperature of the tube metal
$U \times A$	Lumped parameter (C) or, for heat transfer, the heat transfer coefficient multiplied by the area
V	Monomer in vapor space of the hopper car, lb
VP	Vapor pressure of the solvent at the dryer temperature
VT	Vapor volume of the hopper car, ft ³
$(X - X_e)$	Driving force for stripping
X	Actual concentration of solvent in a polymer
X	Concentration of component X
X_e	Equilibrium concentration of solvent in the polymer
X_f	Concentration of solvent in the outlet polymer
X_o	Concentration of solvent in the inlet polymer
Y	Concentration of component Y or the concentration of the solvent in the vapor phase
π	Total pressure, psia