

16

Tanks, Vessels, and Special Reaction Systems

The actual physical design and detailed specification of tanks and vessels (wall thickness, exact metal alloy, etc.) are done by mechanical and structural engineers. However, chemical engineering input is required to decide the general geometry and geometrical ratios, pressure and vacuum requirements, and materials needed to resist corrosion of the liquids, solids, and gases being contained.

Categories

Tanks and vessels can be divided into three broad categories:

- 1) Storage or Batch Vessels. In this case we are using a tank or vessel to store a raw material, an intermediate, or a final product. Storage can refer to raw materials, intermediates, final products, and inventory. It can also refer to “day tanks” where a “lot” of material is quarantined for analysis prior to being forwarded for further processing. This type of tank can also be used as an intermediate process point for settling layers or letting solids or “rag layers” to settle out. Occasionally, these tanks may be used as precipitators after a reaction or crystallization. Though these situations and uses may appear to be benign, safety issues that must be considered include leaks, overflowing, product contamination, and corrosion.
- 2) Pressure and Vacuum. Most storage tanks operate under atmospheric pressure unless the contents are a liquefied compressed gas. Because of the typical conservative design of such tanks, these tanks can normally handle a small amount of pressure. However, these types of tanks have little or no capability to handle vacuum and can collapse under vacuum. If the tank is expected to store materials under pressure, its pressure rating must accommodate this. It is essential that vents from a tank, if designed to maintain atmospheric pressure, do not become closed or clogged. This can happen

because covered vents are not uncovered after maintenance or, as shown in this illustration, a vent is plugged by an insect nest! (Figure 16.2).

- 3) Process and Agitated Tanks. This would refer to reaction vessels and storage vessels that are agitated. Most of the time we are concerned about process reaction vessels. We discussed reaction rates and kinetics earlier, and the design of an actual chemical reactor incorporates these fundamentals into its design. There is an overlap between these two basic concepts in some situations such as crystallization and settling.

Corrosion

In addition to the normal concerns about corrosion to the tank from its contents and the outside environment, tanks that are situated at ground level in contact with soil are subject to what is known as galvanic corrosion, where the tank metal, in contact with moisture in the soil, becomes part of an electrochemical circuit (a battery). It is a normal practice to monitor this and provide a reverse current to counteract this current to ensure that the bottom sections of the tank (frequently unseen) do not collapse or leak.

The physical design of any tank or vessel includes not only such obvious items such as volume and pressure rating (especially if used as a reactor, which handles or generates gases) but also such geometric factors such as diameter, height-to-width ratio, the nature of the flanges, wall thickness (including corrosion concerns), materials of construction, and the nature of jackets that might be used around the tank for cooling or heating. Mechanical and civil engineers will be involved in ensuring that a vessel meets codes and that welding done during tank construction and assembly meets appropriate codes.

It is tempting to think of tanks and storage vessels as nonhazardous equipment. However, when such tanks and vessels contain large volumes of hazardous materials, release of these materials can cause serious safety incidents. The Center for Chemical Process Safety (<http://www.aiche.org/ccps>), a consortium of over 150 chemical companies, which studies and provides learning examples for chemical engineers, reported this major incident in England in 2005, which provides a classic example of the hazards of simple storage tanks (Figure 16.1).

The learnings from the incident are discussed in detail in the Summary section, but let's review some of the following key points:

- 1) It is critical to know the inventory of a tank at all times for a number of important reasons:
 - a) Overfilling or under filling of a tank, resulting in overflow or damage to pumps associated with the storage tank. Overfilling can also result in discharge of flammable materials (which will ultimately find an ignition source),




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<p>http://www.aiche.org/ccps/safetybeacon.htm</p>		<p style="text-align: right;">September 2006</p>
<h2>Overfilling Tanks — What Happened?</h2>		
	<p>On Sunday, December 11, 2005, gasoline (petrol) was being pumped into a storage tank at the Buncefield Oil Storage Depot in Hertfordshire, U.K. At about 1:30 A.M., a stock check of the tanks showed nothing abnormal. From about 3 A.M., the level gage in one of the tanks recorded no change in reading, even though flow was continuing at a rate of about 550 m³/h (2,400 U.S. gal/min). Calculations show that the tank would have been full at about 5:20 A.M., and that it would then overflow. Pumping continued, and the excess gasoline overflowed from the top of the tank and cascaded down the sides, forming a liquid pool and a cloud of flammable gasoline vapor. At about 6 A.M., the cloud ignited, and the first explosion occurred. This was followed by additional explosions and a fire that engulfed 20 storage tanks. Fortunately, there were no fatalities, but 43 people were injured. Approximately 2,000 people were evacuated. There was significant damage to property in the area, and a major highway was closed. The fires burned for several days, destroying most of the site and releasing large clouds of black smoke, which impacted the environment over a large area.</p>	
<p><i>Photograph courtesy of Royal Chiltern Air Support Unit.</i></p>		
<h3>Did You Know?</h3>  <p><i>Photo courtesy of Royal Chiltern Air Support Unit.</i></p> <ul style="list-style-type: none"> ▶ Overfilling of process vessels has been one of the causes of a number of serious incidents in the oil and chemical industries in recent years — for example, the explosion at an oil refinery in Texas City, TX, in March 2005. ▶ The tank involved in this incident had an independent high-level alarm and interlock, but these components did not work. The cause of the failure is still under investigation. ▶ A spill of flammable material, such as gasoline, can form a dense, flammable vapor cloud. This cloud can grow and spread at ground level until it finds an ignition source. This ignition source can cause the cloud to explode. 	<h3>What Can You Do?</h3>  <p><i>Photo courtesy of Hertfordshire Constabulary.</i></p> <ul style="list-style-type: none"> ▶ When you transfer material, make sure that you know where the material is going. ▶ When you are pumping into a tank, and the level or weight indicator in that tank does not increase as you would expect, stop the transfer and find out what is happening. ▶ Make sure that all safety alarms and interlocks are tested at the frequency recommended in the plant process-safety-management procedures. ▶ If you have alarms and interlocks that are not regularly tested, ask the plant process safety manager if they are safety critical and whether they should be on a regular testing program. <p>Read the reports about this incident at: http://www.buncefieldinvestigation.gov.uk</p>	
<p>If you are pumping material, be sure you know where it is going!</p>		
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Figure 16.1 Consequences of overfilling a tank. Source: Chemical Engineering Progress 7/06, p17. Reproduced with permission of American Institute of Chemical Engineers.





a release of material that will cause environmental damage, or human exposure. There are many state and federal regulations regarding diking requirements, but not having any leaks at all should be the primary objective.

- b) If the tank contents and volume are not known accurately, upstream and downstream processing units can be negatively affected.
- c) The pressure within the tank or vessel must also be known for two primary reasons. The first, the one that immediately comes to mind, is rupture of a vessel by exposing it to an internal pressure greater than its design. However, the second and just as important a consideration is the potential exposure of tank contents to vacuum, as mentioned earlier. Atmospheric pressure is NOT zero—it is approximately 14.7 psig at sea level and slightly lesser at high altitudes. Many tanks and vessels can withstand a moderate amount of pressure but cannot withstand even a small amount of *external* pressure (i.e., the difference between atmospheric pressure and vacuum in the tank). Figure 16.2 (from the Center for Chemical Process Safety publication, the Beacon) shows the consequences of plugging a vent from a vessel not designed to handle vacuum. This can happen because covered vents are not uncovered after maintenance or, as shown in Figure 16.2, a vent is plugged by an insect nest!

Agitated tanks and vessels are used for many purposes, including reactions, crystallizers, blend tanks, and precipitators. A general diagram of an agitated vessel is shown in Figure 16.3.

From a physical design standpoint, there are a number of parameters that must be chosen:

- 1) Diameter and Height. The product of these will determine the overall volume of the tank. It is important, when designing a reactor tank's volume, to take into account the gas volume, which may be from a reactant or an evolved gas from a reaction. If a batch reaction is the primary function of the vessel, the volume needed must also be taken into account as well as the time spent filling, draining, and cleaning the reactor vessel.
- 2) Height-to-diameter Ratio (Z/T). This refers to the ratio of the height of liquid in the tank to the inside tank diameter. This ratio will affect the physical stress on the agitator system and its motor and drive system. For example, if the vessel is very short and wide in diameter, there will be a great deal of stress on the shaft in the latitudinal direction and the agitation system may have difficulty in mixing side to side. At the other extreme, if the vessel is very tall and skinny, there will be excellent sideways mixing, but poor top-to-bottom mixing, and the longitudinal stress on the agitator shaft will be large. These effects will be exaggerated if baffles are attached to the shaft or if the liquid viscosity and densities are high, requiring more energy to mix the fluids.

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<h2>Vacuum Hazards — Collapsed Tanks</h2>		<p>February 2007</p>
	<p>The tank on the left collapsed because material was pumped out after somebody had covered the tank vent to atmosphere with a sheet of plastic. Who would ever think that a thin sheet of plastic would be stronger than a large storage tank? But, large storage tanks are designed to withstand only a small amount of internal pressure, not vacuum (external pressure on the tank wall). It is possible to collapse a large tank with a small amount of vacuum, and there are many reports of tanks being collapsed by something as simple as pumping material out while the tank vent is closed or rapid cooling of the tank vapor space from a thunder storm with a closed or blocked tank vent. The tank in the photograph on the right collapsed because the tank vent was plugged with wax. The middle photograph shows a tank vent that was blocked by a nest of bees! The February 2002 Beacon shows more examples of vessels collapsed by vacuum.</p>  	
<h3>Did you know?</h3> <ul style="list-style-type: none"> ▶ Engineers calculated that the total force from atmospheric pressure on each panel of the storage tank in the left photograph was about 60,000 lbs. ▶ The same calculation revealed that the total force on the plastic sheet covering the small tank vent was only about 165 lbs. Obviously this force was not enough to break the plastic, and the tank collapsed. ▶ Many containers can withstand much more internal pressure than external pressure — for example, a soda can is quite strong with respect to internal pressure, but it is very easy to crush an empty can. 	<h3>What can you do?</h3> <ul style="list-style-type: none"> ▶ Recognize that vents can be easily blocked by well intended people. They often put plastic bags over tank vents or other openings during maintenance or shutdowns to keep rain out of the tank, or to prevent debris from entering the tank. If you do this, make sure that you keep a list of all such covers and remove them before startup. ▶ Never cover or block the atmospheric vent of an operating tank. ▶ Inspect tank vents routinely for plugging when in fouling service. 	
<p style="text-align: center;">Vacuum — It is stronger than you think!</p>		
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Figure 16.2 Consequences of pulling vacuum on storage vessel. Source: Chemical Engineering Progress, 3/10, pp. 25–32. Reproduced with permission of American Institute of Chemical Engineers.

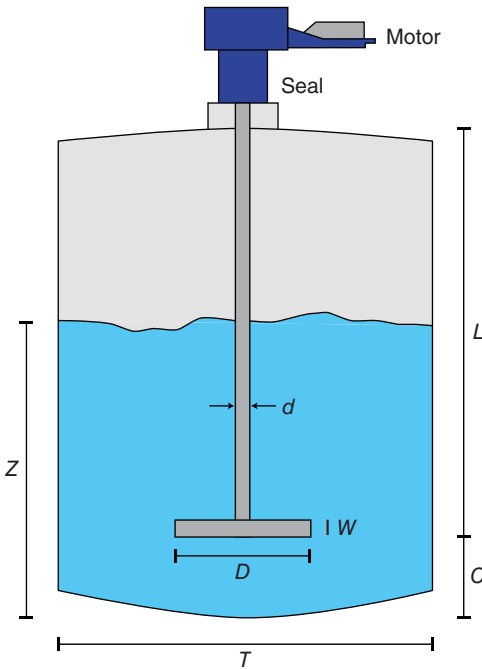


Figure 16.3 Agitated vessel parameters. Source: Chemical Engineering Progress, 8/15, pp. 35–42. Reproduced with permission of American Institute of Chemical Engineers.

3) Impellers. Figure 16.3 shows only one impeller near the bottom of the agitator shaft. There could be multiple impellers installed vertically. The number needed will be a function of the physical property differences, the Z/T ratio in the tank, and the agitator horsepower available.

As a rule of thumb, 20% of the volume in a tank is left for gas volume and the diameter-to-height ratio is between 0.8 and 1.4. Whatever choices are made in the agitator system, they must meet the standard horsepower and gear box requirements.

If a tank contains solids, the settling rate of these materials may be important and may indirectly impact any agitation design. The settling rate will not only be a function primarily of density difference and solids concentration, as shown in Figure 16.4, but will also be affected by viscosity.

There are numerous types of agitators used in vessels including the following:

- 1) Marine Propellers. These are commonly used in boats and are fairly expensive since they are made from a casting process (Figure 16.5).
- 2) Rushton Turbine Agitators. These were developed as an alternative to cast mixers and propellers and are multipurpose and multifunctional agitators whose geometry can be varied and adjusted to suit various process conditions. They are also relatively inexpensive to manufacture. Example of such agitators are shown in Figure 16.6.

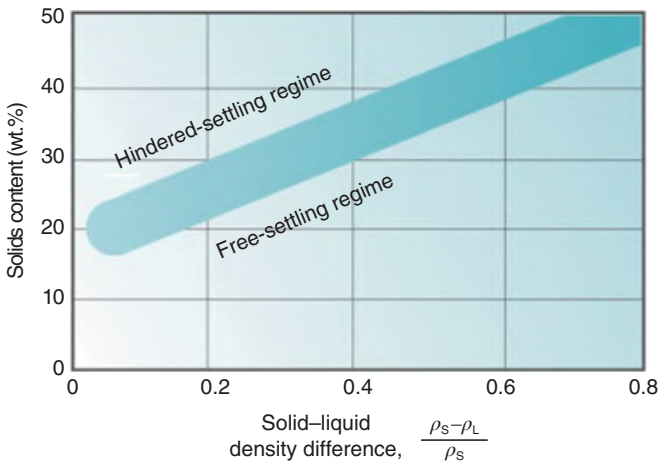


Figure 16.4 Settling versus density and solids concentration. Source: Chemical Engineering Progress, 1/14, pp. 30–36. Reproduced with permission of American Institute of Chemical Engineers.



Figure 16.5 Propeller agitator. Source: PublicDomainPictures.com.

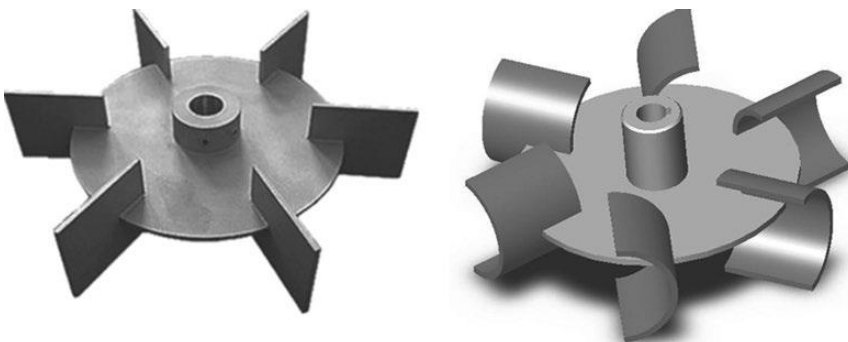


Figure 16.6 Rushton turbine agitators. Source: Reproduced with permission of Yahoo.

The pitch and number of blades can be modified to adapt to different mixing requirements, different liquid-to-gas ratios, and differences in liquid viscosities and densities. The diameter of the plane blade compared to the shaft diameter and nature of the attachments can also be modified. The attached blades can also be curved, increasing the pumping versus agitation ratio.

These geometric differences will affect the ratio of side-to-side (agitation) and top-to-bottom (pumping) aspects of the agitator's function as shown in Figure 16.7.

It is also possible to insert into a vessel a slow moving "scraper" that will remove solids from the walls of the vessel in cases where solids are precipitating out of a reaction and coating of the vessel walls would inhibit heat transfer.

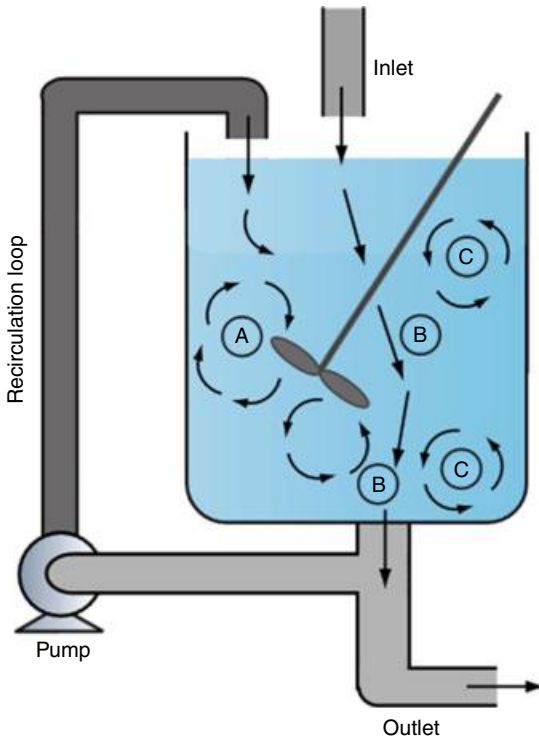


Figure 16.7 Flow patterns induced by agitation: side to side and top to bottom. Source: *Chemical Engineering Progress*, 3/10, pp. 25–32. Reproduced with permission of American Institute of Chemical Engineers.

Heating and Cooling

When reactor vessels and tanks must be heated or cooled, there are three basic options as follows:

- 1) Jacket of the Vessel. Steam or a cooling fluid can be injected into the jacket of the vessel. The rate of heat transfer will be governed by the general heat transfer equation we have discussed previously:

$$Q = UA\Delta T$$

In the case of a stirred tank, the overall heat transfer coefficient, U , will be affected by the properties of the fluid (viscosity, density, heat capacity) as well as the agitation rate. If a chemical reaction is being carried out in the vessel, these properties will change with time as the chemical reaction proceeds (with physical properties changing), and these differences must be taken into account. If gases are evolved during the reaction, this will make the heat transfer calculations more complex.

- 2) Coils Inserted into the Vessel. The same issues apply as mentioned in the case of the use of jackets.
- 3) Direct Steam or Cooling Injection. As long as the heat and material balance issues are taken into account, it is possible to directly inject steam (for heating) or water into a reactor for heating or cooling. Dilution of the process stream must be taken into account. Since there is no material barrier between the steam and the material being heated, the heat transfer rates are much higher than indirect heating mechanisms.
- 4) Addition of turbulence into the jacket of the reactor and internal baffling can also be considered as seen in Figure 16.8.

Power Requirements

The amount of power required for a tank or a vessel agitator will be affected by many factors including the following:

- 1) Amount of agitation required
- 2) Physical properties of the liquids or gases in the tank or vessel (density, viscosity)
- 3) Ratio of gas to liquid and gas/liquid to solids (if any)
- 4) Geometric design of the tank

There are several different equations used to calculate the relationships between physical properties and turbulence, agitation, and energy requirements

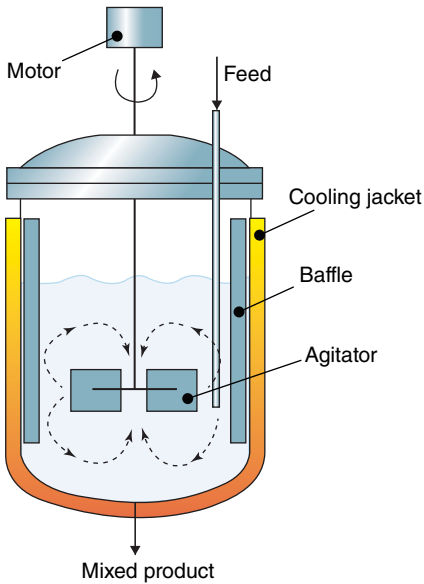


Figure 16.8 Agitated, baffled, and jacketed reactor vessel. Source: Reproduced with permission of Sulzer.

in an agitated tank system. The turbulence in the tank (the impeller Reynolds number) can be estimated by

$$N_{\text{Re}} = \frac{D^2 N \rho}{\mu}$$

where D is the impeller diameter, N is the shaft speed, ρ is the fluid density, and μ is the liquid viscosity. As we increase the diameter, rotational speed, and density, the turbulence increases; as the viscosity increases, it decreases. It is important to calculate these numbers based on the properties and conditions in the vessel at the time of concern and not the feed materials.

We will also see a number called the impeller “pumping number”:

$$N_p = \frac{P}{\rho N^3 D^5}$$

This equation shows the strong dependency of power requirement on shaft speed and impeller diameter. This relationship explains, in part, the reason why extreme vessel and tank designs are not used (tall and skinny or short with wide diameter).

Tank agitation can also be done with a combination of mechanical agitation and aeration (or other gas) flow. The power used by the agitator plus the power used by the gas compression system may result in a minimum energy cost point as shown in Figure 16.9.

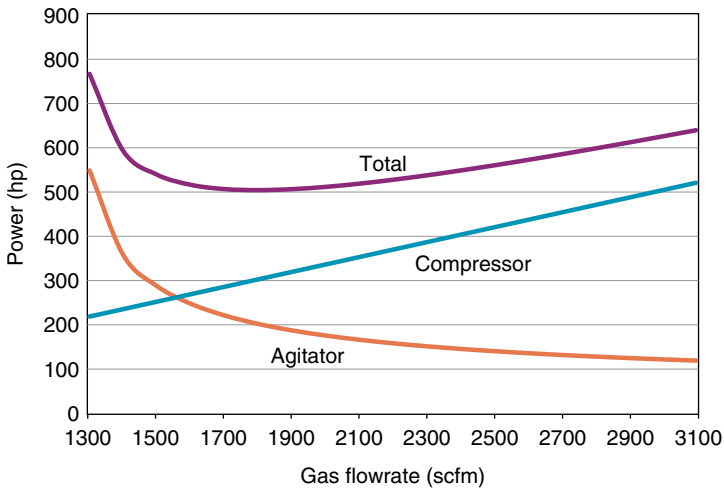


Figure 16.9 Minimal power consumption. Source: Chemical Engineering Progress, 8/15, pp. 35–42. Reproduced with permission of American Institute of Chemical Engineers.

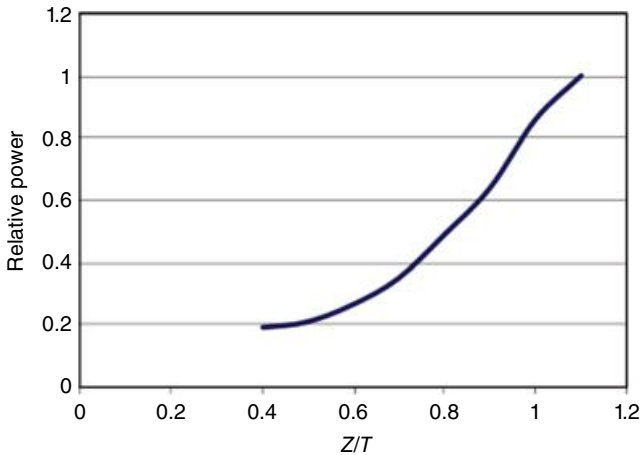


Figure 16.10 Power requirements versus liquid level. Source: Chemical Engineering Progress, 8/15, pp. 35–42. Reproduced with permission of American Institute of Chemical Engineers.

Agitation power requirements are also affected by the liquid level in the tank as shown in Figure 16.10.

Power requirements are also affected by the number of baffles and the Z/T ratio in the vessel, as summarized in Table 16.1.

Table 16.1 Relative power requirements versus Z/T ratio and number of impellers.

Table 3. Looking at relative torque as a function of Z/T can also help you determine power requirements.							
Z/T	Number of impellers	Square batch power split basis					
		50/50		70/30		90/10	
		Relative torque	Relative power	Relative torque	Relative power	Relative torque	Relative power
0.5	1	1.00	0.79	1.41	1.12	1.80	1.43
1	2	1.00	1.00	1.00	1.00	1.00	1.00
1.5	3	1.00	1.15	0.86	0.99	0.73	0.84
2	4	1.00	1.26	0.80	1.00	0.60	0.75
2.5	5	1.00	1.36	0.75	1.02	0.52	0.70

Source: Chemical Engineering Progress, 2/12, pp. 45–48. Reproduced with permission of American Institute of Chemical Engineers.

Using tanks as blending systems is frequently done, and the time necessary to blend two different fluids will be affected by their differences in viscosity and density, as well as the mechanical design of the agitator and input power.

Tanks can also be used as settling vessels to allow solids to settle out after reactions or prior to filtration. As the solids concentration increases, the settling rate decreases as the solids settling will hinder each other. This phenomenon is especially visible at solids concentrations above 40% and with high viscosity fluids.

Flow patterns with a mixing vessel are important to consider, especially if uniformity is critical. The mixing within a vessel from top to bottom will require higher energy input than simple side-to-side mixing. If a gas is being generated or used as a reactant, or if a gas is being used as part of the agitation system, there will be an optimum ratio of agitator power to gas velocity, which will minimize overall power requirement.

Tanks and Vessels as Reactors

When tanks are used as reaction vessels, sizing is important and also the total cycle time. When a vessel is being used as a batch reactor, the size required must take into account not only the reaction time but also the fill time, drain time, and cleaning time that may be required. Occasionally we will see a tank reactor used in what would be described as a “semi-continuous” mode. This refers to the input into the reactor of reacting components and the reaction occurs during the filling process. This would normally be a fast reacting system. When the vessel is full, the flows are stopped and the products removed.

Another common use of tanks and vessels in reaction systems is what is known as a continuously stirred tank reactor (CSTR). In this case, reactants flow into the vessel continuously, reactants have a certain residence time in the vessel for the reaction to occur, and the flow constantly leaves the reactor. If we take a look at the previous illustration of a tank design, we can focus on how the feed is introduced. Depending on physical property differences (viscosity, density) and if any of the feed materials are gases as opposed to liquids, the feed could be introduced as shown in Figure 16.11 (near the impeller) to maximize immediate mixing.

A cooling jacket could also be used on the reaction vessel if the reaction is exothermic and needs cooling, or if the agitation energy needs to be balanced). Baffles can be used to improve mixing within the vessel. The required size of the reaction vessel will be related to the kinetics of the reaction(s) that are occurring. The slower the reaction rate, the larger the vessel volume will need to be. It is also possible to configure cooling or heating of such a system via external cooling or internal heat exchange piping.

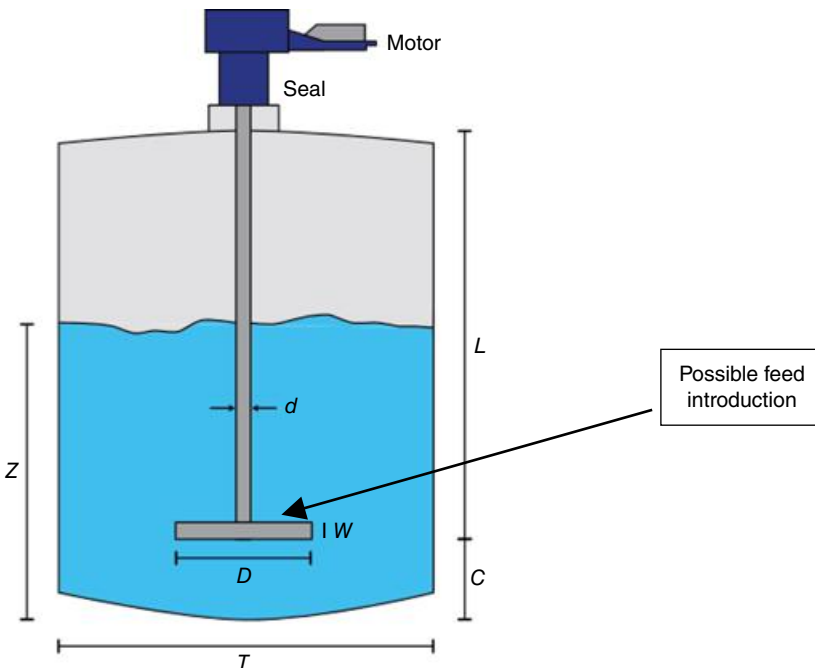


Figure 16.11 Feed introduction into an agitated vessel. Source: Reproduced with permission of Sulzer.

Static Mixers

If the reaction rates are extremely fast or the physical property differences between materials are minimal, it is possible for a static mixer to be used to mix and/or react materials within a pipeline, as shown in Figure 16.12.

These in-line mixers provide very intense mixing in a short piping length with the primary drawback being high pressure drop. These devices are suitable for in-line mixing of solutions and liquids of different compositions and physical properties as well as to conduct chemical reactions, precipitations, and dissolutions when the required time is very short. The primary downside to these devices is their very high pressure drop. A secondary concern may be erosion to the inserts if the liquids or slurries being processed have a high abrasive content.

Summary

Tanks and vessels have many uses within the chemical process industries, including storage, decanting, settling, product isolation for analysis, and chemical reaction systems. Their specific design will be affected by pressure and agitation requirements, gas/liquid/solids ratios, vessel codes, and the nature of the reaction kinetics if used as reactors. The detailed design of vessels and tanks must meet various codes specified by ASME. In-line mixers are low cost alternatives to tank mixing when lot isolation is not required and high pressure drop is not a barrier to their usage.



Figure 16.12 Static mixer. Source: Reproduced with permission of Sulzer.

Coffee Brewing Tanks and Vessels

The two most obvious are the carafe into which the brewed coffee drops and the cup that holds the final cup of coffee that is consumed. Carafes can be either glass or metal. Glass can easily break and protection against thermal burns is advisable, no different than if a similar situation existed in industry. Glass is usually corrosion resistant but can build up coatings that need to be removed. A metal container will be safer but will certainly have a corrosion rate. In the case of hot coffee, this is probably so small that it is of no practical concern, but it is not zero.

Previously ground coffee is occasionally stored in vacuum containers. These must be strong enough not to collapse under atmospheric pressure.

The final coffee cup is an agitated vessel if cream and sugar/sweetener (solids!) are added. The uniformity of the coffee flavor will be a function of how long the agitation lasts and what kind of agitator is used (spoon, stick, etc.).

Discussion Questions

- 1 How are tanks and agitated vessels used in your processes? How was the design and type of agitation chosen? Have these decisions been reviewed recently in light of new types of equipment availability?
- 2 What is the response of the agitation system to changes in physical properties (density, viscosity)?
- 3 Could static mixers replace tank mixers?
- 4 Is the possibility of vacuum collapse of storage vessels been reviewed?
- 5 Is there a more optimum combination of heat transfer and tank agitation that could be more optimal?
- 6 Have wall thicknesses of tanks and vessels been checked? How often?

Review Questions (Answers in Appendix with Explanations)

- 1 Simple storage tanks can be hazardous due to:
 - A __Leakage
 - B __Overfilling and under filling
 - C __Contamination
 - D __All of the above

- 2 A key design feature in an agitated vessel (its Z/T ratio) is:
A __ Its height-to-diameter ratio
B __ Which company manufactured it
C __ The engineer who designed it
D __ When it was placed into service
- 3 Choosing an agitator for a tank will be affected by:
A __ Densities of liquids and solids
B __ Viscosity of liquids
C __ Ratios of gases/liquids/solids
D __ All of the above
- 4 The significance of top-to-bottom agitation will be affected by:
A __ Gas and liquid densities and their changes over time
B __ Formation of solids as a reaction proceeds
C __ Necessity for liquid/solid/gas mixing
D __ Any of the above
- 5 Shaft horsepower requirements for an agitated vessel will be MOST affected by:
A __ Air flow available and ability to clean an exiting air stream
B __ Physical properties of materials being mixed and agitated
C __ Particle size degradation
D __ All of the above

Additional Resources

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17

Chemical Engineering in Polymer Manufacture and Processing

Polymers have unique properties from a chemical engineering standpoint. They are long chain molecules with unique physical properties, and these properties change with the nature of the polymer being manufactured, how it is manufactured, and how it is used. Different polymers can be blended together to achieve certain properties. In addition, different monomers (the building blocks from which polymers are made) can be combined in many different ways to achieve further differentiation in product performance. When we formulate polymers with additives and pigments, we usually use the term plastics, but it is common to see both terms used to describe the starting polymer material.

What are Polymers?

Basically, polymers are products produced from joining together chains of reactive monomers, the starting molecules. One type of “joining” process is initiated with energy to activate a double bond in the starting molecule, allowing additional monomers to react with it, creating long chains of monomers. The length of this chain can be controlled and limited. A common term used is the “molecular weight” (MW) of the polymer.

In one example, the double bond within ethylene ($\text{CH}_2=\text{CH}_2$) is activated by heat or a catalyst to produce a monomer that we would describe as (CH_2-CH_2). This activation allows the ethylene to react with other ethylene molecules multiple times and produce “polyethylene,” which we describe as ($\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$)_x where “x” is the number of ethylene monomers joined together. We commonly refer to “x” as the MW of the polymer. The higher the MW, the higher the “melting point” of the polymer will be and the higher will be its viscosity. Its mechanical strength, in general, will also be higher. There are numerous types of monomers that can be polymerized

including propylene, styrene, butadiene, and vinyl chloride, all having double bonds that can be activated. All the chains in a polymer system do not necessarily have the same chain length. There can be a variety and distribution of chain lengths. We use the term *molecular weight distribution* (MWD) to describe this. The more even this characteristic is, the more uniform the polymer properties will be under processing and use conditions. MWD can be viewed in the same way the particle size distribution was seen in the discussion on solids handling (see Figure 17.1).

Polymers, when made, can also display a property known as *crystallinity* meaning that portions of the long polymer chains have grouped together in such a way that there are structured domains of polymers within the overall polymer structure as shown in Figure 17.2.

When this type of characteristic is present, there will be multiple softening points as the polymer is heated and the various regions reach their softening points.

In addition to higher thermal stability than their starting monomers, polymers will also have some degree of thermal, chemical, and abrasion resistances. Their melting points will vary with the monomer used as well as the MW, and these two variables will affect their uses. Polymers are used in the manufacture of plastic garbage bags, blood tubing, fuel-resistant parts in automobiles, bake ware, kitchenware, and piping. In modified forms they are also used as foamed insulation, carpet backings, and house siding.

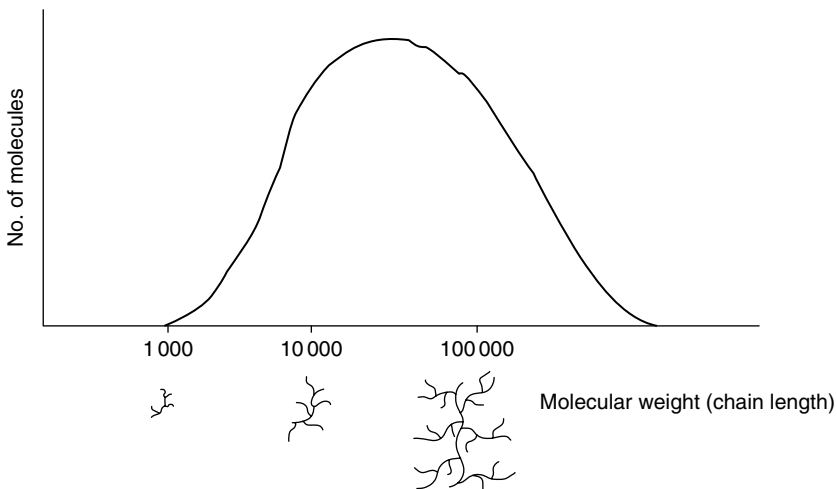
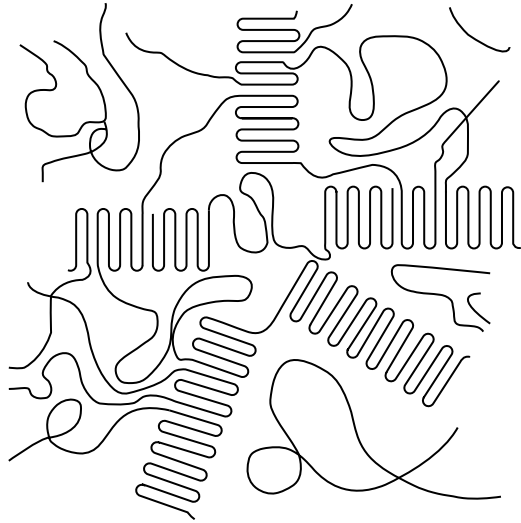


Figure 17.1 Molecular weight distribution.

Figure 17.2 Crystallinity areas in polymers.

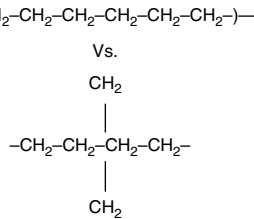


Polymer Types

In addition to a basic linear polymer, there are other possible types of polymers, described by a combination of their make up or how they are manufactured.

- 1) Linear versus Branched Polymers. The method of polymerization (primarily the catalyst used) can control whether the monomers are linked together in a linear fashion or in a branched fashion:

Figure 17.3 Linear versus branched polymers.



The MW may be the same, but the branched structure produces a polymer of lower density and greater strength per unit volume. The change from linear to branched structure was a major breakthrough in polyethylene manufacturing and is the primary reason why typical trash bags, made from polyethylene, use far less material to achieve the same strength, compared to decades ago.

- 2) Copolymers. It is possible to copolymerize two different monomers, both of which having a reactive bond, as previously discussed, or a reactive chemistry

between the molecules. Combinations of styrene and butadiene (the basis for many synthetic rubber materials) are an example of this:

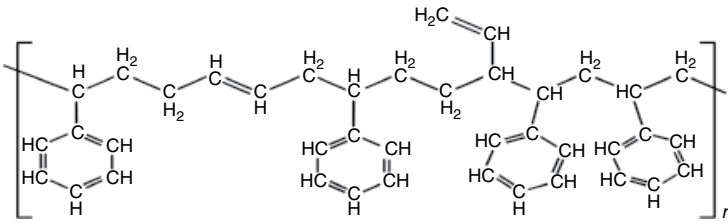


Figure 17.4 Styrene-butadiene copolymer.

In addition to the ratio of the two monomers, it is also possible to change the manner in which the monomers are arranged in the chain:

- A+B+A+B+A+B (alternating) **Figure 17.5** Polymerization structures.
- A+A+A+A+B+B+B+B (block)
- A+A+B+A+B+B+A+A (random)

Polymer Properties and Characteristics

There are a number of unique physical properties that are used to describe the properties and behavior of polymers beyond their chemical composition. One of the most important is the *glass transition temperature*, commonly represented as T_g . It would be similar to the melting point of a solid except that for polymeric materials, it is not usually at a specific temperature. The polymer can soften over a range of temperature and has a number of different shapes. This shape is a function of a number of factors including MW and MWD. T_m is the temperature at which the polymer has totally liquefied. A laboratory device is used to melt the polymer, and its softening measured against a reference point. An output graph would look like Figure 17.6:

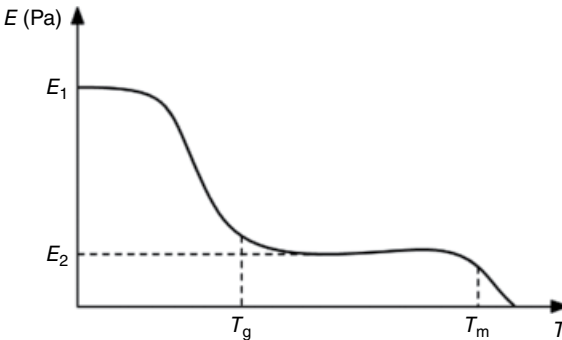


Figure 17.6 Differential scanning calorimetry (DSC) graph: energy (Pa) versus temperature.

With these properties in mind, we can describe the general nature of the various types of polymers as follows:

- 1) **Thermoplastics.** This refers to a polymer that can be melted into a liquid phase and then cooled to reform the original solid polymer. For most thermoplastics, this cycle can be repeated numerous times; however, over a long period of time, some degradation in the MW of the polymer will be seen (this is one of the limitations of plastics recycling where the properties of the recycled polymer may limit its potential uses to less valuable products than the original polymer). The T_g would typically be at room temperature or above. Polyethylene, polypropylene, and polystyrene are examples of such materials and find use in molded toys, food wrap films, and molded shapes of many types.
- 2) **Thermosets.** These types of polymers are chemically cross-linked in such a way that they do not have the ability to “melt” in the traditional sense. Epoxy resins are examples of such materials. When heated, they will tend to char and burn. They are suitable for rigid plastic structures such as tanks. Because they cannot be melted in a normal sense, it is not possible to recycle these types of plastics in an economical way.
- 3) **Elastomers.** These are polymers whose T_g is below room temperature and thus can be stretched or fitted around a mold at room temperature. A simple rubber band is an example of such a material. These materials find use in applications where flexibility at room temperature is important, such as gaskets or medical tubing.
- 4) **Emulsions and Latexes.** These are suspensions of polymers in either an aqueous or organic liquid where the polymer is suspended in the solution by means of surface chemistry which interacts with the solution. A household latex paint is an example of such a system. The paint may look as if it is a solution of polymer in water, but if a paint can is left unused, but covered, for an extended period of time and then opened, a clear water layer is seen at the top. Agitation will re-disperse the latex polymer in the water solution. This behavior is enabled via a unique polymerization technology that coats the surface of the polymer beads with functional groups that are attracted to polar molecules such as water.
- 5) **Engineering thermoplastics.** This general term is used primarily to designate thermoplastics with very high temperature resistance (i.e., high T_g) and/or having a high degree of chemical resistance to solvents and acids. Examples of such materials include nylon (frequently used in “under the hood” automobile applications where gasoline resistance is critical), polycarbonate (having high temperature resistance and high impact strength), acrylonitrile–butadiene–styrene terpolymer (ABS), and fluorinated polymers.

Polymer Processes

The polymerization of monomers has the same aspects of kinetics as discussed in Chapter 4. However, in polymerization we have several different reactions occurring simultaneously: First, the rate of the polymer chain growth, second, the rate of chain growth termination, and finally, the rate of branching of the polymer chains.

Monomers can be combined to obtain polymers, with the aforementioned characteristics in various ways as follows:

- 1) **Thermal.** The double bonds of many monomers, such as ethylene or styrene, will be activated by thermal energy and can be polymerized through simple thermal processes. There is usually little control over the characteristics of the polymer produced. This was the primary process for polymerization of compounds such as styrene and methyl methacrylate in the 1940s and 1950s prior to the discovery of catalytic processes.
- 2) **Catalytic.** The use of catalysts to polymerize monomers has been used for many decades, allowing the control of chain length (MW) and branching. These processes can be either liquid phase (under pressure in liquid monomer) or vapor phase, producing a particulate product. Vapor-phase and liquid-phase catalytic processes will produce different products in terms of density and other physical properties. Until recently these processes were required to be shut down when the catalyst activity diminished below an acceptable point. Recent developments in polymerization catalysis have produced catalysts that are so active that the amount required does not justify recovery and they can be left in the polymer product as a trace residue, which does not affect its performance or properties. These types of processes can be run in the liquid phase (frequently under pressure due to the low boiling points of many monomers) or in the gas phase.
- 3) **Condensation.** This refers to a copolymerization involving not only joining two different monomers but also generating a chemical by-product such as water or HCl in this process. The polymerization of amides and amine functional groups in various ratios to produce different forms of nylon is such a process as shown in Figure 17.7.

The process of producing polycarbonates via reacting phosgene and bis-phenol is another common process of this nature.

In condensation polymerizations, a by-product produced as part of the coupling reaction (H_2O or HCl) must be removed from the process, complicating the process from a chemical engineering standpoint, especially since the polymer streams are high viscosity.

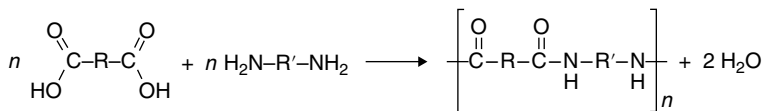


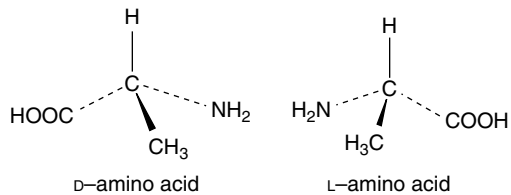
Figure 17.7 Formation of nylon from an amide and carboxylic acid.

4) Copolymerization. If we want to copolymerize two or more different monomers, we can use heat and free radical activation to produce some combination of polymers A and B (and C, D, etc.). Examples of such materials would include styrene–butadiene rubber (SBR) and ABS. These reactions also couple two or more different monomers, but as opposed to condensation polymerization, they do not split out a third molecule.

Suspension polymers, such as latexes, are typically produced in the liquid phase, in a sequential batch process that builds layers of the desired polymer composition, and then in a final layer including a “water-loving” molecule that attracts water and allows these polymers to be suspended in water.

5) Chiral and Tactic Polymerizations. The carbon atom is somewhat unique in that it does not have a “linear” geometric center. The carbon atom has four bonds, which are in the shape of a pyramid and two identical chemical compounds (by chemical formula) and can be represented by two different structures. This is the case with the amino acid alanine as shown in Figure 17.8.

Figure 17.8 Chiral molecule illustration.



These two structures are not superimposable on each other. One, as seen in Figure 17.8, is “left handed” while the other is “right handed.” If a polymerization involves a monomer with such a chiral center and a double bond, the polymers manufactured will generally have very different properties.

If we use the generic symbol “R” to represent a functional group, it is possible to produce a polymer with the “R” being randomly distributed by position (called *syndiotactic* polymers), virtually all on one side of the polymer chain (called *isotactic* polymers), or randomly distributed (*atactic* polymers). These polymer structures would be seen in Figure 17.9.

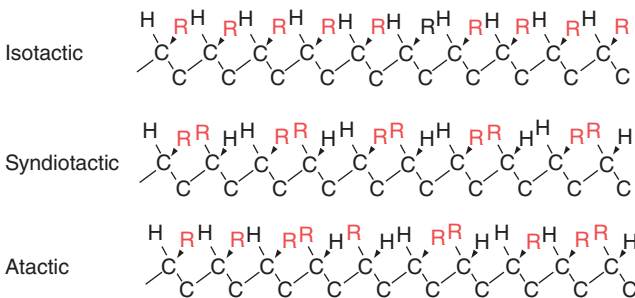


Figure 17.9 Polymer “tacticity” structure.

If these three polymers were polybutadiene, the differences in T_g and physical properties are significant. One can be hard enough to use as a golf ball cover and another a low T_g material with no practical use. These polymers are examples of *chiral* polymers. Figure 17.10 shows this difference in the polymerization of isoprene monomer, with the methyl groups either alternating or totally atactic.

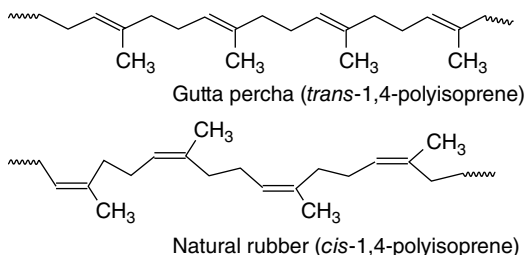


Figure 17.10 *trans* versus *cis* isomers.

The “Gutta” version is hard and rigid while natural rubber is soft and stretchy. One of the processes for the manufacture of polyethylene is shown in Figure 17.11.

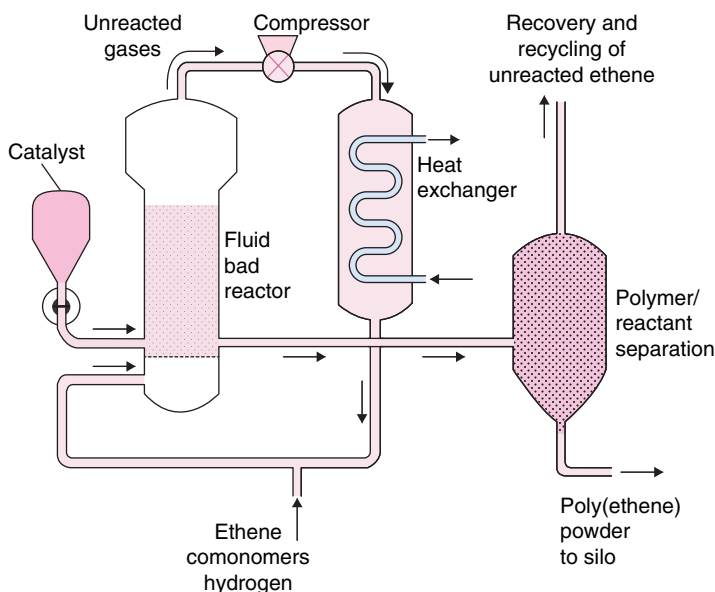


Figure 17.11 Gas phase polyethylene process. Source: Diagram was produced by the Centre for Industry Education Collaboration, a non-profit organization and an integral part of the Department of Chemistry, University of York, UK. <http://www.essentialchemicalindustry.org/>

This is what is known as a catalyzed gas-phase reaction system. The polymerization reaction itself is exothermic and occurs in a fluidized bed. A heat exchanger is used to recover the heat of the exothermic reaction and use some of it to preheat the inlet ethane (ethylene) feed gas. The polymer product is separated from the unreacted ethylene/ethane and recycled. The final product is in a powdered form and is sent to storage silos. We can see many unit operations, which we have already discussed, used in this process, including reaction engineering and kinetics, thermodynamics, heat transfer, solids handling, and liquid–solid separation.

Polymer Additives

Very few polymers are used in the “as produced” condition. In the case of thermoplastics, it is common for the end product of manufacturing to be a small plastic pellet, which is shipped to the customer in bags, boxes, or bulk rail cars. The pellet is produced from a high temperature process stream or molded from fine particles produced from a vapor-phase reaction.

As the end user produces a final product (i.e., piping, tubing, molded shell, or building siding), colorants, flow processing aids, viscosity modifiers, and other additives are added to the molten polymer stream prior to its molding into a final useful product. The final polymer properties must match the final end-use demands in terms of temperature and solvent resistance, color, resistance to UV light, and abrasion.

End-Use Polymer Processing

The type of process used to fabricate the final product will be primarily determined by its end use and can include blow molding, extrusion, injection molding, or fiber spinning in the case of such materials as nylon and polyesters. The unique chemical engineering challenges in designing such process equipment include the typical high viscosity of molten polymers, which in turn reduces heat and mass transfer rates, resulting in long times to heat and cool and long times to mix and disperse materials.

The formation of polymers into final products is done in numerous ways, depending upon the application and properties of the starting polymer.

- 1) Extrusion. In this process, the polymer (or copolymer) is melted and then pushed through (“extruded”) a die, which contains the form of the desired product. Plastic shapes, sheets, and toys would be produced by such a process.
- 2) Blow Molding. This is the type of process used to make plastic bottles. The polymer is extruded as a rod and then inserted into a die. A gas

stream is then injected into the rod, causing it to expand into the die shape, leaving the inside hollow.

- 3) Injection Molding. In this case, the entire cavity of a mold is filled with a molten polymer, and after cooling, is rejected and the process repeated.

In all of the aforementioned processes, the thermal and flow properties discussed are critical in designing the correct type of process and specifying the optimal processing equipment.

- 4) Spinning. In this case a polymer is extruded into a very fine diameter rod and these “fibers” are spun together into what amounts to a multicomponent thread wound up on to a spool. These threads (typically nylon, polyester, etc.) are ultimately unwound and spun into clothing.

As opposed to specific chemical entities, polymers and multicomponent polymers will have a broad range of properties, and many product demands can be met by several different polymer systems and blends. In any case, the polymer properties must match what is required in the final end use. Examples include impact strength, tensile strength, clarity, glass transition temperature, and others. Specific chemicals such as acetone have a specific boiling point, freezing point, vapor pressure, viscosity, density, and surface tension, which are independent of the process by which they are made. This is not the case with polymers and makes polymer processing much more empirical in nature.

Plastics Recycling

There is much activity in this area directed at trying to reduce the volume of plastics in landfills. There are several challenges in accomplishing the goal of total plastics recycling as follows:

- 1) Polymer Degradation. Polymers are subject to degradation in terms of their MW and physical properties each time they are melted and reprocessed. We can see this in commercial products made from recycled plastics when the label says “made with 10, 20, etc. % recycled plastics.” Few materials can be reprocessed to their original condition due to degradation and the contamination of one plastic with another, not allowing accurate process control to achieve the needed physical properties.
- 2) Additives. The color and physical property modifiers added for the original end use may or may not be suitable for the recycled use, thus eliminating all but the least severe applications such as low quality plastic garbage bags. The cost of separating the various polymers and additives to the degree necessary is currently much too cost prohibitive for commercial use, with some sort of subsidy or tax credit.
- 3) Depolymerization or Pyrolysis. In this form of plastics recycling, the plastics are “burned” in an anaerobic system in the absence of oxygen. In this

type of process, the polymer decomposes back into its starting monomers (i.e., ethylene, styrene, etc.), which are then separated via conventional chemical engineering separation techniques such as distillation or absorption. This type of process provides much more flexibility in the use of the recycled monomers.

Summary

The chemical engineering issues with polymer manufacture, processing, and end use are more complicated than traditional chemical processing. The properties of polymers are orders of magnitude different from traditional chemicals, impacting fluid flow, heat transfer, and reaction engineering. In addition, end-use properties (in the eye of the end user) can be achieved by many different types of polymers, including additives. The product and process are mutually connected far more than in the case of traditional chemicals and chemical engineering. The use of catalysts to produce many different forms and types of polymers is also unique challenge.

Coffee Brewing and Polymers

The bag in which much coffee is packaged is usually a foil-lined (to prevent oxygen and water from entering) plastic bag, which must be strong enough to withstand normal handling in the grocery store, distribution channel, and home. It must not rupture when dropped from reasonable heights. This value can be measured in lab tests. The materials used in containing the coffee, including the new “pods” used in single serving systems, must have a high enough T_g to withstand the temperature of the brewing water and not melt in the coffee brewer or in the dishwasher.

If your coffee cup is a foamed polystyrene cup, do you recycle it?

Discussion Questions

- 1 How many different types of polymerization processes are run at your location? Is it clearly understood why a particular process is used to produce a particular product?
- 2 For the polymerization processes to run, are their limitations clearly understood in terms of MW, MWD, tensile strength, etc.?
- 3 How are the polymers formulated? With what type of equipment? How was it chosen? Are you prepared for possible customer requests for changes?

- 4 What possible new products could be produced in your current equipment?
- 5 How well is the heat transfer in and out of the polymer streams understood? What possible improvements are possible?
- 6 Are you familiar with all the possible crystallinity and density forms of your products and how they could be changed?

Review Questions (Answers in Appendix with Explanations)

- 1 Polymers are long chains of:
A Polys
B Mers
C Various mixtures of polys and mers
D Monomers
- 2 Latex polymers are unique in that they:
A Are used in tennis shoes
B Are stretchable
C Are suspensions of polymers in solution
D Are combinations of thermoplastic and thermoset polymers
- 3 The uniqueness of elastomers is that they:
A Have a T_g below room temperature
B Have a T_g at room temperature
C Have a T_g above room temperature
D Have a T_g that is controllable
- 4 *cis*- and *trans*-isomers differ in:
A Where functional groups are positioned on the monomer backbone
B Their preference for being *cis* or *trans*
C Their ability to change positions
D Cost
- 5 “Condensation” polymerizations are unique in that they:
A Produce polymers that condense when it is cold
B Split out a molecule during the polymerization process
C Prevent another monomer from entering the process
D Provide a barrier to another polymerization process occurring

- 6 Polymer additives can be used to affect or change:
- A __Color
 - B __Flowability
 - C __Ability to foam
 - D __All of the above
- 7 A differential scanning calorimetry (DSC) tells us:
- A __Softening temperature range of a polymer
 - B __Softening temperature ranges within a polymer
 - C __Degree of crystallinity within a polymer
 - D __All of the above
- 8 Chemical engineering challenges presented in processing polymers include all but:
- A __High viscosity
 - B __Slow heat transfer rates
 - C __Knowledge of the polymers being processed
 - D __Difficulty in mixing
- 9 The technical challenges in recycling of plastics and polymers can be affected by all but:
- A __Purity of plastics and ability to separate into various types
 - B __Energy value of plastics
 - C __Legislation
 - D __Landfill availability

Additional Resources

- Sharpe, P. (2015) "Making Plastics: From Monomer to Polymer" *Chemical Engineering Progress*, 9, pp. 24–29.
- Stein, H. (2014) "Understanding Polymer Weld Morphologies" *Chemical Engineering Progress*, 7, p. 20.
- Villa, C.; Dhodapkar, S.; and Jain, P. (2016) "Designing Polymerization Reaction Systems" *Chemical Engineering Progress*, 2, pp. 44–54.
<https://www.usm.edu/polymer>.

18

Process Control

It almost goes without saying that a chemical process needs to be controlled. But why? This is an important question to answer prior to deciding *how* we want to control the process. Some typical reasons include the following:

- 1) Internal Process Disturbances and Changes. These can take many forms including changes in feed rates, temperatures, pressures, and compositions of incoming process streams. Examples include cooling water temperature and pressure, steam temperature and pressure, and changes in air pressure and electrical voltage used to control process equipment.
- 2) External Conditions. These would include weather (primarily external temperature and weather conditions such as wind, rain, and humidity) and changes in items mentioned in #1 earlier if the sources of the variations are outside the control of the process operation. If a feedstock or raw material being used is coming from a source outside the organization's direct control (feedstock arriving in a tank truck, tank car, or pipeline), there must be a process in place to ensure that the composition and quality of this material is what is specified.
- 3) Safety and Environmental Impacts and Regulations. Many processes, if not under control, could emit hazardous materials that could injure the people within the plant's perimeters or in the surrounding communities. Most chemical process operations also operate under several kinds of operation permits issued by local, state, or federal authorities. These permits frequently limit environmental discharges to the air and water. Any process control strategy must assist in complying with such regulations. From a safety standpoint, the means by which a process is controlled *must* ensure that operating personnel are not subject to situations where their safety and lives are threatened. The reactive chemicals area discussed earlier is one of these areas.
- 4) Planned Changes. In many chemical operations, the "normal" process operations may be deliberately changed as a function of customer demand,

regulatory requirements, or external conditions. Examples here would include changing gasoline composition due to differences in volatility requirements as the seasons change, especially in geographic areas where winter and summer weather conditions are quite different, and specialty chemical operations to reflect changes in product composition or changes in ratios or temperatures within a semi-continuous operation.

Other reasons we desire to document, as well as control chemical operations, include the following:

- 1) **Regulatory and Process Documentation.** For example, when a pharmaceutical is registered by the Food and Drug Administration (FDA) in the United States, it is necessary to document not only the final product composition but also the process variables and conditions used to produce the product, as they are tied directly to the FDA registration approval process.
- 2) **Product Quality Issues.** Many customers using chemical products have defined specifications for their products, which must be met; however, in some cases the performance of the product in the end-use applications has not been defined adequately by measurable items. In some of these cases, the process operating conditions can be used to provide information to better control a process for a particular customer to partially substitute for end-product analytical information.
- 3) **Process Learning.** There is no chemical process operating today where everything is known about how all variables will respond to all possible changes. It is common for a newly built plant to have instrumentation, analytical devices, corrosion coupons, and other such items installed within it for the simple reason of data collection to learn more about the process to improve understanding and how it might be better monitored and controlled in the future. This information is analyzed offline for its learning value, but is typically not used to control the current plant operation.

Elements of a Process Control System

We first need to have a desired value for something we are measuring. This could be temperature, level, mass weight, flow rate, composition, or pressure. This has usually been determined by previous experience, process knowledge, and input from customers. (Customers in this context could mean the next unit process within a larger process run by the same company.) As a simple example, consider the human body temperature. We know the normal desired number for this is 98.6°F.

The second part of the system is a way to measure what is of concern to us. This could be a thermocouple or RTD device for temperature, a differential bubbling device for level, an orifice plate for flow, an online (or offline) analytical

device to measure composition, or a diaphragm type of device to measure pressure. At home, we do this with a thermometer, inserted under the tongue and held there until the temperature reading does not change. This allows us to know whether our body temperature is at the “set point.”

The third part of the system is the way to connect these two parts. In other words, what do we do if the measurement is not what it needs to be? We need an action of some sort to make these two measurements to be the same. We refer to this as a control action. This could be a change in heating or cooling to control temperature, an increase or decrease in flow rate or pump speed to control flow or level, or a change in one feed rate relative to another to change composition. Another peripheral question is to ask what are the consequences of this variable not being what it is supposed to be? To what degree? And for how long? The answer to these last two questions will have a great impact on the nature of the response (what we will now call the *control action*). In our simple example, it might be to take an aspirin tablet, drink something cold, or call the doctor (or possibly some combination of these three actions). In a chemical process, this action could be either manual or automatic, depending on the seriousness of the deviation and the speed of the response necessary.

In our human body temperature case, a minor deviation from normal body temperature might just call for taking two aspirin tablets and getting some extra rest and fluid consumption. If, however, the measurement rises to 103°F, we now are concerned about something far more serious such as the flu or pneumonia. We take more serious action such as seeing the doctor or going to an emergency room. Our response is *proportional* to the deviation from normal.

1) Measurement. First of all, we need a way to measure what is of concern to us, for example, level, pressure, or composition. The exact way we do this will be a function of the desired accuracy and response time of the measurement system (how long does it take for the measurement device to detect a change and transmit it to the part of the system, which will analyze and react to the measurement?). If we are measuring pressure, differential pressure instruments are typically used. If direct contact with the fluid is not possible, then various types of electronic or ultrasonic devices may be used. In some cases, depending on the nature of the fluid, magnetic property differences can be used to measure the level external to the tank, avoiding contact. When using differential pressure as a measurement approach, it is important to take into account any density changes in the fluid due to compositional or temperature changes. A bubbling device responds to pressure of a height of liquid, and if the density of the fluid is increased, a change in density will be seen as a change in level. It is also important to remember that any gas introduced to measure level must be able to be vented from the process in a safe way and not contribute to flammability or environmental concerns.

Temperatures are typically measured by thermocouple or RTD devices, which use the difference in two different metals' change in conductivity or electrical resistance as a function of temperature.

Flow measurements are typically made with a device that temporarily restricts the flow of fluid through a hole smaller than the diameter of the pipe. These devices were reviewed in Chapter 5.

- 2) Comparing and Evaluating. After a measurement is made, we need to decide what we should do in response. What is the difference between what we observe and what we need? How fast is the change occurring? What are the consequences if a change is not made? How fast do we need to respond? Under what conditions? This is sometimes written as E (error) = MV (measured value) – SP (set point).
- 3) Responding. After we have measured or observed and compared what we see or measure to what we need, we need to decide how to respond to the difference. This can be done in a myriad of ways depending on the nature of the difference (error) we see, the necessary speed of response, and the nature of the response. The most often seen aspect of this last part of the cycle is some kind of control valve that regulates flow, heating or cooling, pressure, or composition. These valves have many different types of design and can be designed and installed in many different ways, which we will discuss later. This cycle of measuring, comparing/evaluating, and responding is what we call a *control loop*.

Control Loops

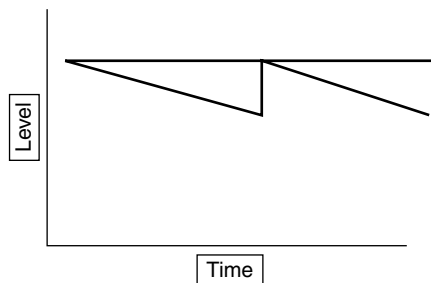
This cycle of measure, evaluate, and take action (or respond) is commonly referred to as a control loop. We continuously measure, evaluate, and respond. The speed at which this is done can be anywhere from many times per second to just several times an hour, depending on the rate of change in the operation being controlled, how critical it is to maintain precise control, and the safety/environmental implications of loss of control. In addition to the simple human thermometer example already discussed, how a turkey is prepared for Thanksgiving is another analogous situation we can all relate to. We have a cookbook that says if the turkey weighs a certain amount and is stuffed, then it should take so many hours to bake at a given temperature range. We prepare the turkey and for the first several hours, we pay little attention. As we get near the end of the cycle, we start to inspect the skin and poke the turkey to “fine-tune” the final cooking temperature. The speed of the control loop is very slow at the beginning and speeds up at the end. The analogy in a chemical reactor might be a slow reaction producing an intermediate, which then reacts very fast with a newly added material to produce a finished product.

There are numerous types of control loops that can be designed and implemented, and with today's advanced measurement, calculation, and computer capabilities we have, it is possible to design an infinite number and types of control loops and systems. We will cover only the most basic concepts here.

On-off Control

This type of control is analogous to the type of control system found in most home heating systems. First of all, a temperature is set. If the temperature deviates from this temperature, the fan and heating/cooling system turns on until the desired temperature is reached and then the system elements shut off. An industrial analogy might be maintaining the temperature of tank contents at a certain temperature with a heating or cooling coil. Another might be controlling level in a tank and turning a pump on or off based on the level measurement. This type of control will always have the possibility of not exactly reaching the desired temperature due to simple overshoot or undershoot based on system volume, lag time, etc. If offset is tolerable and the system is not demanding in some way, this may be an acceptable control approach. For a tank level on-off system, with pumping in and out, we might see a control room graph that looks something like that shown in Figure 18.1.

Figure 18.1 On-off control for tank level.



This would be similar to what occurs in a home heating system, except that we typically do not see the graph. The manufacturer of the thermostat has preset (which might be adjustable by the homeowner) a certain deviation, at which point the gas flame is ignited by the pilot light and the blower starts. The small differences in the actual temperature in the house might be less than 0.5°F , too small for anyone to notice. Since sometimes the error is high and sometimes it is low, the average of the error is acceptable. The same logic applies to the start of an air conditioning compressor or a sump pump in the basement of a house. This type of control will always have some level of error that is not automatically compensated for since there is no way to integrate the total error over time. In the case of small variations in a tank level or a small degree of temperature change in a home, these differences average out over

time in a way that is not noticeable from a practical standpoint. This type of control may put process equipment under abnormal stress as the final control element (pump, heater, compressor, etc.) is starting and stopping on an irregular basis as opposed to running continuously.

Proportional Control

This type of control includes a response to the error that is proportional to the amount of the error. In our home heating example, the fan speed could be increased (requiring a variable speed motor) if the temperature was much higher or lower than the normal. In our tank system the output of the pump (which is now running continuously and has a control valve throttling its output) will be changed in response to the *amount* of error, not just the fact that there is an error. Mathematically, we would describe this type of control as follows:

$$CE = K_c e + m$$

where CE, the position of the control element, is proportional to the amount of error plus the reset value; K_c is the controller gain (sensitivity is one way to look at this or how fast and how much the controller reacts to an error); and m , the reset value, is the position of the control element when the process is at the set point. We need to ensure that we understand the value of “ m .” At any point in time, a control valve has a position, “ m .” When asked to change, its position moves according to the aforementioned equation, proportional to the amount of error and the speed with which we desire a response (K_c), but the initial valve setting, “ m ,” is not changed. Without a change in this value, we have a permanent offset in the valve position versus what we want. This produces an “offset.” A graphical display of this response would look like Figure 18.2, if displayed on a control graph.

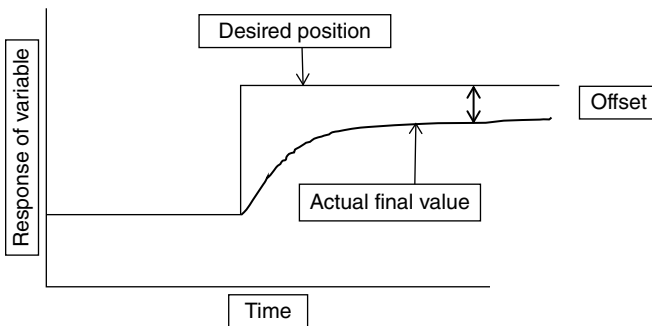


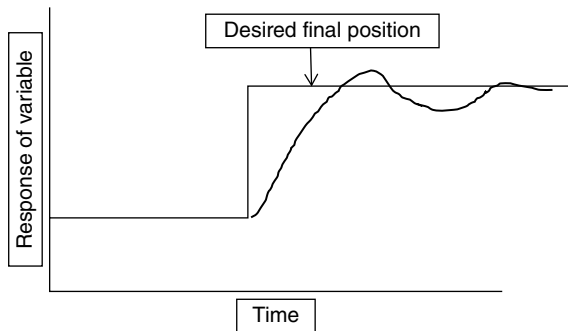
Figure 18.2 Response of proportional control: offset.

Though a home heating or cooling system is normally not a proportional system, it will typically display a response such as this, and the reason we don't notice is that on occasion it is above and in others below (depending on where the system starts from) and the small difference and the average temperature in the room being close enough for us to feel comfortable. Whether an offset is tolerable in a chemical process, control loop is quite another matter. We need to think carefully about the consequences of the variable of concern not being where it is desired to be and for how long.

Proportional–Integral Control

In this type of control, the error around the desired set point is constantly evaluated and the valve position is changed until the desired value of the controlled value is reached. In effect, “ m ” is constantly adjusted until the desired set point is reached. A graph of this type of control would look something like that shown in Figure 18.3.

Figure 18.3 Control response with integral control.



There will be both an “overshoot” and “undershoot” as the system integrates the error until the desired final control point is reached. The primary advantage of this type of control loop is that it will eventually reach the truly desired set point. However, there will be an overshoot and undershoot on the way to the final steady state, and the implications of this must be considered. There are two parameter choices in this type of control. First is the gain (K_c), the same as discussed for simple proportional control (how much reaction is there to a given amount of error?). The second design aspect of this type of control is what we call the “reset” time. In other words, how often does the control system measurement check to see if it has reached its final desired point and whether it is over or under that desired set point? This could be milliseconds to minutes, depending on the nature of the system being controlled and its response to change.

We can view two extremes of these settings as seen in Figure 18.4.

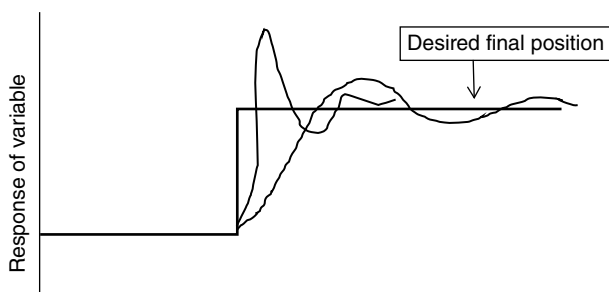


Figure 18.4 Impact of choice of integral reset time.

Line “A” would represent a high K_c and short reset time, while line “B” would represent a lower “K” and a slower reset time. The choice of this setting will depend on the impact of overshoot, the amount of time where not being at the final set point is tolerable, the impact of these controlled variables on downstream operations, and the nature of the controlled variable itself and what affects its change. In a typical plant start-up, the gain and reset time would be estimated based on process knowledge and typically programmed into a process control computer or set manually in a simple controller. Based on actual process behavior and response, these settings would be adjusted during a plant start-up.

Derivative Control

This additional level of sophistication can be added to either of the aforementioned strategies. In derivative control, we assume that we have enough knowledge about the process that we can estimate, ahead of time, how the process will respond to a known change. For example, if we are running a reaction that has a known ratio of “A” to “B” and we increase the rate of “B,” we know that if we increase “B” by 50%, the rate of “A” should also be increased by 50%. There should be no need to have a downstream analysis output telling us that the amount of “A” should also be increased by 50%. A more complex illustration of this strategy would be changing cooling or heating to a reactor based on a change in feed rates or temperatures of feeds to a reactor based on our knowledge of heats of reactions, heat capacities of materials, etc. There is always some uncertainty in this type of control as it assumes that the effects of upstream changes in process variables are all known and can be programmed into a process control scheme. This is rare, but the need for a set point to be ultimately achieved is often critical, and the result is that the large majority of chemical process control loops are based on a proportional–integral (PI) scheme.

We can view a summary of these approaches to control in Figure 18.5.

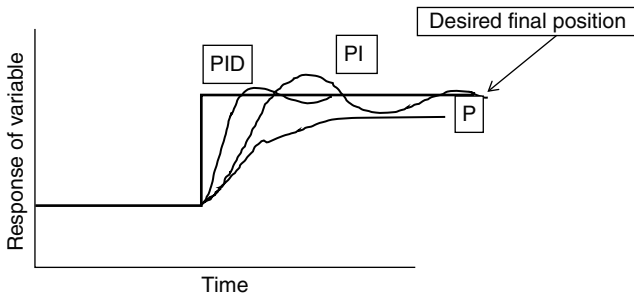


Figure 18.5 Response of various control system types.

Both PI and PID control systems will eventually reach the desired set point, and both will overshoot the desired set point to some extent. The control loop settings that will determine to what extent this happens will be fine-tuned during a plant start-up.

Other factors that must be considered in the design of a control system include “dead time,” meaning the time difference between when the variable is measured and when response to that measurement is made. If this time differential is high, the response of the control system to changes or errors may become out of phase with the dynamics of the process. The same kind of result is possible if the time for the actual measurement is much slower than the process response to change.

There are many sophisticated mathematical modeling techniques for determining the various control scheme constants, including what is known as Ziegler–Nichols, allowing tuning of a control loop based on empirical process information.

Other types of process control structural design include the following:

Ratio Control

If we know that a change in one feed rate should be accompanied by a known change in another variable, we can make this change at the same time. It is important that we understand all the impacts of a feed change, including heat release in an exothermic reaction or gas production in a reaction.

Cascade Control

We can think of this type of control as “embedded.” For example, if we have a very slow chemical reaction system providing the feed to another, a much faster reaction system, the control loops for these systems would be very different as one is feeding the other and their rates are very different.

Measurement Systems

In order for a variable to be controlled, it must be measured and that measurement information must be used in the control loop design.

Flow measurements were discussed previously in the unit on fluids and pumps. *Pressure measurements* are most frequently done by a mechanism that senses differential pressure against a reference point. A diaphragm device outputting an electronic signal can serve this purpose.

Temperature measurements are done with thermocouples or with RTDs, where resistance changes between two different metals generate an electronic signal.

Level measurements can be done through the use of differential pressure measurements, magnetic resonance, or ultrasonic measurements.

Control Valves

The final element in a control loop is the control valve. This valve is actuated via air or an electronic signal and moved to varying degrees depending on the difference in measurement between the actual versus the desired value of a particular measurement. There are many choices in such valves, and the choice needs to be made based on the desired response we want as a function of the amount of error measurement and how fast the response needs to be. Basically, control valves are characterized in two ways as follows:

- 1) Size. This relates to the maximum flow that a given valve will allow. This will vary as a function of pressure drop available and fluid properties, as discussed earlier.
- 2) Flow versus % Opening Response. This is basically a plot of percentage of maximum flow (which will vary with fluid properties already discussed) as a function of what % open the valve is. This is not necessarily a linear function as the geometric design of internals of the valve can greatly affect this relationship and these differences are a major part of the valve choice decision.

Though there are many more possibilities based on internal geometric valve design, we can classify many valves as linear, fast opening, or equal percentage as shown in Figure 18.6.

It is also possible to design a valve with a more complicated response curve if desired. A globe valve is illustrated in Figure 18.7.

We can see that a very small adjustment in the valve stem will allow a great deal of flow, and this type of valve would typically be characterized as a fast opening valve. “Trim” is the word used to describe the degree of flow response

Figure 18.6 Flow versus % valve opening. Source: Reproduced with permission of Engineering Toolbox.

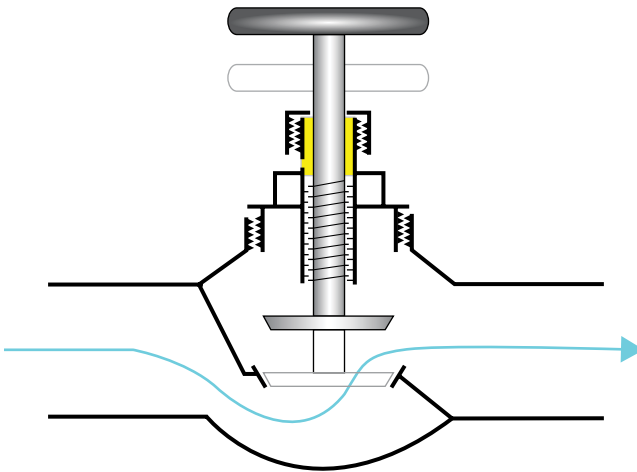
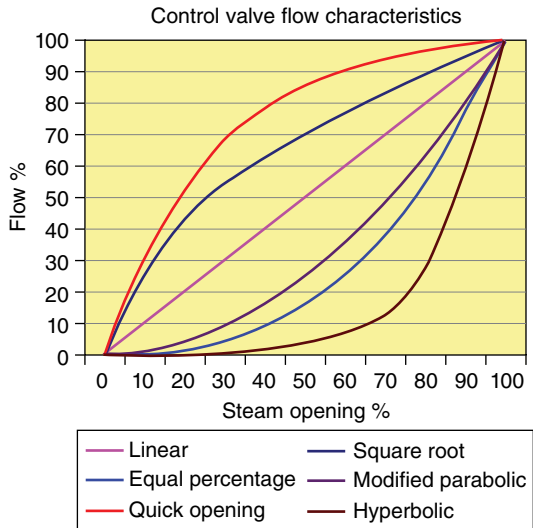


Figure 18.7 Elements of a globe valve. Source: Padleckas, https://commons.wikimedia.org/wiki/File:Valve_cross-section.PNG. Used under CC BY-SA 3.0, <https://creativecommons.org/licenses/by-sa/3.0/deed.en>. © Wikipedia.

to valve opening. The geometry of this valve trim can be designed to give almost any response as shown in Figure 18.6.

An equal percentage valve has an internal design that very slowly allows flow versus its physical opening (see Figure 18.6). These valves are excellent for close control over a broad range of conditions.

A ball valve is shown in Figure 18.8.



Figure 18.8 Ball valve. Source: Castelnovo, https://commons.wikimedia.org/wiki/File:Seccion_valvula_de_bola.jpg. Used under CC BY-SA 4.0, <https://creativecommons.org/licenses/by-sa/4.0/>. © Wikipedia.

A quarter turn will move the valve from no flow to 100% flow. This type of valve will produce a more linear response curve.

A gate valve is one where a simple linear plate is installed perpendicular to the flow and the valve moved up and down as desired, as seen in Figure 18.9.

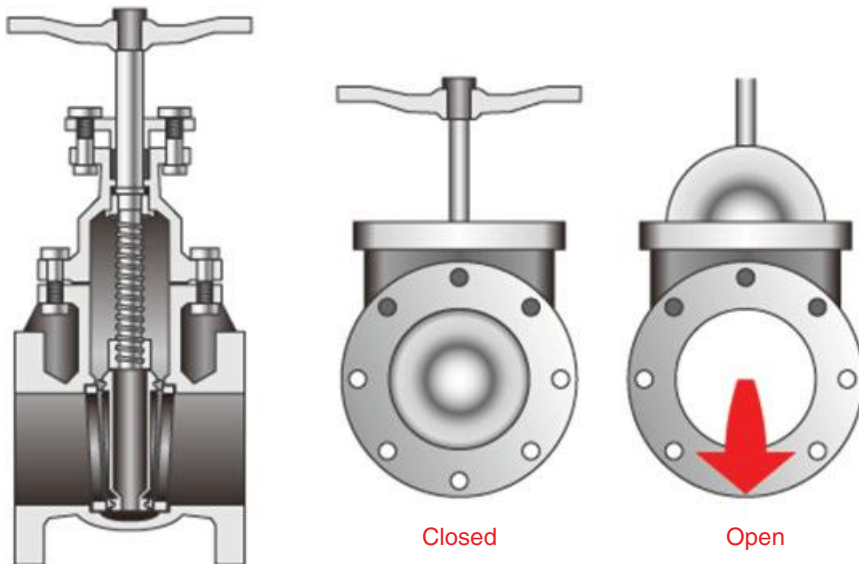


Figure 18.9 Gate valve. Source: Reproduced with permission of Google.

This type of valve will typically have a linear response curve. A butterfly valve is shown in Figure 18.10.



Figure 18.10 Butterfly valve. Source: Qurren. https://commons.wikimedia.org/wiki/File:Yagisawa_power_station_inlet_valve.jpg. Used under CC BY-SA 3.0, <https://creativecommons.org/licenses/by-sa/3.0/deed.en>. © Wikipedia.

Because of their reliance on sealing against an interior surface, it is difficult to ensure 100% shut off in this type of valve.

One other type of “on–off”-type valve sometimes is a check valve, which is intended to prevent flow in a particular direction primarily due to safety or quality concerns. This can be done via a flap that is designed to be totally open in one direction and allow no flow in the other direction (see Figure 18.11).



Figure 18.11 Check valve with flow indication.

When this type of valve is installed, it is critical to ensure that the arrow (indicating the direction that flow is allowed) is in the correct direction. Obviously, if such a valve were to be installed in reverse, the safety or environmental consequences could be severe, allowing the flow to go in the exact opposite direction vs. intended.

Valve Capacity

The capacity of a valve is normally given by its C_v or capacity of water flow at 1 psi pressure drop with the water at 60°F. The higher the C_v of a valve, the greater its capacity. This provides a standardized way of comparing different valves in the same service and can assist in choosing a valve when pressure drop is a prime consideration. For example, if a particular valve had a C_v of 12 versus a C_v of another valve at 4, we would expect three times the flow at the same fluid conditions and pressure drop across the valve. When doing these calculations or comparisons, remember to maintain the same set of units.

Table 18.1 shows the relative capacities of different valve sizes.

Utility Failure

Since the movement of control valves is driven typically by electrical or mechanical energy, it is important to decide, prior to installation and start-up, how a particular valve should respond if the utility driving its change is lost.

Table 18.1 Relative valve capacity.

Control valve flow capacities (Cv*)							
Valve type	Valve size (in.)						
	0.75	1.5	2	4	6	8	10
Single-seat globe	6	26	46	184	414	736	1150
Double-seat globe	7	27	48	192	432	768	1200
Sliding gate	5	20	36	144	324	576	900
Single-seat Y	11	43	76	304	684	1216	1900
Throttling ball	14	56	100	400	900	1600	2500
Single-seat angle	15	59	104	416	936	1664	2600
90%-open butterfly	18	72	128	512	1152	2048	3200

Source: Chemical Engineering Progress, 3/16, pp. 51–58. Reproduced with permission of American Institute of Chemical Engineers.

When should a valve fail in the “open” position? Any time the valve is controlling cooling water or other utility that is designed to reduce the rate of an exothermic chemical reaction. The reaction will not stop just because utilities are lost. In fact, if it is a reactor vessel and the agitation is lost for the same reason, this will only increase the potential danger of the situation. A backup electrical supply may also be necessary to keep the process under control.

When should a valve fail in the “closed” position? If we are running an exothermic reaction, we would want all of the feed materials into the reactor to stop, in combination with the cooling water failing to open.

When might we want a valve to fail in its “last position?” If we are melting a heat-sensitive material, we might choose this option versus having the material freeze or decompose if exposed to a higher temperature.

It is possible to design a valve and utility system to do any of these aforementioned options. The important thing is to think about the ramifications of utility loss prior to designing and installing a control valve system.

Process Control as a Buffer

It is important to remember that process control is used not only to control a specific process variable but also to provide a buffer between unit operations within a process or plant. Examples of these include the following:

- 1) Inventory Management. A unit operation such as a reaction system may be providing the feed to a separation unit. Either rates may need to be slowed to take into account another’s slower rate or downtime. Restrictions in raw material availability or product storage are also examples.

- 2) **Utility Restrictions.** If there is an outage at a utility, either on-site or off-site, there may be a need to slow a unit operation or change the conditions under which it operates.
- 3) **Emergencies.** We must always consider the possibility of utility loss. The process control system must be designed to react to this situation in a safe way. In many large plant situations, backup electrical generations units are designed to activate and keep a process's key units and controls operating for a specified amount of time.

Instruments that “Lie”

In many situations, an instrument's output is calculated based on physical properties that are assumed to be constant when this is not necessarily true. For example, a level instrument that is not calibrated and corrected by density of a fluid may show level decreasing when it is actually increasing. This will cause the control system to add liquid instead of the proper response. This was actually one key cause of the large Texas City fire and explosion in Texas City, TX, in 2005 (see Figure 18.12).


It is important in process control design and instrument selection that we consider all the variables that might affect the measurement we are reacting to, such as the following:

- 1) **Temperature.** What is the effect of a temperature change in the reading? This applies especially to measurements of level and density and especially, in the latter case, to gases.
- 2) **Pressure.** An instrument calibrated for one set of pressure conditions can give off the wrong output if this is not compensated for, especially for gases.
- 3) **Composition.** There is a tendency to take averages of composition measurements and rely on them to provide an output. The exact compositional outputs as a function of concentration need to be measured.
- 4) **Density.** How can compositional change affect this measurement?
- 5) **Viscosity.** Temperature, as well as composition, can affect this measurement greatly. Have these differences been taken into account?


Summary

Process control is a critical part of any chemical process, no matter its level of sophistication. The control logic and design of the control loops must be thoroughly thought out, and all variables that may affect measurements and how the control system will respond to them must be considered.

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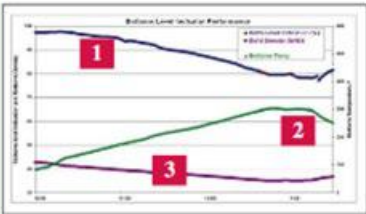
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Instrumentation — Can you be fooled by it?

March 2007



What happened?

A column was overfilled. However, before the incident, as shown in this instrument chart, the level *indication* in the bottom of the column (the dark blue line - 1) slowly decreased!



YES you can!

The level was measured with a displacement level indicator. Normally, when the displacer (green) is partially covered with liquid, it properly indicates level based on the changing force on the displacer as the liquid level changes (first and second drawings). But, on the day of the incident, the column was overfilled with cold liquid, completely submerging the displacer in cold liquid (third drawing). The level was above 100%, and the level indicator showed a high level alarm condition continuously. A high level alarm indicates an abnormal condition, and this should be an alert that something is not normal. In this incident, there was no response to the alarm condition.

With the liquid completely covering the displacer, the instrument did not indicate liquid level. Instead, the force on the displacer gave a measure of the relative density of the displacer and the liquid in which it was submerged. In other words, the instrument was not designed to function properly if the level was high enough to completely submerge the displacer. The column was heated during the startup. As the temperature of the liquid increased (the green line in the graph above - line 2), the density of the liquid decreased (the purple line - 3). The change in density of the liquid changed the force on the displacer, resulting in a decrease in the "level" indication (fourth drawing, with hot liquid), even though the column level was actually increasing. The column overflowed, flammable material was released, and there was a major explosion and fire.

What you can do

Know what can fool you. Review examples of incidents where the instrumentation provided information that did not represent the data that was wanted (for example, density of the liquid, not level). This is not always an easy concept to grasp, so consult with the engineers and technicians who know the system best.

Understand how instrumentation works, and how it will respond to conditions outside the normal operating range, including, for example, control loops, venturis, orifice plates and impulse lines, differential pressure cells, level floats. Know whether instrumentation is normally energized, and the failure mode for valves, instruments and control loops following loss of pneumatic or electrical energy.

Know what you should be observing as part of normal operations, for example, balancing transfers into and out of equipment, changes in level. And, *NEVER* ignore alarms — find out what caused the alarm!

Understand whether components can be tested on line or whether an "out of service" test is required to confirm that an instrument is working.

PSID members use Free Search for "Instrumentation" or "Level Control."

Understand how your equipment works — and how it can fool you!

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CEP March 2007 www.aiche.org/cep **25**

Figure 18.12 Understanding all variables that affect instrumentation response. Source: Chemical Engineering Progress and Center for Chemical Process Safety. Reproduced with permission of American Institute of Chemical Engineers and Chemical Process Safety.

Control of Coffee Brewing

Any coffee machine today has some kind of “control panel.” The selection of coffee type, size of cup, and occasionally water temperature may be set points that a consumer can decide. The coffee drinker also decides how long the coffee is left on the hot plate or left in the vacuum container. The ratio of flavor additives and water type are also control points. The amount of mixing of the final product with cream and sugar or sweetener is also a control point. From a safety standpoint, most coffee makers are located in the kitchen, and building codes require them to use a ground fault interrupter (GFI) circuit, which will automatically cut power if any fluid comes in contact with the electrical circuit.

Discussion Questions

- 1 How are the various parts of your process controlled? How was this decided? Has anything changed about your raw material or products that would warrant a review?
- 2 Is it well understood why certain types of valves were chosen? Are the response curves available? If not, why not? When was the last time they were reviewed?
- 3 Are the control systems and hardware appropriate for the current list of concerns in the areas of safety and reactive chemicals?
- 4 Is it well understood what secondary variables could affect a critical process control loop?
- 5 Is it well understood how changes in process chemistry could affect process control?

Review Questions (Answers in Appendix with Explanations)

- 1 Proper process control is necessary because:
A __ Specifications must be met on products produced
B __ Environmental emissions must be within permitted limits
C __ Safety and reactive chemicals issues must be controlled
D __ All of the above

- 2 The elements of a process control loop include all but:
- A __Method to measure
 - B __Manager's approval
 - C __Way to evaluate the measurement versus what is desired
 - D __Corrective action
- 3 Characteristics of a process which affect how it should be controlled include all but:
- A __Customer quality requirements
 - B __Response time of measurements
 - C __Degree of deviation permitted around the set point
 - D __The mood of the process operator that day
- 4 The least sophisticated process control strategy is:
- A __On-off
 - B __Off-on
 - C __Off sometimes, on other times
 - D __On-on, off-off
- 5 Integral control has a key advantage in that it:
- A __Has the capability to integrate
 - B __Will eventually result in the process reaching its desired set point
 - C __Oscillates around the desired set point
 - D __Oscillates in a controlled manner around the desired set point
- 6 Derivative control allows a control system to:
- A __Anticipate a change in process based on input changes
 - B __Preplan batch operations
 - C __Provide a more uniform break structure for process operators
 - D __React sooner to post process changes
- 7 If a process has a slow reaction rate process feeding into a very fast final reaction process, the type of process control likely to be used is:
- A __Proportional
 - B __Follow the leader
 - C __Wait 'til it tells me
 - D __Cascade
- 8 Control valves can be characterized, in terms of their process response, by all but:
- A __Capacity
 - B __Speed of response

- C Type of response
D Materials of construction
- 9 A control valve curve plots:
A % Open versus % closed
B % Closed versus flow rate
C % Flow versus % open
D Flow rate versus air pressure supplied
- 10 A water cooling control valve, with loss of utilities, should fail to open if:
A An endothermic reaction is being run
B An exothermic reaction is being run
C The utility water rates are temporarily dropping
D There is no mechanic available to close
- 11 A control valve, with loss of utilities, should fail to close if:
A An endothermic reaction is being run
B It controls feed to an exothermic reaction
C There is one person strong enough to close it
D There is no other option
- 12 A control room variable may not indicate the actual process conditions if:
A The sensor has failed or been disconnected
B A physical property effect has not been taken into account
C The operator is not looking at the correct screen
D Any of the above

Additional Resources

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- Smith, C. (2016) "PID Explained for Process Engineers: Part I: The Basic Control Equation" *Chemical Engineering Progress*, **1**, pp. 37–44.
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