

CHAPTER III

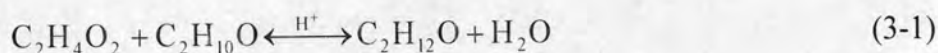


THEORY

3.1 Synthesis of Butyl Acetate via Esterification Process

n-Butyl acetate (BuOAc), also known as 1-butyl ethanoate or acetic acid butyl ester, has three isomers: tert-butyl acetate, sec-butyl acetate and iso-butyl acetate. It is a colorless flammable liquid with fruity odor. BuOAc is a typical representative of the class of esters of small organic acids and alcohols and an industrially important chemical. It is used in large quantities as a solvent in lacquer and coating manufactures. It has also been applied in pharmaceutical industries and cosmetic formulations as an artificial flavor in recent years. In addition, due to its pleasant fruity (rather like pears) odor, it is also used as a component in synthetic flavors of fruits. It may also be used in photographic industries, as a reaction medium for adhesives, a solvent for leather dressings, an extraction solvent, and a process solvent in various industrial applications. Therefore, the consumption of BuOAc is expected to grow in near future because of its low toxicity and environmental impact, compared to some other types of solvent. Being less harmful to the environment, BuOAc is frequently used as a substitution for aromatics in many coatings and lacquer compositions.

The production of BuOAc by esterification of acetic acid (HOAc) with butanol (BuOH) in the presence of an acid catalyst either homogeneous or heterogeneous generally follows the elementary reaction



The kinetics of esterification catalyzed by acidic cation-exchange resin (Amberlyst-15) was studied by Steinigeweg and Gmehling (2002). The reaction rate based on a pseudo-homogeneous model can be expressed by

$$r = k_f \left(a_{HOAc} a_{BuOH} - \frac{a_{BuOAc} a_{H_2O}}{K_{eq}} \right) \quad (3-2)$$

where k_f and K_{eq} are the forward rate and the reaction equilibrium constants which are the function of temperature as follows,

$$k_f = 6.1084 \times 10^4 \exp\left(-\frac{56.67 \text{ kJ/mol}}{RT}\right) \quad (3-4)$$

$$K_{eq} = 0.6206 \exp\left(-\frac{10.99 \text{ kJ/mol}}{RT}\right) \quad (3-5)$$

3.1.1 Vapor-Liquid-Liquid Equilibrium

Venimadhavan et al. (1999) studied the formation of azeotropic mixture consisting of BuOH, HOAc, BuOAc and H₂O. It was found that there are three minimum-boiling binary azeotropes (BuOH - BuOAc, H₂O- BuOH, H₂O -BuOAc) and one ternary azeotrope (H₂O-BuOH-BuOAc). While the azeotrope between BuOH-BuOAc is homogeneous, the others are heterogeneous. There is an uncertainty in the relative boiling temperature of the two lightest azeotropes. Some sources report that the lightest boiler is the heterogeneous ternary azeotrope between H₂O-BuOH-BuOAc (McKetta et al., 1983), while others report that the heterogeneous binary azeotrope between H₂O -BuOAc is the lightest (Karpilovskiy et al., 1997). Experimental values of the normal boiling points of these azeotropic vary over an interval of ~2 °C and overlap. The boiling point of the ternary azeotrope ranges from 89.40 to 90.60 °C, while the boiling point of the H₂O -BuOAc azeotrope ranges from 90.20 to 91.40 °C (see Table 3.1).

If the binary azeotrope is the lightest boiler, then the design would be quite easy. Because this is an azeotrope between the reaction products, its removal allows for complete conversion of the limiting reactant in a distillation process. In addition, the overhead products are separated in condenser/decanter into two liquid phases: an aqueous phase of nearly pure water and an organic phase which contains 83 mol% BuOAc and 17 mol% H₂O. As a result, the water phase is removed from the process, and BuOAc is purified in a stripper (the overhead vapor from the stripper can be

recycled to the decanter). On the other hand, if the ternary azeotrope is the lightest boiler, the second liquid phase in the condenser/decanter has a composition of 56 mol% BuOAc, 23 mol% H₂O, and 21 mol% BuOH (see Table 3-1). In this case, the design would be very different.

Table 3-1 Boiling points of pure components and azeotropes in a ternary mixture of HOAc, BuOH, H₂O and BuOAc under atmospheric pressure (Venimadhavan et al., 1999)

Pure components and azeotropes	Normal boiling temperature (°C)
H ₂ O - BuOH - BuOAc	89.40-90.60
H ₂ O - BuOAc	90.20-91.04
H ₂ O - BuOH	92.83
H ₂ O	100.0
BuOH - BuOAc	116.94
BuOH	117.74
BuOAc	125.95

Table 3-2 Mole fractions of two heterogeneous azeotropes containing H₂O and BuOAc (Venimadhavan et al., 1999)

Component	Overall composition	Aqueous phase	Organic phase
Ternary azeotrope			
H ₂ O	0.712	0.995	0.232
BuOH	0.085	0.004	0.206
BuOAc	0.203	0.001	0.562
Binary azeotrope			
H ₂ O	0.7228	0.9988	0.1694
BuOAc	0.2772	0.0012	0.8309

3.2 Reactive Distillation

Currently there is considerable academic and industrial interest in multi-functional reactors, involving in-situ separation of products from reactants. Reactive distillation is one of the most common means of in-situ product removal and has been received increasing attention in recent years as an alternative to the conventional reactor followed by distillation processes. Reactive distillation is potentially attractive whenever a liquid phase reaction must be carried out with a large excess of one reactant. Under such circumstance, conventional processes involve large recycle costs for excess reactant. Reactive distillation, on the other hand can be carried out closer to stoichiometric feed conditions, thereby eliminating recycle costs. Both homogeneous and heterogeneous catalyzed chemical reactions can be performed in a reactive distillation column.

3.2.1 Reactive Distillation Configuration

A typical set-up used for a reactive distillation is shown in Figure 3-1. The column usually is divided into three sections: rectifying, reactive and stripping sections. In the reactive section, the reactants are converted into products and by means of distillation; the products are separated out of the reactive zone. The tasks of the rectifying and stripping sections depend on the boiling points of reactants and products. If the product is the lowest boiling component in the process, the rectifying section is used for product purification and reactant recycle, and the stripping section mainly used for inert and by-product removal as well as reactant recycles. On the other hand, for the case that the product is the highest boiling component, the tasks of the rectifying and stripping sections are switched. With the set-up as shown in Figure 3-2, it is possible to virtually eliminate an entire post processing train in a process. One of the most spectacular examples of the use of reactive distillations is the Eastman process for production of methyl acetate (Sirola et al., 1995).

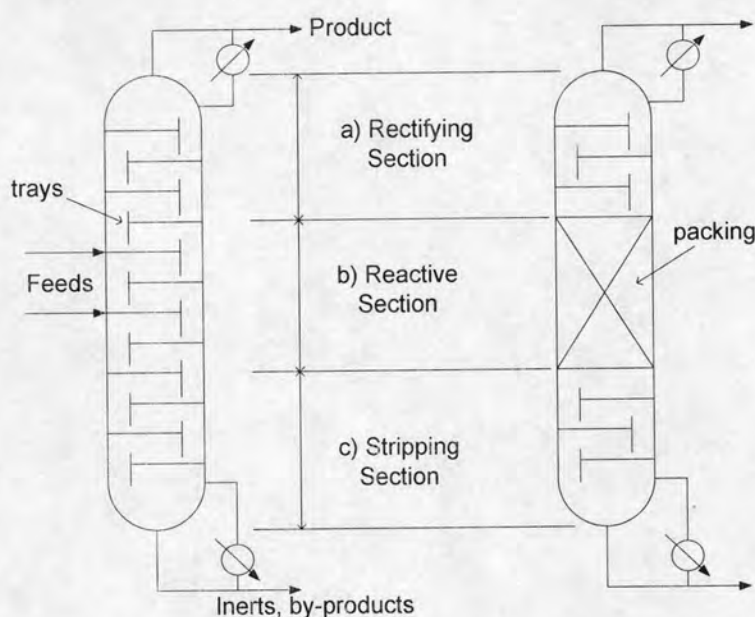


Figure 3-1 Typical configuration of a reactive distillation tray column consisting of three sections: (a) rectifying section. (b) reactive section and (c) stripping section (Siirola et al., 1995).

Considering a reversible reaction scheme $A + B \rightleftharpoons C + D$ where the boiling points of the components follow the sequence A, C, D and B, the traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns (Figure 3-2 (a)). The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst and reached equilibrium. A distillation train is required to produce pure product C and D. The unreacted components, A and B, are recycled back to the reactor. In practice the distillation train could be much complex than the one portrayed in Figure 3-2 (a) if one or more azeotropes are formed in the mixture. An alternative reactive distillation configuration is shown in Figure 3-2 (b). The reactive distillation column consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section the products are separated in-situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A or B with the product C or D. For a properly designed reactive distillation column, virtually 100% conversion can be achieved.

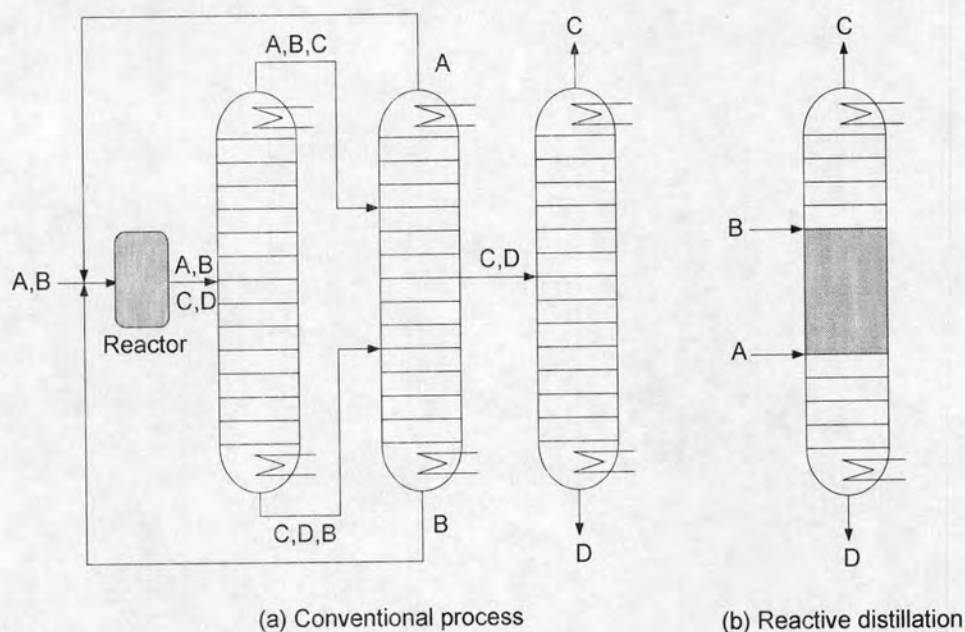


Figure 3-2 Processing schemes for a reaction sequence $A + B \rightleftharpoons C + D$ where C and D are both desired products. (a) Typical configuration of a conventional process consisting of a reactor followed by a distillation train. (b) The reactive distillation configuration. (Stichlmair et al., 1999).

From the example mentioned earlier, it can be seen that the overall flowsheet of the reactive distillation process is less complicated than traditional multi-unit processes consisting of a train of reaction and separation processes with recycle streams. However, it should be noted that the design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in-situ separation function within the reaction zone leads to complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics.

3.2.2 Advantages of Reactive Distillation Column

Carrying out reaction and distillation in a single unit offers several advantages compared to conventional reactor-separator sequences, including

- (a) Reduction in the amount of plant items of equipment. By carrying out the chemical reaction and distillation in the same vessel, one process step is eliminated, along with the associated pumps, piping and instrumentation.
- (b) Shifting of equilibrium. Removing one or more products from the reaction phase causes the equilibrium to be reestablished at a higher conversion. If the relative volatilities are favorable it may be possible to maintain the reagents in the column and draw off only the products. Even if only one product can be separated from the reaction phase, the increase in conversion still gives a benefit in reduced recycle costs.
- (c) Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
- (d) Significantly reduced catalyst requirement for the same degree of conversion.
- (e) Avoidance of azeotropes. Reactive distillation is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. In such cases a conventional separation scheme would require many distillation columns and use of entrainers to break the azeotropes. Instead, careful choice of reactive distillation conditions can allow the azeotropes to be “reacted away” in a single vessel. Azeotropic behavior can also be exploited to maintain high concentrations of the reagents in the reaction zone of the column, or to separate close-boiling mixtures of a reagent and product.
- (f) Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty. Other heat integration benefits can be obtained through use of intermediate condensers, reboilers and pump-arounds.

- (g) Reduced by-product formation.

However, the applications of reactive distillation technology in industrial scale is somewhat limited by several constraints, for examples,

- (a) The boiling point sequence of the components should allow separation of the products. The reactants should not be key components. Any side products or any undesired intermediate products should be medium boiling components so that a high concentration of reactants and a low concentration of products exist in the reaction zone.
- (b) Difficulties in providing proper residence time characteristics. If the residence time for the reaction is long, it may require a large column size and a large hold-up leading to the process becoming uneconomical compared with standard separate reactor and distillation column setup.
- (c) If the scale-up of the process is high, it may get liquid distribution problems especially in a packed reactive distillation column.
- (d) The use of reactive distillation technology is only possible, if the temperature window of the vapor-liquid equilibrium is equivalent to the reaction temperature. By changing the column operating pressure, this temperature window can be altered. However, the thermal stability in the catalyst can limit the upper operation temperature of the distillation column
- (e) Because of the necessity of wet catalyst pellets, the chemical reaction has to take place entirely in the liquid phase.

3.3 Control of Reactive Distillation

A reactive distillation column must be operated so that the product purity and reaction conversion are maintained close to their design values when disturbances enter the column. A efficient control system is needed to put in place that can regulate the column for changes in production rate and the feedstock composition, In the design of such a control system, the selection of the control structure is the most crucial decision.

When determining the control system design for a multivariable process, the terms control strategy, control structure, and controller structures are used interchangeably. However, the three terms can also have individual meanings. Control strategy can describe how the control loops in a process are configured to meet a given overall objective, such as the purity of a given stream. Control structure, on the other hand, is the selection of controlled and manipulated variables from a set of many choices. Finally, controller structure means the specific pairing of controlled and manipulated variables by way of feedback controller.

A column control system has three main objectives: to set stable conditions for column operation, to regulate conditions in the column so that the products always meet the required specifications and to achieve the above objectives most efficiently. This could mean maximizing product recovery, minimizing energy consumption and often both. The variables typically controlled in a column. Excluding flows, these include pressure, bottom level, accumulator level, top product composition and bottom product composition. These can be classified into two groups:

1. Single-loop variables: these include pressure and levels. They are controlled in order to achieve the first objective, i.e., setting stable conditions for column operation. The set points at which these are controlled are established by stability considerations alone, regardless of product specifications. Controlling pressures and levels regulates material accumulation in the column. Keeping the levels constant prevents liquid accumulation, while keeping the pressure constant prevents vapor accumulation. Unless accumulation (positive or negative) is prevented, a continuous system will not operate at steady-state and will not be stable.
2. Unit objective variables: these include top and bottom compositions. They are regulated to achieve the second objective, i.e., meeting product specifications. The set points at which these are controlled are determined by product purity considerations alone. Composition controls can be direct, i.e., using composition measurements of the product streams, or indirect, using a physical property representative of product composition. Typical physical properties used are

refractive index, density, vapor pressure, freezing point, and most commonly, tray temperature.

In summary, beside flows, five variables are controlled in a typical column. Three of these (pressure and two levels) are controlled to set stable conditions, and two (composition) are controlled to achieve the desired product purities.

A stream is manipulated by varying the opening of its control valve. The stream flow rate is thereby varied to control a desired variable. Figure 3-3 shows positions of control valves in a typical distillation system. There are five manipulated streams: top and bottom product flowrates, condensation rate, boilup rate and reflux flowrate.

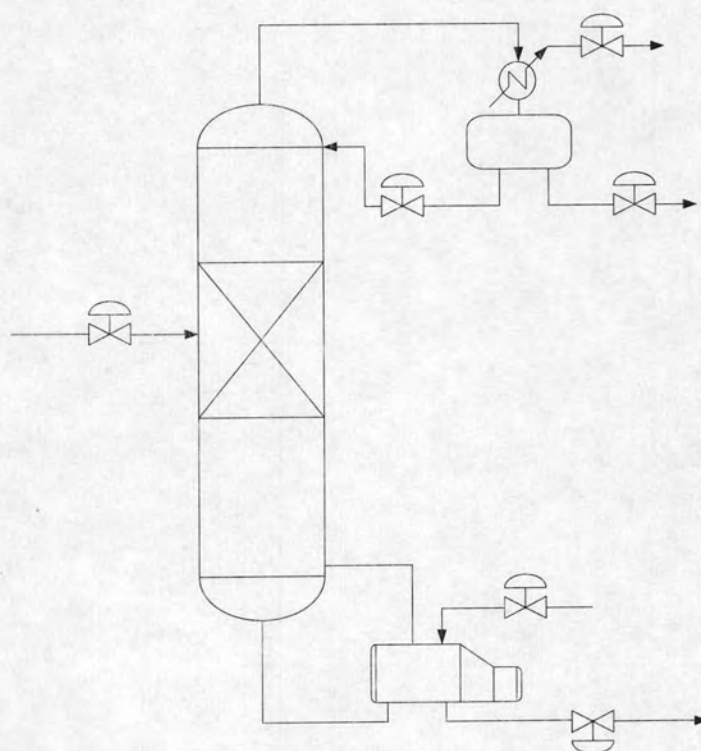


Figure 3-3 Controlled variables and manipulated streams in a typical column

3.3.1 Moving from Steady-State to Dynamic Simulation

The steady-state simulation does not need information that has no effect on steady-state results. These items include column diameters, sizes of all surge vessels, sizes of control valves, etc. However, a process unit depends on the size of the equipment. The capacitance of the system (its time constant) is dictated by its size (volume or mass) relative to the reflux (flowrate, heat-transfer rate, etc.). Therefore all equipment must be sized (at least approximately) before dynamic simulations can be performed.

Sizing Equipment

- **Column Diameter:** The diameter of a column is set by the maximum vapor velocity. This often occurs at the top of the column where the pressure is the lowest, resulting in the lowest vapor density. However, if the feed is subcooled liquid, the maximum vapor rate can occur just below the feed tray because the extra vapor needed to bring the feed up to the temperature of the feed tray. Change in molar heats of vaporization, temperature and molecular weights can move the location of the worst-case tray location to other positions in the column. The steady-state vapor profiles should be checked to find the tray with the maximum vapor velocity.

A simple way to calculate the maximum allowable vapor velocity is to use the “*F-Factor*” parameter.

$$V_{\max} = \frac{F - \text{Factor}}{\sqrt{\rho_v}} \quad (3-6)$$

In English Engineering units, the velocity V_{\max} has units of ft/sec and the vapor density ρ_v has units of lb/ft³. In SI units, velocity is in m/sec and density is in kg/m³. An *F-Factor* of 1 in English Engineering units or 1.22 in SI units can be used to determine the diameter of the column. From

- Reflux Drum and Column Base: Using the heuristic approach with 10 minutes of total holdup, we can calculate the volumes in the reflux drum and in the column base.

3.3.2 Level, pressure, temperature and composition control

- Level control: Accumulator level is usually controlled by manipulating liquid product flow, reflux flow, or condensation rate. The latter is often used when the column has a vapor product. It is normally unnecessary to tightly control accumulator level when the level manipulates product flow. In trains of columns, it is even undesirable, because the accumulator volume should be used to smooth product flow overflowing or emptying out. However, when accumulator level controls reflux or condensation rate, a tighter level control is desirable. The accumulator level controller must be properly tuned, otherwise it may interact with composition or pressure control loops.

Base-level is controlled by bottom product flow. This loop arrangement is considered stable and responsive except for kettle reboilers, particularly where a feed bottoms heat exchanger is used. However, if bottom product flow is extremely small compared with other stream flows, then it cannot control level well and will undergo wide fluctuations in the attempt. In situations such as this, it may be wise to use it for composition control, in which case base level is to be controlled by heat input to the reboiler. As overhead composition response to distillate flow depended on tight control of accumulator level, so bottom composition response to bottom product flow depends on tight control of base level. In most columns, the volume of product stored in the base is much smaller than that in the accumulator. However, turbulence associated with boiling produces a much higher noise level, requiring a wider proportional band for the level controller. As the result, the time lags of the accumulator and

base-level loops in response to changes in product flows tend to be quite similar.

- Pressure control: Pressure control is a primary requirement for all columns because of its direct influence on the separation process. Columns are typically designed to operate at sub-atmospheric, atmospheric, or above atmospheric pressure. Column pressure control configurations can also be required to vent varying amounts of inerts from the overhead accumulator. The venting of inerts or maintaining the desired operating pressure is often the crux of the control problem.

The same general principle is followed when finding manipulated variables for pressure control as for level control. Column pressure is generated by boil-up and is relieved by condensation and venting. To find an effective variable for pressure control, it is necessary to determine what affects pressure the most. For example, in a column with a total condenser, either the reboiler heat or the condenser cooling is a good candidate for pressure control. On a column with a partial condenser, it is necessary to determine whether removing the vapor stream affects pressure more than condensing the reflux. Sometimes the dominating effect is not obvious. If the vent stream is small, then it might be assumed that the condenser cooling should be manipulated for pressure control. However, if the vent stream contains non-condensables, these will blanket the condenser and affect the condensation significantly. In this situation, the vent flow although small, is the best choice for pressure control.

The location of a column pressure control point is not restricted by dynamic considerations. The response time of pressure changes in a column and the dynamic measuring lag has been found to be equally fast for any location in the column when the manipulated energy source used to control pressure is either condenser cooling or reboil heat. Pressure is regulated at a constant value and is rarely used as a variable to control a product specification. Generally, temperature is used to control

composition, making pressure compensation necessary to sustain accurate control.

- Temperature control: Composition control of products from a column is usually realized via temperature control. Temperature sensors are inexpensive, highly reliable, repeatable, continuous, and fast compared with composition sensors. The accuracy of the correlation of column temperature to product composition depends on the sensitivity of the controlled temperature to composition changes and pressure variations at the temperature measuring point. The sensitivity of the temperature measurement to key or major component composition changes for each tray can be determined if tray-by-tray composition changes are large and the other component changes are small. It must be determined which stage exhibits the composition-related temperature response in all disturbance situations.

The temperature-composition correlations of key components are often affected by changes in the concentration of other components, i.e. column feed composition changes. If the magnitude of these changes can be estimated, then a calculation using equilibrium constants can be made to determine the effect on the temperature composition correlation. Then a control tray can be selected where the effect of non-key component variations is small.

Stable column temperature control, from the tray selected by the foregoing static considerations, depends on the dynamic measuring lag or response of the tray temperature with respect to the manipulated energy source used to control the temperature. Based on experimental tests, the following observations are cited for use as guides:

1. Temperature control is made less stable by thermowell and measuring instrument lag or response times.

2. The speed of response and control stability of tray temperature, when controlled by reboiler heat, is the same for all tray locations.
 3. The speed of response and control stability of tray temperature, when controlled by reflux, decreases in direct relation with the number of trays below the reflux tray.
 4. When pressure is controlled at the temperature control tray, the speed of response of the temperature instrument can vary considerably with tray location, and is normally slower.
- **Composition control:** The composition control loops on a column are the most important steady-state controls. The purpose of composition control is to satisfy the constraints defined by product quality specifications. These constraints must be satisfied at all times, particularly in the face of disturbances. The objective of composition control is then to hold the controlled composition as close as possible to the imposed constraint without violating the constraint. This objective translates to on-aim, minimum variance control. To achieve good composition control, two things must be examined: process dynamics and disturbance characteristics. Process dynamics includes measurement dynamics, process dynamics and control-valve dynamics. Tight process control is possible if the equivalent deadtime in the loop is small compared with the shorted time constant of a disturbance with significant amplitude. To ensure small overall deadtime in the loop, it is necessary to find a rapid measurement along with a manipulated variable that gives an immediate and appreciable response. In distillation, a rapid measurement for composition control often translates into a tray temperature. A good manipulated variable is vapor flow, which travels quickly up through the column and usually has a significant gain on tray temperatures and indirectly on composition.

3.3.3 Tuning Flow, Level and Pressure Loops

- **Flow Controllers:** The tuning of flow controllers is usually a no-brainer. The majority of flow control loops feature an orifice-plate sensor, a differential-pressure transmitter, a PI controller and a control valve. The dynamics of flow measurement are fast. The time constants for moving control valves are small (several seconds unless very large valves are involved). Therefore, the controller can be tuned with a small integral or reset time constant τ_I . A value of $\tau_I = 0.3$ minutes works in most flow controllers.

The value of controller gain should be kept modest because flow-measurement signals are sometime noisy due to the turbulent flow through the orifice plate. A value of controller gain of $K_c = 0.5$ is often used. Derivative action should not be used. So the controller tuning constants for a typical PI flow controller are:

$$K_c = 0.5 \quad (3-7)$$

$$\tau_I = 0.3 \text{ minutes} \quad (3-8)$$

- **Level Controller:** Most level controller should use proportional-only action with a gain of 1 to 2. This provides the maximum amount of flow smoothing. Proportional control means there will be steady-state offset (the level will not be returned to its setpoint value). However, maintaining a liquid level at a certain value is often not necessary when the liquid capacity is simply being used as surge volume. So the recommended tuning parameter of a level controller is $K_c = 2$.

Typical hold-up times for condenser accumulators and reboiler are of the order of 5-10 min and 20 min (large enough to hold all the liquid from the trays if dumped), respectively.

- **Pressure Controllers:** Most pressure controllers can be fairly easily tuned. The process time constant is estimated by dividing the gas volume of the system by the volumetric flowrate of gas flowing through the system. Setting the integral time equal to about 2 to 4 times the process time constant and using a reasonable controller gain usually gives satisfactory pressure control. Of course the gain used depends on the span of the pressure transmitter. Some simple step tests can be used to find the value of controller gain that yields satisfactory pressure control. Typical pressure controller tuning constants for columns and tanks are $K_c = 2$ and $\tau_I = 10$ minutes. Pressure controller settings in very fast loops such as compressor controls have much smaller integral times.
- **Temperature Controllers:** Temperature dynamic responses are generally slow, so PID control is used. Typically, the controller gain, K_c , should be set between 2 and 10, the integral time, τ_I , should be set between 2 and 10 minutes, and the derivative time τ_D , should be set between 0 and 5 minutes.

3.3.4 Inclusion of Lags

Once the simple controllers are tuned, we are left with a significant number of other controllers that require more detailed engineering. These are typically temperature and composition controllers. These loops have significant dynamic lags and/or deadtimes, so arbitrarily tight tuning is not physically possible. Any real physical system has many lags. Measurement and actuator lags always exist. In simulations, however, these lags are not part of the unit models. Much more aggressive tuning is often possible on the simulation than is possible in the real plant. Thus the predictions of dynamic performance can be overly optimistic. Realistic dynamic simulations require that we explicitly include lags and/or deadtimes in all the important loops. Usually this means controllers that affect product quality (temperature or composition) or process constraint (safety, environmental, etc.). Table 3-3

summarizes some recommended lags to be included in several different types of control loops.

3.4 HYSYS Simulator

HYSYS is powerful software for simulation of chemical plants and oil refineries. It includes tools for estimation of physical properties and liquid vapor phase equilibrium, heat and material balances, and simulation of many types of chemical engineering equipment. The goal of HYSYS is, of course, to provide the capability to design an entire process as completely and accurately as possible. With HYSYS, rigorous steady-state and dynamic models can be used for plant design, performance monitoring, troubleshooting, operational improvement and asset management.

Table 3-3 Typical Measurement Lags

		Number	Time Constant (minutes)	Type
Temperature	Liquid	2	0.5	First-order Lag
	Gas	3	1	First-order Lag
Composition	Chormatograph	1	3 to 10	Deadtime

