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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I - Basics of Modelling – SCH1401

1.INTRODUCTION

Analysis of the cognition methods which have been used since early times reveals that the general methods created in order to investigate life phenomena could be divided into two groups: (i) the application of similitude, modeling and simulation, (ii) experimental research which also uses physical models. These methods have always been applied to all branches of human activity all around the world and consequently belong to the universal patrimony of human knowledge. The two short stories told below aim to explain the fundamental characteristics of these cognition methods.

First story. When, by chance, men were confronted by natural fire, its heat may have strongly affected them. As a result of these ancient repeated encounters on cold days, men began to feel the agreeable effect of fire and then wondered how they could proceed to carry this fire into their cold caves where they spent their nights. The precise answer to this question is not known, but it is true that fire has been taken into men’s houses. Nevertheless, it is clear that men tried to elaborate a scheme to transport this natural fire from outside into their caves. We therefore realize that during the old times men began to exercise their minds in order to plan a specific action. This cognition process can be considered as one of the oldest examples of the use of modeling research on life.

So we can hold in mind that the use of modeling research on life is a method used to analyze a phenomenon based on qualitative and quantitative cognition where only mental exercises are used.

Second Story. The invention of the bow resulted in a new lifestyle because it led to an increase in men’s hunting capacity. After using the bow for the first time, men began to wonder how they could make it stronger and more efficient. Such improvements were repeated continually until the effect of these changes began to be analyzed. This example of human progress illustrates a cognition process based on experimentation in which a physical model (the bow) was used. In accordance with the example described above, we can deduce that research based on a physical model results from linking the causes and effects that characterize an investigated phenomenon. With reference to the relationships existing between different investigation methods, we can conclude that, before modifying the physical model used, modeling research has to be carried out. The modeling can then suggest various strategies but a single one has to be chosen. At the same time, the physical model used determines the conditions required to measure the effect of the adopted strategy. Further improvement of the physical model may also imply additional investigation.

If we investigate the scientific and technical evolution for a random selected domain, we can see that research by modeling or experimentation is fundamental. The evolution of research by modeling and/or experimentation (i.e. based on a physical model) has known an important particularization in each basic domain of science and techniques. Research by modeling, by simulation and similitude as well as experimental research, have become fundamental methods in each basic scientific domain . However, they tend to be considered as interdisciplinary activities. In the case of modeling simulation and similitude in chemical engineering, the interdisciplinary state is shown by coupling the phenomena studied with mathematics and computing science.

1.1 CLASSIFICATION OF MODELS

The advances in basic knowledge and model-based process engineering methodologies will certainly result in an increasing demand for models. In addition, computer assistance to support the development and implementation of adequate and clear models will be increasingly used, especially in order to minimize the financial support for industrial production by optimizing global production processes. The classification of models depending on their methodology, mathematical development, objectives etc. will be a useful tool for beginners in modeling in order to help them in their search for the particular model able to solve the different and variable products synthesis.

Highly-diversified models are used in chemical engineering, consequently, it is not simple to propose a class grouping for models. The different grouping attempts given here are strongly related to the modeled phenomena. In the case of a device model or plant model, the assembly of the model parts creates an important number of cases that do not present any interest for class grouping purposes. In accordance with the qualitative process theory to produce the class grouping of one phenomenon or event, it is important to select a clear characterization criterion which can assist the grouping procedure. When this criterion is represented by the theoretical base used for the development of models, the following classification is obtained:

. mathematical models based on the laws of transport phenomena

. mathematical models based on the stochastic evolution laws

. mathematical models based on statistical regression theory

. mathematical models resulting from the particularization of similitude and dimensional analysis.When the grouping criterion is given by the mathematical complexity of the process model (models), we can distinguish:

. mathematical models expressed by systems of equations with complex derivatives

. mathematical models containing one equation with complex derivatives and one (or more) ordinary system(s) of differential equations.

.mathematical models promoted by a group of ordinary systems of differential equations

. mathematical models with one set of ordinary differential equations complete with algebraic parameters and relationships between variables

. mathematical models given by algebraic equations relating the variables of the process.

For the mathematical models based on transport phenomena as well as for the stochastic mathematical models, we can introduce new grouping criteria. When the basic process variables (species conversion, species concentration, temperature, pressure and some non-process parameters) modify their values, with the time and spatial position inside their evolution space, the models that describe the process are recognized as models with distributed parameters. From a mathematical viewpoint, these models are represented by an assembly of relations which contain partial differential equations The models, in which the basic process variables evolve either with time or in one particular spatial direction, are called models with concentrated parameters.

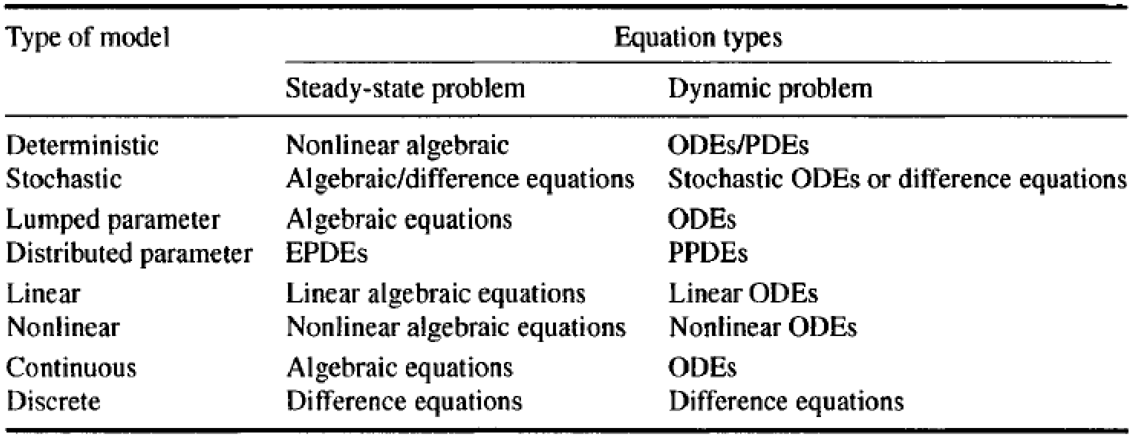
When one or more input process variable and some process and non-process parameters are characterized by means of a random distribution (frequently normal distributions), the class of non-deterministic models or of models with random parameters is introduced. Many models with distributed parameters present the state of models with random parameters at the same time.

The models associated to a process with no randomly distributed input variables or parameters are called rigid models. If we consider only the mean values of the parameters and variables of one model with randomly distributed parameters or input variables, then we transform a non-deterministic model into a rigid model.

The stochastic process models can be transformed by the use of specific theorems as well as various stochastic deformed models, more commonly called diffusion models. In the case of statistical models, we can introduce other grouping criteria.

1.1.1 Type of model Criterion of classification

Mechanistic	- Based on mechanisms/underlying phenomena
Empirical	- Based on input-output data, trials or experiments
Stochastic	- Contains model elements that are probabilistic in nature
Deterministic	- Based on cause-effect analysis
Lumped parameter	- Dependent variables not a function of spatial position
Distributed parameter	- Dependent variables are a function of spatial position
Linear	- Superposition principle applies
Nonlinear	- Superposition principle does not apply
Continuous	-Dependent variables defined over continuous space-time
Discrete	- Only defined for discrete values of time and/or space
Hybrid	- Containing continuous and discrete behavior



Type of model	Equation types	
	Steady-state problem	Dynamic problem
Deterministic	Nonlinear algebraic	ODEs/PDEs
Stochastic	Algebraic/difference equations	Stochastic ODEs or difference equations
Lumped parameter	Algebraic equations	ODEs
Distributed parameter	EPDEs	PPDEs
Linear	Linear algebraic equations	Linear ODEs
Nonlinear	Nonlinear algebraic equations	Nonlinear ODEs
Continuous	Algebraic equations	ODEs
Discrete	Difference equations	Difference equations

1.2 MATHEMATICAL MODEL

Mathematical Model (Eykhoff, 1974)

"a representation of the essential aspects of an existing system (or a system to be constructed) which represents knowledge of that system in a usable form"

Everything should be made as simple as possible, but no simpler.

General Modeling Principles

- The model equations are at best an approximation to the real process.
- *Adage*: “All models are wrong, but some are useful.”
- Modeling inherently involves a compromise between model accuracy and complexity on one hand, and the cost and effort required to develop the model, on the other hand.
- Process modeling is both an art and a science. Creativity is required to make simplifying assumptions that result in an appropriate model.
- Dynamic models of chemical processes consist of ordinary differential equations (ODE) and/or partial differential equations (PDE), plus related algebraic equations.

1.3 USES OF MATHEMATICAL MODELS

- to improve understanding of the process
- to optimize process design/operating conditions
- to design a control strategy for the process
- to train operating personnel

The most important result of developing a mathematical model of a chemical engineering system is the understanding that is gained of what really makes the process “tick.” This insight enables you to strip away from the problem the many extraneous “confusion factors” and to get to the core of the system. You can see more clearly the cause-and-effect relationships between the variables.

Mathematical models can be useful in all phases of chemical engineering, from research and development to plant operations, and even in business and economic studies.

- Research and development: determining chemical kinetic mechanisms and parameters from laboratory or pilot-plant reaction data; exploring the effects of different operating conditions for optimization and control studies; aiding in scale-up calculations.
- Design: exploring the sizing and arrangement of processing equipment for dynamic performance; studying the interactions of various parts of the process, particularly when material recycle or heat integration is used; evaluating alternative process and control

structures and strategies; simulating start-up, shutdown, and emergency situations and procedures.

- Plant operation: troubleshooting control and processing problems; aiding in start-up and operator training; studying the effects of and the requirements for expansion (bottleneck-removal) projects; optimizing plant operation. It is usually much cheaper, safer, and faster to conduct the kinds of studies listed above on a mathematical model than experimentally on an operating unit. This is not to say that plant tests are not needed. As we will discuss later, they are a vital part of confirming the validity of the model and of verifying important ideas and recommendations that evolve from the model studies.

1.4 SCOPE OF COVERAGE

We will discuss in this subject only deterministic systems that can be described by ordinary or partial differential equations. Most of the emphasis will be on lumped systems (with one independent variable, time, described by ordinary differential equations). Both English and SI units will be used. You need to be familiar with both.

1.5 PRINCIPLES OF FORMULATION

BASIS. The bases for mathematical models are the fundamental physical and chemical laws, such as the laws of conservation of mass, energy, and momentum.

To study dynamics we will use them in their general form with time derivatives included.

ASSUMPTIONS. Probably the most vital role that the engineer plays in modeling is in exercising his engineering judgment as to what assumptions can be validly made. Obviously an extremely rigorous model that includes every phenomenon down to microscopic detail would be so complex that it would take a long time to develop and might be impractical to solve, even on the latest supercomputers. An engineering compromise between a rigorous description and getting an answer that is good enough is always required. This has been called “optimum sloppiness.” It involves making as many simplifying assumptions as are reasonable without “throwing out the baby with the bath water.” In practice, this optimum usually corresponds to a model which is as complex as the available computing facilities will permit. More and more this is a personal computer.

The development of a model that incorporates the basic phenomena occurring in the process requires a lot of skill, ingenuity, and practice. It is an area where the creativity and innovativeness of the engineer is a key element in the success of the process.

The assumptions that are made should be carefully considered and listed. They impose limitations on the model that should always be kept in mind when evaluating its predicted results.

MATHEMATICAL CONSISTENCY OF MODEL. Once all the equations of the mathematical model have been written, it is usually a good idea, particularly with big, complex systems of equations, to make sure that the number of variables equals the number of equations. The so-called “degrees of freedom” of the system must be zero in order to obtain a solution. If this is not true, the system is underspecified or over specified and something is wrong with the formulation of the problem. This kind of consistency check may seem trivial, but I can testify from sad experience that it can save many hours of frustration, confusion, and wasted computer time. Checking to see that the units of all terms in all equations are consistent is perhaps another trivial and obvious step, but one that is often forgotten. It is essential to be particularly careful of the time units of parameters in dynamic models. Any units can be used (seconds, minutes, hours, etc.), but they cannot be mixed. We will use “minutes” in most of our examples, but it should be remembered that many parameters are commonly on other time bases and need to be converted appropriately, e.g., overall heat transfer coefficients in Btu/h “F ft’ or velocity in m/s. Dynamic simulation results are frequently in error because the engineer has forgotten a factor of “60” somewhere in the equations.

SOLUTION OF THE MODEL EQUATIONS. the available solution techniques and tools must be kept in mind as a mathematical model is developed. An equation without any way to solve it is not worth much.

VERIFICATION. An important but often neglected part of developing a mathematical model is proving that the model describes the real-world situation. At the design stage this sometimes cannot be done because the plant has not yet been built. However, even in this situation there are usually either similar existing plants or a pilot plant from which some experimental dynamic data can be obtained. The design of experiments to test the validity of a dynamic model can sometimes be a real challenge and should be carefully thought out.

1.6 FUNDAMENTAL LAWS

1.6.1 Continuity Equations

Total continuity equation (mass balance). The principle of the conservation of mass when applied to a dynamic system says

$$\left[\begin{array}{l}\text{Mass flow}\\ \text{into system}\end{array}\right]-\left[\begin{array}{l}\text{mass flow}\\ \text{out of system}\end{array}\right]=\left[\begin{array}{l}\text{time rate of change}\\ \text{of mass inside system}\end{array}\right]$$

The units of this equation are mass per time. Only one total continuity equation can be written for one system.

Component continuity equations (component balances).

If a reaction occurs inside a system, the number of moles of an individual component will increase if it is a product of the reaction or decrease if it is a reactant. Therefore, the component continuity equation of the jth chemical species of the system says

$$\begin{aligned}&\left[\begin{array}{l}\text{Flow of moles ofjth}\\ \text{component into system}\end{array}\right]-\left[\begin{array}{l}\text{flow of moles ofjth}\\ \text{component out of system}\end{array}\right]\\ &\qquad+\left[\begin{array}{l}\text{rate of formation of moles of jth}\\ \text{component from chemical reactions}\end{array}\right]\\ &\qquad\qquad=\left[\begin{array}{l}\text{time rate of change of moles of jth}\\ \text{component inside system}\end{array}\right]\end{aligned}$$

The units of this equation are moles of component j per unit time. The flows in and out can be both convective (due to bulk flow) and molecular (due to diffusion). We can write one component continuity equation for each component in the system. If there are NC components, there are NC component continuity equations for any one system. However, the one total mass balance and these NC component balances are not all independent, since the sum of all the moles times their respective molecular weights equals the total mass. Therefore a given system has only NC independent continuity equations. We usually use the total mass balance and NC - 1 component balances. For example, in a binary (two-component) system, there would be one total mass balance and one component balance.

1.6.2 Energy Equation

The first law of thermodynamics puts forward the principle of conservation of energy. Written for a general "open" system (where flow of material in and out of the system can occur) it is

$$\left[\begin{array}{l}\text{Flow of internal, kinetic, and}\\ \text{potential energy into system}\\ \text{by convection or diffusion}\end{array}\right] - \left[\begin{array}{l}\text{flow of internal, kinetic, and}\\ \text{potential energy out of system}\\ \text{by convection or diffusion}\end{array}\right]$$

$$+ \left[\begin{array}{l}\text{heat added to system by}\\ \text{conduction, radiation, and}\\ \text{reaction}\end{array}\right] - \left[\begin{array}{l}\text{work done by system on}\\ \text{surroundings (shaft work and}\\ \text{PV work)}\end{array}\right]$$

$$= \left[\begin{array}{l}\text{time rate of change of internal, kinetic,}\\ \text{and potential energy inside system}\end{array}\right]$$

1.6.3 Equations of motion

The equation which links acceleration, initial and final velocity, and time is the first of the equations of motion.

These equations are used to describe motion in a straight line with uniform acceleration. You must to be able to:

- select the correct formula
- identify the symbols and units used

- carry out calculations to solve problems of real life motion
- carry out experiments to verify the equations of motion.

You should develop an understanding of how the graphs of motion can be used to derive the equations. This is an important part of demonstrating that you understand the principles of describing motion, and the link between describing it graphically and mathematically.

$$a = \frac{v - u}{t}$$

a = acceleration in metres per second per second ($\mathrm{m\ s^{-2}}$)
v = final velocity in metres per second ($\mathrm{m\ s^{-1}}$)
u = initial velocity in metres per second ($\mathrm{m\ s^{-1}}$)
t = time in seconds (s)

$v = u + at$ Equation of motion 1

$s = ut + \frac{1}{2}at^2$

s = displacement in metres (m)
u = initial velocity in metres per second ($\mathrm{m\ s^{-1}}$)
t = time in seconds (s)
a = acceleration in metres per second per second ($\mathrm{m\ s^{-2}}$)

$s = ut + \frac{1}{2}at^2$ Equation of motion 2

The third equation of motion is derived from with Equation 1.

Equation 1 $v = u + at$
square each side to give $v^2 = (u + at)^2$
$v^2 = u^2 + 2uat + a^2t^2$
$v^2 = u^2 + 2a(ut + \frac{1}{2}at^2)$
substitute in Equation 2 $v^2 = u^2 + 2as$

$v^2 = u^2 + 2as$ Equation of motion 3

1.7 REGRESSION AND CORRELATION ANALYSIS

Suppose we have a set of 30 students in a class and we want to measure the heights and weights of all the students. We observe that each individual (unit) of the set assumes two values – one relating to the height and the other to the weight. Such a distribution in which each individual or unit of the set is made up of two values is called a bivariate distribution. The following examples will illustrate clearly the meaning of bivariate distribution.

(i) In a class of 60 students the series of marks obtained in two subjects by all of them.

(ii) The series of sales revenue and advertising expenditure of two companies in a particular year.

(iii) The series of ages of husbands and wives in a sample of selected married couples.

Thus in a bivariate distribution, we are given a set of pairs of observations, wherein each pair represents the values of two variables. In a bivariate distribution, we are interested in finding a relationship (if it exists) between the two variables under study.

The concept of 'correlation' is a statistical tool which studies the relationship between two variables and Correlation Analysis involves various methods and techniques used for studying and measuring the extent of the relationship between the two variables.

"Two variables are said to be in correlation if the change in one of the variables results in a change in the other variable".

1.7.1 Types of Correlation

There are two important types of correlation. They are (1) Positive and Negative correlation and (2) Linear and Non – Linear correlation.

Positive and Negative Correlation

If the values of the two variables deviate in the same direction i.e. if an increase (or decrease) in the values of one variable results, on an average, in a corresponding increase (or decrease) in the values of the other variable the correlation is said to be positive.

Some examples of series of positive correlation are:

(i) Heights and weights;

(ii) Household income and expenditure;

(iii) Price and supply of commodities;

(iv) Amount of rainfall and yield of crops.

Correlation between two variables is said to be negative or inverse if the variables deviate in opposite direction. That is, if the increase in the variables deviate in opposite direction. That is, if increase (or decrease) in the values of one variable results on an average, in corresponding decrease (or increase) in the values of other variable.

Some examples of series of negative correlation are:

(i) Volume and pressure of perfect gas

(ii) Current and resistance [keeping the voltage constant

(iii) Price and demand of goods.

1.7.2 Regression Equation

Suppose we have a sample of size 'n' and it has two sets of measures, denoted by x and y. We can predict the values of 'y' given the values of 'x' by using the equation, called the REGRESSION EQUATION.

$y^* = a + bx$

where the coefficients a and b are given by

$$b = \frac{n\sum xy - (\sum x)(\sum y)}{n(\sum x^2) - (\sum x)^2}$$

$$a = \frac{\sum y - b\sum x}{n}$$

The symbol y* refers to the predicted value of y from a given value of x from the regression equation.

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UNIT – II - Modeling of Heat Transfer and other Equipment's –SCH1401

2.1 HEAT EXCHANGER

Consider the shell and tube heat exchanger shown in figure 2.1. Liquid A of density $\square_A$ is flowing through the inner tube and is being heated from temperature T_{A1} to T_{A2} by liquid B of density $\square_B$ flowing counter-currently around the tube. Liquid B sees its temperature decreasing from T_{B1} to T_{B2}. Clearly the temperature of both liquids varies not only with time but also along the tubes (i.e. axial direction) and possibly with the radial direction too. Tubular heat exchangers are therefore typical examples of distributed parameters systems. A rigorous model would require writing a microscopic balance around a differential element of the system. This would lead to a set of partial differential equations. However, in many practical situations we would like to model the tubular heat exchanger using simple ordinary differential equations. This can be possible if we think about the heat exchanger within the unit as being an exchanger between two perfect mixed tanks. Each one of them contains a liquid.

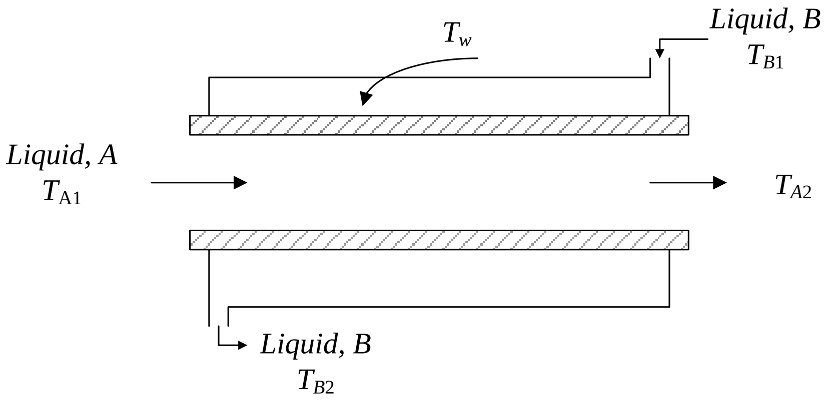


Figure 2-1 Heat Exchanger

For the time being we neglect the thermal capacity of the metal wall separating the two liquids. This means that the dynamics of the metal wall are not included in the model. We will also assume constant densities and constant average heat capacities.

One way to model the heat exchanger is to take as state variable the exit temperatures T_{A2} and T_{B2} of each liquid. A better way would be to take as state variable not the exit temperature but the average temperature between the inlet and outlet:

$$T_A = \frac{T_{A1} + T_{A2}}{2}$$

$$T_B = \frac{T_{B1} + T_{B2}}{2}$$

For liquid *A*, a macroscopic energy balance yields:

$$\rho_A C_{p_A} V_A \frac{dT_A}{dt} = \rho_A F_A C_{p_A} (T_{A1} - T_{A2}) + Q$$

where Q (*J/s*) is the rate of heat gained by liquid A. Similarly for liquid B:

$$\rho_B C_{p_B} V_B \frac{dT_B}{dt} = \rho_B F_B C_{p_B} (T_{B1} - T_{B2}) - Q$$

The amount of heat Q exchanged is:

$$Q = UA_H (T_B - T_A)$$

Or using the log mean temperature difference:

$$Q = UA_H \Delta T_{lm}$$

where

$$\Delta T_{lm} = \frac{(T_{A2} - T_{B1}) - (T_{A1} - T_{B2})}{\ln \frac{(T_{A2} - T_{B1})}{(T_{A1} - T_{B2})}}$$

with U (J/m^2s) and A_H (m^2) being respectively the overall heat transfer coefficient and heat transfer area.

Degrees of freedom analysis

- Parameter of constant values: □□□□Cp_A, V_A, □□, Cp_B, V_B, U, A_H
- (Forced variable): T_{A1}, T_{B1}, F_A, F_B
- Remaining variables: T_{A2}, T_{B2}, Q
- Number of equations: 3

The degree of freedom is 5 − 3 = 2. The two extra relations are obtained by noting that the flows F_A and F_B are generally regulated through valves to avoid fluctuations in their values.

So far we have neglected the thermal capacity of the metal wall separating the two liquids. A more elaborated model would include the energy balance on the metal wall as well. We assume that the metal wall is of volume V_w, density □$_w$ and constant heat capacity Cp_w. We also assume that the wall is at constant temperature T_w, not a bad assumption if the metal is assumed to have large conductivity and if the metal is not very thick. The heat transfer depends on the heat transfer coefficient $h_{o,t}$ on the outside and on the heat transfer coefficient $h_{i,t}$ on the inside. Writing the energy balance for liquid B yields:

$$\rho_B C_{p_B} V_B \frac{dT_B}{dt} = \rho_B F_B C_{p_B} (T_{B1} - T_{B2}) - h_{o,t} A_{o,t} (T_B - T_W)$$

where $A_{o,t}$ is the outside heat transfer area. The energy balance for the metal yields:

$$\rho_w C_{p_w} V_w \frac{dT_w}{dt} = h_{o,t} A_{o,t} (T_B - T_w) - h_{i,t} A_{i,t} (T_w - T_A)$$

where $A_{i,t}$ is the inside heat transfer area. . The energy balance for liquid A yields:

$$\rho_A C_{p_A} V_A \frac{dT_A}{dt} = \rho_A F_A C_{p_A} (T_{A1} - T_{A2}) + h_{i,t} A_{i,t} (T_w - T_A)$$

Note that the introduction of equation does not change the degree of freedom of the system.

2.2 HEAT EXCHANGER WITH STEAM

A common case in heat exchange is when a liquid *L* is heated with steam (Figure 2.2). If the pressure of the steam changes then we need to write both mass and energy balance equations on the steam side.

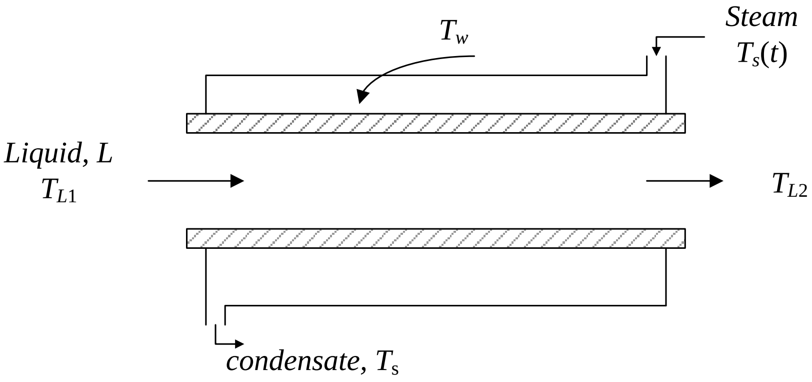


Figure 2.2 Heat Exchanger with Heating Steam

The energy balance on the tube side gives:

$$\rho_L C_{p_L} V_L \frac{dT_L}{dt} = \rho_L F_L C_{p_L} (T_{L1} - T_{L2}) + Q_s$$

where

$$T_L = \frac{T_{L1} + T_{L2}}{2}$$

$$Q_s = UA_s (T_s - T_L)$$

The steam saturated temperature T_s is also related to the pressure P_s:

$T_s = T_s(P)$

Assuming ideal gas law, then the mass flow of steam is:

$$m_s = \frac{M_s P_s V_s}{R T_s}$$

where M_s is the molecular weight and R is the ideal gas constant. The mass balance for the steam yields:

$$\frac{M_s V_s}{R T_s} \frac{dP}{dt} = \rho_s F_s - \rho_c F_c$$

where F_c and ρ_c are the condensate flow rate and density. The heat losses at the steam side are related to the flow of the condensate by:

$Q_s = F_c \rho_s$

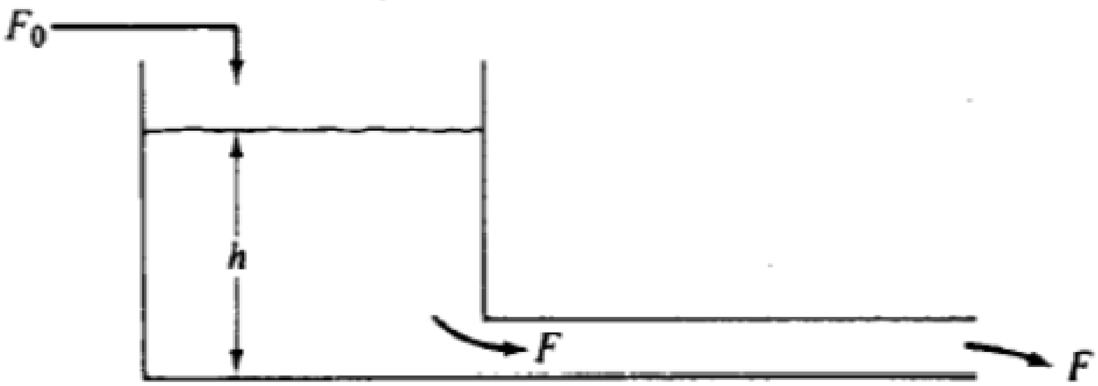
Where ρ_s is the latent heat.

Degrees of freedom analysis

- Parameter of constant values: Cp_L, M_s, A_s, U , M_s, R
- (Forced variable): T_{L1}
- Remaining variables: T_{L2}, F_L, T_s, F_s, P_s, Q_s, F_c
- Number of equations: 5

The degrees of freedom is therefore 7 – 5 = 2. The extra relations are given by the relation between the steam flow rate F_s with the pressure P_s either in open-loop or closed-loop operations. The liquid flow rate F_1 is usually regulated by a valve.

2.3 GRAVITY-FLOW TANK.



Gravity-flow tank.

Figure shows a tank into which an incompressible (constant density) liquid is pumped at a variable rate F, (ft^3/s). This inflow rate can vary with time because of changes in operations upstream. The height of liquid in the vertical cylindrical tank is h (ft). The flow rate out of the tank is F (ft’/s). Now F, , h, and F will all vary with time and are therefore functions of time t.

Equations of Motion

Newton’s second law of motion says that force is equal to mass times acceleration for a system with constant mass M

$$F = \frac{Ma}{g_c}$$

This is the basic relationship that is used in writing the equations of motion for a system. In a slightly more general form, where mass can vary with time,

$$\frac{1}{g_c}\frac{d(Mv_i)}{dt} = \sum_{j=1}^{N} F_{ji}$$

where v_i = velocity in the i direction, ft/s
F_{ji} = jth force acting in the i direction

The gravity-flow tank system provides a simple example of the application of the equations of motion to a macroscopic system. Referring to Fig., let the length of the exit line be L (ft) and its cross-sectional area be A, (ft’). The vertical, cylindrical tank has a cross-sectional area of A, (ft’). The part of this process that is described by a force balance is the liquid flowing through the pipe. It will have a mass equal to the volume of the pipe (APL) times the density of the liquid p. This mass of liquid will have a velocity v (ft/s) equal to the volumetric flow divided by the cross-sectional area of the pipe. Remember we have assumed plug-flow conditions and incompressible liquid, and therefore all the liquid is moving at the same velocity, more or less like a solid rod. If the flow is turbulent, this is not a bad assumption.

$$M = A_p L \rho$$
$$v = \frac{F}{A_p}$$

The amount of liquid in the pipe will not change with time, but if we want to change the rate of outflow, the velocity of the liquid must be changed. And to change the velocity or the momentum of the liquid we must exert a force on the liquid. The direction of interest in this problem is the horizontal, since the pipe is assumed to be horizontal.

The force pushing on the liquid at the left end of the pipe is the hydraulic pressure force of the liquid in the tank.

$$\text{Hydraulic force} = A_p \rho h \frac{g}{g_c}$$

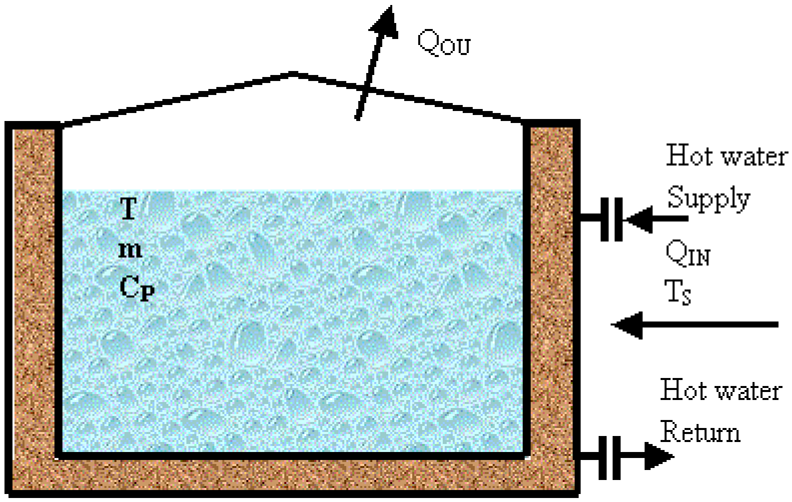
$$\text{Frictional force} = K_F L v^2$$

$$\frac{1}{g_c}\frac{d(A_p L \rho v)}{dt} = A_p \rho h \frac{g}{g_c} - K_F L v^2$$

$$\frac{dv}{dt} = \frac{g}{L} h - \frac{K_F g_c}{\rho A_p} v^2$$

2.4 MODELING A PROCESS - A TANK HEATING SYSTEM

Think about the tank below. It could be the hot water cylinder in your home which is a hot water tank heated by a heating coil that is connected to the central heating system (it can also be heated electrically like a kettle by an electric heater immersed in the water in the tank).



Hot water is used to heat the contents of a reactor. It is supplied to the jacket at a temperature of Ts. Heat is transferred at a rate of Qin (J/sec = Watts) from the jacket to the reactor contents. This input causes a change in the reactor temperature, T. The liquid in the reactor has a mass, m (kg), and a specific heat capacity of Cp (kJ/kgK). Heat is removed from the reactor at a rate of Qout (W).

The input to the system is the temperature of the hot water, T_S. This variable determines how much heat is added to the system, i.e. Q_{in}.

The output from the system is the temperature of the reactor, T. This variable determines how much heat is removed from the system in Q_{out}.

Any difference between the heat added and removed will result in an accumulation of energy (either positive or negative). A mass/energy balance on the system gives:

$$\begin{aligned} &In - Out = Accumulation \\ &Q_{in} - Q_{out} = Rate\ of\ Change\ in\ Internal\ Energy \\ &Q_{in} - Q_{out} = \frac{Change\ in\ Internal\ Energy}{\Delta t} \end{aligned}$$

Internal energy is a function of the mass of liquid, its specific heat capacity and its temperature and is equal to mC_pT. m and C_p are constants. The *change* in internal energy is equal to mC_p x the *change* in temperature.

$$\begin{aligned} &Q_{in} - Q_{out} = \frac{mC_p \Delta T}{\Delta t} \\ &\Delta t \rightarrow 0 \\ &\Rightarrow Q_{in} - Q_{out} = mC_p \frac{dT}{dt} \end{aligned}$$

If the top of the reactor is sealed and insulated the heat loss becomes minimal, i.e. Qout = 0.

The heat added to the system, Qin, is a function of the overall heat transfer coefficient, U (W/m^2K), the area available for heat transfer, A (m^2), the driving force for heat transfer which is the difference between the jacket temperature and the reactor temperature. Qin is given by:

$$Q_{in} = UA(T_S - T)$$

Rearranging the above equation, we get:

$$\begin{aligned} &UA(T_S - T) - 0 = mC_p \frac{dT}{dt} \\ &T_S - T = \frac{mC_p}{UA} \frac{dT}{dt} \\ &\frac{mC_p}{UA} \frac{dT}{dt} + T = T_S \end{aligned}$$

This is a first order differential equation which means that this is a first order system. The time constant is equal to mC_p/UA and the steady state gain is 1, i.e. the reactor temperature will eventually reach the temperature of hot water in the heating coil if left for long enough.

What if the reactor is not insulated? Well, Qout is not equal to zero but is equal to *uaDT*, where *u* is the overall heat transfer coefficient for the path from the reactor to outside (and *u ¹ U*), *a* is the area available for this heat transfer (and *a ¹ A*), and DT is the difference between the reactor temperature, T, and the outside temperature, T_o.

$$Q_{out} = ua\left(T - T_o\right)$$

Adding to the equation above, we get:

$$UA\left(T_S - T\right) - ua\left(T - T_o\right) = mC_p \frac{dT}{dt}$$

$$UAT_S - UAT - uaT + uaT_o = mC_p \frac{dT}{dt}$$

$$UAT_S + uaT_o = mC_p \frac{dT}{dt} + UAT + uaT$$

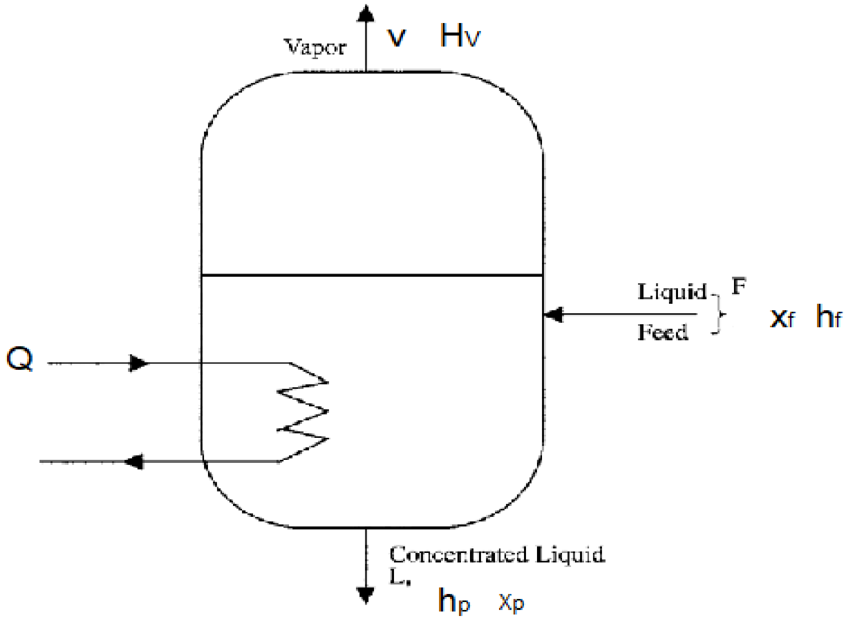
$$mC_p \frac{dT}{dt} + T\left(UA + ua\right) = UAT_S + uaT_o$$

$$\frac{mC_p}{\left(UA + ua\right)} \frac{dT}{dt} + T = \frac{UA}{\left(UA + ua\right)} T_S + \frac{ua}{\left(UA + ua\right)} T_o$$

The time constant in this equation is different. It has the extra *ua* term which makes it smaller, i.e. a shorter time constant.

Compare the insulated model to the non insulated one. The steady state temperature is a combination of the hot water temperature and the outside temperature. The contribution of the hot water temperature is reduced. The higher the outside temperature the higher the tank temperature will be.

2.5 MATHEMATICAL MODELING OF EVAPORATOR



$$F X_f = L X_p$$

$$F (1 - X_f) = V + L (1 - X_p)$$

Respectively, Where

F = feed rate kg/sec

L = concentrated liquid rate kg/sec

V = vapour rate kg/sec

X_f = mass fraction of solute in feed

X_p =mass fraction of solute in the product

Total material balance is given by-:

$$F = V + L$$

An enthalpy balance on the process stream yields-:

$$F.h_f + Q = V.H_v + L.h_p$$

Or $$F.h_f + Q = (F - L)H_v + Lh_p + F.h_p - Fh_p$$

Or $$F\ (h_f - h_p) + Q = (F-L)\ Hv - (F-L)\ hp$$

Or $$F\ (h_f - h_p) + Q - (F-L)\ (H_v - h_p) = 0$$

Where,

h_f = enthalpy of feed

h_p = enthalpy of product

H_v = enthalpy of vapour at the boiling point temperature of the feed, kJ/kg.

Q= rate of heat transfer across the tubes (from the steam to the thick liquor) kJ/sec

The enthalpy balance on the stream is given by-:

$$Q = V_0\ (H_o - h_o) = V_o\ \lambda_o$$

The rate of heat transfer Q is commonly approximated by use of the relationship-:

$$Q = UA\ (T_0 - T)$$

Where-:

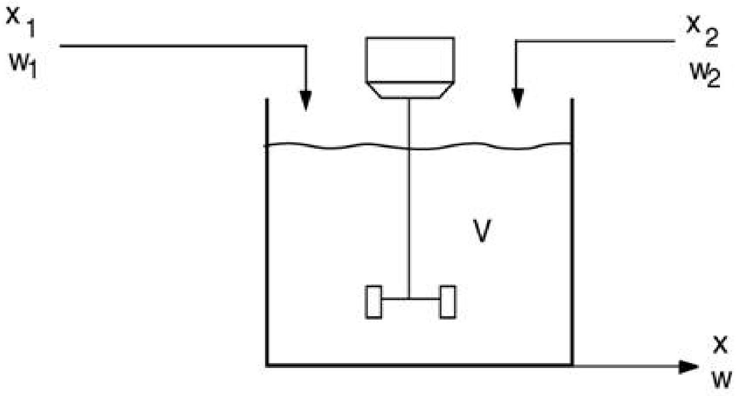
U = overall heat transfer coefficient

A =surface area of the tubes available for heat transfer.

T_o = saturation temperature of the steam entering the chest.

T = boiling point temperature of thick liquor at the pressure of the vapour space

2.5 MIXING PROCESS



Stirred-tank blending process.

$$\begin{Bmatrix}\text{rate of accumulation}\\ \text{of mass in the tank}\end{Bmatrix} = \begin{Bmatrix}\text{rate of}\\ \text{mass in}\end{Bmatrix} - \begin{Bmatrix}\text{rate of}\\ \text{mass out}\end{Bmatrix}$$

or

$$\frac{d(V\rho)}{dt} = w_1 + w_2 - w$$

where w_1, w_2, and w are mass flow rates.

The unsteady-state component balance is:

$$\frac{d(V\rho x)}{dt} = w_1 x_1 + w_2 x_2 - wx$$

The corresponding steady-state model

$$0 = \bar{w}_1 + \bar{w}_2 - \bar{w}$$
$$0 = \bar{w}_1 \bar{x}_1 + \bar{w}_2 \bar{x}_2 - \bar{w}\bar{x}$$

For constant ρ,

$$\rho \frac{dV}{dt} = w_1 + w_2 - w$$

$$\frac{\rho d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx$$

Equation can be simplified by expanding the accumulation term using the "chain rule" for differentiation of a product:

$$\rho \frac{d(Vx)}{dt} = \rho V \frac{dx}{dt} + \rho x \frac{dV}{dt}$$

$$\rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} = w_1 x_1 + w_2 x_2 - wx$$

$$\rho V \frac{dx}{dt} + x(w_1 + w_2 - w) = w_1 x_1 + w_2 x_2 - wx$$

After canceling common terms and rearranging a more convenient model form is obtained:

$$\frac{dV}{dt} = \frac{1}{\rho}(w_1 + w_2 - w)$$

$$\frac{dx}{dt} = \frac{w_1}{V\rho}(x_1 - x) + \frac{w_2}{V\rho}(x_2 - x)$$

2.6 MATHEMATICAL MODELING OF TWO CONICAL TANKS OF NON-INTERACTING SYSTEM

System is said to be non-interacting the dynamic behaviour of the first system will affect the dynamic behaviour of the second system while the dynamic behaviour of the second system does not affect the first system.

Let us define,

H_1=height of the conical tank 1 cm

H_2=height of the conical tank 2 cm

V = total volume of the conical tank

qin(s)=volumetric flow rate of the inlet stream (lph)

q1(s)volumetric flow rate of the outlet stream (lph)

R_1=Restriction element

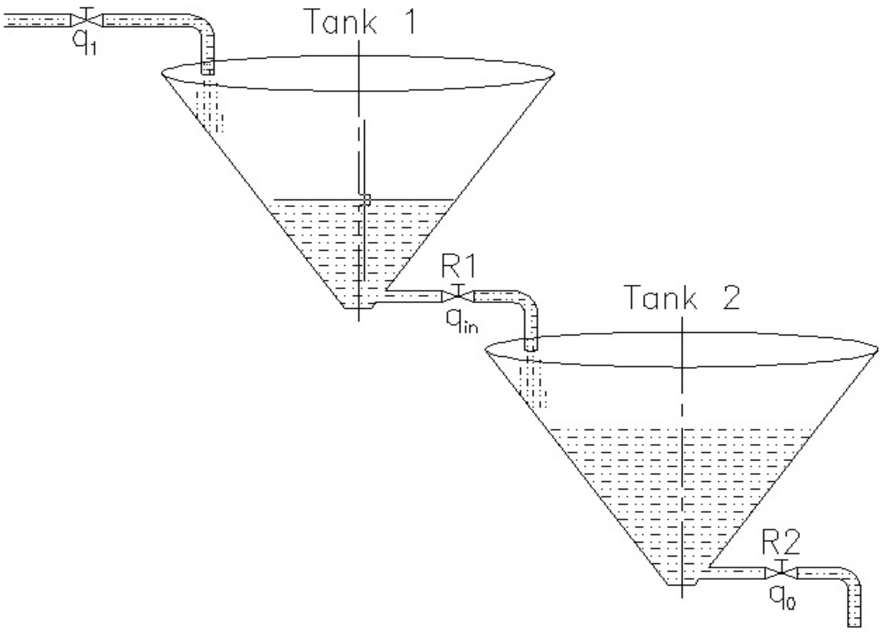


Fig - Two Conical Tanks of Non-Interacting System

H=Maximum height of the conical tank

According to law of conservation of mass,

Accumulation of mass within a system = Flow of mass into the system - Flow of mass out to the system

$$v1 * \frac{dh1}{dt} = q_{in} - q_1$$

For laminar flow,

$q_1=h_1/R_1$

Sub (2) in (1)

$$V_1 * \frac{dh_1}{dt} = q_{in} - \frac{h_1}{R_1}$$

2.7 MATHEMATICAL MODELING OF TWO CONICAL TANKS OF INTERACTING SYSTEM

System is said to be interacting then the dynamic behavior of the first system will affects the dynamic behavior of the second system while the dynamics of second system will affects the dynamics of first system.

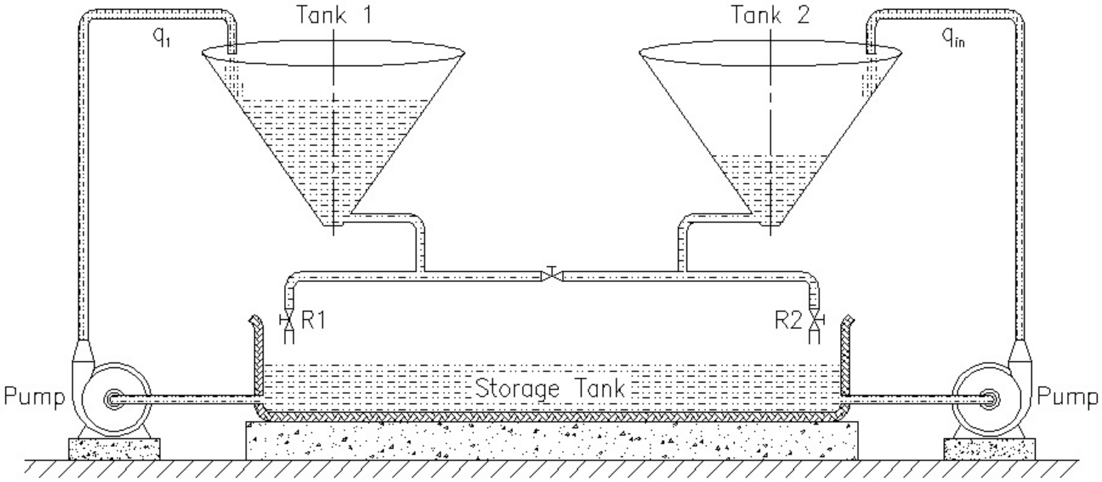


Figure-two conical tank of interacting system

For tank 1,

$$v1 * \frac{dh1}{dt} = q_{in} - q_1$$

$$q_1 = \frac{h_1 - h_2}{R_1}$$

$$v1 * \frac{dh1}{dt} = q_{in} - \frac{h_1 - h_2}{R_1}$$

For tank-2,

$$v_2 * \frac{dh_2}{dt} = q_1 - q_0$$

Let $q_0 = \frac{h_2}{R_2}$

$$v_2 * \frac{dh_2}{dt} = \frac{h_1 - h_2}{R_1} - \frac{h_2}{R_2}$$

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III- Modeling of Reactors – SCH1401

3.INTRODUCTION

In this chapter we develop mathematical models for a number of elementary chemical processes that are commonly encountered in practice. We will apply the methodology discussed in the previous chapter to guide the reader through various examples. The goal is to give the reader a methodology to tackle more complicated processes that are not covered in this chapter and that can be found in books listed in the reference. The organization of this chapter includes examples of systems that can be described by ordinary differential equations (ODE), i.e. lumped parameter systems followed by examples of distributed parameters systems, i.e those described by partial differential equations (PDE). The examples cover both homogeneous and heterogeneous systems. Ordinary differential equations (ODE) are easier to solve and are reduced to simple algebraic equations at steady state. The solution of partial differential equations (PDE) on the other hand is a more difficult task. But we will be interested in the cases were PDE's are reduced to ODE's. This is naturally the case where under appropriate assumptions, the PDE's is a one-dimensional equation at steady state conditions. It is worth to recall, as noted in the previous chapters, that the distinction between lumped and distributed parameter models depends sometimes on the assumptions put forward by the modeler. Systems that are normally distributed parameter can be modeled under appropriate assumptions as lumped parameter systems. This chapter includes some examples of this situation.

3.1 LIQUID STORAGE TANK

Consider the perfectly mixed storage tank shown in figure 3.1. Liquid stream with volumetric rate F_f (m^3/s) and density ρ_f flow into the tank. The outlet stream has volumetric rate F_o and density ρ_o. Our objective is to develop a model for the variations of the tank holdup, i.e. volume of the tank. The system is therefore the liquid in the tank. We will assume that it is perfectly mixed and that the density of the effluent is the same as that of tank content. We will also assume that the tank is isothermal, i.e. no variations in the temperature. To model the tank we need only to write a mass balance equation.

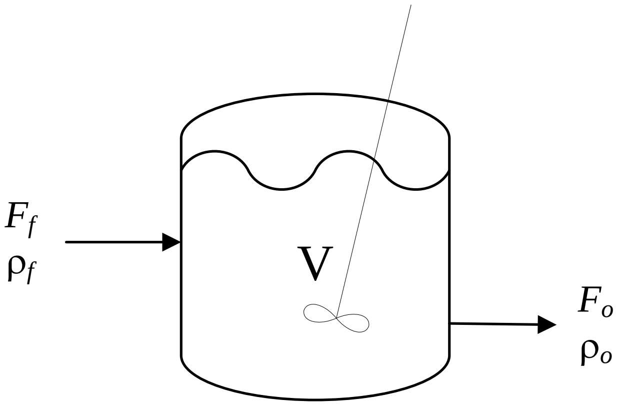


Figure 3.1 Liquid Storage Tank

Since the system is perfectly mixed, the system properties do not vary with position inside the tank. The only variations are with time. The mass balance equation can be written then on the whole system and not only on a differential element of it. This leads to therefore to a macroscopic model.

We apply the general balance equation to the total mass $m = \rho V$. This yields:

Mass flow in:

$$\rho_f F_f \tag{3.1}$$

Mass flow out:

$$\rho_o F_o \tag{3.2}$$

Accumulation:

$$\frac{dm}{dt} = \frac{d(\rho V)}{dt} \tag{3.3}$$

The generation term is zero since the mass is conserved. The balance equation yields:

$$\rho_f F_f = \rho_o F_o + \frac{d(\rho V)}{dt} \tag{3.4}$$

For consistency we can check that all the terms in the equation have the SI unit of *kg/s*. The resulting model (Eq. 3.4) is an ordinary differential equation (ODE) of first order where time (*t)* is the only independent variable. This is therefore a lumped parameter model. To solve it we need one initial condition that gives the value of the volume at initial time t_i, i.e.

$$V(t_i) = V_i \tag{3.5}$$

Under isothermal conditions we can further assume that the density of the liquid is constant i.e. $\rho_f = \rho_o = \rho$. In this case Eq. 3.4 is reduced to:

$$\frac{dV}{dt} = F_f - F_o \tag{3.6}$$

The volume V is related to the height of the tank L and to the cross sectional area A by:

$$V = AL \tag{3.7}$$

Since (A) is constant then we obtain the equation in terms of the state variable L:

$$A\frac{dL}{dt} = F_f - F_o \tag{3.8}$$

with initial condition:

$$L(t_i) = L_i \tag{3.9}$$

Degree of freedom analysis

For the system described by Eq. 3.8 we have the following information:

- Parameter of constant values: A
- Variables which values can be externally fixed (Forced variable): F_f
- Remaining variables: L and F_o
- Number of equations: 1 (Eq. 3.8)

Therefore the degree of freedom is:

Number of remaining variables – Number of equations = 2 – 1 = 1

For the system to be exactly specified we need therefore one more equations. This extra relation is obtained from practical engineering considerations. If the system is operated without control (at open loop) then the outlet flow rate F_o is a function of the liquid level L. Generally a relation of the form:

$$F_o = \alpha\sqrt{L} \tag{3.10}$$

could be used, where α is the discharge coefficient.

If on the other hand the liquid level is under control, then its value is kept constant at certain desired value L_s. If F_o is used to control the height then a control law relates F_o to L and L_s:

$$F_o = F_o(L,L_s) \tag{3.11}$$

For instant, if a proportional controller K_c is used then the control law is given by:

$$F_o = K_c(L - L_s) + F_{ob} \tag{3.12}$$

Where F_{ob} the bias, i.e. the constant value of F_o when the level is at the desired value i.e., $L = L_s$.

Note that at steady state, the accumulation term is zero (height does not change with time), i.e., $dL/dt = 0$. The model of the tank is reduced to the simple algebraic equation:

$$F_0 = F_f \tag{3.13}$$

3.2 ISOTHERMAL CSTR

We revisit the perfectly mixed tank of the first example but where a liquid phase chemical reaction taking place:

$$A \xrightarrow{k} B \qquad (3.14)$$

The reaction is assumed to be irreversible and of first order. As shown in figure 3.2, the feed enters the reactor with volumetric rate F_f (m^3/s), density ρ_f (kg/m^3) and concentration C_{Af} ($mole/m^3$). The output comes out of the reactor at volumetric rate F_o, density ρ_0 and concentration C_{Ao} ($mole/m^3$) and C_{Bo} ($mole/m^3$). We assume isothermal conditions.

Our objective is to develop a model for the variation of the volume of the reactor and the concentration of species *A* and *B*. The assumptions of example 3.1 still hold and the total mass balance equation (Eq. 3.6) is therefore unchanged

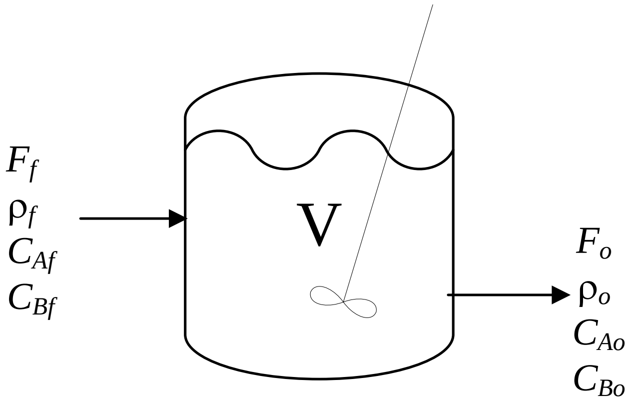


Figure 3.2 Isothermal CSTR

The component balance on species A is obtained by the application of law of conservation of mass to the number of moles ($n_A = C_A V$). Since the system is well mixed the effluent concentration C_{Ao} and C_{Bo} are equal to the process concentration C_A and C_B.

Flow of moles of *A* in:

$$F_f C_{Af} \qquad (3.15)$$

Flow of moles of *A* out:

$$F_o C_{Ao} \qquad (3.16)$$

Rate of accumulation:

$$\frac{dn}{dt} = \frac{d(VC_A)}{dt} \tag{3.17}$$

Rate of generation: $-rV$

where r (*moles/m*^{3}*s*) is the rate of reaction.

Substituting these terms in the general equation yields:

$$\frac{d(VC_A)}{dt} = F_f\, C_{Af} - F_o\, C_A - rV \tag{3.18}$$

We can check that all terms in the equation have the unit (*mole/s*).

We could write a similar component balance on species B but it is not needed since it will not represent an independent equation. In fact, as a general rule, a system of n species is exactly specified by n independent equations. We can write either the total mass balance along with $(n-1)$ component balance equations, or we can write n component balance equations.

Using the differential principles, equation (3.18) can be written as follows:

$$\frac{d(VC_A)}{dt} = V\frac{d(C_A)}{dt} + C_A\frac{d(V)}{dt} = F_f\, C_{Af} - F_o\, C_A - rV \tag{3.19}$$

Substituting Equation (3.6) into (3.19) and with some algebraic manipulations we obtain:

$$V\frac{d(C_A)}{dt} = F_f\,(C_{Af} - C_A) - rV \tag{3.20}$$

In order to fully define the model, we need to define the reaction rate which is for a first-order irreversible reaction:

$$r = k\, C_A \tag{3.21}$$

Equations 3.6 and 3.20 define the dynamic behavior of the reactor. They can be solved if the system is exactly specified and if the initial conditions are given:

$$V(t_i) = V_i \text{ and } C_A(t_i) = C_{Ai} \tag{3.22}$$

Degrees of freedom analysis

- Parameter of constant values: A
- (Forced variable): F_f and C_{Af}
- Remaining variables: V, F_o, and C_A

- Number of equations: 2 (Eq. 3.6 and Eq. 3.20)

The degree of freedom is therefore 3 − 2 =1. The extra relation is obtained by the relation between the effluent flow F_o and the level in open loop operation (Eq. 3.10) or in closed loop operation (Eq. 3.11).

The steady state behavior can be simply obtained by setting the accumulation terms to zero. Equation 3.6 and 3.20 become:

$$F_0 = F_f \tag{3.23}$$

$$F_f(C_{Af} - C_A) = rV \tag{3.24}$$

3.3 GAS-PHASE PRESSURIZED CSTR

So far we have considered only liquid-phase reaction where density can be taken constant. To illustrate the effect of gas-phase chemical reaction on mass balance equation, we consider the following elementary reversible reaction:

$$A \leftrightarrow 2B \tag{3.25}$$

taking place in perfectly mixed vessel sketched in figure 3.3. The influent to the vessel has volumetric rate F_f (m^3/s), density ρ_f (kg/m^3), and mole fraction y_f. Product comes out of the reactor with volumetric rate F_o, density ρ_o, and mole fraction y_o. The temperature and volume inside the vessel are constant. The reactor effluent passes through control valve which regulate the gas pressure at constant pressure P_g.

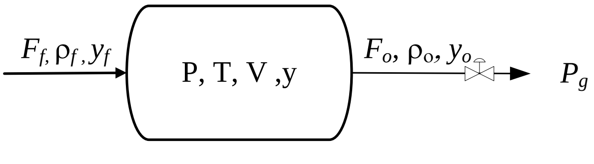


Figure 3.3 Gas Pressurized Reactor

Writing the macroscopic total mass balance around the vessel gives:

$$\frac{d(\rho V)}{dt} = \rho_f F_f - \rho_o F_o \tag{3.26}$$

Since V is constant we have:

$$V\frac{d\rho}{dt} = \rho_f F_f - \rho_o F_o \tag{3.27}$$

Writing the component balance, for fixed V, results in:

$$V\frac{dC_A}{dt} = F_f C_{Af} - F_o C_{A_0} - r_1 V + r_2 V \tag{3.28}$$

The reaction rates for the reversible reaction are assumed to be:

$$r_1 = k_1\, C_A \tag{3.29}$$

$$r_2 = k_2 C_B{}^2 \tag{3.30}$$

Equations (3.27) and (3.28) define the variations of density and molar concentration. One can also rewrite the equation to define the behavior of the pressure *(P)* and mole fraction *(y)*. The concentration can be expressed in term of the density through ideal gas law:

$$C_A = yP/RT \tag{3.31}$$

$$C_B = (1 - y)P/RT \tag{3.32}$$

Similarly, the density can be related to the pressure using ideal gas law:

$$\rho = MP/RT = [M_A y + M_B\,(1 - y)]P/RT \tag{3.33}$$

Where M_A and M_B are the molecular weight of A and B respectively. Therefore one can substitute equations (3.31) to (3.33) into equations (3.27 & 3.28) in order to explicitly write the latter two equations in terms of y and P. Or, alternatively, one can solve all equations simultaneously.

Degrees of freedom analysis:

- Parameters: V, k_1, k_2, R, T, M_A and M_B
- Forcing function: F_f, C_{Af}, y_f
- Variables: C_A, C_B, y, P, ρ, F
- Number of equations: 5
- The degree of freedom is therefore 6 − 5 =1. The extra relation relates the outlet flow to the pressure as follows:

$$F_o = C_v \sqrt{\frac{P - P_g}{\rho}} \tag{3.34}$$

where C_v is the valve-sizing coefficient. Recall also that P_g is assumed to be constant.

3.4 NON-ISOTHERMAL CSTR

We reconsider the previous CSTR example but for non-isothermal conditions. The reaction A → B is exothermic and the heat generated in the reactor is removed via a cooling system as shown in figure 3.4. The effluent temperature is different from the inlet temperature due to heat generation by the exothermic reaction.

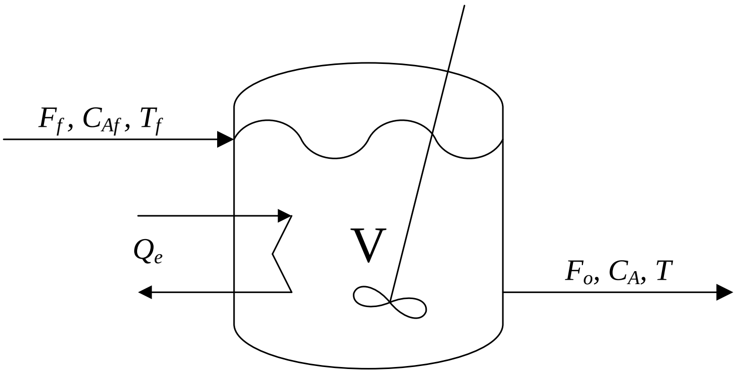


Figure 3.4 Non-isothermal CSTR

Assuming constant density, the macroscopic total mass balance (Eq. 3.6) and mass component balance remain the same as before. However, one more ODE will be produced from the applying the conservation law for total energy balance. The dependence of the rate constant on the temperature:

$$k = k_o e^{-E/RT} \tag{3.35}$$

should be emphasized.

The general energy balance for macroscopic systems applied to the CSTR yields, assuming constant density and average heat capacity:

$$\rho \tilde{C}_p \frac{d\left(V(T - T_{ref})\right)}{dt} = \rho F_f \tilde{C}_p (T_f - T_{ref}) - \rho F_o \tilde{C}_p (T - T_{ref}) + Q_r - Q_e \tag{3.36}$$

where Q_r (J/s) is the heat generated by the reaction, and Q_e (J/s) the rate of heat removed by the cooling system. Assuming $T_{\text{ref}} = 0$ for simplicity and using the differentiation principles, equation 3.36 can be written as follows:

$$\rho\tilde{C}_p V \frac{dT}{dt} + \rho\tilde{C}_p T \frac{dV}{dt} = \rho F_f \tilde{C}_p T_f - \rho F_o \tilde{C}_p T + Q_r - Q_e \tag{3.37}$$

Substituting Equation 3.6 into the last equation and rearranging yields:

$$\rho\tilde{C}_p V \frac{dT}{dt} = \rho F_f \tilde{C}_p (T_f - T) + Q_r - Q_e \tag{3.38}$$

The rate of heat exchanged Q_r due to reaction is given by:

$$Q_r = -(\Delta H_r) Vr \tag{3.39}$$

where ΔH_r (J/mole) is the heat of reaction (has negative value for exothermic reaction and positive value for endothermic reaction). The non-isothermal CSTR is therefore modeled by three ODE's:

$$\frac{dV}{dt} = F_f - F_o \tag{3.40}$$

$$V \frac{d(C_A)}{dt} = F_f (\, C_{Af} - C_A) - rV \tag{3.41}$$

$$\rho\tilde{C}_p V \frac{dT}{dt} = \rho F_f \tilde{C}_p (T_f - T) + (-\Delta H_r) Vr - Q_e \tag{3.42}$$

where the rate (r) is given by:

$$r = k_o e^{-E/RT} C_A \tag{3.43}$$

The system can be solved if the system is exactly specified and if the initial conditions are given:

$$V(t_i) = V_i \qquad T(t_i) = T_i \qquad \text{and} \qquad C_A(t_i) = C_{Ai} \tag{3.44}$$

Degrees of freedom analysis

- Parameter of constant values: ρ, E, R, C_p, ΔH_r *and* k_o
- (Forced variable): F_f , C_{Af} and T_f
- Remaining variables: V, F_o, T, C_A and Q_e
- Number of equations: 3

  The degree of freedom is 5−3 = 2. Following the analysis of example 3.3, the two extra relations are between the effluent stream (F_o) and the volume (V) on one hand and between the rate of heat exchanged (Q_e) and temperature (T) on the other hand, in either open loop or closed loop operations.

A more elaborate model of the CSTR would include the dynamic of the cooling jacket (Fig. 3.5). Assuming the jacket to be perfectly mixed with constant volume V_j, density ρ_j and constant average thermal capacity Cp_j, the dynamic of the cooling jacket temperature can be modeled by simply applying the macroscopic energy balance on the whole jacket:

$$\rho_j \tilde{C}_{p_j} V_j \frac{dT_j}{dt} = \rho_j F_j \tilde{C}_{p_j} (T_{jf} - T_j) + Q_e \tag{3.45}$$

Since V_j, ρ_j, Cp_j and T_{jf} are constant or known, the addition of this equation introduces only one variable (T_j). The system is still exactly specified.

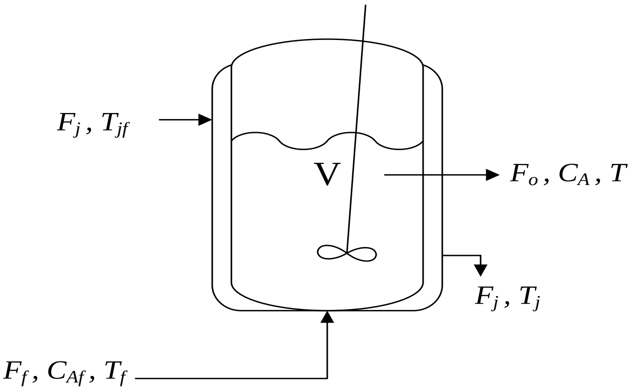


Figure 3.5 Jacketed Non-isothermal CSTR

3.5 TWO-PHASE REACTOR

Consider the two-phase reactor shown in figure 3.6. Gaseous *A* and liquid *B* enters the reactor at molar flow rates F_A and F_B respectively. Reactant *A* diffuses into the liquid phase with molar flux (N_A) where it reacts with *B* producing *C*. The latter diffuses into the vapor phase with molar flux (N_C). Reactant *B* is nonvolatile. The product *C* is withdrawn with the vapor leaving the reactor. The objective is to write the mathematical equations that describe the dynamic behavior of the process. We consider all flows to be in molar rates.

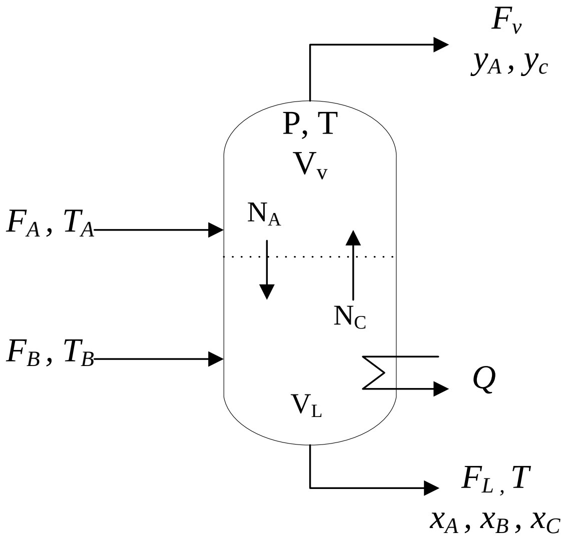


Figure 3.6 Two Phase Reactor

Assumptions:

- The individual phases are well mixed and they are in physical equilibrium at pressure *P* and temperature *T*.
- The physical properties such as molar heat capacity *Cp*, density ρ , and latent heat of vaporization λ are constant and equal for all the species.
- The reaction mechanism is: $A+B \rightarrow C$ and its rate has the form: $R_c = k\, C_A\, C_B\, V_L$
- The two phases are in equilibrium and follows the Raoult's law.
- Total enthalpy for the system is given as: $H = N_L H_L + N_v H_v$ where H_L and H_v are molar enthalpies in the liquid and vapor phases respectively, and N_L and N_v are their corresponding molar holdups.

The assumption of well mixing allows writing the following macroscopic balances:

Vapor phase:

Total mass balance:

$$\frac{dN_v}{dt} = F_A - N_A + N_c - F_v \qquad (3.46)$$

Component balance for *A*:

$$\frac{d(N_v y_A)}{dt} = F_A - N_A - F_v y_A \qquad (3.47)$$

Since $d(N_v y_A)/dt = N_v\, dy_A/dt + y_A\, dN_v/dt$, and using equation (3.46), equation (3.47) can be written as follows:

$$N_v \frac{dy_A}{dt} = F_A(1 - y_A) - N_A(1 - y_A) - N_c y_A \qquad (3.48)$$

Liquid phase:

Total mass balance:

$$\frac{dN_L}{dt} = F_B + N_A - N_c - F_L - R_c \qquad (3.49)$$

Component balance for *A*:

$$\frac{d(N_L x_A)}{dt} = N_A - F_L x_A - R_c \qquad (3.50)$$

Since $d(N_L x_A)/dt = N_L\, dx_A/dt + x_A\, dN_L/dt$, and using equation (3.49), equation (3.50) can be written as follows:

$$N_L \frac{dx_A}{dt} = N_A(1-x_A) - F_B x_A - R_c(1-x_A) + N_c x_A \qquad (3.51)$$

Component balance for *B*:

Repeating the same reasoning used for component *A*, we can write:

$$N_L \frac{dx_B}{dt} = N_A(1-x_B) + F_B x_B - R_c(1-x_B) + N_c x_B \qquad (3.52)$$

Energy balance, assuming $T_{\mathrm{ref}} = 0$:

$$\frac{d(N_L H_L + N_v H_v)}{dt} = F_B Cp T_B + F_A(Cp T_A + \lambda) - F_L Cp T - F_v Cp T - R_c \Delta H_r + Q \qquad (3.53)$$

Note that:

$$\frac{d(N_L H_L)}{dt} = N_L \frac{d(H_L)}{dt} + H_L \frac{d(N_L)}{dt} = N_L Cp \frac{d(T)}{dt} + Cp T \frac{d(N_L)}{dt} \qquad (3.54)$$

$$\frac{d(N_v H_v)}{dt} = N_v \frac{d(H_v)}{dt} + H_v \frac{d(N_v)}{dt} = N_v Cp \frac{d(T)}{dt} + (Cp T + \lambda) \frac{d(N_v)}{dt} \qquad (3.55)$$

Substituting the last two equations, and using the definition of dN_L/dt and dN_v/dt from equations (3.46) and (3.49), in equation (3.55) yields:

$$N_L + N_v \frac{d(T)}{dt} = F_A(T_A - T) + F_B(T_B - T) + R_c(T - \frac{\Delta H_r}{Cp}) + \frac{\lambda}{Cp}(N_A - N_c) + \frac{Q}{Cp} \qquad (3.56)$$

The following additional equations are needed:

Vapor-liquid equilibrium relations:

$$y_A P - x_A P_A^s = 0 \tag{3.57}$$

$$y_A P - (1 - x_A - x_B) P_c^s = 0 \tag{3.58}$$

Total volume constraint:

$$V = V_L + V_v \tag{3.59}$$

Or, using ideal gas law for vapor volume and total volume and knowing that $V_L = N_L/\rho$, we can write:

$$nRT = N_v RT + N_L P/\rho \tag{3.60}$$

or

$$V = N_v RT/P + N_L/\rho \tag{3.61}$$

Degrees of freedom analysis:

- Forcing variables: F_A, F_B, T_A, T_B, Q, P
- Physical properties and parameters: $\Delta H_r, Cp, \lambda, R, \rho, V, P_A^s, P_C^s$
- Remaining variables: $N_A, N_c, N_L, N_v, F_L, T, x_A, x_B, y_A$
- Number of equations: 9
- The degree is freedom is 9-9=0 and the problem is exactly specified. Note that the reaction rate R_c is defined and that the outlet flow F_v can be determined from the overall mass balance.

3.7 ISOTHERMAL PLUG FLOW REACTOR

Let consider a first-order reaction occurring in an isothermal tubular reactor as shown in figure 3.8. We assume plug flow conditions i.e. the density, concentration and velocity change with the axial direction only. Our aim is to develop a model for the reaction process in the tube.

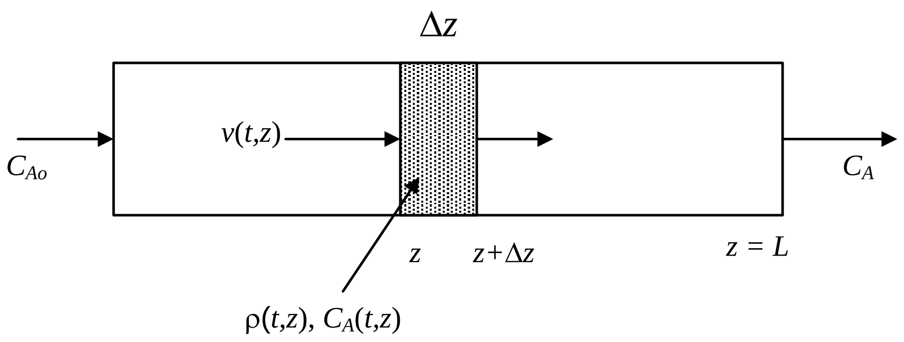


Figure 3.8 Isothermal Plug flow reactor

In the following we derive the microscopic component balance for species (A) around differential slice of width Δz and constant cross-section area (S).

Flow of moles of A in:

Mass transfer occurs by two mechanism; convection and diffusion. The flow of moles of species A into the shell is therefore the sum of two terms:

$$(vC_A\, S\, \Delta t)\,|_z + (N_A\, S\, \Delta t)|_z$$

where N_A is the diffusive flux of A (*moles of* $A/m^2\, s$).

Flow of moles of A out:

$$(vC_A\, S\, \Delta t)\,|_{z+\Delta z} + (N_A\, S\, \Delta t)|_{z+\Delta z}$$

Accumulation:

$$(C_A\, S\, \Delta z)\,|_{t+\Delta t} - (C_A\, S\, \Delta z)\,|_t$$

Generation due to reaction inside the shell:

$$-\, r(S\Delta z\Delta t)$$

where $r = k\, C_A$ is the rate of reaction.

Substituting all the terms in the mass balance equation and dividing by Δt and Δz gives:

$$\frac{(C_A S)|_{t+\Delta t} - (C_A S)|_t}{\Delta t} = \frac{(vC_A S + N_A S)|_z - (vC_A S + N_A S)|_{z+\Delta z}}{\Delta z} - kC_A S$$

Taking the limit of Δt → 0 and Δz → 0 and omitting S from both sides give the following PDE:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial v C_A}{\partial z} - \frac{\partial N_A}{\partial z} - kC_A$$

where N_A is the molar flux given by Fick's law as follows:

$$N_A = -D_{AB}\frac{dC_A}{dz}$$

where D_{AB} is the binary diffusion coefficient. Equ can be then written as follows:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial (vC_A)}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$

Expanding the derivatives, the last equation can be reduced to:

$$\frac{\partial C_A}{\partial t} = -v\frac{\partial C_A}{\partial z} - C_A\frac{\partial v}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$

This equation can be further simplified by using the mass balance equation for incompressible fluids . We get then:

$$\frac{\partial C_A}{\partial t} = -v\frac{\partial C_A}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$

The equation is a PDE for which the state variable (C_A) depends on both t and z.

The PDE is reduced at steady state to the following second order ODE,

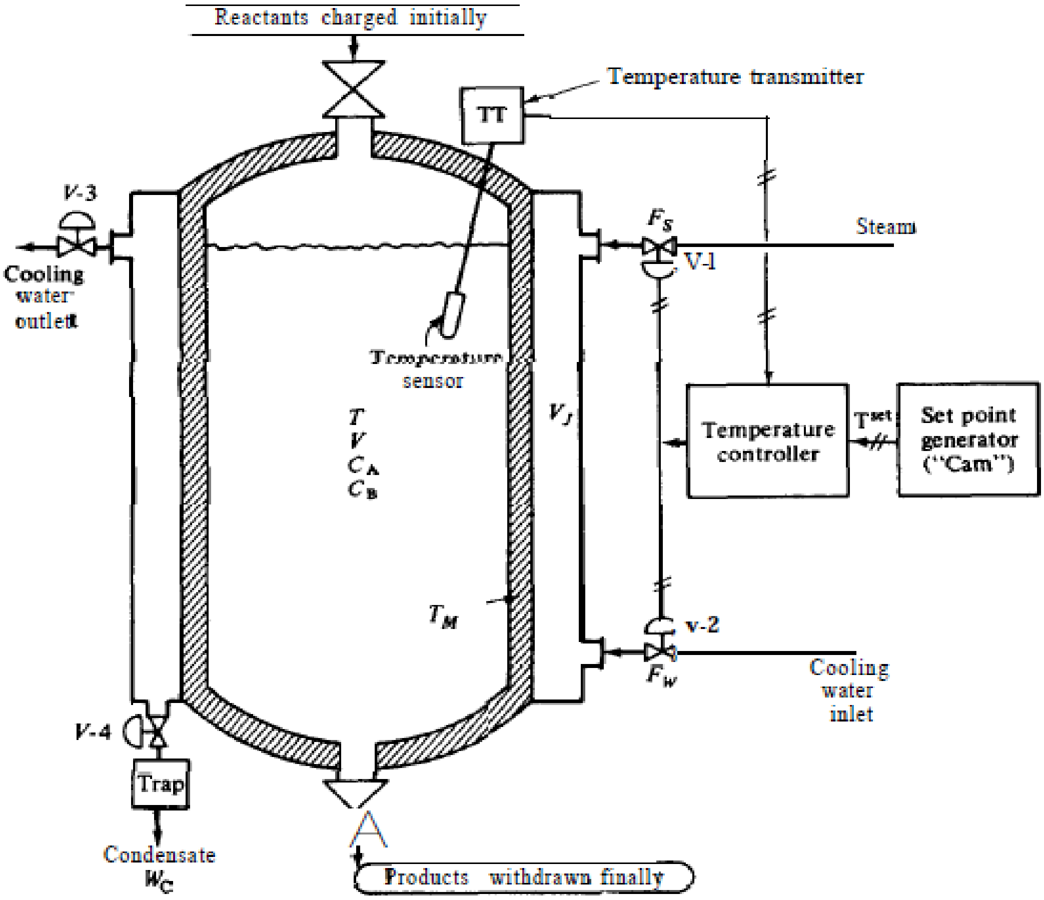
$$0 = -v\frac{dC_A}{dz} + D_{Ab}\frac{d^2 C_A}{dz^2} - kC_A$$

The ODE can be solved with the following boundary conditions (BC):

BC1: at $z = 0$ $C_A(0) = C_{A0}$

BC2: at $z = L$ $\frac{dC_A(z)}{dz} = 0$

The first condition gives the concentration at the entrance of the reactor while the second condition indicates that there is no flux at the exit length of the reactor.



Batch reactor.

Batch processes offer some of the most interesting and challenging problems in modeling and control because of their inherent dynamic nature. Although most large-scale chemical engineering processes have traditionally been operated in a continuous fashion, many batch processes are still used in the production of smaller-volume specialty chemicals and pharmaceuticals. The batch chemical reactor has inherent kinetic advantages over continuous reactors for some reactions (primarily those with slow rate constants). The wide use of digital process control computers has permitted automation and optimization of batch processes and made them more efficient and less labor intensive

Let us consider the batch reactor sketched in Fig. 3.9. Reactant is charged into the vessel. Steam is fed into the jacket to bring the reaction mass up to a desired temperature. Then cooling water must be added to the jacket to remove the exothermic heat of reaction and to make the reactor temperature follow the prescribed temperature-time curve. This temperature profile is fed into the temperature controller as a setpoint signal. The setpoint varies with time. First-order consecutive reactions take place in the reactor as time proceeds.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The product that we want to make is component B. If we let the reaction go on too long, too much of B will react to form undesired C; that is, the yield will be low. If we stop the reaction too early, too little A will have reacted; i.e., the conversion and yield will be low. Therefore, there is an optimum batch time when we should stop the reaction. This is often done by quenching it, i.e., cooling it down quickly.

There may also be an optimum temperature profile. If the temperature dependences of the specific reaction rates k_l and k_2 are the same (if their activation energies are equal), the reaction should be run at the highest possible temperature to minimize the batch time. This maximum temperature would be a limit imposed by some constraint: maximum working temperature or pressure of the equipment, further undesirable degradation or polymerization of products or reactants at very high temperatures, etc.

If k1 is more temperature-dependent than k,, we again want to run at the highest possible temperature to favor the reaction to B. In both cases we must be sure to stop the reaction at the right time so that the maximum amount of B is recovered.

If kl is less temperature-dependent that k2 the optimum temperature profile is one that starts off at a high temperature to get the first reaction going but then drops to prevent the loss of too much B.

With this background, let us now derive a mathematical model for this process. We will assume that the density of the reaction liquid is constant. The total continuity equation for the reaction mass, after the reactants have been charged and the batch cycle begun, is

$$\frac{d(\rho V)}{dt} = 0 - 0$$

There is no inflow and no outflow. Since p is constant, $dV/dt = 0$. Therefore the volume of liquid in the reactor is constant.

Component continuity for A:

$$V\frac{dC_A}{dt} = -Vk_1C_A$$

Component continuity for B :

$$V\frac{dC_B}{dt} = Vk_1C_A - Vk,\ C_B$$

Kinetic equations :

$$k_1 = \alpha_1 e^{-E_1/RT} \qquad k_2 = \alpha_2\, e^{-E_2/RT}$$

Using a lumped model for the reactor metal wall and the simple enthalpy equation $h = C_p\, T$, the energy equations for the reaction liquid and the metal wall are :

Energy equation for process :

$$\rho V C_p\frac{dT}{dt} = -\lambda_1 Vk_1C_A - \lambda_2\, Vk,\ C_B - h_i\, A_i(T - T_M)$$

where λ_1 and λ_2 are the exothermic heats of reaction for the two reactions.

3.9SERIES OF ISOTHERMAL, CONSTANT-HOLDUP CSTRs

The system is sketched in Fig. Product B is produced and reactant A is consumed in each of the three perfectly mixed reactors by a first-order reaction occurring in the liquid. For the moment let us assume that the temperatures and holdups (volumes) of the three tanks can be different, but both temperatures and the liquid volumes are assumed to be constant (isothermal and constant holdup). Density is assumed constant throughout the system, which is a binary mixture of A and B. With these assumptions in mind, we are ready to formulate our model. If the volume and density of each tank are constant, the total mass in each tank is constant. Thus the total continuity equation for the first reactor is

$$\frac{d(\rho V_1)}{dt} = \rho F_0 - \rho F_1 = 0$$

or $F_1 = F_0$.

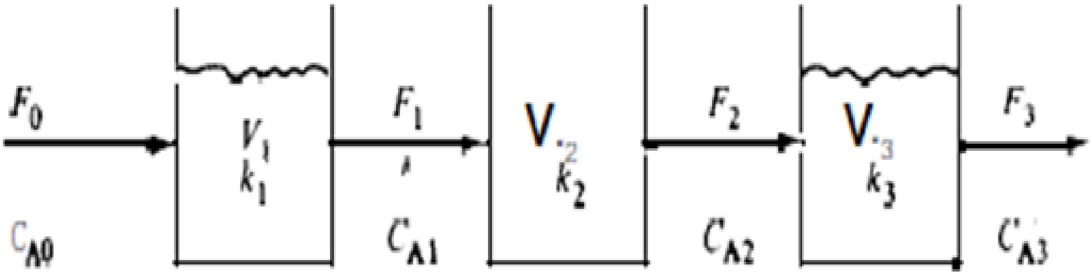
Likewise total mass balances on tanks 2 and 3 give

$$F_3 = F_2 = F_1 = F_0 \equiv F$$

where F is defined as the throughput (m^3/min)

$$\frac{d(\rho V)}{dt} = \rho F - \rho F = 0$$

$$\frac{d(\ V)}{dt} = 0$$



Series of CSTRs.

We want to keep track of the amounts of reactant A and product B in each tank, so component continuity equations are needed. However, since the system is binary and we know the total mass of material in each tank, only one component continuity equation is required. Either B or A can be used. If we arbitrarily choose A, the equations describing the dynamic changes in the amounts of reactant A in each tank are (with units of kg - mol of A/min) reactant A in each tank are (with units of kg • mol of A/min)

$$V_1 \frac{dC_{A1}}{dt} = F(C_{A0} - C_{A1}) - V_1 k_1 C_{A1}$$

$$V_2 \frac{dC_{A2}}{dt} = F(C_{A1} - C_{A2}) - V_2 k_2 C_{A2}$$

$$V_3 \frac{dC_{A3}}{dt} = F(C_{A2} - C_{A3}) - V_3 k_3 C_{A3}$$

The specific reaction rates k_n are given by the Arrhenius equation

$$k_n = \alpha e^{-E/RT_n} \qquad n = 1, 2, 3$$

The volumes V, can be pulled out of the time derivatives because they are constant .The flows are all equal to F but can vary with time. An energy equation is not required because we have assumed isothermal operation. Any heat addition or heat removal required to keep the reactors at constant temperatures could be calculated from a steady state energy balance (zero time derivatives of temperature). The three first-order nonlinear ordinary differential equations obtained are the mathematical model of the system. The parameters that must be known are V_1, V_2, , V_3, , k_l, k_2, and k_3, . The variables that must be specified before these equations can be solved are F and CA_o. “Specified” does not mean that they must be constant. They can be time-varying, but they must be known or given functions of time. They are the forcing functions. The initial conditions of the three concentrations (their values at time equal zero) must also be known

Let us now check the degrees of freedom of the system. There are three equations and, with the parameters and forcing functions specified, there are only three unknowns or dependent variables: CA_1, CA_2, and CA_3. Consequently a solution should be possible.

When we use it for controller design and stability analysis, we will use an even simpler version. If the throughput F is constant and the holdups and temperatures are the same in all three tanks, the above Eqs. become

$$\frac{dC_{A1}}{dt} + \left(k + \frac{1}{\tau}\right)C_{A1} = \frac{1}{\tau}\,C_{A0}$$

$$\frac{dC_{A2}}{dt} + \left(k + \frac{1}{\tau}\right)C_{A2} = \frac{1}{\tau}\,C_{A1}$$

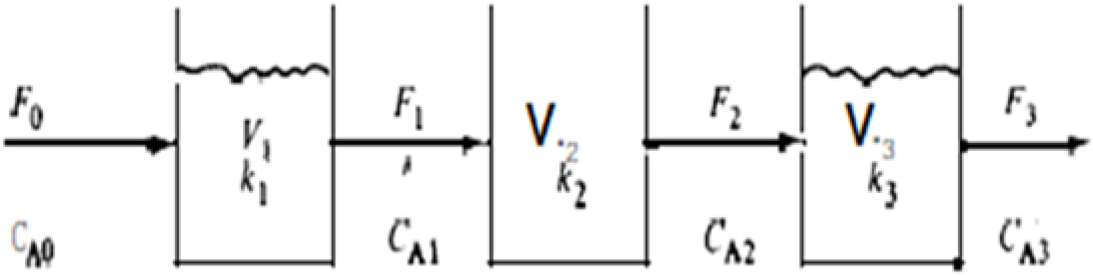
$$\frac{dC_{A3}}{dt} + \left(k + \frac{1}{\tau}\right)C_{A3} = \frac{1}{\tau}\,C_{A2}$$

where $\tau = V/F$ with units of minutes.

There is only one forcing function or input variable, C_{A0} .

3.10 CSTRs WITH VARIABLE HOLDUPS

If the previous example is modified slightly to permit the volumes in each reactor to vary with time, both total and component continuity equations are required for each reactor. To show the effects of higher-order kinetics, assume the reaction is now nth-order in reactant A



Series of CSTRs.

$$F_1 = f_{(V_1)} \qquad F_2 = f_{(V_2)} \qquad F_3 = f_{(V_3)}$$

Reactor 1:

$$\frac{dV_1}{dt} = F_0 - F_1$$

$$\frac{d}{dt}(V_1 C_{A1}) = F_0\, C_{A0} - F_1 C_{A1} - V_1 k_1 (C_{A1})$$

Reactor 2:

$$\frac{dV_2}{dt} = F_1 - F_2$$

$$\frac{d}{dt}(V_2\, C_{A2}) = F_1 C_{A1} - F_2\, C_{A2} - V_2\, k_2 (C_{A2})$$

Reactor 3 :

$$\frac{dV_3}{dt} = F_2 - F_3$$

$$\frac{d}{dt}(V_3\, C_{A3}) = F_2\, C_{A2} - F_3\, C_{A3} - V_3\, k_3 (C_{A3})$$

Our mathematical model now contains six first-order nonlinear ordinary differential equations. Parameters that must be known are k_1, k_2, k_3, and n. Initial conditions for all the dependent variables that are to be integrated must be given: CA1, cA2, CA3, VI, V2, and V, . The forcing functions $C_{Ao(t)}$ and $F_{o(t)}$, must also be given.

Let us now check the degrees of freedom of this system. There are six equations. But there are nine unknowns: C_{A1}, C_{A2}, C_{A3}, V_I, V_2, V_3, F_1, F_2, and F_3. Clearly this system is not sufficiently specified and a solution could not be obtained. What have we missed in our modeling? A good plant operator could take one look at the system and see what the problem is. We have not specified how the flows out of the tanks are to be set. Physically there would probably be control valves in the outlet lines to regulate the flows. How are these control valves to be set? A common configuration is to have the level in the tank controlled by the outflow, i.e., a level controller opens the control valve on the exit

How are these control valves to be set? A common configuration is to have the level in the tank controlled by the outflow, i.e., a level controller opens the control valve on the exit line to increase the outflow if the level in the tank increases. Thus there must be a relationship between tank holdup and flow.

3.11 SEMI BATCH REACTOR

we focus attention primarily on the one with constant molar feed. A schematic diagram of this semi batch reactor is shown in Figure below. We shall consider the elementary liquid-phase reaction

$$A + B \rightarrow C$$

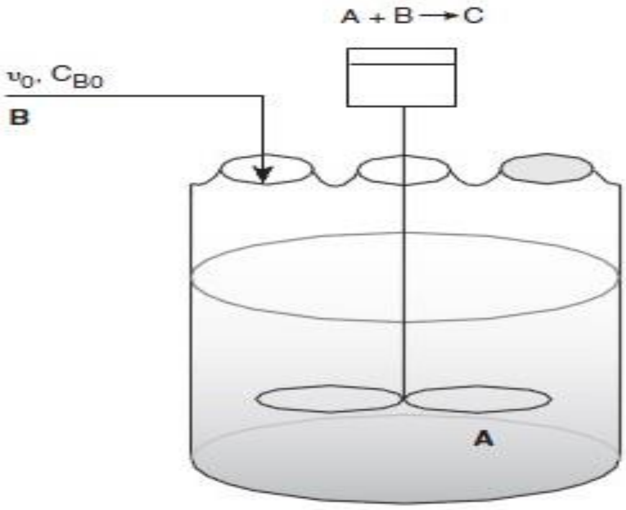


Figure Semibatch reactor.

in which reactant B is slowly added to a well-mixed vat containing reactant A.

A **mole balance on species A yields**

$$\begin{bmatrix}\text{Rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$\overbrace{0} - \overbrace{0} + \overbrace{r_A V(t)} = \overbrace{\frac{dN_A}{dt}}$$

Three variables can be used to formulate and solve semibatch reactor problems: the concentrations, C_j, the number of moles, N_j, and the conversion, X.

Writing the Semibatch Reactor Equations in Terms of Number of Moles

Recalling that the number of moles of A, N_A, is just the product of concentration of A, C_A, and the volume, V, we can rewrite above Equation as

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt}$$

We note that since the reactor is being filled, the volume, V, varies with time. The reactor volume at any time t can be found from an **overall mass balance** of all species:

$$\begin{bmatrix}\text{Rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$\overbrace{\rho_0 v_0} - \overbrace{0} + \overbrace{0} = \overbrace{\frac{d(\rho V)}{dt}}$$

For a constant-density system, $\rho=\rho_0$, and

$$\frac{dV}{dt} = v_0$$

with the initial condition V= V_0 at t=0, integrating for the case of constant volumetric flow rate v_0 yields

$$\boxed{V = V_0 + v_0 t}$$

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt}$$

$$-v_0 C_A + V r_A = \frac{V dC_A}{dt}$$

The balance on A can be rewritten as

$$\boxed{\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A}$$

A mole balance on B that is fed to the reactor at a rate F_{B0} is

$$\begin{array}{ccccccc} \text{In} & + & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\ \overbrace{F_{B0}} & - & \overbrace{0} & + & \overbrace{r_B V} & = & \overbrace{\frac{dN_B}{dt}} \end{array}$$

Rearranging

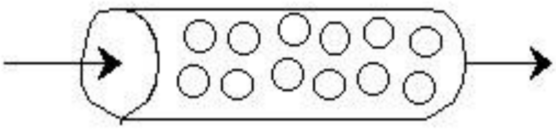
$$\frac{dN_B}{dt} = r_B V + F_{B0}$$

$$\frac{d(VC_B)}{dt} = \frac{dV}{dt} C_B + \frac{VdC_B}{dt} = r_B V + F_{B0} = r_B V + \nu_0 C_{B0}$$

$$\boxed{\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V}}$$

At time t = 0, the initial concentration of B in the vat is zero, $C_{Bi} = 0$. The concentration of B in the feed is C_{B0}. If the reaction order is other than zero- or first-order, or if the reaction is nonisothermal, we must use numerical techniques to determine the conversion as a function of time.

3.12 PACKED BED REACTORS (PBRS)



From the PFR module we have

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

The catalyst weight and rector volume are related by the catalyst bulk density (g/dm^3)

$$\underset{(\mathrm{gm})}{W} = \underset{\left(\frac{\mathrm{gm}}{\mathrm{dm}^3}\right)}{\rho_b} \; \underset{(\mathrm{dm}^3)}{V}$$

The reaction rate per unit volume and the reaction rate per unit catalyst weight are also related by the bulk density, r_b

$$-r_A = \rho_b(-r'_A)$$

$$\left(\frac{\mathrm{mol}}{\mathrm{dm}^3 \cdot \mathrm{s}}\right) = \left(\frac{\mathrm{gcat}}{\mathrm{dm}^3}\right) \frac{\mathrm{mol}}{(\mathrm{g})\mathrm{cat} \cdot \mathrm{s}}$$

$$-r'_A = \frac{-r_A}{\rho_b}$$

The differential form of the PBR mole balance is

$$\boxed{\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}}$$

Use the ABOVE differential form of the mole balance on PBRs when there is pressure drop or catalyst decay.

In the absence of pressure drop (i.e. $\Delta P = 0$) and catalyst decay ($a = 1$) we can integrate the differential form.

$$\boxed{W = F_{A0}\int_0^X \frac{dX}{-r'_A}}$$

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT–IV -Modeling of Heat and Mass Transfer Operations –SCH1401

4.1 MULTI-COMPONENT FLASH DRUM

The previous treated examples have discussed processes that occur in one single phase. There are several chemical unit operations that are characterized with more than one phase. These processes are known as heterogeneous systems. In the following we cover some examples of these processes. Under suitable simplifying assumptions, each phase can be modeled individually by a macroscopic balance.

A multi-component liquid-vapor separator is shown in figure 4.3. The feed consists of N_c components with the molar fraction z_i (i=1,2… N_c). The feed at high temperature and pressure passes through a throttling valve where its pressure is reduced substantially. As a result, part of the liquid feed vaporizes. The two phases are assumed to be in phase equilibrium. x_i and y_i represent the mole fraction of component i in the liquid and vapor phase respectively. The formed vapor is drawn off the top of the vessel while the liquid comes off the bottom of the tank. Taking the whole tank as our system of interest, a model of the system would consist in writing separate balances for vapor and liquid phase. However since the vapor volume is generally small we could neglect the dynamics of the vapor phase and concentrate only on the liquid phase.

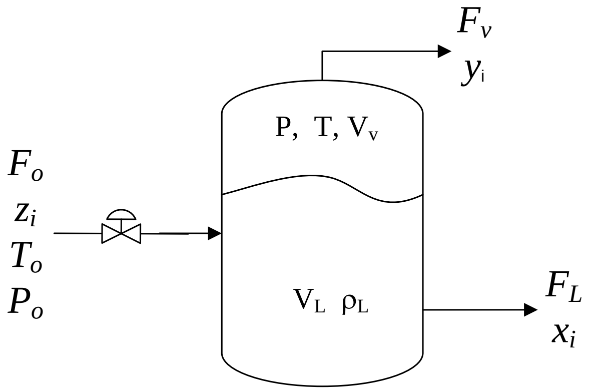


Figure 4.1 Multicomponent Flash Drum

For liquid phase:

Total mass balance:

$$\frac{d(\rho_L V_L)}{dt} = \rho_f F_f - \rho_L F_L - \rho_v F_v$$

Component balance:

$$\frac{d(\rho_L V_L x_i)}{dt} = \rho_f F_f z_i - \rho_L F_L x_i - \rho_v F_v y_i \quad (i=1,2,\ldots,N_c\text{-}1)$$

Energy balance:

$$\frac{d(\rho_L V_L \tilde{h})}{dt} = \rho_f F_f \tilde{h}_f - \rho_L F_L \tilde{h} - \rho_v F_v \tilde{H}$$

where $\tilde{h}$ and $\tilde{H}$ are the specific enthalpies of liquid and vapor phase respectively.

In addition to the balance equations, the following supporting thermodynamic relations can be written:

- Liquid-vapor Equilibrium:

Raoult's law can be assumed for the phase equilibrium

$$y_i = \frac{x_i P_i^s}{P} \quad (i=1,2,\ldots,N_c)$$

Together with the consistency relationships:

$$\sum_{i=1}^{Nc} y_i = 1$$

$$\sum_{i=1}^{Nc} x_i = 1$$

- Physical Properties:

The densities and enthalpies are related to the mole fractions, temperature and pressure through the following relations:

$\rho_L = f(x_i,T,P)$

$\rho_V = f(y_i,T,P) \approx M_V^{ave} P/R\,T$

$$M_V^{ave} = \sum_{i=1}^{Nc} y_i M_i$$

$$h = f(x_i,T) \approx \sum_{i=1}^{Nc} x_i Cp_i (T - T_{ref})$$

$$H = f(y_i,T) \approx \sum_{i=1}^{Nc} y_i Cp_i (T - T_{ref}) + \lambda_m$$

$$\lambda_m = \sum_{i=1}^{Nc} y_i \lambda_i$$

Degrees of freedom analysis:

- Forcing variables: F_f, T_f, P_f, z_i $(i=1,2..N_c)$,
- Remaining variables: $2N_c+5$: V_L, F_L, F_V, P, T, x_i $(i=1,2..N_c)$, $y_i(i=1,2,\ldots N_c)$
- Number of equations: $2N_c+3$:

Note that physical properties are not included in the degrees of freedom since they are specified through given relations. The degrees of freedom is therefore $(2N_c+5)-(2N_c+3)=2$. Generally the liquid holdup (V_L) is controlled by the liquid outlet flow rate (F_L) while the pressure is controlled by F_V. In this case, the problem becomes well defined for a solution.

4.2 BINARY ABSORPTION COLUMN

Consider a N stages binary absorption tower as shown in figure 4.5. A Liquid stream flows downward with molar flow rate (L) and feed composition (x_f). A Vapor stream flows upward with molar flow rate (G) and feed composition (y_f). We are interested in deriving an unsteady state model for the absorber. A simple vapor-liquid equilibrium relation of the form of:

$$y_i = a\,x_i + b$$

can be used for each stage i (i=1,2,…,N).

Assumptions:

- Isothermal Operation
- Negligible vapor holdup
- Constant liquid holdup in each stage
- Perfect mixing in each stage

According to the second and third assumptions, the molar rates can be considered constants, i.e. not changing from one stage to another, thus, total mass balance need not be written. The last assumption allows us writing a macroscopic balance on each stage as follows:

Component balance on stage *i*:

$$H\frac{dx_i}{dt} = G(y_{i-1} - y_i) + L(x_{i+1} - x_i) \text{ (i=2…,N-1)}$$

where H is the liquid holdup, i.e., the mass of liquid in each stage. The last equation is repeated for each stage with the following exceptions for the last and the first stages:

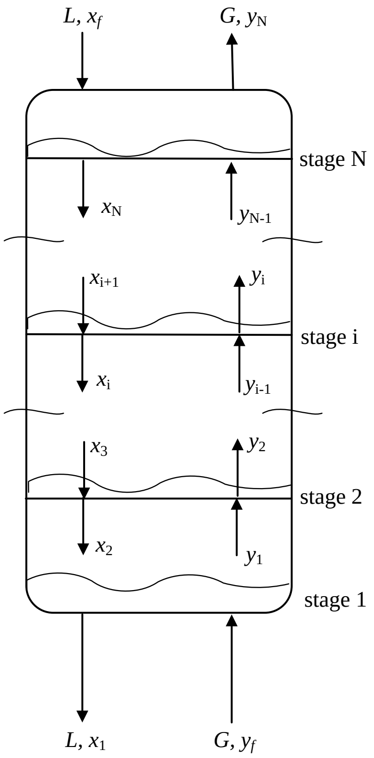


Figure 4.5 N-stages Absorbtion Tower

In the last stage, x_{i+1} is replaced by x_f

In the first stage, y_{i-1} is replaced by y_f

Degrees of freedom analysis

- Parameter of constant values: H, a, b
- (Forced variable): G, L, x_f, y_f
- Remaining variables: x_i (i=1,2…,N), y_i (i=1,2…,N)
- Number of equations:2N (Eqs4.37,4.38)

The problem is therefore is exactly specified.

4.3 MULTI-COMPONENT DISTILLATION COLUMN

Distillation columns are important units in petrochemical industries. These units process their feed, which is a mixture of many components, into two valuable fractions namely the top product which rich in the light components and bottom product which is rich in the heavier components. A typical distillation column is shown in Figure 4.6. The column consists of n trays excluding the re-boiler and the total condenser. The convention is to number the stages from the bottom upward starting with the re-boiler as the 0 stage and the condenser as the n+1 stage.

Description of the process:

The feed containing *nc* components is fed at specific location known as the feed tray (labeled *f*) where it mixes with the vapor and liquid in that tray. The vapor produced from the re-boiler flows upward. While flowing up, the vapor gains more fraction of the light component and loses fraction of the heavy components. The vapor leaves the column at the top where it condenses and is split into the product (distillate) and reflux which returned into the column as liquid. The liquid flows down gaining more fraction of the heavy component and loses fraction of the light components. The liquid leaves the column at the bottom where it is evaporated in the re-boiler. Part of the liquid is drawn as bottom product and the rest is recycled to the column. The loss and gain of materials occur at each stage where the two phases are brought into intimate phase equilibrium.

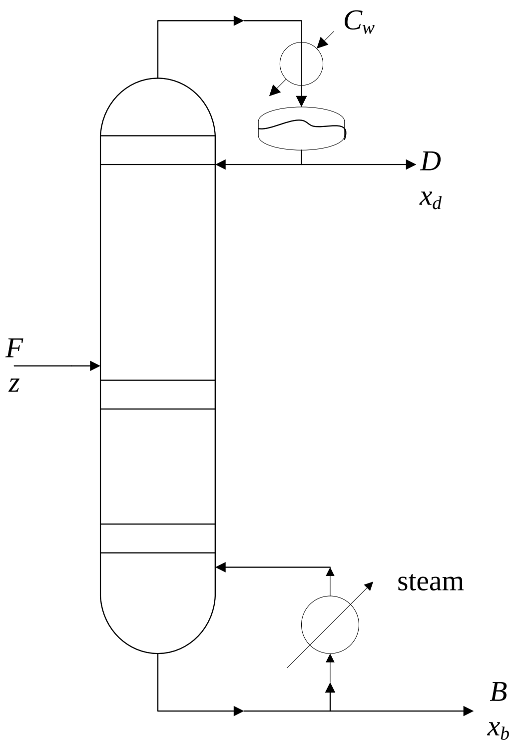


Figure 4.3 Distillation Column

Modeling the unit:

We are interested in developing the unsteady state model for the unit using the flowing assumptions:

- 100% tray efficiency
- Well mixed condenser drum and re-boiler.
- Liquids are well mixed in each tray.
- Negligible vapor holdups.
- liquid-vapor thermal equilibrium

Since the vapor-phase has negligible holdups, then conservation laws will only be written for the liquid phase as follows:

Stage *n*+1 (Condenser),

Total mass balance:

$$\frac{dM_D}{dt} = V_n - (R + D)$$

Component balance:

$$\frac{d(M_D x_{D,j})}{dt} = V_n y_{n,j} - (R + D) x_{D,j} \qquad j = 1, nc - 1$$

Energy balance:

$$\frac{d(M_D h_D)}{dt} = V_n h_n - (R + D) h_D - Q_c$$

Note that $R = L_{n+1}$ and the subscript D denotes $n+1$

Stage n,

Total Mass balance:

$$\frac{dM_n}{dt} = V_{n-1} - V_n + R - L_n$$

Component balance:

$$\frac{d(M_n x_{n,j})}{dt} = V_{n-1} y_{n-1,j} - V_n y_{n,j} + R x_{D,j} - L_n x_{n,j} \qquad j = 1, nc - 1$$

Energy balance:

$$\frac{d(M_n h_n)}{dt} = V_{n-1} H_{n-1} - V_n H_n + R h_D - L_n h_n$$

Stage i,

Total Mass balance:

$$\frac{dM_i}{dt} = V_{i-1} - V_i + L_{i+1} - L_i$$

Component balance:

$$\frac{d(M_i x_{i,j})}{dt} = V_{i-1} y_{i-1,j} - V_i y_{i,j} + L_{i+1} x_{i+1,j} - L_i x_{i,j} \qquad j = 1, nc-1$$

Energy balance:

$$\frac{d(M_i h_i)}{dt} = V_{i-1} H_{i-1} - V_i H_i + L_{i+1} h_{i+1} - L_i h_i$$

Stage f (Feed stage),

Total Mass balance:

$$\frac{dM_f}{dt} = V_{f-1} - (V_f + (1-q)F) + L_{f+1} - (L_f + qF)$$

Component balance:

$$\frac{d(M_f x_{f,j})}{dt} = V_{f-1} y_{f-1,j} - (V_f y_{f,j} + (1-q)Fz_j) + L_{f+1} x_{f+1,j} - (L_f x_{f,j} + qFz_j)$$
$$j = 1, nc-1$$

Energy balance:

$$\frac{d(M_f h_f)}{dt} = V_{f-1} H_{f-1} - (V_f H_f + (1-q)Fh_f) + L_{f+1} h_{f+1} - (L_f h_f + qFh_f)$$

Stage 1,

Total Mass balance:

$$\frac{dM_1}{dt} = V_B - V_1 + L_2 - L_1$$

Component balance:

$$\frac{d(M_1 x_{1,j})}{dt} = V_B y_{B,j} - V_1 y_{1,j} + L_2 x_{2,j} - L_1 x_{1,j} \qquad j = 1, nc-1$$

Energy balance:

$$\frac{d(M_1 h_1)}{dt} = V_B H_B - V_1 H_1 + L_2 h_2 - L_1 h_1$$

Stage 0 (Re-boiler),

Total Mass balance:

$$\frac{dM_B}{dt} = -V_B + L_1 - B$$

Component balance:

$$\frac{d(M_B x_{B,j})}{dt} = -V_B y_{B,j} + L_1 x_{1,j} - B x_{B,j} \qquad j = 1, nc-1$$

Energy balance:

$$\frac{d(M_B h_B)}{dt} = -V_B H_B + L_1 h_1 - B h_B + Q_r$$

Note that $L_0 = B$ and B denotes the subscript 0

Additional given relations:

Phase equilibrium: $y_j = f(x_j, T, P)$

Liquid holdup: $M_i = f(L_i)$

Enthalpies: $H_i = f\,(T_i, y_{i,j})$, $h_i = f\,(T_i, x_{i,j})$

Vapor rates: $V_i = f\,(P)$

Notation:

L_i, V_i	Liquid and vapor molar rates
H_i, h_i	Vapor and liquid specific enthalpies
x_i, y_i	Liquid and vapor molar fractions
M_i	Liquid holdup
Q	Liquid fraction of the feed
Z	Molar fractions of the feed
F	Feed molar rate

Degrees of freedom analysis

Variables

M_i	n
M_B, M_D	2
L_i	n
B,R,D	3
$x_{i,j}$	$n(nc-1)$
$x_{B,j}$,$x_{D,j}$	$2(nc-1)$
$y_{i,j}$	$n(nc-1)$
$y_{B,j}$	$nc-1$
h_i	n
h_B, h_D	2
H_i	n
H_B	1
V_i	n
V_B	1
T_i	n
T_D, T_B	2
Total	$11+6n+2n(nc-1)+3(nc-1)$

Equations:

Total Mass	$n + 2$
Energy	$n + 2$
Component	$(n + 2)(nc - 1)$
Equilibrium	$n(nc - 1)$
Liquid holdup	n
Enthalpies	$2n+2$
Vapor rate	n
$h_B = h_1$	1
$y_B = x_B$	$(nc - 1)$
Total	$7+6n+2n(nc-1)+3(nc-1)$

Constants: P, F, Z

Therefore; the degree of freedom is 4

To well define the model for solution we include four relations imported from inclusion of four feedback control loops as follows:

- Use B, and D to control the liquid level in the condenser drum and in the re-boiler.
- Use V_B and R to control the end compositions i.e., x_B, x_D

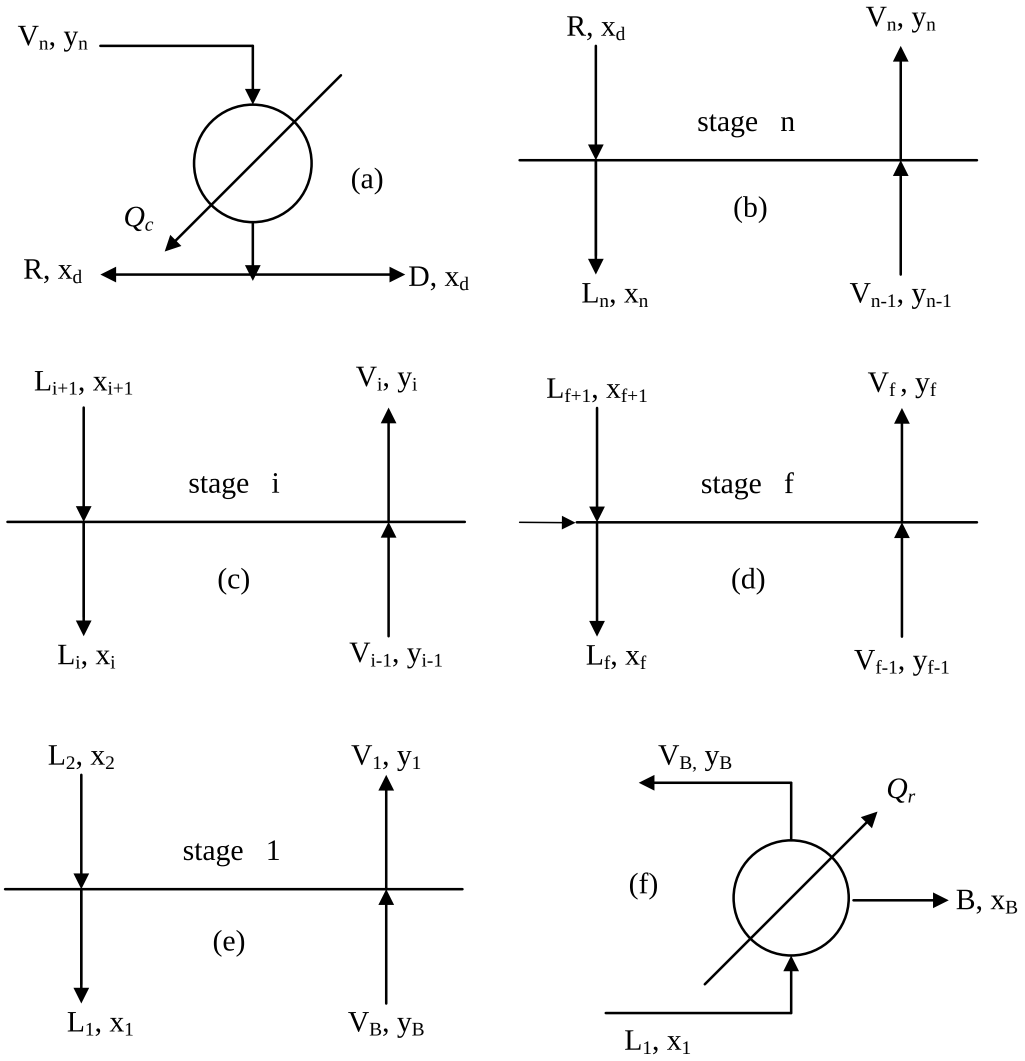


Figure Distillation Column Stages

Simplified Model

One can further simplify the foregoing model by the following assumptions:

(a) Equi-molar flow rates, i.e. whenever one mole of liquid vaporizes a tantamount of vapor condenses. This occur when the molar heat of vaporization of all components are about the same. This assumption leads to further idealization that implies constant temperature over the entire column, thus neglecting the energy balance. In addition, the vapor rate through the column is constant and equal to:

$$V_B = V_1 = V_2 = \ldots = V_n$$

(b) Constant relative volatility, thus a simpler formula for the phase equilibrium can be used:

$$y_j = \alpha_j\, x_j/(1+(\alpha_j - 1)\, x_j)$$

Degrees of Freedom:

Variables:

M_i, M_B, M_D	$n + 2$
L_i, B,R,D	$n + 3$
x_i,x_B,x_D	$(n + 2)(nc - 1)$
y_j, y_B	$(n + 1)(nc - 1)$
V	1
Total	$2 + 2n + (2n + 3)(nc - 1)$

Equations:

Total Mass	$n + 2$
Component	$(n + 2)(nc - 1)$
Equilibrium	$n(nc - 1)$
Liquid holdup	n
$y_B = x_B$	1
Total	$2+2n+(2n+3)(nc-1)$

It is obvious that the degrees of freedom is still 4.

4.4 MASS EXCHANGE IN PACKED COLUMN

In previous section we presented some examples of mass transfer units that can be described by simple ODE's. This includes all the operations that can occur in tray or spray-tray towers. In this section we present an example of modeling a mass transfer operation that occurs in packed tower. Absorption is a mass transfer process in which a vapor solute (A) in a gas mixture is absorbed by contact with a liquid phase in which the solute is more or less soluble. The gas phase consists usually of an inert gas and the solute. This process involves flow transfer of the solute A through a stagnant non diffusive gas B into a stagnant liquid C. The liquid is mainly immiscible in the gas phase. An example is the absorption of ammonia (A) from air (B) by liquid water (C). The operation can be carried out either in tray (plate) towers or in packed towers. The operation in tray towers can be modeled similarly to the liquid-liquid extraction process. We consider here the absorption taking place in a packed tower.

Consider the binary absorption tower shown in Figure 4.10. A liquid stream flow downward with molar flow rate L and feed composition (X_{Af}). Vapor stream flows upward with molar flow rate (G) and feed composition (Y_{Af}). A simple vapor-liquid equilibrium relation of the form of:

$$Y_A = HX_A$$

is used, where H (mole fraction gas/mole fraction liquid) is the Henry's law constant. This assumption is valid for dilute streams. The molar rates can be considered constants, i.e. not changing from one stage to another, thus the total mass balance need not be written. To establish the model equations we need to write equations for liquid and vapor phase. To simplify the problem we assume constant liquid and vapor holdup in each stage. We also assume isothermal conditions. An energy balance therefore is not needed.

The flux N_A transferred from bulk liquid to bulk gas is given by:

$$N_A = K_Y\,(Y_A - Y_A^*)$$

Where K_Y is the overall mass transfer in the gas-phase (*kgmole*/*m*^{2}*s mole fraction*) and Y_A^* is the value that would be in equilibrium with X_A. The flux can also be expressed as:

$$N_A = K_X\,(X_A - X_A^*)$$

Where K_X is the overall mass transfer coefficient in the liquid-phase and X_A^* is the value that would be in equilibrium with Y_A.

A mass balance on the liquid phase for a differential volume (Fig. 4.10) of the column length z and cross sectional area S yields:

Flow of mole in:

$$[(SLX_A)\Delta t|_z + (N_A S\Delta t)\,|_z]\Delta z$$

Flow of moles out:

$$(SLX_A)\Delta t|_{z+\Delta z}$$

Rate of accumulation:

$$(SH_L X_A \Delta z)|_{t+\Delta t} - (SH_L X_A \Delta z)|_t$$

where X_A is the liquid fraction of A and H_L the liquid holdup (*mole/m*^{3}).

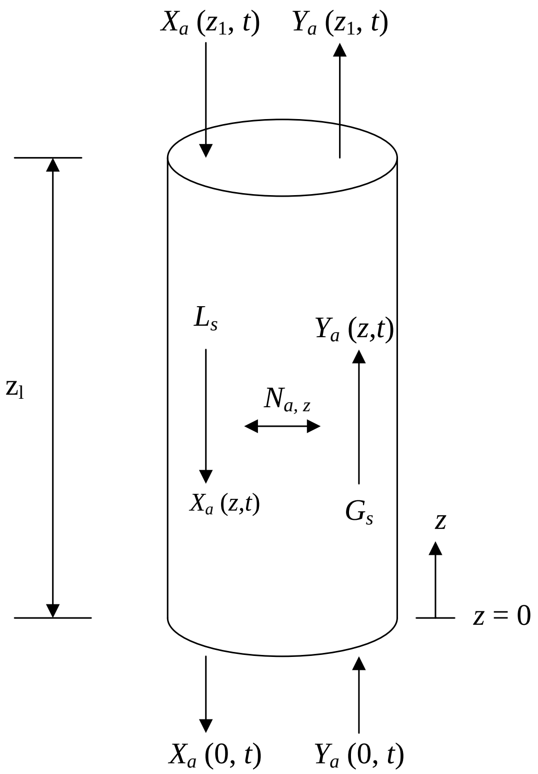


Figure 4.4 Packed column

The balance equation yields:

$$(SH_L X_A \Delta z)|_{t+\Delta t} - (SH_L X_A \Delta z)|_t = (SLX_A)\Delta t|_{z+\Delta z} - [(SLX_A)\Delta t|_z + (N_A S\Delta t)\Delta t|_z]\Delta z$$

Dividing by $S\Delta t\Delta z$ and taking the limits as Δz and Δt goes to zero yield:

$$H_L \frac{\partial X_A}{\partial t} = L\frac{\partial X_A}{\partial z} + N_A$$

which is equivalent to

$$H_L \frac{\partial X_A}{\partial t} = L\frac{\partial X_A}{\partial z} + K_Y(Y_A - Y_A^*)$$

We could also use the expression of flux (Eq. 4.92):

$$H_L \frac{\partial X_A}{\partial t} = L\frac{\partial X_A}{\partial z} + K_X(X_a^* - X_A)$$

We can develop material balances for the gas phase that are similar . This gives:

$$H_G \frac{\partial X_A}{\partial t} = -G\frac{\partial Y_A}{\partial z} + K_Y(Y_A - Y_A^*)$$

or alternatively:

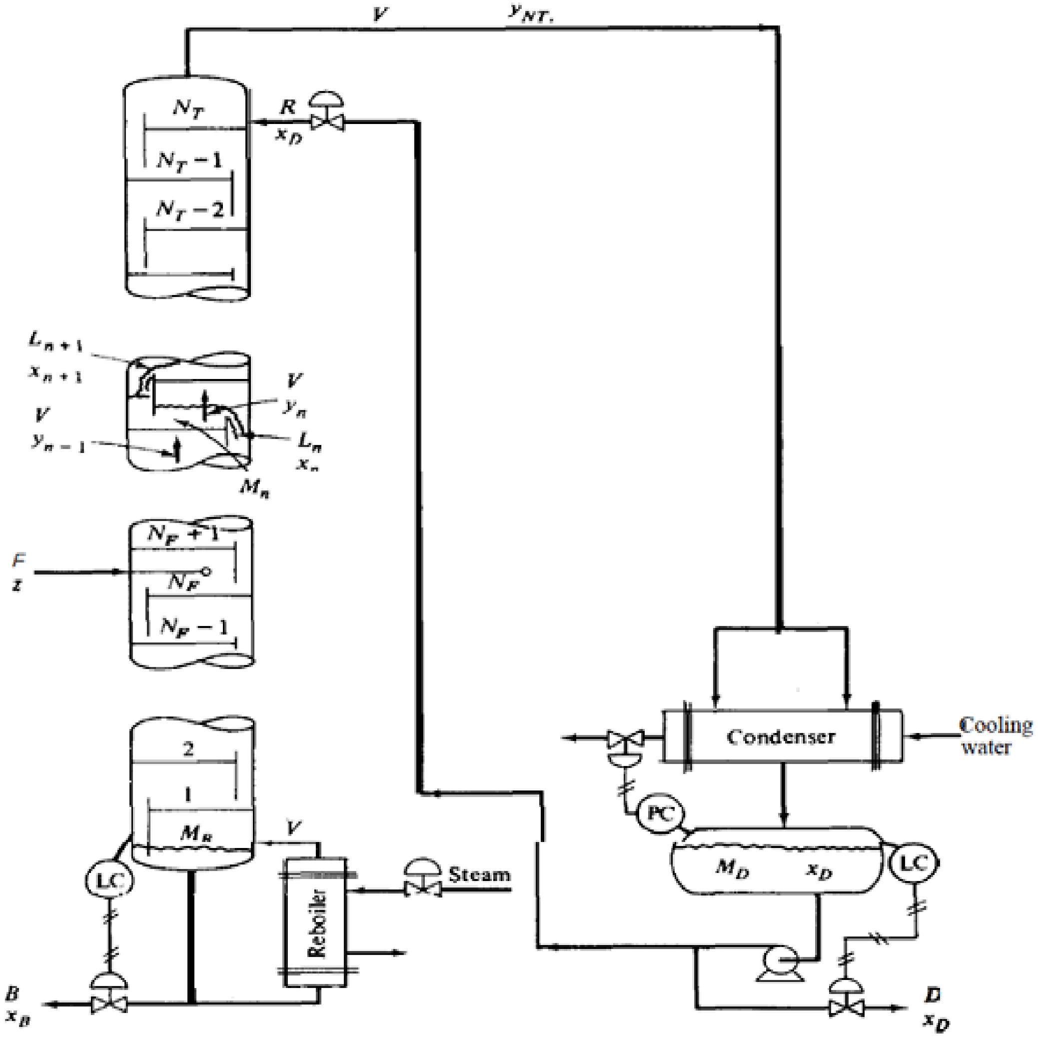
$$H_G \frac{\partial Y_A}{\partial t} = -G\frac{\partial Y_A}{\partial z} + K_X(X_a^* - X_A)$$

It should be noted that the analysis carried here can be used for a number of operations where packed columns are used. This includes liquid-liquid extraction, gas-liquid absorption and gas-solid drying. In each of these operations an equilibrium relation of the type:

$$Y_A = f(X_A)$$

is generally available

4.5 IDEAL BINARY DISTILLATION COLUMN



Binary distillation column.

The liquid rates throughout the' column will not be the same dynamically. They will depend on the fluid mechanics of the tray. Often a simple Francis weir formula relationship is used to relate the liquid holdup on the tray (M,) to the liquid flow rate leaving the tray (L_n).

$$F_L = 3.33 L_w (h_{ow})^{1.5}$$

where F_L = liquid flow rate over weir (ft^3/s)
L_w = length of weir (ft)
h_{ow} = height of liquid over weir (ft)

Condenser and Reflux Drum

Total continuity:

$$\frac{dM_D}{dt} = V - R - D$$

Component continuity (more volatile component):

$$\frac{d(M_D x_D)}{dt} = V y_{NT} - (R + D) x_D$$

Top Tray (n = N_T)

Total continuity:

$$\frac{dM_{NT}}{dt} = R - L_{NT}$$

Feed Tray (n = N_F)

Total continuity:

$$\frac{dM_{NF}}{dt} = L_{NF+1} - L_{NF} + F$$

Component continuity :

$$\frac{d(M_{NF} x_{NF})}{dt} = L_{NF+1} x_{NF+1} - L_{NF} x_{NF} + V y_{NF-1} - V y_{NF} + Fz$$

First Tray (n = 1)

Total continuity :

$$\frac{dM_1}{dt} = L_2 - L_1$$

Component continuity :

$$\frac{d(M_1 x_1)}{dt} = L_2 x_2 - L_1 x_1 + V y_B - V y_1$$

Reboiler and Column Base

Total continuity:

$$\frac{dM_B}{dt} = L_1 - V - B$$

Component continuity :

$$\frac{d(M_B x_B)}{dt} = L_1 x_1 - V y_B - Bx,$$

vapor-liquid equilibrium relationship

$$y_n = \frac{\alpha x_n}{1 + (a - 1)x_n}$$

where x_n = liquid composition on the nth tray (mole fraction more volatile component)
y_n = vapor composition on the nth tray (mole fraction more volatile component)
α = relative volatility

4.6 BATCH DISTILLATION WITH HOLDUP

Batch distillation is frequently used for small-volume products. One column can be used to separate a multicomponent mixture instead of requiring NC - 1 continuous columns. The energy consumption in batch distillation is usually higher than in continuous, but with small-volume, high-value products energy costs seldom dominate the economics

Fresh feed is charged into the still pot and heated until it begins to boil. The vapor works its way up the column and is condensed in the condenser. The condensate liquid runs into The column is run on total reflux until the overhead distillate composition of the lightest component (component 1) reaches its specification purity. Then a distillate product, which is the lightest component, is withdrawn at some rate.

Eventually the amount of component 1 in the still pot gets very low and the purity of the distillate drops. There is a period of time when the distillate contains too little of component 1 to be used for that product and also too little of component 2 to be used for the next heavier product. Therefore a “slop” cut must be withdrawn until xD2 builds up to its specification. Then a second product is withdrawn. Thus multiple products can be made from a single column. The total amount of material charged to the column is MB0 (moles). This material can be fresh feed with composition zj or a mixture of fresh feed and the slop cuts. The composition in the still pot at the beginning of the batch is XBoj. The composition in the still pot at any point in time is xBj. The instantaneous holdup in the still pot is MB. Tray liquid holdup and reflux drum holdup are assumed constant. The vapor boilup rate is constant at V (moles per hour). The reflux drum, column trays, and still pot are all initially filled with material of composition xBj.

The equations describing the batch distillation of a multicomponent mixture are given below.

Still pot:

$$\frac{dM_B}{dt} = -D$$

$$\frac{d[M_B x_{Bj}]}{dt} = Rx_{1j} - Vy_{Bj}$$

$$y_{Bj} = \frac{\alpha_j x_{Bj}}{\sum_{k=1}^{NC} \alpha_k x_{Bk}}$$

Tray n:

$$M_n \frac{dx_{nj}}{dt} = R[x_{n+1,j} - x_{nj}] + V[y_{n-1,j} - y_{nj}]$$

$$y_{nj} = \frac{\alpha_j x_{nj}}{\sum_{k=1}^{NC} \alpha_k x_{nk}}$$

Tray N_T (top tray):

$$M_{NT} \frac{dx_{NT,j}}{at} = R[x_{Dj} - x_{NT,j}] + V[y_{NT-1,j} - y_{NT,j}]$$

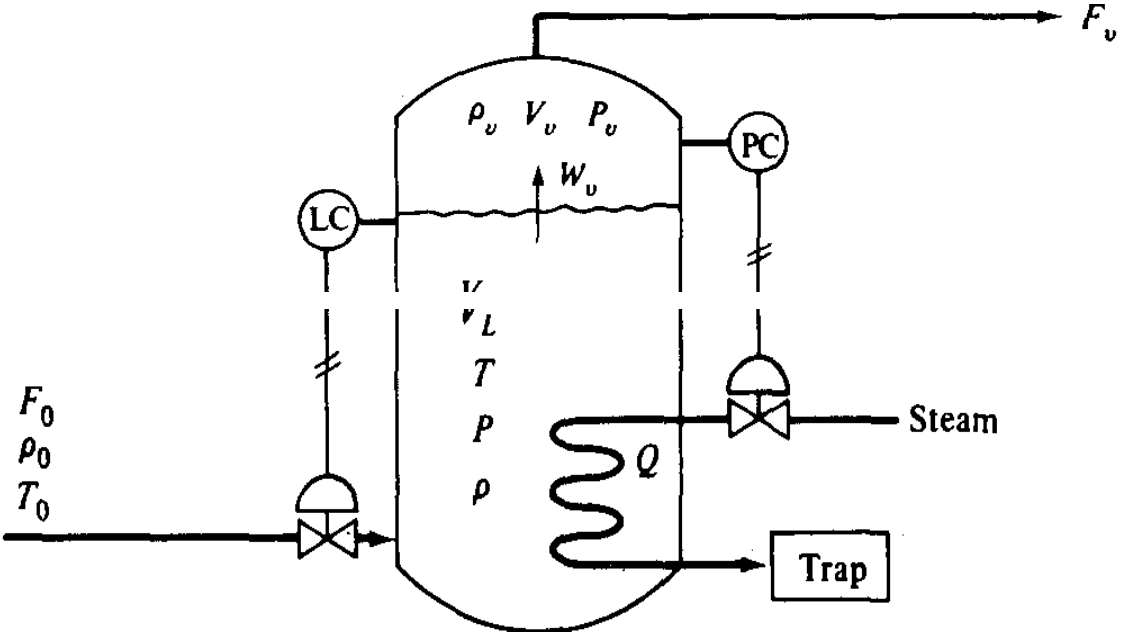
$$y_{NT,j} = \frac{\alpha_j x_{NT,j}}{\sum_{k=1}^{NC} \alpha_k x_{NT,k}}$$

4.7 SINGLE-COMPONENT VAPORIZER

Boiling systems represent some of the most interesting and important operations in chemical engineering processing and are among the most difficult to model.

The basic problem is finding the rate of vaporization of material from the liquid phase into the vapor phase. The equations used to describe the boiling rate should be physically reasonable and mathematically convenient for solution.

Consider the vaporizer as shown in Fig. below. Liquefied petroleum gas (LPG) is fed into a pressurized tank to hold the liquid level in the tank. We will assume that LPG is a pure component: propane.



LPG vaporizer.

LIQUID-PHASE DYNAMICS MODEL.

A somewhat more realistic model is obtained if we assume that the volume of the vapor phase is small enough to make its dynamics negligible. If only a few moles of liquid have to be vaporized to change the pressure in the vapor phase, we can assume that this pressure is always equal to the vapor pressure of the liquid at any temperature

Total continuity Equation:

$$\rho \frac{dV_L}{dt} = \rho_0 F_0 - \rho_v F_v$$

Energy Equation:

$$C_p\rho\frac{d(V_L T)}{dt} = \rho_0 C_p F_0 T_0 - \rho_v F_v(C_p T + \lambda_v) + Q$$

LIQUID AND VAPOR DYNAMICS MODEL.

If the dynamics of the vapor phase cannot be neglected (if we have a large volume of vapor), total continuity and energy equations must be written for the gas in the tank. The vapor leaving the tank, ρv Fv, is no longer equal, dynamically, to the rate of vaporization Wv, .The key problem now is to find a simple and reasonable expression for the boiling rate Wv, The equations describing the system are:

Total continuity Equation:

$$\rho\frac{dV_L}{dt} = \rho_0 F_0 - W_v$$

Energy Equation:

$$\rho\frac{d(V_L U_L)}{dt} = \rho_0 F_0 h_0 - W_v H_L + Q$$

Vapor phase

Total continuity Equation:

$$\frac{d(V_v \rho_v)}{dt} = W_v - \rho_v F_v$$

Energy Equation:

$$\frac{d(V_v \rho_v U_v)}{dt} = W_v H_L - \rho_v F_v H_v$$

where UL = Internal energy of liquid at temperature T

HL = Enthalpy of vapor boiling off liquid

Uv, = Internal energy of vapor at temperature Tv,

Hv = Enthalpy of vapor phase

REFERENCES

1. William L.Luyben, Process Modelling, Simulation and Control For Chemical Engineers, 2nd Edition, McGraw Hill International Editions,New York ,1980.

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3. Denn M.M., Process Modelling, 2nd Edition, Wiley, New York, 1986.

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5. Mickley. H.S.Sherwood.T.S. and Reed C.E., Applied Mathematics for Chemical Engineers, 1st Edition, Tata McGraw Hill Publishing Co. Ltd, New Delhi, 1989

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V- Dynamic Simulation – SCH1401

5. INTRODUCTION

Process simulation is the representation of industrial processes by means of the application of mathematics and first principles (i.e. conservation laws, thermodynamics, transport phenomena and reaction kinetics). Steady State models have been widely used in the industry, becoming a common or even more, a required practice. Steady state modeling is key for process conceptualization, design and evaluation and it is indeed a mature technology tool. However, the steady state is an idealistic definition used by engineers as a representation of "design" conditions which are not always accomplished due to change in raw materials, product specification, change in capacity due to marketing requirements, and the inherent dynamic behavior of processes. This article will help the reader to easily identify typical engineering problems where dynamic modeling would be an ideal tool to answer their questions.

What is a Dynamic Model?

Similar to a steady state model, dynamic models are based on first principles that cannot be violated. Conservation laws, phase equilibria, heat and mass transfer, and kinetics are also applied in dynamic models. The most significant difference between steady state and dynamic simulation is that steady state assumes that variables are constant with respect to the time. This means that in steady state there is no accumulation in the system so the overall mass and energy input matches its output. Conversely, dynamic models take into account the mass and energy rate of accumulation within the system, which allows one to determine the how long it would take to reach a stable condition starting from a specified initial state. Figure 1, below, represents the simulation scope for steady state and dynamic simulation models.

Why use dynamic simulation?

The industrial application of dynamic simulation was limited decades ago, however, with the development in the computing sciences and the improvement of computer processor speeds those limitations have been overcome. Now, we can incorporate a high level of detail in modelling and we can also develop fairly large models. Some application areas of this technology are:

Process design is a task that can be performed by using dynamic simulator. Since dynamic models consider equipment holdup, equipment size is required for running simulations. In the case of a new design, an initial sizing can be obtained by means of a steady state simulation and then it can be optimized based on its dynamic behaviour. Significant reduction in CAPEX is possible using dynamic simulation in different types of equipment, such as pressure vessels, tanks, control valves, etc.

Process evaluation and de-bottlenecking involves performance evaluation of an existing piece of equipment or facility running under process conditions different from the design case(s). If the analysis shows that its capacity is limiting the process then the "bottleneck" has been identified. The use of a dynamic model will quickly allow the engineer to determine the optimum design, if equipment resizing is an option, stream rerouting options (change in topology), and storage capacities among other options.

Safety analyses (what-if) can be easily run with dynamic models which allow the determination of unsafe and hazardous conditions during operation. The impact of equipment malfunction scenarios, such as distillation column overpressure, heat exchanger pipe ruptures, valve leakage, pump failure, indicator drift, and many others can also be studied.

Distribution and gathering system piping network studies can be also carried out due to the nature of the "pressure-driven" solver typically implemented in dynamics simulators, which allows a more accurate representation of real processes in which hydraulics and fluid mechanics are of vital importance (Luyben, 2002). Flow and fluid velocity estimation, change in production rates, pressure specifications and evaluation of pigging scenarios are some of the features available in this sort of model.

Relief and blowdown systems is a specific application where dynamic simulation can improve design. Blowdown valves and pressure safety valves may be oversized if API 521 is applied. The application of dynamic simulation leads to more precise calculations of relief loads. Consequently there would be decreased flare loads, with reduced CAPEX. Dynamic simulation also allows the study of controlled blowdown procedures to avoid unnecessary flowrate peaks especially in the initial stages.

Batch and semi-batch processes can only be successfully modelled in dynamic simulators. Examples of these processes are: batch distillation, batch reactors, catalyst regeneration processes, delayed coking process, etc.

Process control strategies can be evaluated and compared in order to determine the best, most cost-effective solution. Traditional and advanced process controllers can be easily “pre-tuned” using dynamic simulation models saving hours of expensive steps tests performed in plants. A current trend is to test Distributed Control Systems (DCS) using these models. Anti-surge controller evaluation on centrifugal compressors is a major area of this application.

Start-up and shutdown procedures can developed, tested and optimized with dynamic models. Tens or hundreds of hours of stabilization time and tons of out-of-spec products can be saved by the determination of optimum start-up/shutdown sequences, in addition to the identification of potential hazardous conditions during these activities.

Operator training is an area that has been gaining an important place in engineering practice. Complete replication of the control room is commonly installed on site to help train operators before plant experience. Operator Training Simulators (OTS), for which a dynamic simulation is essential, include grading methodologies which allow for certifying operators before they face routine (normal operation, start-up and shutdown) and non-routine (equipment malfunction) scenarios in real plants.

Dynamic simulation (or dynamic system simulation) is the use of a computer program to model the time-varying behavior of a dynamical system. The systems are typically described by ordinary differential equations or partial differential equations. A simulation run solves the state-equation system to find the behavior of the state variables over a specified period of time.

Process simulation is used to determine the size of equipment in a chemical plant, the amount of energy needed, the overall yield, and the magnitude of the waste streams. Because the results of process simulation depend upon thermodynamics and transport processes, the mathematical models are complicated and would be time-consuming to solve without a computer. In this chapter some of the problems are solved by using **chemcad**

Examples

5.4.1 A gas mixture of air (4 kmol/hr) and hydrogen sulfide (2 kmol/hr) is to be absorbed by water so that 99% of hydrogen sulfide is recovered from the bottom stream. The absorber has 10 trays. Water enters the absorber from 1st tray at 298 K and 1 atm and gas feed enters from 10th tray at the same temperature and pressure as those of water. Simulate this absorber in CHEMCAD to determine the mole rate of water needed to recover 99% of hydrogen sulfide in the bottom stream.

Procedure:

Step 1: Creating the flow sheet

Step 2: Entering the components and formatting engineering units

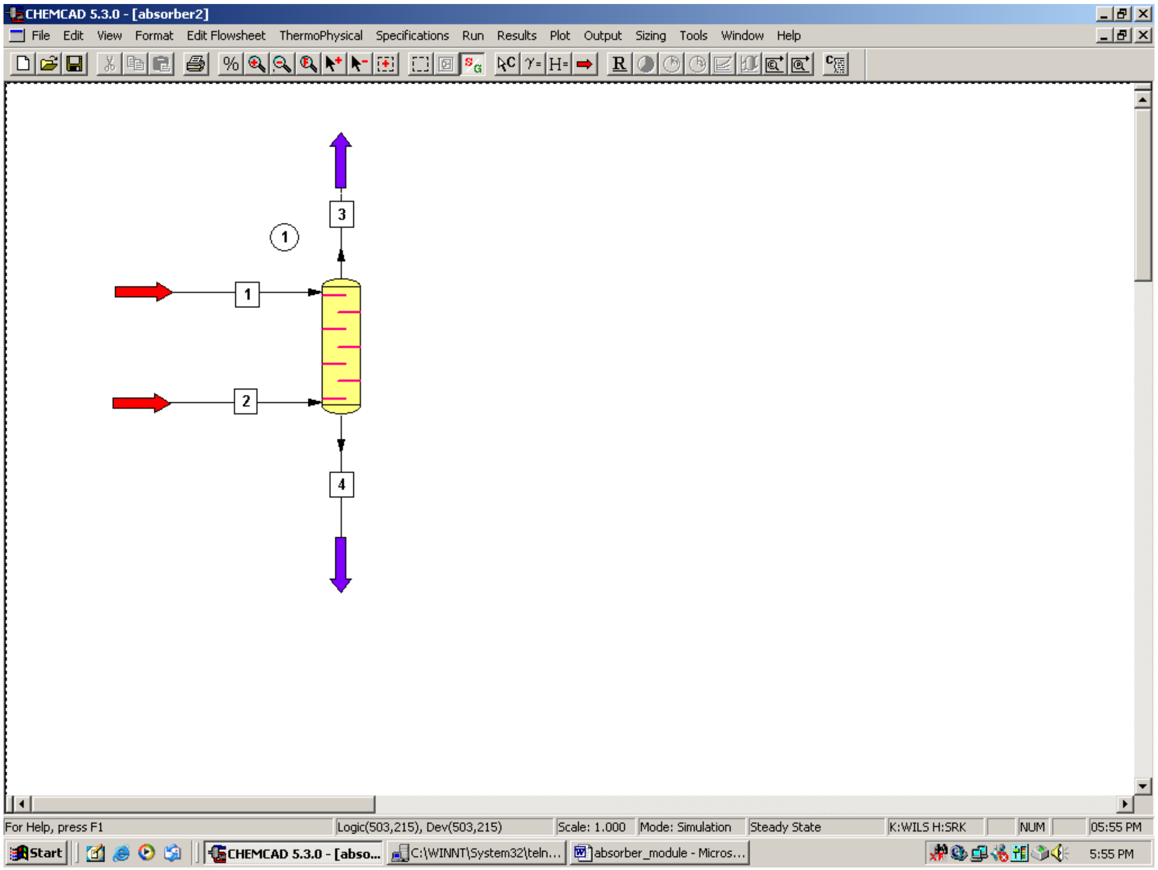
Step 3: Entering the feed stream composition

Step 4: Entering the absorber specs

Step 5: Running the simulation and retrieving the results

Step 1: Creating the flow sheet

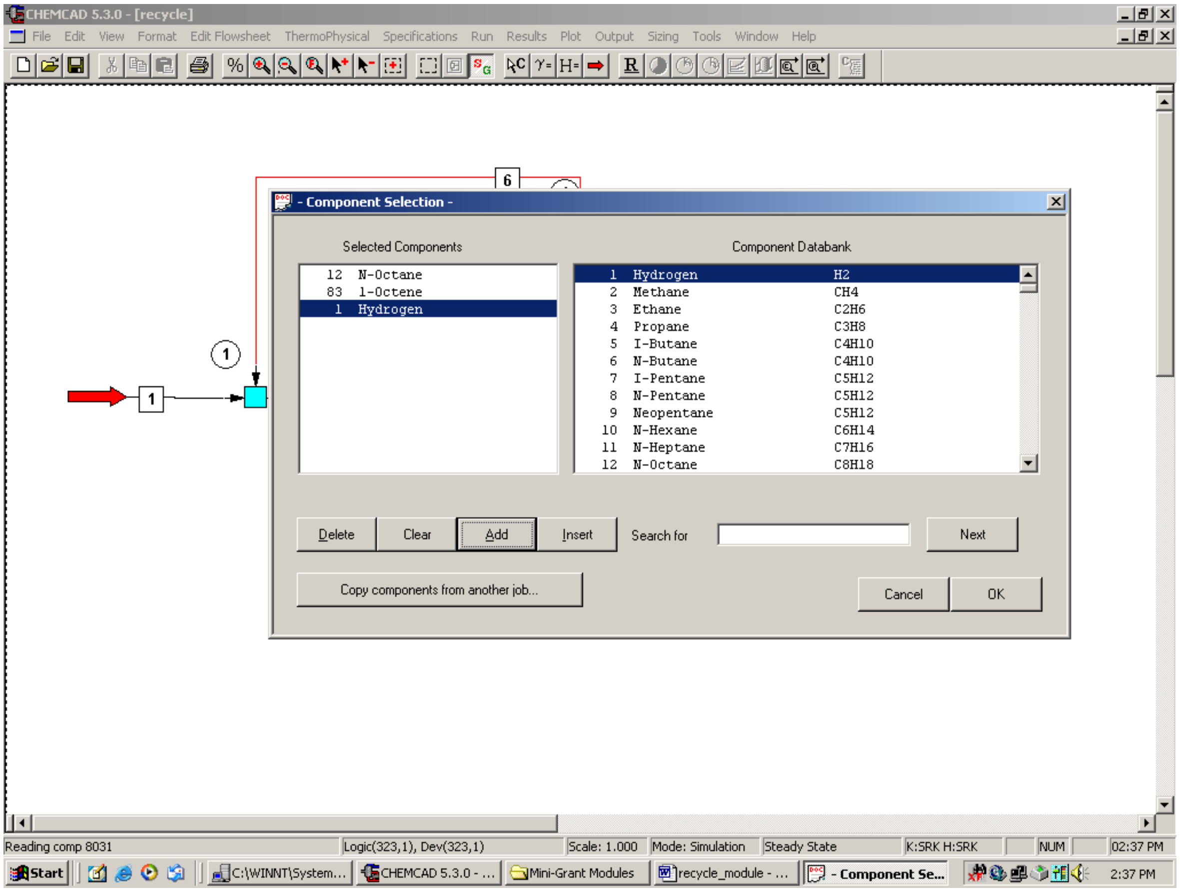
Select and click *feed (2), SCDS column* #3 (right click on the regular SCDS icon to find the icon representing absorber mode) and *product(2)* icons on the workspace. Connect the icons appropriately using *Stream.* Click once on the **S/G** icon on the menu bar to switch the simulation mode from *Edit Simulation* to *Run Simulation.*



Step 2: Entering the components and formatting engineering units

Go to the *Thermophysical* on the menu bar and click on *Components List*. Find air, hydrogen sulfide and water from the CHEMCAD components list and add them to the component list. Go

to the *Format* menu and click on *Engineering Units* and select the desired units for such properties as temperature, pressure etc. Click OK to continue.



Selected Components

12	N-Octane
83	1-Octene
1	Hydrogen

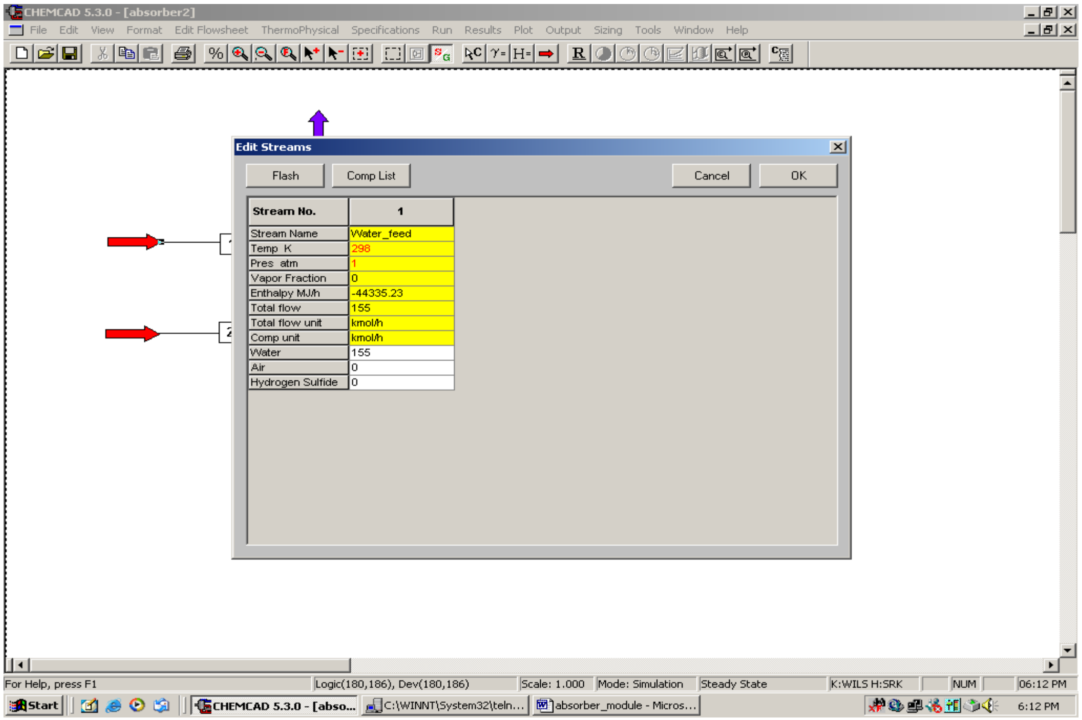
Component Databank

1	Hydrogen	H_2
2	Methane	CH_4
3	Ethane	C_2H_6
4	Propane	C_3H_8
5	I-Butane	C_4H_{10}
6	N-Butane	C_4H_{10}
7	I-Pentane	C_5H_{12}
8	N-Pentane	C_5H_{12}
9	Neopentane	C_5H_{12}
10	N-Hexane	C_6H_{14}
11	N-Heptane	C_7H_{16}
12	N-Octane	C_8H_{18}

Reading comp 8031 | Logic(323,1), Dev(323,1) | Scale: 1.000 | Mode: Simulation | Steady State | K:SRK H:SRK | NUM | 02:37 PM

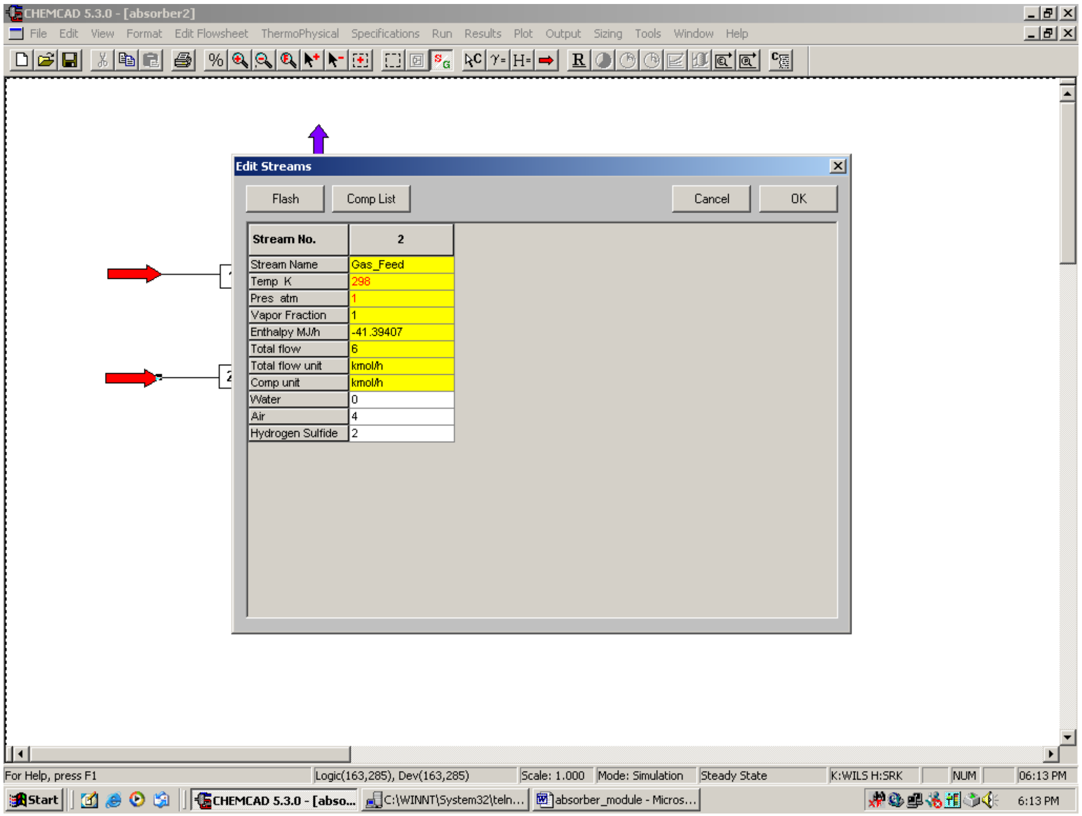
Step 3: Entering the feed stream composition

Double click on the first feed stream (water stream). Enter the feed information (temperature, pressure, and an initial guess, say 100 kmol/hr for flow rate of water) given in the problem statement. Click once on *Flash* to get the feed stream enthalpy and vapor fraction in feed at the feed conditions.



Stream No.	1
Stream Name	Water_feed
Temp K	298
Pres atm	1
Vapor Fraction	0
Enthalpy MJ/h	-44335.23
Total flow	155
Total flow unit	kmol/h
Comp unit	kmol/h
Water	155
Air	0
Hydrogen Sulfide	0

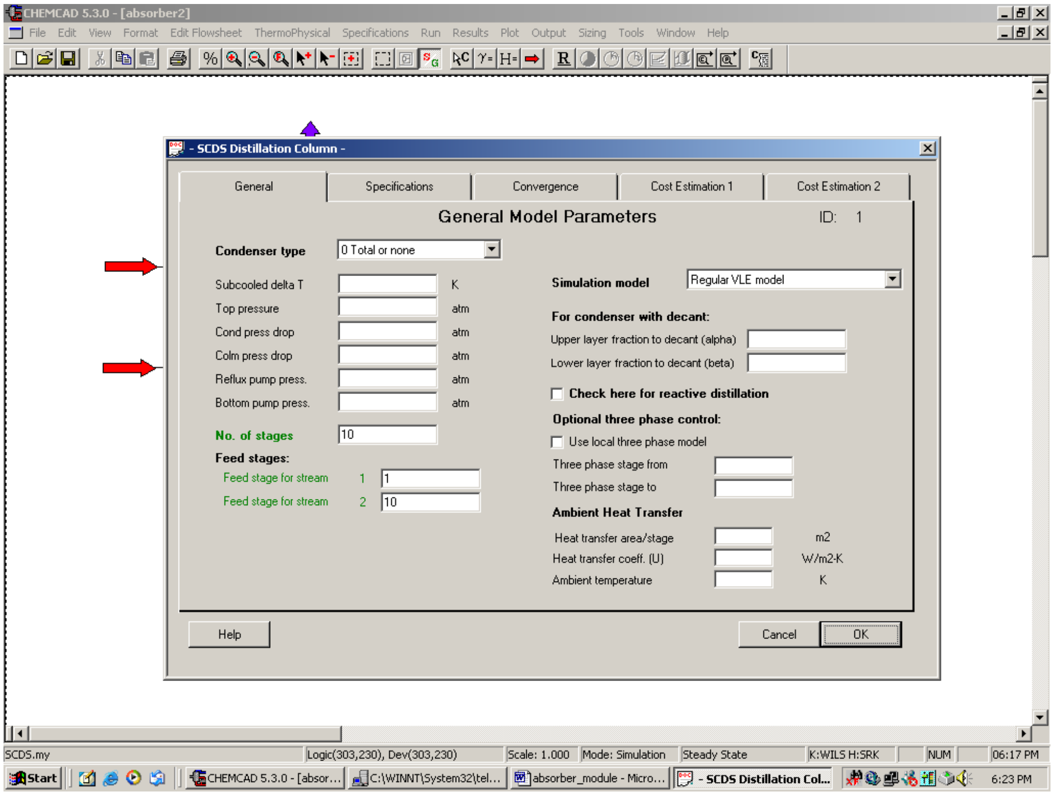
Similarly, enter the feed conditions for the second stream (gas stream).



Stream No.	2
Stream Name	Gas_Feed
Temp K	298
Pres atm	1
Vapor Fraction	1
Enthalpy MJ/h	-41.39407
Total flow	6
Total flow unit	kmol/h
Comp unit	kmol/h
Water	0
Air	4
Hydrogen Sulfide	2

Step 4: Entering the absorber specs

Double click on the SCDS column. This can be used as an absorber.



Condenser type: 0 Total or none

Simulation model: Regular VLE model

No. of stages: 10

Feed stage for stream 1: 1

Feed stage for stream 2: 10

The required inputs in this page are the same as those for a distillation column and are described below:

No. of stages: Enter the number of stages (10)

Feed stage for stream 1: Enter the stage number at which water enters the column (1)

Feed stage for stream 2: Enter the stage number at which gas mixture enters the column (10)

The other inputs on this page are optional and can be neglected.

Don't click *OK* yet!

Click on the *Specifications* tab. Note that the default options for *Condenser mode* and *Reboiler mode* are *No Condenser* and *No Reboiler* respectively. These options are always left to default when simulating for an absorber using an SCDS column.

Click *OK* to continue.

Step 5: Running the simulation and retrieving the results:

Now the simulation is ready to be run. Click once on ***R*** to run the simulation. Alternatively, one can run the simulation by clicking on *Run* on the menu bar and selecting *Run all.* The status of the simulation can be found at the bottom left hand corner of the screen. The message, *Run Finished,* appears if the run is successfully completed. The product stream properties can be found by double clicking the product streams. At this point, a check is made to see the mole rate of hydrogen sulfide in the bottom stream. If this is more than 1.98 kmol/hr (99% of hydrogen sulfide in feed, as per the problem statement), the guessed flow rate of water is too high. Decrease the flow rate of water in feed stream and repeat the above steps. Conversely, if the mole rate of hydrogen sulfide exiting from the bottom is less than 1.98 kmol/hr, increase the flow rate of water in the feed stream and repeat the above steps until the flow rate of hydrogen sulfide from the bottom is approximately 1.98 kmol/hr.

Alternatively, a sensitivity analysis can made with water feed flow rate as the independent variable and the hydrogen sulfide product flow rate in the bottom as the dependent variable. The plot obtained after running the sensitivity analysis can be used to read the water flow rate at which the flow rate of hydrogen sulfide from the bottom is 1.98 kmol/hr.

It can be verified that the water flow rate to meet the specifications in problem staement is 145 kmol/hr

The Problem Statement:

5.4.2 Reaction:

Decomposition of di-t-butyl peroxide (DTBP) to acetone and ethane

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO + C_2H_6$$

Reaction kinetics:

$$k_c = 2.095*10^{-2}\ \text{min}^{-1}$$
$$-r_A = k_c C_A$$

Reaction conditions:

Temperature 154.6 ^{o}C

Pressure 491.8 mmHg

Feed and initial conditions:

100 kmol/h of (DTBP) at 110 ^{o}C and 760 mmHg

Information for steady state:

1. Reaction is isothermal
2. Conversion with respect to DTBP is 85%
3. Reference temperature for heat of reaction is 25 ^{o}C

Perform a simulation to determine the volume of the reactor at steady state to achieve the desired conversion, the steady state heat duty and the steady-state mole rates of components in the product stream.

Procedure:

Step 1: Creating the Flow sheet

Step 2: Formatting Engineering Units and Selecting Components

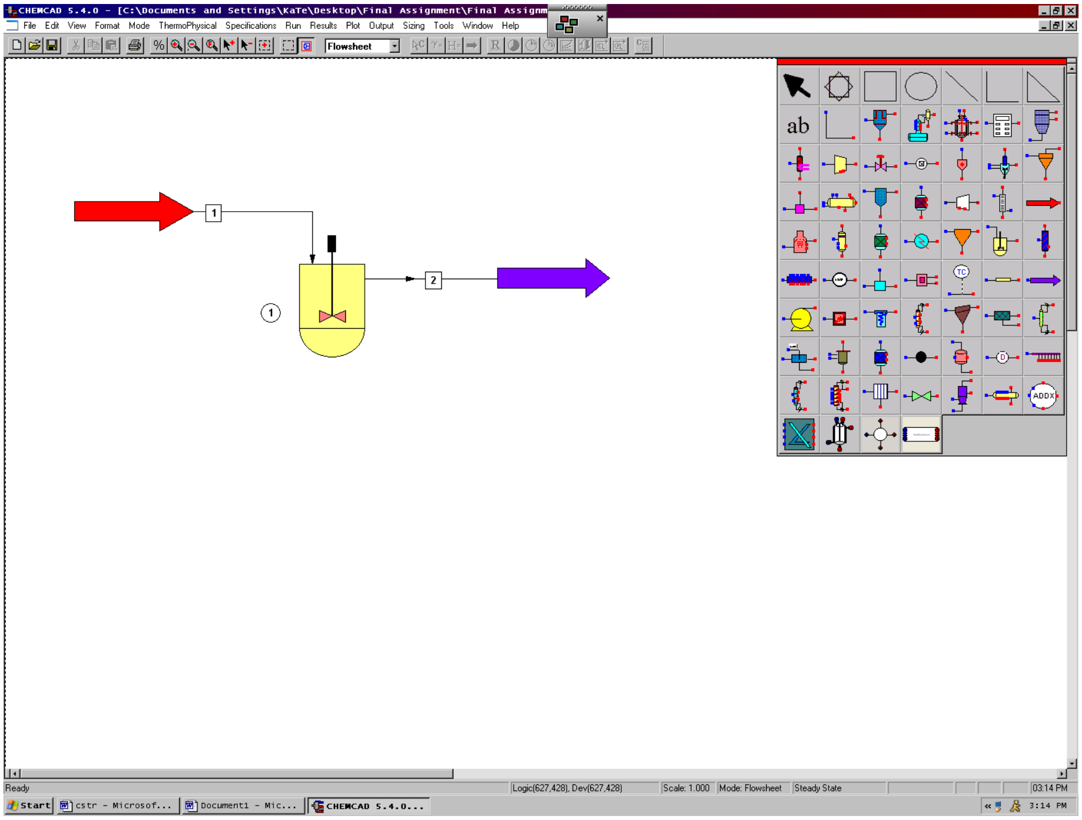
Step 3: Entering the feed stream composition

Step 4: Entering the reactor specs

Step 5: Running the simulation and retrieving the results

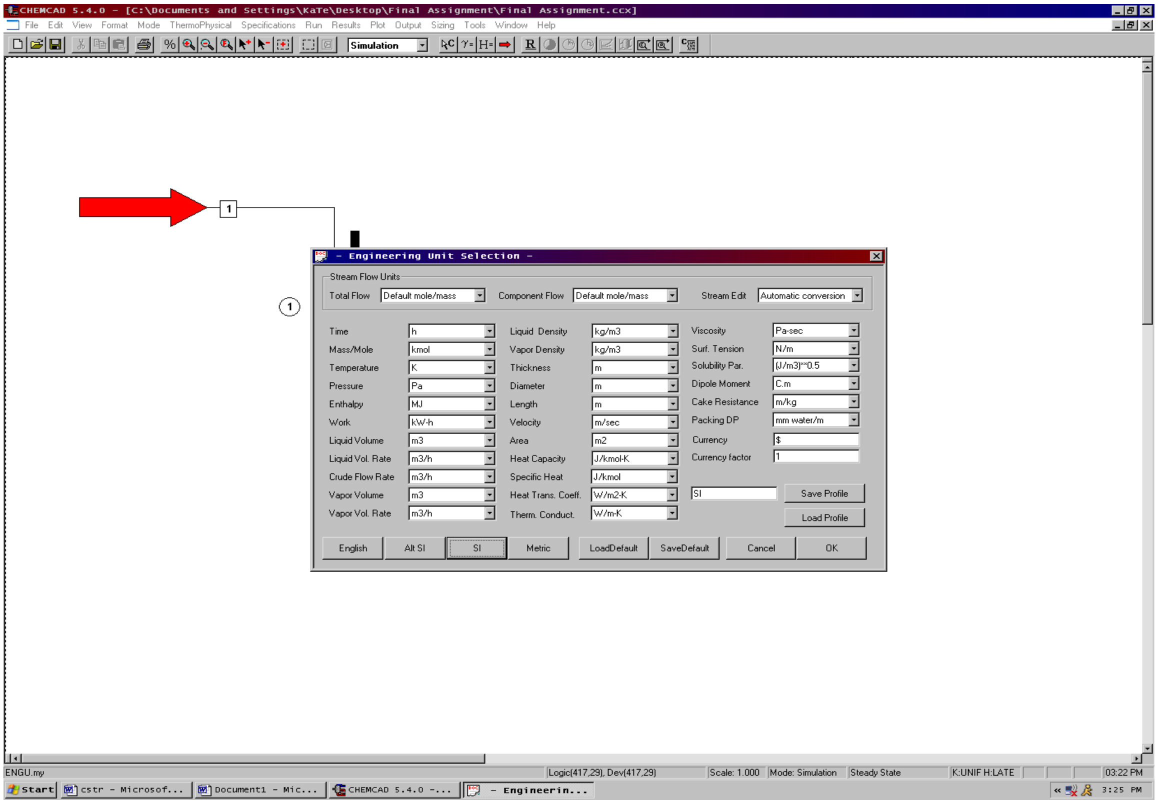
Step 1: Creating the flow sheet

From the File menu select New, save to desired directory. Select and click the *kinetic reactor, feed* and *product* icons on the workspace. Connect the three using the *stream icon.*



Step 2: Formatting Engineering Units and Selecting Components

At the top of the screen change the scroll down menu from Flowsheet to Simulation. Go to the *Format* menu and select *Engineering Units.* Use the *SI* option at the bottom to convert all units at the same time. The desired units for each category may also be selected individually. Click OK to continue.

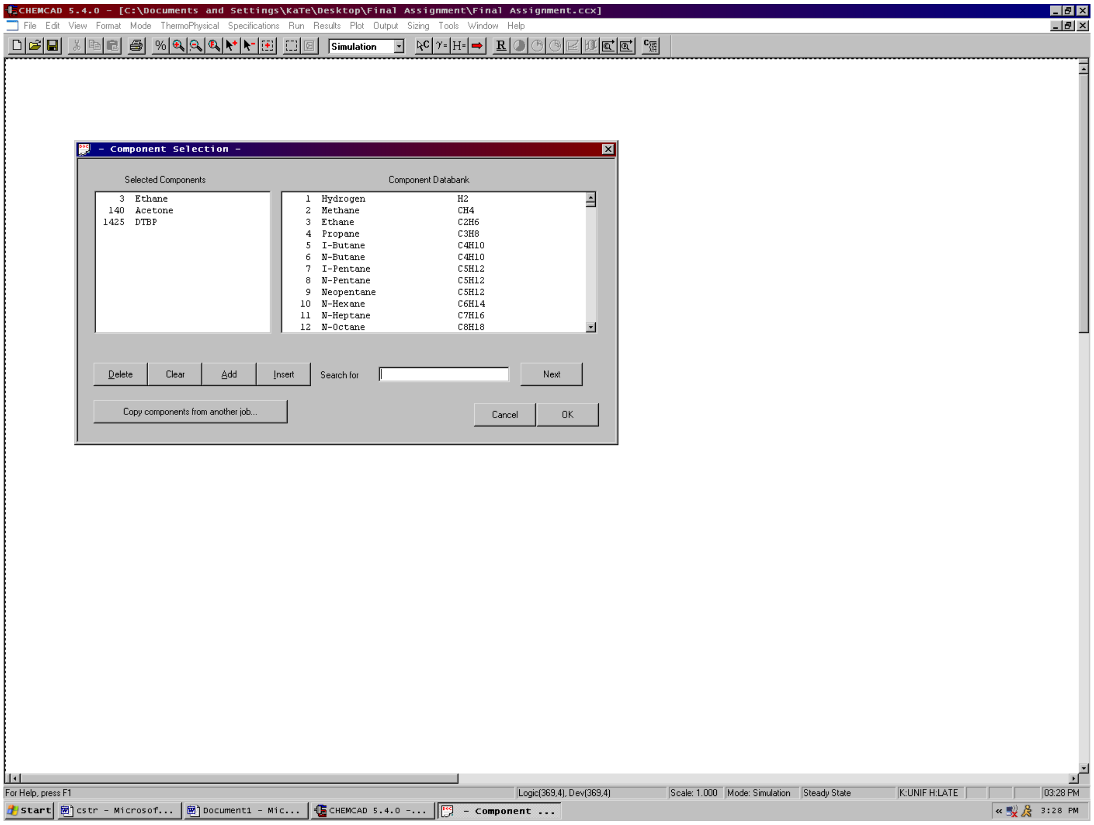


Stream Flow Units

Total Flow: Default mole/mass
Component Flow: Default mole/mass
Stream Edit: Automatic conversion

Time	h	Liquid Density	kg/m3	Viscosity	Pa-sec
Mass/Mole	kmol	Vapor Density	kg/m3	Surf. Tension	N/m
Temperature	K	Thickness	m	Solubility Par.	(J/m3)**0.5
Pressure	Pa	Diameter	m	Dipole Moment	C.m
Enthalpy	MJ	Length	m	Cake Resistance	m/kg
Work	kW-h	Velocity	m/sec	Packing DP	mm water/m
Liquid Volume	m3	Area	m2	Currency	$
Liquid Vol. Rate	m3/h	Heat Capacity	J/kmol-K	Currency factor	1
Crude Flow Rate	m3/h	Specific Heat	J/kmol		
Vapor Volume	m3	Heat Trans. Coeff.	W/m2-K		SI
Vapor Vol. Rate	m3/h	Therm. Conduct.	W/m-K		

Next Go to *Thermophysical* on the menu bar and click on *Components List*. Find DTBP (Di tertiary butyl peroxide), acetone, and ethane from the CHEMCAD components list and add them to the component list. Click OK to continue.



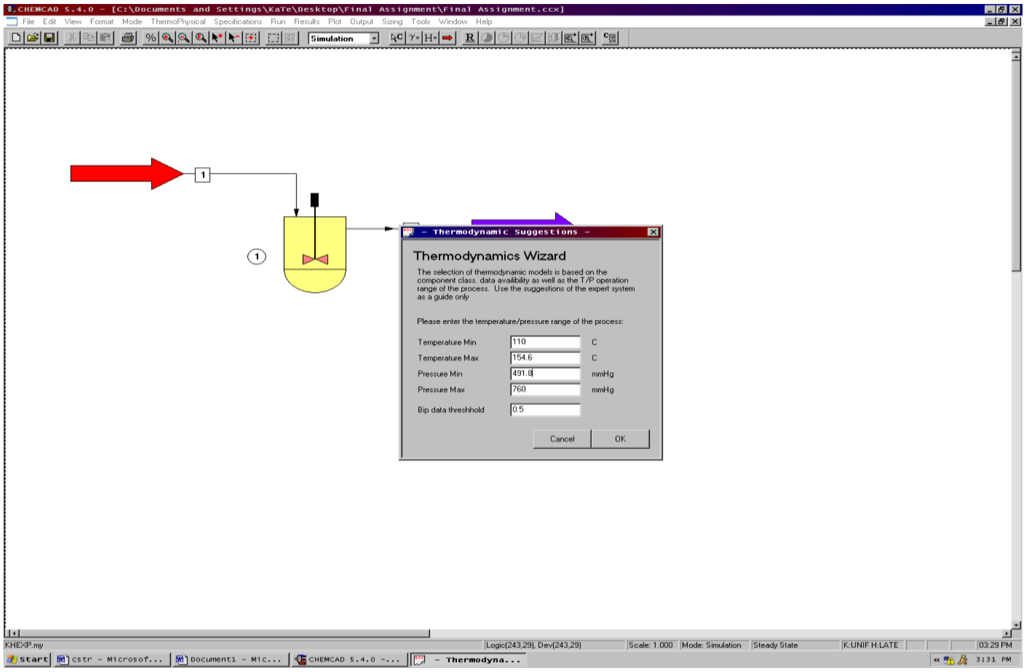
Selected Components

3	Ethane
140	Acetone
1425	DTBP

Component Databank

1	Hydrogen	H2
2	Methane	CH4
3	Ethane	C2H6
4	Propane	C3H8
5	I-Butane	C4H10
6	N-Butane	C4H10
7	I-Pentane	C5H12
8	N-Pentane	C5H12
9	Neopentane	C5H12
10	N-Hexane	C6H14
11	N-Heptane	C7H16
12	N-Octane	C8H18

The Thermodynamics Wizard will then appear, enter the desired information. Click OK to Continue. The K-Value Wizard can be accessed any time by clicking on the *Thermo physical menu* and then scrolling down to K-Value Wizard. Click OK. On the second screen select the SRK equation of state if the UNIFAC equation of state does not work. Click OK.



Thermodynamics Wizard

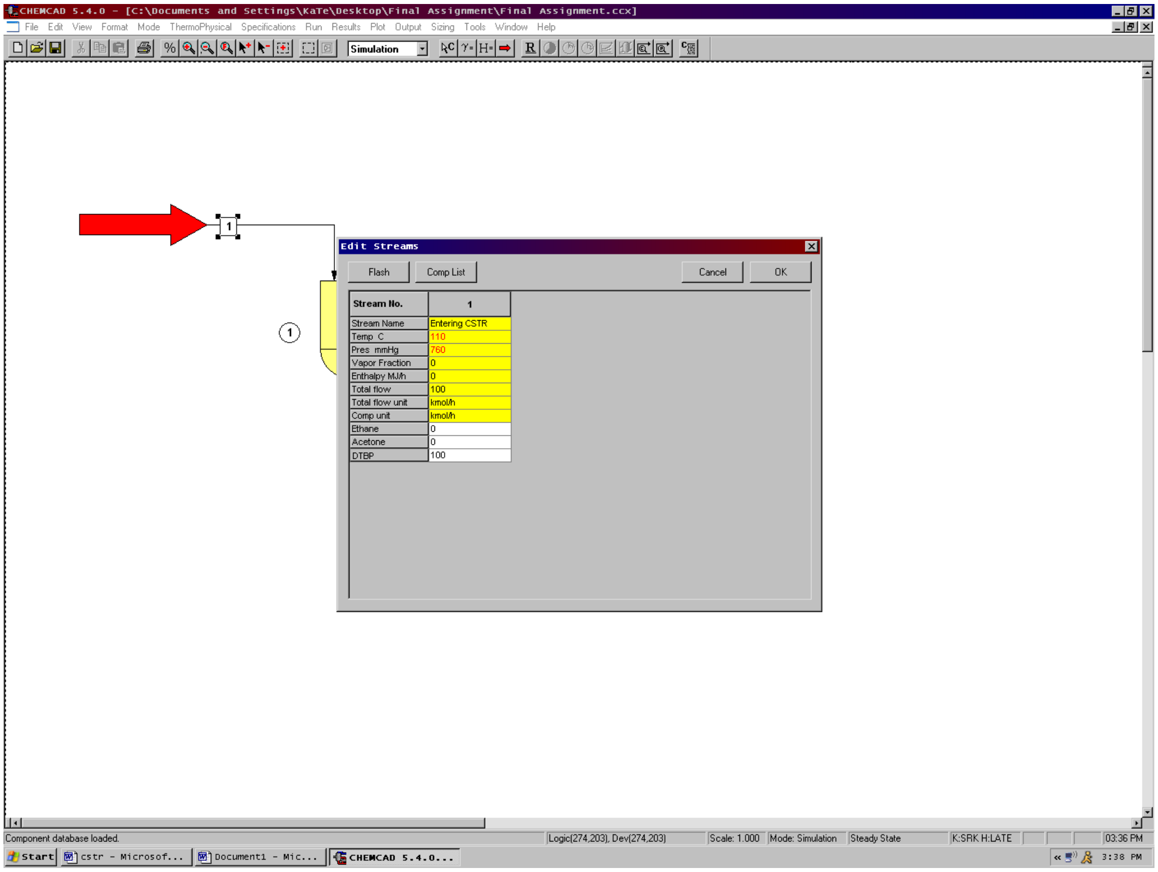
The selection of thermodynamic models is based on the component class, data availibility as well as the T/P operation range of the process. Use the suggestions of the expert system as a guide only

Please enter the temperature/pressure range of the process:

Temperature Min 110 C
Temperature Max 154.6 C
Pressure Min 491.8 mmHg
Pressure Max 760 mmHg
Bip data threshhold 0.5

Step 3: Entering the feed stream composition

Double click on the feed stream and enter the feed information (temperature, pressure, total flow rate and component mole fractions) given in the problem statement. Click once on *Flash* to get the feed stream enthalpy and vapor fraction in feed at the feed conditions. Click OK. Click on the Exit stream and input the isothermal temperature and pressure. Click Flash. Click OK.



Stream No.	1
Stream Name	Entering CSTR
Temp C	110
Pres mmHg	760
Vapor Fraction	0
Enthalpy MJ/h	0
Total flow	100
Total flow unit	kmol/h
Comp unit	kmol/h
Ethane	0
Acetone	0
DTBP	100

Step 4: Entering the reactor specs

Double click on the reactor.

General Specifications Page:

Number of reactions*:* As there is only one reaction in the problem statement, enter ‘1’

Reactor Pressure*:* Enter the reactor pressure as given in the problem statement (491.8 mmHg)

Pressure Drop*:* As there is no pressure drop specified within the reactor. Leave this blank.

Kinetic Rate Expression*:* There are two options for this. The default option *(Standard)* is used when the rate equation is in standard Arrhenius form. The other option *(User Specified)* is used when the rate law is not in its standard form and the user needs to enter this manually. For more information on this, the user can always click on the *help* button that appears at the bottom left corner on this page. For this problem, the kinetic rate expression is given to the user. So, the *User Specified* option should be selected.

Reaction Phase*:* As the reactant, DTBP and one product, ethane, are in vapor phase at reaction pressure and temperature and the other product, acetone is in liquid phase, *Vapor Reaction, Mixed Phase* radio button should be selected.

Specify Reactor Type*:* As the reactor described in the problem statement is a CSTR, *CSTR* should be selected form the drop box.

Thermal Mode*:* As the temperature of the reaction is given as 154.6 ^{o}C, *Isothermal* option should be selected.

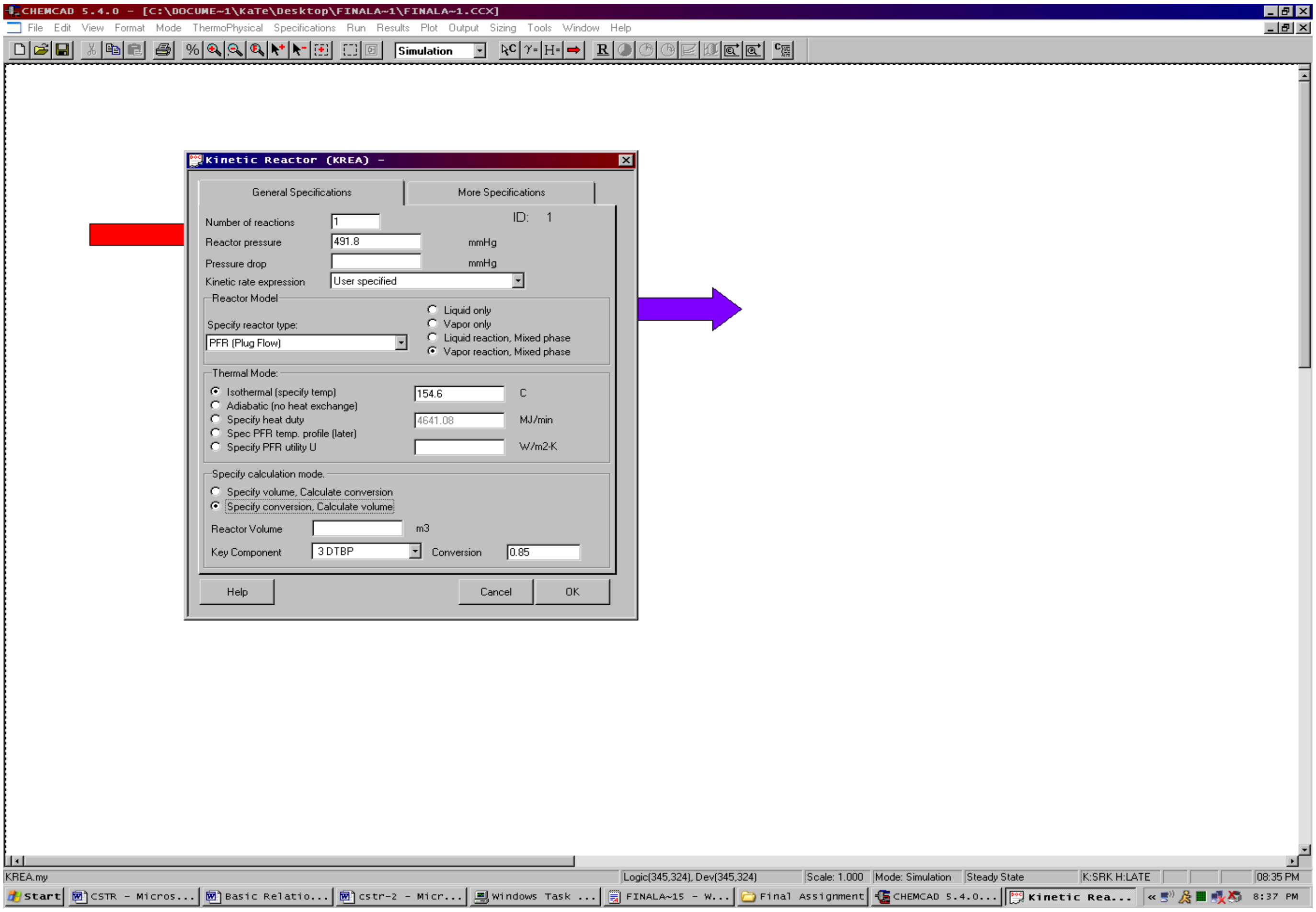
Specify Calculation Mode*:* As the desired conversion is given in the problem statement, *Specify Conversion, Calculate Volume* option should be selected.

Reactor Volume*:* This needs to left blank as this is the value that is required to be calculated in the simulation.

Key Component*:* The key component to specify conversion is DTBP and this is selected from the drop box.

Conversion*:* The conversion with respect to the key component, DTBP is given as 85% and this conversion (0.85) is entered in this field.

Don’t Click *OK* yet! There is more to complete in the *More Specifications* page!



ID: 1

Number of reactions: 1

Reactor pressure: 491.8 mmHg

Pressure drop: mmHg

Kinetic rate expression: User specified

Reactor Model

Specify reactor type: PFR (Plug Flow)

○ Liquid only
○ Vapor only
○ Liquid reaction, Mixed phase
● Vapor reaction, Mixed phase

Thermal Mode:

● Isothermal (specify temp) 154.6 C
○ Adiabatic (no heat exchange)
○ Specify heat duty 4641.08 MJ/min
○ Spec PFR temp. profile (later)
○ Specify PFR utility U W/m2-K

Specify calculation mode.

○ Specify volume, Calculate conversion
● Specify conversion, Calculate volume

Reactor Volume m3

Key Component 3 DTBP Conversion 0.85

+

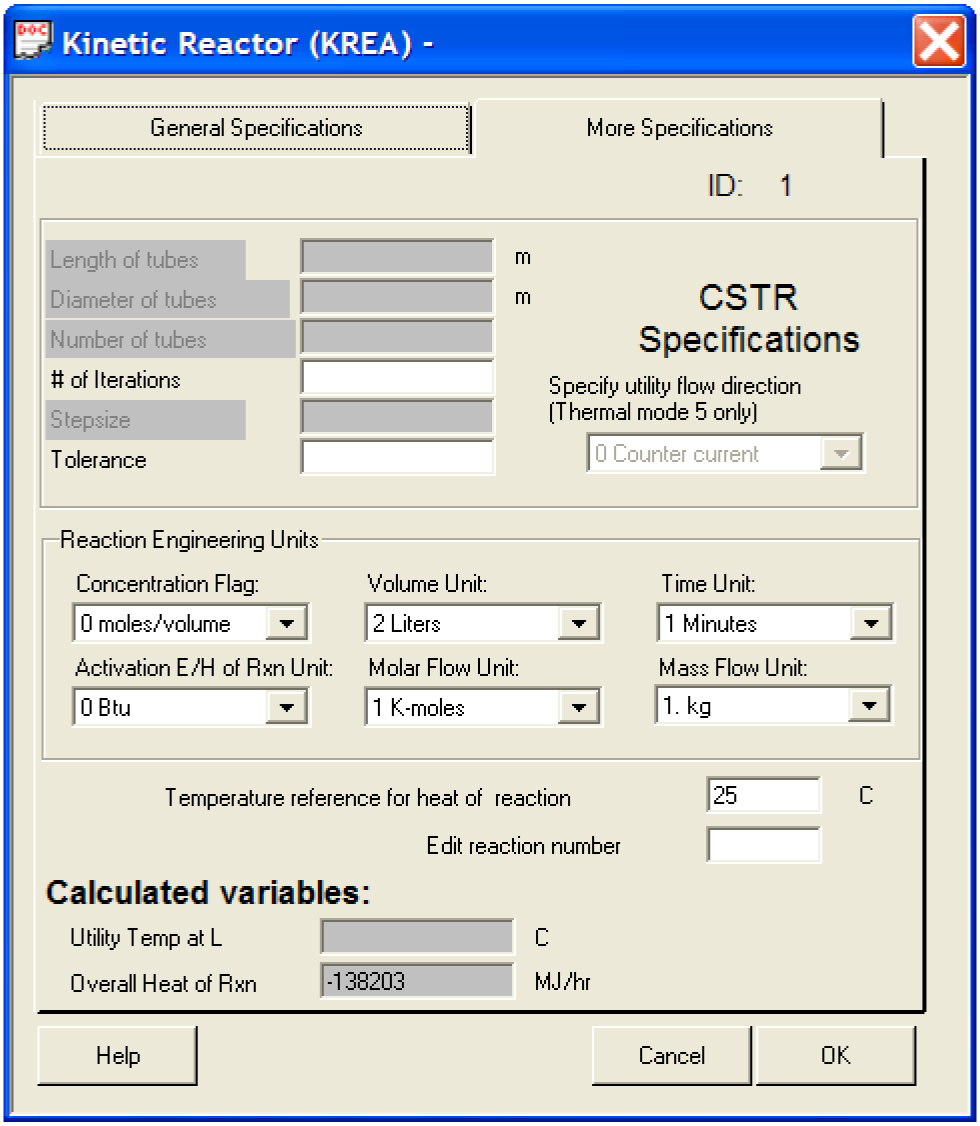
More Specifications:

# of Iterations and ***Tolerance*** can be left blank as these are optional fields.

***Reaction Engineering Units**:* Change the units so that the units are consistent with the rate law (Change *time* units to *min*)

***Temperature reference for heat of reaction**:* Enter 25 °C in this field.

***Edit reaction number**:* Can be left blank.



Kinetic Reactor (KREA) -

ID: 1

Length of tubes m
Diameter of tubes m
Number of tubes
# of Iterations
Stepsize
Tolerance

CSTR Specifications

Specify utility flow direction (Thermal mode 5 only)
0 Counter current

Reaction Engineering Units

Concentration Flag: 0 moles/volume
Volume Unit: 2 Liters
Time Unit: 1 Minutes
Activation E/H of Rxn Unit: 0 Btu
Molar Flow Unit: 1 K-moles
Mass Flow Unit: 1. kg

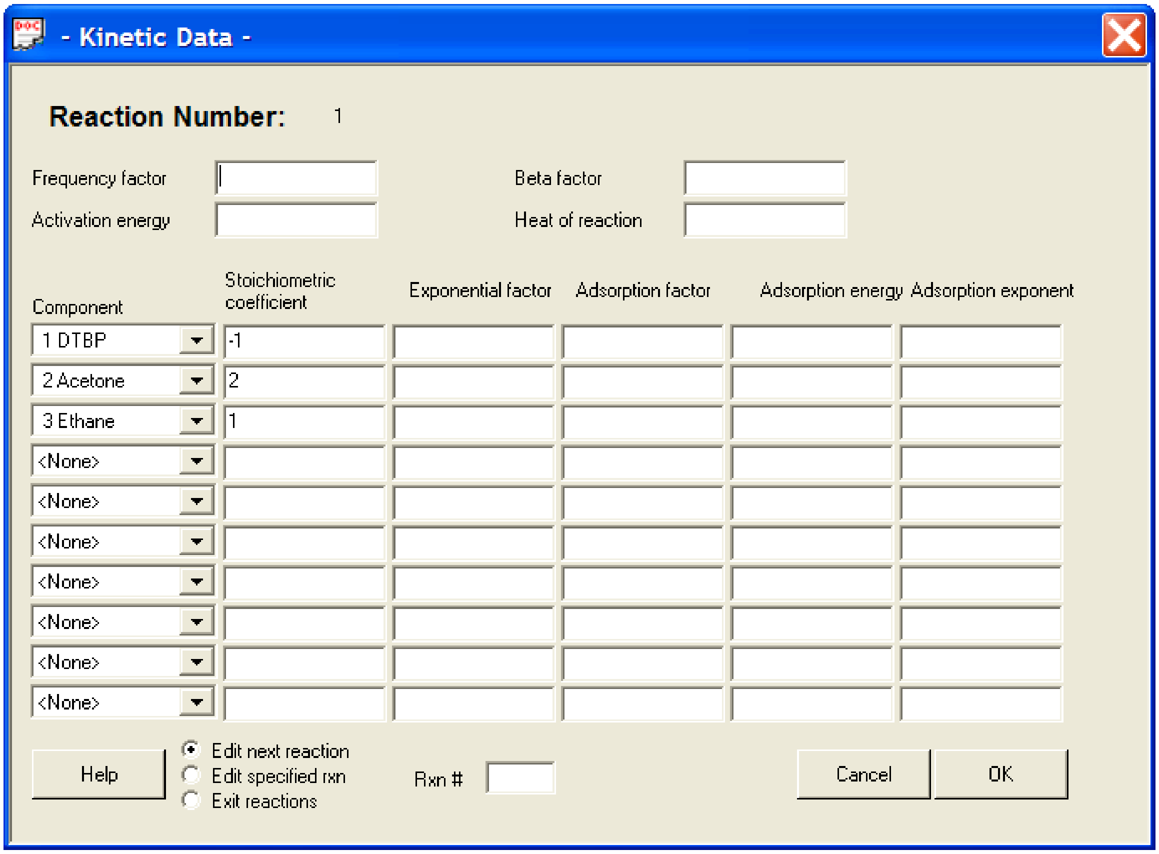
Temperature reference for heat of reaction 25 C

Edit reaction number

Calculated variables:

Utility Temp at L C
Overall Heat of Rxn -138203 MJ/hr

Click *OK* after completing the specifications page. A new window will appear and the stoichiometric coefficients should be entered in this window. Remember Reactants are negative (-), while products are positive (+). Click *OK* after entering the coefficients.



Reaction Number: 1

Component	Stoichiometric coefficient	Exponential factor	Adsorption factor	Adsorption energy	Adsorption exponent
1 DTBP	-1				
2 Acetone	2				
3 Ethane	1				
<None>					
<None>					
<None>					
<None>					
<None>					
<None>					
<None>					

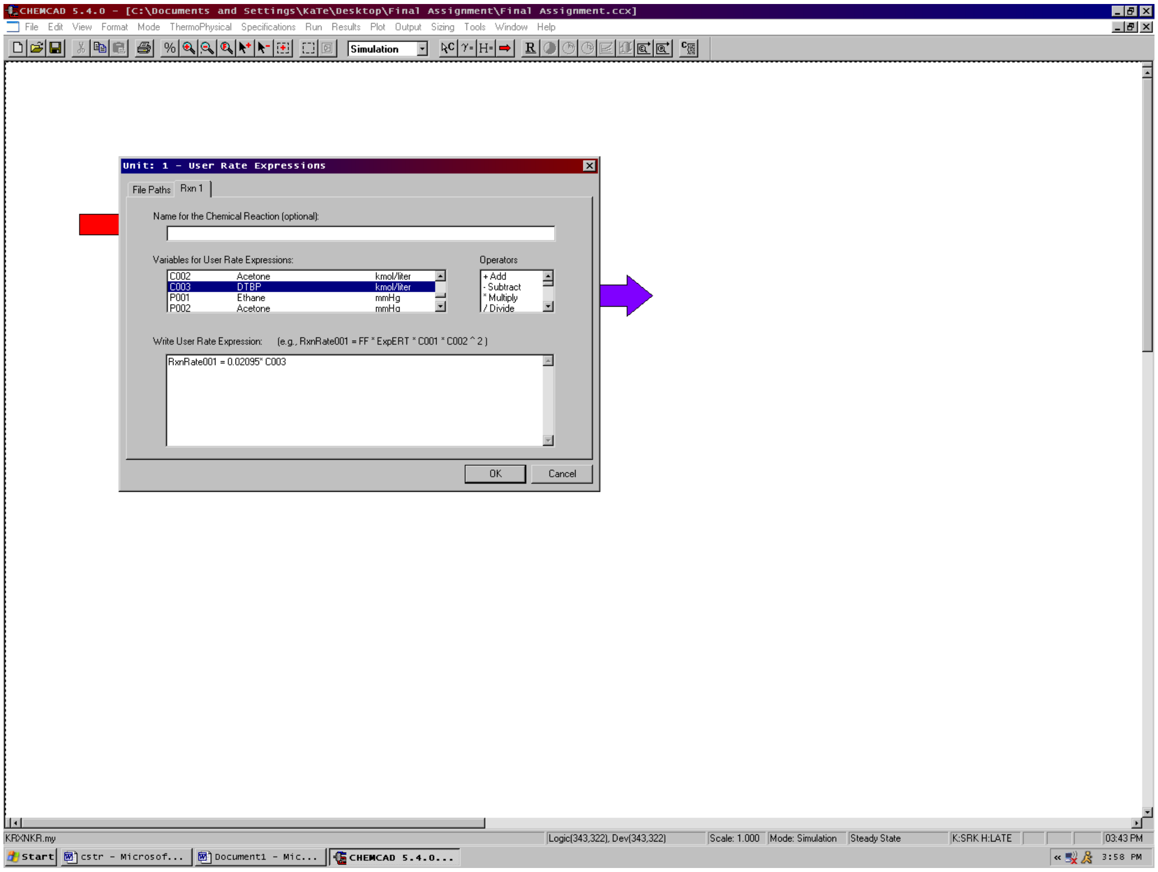
● Edit next reaction
○ Edit specified rxn
○ Exit reactions

Because the *User Specified* option is selected for kinetic rate expression, another window with the title *Unit: 1-User Rate Expressions* appears. If a separate Visual Basic code is available, the user can browse those files using options available on *File path* tab. For most practical purposes, the user can go directly to the *Rxn1* tab and complete the information as follows:

Name for the Chemical Reaction: DTBP decomposition

Variables for User Rate Expressions: CHEMCAD supplies the user with the variables described in this section to be used for user rate expressions.

Write User Rate Expression: 0.02095*C003



Name for the Chemical Reaction (optional):

Variables for User Rate Expressions:

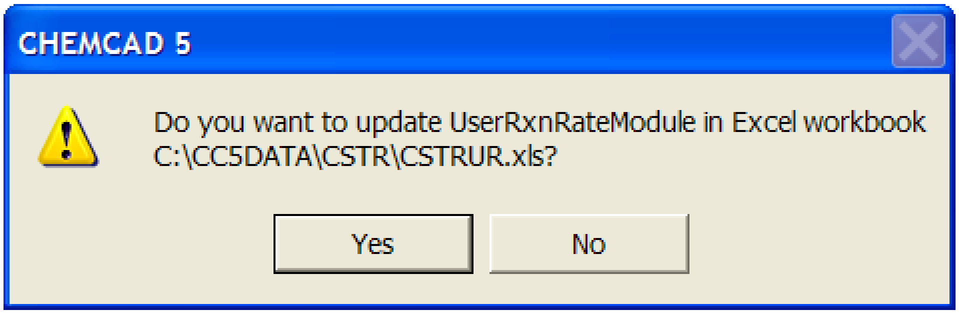
C002	Acetone	kmol/liter
C003	DTBP	kmol/liter
P001	Ethane	mmHg
P002	Acetone	mmHg

Operators
+ Add
- Subtract
* Multiply
/ Divide

Write User Rate Expression: (e.g., RxnRate001 = FF * ExpERT * C001 * C002 ^ 2)

```
RxnRate001 = 0.02095* C003
```

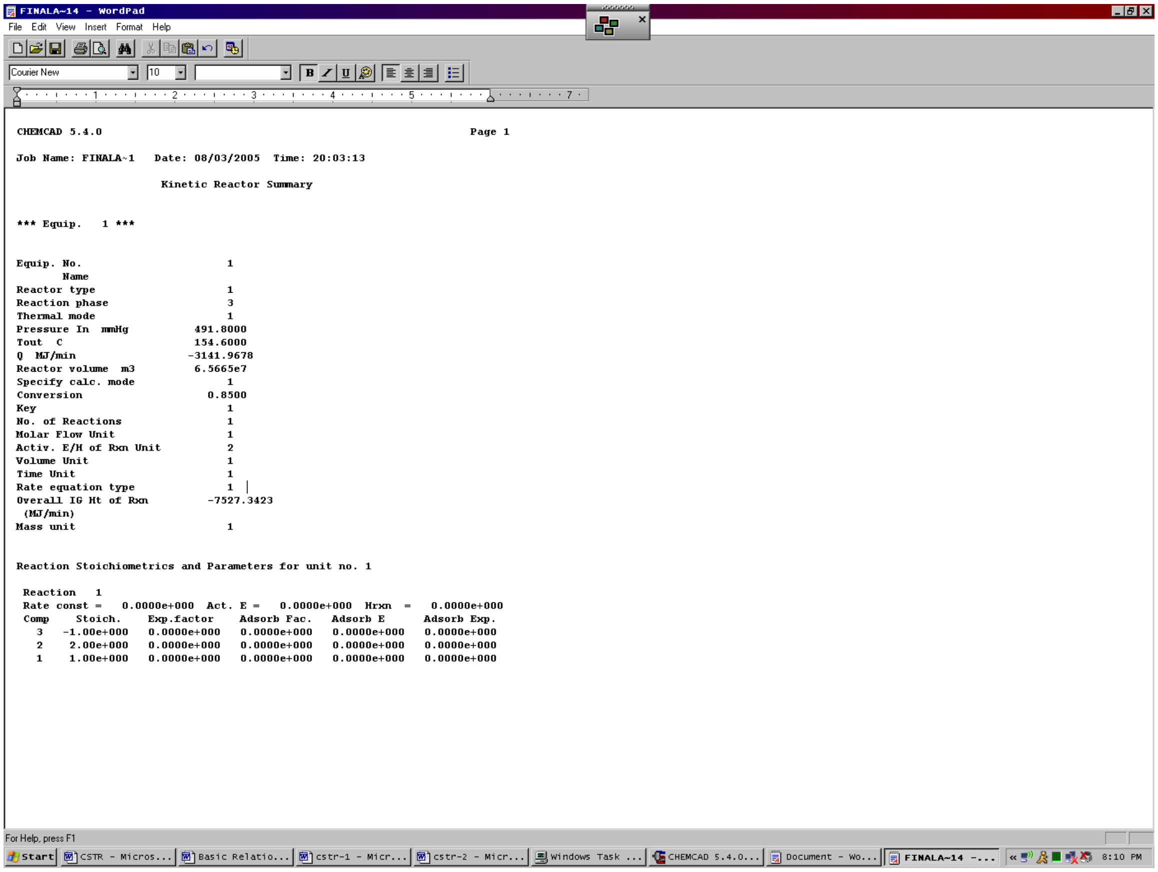
Click *OK* when finished. The following window will appear to confirm that we are allowing the cookies from an existing excel file so that the Visual Basic program accesses the rate expression specified by us. Click on *Yes* to continue.



Do you want to update UserRxnRateModule in Excel workbook C:\CC5DATA\CSTR\CSTRUR.xls?

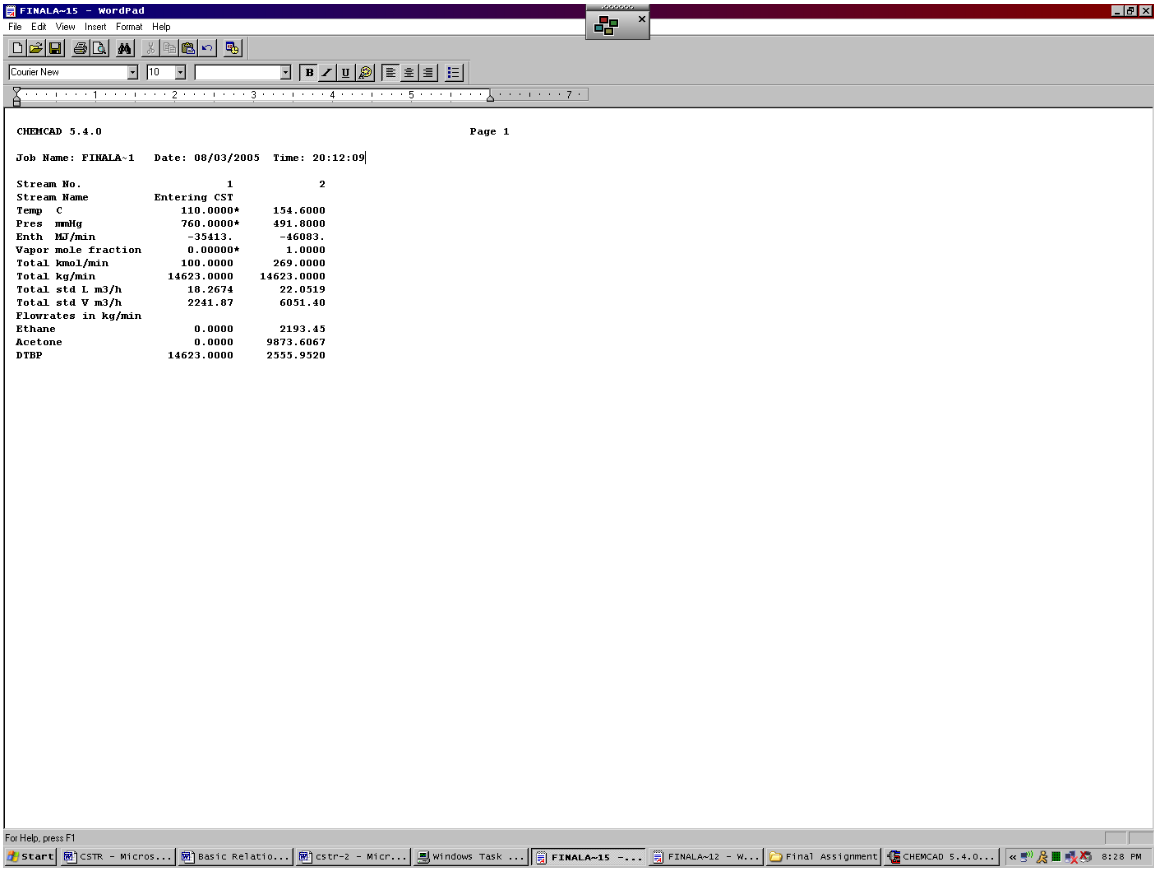
Step 5: Running the simulation and retrieving the results:

Now the simulation is ready to run. Click once on *R* at the top of the screen to run the simulation. Alternatively, one can run the simulation by clicking on *Run* on the menu bar and selecting *Run all*. The status of the simulation can be found at the bottom left hand corner of the screen. The message, *Run Finished* appears in this place if the run is successfully completed. The volume of the reactor for the desired conversion can be found from the *General specifications page* (double click on the reactor for this screen) to be 6.53e4 m^3. Alternatively, all the results associated with the Unit operation, CSTR can be found by clicking *Results* on the menu and selecting *Unit Op's* and entering the number the CSTR is associated with ('1' in this case) on the flow sheet. The CSTR results will then be available in a WordPad file.



```
CHEMCAD 5.4.0                                                   Page 1

Job Name: FINALA~1   Date: 08/03/2005  Time: 20:03:13

                      Kinetic Reactor Summary


*** Equip.   1 ***


Equip. No.                      1
       Name
Reactor type                    1
Reaction phase                  3
Thermal mode                    1
Pressure In  mmHg          491.8000
Tout  C                    154.6000
Q  MJ/min                 -3141.9678
Reactor volume  m3         6.5665e7
Specify calc. mode              1
Conversion                   0.8500
Key                             1
No. of Reactions                1
Molar Flow Unit                 1
Activ. E/H of Rxn Unit          2
Volume Unit                     1
Time Unit                       1
Rate equation type              1
Overall IG Ht of Rxn         -7527.3423
 (MJ/min)
Mass unit                       1


Reaction Stoichiometrics and Parameters for unit no. 1

 Reaction   1
 Rate const =   0.0000e+000  Act. E =   0.0000e+000  Hrxn  =   0.0000e+000
 Comp    Stoich.     Exp.factor    Adsorb Fac.   Adsorb E      Adsorb Exp.
   3   -1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   2    2.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   1    1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
```

Similarly, the product stream properties can found either by clicking once on the product stream or by clicking once on *Results* on the menu, selecting *Stream Composition* and then clicking on *All Streams.* The results will again be available in a WordPad file.



```
CHEMCAD 5.4.0                                                    Page 1

Job Name: FINALA~1   Date: 08/03/2005   Time: 20:12:09

Stream No.                      1              2
Stream Name               Entering CST
Temp   C                    110.0000*      154.6000
Pres   mmHg                 760.0000*      491.8000
Enth   MJ/min               -35413.        -46083.
Vapor mole fraction          0.00000*        1.0000
Total kmol/min              100.0000       269.0000
Total kg/min              14623.0000     14623.0000
Total std L m3/h             18.2674        22.0519
Total std V m3/h             2241.87        6051.40
Flowrates in kg/min
Ethane                        0.0000        2193.45
Acetone                       0.0000      9873.6067
DTBP                      14623.0000      2555.9520
```

You Are Done!

A few hints:

If CHEMCAD gives you a 0 slope error, you need to make sure your More Specifications have been typed in correctly.

You may have to run the reactor as a PFR then as a CSTR.

If you get a mass balance error make sure your reaction rate and stoichiometric coefficients are typed in correctly.

If you have checked all of the above and you are still getting an error, you may want to close CHEMCAD and try again. Sometimes the program stops taking your corrections. You may actually have to close the program several times before you get it to run.

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5. Mickley. H.S.Sherwood.T.S. and Reed C.E., Applied Mathematics for Chemical Engineers, 1st Edition, Tata McGraw Hill Publishing Co. Ltd, New Delhi, 1989