Equation Forms in Process Modelling

Introduction

1. Introduction

A modern chemical plant consists of interconnected units such as heat exchangers, reactors, distillation columns, mixers etc. with high degree of integration to achieve energy efficiency. Design and operation of such complex plants is a challenging problem. Mathematical modeling and simulation is a cost effective method of designing or understanding behavior of these chemical plants when compared to study through experiments. Mathematical modeling cannot substitute experimentation, however, it can be effectively used to plan the experiments or creating scenarios under different operating conditions. Thus, best approach to solving most chemical engineering problems involves judicious combination of mathematical modeling and carefully planned experiments.

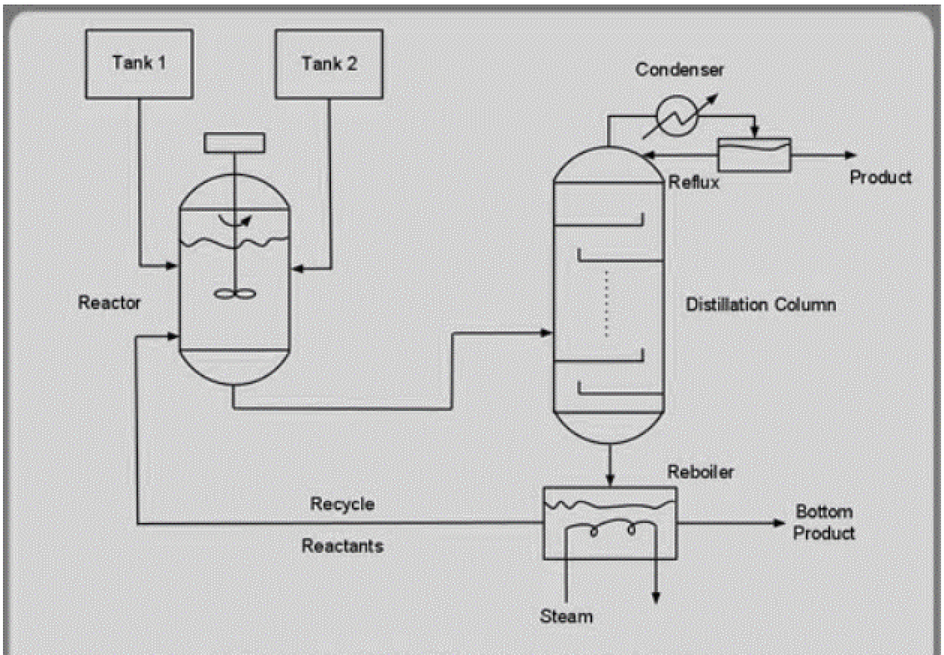

Figure 1: Typical Processing Plant

To begin with, let us look at types of problems that can arise in context of modeling and simulation. Consider a typical small chemical plant consisting of a reactor and a distillation column, which is used to separate the product as overhead (see Figure 1). The reactants, which are separated as bottom product of the distillation column, are recycled to the reactor. We can identify following problems

- **Process Design problem**

  Given: Desired product composition, raw material composition and availability.

- **To Find**: Raw material flow rates, reactor volume and operating conditions (temperature, pressure etc.), distillation column configuration (feed locations and product draws), reboiler,condenser sizes and operating conditions (recycle and reflux flows, steam flow rate, operating temperatures and pressure etc.)

- **Process Retrofitting**: Improvements in the existing set-up or operating conditions Plant may have been designed for certain production capacity and assuming certain raw material quality. We are often required to assess whether
  — Is it possible to operate the plant at a different production rate?
  — What is the effect of changes in raw material quality?
  — Is it possible to make alternate arrangement of flows to reduce energy consumption?

- **Dynamic behavior and operability analysis**: Any plant is designed by assuming certain ideal composition of raw material quality, temperature and operating temperatures and pressures of utilities. In practice, however, it is impossible to maintain all the operating conditions exactly at

the nominal design conditions. Changes in atmospheric conditions of fluctuations in steam header pressure, cooling water temperature, feed quality fluctuations, fouling of catalysts, scaling of heat transfer surfaces etc. keep perturbing the plant from the ideal operating condition. Thus, it becomes necessary to understand transient behavior of the system in order to
— reject of effects of disturbances on the key operating variables such as product quality
— achieve transition from one operating point to an economically profitable operating point.
— carry out safety and hazard analysis

In order to solve process design or retrofitting problems, mathematical models are developed for each unit operation starting from first principles. Such mechanistic (or first principles) models in Chemical Engineering are combination of mass, energy and momentum balances together with associated rate equations, equilibrium relation and equations of state.

- **Mass balances**: overall, component.

- **Rate equations**: mass, heat and momentum transfer rates (constitutive equations.), rate of chemical reactions

- **Equilibrium principles** : physical(between phases) and chemical (reaction rate equilibrium).

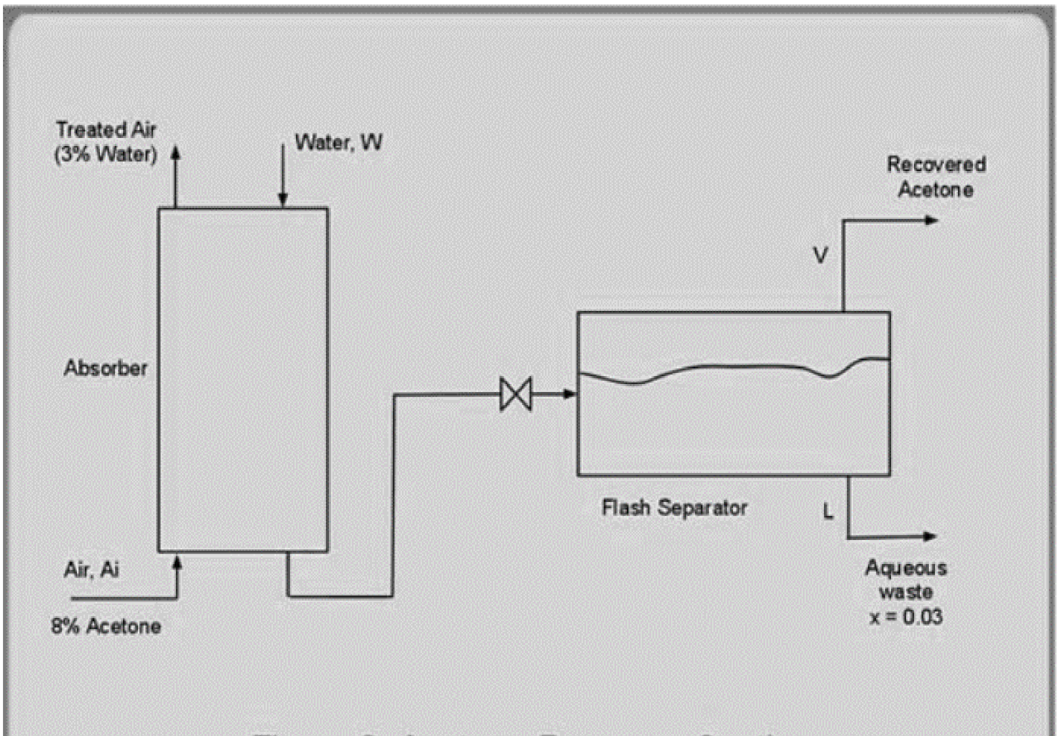

Figure 2: Acetone Recovery Section

• **Equations of state**: primarily for problems involving gases. From mathematical viewpoint, these models can be classified into two broad classes

• Distributed parameter model: These models capture the relationship between the variables involved as functions of time and space.

• Lumped parameter models: These models lump all spatial variation and all the variables involved are treated as functions time alone.

The above two classes of models together with the various scenarios under consideration give rise to different types of equation forms such as linear / nonlinear algebraic equations, ordinary differential equations or partial differential equations. In order to provide motivation for studying these different kinds of equation forms, we present examples of different models in chemical engineering and derive abstract equation forms in the following section.

2. Mechanistic Models and Equation Forms

2.1 Linear Algebraic Equations

Plant wide or section wide mass balances are carried out at design stage or later during operation for keeping material audit. These models are typical examples of systems of simultaneous linear algebraic equations..

Example 1 *Recovery of acetone from air -acetone mixture is achieved using an absorber and a flash separator (Figure 2). A model for this system is developed under following conditions*

- All acetone is absorbed in water
- Air entering the absorber contains no water vapor
- Air leaving the absorber contains 3 mass % water vapor

The flash separator acts as a single equilibrium stage such that acetone mass fraction in vapor and liquid leaving the flash separator is related by relation

$$y=20.5x \qquad \text{-----(1)}$$

where y mass fraction of the acetone in the vapor stream and x mass fraction of the acetone in the liquid stream. Operating conditions of the process are as follows

- Air in flow: 600 lb /hr with 8 mass % acetone
- Water flow rate: 500 lb/hr

It is required that the waste water should have acetone content of 3 mass % and we are required to determine concentration of the acetone in the vapor stream and flow rates of the product streams.

Mass Balance:

$$0.92Ai = 0.97Ao \qquad \textit{(Air)} \qquad \text{-----(2)}$$

$$0.08Ai = 0.03L + yV \qquad \textit{(Acetone)} \qquad \text{-----(3)}$$

$$W = 0.03Ao + (1-y)V + 0.97L \qquad \textit{(Water)} \qquad \text{-----(4)}$$

$$x = 0.03 \qquad \textit{(Design requirement)} \qquad \text{-----(5)}$$

Equilibrium Relation:

$$y = 20.5x \qquad \text{-----(6)}$$

$$\Rightarrow \quad y = 20.5 \times 0.03 = 0.615 \qquad \text{-----(7)}$$

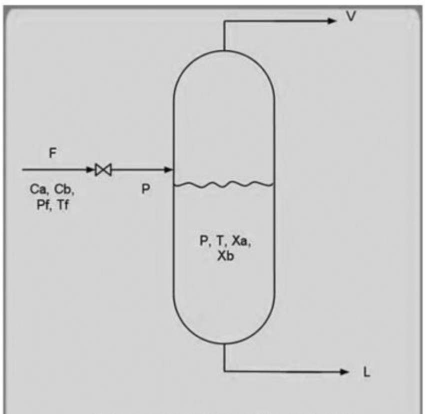

Figure 3: Flash Drum Unit

Substituting for all the known values and rearranging, we have

$$\begin{bmatrix} 0.97 & 0 & 0 \\ 0 & 0.03 & 0.615 \\ 0.03 & 0.385 & 0.97 \end{bmatrix} \begin{bmatrix} Ao \\ L \\ V \end{bmatrix} = \begin{bmatrix} 0.92 \times 600 \\ 0.08 \times 600 \\ 500 \end{bmatrix} \qquad \text{-----(8)}$$

The above model is a typical example of system of linear algebraic equations, which have to be solved simultaneously. The above equation can be represented in abstract form set of linear algebraic equations

$$A\mathbf{x} = \mathbf{b} \qquad \text{-----(9)}$$

where $\mathbf{x}$ and $\mathbf{b}$ are a $(n \times 1)$ vectors (i.e. $\mathbf{x}, \mathbf{b} \in R^n$) and A is a $(n \times n)$ matrix.

2.2 Nonlinear Algebraic Equations

Consider a stream of two components A and B at a high pressure P_f and temperature T_f as shown in Figure 3. If the P_f is greater than the bubble point pressure at T_f, no vapor will be present. The liquid stream passes through a restriction (valve) and is flashed in the drum, i.e. pressure is reduced from P_f to p. This abrupt expansion takes place under constant enthalpy. If the pressure p in the flash drum is less than the bubble point pressure of the liquid feed at T_f, the liquid will partially vaporize and two phases at the equilibrium with each other will be present in the flash drum. The equilibrium relationships are

Table 1: Flash vaporization Unit Example: k-values and compositions

Component	$\mathbf{z}_i$	$\mathbf{k}_i$
n-butane	0.25	2.13
n-pentane	0.45	1.10
n-hexane	0.30	0.59

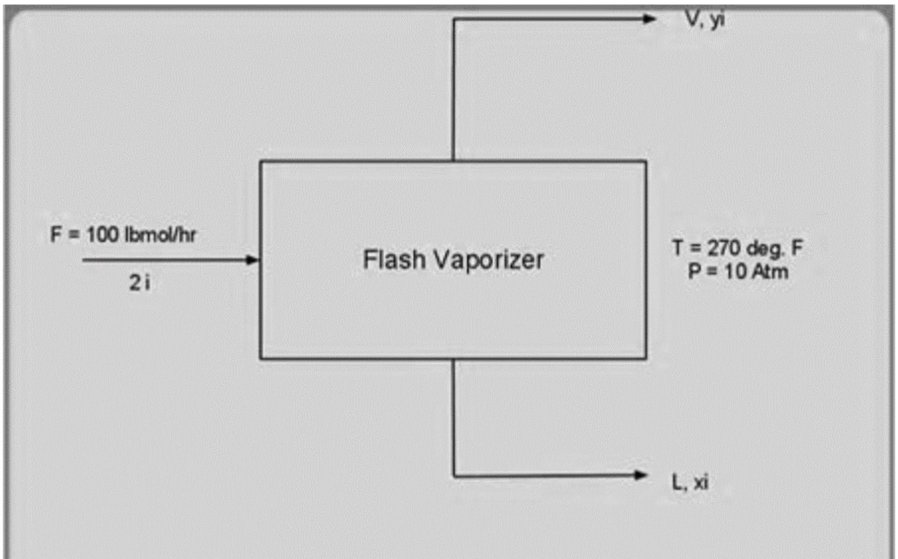

Figure 4: Flash Vaporizer

- Temperature of the liquid phase = temperature of the vapor phase.
- Pressure of the liquid phase = pressure of the vapor phase.
- Chemical potential of the $i'th$ component in the liquid phase = Chemical potential of the $i'th$ component in the vapor phase

Example 2

Consider flash vaporization unit shown in Figure 4. A hydrocarbon mixture containing 25 mole % of n butane, 45 mole %of n -hexane is to be separated in a simple flash vaporization process operated at 10 atm. and $270^0 F$. The equilibrium k- values at this composition are reported in Table 1. Let x_i represent mole fraction of the component i in liquid phase and y_i represent mole fraction of the component i in vapor phase. Model equations for the flash vaporizer are

- Equilibrium relationships

$$k_i = y_i/x_i \qquad (i = 1,2,3) \qquad \text{-----(10)}$$

- Overall mass balance

$$F = L + V \qquad \text{-----(11)}$$

- Component balance

$$z_i F = x_i L + y_i V \qquad (i = 1,2,3) \qquad \text{-----(12)}$$

$$= x_i L + k_i x_i V \qquad \text{-----(13)}$$

$$\sum x_i = 1 \qquad \text{-----(14)}$$

Note that this results in a set of simultaneous 5 nonlinear algebraic equations in 5 unknowns Equations

(11-14) can be written in abstract form as follows

$$f_1(x_1, x_2, x_3, L, V) = 0 \quad \text{-----(15)}$$

$$f_2(x_1, x_2, x_3, L, V) = 0 \quad \text{-----(16)}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots = 0$$

$$f_5(x_1, x_2, x_3, L, V) = 0 \quad \text{-----(17)}$$

which represent coupled nonlinear algebraic equations. These equations have to be solved simultaneously to find solution vector

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & x_3 & L & V \end{bmatrix}^T \quad \text{-----(18)}$$

The above 5 equations can also be further simplified as follows

$$x_i = z_i / \left[1 + \left(\frac{V}{F} \right)(k_i - 1) \right]$$

Using $\sum x_i = 1$, we have

$$f(V/F) = \sum \frac{zi}{1 + (V/F)(ki - 1)} - 1 = 0 \quad \text{-----(19)}$$

In general, we encounter n nonlinear algebraic equations in n variables, which have to be solved simultaneously. These can be expressed in the following abstract form

$$f_1(x_1, x_2, x_3, \ldots\ldots x_n) = 0 \quad \text{-----(20)}$$

$$f_2(x_1, x_2, x_3, \ldots\ldots x_n) = 0 \quad \text{-----(21)}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots = 0$$

$$f_n(x_1, x_2, x_3, \ldots\ldots x_n) = 0 \quad \text{-----(22)}$$

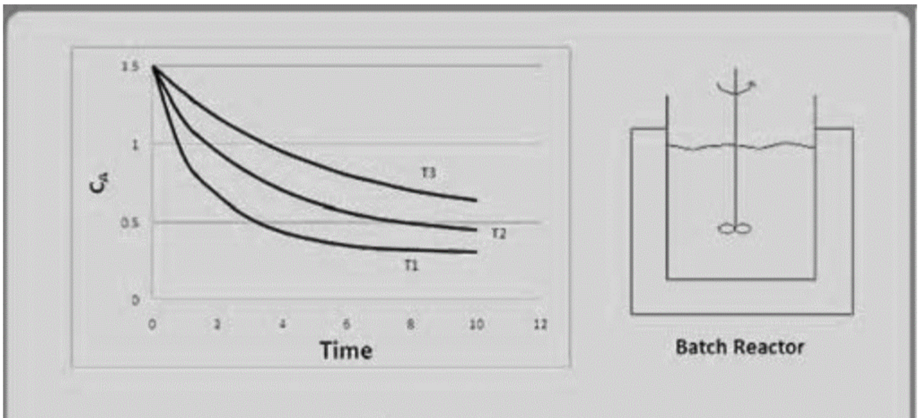

Figure 5: Batch Reactor

Using vector notation, we can write

$$F(\mathbf{x}) = \overline{0} \quad ; \quad \mathbf{x} \in R^n \quad \text{-----(23)}$$

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \ldots & x_n \end{bmatrix}^T$$

where represents zero vector. Here represents dimensional function vector defined as $\bar{0}$ $n \times 1$ $F(\mathbf{x}) \in R^n$ n

$$F(\mathbf{x}) = \begin{bmatrix} f_1(\mathbf{x}) & f_2(\mathbf{x}) & \ldots & f_n(\mathbf{x}) \end{bmatrix}^T \qquad \text{-----(24)}$$

2.3 Optimization Based Formulations

Variety of modeling and design problems in chemical engineering are formulated as optimization problems.

Example 3

Consider a simple reaction modelled using the following reaction rate equation

$$A \rightarrow B$$

modelled using the following reaction rate equation

$$-r_a = -dC_a/dt = k_o(C_a)^n \exp(\frac{-E}{RT}) \qquad \text{-----(25)}$$

Table 2: Reaction Rates at Different Temperaturtes and Concentrations in a batch experiment

Reaction Rate	Concentration	Temperature
$-r_{a1}$	C_{a1}	T_1
$-r_{a2}$	C_{a2}	T_2
....	....	....
$-r_{aN}$	C_{aN}	T_N

carried out in a batch reactor (see Figure 5). It is desired to find the kinetic parameters k_o, E and n from the experimental data. The data reported in Table 5 is collected from batch experiments in a reactor at different temperatures
Substituting these values in the rate equation will give rise to N equations in three unknowns, which forms an overdetermined set equations. Due to experimental errors in the measurements of temperature and reaction rate, it may not be possible to find a set of values of $\{k_o, E, n\}$ such that the reaction rate equation is satisfied at all the data points. However one can decide to select $\{V_O, E, n\}$ such that the quantity

$$\Phi = \sum_{i=1}^{N} \left[-r_{ai} - k_o(C_{ai})^n \exp(\frac{-E}{RT_i}) \right]^2 \qquad \text{----(26)}$$

is minimized with respect to $\{k_o, E, n\}$. Suppose we use $-\widehat{r}_{ai}$ to denote the estimated reaction rate

$$-\widehat{r}_{ai} = k_o \, C_{ai}^n \quad \exp(\frac{-E}{R * T_i}) \qquad \text{----(27)}$$

then, the problem is to choose parameters $\{k_o, E, n\}$ such that the sum of the square of errors between the measured and estimated rates is minimum, i.e.

----(28)

$$\underset{k_o, E, n}{Min} \quad \Phi(k_o, E, n) = \sum_{i=1}^{N} [-r_{ai} - (-\hat{r}_{ai})]^2$$

Example 4

Cooling water is to be allocated to three distillation columns. Up to 8 million liters per day are available, and any amount up to this limit may be used. The costs of supplying water to each equipment are

Equip. 1: $f_1 = |1 - D_1| - 1$ for $0 \leq D_1 \leq 2$

$= 0 \ (otherwise)$

Equip. 2: $f_2 = -\exp(\frac{-1}{2}(D_2 - 5)^2)$ for $0 \leq D_2 \leq \infty$

Equip. 3: $f_3 = D_3^2 - 6D_3 + 8$ for $0 \leq D_3 \leq 4$

Minimize $\Phi = \sum f_i$ to find $D_1, D_2,$ and D_3

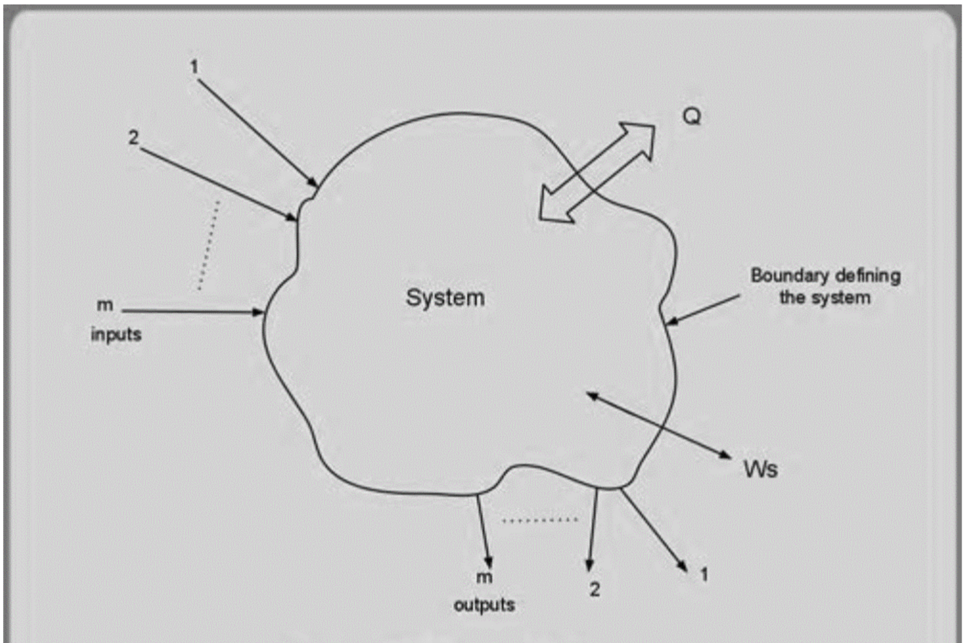

Figure 6: General System

Note that this is an example of a typical multi-dimensional optimization problem, which can be expressed in abstract form

$$\underset{\mathbf{x}}{Min} \quad \Phi(\mathbf{x}) \qquad \text{----(29)}$$

where $\mathbf{x} \in R^n$ and $f(\mathbf{x}) : R^n \rightarrow R$ is a scalar objective function. A general problem of this type may include constraints on $\mathbf{x}$ or functions of $\mathbf{x}$.

The Ordinary Differential Equations - Initial Value Problem (ODE-IVP) will be continued in lecture 2

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