

CHAPTER 2

ACETYLENE HYDROGENATION REACTOR

2.1 Introduction

Acetylene is chemically formed as a by-product during the manufacturing of ethylene. It is an undesirable contamination in polymer grade ethylene. In plant operation, the removal of this compound is very crucial for purification. In general, the most effective method for removing acetylene, down to the typical levels of 2-3 ppm, is the selection of hydrogenation over palladium catalysts in a multi-bed adiabatic reactor. The term selection of hydrogenation is used to describe the conditions leading to promotion of hydrogenation of acetylene to ethylene, as well as leading to promotion of hydrogenation of ethylene to ethane. However, it is obvious that the second reaction is highly chemically undesirable.

In some ethylene crackers, the acetylene converters are located after the cold-train where hydrogen is intentionally removed from the cracked gas. Hydrogen must be injected in to the feed before entering the converters and hydrogen concentration is considered as a control variable, as well as the inlet temperature entering the reactor beds. In some other case, the converters could be alternatively located before the cold-train.

The process for removal of acetylene in industry could be categorized into 4 types as follows:

1. Solvent absorption
2. Cracked gas train hydrogenation reactor
3. Back-end catalytic reactor: Hydrogenation of C₂ fraction of the cracked gas
4. Front-end selective catalytic reactor: Hydrogenation of C₂ or C₃ and lighter portion of the cracked gas

In chemical industry operation, the above four process types evolved and have been used over time as listed order. However, in this study, the last two systems listed above will be totally focused and studied since they are commonly accepted and widely used.

2.2 Back-End Catalytic Reactors

In this type of operation reactors, the units are commonly located after the cold-train where hydrogen is directly removed from the cracked gas. Hence, hydrogen used in the unit must come from the top ethylene rich stream of the deethanizer unit. Hydrogen must be directly injected into the feed before entering the converters. The concentration of hydrogen being injected is a control variable controlling both amount and rate of reaction occurring in the back-end catalytic reactor unit. (Nasi, 1985). Commonly, this type of reactor could also be called as a “tail-end type” of reactor in comparison with the front-end type.

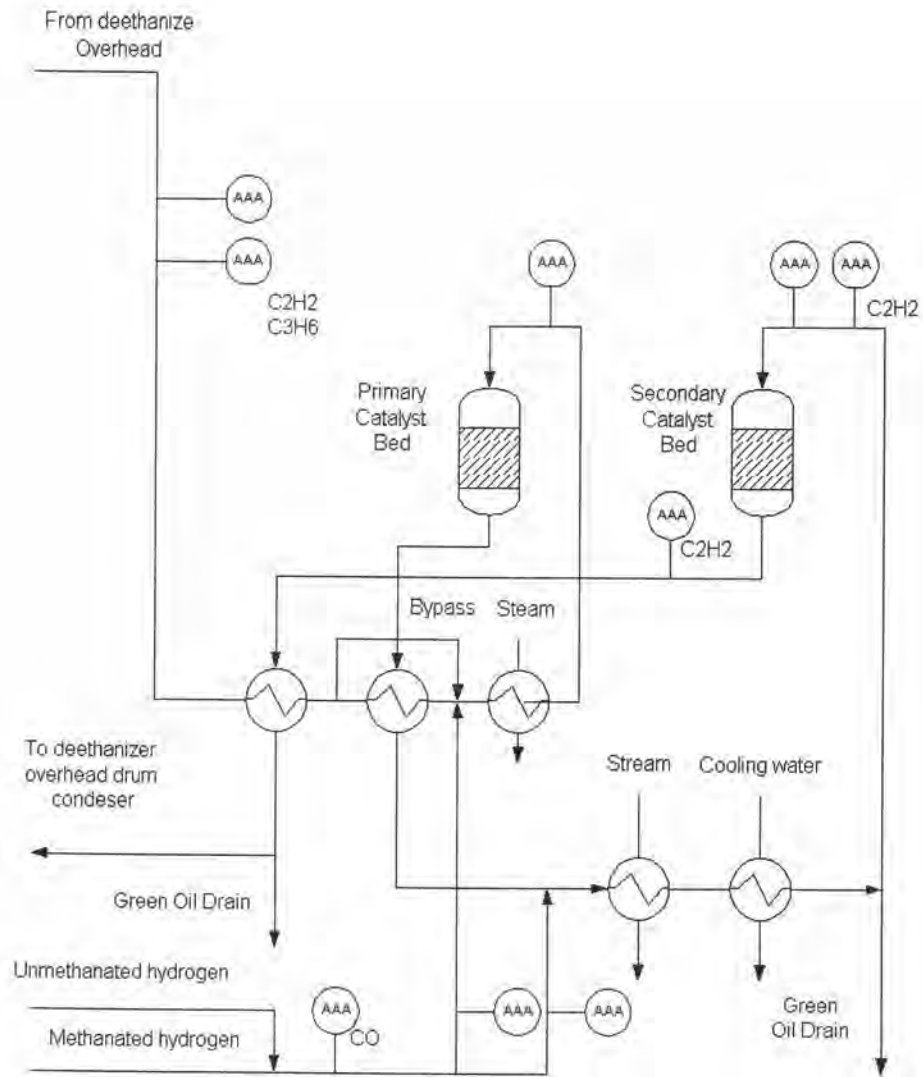
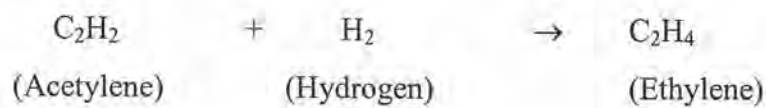


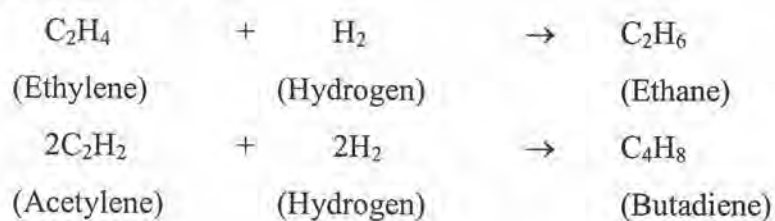
Figure 2.1 Back-end catalytic reactor

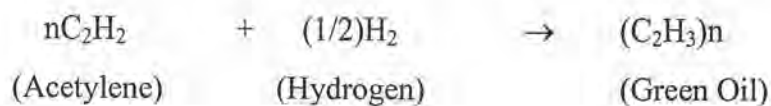
The kinetic reactions occurring in the back-end catalytic reactor could be shown as follows:

The desired reaction is:



The undesired reactions are:





The hydrogenation process is an exothermic reaction in nature. In each reaction process, products are commonly produced with heat release.

2.3 Front-End Acetylene Hydrogenation Reactors

The units are generally located prior to the cold train of the ethylene plant. Practically, they are located after the cracking section, following a caustic scrubbing treatment to remove CO_2 . This means that only the inlet temperature is available as a control variable while the cracked gas already has significant quantity of hydrogen in itself. This system, known as front-end acetylene hydrogenation, is considerably crucial to be studied in this research. The industrial step in this thesis comprised of a heater followed by three fixed bed adiabatic reactors with an inter stage cooling heat exchanger. In this unit, the hydrogenation of acetylene occurred directly in the raw cracked gas mixture, which contains high ratio of $\text{H}_2/\text{C}_2\text{H}_2$ ($\geq 100/1$).

Several acetylenic, olefin and diolefinic by-products, together with the carbon monoxide (CO) produced in the universe water-gas shift reaction are occurring in the cracked furnaces. In this system, it is commonly reported that CO is the main inhibitor of C_2H_2 hydrogenation reaction. (Wilfred, 1990)

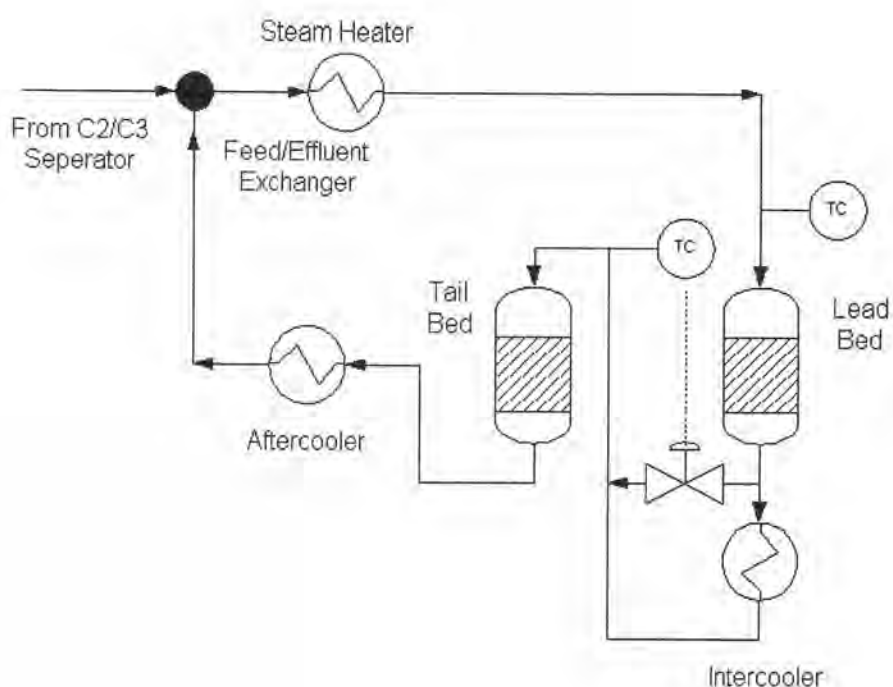
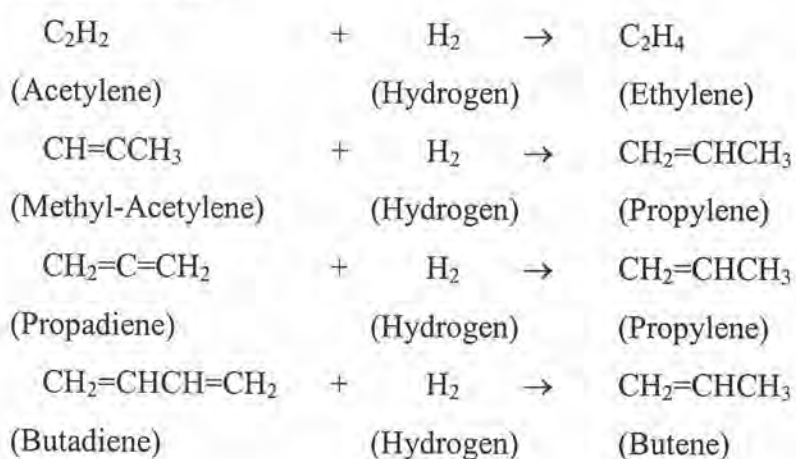


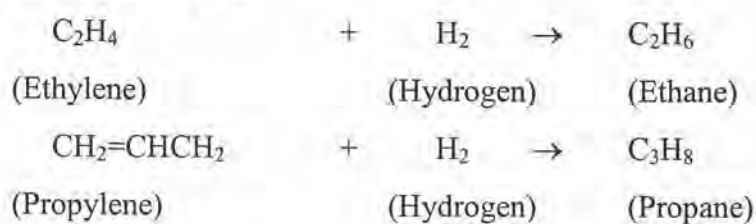
Figure 2.2 Front-end acetylene hydrogenation reactor

The kinetic reactions occurring in the front-end acetylene hydrogenation reactor could be summarized as follows:

The desired reactions are:



The undesired reactions are:



According to literatures reported in the past, most of the research on acetylene hydrogenation reactor were made on the tail-end type. For example, the study on sensitivity of the reactor has been revealed by Huang, 1979. An optimization based on a reactor model was made to minimize the ethylene loss while maintaining the outlet of acetylene specification. The conjugated gradient method was used to perform the minimization and arrived at the set of optimal operating parameters.

In addition, a general method on establishing advanced control schemes of the acetylene hydrogenation reactors has been published (Nasi, 1955). In that study, he presented crucial issue on on-line modeling and optimization of reactors in an ethylene plant.

Nevertheless, the control scheme adopted in his research was based on a static presentation of the acetylene hydrogenation system and could not examine the effects of the manipulated variables on the deactivation occurring over time, and thus the model could not calculate the catalyst regeneration requirement of the hydrogenation process. In order to overcome this problem, Brown, 1991, presented a technique of an optimal and sub-optimal operational way to minimize the ethylene loss over time.

However, in the front-end type acetylene hydrogenation reactor, very few studies have been made and reported due to that only a good number of such reactor type have been installed worldwide. For instance, a dynamic simulation of a front-end industrial acetylene converter and its closed-loop performance under three different control strategies have been reported (Schbib, 1994). In his report, the results is obtained from a mathematical model derived from fundamental equations checking against industrial data. Furthermore, he explained the kinetic model of the front-end acetylene hydrogenation reactor (Schbib, 1996) in order to make confidence that the model was more accurate. Moreover, Weiss (1996) reported results from his study on the modeling and control of an acetylene converter. The results showed that a nonlinear dynamic model of process could assist in the development of linear model suitable for controller design. It also showed that a model-based controller should be considered as a control prediction of the reactor outlet temperature in industrial acetylene converter.

2.4 Process Description

In the area of the acetylene hydrogenation reactor, it is well understood among the industrial engineers that there are four types of reactors. However, only the front-end hydrogenation reactor will be addressed and thoroughly studied. In the operation of the acetylene converter, the primary objective is to remove acetylene from the cracked gas so that its concentration is confined in the polymer-grade ethylene product. In addition, minimizing the ethylene losses in the acetylene hydrogenation reactor is the second objective.

A schematic diagram of the mentioned process could be summarized as follows:

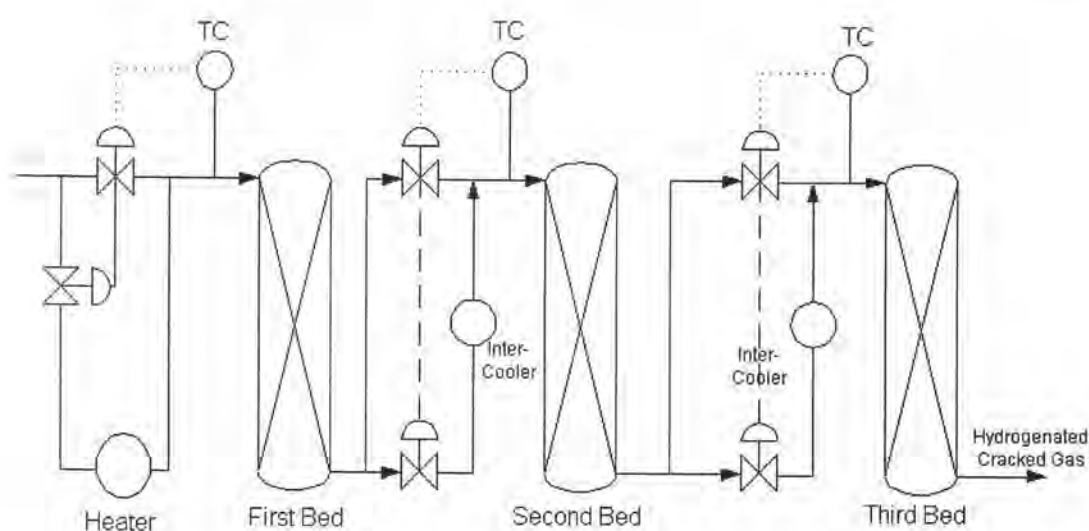


Figure 2.3 Acetylene hydrogenation reactor for TOC

In general of acetylene hydrogenation, three catalyst beds are used to hydrogenate the cracked gas. However, a total of four catalyst beds are provided practically for expanded capacity operation when ethylene production reaches a limit of 380,000 MTA, the spared reactor is then reserved for additional utilization when needed. For a normal design case, only three reactor beds with intercoolers are required. This is due to lower furnace severity with a lower acetylene concentration in the cracked gas effluent.

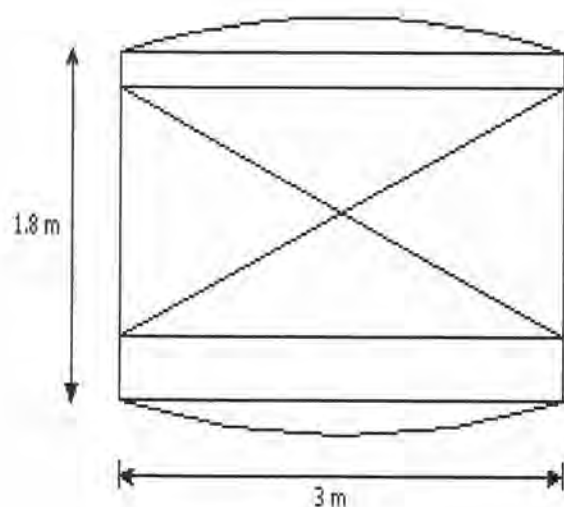


Figure 2.4 Bed Reactor

The bed reactor size is 3 meters in diameter and 1.8 meters in height. The details of the reactor are as followed

1. The volume of the reactor = 10.815 m^3
2. The volume of catalyst in reactor = 10.8 m^3
3. Pressure drop = 0.25 Kg/cm^2
4. Weight of catalyst = 11340 Kilograms

Composition analysis of the feed streams to each reactor and process effluent was carried out every 200 seconds. The on-line gas chromatographers analyze the process gas streams for acetylene, methyl acetylene, propadiene, methane, ethylene and ethane. The complete analysis on each stream was performed off-line once a day. The temperature, pressure and flow rates of the feed stream were recorded for each sample.

The normal acetylene concentration in the converter feed is 0.3 to 0.5 mole % and the acetylene specification in the ethylene product is 1 ppmv. The chemical feed to the converter (few C_3 , C_2 and lighter, and CO) comes from the mercury and arsine removal unit locating after the caustic scrubbing unit. Mercury and arsine must be removed from the cracked gas because they are poison to the palladium catalyst used for acetylene hydrogenation reactor. Depending on the catalyst activity, the clean cracked gas lets acetylene flow through the acetylene hydrogenation feed heater before entering the first acetylene hydrogenation reactor. Heat of reaction from acetylene hydrogenation reactors was removed by cooling water in the acetylene hydrogenation

inter-coolers. The pre-heater and inter-cooler heat exchangers each contain a surface area of 256.1 m^2 . The effluent from the third acetylene hydrogenation reactor was then cooled in the acetylene hydrogenation after-cooler. In overall, the cracked gas contains sufficient hydrogen to hydrogenate all acetylene to become ethylene.

2.5 Kinetics of a Catalyst Reaction

A catalyst is a substance that affects the rate of a reaction but emerges from the process unchanged. Normally, a catalyst is generally referred to one that speeds up a reaction although, a catalyst can either accelerate or slow the formation of a particular product species. A catalyst changes only the rate of reaction but does not affect the equilibrium.

2.5.1 Steps in a Catalyst Reaction

A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Figure 2.5. The overall process by which heterogeneous catalytic reactor could be broken down into the sequential steps as shown in Table 2.1 and picture in Figure 2.6

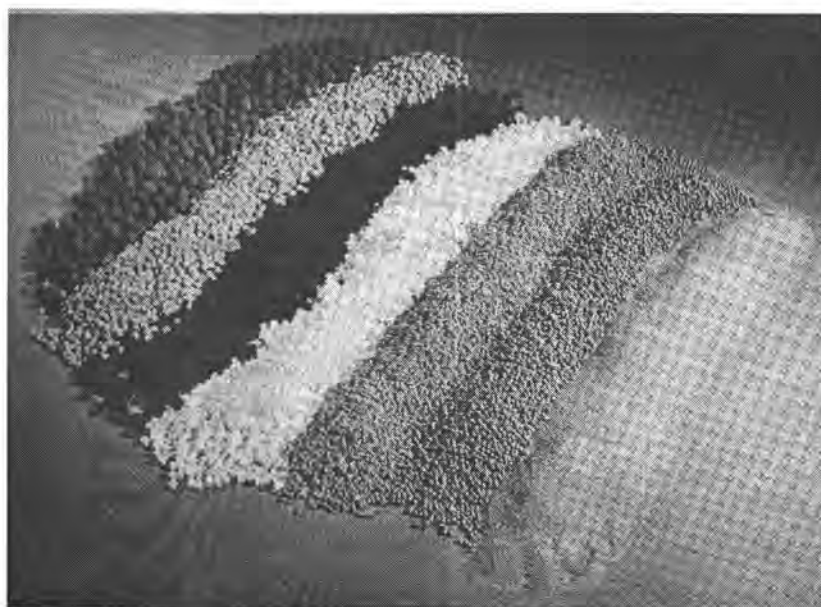


Figure 2.5 Different shapes and size of catalyst.

The overall rate of reactions equals to the rate of the slowest step in mechanism. When the diffusion steps (1, 2, 6, and 7 In Table 2.1) are very fast compare with the reaction step (3, 4, and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion step, mass transport does affect the reaction rate. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate. In porous catalysts, on the other hand, diffusion within the catalyst pores may limit the rate of reaction. Under these circumstances, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate.

There are many variations of the situation described In Table 2.1. Sometimes, of course, two reactants are necessary for a reaction to occur, and both of these may undergo the steps listed above. Other reactions between two substances have only one of them adsorbed.

Table 2.1 Steps in a catalytic reaction

1. Mass transfer (diffusion) of the reactant(s) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst
5. Desorption of the products from the surface
6. Diffusion of the products from the interior of the pellet to the pore month at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

It is assumed that the diffusion steps (1, 2, 6, and 7) are very fast, such that mass transfer does not affect the overall reaction rate.

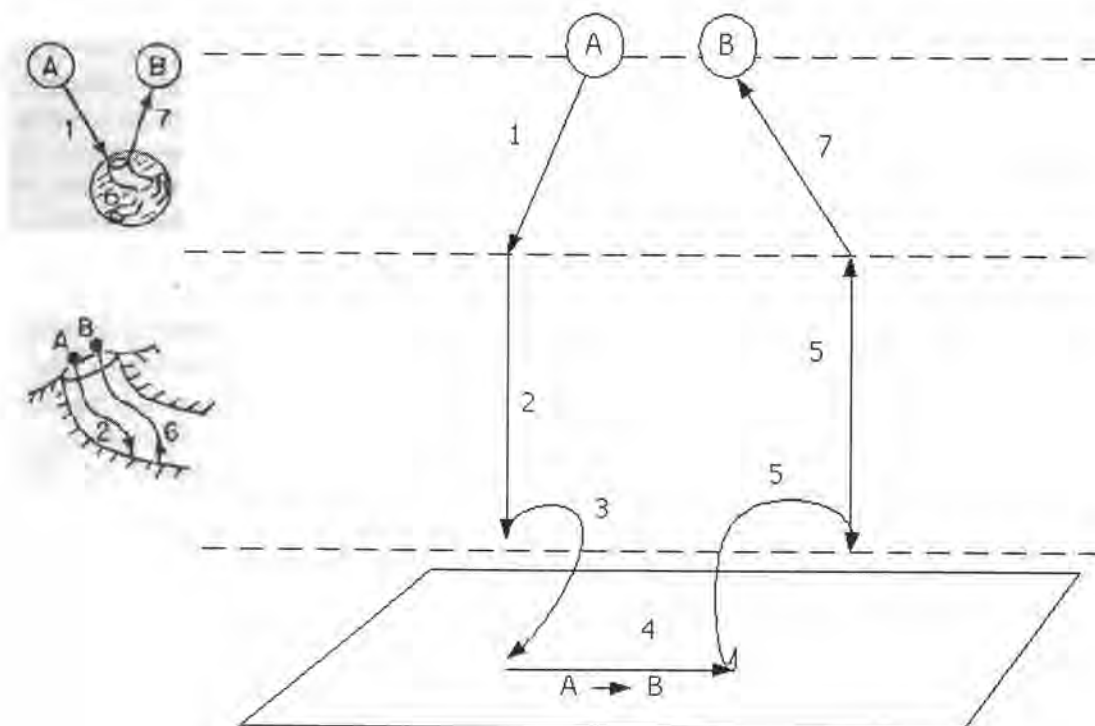


Figure 2.6 Steps in heterogeneous catalytic reaction

The mathematical model of the reactor forms set of constraints internally upon which the optimization was performed. This model is similar to ones developed in studies of the fixed bed catalytic reactors by Saurod (1998), Schbib (1994) and Schbib (1996). The accuracy and reliability of the mathematical description is dependent on the character of the mixing and the heat and mass transfer coefficients in the reactor, as well as the validity and analysis of the experimental data used to model the chemical reactions. The process fixed bed catalytic reactors were modeled in Aspen Plus Simulation Package with the plug flow reactor unit model. Oversimplification model should be avoided due to necessity in computation time although it could provide better accuracy. However, reducing the number of complex calculations by simplifying vigorous models could lead to the implementation of real time process control and optimization solutions.

Fixed bed catalytic reactors are essentially tubular reactors through which a mixture of reactant, products and inert flow through. The concentration of the reacting species is not constant throughout the reactor and varies as a function of the reactor length or axial distance.

If the processing conditions allow the tubular reactor be modeled as a plug flow reactor, the underlying characteristics of the plug flow reactor then form the basis of the assumptions made. This allows modeling of this process as a PFR in Aspen Plus Simulation Package and reduces the distributed system to the simpler lumped parameter model. The following are a list of the basic characteristics of a PFR:

1. The reactor operates in plug flow.
2. Axial and radial dispersion are negligible,
3. The “pseudo-steady state” assumption is valid since the deactivation of the catalyst is slow with respect to the reaction dynamics. Thus, the model will use a constant catalyst activity during each reactor interval as if the deactivation process was at some steady state.
4. The physical properties of the gas stream, including density, are constant along the reactor bed length.
5. The acetylene reactor has a constant sectional area.
6. The pressure drop across the reactor bed length is negligible, so that partial pressure can be substituted for mole fractions, which are available from laboratory daily data.
7. The flow through the vessel is plug flow and continuous but unnecessarily at a fixed rate.

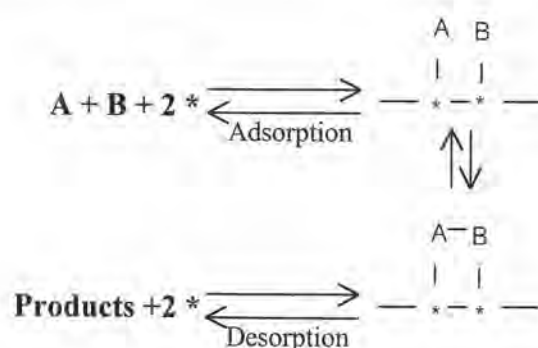
2.5.2. Langmuir-Hinshelwood Kinetics

Determination of the rate law for heterogeneous catalyst was by using a method proposed by Langmuir-Hinshelwood kinetics concept. In this concept, the adsorption equilibrium is assumed to be established at all times; for example, the rate of reaction is taken to be much less than the potential rate of adsorption or desorption. The concentrations of adsorbed species are therefore determined by adsorption equilibria as given by the Langmuir isotherm. If two or more species are present, they compete with each other for adsorption on a fixed number of active sites.

Reaction is assumed to occur between adsorbed species on the catalyst. If a single reactant is decomposed, the process may be assumed to be either unimolecular or bimolecular, depending on the number of product molecules formed per reactant molecule and whether or not the products are adsorbed. A simple decomposition in which products are not adsorbed is usually taken to be unimolecular. (Case 1). If two

adsorbed product molecules are formed for each reactant molecule decomposed, it is postulated that an empty site must be adjacent to the adsorbed reactant molecule to accommodate the additional molecule formed. The reaction is then “bimolecular” in the sense that the rate is proportional to the product of the concentration of adsorbed reactants and of empty sites.

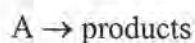
If reaction takes place between adsorbed A and adsorbed B and these species are immobile, they must be adsorbed on neighboring sites in order for reaction to occur. The mechanism may be visualized as follows, where θ_i represents the fraction of available sites on which species i is adsorbed.



The probability of reaction here is taken to be proportional to the product $\theta_A \theta_B$.

By the foregoing and analogous procedures, rate expressions can be derived for any type or postulated mechanism. The form and complexity of the expression depend on the assumptions made concerning this the mechanism. A few case are presented below:

Case 1: Decomposition, Products not adsorbed



The reaction rate is taken to be proportional to the quantity of adsorbed A molecules. Then,

$$-r, \frac{(\text{moles})}{(\text{time})(\text{area})} = k\theta_A \quad (2.1)$$

The value of θ_A is given by the Langmuir adsorption isotherm

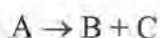
$$\theta_A = \frac{KP_A}{1 + KP_A} \quad (2.2)$$

Combining these two equations,

$$-r = \frac{kKP_A}{1 + KP_A} \quad (2.3)$$

If the system follows this model, the reaction rate should be first order at sufficiently low values of P_A . As P_A increases, the order of the reaction should gradually drop and becomes zero order. Similarly, the reaction rate should be first order if A is weakly adsorbed – for example, K is small – and zero order if A is strongly adsorbed. The type of behavior is indeed found for a number of decompositions.

Case 2. Decomposition, Products Adsorbed



Assume:

1. A, B, C all may be appreciably adsorbed.
2. The reaction rate is proportional to the quantity of adsorbed A molecules.
3. No dissociation of molecules occurs on adsorption.
4. Reverse reaction is negligible.

Again using the Langmuir adsorption isotherm, the fractions of surface covered by A, B and C can be derived from the adsorption/desorption equilibrium to be as follows:

$$k_A [1 - \sum \theta] P_A = k'_A \theta_A$$

where $\sum \theta$ is the fraction of available sites covered with A, B and C.

$$\theta_A = K_A P_A [1 - (\theta_A + \theta_B + \theta_C)] = K_A P_A (1 - \sum \theta) \quad (2.4)$$

$$\theta_B = K_B P_B (1 - \sum \theta) \quad (2.5)$$

$$\theta_C = K_C P_C (1 - \sum \theta) \quad (2.6)$$

Addition equation (2.4), (2.5) and (2.6),

$$\sum \theta = (1 - \sum \theta) [K_A P_A + K_B P_B + K_C P_C] \quad (2.7)$$

Subtracting both sides of equation (2.7) from unity and rearranging,

$$(1 - \sum \theta) = \frac{1}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (2.8)$$

Two modules are formed for each one that reacts, and both product molecules are postulated to be adsorbed. It thus seems plausible that it is necessary for an empty site to be present adjacent to the reacting molecule to accommodate one of the product molecules.

In that event

$$-r = k\theta_A(1 - \sum \theta) \quad (2.9)$$

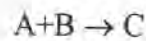
Combining equation (2.4), (2.8) and (2.9) gives

$$-r = \frac{kK_A P_A}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (2.10)$$

If an inert material X is present that is significantly adsorbed, then a term $K_X P_X$ must be added in the denominator, and equation (2.10) would become

$$-r = \frac{kK_A P_A}{(1 + K_A P_A + K_B P_B + K_C P_C + K_X P_X)^2} \quad (2.11)$$

Case 3. Bimolecular Reaction



The same assumption as in Case 2 are made except that the reaction rate now is assumed to be proportional to the product of the concentration of adsorbed A and adsorbed B. The rate expression then becomes.

$$-r = k\theta_A \theta_B \quad (2.12)$$

Combining equation (2.4), (2.5), (2.7), (2.12) gives

$$-r = \frac{kK_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C + K_X P_X)^2} \quad (2.13)$$

Case 4. Adsorption/Desorption with Dissociation



Assume that A dissociates upon adsorption and associates on desorption. In order for dissociation to occur, a gas molecule must plausibly impinge on the surface at a location where two sites are adjacent to one another. Up to fairly high fractional coverage, the number of pairs of adjacent sites is proportional to the square of the number of single sites. Then the rate of adsorption is given by

$$\left(\frac{dn}{dt}\right)_{\text{ads}} = kP_A(1 - \theta_A)^2 \quad (2.14)$$

where P_A is the pressure of the undissociated A. Assuming desorption involves interaction of two neighboring adsorbed atoms.

$$\left(\frac{dn}{dt}\right)_{\text{des}} = k'\theta_A^2 \quad (2.15)$$

At equilibrium, $kP_A(1 - \theta_A)^2 = k'\theta_A^2$ and

$$\theta_A = \frac{(K_A P_A)^{1/2}}{1 + (K_A P_A)^{1/2}} \quad (2.16)$$

This simple equation applies to mobile adsorbed atoms at all degrees of surface coverage or to immobile adsorbed atoms at small values of θ_A . At high coverage, some unused single sites exists in the “fully covered” region, and they are not available for chemisorbing a molecule as atoms if adsorbed atoms are immobile. The exact equation for any case depends on whether or not individual atoms are mobile and the extent of coverage.

The rate of reaction might plausibly be either first order or second order with respect to dissociated A, depending on circumstances.

If $-r = k\theta_A$, upon substituting in equation (2.16)

$$-r = \frac{k(K_A P_A)^{1/2}}{1 + (K_A P_A)^{1/2}} \quad (2.17)$$

Alternately,

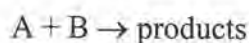
$$-r = k\theta_A^2 = \frac{kK_A P_A}{\left[1 + (K_A P_A)^{1/2}\right]^2} \quad (2.18)$$

If two atoms of dissociated A react simultaneously with B, and product adsorption is negligible, then

$$-r = k\theta_A^2 = \frac{kK_A P_A K_B P_B}{\left[1 + \sqrt{K_A P_A} + (K_B P_B)\right]^2} \quad (2.19)$$

The most common example of dissociative adsorption is encountered with hydrogen on most metals. However, hydrogenation reactions are frequently approximately first order with hydrogen rather than half orders. Equation (2.19) shows that even if the hydrogen dissociated, a first-order process with respect to hydrogen (for example, A) will be observed if it is not strongly adsorbed relative to B ($K_A < K_B$). Plausibly, hydrogen atoms may add to B one at a time, one of the additions begin at equilibrium and the addition of the other begin the rate limiting process. Assume, for example, that the first addition, to form adsorbed HB, is in equilibrium and the reaction $HB + H \rightarrow C$ is the rate limiting step. Assume further that that concentration of adsorbed HA is small, and that of adsorbed C is negligible. Then the rate expression is of the identical form of equation (2.19), except that a term $k'K$ replaces k . Here k' is the rate constant for the rate limiting process and K is an equilibrium constant in terms of concentrations of surface-adsorbed species.

Case 5. Adsorption of two gases on separate sites



In this case, A and B molecules are assumed to adsorb independently on different sites. Applying the usual assumptions,

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A} \quad (2.20)$$

$$\theta_B = \frac{K_B P_B}{1 + K_B P_B} \quad (2.21)$$

If the reaction rate is proportional to the product of adsorbed A and B molecules and sites are randomly distributed,

$$-r = \frac{kK_A P_A K_B P_B}{(1 + K_A P_A)(1 + K_B P_B)} \quad (2.22)$$

This type of behavior appears to be less common than competition for the same type of site, but it may be a plausible formalism to apply where the catalyst clearly has two kinds of sites, e.g., some dual function catalysts. The behavior of some systems suggests a mixture of independent adsorption and competition adsorption.

In this study, the main reactions involved in a acetylene hydrogenation processes are as follows: (Godinez *et al.*, 1996)

1. Alkynes and diolefins hydrogenation

Acetylene Hydrogenation



Methyl Acetylene Hydrogenation



Propadiene Hydrogenation



2. Olefins Hydrogenation

Ethylene Hydrogenation



Most kinetic results are given in a power rate equation from with hydrogen and acetylene concentration are as the only variables. Some researchers find that the rate of acetylene hydrogenation is zero order in acetylene and first order in hydrogen (McGown *et al.*, 1977, Moses *et al.*, 1984, Weiss, 1996). However, the rate order in hydrogenation depends on the reaction temperature. For example, the first order in hydrogen is valid for hydrogenation at 0 - 30 °C, whereas a reaction order of 1.14 is recorded at 125 °C (Bond and Wells, 1965).

The derived of the kinetic model used in this study derived from Wilfred K. Lam (1990) which posses the following details:

Let c_1, c_2, \dots, c_n be the surface concentration of n species adsorbed on the catalyst surface in the reactor and x_1, x_2, \dots, x_n be the corresponding concentration in gaseous phase. Let C_t be the total surface concentration of all the species if they were all adsorbed on the catalyst. Let C_v be the vacant surface concentration. By definition

$$C_v = C_t - \sum_{j=1}^n c_j \quad (2.23)$$

Let the adsorption rate of j th species be R_{aj}

$$R_{aj} = k_{aj} C_v x_j - k_{dj} c_j \quad (2.24)$$

and define the equilibrium constant for adsorption description, K_j , as

$$K_j = \frac{k_{aj}}{k_{dj}} \quad (2.25)$$

where k_{aj} and k_{dj} are the adsorption and desorption rate constants.

At equilibrium, $R_{aj} = 0$, and

$$K_j \left(C_t - \sum_{j=1}^n c_j \right) x_j - c_j = 0 \quad (2.26)$$

$$c_j = K_j \left(C_t - \sum_{j=1}^n c_j \right) x_j \quad (2.27)$$

By summing j from 1 to n in equation (2.27) we then have,

$$\sum_{j=1}^n c_j = \left(C_t - \sum_{j=1}^n c_j \right) \sum_{j=1}^n K_j x_j \quad (2.28)$$

$$\sum_{j=1}^n c_j + \left(\sum_{j=1}^n c_j \right) \left(\sum_{j=1}^n K_j x_j \right) = C_t \sum_{j=1}^n K_j x_j \quad (2.29)$$

Rearranging equation (2.29) gives

$$\sum_{j=1}^n c_j = \frac{C_t \sum_{j=1}^n K_j x_j}{1 + \sum_{j=1}^n K_j x_j} \quad (2.30)$$

Substituting equation (2.30) into equation (2.27) gives

$$c_j = \frac{K_j C_t x_j}{1 + \sum_{j=1}^n K_j x_j} \quad (2.31)$$

There are four possible pairs of reaction in the catalytic hydrogenation reaction. They are the reactions between:

- Adsorbed hydrogen and adsorbed jth species
- Adsorbed hydrogen and gaseous jth species
- Gaseous hydrogen and adsorbed jth species
- Gaseous hydrogen and gaseous jth species

Denoting their respective reactive rate to be R_{1j} , R_{2j} , R_{3j} , R_{4j} , the reaction rate of jth species may be written as

$$R_j = R_{1j} + R_{2j} + R_{3j} + R_{4j} \quad (2.32)$$

where:

$$R_{1j} = k_{1j} c_1^{a1} c_j^{b1} \quad (2.33)$$

$$R_{2j} = k_{2j} c_1^{a2} c_j^{b2} \quad (2.34)$$

$$R_{3j} = k_{3j} c_1^{a3} c_j^{b3} \quad (2.35)$$

$$R_{4j} = k_{4j} c_1^{a4} c_j^{b4} \quad (2.36)$$

and k_{1j} , k_{2j} , k_{3j} , k_{4j} are the reaction rate constants and a_1 , a_2 , a_3 , a_4 , b_1 , b_2 , b_3 , b_4 are empirical parameters.

Substituting equation (2.31) into equation (2.32) and (2.33) through (2.36) gives

$$\begin{aligned}
 R_j = & k_{1j} K_1^{a_1} K_j^{b_1} \left(\frac{C_t}{1 + \sum_{j=1}^n K_j X_j} \right)^{(a_1+b_1)} X_1^{a_1} X_j^{b_1} + \\
 & k_{2j} K_1^{a_2} \left(\frac{C_t}{1 + \sum_{j=1}^n K_j X_j} \right)^{a_2} X_1^{a_2} X_j^{b_2} + \\
 & k_{3j} K_1^{a_3} \left(\frac{C_t}{1 + \sum_{j=1}^n K_j X_j} \right)^{b_3} X_1^{a_3} X_j^{b_3} + k_{4j} X_1^{a_4} X_j^{b_4}
 \end{aligned} \tag{2.37}$$

Equation (2.37) represents the most general case in the hydrogenation reactions in the catalytic reactor. To apply this equation to an industrial acetylene reactor requires simplification and modification of the equation. The value of equation (2.37) lies in that it gives a starting form of reaction rate equation for a series of complex reactions occurring in the catalytic hydrogenation of reaction mixture, and inert species that were absorbed on the catalyst surface.

It is also noted that all the constants in equation (2.37) happened with respect to concentrations. They are temperature dependant. Industrial acetylene reactors are mostly adiabatic and the temperature profile along the reaction length is not constant. Assumptions based on practical experience and empirical correlation of plant data are necessary to arrive at an equation for practical purpose.

The numerical values for constants in equation (2.37) were developed based on extensive plant operation data available from Braun-built front-end reactors. As a result, equation (2.37) was simplified to obtain a set of rate equations that forms the basis of Bruan's reaction kinetic model.

Applying to a C_3 and lighter front-end reactor, one could reach a conclusion that there are six species in the kinetic model. The species are Hydrogen, Acetylene, Ethylene, Methyl Acetylene, Propadiene and Carbon monoxide. Their concentrations were denoted by the following symbols:

z = hydrogen concentration

v = acetylene concentration

w = ethylene concentration

y = methyl acetylene concentration

u = Propadiene concentration

x = carbon monoxide concentration

The reaction rate equations are given by the following:

$$R_v = K_{C_2H_2} f_v e^{\frac{E_v}{RT}} z^{a_1} v^{b_1} \quad (2.38)$$

$$R_w = K_{C_2H_4} f_w e^{\frac{E_w}{RT}} z^{a_2} w^{b_2} \quad (2.39)$$

$$R_y = K_{MA} f_y e^{\frac{E_y}{RT}} z^{a_3} y^{b_3} \quad (2.40)$$

$$R_u = K_{PD} f_u e^{\frac{E_u}{RT}} z^{a_4} u^{b_4} \quad (2.41)$$

where $a_1, a_2, a_3, a_4, b_1, b_2, b_3, b_4$ are parameters independent of temperature as well as concentrations. $f_v, f_w, f_y, f_u, E_v, E_w, E_y, E_u$ are related to Arrhenius type of rate equations. $K_{C_2H_2}, K_{C_2H_4}, K_{MA}, K_{PD}$ are factors involving adsorbing on the catalyst surface. They are given by the following:

$$K_{C_2H_2} = \frac{(A_{v1} + A_{v2}z + A_{v3}v + A_{v4}y + A_{v5}u + A_{v6}x)^{m_1}}{K} \quad (2.42)$$

$$K_{C_2H_4} = \frac{(A_{w1} + A_{w2}z + A_{w3}v + A_{w4}y + A_{w5}u + A_{w6}x)^{m_2}}{K} \quad (2.43)$$

$$K_{MA} = \frac{(A_{y1} + A_{y2}z + A_{y3}v + A_{y4}y + A_{y5}u + A_{y6}x)^{m_3}}{K} \quad (2.44)$$

$$K_{PD} = \frac{(A_{u1} + A_{u2}z + A_{u3}v + A_{u4}y + A_{u5}u + A_{u6}x)^{m_4}}{K} \quad (2.45)$$

$$K = (B + K_z z + K_v v + K_w w + K_y y + K_u u + K_x x)^m \quad (2.46)$$

Where:

$K_z, K_v, K_w, K_y, K_u, K_x$ are the equilibrium constants defined in Equation (2.25).

B and all the A s and m s are empirical parameters.

However, Saurod (1998) had developed and concluded the kinetic model into 12 types. The important variables on the criteria of model selected were the temperature and acetylene concentration since temperature effects the rate of reaction, physical and chemical properties of the process. While acetylene concentration was the control variable of the process.

1. The rate-limiting step is a surface rate of reaction.

The rates of the reactions are

$$-r_{Ac} = k_{Ac} \theta_{Ac} \theta_{H_2} \quad (2.47)$$

$$-r_{Eth} = k_{Eth} \theta_{Eth} \theta_{H_2} \quad (2.48)$$

$$-r_{MA} = k_{MA} \theta_{MA} \theta_{H_2} \quad (2.49)$$

$$-r_{PD} = k_{PD} \theta_{PD} \theta_{H_2} \quad (2.50)$$

2. The hydrogen breaks into free atoms
3. The product is not adsorbed on the catalytic surface
4. The catalyst activity is

$$\text{activity} = 1 / (1 + K_{\text{activity}} \sum A_c) \quad (2.51)$$

Use the Langmuir-Henshelwood kinetic concept will obtain

$$\theta_{Ac} = K_{Ac} C_{Ac} (1 - \sum \theta) \quad (2.52)$$

$$\theta_{Eth} = K_{Eth} C_{Eth} (1 - \sum \theta) \quad (2.53)$$

$$\theta_{H_2} = (K_{H_2} C_{H_2})^2 (1 - \sum \theta) \quad (2.54)$$

$$\theta_{MA} = K_{MA} C_{MA} (1 - \sum \theta) \quad (2.55)$$

$$\theta_{PD} = K_{PD} C_{PD} (1 - \sum \theta) \quad (2.56)$$

$$\theta_{CO} = K_{CO} C_{CO} (1 - \sum \theta) \quad (2.57)$$

$$\sum \theta = \theta_{Ac} + \theta_{Eth} + \theta_{H_2} + \theta_{MA} + \theta_{PD} + \theta_{CO} \quad (2.58)$$

$$\begin{aligned} \sum \theta = (1 - \sum \theta) & (K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H_2} C_{H_2})^{0.5} \\ & + K_{MA} C_{MA} + K_{PD} C_{PD} + K_{CO} C_{CO}) \end{aligned} \quad (2.59)$$

In comparison with others $K_{MA} C_{MA}$ and $K_{PD} C_{PD}$ are very small, thus it can be ignored (Schbib et al, 1996)

$$\sum \theta = (1 - \sum \theta) (K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H_2} C_{H_2})^{0.5} + K_{CO} C_{CO}) \quad (2.60)$$

$$(1 - \sum \theta) = 1 / (1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO}) \quad (2.61)$$

Replacing θ_{Ac} , θ_{Eth} , θ_{MA} , θ_{PD} and θ_{H2} in the rate equations. One could obtain (Schbib *et. al*, 1994)

$$-r_{Ac} = \frac{k_{Ac} K_{Ac} C_{Ac} (K_{H2} C_{H2})^{0.5}}{(1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO})^2} \quad (2.62)$$

$$-r_{Ac} = \frac{K_1 C_{Ac} C_{H2}^{0.5}}{(1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO})^2} \quad (2.63)$$

and

$$-r_{Eth} = \frac{K_2 C_{Eth} C_{H2}^{0.5}}{(1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO})^2} \quad (2.64)$$

$$-r_{MA} = \frac{K_4 C_{MA} C_{H2}^{0.5}}{(1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO})^2} \quad (2.65)$$

$$-r_{PD} = \frac{K_5 C_{PD} C_{H2}^{0.5}}{(1 + K_{Ac} C_{Ac} + K_{Eth} C_{Eth} + (K_{H2} C_{H2})^{0.5} + K_{CO} C_{CO})^2} \quad (2.66)$$

Where:

K_{Ac} = adsorption equilibrium constant of acetylene

K_{Eth} = adsorption equilibrium constant of acetylene

K_{H2} = adsorption equilibrium constant of acetylene

K_{CO} = adsorption equilibrium constant of acetylene

k = reaction rate constant

C_{Ac} = acetylene concentration

C_{Eth} = ethylene concentration

C_{H2} = hydrogen concentration

C_{MA} = Methyl Acetylene concentration

C_{PD} = propadiene concentration

On which the parameter estimation is given in Table 2.2

Table 2.2 The solute parameter values from dynamic parameter estimation (Saurod, 1998)

Parameter type	Value
K_1	4.6512E11
K_2	1.8857E13
K_4	5.1204E11
K_5	6.4480E24

Table 2.3 Equilibrium Constant values for the rate equation (Saurod, 1998)

K ($m^3/kmol$)	Log (A)	E (kcal/gmol)
K_{H_2}	20.2	21.22
K_{CO}	13.6	9.95
K_{Eth}	0.26	0.005
K_{Ac}	-16	0.001

Where:

A = pre-exponential factor in Arrhenius expression

E = activation energy in Arrhenius expression

From literature review, the initial step of mathematically modeling the kinetics of acetylene hydrogenation consisted of a consultation of the literature in order to find a starting proposal of the model. However, literature about acetylene hydrogenation in the presence of palladium catalysts gives a rather contradictory picture of the kinetic parameters. Most kinetic results are given in a power rate equation form with hydrogen and acetylene pressure as the only variables. Many authors like McGown et al, (1977) and Mosses et al. (1984) found that the rate of acetylene hydrogenation is zero order in acetylene and first order in hydrogen. Other authors (e.g., Sheridan (1945) and Bond and Wells (1965)) stated that the reaction order with respect to acetylene is -0.5 or more

negative. Aduriz et al. (1990) found that the reaction order with respect to acetylene was dependent on the palladium dispersion. At low dispersion was zero order, whereas at high dispersion the reaction order decreased to -0.5 . The negative reaction order in acetylene is said to reflect the strong absorption of acetylene on the catalyst surface.

The reaction order in hydrogen has also been a subject of many debates. Bond and Wells (1965), for example, found that first-order in hydrogen was valid for hydrogenation at $0-30$ °C, whereas a reaction order of 1.4 was recorded at 125 °C. Aduriz et al. (1990), however, found a reaction order of 1.3-1.6 even at 15 °C and found this reaction order to be independent of the dispersion of palladium.

Many authors (e.g., Margitfalvi et al. (1980, 1981)) reported that the rate of hydrogenation of acetylene increases in the presence of even a small excess of ethylene. This influence has not been taken into consideration by the power rate equations published.

Only a few authors have reported their kinetic results in a Langmuir-Hinshellwood rate equation. Among them are Cremer et al. (1941) in an early work from 1941 and Tamaru (1950) in a work from 1950. The reason for the dominating use of the power rate equation may be the fact the acetylene is strongly adsorbed on the catalyst. On the other hand, a power rate equation cannot describe the possibility that the rate of hydrogenation passes a maximum value, when increasing the acetylene pressure.

Margitfalvi et al. (1980,1981) and LeViness et all (1984) found a maximum value of the hydrogenation rate for an acetylene partial pressure of about 0.1 kPa at a total pressure of 101.3 kPa and in the presence of an excess of hydrogen. The maximum was found in experiments between 0 and 42 °C (LeViness et al., 1984), and it may be seen from the data that the activation energy is higher after the rate maximum than before. The data, moreover, show a decrease in reaction order in acetylene from about first order before the maximum rate value to reaction order -0.5 after this maximum. The fact that the reaction rate has a clear maximum value as a function of the starting acetylene pressure has not resulted in any revised rate equation. It should be noted, in connection with this, that Moyes et al. (1989) recently found that the initial reaction rate when increasing the acetylene partial pressure did not continuously pass a maximum value, but instead dropped sharply with a corresponding change of the reaction order in acetylene from a positive to a slightly negative value. The activation energy was also

shown to be quite different, parallel to this sharp change of the rate of reaction. The phenomenon was supposed by the authors to be interpretable on the basis of two different modes of packing the adsorbed acetylene molecules on the catalyst surface.

This conclusion allows us to establish that the adsorption of acetylene is known to give rise to different adsorbed species, but little is known about the hydrogenation kinetics of these species. Moreover, acetylene has also been found to hydrogenate both on metallic active sites and on a hydrocarbon overlayer (Thomas and Webb (1976) and Brendt et al. (1983)), and very little is known about the possible difference in kinetics between these two reactions routes.

Although, Schbib et al. (1996) modeled their rate equations using a Langmuir-Hinshelwood model, it was found that the desorption rates of ethylene, ethane and acetylene are negligible. Consequently they selected a model that incorporated only the effects of CO and H₂ on the number of free surface sites. However, due to rate modeling inadequacies, positive values were obtained for CO and H₂ adsorption energies. This is inconsistent with the expectation that adsorption which is highly exothermic should decrease when temperature increases. Due to difficulties in expressing hydrogenation rates using a Langmuir-Hinshelwood model, it was decided to incorporate the effects of surface interactions into a power-law model by solving for a process determined kinetic reaction rate. Furthermore, process data for six months exhibited a constant CO:H₂ ratio. Board operators closely monitor CO at the plant and sudden increases are compensated for by an increase in temperature. Therefore the role of CO on acetylene hydrogenation was not included.

2.6 Catalyst Deactivation

The observed deactivation of a porous catalyst pellet is dependent on a number of factors: the actual decay reactions, the presence or absence of pore diffusion for reacting species and poisons, the way poisons act on the surface, etc.

- **Decay Reaction**

Decay can occur in four ways, first, the reactant may produce a side product, which deposits on and deactivates the surface. This is called parallel deactivation. Secondly, the reaction product may decompose or react further to produce a material, which then deposits on and deactivates the surface. This is called series deactivation.

Thirdly, an impurity in the feed may deposit on and deactivate the surface. This is called side-by-side deactivation.

The key difference in these three forms of decay reaction is that the deposition depends respectively on the concentration of reactant, product, and some other substance in the feed. Since the distribution of these substances will vary with position in the pellet, the location of deactivation will depend on which decay reaction is occurring.

A fourth process for catalyst decay involves the structural modification or sintering of the catalyst surface caused by exposure of the catalyst to extreme conditions. This type of decay is dependent on the time that the catalyst spends in the high temperature environment, and since it is unaffected by the materials in the gas stream we call it independent deactivation.

- **Pore Diffusion.**

For a pellet, pore diffusion may strongly influence the progress of catalyst decay. First consider parallel deactivation. By knowing that reactant may either be evenly distributed throughout the pellet ($mL < 1$ and $\varepsilon = 1$) or may be found close to the exterior surface ($mL > 1$ and $\varepsilon < 1$). Thus the poison will be deposited in a like manner; uniformly for no pore resistance, and at the exterior for strong pore resistance. In the extreme of very strong diffusional resistance a thin shell at the outside of the pellet becomes poisoned. This shell thickens with time and the front moves inward. We call this the shell model for poisoning.

On the other hand, consider series deactivation. In the regime of strong pore resistance the concentration of product R is higher within the pellet than at the exterior. Since R is the source of the poison, the latter deposits in higher concentration within the pellet interior. Hence we can have poisoning from the inside out for series deactivation.

Finally, consider side-by-side deactivation. Whatever the concentration of reactants and products may be, the rate at which the poison from the feed reacts with the surface determines where it deposits. For a small rate constant the poison penetrates, the pellet uniformly and deactivates all elements of the catalyst surface in the same way. For a large rate constant poisoning occurs at the pellet exterior, as soon as the poison reaches the surface.

The above discussion shows that the progress of deactivation may occur in different ways depending on the type of decay reaction occurring and on the value of a

pore diffusion factor. For parallel and series poisoning the Thiele modulus for the main reaction is the pertinent pore diffusion parameter, for side-by-side reactions the Thiele modulus for the deactivation is the prime parameter.

Non-isothermal effects within pellets may also cause variations in deactivation with location, especially when deactivation is caused by surface modifications due to high temperatures.

Figure 2.7 summarizes this discussion by showing the various ways that the surface can be deactivated.

- **Form of Surface Attack by Poison.**

Consider an element of active catalyst surface in a reactive gas environment. The active sites of this surface may be immobilized in distinctly different ways. On one hand, this may take place uniformly; in other words all sites, the very active and the slightly active, are attacked indiscriminately. On the other hand, it may be that the more active sites are preferentially attacked and immobilized. Let us call these cases homogeneous site-attack and preferential site-attack.

Homogeneous site-attack is representative of poisoning by physical deposition on the surface, such as fouling. On the other hand, preferential site-attack is likely to occur during chemisorption of small amounts of poisons.

In homogeneous site attack another factor may be at work. If the physical deposition produces a growing porous layer the activity may decrease gradually as reactant experiences increasing difficulty in diffusing through this thickening layer.

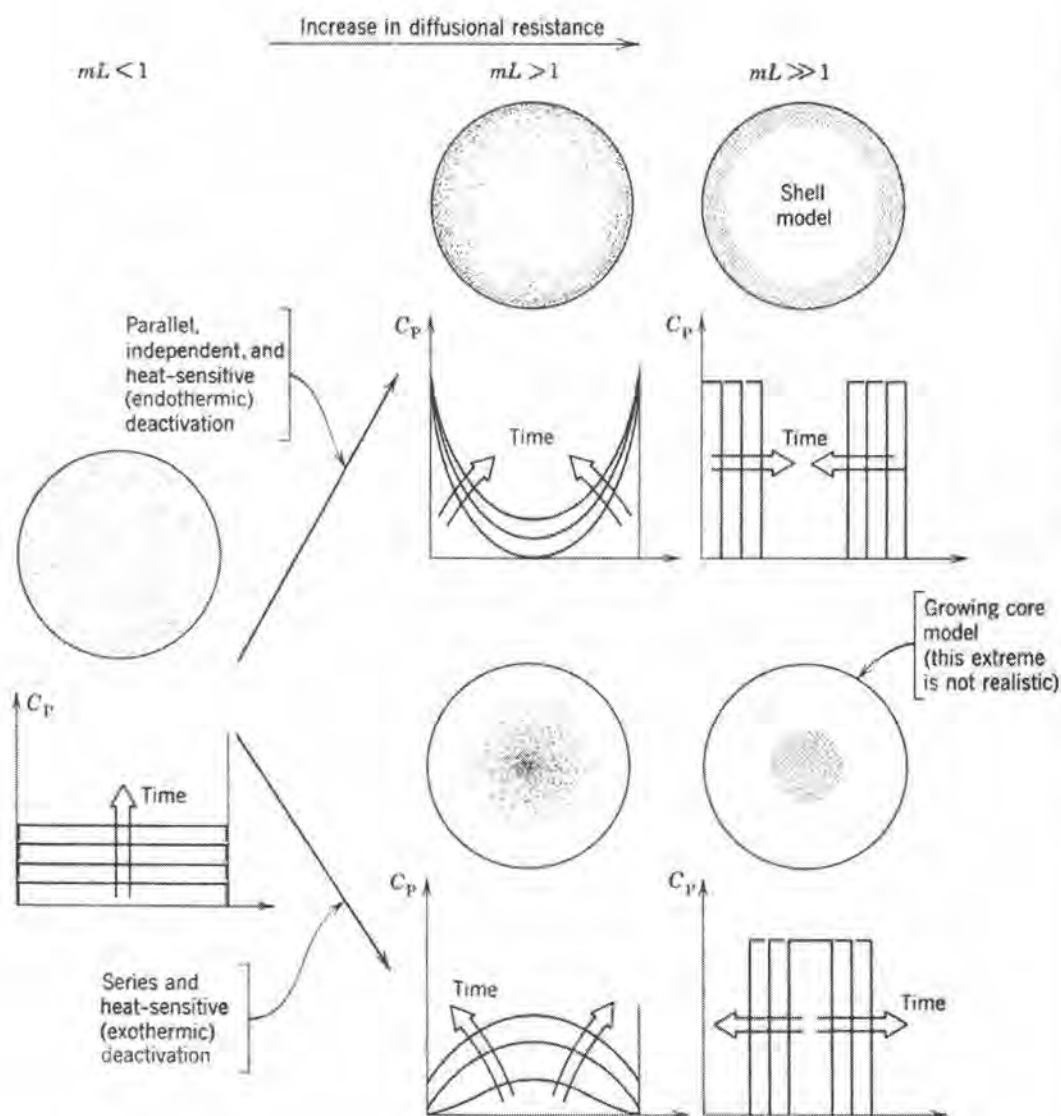


Figure 2.7 Location of poison deposit is influenced by the diffusional effect and by the type of decay reaction.

- **Additional Factors Influencing Decay.**

Numerous other factors may influence the observed change in activity of catalyst. These include pore mouth blocking by deposited solid, equilibrium or reversible poisoning where some activity always remains, the action of regeneration (this often leaves catalyst with an active exterior but inactive core).

Most important of all, the observed deactivation may result from a number of processes at work simultaneously; for example, the speedy immobilization of the most

active sites by P_1 which will not attack the less active sites, and then the slower attack of the remainder of the sites by P_2 .

Although the possible influence of all these factors should be examined in the real case, in this introductory treatment we will concentrate on the first two factors: the decay reaction and pore diffusion. There are enough lessons here to illustrate how to approach the more complete problem.

The mechanism responsible for catalyst deactivation in the acetylene hydrogenation process is fouling or coking. Deactivation occurs when carbonaceous residues from the reactants, products or intermediate are deposited on the catalyst surface. The mechanism of coke deposition is a very complex multi-step reaction sequence. The reaction path may consist of adsorption, dehydrogenation, condensation-polymerization, or cyclization of hydrogen-deficient intermediates. Gas-phase reactions may lead to coke via free radical reactions.

Larsson (1995) investigated the decrease in selectivity of ethylene formation, during acetylene hydrogenation, on palladium catalysts. It was found that the change in selectivity was not an effect of coke concentration. Instead, a low surface coverage of hydrogen resulted in less overall coke formation, but the coke was more harmful and affected the selectivity for ethylene formation negatively. It was therefore proposed that the coke was formed via the half-hydrogenated surface species, C_2H_3 . This surface intermediate may either be hydrogenated and form ethylene or in the case of a low hydrogen surface coverage, react with other species on the surface and form coke and coke precursors. At low surface coverage of hydrogen, the coke formation would be suppressed because the formation of the half-hydrogenated species would be the rate-limiting step. At higher hydrogen coverage, the formation of coke precursors would be reduced because the half-hydrogenated species would react with hydrogen and form ethylene. Although a number of studies have dealt with the modeling of catalyst deactivation in tail end acetylene hydrogenation processes, very few have focused on the front end hydrogenation process.

The activity of a catalyst pellet at any time is defined as:

$$a = \frac{\text{rate at which the pellet converts reactant A}}{\text{rate of reaction of A with fresh pellet}} = \frac{-r_A}{-r_{A0}}$$

2.7 Multiple-Reactor Systems

2.7.1 Plug Flow Reactors in Series and/or in Parallel

Consider N plug flow reactors connected in series, and let X_1, X_2, \dots, X_N be the fractional conversion of component A leaving reactor 1, 2, ..., N . Basing the material balance on the feed rate of A to the first reactor, we find for the i th reactor from equation (2.67)

$$\frac{V_i}{F_0} = \int_{X_{i-1}}^{X_i} \frac{dX}{-r} \quad (2.67)$$

or for the N reactors in series

$$\begin{aligned} \frac{V}{F_0} &= \sum_{i=1}^N \frac{V_i}{F_0} = \frac{V_1 + V_2 + \dots + V_N}{F_0} \\ &= \int_{X_0=0}^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \dots + \int_{X_{N-1}}^{X_N} \frac{dX}{-r} = \int_0^{X_N} \frac{dX}{-r_A} \end{aligned}$$

Hence N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V .

For plug flow reactors connected in parallel or in any parallel-series combination, one could treat the whole system as a single plug flow reactor of volume equal to the total volume of the individual units if the feed is distributed. Thus for reactors in parallel V/F or τ must be the same for each parallel line. Any other way of feeding is usually less efficient.

2.7.2 Equal-size Mixed Reactors in Series

In plug flow the concentration of reactant decreases progressively through the system; in mixed flow the concentration drops immediately to a low value. Because of this fact a plug flow reactor is more efficient than a mixed reactor for reactions whose rates increase with reactant concentration, such as n th-order irreversible reactions, $n > 0$.

Consider a system of N mixed reactors connected in series. Though the concentration is uniform in each reactor, there is nevertheless a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in figure 2.8, suggests that the larger the number of units in series the closer should the behavior of the system approach plug flow. This will be shown to be so.

Let us now quantitatively evaluate the behavior of a series of N equal-size mixed reactors. Density changes will be assumed to be negligible; hence $\varepsilon = 0$ and $t = \tau$. As a rule, with mixed reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions; therefore we use this approach. The nomenclature used is shown in figure 2.9 with subscript i referring to the i^{th} vessel.

First-order Reactions. From equation (2.68) a material balance for component A about vessel i gives

$$\tau_i = \frac{C_0 V_i}{F_0} = \frac{V_i}{v} = \frac{C_0 (X_i - X_{i-1})}{-r_i} \quad (2.68)$$

Because $\varepsilon = 0$, this may be written in terms of concentrations. Hence

$$\tau_i = \frac{C_0 [(1 - C_i/C_0) - (1 - C_{i-1}/C_0)]}{kC_i} = \frac{C_{i-1} - C_i}{kC_i}$$

or

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i \quad (2.69)$$

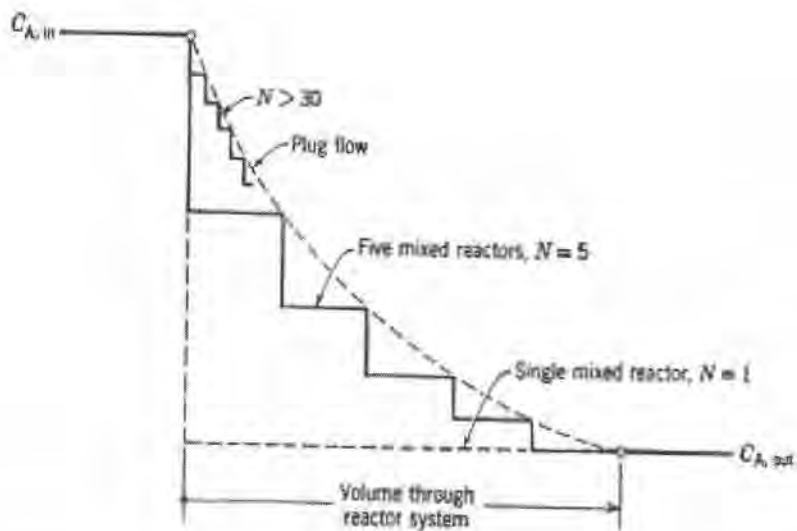


Figure 2.8 Concentration profile through an N -stage mixed reactor system compared with single flow reactors.

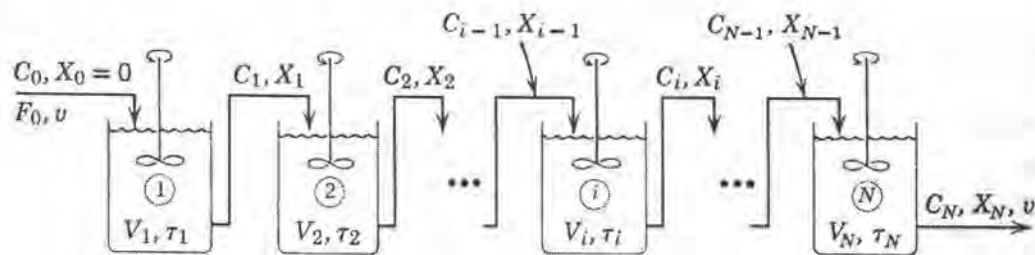


Figure 2.9 Notation for a system of N equal-size mixed reactors in series.

Now the space-time τ (or mean residence time t) is the same in all the equal-size reactors of volume V_i . Therefore

$$\frac{C_0}{C_N} = \frac{1}{1 - X_N} = \frac{C_0}{C_1} \frac{C_1}{C_2} \dots \frac{C_{N-1}}{C_N} = (1 + k\tau_i)^N \quad (2.70a)$$

Rearranging, we find for the system as a whole

$$\tau_{\text{Nreactors}} = N\tau_i = \frac{N}{k} \left[\left(\frac{C_0}{C_N} \right)^{1/N} - 1 \right] \quad (2.70b)$$

In the limit, for $N \rightarrow \infty$, this equation reduces to the plug flow equation

$$\tau_p = \frac{1}{k} \ln \frac{C_0}{C} \quad (2.71)$$

With equations 2.70b and 2.71 we can compare performance of N reactions in series with a plug flow reactor or with a single mixed reactor. This comparison is shown in figure 2.10 for first-order reactions in which density variations are negligible.

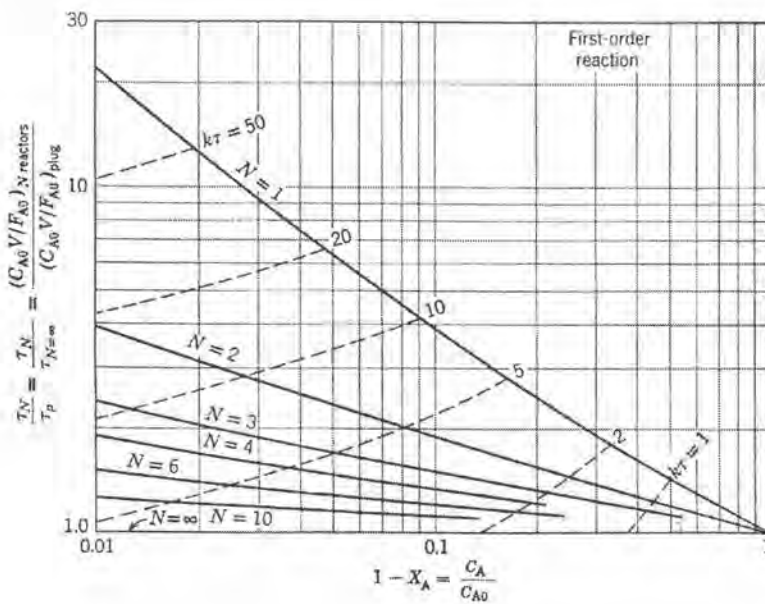
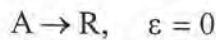


Figure 2.10 Comparison of performance of a series of N equal-size mixed reactors with a plug flow reactor for the first-order reaction



For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_P directly.

Second-order Reactions. We may evaluate the performance of a series of mixed reactors for a second-order, bimolecular-type reaction, no excess of either reactant by a procedure similar to that for a first-order reaction. Thus for N reactors in series we find

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \cdots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0 k \tau_i}}} \right) \quad (2.72a)$$

Whereas for plug flow

$$\frac{C_0}{C} = 1 + C_0 k \tau_p \quad (2.72b)$$

The results are presented in figure 2.11

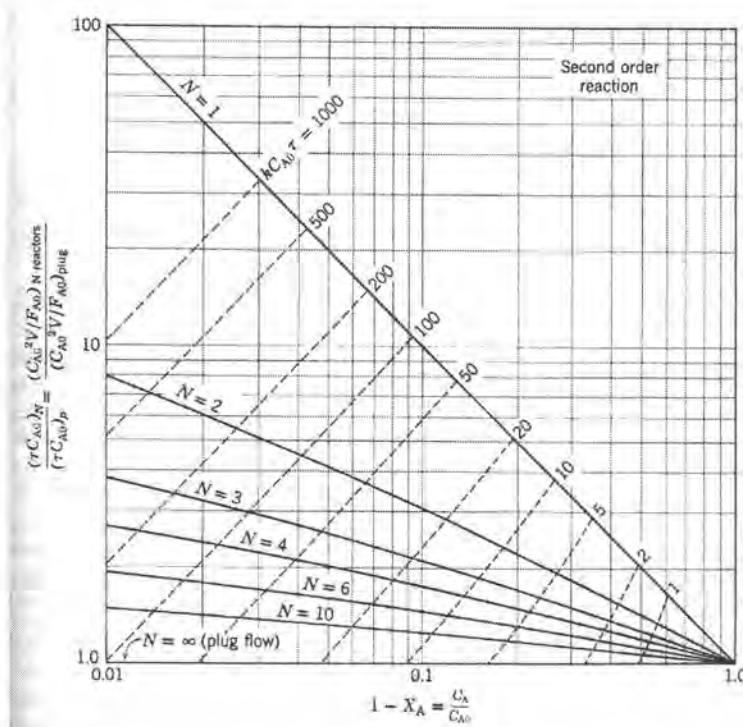
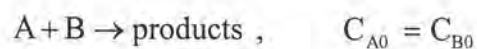
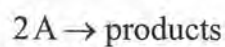


Figure 2.11 Comparison of performance of a series of N equal-size mixed reactors with a plug flow reactor for elementary second-order reactions



with negligible expansion. For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p or space-time ratio τ_N/τ_p directly.

Figure 2.10 and 2.11 support our intuition by showing that the volume of system required for a given conversion decrease to plug flow volume as the number of reactors in series is increased, the greatest change taking place with the addition of a second vessel to a one-vessel system.

Example 1 Substance A reacts according to second-order kinetics and conversion is 95% from a single flow reactor. We buy a second unit identical to the first. For the same conversion, by how much is the capacity increased if we operate these two units in parallel or in series?

- (a) The reactors are both plug flow.
- (b) The reactors are both mixed flow.

Solution

(a) For 2 plug flow units in series or in parallel we have

$$\frac{V}{F_{A_0}} = \int_0^{0.95} \frac{dX_A}{-r_A}$$

the feed rate F_{A_0} can be doubled

(b) For 2 mixed reactors in parallel

$$\frac{V}{F_{A_0}} = \frac{X_A}{-r_A}$$

the feed rate F_{A_0} can be doubled

For 2 mixed reactors in series things are not as simple, and we can solve the problem in two ways

Method 1 Use the performance charts of figure 2.11

From the figure

$$\frac{\tau_2}{\tau_1} = \frac{80}{380} \quad (i)$$

$$\text{but } \frac{\tau_{2 \text{ vessels}}}{\tau_{1 \text{ vessel}}} = \frac{C_0 V_2 / F_{0,2}}{C_0 V_1 / F_{0,1}} = \frac{2 V_1 / F_{0,2}}{V_1 / F_{0,1}} \quad (ii)$$

Combining (i) & (ii) gives feed rate for 2 vessels = $2 \left(\frac{380}{80} \right) = 9.5$ that for the single vessel

Method 2 Solve the performance equations. Thus

$$\text{for 1 vessel : } \tau = \frac{C_0 - C_f}{k C_f^2} \quad \text{where } C_f = \frac{5}{100} C_0$$

$$\text{for 2 vessel in series : } \tau = \frac{C_0 - C_1}{k C_1^2} = \frac{C_1 - C_f}{k C_f^2}$$

By trail and error we find first that $C_1 = \frac{15}{100} C_0$, or 85% conversion after the first stage

From this we find that $k \tau_1 C_0 = \frac{1 - 0.15}{(0.15)^2} = 37.5$, and finally that

$$\text{Feed rate for 2 vessels} = \frac{380}{375} = 10.1 \text{ times that for a single vessel}$$

Combination (f) consists of n perfectly mixed reactors arranged in tandem so that the effluent of one vessel is the feed to the next. Focusing first, upon two CSTRs in series, each of equal volume. The residence time or response to step input of inert tracer will be developed before considering reaction in such a system. For the first vessel the effluent tracer concentration C is

$$C_1 = C_0 \left[1 - \exp\left(-\frac{2t}{\theta_1}\right) \right] \quad (2.74)$$

Where: $\theta_1 = (V_1 + V_2) / Q$

$$\theta_2 = \frac{\theta_1}{2}$$

For the second CSTR, a material balance gives

$$QC_1 = QC_2 + V_2 \frac{dC_2}{dt} \quad (2.75)$$

$$\frac{dC_2}{dt} = \frac{2}{\theta_1} (C_1 - C_2) = \frac{2}{\theta_1} \left\{ C_0 \left[1 - \exp\left(-\frac{2t}{\theta_1}\right) \right] - C_2 \right\} \quad (2.76)$$

or

$$\frac{dC_2}{dt} + \frac{2C_2}{\theta_1} = \frac{2C_0}{\theta_1} \left[1 - \exp\left(-\frac{2t}{\theta_1}\right) \right] \quad (2.77)$$

which is a first order linear differential equation of the form

$$\frac{dy}{dx} + yP(x) = Q(x)$$

The general solution is

$$y = \left[\exp\left(-\int P dx\right) \right] \left\{ \left[\int Q \exp\left(\int P dx\right) dx + \text{const} \right] \right\}$$

For a step input $C = 0, t = 0,$

$$C_2 = \left[\exp\left(-\frac{2t}{\theta_1}\right) \right] \left(\left\{ K_1 \int \left[1 - \exp\left(-\frac{2t}{\theta_1}\right) \right] \left(\exp \frac{2t}{\theta_1} \right) dt \right\} + K_2 \right)$$

Therefore

$$J(t) = \frac{C_2}{C_0} = 1 - \left(1 + \frac{2t}{\theta_1} \right) \exp\left(-\frac{2t}{\theta_1}\right)$$

This procedure can be extended to any number of equal-volume CSTRs in series. The resulting response for $n=1, 2, 10, 20$ and an infinite number of CSTRs in series are shown in figure 2.12. It is apparent that as the number of CSTRs in series is increased, the residence-time function approaches that of a PFR ($n \rightarrow \infty$). The corresponding pulse response are shown in figure 2.13, representing the derivatives of the $J(t)$ curves.

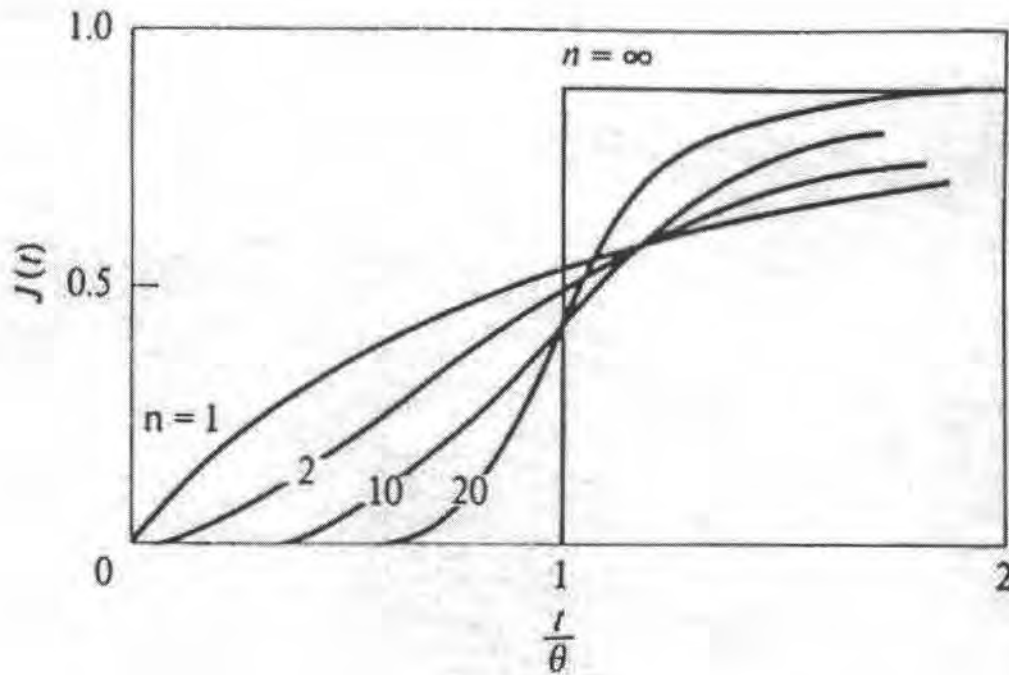


Figure 2.12 Step-input response for n CSTRs in series ($n=1$ to ∞)

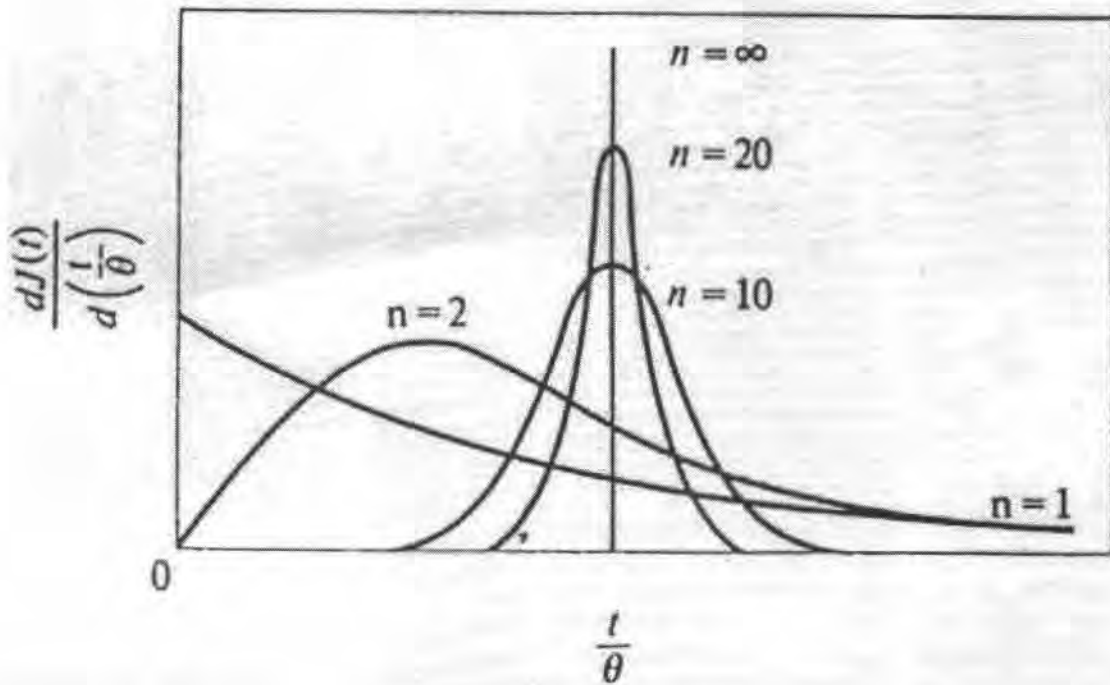


Figure 2.13 Pulse-input response for n CSTRs in series ($n=1$ to ∞)

The series of network of CSTRs provides an illustration of residence-time distribution intermediate between plug flow and the uniform environment characteristic of a CSTR with its exponential distribution of residence times. The usefulness of the CSTR series network is that a reactor, which reveals neither a PFR nor a single-CSTR response may be described in terms of n CSTRs. If an n -CSTR residence-time distribution does in fact exist, reactor performance is capable of being predicted for first-order kinetics. Once again it must be emphasized that in other than first-order cases, more must be known about the nature of mixing (segregated and/or nonsegregated) before a precise prediction of performance is feasible.

It is worth noting at this point that complex-reactor geometries, while revealing residence-time functions intermediate between PFR and single-CSTR character, are often not easily described by n CSTRs in series. The fluidized-bed reactor is typical of a unit displaying a J curve, which does not conform to the n -CSTR pattern.

In a series of CSTRs, each of equal volume V , in which reaction occurs in steady state, we have for the first vessel, for the first order kinetics

$$QC_0 = QC_1 + VkC_1$$

$$\text{or } C_1 = \frac{C_0}{1 + k\theta_1}$$

For the second and n^{th} vessels, respectively,

$$C_2 = \frac{C_1}{1 + k\theta_2}$$

$$\text{and } C_n = \frac{C_{n-1}}{1 + k\theta_n}$$

At constant flow rate for equal-volume vessels, $\theta_1 = \theta_2 = \theta_3$, and thus by successive substitutions

$$\frac{C_n}{C_0} = \frac{1}{(1 + k\theta_1)^n} = \frac{1}{\left(1 + \frac{k\theta_1}{n}\right)^n} \quad (2.78)$$

where θ_1 is total holding time for the system.

A useful and instructive comparison between PFR and n-CSTR performance can now be undertaken. Conversion $(1 - C/C_0)$ in a PFR is given by

$$X_{\text{PFR}} = 1 - \frac{C}{C_0} = 1 - \exp(-k\theta_p) \quad (2.79)$$

compared with that in an n-CSTR network

$$X_{\text{n-CSTR}} = 1 - \frac{1}{(1 + k\theta_1)^n} \quad (2.80)$$

Solving for $n\theta_1$ in (2.80) and θ_p in (2.79) gives

$$\text{n-CSTRs} \quad \theta_t = n\theta_1 = \left[\frac{(1-x)^{-1/n} - 1}{k} \right] n \quad (2.81)$$

$$\text{PFR} \quad \theta_p = -\frac{\ln(1-x)}{k} \quad (2.82)$$

Then $\frac{\theta_p}{n\theta_1}$ represents the respective holding time in a PFR (or batch reactor) and n-CSTR network for a given conversion level of x

$$\frac{\theta_p}{n\theta_1} = \frac{-\ln(1-x)}{[(1-x)^{-1/n} - 1] n} \quad (2.83)$$

As an exercise show at what values of n, $\frac{\theta_p}{n\theta_1}$ becomes 90 or 99 percent of unity. The exercise should demonstrate that as n increases in the n-CSTR series network, PFR (or batch) performance is realized. This must, of course, follow logically from the previous demonstration that the residence-time behavior of n CSTRs approaches character with increasing n.