

CHAPTER 7

NUMERICAL INVESTIGATION OF CONTINUOUS SYNTHETIC POLYISOPRENE HYDROGENATION PROCESS

Experimental work on the homogeneous catalytic hydrogenation of CPIP was performed in a semi-batch process with hydrogen transfer from the gas phase into the liquid phase (Chapter 3). While batch processing is very efficient for achieving high olefin conversions, one disadvantage is the hydrogenation output, which is an important aspect of the overall production cycle. Effective catalysts and the use of efficient reactors are key among the hydrogenation techniques. A continuous process can offer an economic advantage. The concurrent upflow plug flow reactor (PFR) for NBR hydrogenation was developed by Parent (1996). A dynamic model for kinetics coupled with mass transfer was investigated for NBR, PBD, and SBR hydrogenation for a semi-batch process (Pan and Rempel, 2000). The coupling behaviors of these processes can be determined by the ability of catalyst in activating hydrogen, the carbon – carbon double bonds loading level, and the relative capacity of reaction over mass transfer. Recently, the dynamic behavior of a continuous process for NBR hydrogenation was established based on the development of coupling models between kinetics and mass transfer (Pan et al., 2002). It was suggested that an optimal reactor for such a hydrogenation system would be small CSTR followed by a large PFR reactor.

In this chapter, an attempt is made to provide insight of the coupling behavior between the reaction and hydrogen transfer for CPIP hydrogenation for the possible development of a potential new continuous process. The consideration taken was based on the knowledge of kinetics and dynamic performance of CPIP hydrogenation in Chapter 3.

7.1 Development of Coupling Models

Since the homogeneous hydrogenation of CPIP is accompanied with hydrogen transfer from gas into the liquid phase, a distinguishing characteristic of this operation is that the process is affected by the gas-liquid mass transfer behavior. A model characterizing the coupling behavior between the reaction and hydrogen transfer is developed here to investigate the coupling behavior.

Modeling of a continuous process is dependent on flow characterization of the investigated process. It is well known that the well-mixed flow, plug-flow and short-cut flow have been models as ideal reactors. In this study, the ideal flows i.e. continuous stirred tank reactor (CSTR) and plug flow reactor (PFR) are investigated.

The mathematical used is based on the following assumptions:

1. The hydrogen transfer takes place from the gas phase to liquid phase.
2. The mass transfer in gas phase could be described with the stagnant film model (Danckwerts, 1970) and the extent of the reaction in the liquid film in the film model is negligible.
3. The instantaneous mixing of catalyst into the reactants is performed.
4. The reactor is operated at isothermal and isobaric conditions.
5. The mass transfer coefficient and the interfacial area for mass transfer are constant during the reaction process.

7.1.1 Continuous Stirred Tank Reactor (CSTR)

The continuous stirred tank reactor (CSTR) or backmix reactor is a common type of reactor used in industrial processing. The CSTR is normally run at steady state and is usually well mixed under operation (Fogler, 1999). Therefore, the CSTR is generally modeled with no variations in concentration, temperature, or reaction rate throughout the vessel. An Eulerian approach, with an arbitrary control volume in a stationary reference frame, is used to derive the basic governing equation for the CSTR (Renade, 2002). Figure 7.1 illustrates conceptual diagram of CSTR for hydrogenation of a diene polymer.

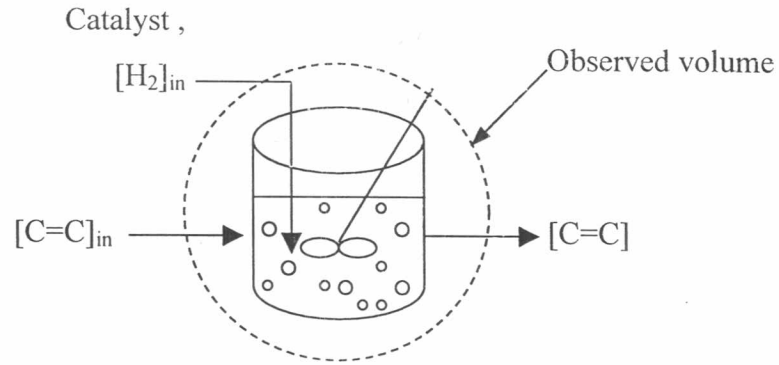


Figure 7.1: Diagram of CSTR for hydrogenation of CPIP

According to the material balance, the following nonlinear ordinary differential equation set represents the hydrogen process:

$$\begin{aligned} \langle \text{accumulated} \rangle &= \langle \text{reactor feed} \rangle - \langle \text{reactor outlet} \rangle + \langle \text{interfacial mass transfer} \rangle \\ &+ \langle \text{reaction in the bulk phase} \rangle \end{aligned}$$

$$\text{For } C=C: \quad \frac{d[C=C]}{dt} = \frac{[C=C]_{in} - [C=C]}{\tau} - R_H \quad (7.1)$$

$$\text{For } H_2: \quad \frac{d[H_2]}{dt} = \frac{[H_2]_{in} - [H_2]}{\tau} + K_L a ([H_2]_e - [H_2]) - R_H \quad (7.2)$$

Initial conditions:

$$[C=C](0) = [C=C]_0 \quad (7.3)$$

$$[H_2](0) = [H_2]_0 \quad (7.4)$$

where $[H_2]_0$ is the hydrogen concentration in the liquid phase at $t = 0$ in the reactor. $[H_2]_e$ is the hydrogen concentration in the liquid phase equilibrated with the hydrogen gas phase in the reactor. $[H_2]_{in}$ and $[C=C]_{in}$ are the concentrations of hydrogen and carbon – carbon double bonds in the inlet of the reactor. τ is the mean residence time in CSTR.

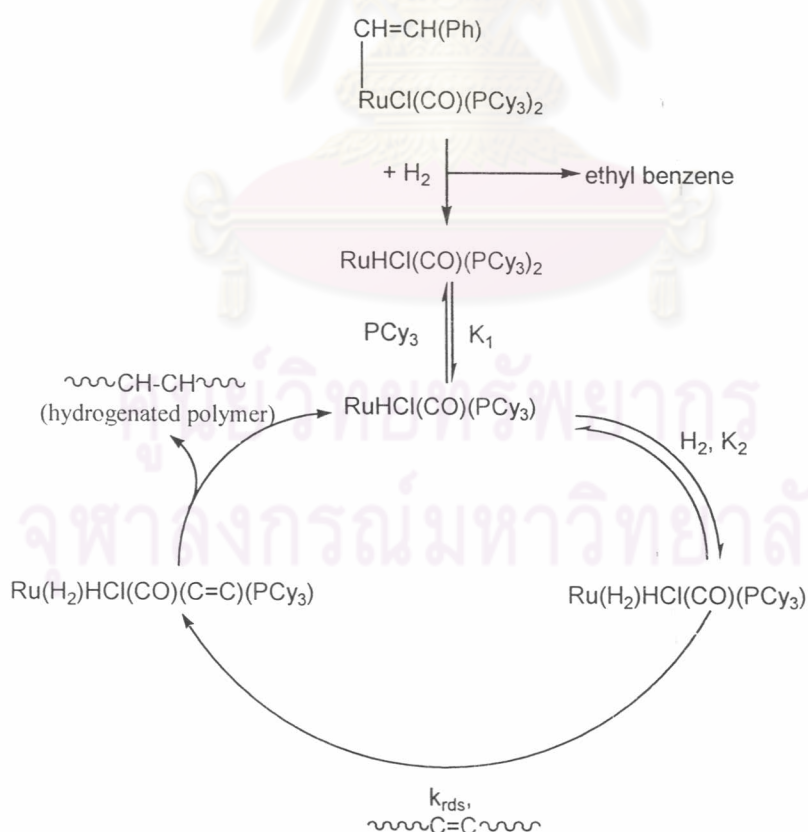
$K_L a$ in Equation 7.2 is the overall volumetric mass transfer coefficient between gas and liquid phases. In the hydrogenation system $K_L a$ is actually equal to $k_L a$, the

volumetric mass transfer coefficient in the liquid phase, because both mass transfer resistance in the gas phase and at the interface between gas and liquid phases may be considered negligible.

R_H in Equation 7.1 and 7.2 is the intrinsic hydrogenation reaction rate that has been investigated for the CPIP hydrogenation over a range of operation conditions (Chapter 3) as shown in Table 7.1. The proposed mechanism for the hydrogenation system is illustrated in Scheme 7.1. The corresponding rate expression for R_H was derived as follows:

$$R_H = \frac{k_{rds} K_1 K_2 [Ru][H_2][C=C]}{K_1 + [PCy_3]} \quad (7.5)$$

The reaction kinetics exhibited an apparent pseudo first order dependence on the olefin substrate. The reaction rate followed a first order with respect to the catalyst concentration and hydrogen pressure. An increase in the amount of tricyclohexylphosphine decreases the rate constant of reaction.



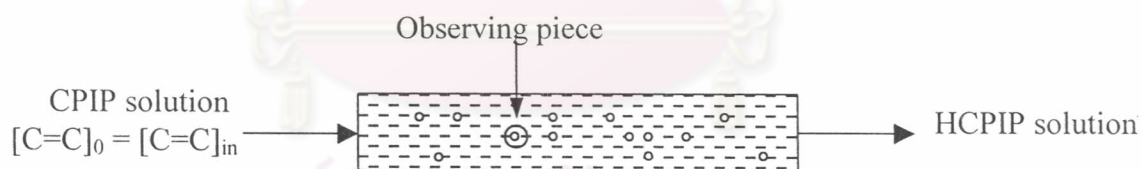
Scheme 7.1: Proposed Mechanism of CPIP Hydrogenation.

Table 7.1: Range of Operation Conditions for CPIP Hydrogenation.

Condition	Range
Polymer concentration; mmol/l	130 - 520
Ruthenium concentration; $\mu\text{mol/l}$	20 - 250
Tricyclohexylphosphine concentration; mmol/l	0 - 1.2
Hydrogen Pressure; bar	6 - 68

7.1.2 Plug Flow Reactor (PFR)

The tubular reactor or plug flow reactor (PFR) is another type of commonly used reactor in industry. It consists of a cylindrical pipe and is normally operates at steady state (Fogler, 1999). The main assumption of the PFR model is that the concentration varies continuously in the axial direction through the reactor. Accordingly, the reaction rate will also vary axially. For a tubular reactor, a Lagrangian approach, which is the equation derived by considering a control volume such as velocity of the control volume surface always equals the local fluid velocity, is used (Renade, 2002). Figure 7.2 illustrates the conceptual diagram of a PFR for hydrogenation of diene polymer.

**Figure 7.2: Diagram of PFR for hydrogenation of CPIP**

The following nonlinear ordinary differential equation set represents the hydrogenation process:

$$\langle \text{accumulated} \rangle = \langle \text{interfacial mass transfer} \rangle + \langle \text{reaction in the bulk phase} \rangle$$

$$\text{For } C=C: \quad \frac{d[C=C]}{dt} = -R_H \quad (7.6)$$

$$\text{For } H_2: \quad \frac{d[H_2]}{dt} = K_l a ([H_2]_e - [H_2]) - R_H \quad (7.7)$$

Initial conditions:

$$[C = C](0) = [C = C]_0 = [C = C]_{in} \quad (7.8)$$

$$[H_2](0) = [H_2]_0 = [H_2]_{in} \quad (7.9)$$

The meaning of the symbols for the equations of the PFR is the same as those for the equations of the CSTR. However, the conditions in the inlet are the same as the initial conditions; and the residence time will be the time of the integrated equations.

7.2 Analysis of Characteristic Parameters

7.2.1 Continuous Stirred Tank Reactor (CSTR)

The dimensionless transformation is carried out according to Equations 7.1 –7.5 in order to reveal the key factors controlling the models and in turn the coupling behaviors. The following expressions are obtained:

$$\frac{dx}{d\theta} = \frac{(x_{in} - x)}{\theta_r} + h(1 - x) \quad (7.10)$$

$$\frac{1}{q} \frac{dh}{d\theta} = \frac{(h_{in} - h)}{q\theta_r} + \frac{1}{R}(1 - h) - h(1 - x) \quad (7.11)$$

with initial conditions

$$x(0) = x_o \quad (7.12)$$

$$h(0) = h_o \quad (7.13)$$

where x is the degree of hydrogenation or conversion. The dimensionless hydrogen concentration, h , dimensionless time, θ , and dimensionless residence time, θ_r , are defined as

$$h = \frac{[H_2]}{[H_2]_c} \quad (7.14)$$

$$\theta = \frac{t}{\tau_r} \quad (7.15)$$

$$\theta_r = \frac{\tau}{\tau_r} \quad (7.16)$$

where τ is mean residence time of the reactor and τ_r is time constant under pure chemical reaction conditions without mass transfer resistance and is defined as

$$\tau_r = \frac{K_1 + [PCy_3]}{k_{rds} K_1 K_2 [Ru][H_2]_e} \quad (7.17)$$

q and R , dimensionless parameters are defined as

$$q = \frac{[C = C]_0}{[H_2]_e} \quad (7.18)$$

$$R = \frac{k_{rds} K_1 K_2 [Ru][C = C]_0}{K_L a (K_1 + [PCy_3])} \quad (7.19)$$

Both dimensionless parameters q and R possess exact physical meaning. It is obvious that q stands for the loading level of carbon-carbon double bonds. R is the relative capacity of the intrinsic hydrogenation reaction over the mass transfer of the reactor.

7.2.2 Plug Flow Reactor (PFR)

Similar to CSTR, the following dimensionless equations for a tubular reactor can be derived as:

$$\frac{dx}{d\theta} = h(1-x) \quad (7.20)$$

$$\frac{1}{q} \frac{dh}{d\theta} = \frac{1}{R} (1-h) - h(1-x) \quad (7.21)$$

with the initial conditions:

$$x(0) = x_o \quad (7.22)$$

$$h(0) = h_o \quad (7.23)$$

The equations for the PFR are actually in the same form mathematically as for a batch process, but with a different meaning physically.

Hereafter, the models and in turn the coupling behavior are determined by the carbon-carbon double bond loading level (q) and the relative capacity (R) between reaction and mass transfer as well as the residence time (θ_τ for CSTR or integrated time for a PFR), besides the initial operation conditions. The effect of these parameters has been studied in an attempt to understand the behavior of these equations.

7.3 Behavior of Continuous Hydrogenation in CSTR

To understand the behaviors of the CSTR based on Equation 7.1 and 7.2, a detailed computation has been made. The Runge-Kutta-Fehlberg method (RK45) (POLYMATH 5.1 program) is used to solve the ordinary differential equation (ODE).

7.3.1 Start-up Period

The trajectories with three dimension reaction on the coordinate of x - h - θ during the starting period from different start points under different residence time are shown in Figure 7.3. The two dimension projections of curves on the plane x - θ in Figure 7.3 are illustrated in Figure 7.4. It is apparent that the system which starts from $h = 1$ is much quicker to reach the steady state with higher conversion than if the system starts from $h = 0$. The effects of mass transfer on the x - θ trajectories are shown in Figure 7.5. It is easier to approach the steady state with higher conversion at superior mass transfer behavior than at the interior. Thus, the start-up period of the system is shortened and the amount of undesirable product produced during the period required to reach the steady state is diminished by superior mass transfer behavior and high hydrogen concentration.

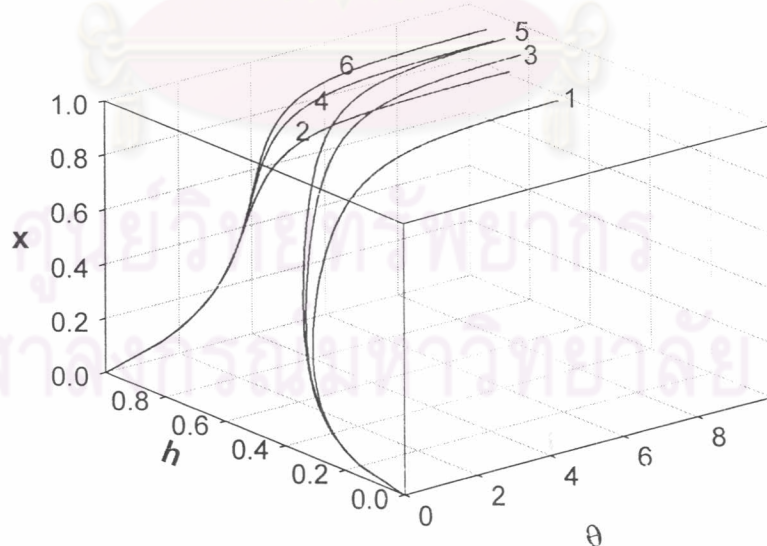


Figure 7.3: Three-dimension reaction trajectories in CSTR: $R=1$, $q=1$.

Curve 1: $(x_0, h_0) = (0, 0)$, $\theta_\tau = 5$

Curve 2: $(x_0, h_0) = (0, 1)$, $\theta_\tau = 5$

Curve 3: $(x_0, h_0) = (0, 0)$, $\theta_\tau = 10$

Curve 4: $(x_0, h_0) = (0, 1)$, $\theta_\tau = 10$

Curve 5: $(x_0, h_0) = (0, 0)$, $\theta_\tau = 15$

Curve 6: $(x_0, h_0) = (0, 1)$, $\theta_\tau = 15$

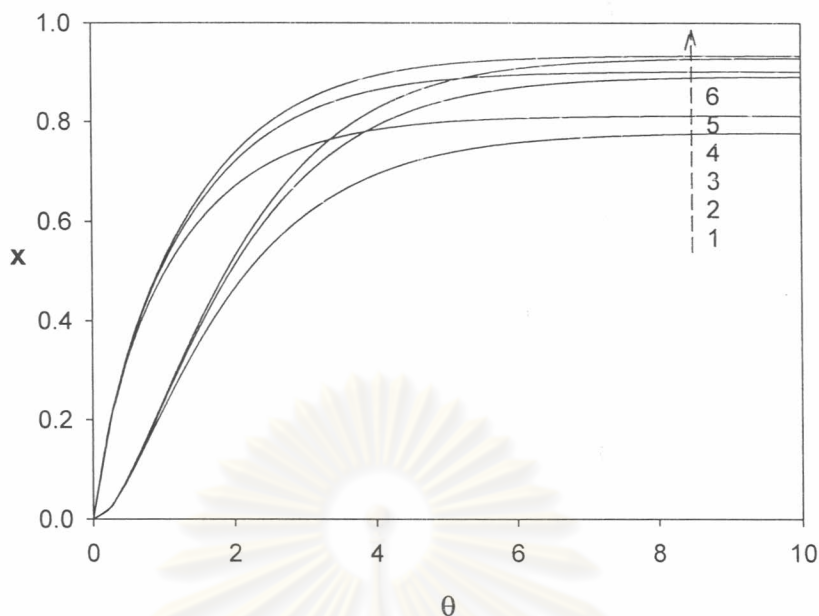


Figure 7.4: The projection of the 3-D reaction trajectories in CSTR of Figure 7.3: $R=1$, $q=1$.

Curve 1: $(x_0, h_0) = (0,0)$, $\theta_\tau = 5$

Curve 2: $(x_0, h_0) = (0,1)$, $\theta_\tau = 5$

Curve 3: $(x_0, h_0) = (0,0)$, $\theta_\tau = 10$

Curve 4: $(x_0, h_0) = (0,1)$, $\theta_\tau = 10$

Curve 5: $(x_0, h_0) = (0,0)$, $\theta_\tau = 15$

Curve 6: $(x_0, h_0) = (0,1)$, $\theta_\tau = 15$

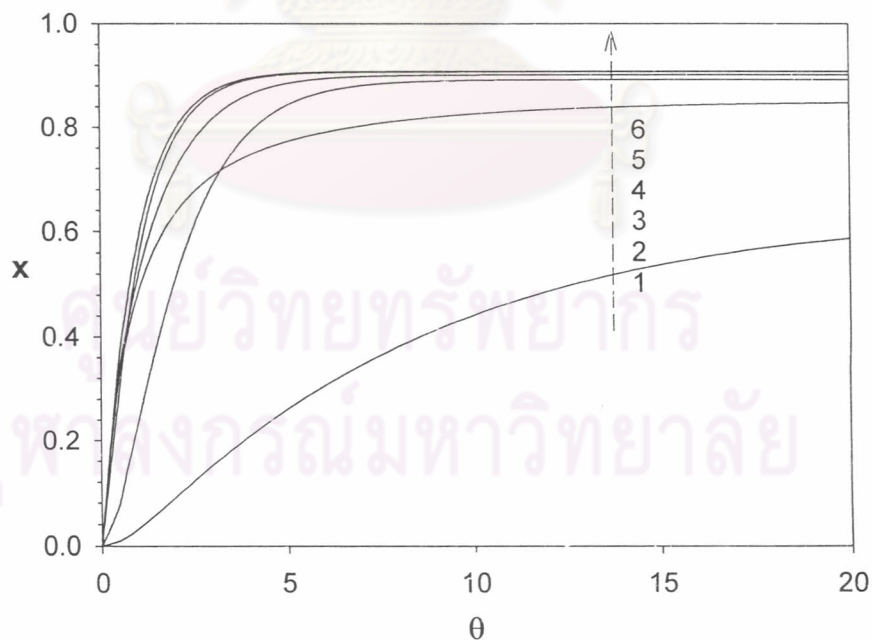


Figure 7.5: Reaction trajectories in CSTR: $q = 1$, $\theta_\tau = 10$.

Curve 1: $(x_0, h_0) = (0,0)$, $R = 10$

Curve 2: $(x_0, h_0) = (0,1)$, $R = 10$

Curve 3: $(x_0, h_0) = (0,0)$, $R = 1$

Curve 4: $(x_0, h_0) = (0,1)$, $R = 1$

Curve 5: $(x_0, h_0) = (0,0)$, $R = 0.1$

Curve 6: $(x_0, h_0) = (0,1)$, $R = 0.1$

7.3.2 Residence Time/ Reactor Volume Required

The required dimensionless residence time for a given conversion under a variety of different operation conditions is illustrated in Figure 7.6. θ_τ is proportional to the reactor volume required to reach a given conversion when the production rate is given. The results indicate that in a single CSTR, θ_τ would be required to increase significantly when the required conversion is higher than 0.9. Therefore, the volume of the reactor should be increased dramatically to reach the given conversion. Thus, it can be concluded that it is not practical to use a single CSTR for hydrogenation of CPIP with the degree of hydrogenation higher than 0.9.

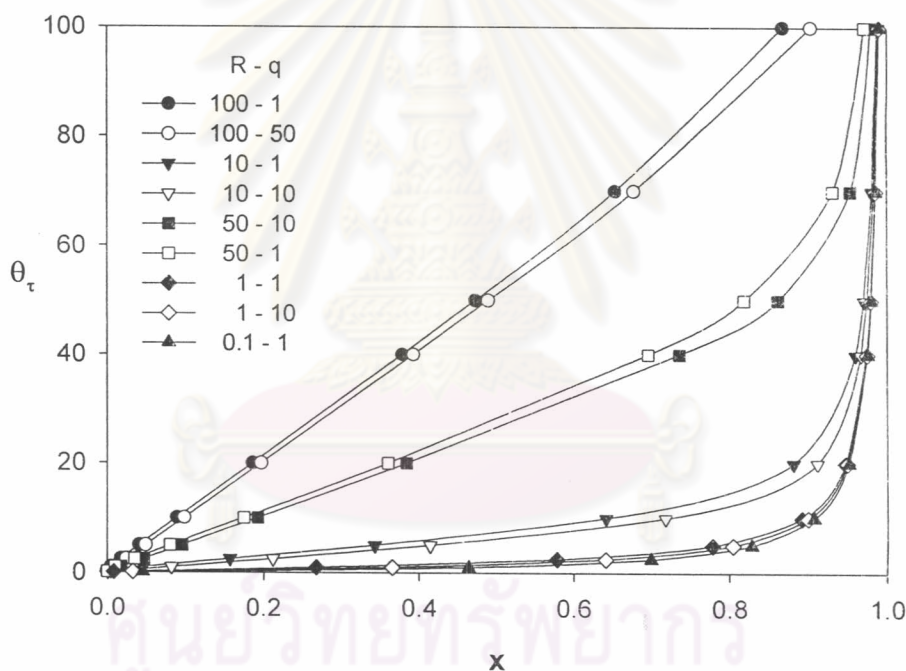


Figure 7.6: Effect of residence time on conversion in CSTR: $(x_0, h_0) = (0, 0)$.

7.3.3 The Effect of Characteristic Parameters

The effect of R shows that the reduction of reactor volume is obtained by a small R as illustrated in Figure 7.6. The mass transfer of hydrogen increases as the value of R decreases. However, the effect from decreasing R on θ_τ is not significant when R is small enough. It is obvious that when $R \leq 1$, the effect of decreasing R is not significant. R_c is defined as the value of critical R . If R is less than the critical

value (R_c), the effect of R is insignificant. R_c is dependent on q , x and the criterion used to estimate R_c itself. The examples of two criteria are shown as follow:

$$\frac{x(R = R_c)}{x(R = 0)} = 0.9 \quad (7.24)$$

and

$$\frac{x(R = R_c)}{x(R = 0)} = 0.95 \quad (7.25)$$

Figure 7.7 shows R_c obtained which is the dotted line for Equation 7.24 and the dashed line for Equation 7.25. It can be seen that there is no significant effect of changing R on the conversion when $R < R_c$. Therefore, the reduction of R is not suggested when $R < R_c$ due to the high energy cost but little gain in conversion. R_c increases with an increase in residence time. This indicates that the effect of mass transfer resistance becomes insignificant when the residence time is long enough. However, the reactor would be low efficient if the residence time is long.

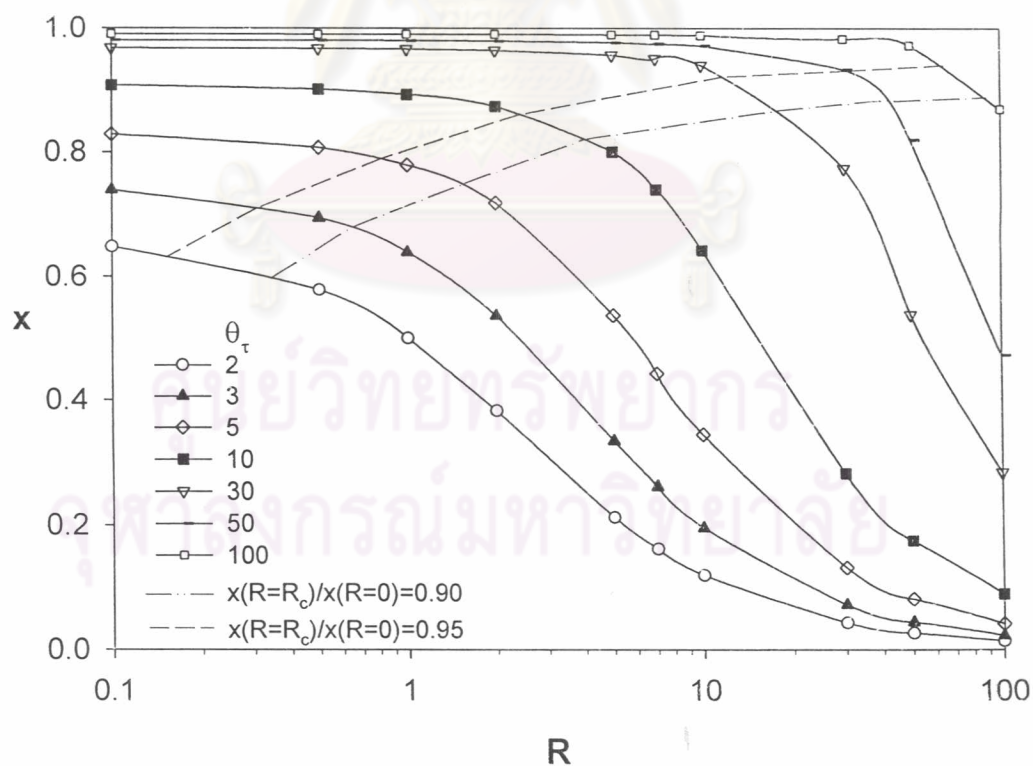


Figure 7.7: Effect of R on conversion in CSTR: $q = 1$, $(x_0, h_0) = (0, 0)$.

The effect of q is positive when $h_{in} = 0$ and the effect of q is negative when $h_{in} = 1$ as shown in Figure 7.8. However, the conversion obtained under $h_{in} = 1$ is always higher than that obtained under $h_{in} = 0$. It can be noticed that the difference between different h_{in} becomes negligible and both approach the same line after $q > 10$. This indicates that the mass transfer rate is equal to the reaction rate and both the effects of q and h_{in} disappear at the steady state. This may be due to a complex competition between the reaction and mass transfer related with the concentration of carbon – carbon double bonds and hydrogen. Higher q results in higher reaction rate due to the higher double bond concentration. Higher inlet hydrogen concentration yields the higher reaction rate. However, fast reaction will result in lower hydrogen concentration in the bulk and then will possibly affect inversely the reaction rate. But lower hydrogen concentration in bulk will accelerate the hydrogen transfer from the gas phase into the liquid phase then reaction rate will increase. These factors are coupled together, and the apparent behavior is dependent on which is the dominant factor at each different case. If mass transfer resistance were negligible, the effects of both q and h_{in} would disappear through the process.

The effect of h_{in} in Figure 7.8 can be understood by considering the material balance equation in Equation 7.11. When $h_{in} = 0$, the hydrogen source of the reaction comes solely from the mass transfer from the gas phase. Some part of the hydrogen is consumed by the reaction and some part flows out of the reactor along with the reaction fluid ($h_{in} - h < 0$). The increase of q results in increasing the amount of hydrogen consumed by reaction and decreasing the proportion of hydrogen flowing out of the reactor. Therefore, the conversion increases with increasing q . When $h_{in} = 1$, there are two sources of hydrogen, one from the mass transfer from gas phase and the other from hydrogen inlet. The increase in q will reduce the gaining of $h_{in} - h$ (see Equation 7.11) and results in a decrease in conversion. However, when q is high enough (e.g. the case of $q > 10$), the effect of hydrogen inlet is negligible because both approach in the same level. Therefore, the process running under $h_{in} = 0$ is more convenient since its procedures are more simple.

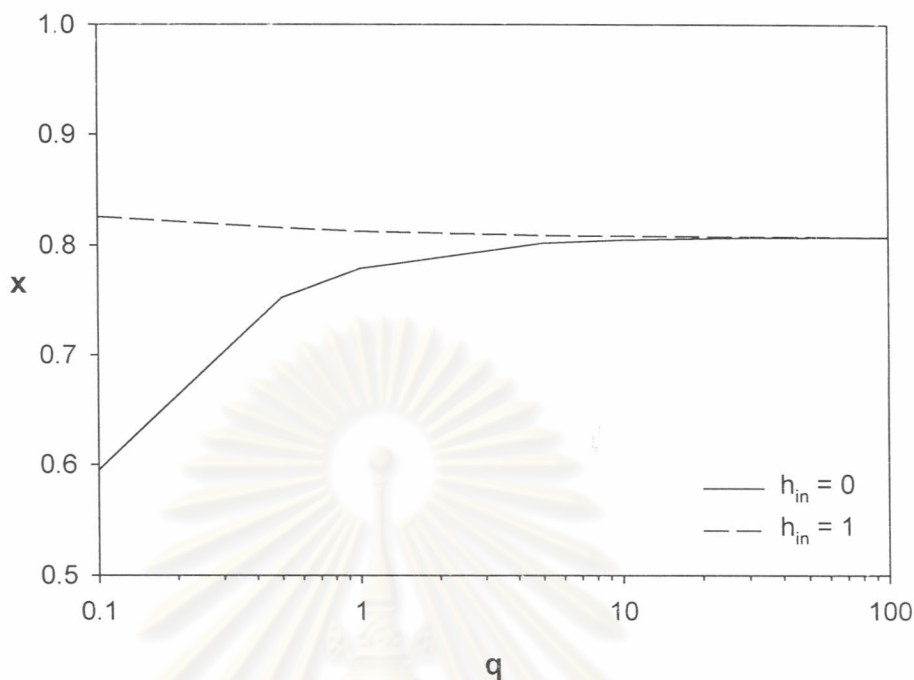


Figure 7.8: Effect of q under different h_{in} : $\theta_{\tau} = 10$.

7.4 Behavior of Continuous Hydrogenation in PFR

In an attempt to understand the behavior in PFR, a similar analysis to the case of the CSTR has been investigated. The behavior of PFR is displayed in Figure 7.9 – 7.12. The results show that the PFR provided shorter residence time to approach the given conversion than in the CSTR. The effect of R , which is the main factor to dominate the behavior of the reaction trajectories in PFR, is stronger than in the CSTR. If R is small enough, the effect of changing R and q can be negligible as shown in Figure 7.10 - 7.11. This behavior is similar to that observed in CSTR. The corresponding of R_c in the same criteria as Equation 7.24 – 7.25 is illustrated in Figure 7.12. The effect of q is similar to the case of CSTR (Figure 7.13). However, the effect of q under different h_{in} in the PFR is caused by change in hydrogen accumulation dh ($dh > 0$, at $h_{in} = 1$; $dh < 0$ at $h_{in} = 0$) in the observing element (Equation 7.21). If $q > 10$, the difference between h_{in} becomes insignificant and in this case running process under $h_{in} = 0$ is preferred.

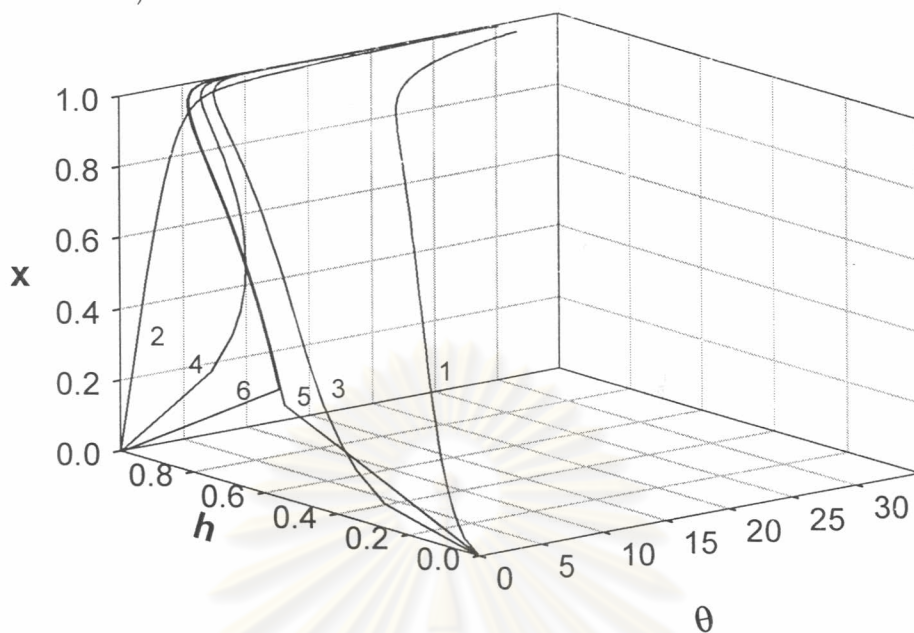


Figure 7.9: Three-dimension reaction trajectories in PFR: $R=1$.

Curve 1: $(x_0, h_0) = (0, 0)$, $q = 0.1$

Curve 2: $(x_0, h_0) = (0, 1)$, $q = 0.1$

Curve 3: $(x_0, h_0) = (0, 0)$, $q = 1$

Curve 4: $(x_0, h_0) = (0, 1)$, $q = 1$

Curve 5: $(x_0, h_0) = (0, 0)$, $q = 10$

Curve 6: $(x_0, h_0) = (0, 1)$, $q = 10$

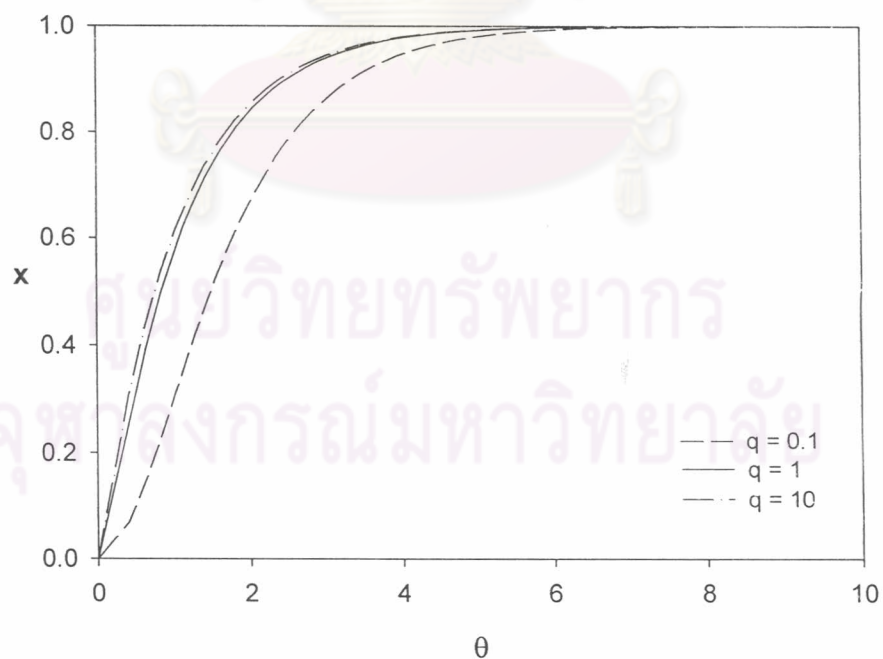


Figure 7.10: Reaction trajectories in PFR: $R = 0.1$, $(x_0, h_0) = (0, 0)$.

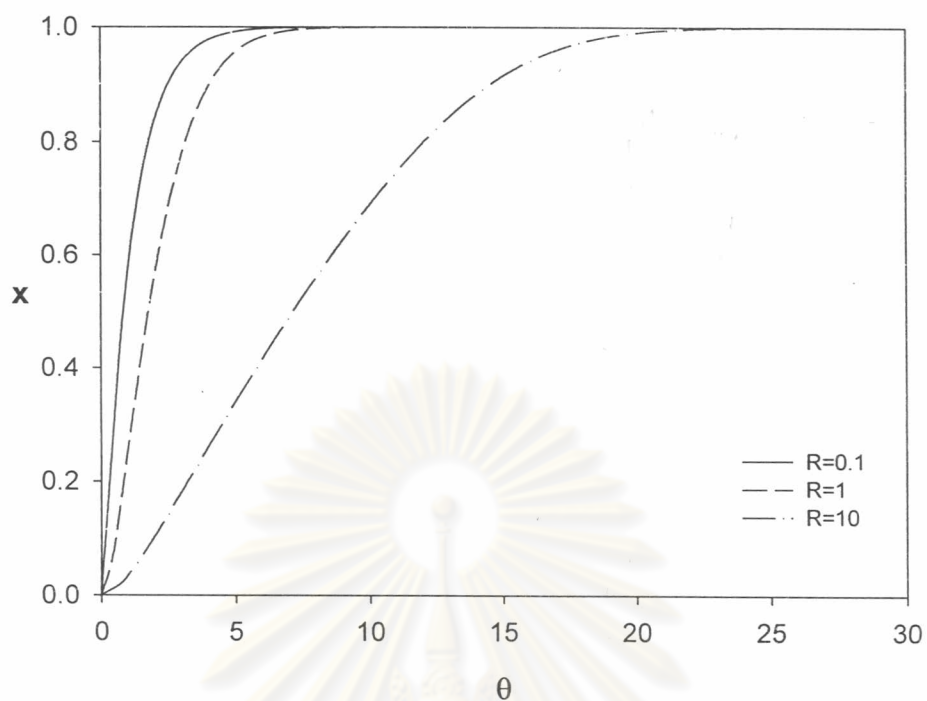


Figure 7.11: Reaction trajectories in PFR: $q = 1$, $(x_0, h_0) = (0, 0)$.

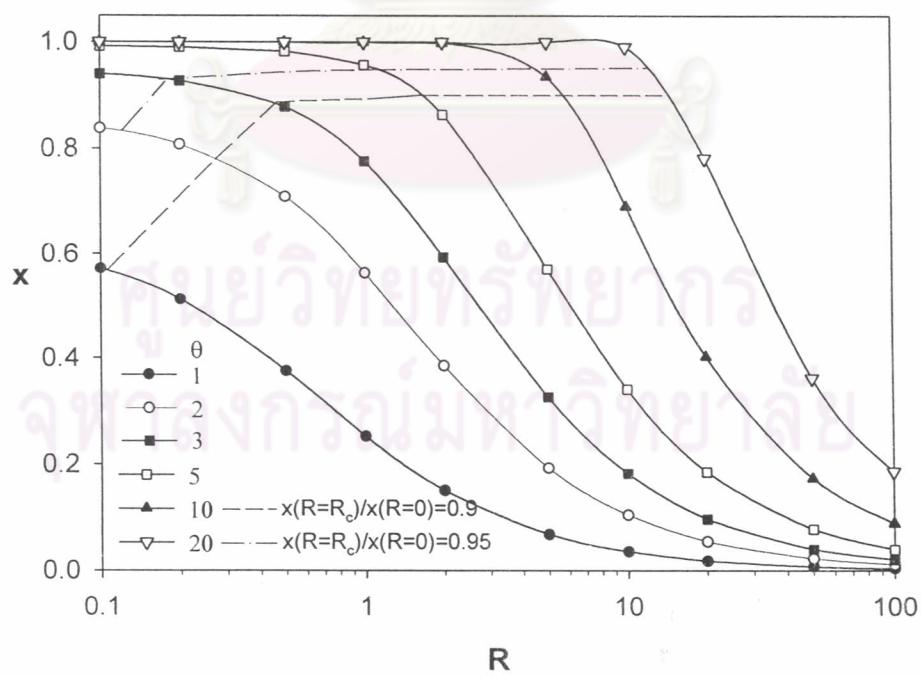


Figure 7.12: Effect of R on conversion in PFR: $q = 1$, $(x_0, h_0) = (0, 0)$.

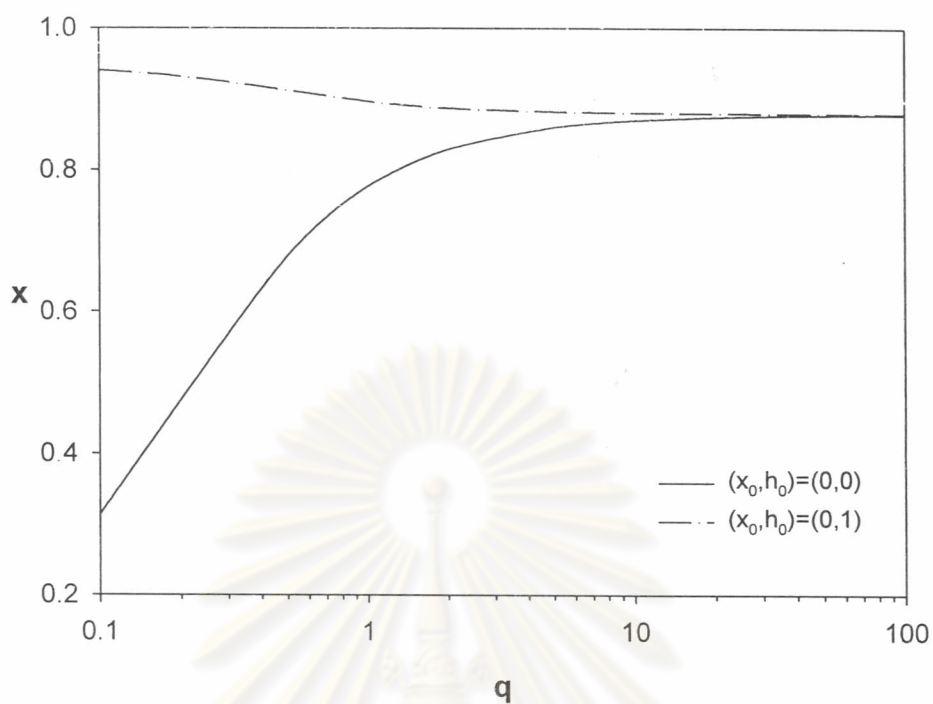


Figure 7.13: Effect of q under different h_{in} in PFR: $R = 1, \theta = 3$.

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7.5 Comparison of CSTR and PFR

Figure 7.14 shows the comparison of CPIP hydrogenation between a CSTR and a PFR under normal operation. It is observed that there is a cross point of two curves. The CSTR is more efficient than PFR when θ_τ is less than $\theta_{\tau c}$, and the PFR is better than CSTR after the cross point. This may be due to the mass transfer resistance. It is evident that decreasing R results in moving the cross point to lower conversion. This means that the higher rate of mass transfer, the higher efficiency of PFR. In fact, in the case without mass transfer resistance, the cross point has been moved to $x = 0$. Therefore, if the resistance is negligible, the PFR is always better than CSTR.

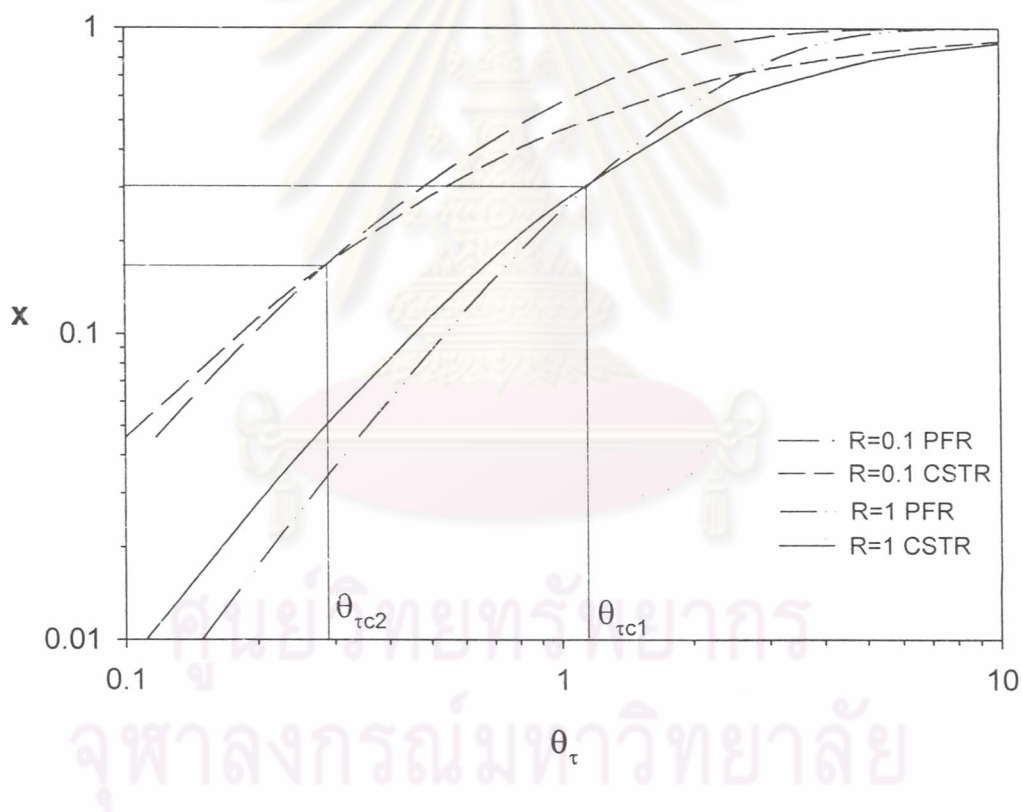


Figure 7.14: Comparison of CSTR and PFR: $q = 1$, $(x_0, h_0) = (0, 0)$.

Notation

- a : interfacial area per unit volume of liquid, m^{-1}
 $[C=C]$: concentration of carbon – carbon double bond, mM
 h : dimensionless concentration of hydrogen, defined in Equation 7.14.
 $[H_2]$: hydrogen concentration; mM
 K_1, K_2 : reaction equilibrium constants, mM^{-1}
 k_{rds} : kinetic rate constant; $(mM\ s)^{-1}$
 $k_{L,a}$: volumetric mass transfer coefficient in liquid phase; s^{-1}
 $K_{L,a}$: overall volumetric mass transfer coefficient; s^{-1}
 $[PCy_3]$: concentration of tricyclohexylphosphine; mM
 q : dimensionless parameter, defined in Equation 7.18
 R : dimensionless parameter, defined in Equation 7.19
 R_H : hydrogenation rate, $mM\ s^{-1}$
 $[Ru]$: concentration of ruthenium based catalyst, mM
 t : time; s
 x : conversion

Greek Letters

- τ : residence time; s
 τ_r : kinetic time constant, define in Equation 7.17
 θ : dimensionless time, define in Equation 7.15
 θ_r : dimensionless residence time, define in Equation 7.16

Subscripts

- 0 : $t = 0$
 c : critical value
 e : equilibrium
 in : inlet