



การมีสภาวะคงที่หลายสภาวะของพอลิเอทิลีนความหนาแน่นต่ำในถังกวน
แบบต่อเนื่องที่มีการแยกและนำกลับมาใช้ใหม่ โดยผลกระทบการย่อยสลาย

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**MULTIPLICITIES OF LOW DENSITY POLYETHYLENE IN
CSTR-SEPARATOR-RECYCLE: THE EFFECT OF ETHYLENE
AND ACETYLENE DECOMPOSITIONS**

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ใบรับรองปริญญาานิพนธ์

ชื่อหัวข้อโครงการ การมีสภาวะคงที่หลายสภาวะของพอลิเอทิลีนความหนาแน่นต่ำในถังกวนแบบต่อเนื่องที่มีการแยกและนำกลับมาใช้ใหม่ โดยผลกระทบการย่อยสลายของเอทิลีนและอะเซทิลีน

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คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี อนุมัติให้ปริญญาานิพนธ์ฉบับนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต สาขาวิชาวิศวกรรมเคมี


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ชื่อหัวข้อโครงการ	การมีสภาวะคงที่หลายสภาวะของพอลิเอทิลีนความหนาแน่นต่ำในถังกวนแบบต่อเนื่องที่มีการแยกและนำกลับมาใช้ใหม่ โดยผลกระทบการย่อยสลายของเอทิลีนและอะเซทิลีน		
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บทคัดย่อ

โครงการนี้ได้สร้างแบบจำลองทางคณิตศาสตร์เพื่อศึกษากระบวนการผลิตพอลิเอทิลีนความหนาแน่นต่ำที่ความดันสูงในระบบปฏิกิริยาพอลิเมอไรเซชันของถังปฏิกรณ์แบบต่อเนื่องและทำการแยกเพื่อนำสารตั้งต้นกลับมาใช้ใหม่ โดยมีวัตถุประสงค์เพื่อศึกษาพฤติกรรมความไม่เชิงเส้นของแบบจำลอง เมื่อรวมปฏิกิริยาการย่อยสลายของเอทิลีนและอะเซทิลีนเข้าในแบบจำลอง แบบจำลองดังกล่าวจะถูกพัฒนาขึ้นในระดับโรงงานอุตสาหกรรมและใช้วิธีการทางตัวเลขเพื่อวิเคราะห์พฤติกรรมไม่เชิงเส้น ตัวแปรการปฏิบัติการต่างๆ เช่น อุณหภูมิขาเข้าระบบและความเข้มข้นขาเข้าระบบของตัวเริ่มต้นปฏิกิริยา (Initiator) จะถูกศึกษาในโครงการนี้ การวิเคราะห์เสถียรภาพและแผนผังตัวแปรเชิงตัวเลข (numerical bifurcation) จะถูกใช้ในการคาดเดาช่วงของการปฏิบัติการที่มีความเสถียรและแสดงถึงข้อจำกัดในการปฏิบัติการเพื่อความปลอดภัย แบบจำลองนี้มีประโยชน์สำหรับการออกแบบถังปฏิกรณ์เคมีที่เหมาะสม การเลือกเงื่อนไขการปฏิบัติการที่ดีที่สุด และการควบคุมระบบเพื่อให้ได้พอลิเมอร์ในปริมาณมากที่สุดด้วย สังเกตได้ว่าเมื่อไม่พิจารณาผลกระทบของการย่อยสลายของเอทิลีนในแบบจำลองจะพบว่ามีความเสถียรที่สภาวะคงที่เกิดขึ้นที่สองช่วง แต่เมื่อพิจารณาการย่อยสลายของเอทิลีนในแบบจำลองจะพบว่ามีความเสถียรที่สภาวะคงที่เกิดขึ้นสามช่วง สภาวะคงที่ที่ส่วนกลางนี้เป็นสภาวะที่ต้องการและเป็นช่วงที่สั้นกว่าช่วงที่ไม่พิจารณาการย่อยสลายของเอทิลีน ซึ่งอาจทำให้เกิดพฤติกรรมที่ไม่สามารถควบคุมได้อย่างฉับพลันจะทำให้อุณหภูมิสูงขึ้นมากกว่า 3,300 องศาเซลเซียส ซึ่งเป็นสภาวะที่มีความเสถียรใหม่ จากการย่อยสลายของเอทิลีนทำให้เกิดอะเซทิลีนเป็นผลิตภัณฑ์ และเมื่อรีไซเคิลกลับเข้าสู่ระบบจะทำให้สภาวะคงที่ที่ส่วนกลางหายไป เมื่อพิจารณาการย่อยสลายของเอทิลีนและอะเซทิลีนในแบบจำลองจะให้ความ

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Title MULTIPLICITIES OF LOW DENSITY POLYETHYLENE
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ETHYLENE AND ACETYLENE DECOMPOSITIONS

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ABSTRACT

Multiple steady states and bifurcation of low density polyethylene (LDPE) in high pressure of Continuous Stirred Tank Reactor (CSTR)-separator-recycle polymerization systems were investigated through simulations. The comprehensive mathematical models considering ethylene and acetylene decompositions in an industrial LDPE plant were developed and numerically solved to analyze the nonlinear behaviors. The bifurcation parameters such as the feed temperature and the inlet concentration of initiator are studied in the paper. A numerical bifurcation and stability analysis are performed to predict the region of stable operation and indicate safe operating limits for certain variables at typical conditions. The models are useful for the design of optimal reactor operating conditions to obtain maximum polymer productivity. Two stable steady states are observed without ethylene decomposition in the model. When the ethylene decomposition is considered in the model there are three stable steady states observed. The middle stable steady state is desired and this stable branch is shorter than that of without ethylene decomposition which can get a runaway behavior easily to raise the upper stable steady state at very high temperature 3,300°C. Acetylene can be produced from ethylene decomposition which would be recycled

back to the process to cause the disappearance of the middle stable branch. When both of the undesired decompositions of ethylene and acetylene are considered in the model the three stable branches are still observed for no recycling. However, the polymer conversion and the reactor temperature regime of the middle stable branch are increased with increasing (i) the ratio of mass recycling and (ii) the percentage of acetylene removed from the recycled stream.



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NOMENLATURE

- C_p = Total specific heat, $\text{cal}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
- E_a = Activation energy of the generalized Arrhenius equation, $\text{cal}\cdot\text{mol}^{-1}$
- f = Initiator decomposition efficiency
- g = acetylene decomposition efficiency
- $[I]$ = Initiator concentration, $\text{mol}\cdot\text{L}^{-1}$
- k_{d_i} = Initiator I decomposition rate constant, s^{-1}
- k_p = Propagation rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- k_{tc} = Termination by combination rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- k_{tt} = Total termination rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- k_{tx} = Termination by inhibition rate constant, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- $[M]$ = Monomer concentration, $\text{mol}\cdot\text{L}^{-1}$
- MW_M = Molecular weight of monomer, $\text{g}\cdot\text{mol}^{-1}$
- $[P]$ = Polymer concentration, $\text{mol}\cdot\text{L}^{-1}$
- Q_{out} = Outlet volumetric flow rate, $\text{cm}^3\cdot\text{s}^{-1}$
- $[R]$ = Free radical concentration, $\text{mol}\cdot\text{L}^{-1}$
- R_i = Species i kinetic rate change, $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- $R_{w_{D_i}}^k$ = Kinetic rate of change of decomposition product i , $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
- V = Volume of reaction mixture, cm^3
- V_a = Activation volume of the generalized Arrhenius equation, $\text{cal}\cdot\text{atm}^{-1}\cdot\text{mol}^{-1}$
- W_i = Weight fraction of species i in the reaction mixture
- ΔH_{decomp} = Heat of ethylene decomposition, $\text{cal}\cdot\text{mol}^{-1}$
- ΔH_{polym} = Heat of polymerization, $\text{cal}\cdot\text{mol}^{-1}$
- ρ_i = Species j density, $\text{g}\cdot\text{cm}^{-3}$
- d = Decomposition
- D_i = Decomposition product i
- I = Initiator
- M = Monomer
- P = Polymerization
- X = Inhibitor species

CHAPTER I

INTRODUCTION

1.1 Significance of the Problem

Low density polyethylene or LDPE is a commodity polymer widely used in a variety of applications, for example, plastic bag, cables, insulation, and wrapping etc. LDPE can be produced from polymerization of ethylene in autoclave and/or tubular [1, 2] reactors. In both reactors, a free radical mechanism using initiators such as peroxides or oxygen takes place at temperatures ranging from 150 to 300°C and pressures ranging from 1,000 to 3,000 atm. The conversion of ethylene is normally in the ranges of 10 and 30%wt while the mean residence time in reactors varies from 15 to 120 seconds [3, 4]. Runaway reaction, or uncontrollable increases of temperature and pressure, happens more frequently in autoclave reactors than in tubular ones because of the existence of multiple steady states in autoclave reactors [3, 5]. Polymerization reaction can exhibit highly non-linear behavior, such as multiple steady states, sustained oscillations, and chaos [6]. As a result, an analysis of the non-linear dynamics of polymerization reactors has been one of important research areas. In particular, polymerization reactions are great interest because of complicated steady-state non-linear bifurcation behavior. This knowledge is important because the non-linear behavior of chemical reactors causes many operational difficulties. Furthermore, the knowledge of this behavior can be used in optimization through elimination of non-linearity. Although the reaction systems involving material recycles are common in industrial practice, a few results concerning its non-linear behavior are available in literature.

In polymerization reactors, both heat effects and autocatalytic kinetics are presented; hence, non-linear phenomena are common. Freitas et al. (1994) [7] considered a generic model of the free radical polymerization, which up to five steady states may exist. They concluded that steady state multiplicity should occur for most polymerization systems. Topalis et al. (1996) and Zhang et al. (1996) [3, 8] demonstrated that multiple steady states could occur in a LDPE CSTR polymerization.

Several authors (Marini and Georgakis, 1984; Chan et al., 1993; Topalis et al., 1996; Zhang et al., 1996; Yuan et al., 2011; Toledo et al., 2005) [3, 8-12] have studied LDPE polymerization reactors and have proposed the reactor model. They reported that the steady state of a continuous autoclave polyethylene reactor was often open-loop unstable at typical industrial process operating conditions. However, one of the well-known phenomena in high-pressure polyethylene reactors is a rapid ethylene decomposition reaction when the reaction heat is not dissipated effectively. In such cases, the reactor temperature rises rapidly (at 300 to 320°C) at which reaction mixture decomposes explosively to lower molecular weight species such as carbon, methane, hydrogen, acetylene, and ethane [13]. It is worthwhile to point out that the decomposition reaction often occurs unexpectedly even after a long period of stable reactor operation with no clearly detectable abnormal symptoms in reactors. When the decomposition reaction takes place, the reactor pressure and temperature build up quickly and reactor must be vented, shut down, and flushed for a long period of time before a new startup is initiated. Quite obviously, the resulting economic loss both from raw material and idle time is significant [14]. Because of these difficulties, the simulation technique is usually preferred over the experimental ones. Consequently, ethylene decomposition kinetics, proposed in the literature, would be included in the model studied in this work. Acetylene is one of the major products of ethylene decomposition and it was known reported that acetylene could decompose into free-radical and induced runaway reactions even the concentration is in ppm [3]. Because the recycling consists of unreacted monomer and ethylene decomposition products including acetylene, the recycle should affect the behavior of LDPE polymerization reactors.

Furthermore, a coupling between a reactor and a separator through the recycle of reactant-rich stream due to the low conversion of ethylene is the other source of multiplicities. Pushpavanam and Kienle (2001) [15] considered an exothermic first-order reaction in a CSTR-separator-recycle system. Twenty-four different bifurcation diagrams which include a maximum of two steady states, isolated solution branches and limit cycle were presented. Although the units were decoupled energetically via heat exchangers, energy feedback was still present. Kiss et al. (2002) [16] studied a case of complex reactions, including polymerization in isothermal CSTR-separator-

recycle systems and a sharp separation between reactants and products was assumed with constant product compositions. It was shown that LDPE polymerization systems can have multiple steady states.

There were several works that study the producing of LDPE in reactor-separator-recycle [16, 17]. However, no one included the ethylene and acetylene decompositions in their model. The main reason for the difference is the assumption of isothermal assumption and the negligence of decomposition in their work. Because of the thick wall of LDPE autoclave due to high pressure and highly exothermic polymerization and decomposition reactions, an adiabatic reactor is unlikely. Consequently, the model developed in our work is a better alternative.

From these reasons, multiple steady states in CSTR-separator-recycle polymerization systems for production of LDPE in the presence of ethylene and acetylene decompositions are investigated in this research. The percentages of mass recycled and acetylene removed are investigated on the desired stable branch. High-pressure free radical polymerization of ethylene in autoclaves is an important process that is widely used in industries. Because of the high operation pressure and the large heat of polymerization, difficulties are encountered in the design and in the operation of the reactor. Hence, the precise selection of the operating conditions such as feed temperature and feed initiator concentration is essential in the economic process operation. In this regard, it is important to analyze the steady states characteristic of the reactor in relationship with the change of various operating conditions by using appropriate mathematical model.

1.2 Research Objectives

1. To study multiple steady-state of a CSTR-separator-recycle-polymerization system for production of LDPE in the presence of decomposition in order to compare with the simulation results from Zhang and coworkers (1996) on bifurcation diagrams.

2. To study the effect of both ethylene and acetylene decomposition on the reactor temperature in the presence of recycles.

3. To study bifurcation behavior of LDPE in a CSTR separator recycle polymerization system in the presence of ethylene and acetylene decomposition with the effect of bifurcation parameters such as feed temperature and feed initiator concentration.

1.3 Scope

The study is divided into second parts. In the 1st part, the analysis of bifurcation behavior of a LDPE CSTR separator recycle polymerization system as an adiabatic non-isothermal system including ethylene decomposition kinetics is performed. The dynamic and steady-state simulation, such as the reactor temperature or conversion to polymer are predicted as a function of bifurcation parameters on the steady-state bifurcation diagrams. In this section, the bifurcation parameters are feed temperature and residence time. In addition, bifurcation behavior obtained in this thesis and those reported by Zhang et al. (1996) are compared. The studied reactor volume constant 1000 L. The pressure is assumed constant at 2,000 atm. The initiator is di-tert-butyl peroxide (DTBP).

In the 2nd part, the analysis of Multiple steady states of percent Acetylene in recycle stream of a LDPE CSTR-separator-recycle polymerization system as an adiabatic non-isothermal reactor in the presence of ethylene and acetylene decomposition kinetics in the model is performed as ethylene decomposes into carbon, methane, acetylene, and ethane and acetylene decompose into free-radical. The separation unit splits the products stream exiting a reactor into two streams with constant compositions. The recycling stream consists of monomer and decomposition products and the product stream consists only of LDPE. In this part, the dynamic and steady-state simulation, such as the reactor temperature, monomer conversion,

conversion to polymer, and polymer selectivity are predicted as a function of bifurcation parameters on the steady-state bifurcation diagrams. The operating parameters used in this part are feed temperature and feed initiator concentration. In addition, the bifurcation behaviors of with and without mass recycle, with and without ethylene and acetylene decomposition is compared.

The steady-state model is solved numerically using Newton method through MATLAB and the stability for steady-state regions are identified with the evaluation of eigenvalue and the eigenvalue technique was validated by solving the unsteady state models with MATLAB.

1.4 Outcomes

It is well recognized that process modeling is useful for the design of optimal reactor operating conditions and reactor controls to obtain maximum polymer productivity and desired polymer properties. In developing a comprehensive process model for high-pressure ethylene polymerization, it is first required to develop a model that gives an accurate prediction of the first level reactor performance, such as temperature, polymer yield, and specific initiator consumption rate. Once these key reactor variables can be predicted by the model, one can further improve the process model to predict important polymer properties; for example, molecular weight, molecular weight distribution, degree of short chain and long chain branching, etc., and optimize the model to design a better LDPE CSTR-separator-recycle system

CHAPTER II

LITERATURE REVIEW AND THEORY

2.1 Process Description

A generic flow diagram of the LDPE process is shown schematically in Figure 2.1. Briefly, the fresh ethylene feed is mixed with the recycled ethylene stream before entering the primary compressor. This stream is then pressurized to the desired reactor pressure in the second compression stage. Polymerization of the monomer is initiated by addition of free-radical initiators. The heat of reaction is usually removed by sensible heat because the thick reactor wall causes the low heat transfer rate. The polymer molecular weight is controlled by adjusting the reactor temperature and pressure and, optionally, by adding a chain-terminating agent. In this process, ethylene is both the reactant and the solvent (here monomer) for the polymer.

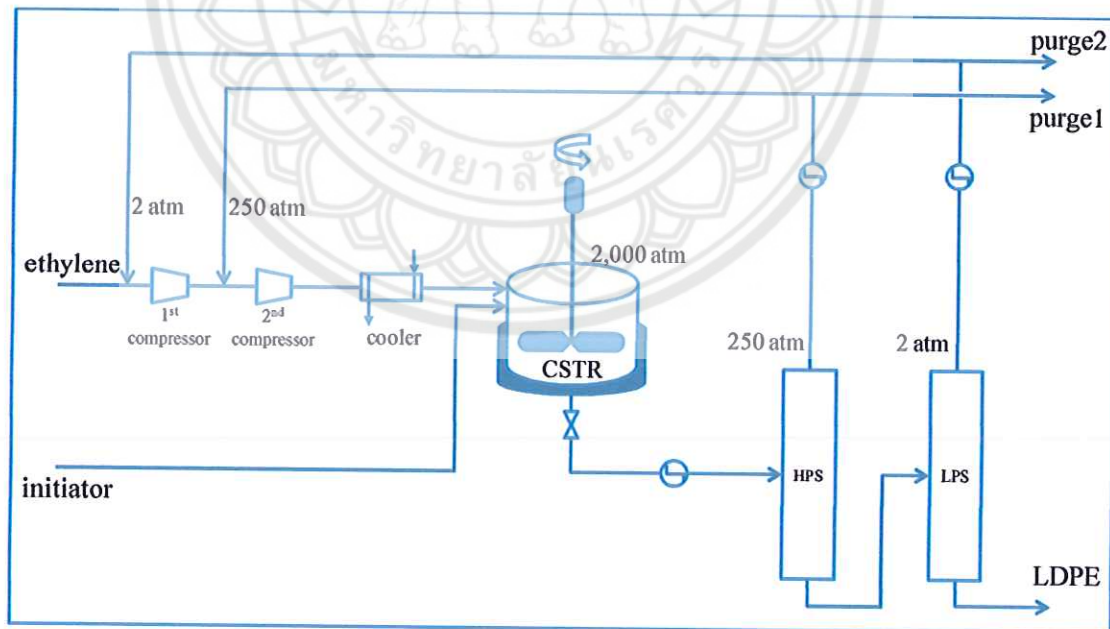


Figure 2.1 Process flow diagram of high-pressure LDPE producing

Due to the short reactor residence time, the monomer conversion is relatively low. The reactor effluent stream is depressurized across a pressure reduction valve down to 250 atm to allow separation of the product from the unreacted ethylene in a high-pressure separator (HPS). The overhead monomer rich stream is cooled and recycled back to the entrance of the secondary compressor whereas the bottom polymer-rich stream undergoes a second separation step at near atmospheric pressures in a low-pressure separator (LPS). The low-pressure gas is recycled to the entrance of the primary compressor from the LPS overhead. Most of the unreacted gas recycles continuously in this process. The byproducts are accumulated until the product qualities are outside the control limits. By that point, the operator is notified to purge the recycled gas in order to maintain the purity of the reacting gas.

2.2 Model Assumptions

The system investigated in this paper obeys the following assumptions:

- (1) Volume of the mixer, compressor, cooler, and separator are insignificant and are neglected.
- (2) Monomer feed at the primary mixer is 4 kg/s.
- (3) The initiator used is di-*tert*-butyl peroxide (DTBP).
- (4) Reactor volume of 1,000 L.
- (5) Autoclave LDPE polymerization reactor is assumed to be a non-isothermal adiabatic CSTR.
- (6) The LDPE reactor has very thick walls because the reactor is pressurized to 2,000 atm. Because of this thickness and fast and highly exothermic reaction, the reactor can be reasonably modeled as an adiabatic reactor.
- (7) The main sources of heat released are the exothermic propagation reaction and the exothermic ethylene decomposition.
- (8) The quasi-steady-state assumption for each of the radical concentrations is used.
- (9) The effect of delay on the behavior of the coupled CSTR-separator-recycle system is neglected.
- (10) Pressure is assumed to be constant.

(11) The gel effect, caused by increasing polymer molecular weight, is neglected.

(12) A sharp separation between reactants and products are assumed with constant product compositions.

(13) Mass and energy balances for mixer, compressor, cooler, and both flash are assumed to be quasi-stationary.

2.3 Decomposition of Ethylene

This study does not only include the standard initiation, propagation, and termination reactions for radical polymerization, but the free radical reactions that describe the decomposition of ethylene ultimately leading to a runaway will also be included. Although it is well known that other mechanisms, such as chain transfer to (monomer, agents, and polymer), β -scission, and back-biting, also contribute significantly to the weight- and number-distribution of polymer, those mechanisms have little effect on the total conversion and stability of LDPE autoclave reactors [18]; thus those mechanisms have not been included. Zhang and co-workers combined polymerization with decomposition reactions on their model. The rate constants of ethylene decomposition were evaluated based on ethylene decomposition kinetic scheme proposed by [13]. However, the rates of decomposition products were erroneous. To close this gap, an estimation of the kinetic parameters of ethylene decomposition was conducted in this work before the decomposition can be used for simulation.

Table 2.1 Ethylene decomposition mechanism

Reaction step	Chemical reaction
Initiation	$2C_2H_4 \xrightarrow{k_1} C_2H_3 \cdot + C_2H_5 \cdot$
	$C_2H_5 \cdot \xrightleftharpoons[k_2]{k_1} C_2H_4 + H \cdot$
Propagation	$C_2H_5 \cdot + C_2H_4 \xrightarrow{k_3} C_2H_6 + C_2H_3 \cdot$
	$H \cdot + C_2H_4 \xrightarrow{k_4} H_2 + C_2H_3 \cdot$
	$C_2H_3 \cdot \xrightarrow{k_5} C + CH_3 \cdot$
	$CH_3 \cdot + C_2H_4 \xrightarrow{k_6} CH_4 + C_2H_3 \cdot$
Termination	$CH_3 \cdot + CH_3 \cdot \xrightarrow{k_7} C_2H_6$
	$C_2H_3 \cdot + CH_3 \cdot \xrightarrow{k_8} C_2H_2 + CH_4$
	$C_2H_3 \cdot + C_2H_3 \cdot \xrightarrow{k_9} C_2H_2 + C_2H_4$

There are many independent parameters to be determined for the full decomposition model and there are few experimental results available in the literature. Therefore, it is not feasible to determine all the rate constants from experimental data. Because of this reason, a simplified decomposition kinetic scheme with a minimum number of independent kinetic parameters proposed by Watanabe et al. (1972) [13] was used. The simplified ethylene decomposition kinetic scheme is presented in Table 2.1 Even with the simplified decomposition kinetic scheme, there are still many rate constants to be determined before the decomposition can be used for simulation. There are four radicals involved in the simplified ethylene decomposition kinetic scheme, $C_2H_5 \cdot$, $C_2H_3 \cdot$, $CH_3 \cdot$, and $H \cdot$. As in other reaction mechanisms, quasi-steady-state assumption (QSSA) can be applied to all radical.

Based on the elementary reaction listed in Table 2.1, the following equations are obtained.

$$\begin{aligned} \frac{d[C_2H_5\cdot]}{dt} &= k_1[C_2H_4]^2 - k_2[C_2H_5\cdot] + k_2'[C_2H_4][H\cdot] \\ &\quad - k_3[C_2H_4][C_2H_5\cdot] = 0 \end{aligned} \quad (2.1)$$

$$\begin{aligned} \frac{d[C_2H_3\cdot]}{dt} &= k_1[C_2H_4]^2 + k_3[C_2H_4][C_2H_5\cdot] + k_4[C_2H_4][H\cdot] \\ &\quad - k_5[C_2H_3\cdot] + k_6[C_2H_4][CH_3\cdot] \\ &\quad - k_8[C_2H_3\cdot][CH_3\cdot] - 2k_9[C_2H_3\cdot]^2 = 0 \end{aligned} \quad (2.2)$$

$$\begin{aligned} \frac{d[CH_3\cdot]}{dt} &= k_5[C_2H_3\cdot] - k_6[C_2H_4][CH_3\cdot] \\ &\quad - 2k_7[CH_3\cdot]^2 - k_8[C_2H_3\cdot][CH_3\cdot] = 0 \end{aligned} \quad (2.3)$$

$$\frac{d[H\cdot]}{dt} = k_2[C_2H_5\cdot] - k_2'[C_2H_4][H\cdot] - k_4[C_2H_4][H\cdot] = 0 \quad (2.4)$$

Rearranging equations (2.1) and (2.4), $[C_2H_5\cdot]$ and $[H\cdot]$ can be represented by

$$[C_2H_5\cdot] = \frac{k_1[C_2H_4]^2(k_2' + k_4)}{k_2k_4 + k_2'k_3[C_2H_4] + k_3k_4[C_2H_4]} \quad (2.5)$$

$$[H\cdot] = \frac{k_1k_2[C_2H_4]}{k_2k_4 + k_2'k_3[C_2H_4] + k_3k_4[C_2H_4]} \quad (2.6)$$

By combination of equations (2.2) and (2.3), we arrive at

$$k_1[C_2H_4]^2 - (k_7[CH_3\cdot]^2 + k_8[[C_2H_3\cdot][CH_3\cdot] + k_9[C_2H_3\cdot]^2) = 0 \quad (2.7)$$

By assuming the rate constants of termination reactions are approximately the same value, k , since carbon and methane are the main products. If $[C_2H_3\cdot]$ is roughly equal to $[CH_3\cdot]$, equation (2.7) then becomes

$$[C_2H_3\cdot] = [CH_3\cdot] = \sqrt{\frac{k_1}{3k}} [C_2H_4] \quad (2.8)$$

where $k = k_7 = k_8 = k_9$ [13]

The rate of consumption of ethylene through ethylene decomposition is represented by equation (2.9).

$$\begin{aligned} -\frac{d[C_2H_4]}{dt} = & 2k_1[C_2H_4]^2 - k_2[C_2H_5\cdot] + k_2'[C_2H_4][H\cdot] \\ & + k_3[C_2H_4][H\cdot] + k_4[C_2H_4][H\cdot] \\ & + k_6[C_2H_4][CH_3\cdot] - k_9[C_2H_3\cdot]^2 \end{aligned} \quad (2.9)$$

The substitution of equation (2.5), (2.6), and (2.8) into (2.9) yields

$$\begin{aligned} -\frac{d[C_2H_4]}{dt} = & \left(2k_1 - \frac{k_1}{3} + k_6\sqrt{\frac{k_1}{3k}} \right) [C_2H_4]^2 \\ & + \frac{k_1k_3[C_2H_4]^3(k_2' + k_4)}{k_2k_4 + k_3[C_2H_4](k_2' + k_4)} \end{aligned} \quad (2.10)$$

Because k_2 is smaller than $k_2'[C_2H_4]$ as described above and k_2k_4 is much smaller than $k_3[C_2H_4](k_2' + k_4)$ [13], equation (2.10) then becomes;

$$-\frac{d[C_2H_4]}{dt} = \left(\frac{8}{3}k_1 + k_6\sqrt{\frac{k_1}{3k}} \right) [C_2H_4]^2 \quad (2.11)$$

The rates of formation of products can, thus, be represented by the following equations.

$$\frac{d[C]}{dt} = k_5[C_2H_3\cdot] = \left(k_6\sqrt{\frac{k_1}{3k}} \right) [C_2H_4]^2 \quad (2.12)$$

$$\begin{aligned}\frac{d[CH_4]}{dt} &= k_6[C_2H_4][CH_3\cdot] + k_8[C_2H_3\cdot][CH_3\cdot] \\ &= \left(\frac{k_1}{3} + k_6\sqrt{\frac{k_1}{k}}\right)[C_2H_4]^2\end{aligned}\quad (2.13)$$

$$\frac{d[C_2H_6]}{dt} = k_3[C_2H_4][C_2H_5\cdot] + k_7[CH_3\cdot]^2 = \left(\frac{4}{3}k_1\right)[C_2H_4]^2 \quad (2.14)$$

$$\frac{d[C_2H_2]}{dt} = k_8[C_2H_3\cdot][CH_3\cdot] + k_9[C_2H_3\cdot]^2 = \left(\frac{2}{3}k_1\right)[C_2H_4]^2 \quad (2.15)$$

2.4 Polymerization

The kinetic model of LDPE polymerization is a form of free-radical addition polymerization with initiator and impurity (C_2H_2) break down to produce the radical ($R\cdot$) and the radical reacts with monomer (M) to produce growing polymer for propagation step. Dead polymer chains (P) are created in the termination step. All of these reactions are shown in Table 2.2.

Table 2.2 Simplified kinetics of free-radical polymerization

Reaction step		Chemical reaction
Initiation		$I \xrightarrow{k_d} 2R\cdot$
		$2C_2H_2 \xrightarrow{gk_d} 2R\cdot$
Propagation		$M + R\cdot \xrightarrow{k_p} R\cdot$
Termination:	By coupling	$R\cdot + R\cdot \xrightarrow{k_{tc}} P$
	Spontaneous	$R\cdot + X \xrightarrow{k_{ts}} P$

From Table 2.2, the rate of formation of the free-radical $R\cdot$ formed by initiator and impurity are first considered. Because there will always be scavenging or recombining

of the primary radicals, only a certain fraction of initiator (f) and of impurities (g) is successful in initiating polymer chains. As a result, with the QSSA for all free radicals, the total free-radical concentration is

$$[R\cdot] = \sqrt{\frac{fk_d[I] + gk_a[C_2H_2]^2}{k_t}} \quad (2.16)$$

where $k_t = k_{tc} + k_{td} + k_{tx} + k_{isp}$

The long-chain approximation (LCA) is then utilized. Briefly, the assumption of LCA is that the rate of propagation is much greater than the rate of initiation. Consequently, the application of LCA yields simplified kinetics of free-radical polymerization

$$-r_M = k_p[M][R\cdot] \quad (2.17)$$

After substitution of $R\cdot$, the rate of disappearance of monomer [3] is

$$-r_M = k_p[M] \sqrt{\frac{fk_d[I] + gk_a[C_2H_2]^2}{k_t}} \quad (2.18)$$

The reaction rate constants in the LDPE model will be calculated from a generalized Arrhenius form shown in equation (2.19)

$$k = k_0 \exp\left[-\frac{E_a}{RT} - \frac{V_a P}{RT}\right] \quad (2.19)$$

where k_0 is the preexponential factor, E_a is the activation energy, R is the gas constant, T is the absolute temperature, P is the absolute pressure, and V_a is the activation volume. The activation volume term is used to account for the effect of pressure on reaction rate for reactions occurring at high pressures.

The initiator being used in the plant and considered in the present study is DTBP. The kinetic parameters for polymerization reaction are listed in Table 2.3. The initiator decomposition efficiency f is 0.9 and 0.1 for the impurity g [3].

Table 2.3 Kinetic parameters

Rate constant	k_0 *(s ⁻¹), **(L/gmol·s)	E_a (cal/gmol)	V_a (cal/atm·gmol)	Reference
k_{dDTBP}	*1.81x10 ¹⁶	38,400	0.0605	Chen et al., 1976
$k_{dC_2H_2}$	*2.944x10 ¹⁰	16,828	0.0	Gay et al., 1965
k_p	**1.14x10 ⁷	7,091	-0.477	Chen et al., 1976
k_{tc}	**3.00x10 ⁹	2,400	0.3147	Chen et al., 1976
ΔH_{poly}	-24,000 (cal/gmol)			Chen et al., 1976
ΔH_{decomp}	-30,200 (cal/gmol)			Huffman et al., 1974

2.5 Model Equations in the Reactor

The model is written in a general way such that different reaction media, outflow types, and thermal conditions can be modeled as special cases of the general model (Figure 2.1). The balance equations of the well-mixed tank reactor include; (1) Material balances for monomer, polymer, decomposition products, and other non-polymer species; (2) Energy balances.

The mixture in the reactor is treated as single-phase mixture consisted of monomer, polymer, solvent (here monomer), and decomposition products considered to have significant physical properties. Other species, such as initiator, impurity, and inhibitor exist only in trace amounts and have negligible physical properties.

Component densities (ρ_k) and heat capacities (C_{pk}) of individual are polynomial functions of temperature and pressure [19-21]. The reacting mixture properties such as the reacting mixture density (ρ) and the reacting mixture heat

capacity (C_p) are calculated from individual-component physical properties assuming zero volume changes of mixing.

$$\frac{1}{\rho} = \sum_{k=1}^N \frac{W_k}{\rho_k} \quad (2.20)$$

$$C_p = \sum_{k=1}^N W_k C_{pk} \quad (2.21)$$

where W_k is the weight fraction of individual-component k , N is number of components with significant volume contributions.

A total material balance around the reactor yields

$$\frac{d(V_{out} \rho_{out})}{dt} = Q_{in} \rho_{in} - Q_{out} \rho_{out} \quad (2.22)$$

where V_{out} is the volume of reaction mixture, Q_{in} is the inlet volumetric flow rate, Q_{out} is the outlet volumetric flow rate, ρ_{in} is the inlet reacting mixture density, ρ_{out} is the outlet reacting mixture density.

The fraction conversion to polymer X_p is defined as the fraction of monomer units being converted into polymer over the total amount of monomer units in the reactor, which includes monomers M , decomposition products D_i and polymers P :

$$X_p = \frac{[P]}{[M] + [D_i] + [P]} \quad (2.23)$$

2.5.1. Total Mass Balance Equation

The total material balance around the reactor is given by:

$$\begin{aligned} \frac{dV_{out}}{dt} = & -Q_{out} + \frac{(Q_{in}\rho_{in})}{\rho_{out}} - V_{out}\rho_{out} \frac{\partial P_{out}}{\partial t} \sum_{k=1}^N \frac{W_{k,out}}{\rho_{k,out}^2} \frac{\partial \rho_{k,out}}{\partial P_{out}} \\ & + V_{out}\rho_{out} \sum_{k=1}^N \frac{1}{\rho_{k,out}} \frac{dW_{k,out}}{dt} - V_{out}\rho_{out} \frac{\partial T_{out}}{\partial t} \sum_{k=1}^N \frac{W_{k,out}}{\rho_{k,out}^2} \frac{\partial \rho_{k,out}}{\partial T_{out}} \end{aligned} \quad (2.24)$$

2.5.2. Component Mass Balance Equations

The balance for monomer in the reactor is:

$$\frac{dW_{M,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}} (W_{M,in} - W_{M,out}) - \frac{MW_M (-R_p - R_d)}{\rho_{out}} \quad (2.25)$$

The balances for other non-polymer species in the reactor are:

$$\frac{dW_{I,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}} (W_{I,in} - W_{I,out}) - fk_{d_i} W_{I,out} \quad (2.26)$$

$$\frac{dW_{D_i,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}} (W_{D_i,in} - W_{D_i,out}) + \frac{MW_{D_i} R_{W_{D_i}}^k}{\rho_{out}} \quad (2.27)$$

$$\frac{dW_{X,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}} (W_{X,in} - W_{X,out}) - k_{ix} W_{X,out} \quad (28)$$

2.5.3. Energy Balance Equation

The total energy balance around the reactor is:

$$\frac{dT_{out}}{dt} = \frac{Q_{in}\rho_{in}(e_{in} - e_{out}) + E_{input} + V_{out}(R_p \Delta H_{poly} + R_d \Delta H_{decomp})}{V_{out}\rho_{out}c_{p,out} + c} \quad (2.29)$$

where c is the reactor wall heat capacity and e is the enthalpy of reaction mixture per unit mass:

$$e = \int_{T_{ref}}^T c_p dT \quad (2.30)$$

2.5.4. Peripheral Units

The mathematical models for the peripheral units (mixer, compressors, and cooler) are derived from balance equations for mass and energy. For simplicity, it is assumed that the separation in the flash units is ideal, only the monomer and the modifier are recycled, and only the product (polymer) is withdrawn from the plant. It is assumed, that the heat capacity and density of modifier is the same as those of ethylene. All volumes are well mixed and for all model equations of the peripheral units the pseudo-steady state approach is used. The ideal controllers that keep the controlled variables at the desired set point are assumed; hence, the temperatures in the recycle lines are assumed constant.

1 Mixer

In the plant there are several units for mixing different streams, e.g. mixing fresh ethylene with the recycle from the low pressure separator, or the injection of new initiator into the reactor tube. For all of these units, the volumes of these units are small in comparison with the flow terms. Thus, the different fluxes mix instantaneously, meaning that the mixer is modelled as a continuous stirred tank reactor with infinitely small volume. Hence these systems can be described solely by algebraic equations. Therefore all mixers in the plant are described by algebraic mass, component and energy balance.

$$0 = Q_{out} \rho_{out} - \sum_{j=1}^J Q_{in,j} \rho_{in,j} \quad (2.31)$$

$$0 = Q_{out} \rho_{out} W_{i,out} - \sum_{j=1}^J Q_{in,j} \rho_{in,j} W_{i,in,j} \quad (2.32)$$

$$0 = T_{out} Q_{out} \rho_{out} - \sum_{j=1}^J Q_{in,j} \rho_{in,j} T_{in,j} \quad (2.33)$$

2 Compressor

It is assumed that both compressors in the plant consist of one stage for an isentropic system.

$$0 = Q_{out} \rho_{out} - Q_{in} \rho_{in} \quad (2.34)$$

$$0 = Q_{out} \rho_{out} W_{i,out} - Q_{in} \rho_{in} W_{i,in} \quad (2.35)$$

$$0 = \frac{-Q_{in} \rho_{in} \left(\int_{T_f}^{T_{out}} C_{p,out} dT - \int_{T_f}^{T_{in}} C_{p,in} dT \right) - W_s}{V_{out} \rho_{out} C_{p,out}} \quad (2.36)$$

3 Heat Exchanger

The total mass balance, components mass balance, and energy balanced are obtained

$$0 = Q_{out} \rho_{out} - Q_{in} \rho_{in} \quad (2.37)$$

$$0 = Q_{out} \rho_{out} W_{i,out} - Q_{in} \rho_{in} W_{i,in} \quad \forall i = 1, \dots, N \quad (2.38)$$

$$0 = \frac{Q_{in} \rho_{in} \int_{T_{in}}^{T_{out}} C_{p,out} dT + Q_k}{V_{out} \rho_{out} C_{p,out}} \quad (2.39)$$

4 Separator

To describe the high-pressure flash unit, the composition of the outlet streams is assumed constant. All polymer and about 10% of unreacted monomer and ethylene decomposition products are separated and fed to the low-pressure separator

unit [20]. So the global mass balance and components mass balance are shown as the following equations.

$$0 = 0.9(Q_{in}\rho_{in} - Q_{P,in}\rho_{P,in})_{out1} + [0.1(Q_{in}\rho_{in} - Q_{P,in}\rho_{P,in}) + Q_{P,in}\rho_{P,in}]_{out2} - Q_{in}\rho_{in} \quad (2.40)$$

$$0 = 0.9(Q_{in}\rho_{in} - Q_{P,in}\rho_{P,in})W_{i,out1} + 0.1(Q_{in}\rho_{in} - Q_{P,in}\rho_{P,in})W_{i,out2} - Q_{in}\rho_{in}W_{i,in} \quad (2.41)$$

The low-pressure flash is modeled to separate ideally the polymer P from the mixture of unreacted monomer M and ethylene decomposition products Di , hence all polymer is withdrawn from the plant. So the model equations for this unit read

$$0 = (Q_M\rho_M + Q_{Di}\rho_{Di})_{out1} + Q_{P,out2}\rho_{P,out2} - Q_{in}\rho_{in}, \quad (2.42)$$

$$0 = (Q_M\rho_M + Q_{Di}\rho_{Di})_{out1}W_{i,out1} - Q_{in}\rho_{in}W_{i,in}, \quad (2.43)$$

where equations (2.41) and (2.43) are component balance for M and Di .

The two flashes are temperature controlled, so that separation temperature is constant.

CHAPTER III

RESEARCH METHODOLOGY

3.1 Simulation Method

The steady-state model is solved numerically with Newton method and the steady-state solutions are presented on bifurcation diagram. The stable steady states are identified from the values of the eigenvalues of the linearized unsteady state model; if the real parts of all eigenvalues are negative, the steady state is the stable steady state. For dynamic simulation, the unsteady state model was first derived. Then, the full set of modeling equations, which are a set of differential algebraic equations, are solved by method of fourth-order Runge-Kutta-Fehlberg [22].

3.2 Parameter Estimation

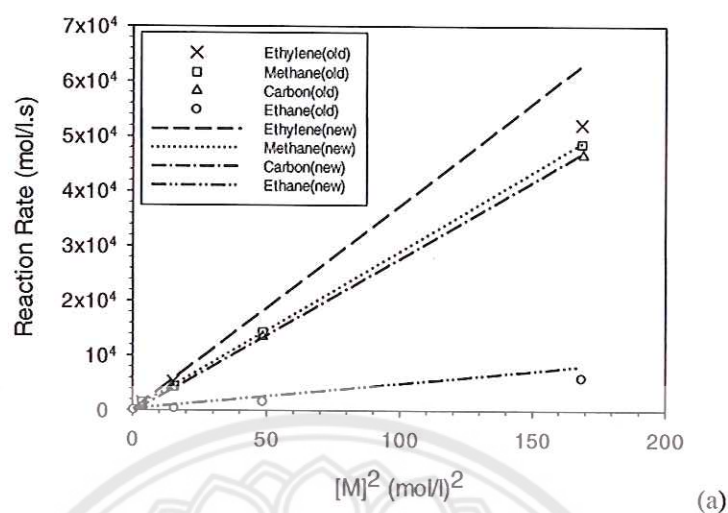
Zhang et al. (1996) combined polymerization with decomposition reactions on their model. Their rate constants of ethylene decomposition were evaluated based on ethylene decomposition kinetic scheme proposed by [13]. They reported that the generation rate of decomposition products consist of two parts: $k_1[C_2H_4]^2$, corresponding to ethylene decomposition into radicals, and $k_6\sqrt{(k_1/k)}[C_2H_4]^2$, representing the consumption of ethylene through propagation steps. There are two independent rate constants required to be determined, k_1 and $k_6k^{-0.5}$, with this simplified decomposition scheme. These rate constants were determined from two pieces of information, the crossing temperature of 310°C of the decomposition reaction rate with the polymerization rate [9, 23] and the decomposition products distribution at a specified temperature [13]. However, their rates of ethylene decomposition products were erroneous with inconsistent stoichiometric coefficients. To overcome this shortcoming, a consistent rate of ethylene decomposition is first derived and the kinetic parameters are estimated from the crossing temperature and decomposition product distribution. The kinetic scheme used here is based on the

scheme originally proposed by Watanabe et al. (1972). The rate constants for our and result from Zhang and coworkers are listed in Table 3.1

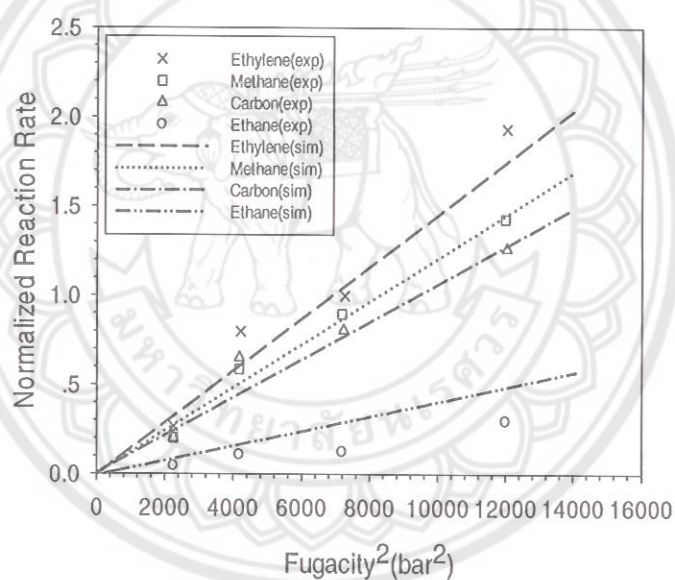
Table 3.1 Kinetic parameters for ethylene decomposition

Rate constant	k_0 (L/gmol·s)	E_a (cal/gmol)	V_a (cal/atm·gmol)	Reference
k_1	6.004×10^{19}	65,000	-0.1937	This study
$k_6 k^{0.5}$	1.587×10^{20}	65,000	0.32185	This study
k_1	4.003×10^{19}	65,000	-0.1937	Zhang et al., 1996
$k_6 k^{0.5}$	1.587×10^{20}	65,000	0.32185	Zhang et al., 1996

Figure 3.1a compares the consumption rate of ethylene and the generation rate of decomposition products as functions of ethylene. The results from the present model are compared with the simulation results from Zhang et al. (1996) at the same conditions. The simulation results from Zhang et al. (1996) are compared with experimental results from Watanabe et al. (1972) as shown in Figure 3.1b, and in good agreement was observed for the cases of methane and carbon. The predicted rate of ethylene decomposition resulting from Zhang et al. (1996) is smaller than the measured rate presented by Watanabe et al. (1972), especially at high pressure. Generally, our derived model yields the increased rate of ethylene decomposition when compared with model of Zhang et al. (1996).



(a)



(b)

Figure 3.1 The consumption rate of ethylene and the production rate of decomposition decomposition products as functions of ethylene concentration; (a) comparison between this work (new) and simulation results from Zhang et al., 1996 (old); (b) comparison between simulation results from Zhang et al. (1996) and experimental data from Watanabe et al. (1972).

3.3 Model Validation

First of all, our model is validated by comparing the numerical results to those presented in Zhang et al. (1996). Since the present decomposition rate is slightly greater than the decomposition rate of Zhang et al. (1996) at a given temperature as shown in Figure 3.2. Furthermore, the polymerization and decomposition rates for both models cross at approximately 310°C. This observation agrees with those of Marini and Georgakis (1984) [9] and Bonsel and Luft (1995) [23] in which it is generally accepted that ethylene decomposition is faster than polymerization at >300°C

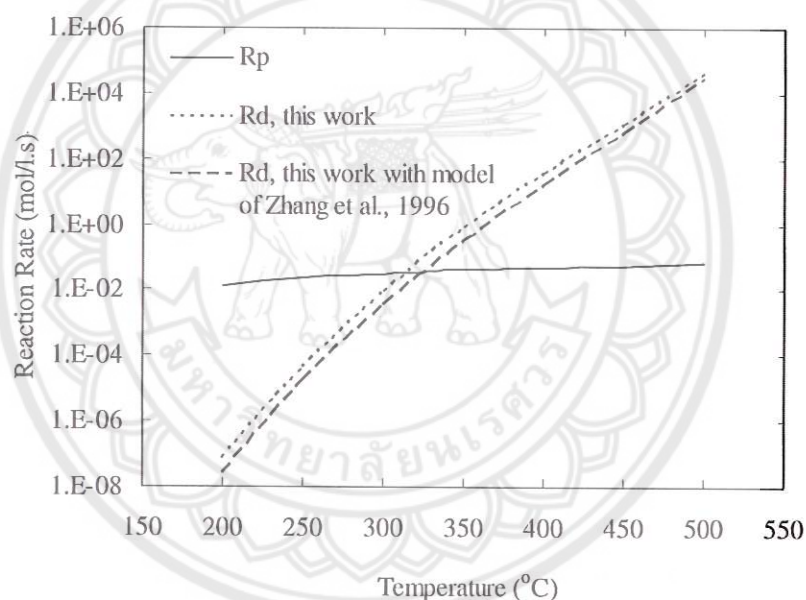


Figure 3.2 Polymerization and decomposition rates of ethylene are shown as function of temperature comparison between our model and a model of Zhang et al. (1996).

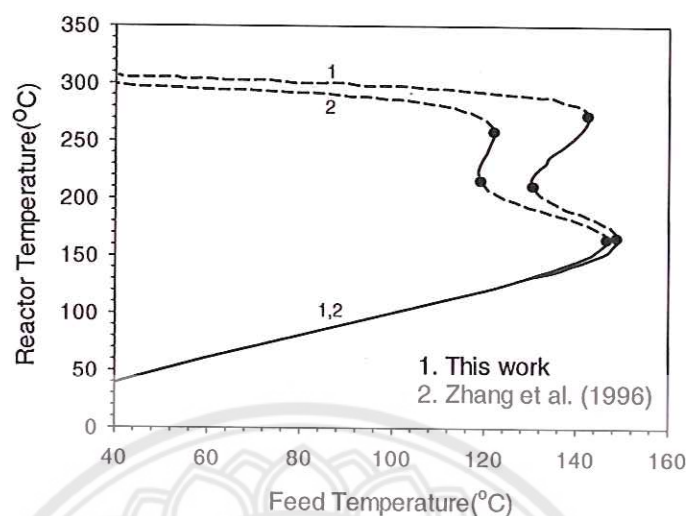


Figure 3.3 The bifurcation diagram of feed temperature on reactor temperature when ethylene decomposition reactions is included in the model. Comparison between our model (variable ethylene heat capacity) and the model of Zhang et al. (1996) (constant ethylene heat capacity) for stand-alone CSTR. Dash line refers to unstable branch and solid line refers to stable branch.

Since the assumption of constant heat capacity was used by Zhang and coworkers, the comparison of our model (with heat capacity of ethylene as a function of temperature and pressure) and Zhang et al. (1996) is made in order to investigate the effect of variable heat capacity. The simulation results of Zhang and coworkers were obtained with the component densities and heat capacities as polynomial functions of reactor temperature and pressure but constant heat capacity of ethylene (0.518 cal/g·K). Figures 3.3 and 3.4 show the steady-state of reactor temperature as a function of feed temperature and residence time with variable heat capacity for standalone CSTR, respectively. From those figures, it is obvious that the heat capacity of ethylene should not be constant when one models a LDPE polymerization reactor. Therefore, the specific heat of ethylene as a function of reactor temperature and pressure are used throughout this study. Nevertheless, the reactor is unstable over a wide range of feed temperature for both models but the middle stable branch of our numerical results exists at the higher feed temperature and residence time due to the

relaxation of the assumption. For both simulation results, the feed and product temperature of the lower stable steady states are similar indicating very low conversion.

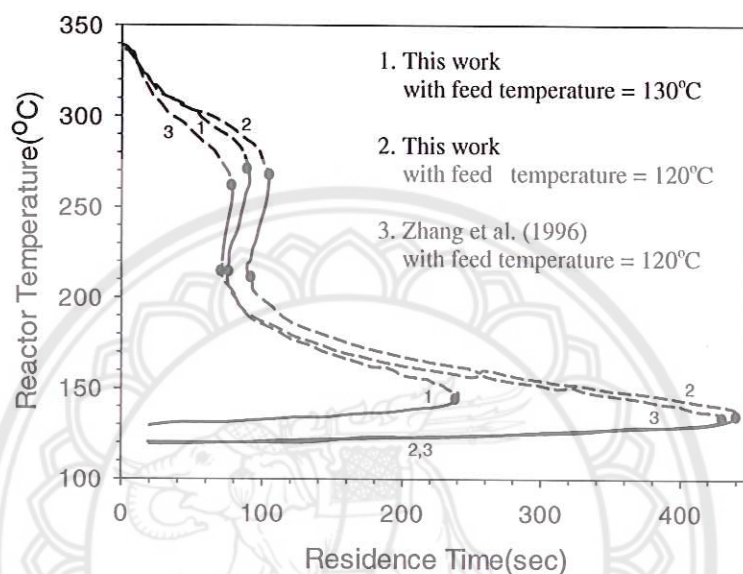


Figure 3.4 The bifurcation diagram of residence time on reactor temperature when ethylene decomposition reactions are included in the model. Comparison between this work (variable ethylene heat capacity) and result from Zhang et al. (1996) (constant ethylene heat capacity)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Ethylene Decomposition

The reactor can be kept below a certain critical temperature, the decomposition can, in principle, be avoided. However, as shown later, it is not easy to maintain a steady reaction temperature due to a fast reaction rate, a short residence time, and no external cooling. Local areas of high temperature or hot spots can also be caused by imperfect mixing and can propagate through the reactor and result in a global decomposition. Figure 4.3 compares the effects of variations in feed temperatures on reactor temperature when ethylene decomposition is included or excluded in the model without recycle and with recycle, respectively. As a result, when ethylene decomposition is included in the model, there are three stable (upper, middle, lower) and two unstable (upper, lower) branches appeared, represented by solid and dashed lines, respectively. In Figure 4.1a and 4.1b, a circle point on the line is called a “fold bifurcation point” or a “transcritical bifurcation point”. When the decomposition reactions are not included in the model, the reactor temperature continuation diagram has the typical S-shape, which is similar to the simulation result from Zhang et al. (1996). However, the upper branch of the continuation diagram is completely different when the decomposition reactions are included. The reactor temperature in upper unstable branch with decomposition reaction included increases as the feed temperature increases. At the temperature on the upper stable branch, the ethylene starts to decompose and the decomposition reactions become the dominant reaction; there appears an upper stable steady state. With ample amount of monomer available for decomposing into free radicals, there is no need for additional initiator to sustain the high-reactor temperature steady state. The calculated upper steady state of 3,300°C agrees the adiabatic temperature rise corresponding to complete ethylene decomposition. Additionally, these results suggest the importance of considering both decomposition and polymerization kinetics in performing process analysis and design.

In this study, the focus is on the four lower branches since these branches are in the normal operating ranges.

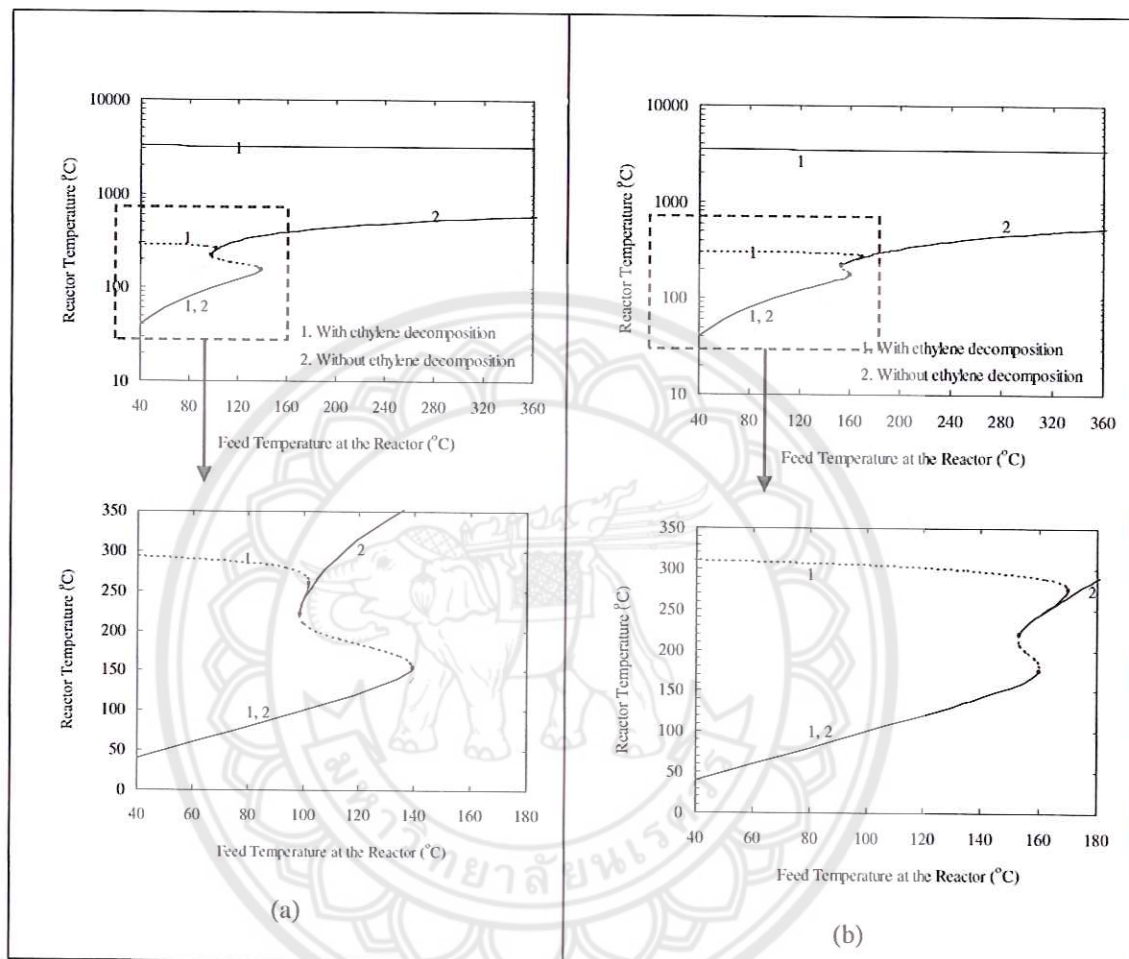


Figure 4.1 The steady-state reactor temperature is shown as a function of feed temperature when ethylene decomposition are included (1) or excluded (2) for system (a) without mass recycled and (b) with mass recycled (70%wt is recycled) at initiator feed concentration of 7.5 ppm. Solid line indicates stable steady-state. Dash line indicates unstable steady-state.

Because a design at an unstable steady state should be avoided in practice, it is of interest to recognize such conditions. In identifying stability steady-state, the technique proposed by [8] in which the eigenvalues of the Jacobian matrix of the system are calculated and analyzed for the stable-unstable steady-state; if all real part of the eigenvalues are negative, the steady state is stable. In order to prove the validity of the eigenvalue technique, the eigenvalue of the unstable steady-state is evaluated and the result is compared with the numerical results obtained from the unsteady state model as shown in Figure 4.2 for no mass recycled and with mass recycled. As a result, the steady-state reactor temperature is set initially at reactor temperature of 190°C. At 10,000 sec, the feed temperature at the primary mixer is changed for a limited period of time. Depending on the disturbance direction, runaway reaction or lower reactor temperature is reached; it proves that at the reactor temperature of 190°C is unstable steady-state. Since the reactor is adiabatic, the negative sign of eigenvalues are both necessary and sufficient stability conditions. A similar technical was used to prove the stability of steady-state solution by [16]. Additionally, Figure 4.3 shows decomposition products' distribution during the runaway reaction for no mass recycled. The decomposition products distribution is in good agreement with experimental observations [13]. Carbon, methane, acetylene, and ethane are the major decomposition products.

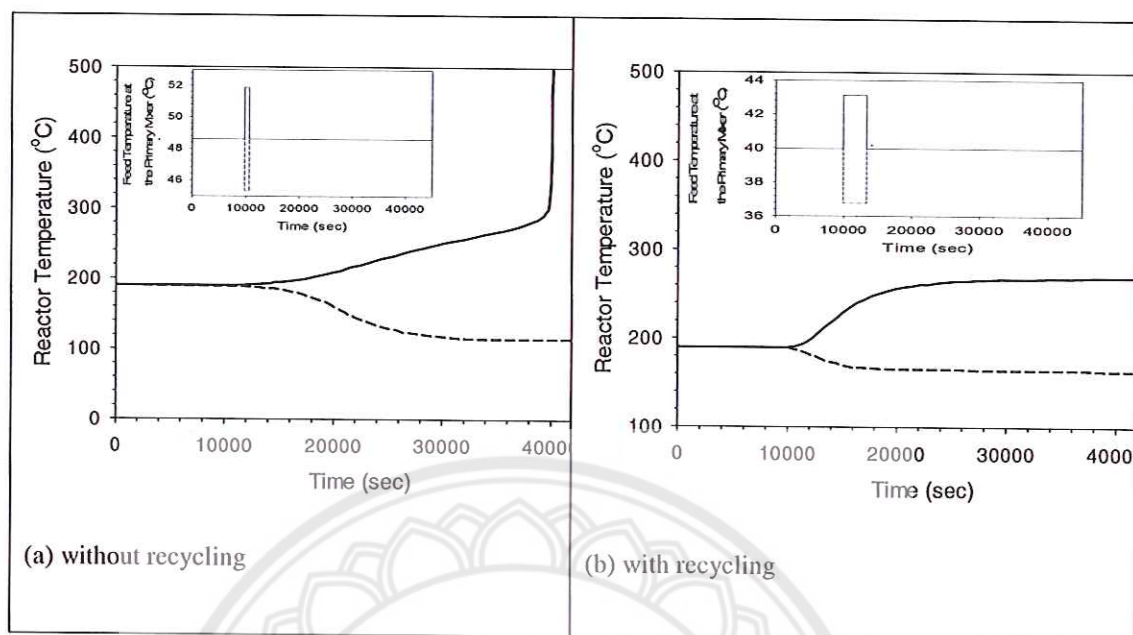


Figure 4.2 Dynamic responses of unstable steady state at reactor temperature of 190°C (a) without recycling and (b) with recycling to a feed temperature at the primary mixer disturbance when ethylene decomposition reactions are included

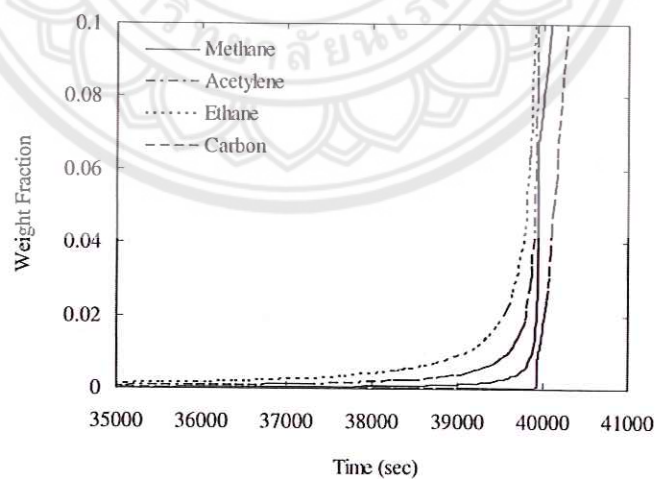


Figure 4.3 Decomposition product distribution during a runaway reaction without recycling corresponding to Figure 4.5a

4.2 Ethylene and Acetylene Decomposition

The acetylene would be in the recycle stream; hence, the model of LDPE CSTR-separator recycle system when ethylene and acetylene decomposition are considered with mass recycled are investigated. Figure 4.4 shows the conversion to polymer and reactor temperature as a function of feed temperature at different of mass recycled from 0 to 95%wt that all are in the case of 100%wt of acetylene is removed from the recycled streams. The middle stable branch is increased with the decreasing of the lower unstable branch when the mass recycled is increased. These two branches become one branch as a stable branch at the recycled mass greater than 80%wt. This is suggested that to avoid the lower unstable state and get more conversion the mass recycled should be greater than 80%.

However, when acetylene is fractionally removed from the recycling, the effect becomes more significant. Figure 4.5 shows the bifurcation diagram at different percentages of acetylene removed of 90% mass recycled. The acetylene decomposition would unstabilize the reactor and the undesirable results occur. The middle stable steady state is decreased if the percentage acetylene removed is decreased which disappeared completely at 0% acetylene removed. From the investigation, it has found that the high efficiency (>95%) of acetylene separation yields the much improved results with the middle stable steady states. However, lower efficiency acetylene separation is difficult to remediate the problems.

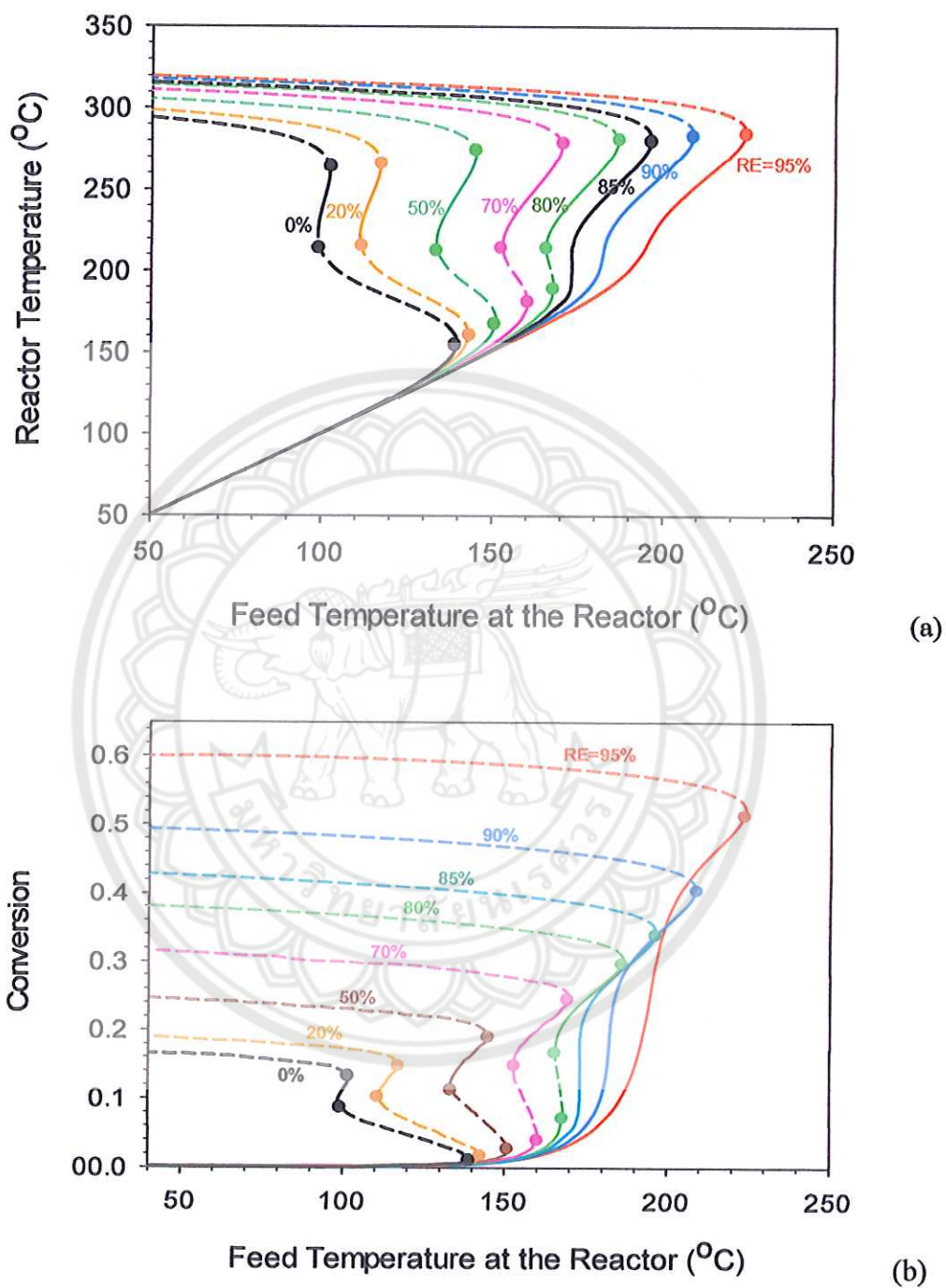


Figure 4.4 (a) reactor temperature and (b) conversion to polymer as a function of feed temperature at a given inlet concentration of initiator of 7.5 ppm and 100% acetylene removed with different mass recycled ratios

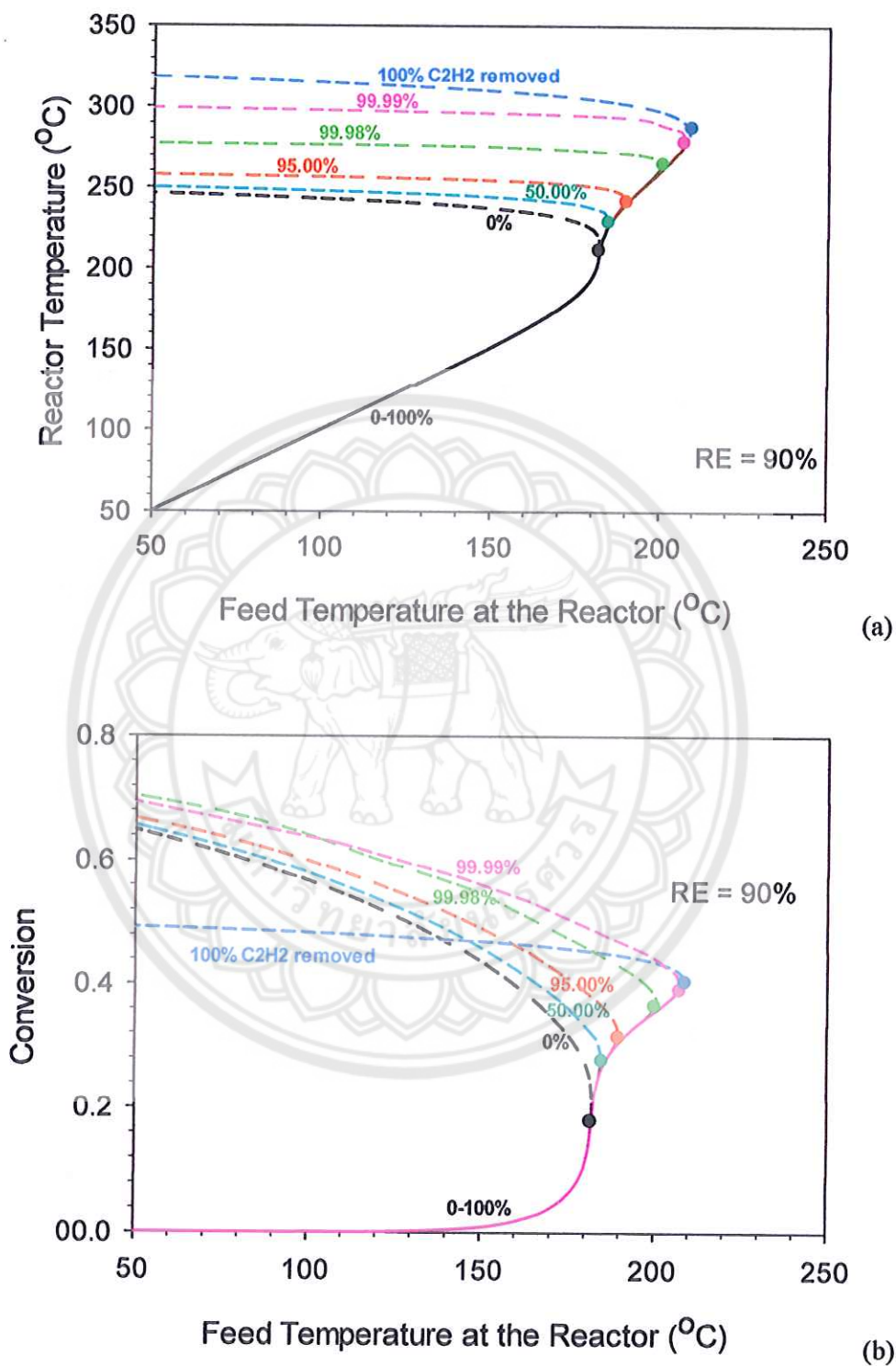


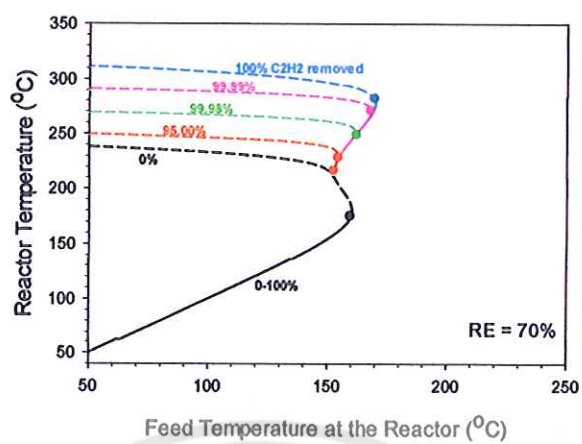
Figure 4.5 (a) Reactor temperature and (b) conversion to polymer as a function of feed temperature at 7.5ppm inlet initiator and 90% mass recycled at differences of acetylene removed

The conversion is a function of this temperature. To obtain higher conversions, the steady-state reactor temperature must be higher. However, increasing reactor temperature moves the reactor close to the unstable boundary. In practice, designs near the transcritical bifurcation points are dangerous, since changing operating conditions or uncertain design parameters can lead to a behavior that is different from the expected one.

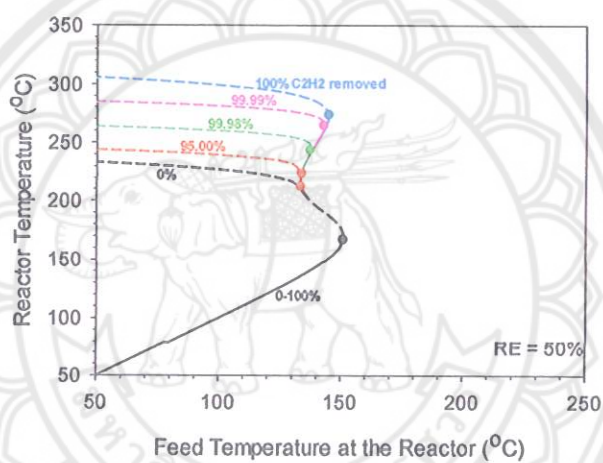
4.3 The Effect of Bifurcation Parameters

4.3.1. Feed Temperature

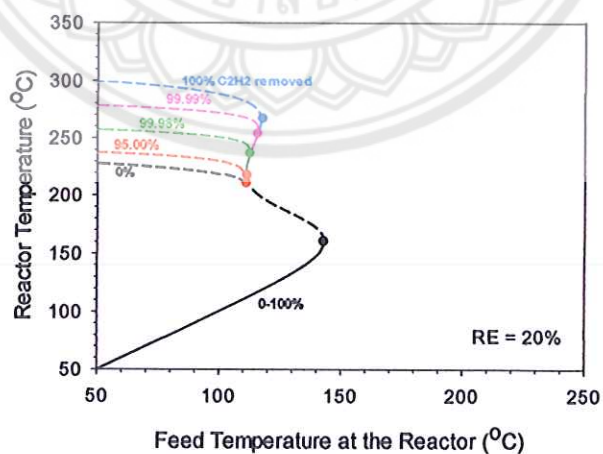
The feed temperature can have an effect on the reactor stability behavior of the system. The effect of feed temperature on the reactor temperature and conversion when the ethylene and acetylene decompositions are considered, Because of Arrhenius, increasing the feed temperature has the beneficial effect of allowing much higher degrees of conversion to polymer at middle stable branch (see Figures 4.5 and 4.6). With the higher recycle ratio, the wider middle stable branch appears with a longer feed temperature range. As the recycle ratio increasing, the conversion to polymer at the middle stable branch is higher. Therefore, the higher overall conversion could be obtained in an economically reasonable region of operation commercial plant.



(a)



(b)

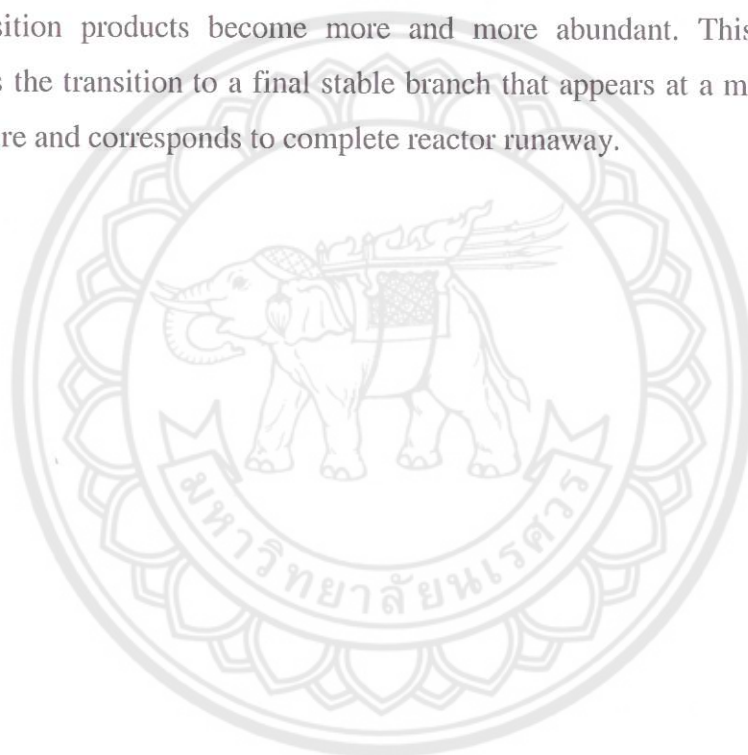


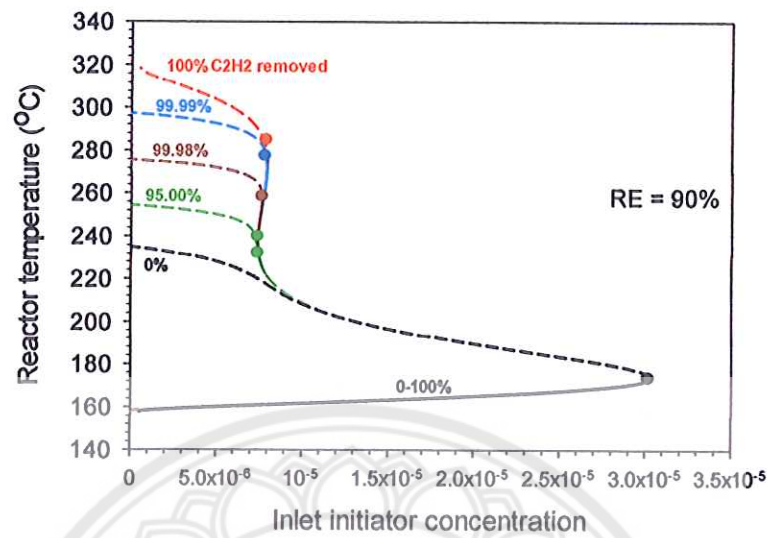
(c)

Figure 4.6 Reactor temperature as a function of feed temperature with constant inlet concentration of initiator of 7.5 ppm; (a) 70% mass recycled, (b) 50% mass recycled and (c) 20% mass recycled

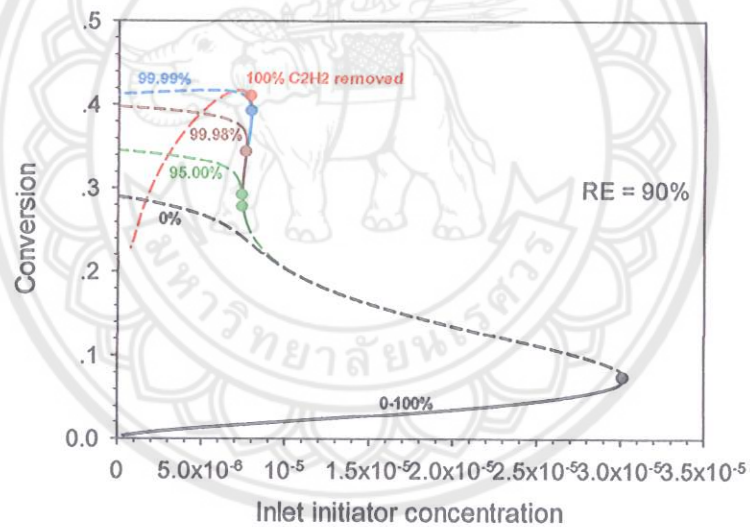
4.3.2 Inlet Initiator Concentration

Due to the adiabatic nature of the LDPE autoclave, inlet initiator is the main operation variable used to control the reactor temperature. Figure 4.7 shows the reactor temperature and conversion to polymer as a function of inlet initiator concentration at 90% recycled ratio. The increase in acetylene removed causes the increase in the middle stable steady-state. The upper unstable branch is characterized by increasing consumption of monomer by decomposition reactions. It is along this branch that conversion to polymer reaches a peak and drops to zero as the decomposition products become more and more abundant. This unstable branch represents the transition to a final stable branch that appears at a much higher reactor temperature and corresponds to complete reactor runaway.





(a)



(b)

Figure 4.7 (a) Reactor temperature and (b) conversion to polymer as a function of inlet initiator concentration for 90% mass recycled and feed temperature at the primary mixer of 30°C with different percentages of acetylene removed.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

We have presented the simulation of multiplicities of LDPE in CSTR-separator-recycle system as an industrial scale. Inclusion of ethylene and acetylene decomposition reactions in the model is important. It can be seen that a maximum of five steady states are possible with three stable (upper, middle, lower) branches and two unstable (upper, lower) branches when the ethylene decomposition reactions is included. The middle stable branch is the desired operating conditions because of its stability and acceptable conversion.

At low conversions, carbon, methane, ethane and acetylene would be present as the product of ethylene decomposition. The ethylene with its impurities, acetylene and other gases, can be recycled to the feed. Acetylene can decompose into free radicals and induce runaway reaction, the model with both ethylene and acetylene decompositions is developed and solved numerically. It can be seen that when both ethylene and acetylene decomposition is considered, the effect becomes more significant. The acetylene decomposition would destabilize the reactor and the undesirable results occur; From further investigation, it is found that the high efficiency (>95%wt) of acetylene separation yields the much improved bifurcation, middle stable steady states. However, low efficiency acetylene separation could not remediate the problems.

As the recycle ratio increasing, the range of reactor temperature at the stable steady-state is wider. Consequently, operating at high recycled ratio can produce various different grade polymer and adequately high overall conversion. A numerical bifurcation and stability analysis are performed to predict the region of stable operation and indicate safe operating limits for certain variables at typical conditions. The models are useful for the design of optimal reactor operating conditions to obtain maximum polymer productivity.

5.2 Recommendations

Since we have done the producing LDPE in on industrial scale CSTR-separator-recycle with including of ethylene and acetylene decomposition in the model. Therefore, in the similar system but the reactor change to a plug flow reactor would be interesting.





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