



สภาวะคงที่หลายสภาวะของระบบพอลิเอทิลีนไฮดรอกซีเมอไรเซชันในถังปฏิกรณ์เคมีพอลิเอทิลีน
ความหนาแน่นต่ำ-เครื่องแยก-การไหลย้อนกลับ: ผลกระทบของปฏิกิริยาการย่อยสลายของเอทิลีน

**Multiple Steady States of LDPE in CSTR-Separator-Recycle Polymerization
Systems: Effect of Ethylene Decomposition**

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บทคัดย่อ

บทความนี้นำเสนอการสร้างแบบจำลองของระบบพอลิเอทิลีนไฮดรอกซีเมอไรเซชันของพอลิเอทิลีนความหนาแน่นต่ำที่ความดันสูงในถังปฏิกรณ์เคมีแบบต่อเนื่องที่มีเครื่องแยกและการไหลย้อนกลับ ซึ่งได้พัฒนาแบบจำลองทางคณิตศาสตร์ของพอลิเอทิลีนความหนาแน่นต่ำในระดับโรงงานอุตสาหกรรม เพื่อวิเคราะห์พฤติกรรมความไม่เชิงเส้นของระบบนี้ เมื่อรวมปฏิกิริยาการย่อยสลายของเอทิลีนไว้ในแบบจำลองด้วย ผลกระทบของตัวแปรในที่นี้คืออุณหภูมิเข้าของระบบที่มีต่ออุณหภูมิของถังปฏิกรณ์เคมี และการเกิดขึ้นของพอลิเมอร์ได้ถูกวิเคราะห์ด้วยเช่นกัน สมการของแบบจำลองทั้งหมดนั้น ประกอบด้วย สมการอนุพันธ์และสมการพีชคณิต โดยที่แบบจำลองที่สภาวะคงที่นั้น ได้ถูกแก้โดยวิธีเชิงตัวเลขด้วยวิธีของนิวตัน และได้ตรวจสอบพฤติกรรมโดยการสร้างแผนผังตัวแปร (bifurcation diagram) พบว่า การรวมปฏิกิริยาการย่อยสลายของเอทิลีนเข้าในแบบจำลองนั้นมีความจำเป็น และการเพิ่มขึ้นของอัตราการไหลย้อนกลับของมวลสารสามารถทำให้เกิดสภาวะคงที่หลายสภาวะได้ และได้มีการวิเคราะห์เสถียรภาพของเงื่อนไขตัวแปรเชิงตัวเลขเพื่อคาดเดาช่วงของการปฏิบัติการที่มีเสถียรภาพ และบ่งชี้ขอบเขตการปฏิบัติการที่มีความปลอดภัย ซึ่งแบบจำลองนี้มีประโยชน์ สำหรับการออกแบบ การหาสภาวะการปฏิบัติการที่เหมาะสม และการควบคุมผลิตภัณฑ์ที่เป็นพอลิเมอร์ให้ได้ปริมาณมากที่สุด เป็นต้น

คำสำคัญ: พอลิเอทิลีนความหนาแน่นต่ำ การย่อยสลายของเอทิลีน ความสัมพันธ์เชิงตัวแปร

Abstract

This paper focuses on simulation inside low-density polyethylene (LDPE) in high pressure CSTR-separator-recycle polymerization systems. A comprehensive mathematical model of an industrial LDPE plant is developed to analyze the non-linear behavior when ethylene decomposition kinetics is included in the model. The effect of bifurcation parameter as feed temperature on reactor temperature and overall conversion to polymer is also investigated. The overall model comprises differential and algebraic equations. The steady-state model is solved numerically with Newton and examined by constructing the bifurcation diagram. It can be seen that the ethylene decomposition is important and must be included in the model. Increasing the mass recycle ratio can lead to multiple steady states. A numerical bifurcation and stability analysis are performed and the regions of stable operation are predicted; the safe operating limits for certain variables at typical conditions are identified. The presented models are useful for the design of optimal reactor operating conditions and reactor controls to obtain maximum polymer productivity.

Keywords: Low-density polyethylene (LDPE), ethylene decomposition, bifurcation

Introduction

Low-density polyethylene (LDPE) is a commodity polymer used in a wide variety of applications; for example, plastic bags, wrapping, cable, insulation and wrapping. LDPE can be produced from polymerization of ethylene in both autoclave reactors and tubular 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 in the ranges of 10 and 30%wt while the mean residence time in reactors varies from 15 to 120 seconds (Gemassmer, 1978; Zhang et al., 1996). Autoclave reactors are preferred if copolymerization or special LDPE properties are desired since the operating condition of autoclave reactors could be changed easier. Because of low conversion of ethylene, recycling of monomer is a common procedure for LDPE production.

Many results can be found on modeling LDPE stand-alone autoclave (Chan et al., 1993; Marini and Georgakis, 1984; Topalis et al., 1996) and there was CSTR-separator-recycled system that proposed by Kiss et al. (2002). But most of these results deal with only polymerization and polymer molecular structure due to the lack of a fundamental understanding of the decomposition reactions. Descriptions of typical decomposition phenomena can be found elsewhere (Zhang et al., 1996). Zhang et al. (1996) combined polymerization with decomposition reactions on their model. The rate constants of ethylene decomposition were evaluated based on ethylene decomposition kinetic scheme proposed by Watanabe et al. (1972). However, the rates of ethylene decomposition products were erroneous. Since, this paper focuses on CSTR-Separator-Recycle LDPE polymerization in the presence of ethylene decomposition.

Consequently, the objective of this paper is to investigate the bifurcation behavior in CSTR-Separator-Recycle LDPE polymerization in the presence of ethylene decomposition. The steady-state model has been extended to include the kinetic of decomposition using the data from Watanabe et al. (1972) and Zhang et al. (1996) and the consistent rates of the reactions are derived in order to estimate rate constant before the decomposition can be used for simulation. The steady-state model is solved and examined by constructing the bifurcation diagram. The stability steady state regions were also identified. In addition, the effect of bifurcation parameter as feed temperature on the reactor temperature and overall conversion at different mass recycle ratio is also investigated and discussed in the paper.

Methods

Process Description

A generic flow diagram of the LDPE process is shown schematically in Figure 1. In brief, fresh ethylene is mixed with recycle gas before entering the primary compressor. This stream is pressurized to the desired reactor pressure of 2,000 atm in a second compression stage. Polymerization of the monomer is initiated by adding free-radical initiators (here *di-tert-butyl peroxide*, DTBP). In this process, ethylene is both the reactant and the solvent for the polymer. 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 will be notified to purge the recycled gas in order to maintain the purity of the reacting gas.

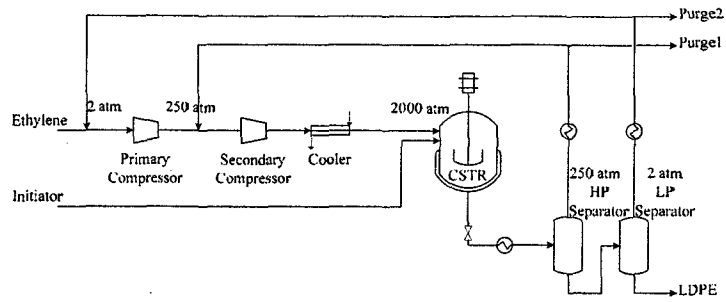


Figure 1. Scheme of a LDPE Polymerization Plant.

Rate of LDPE Polymerization

The kinetic model of LDPE polymerization is a form of free-radical addition polymerization with initiator and impurity 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 1. Rate of LDPE polymerization reaction can also be seen in Zhang et al. (1996).

Table 1. Simplified kinetics of free-radical polymerization (Zhang et al., 1996)

Initiation:		$I \xrightarrow{k_d} 2R\cdot$
Initiation:		$2C_2H_2 \xrightarrow{k_{d_1}} 2R\cdot$
Propagation:		$M + R\cdot \xrightarrow{k_p} R\cdot$
Termination:	By coupling	$R\cdot + R\cdot \xrightarrow{k_{tc}} P$
	By inhibition	$R\cdot + X \xrightarrow{k_{ti}} P$

Rate of Reaction for Ethylene Decomposition

Using the kinetic mechanisms proposed in Watanabe et al. (1972) and shown in Table 2, the following rates of reaction were derived.

$$-\frac{d[C_2H_4]}{dt} = \left(\frac{8}{3}k_1 + k_6\sqrt{\frac{k_1}{3k}} \right) [C_2H_4]^2 \quad (1)$$

$$\frac{d[C]}{dt} = k_3[C_2H_3\cdot] = \left(k_6\sqrt{\frac{k_1}{3k}} \right) [C_2H_4]^2 \quad (2)$$

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

$$\frac{d[C_2H_6]}{dt} = k_3[C_2H_4][C_2H_3\cdot] + k_7[CH_3\cdot]^2 = \left(\frac{4}{3}k_1 \right) [C_2H_4]^2 \quad (4)$$

$$\frac{d[C_2H_2]}{dt} = k_8[C_2H_3\cdot][CH_3\cdot] + k_9[C_2H_3\cdot]^2 = \left(\frac{2}{3}k_1 \right) [C_2H_4]^2 \quad (5)$$

Table 2. Ethylene decomposition mechanism (Watanabe et al., 1972)

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



It should be noted that the rate of ethylene decomposition presented here is consistent as compared with Watanabe et al., (1972).

The kinetic parameters for ethylene decomposition were obtained by fitting with Watanabe and coworkers' results and listed in Table 3. The rate of ethylene decomposition with our model is good agreement with the result from Zhang et al. (1996) as shown in Figure 2. The crossing temperature of decomposition and polymerization are both around 310°C that reasonable to concluding of Marini and Georgakis, (1984).

Table 3. Kinetic parameters for polymerization and ethylene decomposition (Zhang et al., 1996)

Rate constant	k_0 *(s ⁻¹), **(L/gmol·s)	E_a (cal/gmol)	V_a (cal/atm·gmol)	Reference
DTBP, k_{dDTBP}	*1.81x10 ¹⁶	38,400	0.0605	Chen et al., 1976
Acetylene, $k_{dC_2H_2}$	*2.944x10 ¹⁰	16,828	0.0	Gray 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
k_1	**6.004x10 ¹⁹	65,000	-0.1937	This study
$k_6k^{-0.5}$	**1.587x10 ²⁰	65,000	0.32185	This study
ΔH_{poly}	-24,000 (cal/gmol)			Chen et al., 1976
ΔH_{decomp}	-30,200 (cal/gmol)			Huffman et al., 1974

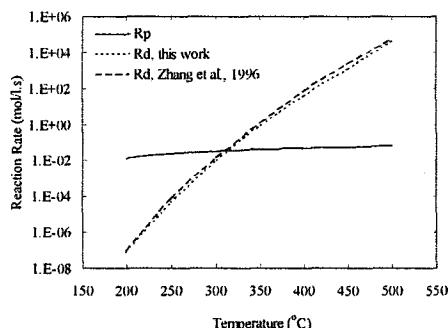


Figure 2. Polymerization and decomposition rates of ethylene are shown as a function of temperature. At typical operating temperatures (200-250°C), polymerization dominates; at elevated temperatures (above 310°C), decomposition of ethylene takes over.

Mathematical Model of LDPE Autoclaved Polymerization Plants

Upon performing unsteady state material and energy balances around reactors assuming a CSTR and adiabatic system, the following ordinary differential equations are obtained;

The total material balance around the reactor is given by:

$$\frac{dV_{out}}{dt} = -Q_{out} + \frac{Q_{in}\rho_{in}}{\rho_{out}} - V_{out}\rho_{out} \frac{\partial \rho_{out}}{\partial t} \sum_{k=1}^N \frac{W_{k,out}}{\rho_{k,out}^2} \frac{\partial \rho_{k,out}}{\partial P_{out}} + V_{out}\rho_{out} \sum_{k=1}^N \frac{1}{\rho_{k,out}} \frac{dW_{k,out}}{dt} - V_{out}\rho_{out} \frac{\partial T_{out}}{\partial t} \sum_{k=1}^N \frac{W_{k,out}}{\rho_{k,out}^2} \frac{\partial \rho_{k,out}}{\partial T_{out}} \tag{6}$$

The balance for monomer in the reactor is:

$$\frac{dW_{M,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}}(W_{M,in} - W_{M,out}) - \frac{MW_M(-R_p - R_d)}{\rho_{out}} \quad (7)$$

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

$$\frac{dW_{I,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}}(W_{I,in} - W_{I,out}) - fk_{d_i}W_{I,out} \quad (8)$$

$$\frac{dW_{D,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}}(W_{D,in} - W_{D,out}) + \frac{MW_{D_i}R_{W_{D_i}}^k}{\rho_{out}} \quad (9)$$

$$\frac{dW_{X,out}}{dt} = \frac{Q_{in}\rho_{in}}{V_{out}\rho_{out}}(W_{X,in} - W_{X,out}) - k_{rx}W_{X,out} \quad (10)$$

The total energy balance around the reactor is:

$$\frac{dT_{out}}{dt} = \frac{Q_{in}\rho_{in}(e_{in} - e_{out}) + E_{input} + V_{out}(R_p\Delta H_{poly} + R_d\Delta H_{decomp})}{V_{out}\rho_{out}C_{p,out} + c} \quad (11)$$

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

The mathematical models for the other units 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 polymer is withdrawn from the plant. All volumes are well mixed is used. For steady-state model, the time derivatives in equations are set to zero and a set of algebraic equations are obtained.

Numerical Analysis of the Mathematical Models

For unsteady state model, fourth-order Runge-Kutta-Fehlberg in MATLAB is used. Newton method is applied to solve the steady state model numerically. In identifying stable steady state, the technique proposed by Topalis et al. (1996) in which the eigenvalue will be calculated and analyzed for the stable-unstable steady state; if all real part of the eigenvalue is less than zero, the steady state is stable. In order to prove the validity of the eigenvalue technique, the eigenvalue of the unstable steady-state was evaluated and the result was compared with the numerical results obtained from the unsteady state model.

Results and Discussion

Model Validation

First of all our model is validated by comparing to the model of Zhang et al. (1996). Our result and the read of picture from Zhang et al. (1996) with the same conditions that the reacting mixture properties are calculated from the individual component physical properties are compared as shown in Figure 3(a). The simulation results from Zhang and coworkers were done with component densities and heat capacities are polynomial functions of reactor temperature and pressure except heat capacity of ethylene is constant. As the result, a good fit between both results of steady-state reactor temperature as function of feed temperature with the same physical properties for stand-alone CSTR are occurred. Furthermore, our simulation result with all of physical properties as function of reactor temperature and pressure is computed to compare with the simulation result from Zhang et al. (1996) and shown in Figure 3(b). So, all of physical properties such as density and specific heat as function of reactor temperature and pressure are used in this study.

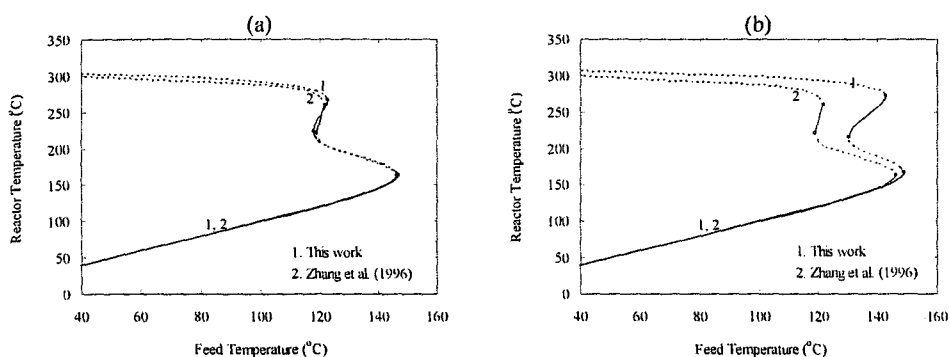


Figure 3. The bifurcation diagram of feed temperature on reactor temperature with ethylene decomposition reactions included, compare between this works and result from Zhang et al. (1996) for stand-alone CSTR. (a) At the same physical properties used. (b) Our all of physical properties used as function of reactor temperature and pressure.

Effect of Ethylene Decomposition

The effects of variations in feed temperature on reactor temperature comparison between with and without ethylene decomposition included in the model for no recycle case and the case of with recycle are shown in Figure 4 and 5, respectively. As the result of ethylene decomposition included in the model, there are three stable (upper, middle, lower) and two unstable (upper, lower) branches appear, represented by solid and dashed lines, respectively. Description, a circle point on the line is called "a turning point" or "a fold bifurcation point" and 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 once the decomposition reactions are included. The upper unstable branch with decomposition reaction included increases in reactor temperature with decreasing feed temperature. At reactor temperatures, the ethylene starts to decompose and the decomposition reactions overcome the polymerization reactions to become the dominant reaction path; 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 upper steady state of 3,300°C is calculated from the adiabatic temperature rise corresponding to complete ethylene decomposition. Additionally, these results suggest the importance of considering both decomposition and polymerization kinetics in doing process analysis, design, and control. In this study, we will focus on the four lower branches because they are in the normal operating range.

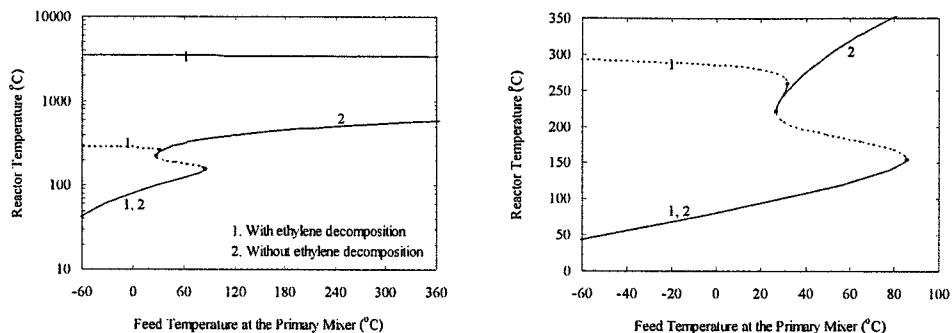


Figure 4. The bifurcation diagram of the steady-state reactor temperature is shown as a function of feed temperature at the primary mixer with either decomposition or non-decomposition kinetics in the model for the case of no recycled at initiator feed concentration of 7.5 ppm.

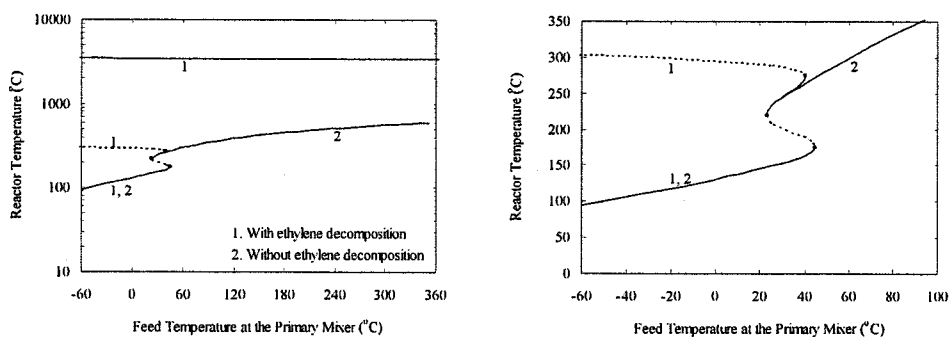


Figure 5. The bifurcation diagram of the steady-state reactor temperature is shown as a function of feed temperature at the primary mixer with either decomposition or non-decomposition kinetics in the model for the case of with recycled at initiator feed concentration of 7.5 ppm.

The Effect of Feed Temperature at Different Mass Recycle Ratio

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 the overall conversion for the case of the ethylene decomposition is considered at initiator feed concentration of 7.5 ppm as shown in Figure 6. Because the reactor temperature is limited by the onset of ethylene decomposition reactions and danger of runaway, increasing the feed temperature has the beneficial effect of allowing much higher degrees of the overall conversion to polymer at middle stable branch. For the higher recycle ratio (r_e), the middle stable branch exists at a wider reactor temperature with a wider feed temperature range. For example the middle stable reactor temperature in the range from 220 to 260°C for no recycle case and 220 to 265°C, 220 to 270°C, and 220 to 275°C for the cases of recycle ratio values of 0.20, 0.50, and 0.70, respectively. And the middle stable exist at a range of feed temperature at primary mixer from 27 to 32°C, 25 to 34°C, 23 to 37°C, and 23 to 40°C for recycle ratio of 0, 0.20, 0.50, and 0.70 respectively. As the recycle ratio increases, the conversion to polymer middle stable branch has higher conversion to polymer with a wider feed temperature range. Description, the overall conversion could be obtained in an economical reasonable region of operation commercial plant. The middle stable branch is the normal operating branch and covers conversion in the range from 10 to 13% for no recycle case and 11 to 15%, 13 to 20%, and 16 to 25% for the cases of recycle ratio values of 0.20, 0.50, and 0.70, respectively. For lower stable branch, increase of recycle ratio causes decrease in a wide range of feed temperature at the primary mixer but increase in a wide range of the reactor temperature.

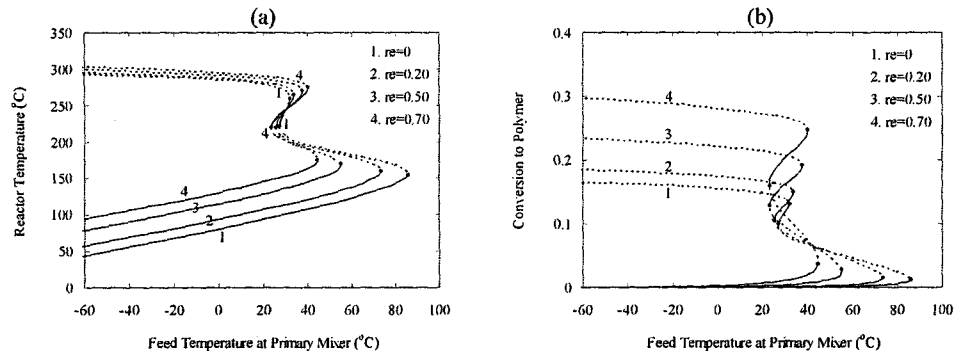


Figure 6. The bifurcation diagram of the steady-state of (a) feed temperature at the primary mixer on the reactor temperature and (b) the overall conversion to polymer with ethylene decomposition reactions included at initiator feed concentration of 7.5 ppm.

Conclusions

Including of ethylene decomposition reactions in the model is important. It can be seen that a maximum of five steady states are possible. The middle stable branch is desired operating conditions and an economical reasonable region of operation commercial plant. Furthermore, During LDPE production, it is often necessary to change the reactor operating conditions to produce a different grade polymer since reactor temperature can significantly affect the polymer molecular structure and subsequently the physical properties. As increasing of recycle ratio, stable steady-state of reactor temperature has a wider over a wider of operating parameters range. So, operating at high recycle ratio can be produced more a different polymer and overall conversion. The present model, the acetylene decomposition in the presence of recycle is neglected. Because of acetylene is one major of ethylene decomposition products at low conversion and can decompose into free radicals. Since, a subsequent article will analyze bifurcation behavior with including both ethylene and acetylene decompositions in the model.

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