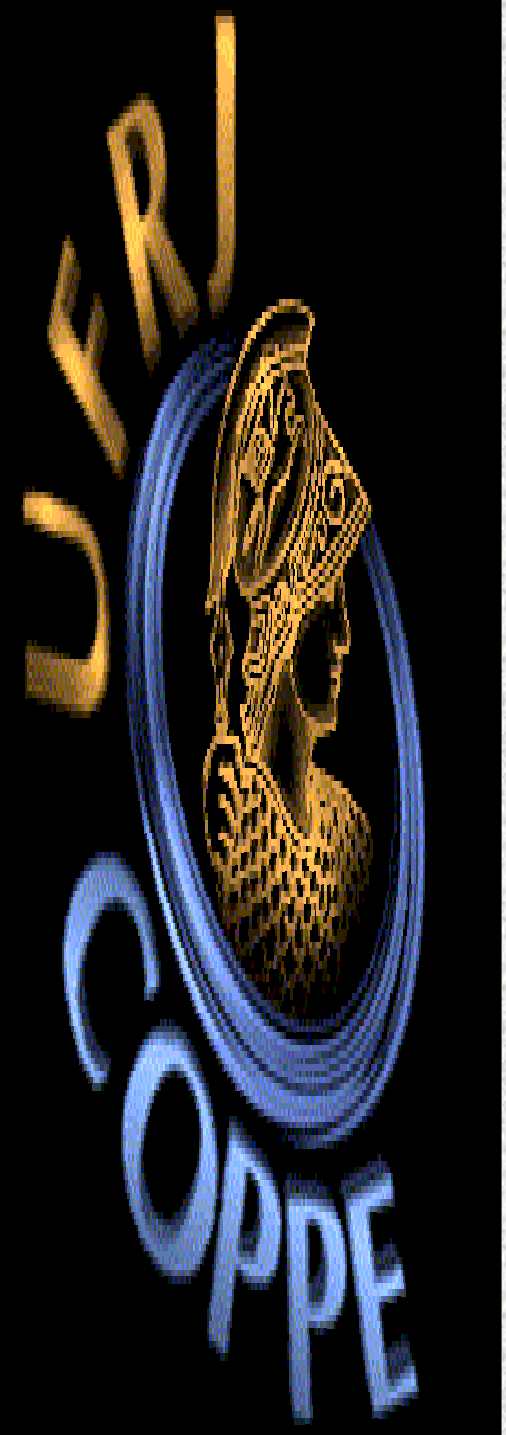

Stability Issues in a Continuous Loop Reactor for Free-Radical Polymerization

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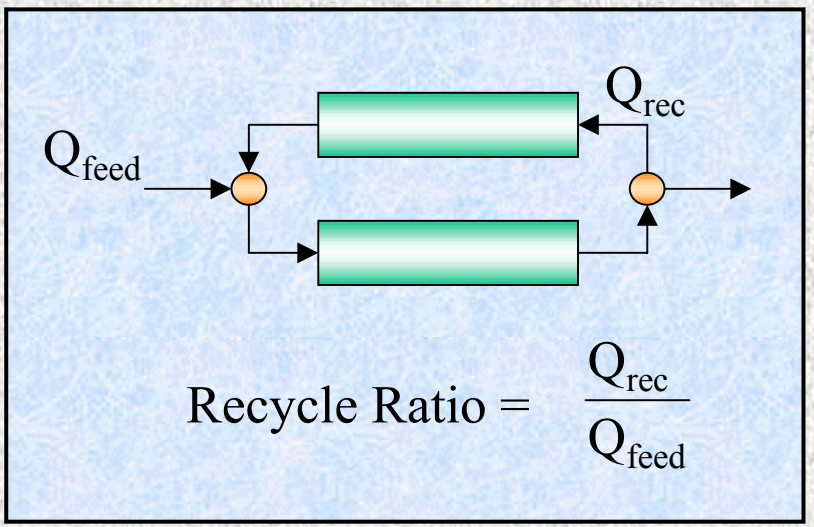
Outline

- Introduction and Motivation
- Polymerization System
- Reactor Modeling
- Numerical Methods and Results
- Conclusions
- Acknowledgements

Introduction and Motivation

- Tank reactors present difficulties for heat transfer and mixing (Gerrens, 1982, *Chemtech*, June);
- Tubular reactors present difficulties related to uncertainty in the MWD & plugging (Hamer & Ray, 1986 *Chem. Eng. Sci.*, **41** (12));

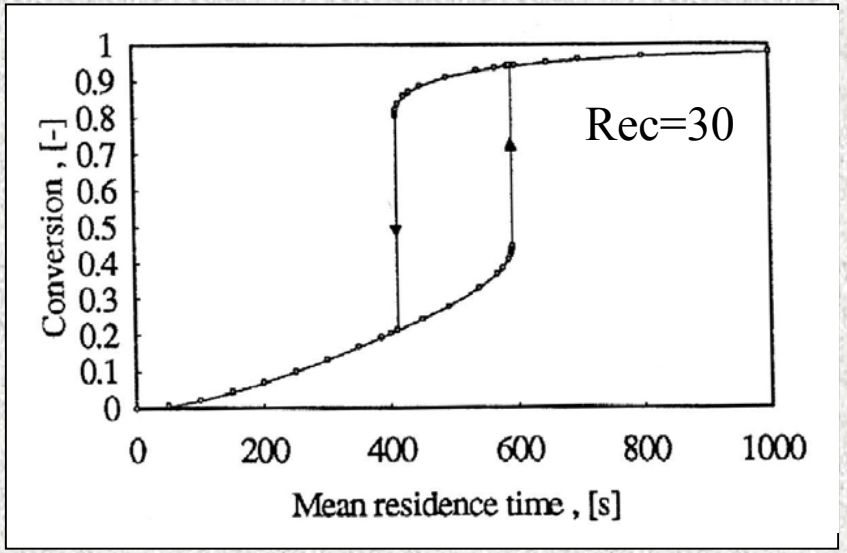


- Loop reactors are tubular and present the RTD of the perfect mixed tanks (Meyer & Renken, *Chem. Eng. Sci.*, **45** (8), 1990, and Asua *et al.*, *Chem. Eng. Sci.*, **49** (24B), 1994);
- Loop reactors are potential candidates for an alternative vessel for the free-radical polymerization systems (Renken *et al.*, *Chem. Eng. Sci.*, **47** (9-11), 1992).

Issues Regarding Reactor Stability

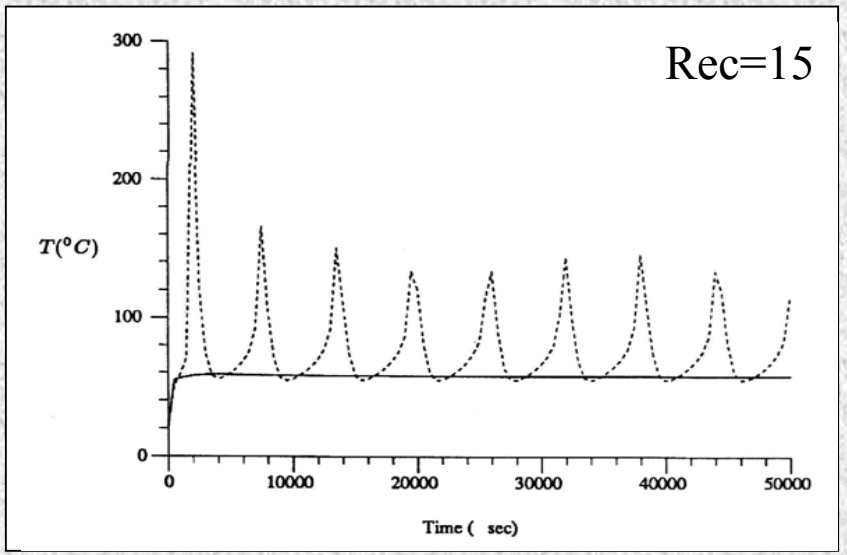
- Multiple steady-states:

Fleury, Meyer & Renken
Chem. Eng. Sci., **47** (9), 1992



- Oscillatory behavior:

Zacca & Ray
Chem. Eng. Sci., **48** (22), 1993



Polymerization System

- Free-radical polymerization of vinyl acetate in methanol initiated by AIBN
- Industrial importance of poly(vinyl acetate) in the adhesive and paint industries and as the key component for the production of poly(vinyl alcohol) and poly(vinyl acetal)
- Availability of kinetic parameters in the open literature
- Previous work in *UWPREL* and *LMSCP* on reactor dynamics using this monomer (Teymour & Ray,1992, *Chem. Eng. Sci.*, **45** (8), and Pinto, 1995, *Chem. Eng. Sci.*, **45** (8))

Polymerization Kinetics

- Polymerization kinetics described by classical free-radical mechanism steps:

Initiation:

$$I \xrightarrow{k_d} 2R$$

$$R + M \xrightarrow{k_{pR}} P_1'$$

Propagation:

$$P_n + M \xrightarrow{k_p} P_{n+1}$$

$$P_n' + M \xrightarrow{k_p} P_{n+1}'$$

Termination by combination:

$$P_n + P_m \xrightarrow{k_{tc}} M_{n+m}$$

$$P_n' + P_m \xrightarrow{k_{tc}} M_{n+m}$$

$$P_n + P_m' \xrightarrow{k_{tc}} M_{n+m}$$

$$P_n' + P_m' \xrightarrow{k_{tc}} M_{n+m}'$$

The prime denotes absence of terminal double bonds

Chain transfer to monomer, solvent and terminal double bond polymerization have also been modeled

Model Equations

- Component molar balance:

$$\frac{\partial y^i(z,t)}{\partial t} + \frac{\partial y^i(z,t)}{\partial z} = \frac{1}{Pe_m^i}\frac{\partial^2 y^i(z,t)}{\partial z^2} - Da^i \cdot \Re_{y,\theta}^i$$

- Energy balance:

$$\frac{\partial \theta^i(z,t)}{\partial t} + \frac{\partial \theta^i(z,t)}{\partial z} = \frac{1}{Pe_h^i}\frac{\partial^2 \theta^i(z,t)}{\partial z^2} + B \cdot Da^i \cdot \Re_{y,\theta}^i + \beta^i(\theta_c - \theta)$$

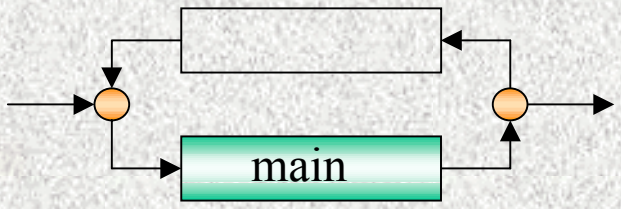
where i=1 for the *main section* and i=2 for *secondary section*

$$\mathbf{y} = \begin{bmatrix} y_{mon} \\ y_{ini} \end{bmatrix} = \begin{bmatrix} C_{mon} / C_{mon\ feed} \\ C_{ini} / C_{mon\ feed} \end{bmatrix}$$

$$\theta = T / T_{feed}$$

Boundary Conditions

- Main Tubular Section



Inlet

$$(1-\alpha)f_c + \alpha y^2(1,t) = y^1(0,t) - \frac{1}{Pe_m^1}\left.\frac{\partial y^1(z,t)}{\partial z}\right|_{z=0}$$

$$(1-\alpha) + \alpha\theta^2(1,t) = \theta^1(0,t) - \frac{1}{Pe_h^1}\left.\frac{\partial \theta^1(z,t)}{\partial z}\right|_{z=0}$$

Outlet

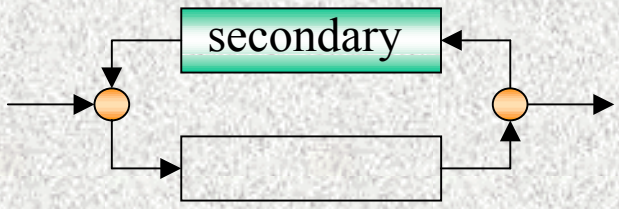
$$\left.\frac{\partial y^1(z,t)}{\partial z}\right|_{z=1} = \left.\frac{\partial y^2(z,t)}{\partial z}\right|_{z=0}$$

$$\left.\frac{\partial \theta^1(z,t)}{\partial z}\right|_{z=1} = \left.\frac{\partial \theta^2(z,t)}{\partial z}\right|_{z=0}$$

Fluxes Continuity

Boundary Conditions

- Secondary Tubular Section



Inlet

$$y^1(1,t) = y^2(0,t)$$

$$\theta^1(1,t) = \theta^2(0,t)$$

State Variables Continuity

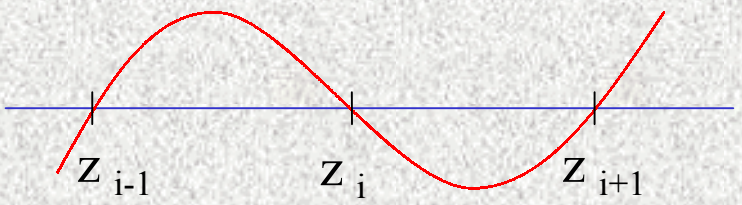
Outlet

$$\left.\frac{\partial y^2(z,t)}{\partial z}\right|_{z=1} = 0$$

$$\left.\frac{\partial \theta^2(z,t)}{\partial z}\right|_{z=1} = 0$$

Numerical Methods

- Reactor model solution: Method of Lines
  - Finite elements technique used to discretize the axial coordinate.
  - Quadratic approximation used to describe the profiles inside each element



  - Resulting set of Differential-Algebraic Equations solved by means of DASSL package (Petzold, 1982, *Technical Report SAND82-8637*)

Numerical Methods - Cont.

- Reactor model stability analysis

  - Reactor model: $$\mathbf{A}\frac{d\mathbf{x}}{dt} + f(\mathbf{x},\lambda) = \mathbf{0}$$

    $\mathbf{x}$ is the vector of states
    λ is a given system parameter
    $\mathbf{A}$ is rank deficient

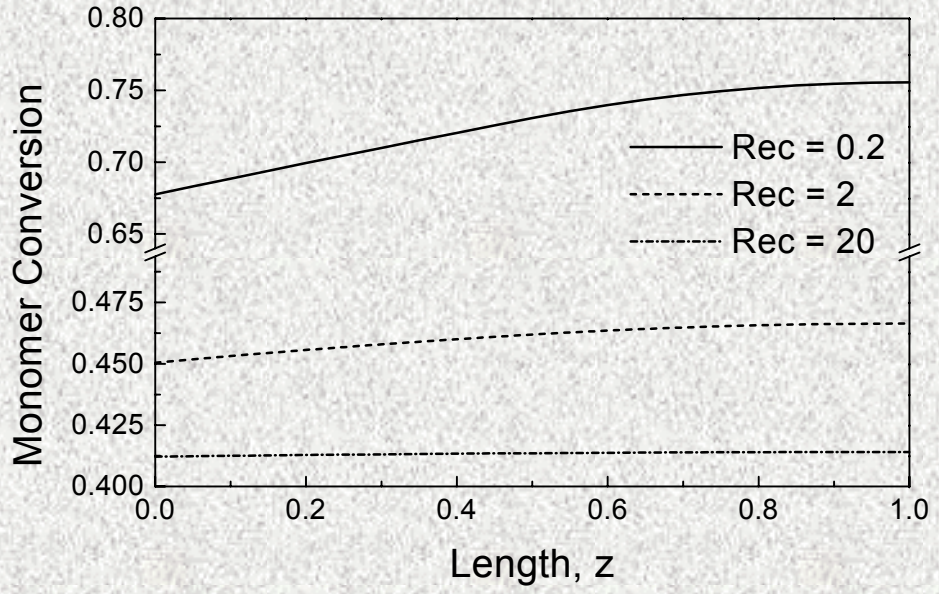
  - Continuation package AUTO (Doedel, 1986, *Caltech Technical Report*) has been chosen. DAE stability evaluation has been added following the procedure proposed by Hyaneck e*t al*. (1995, *Ind. Eng. Chem. Res*. **34**)

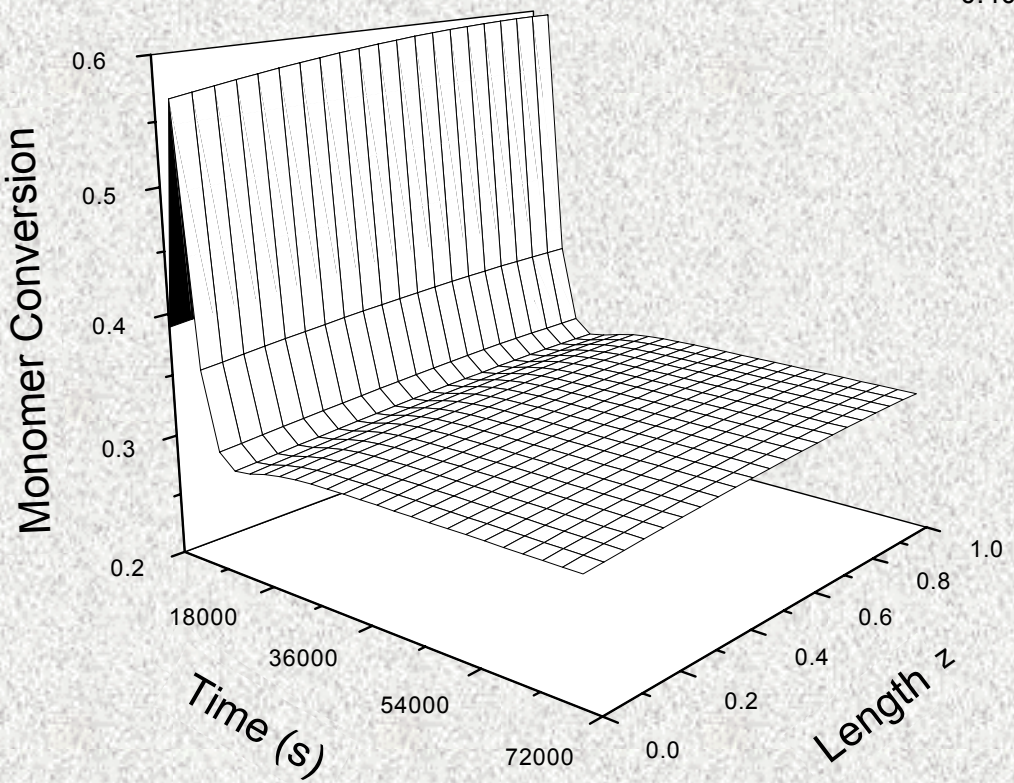
Simulation Results

- Simulation data:

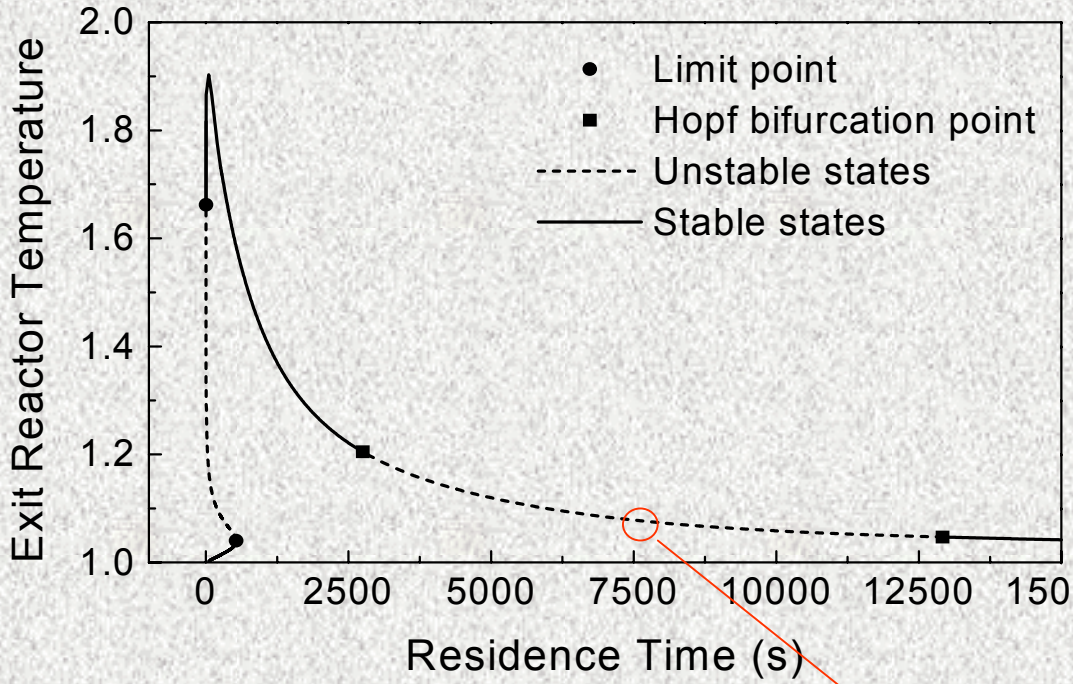
Definition	Value
Length of tubular sections	106.5 cm
Diameter of tubular sections	1.7272 cm
Coolant temperature	45^{o}C
Heat of polymerization	21 kcal/gmol
Feed temperature	42^{o}C
Feed monomer concentration	$7.34*10^{-3}$ gmol/cm^3
Feed solvent concentration	$7.34*10^{-3}$ gmol/cm^3
Feed initiator concentration	$3.80*10^{-5}$ gmol/cm^3

Steady-state profiles for different recycling ratios

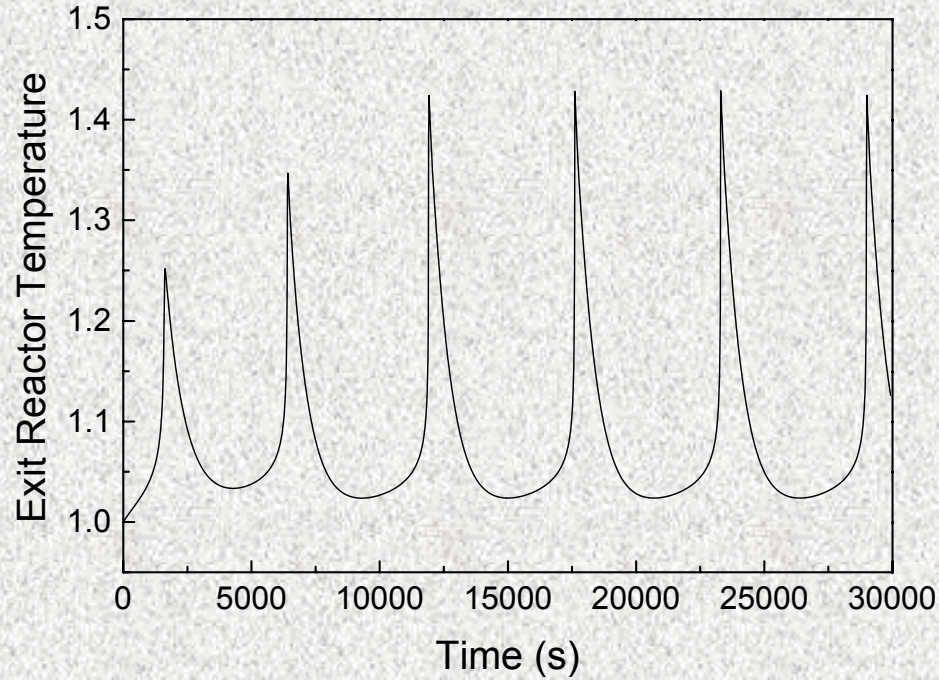




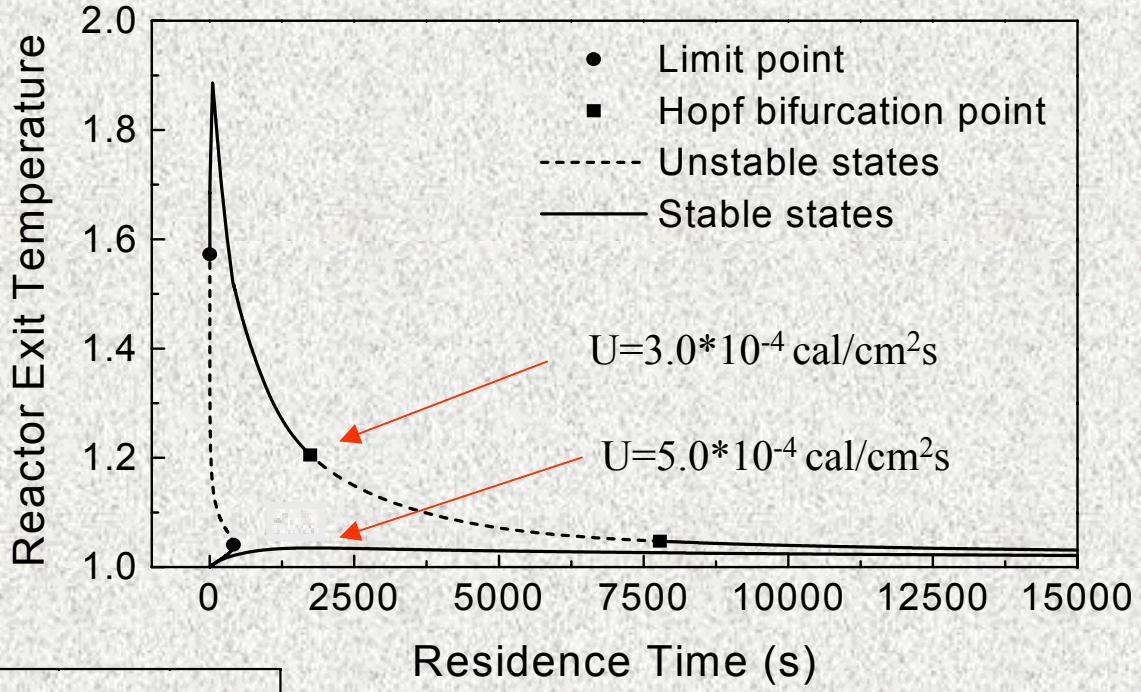
Axial-temporal profiles for Rec=1.0

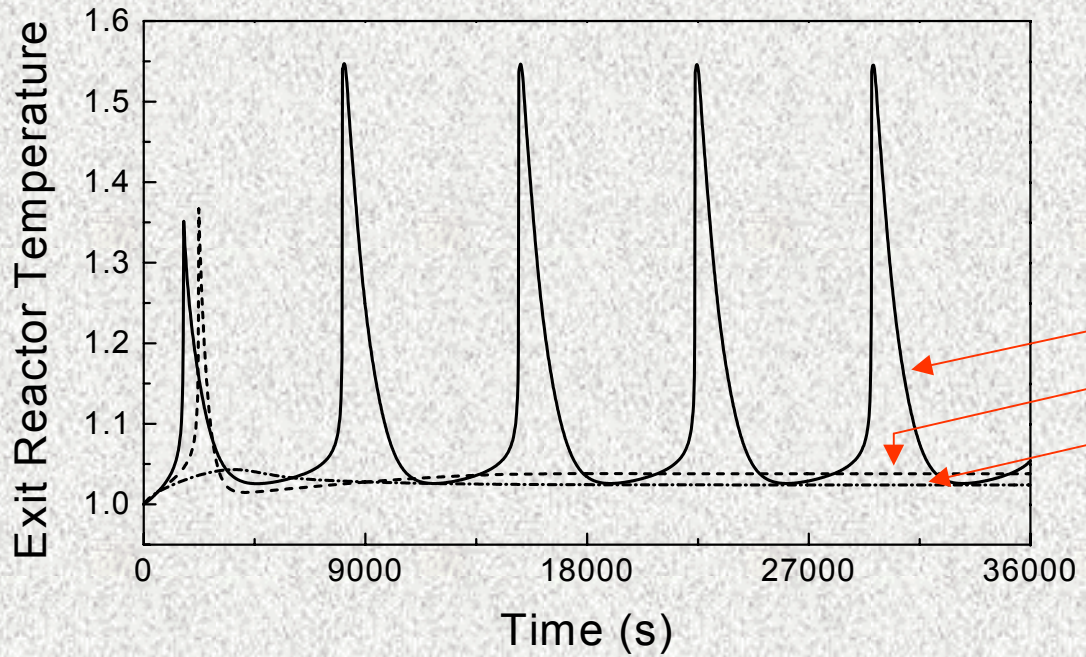


Bifurcation diagram for
Rec=50, U=3.0*10^{-4} cal/cm^{2}s



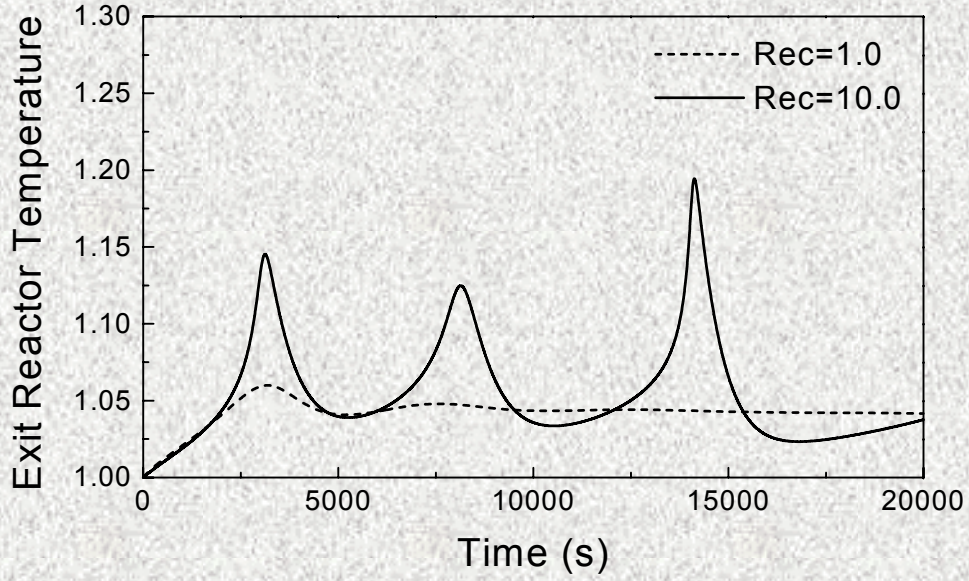
The role of the overall heat transfer coefficient on the bifurcation structure for Rec=1.0





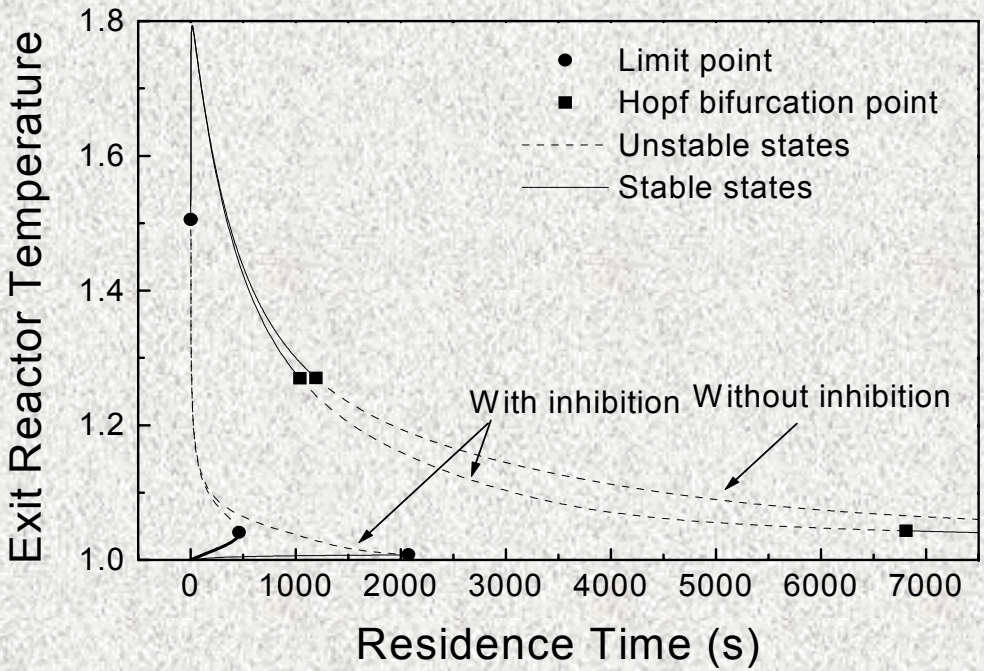
Dynamic profiles of reactor exit temperatures Rec=1.0, τ=167min

U=3.0*10-4 cal/cm2s
U=5.0*10-4 cal/cm2s
U=7.0*10-4 cal/cm2s



Recirculation may induce oscillatory behavior (τ=167 min and U=3.0*10^{-4} cal/cm^{2}s)

Impurities in the feed stream may widen the steady-state multiplicity region (Rec=100; U=3.0*10^{-4} cal/cm^{2}s)



Conclusions

- Theoretical results on stability of loop reactors applied in free-radical polymerization processes have been presented in this work.
- The non-linear analysis of the reactor mathematical model has shown the reactor's high sensitivity to some operating parameters such as residence time, recycle ratio and overall heat transfer coefficient.
- It has been observed the induction of oscillatory behavior by varying the recycle ratio.
- Oscillations are also induced depending on the heat removal rates imposed on the reactor operation. The lower the overall heat transfer coefficient the greater are the chances for nonlinear behavior to arise
- Although steady-state multiplicity region lies in a narrow range of residence times, the simulation results have shown that impurities in the feed may widen this region.

Acknowledgments

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