Chemical Engineering Journal 134 (2007) 175–179

Chemical Engineering Journal

www.elsevier.com/locate/cej

Mathematical modeling and experimental study of high-pressure ethylene polymerization reactors

S.S. Ivanchev[b,*], M.V. Goncharenko[a,1], Yu.N. Kondratiev[a,1], A.M. Saveliev[a,1], A.E. Sofiev[a,1]

[a] Central R&D Institute for Complex Automation, 8 Mozhaisky Val, Moscow, Russia
[b] St. Petersburg Department of the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, 14 Prospect Dobrolubova, 197198 St. Petersburg, Russia

Abstract

Mathematical models and experimental data are discussed for high-pressure ethylene polymerizations in stirred autoclaves and tubular reactors. The models are based on free radical mechanism of ethylene polymerization using material and energy balance equations as well as impact balance (for tubular reactors). A stirred autoclave reactor is modeled taking into account mixing modes in the reactor on the basis of the segregation approach.

The developed mathematical model was used to study the stability of stirred autoclave reactor and determine the range of the process parameters corresponding to their sustainable functioning.

Keywords: Mathematical modeling; Polymerization; Tubular reactors

1. Stirred tank reactor

The experimental data show (Fig. 1) that as the temperature increases in the top S1-section of the reactor due to the control of the initiator amount supplied in this zone the temperature growth profile in the next S2-section gradually drops and the polymerization zone continuously shifts towards S1.

This phenomenon is accompanied by the decrease of the polymer molecular weight and initiator efficiency.

Also Fig. 1 shows the influence of reaction temperature diapason to the temperature profiles and the temperature gradients in stirred tank reactor. In particular, Fig. 1a shows that if the initiator feed is increased in the top part of the reactor then the temperatures in sections S1 and S2 are increased; also if the temperature in section S1 is higher then the temperature increase in section S2 is smaller. From Fig. 1b is evident that for ensuring a constant for temperature increases in the S1- and S2-sections it is necessary to feed larger initiator if the temperature in the sections is higher.

All results and issues above are confirmed by large volume of experimental data obtained for industrial stirred autoclaves.

Industrial stirred autoclaves (Fig. 2) operate in a nearly adiabatic mode with the ratio $G \times C_P/K \times F > 50$ and the temperature difference between the sections S2 (T2) and S1 (T1) being always positive. (Here G, C_P are the reaction medium mass flow and heat capacity and K, F are the heat transfer constant and surface area in the reactor accordingly).

However, for pilot stirred autoclave installations at $G \times C_P/K \times F < 0.5$ the temperature growth in the section S1 (T1) tends to negative values of the temperature gradient between these sections confirming the process shifts towards S1 (T1).

At reduced temperatures in T1, for a certain initiator the process temperature should be controlled on the basis of the temperatures in this section while at higher T1 temperatures the control can be based on the levels for either T1 or T2.

The further increase of T1 temperature with T2 − T1 temperature gradient approaching zero is undesirable in view of a high risk of the process thermal stability loss.

For Trigonox-36 the low temperature level is 170–175 °C whereas for Trigonox-42 this value is about 215 °C.

---

* Corresponding author. Fax: +7 812 2330002.
E-mail addresses: ivanchev@SM2270spb.edu (S.S. Ivanchev), AMSAVELIEV@mtu-net.ru (A.M. Saveliev).
[1] Fax: +7 495 2404206.

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.03.075

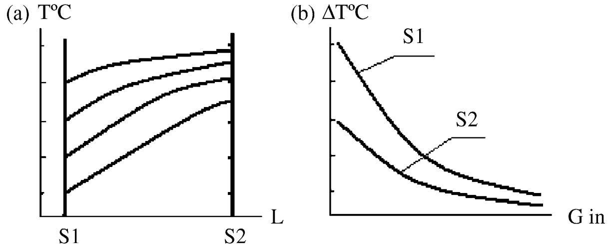

Fig. 1. Stirred tank reactors. (a) Temperature profiles in S1-section and S2-section: ΔT S1-const and (b) temperature gradient: $\Delta T = T(i+1) - T_i$.

2. Continuous stirred tank reactor with semi-segregation

In the process of modeling of continuous stirred tank reactors (CSTR) it is in general supposed the ideal mixing, i.e. every small aggregate of reaction medium can be considered as being in same conditions and the species concentrations are instantly established over whole reactor volume. Owing to simplicity of describing equations it turned out that some important behavior properties of the CSTR can be studied by means of those simple equations, for example, the existence of regions with high and low parametric sensitivity [1], the phenomenon of multiple steady-states and the existence of the auto-oscillations [2].

However, if we use a model obtained in supposing of the ideal mixing for real calculations in the chemical engineering, for example for calculations of temperatures in a reactor, the reaction conversion then it is revealed an essential difference between real and modeled values of those state variables. So it seems reasonable to look for a model in which some effects of mixing mechanism are considered in detail. In the following, we consider only one way to introduce a non-ideal mixing in the model of a continuous-stirred-tank-reactor. In particular, we will study a stability problem for this model which has some specific properties.

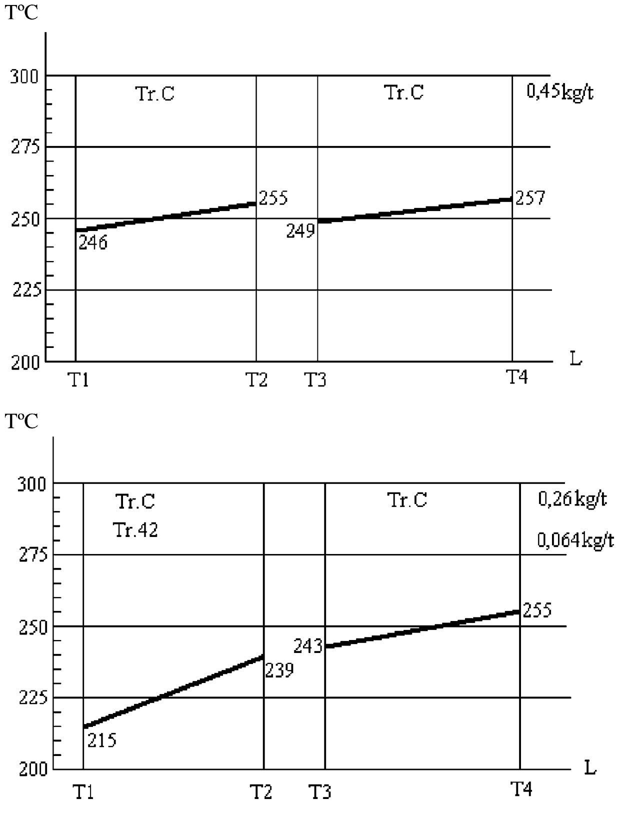

Fig. 2. Temperature profiles for industrial stirred tank reactors.

According to this way we look for the process of mixing in CSTR as a mixing of a large number of small “elementary” aggregates in which the species concentrations are different while the temperature is the same. Additionally every small aggregate is considered as a small periodic reactor with the stochastic residence time τ. This approach we call “semi-segregation” [3,4].

We will suppose in the following that the density distribution function $\gamma(\tau)$ for a CSTR was reconstructed in the range $[0,\infty)$ on the base of a detailed quantitative analysis of experimental data. Assuming the following notations: $c(\alpha,t)$ is the species concentration in a small aggregate, T the temperature in reactor and $f(c,t)$ is the right-hand side of the kinetic equation, we consider mass balance and energy balance equations for CSTR with semi-segregation, respectively,

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = f(c, t) \tag{1}$$

$$\frac{dT}{dt} = \frac{G}{\rho V}(T_{\text{in}} - T) - \frac{q}{Q\rho}\int_0^{\infty} \gamma(\tau) f(c, T)\, d\tau - \frac{kF}{Q\rho V}(T - T_{\text{w}}) \tag{2}$$

$$c(t, 0) = c_{\text{in}},\ T(0) = T_0,\ c(0, \tau) = c_0(\tau). \tag{3}$$

Here, we use the index of symbols: G is the mass flow, ρ the reaction medium density, V the reactor volume, F the internal surface area, Q the thermal capacity of reaction medium, q the reaction heat effect, k the heat transfer coefficient and T_{w} is the reactor wall temperature.

Eq. (1) is evident. The first term on the right-hand in Eq. (2) describes the energy, introduced in and exited from reactor with reaction medium, the second term describes the integral thermal effect of the reaction and the third one—thermo-exchange through reactor wall. We suppose $f(c,T) < 0$ also.

The problems (1)–(3) may be solved in MatLab-medium. As it turned out Eqs. (1)–(3) allow to study the dynamical behavior of CSTR depending on a mixing regime unlike standard models of a reactor with complete mixing.

For Eqs. (1)–(3), we can formulate and solve the stability problem for some stationary state $[c_{\text{s}}(\tau), T_{\text{s}}]$. With that end in view we pass to the linear equations in a neighbourhood of the stationary state

$$\frac{\partial s}{\partial t} + \frac{\partial s}{\partial \tau} = A(\tau)s(t, \tau) + B(\tau)\theta(t) \tag{4}$$

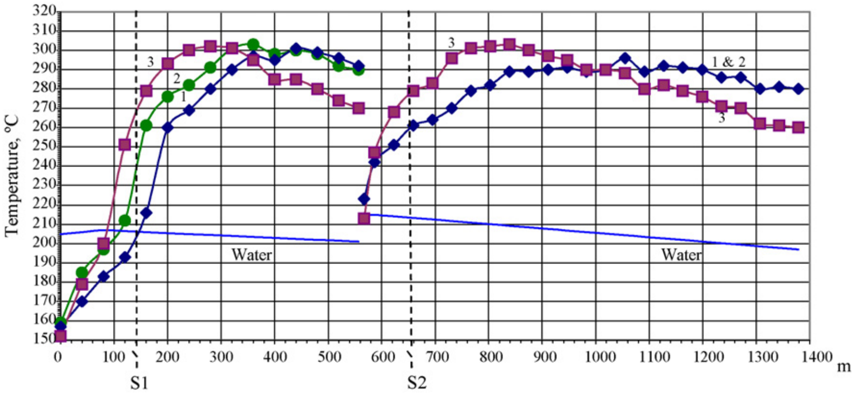

Fig. 3. Temperature profiles in a double-zone tubular reactor with different initiating systems. Oxygen initiation in both zones: first zone, oxygen + Trigonox-36 (1.9 kg/h); second zone, oxygen; first zone, oxygen + Trigonox-36 (1.3 kg/h + Trigonox-C (0.52 kg/h); second zone, oxygen + Trigonox-C (1.9 kg/h). Conversion is up to 23%. S1, S2 are control points.

$$\frac{d\theta}{dt}=-C\int_0^\infty[A(\tau)s(t,\tau)+B(\tau)\theta(t)]\gamma(\tau)d\tau-D\theta(t) \qquad (5)$$

for initial and boundary conditions

$$s(t,0)=0,\ s(0,\tau)=c_s(\tau),\ \theta(0)=\theta_s. \qquad (6)$$

Here A,B,C and D are some expressions which can be obtained from (1) to (2) in the process of the right-hand side linearization.

The solution to Eq. (4) has the form

$$s(t,\tau)=\left[\Omega(t-\tau)+\int_0^\tau B(\xi)\theta(t-\tau+\xi)\ \exp(-\int_0^\xi A(x)\,dx\right]\exp\left(\int_0^\tau A(\xi)\,d\xi\right),$$

where $\Omega(t-\tau)\ \exp(\int_0^\tau A(\xi)\,d\xi$ is a solution to the homogeneous equation corresponding to Eq. (4) and the function $\Omega(t)$ is defined by condition (6).

If the boundary condition is null as in (6) then

$$s(t,\tau)=\exp\left(\int_0^\tau A(\xi)\,d\xi\right)\int_0^\tau B(\xi)\theta(t-\tau+\xi)\exp\left(-\int_0^\xi A(x)\,dx\right)\,d\xi. \qquad (7)$$

By substitution (7) to (5) we have

$$\frac{d\theta}{dt}=-C\int_0^\infty K(\tau)\int_0^\tau M(\xi)\theta(t-\tau+\xi)\,d\xi\,d\tau-(CB+D)\theta(t) \qquad (8)$$

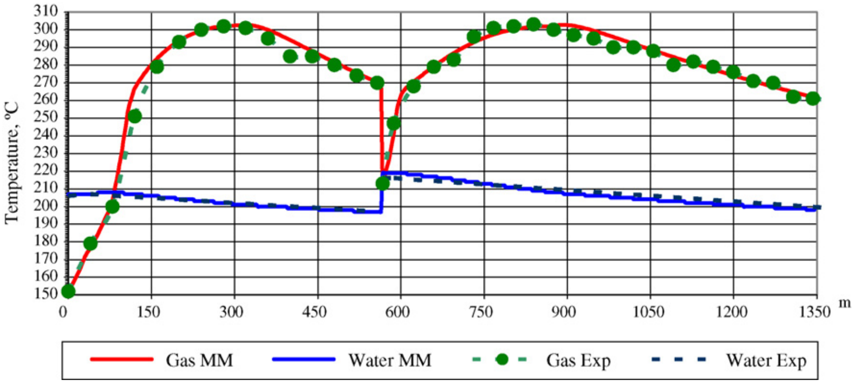

Fig. 4.

Initiator		Tr-36 (ppm)	Tr-C (ppm)	Oxygen (ppm)
Experiment	Zone 1	23	15	11.6
	Zone 2	–	36	4
MM	Zone 1	26	15.4	10.7
	Zone 2	–	30.2	4.3

where

$$K(\tau) = A(\tau)\gamma(\tau)\,\exp\int_0^{\tau} A(\xi)\,\mathrm{d}\xi$$
$$\bar{B} = \int_0^{\infty} B(\tau)\gamma(\tau)\,\mathrm{d}\tau \qquad .$$
$$M(\xi) = B(\xi)\,\exp\left(-\int_0^{\xi} A(x)\,\mathrm{d}x\right)$$

The solution to (8) is constructed in the form

$\theta(t) = \theta_0\,\mathrm{e}^{at}$.

For the constant a, we have

$$a = -C\int_0^{\infty} K(\tau)\,\mathrm{e}^{-at}\int_0^{\tau} M(\xi)\,\mathrm{e}^{a\xi}\,\mathrm{d}\xi\,\mathrm{d}\tau - (C\bar{B} + D).$$

The stationary state $[c_s(\tau), T_s]$ is stable if the roots of this equation lie in the left semi-plane.

3. Multi-zone tubular reactor

For a multi-zone tubular reactor, the mathematical model is based on the plug-flow admission and the following aspects are presented and discussed:

- Calculation results and experimental data for a series of industrial ethylene polymerization reactors.
- Recommendations for the selection of optimum technological conditions and modes for the exploration of such reactors as well as for their geometric (length, number of zones and their diameters) parameters and heat exchange system design.

The adequacy of the developed mathematical models was tested using experimental data obtained for various commercial tubular polyethylene production reactors.

At first the sensitivity to the main process parameters was analyzed followed by the determination of criteria to the experimental data.

Table 1
Double-zone tubular reactor

	Mathematical model (MM)	Experimental data
1 Zone		
1.1 Trigonox 36 + O_2	1.5–2.0 kg/h	1.9 kg/h
ДL T_{max}	60–70 m	60 m
S_1	–	–
1.2 Trigonox (36 + C) + O_2	1.5 + (0.4–0.6) kg/h	1.3 + 0.5 kg/h
ДL T_{max}	130 m	150 m
S_1	105 m	118 m
2 Zone		
Trigonox C + O_2 (213 °C)	1.5–1.6 kg/h	1.9 kg/h
ДL T_{max}	170 m	200 m
S_1	87 m	68 m

3.1. *Mathematical models for ethylene polymerization in tubular reactor*

Initiating system—oxygen and peroxides (Trigonox 36 and Trigonox C)

$$\begin{aligned}
w\frac{\mathrm{d}g_M}{\mathrm{d}l} &= -k_{oM}\exp\left\{\frac{-E_M + \Delta V(p-1000)}{T+273.16}\right\} g_M^{3/2} g_C^{1/2}\rho \\
&\quad - k_{oM36}\exp\left\{\frac{-E_{M36} + \Delta V_{36}(p-1000)}{T+273.16}\right\} g_M g_{36}\rho \\
&\quad - k_{oMC}\exp\left\{\frac{-E_{MC} + \Delta V_C(p-1000)}{T+273.16}\right\} g_M g_C\rho; \\
w\frac{\mathrm{d}g_K}{\mathrm{d}l} &= -k_{oK}\exp\left\{\frac{-E_K}{T+273.16}\right\} g_M g_K\rho; \\
w\frac{\mathrm{d}g_{36}}{\mathrm{d}l} &= -k_{036}\exp\left\{\frac{-E_{36}}{T+273.16}\right\} g_{36}; \\
w\frac{\mathrm{d}g_C}{\mathrm{d}l} &= -k_{0C}\exp\left\{\frac{-E_C}{T+273.16}\right\} g_C; \\
w\frac{\mathrm{d}T}{\mathrm{d}l} &= \frac{\Delta H}{c_p}\left(-w\frac{\mathrm{d}g_M}{\mathrm{d}l}\right) - \frac{4K_{m,H}}{\pi d_H^2\rho c_p}(T - T_{cm}); \\
T_{cm} &= K_1 T + K_2 T_m; \\
w_m\frac{\mathrm{d}T_m}{\mathrm{d}l} &= -\frac{4K_{m'_,}}{\pi(d_m^2 - d_{,}^2)\rho_m c_{p,m}}(T_m - T_m).
\end{aligned}$$

where:

$w = 4G/\pi d_B^2\rho$; $w_m = 4G_m/\pi(d_m^2 - d_H^2)\rho_m$ are the reaction medium and cooling water velocity accordingly;

$\rho = (3780.0 - 264.0\ln P) + (63.0\ln P - 695.0)\ln(T + 273.16)$ is the density of reaction medium;

$c_{cm} = \pi/4(d_{i}^2 - d_B^2)\rho_{cm}c_{p,cm}$; $d_0 = d_H + d_B/2$ are the heat capacity and tube diameter accordingly.

The heat transfer constants are calculated as

$$k_{m,B} = \frac{\pi}{1/\alpha_B d_B + 1/2\,\lambda_{cm}\ \ln\ d_0/d_B + R_f};$$
$$k_{m,n} = \frac{\pi}{1/\alpha_n d_n + 1/2\,\lambda_{cm}\ \ln\ d_{,}/d_0}.$$

The studies were carried out relating to industrial high-pressure reactors with oxygen and complex of different initiators.

The results of mathematical modeling for a double-zone tubular reactor with different initiating systems are shown in Fig. 3 and fitting of the calculated and experimental temperature profiles are illustrated in Fig. 4.

The theoretically expected and measured data for the initiator consumption, temperature profiles and process control parameters are found to be in a good agreement (see Table 1 below).

References

[1] M.V. Goncharenko, A.E. Sofiev, I.I. Sluch, Theor. Osn. Chem. Tehn. 20 (2) (1996) 169–178.
[2] Yu.N. Kondratiev, A.E. Sofiev (Eds.), High Pressure Polyethylene, Khimia, Leningrad, 1988.
[3] A.A. Lapin, A.V. Zaev, A.E. Sofiev, Theor. Osn. Chem. Tehn. 8 (3) (1974) 387–393.
[4] A.M. Tsirlin, L.E. Shnaider, M.V. Goncharenko, A.E. Sofiev, Theor. Osn. Chem. Tehn. 11 (6) (1977) 861–865.