Simulation and control of monomer conversion in a continuous emulsion polymerization reactor

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Abstract: A detailed pseudo-bulk model has been used for prediction of conversion and particle size distribution (PSD) of vinyl acetate in a continuous emulsion polymerization reactor. Finite volume (FV) and moment techniques are applied for solving population balance equation under continuous operation. It is found that both methods can predict sustained oscillations in the monomer conversion, however the FV method matches the experimental data better than the moment method. The monomer conversion and free surfactant concentration are controlled via two single control loops. In this work, a new control strategy for controlling monomer conversion has been proposed. It has been shown that monomer conversion and free surfactant concentration can be controlled simultaneously by manipulating initiator and surfactant feed rates.

***Keywords**:* Mathematical Models, Closed-loop Control, Emulsion polymerization, Continuous reactor.

1. INTRODUCTION

Emulsion polymerization in both batch and continuous reactors is a major processing step in the manufacture of polymer products such as paints, inks, coating, adhesives, high-impact strength copolymers, etc. Continuous emulsion polymerization is more economically advantageous over batch process for the production of large amounts of polymer and avoids product differences (Sayer et al. 2002). However, oscillations in conversion and polymer particles number are usually observed when water-soluble monomers such as vinyl acetate are polymerized in a continuous stirred tank reactor (Fang et al. 2003).

The pseudo-bulk and the zero–one models are widely used for modeling the emulsion polymerization (Vale & McKenna 2005; Lovel & El-Aasser 1997). Several researchers have used the pseudo-bulk model for modeling emulsion polymerization of vinyl acetate (Vale & McKenna 2005), and in the present work we have also used this modeling approach.

Various solution techniques have been proposed for solving these equations. Method of moments and discretization techniques such as finite difference and finite volume methods are two common approaches for solving the population balance equation. Simulation and experimental studies have revealed that polymer conversion can go under oscillation in continuous polymerization reactors.

There are very few reports in the literature of attempts to control continuous stirred emulsion polymerization tank reactors in the presence of sustained oscillations. Semino and Ray (D Semino & Ray 1995; Daniele Semino & Ray 1995) designed single-input single-output PI and PID controllers for all possible couplings of controlled and manipulated variables. They have found that the sustained oscillations in monomer conversion can be damped by control of the free surfactant concentration or the total particles number. However, it cannot be controlled directly by manipulating the surfactant and initiator concentrations in the feed in the absence of inhibitor.

In the present study, we proposed a new control strategy for direct control of monomer conversion. We simulated the evaluations of vinyl acetate conversion and particle size distribution (PSD) in a continuous emulsion polymerization reactor by using a detailed dynamical model. Material balances and population balance equations based on pseudo-bulk model are used to predict the monomer conversion (Immanuel & Doyle III 2002). Finite volume and moment methods are used for solving system equations and the result obtained for conversion is compared with experimental data given in the literature (Kiparissides et al. 1980a). To overcome the problem associated with control of conversion, different loop pairings are tested. It has been shown that monomer conversion and free surfactant concentration can be controlled simultaneously by manipulating initiator and surfactant feed rates.

2. VINYL ACETATE EMULSION POLYMERIZATION MODELING

In this Study, the general structure of the pseudo-bulk model of Immanuel et al. (Immanuel et al. 2002) is implemented, using the results of other works (Rawlings & Ray 1988; Zeaiter & Romagnoli 2002; Abedini & Shahrokhi 2010).

2.1 Pseudo-Bulk Model for Polymer Particles

The polymer particles are characterized by a population density. It is assumed that particle density ($f(r,t)$) can be expressed by pseudo-bulk model. The particle density is described by population balance equations, which account for the nucleation of new particles, and their growth by polymerization. Particles are assumed colloidally stable, and therefore coagulation is not considered. The particle population is described by (Immanuel et al. 2002):

$$\frac{\partial}{\partial t}f(r,t)+\frac{\partial}{\partial r}\left(f(r,t)\frac{dr}{dt}\right)=R_{nuc}\delta(r-r_{nuc})-\frac{Q}{V_R}f(r,t) \qquad (1)$$

The particle density $f(r,\ t)\ dr$ is defined as the moles of particles of unswollen size between r and $r+dr$ at time t. R_{nuc} is the rate of nucleation and $\delta(r-r_{nuc})$ is the Dirac delta function which is unity at $r = r_{nuc}$ and zero elsewhere. It is assumed that $r_{nuc} = r_{micellar}$ for both homogenous and micellar nucleation.

2.2 Solution Technique

Method of moments and discretization techniques such as finite difference and finite volume methods are two common approaches for solving the population balance equation. In our previous work (Barazandegan et al. 2009), two different methods, finite volume (FV) and moment techniques were applied for solving the population balance equation and the result obtained for conversion was compared. In the FV method, the truncated radius domain is subdivided into N cells and the average value of the density function over cell j at time t is defined as (Vale & McKenna 2005; Barazandegan et al. 2009):

$$\bar{f}_j=\frac{1}{\Delta r_j}\int_{r_{j-1}}^{r_j} f(r,t)dr; \qquad j=2,3,\dots,N$$
$$\bar{f}_1=\frac{1}{\Delta r_1}\int_{r_{nuc}}^{r_1} f(r,t)dr \qquad (2)$$

According to the FV method, the population balance equation is not solved directly, but its integrated version is used. Integrating (1) over the jth cell, changing the order of differentiation and integration and dividing by Δr_j results in (Vale & McKenna 2005; Barazandegan et al. 2009):

$$\frac{d\bar{f}_j}{dt}+\frac{\bar{f}_j\left(\frac{dr}{dt}\right)_{r_j}-\bar{f}_{j-1}\left(\frac{dr}{dt}\right)_{r_{j-1}}}{\Delta r_j}=-\frac{Q}{V_R}\bar{f}_j \qquad (3)$$

The conventional method of moments may be used to determine evolution of the lower-order moments of an unknown distribution. The kth radial moment of a population density function $f(r,\ t)$, is defined as follows (McGraw 1997):

$$\mu_k=\int_0^\infty r^k f(r,t)dr \qquad (4)$$

which, r is internal coordinate of the population density function. By applying the moment equation (4) to the population balance equation (1), the following moment equation for particle density function can be obtained:

$$\frac{d}{dt}\mu_k + G(k\mu_{k-3}) = \delta_{k,0}R_{nuc} - \frac{Q}{V_R}\mu_k \qquad (5)$$

$$G = \frac{1}{4\pi\rho_p N_A} k_p \bar{n}_{ave}[M]_p M_{w_m} \qquad (6)$$

3. SIMULATION RESULTS

For simulation purposes, emulsion polymerization of vinyl acetate in a continuous reactor has been considered. Sodium dodecyl sulfate and potassium persulfate are used as surfactant and initiator, respectively. In this work, critical micellar concentration (CMC) is set to 0.001 *mol/l*. Simulation results obtained by finite volume and moment methods along with experimental data of vinyl acetate conversion are shown in Fig. 1. As can be seen, both methods can predict oscillation in monomer conversion. However, finite volume method fits to the experimental data more satisfactorily than moment method. Therefore, for the rest of simulation runs, the FV method has been used.

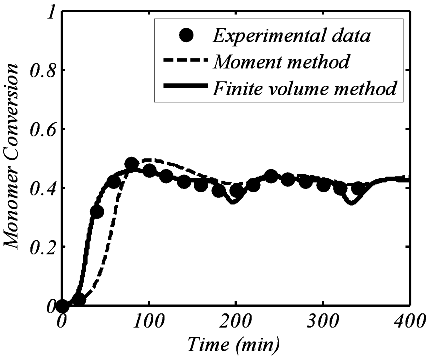

Fig. 1. Comparison between experimental data (Kiparissides 1978; Kiparissides et al. 1980a; Kiparissides et al. 1980b) and simulation results of vinyl acetate conversion, T=50 °C, S_f =0.01 mol/l, V_{wf} =0.6, I_f = 0.01 mol/l and residence time =30 min.

Oscillations, which are undesirable for a stable continuous operation, are generated due to two distinct mechanisms (Rawlings & Ray 1988; Immanuel et al. 2008). The first one pertains to periodic (on-off) particle nucleation, and the second one is related to the oscillation in the average number of radicals per particle (Fig. 2). Due to the first mechanism, the particles number decreases because of washout in the outlet stream when nucleation is off. This causes the surfactant concentration to increase and eventually exceed the CMC barrier, leading to restart of particle nucleation. By increasing the total number of particles, the surface area is increased and the free surfactant concentration drops below the CMC, which leads to nucleation stoppage (Immanuel et al. 2008). The oscillating rate of micellar nucleation is shown in Fig. 2a. The simulation result indicates that the rate of homogenous nucleation can be ignored and therefore particle nucleation occurs only by the micellar nucleation. Periodic (on-off) particle nucleation can be seen in Fig. 2b. Further, it can be seen from Fig. 2c that the average number of radicals per particle is oscillatory due to the second mechanism. As the average number of radicals per particle increases, the particle growth rate increases and rate of monomer consumption exceeds the monomer feed rate. The increase in particle growth rate eventually leads to decrease of the monomer concentration, which in turn causes a decrease in the average number of radicals per particle and the growth rate. This again leads to the conversion oscillatory behavior (Immanuel et al. 2008).

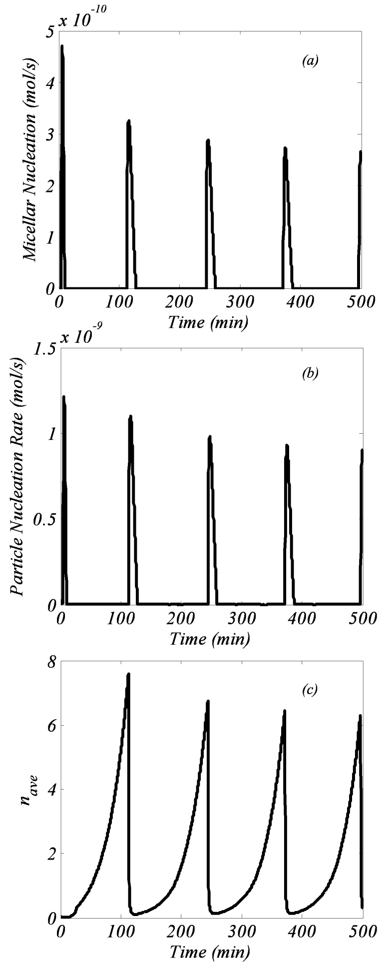

Fig. 2. Oscillations as predicted by FV model for vinyl acetate polymerization, T=50 °C, Sf=0.01 mol/l, V_{wf}=0.6, I_f= 0.01 mol/l and residence time=30 minutes. (a) Rate of micellar nucleation vs. time; (b)Particle nucleation rate vs. time; (c) Average number of radicals per particle vs. time.

4. CLOSED-LOOP CONTROL OF SUSTAINED OSCILLATIONS APPEARED IN VINYL ACETATE POLYMERIZATION

Selection and pairing of manipulated and output variables is of primary steps in the design of controllers for continuous emulsion polymerization reactors (Daniele Semino & Ray 1995). The suitable manipulated variables for controlling such reactors have been found through controllability analysis by Semino and Ray (D Semino & Ray 1995). They have shown that using surfactant and initiator feed rates as manipulated variables can make the system controllable. Output variables should be measurable or at least easily observable. Monomer conversion usually is measured using an on-line densitometer and the total number of particles can be determined on-line via light scattering measurements (Daniele Semino & Ray 1995). Free ionic surfactant concentration can be inferred through surface tension or conductivity measurements (Abedini & Shahrokhi 2008).

Since PID controller has a simple structure and it has been turned out that its performance is satisfactory for the reactor under consideration, this controller has been used to control the monomer conversion and eliminate the undesirable oscillations. In order to tune the controller parameters, the extended tuning technique introduced by Åström and Hägglund (Åström & Hägglund 1983) has been used.

4.1 Closed-Loop Control of Free Surfactant Concentration By Surfactant Feed Rate

Controlling the free surfactant concentration via surfactant feed rate is considered first. A PI controller tuned according to the above technique (K_c=23, τ_I =103) has been used for control purposes. Closed-loop free surfactant concentration along with monomer conversion and surfactant feed rate are plotted in Fig. 3. As can be seen from Figs. 3a and 3b, free surfactant concentration is controlled at the desired value, 1.05×10^{-3} *mol/l*, and oscillations in conversion are damped. The corresponding control action is shown in Fig. 3c. Although the conversion oscillations are eliminated, but it's steady state value is not necessarily the desired one. To fix the conversion at the desired level, additional loop is needed which will be discussed later.

4.2 Closed-Loop Control of Total Number of Particle By Surfactant Feed Rate

Controlling the total number of particle via surfactant feed rate is considered in this section. The tuned parameters of PI controller are K_c=0.5, τ_I=833. Closed-loop total number of particle along with monomer conversion and surfactant feed rate are plotted in Fig. 4. It can be seen from Figs 4a and 4b that the total number of particles has been controlled at the desired value, 2.5×10^{16}, and conversion oscillations are damped. The corresponding control action is depicted in Fig. 4c.

4.3 Simultaneous Closed-Loop Control of Free Surfactant Concentration and Monomer Conversion

Previously, Semino and Ray (D Semino & Ray 1995; Daniele Semino & Ray 1995) have found that the sustained oscillations in monomer conversion cannot be controlled directly by manipulating the surfactant and initiator concentrations in the feed in the absence of inhibitor. Also, it was showed in the previous section that polymer conversion oscillations can be eliminated by controlling free surfactant concentration or total particle number, however, it cannot be controlled directly by initiator or surfactant feed rates. Since polymer conversion is an important factor in polymer production, controlling its value at the desired point is very crucial. In this section, a control strategy for this purpose has been proposed.

By this strategy, controls of free surfactant concentration and monomer conversion are achieved simultaneously by two single control loops. The surfactant feed rate is used as manipulated variable for controlling the free surfactant concentration while the initiator feed rate is used to control the monomer conversion. The controller parameters for first and second loops are K_{c1}=76, τ_{I1}=415, K_{c2}=0.74, τ_{I2}=1829 respectively. Closed-loop controls of monomer conversion and free surfactant concentration with their corresponding control actions are shown in Fig. 5 using the proposed strategy. As can be seen from Figs. 5a and 5b, free surfactant concentration and monomer conversion have been controlled at their desired values, 1.05×10^{-3} mol/l and 0.9, and the performances of two PI controllers are quite satisfactorily. The corresponding control actions are shown in Figs. 5c and 5d.

To check the performance of the proposed control strategy in the presence of load, first set-points of monomer conversion and free surfactant concentration have been set to 0.9 and 1.05×10^{-3} mol/l, respectively and at t=1000 min, the water volume fraction has been changed from 0.6 to 0.7. Simulation results are shown in Fig. 6. As can be seen from Figs. 6a and 6b, monomer conversion and free surfactant concentration are controlled at their desired values. The corresponding control actions are shown in Figs. 6c and 6d.

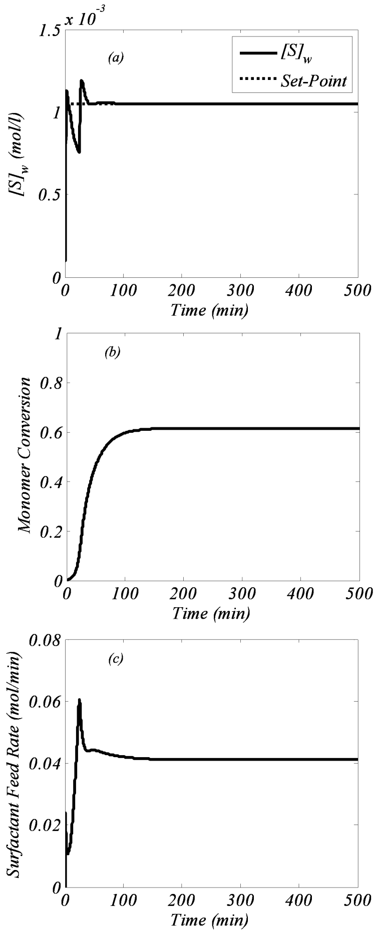

Fig. 3. Control of free surfactant concentration by surfactant feed rate. (a) Free surfactant concentration; (b) Monomer conversion; (c) Surfactant feed rate.

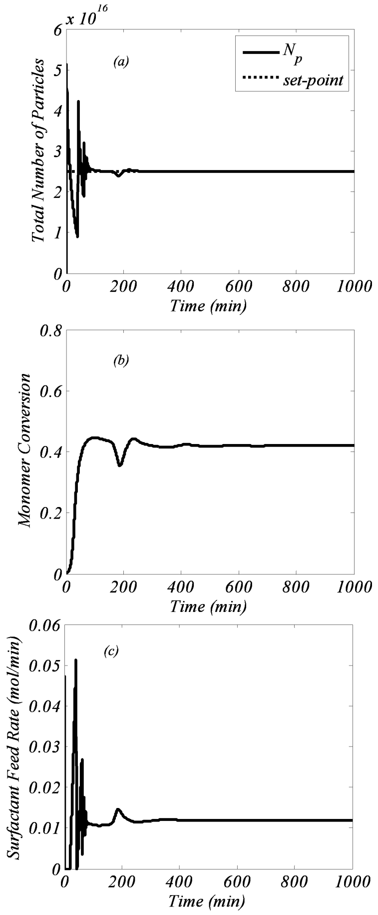

Fig. 4. Control of total number of particles by surfactant feed rate. (a) Total number of particles; (b) Monomer conversion; (c) Surfactant feed rate.

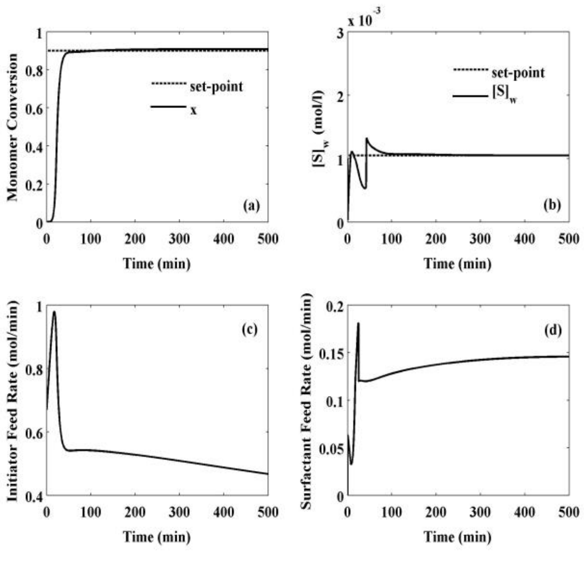

Fig. 5. Simultaneous control of free surfactant concentration and monomer conversion by surfactant and initiator feed rates: (a) Monomer conversion; (b) Free surfactant concentration; (c) Initiator feed rate; (d) Surfactant feed rate.

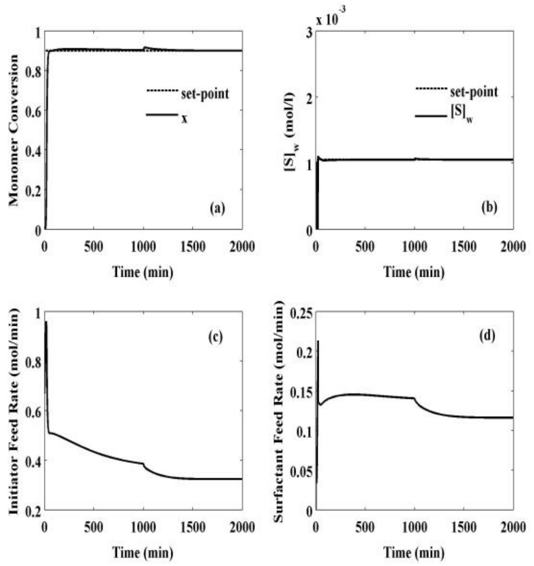

Fig. 6. Simultaneous control of free surfactant concentration and monomer conversion by surfactant and initiator feed rates in the presence of disturbance: (a) Monomer conversion; (b) Free surfactant concentration; (c) Initiator feed rate; (d) Surfactant feed rate.

5. CONCLUSION

In this paper, the pseudo-bulk model was employed for simulating the dynamic behavior of vinyl acetate emulsion polymerization in a continuous reactor and predicting the sustained oscillation of monomer conversion. Finite volume and moment techniques have been used for solving the population balance equation. Comparing experimental data with simulation results has validated model. It has been turned out that the FV method has a better match with the experimental data. PI controllers have been used for control purposes and controller tuning has been achieved by the relay feedback technique. Different loop pairings are tested and it has been shown that if a single control loop is used, only free surfactant concentration or total number of particle can be controlled by manipulating the surfactant feed rate and direct control of monomer conversion is not possible. If two single PI control loops are used, free surfactant concentration and monomer conversion can be controlled simultaneously by manipulating surfactant and initiator feed rates.

NOMENCLATURE

k_p = Coefficient of propagation rate in the polymer phase $\left(dm^3 mol^{-1} s^{-1} \right)$

$[M]_p$ = Concentration of monomer in the particle phase, $\left(mol\, dm^{-3} \right)$

M_{W_m} = Molecular weight of monomer, $\left(gr\, mol^{-1} \right)$

N_A = Avogadro’s number , $\left(mol^{-1} \right)$

$n_{ave}(t)$ = Global average number of radicals per particle, $\left(mol \right)$

Q = Volumetric flow rate, $\left(dm^3 s^{-1}\right)$
r_{nuc} = Radius of particle produced by nucleation, $\left(dm\right)$
V_R = Total volume of the contents of the reactor, $\left(dm^3\right)$
ρ_p = Mass density of monomer and polymer, $\left(gr\, dm^{-3}\right)$

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