CHARACTERIZING A TUBULAR POLYMERIZATION REACTOR BY WASHOUT INITIATOR PERTURBATION

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Abstract—The fluid dynamics of three styrene tubular polymerization reactors were analyzed theoretically and experimentally through washout perturbation. The analysis was developed through initiator negative step inputs and monomer conversion outputs, and thus additional analytic methods were not necessary as no tracer was used. The results were evaluated by an axial-dispersion model and a system of partial differential equations was obtained. This system was reduced by orthogonal collocation into a new system of differential algebraic equations, and these were numerically integrated over time by DASSL. The model parameter – Peclet number - and mean residence time were estimated by fitting the experimental data to the simulation. As these values were correlated, a maximum-likelihood procedure was carried out to estimate the values. Qualitative conclusions were obtained and different fluid dynamic patterns were observed.

Keywords—fluid dynamics, dispersion, modeling, simulation.

I. INTRODUCTION

The final properties of a polymer depend on polymerization kinetics (reaction mechanism), physical properties of transport (heat and mass transfer, mixing), reactor configuration (tubular or tank), and reactor operating conditions (Kiparissides, 1996; Theodorou, 2007). Specific end-use properties can be obtained via special reactor configurations (Covezzi and Mei, 2001). However, the question is how a qualitative evaluation of new reactor configuration can be carried out. The fluid-dynamic characterization can be done by dynamic tracer-response testing (Danckwerts, 1953), which reveals ideal or non-ideal behavior. The PFR and CSTR are two ideal models for mixing in tubular and tank chemical reactors, respectively. The non-ideal models are represented by almost everything between a plug-flow pattern and a total mixing (macro and micro). These models involve some or no parameters, like complete segregation and maximum mixing, or axial dispersion and the number of ideal tanks in series.

The non-idealities can be determined only through experimental methods. The idea is “to mark” each fluid element with a different, nonreacting species (a tracer) and then look at the response of the system to a perturbation (Danckwerts, 1953). For this purpose, the tracer is ideally a substance which does not modify the reactor hydrodynamics, does not interact with the reagents or products, and is easily detected by instruments (de Nadri et al., 1999). Adding a tracer could affect the form of the residence-time distribution (RTD) curve and the apparent degree of mixing (Chen and Nauman, 1989). The more common types of perturbation are impulse, step and sinusoidal, as the impulse and step responses are directly associated with the concept of RTD. In spite of this, one need not necessarily use a tracer because any property can be measured at the outlet, and the input perturbation can be carried out, for example, in pressure (Giudici et al., 1997), temperature (Vega et al., 1997), or reagent concentration (Vega et al., 1997).

Danckwerts (1953) is the fundamental reference in the systematic analysis of fluid dynamics. In this work, Danckwerts mathematically evaluated the RTD results from step and pulse inputs for ideal and real reactors, obtaining the $F(t)$ and $C(t)$ curves and the segregation from the mean residence time.

Fluid-dynamic characterization by tracer-response testing has been used in polymerization systems as well (Chen and Nauman, 1989; Yoon and Choi, 1996; Giudici et al., 1997).

The model of the axial dispersion has previously been applied to polymeric systems (Chen and Nauman, 1989; Yoon and Choi, 1996; Giudici et al., 1997). Sayer et al. (1995) evaluated a pulsed tubular reactor for styrene emulsion polymerization through the axial-dispersion model. Mayer et al. (1995) applied the model to styrene continuous-emulsion polymerization accomplished in a pulsed packed column. Melo Jr. et al. (2001a, b) characterized a tubular reactor with recycle used for styrene polymerization.

In the present work, the fluid dynamics of three tubular polymerization reactors were evaluated theoretically and experimentally in an empty tubular reactor, a tubular reactor packed with continuous mixing elements, and a tubular reactor packed with discontinuous mixing elements. The polymerization of styrene in solution was chosen as the subject, with radical free initiation at 85°C. The fluid-dynamic characterization was performed through a dynamic response technique, using a washout initiator perturbation as the input, where the response was a negative step in monomer conversion. There was no heterogeneous species like an inert tracer, thus it was not necessary to use another method of analysis. Qualitative conclusions were obtained from the three tubular reactors, and different fluid dynamics were observed.
II. EXPERIMENTAL

Three reactors were used in the present work. The empty tubular reactor has been used in previous works (Vega et al., 2001; Cabral et al., 2003; Vianna Jr. et al., 2006; 2007). Two different packing configurations were also used in order to observe whether the fluid-dynamic characteristics of the reactor were sensitive to packing (Vianna Jr. et al., 2007). In the first case, a continuous packing consisted of stainless-steel wire, with five spirals/cm and a diameter of 0.5 mm. In the second case, ten static discontinuous mixing elements, each with a length of 10.0 cm, were introduced regularly along the tubular reactor. The static mixing elements were formed by filling 1.0 gram of stainless-steel wool into stainless tubes with an internal diameter of 0.4 cm and a length of 10.0 cm. The mixing elements (with a porosity of 10%) were connected by eleven empty tubes the same dimensions. The three reactors were made of stainless steel tube with an external diameter of 0.63 cm (I.D. 0.4 cm) and were 12.0 meters long. The polymerization runs were performed at 85°C.

A. Reagents

The reagents used were styrene, provided by Nitriflex, Rio de Janeiro, Brazil (polymer grade with a minimum purity of 99.9%); toluene, provided by Vetec, Rio de Janeiro, Brazil (analytical grade with a minimum purity of 99.9%); benzoyl peroxide (95% purity) from Reagen, Rio de Janeiro, Brazil; and nitrogen, provided by AGA, Rio de Janeiro, Brazil (99% purity). All reagents were used as received.

B. Reactor Setup

The polymerization unit comprised the feed section; the tubular reactor, the heating system, and the in-line analysis system (see Figure 1). The feed section consisted of a feed tank and a Masterflex pump (model 7550-62). The flow was monitored continuously and was controlled by a process computer. The heating system consisted of an air blower, an electrical resistance heater, a variable-voltage controller, and two thermocouples. The thermocouples indicated the temperatures of the hot air (used to control the reactor temperature) at two points close to the reactor walls and 50 cm apart. Previous studies have indicated that these temperature readings are essentially equal to the reaction temperatures (Vega et al., 2001; Melo Jr. et al., 2001a; b; Cabral et al., 2003; Vianna Jr. et al., 2006; 2007). The variable-voltage controller and the thermocouples were linked to the process computer, which controlled the reaction temperature through manipulation of the heat released by the electrical resistance. The tubular reactors were coiled into a spiral form approximately 40 cm in diameter. The reactor was placed inside the heating section, which was isolated from the ambient with corrugated aluminum, glass wool, and asbestos. The in-line analysis was performed by a Digital Anton Paar Density meter (model mPDS 2000) placed at the outlet stream of the reactor. The density meter provided the temperature and the density of the product mixture at the outlet; the precision of the meter was 0.001 g/mL. The monomer conversion was calculated from the density values with the help of an empirical correlation obtained by Vega et al. (2001).

Samples of the reaction product were regularly collected in sampling jars. Known amounts of ethanol were then used to precipitate the polystyrene product. The molecular weights were measured off line by gel-permeation chromatography using a Waters 600 E GPC with four ULTRASTYRAGEL columns with porosities of 10^5, 10^4, 10^3, and 500A. The fluid phase was tetrahydrofuran (THF) and the feed flow was 1 mL/min.

C. Experimental Procedures

Known amounts of styrene and toluene were measured in test tubes and added into the feed tank. Then, the feed tank was covered and the nitrogen flow was initiated, in order to agitate the feed mixture and to purge oxygen. After a few minutes, the initiator was weighed on an analytical balance and added into the feed tank. The pump was turned on and the flow-calibration procedure was started. A feed flow rate of 2 mL/min was used.

D. Washout Initiator Perturbation

The reactor-flow characterization was carried out through a negative step perturbation of the initiator. First, the reaction was stabilized at the desired reaction conditions as indicated by the in-line density meter. The initiator concentration was then suddenly reduced by adding a known volume of solvent and monomer into the feed tank and mixing vigorously. Thereafter, the degree of monomer conversion was monitored by the product density as described.

III. MATHEMATICAL METHODOLOGY

The model represents the three steps of the experiment. First, cold reagents were supplied to the reactor. Then, the reactor was warmed, and the operational conditions were imposed. When the proprieties of the system were unchanging in time, the system was considered to be at steady state. Finally, it was perturbed by a step change in the input initiator concentration.

To represent the washout perturbation responses, a transient model was necessary. Additionally, a non-ideal flow pattern was observed in the polymerization reactors. Thus, the axial-dispersion model was used in the
The present work to fit the experimental data. The core objective was reactor flow characteristic and determination of the fluid-dynamic parameters. To achieve this, a three-level algorithm was used. On the first level, a system of partial differential equations was reduced to a simple system of differential algebraic equations (DAE). The numerical integration of this DAE by DASSL (Brenan et al., 1989) was the second level. Finally, parameter estimation was performed using the ESTIMA software (Santos and Pinto, 1998), the two levels cited above and the experimental data. Mathematical consistency was ensured by imposing boundary conditions matching the experimental conditions, such as the initial conditions and the washout implementation.

A. Modeling

The axial-dispersion model is a model for real reactors with one experimentally obtained parameter, the axial-dispersion coefficient. This model involves a modification of the plug-flow reactor pattern by imposing axial dispersion over it. In an analogy to Fick’s Law, the model is represented by Eq. 1:

$$\frac{\partial C_i}{\partial t} + v_i \frac{\partial C_i}{\partial z} = D_{axial} \frac{\partial^2 C_i}{\partial z^2} + R_x,$$

where $C_i$ is the concentration of species $A$, $t$ is time, $v_i$ is the axial velocity, $z$ is the axial position, $D_{axial}$ is the axial dispersion, and $R_x$ is the rate of reaction.

The system of equations that represents the model is obtained by assuming these hypotheses: transient state, isothermal conditions, quasi-steady-state approximation (QSSA) to macroradicals, QSSA to the first center ($R_0$), chain transfer of active center to solvent and monomer, constant axial velocity (i.e., constant flow rate), incompressible fluid, constant density, and the gel effect. The reactor was considered to be in an isothermal condition, because the difference between the entrance and the exit thermocouples was generally limited to 4-5°C; in some experiments using the reactor with discontinuous mixing elements, the difference reached 9°C.

To reduce the number of equations, we considered the macroradicals ($\lambda_i$’s) and final polymer ($\mu_i$’s) moments, as shown in Eq. 2:

$$\lambda_i = \sum_{j=0}^{M} j^p R_j, \quad \mu_i = \sum_{j=0}^{M} k^p P_j.$$

The first three moments for each distribution were sufficient to obtain the number-average molecular weight ($M_n$) and weight average molecular weight ($M_w$), as defined in Eqs. 3 and 4:

$$M_n = MW_{average} \frac{\mu_3}{\mu_2},$$

$$M_w = MW_{average} \frac{\mu_3}{\mu_1}.$$

The polydispersity index (PI) is calculated by dividing $M_w$ by $M_n$.

All species were considered: solvent (S), initiator (I), inhibitor (Z), and monomer (M) as well as the moments of macroradicals and polymers. The equations are Eqs. 5-14:

$$\frac{\partial S}{\partial t} = v \frac{\partial S}{\partial z} - D_S \frac{\partial^2 S}{\partial z^2} - k_S \lambda,$$

$$\frac{\partial I_0}{\partial t} = v \frac{\partial I_0}{\partial z} - D_I \frac{\partial^2 I_0}{\partial z^2} - 2k_{I} \lambda,$$

$$\frac{\partial Z}{\partial t} = v \frac{\partial Z}{\partial z} - D_Z \frac{\partial^2 Z}{\partial z^2} - k_{inh} \lambda,$$

$$\frac{\partial M}{\partial t} + v \frac{\partial M}{\partial z} = D_M \frac{\partial^2 M}{\partial z^2} - k_{M} \lambda - 3k_{M} \lambda^3 - k_{M} M \lambda^2,$$

$$\frac{\partial \lambda}{\partial t} + v \frac{\partial \lambda}{\partial z} = D_{polym} \frac{\partial^2 \lambda}{\partial z^2} + 2f \mu \frac{\partial \lambda}{\partial z} + (k_{S} + k_{X} M) \lambda,$$

$$\frac{\partial \mu}{\partial t} + v \frac{\partial \mu}{\partial z} = D_{polym} \frac{\partial^2 \mu}{\partial z^2} + (k_{S} + k_{X} M) \mu + k_{M} \lambda^3,$$

$$\frac{\partial C_i}{\partial t} = \sum_{j=0}^{M} j^p R_j \quad \text{with } C_i = S, I_0, Z, \lambda, \mu.$$

The initial concentrations (conditions) were when $t=0$, $S = S_0; I = I_0; M = M_0; \lambda_i’s$ and $\mu_i’s = 0$.

The boundary conditions are the closed-closed conditions of Danckwerts (1953), see Eq. 15:

$$B.C.1 \quad v \cdot X = \left( X - D_s \frac{dX}{dz} \right)_{z=0} = 0,$$

$$B.C.2 \quad \frac{dX}{dz} = 0 \quad \text{for } X = M, I, S, \lambda, \mu \quad \text{and } i = 0,1,2.$$

The gel effect was considered by assuming the chain-length dependence of termination to be a power law (Olaj et al., 2001) of the form given by Eq. 16:

$$k_{inh} = k_{inh}(\nu)^{-b},$$

where $k_{inh}$ is the initial rate constant of termination, $\nu$ is related to the number-average degree of polymerization, and $b$ is a parameter, here assumed to equal 0.1.

B. Simulation

The model is composed of very similar equations, and an example equation is used for the mathematical considerations. First, the equation is put in dimensionless units by using $y = c/c_0; x = z/L$ (length of reactor) and $t’ = t v/L$, thus

$$\frac{\partial y}{\partial t} + \frac{1}{Pe} \frac{\partial y}{\partial x} - \frac{L}{v} R,$$

I.C: $y_0 = 1$ or 0

$$B.C.1 \quad y = \left( y - \frac{1}{Pe} \frac{dy}{dx} \right)_{x=0} = 0 \quad \text{to } x = 1.$$

The axial dispersion is transformed to a Peclet number, which is the parameter to be explored herein. Applying the orthogonal-collocation method (Finlayson, 1976; Villadsen and Michelsen, 1978), a system of differential algebraic equations is obtained:
C. Washout Initiator Perturbation

A negative step in initiator concentration was realized by adding monomer and solvent in the same proportions as the initial charge to the feeding tank, but without initiator. Mathematically, the perturbation was obtained as the initial charge to the feeding tank, but without inconsistency (Vieira and Biscaia, 2001). The typical experimental operational parameters are given in Table 2. To simplify the parameter estimation, the Peclet parameter and the mean residence time were evaluated by this estimation procedure.

D. Parameter estimation

A fundamental step in the process of the generation of a mathematical model is parameter estimation. These values are usually evaluated by fitting model responses to experimental data. Parameter-estimation procedures generally lead to the minimization of a scalar function, which measures the adequacy of the model response. Parameter estimation has been largely concentrated on the development of numerical techniques for fast and reliable minimization of nonlinear quadratic scalar objective functions (Vega et al., 2001). One of the best methods of taking variable correlation into consideration is the maximum-likelihood method, because it is easy to use and produces estimators with good statistical properties. In the present work, the Peclet parameter and the mean residence time were evaluated by this estimation procedure.

IV. RESULTS

The final model simulation demanded additional information. The kinetic constants of polymerization are a very difficult choice, as widely varying values have been reported in the literature (Brandup et al., 1999). The values used herein are listed in Table 1 (Cutter and Drexler, 1982; Brandup et al., 1999; Beuermann and Buback, 2001). The typical experimental operational parameters are given in Table 2. To simplify the parameter...
Table 1. Kinetic constants for styrene polymerization.

<table>
<thead>
<tr>
<th>Kinetic constants</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal initiation ($K_i$)</td>
<td>$1.99 \times 10^6 \exp(-14.842/T)$, m$^3$/kgmol$^2$/s</td>
</tr>
<tr>
<td>Chemical initiation ($K_d$)</td>
<td>$1.71 \times 10^{15} \exp(-15.924/T)$, 1/s</td>
</tr>
<tr>
<td>Propagation ($K_p$)</td>
<td>$4.27 \times 10^7 \exp(-3.909/T)$, m$^3$/kgmol/s</td>
</tr>
<tr>
<td>Transfer to solvent ($K_{ts}$)</td>
<td>$1.25 \times 10^{-5} K_p$, m$^3$/kgmol/s</td>
</tr>
<tr>
<td>Transfer to monomer ($K_{tm}$)</td>
<td>$7.0 \times 10^{-5} K_p$, m$^3$/kgmol/s</td>
</tr>
<tr>
<td>Terminating (combination) ($K_{tc}$)</td>
<td>$1.06 \times 10^9 \exp(-753/T)$, m$^3$/kgmol/s</td>
</tr>
<tr>
<td>Inhibition ($K_{init}$)</td>
<td>0.36 $K_p$</td>
</tr>
</tbody>
</table>

Table 2. Typical operational parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the reactor (L)</td>
<td>12.0 m</td>
</tr>
<tr>
<td>Diameter of the reactor</td>
<td>0.4 cm</td>
</tr>
<tr>
<td>Flow</td>
<td>2.0 mL/min</td>
</tr>
<tr>
<td>Initiator concentration</td>
<td>0.0386 mol/L</td>
</tr>
<tr>
<td>Solvent concentration</td>
<td>60% by volume</td>
</tr>
<tr>
<td>Monomer concentration</td>
<td>40% by volume</td>
</tr>
<tr>
<td>velocity</td>
<td>$3.3 \times 10^{-3}$ m/s</td>
</tr>
</tbody>
</table>

analysis, it was assumed that a single value of the axial-dispersion coefficient would suffice for all reactors.

The algorithm used herein is effective, as only seven collocation points were necessary to solve the DAE system (Eqs. 17-20), and twelve points were needed for the washout-initiator modeling, so this is the number considered ideal for the algorithm; if the Peclet number does not exceed 30, a reduced number of points can be used.

The results of the monomer-conversion response tests presented three distinct parts (see Figs. 4-6). The initial value is the unperturbed one, so this is the original steady-state conversion and is completely defined by initial conditions, constants, and parameters. This first steady state was used to determine the kinetic constants of polymerization. The second part was characterized by the intensity of the decrease in conversion, and if the Peclet number was increased then the step inclination was decreased, that is, it became similar to a PFR pattern. The third part was the new steady-state conditions which were imposed by the new concentrations of initiator and inhibitor.

A parametric evaluation demonstrated that the model was more sensitive to the mean residence time, the polymerization temperature, and to the efficiency factor of the initiator. Good consistency of the simulated results was observed, because as the temperature of polymerization and the mean residence time were increased then the monomer conversion simulation also increased. Additionally, the difference between the old and new steady states of monomer conversion was increased when the Peclet number decreased. These variations indicate trends useful for parameter estimation.

The inhibition concentration was well represented by the model, and consistent values were obtained up to the point where the kinetic constant of inhibition was equal to twenty times the $K_p$ value; above this value, oscillations in the inhibition concentration were observed.

An intermediate Peclet number value, 0.9, was obtained for the empty tubular reactor (see Fig. 5). This indicates a non-ideal behavior and it is very different from the PFR model; it more resembles an elongated parabolic velocity profile. The reactor with continuous packing had a high Peclet number (see Fig. 4), and therefore it could be considered as plug flow. Thus, this packing is a good choice when only one residence time is necessary. The reactor with discontinuous packing also had an intermediate Peclet number of 2.4 (see Fig. 7). The velocity profile developed in the empty reactor prevailed; therefore the mixing elements were not very effective. Using these Peclet numbers and mean residence times, it was possible to evaluate the monomer conversion and molecular weights in the three tubular reactors. It was concluded that very different fluid-dynamic patterns can be studied with washout-initiator perturbations.

Typical experimental values for monomer conversion and molecular weights were obtained for each reactor at $85^\circ C$. The monomer conversions were 35-40% (Figs. 7, 8, and 9), and the number-average molecular weight ($M_n$) was in the range of 8,000-12,000. The weight-average molecular weights ($M_w$) were 14,000-20,000.

![Figure 4. Comparison of model step predictions (line) and monomer-conversion measurements (points). Unpacked tubular reactor, $tr = 47$ min, $Pe = 0.9$.](image)

![Figure 5. Comparison of model step predictions (line) and monomer-conversion measurements (points). Reactor with continuous packing, $tr = 68$ min, $Pe = 54$.](image)
Figure 6. Comparison of model step predictions (line) and monomer-conversion measurements (points). Reactor with discontinuous packing, \( t_r = 58 \) min, \( Pe = 2.4 \).

Figure 7. Comparison of model predictions (line) and monomer-conversion measurements (points) in an unpacked tubular reactor.

The polydispersity indices (PI) were in the range of 1.5 to 2.0, in accord with the molecular-weight values and termination controlled by combination, with a possible contribution by chain transfer by uncontrolled contaminants.

Fluctuations in the monomer-conversion curves can be seen in Figure 5, which indicates a complex fluid dynamic behavior, as has been reported elsewhere (Vianna et al., 2006, 2007). However, a deep error analysis would be required to affirm this interpretation.

The Peclet numbers and mean residence times estimated herein represented monomer conversions well in all three reactors, as can be seen in Figures 7, 8, and 9. Unfortunately, the model values for the molecular weights were twice the experimental values. If the model better represented molecular weights, it may be possible to study these negative step-variable responses, and a specific macromolecular Peclet number could be obtained.

V. CONCLUSIONS

The washout perturbation of a reagent can be used to characterize the fluid dynamics of a tubular polymerization reactor, as different fluid dynamic patterns were identified herein. Additional analytic equipment was not necessary, because no tracer was used. However, a transient model was needed to represent the monomer conversion step. Additionally, there are some systems that cannot accept heterogeneous tracers, for example, industrial plant (Giudici et al., 1997) and metabolic systems (Nasution et al., 2006).

The negative-step response to washout initiator perturbation was very similar to a tracer-step response, and a similar family of curves can be plotted to identify the fluid dynamics as well (Giudici et al., 1997). The slope of the response was directly related to the Peclet number and the mixing conditions.

The conversion and average molecular weights of the three reactors were not significantly different, which indicates that the ultimate differences induced by the different fluid-dynamic behaviors were not the most important effects. This is in agreement with studies performed by Cabral et al. (2003), Hamer and Ray (1986a, b), and Vianna et al. (2006, 2007).
ACKNOWLEDGMENTS

The author gratefully acknowledges D.Sc. Evaristo C. Biscaia Jr. and D.Sc. José Carlos Pinto for the experimental support of LMSCP (PEQ/UFRJ, Brazil) and their many constructive suggestions.

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Received: January 12, 2009.
Accepted: March 4, 2010.
Recommended by Subject Editor Orlando Alfano.