

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 Nardi *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.