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Detailed steady-state simulation of tubular reactors for LDPE production: Influence of numerical integration accuracy

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ABSTRACT

Simulators are widely used for analyzing and optimizing the production of low density polyethylene in tubular reactors under steady state conditions. This steady state is in practice often simulated by chemical engineers using a series of CSTRs type model due to its stable behavior with respect to spatial discretization and smooth convergence for the underlying stiff model equations. Although already a large number of CSTRs is used, this number appears to be too low for the physical reality. Here, this traditional cascaded CSTR approach is compared with a plug flow type approach for a highly detailed reaction model describing the free radical copolymerization. Additionally, the influence of the discretization is rigorously investigated and quantified. It is shown that the discretization does not significantly affect the temperature and the conversion profile, but has a major impact (deviations up to 30%) on the properties which determine the end product. However, this impact of discretization is in practice often overlooked.

1. Introduction

Polyethylene is one of the most widespread polymers worldwide. Its annual production is estimated to 80 million tonnes. Low-density polyethylene (LDPE), made in high-pressure reactors, represents about 30% of the total volume of produced polyethylene and is used for a large number of applications, e.g., packaging, adhesives, insulators, coatings and films. This widespread use is the result of the broad range of possible molecular and structural properties of the various grades of LDPE and its copolymers.

LDPE and its copolymers are commonly produced in high-pressure autoclaves and tubular reactors. From the 1990s on, when the majority of LDPE (60%) was produced in autoclave reactors, the tubular reactors gradually replaced the autoclave capacity. Most recent research and development was put into tubular reactors, which lead to an increased capacity and efficiency. Nowadays, the tubular reactor stands for 60% of the total production of LDPE. A high-pressure LDPE tubular reactor consists of a spiral wrapped metallic pipe with a large length to diameter ratio and a total length ranging from 1500 to 3000 m. The free-radical (co)polymerization of ethylene is carried out under extreme conditions, i.e., very high pressures between 2000 and 3000 bar and reactor temperatures between 400 and 600 K. Due to the pressure, the thickness of the reactor wall is of the same order as the inner diameter of the tube. The heat of reaction of this exothermic process is removed through the reactor wall by a cooling jacket around the tube. The ethylene conversion in this process is known to be low, in the order of 25–35%, and the polymer produced in these tubular reactors has a typical density of 915–930 kg/m^3. A commercial reactor has multiple reaction and cooling zones and includes a number of initiators and monomers feeding points (Fig. 1).

Mathematical models have proven to be extremely valuable tools for analyzing and optimizing the design, control and operation of chemical processes. Also for tubular LDPE reactors models of different complexity have been employed for (i) steady-state simulation (Bokis et al., 2002; Brandolin, Lacunza, Ugrin, & Capiati, 1996; Kiparissides, 1996; Zabisky & Chan 1992) and optimization (Brandolin, Valles, & Farber, 1991; Yao, Lohi, Upreti, & Dhib, 2004; Yoon & Rhee, 1985) as well as (ii) transient simulation (Häfele, Kienle, Boll, Schmidt, & Schwibach, 2005, 2006; Zavala & Biegler, 2009a, 2009b) and optimization (Asteasuain, Tonelli, Brandolin, & Bandoni, 2001). All examples prove that model based approaches lead to significant improvements for the manufacturers.

In general, two simulation approaches are used to model the multipeak reactor under steady state conditions, i.e., a direct simulation as a steady state plug flow reactor (PFR) (e.g., Zabisky and Chan (1992)) or a false transient simulation as a cascade of continuous stirred tank reactors (cascaded CSTRs) (e.g., Häfele et al. (2006)). The cascaded CSTR is often preferred in practice by chemical engineers because of its stable behavior with respect to spatial discretization and its smooth convergence for the underlying stiff

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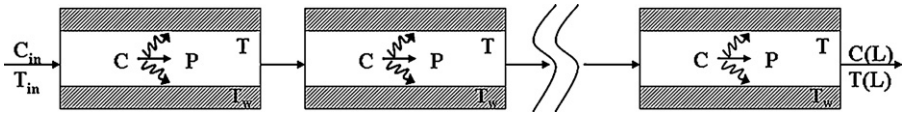

Fig. 1. Schematic view of a high pressure multizone jacketed tubular reactor for the production of LDPE.

model equations. On the other hand, the plug flow approach may be closer to the physical and chemical reality, as in principle a high number of CSTRs (i.e., a fine discretization grid) is required to capture accurately fast kinetics and thus steep gradients, which gives rise to large computation times. Although the two simulation approaches should yield similar predictions, if an infinite number of CSTRs is used, several aspects are numerically non-trivial (e.g., the large, complex, highly nonlinear system of equations with largely different time-scales) and may give rise to discrepancies. In case the models are implemented to perform online tasks such as real-time optimizations or moving horizon estimations, certain errors due to process or model mismatch can be eliminated by the use of online estimation strategies (Kiparissides, Verros, & Pertsinides, 1994; Zavala & Biegler, 2006, 2009a). Additionally, coarse CSTR-like discretizations can in these cases be used to provide a hot-start. Since our research is situated more in the field of offline design optimizations, these discrepancies will be of major importance. The accuracy of the two simulation approaches has hardly been compared in literature, nor has the impact of the discretization rigorously been studied.

In this paper, a rigorous comparison for the steady state simulations is presented based on a highly detailed reactor model, including all zones and a higher order approximation of the molecular weight distribution than what is typically used. Section 2 first links the two simulation approaches to the chemical process reality. Section 3 introduces the main characteristics of the detailed reaction model. Afterwards Section 4 discusses the two steady state simulation approaches, while Section 5 presents the simulation results and analyzes the importance of discretization. Finally, Section 6 summarizes the conclusions.

2. Tubular reactor modelling methods

Most of the industrial reactors deviate from the idealized model reactors, i.e., not all tank reactors are perfectly mixed, nor do all tubular reactors exhibit plug flow behavior. In general, for a tubular reactor the deviation from the ideal plug flow reactor can be traced back to three causes, i.e., (i) vortices and turbulent eddies, which may produce axial mixing and give rise to back-mixing, (ii) a not uniform distribution of the velocity over the cross section and (iii) the molecular diffusion which always takes place, but has a minor influence. In practice, axial back-mixing in tubular reactors is represented by axial dispersion. Two models, i.e., the dispersion plug flow (DPFR) model and the cascaded CSTRs model, use a single parameter that accounts for the non-ideality of the tubular reactors, i.e., the axial dispersion coefficient D_a and the number of CSTRs in series N, respectively. By varying the axial dispersion coefficient D_a in the dispersion plug flow model, behavior ranging from a pure PFR to a CSTR can be induced. The level of dispersion is often indicated by the dimensionless Peclet number Pe, which is defined as the ratio between the transport rate by convection and the transport rate by dispersion (Eq. (1)).

$$Pe = \frac{vL}{D_a} = Pe_a \frac{L}{d_t} \tag{1}$$

$$Pe_a = \frac{vd_t}{D_a} \tag{2}$$

here Pe_a is the axial Peclet number, v is the reaction mixture velocity, L is the reactor length and d_t is the inner diameter of the tube.

Axial dispersion data are correlated based on the axial Peclet number Pe_a (Eq. (2)) to process conditions by means of dimensionless numbers, e.g., Reynolds number Re and Schmidt number Sc. For the turbulent flow of LDPE reaction mixture with a Reynolds number Re of approximately 2.5×10^6, the axial Peclet number Pe_a can be derived using the correlation of Wen and Fan (1975):

$$\frac{1}{Pe_a} = \frac{3 \times 10^7}{Re^{2.1}} + \frac{1.35}{Re^{0.125}} \qquad Re > 3000 \tag{3}$$

If the second approach of the cascaded CSTRs is preferred, it is easy to calculate the corresponding number of CSTRs in series N of this model by following equation:

$$\frac{Pe}{2} = N - 1 \tag{4}$$

The actual LDPE tubular reactor has on average a $\frac{L}{d_t}$ ratio in the order of 5×10^4, which results in a Peclet number Pe of 2.0×10^5. Thus, it is safe to assume that a plug flow reactor (PFR) model approaches the operation characteristics of the LDPE reactor. In order to obtain an equivalent cascaded CSTRs model in principle 100,000 tanks in series would be necessary. In practice however, much less CSTRs in series ($\sim 10^2 - 10^3$) are used in order to reduce the computational effort. Nevertheless, the cascaded CSTRs model is often preferred in practice by chemical engineers because of its stable behavior and its smooth convergence for the underlying stiff model equations.

3. Model

The detailed model describes the free radical copolymerization of ethylene in the presence of several initiators and chain-transfer agents (CTAs) under supercritical conditions and is based on industrial data. In general, an LDPE reactor model consists of three main elements, i.e., (i) the reaction kinetics, (ii) the mass, energy and momentum balances, and (iii) the physical, transport and thermodynamic properties. Due to the high complexity of the model equations, only the general aspects of the model are highlighted and some general equations of the PFR model are shown.

3.1. Reaction kinetics

Extensive studies have shown that the free radical (co)polymerization of ethylene exists of (i) three main reactions, i.e., initiation, propagation and termination, and (ii) numerous side reactions, e.g., chain transfer to monomer and polymer, β-scission and backbiting. Mostly a mixture of peroxides initiates the polymerization, each of them start decomposing at a different temperature. Every reaction taken into account is presented in Table 1. Here, the symbols M_1, M_2 and CTA represent the monomer, comonomer and chain transfer agent, respectively, while $I_{2,\nu}$ and I^*_ν with $\nu \in 1, \ldots, N_{I_2}$ denote N_{I_2} initiator types and the corresponding initiator radicals. The symbols $R^*_{1,i}$ and $R^*_{2,i}$ denote the *live* polymer chains of length i ending with a monomer 1 unit, respectively monomer 2 unit (comonomer). Finally, D_i are the *dead* polymer chains of length i. The respective reaction rates are for