This document contains the **post-print pdf-version** of the refereed paper:

“Detailed steady-state simulation of tubular reactors for LDPE production: influence of numerical integration accuracy.”

by *Peter Van Erdeghem, Filip Logist, Christoph Dittrich and Jan Van Impe*

which has been archived in the university repository Lirias (<https://lirias.kuleuven.be/>) of the Katholieke Universiteit Leuven.

The content is identical to the content of the published paper, but without the final typesetting by the publisher.

When referring to this work, please cite the full bibliographic info:

Van Erdeghem, P., Logist, F., Dittrich, C., Van Impe, J. (2012). Detailed steady-state simulation of tubular reactors for LDPE production: influence of numerical integration accuracy. Computers & Chemical Engineering, 37, 40-47.

The journal and the original published paper can be found at:

<http://www.sciencedirect.com/science/journal/00981354>
<http://dx.doi.org/10.1016/j.compchemeng.2011.09.003>

The corresponding author can be contacted for additional info.

Conditions for open access are available at:

<http://www.sherpa.ac.uk/romeo/>

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

Peter M.M. Van Erdeghem^a, Filip Logist^a, Christoph Dittrich^b, Jan F. Van Impe^a

*^aBioTeC & OPTEC, Department of Chemical Engineering,
Katholieke Universiteit Leuven,
W. de Croylaan 46, B-3001 Leuven, Belgium.*

(Tel: +32-16-32.26.75, e-mail: jan.vanimpe@cit.kuleuven.be)

*^bSABIC Technology Center Geleen,
P.O. Box 319, 6160 AH Geleen, The Netherlands*

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 profiles, 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.

Keywords: Tubular reactor, discretization, differential equations, LDPE (co)polymerization, steady state simulation.

Postprint of manuscript accepted for Computer and Chemical Engineering

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

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 90's 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 to 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/m³. A commercial reactor has multiple reaction and cooling zones and includes a number of initiators and monomers feeding points (Figure 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 (Zabisky and Chan, 1992; Kiparissides, 1996; Brandolin et al., 1996; Bokis et al., 2002) and optimization (Yoon and Rhee, 1985; Brandolin et al., 1991; Yao et al., 2004) as well as *(ii)* transient simulation (Häfele et al., 2005, 2006; Zavala and Biegler, 2009a,b) and optimization (Asteasuain et al., 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 multippeak 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 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 et al., 1994; Zavala and 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 (Equation (1)).

$$Pe = \frac{vL}{D_a} = Pe_a \frac{L}{d_t} \quad (1)$$

$$Pe_a = \frac{vd_t}{D_a} \quad (2)$$

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 (Equation (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

$2.5 \cdot 10^6$, the axial Peclet number Pe_a can be derived using the correlation of Wen and Fan (1975):

$$\frac{1}{Pe_a} = \frac{3 \cdot 10^7}{Re^{2.1}} + \frac{1.35}{Re^{0.125}} \quad Re > 3000 \quad (3)$$

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:

$$\frac{Pe}{2} = N - 1. \quad (4)$$

The actual LDPE tubular reactor has on average a $\frac{L}{d_t}$ ratio in the order of $5 \cdot 10^4$, which results in a Peclet number Pe of $2.0 \cdot 10^5$. 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 100000 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

Table 1: Free radical copolymerization of LDPE

Initiation		
$I_{2,\nu} \xrightarrow{k_{d,\nu}} 2I_\nu^*$	Initiator(s) decomposition	
$I_\nu^* + M_1 \xrightarrow{k_{i,1}} R_{1,1}^*$	Chain initiation	
$I_\nu^* + M_2 \xrightarrow{k_{i,2}} R_{2,1}^*$		
Propagation		
$R_{1,i}^* + M_1 \xrightarrow{k_{p,11}} R_{1,i+1}^*$	Chain propagation	
$R_{2,i}^* + M_1 \xrightarrow{k_{p,21}} R_{1,i+1}^*$		
$R_{1,i}^* + M_2 \xrightarrow{k_{p,12}} R_{2,i+1}^*$		
$R_{2,i}^* + M_2 \xrightarrow{k_{p,22}} R_{2,i+1}^*$		
Termination		
$R_{1,i}^* + R_{1,j}^* \xrightarrow{k_{t,rec,11}} D_{i+j}$	Recombination	
$R_{1,i}^* + R_{2,j}^* \xrightarrow{k_{t,rec,12}} D_{i+j}$		
$R_{2,i}^* + R_{2,j}^* \xrightarrow{k_{t,rec,22}} D_{i+j}$		
$R_{1,i}^* + R_{1,j}^* \xrightarrow{k_{t,rec,11}} D_i + D_j$	Disproportionation	
$R_{1,i}^* + R_{2,j}^* \xrightarrow{k_{t,rec,12}} D_i + D_j$		
$R_{2,i}^* + R_{2,j}^* \xrightarrow{k_{t,rec,22}} D_i + D_j$		

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 $\nu \in 1, \dots, N_{I_2}$ 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 each reaction described by an Arrhenius law, dependent on both the temperature T and pressure P :

$$k = k_0 \cdot \exp \left[\frac{-E_a - PdV}{RT} \right] \quad (5)$$

with the frequency factor k_0 , the activation energy E_a , the activation volume dV and the ideal gas constant R .

Table 1: (continued) Free radical copolymerization of LDPE

Side reactions		
$R_{1,i}^* + M_1 \xrightarrow{k_{tr,mon,1}} D_i + R_{1,1}^*$	Transfer to monomer	
$R_{2,i}^* + M_1 \xrightarrow{k_{tr,mon,1}} D_i + R_{1,1}^*$		
$R_{1,i}^* + M_2 \xrightarrow{k_{tr,mon,2}} D_i + R_{2,1}^*$		
$R_{2,i}^* + M_2 \xrightarrow{k_{tr,mon,2}} D_i + R_{2,1}^*$		
$R_{1,i}^* + D_j \xrightarrow{k_{tr,pol,1}} D_i + R_{1,j}^*$	Transfer to polymer	
$R_{2,i}^* + D_j \xrightarrow{k_{tr,pol,1}} D_i + R_{1,j}^*$		
$R_{1,i}^* + D_j \xrightarrow{k_{tr,pol,2}} D_i + R_{2,j}^*$		
$R_{2,i}^* + D_j \xrightarrow{k_{tr,pol,2}} D_i + R_{2,j}^*$		
$R_{1,i}^* + CTA \xrightarrow{k_{tr,1}} D_i + CTA^*$	Transfer to CTA	
$R_{2,i}^* + CTA \xrightarrow{k_{tr,1}} D_i + CTA^*$		
$R_{1,i}^* \xrightarrow{k_{bb,1}} R_{1,i}^*$	Backbiting	
$R_{1,i}^* \xrightarrow{k_{bb,1}} R_{2,i}^*$		
$R_{2,i}^* \xrightarrow{k_{bb,2}} R_{1,i}^*$		
$R_{2,i}^* \xrightarrow{k_{bb,2}} R_{2,i}^*$		
$R_{1,i}^* + D_j \xrightarrow{k_\beta} D_i + R_{1,j-k}^* + D_k$	β -scission	
$R_{1,i}^* + D_j \xrightarrow{k_\beta} D_i + R_{2,j-k}^* + D_k$		
$R_{2,i}^* + D_j \xrightarrow{k_\beta} D_i + R_{1,j-k}^* + D_k$		
$R_{2,i}^* + D_j \xrightarrow{k_\beta} D_i + R_{2,j-k}^* + D_k$		

3.2. Balance equations

3.2.1. Mass balances.

To obtain a complete description of the molecular weight distributions of the copolymerization, an infinite number of mass balances for every polymer chain length is required. Hence, the *method of moments* (Katz and Saidel, 1967) is used to reduce the infinite system of balance equations into a low-order system of differential moment equations. This method is based on the statistical representation of the average molecular weight distribution and the properties of the copolymer in terms of the leading moments of the number

chain-length distributions of *dead* and *live* copolymer chains. The first four moments, i.e., zeroth till third, are used to reconstruct information about the molecular weight distribution and to obtain the characteristic quantities, e.g., the number, weight and z-average molecular weight M_n , M_w and M_z . The n leading moments for *dead* and *live* copolymer chains are defined as follows:

$$\mu_n = \sum_{i=1}^{\infty} i^n \cdot D_i \quad n \in \{0, 1, 2, 3\} \quad (6)$$

$$\lambda_n^m = \sum_{i=1}^{\infty} i^n \cdot R_{m,i}^* \quad n \in \{0, 1, 2, 3\}, m \in \{1, 2\}. \quad (7)$$

Since the moment equations for the dead polymer do not close, i.e., the n th moment depends on higher ones, for the fourth moment an algebraic closure equation, derived from Hulbert and Katz (1964), is introduced. One of the novelties in this model is the elaborate derivation of the third moment equation such that next to the mean and variance of the molecular weight distribution also the skewness, which is function of the third moment, is calculated accurately. In literature, most often a closure equation on the third moment is used (Asteasuain and Brandolin, 2008; Häfele et al., 2005).

Beside the moment balances of the copolymer, also the mass balances of the two monomers M_1 and M_2 , the different initiators $I_{2,\nu}$, the initiator radicals I_ν^* and the CTAs are taken into account. By incorporating the balances of the long chain branching (LCB) and short chain branching (SCB) frequencies additional information on the molecular properties is gathered.

3.2.2. Heat balance.

The temperature along the reactor is determined by (i) the heat of reaction of the propagation H_r , (ii) the heat exchange with the cooling water and (iii) the pressure dependence of the enthalpy of the mixture h_m :

$$\frac{dT}{dz} = \frac{H_r}{\dot{m}C_p} - \frac{U(T - T_{\text{cool}})\pi d_i}{\dot{m}C_p} - \frac{1}{C_p} \frac{\partial h_m}{\partial P} \frac{dP}{dz} \quad (8)$$

with the mass flow rate $\dot{m}$, the heat capacity C_p , the total heat transfer coefficient U , the temperature of the cooling water T_{cool} and the inner tube

diameter d_i . The overall heat-transfer coefficient U is calculated by the following equation:

$$\frac{1}{U} = R_o + R_w + R_i + R_f \quad (9)$$

where R_o , R_w , R_i and R_f denote the corresponding outside, wall, inside, and wall fouling heat resistances.

3.2.3. Momentum balance.

The pressure drop is defined as function of (i) friction factor f_r , (ii) the density of the mixture ρ_m and (iii) the velocity of the mixture v_m :

$$\frac{dP}{dz} = -C f_r \rho_m v_m^2. \quad (10)$$

3.3. Properties of the mixture

As a detailed description of the physical, transport and thermodynamic properties of the reaction mixture is essential for an accurate simulation, hardly any simplification is made. These properties strongly depend on the reactor operating conditions, e.g., temperature, pressure, and compositions of the mixture. A description of, e.g., density ρ , heat capacity C_p , thermal conductivity k , thermal convection h and viscosity η , is given in Van Erdeghem (2010).

4. Steady state simulation

Two approaches can be used to find the steady state solution, i.e., by directly solving the steady state equations or by solving relevant transient equations until the time derivatives stop to change significantly. Here, the LDPE high-pressure tubular reactor is simulated (i) as a steady state continuous PFR (Section 4.1) and (ii) as transient system of cascaded CSTRs (Section 4.2). Some implicit differences of the two methods are compared in Section 4.3 and 4.4. Both models contain all the features described in the previous section.

4.1. PFR

As mentioned, LDPE reactors consist of multiple reaction zones and exhibit characteristic multi-peak temperature and conversion profiles along the tube. The set of reactions stays the same in each zone and the length and distribution of the reaction zones along the tube are mainly defined by the

initiator, i.e., the location, the amount and composition of the initiator cocktail. Thus, the multizone reactor can directly be modelled as a series of 1-peak PFR modules. Hence, the model simulates the steady state profiles directly by integrating the time-invariant, but stiff ODEs along the reactor length.

4.2. Cascade of CSTRs

A transient tubular model can be approximated by a model of N cascaded CSTRs (Figure 2). In theory an infinite number is needed for an ideal plug flow behavior. Hence, the cascaded CSTRs can be interpreted as a discretization of the PDE model equation along the reactor length, i.e., every CSTR represents the transient working of the reactor along a distance Δz .

Figure 2: Schematic representation of the transient system of cascaded CSTRs.

Obtaining the steady-state solution by solving the transient CSTR equations until the state profiles stop changing significantly is also known as the *false transient method* (Kubíček and Hlaváček, 1983). In general this method is described as follows, an element y^* for which:

$$F(y^*) = 0 \quad (11)$$

is called the steady state solution of the transient system:

$$\frac{dy}{dt} = F(y) \quad \text{with} \quad y(0) = y_0. \quad (12)$$

For a stable steady state y^* and an initial condition y_0 near y^* convergence to this steady state is assumed:

$$y^* = \lim_{t \rightarrow \infty} y(t), \quad (13)$$

where $y(t)$ is a solution of the false transient equation (12) subject to an initial condition:

$$y(0) = y_0. \quad (14)$$

Important to note is that CSTRs in which large exothermic reactions occur, can exhibit multiple steady states, e.g., where no reaction takes place or the reaction runs away. Even open-loop unstable steady states are possible, in which case the false transient method will not detect it (Nauman, 2002). Hence, a CSTR discretization of a tubular reactor could introduce a very large number of parasitic steady-states (Flores-Tlacuahuac et al., 2005).

4.3. Order of the integration method

The steady state PFR model, consisting of a system of about 30 ODEs, is integrated along the reactor length by the **Matlab** (The MathWorks, Natick) routine **ode15s**. This routine is based on numerical differentiation formulas, where the integration is executed with a maximum order less than the default of fifth order. Moreover, the routine is especially suited for stiff systems.

As for the false transient method with the cascaded CSTRs, the integration order can be derived. In general, a balance equation states that the total or a component of a quantity m (e.g., mass) in the i th CSTR is modelled by:

$$\underbrace{\frac{dm_i}{dt}}_{\text{Accumulation}} = \underbrace{m_{i-1}}_{\text{In}} - \underbrace{m_i}_{\text{Out}} + \underbrace{r_i A \Delta z}_{\text{Generation}} \quad \text{with } i \in 1 \dots N \quad (15)$$

with r the reaction-consumption rate per volume reactor, A the inner area of the reactor tube and Δz the reactor length represented by one CSTR. If we assume the steady state solution per CSTR i , the balance equation (15) is rewritten as:

$$\frac{m_i - m_{i-1}}{\Delta z} = r_i A. \quad (16)$$

Thus, by applying the cascaded CSTR approach, the implicit or backwards Euler method, is used as integration method in space. As the LDPE polymerization exhibits for example very steep and mild slopes in the temperature profiles or initiators which are totally consumed instantaneously after injection, the implicit methods such as backwards Euler method are stable for solving these stiff equations in space, meaning that a larger step size Δz can be used. Hence, the cascaded CSTRs approach is more robust with respect to the spacial discretization as the implicit Euler introduces extra dispersion which results in a moderation of the steep gradients. Nevertheless, the cascaded CSTRs approach, compared to PFR model, is just a first order integration method instead of fifth order.

4.4. Size of the resulting ODE system

Another disadvantage of the false transient approach is the size of the resulting ODE system. For every CSTR the model contains 30 differential equations, so for N cascaded CSTRs a system of $30 \times N$ has to be solved. Knowing that an LDPE reactor is longer than 2000 m, even a coarse grid with discretization points every 10 m results into a system of at least 6000 ODEs. For the PFR model on the other hand, only 30 ODEs per peak have to be solved, independent of the discretization along the reactor (Table 2). It should be mentioned that `ode15s` is discretizing the PFR internally with an adaptive grid size, which is the main cause of the numerical advantage of the PFR model.

Table 2: Computational effort versus the size of resulting ODE system for the different discretization grids of the cascaded CSTRs approach and PFR reference.

grid	zones	computation time [s]	# of ODEs
10 m	R+C	4	$\gg 6000$
5 m	R	34	$\gg 8000$
5 m	R+C	88	$\gg 12000$
2 m	R	158	$\gg 13000$
1 m	R	623	$\gg 19000$
PFR		6	≈ 120

5. Results and discussion

As mentioned, the importance of a correct discretization along the reactor length is hardly studied and certainly not for a complete 4-peak reactor and detailed moment balances up to the third moment. For instance, Häfele et al. (2005) described the influence of discretization on the simulation results, though only for the first peak and moment balances up to the second moment. Here, five fixed grids for the cascaded CSTRs are chosen, i.e., 5 and 10 meter discretization along the complete reactor and 1, 2 and 5 meter discretization in the reaction zone (R) while in the cooling zones (C) it remains 10 meters. For the PFR approach, the integrator `ode15s` uses a high resolution adaptive grid. The size of the resulting ODE system for all grids, discussed in Section 4.4, and the corresponding computation time are comprised in Table 2. All calculations are performed on a Intel core2duo laptop

(2.5 Ghz). The coarse discretization of 10 meters tube per CSTR converges faster than the PFR approach obtains the steady state profiles. As the grid is refined, the computational effort escalates as the number of ODE equations vastly increases. Important to note is that the obtained profiles of the coarse discretization provides a good warm-start for the fine discretization steady state simulations, e.g., the computation time for the 2 meter and 1 meter grid substantially reduces from 158 and 623 s to 79 and 162 s, respectively.

The PFR results will serve as reference profile in the comparison and is drawn in Figures 3 - 7 with a dotted black line. For the sake of generality, only the trends are shown and the numbers have been removed. The relative deviations from this reference (1-norm) are calculated both along the reactor and at the reactor outlet. All obtained results are summarized in Table 3.

As depicted in Figure 3, the number of grid points or the fineness of discretization has hardly any influence on the temperature profile and all profiles are located within a bound of about 1.11 %. Also the influence on the conversion in the first reaction peak appears to be limited, but as the reaction mixture progresses along the reactor, the conversion decreases as the number of grid points increases and converges towards the PFR reference profile. Thus, although the temperature profile remains the same, just by refining the grid a conversion drop of about 7.97 % is visible. Important to note is that the difference in conversion only becomes clearly visible by examining the full multi-peak model instead of just one peak (Häfele et al. (2005)). This can be explained by conversion being an accumulated quantity with accumulated deviation while temperature is a local intensive quantity which starts with a deviation near zero in each valley.

Not only the differences on macroscopic scale, i.e., the conversion and reactor temperature profile, are of interest, also the influence on the microscopic properties of the produced LDPE are important. Even significantly larger deviations can be observed in Figure 4, where the zeroth and the third moment of the dead polymer are plotted. These quantities are of major interest in terms of product properties, i.e., the molecular weight distribution. For the zeroth moment of the dead polymer a large average deviation of 15.37 % is obtained for the 10 m grid with respect to the reference profile. The first moment is less sensitive for discretization, but the influence increases again for the second moment and certainly for the third moment. Moreover, different trends can be observed in the bottom picture of Figure 4, i.e., for a

coarse grid the third moment decreases in the two last peaks instead of the expected increasing trend. These discrepancies are ascribed to fast dynamics of the living polymers, i.e., the discretization grid is too coarse to resolve the formation of living polymer precisely. Hence, these deviations sum up in the higher moments of living polymer and are transferred to the moments of the dead polymer. It must be noted that in contrast to existing literature results, the exact third moment is calculated in this model and not approximated by a closure equation dependent on the previous moments, such that the results on the molecular weight distribution properties, e.g., variance and skewness, are not biased.

Figure 5 obviously shows that the physical properties of the supercritical mixture in the reactor, e.g., viscosity, are very sensitive to the integration grid choice. For physical properties, which are not only dependent on temperature, but also on concentration and n^{th} order moments of dead polymer, deviations of 25.28 % can be observed at the outlet of the reactor.

Many properties of the produced LDPE are determined by the polymer molecular weight distribution. Thus, typically every polymer grade can be characterized by the *number average molecular weight* M_n (Equation (17)), the *weight average molecular weight* M_w (Equation (18)) and the *z-average molecular weight* M_z (Equation (19)).

$$M_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = m_0 \frac{\mu_1}{\mu_0} \quad (17)$$

$$M_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} = m_0 \frac{\mu_2}{\mu_1} \quad (18)$$

$$M_z = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = m_0 \frac{\mu_3}{\mu_2} \quad (19)$$

where N_i is the number of polymers with molecular weight M_i and m_0 is the molecular weight of one monomer unit. The number average or arithmetic mean, is more sensitive to molecules of low molecular mass, while the weight and z-average is more sensitive to molecules of high molecular mass. As depicted in Figure 6, the error due to discretization on the number average molecular weight M_n is limited, while the weight average molecular weight M_w alters on average between 2.47 and 27.65 % along the different grides with a maximum relative error of 41.26 % on the end product. For the z-average molecular weight M_z , where the larger polyethylene molecules play

an even more important role, errors of similar order of magnitude as M_w are observed. Moreover, different profile trends are observed, e.g., for a coarse grid the weight average molecular weight M_w decreases as the polymer progresses along the reactor, while for the finer grids it keeps increasing.

In order to represent the molecular weight distribution (MWD) from the more mathematical or statistical perspective, specific quantities have to be derived of the dead polymer moments, i.e., the mean μ_{MWD} , the variance σ_{MWD}^2 and the skewness γ_{MWD} . The mean can be expressed in terms of the number average molecular weight,

$$M_n = \mu_{\text{MWD}} = \frac{\mu_1}{\mu_0} m_0 \quad (20)$$

with m_0 the molecular weight of one monomer unit.

This results into the following expression for the variance σ_{MWD}^2 :

$$\sigma_{\text{MWD}}^2 = \frac{\mu_2 \mu_0 - \mu_1^2}{\mu_0^2} m_0^2 \quad (21)$$

and the skewness γ_{MWD} :

$$\gamma_{\text{MWD}} = \frac{\mu_0^2 \mu_3 - 3\mu_0 \mu_1 \mu_2 + 2\mu_1^3}{\mu_0^3} m_0^3 \quad (22)$$

where the exact moments μ_0 till μ_3 are used.

Large deviations are observed for the quantities of the molecular weight distribution, i.e., for the variance σ_{MWD}^2 up to a relative error (increase) of 47.97 % on the end product and even 67.21 % for the skewness. As the variance σ_{MWD}^2 is the averaged squared deviation from the arithmetic mean, the resulting molecular weight distribution of the produced LDPE broadens. The skewness γ_{MWD} on the other hand is a measure for the asymmetry of the distribution, i.e., for a normal distribution the skewness calculated with centralized moments is zero but if the right tail is longer than the left one, which is the case for molecular weight distributions, the skewness γ_{MWD} is positive. Thus, as the grid is refined the skewness γ_{MWD} increases, even doubles in some cases, and pushes the distribution towards the left with a longer tail towards the high molecular weights.

In general, the deviation mainly occurs in the reaction zone of the peaks, i.e., the zones with the fast kinetics and larger temperature gradients, which

is proven by comparing the simulation results of the two 5 m grids, i.e., one along the complete reactor (magenta solid line) and one only in the reaction zones (green solid line). Figures 3 - 7 show that a finer grid in the cooling zones does not result into improved simulation results. The obtained profiles are practically the same with for example a relative deviation of about 10.1 % for the weight average molecular weight M_w . Hence, the discretization in the cooling zones remains 10 m while the grid of the reaction zones are further refined in order to avoid an too large system of ODEs.

Last but not least, it is important to note is that all observed properties (see Fig. 3 - 7 and Table 3) converge towards the reference profile as the number of discretization points increases. Thus, the steady state profiles obtained by the CSTRs in series evolves to the unique steady state of the PFR. Moreover, deviations on the initial values and profiles have no effect on the resulting steady state. Also no difference is observed when the steady state solutions of the PFR approach are used as initialization for all the cascaded CSTRs cases. Hence, it is safe to assume the CSTR discretizations do not converge to a spurious steady state.

6. Conclusion

In this paper two simulation approaches for the production of LDPE, i.e., as a plug flow reactor or as a cascade of CSTRs, are discussed and compared. The latter approach is in practice often preferred due to its easy interpretation, its stable behavior with respect to spatial discretization and its smooth convergence. Both detailed reactor models based on industrial data describe the complete reaction mechanism of the free radical copolymerization of ethylene with a comonomer under supercritical conditions, resulting into about 30 ODEs for the PFR or each CSTR. Moreover, as the closure is on the fourth moment, the level of detail of the current model exceeds those of the models found in literature which mostly have the closure on the third moment. The comparison of both approaches mainly boils down to one important numerical aspect, i.e., the discretization. The use of either approaches already implies some intrinsic differences. First, the integration routine for the PFR is free of choice, in the current case of the fifth order `matlab` routine `ode15s`, while the classic cascaded CSTR approach is equivalent to the implicit Euler method of first order. Second, the size of the resulting ODE system increases for the CSTR approach as the grid is refined, i.e., 30 ODEs per grid point,

while the number of ODEs for the PFR model remains the same, independent of the grid choice.

While observing the temperature profiles for the different grids, the discretization seems to have no significant influence. For the conversion profile however, the deviation increases towards the end of the reactor, i.e., for the first peak no distinct difference is detected, but at the fourth and last peak the relative deviation is up to 7.97 %. This is important as a previous analysis by Häfele et al. (2005) only considered the first peak. However, it is a completely different story for the physical properties of the mixture in the tube. From the start on a large influence from discretization is observable, e.g., an increasing deviation in viscosity ends up to 25.28 % at the end of the reactor. Also all the n^{th} moments are influenced by discretization and the higher the moment, the larger the deviations. For the third moment even different trends are observed, which results into other grades of LDPE with different molecular weight distributions. The number average molecular weight M_n is slightly altered with refined grids, but the weight average molecular weight M_w differs up to 27.65 % with the reference profile and even a different profile trend is observed. Similar deviations are observed for the z-average molecular weight M_z . Thus, the use of different discretization schemes leads to molecular weight distributions where the mean μ_{MWD} , variance σ_{MWD} and skewness γ_{MWD} deviate on average up to 8.38 %, 33.93 % and 44.85 % respectively.

In general, as the number of grid points increases, all the observed profiles converge towards the reference values. Hence, coarse CSTR like discretizations can be used for fast warm-starting of online applications. However, the size of the resulting ODE system and accordingly the computational time largely increases. Finally, the deviations mainly occur in the reaction zones with the fast reactions of the radicals and the large temperature gradients. Future work relates to a rigorous multi-objective optimisation based on methods similar to (Logist et al., 2009) and (Logist et al., 2010).

Acknowledgements

Work supported in part by SABIC Technology Center Geleen (The Netherlands) and Projects OT/10/035 and PFV/10/002 (Center-of-Excellence Op-

timization in Engineering) of the Research Council of the Katholieke Universiteit Leuven, Project KP/09/005 (SCORES4CHEM) of the Industrial Research Council of the Katholieke Universiteit Leuven, and the Belgian Program on Interuniversity Poles of Attraction, initiated by the Belgian Federal Science Policy Office. J. Van Impe holds the chair Safety Engineering sponsored by the Belgian chemistry and life sciences federation essenscia. The scientific responsibility is assumed by its authors.

References

- Asteasuain, M., Brandolin, A., 2008. Modeling and optimization of a high-pressure ethylene polymerization reactor using gproms. *Computers and Chemical Engineering* 32 (3), 396–408.
- Asteasuain, M., Tonelli, S., Brandolin, A., Bandoni, J., 2001. Dynamic simulation and optimisation of tubular polymerisation reactors in gPROMS. *Computers and Chemical Engineering* 25, 509–515.
- Bokis, C., Ramanathan, S., Franjione, J., Buchelli, A., Call, M., Brown, A., 2002. Physical properties, reactor modeling and polymerization kinetics in the low-density polyethylene tubular reactor process. *Industrial and Engineering Chemistry Research* 41 (5), 1017–1030.
- Brandolin, A., Lacunza, M., Ugrin, P., Capiati, N., 1996. High pressure polymerization of ethylene. An improved mathematical model for industrial tubular reactors. *Polymer Reaction Engineering* 4, 193–241.
- Brandolin, A., Valles, E., Farber, J., 1991. High pressure tubular reactors for ethylene polymerization optimization aspects. *Polymer Engineering and Science* 31, 381–390.
- Flores-Tlacuahuac, A., Zavala, V., Saldivar-Guerra, E., 2005. Complex non-linear behavior in the full-scale high-impact polystyrene process. *Industrial & Engineering Chemistry Research* 44 (8), 2802–2814.
- Häfele, M., Kienle, A., Boll, M., Schmidt, C.-U., Schwibach, M., 2005. Dynamic simulation of a tubular reactor for the production of low-density polyethylene using adaptive method of lines. *Journal of Computational and Applied Mathematics* 183, 288–300.
- Häfele, M., Kienle, A., Boll, M., Schmidt, C.-U., Schwibach, M., 2006. Modeling and analysis of a plant for the production of low density polyethylene. *Computers and Chemical Engineering* 31 (2), 51–65.
- Hulbert, H., Katz, S., 1964. Some problems in particle technology: A statistical mechanical formulation. *Chemical Engineering Science* 19, 555–574.
- Katz, S., Saidel, G. M., 1967. Moments of the size distribution in radical polymerization. *AIChE Journal* 13 (2), 319–326.

- Kiparissides, C., May 1996. Polymerization reactor modeling: a review of recent developments and future directions. *Chemical Engineering Science* 51 (10), 1637–1659.
- Kiparissides, C., Verros, G., Pertsinides, A., December 1994. On-line optimization of a high pressure low-density polyethylene tubular reactor. *Chemical Engineering Science* 49 (24), 5011–5024.
- Kubíček, M., Hlaváček, V., 1983. Numerical Solution of Nonlinear Boundary Value Problems with Applications. Prentice-Hall, Englewood Cliffs, New Jersey.
- Logist, F., Van Erdeghem, P., Van Impe, J. 2009. Efficient deterministic multiple objective optimal control of (bio)chemical processes. *Chemical Engineering Science*, 64 (11), 2527-2538.
- Logist, F., Houska, B., Diehl, M., Van Impe, J. 2010. Fast Pareto set generation for nonlinear optimal control problems with multiple objectives. *Structural and Multidisciplinary Optimization*, 42 (4), 591-603.
- Nauman, E., 2002. Chemical Reactor Design, Optimization, and Scaleup. McGRAW-HILL.
- Van Erdeghem, P., 2010. Model based simulation and optimisation of tubular reactors for the production of LDPE. Phd thesis, in preperation, K.U.Leuven.
- Wen, C., Fan, L., 1975. Models for flow systems and chemical reactors. Dekker (New York).
- Yao, F., Lohi, A., Upreti, S., Dhib, R., 2004. Modeling, simulation and optimal control of ethylene polymerization in non-isothermal, high-pressure tubular reactors. *International Journal of Chemical Reactor Engineering* 2.
- Yoon, B., Rhee, H., 1985. A study of the high-pressure polyethylene tubular reactor. *Chemical Engineering Communications* 34, 253–265.
- Zabisky, R., Chan, W.-M., 1992. A kinetic model for olefin polymerization in high-pressure tubular reactors: a review and update. *Polymer* 33 (11), 2243–2262.

- Zavala, V. M., Biegler, L., 2009a. Optimization-based strategies for the operation of low-density polyethylene tubular reactors: Moving horizon estimation. *Computers and Chemical Engineering* 33 (1), 379–390.
- Zavala, V. M., Biegler, L., 2009b. Optimization-based strategies for the operation of low-density polyethylene tubular reactors: nonlinear model predictive control. *Computers and Chemical Engineering* 33 (10), 1735–1746.
- Zavala, V. M., Biegler, L. T., 2006. Large-scale parameter estimation in low-density polyethylene tubular reactors. *Industrial & Engineering Chemistry Research* 45, 7867–7881.

Table 3: Overview of the relative error (1-norm) with respect to the PFR reference for the different discretization grids over the reaction (R) and cooling (C) zones. For every grid, AD is the averaged relative deviation along the entire reactor [%] and ED is the relative deviation on specifications of the end product [%].

	Discretization grids									
	10 m (R+C)		5 m (R+C)		5 m (R)		2 m (R)		1 m (R)	
	AD[%]	ED[%]	AD[%]	ED[%]	AD[%]	ED[%]	AD[%]	ED[%]	AD[%]	ED[%]
T	1.11	0.52	0.86	0.59	0.87	0.51	0.75	0.54	0.72	0.55
Conv	5.99	7.97	3.66	5.18	3.44	4.87	2.27	3.03	1.87	2.30
η	30.01	25.28	15.40	11.95	16.05	12.82	7.24	4.56	3.36	0.73
μ_0	15.37	15.88	7.59	8.11	7.36	7.79	3.22	3.50	1.90	2.10
μ_1	6.16	8.15	3.84	5.36	3.62	5.05	2.38	3.21	1.98	2.48
μ_2	27.49	36.33	8.52	12.93	8.77	13.25	3.24	5.39	1.32	2.11
μ_3	45.27	60.27	26.04	36.84	26.27	37.07	13.22	20.26	6.60	10.97
M_n	8.38	6.88	4.01	2.77	4.02	2.76	1.77	0.51	1.24	0.14
M_w	27.65	41.26	10.10	17.55	10.14	17.61	4.69	8.53	2.47	4.70
M_z	26.13	37.61	17.27	27.46	17.29	27.46	9.03	15.72	4.93	9.05
σ_{MWD}^2	33.93	47.97	12.17	20.78	12.22	20.83	4.94	9.31	2.47	4.57
γ_{MWD}	44.85	67.21	27.10	43.46	27.17	43.50	13.72	24.28	7.12	13.65

Figure 3: Temperature and conversion profiles.

Figure 4: Profiles of the zeroth and third moment.

Figure 5: Influence on physical properties: viscosity.

Figure 6: The evolution of the number, weight and z-average molecular weight along the reactor length.

Figure 7: Discretization influence on the variance (top) and skewness (bottom) of the molecular weight distribution.