Detailed steady-state simulation of tubular reactors for LDPE production: plug flow versus cascaded CSTR model

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Abstract: This paper compares two approaches for simulating the steady state of tubular reactors for the production of LDPE, i.e., the plug flow and the cascaded CSTR approach. In principle, both strategies should yield similar predictions. However, numerical discretization issues related to, e.g., the large-scale and complex system of equations with various time scales needed to model this polymerization, may lead to serious discrepancies. First, this paper gives a condensed overview of the detailed model, i.e., the reaction mechanisms, the balance equations and the physical, transport and thermodynamical properties. Then, the two simulation approaches are discussed and the intrinsic differences are unraveled. Finally, the influence of discretization during integration is studied in simulation. Although this aspect is crucial to ensure accurate steady-state simulations, it is in practice too often overlooked.

Keywords: Chemical industry; discretization; differential equations.

1. INTRODUCTION

Low-density polyethylene (LDPE) is without a doubt one of the most widespread polymers worldwide. Its annual production is estimated at 24 million tonnes and it is used for a large number of applications, e.g., packaging, adhesives, insulators, coatings and films. Most of the LDPE nowadays produced in tubular reactors, which consist of a spiral wrapped metallic tube with a total length ranging from 2000 to 3000 m and an inner diameter of 5 to 7 cm, and which operate under extreme conditions (i.e., pressures between 2000 and 3000 bar and temperatures between 400 to 600 K). Due to the exothermicity of the free-radical polymerization reaction, the heat of reaction has to be removed through a surrounding cooling jacket. A commercial reactor has multiple reaction (R) and cooling (C) zones (so-called peaks) and includes a number of initiator and monomer feeding points.

Mathematical models have proven over the past decades to be extremely valuable tools for analysing and optimising the operation, control and design of chemical processes. Also for tubular LDPE reactors models of different complexity have been developed and 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 [Häfle et al., 2005, 2006] 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 steady state reactor, i.e., a direct simulation as a 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., Häfle et al. [2006]). Although the two simulation approaches should yield similar predictions, 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. However, the accuracy of the two simulation approaches have hardly been compared in literature. In this paper, a rigorous comparison for the steady-state simulations is presented based on a complete and detailed reactor model, including all zones and an accurate description of the molecular weight distribution. Section 2 introduces the detailed reactor model. Section 3 discusses the two types of steady state simulation approaches, while Section 4 presents the simulation results and analyses the importance of a correct discretization.

2. MODEL

The detailed model describes the free radical copolymerization of ethylene with a comonomer in the presence of several initiators and chain-transfer agents (CTAs) under supercritical conditions. In general, an LDPE reactor model consists of three main elements, i.e., (i) the reaction mechanism, (ii) the mass, energy and momentum balances, and (iii) the physical, transport and thermodynamical properties. Due to the high complexity of the model equations and the limited amount of space, only the general aspects of the model are highlighted.
Table 1. Free radical copolymerization of LDPE

<table>
<thead>
<tr>
<th>Initiation</th>
<th>Propagation</th>
<th>Termination</th>
<th>Side reactions</th>
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<tr>
<td>$I^<em><em>n + M_1 \xrightarrow{k</em>{p,1}} R_1^</em>$</td>
<td>$R_{1,i}^* + M_1 \xrightarrow{k_{p,1}} R_{1,i+1}^*$</td>
<td>$R_{1,i}^* + R_{1,j}^{<em>} \xrightarrow{k_{r,1}^{</em>}} D_{i} + CTA^*$</td>
<td>$R_{1,i} + M_1 \xrightarrow{k_{p,1}} R_{1,i}^*$</td>
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<tr>
<td>$I^<em><em>n + M_2 \xrightarrow{k</em>{p,2}} R_{2,i}^</em>$</td>
<td>$R_{2,i}^* + M_2 \xrightarrow{k_{p,2}} R_{2,i+1}^*$</td>
<td>$R_{2,i}^* + R_{2,j}^{<em>} \xrightarrow{k_{r,1}^{</em>}} D_{i} + CTA^*$</td>
<td>$R_{2,i} + M_1 \xrightarrow{k_{p,1}} R_{2,i}^*$</td>
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<tr>
<td>$\rightarrow 2 I_0^*$</td>
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<td>$\rightarrow 2 I_0^*$</td>
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<tr>
<td>Initiator(s) decomposition</td>
<td>Chain propagation</td>
<td>Chain propagation</td>
<td>Transfer to monomer</td>
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<td>$\rightarrow$</td>
<td>$\rightarrow$</td>
<td>$\rightarrow$</td>
<td>$\beta$-scission</td>
</tr>
</tbody>
</table>

2.1 Reaction kinetics

Extensive studies have shown that the free radical (co)polymerization of LDPE exists out of (i) three main reaction mechanisms, i.e., initiation, propagation and termination, and (ii) numerous side reactions, e.g., chain transfer to monomer and polymer, β-scission and backbiting. Most often a mixture of peroxides initiates the polymerization, each of them decomposing at a different temperature. At high temperatures also thermal initiation of ethylene is a source of radicals. 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 $I_{2,n}$ and $I_n^*$ with $n \in 1, \ldots, N_{I}$ denote $N_{I}$ 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 unit, respectively comonomer unit. 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 the temperature $T$ and pressure $P$:

$$k = k_0 \cdot \exp \left( \frac{-E_a - P dV}{RT} \right)$$ (1)

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

2.2 Balance equations

Mass balances. To obtain a complete description of the molecular weight distributions of the copolymerization, an infinite amount of mass balances for every polymer chain 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 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 to third, are needed to reconstruct 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:

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

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

Because 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, proposed by Huibert and Katz [1964], is introduced.

Besides the moment balances of the copolymer, also the mass balances of the two monomers $M_1$ and $M_2$, the different initiators $I_{2,n}$, initiator radicals $I_n^*$ and CTA's 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.

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

$$\frac{dT}{dz} = \frac{H_p}{mC_p} - \frac{U(T - T_{cool}) \pi dt}{mC_p} - \frac{1}{C_p} \frac{\partial h_m}{\partial P} \frac{dP}{dz}$$ (4)

with $\dot{m}$ the mass flow rate, and $C_p, U, T_{cool}$ and $d_t$, the heat capacity, the total heat transfer coefficient, the temperature of the cooling water, and the inner tube diameter, respectively.
respectively. The overall heat-transfer coefficient $U$ is calculated by the following equation:

$$
\frac{1}{U} = R_o + R_w + R_i + R_f
$$

(5)

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

**Momentum balance.** The pressure drop is defined as function of (i) friction factor $f_r$, (ii) the density of the mixture $\rho_m$ and (iii) the velocity of the mixture $v_m$:

$$
\frac{dP}{dz} = -C_f\rho_m v_m^2.
$$

(6)

### 2.3 Properties of the mixture

As a detailed description of the physical, transport and thermodynamical properties of the reaction mixture is essential for an accurate simulation, no simplifications are made. These properties strongly depend on reactor operating conditions, e.g., temperature, pressure, and compositions of the mixture. A description of, e.g., density $\rho$, heat capacity $C_p$, thermal conductivity $k$, thermal convection $h$ and viscosity $\eta$, is given in Van Erdeghem [2011].

### 3. PFR VS CSTR APPROACH

Two simulation approaches are used to find the steady state solution, i.e., by directly solving the steady state equations or by solving relevant transient equations until the solutions stop to change significantly. Here, the LDPE high-pressure tubular reactor is modelled (i) as a steady state continuous PFR (Section 3.1) and (ii) as transient system of cascaded CSTRs (Section 3.2). Both models contain all the features described in the previous section.

#### 3.1 PFR

As mentioned, LDPE reactors consist of multiple reaction zones and exhibit characteristic multi-peak temperature and conversion profiles along the tube. The reaction mechanism 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 (Figure 1).

**Fig. 1.** Steady state continuous PFR approach.

#### 3.2 Cascade of CSTRs

A transient PFR model can be approximated by a model of $N$ cascaded CSTRs (Figure 2). In theory an infinite number is needed for an identical result. 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 $\Delta z$.

**Fig. 2.** 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:

$$
F(y^*) = 0
$$

(7)

called the steady state solution of the transient system:

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

(8)

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

$$
y^* = \lim_{t \to \infty} y(t).
$$

(9)

#### 3.3 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 (NDF), 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:

$$
\frac{dm_i}{dt} = m_{i-1} - m_i + r_i A \Delta z \quad \text{with} \quad i \in 1 \ldots N
$$

(10)

with $r$ the reaction-consumption rate per volume reactor, $A$ the inner area of the reactor tube and $\Delta z$ the reactor length represented by one CSTR. If we assume the steady state solution per CSTR $i$, the balance equation (10) is rewritten as:

$$
m_i = m_{i-1} + r_i A \Delta z
$$

(11)

Thus, by applying the cascaded CSTR approach, the implicit or backwards Euler method, is used as integration method. The advantage of implicit methods such as backwards Euler method is that they are more stable for solving a stiff equation, meaning that a larger step size $\Delta z$ can be used. Nevertheless, the cascaded CSTRs approach, compared to PFR model, is just a first order integration method instead of fifth order.

#### 3.4 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 have to be solved, independent of the discretization along the reactor.
4. RESULTS AND DISCUSSION

As mentioned, the importance of a correct discretization along the reactor length is hardly studied and certainly not for the complete 4-peak reactor and detailed moment balances up to the third moment. For instance, [Häfele et al., 2005] describes 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 PFR results will serve as reference profile in the comparison and is drawn in Figures 3 - 7 with a dotted black line. Due to confidentiality reasons only the trends are shown and the numbers have been removed. Also the deviations from this reference are calculated both along the reactor and at the reactor outlet. All numbers are summarized in Table 2.

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%. 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 8% 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]).

Not only the differences on macroscopic scale, i.e., the conversion 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 entities 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 15.4% is obtained for the 10 meter grid with respect to the reference profile. The first moment is less sensitive for discretization, but the influence reincreases 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.,

**Table 2. Overview of the relative error (1-norm) with respect to the PFR reference for the different discretization grids.** The first value is the averaged deviation along the entire reactor and the value between brackets is the relative deviation on specifications of the end product.

<table>
<thead>
<tr>
<th>Discretization</th>
<th>Relative error using the 1-norm [%] (deviation on end product [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>grid</td>
<td>$\mu_0$</td>
</tr>
<tr>
<td>10 m R+C</td>
<td>15.4 (15.9)</td>
</tr>
<tr>
<td>5 m R+C</td>
<td>7.6 (8.1)</td>
</tr>
<tr>
<td>5 m R</td>
<td>7.4 (7.8)</td>
</tr>
<tr>
<td>2 m R</td>
<td>3.2 (3.5)</td>
</tr>
<tr>
<td>1 m R</td>
<td>1.9 (2.1)</td>
</tr>
</tbody>
</table>

**Fig. 3. Temperature and conversion profiles.**

**Fig. 4. Profiles of the zeroth and third moment.**
instead of increasing, for a coarse grid the third moment decreases in the two last peaks. 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 higher moments of living polymer and are transferred to the moments of the dead polymer. Note that, in this model the exact third moment is calculated 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 obvious 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 25.3% can be observed at the outlet of the reactor.

Because many properties of the produced LDPE are determined by the polymer molecular weight distribution, every polymer grade can be characterized by the number average molecular weight \( M_n \) (Equation (12)) and the weight average molecular weight \( M_w \) (Equation (13)).

\[
M_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{m_0 \mu_1}{\mu_0} \quad (12)
\]
\[
M_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{m_0 \mu_2}{\mu_1} \quad (13)
\]

Where \( N_i \) is the number of polymers with molecular weight \( M_i \) and \( m_0 \) 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 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 2.5 and 27.7% along the different grids with a maximum relative error of 41.3% on the end product. Moreover, different profile trends are observed, i.e., 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.

Assuming a log-normal molecular weight distribution, its curve is calculated with the probability density function:

\[
f(x) = \frac{1}{\sqrt{2\pi}\sigma x} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}}, x > 0 \quad (14)
\]

with \( \mu \) and \( \sigma \) the mean and standard deviation of the variables natural logarithm \( \ln x \). The mean \( \mu \) and standard
deviation $\sigma$ are computable from the $n^{th}$ order moments of
dead polymer and the resulting distributions are plotted
in Figure 7. As the discretization grid is refined, the mean
$\mu$ decreases and standard deviation $\sigma$ increases (bottom
picture Figure 7) which result into lognormal distribution
with an increasing skewness (top picture Figure 7).

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 meter grids, i.e., one along
the complete reactor (magenta solid line) and one only
in the reaction zones (green dotted 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 10.1% for the weight average molecular weight $M_w$.
Hence, the discretization in the cooling zones remains 10
meter while the grid of the reaction zones are further
refined in order to avoid an oversized system of ODEs.

Last but not least, it is important to note is that all ob-
served properties (see Figures 3 - 7 and Table 2) converge
towards the reference profile as the number of discretiza-
tion points increases.

5. CONCLUSION

In this paper two simulation approaches for the production
of LDPE, i.e., as a plug flow or as cascade of CSTRs,
are discussed and compared. Both detailed reactor models
describe the complete reaction mechanism of the free rad-
cal copolymerization of ethylene with a comonomer under
supercritical conditions, resulting into about 30 ODEs for
every 1-peak PFR module or CSTR. The comparison of
both approaches mainly boils down to one important re-
search aspect, i.e., the discretization. The use of either ap-
proaches already implies some intrinsic differences. First,
the integration routine for the PFR is free of choice, in our
case of the fifth order matlab routine ode15s, while the
 cascaded CSTR approach boils down 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 for the PFR
model it remains the same, independent of the grid choice.

While observing the temperature profiles for different
discretization schemes, the discretization seems to have
no significant influence on the process variable. 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 8%. 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., a increasing deviation in viscosity ends
up to 25.3% 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 27.7% with the reference
profile and even a different profile trend is observed.

In general, as the number of grid points increases, all the
observed profiles converge towards the reference values.
However, the size of the resulting ODE system and accord-
ingly the computational time largely increases. Finally, the
deviations mainly occur in the reaction zones with the fast
kinetics of the radicals and large temperature gradients.

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