Computers and Chemical Engineering 106 (2017) 744–757

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Simulation and optimization of polymer molecular weight distribution with nonideal reactors

Chi Zhang [a], Zhijiang Shao [a], Xi Chen [a,*], Chaozhong Xu [b], Jiajun Wang [b], Lianfang Feng [b]

[a] State Key Laboratory of Industrial Control Technology, College of Control Science and Engineering, Zhejiang University, Hangzhou, 310027, PR China
[b] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, PR China

ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form 26 January 2017
Accepted 17 March 2017
Available online 20 March 2017

Keywords:
Molecular weight distribution
Computational fluid dynamics
Polymerization
Process optimization
Non-ideal reactors

ABSTRACT

Molecular weight distribution (MWD) is essential for describing the microstructural quality of a polymer. However, most of the studies on MWD are limited to ideal reactors. Computational fluid dynamics (CFD) methods is a useful tool to deal with the nonideal reactors. Few studies on CFD have been extended to the simulation and optimization of polymer MWD due to the computational difficulties. In this study, a new strategy is proposed to simulate the spatial MWD for a type of nonideal reactors using the method of moments with interfacing to the CFD software. Subsequently, given a target MWD curve, process optimization is proposed to achieve the optimal operating conditions. The tubular and autoclave reactors of the low-density polyethylene process are demonstrated for the simulations and optimizations. The influences of the decision variables on the feasibility and objective function are also discussed.

1. Introduction

Recently, studies on molecular weight distribution (MWD) have been the focus of increasing attention, as it reveals more detailed polymer microstructures than scalar quality indices, such as average molecular weight and melt index. The end-use properties of polymers are largely dependent on their MWDs, which affect processing through the polymer melting point and the flow properties of melted polymers. The MWD also determines many mechanical properties of the processed product, such as strength and impact resistance (Crowley and Choi, 1997). Thus, calculating and optimizing polymer MWD are important in industrial polymerization processes.

Considerable research on calculating the MWD, including the methods of molecular weight moment (Crowley and Choi, 1997), transformed domains (Mills, 1986), Monte Carlo (Lu et al., 1993; Weng et al., 2015a), probability generating function (Brandolin et al., 2001), and parallel computation (Chen et al., 2013; Weng et al., 2015b), has been conducted. Several studies focused on determining the optimal operating policies to achieve the desired MWD. Thompson et al. (2010) presented a development of optimal sequential experimental designs for improving parameter precision in a MWD model. Zhang et al. (2012) proposed an equation-oriented model for productivity optimization with a specified MWD as a constraint for slurry high-density polyethylene processes. Optimal flowsheet configurations based on a superstructure were further developed to extend the diversity of the polymer products of a given process (Zhang et al., 2015).

Most of the aforementioned studies assumed an ideal reactor with perfect mixing. In reality, however, polymer reactor behavior is complex because of the inherent nonlinearity arising from the polymerization kinetics and rapidly changing viscosity (Roudsari et al., 2013). A large scale industrial reactor can behave differently from a lab scale one (Behrens and Armaou, 2010), which usually results in poor mixing and contradicts to the ideal reactor assumption. Shastry et al. (1973) considered the free radical polymerization reactor as a tanks-in-series model with backflow instead of a continuous stirred-tank reactor and improved the simulation results to deal with the nonideal property of reactors. In recent years, researchers have used computational fluid dynamics (CFD) method to conduct more accurate simulations. However, only a few researchers considered polymerization reactions in the CFD study. Most studies only focused on investigating the micromixing and macromixing effects and the influence of impeller diameter in stirred-tank reactors (Han et al., 2012; Bao et al., 2012), and design of polymerization reactor components (Yan et al., 2012). Among the limited literatures involving the reactions, Baillagou and Soong investigated the polymerization in a tubular reactor both theoretically and experimentally (Baillagou and Soong, 1985). Read et al. (1997) used CFD to simulate a low-density polyethylene (LDPE)

* Corresponding author.
E-mail address: xi.chen@zju.edu.cn (X. Chen).

http://dx.doi.org/10.1016/j.compchemeng.2017.03.017
0098-1354/

Nomenclature

A	Initiator radical
E	Energy, J
E_a	Activation energy, J/kmol
g	Gravitational acceleration, m/s^2
I	Initiator
J	Diffusion flux, kg/(m^2 s)
k	Reaction rate, kmol/s
k_0	Rate constant, 1/s for first-order reactions and m^3/(kmol s) for second-order reactions
k_{eff}	Effective conductivity, m/s^2
M	Monomer
P	Polymer
p	Pressure, kPa
Q	Source term due to reaction, kg/(m^3 s)
R	Radical
R_g	Gas constant, 8314 J/(kmol K)
S	Source term
T	Temperature, K
t	Time, s
U	Velocity, m/s
V_a	Activation volume, J/(kmol kPa)
W	Molecular weight distribution
X	Manipulated variable
x	Inlet initiator mass fraction
x_i	Spatial coordinate, m
Y	Mass fraction

Greek letters

ϕ	User defined scalar
Γ	Diffusion coefficient
η	Viscosity, m/s^2
λ	Moment of radical
μ	Moment of polymer
ρ	Density, kg/m^3
τ_{ij}	Shear stress

Subscripts

d	Initiator decomposition
ini	Chain initiation
m	Chain length
n	Chain length
p	Propagation
s	Species type
tc	Termination by combination
td	Termination by disproportionation
trm	Chain transfer reaction

autoclave reactor under normal operating conditions. Tosun and Bakker (1997) used the commercial software Fluent to model the polymerization reaction in an autoclave reactor and determined the concentration distribution of the reactants. Tsai and Fox (1996) and Kolhapure et al. (2005) used the probability density function method to simulate turbulent flow in a tubular reactor. Garg et al. (2014) proposed a new transformation to improve the accuracy of CFD modeling and simulations of free radical polymerization reactions. However, the aforementioned studies did not simulate product quality. Zhou et al. (2001) assessed product quality by establishing a CFD model of LDPE and by obtaining the weight, average MWD, and monomer conversion distribution. Wells and Ray (2005) solved the polymerization reaction in autoclave reactors and analyzed the effect of different inlet temperatures on reactor stability. Serra et al. (2007) investigated polymerization in microreactors, and calculated the polydispersity index and the monomer conversion distribution. Roudsari et al. (2013, 2015) modeled the polymerization of methyl methacrylate in a laboratory-scale reactor with CFD and investigated the influence of impeller type and speed on conversion, polymer particle size, and average molecular weight.

Though MWD has advantages over the aforementioned indexes for describing product quality of a polymer, studies on the CFD method of polymerization scarcely include MWD mainly because of its computational complexity. As a vector, the dimension of the MWD could be as large as 10^5 to 10^6 for some typical polymers. The CFD simulation derives the spatial distributions of all attributes. These two factors combined together significantly increase the computational cost. To enable the simulation and optimization of MWD with CFD method, a new strategy is proposed in this study for a type of polymerization with the moment method. An interfacing technique is developed for the CFD simulation of nonideal reactors, with the spatial MWD being computed externally as the final output. Given a target MWD curve, optimization of the operating conditions that maximizes the monomer conversion with the desired MWD constraints is conducted for the nonideal reactors.

2. CFD model and simulation for MWD

2.1. Kinetic model of free radical polymerization for MWD

This study focuses on free radical polymerization, which involves initiator decomposition, chain initiation, propagation, chain transfer to monomer, termination by combination, and termination by disproportionation. The reaction mechanism is illustrated by Eq. (1):

Initiator decomposition:

$$I \xrightarrow{k_d} 2A, \tag{1}$$

Chain initiation:

$$A + M \xrightarrow{k_{ini}} R_1,$$

Propagation:

$$R_n + M \xrightarrow{k_p} R_{n+1},$$

Chain transfer to monomer:

$$R_n + M \xrightarrow{k_{trm}} P_n + R_1,$$

Disproportionation termination:

$$R_n + R_m \xrightarrow{k_{td}} P_n + P_m,$$

Combination termination:

$$R_n + R_m \xrightarrow{k_{tc}} P_{n+m},$$

where I is the initiator; M is the monomer; A and R_n are radicals, P_n is the polymer; m and n are the chain number of radicals or polymers, varying from 1 to theoretical infinity; and k is the rate of reaction. These equations cannot be solved directly because R_n and P_n represent countless reactions involved in the polymerization processes. The source terms or reaction rates for the transport equations of R_n and P_n can be derived as Eqs. (2) and (3):

$$S_{R_n} = -k_p[R_n][M] + k_p[R_{n-1}][M] - k_{trm}[R_n][M] - (k_{td} + k_{tc})[R_n]\sum_{m=1}^{\infty}[R_m], \tag{2}$$

$$S_{P_n} = k_{td}[R_n]\sum_{m=1}^{\infty}[R_m] + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[R_{n-m}][R_m] + k_{trm}[R_n][M], \tag{3}$$