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Numerical solution of mixed continuous–discrete population balance models for depolymerization of branched polymers

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ABSTRACT

A simulation technique to describe the depolymerization of branched polymers via bivariate population balance modeling was developed. The polymers were characterized by two internal coordinates: the number of monomer units and branching bonds. Three commonly used mechanisms for depolymerization (random chain, end chain, and random debranching scission) were applied and formulated such that only physically possible polymers were created. The mechanisms and the population balance equation were formulated in a mixed continuous–discrete manner. The population balance equation was solved using the Direct Quadrature Method of Moments (DQMOM). With this algorithm, the time evolution of the distribution with respect to the internal coordinate was computed. In addition, the algorithm was validated through comparison with Monte Carlo simulations. Notably, the accuracy of the mixed continuous–discrete formulation was significantly higher that of the continuous formulation. However, DQMOM was found to be unsuitable for describing the temporal evolution of the distribution for random scission.

1. Introduction

Branched polymers are depolymerized in several industrially relevant or promising processes, e.g., the pyrolysis of plastic waste (Siddiqui and Redhwi, 2009) and the production of glucose from starch (Eßlinger, 2009) and lignocellulose (Jae et al., 2014). Furthermore, the depolymerization of branched polymers is a side reaction during the polymerization (Iedema et al., 2000) and pyrolysis of linear polymers (Kruse et al., 2002). Therefore, to understand, optimize, and control these processes, there is an interest in developing simulation tools (Besselink et al., 2008; Iedema et al., 2000; Koljonen et al., 1995; Kruse et al., 2002). The goal of the present study was to develop a model and simulation technique for the depolymerization of highly branched polymers that requires only a moderate computational effort, yet provides a fine product resolution (low molecular weight polymers).

The simplest models assume that all the polymers have a constant number of monomer units and a constant degree of branching (e.g., Koljonen et al., 1995). These models therefore allow only highly simplified kinetics. To take the variations between the polymers into account, a population balance equation for the number density function (NDF) of the different polymers can be formulated and solved. Such a population balance equation has previously been solved for univariate cases (Griggs et al., 2012; Madras et al., 1996; Watanabe and Kawai, 2003). This approach is suitable for the linear polymers studied by these groups. However, for branched polymers the variation in the number of monomer units and the degree of branching must be considered. A problem in solving the discretely formulated population balance equation for this situation is that an unacceptably high number of ordinary differential equations (ODEs) must be considered for realistic polymers.

The branching of linear polymers during depolymerization has been described by Kruse et al. (2002), but the branched species were not tracked with high accuracy. Monte Carlo (MC) techniques have also been employed for the simulations of the depolymerization of branched polymers with high accuracy and a solid chemical basis (Besselink et al., 2008; Marchal et al., 2003; Tobita, 1996; Wojciechowski et al., 2001). However, because of the large computational effort required, MC techniques are not suitable for model-based optimization and control.

Even for polymerization rather than depolymerization, bivariate solutions of population balance equations are scarce. Generally, either highly simplified kinetics (Iedema et al., 2003) or nearly linear polymers (Saidel and Katz, 1968) are considered, both of which simplify the solution of the population balance equation significantly. Authors, who have used classical discretization techniques, reported that large numbers of ODEs were required, e.g.,

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Nomenclature

b	amount of bonds associated with branching (branching bonds)
d	arbitrary domain
k	amount of monomer units
$\check{k}_c$	amount of monomer units above which continuity is assumed
n	number density distribution
t	time
w	weight
$\mathbf{A}$	inversion matrix
B	rate of polymer production
C	reaction rate constant
D	death term of polymer
L	type of element
N	number of quadrature points
T	type of element

Greek letters

α	moment of the rate of polymer production
β	beta function
δ	Dirac delta
γ	fragment distribution function
σ	parameter of initial distribution
μ	moment of the number density distribution
ω	moment of the death rate
Γ	gamma function
Θ	parameter of initial distribution

Indices

l	counting variable
$\bullet$	arbitrary mechanism
$\sum$	all mechanisms

Superscripts and accents

i	order of moment with respect to number of monomer units
j	order of moment with respect to number of branching bonds
$\tilde{}$	normalized
$\bar{}$	continuous
$\hat{}$	semi-discrete
$\breve{}$	discrete

Abbreviations

ll	lower left
lr	lower right
ul	upper left
ur	upper right
DQMOM	Direct Quadrature Method of Moments
ECS	end chain scission
MC	Monte Carlo
NDF	number density function
ODE	ordinary differential equation
RCS	random chain scission on linear bonds
RDS	random debranching scission

a solution based on the method of classes required approximately 800 ODEs to describe a bivariate polymerization process (Krallis and Kiparissides, 2007). Given this system size, none of the current simulation techniques appears to be appealing for model-based optimization and control.

The most well studied mechanisms for the depolymerization include random chain scission (RCS) and end chain scission (ECS) (Griggs et al., 2012; McCoy and Madras, 1997). Solving RCS with high-resolution methods has been reported to be problematic (Iedema, 2012). Solver for the ECS based on the method of moments are also difficult to implement and require a very fine resolution using high-resolution methods (Stickel and Griggs, 2012). Random debranching scission (RDS) is not as well studied (refer to Wojciechowski et al., 2001 for an example). In the present study, all the three mechanisms were considered in both a coupled and decoupled manner. To the best of our knowledge, a formulation for the RCS mechanism for a non-crosslinked branched polymer has not yet been reported, and therefore the formulation and implementation is demonstrated for the first time for this particular mechanism.

Generally, the class of Quadrature Method of Moments appears to yield approximate solutions of population balance equations at a moderate computational cost. The method reduces the partial differential equation to a system of ODEs by taking the moments of the distribution and providing closure by using a quadrature rule (McGraw, 1997). Typically, monomials of the internal coordinates are used to generate the moments. For several systems, only a few moments have been required to provide meaningful results (Grosch et al., 2007; McGraw, 1997; Santos et al., 2013; Wright et al., 2001). To avoid the ill-conditioned quadrature, Marchisio and Fox (2005) developed the Direct Quadrature Method of Moments (DQMOM), which has been successfully applied to several problems (Marchisio and Fox, 2013). DQMOM has also been shown to be suitable for bivariate (Fox, 2006; Frances and Line, 2014; Zucca et al., 2007) and breakage (Frances and Line, 2014) problems. To efficiently use DQMOM, the population balance equation must be formulated continuously. McCoy and Madras (2001) have shown that this is an appropriate simplification for polymers with a large number of monomer units. However, because the desired product of depolymerization often has a very small number of monomer units, a mixed continuous–discrete formulation, as reported by Kostoglou (2000), is necessary to describe the time evolution of the end product. To the best of our knowledge, no depolymerization population balance model that reflects highly branched polymers has been formulated yet. In addition, the mixed continuous–discrete formulations for bivariate cases have not yet been studied. Furthermore, there appears to be no experience in using DQMOM for the mixed continuous–discrete formulation not even for univariate cases. However, there have been reports of the use of the method of moments for the mixed continuous–discrete formulation (Kruse et al., 2002).

The novelty of the given approach (application of DQMOM for the mixed continuous–discrete formulation, the mixed continuous–discrete formulation of bivariate problems, and the modeling of RCS for branched polymers) led to several technical problems, which are discussed herein.

2. Population balance model

To describe the depolymerization process using a population balance some simplifying assumptions must be made. All polymers with the same numbers of monomer units k and bonds associated with branching (called branching bonds for brevity) b are assumed to behave identically and deterministically. This assumption prohibits the inclusion of steric effects due to the structure of the polymer and implies that all the polymers are ideally dissolved. In addition, the reaction is assumed to occur in an ideally stirred batch reactor, and thus no spatial distribution is considered.

In the following equations, the explicit dependence on k, b, and time t is only denoted if it significantly enhances the discussion.