Chemical Engineering Journal 350 (2018) 37–48

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Population ensemble modeling of biomass dissolution

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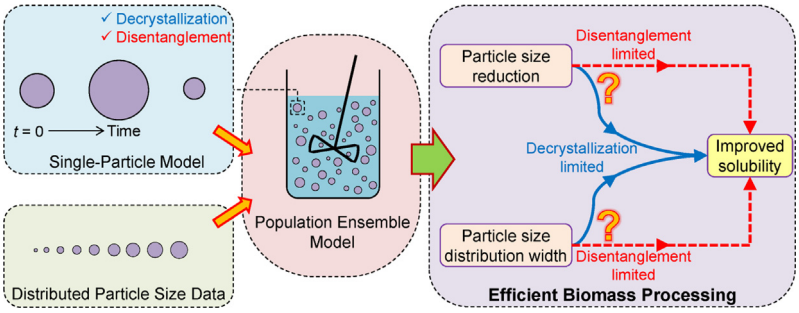
HIGHLIGHTS

- Dissolution of biomass particles is described using population ensemble modeling.
- Dissolution of an individual particle involves decrystallization and disentanglement.
- Impact of size distribution width and mean size is examined at different conditions.
- At disentanglement control, having a wider size distribution increases the solubility.
- At decrystallization control, having a narrower distribution is beneficial at the end.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polymer dissolution
Polydisperse system
Ensemble model
Cellulose
Pretreatment

ABSTRACT

A major barrier to the efficient utilization of biomass is the recalcitrance to dissolution of semicrystalline cellulose. The present study addresses the kinetics of swelling and dissolution of cellulose particles at conditions emulating large-scale biomass processing where the particles exhibit a broad distribution of size. To this end, we have developed a model in which the behavior of a population of particles is obtained from an ensemble of individual particle dissolution models. The dissolution of an individual semicrystalline polymer particle involves decrystallization and disentanglement as two important and potentially rate-determining steps in the process. Using this population ensemble model, novel results on the evolution of cellulose particle size distribution and polydispersity over the dissolution time have been obtained, and the impact on dissolution of the particle size distribution width and mean particle size has been examined at different conditions. The high number of smaller particles determines initially the dissolution behavior of a polydisperse system, however, at long dissolution times, relatively small numbers of larger particles dictate the overall dissolution behavior. Reducing the mean particle size increases the dissolved fraction more at disentanglement control conditions than at decrystallization control conditions. Having a wider particle size distribution would always increase the cellulosic biomass solubility at disentanglement control conditions. At decrystallization control conditions, a wider size distribution is beneficial initially, however, at long times a system with narrower particle distribution dissolves more. Findings from this study would benefit the rational design and optimization of pretreatment processes to reduce the particle size for enhanced biomass utilization. The developed model can be applied to the dissolution of polydisperse particles for various polymers of interest to drug delivery and plastics recycling.

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https://doi.org/10.1016/j.cej.2018.05.167
Received 17 April 2018; Received in revised form 24 May 2018; Accepted 28 May 2018
Available online 28 May 2018
1385-8947/

1. Introduction

Lignocellulosic biomass is a promising renewable, carbon-neutral, and low-cost feedstock which is being explored as raw material for the sustainable production of fuels, platform chemicals, and functional polymers [1,2]. However, biomass is recalcitrant to processing due to the high crystallinity of cellulose, low accessible surface area (low porosity), protection of cellulose by lignin and hemicellulose, and fiber strength [3]. Solvent processing of biomass can be an efficient way to add value to this renewable feedstock through breaking down the lignin structure and disrupting the network of crystalline cellulose, so that the polymer chains become readily accessible to solvents and enzymes [4,5].

Prior to solvent processing, biomass is pretreated in various ways, including mechanical size reduction such as chipping, shredding, grinding, and milling [3]. These steps are required in order to increase the specific surface area and to enhance the solubility [6] and the reactivity of cellulose in biorefinery processes such as enzymatic hydrolysis [7] and anaerobic digestion [8]. For example, the production yield of glucose in the enzymatic hydrolysis of bagasse increased from 55.2% to 75.2% following an increase in the ball-milling time from 24 h (median particle size = 39.7 μm) to 72 h (median particle size = 18.8 μm) [9].

In the case of dissolution, of interest to this study, it was found that the dissolution rate of cellulosic biomass is highly dependent on the particle size [10]. For example, the solubilization efficiency in ionic liquids was found to follow the order: ball-milled wood powder > fine sawdust (particle size 0.1–2 mm with complete dissolution in a few hours) ≥ thermomechanical pulp fibers ≫ wood chips (size in excess of $5 \times 5 \times 1\ mm^3$ where complete dissolution took several weeks) [10]. Further, it was demonstrated that, following extensive ball-milling, wood became soluble in the solvent systems dimethyl sulfoxide + tetrabutyl ammonium fluoride and in dimethyl sulfoxide + imidazole [11].

Mechanical size reduction methods result in polydisperse systems comprising particles having different sizes. The particle size distribution and its characteristics, such as distribution width and mean particle size, are expected to be important in the overall dissolution behavior. However, to the best of our knowledge, there is no study available that assesses the impact of particle size distribution on the dissolution behavior of polymeric particles, including biomass.

This study aims to (i) assess the evolution of particle size distribution over the time of dissolution in order to provide insights into the dissolution behavior of a polydisperse system of semicrystalline polymer particles, and (ii) investigate the effect of mean particle size and size distribution width on the dissolution performance of the system in order to present guidelines for the physical pretreatment of cellulosic biomass.

To this end, a comprehensive population ensemble model of polymer dissolution is developed here that can describe the kinetics of swelling and dissolution of semicrystalline polymer particles in conditions that emulate large-scale solvent processing where the particles have a broad size distribution.

The polydispersity within populations of a system can be handled by the introduction of multiple distinct sub-populations with individual properties using two modeling approaches: population balance equation models and population ensemble models.

The population balance equation method [12,13] has been applied to various chemical engineering processes such as crystallization [14], drying [15], granulation [16], leaching [17], and dissolution of polydisperse particles [18–24]. The population balance equation defines how a population of polydisperse system of particles evolves in size over time. It is a set of integro-partial differential equations which provide the mean-field behavior of a population of particles from an analysis of the behavior of a single particle at local conditions. In the case of dissolution of polydisperse particles, at the core of the population balance equation is the dissolution of single particles in the size distribution [24]. An analytical solution does not exist for most conditions, and the population balance equation must be solved numerically.

Rather than formulating the governing population balance equation, the population ensemble model involves an ensemble of single-particle models which differ in key properties, such as the particle size. The population ensemble approach is based on the implicit assumption that the continuum framework of the population balance equation model can be approximated by a sufficiently large number of individual single-particle models [25]. In this sense, the population ensemble approach is similar to the use of spatial discretization methods to solve differential equations, where a converged solution is obtained by increasing the number of discretization points until the solution remains effectively unchanged [26]. Based on this analogy, the individual single-particle models play the role of the discretization points. For example, the ensemble modeling approach has been used to describe microbial cell populations [26–29].

While the population balance equation modeling method is not limited with regard to the number of single-particle models, the variables that change over the particles must be restricted to a small number in order to ensure the computational feasibility of the discretized model [25]. In contrast, the population ensemble method allows for direct incorporation of arbitrarily complex single-particle models with many variables. Another key advantage of the population ensemble approach is that the number distribution function of any property that is captured by the single-particle model can be calculated from ensemble simulation data [26].

The population balance modeling approach has been used to study the dissolution of polydisperse solid particles (mostly minerals) [18–24], however, it has not yet been applied for modeling the dissolution of polymers which are governed by different mechanism [30] than non-polymeric materials. Further, there is no report to date on the application of the ensemble modeling approach for the dissolution of a polydisperse system of particles (polymeric or non-polymeric). This is the first report of a comprehensive population ensemble model of polydisperse semicrystalline polymer particle dissolution that allows the investigation of the dissolution behavior of a system with a wide particle size distribution. We employed the developed population ensemble model to evaluate the impact of particle size distribution width and size reduction on the dissolution performance of semicrystalline polymer at different conditions. The findings reported here would be useful in suggesting efficient physical pretreatment conditions (e.g., milling) for the efficient utilization of biomass.

2. Methods

We present here a comprehensive model that describes the kinetics of swelling and dissolution of semicrystalline polymer particles in conditions emulating large-scale processing where the particles have a size distribution. In the first part of this section, a phenomenological model for the dissolution of a single semicrystalline polymeric particle is highlighted. In the second part, a population ensemble model of polydisperse particle dissolution is developed. The third part presents the initial particle size distributions and the model parameters considered here.

2.1. Dissolution model of a single particle

The swelling and dissolution of an individual semicrystalline polymer particle is described according to a newly-developed model [30] that captures the mechanism of dissolution of a semicrystalline polymer (e.g., cellulose) particle (Fig. 1). Following the diffusion of solvent inside the solid polymer, crystalline polymer domains are gradually disrupted to form amorphous domains, and the solid polymer gradually transforms into a swollen gel-like medium [30]. The polymer