Multiphysics modeling and simulation of high-solids dilute-acid pretreatment of corn stover in a steam-explosion reactor

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HIGHLIGHTS

- A mathematical model for biomass pretreatment is developed and validated.
- The model is a set of unsteady multiphase reaction-diffusion equations.
- The strongly coupled equations are solved using spectral finite-element method.
- Chemical reactions are driven by spatio-temporal acid molarity variation.
- Steam diffusion, condensation, and evaporation strongly affect local acid molarity.

ARTICLE INFO

ABSTRACT

Pretreatment of lignocellulosic biomass, by which the accessibility of cellulose to enzymes is enhanced, is an important step in the biochemical conversion of biomass feedstocks to biofuels. A mathematical model that considers both spatial and temporal phenomena in a biomass particle has the potential to accurately predict carbohydrate conversion and macroscopic structural changes during pretreatment. The development, implementation, and validation of a multiphysics model for high-solids (44%) dilute-acid pretreatment of a pre-impregnated corn-stover particle is presented. The model consists of tightly coupled time-dependent reaction-diffusion equations with finite-rate chemistry. The model partial-differential equations were discretized and solved numerically by the Legendre spectral finite element method. The simulation results were compared to experimental data that were obtained by performing pretreatment on pre-impregnated corn stover in a steam-explosion reactor. The majority of the modeling parameters were set by established science, obtained from the literature, or were experimentally measured initial conditions. The remaining unknown kinetic rate parameters were obtained by fitting simulation results to a limited set of experimental data. Reasonable quantitative agreement was subsequently obtained between simulation results and a larger set of experimental data. The model simulations illustrate the strong dependence of the biomass conversion rate on the spatially dependent and transient acid concentration within the particle. It is observed that time scales of thermal-diffusion are much shorter than those for chemical reactions, which results in an isothermal condition for long pretreatment times. Diffusion of steam within the biomass particle dictates acid dilution and the zone where reactions occur.

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1. Introduction

The biochemical conversion of lignocellulosic biomass to alcohol or hydrocarbon fuels involves three distinct operations, namely, pretreatment, enzymatic hydrolysis, and fermentation. Pretreatment of biomass is performed mainly to reduce the resistance of biomass cell walls to enzymatic hydrolysis (so-called biomass recalcitrance) [1,2]. Exposed cellulose chains in lignocellulosic materials after pretreatment are more easily hydrolyzed to sugars via enzymatic hydrolysis and are subsequently converted to ethanol by fermentation. Pretreatment can be performed using several mechanical and physicochemical methods that include vibratory ball milling [3], steam explosion [4], ammonia fiber expansion [5], dilute-acid hydrolysis [6–8], alkali hydrolysis [9,10] and using ionic liquids [11].

Among these techniques, steam explosion disrupts the outer lignin structure, while dilute-acid pretreatment catalyzes the conversion of hemicellulose components such as xylan to simpler sugars [12]. A combination of these two methods, commonly called steam-assisted dilute-acid pretreatment, is a leading pretreatment process currently being developed in several laboratories. In its basic form, dilute-acid pretreatment involves the impregnation of milled biomass particles with sulfuric acid and subsequent rapid exposure of the biomass to saturated steam [13].

Acid-impregnated biomass particles undergoing steam explosion is a complex process that includes heat and mass transfer, steam-water phase transitions, and chemical reactions. Thermal-diffusion time scales are typically much shorter than chemical reactions and species mass transfer in the pretreatment processes. Acid-catalyzed hydrolysis tends to be strongly dependent on water content in the biomass particles due to dilution of local acid concentrations. Steam diffusion, condensation, and liquid evaporation contribute to the spatio-temporal variation of acid concentration in the particle. There are several mathematical models in the literature that studied the different aspects of pretreatment, including chemical kinetics, phase transitions, and diffusive transport. These models have been used for biomass pretreatment, pulping processes in the paper industry, and also in food processing. We describe these models in the order of complexity with which the different aspects of pretreatment are addressed.

Modeling of pretreatment chemical kinetics have been performed by solving coupled ordinary-differential equations (ODEs) for concentrations of various participating species that include xylan, xylooligomers, xylose, and furfural. Esteghlalian et al. [6] studied detailed kinetics of dilute-acid pretreatment using first-order Arrhenius reaction rates. The rate constants were fit to experimental data for a simple analytically solved kinetics model, and optimum pretreatment conditions were determined for maximizing sugar yield. Mittal et al. [14] simulated hydrothermal pretreatment using coupled ODEs, where xylan undergoes autohydrolysis to yield xylooligomers, xylose, and furfural. The spatial variations of species concentrations via diffusive mass transport were neglected in this model and an average mass-transfer coefficient was used as a source term to account for non-reactive mass transfer. Gustafson et al. [15] developed a model for the kraft pulping process, which involves both diffusive mass transfer and chemical reactions. The pulping reactions consume alkali and release carbohydrates, lignin, and acetyl groups that diffuse out of the wood chips. The reduction in alkali concentration augments diffusive mass transfer from the bulk into the particle. The model was used to predict the time evolution of the chip lignin and carbohydrate content during the pulping reactions and the effective alkali concentration as a function of wood lignin content. Sensitivity of chip thickness to various metrics pertinent to the kraft pulping process, such as total yield, screened kappa number, and effective alkali consumption, was also explored using this model.

Abasaeed et al. [16] simulated acid hydrolysis of hardwood cellulose using a one-dimensional model comprised of both transient and spatially dependent heat transfer and chemical reactions. Typically, the wood particle is assumed to be isothermal when time scales of thermal conduction are much shorter than those of chemical reactions. The time scales become comparable for sufficiently large particles, and transient temperature effects become important. The model was used to investigate the effect of the chip size on sugar yield and reaction-completion times at different temperatures and acid concentrations.

Xu et al. [17] developed a steady-state model for heat and moisture transfer through textiles. This model included heat and mass transfer, phase transitions, and kinetics pertaining to condensation and evaporation. Coupled ODEs for temperature, water-vapor pressure, water-vapor mass flux through textile pores, and steam condensation on the surface of the textile were solved in this model. The mass transfer of water was modeled using approximate kinetic coefficients and not through diffusive transport.

Sprague and Colvin [18] developed a model that included heat and mass transfer, phase transitions, and chemical reactions for food-processing applications. Their model accounted for heat and liquid-water transport, evaporation of liquid water into steam, steam transport, and heterocyclic amine formation in a frying beef patty. It was used to simulate the spatio-temporal variation of temperature and to estimate the average heterocyclic amine concentration in the patty as a function of the initial frying-pan temperature. A beef patty is a porous and fibrous medium like biomass and the modeling concepts employed are relevant to the multi-physics model developed in this paper.

The focus of this work was to develop a multiphysics model for an individual biomass (corn stover) particle that accounts for the above-mentioned transient reaction-diffusion processes for steam, various chemical species, and temperature. We combined several of the modeling concepts discussed above and develop additional components as needed based on our current understanding of the high-solids pretreatment process. Simulation results were validated with experimental results obtained from a steam-explosion reactor in which pre-impregnated biomass particles at high solids are fully fluidized and well mixed.

2. Mathematical model

2.1. Assumptions

The model assumes high-solids pretreatment of a pre-impregnated cylindrical biomass particle, with length 2ℓ and diameter d as shown in Fig. 1, that consists of solid, liquid, and gas phases at any point during pretreatment. The representative mass and volume fractions, which can vary along the length of the particle are also shown. The gas phase, which is mainly steam, has negligible mass fraction but can occupy a major portion of the volume. The volume fractions of the three different phases in a biomass particle are related as

$$\begin{aligned} \epsilon_P + \epsilon_S &= 1, \\ \epsilon_P &= \epsilon_L + \epsilon_G, \end{aligned} \qquad (1)$$

where $\epsilon_P, \epsilon_S, \epsilon_L$ and ϵ_G represent porosity, solid volume fraction, liquid volume fraction, and gas volume fraction in the particle, respectively. The heat and mass transfer are assumed to occur along the length of the particle. Plant biomass is known to have a porous structure that is highly anisotropic [19], and hence we assume a
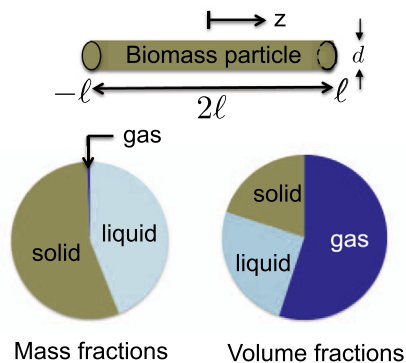

Fig. 1. Cylindrical biomass particle with pie charts depicting typical mass and volume fractions of solid, liquid, and gas phases.