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Research Article

Two-Dimensional Simulation of Diffusion and Advection Effects in Enzymatic Hydrolysis of Cellulose

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Abstract. Enzymatic hydrolysis process to transform lignocellulosic cellulose into sugar in a bioreactor tank involves different controlling factors such as advection, diffusion and fragmentation of cellulose chains. Although it has been observed experimentally that enzymatic hydrolysis is strongly influenced by the environmental effects in a tank, these effects have not been adequately quantified. In this work, a current kinetic model for enzymatic hydrolysis of cellulose was extended by coupling the *population balance equations* (PBE) with advection and diffusion terms to model the spatial evolution of the system. The mathematical model was solved using the DAE-QMOM technique. The aim of this study was to simulate the effect of diffusion and advection on the fragmentation of cellulose chains during enzymatic hydrolysis in two-dimensional domain. This study demonstrated the applicability and usefulness of a commercial software (*COMSOL Multiphysics*) for finding the solution of PBE-advection-diffusion in cellulosic hydrolysis problem. The key implication of this work is that advection is a significant phenomenon which could increase the number of cellulose particles. Also, diffusion alone cannot increase hydrolysis rate, but the combination of advection and diffusion increases hydrolysis rate.

Keywords. Enzymatic hydrolysis; Advection; Diffusion; Population balance equations

MSC. 76R50

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1. Introduction

Bioethanol production from lignocellulosic biomass consists of three fundamental processes: pretreatment, enzymatic hydrolysis, and fermentation. In the enzymatic hydrolysis phase, enzymes break cellulose chains into sugar in the form of cellobiose and glucose. The enzymatic hydrolysis process in transforming lignocellulosic cellulose into sugar in a bioreactor tank involves different kinds of controlling factors such as advection, diffusion and fragmentation of cellulose chains. During the hydrolysis process, certain amount of enzymes will be added to the biomass suspension in the tank and the solution will be stirred by an impeller in the reactor. In other words, cellulose particles are advected (by the velocity terms) and diffused. Both advection and diffusion move the particles from one place to another, but each accomplishes this differently. Advection goes by following the streamline, while diffusion will diffuse regardless of the stream direction.

The basic formulation for studying the evolution of cellulose chains during hydrolysis was proposed by Griggs et al. [1] using the *population balance equations* (PBE). PBE is considered to be a statement which describes the changes in cellulose chains length distribution. PBE employs continuous distribution which tracks the evolution of the spectrum of chain lengths [7]. In PBE, one independent variable represents time, and the other represents property coordinate, which is the particle size. They typically describe the temporal evolution of the population distribution function.

In the present study, we coupled PBE with advection and diffusion terms to model the spatial evolution of a system. In other words, we took into account the fact that particles move through space due to diffusion and advection. To the best of our knowledge, there is no kinetic model for cellulosic hydrolysis process which takes into consideration both advection and diffusion simultaneously. However, in the context of PBE, much research has been conducted to study the PBE-advection-diffusion model for other problems, for instance, coagulation of nanoparticles [2], fluidization [3], and antisolvent crystallization [4]. Based on their findings, moment-based techniques such as MOM, QMOM, DQMOM, and TEMOM came into view as promising choices of PBE-advection-diffusion coupling.

The aim of this paper was to simulate the effect of two-dimensional diffusion and advection on the fragmentation of cellulose chains during enzymatic hydrolysis. Hence, a better understanding on the dynamic process in cellulosic hydrolysis process could be obtained. Moreover, this paper will demonstrate the applicability and usefulness of DAE-QMOM to solve PBE-advection-diffusion in cellulosic hydrolysis problem.

2. Mathematical Modeling

The current kinetic model of enzymatic hydrolysis of cellulose by Griggss et al. [1] was extended to study the effect of advection and diffusion to cellulose particles. The DAE-QMOM technique, which originally solves the pure PBE problem developed by Gimbun et al. [5] was tested to solve the coupled PBE-advection-diffusion model for cellulosic hydrolysis. In this work, PBE, which describes how the particles size distribution changes as time progresses due to polymer breakage during cellulosic hydrolysis, was coupled with advection-diffusion. In this case, there are two physics under study; one is PBE, and the other one is the advection-diusion equation. In mathematical modeling, we believe that, the more physics is correlated to the process we coupled, the more realistic the model is.

In describing the state of the particles, there are two types of coordinates involve: internal and external coordinates. Internal coordinate represents the length of cellulose particles, whereas external coordinate represents the spatial location of the particle. Together, internal and external coordinates create the state space of the particles. In the PBE-advection-diffusion model for enzymatic hydrolysis of cellulose, we allowed for spatial variation in all components of the well mixed PBE model i.e.

$$p(\chi,t) \to p(\chi,\mathrm{x},t) \tag{2.1}$$

where $\mathbf{x}$ denotes spatial coordinates and χ is the cellulose particle length. The transport equations for the cellulose particles are governed by:

$$\left.\begin{array}{l} \frac{\partial p}{\partial t} = f_p - v\cdot\nabla p + \nabla\cdot\left(D_p\nabla p\right) \\ \frac{\partial p_B}{\partial t} = f_{p_B} - v\cdot\nabla p_B + \nabla\cdot\left(D_{p_B}\nabla p_B\right) \\ \frac{\partial R}{\partial t} = f_R - v\cdot\nabla R \end{array}\right\} \tag{2.2}$$

where p is the population distribution of enzyme-accessible cellulose chains of length χ, p_B is the population distribution of CBH-threaded cellulose chains of length χ, and R is the radius of cellulose particles. Here $\mathrm{v} = \mathrm{v}(\mathrm{x},t)$ is the particle velocity, and D_p and Dp_B are the diffusion coefficients for p and p_B of length χ respectively. The second term on the right-hand-side of eq. (2.2) describes the loss or gain of particles due to advection, while the third term denotes the influence of diffusion on the particles. The source terms f_p; f_{pB}, and f_R represent the reaction terms due to the breakage process of cellulose chains and are given by Griggs et al. [1].

In order to describe the particle field in time and space, moment operators were utilized. The k-th order moment $p^{(k)}$ and $p_B^{(k)}$ of the particle distribution are defined as:

$$p^{(k)}(\mathrm{x},t) = \int_0^\infty p(\chi,\mathrm{x},t)\chi^k d\chi \tag{2.3}$$

and

$$p_B^{(k)}(\mathrm{x},t) = \int_0^\infty p_B(\chi,\mathrm{x},t)\chi^k d\chi \tag{2.4}$$

By multiplying both sides of eq. (2.2) with χ^k and integrating over all particle lengths, a system of transport equations for $p^{(k)}$, $p_B^{(k)}$ and R is obtained. Thus, the transport equations for the k-th order moment are expressed as:

$$\left.\begin{array}{l} \frac{\partial p^{(k)}}{\partial t} = f_p^{(k)} - v\cdot\nabla p^{(k)} + \nabla\cdot\left(D_p\nabla p^{(k)}\right) \\ \frac{\partial p_B^{(k)}}{\partial t} = f_{p_B}^{(k)} - v\cdot\nabla p_B^{(k)} + \nabla\cdot\left(D_{p_B}\nabla p_B^{(k)}\right) \\ \frac{\partial R}{\partial t} = f_R - v\cdot\nabla R \end{array}\right\} \tag{2.5}$$

The QMOM technique [6] was used to close the moment equations such that:

$$p^{(k)}(\mathrm{x},t)=\sum_{i=1}^{n_q} w_i(\mathrm{x},t)\xi_i^k(\mathrm{x},t) \tag{2.6}$$

and

$$p_B^{(k)}(\mathrm{x},t)=\sum_{i=1}^{n_q} e_i(\mathrm{x},t)L_i^k(\mathrm{x},t) \tag{2.7}$$

where n_q is the order of the quadrature formulation, ξ_i and L_i are particle length and w_i and c_i are quadrature weights for p and p_B, respectively.

By combining the partial differential equations from the moment transport equations and the algebraic equations from the QMOM definitions, we obtained a *differential algebraic equations* (DAE) system, which can be written as:

$$\begin{aligned}
\frac{\partial p^{(k)}}{\partial t} &= f_p^{(k)} - v\cdot\nabla p^{(k)} + \nabla\cdot\left(D_p\nabla p^{(k)}\right)\\
\frac{\partial p_B^{(k)}}{\partial t} &= f_{p_B}^{(k)} - v\cdot\nabla p_B^{(k)} + \nabla\cdot\left(D_{p_B}\nabla p_B^{(k)}\right)\\
\frac{\partial R}{\partial t} &= f_R - v\cdot\nabla R\\
0 &= \sum_{i=1}^{n_q} w_i\xi_i^k - p^{(k)}
\end{aligned}$$

This combination of QMOM and DAE in solving population balance equation has been proposed by Gimbun et al. [5].

Next, we introduced the dimensionless variables as follows:

$$\tau=\frac{t}{l/u},\ \hat{x}=\frac{x}{l},\ \hat{p}(\hat{x},\tau)=\frac{p(x,t)}{p^{(0)}(0)},\ \hat{p}_B(\hat{x},\tau)=\frac{p_B(x,t)}{p^{(0)}(0)}$$

$$\hat{p}^{(1)}(\hat{x},\tau)=\frac{p^{(1)}(x,t)}{p^{(0)}(0)},\ \hat{p}_B^{(1)}(\hat{x},\tau)=\frac{p_B^{(1)}(x,t)}{p^{(0)}(0)},\hat{p}_B^{(0)}(\hat{x},\tau)=\frac{p_B^{(0)}(x,t)}{p^{(0)}(0)},\hat{K}_d=\frac{K_d}{p^{(0)}(0)},\hat{R}=\frac{R}{R_0},\hat{v}=\frac{v}{u}$$

where t is time, l is the characteristic length (length of the domain), u is the characteristic velocity, $p^{(0)}(0)$ is the initial total number of enzyme accessible cellulose particles, and R_0 is the thickness of single cellulose chains. Several parameters were grouped together to form dimensionless parameters. Therefore, the transport equations became dimensionless.

3. 2D PBE-Advection-Diffusion Model

We solved the two-dimensional PBE-advection-diffusion model of enzymatic hydrolysis of cellulose utilizing the DAE-QMOM in COMSOL 4.3b. Consider a tank where the cellulose particles are suspended in water. The geometry of the computation domain is chosen as a rectangle with length 1 and height 0.2. Initially, the particles are concentrated in $x=(0:25;0:6)$ and $(0:75;1)$ and the other domain is free of particles. This represents the inhomogeneity throughout the domain. We enforce Robin boundary conditions on the boundaries of the rectangular domain by applying the zero flux condition. This represents boundaries where no mass flows in or out across the boundary.

3.1 Case I: 2D Reaction-Diffusion Only

In the case of a reaction-diffusion equation for cellulosic hydrolysis in two-dimensional, we elucidate the role of diffusion in the system. The distribution of the total number of CBH1-threaded cellulose chains, $p_B^{(0)}$ and the total number of enzyme-accessible cellulose chains, $p^{(0)}$ on the rectangular domain at time $t = 0; 20; 60; 200; 400; 600$ are illustrated in Figure 1 (a) and (b), respectively. We consider an isotropic diffusion coefficient $D = 1$ for both distributions.

At $t = 0$, we placed a high population of cellulose particles in the region of $x = (0:25;0:6)$ and $(0:75;1)$. We, therefore, see red area in that region with blue areas in the other space where there are initially very little cellulose particles. Particles move through space from high to low concentration areas due to diffusion. The variation of the color scheme in the domain is due to the reaction from the population balance equation and diffusion effect. From the last time it is clear that the domain for both distribution is filled homogeneously and a stable distribution is formed along the spatial axis x.

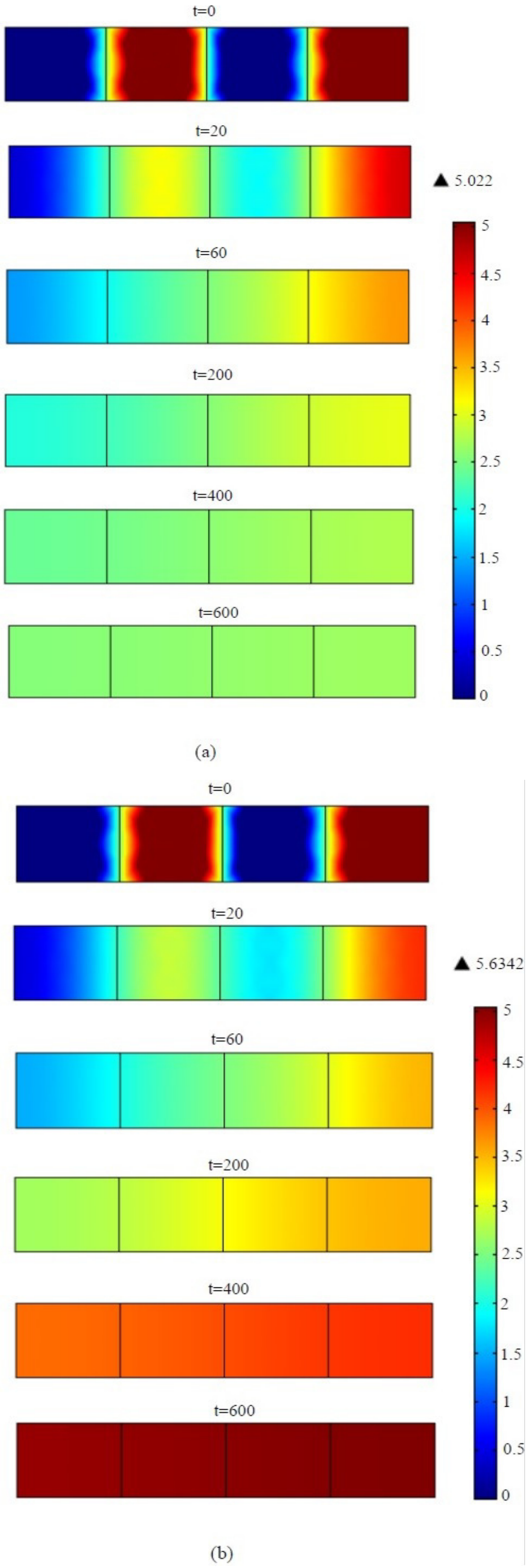
In the last simulation time, $p^{(0)}$ has a higher value than $p_B^{(0)}$. No increase in $p_B^{(0)}$ was detected. This result may be explained by the fact that the CBH1-threaded chains, p_B are transformed into enzyme-accessible cellulose chains, p by the action of EG1 enzyme during the hydrolysis. And also, the population of $p^{(0)}$ increases because of the reaction effect which breaks the long cellulose chains into shorter chains due the action of CBH1 and EG1 enzymes during the hydrolysis.

3.2 Case II: 2D Reaction-Diffusion-Advection

For the case of simultaneous effects of reaction, diffusion, and advection to the enzymatic hydrolysis of cellulose process, the distribution of $p_B^{(0)}$ and $p^{(0)}$ on the domain at time $t = 0$; 20; 60; 200; 400; 600 can be seen in Figure 2. Likewise in the previous case, we placed a high population of cellulose particles in the region of $x = (0:25;0:6)$ and $(0:75;1)$ at initial time. We set the isotropic diffusion coefficient $D = 1$ and velocity field $v = (0.1;0)$.

The cellulose particles are advected with the flow and diused as time goes on. The variation of color scheme in the domain as shown in the figure is due to the simultaneous advection and diffusion effects to the PBE system. The highest concentration decreases over time, because of diffusion into the unoccupied interior of the domain. We soon have the population all over the domain.

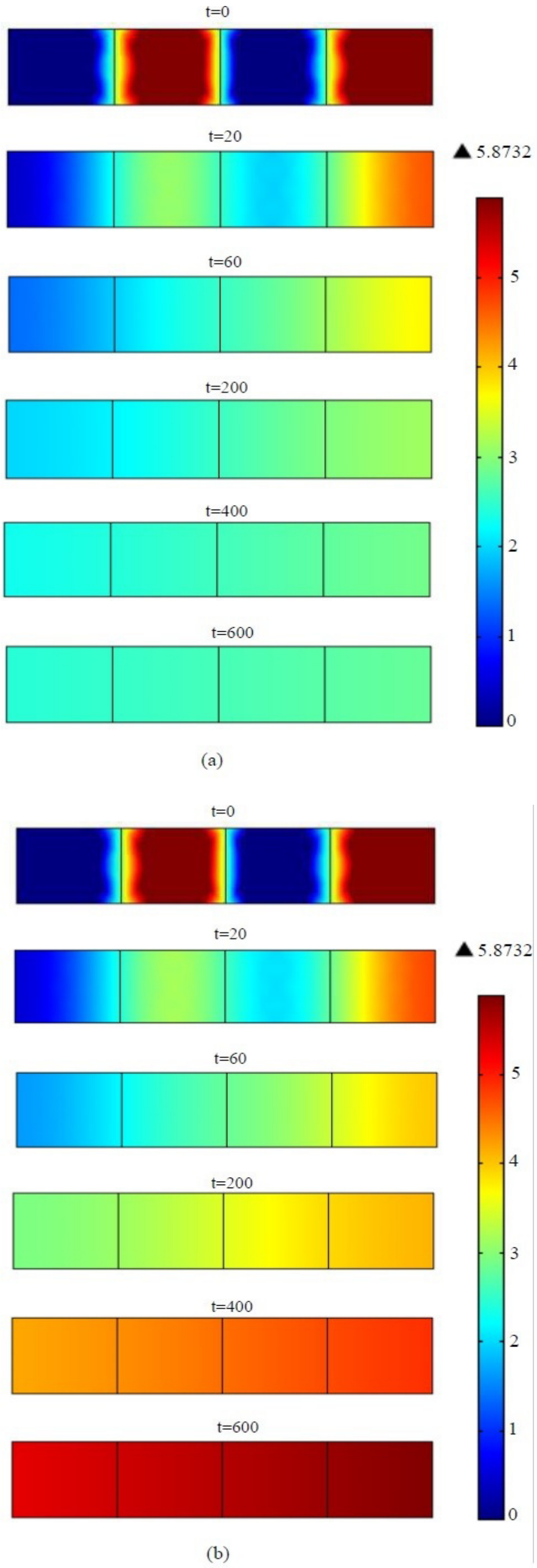
After sufficient long time, the highest concentration is located at the right-end of the boundary due to the velocity moves the particles to the right which is known as advection effect. At the same time, the total number of enzyme-accessible cellulose chains, $p^{(0)}$ is increasing with respect to time due to the breakage process in the cellulosic hydrolysis.



(a)

(b)

Figure 1. The effect of diffusion on (a) $p_B^{(0)}$, and (b) $p^{(0)}$ (blue colour indicates a minimum and red a maximum)



(a)

(b)

Figure 2. The effect of advection and diffusion on (a) $p_B^{(0)}$, and (b) $p^{(0)}$ (blue colour indicates a minimum and red a maximum)

4. Conclusion

In the present study, we extended the Griggs kinetic model for cellulosic hydrolysis by adding diffusion and advection terms into the system. This model was developed to study the effect of advection, as well as the diffusion process as a drift phenomenon on cellulose particles in a two-dimensional domain. The key implication of this work is that advection is a significant phenomenon which could increase the number of cellulose particles. Diffusion alone could not increase the hydrolysis rate, but the combination of advection and diffusion increased the hydrolysis rate. By incorporating the advection and diffusion effects on cellulose chain length evolution, an improved understanding of cellulose depolymerization can be achieved. In this work, we succeeded in carrying out an important coupling of PBE-advection-diffusion model for enzymatic hydrolysis of cellulose for the firrst time.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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