

One-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 study, 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 one-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

Mathematics Subject Classification 2000: 22E46, 53C35, 57S20

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.*, 2012) 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. 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 (Wang *et al.*, 2012), fluidization (Mazzei *et al.*, 2009) and antisolvent crystallization (Woo *et al.*, 2006). 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 one-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.

Mathematical Modeling

The current kinetic model of enzymatic hydrolysis of cellulose by (Griggs *et al.*, 2012) 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.*, 2009) was tested to solve the coupled PBE-advection-diffusion model for cellulosic hydrolysis. In this study, 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-diffusion 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.:

$$p(X, t) \rightarrow p(X, x, t) \quad (2.1)$$

where, x denotes spatial coordinates and X is the cellulose particle length. The transport equations for the cellulose particles are governed by:

$$\frac{\partial p(X, x, t)}{\partial t} = f_p(p, p_B, R, X, t) - v \cdot \nabla p + \nabla \cdot (D_p \nabla p) \quad (2.2)$$

$$\frac{\partial p_B(X, x, t)}{\partial t} = f_{p_B}(p, p_B, R, X, t) - v \cdot \nabla p_B + \nabla \cdot (D_{p_B} \nabla p_B) \quad (2.3)$$

$$\frac{\partial R(x, t)}{\partial t} = f_R(p, p_B, R, X, t) - v \cdot \nabla R \quad (2.4)$$

where, p is the population distribution of enzyme-accessible cellulose chains of length X , p_B is the population distribution of CBH-threaded cellulose chains of length X and R is the radius of cellulose particles. Here $v = v(x, t)$ is the particle velocity and D_p and D_{p_B} are the diffusion coefficients for p and p_B of length X , respectively. The second term on the right-hand-side of Equation 2.2-2.4 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_{p_B} and f_R represent the reaction terms due to the breakage process of cellulose chains and are given by (Griggs *et al.*, 2012).

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 distributions are defined as:

$$p^{(k)}(x, t) = \int_0^\infty p(X, x, t) X^k d_X \quad (2.5)$$

And:

$$p_B^{(k)}(x, t) = \int_0^\infty p_B(X, x, t) X^k d_X \quad (2.6)$$

By multiplying both sides of Equation 2.2-2.3 with X^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 of one-dimensional domain are expressed as:

$$\frac{\partial p^{(k)}}{\partial t} = f_p^{(k)} - v \frac{\partial p^{(k)}}{\partial x} + \frac{\partial}{\partial x} \left(\kappa_p \frac{\partial p^{(k)}}{\partial x} \right) \quad (2.7)$$

$$\frac{\partial p_B^{(k)}}{\partial t} = f_{p_B}^{(k)} - v \frac{\partial p_B^{(k)}}{\partial x} + \frac{\partial}{\partial x} \left(\kappa_{p_B} \frac{\partial p_B^{(k)}}{\partial x} \right) \quad (2.8)$$

$$\frac{\partial R}{\partial t} = f_R - v \frac{\partial R}{\partial x} \quad (2.9)$$

where, the length-independent diffusivity of the particle is κ_p and κ_{p_B} for p and p_B , respectively. According to the definition of moments, $p^{(0)}$ is the total number of enzyme accessible cellulose particles and $p_B^{(0)}$ is the total number of CBH-threaded cellulose particles.

Furthermore, $p^{(1)}$ is the total number of monomeric glucans for enzyme accessible cellulose particles and $p_B^{(0)}$ is the total number of monomeric glucans for CBH-threaded cellulose particles.

The QMOM technique (McGraw, 1997) was used to close the moment equations such that:

$$p^{(k)}(x,t) = \sum_{i=1}^{n_q} w_i(x,t) \xi_i^k(x,t) \quad (2.10)$$

And:

$$p_B^{(k)}(x,t) = \sum_{i=1}^{n_q} e_i(x,t) L_i(x,t)^k \quad (2.11)$$

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:

$$\frac{\partial p^{(k)}}{\partial t} = f_p^{(k)} - v \frac{\partial p^{(k)}}{\partial x} + \frac{\partial}{\partial x} \left(\kappa_p^* \frac{\partial p^{(k)}}{\partial x} \right) \quad (2.12)$$

$$\frac{\partial p_B^{(k)}}{\partial t} = f_{p_B}^{(k)} - v \frac{\partial p_B^{(k)}}{\partial x} + \frac{\partial}{\partial x} \left(\kappa_{p_B}^* \frac{\partial p_B^{(k)}}{\partial x} \right) \quad (2.13)$$

$$\frac{\partial R}{\partial t} = f_R - v \frac{\partial R}{\partial x} \quad (2.14)$$

$$0 = \sum_{i=1}^{n_q} w_i \xi_i^k - p^{(k)} \quad (2.15)$$

$$0 = \sum_{i=1}^{n_q} e_i L_i^k - p_B^{(k)} \quad (2.16)$$

This combination of QMOM and DAE in solving population balance equation has been proposed by (Gimbin *et al.*, 2009).

Next, we introduced the dimensionless variables as follows:

$$\begin{aligned} \tau = \frac{t}{\ell/u}, \hat{x} = \frac{x}{\ell}, \hat{p}(\hat{x}, \tau) = \frac{p(x,t)}{p^{(0)}(0)}, \hat{p}_B(\hat{x}, \tau) = \frac{p_B(x,t)}{p^{(0)}(0)}, \\ \hat{p}^{(1)}(\hat{x}, \tau) = \frac{p^{(1)}(x,t)}{p^{(0)}(0)}, \hat{p}_B^{(1)}(\hat{x}, \tau) = \frac{p_B^{(1)}(x,t)}{p^{(0)}(0)}, \\ \hat{p}_B^{(0)}(\hat{x}, \tau) = \frac{p_B^{(0)}(x,t)}{p^{(0)}(0)}, \hat{K}_d = \frac{K_p}{p^{(0)}(0)}, \hat{R} = \frac{R}{R_0}, \hat{v} = \frac{v}{u} \end{aligned} \quad (2.17)$$

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:

$$\begin{aligned} \frac{\partial \hat{p}^{(k)}}{\partial \tau} + \hat{v} \frac{\partial \hat{p}^{(k)}}{\partial \hat{x}} - \frac{\partial}{\partial \hat{x}} \left(\kappa_p^* \frac{\partial \hat{p}^{(k)}}{\partial \hat{x}} \right) \\ = (-a^* + E^* \hat{p}_B^{(0)}) \frac{\hat{p}^{(1)} + \hat{p}_B^{(1)}}{\hat{p}^{(1)} + \hat{p}_B^{(1)} + \hat{K}_d^{CBH}} \hat{p}^{(k)} \\ + \left(\frac{0.004}{k+1} - 0.002 \right) b^* \frac{\hat{p}^{(1)} + \hat{p}_B^{(1)}}{\hat{p}^{(1)} + \hat{p}_B^{(1)} + \hat{K}_d^{EG}} \hat{p}^{(k+1)} \\ + \frac{0.002}{k+1} b^* \frac{\hat{p}^{(1)} + \hat{p}_B^{(1)}}{\hat{p}^{(1)} + \hat{p}_B^{(1)} + \hat{K}_d^{CBH}} \hat{p}^{(k)} \\ - c^* \left(\frac{\hat{R}-1}{2\hat{R}-1} \right) \left(\frac{d\hat{p}^{(1)}}{d\tau} + \frac{d\hat{p}_B^{(1)}}{d\tau} \right) (\hat{p}^{(k)} + \hat{p}_B^{(k)}) \end{aligned} \quad (2.18)$$

$$\begin{aligned} \frac{\partial \hat{p}_B^{(k)}}{\partial \tau} + \hat{v} \frac{\partial \hat{p}_B^{(k)}}{\partial \hat{x}} - \frac{\partial}{\partial \hat{x}} \left(\kappa_{p_B}^* \frac{\partial \hat{p}_B^{(k)}}{\partial \hat{x}} \right) \\ = (-a^* + e^* \hat{p}_B^{(0)}) \frac{\hat{p}^{(1)} + \hat{p}_B^{(1)}}{\hat{p}^{(1)} + \hat{p}_B^{(1)} + \hat{K}_d^{CBH}} \hat{p}^{(k)} \\ + d^* \left[-X_2 k \hat{p}_B^{(k-1)} + \frac{X_2^2}{2} k(k-1) \hat{p}_B^{(k-2)} \right] \\ + \left(\frac{1}{k+1} - 1 \right) 0.002 b^* \frac{\hat{p}^{(1)} + \hat{p}_B^{(1)}}{\hat{p}^{(1)} + \hat{p}_B^{(1)} + \hat{K}_d^{EG}} \hat{p}^{(k)} \end{aligned} \quad (2.19)$$

$$\frac{\partial \hat{R}}{\partial \tau} + \hat{v} \frac{\partial \hat{R}}{\partial \hat{x}} = \frac{c^*}{2} \left(\frac{d\hat{p}^{(1)}}{d\tau} + \frac{d\hat{p}_B^{(1)}}{d\tau} \right), \hat{R} \geq 1 \quad (2.20)$$

where, a^* , b^* , c^* , d^* , e^* , κ_p^* and $\kappa_{p_B}^*$ are dimensionless parameters.

1D PBE-Advection-Diffusion Model

Computational programs were used using a finite element based software, i.e., COM-SOL for one-dimensional domain. The length of the computation domain was chosen as [0,1]. Initially, the particles concentrated in the range of $x = (0.25, 0.6)$ and $(0.75, 1)$ while the other domain was free of particles. We enforced no flux boundary conditions on the left-end and right-end. Throughout the investigation, the parameters were taken as $K_d = 1 \text{ mol/m}^3$, $p^{(0)}(0) = 100 \text{ mL} = \text{m}^3$, $R_0 = 1 \text{ nm}$, $k_h^{CHBH} = 1 \text{ hr}^{-1}$, $\tilde{k}_h^{EG} = 1 \text{ m}^3 \text{ mol}^{-1} \text{ hr}^{-1}$, $k_f^{CBH} = 2 \text{ m}^3 \text{ mol}^{-1} \text{ hr}^{-1}$, $E_T^{EG} = E_T^{CBH} = 32.5 \text{ mol} = \text{m}^3$, $\rho = 0.8 \text{ mol} = \text{m}^6$, $n = 1$ and $L = 0.1 \text{ m}$. We set $n_q = 2$ for the DAE-QMOM formulation. We assumed that the

initial k -th moments for $k = 0, 1, 2$ of p and p_B with their quadrature length and weight and also the initial value for radius R was [5.0183, 1.0794, 0.3722, 0.2058, 5.0183, 1.0794, 0.3722, 0.2058, 100], respectively.

The evolution of particle moments in the PBE-advection-diffusion model with zero diffusion coefficient and advection velocity is shown in Fig. 1. The result shows that the total number of cellulose particles and the total number of monomeric glucans, which are represented by $p^{(0)}$ and $p^{(1)}$ respectively, increased due to particle breakage. On the other hand, $p_B^{(0)}$ and $p_B^{(1)}$ decreased because the CBH1-threaded cellulose chains were transformed into enzyme-accessible cellulose chains by the action of EG_1 enzyme.

Moreover, all curves in Fig. 1 eventually stopped increasing or decreasing at certain time and became a straight line. This behaviour indicates that, at certain time, all cellulose chains reached the minimum length and all cellulose cylindrical particles reached its minimum radius owing to the depletion of insoluble substrate during the hydrolysis process. In this situation, both enzymes (CBH_1 and EG_1) stopped their activities of cutting the cellulose chains. Next, we describe the reaction-diffusion process of cellulosic hydrolysis in 1D domain before expanding the model to include the advection term.

Case I: 1D Reaction-Diffusion Only

In Fig. 2, the evolution of the total number of CBH1-threaded cellulose chains, $p_B^{(0)}$ and the total number of enzyme-accessible cellulose chains, $p^{(0)}$ undergoing the process of one-dimensional diffusion and reaction are illustrated. Initially the particles concentrated heterogeneously i.e., in the range of (0.25, 0.5) and (0.75, 1), while other places were free of particles. It is apparent from both graphs in Fig. 2 that diffusion caused the particles to move from high to low concentrations so that the domain were filled up with the species over time. After a sufficiently long time, the whole domain would be filled homogeneously.

We can see the difference between the two graphs: (a) $p_B^{(0)}$ and (b) $p^{(0)}$ in Fig. 2. p_B was lost by degradation and reached a steady state, brought about by the combination of fragmentation and diffusion. On the contrary, there is a clear trend of increasing $p^{(0)}$. The spatial evolution of $p^{(0)}$ increased with respect to time due to particle breakage by the enzymes and, also, from CBH1-threaded cellulose chains. This is because, CBH1-threaded chains were transformed into enzyme-accessible cellulose chains, $p^{(0)}$ by the action of EG_1 enzyme.

Also, we studied the effect of diffusion on the distribution of $p_B^{(0)}$ and (b) $p^{(0)}$. In order to reveal the effects of diffusion on the particle moments evolution,

simulations for various diffusion coefficients $D = 0.5, 1, 2$ at $t = 40$ were performed as demonstrated in Fig. 3. As the diffusion coefficient increased, the distribution became less fluctuating. The difference between different diffusion coefficients mainly focused on the neighborhood of the interface; not in increasing the generation of shorter chains. Diffusion took place and moved the particles, but did not significantly alter the solution.

Case II: 1D Reaction-Diffusion-Advection

Next, we studied the effect of advection on reaction-diffusion patterns. Here, we considered v , which exhibits advection in addition to diffusion through the surrounding medium. The evolution of particle moments $p^{(0)}$ and $p_B^{(0)}$ with reaction, diffusion and advection in 1-D domain are shown in Fig. 4. Initially, cellulose particles concentrated at (0.25, 0.5) and (0.75, 1). The results for $p^{(0)}$ and $p_B^{(0)}$ show similar pattern at earlier period during the reaction due to diffusion and particle breakage by the action of enzymes. However, there is a slight difference between $p^{(0)}$ and $p_B^{(0)}$ at longer period during the reaction where $p^{(0)}$ shows higher value than $p_B^{(0)}$ due to the reaction and advection effects. This is because, the CBH1-threaded chains, p_B generates enzyme-accessible cellulose chains, p by the action of EG_1 enzyme. The value of $p^{(0)}$ and $p_B^{(0)}$ in the neighborhood of the interface in the right zone was greater than that in other places which was brought about by the presence of advection velocity.

In order to reveal the effects of advection to reaction-diffusion on particle moments evolution, simulations for various velocities i.e., $v = 0, 3, 5$ are performed at time $t = 40$. The spatial distribution of $p^{(0)}$ and $p_B^{(0)}$ at $t = 40$ is presented in Fig. 5. The advection takes place and accelerates the movement of particles and significantly alters the solution. The particle moments have a larger value at bigger v throughout the domain, which indicates a significant contribution of advection velocity to the reaction-diffusion system. The fundamental new phenomenon resulting from the inclusion of advection is that the pattern of solution is spatially distributed dynamically with increasing number of cellulose particles. The results from this study showed an agreement with the analysis reported in our previous paper (Jamil and Wang, 2016) in terms of the generation of shorter cellulose chains throughout the hydrolysis process. To summarize, advection is a significant phenomenon which could increase the number of cellulose particles. Diffusion alone could not increased the hydrolysis rate, but the combination of advection and diffusion increase the hydrolysis rate.

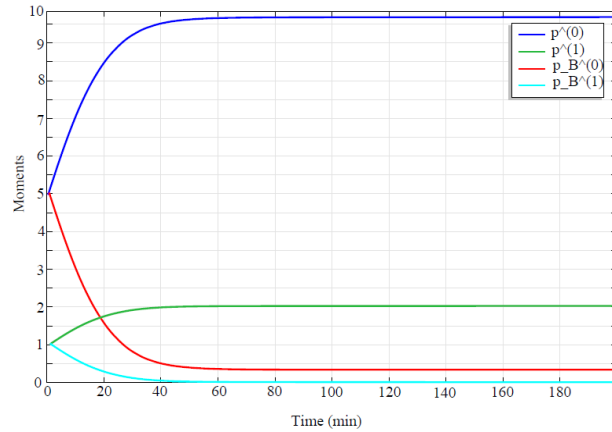


Fig. 1. The evolution of particle moments of PBE-advection-diffusion equation with zero diffusion coefficient and advection velocity

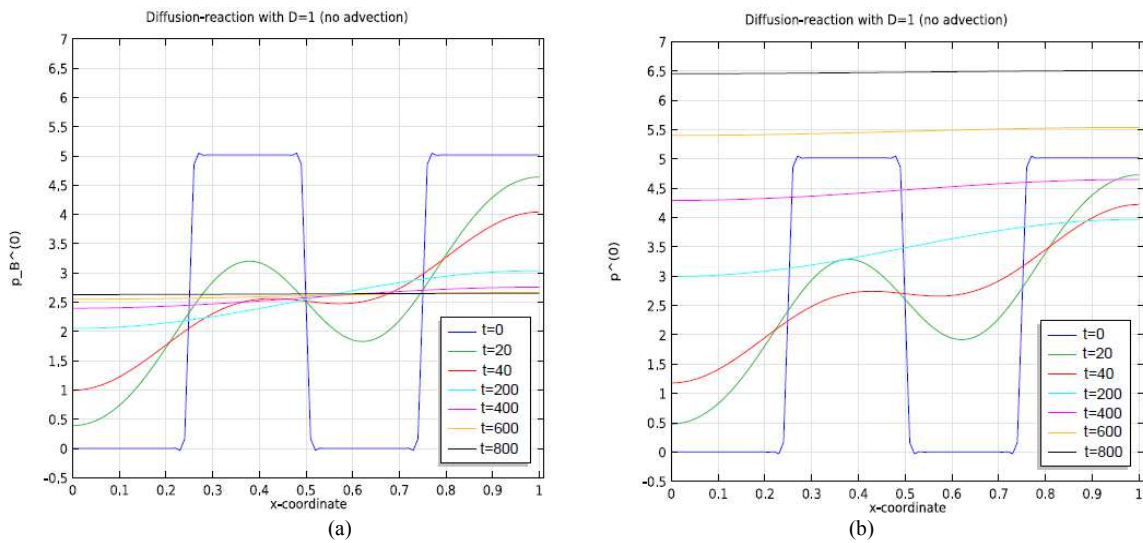


Fig. 2. The evolution of particle moments for (a) p_B and (b) p with diffusion coefficient $D = 1$ at velocity $v = 0$.

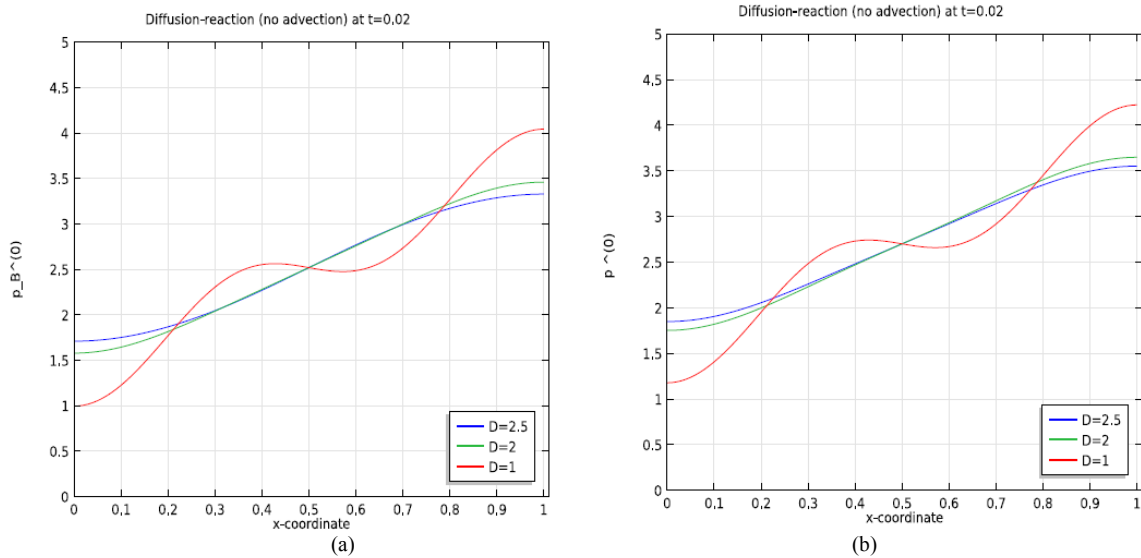


Fig. 3. The distribution of (a) $p_B^{(0)}$ and (b) $p^{(0)}$ for different diffusion coefficient in 1-D at zero velocity at time $t = 40$

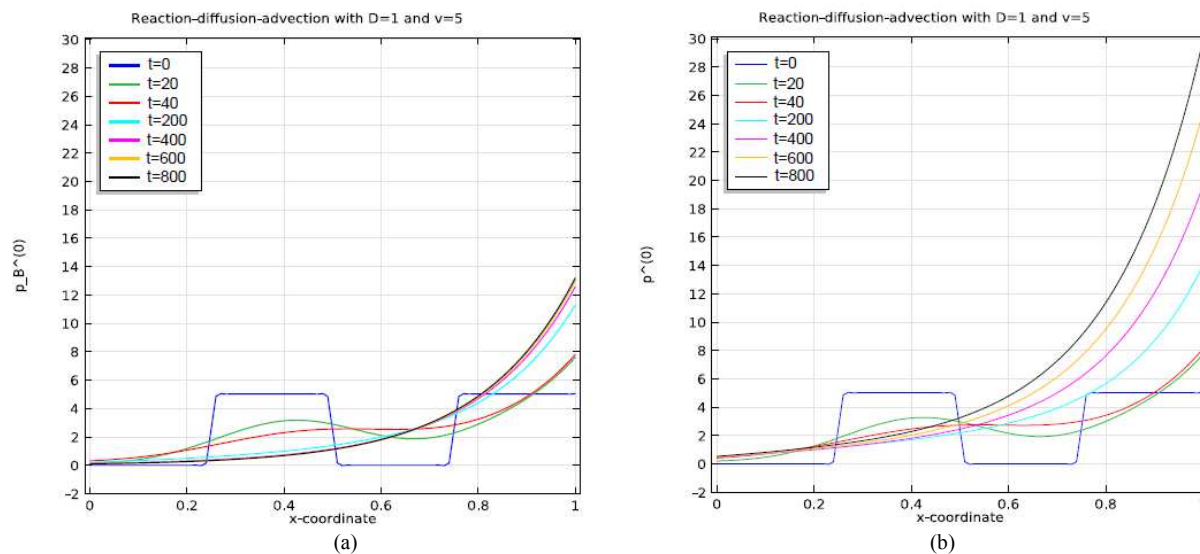


Fig. 4. The evolution of particle moments for (a) $p_B^{(0)}$ and (b) $p^{(0)}$ with diffusion coefficient $D = 1$ at velocity $v = 5$

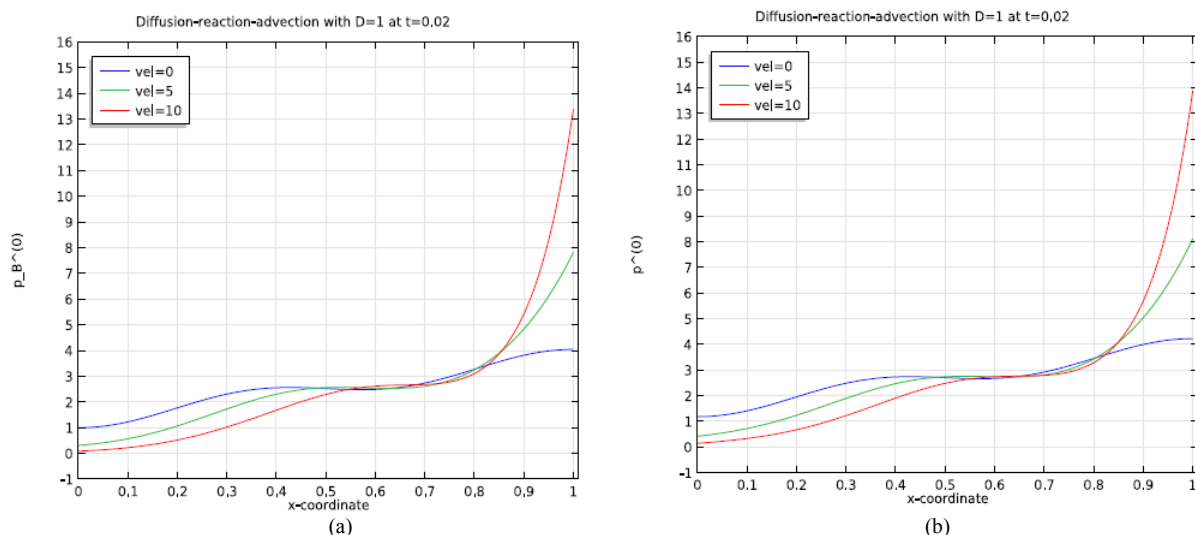


Fig. 5. The distribution of (a) $p_B^{(0)}$ and (b) $p^{(0)}$ for different velocity in 1-D at diffusion coefficient $D = 1$ at time $t = 0.02$

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 one-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 study, we succeeded in carrying out an important coupling of PBE-advection-diffusion model for enzymatic hydrolysis of cellulose for the first time.

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Author's Contributions

Norazaliza Mohd Jamil: Did the research, analysed and interpreted the result, prepared the manuscript and

responsible for the manuscript correction, proof reading and paper submission.

Qi Wang: Designed the research plan and organized the study, assisted in research work, provided the intellectual input and designs in the study and reviewed it critically for significant intellectual content.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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