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A mathematical model for the effects of volume fraction and fiber aspect ratio of biomass mixture during enzymatic hydrolysis

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Abstract. Renewable energy or biofuel from lignocellulosic biomass is an alternative way to replace the depleting fossil fuels. The production cost can be reduced by increasing the concentration of biomass particles. However, lignocellulosic biomass is a suspension of natural fibres, and processing at high solid concentration is a challenging task. Thus, understanding the factors that affect the rheology of biomass suspension is crucial in order to maximize the production at a minimum cost. Our aim was to develop a mathematical model for enzymatic hydrolysis of cellulose by combining three scales: the macroscopic flow field, the mesoscopic particle orientation, and the microscopic reactive kinetics. The governing equations for the flow field, particle stress, kinetic equations, and particle orientation were coupled and were simultaneously solved using a finite element method based software, COMSOL. One of the main results was the changes in rheology of biomass suspension were not only due to the decrease in volume fraction of particles, but also due the types of fibres. The results from the simulation model agreed qualitatively with the experimental findings. This approach has enables us to obtain better predictive capabilities, hence increasing our understanding on the behaviour of biomass suspension.

1. Introduction

Our previous paper [1] bridges the existing gap between PBE reaction kinetics and Navier-Stokes equation for enzymatic hydrolysis of cellulose. A solution strategy was introduced to resolve the modeling and the simulation of the PBE-advection-diffusion system, coupled with fluid medium surrounding the cellulose particles. As discovered, the quality of mixing within the reactor had been crucial in optimizing the hydrolysis product. Practically, the usage of high solid concentration of cellulose particles reduced the operating cost and energy. However, processing high solids concentration of the biomass suspensions consisting of cellulose fibers had been challenging due to the properties of the fibers. This means that understanding the factors that affect the rheology of the biomass suspension is essential for optimization of biomass processes.

This paper, therefore, depicts the development of a kinetic theory for cellulosic biomass mixture consisting of water, glucose, cellobiose, cylindrical shaped cellulosic rods, and enzyme. This theory extends those discussed in the previous paper [1]. A multi-scale modeling for enzymatic hydrolysis of cellulose was developed by combining three scales: the macroscopic



flow field, the mesoscopic particle orientation, and the microscopic reactive kinetics. Here, the macroscopic flow field was described by the mass and the momentum conservation equations. Meanwhile, the mesoscopic scale had been related to the prediction of fiber orientation that was obtained by the orientation tensor equation, whereas the microscopic kinetic model was obtained from the Population Balance Equations established by Griggs et. al [2]. In addition, the model captured the plasticity of the biomass mixture.

2. Mathematical Modelling

2.1. Microscopic Dynamics

Population balance equations serves as a microscopic equation, where the radius of the cellulosic rods was coupled with the macroscopic equation (momentum balance equation) for elastic stress and volume fraction of particles. The microscopic kinetic model was obtained by extending a mechanistic model proposed by Griggs et. al [2] and also by inserting diffusion and advection terms. By using DAE-QMOM method [3], the microscopic system can be expressed as:

$$\frac{\partial p^{(k)}}{\partial t} + \mathbf{v}_c \cdot \nabla p^{(k)} - k_p \nabla^2 p^{(k)} = \int_0^\infty f_p \chi^k d\chi \quad (1)$$

$$\frac{\partial p_B^{(k)}}{\partial t} + \mathbf{v}_c \cdot \nabla p_B^{(k)} - k_{p_B} \nabla^2 p_B^{(k)} = \int_0^\infty f_{p_B} \chi^k d\chi \quad (2)$$

$$\frac{\partial R}{\partial t} + \mathbf{v}_c \cdot \nabla R = S_R \quad (3)$$

$$0 = \sum_{i=1}^{n_q} w_i \xi_i^k - p^{(k)} \quad (4)$$

$$0 = \sum_{i=1}^{n_q} e_i L_i^k - p_B^{(k)} \quad (5)$$

In this formulation, $p(\mathbf{x}, \chi, t)$ is the population of enzyme accessible chains in the cellulose rods of chain length χ , $p_B(\mathbf{x}, \chi, t)$ is the population of CBH₁-threaded cellulose chains, and R is the radius of cellulose particles. \mathbf{x} denotes spatial coordinates and χ is the cellulose chain length [1]. On top of that, k_p and k_{p_B} are the diffusion coefficients for the corresponding species. Meanwhile, \mathbf{v}_c is the cellulose velocity. The source terms f_p , f_{p_B} and S_R represent the reaction terms due to the breakage process by EG1 and CBH1 enzymes of the cellulose chains. n_q is the order of the quadrature formulation, ξ_i and L_i are the particle length and w_i and c_i are the quadrature weights for p and p_B , respectively.

2.2. Mesoscopic Fiber Orientation

Lignocellulosic biomass suspension mainly consists of natural fibers. The mesoscopic continuum theories introduce intermolecular forces (or intermolecular interactions) into hydrodynamic equations of motion. In fact, ideas from a liquid crystal theory [4] concerning the behavior of cylindrical shape of cellulose particles in a solvent was adopted. Hence, it had been considered as an ensemble of cellulosic rods suspended in a viscous solution consisting of water, glucose, cellobiose and enzyme. Furthermore, the kinetic theory formulation for suspensions was used to present the mesoscopic kinetic theory of the rod suspension solutions. Mesoscopic models can be obtained from the kinetic theories governed by the Smoluchowski equation. By applying the moment operators to Smoluchowski equation, time evolution for the second order fiber orientation tensor \mathbf{M} can be written as

$$\begin{aligned}
& \left\{ \frac{\partial \mathbf{M}}{\partial t} + \nabla \cdot ((\mathbf{v} + \mathbf{V})\mathbf{M}) - \boldsymbol{\Omega} \cdot \mathbf{M} + \mathbf{M} \cdot \boldsymbol{\Omega} \right. \\
& \quad \left. - ac_2[\mathbf{D} \cdot \mathbf{M} + \mathbf{M} \cdot \mathbf{D}] \right\}_{\alpha\beta} \\
& = \left\{ -2ac_2 \mathbf{D} : \mathbf{M}\mathbf{M} \right. \\
& \quad \left. - 6D_r \left[\mathbf{M} - \frac{\mathbf{I}}{3} - c_1 N \mathbf{M} \cdot \mathbf{M} + c_1 N \mathbf{M} : \mathbf{M}\mathbf{M} \right] \right. \\
& \quad \left. + D_{\perp} \nabla \mathbf{M} \right\}_{\alpha\beta} + D_{\perp} \nabla_i \langle \mathbf{m}_{\alpha} \mathbf{m}_{\beta} \nabla_i U \rangle. \tag{6}
\end{aligned}$$

where \mathbf{m} is the unit vector along the primary axis of the fiber. Meanwhile, $\boldsymbol{\Omega}$ is the vorticity tensor and \mathbf{D} is the rate of strain tensor (rate of deformation tensor). \mathbf{v} is the velocity vector field for the flowing cellulose particles, \mathbf{V} is the sedimentation velocity and D_r is the diffusion matrix for the rotary diffusion. Here, N is a dimensionless measure of polymer concentration that characterizes the strength of the intermolecular Maier-Saupe potential responsible for orienting molecules in the same direction. c_1 and c_2 are the interpolation parameters. a is the molecular shape parameter. D_{\perp} is the translational diffusion coefficient perpendicular to the rod axis. U is the excluded volume potential given by Maier-Saupe type interaction potential.

2.3. Macroscopic Flow

The time evolution equation for the volume fraction, ϕ can be written as

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{v}_c \phi) = \frac{2S_R}{R} \phi. \tag{7}$$

It had been noted that this equation effectively coupled with the microscopic process due to the enzymatic reaction of the cellulose particles to the volume fraction transport equation of the cellulose component. The volume fraction was expected to be an adequate variable for correlating both concentration and rheology. The continuity equation for the mixture is given by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{8}$$

where ρ is the total density of the mixture and \mathbf{v} is the fluid velocity.

The coupled linear momentum balance equation, the conservation equation of mass, and the evolution of volume fraction reduced to

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p - \phi \frac{\delta A}{\delta \phi} + \nabla \cdot (\boldsymbol{\sigma}) \tag{9}$$

where p is the scalar pressure, $\boldsymbol{\sigma}$ is the stress tensor and $\frac{\delta A}{\delta \phi}$ is the chemical potential of the material system. In addition, the biomass mixture exhibited elastic behavior, depending on the times-scale of interest. The elastic stress is derived through a virtual work principle [5].

3. Results and Discussions

The governing equations for the flow field, particle stress, microscopic kinetic equations, and particle orientation (Equation 1-9) were coupled and were simultaneously solved using a finite element method (FEM) based software i.e. COMSOL 4.3b. This study solved the 2-dimensional multi-scale model for enzymatic hydrolysis of cellulose by utilizing the DAE-QMOM technique and by adopting liquid crystal theory in COMSOL.

3.1. The effect of volume fraction and fiber aspect ratio to the viscosity

Viscosity is an important rheological property of fiber suspensions and polymer solutions. A Newtonian fluid has constant viscosity. However, a large variation of viscosity within a narrow range of shear rates in figure 1 indicates shear thinning behavior. As shown in the figure, the fluid was highly viscous at low shear stress, followed by a shear-thinning region, and then, the viscosity decreased as the shear rate increased. Besides, the shear thinning behavior of biomass suspension had been consistent with previous experimental reports [6], [7], [8] [9], and [10].

Based on the figure, the viscosity of the suspension increased as the volume fraction of particles increased. Shear thinning became more pronounced as the volume fraction increased. Higher volume fraction of particles needed higher shear stress to reduce the viscosity of the biomass suspension. The specific viscosity of suspensions, as defined as $\mu = \phi\eta_c + (1 - \phi)\eta_w$, reflected the contribution of particles in the suspensions to the viscosity. These findings are in agreement with [11] findings that showed that the viscosity was proportional to the concentration in semi-concentrated suspensions of rigid nylon and copper fibers. In other study, [12] reported that the relative viscosity depended on the volume fraction in suspensions of randomly oriented polymethyl methacrylate rods.

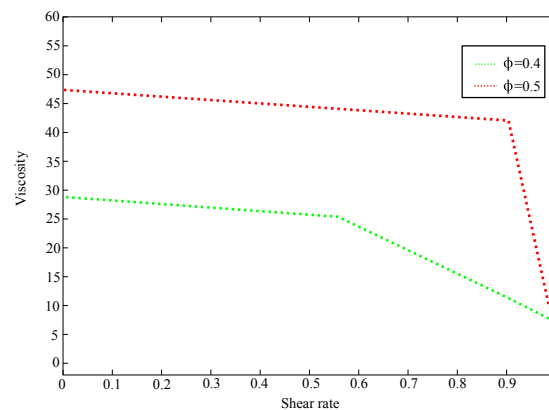


Figure 1. Viscosity vs shear stress at different initial volume fractions $\phi = 0.4, 0.5$.

Besides, another study by [13] found that cellulose suspension properties depended on the aspect ratio of cellulose fibers. Meanwhile, in 2005, Dalpke and Kerekes [14] analyzed the effects of fiber aspect ratio for pulps on its rheological properties. The viscosity is plotted as a function of shear rate in figure 2 for suspensions of fibers with different aspect ratios, whereby longer fibers had larger initial aspect ratio. For both long and short fibers, the viscosity decreased with the increase in shear rate. These trends indicated the attributes of shear-thinning. From the figure, long fibers had higher viscosity at low shear rate and the shift of the viscosity curves was more pronounced than the short fibers. Therefore, in this context, the changes in rheology of biomass suspension were not only due to the decrease in volume fraction of particles, but also due to the types of fibers. The viscosity was also influenced by fiber interactions. Figure 3 shows the curves of viscosity as a function of time for the two types of fibers obtained. Long fibers showed flow resistance behavior due to the entanglement of fibers, which is in agreement with the findings by Tozzi et al. [9].

3.2. First normal stress difference

On the other hand, the non-Newtonian fluid might have non-zero value for the first normal stress difference ($N_1 = \sigma_{xx} - \sigma_{yy}$). The existence of normal stress difference caused both the rod-climbing effect and die swell [15]. Figure 4 presents the first normal difference N_1 as a function

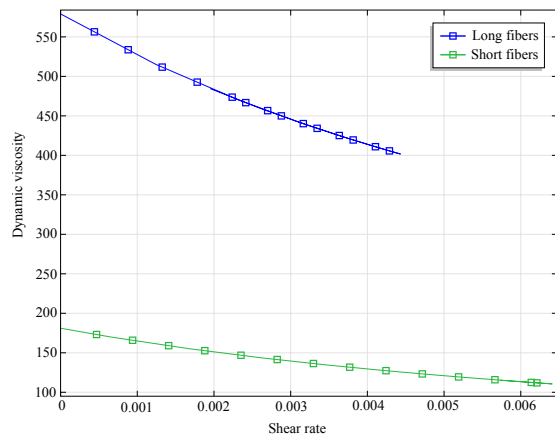


Figure 2. Viscosity as a function of shear rate for long and short fibers.

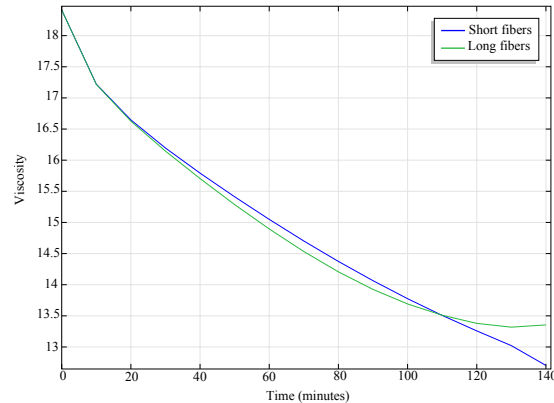


Figure 3. Viscosity as a function of time for long and short fibers at the early stage of hydrolysis.

of the shear rate $\dot{\gamma}$ for biomass slurry with different initial volume fraction $\phi = 0.3, 0.4, 0.5$. As shown in the figure, there were two regimes of N_1 : a low-shear-rate regime where $N_1 < 0$ and a high-shear-rate regime, where $N_1 > 0$. The first normal stress difference changed its sign from negative to positive. As the particle volume fraction increased, the two regimes persisted, but the range of shear rates over which N_1 was negative shifted downwards. The behavior of the non-zero first normal difference on shear rate had been due to the contact of fibers with each other during the collision.

3.3. The evolution of glucose concentration

As alluded earlier, through hydrolysis, biomass was converted into glucose and cellobiose over time. Glucose is the main sugar produced during the conversion of cellulose particles that acted as enzymes [9]. The time evolution of glucose concentration for each fiber aspect ratio is shown in figure 5. As expected, larger concentrations of glucose were produced by short fibers. The rate of sugar production in the flow reactor discovered in the simulation model had been similar qualitatively to the experimental results retrieved by [9]. This is because; it was easier for enzymes to adsorb cellulose substrate with shorter lengths.

4. Conclusion

A multi-scale model was developed to capture the reaction kinetics of cellulose chains in PBE form, cellulose rod orientation and interaction, hydrodynamics and plasticity of the biomass mixture at the same time. One of the main results was the changes in rheology of biomass suspension were not only due to the decrease in volume fraction of particles, but also due to the types of fibres. The results from the simulation model agreed qualitatively with the experimental findings. This approach has enabled us to obtain better predictive capabilities, hence increasing our understanding on the behaviour of biomass suspension. Moreover, the results from the simulation model agreed qualitatively with the experimental findings. This approach has enabled us to obtain better understanding of the multi-scale model during enzymatic hydrolysis.

Acknowledgments

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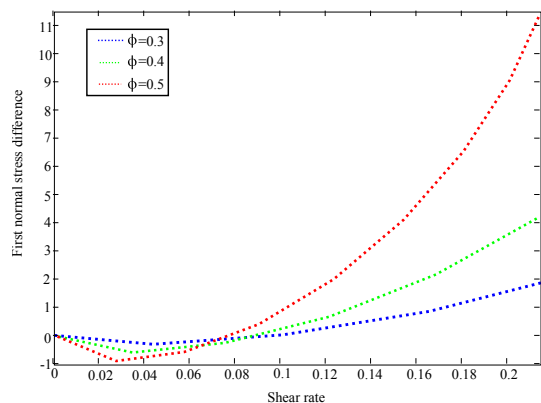


Figure 4. First normal stress difference as a function of shear rate for fiber suspensions at different initial volume fractions.

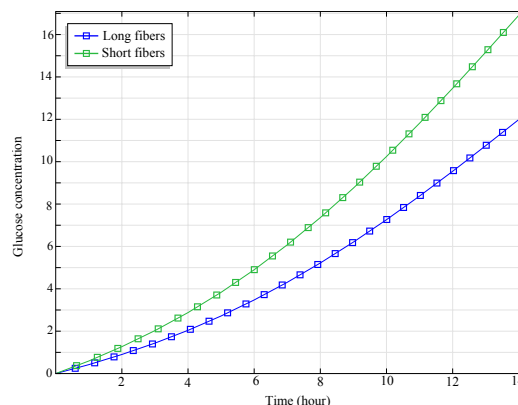


Figure 5. The time evolution of glucose concentration for each fiber type (long and short fibers).

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