MATHEMATICAL MODE



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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 fibers, and processing at high solid concentration is a challenging task because it will affect the mixing quality between enzyme and cellulose particles and the generation of sugars. Thus, understanding factors that affect the rheology of biomass suspension is crucial in order to maximize the production at a minimum cost. Our aim is to develop a solution strategy for the modeling and simulation of high solid concentration of biomass suspension during enzymatic hydrolysis. Also, we intend to develop a multi-scale model for enzymatic hydrolysis that captures the reaction kinetics of cellulose chains in PBE form, cellulose rod orientation and interaction, as well as hydrodynamics and plasticity of the biomass mixture. We extended and improved the established kinetic model proposed by Griggs et al.[Griggs et al., 2012a]. We built the reduced order models by ignoring significantly small terms and determined the approximate solutions by employing asymptotic analysis method. Liquid crystal theory was adopted to study the cellulose fibers. The complete model was solved using DAE-QMOM technique in finite-element software package, COMSOL. Essentially, we made a clear connection between microscopic, mesoscopic, and macroscopic properties of biomass slurries undergoing enzymatic hydrolysis. The results show that the quality of mixing within a reactor is crucial in optimizing the hydrolysis product. Also, the biomass suspension shows non-Newtonian behaviors such as shear thinning, yield stress, and normal stress difference, which is in agreement

with experimental results. The extended model improved the predictive capabilities, hence increased our understanding on the behavior of biomass suspension.

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# LIST OF SYMBOLS

p(x,t)	The distribution of cellulose chain with length $x$
p(x,t)dx	The number of cellulose chains per volume in the length range $x, x + dx$
$p_B(x,t)$	The distribution of CBH-threaded cellulose chain with length $x$
x	The number of glucan units (treated as a continuous variable) $x$
$p^{(0)}(t)$	The total number of cellulose chains at time $t$
$p^{(1)}(t)$	The total number of monomeric glucans at time $t$
$x_N$	The number-average chain length
$q_1(t)$	The concentration of glucose
$q_2(t)$	The concentration of cellobiose
$k_f^{CBH}$	The rate for $CBH_1$ to adsorb on the cellulose chains
$k_h^{CBH}$	The rate for $CBH_1$ to find and thread the $CBH_1$ -threaded cellulose chains
$E_S^{EG}$	Surface-adsorbed EG <sub>1</sub>
$E_S^{CBH}$	Surface-adsorbed CBH <sub>1</sub>
$\Omega(x,y)$	Breakage kernel
$k_h^{EG}(x)$	The rate for $\mathrm{EG}_1$ to find and cleave the cellulose chain of length $x$
R	Radius of the cylindrical shaped cellulose particle
L	Length of the cylindrical shaped cellulose particle
$R_{0}$	The thickness of the accessible layer of cellulose chains
V(t)	The total volume of particles
$V_S(t)$	The volume of the reactive surface layer of cellulose
$p_T(x,t)$	The total cellulose population
$p_S(x,t)$	The population distribution of surface-accessible cellulose
$p_i(x,t)$	The population of inaccessible cellulose

$r_{loss}(x,t)$	The rate of cellulose loss during enzymatic hydrolysis
$r_{exp}(x,t)$	The rate of cellulose exposed during enzymatic hydrolysis
$K_d^E$	The dissociation equilibrium constant
$p_B^{(0)}$	The total number of CBH <sub>1</sub> -threaded cellulose chains
u	The mean velocity vector
$D_p, D_{p_B}$	The particle diffusion constants
m	The unit vector along the primary axis of a fiber
a	Molecular shape parameter
r	Aspect ratio
Ω	Vorticity tensor
D	The rate of strain tensor
$f(\mathbf{m}, \mathbf{x}, t)$	The orientation distribution function
${\cal R}$	The rotational gradient operator
v	The velocity vector field for the flowing cellulose particles
V	The sedimentation velocity
$D_s$	The diffusion matrix for the translational diffusion
$D_r$	The diffusion matrix for the rotary diffusion
$U_{ms}(\mathbf{x},\mathbf{m},t)$	The excluded volume potential
A	The free energy
$\mu$	The chemical potential
Μ	The second moment of the orientation tensor
$\mathbf{M}_4$	The fourth moment of the orientation tensor
$\phi$	The volume fraction of cellulose particles
$\sigma_e$	The elastic stress

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# LIST OF ABBREVIATIONS

- EG<sub>1</sub> Endoglucanase I
- $CBH_1$  Cellobiohydrolase I
- PBE Population Balance Equation
- DAE Differential Algebraic Equation
- QMOM Quadrature Method of Moments
- CM Class Method
- MOM Method of Moments
- DQMOM Direct Quadrature Method of Moments
- SMM Standard Method of Moments
- PD Product-difference
- CFD Computational Fluid Dynamics

## Chapter 1

## INTRODUCTION

#### 1.1 BACKGROUND

In recent years, energy crises and environmental pollution have become vital sustainable problems to the human society. Rapid industrialization has increased the demand for oil; however, the energy supply from fossil fuels worldwide is limited and will eventually be depleted. Due to burning of fossil fuels, pollutant emissions have increased. To reduce pollution caused by fossil fuel burnings, one solution is to use renewable energy as an alternative to replace fossil fuels. Renewable energy fields use ethanol, where ethanol is produced from various lignocellulosic biomass, such as palm trees [Hosseini and Wahid, 2012], [Basiron, 2007], corn stover [Griggs et al., 2012a], [Selig et al., 2008], wood, agricultural products, waste, and grasses. Generally, lignocellulosic biomass is composed of lignin, hemicellulose and cellulose [Abnisa et al., 2011].

The production of ethanol from lignocellulosic biomass consists of three fundamental processes; pretreatment, enzymatic hydrolysis, and fermentation [Limayem and Ricke, 2012]. Pretreatment modifies the structure of biomass to make the cellulose more exposed to enzymes for sugar conversion [Himmel et al., 2007]. Enzymatic hydrolysis breaks cellulose chains into sugar such as cellobiose and glucose, whereas fermentation converts sugar into ethanol [Griggs et al., 2012a], [Griggs et al., 2012b], [Bansal et al., 2009]. As a matter of fact, cellulose molecules are locked-in by the lignin-hemicellulose network; therefore, the hydrolysis step is the most crucial part of biomass to ethanol conversion process, in which this project is focused most specifically on. The production cost of cellulosic hydrolysis can be reduced by increasing the concentration of biomass particles. However, lignocellulosic biomass is a suspension of natural fibers, and processing at high solid concentration is a challenging task because it will affect the mixing quality between enzyme and cellulose particles, as well as hydrolysis yield. Thus, understanding factors that affect the rheology of biomass suspension is crucial in order to maximize the production of ethanol at minimum cost.

Lignocellulosic biomass suspension mainly consists of natural fibers. There are various types of shapes, sizes, and material properties of lignocellulosic fibers. According to Roche et. al, fibers in pretreated corn stover have a size of  $(1-2,000 \ \mu m)$  and the aspect ratio is reported to be in the range of 1-20 [Roche et al., 2009a]. There are three types of regimes for biomass suspension. Firstly, for regime with low concentration of fibers, it is known as dilute regime, in which a fiber is free to rotate without having any contact with other fibers. Secondly, when hydrodynamic interaction is dominant over a few physical contacts between fiber, the regime is called semi-dilute regime. The last category is for the concentrated suspensions where fibers cannot rotate freely and the fibers interact by both hydrodynamic and direct contact forces.

In Malaysia, palm oil becomes the main source of biomass to produce renewable energy. Palm oil industry is very important in Malaysia as the country has maintained its position as the world's leading palm oil producing country [Hamisan et al., 2009]. Their main products of palm oil are foods, oleochemicals, biofuels, and renewable energy source. Ongoing research and development of palm biomass by governmental institutions and universities improves process efficiencies [Mohd Basyaruddin et al., 2012], [Aziz et al., 2002], [Hii et al., 2012], [You and Baharin, 2006]. For enzymatic hydrolysis process of palm oil biomass in Malaysia, cellulase (celluclast 1.5 L, Novozymes A/S, Denmark) and cellobiase (Novozyme 188, Novozymes A/S, Denmark) enzymes were tested experimentally [Iberahim et al., 2013].

Empirical models based on experimental outcomes have been applied frequently to study the enzymatic hydrolysis of cellulose, as surveyed in [Bansal et al., 2009]. These models often offer only limited insight into the fundamental mechanisms of enzymatic hydrolysis. On the other hand, a kinetic model for enzymatic hydrolysis offers several advantages. It can provide a deeper understanding, improve predictive capabilities, and in the end provide more directed and rational approaches for process design and optimization [Griggs et al., 2012a].

Initial studies in kinetic models of enzymatic hydrolysis of cellulose indicated that Michaelis-Menten-type kinetics can be used to take account of random and endwise attack of the substrate by three types of enzymes [Okazaki and Moo-Young, 1978]. Since then, the study of kinetic models for this process has undergone several innovations. In 1983, Fan and Lee [Fan and Lee, 1983] added several key factors in their kinetic model, i.e. the structure of cellulose and the nature of enzyme system. Then in 2012, Griggs et al. [Griggs et al., 2012a] adapted Population Balance Equation (PBE), where the model structure leads to a Partial Differential Equation forming a system of integral-differential equations. In their work, biomass particles are represented as monodispersed cylindrical shaped particles comprised of cellulose chains of varied length.

### 1.2 PROBLEM STATEMENT

Lignocellulosic ethanol production is cost sensitive to operation energy and enzyme prices. Most kinetic models have incorporated several major factors such as mixed type of enzymes, pore size distribution, high solid operation, cellulose structure and a distribution of chain lengths. However, these studies have not demonstrated a sufficiently meaningful scale to evaluate the hydrolysis system. Studies on enzymatic hydrolysis of cellulose that have been reported to date focused on a single scale i.e. at the microscopic level only. The problem is that as the studies employed a single scale model, the effect of fluid behavior, transport process and the interaction between solid particles in the suspension environment are not captured.

As stressed by [Yeoh et al., 2013], many different physical characteristics can be observed at different length scales. At the microscale, it is essential to understand the behavior of particles due to breakage of chains. At the mesoscale, the interaction between particles may become significant, resulting in local structural changes. At the macroscale, the hydrodynamic behavior of the background fluid influences the system. To the best of our knowledge, no kinetic model for enzymatic hydrolysis of cellulose, so far, has been published from a multi-scale point of view.

A combination of several features at different scales is essential in order to obtain a better understanding of the complex system. For this purpose, research is needed to investigate how to integrate the hydrolysis model from micro-scale to macro-scale in a seamless fashion. This is the intention of this study, which is to design a multiscale model for enzymatic hydrolysis of cellulose. The use of multi-scale approach will add value to the model and will also increase the understanding of the fundamental scientific phenomena and processes in order to optimize the production of ethanol. The challenge is to develop a cellulosic hydrolysis model that will give a holistic view on different aspects.

### 1.3 Objectives

This thesis is concerned with the study of mathematical modeling and simulation of biofuel production from lignocellulosic biomass. The aims of this study are:

1. To capture the most important chemical and physical phenomenon in the complex system of enzymatic hydrolysis of biomass.

- 2. To analyze a mechanistic model proposed by Griggs et al. [Griggs et al., 2012a] and improve the predictive capabilities to obtain a better understanding and ultimately provides more directed and rational approaches for process design and optimization.
- 3. To couple the microstructure kinetic equations with hydrodynamics so that we can model the plastic phase of the material all the way into the viscous liquid phase.
- 4. To examine the effect of advection, as well as the diffusion process as a drift phenomena on cellulose particles in a one- and two-dimensional domains.
- 5. To develop a multi-scale model for enzymatic hydrolysis of cellulose that captures the reaction kinetics of cellulose chains in PBE form, cellulose rod orientation and interaction, hydrodynamics and plasticity of the biomass mixture.
- 6. To elucidate the relationship of the three scales and manifest the impact of cellulosic enzymatic hydrolysis on the rheological property of the mixture.
- 7. To develop a solution strategy for the modeling and simulation of high solid concentration of biomass suspension during enzymatic hydrolysis.

### 1.4 RESEARCH FRAMEWORK, DESIGN, AND SCOPE

The first step of our work is to grasp and study the established kinetic model proposed by Griggs et al.[Griggs et al., 2012a] for enzymatic hydrolysis of cellulose. The PBE system derived by Griggs et al. [Griggs et al., 2012a] does not admit an analytical solution due to its complexity. To solve the system of equations, we may have to resort to numerical methods, which can incur significant computational cost. Our strategy here was to search for reduced order models by ignoring significantly small terms in the governing system of equations. Therefore, we reduce the number of parameters in the Griggs' model by using nondimensionalization technique and performing mathematical analysis to the system. Then, we develop separate models for individual action of enzymes. Next, we explore and describe the approximate solution for each of the separated models by employing asymptotic analysis for dynamical systems to reduce the complex model to a set of simple equations. In addition, we carry out a sensitivity analysis to study the effect of several parameters on the overall performance.

The separated models are combined into a full model and the model is solved numerically using DAE-QMOM approach. DAE-QMOM technique [Gimbun et al., 2009] consists of differential equations for the moments and the system of nonlinear equations resulting from the quadrature approximation as a differential algebraic equation system. Then, we compare the solutions from the DAE-QMOM method with the results from Griggs [Griggs et al., 2012a].

The second stage of this work involves the coupling of PBE and advection-diffusion term in order to model the spatial evolution of the system. We simulate the effect of diffusion and advection on the fragmentation of cellulose chains during enzymatic hydrolysis. Further, we couple the PBE-advection-diffusion model with Navier-Stokes equation. In this extended version, we simulate the mixing between biomass suspension and cellulase enzymes in a cylindrical stirred tank mechanically agitated by a stirrer. The influence of mixing speed of the stirred tank and different locations of enzyme injection point in the mixer on hydrolysis yield are investigated.

Finally, we develop a multi-scale model that combines three scales: the macroscopic flow field, the mesoscopic particle orientation and the microscopic reactive kinetics. We investigate the flow of a viscoelastic biomass slurry with different volume fractions and fiber aspect ratios of cellulose particles using COMSOL software package.

#### 1.5 Thesis outline

This dissertation consists of eight chapters and covers the enzymatic hydrolysis of cellulose. Chapter 1 describes the introduction and discusses the background about lignocellulosic biomass and ethanol as a fuel, as well as reviews the current state of knowledge. Chapter 2 provides an overview of the kinetic model for enzymatic hydrolysis of cellulose. The theoretical and mathematical developments required to describe the hydrolysis of insoluble cellulose chains by Griggs et al. [Griggs et al., 2012a] are discussed. Their model is the fundamental base of our study. Furthermore, the idea of splitting the model is also discussed. Asymptotic solutions of the kinetic model are described in Chapter 3. The mathematical analysis of the independent action of EG<sub>1</sub> and CBH<sub>1</sub> is presented. At this point, it is shown how the mathematical model can be reduced to a simple form. The solution of population balance equations (PBE) using numerical technique DAE-QMOM is given in Chapter 4.

Chapter 5 discusses the solution of PBE-advection-diffusion model. We take into account the fact that particles move through space due to diffusion and advection. Chapter 6 focuses on the coupling of the PBE-advection-diffusion model with hydrodynamics. Chapter 7 explains a kinetic theory for cellulosic biomass mixtures and a reduced order model for a multi-scale model. Developing multiple scales is an effort to describe the hydrolysis process more comprehensively. Finally, conclusion and suggestions for future work are presented in Chapter 8.

# CHAPTER 2

# KINETIC MODEL FOR ENZYMATIC HYDROLYSIS OF CELLULOSE

### 2.1 INTRODUCTION

The conversion of lignocellulosic biomass to ethanol involves a large number of physical and chemical transformations that happen in several separate processing steps i.e. pretreatment, enzymatic hydrolysis, and fermentation. The enzymatic hydrolysis step is the most important part of the process, and is the focus of this project. The chemical properties of biomass material are complex, and the reaction kinetics for the degradation of biomass are not well understood.

Kinetic theory is a way to describe the time evolution of probability distributions of various elementary objects in a system. The scheme is formulated as partial differential equations called kinetic equations for the probability distributions. Kinetic equations have been used in describing polymeric fluid flows [Edwards and Doi, 1986], [Bird et al., 1987], [Larson, 1988], active biological systems [Joanny et al., 2013], [Marchetti et al., 2012], and solid materials. Meanwhile, the kinetics equations of enzymatic cellulose hydrolysis in creating ethanol in green energy has been extensively studied, and many kinetic models have been proposed.

Some of the kinetic models of enzymatic hydrolysis of cellulose take into account several contributing factors such as mixed type of enzymes to enhance the rate of reaction [Fujii and Shimizu, 1986]; [Beltrame et al., 1984]; [Griggs et al., 2012a]; [Fan and Lee, 1983]; [Zhou et al., 2010]; [Okazaki and Moo-Young, 1978], pore size distribution to predict the biomass fraction accessible to degradation [Luterbacher et al., 2013], high solids operation to increase the product concentration [Hodge et al., 2009], the structure of cellulose [Fan and Lee, 1983]; [Griggs et al., 2012a], the distribution of chain lengths [Griggs et al., 2012a]; [Suga et al., 1975], and the negative role of lignin [Zheng et al., 2009]. Most of these works are successful, at least partially, in tracing the complicated cellulose-cellulase system quantitatively. However, most of the kinetic models do not take into account all important features simultaneously.

Griggs et al. [Griggs et al., 2012a] tackled the major factors mentioned in the previous paragraph. Griggs's model incorporates two distinct types of enzyme, which are endoglucanase (endoglucanase I, EG<sub>1</sub>) and exoglucanase (cellobiohydrolase I, CBH<sub>1</sub>). The population-balance equations (PBE) technique is used to describe the changes in cellulose chain length distribution. PBE employs continuous distribution that tracks the evolution of the spectrum of chain lengths. For the cellulose substrate structure, Griggs et al. assumed that there are enzyme-accessible chains and inaccessible interior chains.

In this chapter, we will discuss the theoretical and mathematical developments needed to describe the hydrolysis of insoluble cellulose chains by Griggs et al. [Griggs et al., 2012a]. Their model will be the fundamental base of our study. An understanding of this model provides a deeper understanding, improves predictive capabilities, and ultimately provides more directed and rational approaches for process design and optimization. This is the first step of our study in capturing the most important chemical and physical phenomenon in enzymatic hydrolysis of biomass. Later, in the next chapter, we will explore the mathematical structure of the system and analyze their properties to predict the behavior of the system. We will apply techniques from mathematical analysis and computation to gain insight into the complex problem, which is notably lacking in their paper.

## 2.2 MODEL FORMULATION

## Cellulose depolymerization

Cellulose is an insoluble polymer, composed of repeating units of glucose linked by  $\beta$ -(1,4)-glycosidic bonds with varying degrees of polymerization [Igarashi et al., 2009]. Naturally-occurring cellulosic particles have a wide distribution of chain lengths. The availability of cellulose accessible for enzyme hydrolysis can depend on the chain length [Kleman-Leyer et al., 1996]. The measure of enzyme-accessible cellulose deviates from the total cellulose in a reaction mixture because of the arrangement of cellulose chains in the cellulose particles.

Griggs et al. treated the cellulosic substrates as "populations" of various chain lengths and denoted P(x) as an insoluble cellulose chain comprising of x anhydroglucose units. Here, x is treated as a continuous variable for the sake of simplicity. Suppose p(x,t) is the population distribution of enzyme-accessible cellulose chains (concentration of the unthreaded surface exposed cellulose) of length x at time t in a unit volume, then p(x,t)dx is the number of cellulose chain in the length range (x, x + dx) per unit volume at time t.

With the distribution function p(x,t), one can define the *n*th moment of the distribution function as follows:

$$p^{(n)}(t) = \int_0^\infty x^n p(x, t) dx.$$
 (2.2.1)

The zeroth moment,  $p^{(0)}(t) = \int_0^\infty p(x,t)dx$ , gives the total number of cellulose chains at time t in a unit volume. The first moment,  $p^{(1)}(t) = \int_0^\infty xp(x,t)dx$  is the total number of monomeric glucans comprising the cellulose chains at time t. The numberaveraged chain length is denoted by  $x_N = p^{(1)}/p^{(0)}$ . The mass-averaged chain length is the ratio of the second to first moments  $x_M = p^{(2)}/p^{(1)}$ , where the number density is proportional to the mass of the cellulose chain by assuming the monomeric glucan unit has a constant mass. With this definition; the polydispersity is the ratio of mass-

## Chapter 1

## INTRODUCTION

#### 1.1 BACKGROUND

In recent years, energy crises and environmental pollution have become vital sustainable problems to the human society. Rapid industrialization has increased the demand for oil; however, the energy supply from fossil fuels worldwide is limited and will eventually be depleted. Due to burning of fossil fuels, pollutant emissions have increased. To reduce pollution caused by fossil fuel burnings, one solution is to use renewable energy as an alternative to replace fossil fuels. Renewable energy fields use ethanol, where ethanol is produced from various lignocellulosic biomass, such as palm trees [Hosseini and Wahid, 2012], [Basiron, 2007], corn stover [Griggs et al., 2012a], [Selig et al., 2008], wood, agricultural products, waste, and grasses. Generally, lignocellulosic biomass is composed of lignin, hemicellulose and cellulose [Abnisa et al., 2011].

The production of ethanol from lignocellulosic biomass consists of three fundamental processes; pretreatment, enzymatic hydrolysis, and fermentation [Limayem and Ricke, 2012]. Pretreatment modifies the structure of biomass to make the cellulose more exposed to enzymes for sugar conversion [Himmel et al., 2007]. Enzymatic hydrolysis breaks cellulose chains into sugar such as cellobiose and glucose, whereas fermentation converts sugar into ethanol [Griggs et al., 2012a], [Griggs et al., 2012b], [Bansal et al., 2009]. As a matter of fact, cellulose molecules are locked-in by the lignin-hemicellulose network; therefore, the hydrolysis step is the most crucial part of biomass to ethanol conversion process, in which this project is focused most specifically on. The production cost of cellulosic hydrolysis can be reduced by increasing the concentration of biomass particles. However, lignocellulosic biomass is a suspension of natural fibers, and processing at high solid concentration is a challenging task because it will affect the mixing quality between enzyme and cellulose particles, as well as hydrolysis yield. Thus, understanding factors that affect the rheology of biomass suspension is crucial in order to maximize the production of ethanol at minimum cost.

Lignocellulosic biomass suspension mainly consists of natural fibers. There are various types of shapes, sizes, and material properties of lignocellulosic fibers. According to Roche et. al, fibers in pretreated corn stover have a size of  $(1-2,000 \ \mu m)$  and the aspect ratio is reported to be in the range of 1-20 [Roche et al., 2009a]. There are three types of regimes for biomass suspension. Firstly, for regime with low concentration of fibers, it is known as dilute regime, in which a fiber is free to rotate without having any contact with other fibers. Secondly, when hydrodynamic interaction is dominant over a few physical contacts between fiber, the regime is called semi-dilute regime. The last category is for the concentrated suspensions where fibers cannot rotate freely and the fibers interact by both hydrodynamic and direct contact forces.

In Malaysia, palm oil becomes the main source of biomass to produce renewable energy. Palm oil industry is very important in Malaysia as the country has maintained its position as the world's leading palm oil producing country [Hamisan et al., 2009]. Their main products of palm oil are foods, oleochemicals, biofuels, and renewable energy source. Ongoing research and development of palm biomass by governmental institutions and universities improves process efficiencies [Mohd Basyaruddin et al., 2012], [Aziz et al., 2002], [Hii et al., 2012], [You and Baharin, 2006]. For enzymatic hydrolysis process of palm oil biomass in Malaysia, cellulase (celluclast 1.5 L, Novozymes A/S, Denmark) and cellobiase (Novozyme 188, Novozymes A/S, Denmark) enzymes were tested experimentally [Iberahim et al., 2013].

Empirical models based on experimental outcomes have been applied frequently to study the enzymatic hydrolysis of cellulose, as surveyed in [Bansal et al., 2009]. These models often offer only limited insight into the fundamental mechanisms of enzymatic hydrolysis. On the other hand, a kinetic model for enzymatic hydrolysis offers several advantages. It can provide a deeper understanding, improve predictive capabilities, and in the end provide more directed and rational approaches for process design and optimization [Griggs et al., 2012a].

Initial studies in kinetic models of enzymatic hydrolysis of cellulose indicated that Michaelis-Menten-type kinetics can be used to take account of random and endwise attack of the substrate by three types of enzymes [Okazaki and Moo-Young, 1978]. Since then, the study of kinetic models for this process has undergone several innovations. In 1983, Fan and Lee [Fan and Lee, 1983] added several key factors in their kinetic model, i.e. the structure of cellulose and the nature of enzyme system. Then in 2012, Griggs et al. [Griggs et al., 2012a] adapted Population Balance Equation (PBE), where the model structure leads to a Partial Differential Equation forming a system of integral-differential equations. In their work, biomass particles are represented as monodispersed cylindrical shaped particles comprised of cellulose chains of varied length.

### 1.2 PROBLEM STATEMENT

Lignocellulosic ethanol production is cost sensitive to operation energy and enzyme prices. Most kinetic models have incorporated several major factors such as mixed type of enzymes, pore size distribution, high solid operation, cellulose structure and a distribution of chain lengths. However, these studies have not demonstrated a sufficiently meaningful scale to evaluate the hydrolysis system. Studies on enzymatic

# CHAPTER 3

# MATHEMATICAL ANALYSIS OF A KINETIC MODEL FOR ENZYMATIC CELLULOSE HYDROLYSIS

### 3.1 INTRODUCTION

Biofuel production such as ethanol from lignocellulosic biomass consists of three fundamental processes: pretreatment, enzymatic hydrolysis, and fermentation. Enzymatic hydrolysis uses two types of enzymes simultaneously: endoglucanase I (EG<sub>1</sub>) and cellobiohydrolase I (CBH<sub>1</sub>), to break cellulose chains into sugar in the form of cellobiose or glucose. For cellulose chains of length x, the population balance equation (PBE) governs the behavior of the particle size distribution (PSD), denoted as p(x, t). We studied an established kinetic model proposed by Griggs et al. [Griggs et al., 2012a] for enzymatic hydrolysis of cellulose using the PBE described in Chapter 2.

A number of analytical solutions for a general case of PBE were derived [Patil and Andrews, 1998], [McCoy and Madras, 2001], [Sterling and McCoy, 2001], [J McCoy and Madras, 2003] using Laplace transform on particle size. In the early work of Ziff and McGrady [Ziff and McGrady, 1985], an analytical solution was found by probabilistic (statistical) argument. The PBE system derived by Griggs et al. [Griggs et al., 2012a] does not admit an analytic solution due to its complexity. To solve the system of equations, we may have to resort to numerical methods, which can incur significant computational cost. Our strategy here was to search for reduced order models by ignoring significantly small terms in the governing system of equations. We employed asymptotic analysis for dynamical systems to reduce the complex model to a set of simple equations. The resulting approximate solutions for a simple model may not fully capture all the details of the complex system. However, they usually capture some important characteristics and provide insights into potential dynamical and chemical mechanisms and their dependence on certain parameters. This chapter will present the mathematical analysis for the independent action of  $EG_1$  or  $CBH_1$  from the kinetic model that has been formulated as Model I and Model II, respectively, in Chapter 2. The goal is to ensure that the mathematical results are consistent with the physical requirements.

### 3.2 DIRAC DELTA FUNCTION

Before we go deep into the mathematical analysis of the kinetic model, first we review the concept of Dirac Delta function as it is used in the model analysis. Any function,  $\delta(x)$ , is said to be a delta function if it satisfies three conditions [Mickens, 2004]: (i)  $\int_{-\infty}^{\infty} \delta(x) dx = 1$ , (ii)  $\delta(x) = 0$ , for  $x \neq 0$ , and (iii)  $\int_{-\infty}^{\infty} \delta(x) f(x) dx = f(0)$ . Generally, for arbitrary real a and b,

$$\int_{a}^{b} \delta(x - x_{0}) f(x) dx = \begin{cases} f(x_{0}) & \text{if } x_{0} \text{ belongs to the open interval } (a, b) \\ \frac{1}{2} f(x_{0}) & \text{if } x_{0} = a \text{ or } x_{0} = b \text{ and } a < b \\ 0 & \text{otherwise.} \end{cases}$$
(3.2.1)

We can view this function as a limit of Gaussian,  $\delta(x) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi\sigma}} e^{-x^2/2\sigma^2}$ . The basic properties of the delta function are as follows [Mickens, 2004]:

1. The delta function is even, i.e.,

$$\delta(-x) = \delta(x), \text{ or } \int_{-\infty}^{\infty} \delta(-x) f(x) \, dx = \int_{-\infty}^{\infty} \delta(x) f(x) \, dx. \tag{3.2.2}$$

2.  $\int_{-\infty}^{\infty} \delta(ax) f(x) \, dx = \frac{1}{|a|} \cdot f(0).$ 

- 3.  $\int_{-\infty}^{\infty} \delta(x-a) f(x) \, dx = f(a).$
- 4.  $\int_{\infty}^{\infty} \delta^{(n)}(x) f(x) dx = (-1)^n f^{(n)}(0)$ , where it is assumed that the required derivative of f(x) exist.

# 3.3 Model I (Independent action of $EG_1$ )

In this section, we will focus on studying how random-chain scission by  $EG_1$  changes a population of cellulose chains that has been formulated in (2.4.66):

$$\begin{cases} \frac{d\hat{p}(x,\tau)}{d\tau} &= 0.004\tilde{k}_{h}^{EG}E_{s}^{EG}t_{0}\int_{x}^{\infty}\hat{p}(y,\tau)\,dy - 0.002\tilde{k}_{h}^{EG}E_{s}^{EG}t_{0}x\hat{p}(x,\tau) \\ &-\left(1-\frac{1}{\hat{R}}\right)\frac{p_{i}(x)}{p_{i}^{(1)}}r_{loss}^{(1)}\frac{t_{0}}{p^{(0)}(0)} \\ \frac{d\hat{R}}{d\tau} &= \frac{r_{loss}^{(1)}t_{0}}{2n\pi\rho\hat{R}R_{0}^{2}L}, \quad \hat{R} \ge 1. \end{cases}$$

$$(3.3.3)$$

Let  $t_0 = \frac{1}{\widetilde{k}_h^{EG} p^{(0)}(0)}$ , hence

$$\begin{cases} \frac{d\hat{p}(x,\tau)}{d\tau} &= 0.004 \frac{E_s^{EG}}{p^{(0)}(0)} \int_x^{\infty} \hat{p}(y,\tau) \, dy - 0.002 \frac{E_s^{EG}}{p^{(0)}(0)} x \hat{p}(x,\tau) \\ &- \left(1 - \frac{1}{\hat{R}}\right) \frac{p_i(x)}{p_i^{(1)}} r_{loss}^{(1)} \frac{1}{(p^{(0)}(0))^2 \tilde{k}_h^{EG}} \\ \frac{d\hat{R}}{d\tau} &= \frac{r_{loss}^{(1)}}{2n\pi\rho \hat{R} R_0^2 L} \frac{1}{\tilde{k}_h^{EG} p^{(0)}(0)}, \quad \hat{R} \ge 1. \end{cases}$$
(3.3.4)

The dimensionless parameter groups are listed in Table 3.1. The reduction in the number of parameters makes theoretical manipulations easier, as the equations are less cluttered. By omitting the 'hat' for notational simplicity, we obtained:

Table 3.1Dimensionlessgroups of parameters

Parameter Group
$\widetilde{a} = \frac{E_s^{EG}}{p^{(0)}(0)}$
$\widetilde{b} = rac{p_i}{p_i^{(1)}}$
$\widetilde{c} = -rac{r_{loss}^{(1)}}{\widetilde{k}_{h}^{EG}(p^{(0)}(0))^2}$
$\widetilde{d} = rac{p^{(0)}(0)}{2n\pi ho R_0^2 L}$