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$_1$) and cellobiohydrolase I (CBH$_1$), 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 $b$,

$$\int_{a}^{b} \delta(x-x_0)f(x) \, dx = \begin{cases} f(x_0) & \text{if } x_0 \text{ belongs to the open interval } (a,b) \\ \frac{1}{2}f(x_0) & \text{if } x_0 = a \text{ or } x_0 = b \text{ and } a < b \\ 0 & \text{otherwise.} \end{cases} \quad (3.2.1)$$

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.,

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

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

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

3.3 **MODEL I (INDEPENDENT ACTION OF EG₁)**

In this section, we will focus on studying how random-chain scission by EG₁ changes a population of cellulose chains that has been formulated in (2.4.66):

\[
\begin{align*}
\frac{d\hat{p}(y, \tau)}{dy} &= 0.004 E^E G_t_0 \int_\infty \hat{p}(y, \tau) \, dy - 0.002 E^E G \psi_0(x, \tau) \\
&\quad - \left( 1 - \frac{1}{k_h} \right) \frac{p(x)}{\psi_0} \frac{1}{\psi_0} \psi_0(x, \tau) \\
\frac{d\hat{r}}{d\tau} &= \frac{r_{loss}}{2n_x R L}, \quad \hat{R} \geq 1.
\end{align*}
\]

Let \( t_0 = \frac{1}{k_h} \), hence

\[
\begin{align*}
\frac{d\hat{p}(y, \tau)}{dy} &= 0.004 E^E G \int_\infty \hat{p}(y, \tau) \, dy - 0.002 E^E G \psi_0(x, \tau) \\
&\quad - \left( 1 - \frac{1}{k_h} \right) \frac{p(x)}{\psi_0} \frac{1}{\psi_0} \psi_0(x, \tau) \\
\frac{d\hat{r}}{d\tau} &= \frac{r_{loss}}{2n_x R L}, \quad \hat{R} \geq 1.
\end{align*}
\]

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>
<thead>
<tr>
<th>Parameter Group</th>
<th>Value</th>
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<tbody>
<tr>
<td>( \hat{a} )</td>
<td>( \frac{E^E G}{\psi_0(0)} )</td>
</tr>
<tr>
<td>( \hat{b} )</td>
<td>( \frac{p_0}{\psi_0} )</td>
</tr>
<tr>
<td>( \hat{c} )</td>
<td>( \frac{r_{loss}}{k_h \psi_0(0)} )</td>
</tr>
<tr>
<td>( \hat{d} )</td>
<td>( \frac{\psi_0(0)}{2n_x R L} )</td>
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Table 3.1 Dimensionless groups of parameters

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