Modeling of a Rotary Drum Pyrolyzer

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A thesis submitted in fulfilment of the requirements for the degree of Master of Science in the Chemical Science and Engineering

September 2015
Declaration of Authorship

I, Aekjuthon Phounglamcheik, declare that this thesis titled, 'Modeling of a Rotary Drum Pyrolyzer' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a Master’s degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:
“The science of today is the technology of tomorrow”

Edward Teller
Abstract

Chemical Science and Engineering

Master of Science

Modeling of a Rotary Drum Pyrolyzer

by Aekjuthon Phounglamcheik

This project focuses on the numerical modeling of a rotary kiln pyrolyzer such as found in the e.g. WoodRoll multistage gasification process. The model consists of two parts: a granular flow model, and a pyrolyzer model. In the first part, Saeman's equation was employed to develop a model which can describe the behavior of solid granular flow in a rotary kiln without reaction. Residence-time distribution (RTD) is the main aim to study in this part, which was simulated by axial dispersion model (ADM). The model requires only one fitting parameter that is dispersion coefficient ($D_{ax}$), which was studied in parallel by two cases: constant value of $D_{ax}$, and $D_{ax}$ as a function of kiln's length. The result of both models show good predictable in comparison to experimental data from literature, and represent narrow distribution of residence times that behave similar to plug flow reactor. Unfortunately, the result still cannot claim which model of $D_{ax}$ is the best model to describe RTD in rotary drum. The second part of the thesis purpose to design the model of rotary kiln pyrolyzer, which contains specific behavior of granular flow, heat transport in a kiln, and primary pyrolysis of wood. The model of steady-state condition with constant wall temperature was simulated to generate temperature profile and conversion along a kiln. This model included all heat transport features such as conduction, convection, and radiation. According to the result, supplied energy from outer surface of the kiln essentially transfer through the kiln via heat conduction, which occur between solid bed and rotating surface of the kiln. Temperature profile that generated by this model looks reasonable to the process of rotary kiln pyrolyzer, which affected by heating system and heat of reaction along the kiln. The result also demonstrated that conversion of wood is strongly dependent of wall temperature or heating rate of the system. Nonetheless, kinetics data for wood pyrolysis still a debatable issue in many research, and this model required validation by experiment of rotary kiln pyrolyzer.
I would never have been able to finish my Master thesis without the assist of my supervisor, friends, and my family.

First of all, I would like to express the deepest appreciation to my supervisor; Associate Professor Dr. Matthäus Bäbler, who gave me a chance to work with this incredibly project. He always gave me valuable guidance as the great teacher, and did not give up to my foolishness. He fulfilled my spirit and motivation as my parent, and also work hard with me as my colleague. Without his persistent help this Master thesis would not have been possible.

Secondly, I would like to express my gratitude to Ramiar Sadegh Vaziri, all of his advise about mathematical computation influence my sense of simulation a lot. And give big thanks to Lina Norberg Samuelsson, for her experience of wood pyrolysis and gasification which evaluate the result of this work to be on the right track. Furthermore, I would like to thank Paramvir Ahlawat, who is my reviewer on this thesis: he help me to read my ugly text to improve my communication skills.

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Finally, all of my knowledge and life never have been existed without my beloved family; especially, Colonel Narawadee Kirdjongrak. Love and best care created the person who I am today. Not only for well training, but also mental advises which help me walked through every problems with success and pride.
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# Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>RTD</td>
<td>Residence-Time Distribution</td>
</tr>
<tr>
<td>ADM</td>
<td>Axial Dispersion Model</td>
</tr>
<tr>
<td>MRT</td>
<td>Mean Residence Time</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary Differential Equation</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial Differential Equation</td>
</tr>
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</table>
Physical Constants

Gravitational acceleration  $g = 9.81 \text{ m/s}$

Universal gas constant  $R = 8.314 \text{ J/mol.K}$

Stefan-Boltzman radiation coefficient  $\sigma = 5.57 \times 10^{-8} \text{ W/m}^2\text{K}^4$
Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>cross-sectional area of species $i$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A$</td>
<td>pre-exponential factor</td>
<td>1/s</td>
</tr>
<tr>
<td>$a$</td>
<td>local propagation speed</td>
<td>m/s</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat</td>
<td>J/kg.K</td>
</tr>
<tr>
<td>$D_{ax}$</td>
<td>dispersion coefficient</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_0$</td>
<td>dispersion factor</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle diameter</td>
<td>m</td>
</tr>
<tr>
<td>$E$</td>
<td>emissive power</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$E(t)$</td>
<td>residence-time distribution function</td>
<td>1/s</td>
</tr>
<tr>
<td>$F$</td>
<td>mass flow rate</td>
<td>kg/s</td>
</tr>
<tr>
<td>$Fr$</td>
<td>rotational Froude number</td>
<td>-</td>
</tr>
<tr>
<td>$H_i$</td>
<td>specific enthalpy of species $i$</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h$</td>
<td>bed height</td>
<td>m</td>
</tr>
<tr>
<td>$h_0$</td>
<td>height of discharge dam</td>
<td>m</td>
</tr>
<tr>
<td>$h_i$</td>
<td>heat transfer coefficient of species $i$</td>
<td>W/m$^2$.K</td>
</tr>
<tr>
<td>$h_z$</td>
<td>grid length</td>
<td>m</td>
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<tr>
<td>$J$</td>
<td>radiosity</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate coefficient</td>
<td>1/s</td>
</tr>
<tr>
<td>$k_i$</td>
<td>thermal conduction of species $i$</td>
<td>W/m.K</td>
</tr>
<tr>
<td>$L$</td>
<td>length of a kiln</td>
<td>m</td>
</tr>
<tr>
<td>$m_s$</td>
<td>solid mass flow rate</td>
<td>kg/s</td>
</tr>
<tr>
<td>$n$</td>
<td>rotational speed</td>
<td>rpm</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$P$</td>
<td>total pressure</td>
<td>N/m$^2$</td>
</tr>
<tr>
<td>$q_i$</td>
<td>volumetric flow rate of species i</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>$q'$</td>
<td>heat rate per unit length</td>
<td>J/m.s</td>
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<tr>
<td>$q''$</td>
<td>heat flux</td>
<td>J/m$^2$.s</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of a kiln</td>
<td>m</td>
</tr>
<tr>
<td>$Re_g$</td>
<td>flow Reynolds number</td>
<td>-</td>
</tr>
<tr>
<td>$Re_w$</td>
<td>rotational Reynolds number</td>
<td>-</td>
</tr>
<tr>
<td>$r$</td>
<td>reaction rate (mass basis)</td>
<td>kg/m$^3$.s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$u$</td>
<td>velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$x_t$</td>
<td>tracer mass fraction</td>
<td>-</td>
</tr>
<tr>
<td>$z$</td>
<td>horizontal axis</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_{rxn}$</td>
<td>specific heat of reaction</td>
<td>J/kg</td>
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Greek symbols

<table>
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<th>Description</th>
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<tbody>
<tr>
<td>$\beta$</td>
<td>angle of inclination</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Dirac delta function</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>emissivity</td>
</tr>
<tr>
<td>$\eta$</td>
<td>percent fill of material</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>dynamic angle of repose</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>heat exchanged area per unit length</td>
</tr>
<tr>
<td>$\nu$</td>
<td>stoichiometry coefficient (mass basis)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>bulk density</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>variance of residence time</td>
</tr>
<tr>
<td>$\tau$</td>
<td>mean residence time</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>combined momentum</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>half central angle of sectional solid bed</td>
</tr>
<tr>
<td>$\chi$</td>
<td>thickness of gas film</td>
</tr>
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</table>

Subscripts
Symbols

\begin{align*}
  s & \quad \text{solid} \\
  w & \quad \text{wood} \\
  c & \quad \text{char} \\
  g & \quad \text{gas} \\
  b & \quad \text{solid bed} \\
  ew & \quad \text{exposured wall} \\
  cw & \quad \text{covered wall} \\
  eb & \quad \text{exposured bed} \\
  cb & \quad \text{covered bed}
\end{align*}

Superscripts

\begin{align*}
  c & \quad \text{heat convection} \\
  cd & \quad \text{heat conduction} \\
  r & \quad \text{heat radiation}
\end{align*}
Dedicated to my family, teachers, and friends...
Chapter 1

Introduction

In the last 20 years, driven by concerns of global warming and climate change, Biomass gasification has played an important role to increase the capacity of renewable energy. Furthermore, the price of fossil fuel such as oil and natural gas, which are limited resources, has been significantly increased and are still the main cause of the greenhouse gas emission. In variety types of renewable energy, only biomass can be supplied in the increased amount of energy in the future, when other resources such as wind or solar energy has lower supply than biomass [1]. Moreover, biomass is available at every place around the world and widely distributed over every country, which is a big advantage of it to avoid transportation cost.

Essentially, all different kinds of biomass can be converted by gasification process into synthesis gas or syngas, which generally consist of hydrogen, carbon monoxide, carbon dioxide, and methane. This syngas is the main feedstock to produce fuels and many downstream chemicals, for example, Fischer-Tropsch diesel, dimethyl ether, methanol, and methane. In principle, gasification of biomass is mainly performed by partial oxidation of the carbon inside the biomass at high temperature condition with controlled amount of an oxidant, which is typically air, pure oxygen, or steam. The quality of product gas depends on the biomass feedstock, type of oxidant, gasifier type, and process conditions that affect to syngas composition and its heating value [1].

Currently, many research groups are working over syngas cleaning topic, because most of syngas applications require high purity of the gas; especially, catalytic reactions and fuel cells. Fly ash particles and tar are the main impurity of syngas, while sulfur compounds, hydrogen chloride, ammonia, and alkalines are the other impurities that have to be released before downstream processes. In biomass gasification, tar formation
can be a cause of clogging of process equipment at lower temperature because of tar condensation, and remaining of tar in syngas also lead to lower the heating value and yield. Therefore, advance concept of biomass gasification has developed to reduce tar content of syngas.

Another problem of gasification technique is that the traditional gasification consists of various overlapping process steps, such as heating, drying, pyrolysis, partial oxidation, and gasification, inside one-stage reactor. As all these steps take place simultaneously in a single reactor environment, it is not possible to control and optimize each step separately in a gasifier [1]. Likewise, interaction between char and volatiles can result negative impact on the reactivity and gasification of the char, which recommend absence of the volatiles during char gasification [2].

In order to solve this problem, one of modern advanced gasification concept called “multi-stage gasification” is introduced, which is a combination of pyrolysis and gasification. This concept separates the pyrolysis and gasification steps in individual controlled stages in reactor system, aims to operate each stage under optimized operating conditions and achieve high purity syngas with relatively low level of tar [1]. In the multi-stage gasification system, tar vapors are generated in pyrolysis reactor (around 600°C), and then are cracked to simple molecules by gasifier at high temperature (1000-1200°C) [1][3].

Nowadayas, there are several developed multi-stage gasification processes. For instance, 75 kW two-stage process Viking gasifier developed by Danish Technical University [4], three-stage gasification FLETGAS process developed at the University of Sevilla [5], two-stage gasifier of LT-CFB gasification process by Dong Energy Company from Denmark [1], and etc. Produced syngas from these processes were reported impressive low tar content, for example Viking gasifier could lower tar content in the produced gas to less than 15 mg/mN³ [1] or around 30 times less than the gas that obtained from single fixed bed downdraft gasifier [6].

Recently, there is a new process of the multi-stage gasification called “WoodRoll® process”, which was developed by Cortus AB in Sweden [7]. The process is 3-stages gasification that consists of separated dryer, pyrolyzer, and gasifier as represent in Figure 1.1. In order to produce cleaned syngas, uniformed size of biomass will be fed into the dryer to lower humidity in the biomass. Then, dried biomass is treated in a rotary drum pyrolyzer to generate solid char and pyrolysis gas that supply the gasifier in the next step. In pyrolysis step the reactor were constantly kept temperature
around 360 to 400°C [7][8]. For the gasifier, heat is supplied by the pyrolysis gas from the pyrolyzer to generate very high temperature, around 1000°C [7][8], in order to transform the solid char into synthesis gas. In the gasifier, steam is used as an oxidant. Because of very high temperature in the gasifier which reach to the optimum condition of it, the produced syngas is expected to have very low tar content and other impurities, as also included in Figure 1.1. Therefore, synthesis gas from the WoodRoll® process can be directly used without cleaning stage.

According to the WoodRoll® process, the pyrolyzer is the main energy source of the process. Because, the pyrolysis gas from this unit will be supplied as heating fuel to either dryer or gasifier. In addition, the unique of this technology of multi-stage gasification is that rotary drum reactor was employed to apply as the unit of pyrolyzer, which is different from the previous processes and can be developed or possible to increase the capacity to be an industrial scale.

Therefore, behavior of the materials inside the rotary drum pyrolyzer is necessary to understand and predict the behavior of the unit. In order to upgrade performance of the WoodRoll® process, model of rotary drum pyrolyzer must be developed, which can be represented to describe the behavior of rotary drum pyrolyzer and also use to predict the results in different operating conditions of the reactor.
Chapter 1. Introduction

1.1 Aims and Objectives

From the motivation, the aim of this Master thesis is to develop a numerical model of a rotary drum pyrolyzer. Where, the model focuses on the behavior of solid mass flow through a rotary drum in axial direction, which is applied the dispersion model from reaction engineering, in particular to simulate the residence-time distribution of granular solid inside a drum.

Furthermore, temperature profile inside a rotary drum pyrolyzer is an important factor to control the conversion of biomass to pyrolysis products. Hence, heat transfer model is needed to study and derive to formulate the numerical model of rotary drum pyrolyzer.

Nevertheless, the model will focuses only on pyrolyzer unit of multi-stage gasification in particular to the idea of WoodRoll® process, neither dryer nor gasifier are concerned. Rotary drum reactor is considered without internal structure i.e., a so-called unflighted rotary drum. Likewise, the model mainly considers variation in axial dimension of the rotary drum only, while radial conditions are assumed to be homogeneous.

1.2 Historical Perspective of Rotary Drum

Rotary drum or rotary kiln reactor have long history of applications since it was employed to play role in cement production. Currently, rotary kilns are involved by many industrial processes; for example, reduction of iron oxide, calcining of petroleum coke, reclamation of hydrated lime, drying, waste incineration and so on. These widespread usages of the rotary kiln were obtained from the ability to handle varied feedstock, which can be applied to broad in particle size or whose physical properties change significantly during processing [9]. Moreover, rotary kiln has ability to maintain unique environments that is not easily achieved by other reactors, such as oxidizing freeboard which can reduce conditions within the bed coexisting [10].

Nonetheless, the process of rotary kiln reactor is not standing without any problems. Rotary kiln require to concern about thermal efficiency and product quality. Even though, the long period of residence time of granular solid within the kiln (typically greater than one hour) assists to receive acceptably uniform product, there is some perspective to improving the kiln performance. To success this improvement, understanding of transport phenomena of granular flow within the kiln is necessary.
Chapter 1. Introduction

The general concept of rotary drum reactor is basically developed from tubular reactor which include inclination and rotation. Material in the kiln can be heated by two different techniques: internal heating, and external heating. For the internally heated rotary kiln, solid material will be received energy by contacting with hot gas that is fed into the kiln, normally counter-current flow. This type of heating technique usually apply for metallurgical processes. While, externally heating technique use the idea of energy supply via the wall shell or internal structure of the rotary kiln. Because of the later technique is indirect heating, application of the process such as pyrolysis or gasification are very useful.

Figure 1.2 represents an example of externally heated rotary kiln for niche applications. In addition, special feature of this type of heating technique in rotary kiln is possible to use multiple heat zones, which electrical heating or gas fired can be applied individually.

Figure 1.2: Schematic of an externally heated rotary kiln [10]

1.3 State of Art

1.3.1 Pyrolysis in Rotary Kiln Reactor

The basic principle of rotary drum pyrolyzer can be illustrated as Figure 1.3. In the beginning, uniform size of biomass will be fed into the kiln, which control rotational speed and inclination. During the process, biomass will travel through the moving
path and receive energy from the kiln’s wall. When the temperature of biomass reach to pyrolysis temperature, pyrolysis gas, char, and tar will be produced.

![Configuration of rotary kiln pyrolyzer](image)

**Figure 1.3:** Configuration of rotary kiln pyrolyzer

According to literature review, rotary kiln reactor is a wide applicable reactor in the field of pyrolysis. For instance, coal pyrolysis [11], oil sludge pyrolysis [12], pyrolysis of olive pits [13], pyrolysis of recycled aluminum waste [14], and pyrolysis of maize [15] have been reported to run in a rotary kiln. Because, the residence time of feedstock in the rotary kiln reactor can be easily controlled to provide optimum heat transfer for the pyrolysis reaction, and the process is flexible in order to adjust operating conditions. Moreover, temperature profile of the kiln can be set by using of different heating zone by individual controlling [16].

Notwithstanding, most of researches on rotary kiln pyrolyzer are apply to non-biomass feedstock, but studies of biomass pyrolysis in rotary kiln reactor are relatively rare. So, this is the reason to push this Master thesis focusing on pyrolysis of biomass in rotary kiln.

### 1.3.2 Study of Residence Time Distribution in Rotary Kiln

As mention before, the factor that is important role in the process of rotary kiln pyrolyzer is residence-time distribution of granular solid. Because, residence-time distribution of solid is the main factor to control performance of heat transfer inside rotary kiln, which affect to kinetics rate of reaction. Thus, modeling of residence time distribution for granular solid in the rotary kiln is the first part of this thesis. In the second part, the residence time model is combined with a model for heat transfer and the pyrolysis reaction, which allows for simulating the rotary drum pyrolyzer.
1.4 Structure of the Report

This report of Master thesis start with introduction part in Chapter 1, and then it is divided to two parts. The first part is granular flow and residence time distribution in a rotary kiln, which consists of 3 chapters: modeling of granular flow in a kiln (Chapter 2), simulation scheme of ADM (Chapter 3), and result of granular flow and RTD (Chapter 4). In the second part of this report, modeling of rotary kiln pyrolyzer that includes granular flow, heat transport, and pyrolysis reaction will be discussed. Chapter 5 is provided for rotary kiln pyrolyzer modeling, and the result of this part will be established in Chapter 6. Finally, conclusion of this Master thesis will be placed in Chapter 7.
Part I

Granular Flow and RTD in a Rotary Kiln
Chapter 2

Modeling of Granular Flow in a Kiln

In this chapter, solid granular flow within rotary kiln in axial direction will be studied in order to predict behavior of solid bed along the length of the kiln. Therefore, granular flow model would be developed to describe the behavior of solid bed inside a kiln, such as bed height, velocity profile, mean residence time and so on. Not only the bed behavior will be achieved from the model in this chapter, but also residence-time distribution which is the crucial information to identify performance of rotary kiln will be demonstrated.

Generally, flow characteristic or transverse motion of rotary kiln can be categorized into 6 different patterns: slipping, slumping, rolling, cascading, cataracting, and centrifuging, which are represented in Figure 2.1. The flow pattern in rotary kiln depends strongly on kiln’s rotational speed and material properties of solid bed. Correlation between rotational speed and type of flow characteristic can be obtained via the rotational Froude number [17], defined as

\[ Fr = \frac{n^2 R}{g} \]  

(2.1)

Where, \( n \) is rotational speed, \( R \) is radius of rotary kiln, and \( g \) is gravitational acceleration. The table in Figure 2.1 is the range of Froude number in each type of flow patterns for the angle of repose of solid material at 35°. The latter is the solid material parameter in this classification of flow patterns. So, given rotational speed and angle of repose can predict type of flow pattern within a rotary kiln.
In among of these flow patterns, *rolling mode* is the condition that mixing in rotary drum reach to maximum. Likewise, the rolling mode has a steady discharge of granular solid from one side to another side of transverse plane, and the angle of repose remain constant. As a consequence, industrial rotary kiln usually prefer to operate at the rolling mode condition. Thus, model of axial granular flow in a rotary kiln will be developed according to the case of rolling flow pattern in cross-sectional plane of rotary kiln.

### 2.1 Model Development

#### 2.1.1 Granular Flow in Axial Direction

The model to describe axial granular flow of solid bed in a rotary kiln was derived from the idea of particle motion in the bed, as represented schematically in Figure 2.2.

In the rolling mode of rotary kiln, granular particles beneath the bed surface layer rotates as a rigid body in the radial direction with rotational speed of the kiln. When the particle transport from bottom of the bed to reach the top surface layer, it falls...
under gravity from the upper to some lower point of the bed surface with a short axial direction, and repeat as a cycle. From this geometry, Saeman (1951) \cite{20} derived an equation to approximate granular bed depth profile in rotary kiln. Saeman’s model is given by this equation

\[
\frac{dh}{dz} = -\frac{3\tan \Theta m_s}{4\pi n \rho_s} \left[ R^2 - (R - h)^2 \right]^{-3/2} + \frac{\tan \beta}{\cos \Theta}
\] (2.2)

Where, \( m_s \) is mass flow rate of solid, \( \rho_s \) is bulk density of the bed, \( n \) is rotational speed, \( R \) is kiln radius, \( \beta \) is inclination of the kiln, and \( \Theta \) is dynamic angle of repose of solid bed, according to Figure 2.3. The boundary condition is given by depth of solid bed at the exit of a kiln, which is height of discharge dam such as

\[
h(z = L) = h_0
\] (2.3)

In case of a kiln without discharge dam, the bed depth at the exit can be assumed equal to mean particle size of solid, i.e. \( h(z = L) = d_p \), in order to avoid singularity in calculation.

Nevertheless, the Saeman’s model can be accurately expressed behavior of granular flow in rotary kiln when the kiln have heavy load, or the fractionally cross-sectional fill of solid bed exceed 5 percent, approximately \cite{10}.

In addition, the Saeman’s equation was checked for its stability by analyzing the right hand side of Equation (2.2) as a function of the bed height \( h \). Figure 2.4 shows the right hand side of Equation (2.2) for a set of typical parameter values. As can be seen, for the given parameter values, the right hand side of Equation (2.2) has a root at \( h^* = 0.0181 \) m, i.e. \( \frac{dh}{dz} \bigg|_{h^*} = 0 \). Also, we notice that the slope of \( \frac{dh}{dz} \) at \( h^* \) is positive. This implies that the Saeman’s equation is an unstable ordinary differential equation. So,
the depth profile of granular bed that is calculated from the model will not be constant along the length axis in any cases.
According to the bed depth profile, cross sectional area of granular bed $A_s$ as a function of bed depth can be calculated by segment area of circle

$$A_s(h) = R^2 \cos^{-1}(\frac{R - h}{R}) - (R - h)\sqrt{2Rh - h^2}$$  \hspace{1cm} (2.4)$$

From constant volumetric flow rate of solid ($q_s$) and cross sectional area from Equation (2.4), granular velocity profile along the bed, $u(z) = q_s/A_s(h(z))$, can be directly computed. Furthermore, the mean residence time of granular transport through a kiln can be expressed as

$$\tau = \frac{V_{bed}}{q_s} = \frac{1}{q_s} \int_0^L A_s(z)dz$$  \hspace{1cm} (2.5)$$

Where, $V_{bed}$ is the total bed volume.

### 2.1.2 Axial Dispersion Model

In this thesis, the axial dispersion of tubular reactor was employed to describe behavior of granular flow in rotary kiln, i.e. residence time distribution. Figure 2.5 represents a model structure of an unflighted rotary kiln with length $L$ and diameter $D$, which is fed with continuous solid mass flow rate $m_s$.

![Figure 2.5: Model structure of the unflight rotary kiln](image)

In particular to derive the axial dispersion model (ADM) of rotary kiln, a differential element $\Delta z$ in the reactor is built. Mass balance of solid over element $\Delta z$ without reaction is given as

$$\text{Now} - \text{Before} = \text{In} - \text{Out}$$

$$\Delta z A_s \rho_s \bigg|_{z,t+\Delta t} - \Delta z A_s \rho_s \bigg|_{z,t} = \Delta t F_s \bigg|_{z,t} - \Delta t F_s \bigg|_{z+\Delta z,t}$$  \hspace{1cm} (2.6)$$
Divide Equation (2.6) by $\Delta z \Delta t$, and taking the limit $\Delta z, \Delta t \rightarrow 0$ the equation will become

$$\frac{A_s \rho_s |_{z,t+\Delta t} - A_s \rho_s |_{z,t}}{\Delta t} = \frac{F_s |_{z,t} - F_s |_{z+\Delta z,t}}{\Delta z}$$  \hspace{1cm} (2.7)

$$\frac{\partial}{\partial t} (A_s \rho_s) = -\frac{\partial F_s}{\partial z}$$  \hspace{1cm} (2.8)

From Fick’s law of diffusion, mass flow rate ($F_s$) is written as

$$F_s = u_s A_s \rho_s - D_{ax} \frac{\partial}{\partial z} (A_s \rho_s)$$  \hspace{1cm} (2.9)

Where, $u_s$, $A_s$, $\rho_s$, and $D_{ax}$ are the solid velocity ($m/s$), cross-sectional area of the bed ($m^2$), bulk density of solid bed ($kg/m^3$), and axial dispersion coefficient ($m^2/s$), respectively.

By substitution of Equation (2.9) into Equation (2.8), the equation will be given as

$$\frac{\partial}{\partial t} (A_s \rho_s) = \frac{\partial}{\partial z} \left( D_{ax} \frac{\partial}{\partial z} (A_s \rho_s) \right) - \frac{\partial}{\partial z} (u_s A_s \rho_s)$$  \hspace{1cm} (2.10)

To simplify the model, the bulk density of solid bed ($\rho_s$) will be considered as constant within the model, and the equation will become

$$\frac{\partial A_s}{\partial t} = \frac{\partial}{\partial z} \left( D_{ax} \frac{\partial A_s}{\partial z} \right) - \frac{\partial}{\partial z} (u_s A_s)$$  \hspace{1cm} (2.11)

Equation (2.11) is essentially a relation to describe the bed cross section area $A_s(t, z)$ in time and space.

In order to develop model to compute residence-time distribution of solid, tracer mass fraction, $x_t$, is introduced into Equation (2.11), and the final form of the axial dispersion equation is given as

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left( D_{ax} \frac{\partial \psi}{\partial z} \right) - \frac{\partial}{\partial z} (u_s \psi)$$  \hspace{1cm} (2.12)

Where, $\psi = x_t A_s$ is propotional to the amount of tracer.

An initial condition of the model depends on the selected method of tracer measurement, which will be explained later in Section 2.2. While, the Danckwerts boundary conditions [21] are applied for Equation (2.12) as show in Equation (2.13) and (2.14).
At $z = 0$,
\[
\psi(0, t) = \psi_f(t) = \psi |_{z=0} - D_{ax} \frac{\partial \psi}{\partial z} |_{z=0}
\]  \hfill (2.13)

At $z = L$,
\[
\frac{\partial \psi}{\partial z} = 0
\]  \hfill (2.14)

As explain above, Equation (2.12) can be used to simulate residence-time distribution of granular particle inside tubular reactor. Whereas, rotary kiln reactor has a unique flow characteristic, which is different from tubular reactor. Consequently, in order to produce accurately result of residence-time distribution for rotary kiln, the unique parameters of a kiln must be implemented to fulfill the ADM.

### 2.1.3 Correlation of Saeman’s consequence to ADM

According to the axial dispersion model, Equation (2.12), consists of three space-dependent parameters in the equation, such as $A_s(z)$, $u_s(z)$, and $D_{ax}(z)$, and these three parameters are based on the geometry of the rotary kiln and material properties. Therefore, the parameters can be obtained from granular bed profile of Saeman’s expression as discussed in the Section 2.1.1.

From the Saeman’s expression, cross-sectional area of the bed, $A_s(z)$, can directly be calculated from Equation (2.4), and the calculation of bed velocity $u_s(z)$ is also obtained. But, the term of dispersion coefficient, $D_{ax}(z)$, is not obviously appear in the Saeman’s expression. However, if we simplify the Equation (2.11) with operating condition of rotary kiln according to the Saeman’s model, such as steady-state and constant volumetric flow rate ($q_s = u_s A_s$), the dispersion equation will be written as

\[
\frac{\partial}{\partial z} \left( D_{ax} \frac{\partial A_s}{\partial z} \right) = 0
\]  \hfill (2.15)

After integration of Equation (2.15), dispersion coefficient for rotary kiln model can be expressed as Equation (2.16) below

\[
D_{ax} = (D_0) \left| \frac{dA_s}{dz} \right|^{-1}
\]  \hfill (2.16)
Where, $D_0$ is dispersion factor that is fitted by experiment, and $\left| \frac{dA_s}{dh} \right|$ is obtained by the chain rule, $\left| \frac{dA_s}{dz} \right|$. In the latter, the differential of cross-sectional area, by bed height is obtained from Equation (2.4) as the following equation

$$\frac{dA_s}{dh} = (2Rh - h^2)^{1/2} - R(1 - (1 - \frac{h}{R})^2)^{-1/2} - (R - h)^2(2Rh - h^2)^{-1/2}$$

(2.17)

While, the differential $\frac{dh}{dz}$ is given by Saeman’s model, Equation (2.2). The example result of the space-dependent parameters of rotary kiln from the Saeman’s model are shown in the Figure 2.6, which can be observed trend of each parameters in the kiln. According to the figure, dispersion coefficient, $D_{ax}(z)$, from the Saeman’s model (Equation(2.16)) is decreasing along the length of the bed. This effect is a result from the absolute slope of cross-sectional area of the granular bed in the kiln.

Hence, in order to study residence-time distribution of rotary kiln, Equation (2.12) can be solved numerically by plugging in the parameters $A_s(z)$, $u_s(z)$, and $D_{ax}(z)$, which are obtained from the Saeman’s expression.

However, in this study the axial dispersion model with $D_{ax}(z)$ from the Saeman’s consequence have been developed in parallel with the axial dispersion model with constant $D_{ax}$. In case of the model with constant dispersion coefficient is identified as constant axial dispersion model, as show in Equation (2.18). While, the model with $D_{ax}(z)$ is named as refined axial dispersion model, as represent in Equation (2.19).

**Constant axial dispersion model**:

$$\frac{\partial \psi}{\partial t} = D_{ax} \frac{\partial^2 \psi}{\partial z^2} - \frac{\partial}{\partial z} (u_s \psi)$$

(2.18)

**Refined axial dispersion model**:

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left( D_{ax} \frac{\partial \psi}{\partial z} \right) - \frac{\partial}{\partial z} (u_s \psi)$$

(2.19)

### 2.2 Distribution of Residence Times in Rotary Kiln

Generally, the residence-time distribution (RTD) of reactor is one important characteristic of mixing inside chemical reactor, which can demonstrates time spending of each material elements in the reactor. Main purpose to observe times distribution of
each elements is because RTD can be benefit to design the reactor and can essentially affect to reaction performance of the reactor.

In practice, the distribution of residence times can be examined by injecting of inert material – tracer – into the reactor at some appropriate time and measure its concentration at the outlet flow. There are two basic methods of tracer experiment to measure RTD of the reactor, which are called pulse tracer and step tracer.

In case of pulse tracer method, an amount of tracer is instantaneously injected in a shot
to the feed stream of the reactor in very short time. Then, the tracer concentration is measured as a function of time, and RTD can be obtained. On another hand, step tracer use the method of RTD measurement by using constant rate of tracer injection during the measurement. So, the result of RTD measurements from two methods will be difference, as illustrate in Figure 2.7 [22].

![Figure 2.7: Methods of RTD measurement [22]](image)

Clearly, the two responses from the two methods are related to each other and the pulse response is readily translated into the step response, and vice-versa. This study is employed pulse tracer method to evaluate the result of residence-time distribution in the rotary kiln reactor. Therefore, all calculation of RTD in simulation and experiment are based on the theory of pulse tracer measurement. In part of simulation, the Dirac delta function is introduced to represent as a perfect pulse input. As a consequence, the initial condition of the axial dispersion model (Equation (2.12)) can be expressed as

\[
\psi(t = 0, z) = \psi_0 = \delta(0) \tag{2.20}
\]

where, \(\delta(0)\) is the Dirac delta function.
2.2.1 Calculation of RTD by Pulse Tracer method

The measurement of residence-time distribution in pulse tracer method is normally represented in the quantity of $E(t)$, which is called the residence-time distribution function. This function describes how much time different that particles spend in the reactor, and $E(t)$ can be defined as [22]

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt}$$  \hspace{1cm} (2.21)

Where, $C(t)$ is concentration, or mass fraction of tracer that leaves the reactor at time $t$. With respect to Equaiton (2.18) and (2.19), $C(t)$ corresponds to $\psi(t, z)$ evaluated at $z = L$.

The second function of RTD is mean residence time or average residence time, $\tau$, which can be calculated by [22]

$$\tau = \int_0^\infty tE(t)dt$$  \hspace{1cm} (2.22)

Another important function to measure and compare RTD is variance, or square of the standard deviation, $\sigma^2$. This function can be used to indicate the spread of the time distribution, the larger value is the larger in a distribution’s spread. Likewise, this function will be used to fit the values of dispersion coefficient $D_{ax}$ for the constant ADM and refined ADM, respectively. The variance is defined by

$$\sigma^2 = \int_0^\infty (t - \tau)^2E(t)dt$$  \hspace{1cm} (2.23)

2.2.2 Techniques of RTD Measurement in Rotary Kiln

According to experimental techniques in literature, RTD of granular particles in rotary kiln can be measured by many techniques. For example, in the study from Sai [23] to measure residence-time distribution of sand in rotary kiln, he introduced the tracer as colored sand to separate the tracer from the bulk sand particles, which is very simple measurement of RTD. Not only colored particles technique is useful to measure RTD in the literature, but RTD can also be measured by using other kind of tracer, such as using of different particle shape, and special compound. From Sheehan et al. [24], lithium chloride (LiCl) was injected to rotary kiln as tracer to measure RTD of
zinc solids in the kiln. The outlet concentration of lithium were determined by using inductively coupled plasma mass spectrometry (ICP-MS).

In Table 2.1, shows the experiment of RTD measurement in rotary kiln from the literature, which is useful in order to validate the model of axial dispersion.

**Table 2.1:** Experiment of RTD measurement in rotary kiln

<table>
<thead>
<tr>
<th>Reference</th>
<th>Diameter (m)</th>
<th>Internal structure</th>
<th>Materials</th>
<th>RTD measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheehan et al. (2014) [24]</td>
<td>3.9</td>
<td>Flight + Unflight</td>
<td>Zinc solid/</td>
<td>Pulse tracer by LiCl</td>
</tr>
<tr>
<td>Sai (2013) [23]</td>
<td>0.122</td>
<td>Unflight</td>
<td>Sand</td>
<td>Pulse tracer by colored sand</td>
</tr>
<tr>
<td>Gao et al. (2013) [25]</td>
<td>0.15</td>
<td>Unflight</td>
<td>Alumina particle</td>
<td>Pulse tracer by different shaped material</td>
</tr>
<tr>
<td>Bensmann et al. (2010) [26]</td>
<td>0.32</td>
<td>Unflight</td>
<td>Quartz sand</td>
<td>Pulse tracer by colored material</td>
</tr>
<tr>
<td>Desideri et al (2007) [27]</td>
<td>0.319</td>
<td>Unflight</td>
<td>Pellet, wood chips</td>
<td>Pulse tracer by different shaped material</td>
</tr>
<tr>
<td>Li et al (2002) [28]</td>
<td>0.3</td>
<td>Flight</td>
<td>MSW, sand</td>
<td>Pulse tracer by dyed shaped of wood chips, paper plates, and waste tyre</td>
</tr>
</tbody>
</table>
Chapter 3

Simulation scheme of ADM

According to Chapter 2, the axial dispersion model, which was developed to predict residence-time distribution of granular solid within rotary kiln, is a partial-differential equation (PDE). Consequently, producing of analytical solution is very complex and sacrifice too much time. Hence, numerical simulation is the better choice to solve the model of axial dispersion.

From the past until now, the method of lines is one of popular solution to solve the system of PDE. However, there is the new alternative method to solve PDE which called ”finite volume method”. Which observed in many computational researches, the finite volume method have succeed very well and produced more accurate result than the method of lines [29]. Therefore, the numerical simulation in this thesis employed the finite volume method to generate the result of residence time distribution from the equation of axial dispersion model.

In this chapter, simulation model of the axial dispersion equation, which is derived from either method of lines or finite volume method will be explained step by step. Then, comparison of calculation performance between method of lines and finite volume method will be illustrated. At the end of this chapter, the simulation procedure of the rotary kiln axial dispersion models derived in the previous section will be described as well as input parameters that use to study in this thesis.
3.1 Derivation of Simulation Model

The rotary kiln axial dispersion model derived in the previous section and given by Equation (2.18) and (2.19) resemble the dispersion model of a tubular reactor. Hence, for the derivation of the numerical scheme presented here, we consider a well-known model for a tubular reactor. The model for a tubular reactor consists of constant bed velocity \( u_s \) and constant dispersion coefficient \( D_{ax} \). Therefore, the axial dispersion model of tubular reactor can be written as

\[
\frac{\partial \psi}{\partial t} = D_{ax} \frac{\partial^2 \psi}{\partial z^2} - u_s \frac{\partial \psi}{\partial z} \tag{3.1}
\]

Where, initial condition and boundary conditions are represent by Equation (2.20), (2.13), and (2.14) respectively.

3.1.1 Method of Lines

The idea of the method of lines is based on finite difference method, which can be applied to solve numerical solution of time-dependent PDEs. In this method, the space derivative terms \( \frac{\partial}{\partial z} \) are discretized, whereas the time derivative term \( \frac{\partial}{\partial t} \) are kept with the original form. This method can be also called semi-discretization [30].

According to the method of lines, the space derivatives will be discretized by these following equations

\[
\frac{\partial \psi}{\partial z} = \frac{\psi_{i+1} - \psi_i}{h_z} \tag{3.2}
\]

\[
\frac{\partial^2 \psi}{\partial z^2} = \frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{h_z^2} \tag{3.3}
\]

Where, \( \psi_i = \psi(z_i) \) and \( z_i \) is the grid-point.

Thus, the Equation (3.1) will be changed to discretized form as Equation (3.4).

\[
\frac{d\psi_i(t)}{dt} = D_{ax} \left[ \frac{\psi_{i+1}(t) - 2\psi_i(t) + \psi_{i-1}(t)}{h_z^2} \right] - u_s \left[ \frac{\psi_{i+1}(t) - \psi_i(t)}{h_z} \right] \tag{3.4}
\]

The initial of the original PDE dictate the initial condition for Equation (3.4), i.e. \( \psi_i(0) = \psi_0(z_i) \), and \( i = 1, 2, ..., N \). Figure 3.1 illustrates the lines of definition for the solution.
For $i = 1$ and $i = N$ Equation (3.4) can be written as

\[
\frac{d\psi_1(t)}{dt} = D_{ax} \left[ \frac{\psi_2(t) - 2\psi_1(t) + \alpha(t)}{h_z^2} \right] - u_s \left[ \frac{\psi_2(t) - \psi_1(t)}{h_z} \right] \tag{3.5}
\]

\[
\frac{d\psi_N(t)}{dt} = D_{ax} \left[ \frac{\beta(t) - 2\psi_N(t) + \psi_{N-1}(t)}{h_z^2} \right] - u_s \left[ \frac{\beta(t) - \psi_N(t)}{h_z} \right] \tag{3.6}
\]

Where, $\alpha(t)$ and $\beta(t)$ are functions reflecting the boundary conditions of the original PDE. According to the Danckwerts boundary conditions, $\alpha(t)$ and $\beta(t)$ can be expressed as Equation (3.7) and (3.8), respectively.

\[
\alpha(t) = \psi_2(t) + \frac{2h_z}{D_{ax}}(\psi_F(t) - \psi_1(t)) \tag{3.7}
\]

\[
\beta(t) = \psi_N \tag{3.8}
\]

From above, the ODEs Equation (3.4) to (3.8) can be written in matrix form

\[
\frac{d\psi}{dt} = A\psi + b(t), \quad \psi(0) = \psi_0 \tag{3.9}
\]

Where, $A$ and $b$ are the matrices of the coefficients. In case of pulse tracer modeling, $\psi_0$ will be set to pulse response $\delta(0)$, and $\psi_F(t)$ will be equal to zero. Consequently, $\psi(z, t)$ can be numerically solved by mathematical program, i.e. MATLAB.
3.1.2 Finite-Volume method

For the derivation of the finite volume scheme, let us re-write Equation (3.1) in the form of a conservation law

$$\frac{\partial \psi}{\partial t} = \frac{\partial F(\psi)}{\partial z} \quad (3.10)$$

Where, $F(\psi) = u_s \psi - D_{ax} \frac{\partial \psi}{\partial z}$ is the flux.

To compute the axial dispersion model via the finite-volume method, we apply the conservation law over the control volume according to Figure 2.5 [29], which will give the result as

$$\int_V \frac{\partial \psi}{\partial t} dV = - \int_S \bar{n} F dS \quad (3.11)$$

Where, $V$ is volume of the considered control volume, $S$ is its surface area, $\bar{n}$ is outward unit normal to surface $S$, and $F$ is the flux term including both convective ($f$) and diffusive ($J$) parts.

$$F = f + J \quad (3.12)$$

In this case, $\psi$ is not a function of volume, and $F_s$ is not a function of surface area. Hence, $\psi$ and $F_s$ can be taken outside of the integrals, and the equation will become

$$\frac{\partial \psi}{\partial t} = -\frac{A_s}{V} F \quad (3.13)$$

According to the illustration in Figure 3.2, which represents an implementation of the conservation law over a fixed control volume. So, Equation (3.13) will be expressed as

$$\frac{\partial \psi_i}{\partial t} = -\frac{1}{\Delta z} F_{j-1/2} - F_{j+1/2} \quad (3.14)$$

where

$$F_{j-1/2} = f_{j-1/2} + J_{j-1/2} \quad (3.15)$$
$$F_{j+1/2} = f_{j+1/2} + J_{j+1/2} \quad (3.16)$$

For the diffusive flux, Fick’s law can be employed to express as Equation (3.17), and reduce to discretized form as Equation (3.18) and (3.19).

$$J = -D_{ax} \frac{\partial \psi}{\partial z} \quad (3.17)$$
Figure 3.2: Implementation of the conservation law over a fixed control volume

\[ J_{j-1/2} = -D_{ax} \frac{\psi_j - \psi_{j-1}}{\Delta z} \] (3.18)

\[ J_{j+1/2} = -D_{ax} \frac{\psi_{j+1} - \psi_j}{\Delta z} \] (3.19)

According to Kurganov and Tadmor [31], the terms of convective flux are recommended to

\[ f_{j-1/2} = \frac{1}{2} \left[ f(\psi_{R,j-1/2}) + f(\psi_{L,j-1/2}) - a_{j-1/2} (\psi_{R,j-1/2} - \psi_{L,j-1/2}) \right] \] (3.20)

\[ f_{j+1/2} = \frac{1}{2} \left[ f(\psi_{R,j+1/2}) + f(\psi_{L,j+1/2}) - a_{j+1/2} (\psi_{R,j+1/2} - \psi_{L,j+1/2}) \right] \] (3.21)

where \( a \) is the local propagation speed, and

\[ \psi_{L,j-1/2} = \psi_{j-1} + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1}) \]

\[ \psi_{R,j-1/2} = \psi_j - 0.5\phi(r_j)(\psi_{j+1} - \psi_j) \] (3.22)

\[ \psi_{L,j+1/2} = \psi_{j+1} + 0.5\phi(r_j)(\psi_{j+1} - \psi_j) \]

\[ \psi_{R,j+1/2} = \psi_{j+1} - 0.5\phi(r_{j+1})(\psi_{j+2} - \psi_{j+1}) \] (3.23)

For Equation (3.22) and (3.23), the term of \( \phi(r) \) is represented for a function of flux limiter, which is guarantee total variation diminishing compliance. The flux limiter will force the function to calculate in stable and accurate area, it is a sole function of consecutive gradients as Equation (3.24). In addition, some examples of flux limiter are shown in Table 3.1 [29].

\[ r_j = \frac{y_j - y_{j-1}}{y_{j+1} - y_j} \] (3.24)
Table 3.1: Flux limiter [29]

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>van Leer[32]</td>
<td>( \phi(r) = (r +</td>
</tr>
<tr>
<td>MC[33]</td>
<td>( \phi(r) = \max[0, \min(2r, 0.5(1 + r), 2)] )</td>
</tr>
<tr>
<td>superbee[34]</td>
<td>( \phi(r) = \max[0, \min(2r, 1), \min(r, 2)] )</td>
</tr>
<tr>
<td>minmod[34]</td>
<td>( \phi(r) = \max[0, \min(1, r)] )</td>
</tr>
<tr>
<td>Koren[35]</td>
<td>( \phi(r) = \max[0, \min(2r, (1 + 2r)/3, 2)] )</td>
</tr>
</tbody>
</table>

In the axial dispersion model, the convective part of the flux is

\[
f = u_s \psi \quad (3.25)
\]

Furthermore, the maximum local propagation speed, \( a_{j+1/2} \) in the Equation (3.20) and (3.21) are \( u_s \). As a consequence, the convective parts after substitution will become

\[
f_{j-1/2} = u[\psi_{j-1} + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1})] \quad (3.26)
\]

\[
f_{j+1/2} = u[\psi_j + 0.5\phi(r_j)(\psi_{j+1} - \psi_j)] \quad (3.27)
\]

Finally, after plug in Equation (3.18), (3.19), (3.26), and (3.27) into Equation (3.14), the final equation will be given as

\[
\frac{\partial \psi_j}{\partial t} = \frac{u_s}{\Delta z} [\psi_{j-1} - \psi_j + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1}) - 0.5\phi(r_j)(\psi_{j+1} - \psi_j)]
+ \frac{D_{ax}}{(\Delta z)^2} [\psi_{j-1} - 2\psi_j + \psi_{j+1}] \quad (3.28)
\]

After applied the boundary conditions as same as Equation (3.7) and (3.8) in Method of lines, the equation at the boundaries will be

For \( j=1 \):

\[
\frac{\partial \psi_1}{\partial t} = \frac{u_s}{\Delta z} [\psi_2 - \psi_1 + 2\frac{\Delta z}{D_{ax}} (\psi_F(t) - \psi_1) + 0.5\phi(r_0)(\psi_1 - \psi_0) - 0.5\phi(r_1)(\psi_2 - \psi_1)]
+ \frac{D_{ax}}{(\Delta z)^2} [2\psi_2 + 2\frac{\Delta z}{D_{ax}} (\psi_F(t) - \psi_1) - 2\psi_1] \quad (3.29)
\]

For \( j=N \):

\[
\frac{\partial \psi_N}{\partial t} = \frac{u_s}{\Delta z} [\psi_{N-1} - \psi_N + 0.5\phi(r_{N-1})(\psi_N - \psi_{N-1})] + \frac{D_{ax}}{(\Delta z)^2} [\psi_{N-1}] \quad (3.30)
\]

Then, \( \psi(z, t) \) can be determined via matrix solution similar to the Method of lines.
3.1.3 Comparison of Method of Lines and Finite Volume method

To compare performance of calculation between method of lines and finite volume method, examples simulation was set up by using simulation parameters from Desideri et al.\[27\], i.e. $L = 0.1$ m, $R = 0.16$ m, $n = 2$ rpm, $m_s = 26.2$ kg/hr. The test were set by Peclet number at value of 100, and refined increment of simulation. By doing this, number of grid points or simulation points will be increasing in each simulation loop. Figure 3.3 represents results of residence-time distribution. Where, Figure 3.3a is calculated by method of line, and Figure 3.3b is calculated by finite volume method.

From the figure, the result that simulated via finite volume method be able to converge with low number of grids points. While, method of line required very fine mesh of simulation to maintain in convergence. Consequently, these results could clarify that finite volume method has higher performance than method of lines.

3.1.4 Computational Equations for Axial Dispersion Models

The derivation of axial dispersion model by finite volume method in Section 3.1.2 is simplified for tubular reactor. However, in order to compute the axial dispersion models for rotary kiln, the equations must be modified.

In case of rotary kiln reactor, velocity and dispersion coefficient in a function of length must be implemented. According to the dispersion term, Equation (3.18) and (3.19)
Chapter 3. Simulation scheme of ADM

will be modified to

\[ J_{j-1/2} = -D_{ax,j} \frac{\psi_j - \psi_{j-1}}{\Delta z} \]  
(3.31)

\[ J_{j+1/2} = -D_{ax,j+1/2} \frac{\psi_{j+1} - \psi_j}{\Delta z} \]  
(3.32)

And the convective term, Equation (3.26) and (3.27) will be changed to

\[ f_{j-1/2} = u_{j-1/2} [\psi_{j-1} + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1})] \]  
(3.33)

\[ f_{j+1/2} = u_{j+1/2} [\psi_j + 0.5\phi(r_j)(\psi_{j+1} - \psi_j)] \]  
(3.34)

So, the final equation after substitution can be expressed as

\[
\frac{\partial \psi_j}{\partial t} = \frac{1}{\Delta z} \left( u_{j-1/2} [\psi_{j-1} + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1})] - u_{j+1/2} [\psi_j + 0.5\phi(r_j)(\psi_{j+1} - \psi_j)] \right) \\
+ \frac{1}{(\Delta z)^2} \left[ D_{ax,j+1/2}(\psi_{j+1} - \psi_j) - D_{ax,j-1/2}(\psi_j - \psi_{j-1}) \right]
\]  
(3.35)

In case of the constant axial dispersion model, the dispersion coefficient is remain constant along the bed length. Therefore, the dispersion coefficients \( D_{ax,j} \) and \( D_{ax,j+1/2} \) will be substituted by constant term of \( D_{ax} \), and Equation (3.35) will be re-written as

\[
\frac{\partial \psi_j}{\partial t} = \frac{1}{\Delta z} \left( u_{j-1/2} [\psi_{j-1} + 0.5\phi(r_{j-1})(\psi_j - \psi_{j-1})] - u_{j+1/2} [\psi_j + 0.5\phi(r_j)(\psi_{j+1} - \psi_j)] \right) \\
+ \frac{D_{ax}}{(\Delta z)^2} [\psi_{j+1} - 2\psi_j + \psi_{j-1}]
\]  
(3.36)

In conclusion, the constant ADM will be simulated by using Equation (3.36), and the refined ADM will be simulated by Equation (3.35)

3.2 Simulation Procedure

Simulation of the axial dispersion model in either the constant ADM (Equation (3.36)) or the refined ADM (Equation (3.35)) require results from the Saeman model, such as velocity profile \((u_s)\) and cross-sectional area of bed \((A_s)\), in particular to substitute into the ADM equations. Moreover, the term of dispersion coefficient \((D_{ax})\) must be
Chapter 3. *Simulation scheme of ADM*

obtained by fitting of experiment. So, in order to complete simulation of the axial dispersion model, the simulation sequence must be follow Figure 3.4.

![Simulation procedure of the axial dispersion model](image)

**Figure 3.4:** Simulation procedure of the axial dispersion model

According to Figure 3.4, in the starting step, $u(z)$ and $A(z)$ are calculated via the Saeman model to put in the ADM. Secondly, standard deviation ($\sigma^2$) which is obtained from the experiment will use to fit the values of dispersion coefficient. Finally, residence time distribution can be achieved from the axial dispersion model when every necessary parameters are assembled.

### 3.3 Simulation Data

This Master thesis validated the model of the axial dispersion for the rotary kiln by using experimental data from literature. Therefore, to evaluate the result, calculation data or operating condition must be according to the literature. This section will show the given values that using in simulation of the axial dispersion model.

To simulate the model of granular flow and ADM, the author selected the experimental data from Sai [23], 2013. This literature mostly work on residence-time distribution of rotary drum in varied conditions, and using sand as granular solid in the system with
cold condition. The input values that necessary to apply in the ADM are represent in Table 3.2.

**Table 3.2: Input data for simulation of the axial dispersion model**

<table>
<thead>
<tr>
<th>Data</th>
<th>Unit</th>
<th>Value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of rotary kiln</td>
<td>m</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Diameter of rotary kiln</td>
<td>m</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>Dam height</td>
<td>mm</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Inclination</td>
<td>deg</td>
<td>3.00, 3.52, 3.90</td>
<td>Process variable</td>
</tr>
<tr>
<td>Mass feed rate</td>
<td>kg/hr</td>
<td>10.38, 15.24, 18.48</td>
<td>Process variable</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>rpm</td>
<td>5.5, 10, 15</td>
<td>Process variable</td>
</tr>
<tr>
<td>Bulk density of sand</td>
<td>kg/m³</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>Angle of repose</td>
<td>deg</td>
<td>-</td>
<td>To be fitted</td>
</tr>
<tr>
<td>Particle size of sand</td>
<td>mm</td>
<td>1 to 1.25</td>
<td></td>
</tr>
</tbody>
</table>

Notwithstanding, the value for angle of repose, which is one important material property, was not reported by Sai [23]. Therefore, the angle of repose must be obtained via the fitting by mean residence time.

In addition, this literature provided the value of Peclet number in every experiments, and it can be used to calculate the standard deviation which is required to calculate the value of dispersion coefficient.
Chapter 4

Results on granular flow & RTD

This chapter will illustrate simulation results of granular flow model and axial dispersion model in a kiln. Simulations presented here aim at describing the experiments run by Sai [23]. Process parameters of the experimental setup used by Sai [23] are given in Table 3.2.

4.1 Comparison between the Constant ADM and the Refined ADM

According to the constant axial dispersion model (Equation (2.18)) and the refined axial dispersion model (Equation (2.19)), only dispersion coefficient ($D_{ax}$) is different between the two models. The constant ADM has constant $D_{ax}$ along the bed length. While, $D_{ax}(z)$ of the refined ADM is decreasing along the bed respect to constant factor $D_0$, as represent in Figure 4.1a.

To compare these two models, the simulation of the models with the same value of standard deviation $\sigma$ are set by adjusting the dispersion coefficient in the constant ADM and dispersion factor in the refined ADM, i.e. we set $D_{ax} = 6.587 \times 10^{-6}$ m$^2$/s, and $D_0 = 2.909 \times 10^{-9}$ m$^3$/s which results in a standard deviation $\sigma = 32.05$ s for both models. The comparison of residence-time distribution between two models are demonstrated in Figure 4.1b, which shows very closed result of RTD between two models.
Figure 4.1: Comparison of the results between constant ADM and refined ADM

However, if the models are considered the distribution of tracer along the bed length from the time at beginning until the empty of tracer, such as Figure 4.2. It could be obviously observed that the tracer distribution in the refined ADM is more spread than the constant ADM around the front part of the kiln, and then it get closer at the end of the kiln. Because, the values of $D_{ax}$ around the front part of the kiln in the refined ADM are higher than the constant model and it decrease to be lower around the end part of the kiln. In addition, for the refined ADM, the front propagate are sharper than the backward, which is because the effect of higher $D_{ax}$ in the entrance than the exit of the kiln. But, the spread of dispersion is mirror in case of the constant ADM.

Figure 4.2: Comparison of tracer mass fraction along the bed length in different time of the two models
Chapter 4. Results on granular flow & RTD

Figure 4.3: Result of the constant axial dispersion model with different Pe

Furthermore, the models are computed with different value of Peclet number to show how is the dispersion coefficient affect to the mean propagation velocity in each models. The definition of Peclet number for the constant ADM and the refined ADM are described by Equation (4.1) and (4.2), respectively.

\[ P_e = \frac{L u}{D_{ax}} \]  
\[ P_e = \frac{L u}{D_0} \left| \frac{dA_s}{dz} \right|^{-1} \]

The position of propagation front is calculated by

\[ \bar{z}(t) = \int_0^L \psi(z, t) dz \]

In case of the constant ADM, Figure 4.3, the result shows that dispersion coefficient does not effect to the mean propagated speed of the distribution, since the results in different Peclet number are not deviate from result of infinite Peclet number. Whereas, the result in the refined model, Figure 4.4, are affected by dispersion coefficient along the bed length. The propagated speed around the front of the kiln length is deviate from the result at infinite Peclet number, especially in the case of low Pe (5000). The reason of this behavior is because of more spread in backward propagation of distribution than the front propagation, which came from the effect of higher \( D_{ax} \) at the front of the kiln in the refined ADM.
Chapter 4. *Results on granular flow & RTD*

4.2 Comparison with Experimental data from Literature

In order to obtain validation of the axial dispersion models, the experimental data of residence time distribution from Sai [23] was applied to evaluate the models. The experimental data contains the results of 27 experiments, which are different in mass flow rate \( (m_s) \), rotational speed \( (n) \), and inclination \( (\beta) \), as show in Appendix A.

Figure 4.5 represents the mean residence time (MRT) from the experiment compare to the results from simulation by the Saeman model with a global angle of repose \( (\Theta) \) at 40°. The figure shows that the simulation results are not exactly equal to the experiment, and some of them deviate from the experiment more than 10 %. Nevertheless, to use the right result from Saeman model to simulate in ADM, individual angle of repose were adjusted to fit mean residence time.

From the simulation of axial dispersion models by using the result from the Saeman model with individually adjusted angle of repose, dispersion coefficient \( (D_{ax}) \) in constant ADM, and dispersion factor \( (D_0) \) can be fitted by using standard deviation of each experiment. In addition, \( D_{ax} \) and \( D_0 \) are fitted by power law equation in particular to estimate the value for all operating conditions. The correlation to estimate \( D_{ax} \) in the constant axial dispersion model can be written as

\[
D_{ax} = (9.576 \times 10^{-8})m_s^{-0.8659}n^{1.891}\beta^{3.549}
\] (4.4)
Chapter 4. Results on granular flow & RTD

While, the correlation to estimate $D_0$ for the refined axial dispersion model is the following equation

$$D_0 = (1.6368 \times 10^{-4}) m_s^{1.9975} n^{-1.145} \beta^{-2.7989}$$  \hspace{1cm} (4.5)

The accuracy of Equation (4.4) and (4.5) can be demonstrated in Figure 4.6. In case of constant ADM, the result reported value of $D_{ax}$ close to the experiment for the range of $D_{ax}$ around 0.1 to 0.6 $\times$ $10^{-5}$ $m^2/s$. While, the refined ADM has accurate $D_0$ around 1.5 to 3 $\times$ $10^{-9}$ $m^3/s$.

In calculation of residence-time distribution, the example of RTD from the axial dispersion models and the experiment are plotted in Figure 4.7. According to the figure, axial dispersion models either constant $D_{ax}$ or refined $D_{ax}$ can be predicted residence time distribution of granular flow in rotary kiln with good agreement respect to experimental result.

Notwithstanding, the result show approximately 200 second of residence time distribution for 400 second of mean residence time, which is relatively narrow for granular flow. As a consequence, as a first order approximation, the granular flow in rotary kiln can be assumed plug flow for the distribution of residence times.
Chapter 4. Results on granular flow & RTD

Figure 4.6: Comparison of $D_{ax}(a)$, $D_0(b)$ from the correlation and the experiment

Figure 4.7: Comparison of RTD from the models and the experiment
(Run no.9: $m_s = 18.48$ kg/h, $n = 5.5$ rpm, $\beta = 3^\circ$)
Part II

Pyrolysis in a Rotary kiln
Chapter 5

Modeling of Rotary Kiln Pyrolyzer

The main aspects to consider in modeling of rotary kiln pyrolyzer are flow of material, gas-solid mass transfer, heat transfer, and reaction kinetics. The modeling of granular flow was already illustrated in the Chapter 2. Henceforth, heat transfer model including reaction kinetics, and mass balance of solid and gas in particular to the system of rotary kiln pyrolyzer will be demonstrated in this chapter.

It is well known that heat transfer is one of the most important aspect in reactor design, because heat transfer can limit kinetics performance of reactor. In comparison to other type of reactor, such as fluidized bed and packed bed, rotary kiln has the unique features of heat transfer that include:[36]

i) Rotational speed of rotary drum influence heat transfer coefficients between kiln’s wall and freeboard gas, and between the wall and solid bed.

ii) Heat transfer between contact surface of inner wall and bulk solid bed is very important.

iii) Radiation heat transfer will play role and cannot be ignored at highly operating temperature, especially when the temperature exceed 1000°C.

Essentially, rotary kiln reactor can be classified as internal heating and external heating. For the internally heated rotary kiln, which typically used in metallurgical processes and waste incinerator, has a concept of supplying high temperature flue gas into the kiln as its heat source in a direction either counter-current or co-current to the solid bed flow. While, externally heated rotary kiln can apply electrical heat flux or by indirect heating at the outer surface of kiln’s wall with high temperature gas flow, or other heat source. The externally heated technique is typically adopted as reactor of gasification and pyrolysis, because these processes require condition of air free in
Chapter 5. *Modeling of rotary kiln pyrolyzer*

42

the system [36]. According to the requirement of pyrolysis reaction, externally heated rotary kiln must be represented to derive heat transfer model in rotary kiln pyrolyzer.

In this chapter, mass and energy balances over an rotary kiln pyrolyzer will be performed in particular to achieve temperature profile and conversion inside a kiln.

### 5.1 Modeling of Rotary Kiln Pyrolyzer

In modeling of rotary kiln pyrolyzer, not only heat transfer is considered in this model, but also pyrolysis reaction must be taken into the model. Therefore, mass balance and energy balance will be derived over rotary kiln pyrolyzer, as represents in Figure 5.1. All material species, including reactant and product materials, flow into a control volume and leave with mass and energy changing by mass and heat transfer in the control volume.

![Figure 5.1: A control volume of the rotary kiln pyrolyzer](image)

Notwithstanding, the modeling of rotary kiln pyrolyzer will be performed under these following assumptions

1) Radially well mixed
2) Constant solid particle size (reduction in density)
3) Gas phase behave similar to ideal gas
4) Gas phase contain only one species which is pyrolysis gas
5) Neglect term of axial dispersion
6) The common mechanism for primary pyrolysis reaction of wood considers a scheme
of parallel reaction. By ignoring tar, the scheme can reads as

\[
\begin{align*}
\text{Wood} & \xrightarrow{k_1} \text{Gas} \\
\text{Wood} & \xrightarrow{k_2} \text{Char}
\end{align*}
\] (5.1)

This simple scheme of parallel first order reactions can equivalently be formulated as a single reaction of the form:

\[
\text{Wood} \rightarrow \nu_g \text{Gas} + \nu_c \text{Char}
\] (5.2)

The parallel reactions in Scheme (5.1) as accounted by the mass coefficients — equivalent to stoichiometry coefficient \( \nu_g \) and \( \nu_c \) — which defined as

\[
\nu_g = \frac{k_1}{k_1 + k_2} \quad \text{and} \quad \nu_c = \frac{k_2}{k_1 + k_2}
\]

Apparently, \( \nu_g \) and \( \nu_c \) are dependent function of temperature.

### 5.1.1 Mass balance

According to Figure 5.1, species \( i \) enters to the control volume at position \( z \) with mass flow rate \( F_i \), bulk density \( \rho_i \), enthalpy \( H_i \), and cross-sectional area \( A_i \). During flowing inside the control volume, mass flow rate of species \( i \) will change by chemical reaction with reaction rate of wood \( r_w \), and individual stoichiometric coefficient \( \nu_i \).

Overall mass balance over the control volume can be perform by

\[
\text{Now} - \text{Before} = \text{In} - \text{Out} + \text{Generation} - \text{Consumption}
\]

\[
\Delta z \left[ \sum_{i=1}^{n} \rho_i A_i \mid_{z,t+\Delta t} - \sum_{i=1}^{n} \rho_i A_i \mid_{z,t} \right] = \Delta t \left[ \sum_{i=1}^{n} F_i \mid_{z,t} - \sum_{i=1}^{n} F_i \mid_{z+\Delta z,t} \right] + \sum_{i=1}^{n} \nu_i r_w A_w \Delta z \Delta t \] (5.3)
Divide Equation (5.3) by $\Delta t \Delta z$

$$\left| \sum_{i=1}^{n} \rho_i A_i \big|_{z,t+\Delta t} - \sum_{i=1}^{n} \rho_i A_i \big|_{z,t} \right| = \left| \sum_{i=1}^{n} F_i \big|_{z,t} - \sum_{i=1}^{n} F_i \big|_{z+\Delta z,t} \right| + r_w A_w \sum_{i=1}^{n} \nu_i$$

(5.4)

Then, taking the limit $\Delta z, \Delta t \to 0$, and overall mass balance equation for a kiln will be written as

$$\sum_{i=1}^{n} \frac{\partial}{\partial t} (\rho_i A_i) = - \sum_{i=1}^{n} \frac{\partial F_i}{\partial z} + r_w A_w \sum_{i=1}^{n} \nu_i$$

(5.5)

According to the overall mass balance equation, Equation (5.5), mass accumulation in a kiln is varied by mass flow rate and chemical reaction.

Furthermore, taking out summation from overall mass balance Equation (5.5), mass balance equation of species $i$ can be obtained

$$\frac{\partial}{\partial t} (\rho_i A_i) = - \frac{\partial F_i}{\partial z} + r_w A_w \nu_i$$

(5.6)

To apply the mass balance equation for the rotary kiln pyrolyzer system, subscript $i$ in Equation (5.6) will be substituted by $w$, $c$, and $g$ which mean wood, char, and gas, respectively.

$$\frac{\partial}{\partial t} (\rho_w A_w) = - \frac{\partial F_w}{\partial z} + r_w A_w \nu_w$$

(5.7)

$$\frac{\partial}{\partial t} (\rho_c A_c) = - \frac{\partial F_c}{\partial z} + r_w A_w \nu_c$$

(5.8)

$$\frac{\partial}{\partial t} (\rho_g A_g) = - \frac{\partial F_g}{\partial z} + r_w A_w \nu_g$$

(5.9)

Where, we notice that $\nu_w = -1$ from definition. And overall mass balance in rotary kiln pyrolyzer can be expressed as

$$\left( \frac{\partial}{\partial t} (\rho_w A_w) + \frac{\partial}{\partial t} (\rho_c A_c) + \frac{\partial}{\partial t} (\rho_g A_g) \right) = - \left( \frac{\partial F_w}{\partial z} + \frac{\partial F_c}{\partial z} + \frac{\partial F_g}{\partial z} \right) + r_w A_w (\nu_w + \nu_c + \nu_g)$$

(5.10)

Which recovers Equation (5.5). As mentioned before, reaction rate and stoichiometric coefficients are temperature dependent function. Therefore, energy balance must be performed to solve with mass balance equations simultaneously.
5.1.2 Energy balance

For rotary kiln pyrolyzer, energy balance equation cannot derive straightforward as mass balance. Because, the system consists of two domains: solid phase, and gas phase. Moreover, generated energy from reaction must be included in the model, also special characteristic of rotary kiln such as cross-sectional area. Consequently, energy balance derivation will be represented step by step in this section.

Energy balance over control volume
Firstly, energy balance of all species in the control volume according to Figure 5.1 will be performed by following

\[
\text{Now} - \text{Before} = \text{In} - \text{Out} + \text{Heat supply}
\]

\[
\Delta z \left[ \sum_{i=1}^{n} \rho_i A_i H_i |_{z,t,\Delta t} - \sum_{i=1}^{n} \rho_i A_i H_i |_{z,t} \right] = \Delta t \left[ \sum_{i=1}^{n} F_i H_i |_{z,t} - \sum_{i=1}^{n} F_i H_i |_{z+\Delta z,t} \right] + q''_{\text{supply}} A_{\text{shell}} \Delta t \tag{5.11}
\]

Where, \( q''_{\text{supply}} \) is heat flux that supply at outer surface of the kiln (\( W/m^2 \)). Then, divide Equation (5.11) by \( \Delta t \Delta z \)

\[
\frac{\sum_{i=1}^{n} \rho_i A_i H_i |_{z,t,\Delta t} - \sum_{i=1}^{n} \rho_i A_i H_i |_{z,t}}{\Delta t} = \frac{\sum_{i=1}^{n} F_i H_i |_{z,t} - \sum_{i=1}^{n} F_i H_i |_{z+\Delta z,t}}{\Delta z} + \frac{q''_{\text{supply}} A_{\text{shell}}}{\Delta z} \tag{5.12}
\]

Take limit into Equation (5.12), the equation will become

\[
\sum_{i=1}^{n} \frac{\partial}{\partial t} (\rho_i A_i H_i) = - \sum_{i=1}^{n} \frac{\partial}{\partial z} (F_i H_i) + q'_{\text{supply}} \tag{5.13}
\]

Where, \( q'_{\text{supply}} \) is heat supply per unit length (\( W/m \)). After applying differential by part in Equation (5.13), the equation will be changed to

\[
\sum_{i=1}^{n} \left( H_i \frac{\partial}{\partial t} (\rho_i A_i) + \rho_i A_i \frac{\partial H_i}{\partial t} \right) = - \sum_{i=1}^{n} \left( H_i \frac{\partial F_i}{\partial z} + F_i \frac{\partial H_i}{\partial z} \right) + q'_{\text{supply}} \tag{5.14}
\]
Notice that enthalpy can be expressed by the form of temperature as

\[ H_i = H_{i0} + \int_{T_0}^{T} C_p \, dT_i \]  \hspace{1cm} (5.15)

So, derivative of enthalpy can be written as

\[ \partial H_i = C_p \partial T_i \]  \hspace{1cm} (5.16)

After changed the terms of enthalpy to temperature function, and substituted term of \( \partial F_i / \partial z \) by mass balance equation (Equation (5.6)), Equation (5.14) will become

\[
\sum_{i=1}^{n} H_i \frac{\partial}{\partial t} (\rho_i A_i) + \sum_{i=1}^{n} (\rho_i A_i C_{p_i}) \frac{\partial T_i}{\partial t} = \sum_{i=1}^{n} H_i \frac{\partial}{\partial t} (\rho_i A_i) - r_w A_w \sum_{i=1}^{n} \nu_i H_i - \sum_{i=1}^{n} F_i C_{p_i} \frac{\partial T_i}{\partial z} + q_{\text{supply}} \]  \hspace{1cm} (5.17)

After canceled similar terms from Equation (5.17), the final form of overall energy balance over the control volume can be expressed as

\[
\sum_{i=1}^{n} \left( \rho_i A_i C_{p_i} \frac{\partial T_i}{\partial t} \right) = -r_w A_w \sum_{i=1}^{n} \nu_i H_i - \sum_{i=1}^{n} F_i C_{p_i} \frac{\partial T_i}{\partial z} + q'_{\text{supply}} \]  \hspace{1cm} (5.18)

Accumulation of energy in rotary kiln is influenced by energy from reaction, energy with material streams, and heat supply.

**Energy balance over solid bed**

The second derivation of energy balance is considered when the overall control volume is divided into solid bed and gas phase. Figure 5.2 is introduced to describe energy streams that flow through the solid bed including energy released with gas stream respect to chemical reaction inside the solid bed.

---

**Figure 5.2:** A control volume of solid bed in the kiln
Chapter 5. Modeling of rotary kiln pyrolyzer

According to the figure, subscript \(j\) and \(k\) are defined as solid species and gas species, respectively. Energy balance over solid bed can be derived by

\[
\Delta z \left[ \sum_{j=1}^{n_j} \rho_j A_j H_j \bigg|_{z,t+\Delta t} - \sum_{j=1}^{n_j} \rho_j A_j H_j \bigg|_{z,t} \right] = \Delta t \left[ \sum_{j=1}^{n_j} F_j H_j \bigg|_{z,t} - \sum_{j=1}^{n_j} F_j H_j \bigg|_{z+\Delta z,t} \right] 
+ \sum_{j=1}^{n_j} q_{\text{add},j} \Delta t - \sum_{j=1}^{n_j} q_{\text{release},j} \Delta t - r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k) \Delta t \Delta z \tag{5.19}
\]

Where, \(q_{\text{add},j}\) is heat rate that transfer from the other phase to solid bed, and \(q_{\text{release},j}\) is heat rate that release from solid bed to the other phase. The last term in Equation (5.19) is represented for energy release with produced gas from reaction to gas phase in unit of W/s.

After divided Equation (5.19) by \(\Delta t \Delta z\) and taking the limit \(\Delta z, \Delta t \to 0\), the equation will become

\[
\sum_{j=1}^{n_j} \frac{\partial}{\partial t} (\rho_j A_j H_j) = - \sum_{j=1}^{n_j} \frac{\partial}{\partial z} (F_j H_j) + \sum_{j=1}^{n_j} q'_{\text{add},j} - \sum_{j=1}^{n_j} q'_{\text{release},j} - r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k) \tag{5.20}
\]

Then, taking differential by part, Equation (5.20) will be expanded to

\[
\sum_{j=1}^{n_j} \left( H_j \frac{\partial}{\partial t} (\rho_j A_j) + \rho_j A_j \frac{\partial H_j}{\partial t} \right) = - \sum_{j=1}^{n_j} \left( H_j \frac{\partial F_j}{\partial z} + F_j \frac{\partial H_j}{\partial z} \right) 
+ \sum_{j=1}^{n_j} q'_{\text{add},j} - \sum_{j=1}^{n_j} q'_{\text{release},j} - r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k) \tag{5.21}
\]

Next, substitute term of \(\frac{\partial F_j}{\partial z}\) in Equation (5.21) by mass balance Equation (5.6) and expand terms of enthalpy, the equation will become

\[
\sum_{j=1}^{n_j} H_j \frac{\partial}{\partial t} (\rho_j A_j) + \sum_{j=1}^{n_j} (\rho_j A_j C_{pj}) \frac{\partial T_j}{\partial t} = \sum_{j=1}^{n_j} H_j \frac{\partial}{\partial t} (\rho_j A_j) - r_w A_w \sum_{j=1}^{n_j} \nu_j H_j 
- \sum_{j=1}^{n_j} F_j C_{pj} \frac{\partial T_j}{\partial z} + \sum_{j=1}^{n_j} q'_{\text{add},j} - \sum_{j=1}^{n_j} q'_{\text{release},j} - r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k) \tag{5.22}
\]

Whereas, every species within solid bed must remain at the same temperature as bed temperature \(T_b\). After rearranged and canceled similar terms, Equation (5.22) will be
left only

\[
\frac{\partial T_b}{\partial t} \sum_{j=1}^{n_j} (\rho_j A_j C_{pj}) = -r_w A_w \left( \sum_{j=1}^{n_j} \nu_j H_j + \sum_{k=1}^{n_k} r_k H_k \right) - \frac{\partial T_b}{\partial t} \sum_{j=1}^{n_j} F_j C_{pj} \\
+ \sum_{j=1}^{n_j} q'_{addj} - \sum_{j=1}^{n_j} q'_{releasej} \quad (5.23)
\]

We notice that the first term on the right hand side of Equation (5.23), i.e.

\[r_w A_w \left( \sum_{j=1}^{n_j} \nu_j H_j + \sum_{k=1}^{n_k} r_k H_k \right) = r_w A_w \left( \sum_{i=1}^{n_i} \nu_i H_i \right),\]

can be represented as heat of reaction \(\Delta H_{rxn}\) at temperature \(T_b\). Hence, the final form of energy balance over solid bed can be expressed as

\[
\frac{\partial T_b}{\partial t} \sum_{j=1}^{n_j} (\rho_j A_j C_{pj}) = -r_w A_w \Delta H_{rxn} - \frac{\partial T_b}{\partial t} \sum_{j=1}^{n_j} F_j C_{pj} - q'_{addj} - q'_{releasej} \quad (5.24)
\]

Equation (5.24) describes that an influence of energy accumulation in solid bed due to heat of reaction, heat flow with solid streams, and energy exchange to other phases.

**Energy balance over gas phase**

The third component of energy balance can be performed over gas phase, which consists of energy flow with gas streams, energy with product gas from solid bed, and energy exchange to the other phases, as represent in Figure 5.3.

![Figure 5.3: A control volume of gas phase in the kiln](image)
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As similar step as before, energy balance over gas phase would be performed by

\[
\Delta z \left[ \sum_{k=1}^{n_k} \rho_k A_k H_k \bigg|_{z,t} - \sum_{k=1}^{n_k} \rho_k A_k H_k \bigg|_{z,t+\Delta t} \right] = \Delta t \left[ \sum_{k=1}^{n_k} F_k H_k \bigg|_{z,t} - \sum_{k=1}^{n_k} F_k H_k \bigg|_{z+\Delta z,t} \right] + \sum_{k=1}^{n_k} q_{\text{add,k}} \Delta t - \sum_{k=1}^{n_k} q_{\text{release,k}} \Delta t + r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k(T_b)) \Delta t \Delta z \quad (5.25)
\]

The last term in the equation is referred to energy that feed in with product gas from solid bed respect to bed temperature \(T_b\). After divided Equation (5.25) by \(\Delta t \Delta z\) and taking the limit \(\Delta z, \Delta t \to 0\), the equation will become

\[
\sum_{k=1}^{n_k} \frac{\partial}{\partial t} \left( \rho_k A_k H_k \right) = -\sum_{k=1}^{n_k} \frac{\partial}{\partial z} (F_k H_k) + \sum_{k=1}^{n_k} q'_{\text{add,k}} - \sum_{k=1}^{n_k} q'_{\text{release,k}} + r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k(T_b)) \quad (5.26)
\]

Then, taking differential by part, Equation (5.26) will be expanded to

\[
\sum_{k=1}^{n_k} \left( H_k \frac{\partial}{\partial t} (\rho_k A_k) + \rho_k A_k \frac{\partial H_k}{\partial t} \right) = -\sum_{k=1}^{n_k} \left( H_k \frac{\partial F_k}{\partial z} + F_k \frac{\partial H_k}{\partial z} \right) + \sum_{k=1}^{n_k} q'_{\text{add,k}} - \sum_{k=1}^{n_k} q'_{\text{release,k}} + r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k(T_b)) \quad (5.27)
\]

Next, substitute term of \(\frac{\partial F_k}{\partial z}\) in Equation (5.27) by mass balance Equation (5.6) and expand terms of enthalpy, the equation will be written as

\[
\sum_{k=1}^{n_k} H_k \frac{\partial}{\partial t} (\rho_k A_k) + \sum_{k=1}^{n_k} (\rho_k A_k C_{p_k}) \frac{\partial T_k}{\partial t} = \sum_{k=1}^{n_k} H_k \frac{\partial}{\partial t} (\rho_k A_k) - r_w A_w \sum_{k=1}^{n_k} \nu_k H_k
\]

\[
- \sum_{k=1}^{n_k} F_k C_{p_k} \frac{\partial T_k}{\partial z} + \sum_{k=1}^{n_k} q'_{\text{add,k}} - \sum_{k=1}^{n_k} q'_{\text{release,k}} + r_w A_w \sum_{k=1}^{n_k} (\nu_k H_k(T_b)) \quad (5.28)
\]

Whereas, every species within gas phase must remain at the same temperature as gas temperature \(T_g\). After rearranged and canceled similar terms out, Equation (5.28) will be left only

\[
\frac{\partial T_g}{\partial t} \sum_{k=1}^{n_k} (\rho_k A_k C_{p_k}) = -r_w A_w \left( \sum_{k=1}^{n_k} \nu_k H_k(T_g) - \sum_{k=1}^{n_k} \nu_k H_k(T_b) \right) + \frac{\partial T_g}{\partial t} \sum_{k=1}^{n_k} F_k C_{p_k}
\]

\[
+ \sum_{k=1}^{n_k} q'_{\text{add,k}} - \sum_{k=1}^{n_k} q'_{\text{release,k}} \quad (5.29)
\]
Hence, the final form of energy balance over gas can be expressed as

\[ \frac{\partial T_g}{\partial t} + \sum_{k=1}^{n_k} (\rho_{k} A_{k} C_{pk}) = -r_w A_w \sum_{k=1}^{n_k} \nu_k (H_k(T_g) - H_k(T_b)) - \frac{\partial T_g}{\partial z} \sum_{k=1}^{n_k} F_k C_{pk} + \sum_{k=1}^{n_k} q'_{add_k} - \sum_{k=1}^{n_k} q'_{release_k} \]  

(5.30)

Therefore, energy accumulation in gas phase is affected by amount of energy required to adjust temperature of product gas from solid bed temperature to gas temperature, energy with gas streams, and energy exchange to other phases.

In finally, apply the energy balance equations to the rotary kiln pyrolyzer system by substitute species subscripts into the equations. Thus, energy balance over solid bed and gas phase will demonstrate as

\[ (\rho_w A_w C_{pw} + \rho_c A_c C_{pc}) \frac{\partial T_b}{\partial t} = -r_w A_w \Delta H_{rxn} - (F_w C_{pw} + F_c C_{pc}) \frac{\partial T_b}{\partial z} + q'_{wall-bed} + q'_{gas-bed} \]  

(5.31)

\[ (\rho_g A_g C_{pg}) \frac{\partial T_g}{\partial t} = -r_w A_w \nu_g [H_g(T_g) - H_g(T_b)] - F_g C_{pg} \frac{\partial T_g}{\partial z} + q'_{wall-gas} - q'_{gas-bed} \]  

(5.32)

In addition, energy balance over kiln wall can be performed as

\[ \rho_{wall} A_{wall} C_{pwall} \frac{\partial T_{wall}}{\partial t} = q'_{supply} - q'_{wall-bed} - q'_{wall-gas} \]  

(5.33)

Finally, overall energy balance of rotary kiln pyrolyzer can be described by this following equation

\[ \begin{align*}
\left[ (\rho_w A_w C_{pw} + \rho_c A_c C_{pc}) \frac{\partial T_b}{\partial t} + & \rho_g A_g C_{pg} \frac{\partial T_g}{\partial t} + \rho_{wall} A_{wall} C_{pwall} \frac{\partial T_{wall}}{\partial t} \right] = \\
- \left[ (F_w C_{pw} + F_c C_{pc}) \frac{\partial T_b}{\partial z} + F_g C_{pg} \frac{\partial T_g}{\partial z} \right] - r_w A_w [\nu_w H_w(T_b) + \nu_c H_c(T_b) + \nu_g H_g(T_g)] \end{align*} \]  

(5.34)
5.1.3 Momentum balance

According to mass balance equations and energy balance equations, mass flow rates \( F_i \) are required in order to complete the set of equations. So, momentum balance can be employed to derive the equation of flow rate changing.

Overall momentum balance over the control volume can be performed as

\[
\Delta z \left[ \sum_{i=1}^{n} F_i |_{z,t+\Delta t} - \sum_{i=1}^{n} F_i |_{z,t} \right] = \Delta t \left[ \sum_{i=1}^{n} \Phi_i |_{z,t} - \sum_{i=1}^{n} \Phi_i |_{z+\Delta z,t} \right] \tag{5.35}
\]

Where, \( \Phi_i \) is “the combined momentum flux” \((\text{kg.m/s}^2)\), which consists of flowing term \( F_i u_i \), pressure force \( P_i A_i \), and shear force \( \tau \). However, the system is assumed low viscosity and shear force can be neglected. After substitution and divided Equation (5.35) by \( \Delta t \Delta z \) and taking limit, the equation will become

\[
\sum_{i=1}^{n} \frac{\partial F_i}{\partial t} = -\sum_{i=1}^{n} \frac{\partial}{\partial z} (F_i u_i) - \sum_{i=1}^{n} \frac{\partial}{\partial z} (P_i A_i) \tag{5.36}
\]

Then, in order to achieve species momentum balance, Equation (5.36) can be applied without summation as

\[
\frac{\partial F_i}{\partial t} = -\frac{\partial}{\partial z} (F_i u_i) - \frac{\partial}{\partial z} (P_i A_i) \tag{5.37}
\]

After taking differential by part to Equation (5.37), the equation will become

\[
\frac{\partial F_i}{\partial t} = -u_i \frac{\partial F_i}{\partial z} - F_i \frac{\partial u_i}{\partial z} - \frac{\partial}{\partial z} (P_i A_i) \tag{5.38}
\]

Nevertheless, Equation (5.38) still consist of mass flow rate \( F_i \) and velocity \( u_i \). To eliminate velocity from the equation, definition of velocity must need to apply as

\[
u_i = \frac{F_i}{\rho_i A_i} \tag{5.39}
\]

\[
\partial u_i = \frac{(\rho_i A_i) \partial F_i - F_i \partial (\rho_i A_i)}{(\rho_i A_i)^2} \tag{5.40}
\]

After substituted Equation (5.39) and (5.40) into Equation (5.38) and rearranged the equation, momentum balance of species \( i \) in form of mass flow rate can be expressed
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as

\[ \frac{\partial F_i}{\partial t} = -2 \left( \frac{F_i}{\rho_i A_i} \right) \frac{\partial F_i}{\partial z} + \left( \frac{F_i}{\rho_i A_i} \right)^2 \frac{\partial}{\partial z} \left( \rho_i A_i \right) - \frac{\partial}{\partial z} \left( P_i A_i \right) \]  

(5.41)

Therefore, momentum balance equations of rotary kiln pyrolyzer can be achieved as

\[ \frac{\partial F_w}{\partial t} = -2 \left( \frac{F_w}{\rho_w A_w} \right) \frac{\partial F_w}{\partial z} + \left( \frac{F_w}{\rho_w A_w} \right)^2 \frac{\partial}{\partial z} \left( \rho_w A_w \right) - \frac{\partial}{\partial z} \left( P_w A_w \right) \]  

(5.42)

\[ \frac{\partial F_c}{\partial t} = -2 \left( \frac{F_c}{\rho_c A_c} \right) \frac{\partial F_c}{\partial z} + \left( \frac{F_c}{\rho_c A_c} \right)^2 \frac{\partial}{\partial z} \left( \rho_c A_c \right) - \frac{\partial}{\partial z} \left( P_c A_c \right) \]  

(5.43)

\[ \frac{\partial F_g}{\partial t} = -2 \left( \frac{F_g}{\rho_g A_g} \right) \frac{\partial F_g}{\partial z} + \left( \frac{F_g}{\rho_g A_g} \right)^2 \frac{\partial}{\partial z} \left( \rho_g A_g \right) - \frac{\partial}{\partial z} \left( P_g A_g \right) \]  

(5.44)

Notwithstanding, the momentum balance equation can be also derived in form of velocity. To change the momentum equation to velocity form, Equation (5.38) can be re written by substitute \( F_i \) with term of \( u_i \) and the equation will become

\[ (\rho_i A_i) \frac{\partial u_i}{\partial t} + u_i \frac{\partial}{\partial t} \left( \rho_i A_i \right) = -u_i \frac{\partial F_i}{\partial z} - u_i \rho_i A_i \frac{\partial u_i}{\partial z} - \frac{\partial}{\partial z} \left( P_i A_i \right) \]  

(5.45)

Substitute term \( \frac{\partial}{\partial t} \left( \rho_i A_i \right) \) by mass balance Equation (5.6), the equation will change to

\[ (\rho_i A_i) \frac{\partial u_i}{\partial t} - u_i \frac{\partial F_i}{\partial t} + u_i \nu_i r_w A_w = -u_i \frac{\partial F_i}{\partial z} - u_i \rho_i A_i \frac{\partial u_i}{\partial z} - \frac{\partial}{\partial z} \left( P_i A_i \right) \]  

(5.46)

After canceled similar terms out and rearrange Equation (5.46), equation of momentum balance in form of velocity will be expressed as

\[ \frac{\partial u_i}{\partial t} = -u_i \frac{\partial u_i}{\partial z} - \frac{1}{\rho_i A_i} \frac{\partial}{\partial z} \left( P_i A_i \right) - \frac{u_i \nu_i r_w A_w}{(\rho_i A_i)} \]  

(5.47)

Equation (5.47) is recognized as equation of motion without term of shear rate, but an additional term of reaction.

Finally, velocity profile of each species in rotary kiln pyrolyzer can be described by these following equations

\[ \frac{\partial u_w}{\partial t} = -u_w \frac{\partial u_w}{\partial z} - \frac{1}{\rho_w A_w} \frac{\partial}{\partial z} \left( P_w A_w \right) - \frac{u_w \nu_i r_w A_w}{(\rho_w A_w)} \]  

(5.48)
5.1.4 Steady-state model

This thesis only interest to simulate rotary kiln pyrolyzer in case of steady-state condition. Therefore, the set of mass and energy balance equations are reduced to a set of ODEs that describe the steady state profiles.

Mass balance equations for steady-state system of rotary kiln pyrolyzer will be expressed as

\[
\frac{dF_w}{dz} = u_w r_w A_b \tag{5.51}
\]

\[
\frac{dF_c}{dz} = u_c r_w A_b \tag{5.52}
\]

\[
\frac{dF_g}{dz} = u_g r_w A_b \tag{5.53}
\]

And energy balance equation for steady-state condition will become

\[
(F_w C_p + F_c C_p) \frac{\partial T_b}{\partial z} = -r_w A_b \Delta H_{rxn} + q'_{wall-bed} + q'_{gas-bed} \tag{5.54}
\]

\[
F_g C_p \frac{\partial T_g}{\partial z} = -r_w A_w u_g [H_g(T_g) - H_g(T_b)] + q'_{wall-gas} + q'_{gas-bed} \tag{5.55}
\]

\[
q'_{supply} = q'_{wall-bed} + q'_{wall-gas} \tag{5.56}
\]

According to the equations, momentum balance is not necessary to implement in the equations. Furthermore, to solve the set of ordinary differential equations, initial conditions must be stated as
At $z=0$,

\begin{align*}
F_w(0) &= F_{\text{bed feeding}} \quad (5.57) \\
F_c(0) &= 0 \quad (5.58) \\
F_g(0) &= 0 \quad (5.59) \\
T_b(0) &= T_{\text{inlet}} \quad (5.60) \\
T_g(0) &= T_{\text{inlet}} \quad (5.61)
\end{align*}

Nevertheless, the system of heat supply for the rotary kiln pyrolyzer is assumed constant kiln’s wall temperature ($T_w$), the system of coupled mass-heat transfer equations can be solved by substituting a constant value of wall temperature into the system of equations.

Moreover, the term of reaction rate is considered as a first-order reaction, which can be written by

$$r(z) = k \rho_w$$

Where, $r(z)$ is reaction rate ($\text{kg/m}^3\text{s}$), $k$ is kinetics rate coefficient ($\text{1/s}$), and $\rho_w$ is density of wood ($\text{kg/m}^3$). The density of wood relate to $F_w$ by $\rho_w = F_i/(u_i A_i)$.

According to the Arrhenius’s expression, the temperature dependency of the kinetics rate coefficient for the reaction can be illustrated as

$$k = A e^{E/R}$$

Where, $A$ is the pre-exponential factor ($\text{1/s}$), $E$ is the activation energy ($\text{J/mol}$), and $R$ is the universal gas constant.

### 5.2 Heat Transfer in Rotary Kiln

According to the section of modeling, Section 5.1, the model requires parameter of heat transfer rate per unit length $q'_i$. Hence, this section will explain behavior of heat transport within rotary kiln pyrolyzer.

In an externally heated rotary kiln, energy transfer to solid bed via two different paths: across the exposed upper surface of the bed and through the covered lower surface of the bed, as represent in Figure 5.4. At the exposed upper surface of the bed, the
solids absorb heat by combination of radiation and convection from the kiln’s wall and freeboard gas. While, the covered lower region of the bed receive heat mostly via conduction heat transfer from the wall, and this path is a part of the regenerative cycle of the kiln’s wall which is the result from rotation of the kiln [37].

Figure 5.4: Schematic diagram of heat transfer in external heated rotary kiln

Agreeing to Figure 5.4, the media of heat transfer in the system consist of three regions: solid bed, freeboard gas, and kiln’s wall. Heat transfer in the externally heated rotary kiln could be expressed by the following five mechanisms:
- $Q_{\text{supply}}$, supplied heat from external source, which would be controlled as constant heat rate or constant wall temperature.
- $Q_{\text{ew-g}}$, heat transfer between exposed surface of the kiln’s wall and the freeboard gas, including both convection and radiation.
- $Q_{\text{ew-eb}}$, heat transfer between exposed upper surface of the bed and exposed surface of the kiln’s wall, which is only via radiation.
- $Q_{\text{g-eb}}$, heat transfer between exposed upper surface of the bed and the freeboard gas, including both convection and radiation.
- $Q_{\text{cw-cb}}$, heat transfer between covered surface of the kiln’s wall and covered lower surface of the bed, which is mostly conduction.

5.2.1 Heat Transfer Rate

According to the energy balance equations in the Section 5.1.4, the equations contain terms of heat transfer rate per unit length ($q'_i$). To simulate the model, heat transfer
rate must be exploited with their heat transfer mechanisms, which are conduction, convection, and radiation.

In general, heat transfer rate can be calculated by using the terms of heat transfer coefficient $h_i$. Therefore, basic equation of heat transfer is introduced, and the heat transfer rate per unit length can be demonstrated as

$$q'_{\text{wall-bed}} = Q_{ew-eb} + Q_{cw-cb} = (h^r_{ew-eb} \Lambda_{eb} + h^{cd}_{cw-cb} \Lambda_{cw}) [T_w - T_b] \quad (5.64)$$

$$q'_{\text{wall-gas}} = Q_{ew-g} = (h^c_{ew-g} + h^r_{ew-g}) \Lambda_{ew} [T_w - T_g] \quad (5.65)$$

$$q'_{\text{gas-bed}} = Q_{g-eb} = (h^c_{g-eb} + h^r_{g-eb}) \Lambda_{eb} [T_g - T_b] \quad (5.66)$$

Where, $h^{cd}$ is conductive heat-transfer coefficient (W/m$^2$K), $h^c$ is convective heat-transfer coefficient (W/m$^2$K), $h^r$ is radiative heat-transfer coefficient (W/m$^2$K), and $\Lambda_i$ is heat exchanged area per unit length (m).

In addition, heat exchanged area per unit length ($\Lambda_i$) can be estimated as a function of the bed depth ($h$), as represent by these following correlations of circular segment

$$\Lambda_{eb}(h) = 2\sqrt{h(2R - h)} \quad (5.67)$$

$$\Lambda_{cw}(h) = \frac{2\pi R}{180} \cos^{-1}\left(\frac{R - h}{R}\right) \quad (5.68)$$

$$\Lambda_{ew}(h) = 2\pi R - \Lambda_{cw}(h) \quad (5.69)$$

Where, subscript $eb$, $cw$, and $ew$ are defined as exposed upper solid bed, covered wall, and exposed wall, respectively. According to Section 2.1.1, the bed depth of granular flow inside rotary kiln can be obtained by the Saeman model and the heat exchanged area per unit length could be directly calculated.

### 5.2.2 Heat Transfer Coefficients

As state in the previous section, heat transfer coefficients ($h_i$) must be determined in order to obtain the value of heat rate per unit length ($q'_i$). According to the system of rotary kiln pyrolyzer, heat transfer by conduction, convection, and radiation are present simultaneously in the kiln. Hence, this section will describe relevant theories to determine these heat transfer coefficients precisely for the rotary kiln pyrolyzer.
Conductive heat transfer between covered wall and covered bed:

According to Li et al. [36], heat transfer between covered wall and covered solid bed, $Q_{cw-cb}$, occur mostly by conduction. Heat flux will transfer from bulk surface of the kiln’s wall to bulk solid bed. Thermal resistance of this behavior must be contained a term of resistance between the two regions and also resistance at the air gap between two surfaces. From the literature [36], total heat transfer coefficient between the covered wall and covered bed can be illustrated as

$$h_{cw-cb}^{cd} = \frac{1}{(\chi d_p/k_g + (2\sqrt{2}k_b\rho_s C_{pb}n/\phi_0)^{-1})}$$

(5.70)

Where, $\chi$ is thickness of gas film (-), $d_p$ is diameter of solid particle (m), $k_g$ is thermal conductivity of gas film (W/mK), $k_b$ is thermal conductivity of the bed (W/mK), $n$ is rotational speed, and $\phi_0$ is half central angle of sectional solid bed ($\phi_0 = \cos^{-1}[(R - h)/R]$).

Convective heat transfer coefficients in rotary kiln:

In rotary kiln, heat transfer by convection includes two features, such as heat transfer between the freeboard gas and exposed wall ($Q^c_{ew-g}$), and heat transfer between the freeboard gas and exposed bed surface ($Q^c_{g-eb}$). The convective heat transfer coefficients in rotary kiln can be computed from the equations based on Tscheng and Watkinson [38] by these following equations

$$h_{ew-g}^c D_e/k_g = 1.54 Re_g^{0.575} Re_w^{-0.292}$$

(5.71)

$$h_{g-eb}^c D_e/k_g = 0.46 Re_g^{0.535} Re_w^{0.104} \eta^{-0.341}$$

(5.72)

Where, flow Reynolds number $Re_g = V_g D_e/\nu$, rotational Reynolds number $Re_w = D_e^2 n/\nu$, percent fill $\eta = (\phi_0 - \sin \phi_0)/2\pi$, and equivalent diameter $D_e = 0.5D(2\pi - \phi_0 + \sin \phi_0)/(\pi - \phi_0/2 + \sin \phi_0/2)$.

Radiative heat transfer coefficients in rotary kiln:

Heat transfer by radiation in rotary kiln — which is a special characteristic of this reactor type — is involved by exposed bed surface, freeboard gas, and exposed wall. The radiative heat transfer is influenced by the emissivity of material and temperature profile of the three phases. According to Gorog et al.[37] and Li et al.[36], a network of
radiative heat transfer resistance between the three phases in the system of externally heated rotary kiln can be drawn as Figure 5.5.

![Radiation analog network within the freeboard zone of externally heated rotary kiln](image)

**Figure 5.5:** Radiation analog network within the freeboard zone of externally heated rotary kiln

According to the figure of radiation network, heat balance over node $J_{ew}$ and $J_b$ can be performed as [39]

$$\frac{E_w - J_{ew}}{(1 - \varepsilon_w) / \varepsilon_w \Lambda_{ew}} = \frac{J_{ew} - E_g}{1 / \varepsilon_w F_{wg} \Lambda_{ew}} + \frac{J_{ew} - J_b}{1 / \varepsilon_w F_{wb} \Lambda_{eb}} \tag{5.73}$$

$$\frac{J_b - E_b}{(1 - \varepsilon_b) / \varepsilon_b \Lambda_{eb}} = \frac{J_{ew} - J_b}{1 / \varepsilon_w F_{wb} \Lambda_{eb}} + \frac{E_g - J_b}{1 / \varepsilon_g F_{gb} \Lambda_{eb}} \tag{5.74}$$

Where, $E$ is emissive power (W/m$^2$), $J$ is radiosity (W/m$^2$), $\varepsilon$ is emissivity (-), and $F$ is view factor (-). Emissive power is defined by Stefan-Boltzmann law, $E = \varepsilon \sigma T^4$ ($\sigma = 5.57 \times 10^{-8} W/m^2 K^4$). Taking $\varepsilon$ and $F$ for both the exposed wall (ew) and the gas as constant, Equation (5.73) and (5.74) can be solved for the unknowns $J_{ew}$ and $J_{eb}$. Therefore, from the heat balance equations over the nodes, heat transfer coefficients of radiation in the externally heated rotary kiln can be expressed as

$$h^r_{ew-eb} = \frac{(J_{ew} - J_{eb})(\varepsilon_w F_{wb})}{(T_w - T_b)} \tag{5.75}$$

$$h^r_{ew-g} = \frac{(J_{ew} - E_g)(\varepsilon_w F_{wg})}{(T_w - T_g)} \tag{5.76}$$

$$h^r_{g-eb} = \frac{(E_g - J_b)(\varepsilon_g F_{gb})}{(T_g - T_b)} \tag{5.77}$$
Apparently, the radiative heat transfer coefficients from Equation (5.75), (5.76), and (5.77) is only dependent of temperature and emissivity.

### 5.3 Simulation Parameters

In order to simulate the model of coupled mass-energy balance in steady-state conditions, the dimension and operating conditions of rotary kiln is described in Table 5.1.

<table>
<thead>
<tr>
<th>Data</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
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<td>Length</td>
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<td>m</td>
<td>1</td>
</tr>
<tr>
<td>Diameter</td>
<td>$D$</td>
<td>m</td>
<td>0.122</td>
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<tr>
<td>Dam height</td>
<td>$h_{\text{dam}}$</td>
<td>mm</td>
<td>14</td>
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<tr>
<td>Inclination</td>
<td>$\beta$</td>
<td>deg</td>
<td>3.00</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>$n$</td>
<td>rpm</td>
<td>5</td>
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<tr>
<td>Mass feed rate</td>
<td>$F_{\text{bed feed}}$</td>
<td>kg/hr</td>
<td>15</td>
</tr>
</tbody>
</table>

Not only dimension and conditions of the kiln that need to implement into the model, but also material properties which is obtain from Baxter et al. [40]. The properties of material that involve in the model are represented in Table 5.2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Wood and Char</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>True density</td>
<td>-</td>
<td>kg/m$^3$</td>
<td>650</td>
</tr>
<tr>
<td>Porosity</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>Bulk density</td>
<td>$\rho_b$</td>
<td>kg/m$^3$</td>
<td>390</td>
</tr>
<tr>
<td>Angle of repose</td>
<td>$\Theta$</td>
<td>deg</td>
<td>30</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$k_b$</td>
<td>W/m.K</td>
<td>0.11</td>
</tr>
<tr>
<td>Emissivity</td>
<td>$\varepsilon_b$</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Product gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>$\nu_g$</td>
<td>m$^2$/s</td>
<td>$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$k_g$</td>
<td>W/m.K</td>
<td>0.026</td>
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<tr>
<td>Molecular weight</td>
<td>$M_{w_g}$</td>
<td>kg/mol</td>
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</tr>
<tr>
<td>Emissivity</td>
<td>$\varepsilon_g$</td>
<td>-</td>
<td>0.9</td>
</tr>
</tbody>
</table>
In addition, specific heat capacity (J/kg.K) of wood, char, and gas can be illustrated by these following equations [40]

\[
C_{pw} = \frac{8.314}{7.72} \left[ e^{\left(\frac{380}{T_b}\right)} \left( \frac{e^{\left(\frac{380}{T_b}\right)} - 1}{380/T_b} \right)^{-2} + 2e^{\left(\frac{1800}{T_b}\right)} \left( \frac{e^{\left(\frac{1800}{T_b}\right)}}{1800/T_b} \right)^{-2} \right]
\]  (5.78)

\[
C_{pc} = \frac{8.314}{11.3} \left[ e^{\left(\frac{380}{T_b}\right)} \left( \frac{e^{\left(\frac{380}{T_b}\right)} - 1}{380/T_b} \right)^{-2} + 2e^{\left(\frac{1800}{T_b}\right)} \left( \frac{e^{\left(\frac{1800}{T_b}\right)}}{1800/T_b} \right)^{-2} \right]
\]  (5.79)

\[
C_{pg} = 770 + 0.629T_g + 0.000191T_g^2
\]  (5.80)

Furthermore, kinetics rate according to the reaction scheme (5.1), can be represented by

\[
r_{\text{wood}} = (k_1 + k_2)p_w
\]  (5.81)

And kinetics data are obtained from Baxter et al. [40], as show in Table 5.3.

We notice that this reference gives the reaction enthalpy for both the reaction wood→gas and wood→char as \( \Delta H_{rxn} = -418 \) kJ/kg, i.e. \( \Delta H_{rxn} < 0 \) implying exothermic reaction. Consulting other literatures, we found that this might be erroneous, and the reactions are likely to be endothermic [41]. However, due to lack of time, an investigation into the heat of reaction was not undertaken and the values provided by Baxter et al. [40] were used as given in their paper.

**Table 5.3: Kinetics data of pyrolysis reaction [40]**

<table>
<thead>
<tr>
<th>Kinetics data</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) (wood to gas)</td>
<td>( A_1 )</td>
<td>1/s</td>
<td>( 1.52 \times 10^7 )</td>
</tr>
<tr>
<td>Pre-factor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation energy</td>
<td>( E_1 )</td>
<td>J/mol</td>
<td>( 1.392 \times 10^5 )</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>( \Delta H_{rxn1} )</td>
<td>kJ/kg</td>
<td>( -418 )</td>
</tr>
<tr>
<td>( k_2 ) (wood to char)</td>
<td>( A_2 )</td>
<td>1/s</td>
<td>( 2.98 \times 10^3 )</td>
</tr>
<tr>
<td>Pre-factor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation energy</td>
<td>( E_2 )</td>
<td>J/mol</td>
<td>( 7.31 \times 10^4 )</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>( \Delta H_{rxn2} )</td>
<td>kJ/kg</td>
<td>( -418 )</td>
</tr>
</tbody>
</table>
Chapter 6

Result on rotary kiln pyrolyzer

This chapter is provided to demonstrate results of rotary kiln pyrolyzer model, which was performed in Chapter 5. The model of steady-state mass and energy balance of rotary kiln pyrolyzer is simulated by using constant wall temperature as supplied energy. The results will be illustrated in two parts: without reaction, and with pyrolysis reaction.

6.1 Heat Transfer in a Kiln without Reaction

In this section, results of the coupled mass-energy balance equation without chemical reaction term at steady-state condition will be represented. First result in Figure 6.1a demonstrates temperature profile of inert material and without consideration of radiation heat transfer at wall temperature of 650 K. In this case, temperature of either solid bed or gas continuously increase from inlet temperature and reach to around 20 K under the wall temperature. Along length of the kiln, gas phase has higher temperature than solid temperature because of very low gas content in the feed.

When the model is implemented term of radiation heat transfer, the result of temperature profile will be changed to Figure 6.1b. According to the figure, temperature of solid bed continuously increase from the inlet temperature (300 K) to reach around 640 K at the end of the kiln as the same trend as no radiation case. Whereas, gas temperature at the beginning of the kiln instantaneously increase which not appear in the first case. Because, heat transport to gas phase is respect to convection and radiation, but convection heat transfer is very low since gas phase remain in stagnant
condition. While, heat transfer by radiation can occur without heat transfer media between two sources, which heat resistance depends only on temperature difference and emissivity coefficient. Therefore, large difference of temperature between kiln wall and gas phase at the entrance produce huge driving force of heat transfer by radiation, which push amount of energy to gas phase.

Nevertheless, almost of supplied energy transfer to solid phase according to Figure 6.2 that represents heat transfer rate within the kiln at wall temperature of 650 K. Furthermore, because heat transfer from kiln wall to solid bed is mostly by conduction, which can be illustrated by Figure 6.3. Consequently, conduction between solid bed and rotating kiln’s wall is the most important role of heat transfer in rotary kiln pyrolyzer.

![Figure 6.1: Temperature profile of inert material at $T_w = 650$ K](image)

![Figure 6.2: Heat transfer rate within rotary kiln pyrolyzer at $T_w = 650$ K](image)
6.2 Heat Transfer and Pyrolysis in Rotary Kiln

After considered the primary pyrolysis reaction in the model, simulation results should be observed conversion and heat of reaction wood pyrolysis.

Figure 6.4 illustrates temperature profile of solid bed and gas with pyrolysis reaction at wall temperature of 650 K. After 20 percent of kiln length, temperature of solid bed significantly increase even higher than wall temperature until reach to maximum point around 900 K, which is the completed conversion point. This behavior can represent effect of exothermic reaction from wood pyrolysis that lead to increase temperature of the system.
By plotting of wood conversion against length of the kiln at different wall temperature as show in Figure 6.5. The figure shows that conversion is very sensitive to wall temperature or heating rate of the system. According to the figure, only increasing of wall temperature at 600 K to 650 K can lead to increase conversion of biomass to be complete. Moreover, in case of 650 K of wall temperature, the curve bend before reach to 100 percent conversion because solid velocity is not constant along the kiln. Importantly, this point shows different behavior between rotary kiln and plug flow reactor.

![Image](image.png)

**Figure 6.5:** Biomass conversion along the length of the kiln

Last but not least, mass flow rate of wood, char, and gas at different wall temperature system can be shown by Figure 6.6. Nothing surprising from the results, mass flow rate of wood is decreasing, but char and gas streams will be increasing by the effect of pyrolysis reaction.

However, the results of temperature profile and heat transfer in wood pyrolysis model may not completely accurate because of unreliable kinetics data. Heat of pyrolysis reaction is still a debatable topic, kinetics parameters from Baxter et al. [40] show strong exothermic reaction in primary stage of wood pyrolysis reaction. While, it has been report in [42] that thermal result of pyrolysis reaction is competition between endothermic and exothermic reactions. During the reaction, heat of pyrolysis reaction changed from high endothermic level to moderately endothermic and finally suddenly to high exothermic values as conversion of biomass feedstock increase [42]. Moreover, it has been well known that pyrolysis of cellulose in biomass is endothermic, but pyrolysis of both hemicellulose and lignin are exothermic during primary pyrolysis reaction [43].
Therefore, the reaction not consists only strong exothermic reaction as described by Baxter et al. [40].

Even though, the result of this model show capability to predict process of rotary kiln pyrolyzer, but validation of the model by comparison with experiment must be required.
Chapter 7

Conclusion

A numerical model of a rotary drum pyrolyzer has been developed. The model consists of two parts: a granular flow model, and a pyrolyzer model. In the first part, characteristics of granular flow within a rotary kiln were modeled and the distribution of residence time were studied as well. While, heat transfer and pyrolysis in rotary kiln were addressed in the second part of this thesis.

As agreement with the results of granular flow model, the model according to Saeman’s expression can be represented to predict flow behavior, such as bed height, velocity profile, cross-sectional area, and mean residence time. Simulation of axial dispersion models generated well predictable results of residence-time distribution compare to experimental data. Two models of dispersion coefficient show different accurate range of using value. For example, based on simulation parameter from Sai [23], constant $D_{ax}$ represent results close to the experiment for range of $D_{ax}$ from 0.1 to $0.6 \times 10^{-5}$ $m^2/s$. While, refined $D_{ax}$ well describeds experimental results for range of $D_0$ around 1.5 to $3 \times 10^{-5}$ $m^3/s$. Therefore, this competition cannot state which model is the best.

Nevertheless, the result of axial dispersion model and experiment reported narrow residence-time distribution. This result can claim that as a first order approximation plug flow model can be represented distribution of residence times for rotary kiln reactor.

In the second part, rotary kiln pyrolyzer was modeled respect to granular flow, all heat transport (conduction, convection, and radiation), and pyrolysis reaction. Calculation of steady-state model for constant wall temperature were generated, and the simulation show reasonable results which predicted by the model. According to the results,
conduction between rotating kiln’s surface and solid bed is the main heat transport path inside rotary kiln.

From the result at 650 K of wall temperature, rotary kiln pyrolyzer is mainly provided to heat up the material in the first 20 percent of length approximately. And later 80 percent of the length observed significant char and gas produced by pyrolysis reaction, also great increasing of temperature by the effect of exothermic reaction. Furthermore, the diagram of biomass conversion respect to length of the kiln resulted spacial characteristic of rotary kiln that was implemented into the model.

Unfortunately, energy accumulation in the kiln that is affected by heat of reaction need to be re-considered, because of dynamic information of kinetics parameters from the literature [40]. Notwithstanding, the main purpose of this Master thesis is to develop numerical model for rotary kiln pyrolyzer, which kinetics data of pyrolysis reaction have been placed at the secondary consideration. As a consequence, substitution of kinetics data for wood pyrolysis by better sources of literature or experiment to this model, can be fulfill and increase degree of rotary kiln pyrolyzer model in the future.
Appendix A

Fitting of Dispersion Coefficient

In order to fit the values of dispersion coefficient in ADM, these experimental data according to Sai [23] was employed, which are represented by Table A.1. Where, the definition of dispersion number in the literature is

\[
\frac{1}{Pe} = \frac{D_{ax}}{uL}
\]  \hspace{1cm} (A.1)

In addition, variance \( \sigma \) can be calculated by

\[
\frac{\sigma^2}{\tau^2} = 2 \left( \frac{D_{ax}}{uL} \right)
\]  \hspace{1cm} (A.2)

Where, \( Pe \) is Peclet number, \( D_{ax} \) is dispersion coefficient, \( u \) is bed velocity, \( L \) is length of a kiln, \( \tau \) is mean residence time.
## Table A.1: Details of experimental conditions from [23]

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed rate [kg/h]</th>
<th>Rotational speed [rpm]</th>
<th>Inclination [deg.]</th>
<th>MRT [s]</th>
<th>Dispersion number [$\times 10^2$]</th>
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</table>
Appendix B

Additional Results of RTD

The further results of residence-time distribution according to experimental condition from Sai [23] in Table A.1 can be represented by the following diagrams.

Figure B.1: Residence-time distribution of run no.1, 2, 3, and 4
Appendix B. Additional results of RTD

Figure B.2: Residence-time distribution of run no.5, 6, 7, 8, 10, and 11
Appendix B. Additional results of RTD

Figure B.3: Residence-time distribution of run no.12, 13, 14, 15, 16, and 17
Figure B.4: Residence-time distribution of run no.18, 19, 20, 21, 22, and 23
Appendix B. Additional results of RTD

Figure B.5: Residence-time distribution of run no.24, 25, 26, and 27
Appendix C

The Original Assignment
Bibliography


