2.1. Reviews on Previous Woods Pyrolysis Researches

2.1.1. Biomass Conversion Processes

All the organic materials have the potential converted into energy. In general, there are two paths in biomass conversion as shown in Figure 2.1. They are the biochemical and thermo chemical processes [9].

Figure 2.1. Chart of the Biomass Conversion Process [9]

Sources: Prabir Basu, Biomass gasification and pyrolysis practical design and theory
Biochemical conversion is the decomposition of biomass into smaller molecules by bacteria or enzymes. This process is much slower than the thermochemical conversion, but process does not require a lot of external energy. The three main methods for biochemical conversion are:

a. Digestion (anaerobic and aerobic)
b. Fermentation
c. Enzymatic or acid hydrolysis

Thermochemical conversion is the decomposition process of solid biomass molecules transformed into liquid and gaseous materials under heat. For example, wood pyrolysis is one of the thermochemical conversion processes. The thermochemical processes are divided into four methods:

a. Combustion
b. Pyrolysis
c. Gasification
d. Melting

As mentioned above, the conversion processes of biomass into energy source are generally divided into two pathways, biochemical and thermochemical. However, in this chapter gasification and pyrolysis of the thermochemical processes focus for discussion.

Gasification is a process in which the molecules of carbon dioxide are converted into a gaseous fuel such as $\text{H}_2$, $\text{CO}$, and $\text{CH}_4$ with various heating values. During a number of the endothermic reactions, gasification process takes place. The
heat required for the endothermic reaction is usually given from an external heat source or internal heat source, for example, partial combustion of biomass. Less-oxygen-air or inert gas is used to obtain excellent products with a high calorific value of 6 to 16 MJ/m³.

Gasification is an important process from which the products can be used for power generation, manufacturing of chemicals and transportation fuel. Physical, chemical and thermal processes are involved with the gasification process, sequentially or simultaneously depending on the reactor design and materials.

Pyrolysis and gasification processes are shown in Figure 2.2. In the gasification process, O₂ free atmosphere or O₂ controlled atmosphere is used. The direct process uses a part of raw materials to generate heat by burning. If heat is supplied from an external source, the process is called indirect gasification. At the bottom of the figure, an outline of pyrolysis process is shown, but the processes and the products of both processes are not substantially different. In principle, gasification process uses the pyrolysis process, but the process is done under high temperature, 900°C or more than usual pyrolysis. Namely, in the gasification process, the products of pyrolysis under 500°C or less are further decomposed under the high temperature [10].
Figure 2.2. The process of gasification and pyrolysis [10].

Pyrolysis is a process of molecular decomposition of biomass of heat without air supply or below atmospheric pressure to produce charcoal (solid), bio-oil (liquid) and gas [9]. Pyrolysis products can be used for fuel with or without return process, or can be used as raw materials for the chemical industry. Pyrolysis product that can be directly used is methane gas for fuel-generators. However, the tar products cannot be used directly, but rather should be further processed through distillation for getting the bio oil. Tar/ bio oil can be changed to conventional hydrocarbon fuels by eliminating the oxygen content through the hydro treating process [11][12].

2.1.2. Thermo chemical Reactions in Wood Pyrolysis

Wood pyrolysis technology has been used to obtain char or chemicals from ancient era as mentioned above. Therefore, many researches concerning pyrolysis have been carried out until now. Several review articles [1] [2] [3] have been
published. According to those papers, wood consists of three main components, namely, cellulose, hemicellulose, and lignin. The results obtained by the previous research works are outlined below [13]. As shown in Figure 2.3, where each component will be decomposed at different temperature conditions.

![Figure 2.3. Thermal stability main components of wood [13].](image)

In devolatilisation process, the main components of wood can be seen in Figure 2.4. Drying process of main components occurs until temperature $100^\circ C$, and
then in temperature between 250 to 300°C, hemicellulose is decomposed into acetic acid, and furfural. At temperature between 200 to 260°C, cellulose is decomposed into levoglucosan, and hydroxyl acetal dehyde. At temperature between 260 to 500°C lignin is decomposed into methoxyphenols (e.g. guaiacol), dimethoxy phenols (e.g. syringol), catechols, phenols, alkyl-phenols, and methanol.

All intact biomasses are decomposed at temperature between 100 and 600°C into charcoal, tar and gases (i.e. H₂, CO, CO₂, and CH₄).

Figure 2.3. Stage Process Of Thermal Decompose Wood Component [13].
2.1.3. Experimental Works of Wood Pyrolysis

Pyrolysis is an important phenomenon in the combustion of wood, and is modeled successfully to predict the evolution of volatiles. Physical and chemical aspects of pyrolysis can be explored by describing how various parameters such as the structure and composition of the wood, the rate of heating and residence time, have effects on reaction rates and volatile yields:

a. Physical Reactions

The basic phenomenon during the pyrolysis is the heat transfer that leads to an increase in the temperature of the fuel/feedstock, namely biomass. At the beginning of pyrolysis, the temperature increase causes the release of volatile and formation of charcoal from fuel. The volatile flow at the surroundings results in heat transfers into wood that has not experienced the pyrolysis. Then, volatile condensation will produce tar and volatile reaction function as an auto-catalysts for the secondary reaction.

b. Chemical Reaction

Chemical properties of pyrolysis are strongly influenced by the composition of the raw material/fuel biomass. The chemical element composition of the broad class of wood can be obtained by proximate and ultimate analyses as shown in the Table 2.1.
Table 2.3. Typical Proximate and Ultimate Analyses of Dry Wood by Weight (%) [14]

<table>
<thead>
<tr>
<th></th>
<th>Proximate (%)</th>
<th>Ultimate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile</td>
<td>Fixed</td>
</tr>
<tr>
<td></td>
<td>Matter</td>
<td>Carbon</td>
</tr>
<tr>
<td>Soft woods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>77.2</td>
<td>22.0</td>
</tr>
<tr>
<td>Bark</td>
<td>73.3</td>
<td>23.7</td>
</tr>
<tr>
<td>Hard wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>77.3</td>
<td>19.4</td>
</tr>
<tr>
<td>Bark</td>
<td>76.7</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Proximate analysis gives information about volatile matter, fixed carbon and ash. In the table, weight fractions of the three components are indicated. It can be seen that the weight fractions are almost same for the trunk and bark of wood, although an ash weight fraction is larger in bark than in trunk for both soft and hard woods. Around 77% of wood is extracted as volatiles and around 20% of the wood remains as char.

Ultimate analysis gives information about chemical elements contained in wood. The soft woods contain 53.0% of C, 6.1% of H, 38.8% of O and 0.15% of N, while the hard woods contain 51.0% of C, 6.2% of H, 39.9% of O and 0.4% of N.

2.1.4. Kinetic Models in Biomass Pyrolysis

Kinetic models of the pyrolysis of ligno-cellulosic fuels like biomass maybe broadly classified into three types [9]. They are:

a. One-stage global single reaction. The pyrolysis is modeled by a one-step reaction using experimentally measured weight-loss rates.
b. One-stage, multiple reactions. Several parallel reactions are used to describe the degradation of biomass into char and several gases. As one-stage simplified kinetic model is used in these parallel reactions. It is useful for the determination of product distribution.

c. Two-stage semi global. This model includes both primary and secondary reactions, occurring in the series.

On the other hand [15], Typical kinetic models of pyrolysis are described as follows:

1. One Step Global Model:

One-step global model was used during the early stages of pyrolysis model development. This Model considers the pyrolysis reaction sequence as one-step. The step of the pyrolysis process is expressed below. Solid biomass are directly converted into gas and char. Sometimes, there is included beside gas and char. This model is very simple and many researchers use this model.

\[
\text{Wood} \xrightarrow{k} \text{Gas} \quad \text{Gas} \xrightarrow{k} \text{Char}
\]

Chemical kinetics of this model are expressed by Arrhenius equation as follow:

\[
k = A \exp \left( \frac{E_a}{RT} \right)
\]

(2.1)
Where $k$ is a reaction rate, $A$ is **pre-exponential factor**, $E_a$ is activation energy, $R$ is the universal gas constant, and $T$ is temperature in Kelvin.

In this model, each yield of the pyrolysis is obtained as a constant fraction.

2. Competing Models:

Thunder et al [15] improved one-step global model by introducing parallel multi-reaction as indicated below. In this model, biomass is simultaneously converted into light gases, tar, and coke by different chemical reaction equations. The chemical reaction rates, are expressed by $k_g$, $k_T$, and $k_C$, the land is given by the similar equations to Eq. (1-1). The different constants $A$ and $E_a$ are given to each reaction equation.

\[
\begin{align*}
\text{Wood} & \xrightarrow{k_g} \text{Light gases} \\
& \xrightarrow{k_T} \text{Tar} \\
& \xrightarrow{k_C} \text{Coke}
\end{align*}
\]

3. Two Step Multi-reaction Model:

The primary chemical reactions in this model are the same as those of the one-step multi-reaction model, but the sequentially secondary reaction takes place [16]. In the secondary reaction, the tar produced by the primary reaction is converted into gases and char. Here the tar will break down or experiencing gas polymerization stepped into a coke on reaction exothermic.
4. Parallel Reaction Model:

Three parallel reaction model for three main components, cellulose, hemicellulose, and lignin of the wood was proposed by Koufopanos et al [9]. In this model, three reactions take place independently. The rate of pyrolysis of one biomass type can be represented by the sum of the corresponding rates of the main biomass components (cellulose, lignin, and hemicellulose).

\[
M_c \xrightarrow{k_c} \text{Gases} + \text{Char} \\
M_h \xrightarrow{k_h} \text{Gases} + \text{Char} \\
M_l \xrightarrow{k_l} \text{Gases} + \text{Char} \\
k_p = k_c + k_h + k_l
\]

Where \(M_c\), \(M_h\), and \(M_l\) are fractions of three main components, cellulose, hemicellulose, and lignin of wood, and \(k_c\), \(k_h\), and \(k_l\) are reaction rates of three components, respectively. In this model, the reactions complete with one-step.
2.1.5. Numerical Analysis of pyrolysis

Numerical analysis of pyrolysis has been carried out using several methods including theoretical approach. First, theoretical approach is executed to reduce kinetic equations for pyrolysis decomposition and energy equation for temperature. These equations are solved simultaneously. Frequently, those equations are numerically solved using finite difference method [17].

Finite difference method can easily be applied to a problem with simple boundary conditions. For instance, it is the case where furnace can be considered as an infinitive because biomass is so small. In case, the temperature is a biomass are considered uniform. Although Baggio P. et all [18] analyzed the pyrolysis process of large particle in which temperature gradient cannot be neglected, particle shape was cylindrical and heat transfer is axisymmetric, which is easily solved.

On the other hand, computational fluid dynamic (CFD) codes, for instance ANSYS Fluent, are used for analysis of pyrolysis process. Papadikis K. Et al [19] applied CFD to analyze fast pyrolysis of biomass. Using CFD code, multiphase flow equations, mass balance equation, momentum equation, and energy equations are solved to calculate behaviors of particle biomass in a cylindrical fluid-bed furnace. If finite element code like Fluent is used, complex shaped biomasses and actual sized furnace can be analysis target.

Researches using CFD to analyze biomass pyrolysis process are summarized by Wang Y. and Yan L [20]. They pointed out that even if CFD numerical analysis code like Fluent is applied to pyrolysis process, since its phenomena and biomass
structures are very complicated, still biggest challenge is necessary to obtain reasonable numerical results.

2.1.5.1. Governing Equations in CDF

According to [21] for all flows, CFD using ANSYS FLUENT solves conservation equations for mass and momentum. For flows involving heat transfer or compressibility, an additional equation for energy conservation is solved. For flows involving species mixing or reactions, a species conservation equation is solved or, if the non-premixed combustion model is used, conservation equations for the mixture fraction and its variance are solved. Additional transport equations are also solved when the flow is turbulent.

a. The Mass Conservation Equation

The equation for conservation of mass, or continuity equation, can be written as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = S_m$$ ......................................................... (2.2)

This is the general form of the mass conservation equation and is valid for incompressible as well as compressible flows. The source $S_m$ is the mass added to the continuous phase from the dispersed second phase (e.g., due to vaporization of liquid droplets) and any user-defined sources. $\rho$ is density, $\vec{v}$ is velocity vector and $T$ is temperature.

For 2D axisymmetric geometries, the continuity equation is given by:
\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho v_x) + \frac{\partial}{\partial r} (\rho v_r) + \frac{\partial}{\partial z} (\rho v_z) = S_m \quad \text{.......................... (2.3)}
\]

where \( x \) is the axial coordinate, \( r \) is the radial coordinate, \( v_x \) is the axial velocity, and \( v_r \) is the radial velocity.

b. Momentum Conservation Equations

\[
\frac{\partial}{\partial t} (\rho V) + \nabla \cdot (\rho V V) = -\nabla p + \nabla \cdot (\tau \ell) + \rho g + F \quad \text{.......................... (2.4)}
\]

Where \( p \) is the static pressure, \( \ell \) is the stress tensor, and \( \rho g \) and \( F \) are the gravitational body force and external body forces (e.g., that arise from interaction with the dispersed phase), respectively. \( F \) also contains other model dependent source terms such as porous-media and user-defined sources.

The stress tensor \( \ell \) is given by:

\[
\ell = \mu \left[ (\nabla \ell)^T - \frac{2}{3} \nabla \cdot \ell \right] \quad \text{.......................... (2.5)}
\]

c. Thermal Conductivity Model of Reactor Chamber

In this study, two software is used to simulate thermal conduction in the reactor chamber. To construct an axisymmetric model of the reactor chamber used for the experiments, software AUTO CAD is used. An axisymmetric model base on eq. 2.6.

\[
\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( k_r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_z \frac{\partial T}{\partial z} \right) = Q \quad \text{.......................... (2.6)}
\]
where:

\[ \rho = \text{Density} \left( \frac{kg}{m^3} \right) \]

\[ C = \text{Specific heat} \left( \frac{J}{kgK} \right) \]

\[ Q = \text{Volume generation heat rate} \]

\[ T = \text{Temperature} (K) \]

\[ t = \text{time (minute)} \]

\[ k = \text{thermal conductivity} \left( \frac{w}{mK} \right) \]

\[ r = \text{radial coordinate} \]

\[ z = \text{axial direction} \]

2.1.5.2. Assumptions of Numerical Analysis

a. The thermal conduction analysis used, only solid model (not fluid model) even in ambient air and chamber air. Heat convection and radiation effects are neglected in this analysis, because the chamber is in vacuum and high temperature part of a chamber inside is covered by wood pieces.

b. Heat transfer inside the chamber was calculated under consideration of thermal conduction alone, prior to pyrolysis decomposition and the results was well compared with experimental data. However, heat and mass transfer analysis with chemical reactions will explain using ANSYS Fluent.
c. In the thermochemical decomposition, a reaction rate is also an important factor. Arrhenius type of kinetic reaction rate model is used here. Kinetic reaction rate $K$ is given by equation 2.1 as follows:

$$k = A \exp\left(-\frac{E}{RT}\right)$$

(2.7)

Where, $A$ is frequency factor, or pre-exponential coefficient, $E$ is activate energy (in this case the active energy is constant), $T$ is reaction temperature, and $R$ is constant gas, for each component of wood, pre-exponent is constant. In this study pre-exponential and active energy were set available in the fluent, we will explain in the next chapter, and the temperature process is setting $T_1 = 300$ K and $T_2 = 1000$ K.

d. Inside the reactor chamber five wood concentric hollow cylinder wood pieces with 241.5 mm of height is calculated $= 5$ Kg are considered 1.0 mm is considered and volatile gases from wood pieces enter the upper part of the pre-vacuum chamber through this space.