CHAPTER 3

REVIEW OF BIOMASS GASIFICATION

3.1 INTRODUCTION

Biomass consists of moisture, volatile matter, fixed carbon and ash. Except ash, all other components undergo thermal degradation on heating. Heating uniformly at different temperature ranges, releases these components one by one. First moisture is released when heated up to 120°C, then volatile matter is released between 200°C to 450°C and fixed carbon is released as oxides of carbon at higher temperatures. During the gasification depending upon the temperature in the bed of biomass, different zones are assumed to be present. These zones are drying, de-volatilization, reduction and combustion. Splitting of the thermal degradation process into definite zones is not realistic but nevertheless theoretically essential.

Since temperature affects the degradation, the attainment of uniform temperature influences the degree of degradation. If the biomasses were powdery and porous, temperature will be uniform throughout the particle and each of the above processes will be occurring separately at each temperature level. The reaction takes place continuously at all points.

On the other hand, if the biomass were lumps, then non-uniformity in temperature occurs within the lump. This results in the processes occurring simultaneously. The physical properties of biomass play a vital role in influencing the degree of degradation.
3.2 VARIABLES AFFECTING GASIFICATION

The physical properties of the biomass and the environment are found to influence the thermal degradation. The variables along with their ranges affecting gasification are given in Table 3.1 (Kirubakaran et al. 2007b). The effect of these variables on gasification is discussed in subsequent sections.

**Table 3.1 Variables Affecting Thermo-Chemical Process**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Variable</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Size and shape</td>
<td>Powdery</td>
</tr>
<tr>
<td>2</td>
<td>Initial porosity</td>
<td>Low</td>
</tr>
<tr>
<td>3</td>
<td>Moisture</td>
<td>Low</td>
</tr>
<tr>
<td>4</td>
<td>Environment</td>
<td>Inert</td>
</tr>
<tr>
<td>5</td>
<td>Flow of medium</td>
<td>Static</td>
</tr>
<tr>
<td>6</td>
<td>Heating rate</td>
<td>Slow</td>
</tr>
<tr>
<td>7</td>
<td>Ash</td>
<td>Catalytic</td>
</tr>
<tr>
<td>8</td>
<td>External diffusion resistance</td>
<td>Low</td>
</tr>
<tr>
<td>9</td>
<td>Temperature</td>
<td>&lt;500°C</td>
</tr>
</tbody>
</table>

3.2.1 Effect of Size and Shape

Particle size of biomass influences the process of gasification. Maa and Bailie (1973) have studied the effect of particle size on the pyrolysis of cellulosic material. They have observed that the pyrolysis of cellulosic material with particle size less than 0.2 cm is reaction-controlled, the particle sizes between 0.2 to 6 cm is both heat transfer and chemical reaction control and above 6 cm heat transfer controls.
Even though spherical particles do not exist in practice, many investigations have been reported due to its simplicity in analysing the data. Pellets or sticks are very commonly available biomass. Several investigators (Galgno and Blasi 2004) have analyzed the route of gasification in detail. Thermal conductivity plays a vital role in deciding the radial temperature profile. Since gasification is a thermal process, non-uniformity in temperature affects degree of gasification considerably. Therefore the bigger the particle size greater would be the non-uniformity in temperature. This leads to drying, devolatilization and gasification taking place simultaneously. This results in non-uniform gas composition with varying rate of reaction. The particle property evolves with the extent of reaction. The weight loss represents the sum of the individual losses due to three phases of gasification at a temperature averaged over the entire radius. The temperature increases from outer radius to centre. Each stage of thermal degradation of biomass takes place whenever the appropriate temperature is reached. For example around 100°C drying releases water vapor creating more pores in the biomass. This change in particle property decreases the density and thermal conductivity. However the product / reacting gases can flow through these pores with least resistances. This shifts the regime of reaction from internal diffusion control initially to chemical reaction control. If the pore gets widened, then wall strength gets reduced. The wall of pores collapses once a critical thickness is reached.

The porosity corresponding to this thickness in called as critical porosity. The onset of peripheral percolation commences at this stage. In the early stages of reaction, the reaction is taking place at the external surface. Afterwards the shrinkage in particle size can be attributed exclusively to the peripheral percolation. The thermal degradation brings about changes in the particle property. Porosity and pore distribution change considerably resulting in variation in thermal conductivity and surface area. If the micro pores get
widened and become mesa pore, the porosity increases with decrease in surface area. Increased pore size reduces the internal diffusion resistances and the regime of reaction is shifted to chemical control. The increase in porosity reduces the thermal conductivity and hence the heat transfer rate. At this stage, the onset of outer peripheral percolation collapses the fragments and the particle becomes devoid of the porous segments.

Therefore the nature of influence of particle size on thermal degradation is highly complex. It depends upon the initial porosity, pore distribution, moisture and ash. However for powdery biomass, the temperature is uniform and the thermal degradation is due to chemical reaction taking place continuously throughout the particle.

3.2.2 Effect of Initial Porosity

If the initial porosity were low with micro pores then the biomass has very high surface area and thermal conductivity. The internal diffusion resistance and heat transfer rate would be high. The thermal degradation will be taking place only on the external surface. As the reaction progresses, the porosity increase due to widening of pores, changing the pores to mesa pores. This reduces the surface area and hence the rate of reaction. Widening of pores reduces the wall thickness. The pore collapses once the porosity become critical. This shifts the reaction regime from diffusion resistance to chemical reaction control. The reaction is attributed exclusively to the peripheral percolation

If the initial porosity were low with mesa pores, then the biomass has low surface area and thermal conductivity. The internal diffusion resistance and the heat transfer rate would be low. The reactant gases diffuse throughout the particle easily. However, non-uniformity in temperature due to poor thermal conductivity is responsible for slowing down the reaction rate.
Initially the reaction is taking place on the external surface, widening the pores further. Once the onset of percolation commences, the particle size shrinks reducing the internal diffusion resistance further. Therefore with low porosity and mesa pore particle, chemical reaction controls for a considerable amount of time.

If the initial porosity were high with micro pores, then surface area, thermal conductivity and strength parameter would be the highest. The internal diffusion resistance would be controlling. The higher heat transfer rates due to high thermal conductivity reduce the radial temperature variations considerably. The overall rate of thermal degradation would be always high. The strength parameter decreases with widening of pores and peripheral percolation commences as discussed earlier. Even though the reaction takes place on the external surface initially, the peripheral percolation controls the reaction further.

If the initial porosity were high with mesa pore, the surface area, thermal conductivity and internal diffusion resistance would be the least. Chemical reaction is controlling always. With pore widening due to drying and devolatilization, the strength of the walls becomes reduced. Upon the onset of percolation, the wall collapses and the particle shrinkage is due to the peripheral percolation. Even though the gases diffuse uniformly, the reaction rate and mechanism are varying radially due to non-uniformity in temperature.

3.2.3 Effect of Moisture

Depending upon the moisture content, the generation of pores or widening of pores occurs at drying temperature. This increases the porosity, and reduces the surface area and internal diffusion resistance. Further the water vapor at high temperature takes part in gasification of char.
3.2.4 Effect of Environment

Generally it is observed that reactive environment (air/oxygen) results in complete gasification of biomass while inert environment (nitrogen/argon) aids devolatilization (pyrolysis) yielding more char. Pyrolysis of biomass has attracted the attention of many investigators (Williams and Besler 1993, 1996 and Shafizadeh 1968) as it yields solid, liquid and gaseous fuel from biomass.

Commercial gasifiers employ air at sub-stoichiometric quantity to generate producer gas. Depending upon the type of contact between biomass and air, the gasifier is called down draft, updraft or cross flow gasifier. Each type has its own advantages and disadvantages in generating quality producer gas. Thus the understanding on the effect of environment on gasification has come to the natural end. Hence the present gasifiers produce gases with low calorific values due to dilution by nitrogen.

Every biomass has carbon, hydrogen and oxygen in major quantities. Raveendran et al (1995) have reported the composition of 13 biomasses. These are reproduced in Table 2.1. A closer look at the carbon and oxygen contents of these biomasses reveals that every biomass has enough oxygen to convert carbon to oxides of carbon either partially or completely.

Using the data, the percentage of carbon that could have been converted to carbon monoxide by oxygen available in the biomass (bio-oxygen) was calculated for each of the biomass and is given in the last but one column of the Table 2.1. It is evident that 56.6 % to 87.08 % of carbon could have been converted to carbon monoxide depending upon the bio-oxygen available. 12.92 to 43.4 % of carbon is yet to be converted. Conversely it is significant that carbon is also consumed in the formation of
methane and in the water gas reaction. Therefore it is possible to gasify the biomass in the absence of air theoretically. This paves way for auto-gasification of solid combustible matter in the biomass by the bio-oxygen itself. The auto gasification is a thermo chemical process of converting solid combustibles in biomass into gaseous fuels using the bio-oxygen and catalytic ash. Kirubakaran et al (2007a) have reported the feasibility of auto gasification of several bioresidues. This needs further investigation. The key objective of this present investigation is to ascertain the achievability of auto-gasification of coir pith powder and its pellet.

3.2.5 Effect of Flow of Medium

Williams and Besler (1993, 1996) have observed that the secondary degradation of char to gases can be prevented in pyrolysis of biomass by sweeping away the devolatilized gases by inert gases such as nitrogen. This has resulted in yield of more char. Therefore many investigators have carried out the pyrolysis studies with flowing nitrogen.

Safi et al (2004) have carried out studies on global degradation kinetics of pine needles in air. An airflow rate of 50 ml/min was maintained. The char obtained at different heating rates were less than the available fixed carbon, due to the presence of reactive medium such as air.

If the medium were static, then there is a possibility of secondary degradation of char taking place. This may result in complete gasification of biomass. However no attempt is reported so far on the effect of static inert or reactive medium on the gasification of biomass. Therefore the present investigation aims at carrying out this study.
3.2.6 Effect of Heating Rate

Bridgwater (1990) reported the influence of pyrolysis reaction parameters such as temperature and heating rates to determine the yield and composition of the derived products. The liquid intermediate products of pyrolysis condenses without further breaking down higher molecular weight species into gaseous products in fast pyrolysis with high heating rates of up to 1000°C/min at temperature below 650°C and with rapid quenching. Formation of char is minimized by high heating rates. Gaseous products form at high heating rates and high maximum temperature. If the desired end product is the liquid hydrocarbon or bio-oil, fast pyrolysis is preferred. Fluidized bed, cyclonic, entrained flow; vortex and ablative reactors are recommended for fast pyrolysis.

Slow pyrolysis requires low heating rates and low maximum temperature. Maximum yield of char via secondary coking and re-polymerization reaction is observed at slow heating rates coupled with a low final maximum temperature (less than 500°C) and with long gas and solid residence times. Therefore slow pyrolysis has been used for the production of char. Fixed bed reactor, multiple hearths and rotary kiln are used for slow pyrolysis.

Even though the rate of purging out of gaseous products to prevent the secondary reaction influences the pyrolysis, no attempt has been made so far to evaluate its effect. Williams and Besler (1996) have carried out a detailed study on the influence of temperature and heating rate on slow pyrolysis of biomass in a static batch reactor at heating rates of 5, 20, 40 and 80 K/min to a final temperature of 300, 420, 600 and 720°C with nitrogen as purging gas. Slow pyrolysis has yielded aqueous, oil, gas and char. The
gaseous, liquid and solid products of pyrolysis are analyzed for composition, yield and calorific value.

The following is the observation made:

- A decrease in the yield of char and a corresponding increase in the yield of oil and gas resulted with increase in temperature for each heating rate.
- At 420°C and above, the aqueous yield remained virtually constant at about 37 Wt %
- Very high char yield has been obtained at 300°C as char has retained partially pyrolysis material such as hydrocarbons of high molecular weight.
- The high molecular weight hydrocarbon within char volatilizes and degrades thermally as the temperature as increased.
- The oil yield increases steadily from 300 to 720°C at all heating rates.
- The oils are highly oxygenated.
- An increase in carbon and hydrogen and a decrease in sulphur and oxygen contents of the oil with heating rates were observed.
- The gas yield also increases with temperature at all heating rates.
- The char yield decreases with temperature and with heating rates.
The calorific values of oils and char were essentially independent of heating rates and were found to be an average of 23 and 32 MJ/kg respectively.

The yields of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), and methane (CH₄) and ethane (C₂H₆) increased with heating rates.

Total calorific values were 13.6, 15.7, and 15.8 MJ/m³ at heating rates of 5, 20, 40 and 80 K/min respectively.

The calorific values of gases were fairly independent of heating rates above 5 K/min.

Water and oil were evolved throughout the higher temperature.

Since pyrolysis and gasification of biomass is a thermo chemical process, the temperature and rates of heating have pronounced effects on the weight loss of biomass. Thermo gravimetric analysis (TGA) measures and records the weight loss of biomass sample as the temperature is raised at desired uniform rate. In addition the effect of environment such as inert and reacting atmosphere with and without flowing can be studied. For determining the characteristics of pyrolysis and also kinetic parameters, thermo gravimetric analysis (TGA) is used extensively. Kinetic parameters are calculated using the net weight loss with simplifying assumptions, which do not necessarily correspond to the complex chemical reaction in the thermal degradation of biomass. However TGA data provide useful comparisons of reaction parameters such as temperature and heating rates.

The thermal degradation of biomass and samples of cellulose, hemicellulose and lignin has been studied extensively using Thermo gravimetric analyzer (TGA). Most of the investigators have studied the effects
of heating rates and temperature on pyrolysis using Thermo gravimetric analyzer (TGA). Since the main objective of their studies is to get maximum char and combustible volatiles, thermo gravimetric analysis studies were reported to carry out in inert atmosphere with flowing nitrogen to purge out the product gases, thus preventing the secondary reactions. Low heating rates with low final temperature were employed to achieve slow pyrolysis of biomass and samples of cellulose, hemicellulose and lignin.

Williams and Besler (1993, 1996) have carried out thermo gravimetric analysis (TGA) of wood and rice husks and samples of cellulose, hemicellulose and lignin at heating rates of 5, 20, 40, and 80 K/min with nitrogen flowing to purge out the product of gases.

The following observations were made at all heating rates:

- Hemi cellulose represented by xylan decomposes between 220 and 320°C and continued heating up to 720°C resulted in yielding char approximately 20 Wt% of the original hemicellulose
- Cellulose decomposes between 250 and 360°C and has yielded char approximately 8 Wt% of the original cellulose after heating to 720°C
- Lignin undergoes gradual decomposition between 80 and 500°C yielding char 55 Wt% of the original lignin after heating to 720°C

From the thermo gravimetric analysis (TGA) data, Differential Thermo gram (DTG) curves have been drawn at different heating rates for cellulose, hemi cellulose and lignin.
The following was observed:

- Only one temperature for maximum weight loss has been observed for hemicellulose, cellulose and lignin.

- Two temperatures for maximum weight losses were observed for wood (one closer to hemicellulose maximum temperature and the other to cellulose).

- As heating rate increases there is a lateral shift in the temperatures for maximum weight loss due to combined effects of heat transfer at the different heating rates and the kinetics of the decomposition resulting in delayed decomposition.

Safi et al (2004) have studied the global degradation kinetics of pine needles in air. Thermo gravimetric analysis (TGA) was carried out with 10 mg of sample in air flowing at 50 ml/min at 5, 10, 15, 25 and 30 K/min. It is interesting to note that three temperatures for maximum weight loss were observed unlike wood and rice husks pyrolysis reported by Williams and Besler (1996). Further there is a lateral shift in the temperatures for maximum weight loss for heating rates 5 and 10 K/min. The temperature for maximum weight loss decreases with increase in heating rates from 15 to 30 K/min.

3.2.7 Effect of Ash

The ash content and its composition in biomass play a vital role in retaining the shape and in catalyzing the reaction. Mineral content in ash has found to influence the rate of gasification (Raveendran et al 1995). The strength parameter of the biomass depends upon the ash content. Higher the ash more would be the strength and onset of percolation will not influence the
reaction. The reaction will be taking place on the shrinking surface of the particle. The particle size and shape do not get altered. On the other hand, with low ash content, the shrinking of particle is due to peripheral percolation. As discussed earlier, the onset of percolation plays a key role in the progress of reaction due to low strength parameter of particle. At higher temperature, ash fuses sealing off the reactants from further reacting. Shafizadeh (1968) and Raveendran et al (1995) have observed that the minerals present in the ash catalyze the degradation at lower temperature.

3.2.8 Effect of External Mass Transfer Resistance

External mass transfer resistance hardly affects the conversion, irrespective of the internal diffusion resistance. The evolution of overall properties of particle does not get alerted with the extent of external mass transfer resistance. This is exclusively attributed to the heat transfer, since the reaction is a thermal process.

3.2.9 Effect of Order of Reaction

The onset of percolation influences the order of reaction. Before the onset of percolation, the diffusion resistance controls the gas concentration within the pores; the reaction order becomes zero, independent of concentration. After the onset of percolation, the reaction depends upon the concentration and order varies between 1/3 to 1.0. Change in order is due to textural evolution of the properties.

3.2.10 Effect of Temperature

Two temperature ranges are normally selected above and below 500°C. Generally temperatures above 500°C are chosen for reduction of carbon dioxide by carbon-to-carbon monoxide. Therefore pyrolysis of
biomass is carried out at temperature less than 500°C for the maximum yield of char with inert medium flowing. Complete gasification is achieved at temperature above 500°C with air flowing. Method of heating also influences the mechanism of thermal degradation.

No attempt is reported on the effect of temperature and method of heating on complete gasification of biomass with static inert / reactive medium. The present investigation proposes to investigate this effect.

3.2.11 Effect of Thermal Properties on Heating

The above discussions clearly indicate that in a porous and powdery biomass such as sawdust, coir pith, the temperature is uniform; the reaction takes place continuously throughout the particle. However, in the case of lumped biomass, the variations in initial porosity, moisture, pore distribution and ash content and its composition influence the thermal degradation of biomass combinedly and make the process very complex.

In lumps, these properties have pronounced effect on the temperature distribution. Temperature distribution decides the course of reaction. Temperature distribution depends upon thermal conductivity (k), specific heat (Cp), and density (ρ). All these are not constant and are changing with conversion. Therefore the variations with conversions should be understood first.

In porous solids, the thermal conductivity (k) is strongly dependent on the void fraction, the pore size and the fluid contained in the pores; in crystalline material the phase and crystallite size are important; in amorphous solids the degree of molecular orientation has considerable effect. Thermal conductivity (k) for non-metals increases with temperature (Bird et al 1960).
For non-porous solids, thermal conductivity \( k \) is a function of temperature, but not a strong one and is independent for a wide range of temperature gradients. For porous solids where radiation between particles becomes an important part of total heat flow the variations does not follow linear law (Mc Cabe et al 1963).

Thermal conductivity \( k \) at room temperature for a considerable variety of biomass may be accurately predicted from Equation (3.1).

\[
k = \rho (0.1159 + 0.00233 M) + 0.01375 \tag{3.1}
\]

where
- \( k \) - thermal conductivity in Btu/hr ft °F,
- \( \rho \) - Density in gm/cc (based on weight when oven dry and volume when green) and
- \( M \) - average moisture content in weight percent (Perry et al 1963).

For \( M > 40\% \),

\[
k = \rho (0.1159 + 0.00316 M) + 0.01375 \tag{3.2}
\]

Specific heat also increases with temperature in the similar way as thermal conductivity \( k \). Density \( \rho \) decreases marginally with temperature due to expansion of solid.

Thermal conductivity \( k \), specific heat \( C_p \) and density \( \rho \) are related by a quantity called thermal diffusivity \( \alpha \) (Bird et al 1960).

\[
\alpha = \frac{k}{\rho C_p} \tag{3.3}
\]

Therefore thermal diffusivity \( \alpha \) may be assumed to be independent of temperature for small temperature ranges.
The thermal diffusivities are generally calculated from thermal conductivity \((k)\), specific heat \((C_p)\) and density \((\rho)\) using Equation (3.3) (Steinhagen 2007).

It would be better if thermal diffusivity \((\alpha)\) is determined at the same operating conditions used for determining conversion. Further thermal diffusivity \((\alpha)\) is influenced by method of heating. In actual gasifiers, there are different zones of varying temperatures. The biomass, while moving from zone to zone, undergoes isothermal and non-isothermal heating during its journey to complete gasification. Under isothermal heating source, the exterior surface is exposed to highest temperature, and as time progresses, temperature increases radially. During non-isothermal heating, the increase in temperature taking place gradually in radial direction. Depending upon the method of heating, the radial temperature profile varies resulting in different evolution of particle properties and conversion. Therefore thermal diffusivity \((\alpha)\) should be evaluated along with conversion for isothermal and non-isothermal heating.

Because of the non-uniform temperature distribution along the radius, drying devolatilization and gasification take place simultaneously yielding different weight losses at different radial positions. However, only the overall weight loss is estimated. Therefore the weight loss should be taken as that had occurred at an average temperature \((\bar{T})\) prevailing at that time. Therefore determination of average temperature is crucial.

Average temperatures \((\bar{T})\) at different time intervals are to be determined. Since thermal diffusivity \((\alpha)\) varies with average temperature \((\bar{T})\), it is possible to relate them using Fourier’s law as follows (Mc Cabe et al 1963):
\[
\frac{Ts - \overline{T}}{Ts - Ta} = 0.692 e^{-5.78 N_{FO}}
\]  
(3.4)

where

\[ N_{FO} = \text{Fourier Number} = \frac{\alpha \ t}{r_m^2} \]  
(3.5)

where \( \alpha \) - Thermal diffusivity, mm\(^2\)/min  
\( t \) - time, minute and  
\( r_m \) - mean radius, mm

The effect of isothermal or non-isothermal heating on thermal diffusivity (\( \alpha \)) at various times can be established for a given type of biomass. From the relationship thus established, thermal diffusivity (\( \alpha \)) can be determined for any heating method at any time. The Fourier number (\( N_{FO} \)) can be determined at that time using Equation (3.5) and the corresponding average temperatures (\( \overline{T} \)) from Equation (3.4). Thus average temperatures (\( \overline{T} \)) at various times can be determined.

The weight fraction yet to be converted (\( w \)) at any time can be obtained experimentally and the corresponding average temperatures (\( \overline{T} \)) can be determined from thermal diffusivity (\( \alpha \)). From weight fraction yet to be converted (\( w \)) versus time data, the rate (-rd) and rate constant (\( k \)) can be calculated. The rate constant and average temperature can be correlated. Using average temperatures (\( \overline{T} \)) and the corresponding rate constant (\( k \)), the weight fraction yet to be converted of coir pith can be determined at any time.
3.3 OBJECTIVES OF THE PRESENT INVESTIGATION

It is evident from the above discussions that powdery biomass could be gasified by bio-oxygen itself and by catalytic ash. In gasification, thermal diffusivity is observed to influence the reaction. The isothermal or non-isothermal heating and size of biomass would affect the thermal diffusivity. Therefore the present investigation is undertaken with a view to:

- elucidate the kinetics of auto gasification of coir pith powder,
- evaluate the effect of isothermal heating on thermal diffusivity,
- develop a procedure for estimating average temperature,
- elucidate the rate of auto gasification of coir pith pellet under isothermal heating,
- evaluate the effect of non-isothermal heating on thermal diffusivity, and
- elucidate the rate of auto gasification of coir pith pellet under non isothermal heating.