

## **2. PYROLYSIS**

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### **2.1. Introduction**

Pyrolysis is the thermal decomposition of fuel into liquids, gases, and char (solid residue) in the absence of oxygen. It is usually understood to be anhydrous (without water). Pyrolytic products can be used as fuels, with or without prior upgrading, or they can be utilized as feedstock for chemical or material industries. Because of the nature of the process, yield of useful products is high compared to the other processes. In general, pyrolytic products are more refined and therefore can be used with greater efficiency. Materials suitable for pyrolysis processing include coal, animal and human waste, food scraps, paper, cardboard, plastics, rubber and biomass.

Biomass contains different components with different thermal properties. Major components are cellulose, hemicellulose and lignin. Upon rapid heating, the carbohydrates (cellulose and hemicellulose) break down to provide low molecular weight volatile products. The lignin is charred to a carbonaceous residue.

The thermal properties of the components of biomass and aggregates are highly influenced by the presence of inorganic materials and various heat treatments. When these materials are heated during pyrolysis, sufficient energy is available for biomass pyrolytic reactions at higher temperatures. This results in a series of complex reactions that occur repeatedly, yielding a variety of products including bio oil, char and gases. As a clean fuel, bio oil has a number of practical advantages including the following:

- It is a renewable and locally produced from organic waste.
- It can be stored and transported similarly to petroleum-based products.
- It is a greenhouse gas neutral and can generate carbon dioxide credits.

- It generates lower NO<sub>x</sub> emissions than light fuel oil in gas turbines and diesel fuel in stationary diesel engines.

## **2.2. Pyrolytic Modes**

There are three primary types of pyrolytic reaction, which are differentiated by temperature and the processing or residence time of the biomass.

### **2.2.1. Slow Pyrolysis**

Conventional or slow pyrolysis is characterized by slow biomass heating rates, low temperatures and, lengthy gas and solids residence times. Depending on the system, heating rates are about 0.1 to 2°C per second and prevailing temperatures are around 500°C. Gas residence time may be greater than five seconds while that of the biomass can be range from minutes to days.

During conventional pyrolysis, the biomass is slowly devolatilized; hence, tar and char are the main products. After the primary reactions have occurred, re-polymerization or recombination reactions are allowed to take place.

### **2.2.2. Flash Pyrolysis**

Flash pyrolysis is characterized by moderate temperatures exist (400-600°C) and rapid heating rates (>2°C/s). Vapor residence times are usually less than two seconds. Compared to slow pyrolysis, considerably less tar and gas are produced. However, the tar and oil products are maximized.

### **2.2.3. Fast Pyrolysis**

The only difference between flash and fast pyrolysis (more accurately defined as thermolysis) is heating rates and hence residence times and products derived. Heating rates are between 200 and 10<sup>5</sup>°C per second and the prevailing temperatures are usually higher than 550°C. Due to the short vapor residence time, products are high quality, ethylene-rich gases that could subsequently be used to produce alcohols or gasoline. Notably, the production of char and tar is considerably less during this process.

## 2.3. Mechanism of Pyrolysis

Mechanism of biomass pyrolysis is inevitable for the engineering of viable continuous fast pyrolysis processes. More work in this area is centered on fast pyrolysis because the products formed are closer in nature to the fossil fuels currently in use. For the comprehension of pyrolysis mechanism, kinetic studies were conducted on cellulose pyrolysis. However, the results obtained appear to be consistent with that obtained in processes involving wood and other forms of biomass.

### 2.3.1. Reactions Involved in Pyrolysis Process

The overall chemical pyrolysis mechanism is depicted in Figure 2.1. The biomass is directly and visibly affected as the pyrolysis process proceeds. For example, the color of the biomass changes from white to brown to black. Size and weight are reduced while flexibility and mechanical strength are lost. At temperatures around 350°C, weight loss reaches about 80% and the remaining biomass is converted to char. Prolonged heating or exposure to temperatures of about 600°C reduces char fraction to about 9% of the original biomass weight. The primary pyrolysis reactions are either dehydration or fragmentation reactions. Thereafter, several products will be produced.

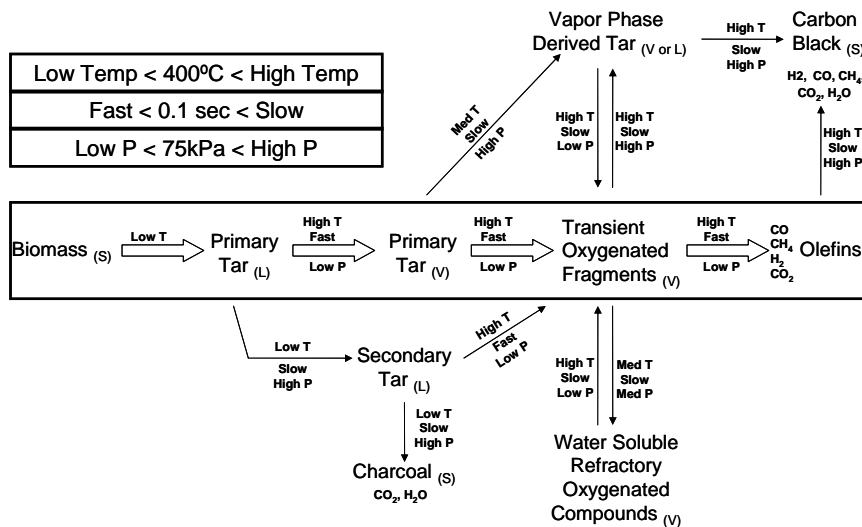


Figure 2.1. Reactions taking place in fast pyrolysis

### **2.3.1.1. Dehydration**

Dehydration, which is dominant at low temperatures, is the primary of the two reactions during slow pyrolysis. These reactions take place below 300°C and result in the reduction of the biomass molecular weight, the evolution of water, CO, CO<sub>2</sub> and, char.

### **2.3.1.2. Fragmentation**

Fragmentation dominates at temperatures above 300°C. It involves the depolymerization of the biomass to anhydro-glucose compounds and other light combustible volatiles. Because of the temperature range involved, fragmentation is of greater interest in flash and fast pyrolysis processes.

## **2.3.2. Formation of Products**

Biomass is complex and heterogeneous, and the information known about it is often limited to the specimen used, the stable end-products and, how some of these products depend on the pyrolytic treatment.

The final products can be divided into three categories: volatile products of molecular weight below 105, such as CO, CO<sub>2</sub>, H<sub>2</sub>O, acetol, furfural and unsaturated aldehydes; tars of higher molecular weight; and chars.

### **2.3.2.1. Basic Products**

Primary products of pyrolysis (volatiles and light tar) fragment or react with free radicals. The direction taken depends on temperature, residence time, and pressure of the process. For the development of specific processes and the maximization of one or more of the products, these secondary reactions must be better characterized.

Lengthy vapor residence times, medium temperatures (200-600°C) and high partial pressures favor the recombination of primary products to subsequently form stable secondary tars. At these conditions, the primary molecules are in close proximity for significant periods of time in the condensed phase. Frequent collisions also occur in the vapor phase. It should be noted however, that long residence times at low temperatures result in the formation of char, water, CO and CO<sub>2</sub> from the secondary tars while at elevated temperatures, secondary tar is cracked to hydrocarbons, H<sub>2</sub>, CO, CO<sub>2</sub>, and carbon black.

### 2.3.2.2. Formation of Volatiles

Pyrolysis can take one of two distinctive routes, both of which lead to the production of char, gaseous and volatile products. The two routes are shown in Figure 2.2.. As temperature is increased, the initiation period and difference between pyrolysis under  $N_2$  diminishes, eventually disappearing at  $310^\circ C$ . At this stage, pyrolysis by the second pathway dominates.

Reaction in the first pathway involves a reduction in molecular weight, appearance of free radicals, elimination of water, evolution of  $CO$  and  $CO_2$ , and the production of charred residue. The primary reaction during the second pathway is depolymerization. This takes place when molecules are sufficiently activated. Further increasing the temperature results in tar formation, which is more pronounced than the production of char and gases.

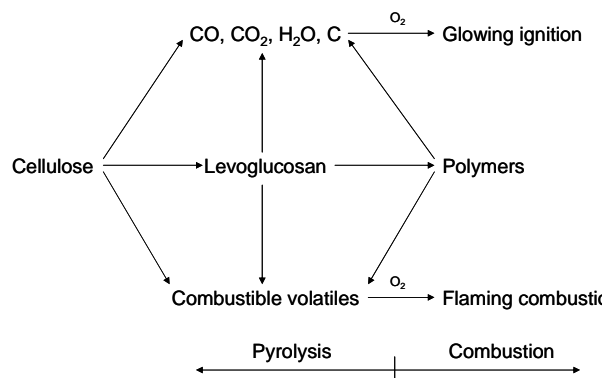


Figure 2.2. Pyrolysis and combustion of cellulose

### 2.3.2.3. Olefin Production

The pyrolytic route for the production of olefin is clearly represented. Initially, it is necessary that liquid tar be formed on the biomass surface. Subsequently, high temperatures, rapid heating rates, and low vapor partial pressures will promote the formation of olefin. The reaction sequence follows: the vaporization of primary tars; cracking of vaporized tars; and cracking of transient oxygenated fragments to yield olefins,  $CO$ ,  $N_2$ , and other hydrocarbons. If extended residence times prevail, olefins and other related products will tend to react and form carbon black, permanent equilibrium gases and condensable aromatic vapors. For the production of olefins therefore, the reactions must be interrupted by rapid quenching of intermediates before equilibrium is reached.

#### **2.3.2.4. Char Formation**

The devolatilization of biomass during pyrolytic reactions yields a solid residue (char). This product does not interact with the biomass or pure carbon. Intermediate chars are also formed, and these can be characterized by the functional groups present (aromatic and olefinic structures), a large surface area, and a high degree of reactivity.

Increasing the heat treatment temperature reduces char yield and also increases the aromatization of char as measured by the aromatic carbon content of the acids. Aromatization processes involve nucleation and the development of isolated aromatic structures at temperatures between 300 and 400°C. When temperatures exceed 400°C, aromatic clusters which are oxidized to acid remain constant, but aromatization continues through condensation and the growth of individual aromatic clusters, resulting in lower H/C ratios.

#### **2.4. Characteristics of bio-oil**

When cooled, some volatiles condense to a liquid referred to as pyrolysis oil or bio-oil. The remaining gases comprise a medium calorific value, non-condensable gas. Bio-oil is typically a liquid, almost black through dark red-brown, depending on its chemical composition and the presence of micro-carbon. Crude pyrolysis liquid or bio-oil is similar to biomass in elemental composition. The density of the liquid is about 1200 kg/m<sup>3</sup>, which is higher than that of fuel oil, and significantly higher than of the original biomass. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications on the design and specification of equipment such as pumps and atomizers in boilers and engines. The viscosity of the oil varies from as low as 25 cP up to 1000 cP depending on water content, the amount of light ends, and the extent to which the oil has aged.

Bio-oil is a liquid mixture of oxygenated compounds containing various chemical functional groups, such as carbonyl, carboxyl and phenolic. It is comprised of the following constituents: 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars, and 10-25% other oxygenated compounds. Due to large amounts of oxygenated components present, the oil has a polar nature and does not mix readily with hydrocarbons. It contains less nitrogen than petroleum products, and almost no metal and sulfur components.

The degradation products from the biomass constituents include organic acids (like formic and acetic acid), which gives the oil its low pH of about 2 to almost 4. Because the oil can corrode mild steels, it should be stored in containers made of acid-proof materials like stainless steel or poly-olefins. Neutralization of the oil is not an interesting option as it can cause polymerization. The (hydrophilic) bio-oils have water contents of typically –15-35 wt%, which can not be removed by conventional methods like distillation. Phase separation may occur when moisture content increases above about 30 to 45%. High water contents of the bio-decreases its viscosity (ease transport, pumping and atomization), improves stability, and lowers the combustion temperature, thus reducing NO<sub>x</sub> emission. The higher heating value (HHV) of the bio-oil is below 20 MJ/kg (compared to 42 - 44 MJ/kg for conventional fuel oils).

The liquid is formed by rapidly quenching and thus “freezing” the intermediate products of flash degradation of hemicellulose, cellulose and lignin. The liquid thus contains many reactive species, which contribute to its unusual attributes. Bio-oil can be considered a micro-emulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products that stabilize the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding. Aging or instability is believed to result from a breakdown in this emulsion. In some ways, it is analogous to asphaltenes found in petroleum. Table 2.1 summarize important characteristics of this liquid.

Bio-oil has a distinctive acrid, smoky odor. The liquid contains several hundred different chemicals in widely varying proportions, ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides. These low molecular weight aldehydes and acids fumes can irritate the eyes if exposure is prolonged.

Bio-oil can tolerate the addition of some water, but there is a limit to the amount of water that can be added to the liquid before phase separation occurs. In other words, the liquid cannot be dissolved in water. It is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels.

**Table 2.1. Properties of wood derived crude bio-oil**

Physical property	Typical value
Moisture content	20-30%
pH	2.5
Specific gravity	1.2
Elemental analysis	
C	55-58%
H	5.5-7.0%
O	35-40%
N	0-0.2%
Ash	0.0-0.2%
HHV as produced	16-19 MJ/kg
Viscosity (40 °C and 25% water)	40-100 cp
Solids (char)	0.1-0.5%
Vacuum distillation residue	0.1-0.5%

Bio-oil liquids cannot be completely vaporized once they have been recovered from the vapor phase. If the liquid is heated to 100°C or more to try to remove water or distill off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid and some distillate containing volatile organic compounds and water. Bio-oil has been successfully stored for several years under normal storage conditions in steel and plastic drums without any deterioration that would prevent its use in any of the applications tested to date. However, it does change slowly with time; most noticeably there is a gradual increase in viscosity.

## 2.5. Kinetics of Pyrolysis

In view of the modes of pyrolysis that are characterized by different heating rates, motion of elements during the respective processes will differ. Consequently, the respective



representation of their kinetics will not be the same. However, due to the slight similarity between flash and fast pyrolysis, a common representation is acceptable.

A simple reaction controls the decomposition kinetics at slow heating rates. There is no generally accepted method for deducing kinetic constants from TGA data. The data can be suitably fit with a range of adjustable constants.

For the pyrolysis of biomass, the assumption that the process rate takes the pattern of a general first order law is accepted. Such a law in mathematical expressions can have the following form:

$$\frac{dW_t}{dt} = K_o (W_\infty - W_t) \exp\left(\frac{-E}{RT}\right) \quad 2.1$$

Where:

- $W_t$  is the particle weight after reaction time, g
- $t$  is the pyrolysis time, s
- $K_o$  is the frequency factor,  $\text{ms}^{-1}$
- $W_\infty$  is the ultimate particle weight, g
- $R$  is the universal gas constant
- $E$  is the activation energy
- $T$  is the temperature, K

However, at high heating rates, the residence time of volatile products is insufficient for further reaction inside the particle. Hence, the reaction may appear to be endothermic. Properties of the biomass, such as density, specific heat, and thermal conductivity, affect the conversion rate and temperature. Such effects can be taken into account by taking their mean values over the conversion range of the experiment.

The reported data on activation energy,  $E$ , and the pre-exponential factor,  $A$ , varies widely.  $E$  varies from 40 to 250 kJ/mole and  $A$  from  $10^4$  to  $10^{20} \text{ sec}^{-1}$ . The measured kinetic data depend on operating conditions such as rate of heating, and on the type of material. Raman et al. (1981) reported mean values of 175 kJ/mole (for  $E$ ) and  $1.67 \times 10^{13} \text{ sec}^{-1}$  (for  $A$ ) for devolatilization of manure.

## **2.6. Variables Affecting Biomass Pyrolysis**

Several variables impact the mechanism and kinetics of pyrolytic reactions. These variables, which include the composition of the substrate, heating rate, bed temperature, bed pressure, ambient atmosphere present and, existence of catalysts, must be fully understood and appreciated. Among other things, these variables have a profound effect on the sequence and kinetics of the reactions, and therefore the yield of products formed. By understanding the influence of these variables on the process, pyrolytic conditions can be anticipated. These conditions can be controlled, thus reducing the unwanted side reactions and promoting the formation of desirable products.

### **2.6.1. Substrate Composition**

Generally, biomass is complex and heterogeneous raw materials derived from different types of living and dead plant cells. Their structure and composition varies according to the species and the plant from which the biomass is derived. Woody tissues contain mainly cell wall materials composed of 30-40% cellulose, 25-30% hemicellulose and 12-30% lignin. These components are responsible for the variety and complexity of products formed during the pyrolysis of biomass.

Above 300°C, cellulose and hemicellulose break down to provide tarry pyrolyzates containing low sugar derivatives and little char while lignin is condensed to carbonaceous char and gives smaller amounts of pyrolyzate containing phenolic compounds. However, the heterogeneity of biomass is a major obstacle to its chemical utilization because of the lower yield of individual products derived from each of its elements. This also affects the yield of charcoal and other types of fuels that are possible products of biomass pyrolysis.

### **2.6.2. Heating Rate**

Length of heating and its intensity affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant products. Pyrolytic reactions proceed over a wide range of temperatures; hence, products formed earlier tend to undergo further transformation and decomposition in a series of consecutive reactions. Further,

various products are formed as secondary reactions to continuous heating of the initial products. Long heating periods allow the sequence of these reactions to take place whereas rapid heating (flash pyrolysis) tends to reduce these secondary reactions and the further degradation of the earlier formed products. If heat is supplied fast enough during flash pyrolysis, little or no char results and subsequent processing is greatly simplified.

There could be substantial difference between the reactor temperature and that of the biomass. Hence, at higher temperatures, the rate of reaction may be controlled by the rate of heat transfer rather than the kinetics of the reactions.

The main products of biomass pyrolysis are char, tar, pyroligneous acid, and gas. At low temperature, char is the dominant product followed by H<sub>2</sub>O. Hardwoods yield less char but more acids than softwoods. The yield of volatile products (gases and liquids) increases with increasing heating rate while solid residue decreases. The effect of heating rate can be viewed as the effect of temperature and residence time. As the heating rate is increased, the residence time of volatiles at low or intermediate temperatures decreases. Most of the reactions that favor tar conversion to gas occur at higher temperatures. At low heating rates, the volatiles have sufficient time to escape from the reaction zone before significant cracking can occur. Heating rate is a function of the feedstock size and the type of pyrolysis equipment. The rate of thermal diffusion within a particle decreases with increasing particle size, thus resulting in lower heating rate. Liquid products are favored by pyrolysis of small particles at high heating rates and high temperature, while char is maximized by pyrolysis of large particles at low heating rates and low temperatures as mentioned earlier.

Scott et al. (1988) have reported over 60% wt (of moisture-free wood) liquid products and 10% char below 600°C in fast pyrolysis of maple wood (120 μm). Aarsen et al. (1985) reported that the pyrolysis of 1 μm wood particles in a fluidized bed at 800°C is nearly complete within 2 seconds. They estimated the heating rate to be about 500°C/s. Small quantities (<10%) of char were produced.

Fast (1,000 °C/s), and flash (10,000 °C/s) pyrolysis processes have recently attracted considerable attention as a means of maximizing gaseous and liquid products from biomass. Ayll'on et al. (2006) studied pyrolysis of meat and bone meal in a fixed bed reactor and investigated the influence of the final pyrolysis temperature and heating rate on the product (char, tar and gas) distribution and composition as well as char characterization. Two sets of

experiments were performed at different final pyrolysis temperatures between 300 and 900°C and heating rates from 2 to 14°C/min. Their results showed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate.

The analysis of pyrolysis product distribution showed that the major products obtained at any temperature or heating rate were bio-oil and char. Most of the decomposition takes place at temperatures lower than 500°C, and no more significant decomposition is produced above 750°C. The chars obtained present a low specific surface area, less than 45 m<sup>2</sup>/g. The bio-oil obtained is mainly composed of more than 60% nitrogenated aliphatic compounds (such as nitriles, amides and cyclic compounds), 15% aliphatic hydrocarbons (such as alkanes and alkenes), 10% oxygenated aliphatic compounds (mostly carboxylic acids) and about 8% oxygenated aromatic compounds (mainly phenolics).

### **2.6.3. Temperature**

The pyrolysis rate of biomass, which increases with temperature, can be determined by weight loss, evolution rate of a primary volatile product, or simultaneous measurement of density and temperature profiles in the pyrolyzing solid. The time required to obtain a certain conversion level decreases with increasing temperature. Koufapanos et al. (1989) recorded an almost instantaneous conversion (about 90%) at 500°C in pyrolysis of wood sawdust. An increase in pyrolysis temperature increases the yield of gaseous products and decreases residue char production.

Scott et al. (1988) recorded in a fast pyrolysis reactor the CO<sub>2</sub> plateau in the temperature range 450°C-550°C and CO yield, which increased monotonically with temperatures over the temperature range studied (400-800°C). In rapid pyrolysis of wood, Nunn et al. (1985) found the CO<sub>2</sub> yield to level off at 680°C while CO reached an asymptotic value near 930°C. This behavior may indicate that gas-phase reactions are taking place at high temperatures. The most probable reaction is the water-gas shift reaction. Utioh et al. (1989) in their pyrolysis studies of wheat grain screenings also reported increasing yields of hydrocarbon gases with temperature. The C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and other higher hydrocarbons reached a maximum near 660°C and then declined with further temperature increases. Similar results have been reported by Nunn et al. (1985) in the pyrolysis of cellulose. This behavior suggests that thermal cracking or reforming of higher hydrocarbons occurs at higher temperatures. The temperature at which reforming heavy

hydrocarbons commences appears to vary depending upon the operating conditions of reported experiments.

Char yield decreases steadily with temperature to an almost constant value above about 650°C when devolatilization is almost complete (Scott et al., 1988). The carbon content of the char, however, increases sharply with increasing temperature while that of H and O decrease.

Another important effect of temperature is product bio oil yields, which increase with pyrolysis temperature to a maximum around 550°C-680°C and then drops with further increases in temperature (Sadakata et al., 1987).

#### **2.6.4. Pressure**

Pressure has a significant influence on pyrolysis of biomass. The effects of pressure on the pyrolysis products can be interpreted by the effect of residence time of the volatile products. In experiments with unmilled wild cherry wood at 300°C, Ward and Braslaw (1985) observed a higher rate of weight loss at 1 atm than at  $4 \times 10^4$  atm. After a reaction time of 50 min, the samples under 1 atm and  $4 \times 10^4$  atm pressure lost about 55% and 40% of their weight, respectively. Blackadder and Rensfelt (1985) pyrolyzed wood, lignin, and cellulose in a pressurized thermobalance and found that at a given temperature, char residue increased pressure in each case. Cellulose, however, displayed the strongest pressure dependency and lignin the weakest. The pressure effect was observable at pyrolysis temperature above about 350°C. Higher pressure increases the residence time of the volatiles in the reaction zone, resulting in increased yield of low molecular weight gas and decreased tar and liquid products due to cracking reactions. Also, at higher temperatures, gas-solid reactions occur (with product gases). At low pressures, and hence short residence times, tar molecules and heavy liquid products will escape before undergoing further decomposition. Product gases will also escape before reacting with the solid residue (char).

#### **2.6.5. Ambient Atmosphere**

During pyrolysis, the ambient atmosphere affects the heat transfer and nature of the secondary reactions. The ambient atmosphere may either be a vacuum or an inert or reactive surrounding.

In a vacuum, primary products are rapidly removed or thinned out in the gas phase, and thus are not available for further decomposition and reaction. The presence of water or steam is known to speed up the breakdown and degradation of molecules by way of hydrolysis of the biomass and rearrangement of the intermediate products. This hydrothermolysis may be catalyzed by acid or alkali reagents.

#### **2.6.6. Catalysis**

The presence of inorganic materials either as additives or natural ash content, strongly affects the pyrolysis of biomass; the effect is more pronounced with alkaline compounds and acidic reagents. Even the natural impurities and ash content can produce significant effects, which can be made clearer by lowering the process temperature and increasing char formation. For an evaluation of this, thermal analysis methods such as thermogravimetry (TG), thermal evolution analysis (TEA), and differential thermal analysis (DTA) could be employed. They also indicate the heats of reaction and vaporization.

Acid catalysts in small amounts catalyze the transglycosylation reactions. When used in larger amounts, catalytic dehydration of the anhydrosugars along with hydrolysis and rearrangement reactions produce dehydration products. The acidic catalysts also enhance the condensation of intermediate compounds and affect some of the char properties. Most affected is the nature of char oxidation. It should be noted, however, that the effect of catalysts is great during cellulose and wood pyrolysis, but almost negligible when lignin is pyrolyzed.

The presence of catalysts has been reported to have a significant influence on the pyrolysis of biomass. The modification of the thermal behavior of wood by impregnation with inorganic salts has long been investigated mainly for use as protection against fire hazards. These compounds are believed to suppress the release of combustible volatiles such as tar, thus suppressing flaming combustion. Utioh et al. (1989) report increased yields in synthesis gas with the addition of 15%  $K_2CO$  during the pyrolysis of grain screenings.  $H_2$  and  $CO_2$  production were enhanced while  $CO$  yields were decreased. Impregnation of biomass with monobasic ammonium phosphate salts reportedly reduce decomposition temperature and increase weight loss during the pyrolysis even at temperatures below  $350^\circ C$ . The salts also enhance char production and reaction rates.

The kinetic data for pyrolysis of wood and its components, reviewed by Roberts (1970), indicates that inorganic salts reduce activation energy from  $E=56$  kcal/mol for pyrolysis of pure cellulose to  $E=30$  kcal/mole. Tsuchiya and Sumi (1970) studied the pyrolysis of untreated and salt-treated cellulose under vacuum and at temperatures ranges of 320-520°C. The presence of inorganic compounds ( $K_2CO$ ,  $KHCO_3$ ,  $ZnCl_2$ ,  $PO_4$ , and  $H_3PO_4$ ) decreased the yield of tar fraction and increased char. Yields of  $CO$ ,  $CO_2$ , and  $H_2O$  were enhanced;  $CO$  was more pronounced with alkali salts.

Nassar et al. (1986) investigated the effects of four inorganic salts (NaCl, KHCO, borax, ammonium phosphate) on the major products of pyrolysis of black spruce sawdust at 500°C under vacuum. Their results show a decreased yield of total flammable gases, especially  $CO$ , decreased tar fraction, and increased water and char yields.  $H_2$  and hydrocarbon gases yields were reduced but  $CO_2$  was increased. Nassar and MacKay (1986) carried out DTA studies on lignin treated with inorganic salts. The results show that lignin is almost inert to the effect of salts during pyrolysis. .

## **2.7. Pyrolysis Reactors**

The thermochemical conversion processes under consideration are interrelated. Pyrolysis is known to be a precursor to both gasification and combustion. As a consequence, it is not necessary to develop or manufacture a reactor specifically for analysis of biomass pyrolytic reactions. Suitable reactors are those already outlined in the previous chapter on gasification, e.g., fixed bed, fluidized bed, entrained flow and suspension flow reactors. Many pyrolytic studies have been conducted in conventional reactors used for gasification and combustion.

### **2.7.1. Bubbling Fluidized Bed Pyrolyzers**

Compared to other types of reactors, fluidized beds are simpler to design and construct. They have several advantages including good gas solids contact, excellent heat transfer characteristics, better temperature control, and large heat storage capacity. Fluidized bed pyrolyzers give good, consistent performance with high liquid yields of typically 60-75%wt. from wood on a dry feed basis. Small biomass particle sizes of less than 2-3 mm are needed to accomplish high biomass heating rates. As mentioned earlier, the rate of particle heating is

usually the rate limiting parameter. Figure 2.3. show a fluidized bed pyrolyzer developed at Iowa State University..

Commercial plants have multiple stages collection systems including de-misters, although aerosol capture is extremely difficult. Since the pyrolysis process is endothermic, external heating was needed. However, heat transfer to bed at large-scales of operation has to be considered carefully due to scale-up limitations of different methods of heat transfer. The fluidizing gas flow rate controls the residence time of solids and vapours. Char acts as a catalyst in cracking vapours during the pyrolysis reaction. Char collection is usually achieved by ejection and entrainment followed by separation in cyclones.

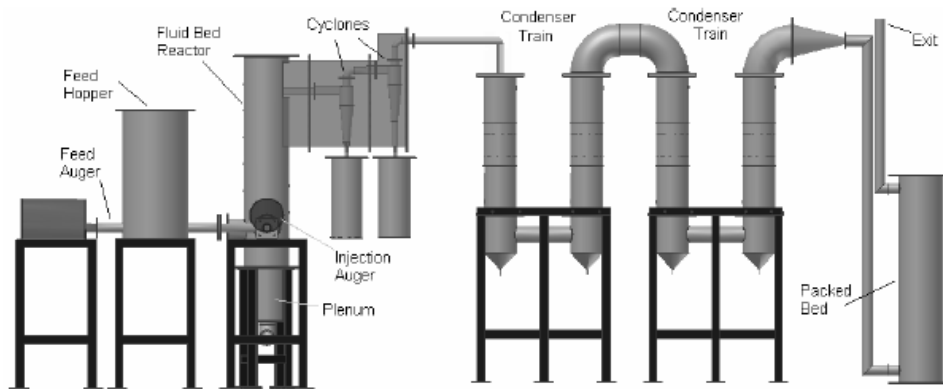


Figure 2.3. Fluidized bed pyrolyzer developed by Iowa State University

Fluidized bed pyrolyzers include the following equipment: hopper and feed system, pyrolysis reactor, cyclone, bio-oil recovery quench system, electrostatic precipitator, and bio-oil tank.

In the BioTherm reactor (Figure 2.4), fluidized sand in a zero-oxygen environment is used to quickly heat feedstock to temperatures  $450^{\circ}\text{C}$ . The biomass decomposed into solid char, gas, vapors and aerosols. The recycled pyrolysis gases are used to fluidize the bed materials and to remove the newly formed pyrolysis products from the reactor. After exiting the reactor, these products pass through two cyclones arranged in series that remove most of the entrained solid char particles. The char is collected in separate char collectors located under the cyclones. The scrubbed gases, vapors and aerosols then enter a direct quenching system where they are rapidly cooled to below  $50^{\circ}\text{C}$  with a liquid, immiscible in bio-oil. The bio-oil portion of the gases is condensed and collected in a product tank. Quench liquid recovered from this tank is cooled in a



heat exchanger then recycled to the recovery system. The non-condensable gas and any residual bio-oil aerosol droplets then enter a precipitator that electrostatically cleans the gas of all these particulates and aerosols. The clean, inert gas is then recycled back to the bubbling fluid bed reactor. The excess non-condensable gas is vented from the system. This medium calorific gas can be combusted to provide heat to the reactor sand. Liquid bio-oil separates from the quench liquid and is then transferred to shipping containers. The quench liquid is decanted from the tank and recycled to the bio-oil recovery system.

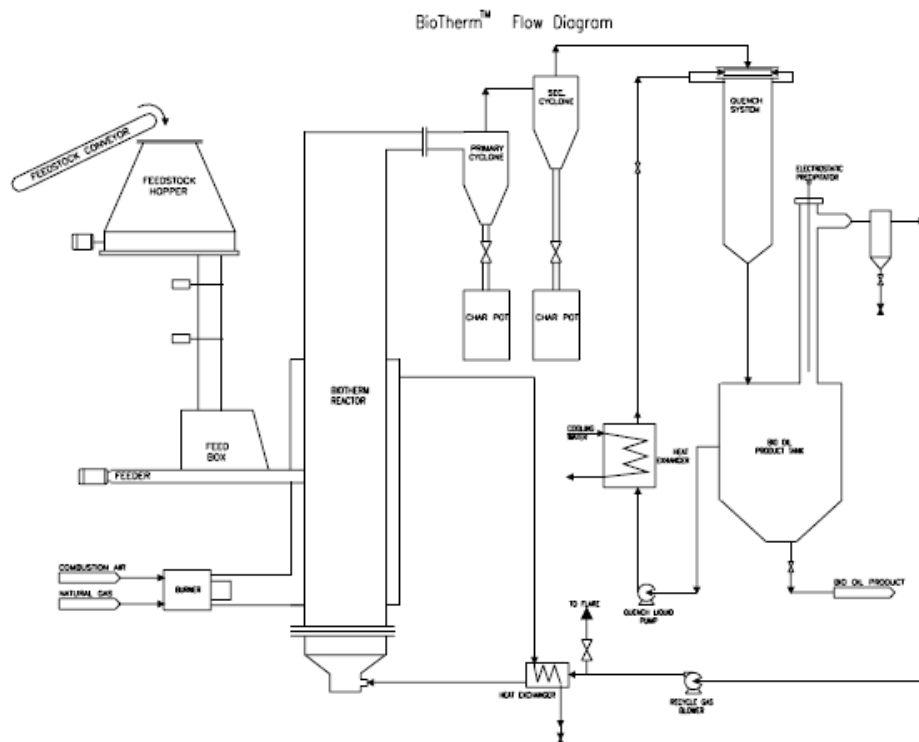


Figure 2.4. BioTherm reactor (BioTherm, 1999)

### 2.7.2. Circulating fluid beds and transported bed

Circulating fluidized bed pyrolyzers have similar characters as bubbling bed pyrolyzers excluding that the residence time for the char and vapours is the faster. Compared to bubbling fluidized bed pyrolyzers, vapor and char escape faster due to higher gas velocities. Therefore, the char content in the bio-oil is higher. Circulating fluidized bed pyrolyzers have high processing capacity, better gas-solid contact, and the ability to handle cohesive solids that might otherwise be difficult to fluidize in bubbling fluidized beds. Despite these advantages, the circulating fluidized beds are still less commonly used. Heat supply is typically from recirculation of heated

sand from a secondary char combustor. This aspect of the process is comparable to a dual fluidized bed gasifier. One of the fundamental research areas is heat transfer at large-scales reactor.

### **2.7.3. Ablative pyrolysis**

The ablative pyrolyzer was designed and built on the premise that heat transferred from a hot reactor wall will soften feedstock that is in contact with it under pressure. The pyrolysis front thus moves in one direction through the biomass particle. As the feedstock is mechanically pushed away, the residual oil film provides lubrication for successive biomass particles but also rapidly evaporates to give pyrolysis vapours for collection in the manner described above. Pressure significantly affects the rate of reaction. In addition, it affects the relative velocity of feedstock on the heat exchange surface. The advantages of ablative pyrolyzers include high pressure of particle on hot reactor wall from mechanical force and high relative motion between particle and reactor wall.

Large feedstock particles could be pyrolyzed in an ablative pyrolyzer since the reaction rates are not limited by heat transfer through the biomass particle. In fact, the process is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolyzing biomass as in other reactors. Another advantage to ablative pyrolyzers is that no inert gas is required, so the processing equipment is smaller and the reaction system is more intensive. However, the process is surface-area controlled so scaling is more costly and the reactor is mechanically driven and thus is more complex.

### **2.7.4. Rotating Cone Pyrolyzer**

Rotating cone fast pyrolysis technology, developed at the University of Twente, is proven gas-solid contactor based on the rotating cone reactor. A schematic of the reactor is presented in Figure 2.5. Biomass particles at room temperature and hot sand particles are introduced near the bottom of the cone where the solids are mixed and transported upwards by the rotating action of the cone. In this type of reactor, rapid heating and a short gas phase residence time can be realized. Pressures were just above atmospheric levels. Biomass, which is initially entrained, enters the reactor tangentially so that the particles are centrifuged against the cyclone walls that were electrically heated to temperatures of about 1000°C.

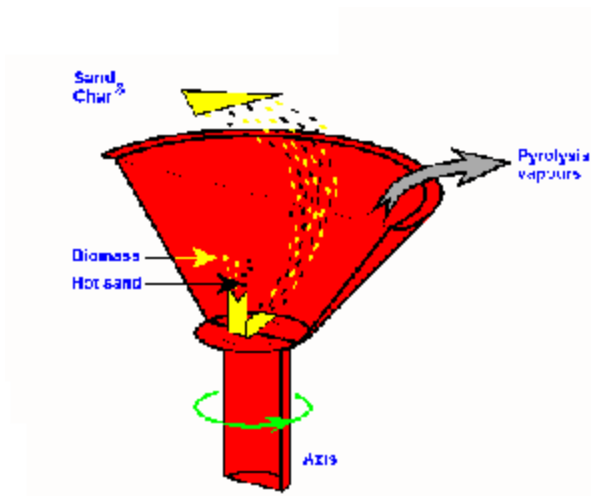


Figure 2.5. A schematic diagram of the cone pyrolyzer

## 2.8. Pyrolysis of Biomass

Cellulose, hemicellulose, and lignin, the principal components of biomass, have different reaction kinetics. Hemicellulose is the most reactive constituent and lignin the least (Probstein and Hicks, 1982). Pyrolysis of whole biomass can be described in terms of the behavior of these components, each of which is discussed separately in the following sections. The reaction rates, products, and other thermal behavior of biomass pyrolysis are considered a combination of the behavior of its main components. Each component contributes to the behavior to an extent proportional to its weight percent contribution to the composition of the raw biomass. This is true in the absence of secondary reactions.

### 2.8.1. Pyrolysis of Cellulose

Of the principal components of biomass, cellulose is the most widely studied. This is mainly because it is the major component of most biomass (43%). In addition, it is the least complicated, best defined component of biomass. Cellulose is the major source of the combustible volatiles that fuel flaming combustion. Cellulose also appears naturally almost in its pure state (e.g., cotton).

Numerous studies of pyrolytic thermal degradation of cellulose under various conditions have been reported and a simplified, two-pathway mechanism of its decomposition has been generally accepted (Figure 2.6).

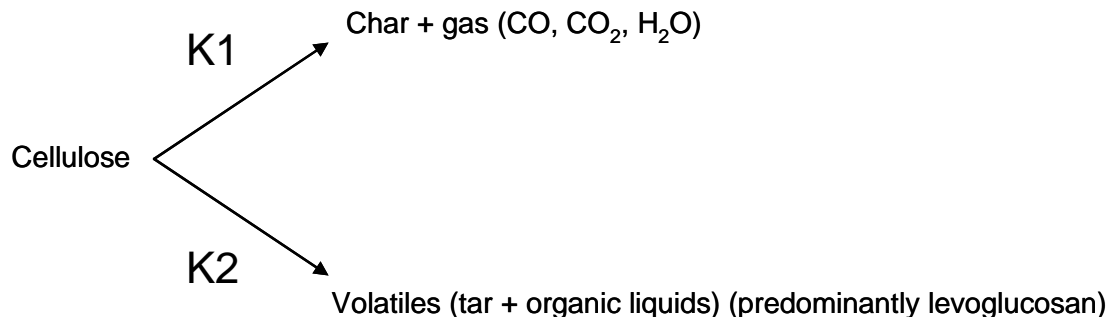


Figure 2.6. Simplified reaction model for cellulose decomposition

Reaction 1 dominates at low temperatures while reaction 2 dominates at high temperatures. The existence of the two pathways is demonstrated by studies of the rates of weight loss of cellulose in nitrogen; the transition is found to occur at about 300°C. Below this temperature, the following chemical reactions may occur: reduction of molecular weight, the appearance of free radicals, oxidation, dehydration, decarboxylation, and decarbonylation. The products are mainly CO, CO<sub>2</sub>, H<sub>2</sub>O, and a char residue.

The second pathway occurs at temperatures above 300°C and involves decomposition of cellulose to tarry pyrolyzate-containing levoglucosan as the major component (22-50%), which vaporizes and then decomposes with increasing temperature. As the temperature is increased from 300°C to 500°C, the amount of tarry products increases while the proportion of char component diminishes and the yields of levoglucosan remain almost constant.

The major products of pyrolysis of cellulose below 500 °C are char, tar (mainly levoglucosan), water, CO<sub>2</sub> and CO (Funakuzuri et al., 1986). The yield of light hydrocarbons, i.e., C<sub>1</sub> - C<sub>4</sub>, is negligible below 500°C but becomes considerable at high temperatures (Scott et al., 1988). Tar yield begins to drop as pyrolysis temperature is raised above 600°C (Hajaligol et al., 1982). A rapid increase in total gas yield was recorded at almost the same temperature at which the tar yield begins to drop. This is an indication that primary tar cracking contributes to the total gas production at elevated temperatures.

Kinetic studies by Bradbury et al. (1979) found the char-forming reaction and the volatiles-forming reaction to have a first-order rate constant of  $7.9 \times 10^{11} \exp(-36000/RT) \text{ min}^{-1}$  and  $1.9 \times 10^{16} \exp(-47300/RT) \text{ min}^{-1}$ , respectively. Pyrolysis of cellulose is essentially complete above 600°C (Funazukuri et al., 1986) and thermal decomposition of tar and some liquid

fractions begin, resulting in a considerable increase in gaseous products. Piskorz et al. (1986) determined the rate constant for tar decomposition to be  $3.4 \times 10^8 \exp(-25000/RT) \text{ min}^{-1}$ .

### **2.8.2. Pyrolysis of Hemicellulose**

Glucuronoxylans (commonly referred to as xylan) are the most important hemicelluloses of hardwoods, and glucomannan is the predominant hemicellulose in softwoods. Xylan has been used in several studies (Koufopoulos et al., 1989) to model the pyrolysis of hemicelluloses. Hemicelluloses are the most reactive major component of wood decomposing in the temperature range 200-260°C. The thermal instability of hemicelluloses is probably due to their lack of crystallines. Decomposition of hemicellulose under pyrolytic conditions is postulated to occur in two steps (Soltes and Elder, 1981). First is the breakdown of the polymer into water soluble fragments followed by conversion to monomeric units, and finally decomposition of these units to volatiles. Hemicelluloses produce more gases and less tar than cellulose, and no levoglucosan. They also produce more methanol and acetic acid than cellulose.

### **2.8.3. Pyrolysis of Lignin**

Lignin, the third major component of woody biomass, is a highly linked (3-D network polymer), amorphous, high molecular weight phenolic compound. Lignin serves as cement between the wood fibers and as a stiffening agent within them. Lignin is the least reactive component of biomass; higher temperatures are necessary for the pyrolysis of most lignin. The time required for complete pyrolysis of woody biomass at a given temperature is controlled by the pyrolysis rate of lignin at the operating conditions. Thermal decomposition of lignin occurs in the temperature range 280°C to 500°C, although some physical and/or chemical changes (e.g., depolymerization, loss of some methanol) may occur at lower temperatures (Koufopoulos et al., 1989). Wenzel (1970) reported that, at a slow heating rate, lignin loses only about 50% of its weight when the pyrolysis is stopped at 800°C.

Pyrolysis of lignin yields more char and tar than cellulose. Soltes and Elder (1981) have reported a product composition of 51-66% char, 14-15% tar, 13-28% pyroligneous acid and about 12% gaseous products (consisting mainly of CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>). The tar residue is a

mixture of phenolic compounds while the aqueous distillate contains, among other compounds, water, methanol, acetic acid, and acetone.

#### **2.8.4. Pyrolysis of Wood**

Studies of the pyrolytic behavior of individual wood components have helped elucidate the different steps involved in the whole wood pyrolysis. Kinetic studies of wood pyrolysis indicated two distinct decomposition regimes. Rate data for the first and second (in time) regimes correlate very closely with those of pyrolysis of pure hemicellulose and cellulose, respectively. This may be interpreted to indicate decomposition of the major wood components is taking place separately.

Pyrolysis of wood takes place in a sequential manner with the least stable component, hemicellulose, decomposing first at temperatures of 200°C to 280°C and lignin, the most stable component, decomposing last at temperatures of 280°C to 500°C. It is not possible to define a strictly lower limit for the beginning of thermal decomposition of wood but the following sequence of events is generally observed at low heating rates:

Up to 200°C: Along with the removal of moisture, other volatile products such as acetic acid and formic acid are released. Non-condensable gases such as CO and CO<sub>2</sub> are also evolved.

–200-280°C: Further decomposition of the (char + wood) residue; decomposition is more vigorous with the release of pyroligneous acids, water, and non-condensable gases (CO, CO<sub>2</sub>). Separation of tar is also observed.

–280-500°C: Release of combustible volatile products such as CO, CH<sub>4</sub>, H<sub>2</sub>, formaldehyde, formic acid, methanol, and acetic acid occur. Formation of char decreases in quantity but increases in carbon content. Release of condensable tar also continues.

Above 500°C: Carbonization is complete. If the reaction products are not removed from the reaction zone as soon as they are formed, secondary reactions begin and char-gas reactions start.

#### **2.9. Problems associated with biomass pyrolysis**

There are three main problems associated with biomass pyrolysis, namely bio oil instability, phase separation, and corrosion of containers.

### **2.9.1. Bio Oil Instability**

Bio-oil is relatively unstable compared to fossil fuels. This is primarily due to slow chemical reactions that produce more polymeric compounds, which gradually increases the molecular weight average of the pyrolysis liquids and consequently the liquid viscosity. Various reactions between the components of the pyrolysis liquids and with the storage environment can occur. With the development of fast pyrolysis for the production of liquid fuel, testing and characterization of these liquids has become a key area of research.

### **2.9.2. Phase Separation**

Bio-oil contains varying amounts of water, which forms a stable single phase mixture. Pyrolysis liquids can accept the addition of some water, but there is a limit to the amount of that can be added before phase separation occurs. In other words, the liquid cannot be dissolved in water.

If an equal volume of water is added to the bio-oil, high molecular weight, largely aromatic compounds are precipitated. Since most of the aromatic compounds can be traced to the lignin content of the biomass, the precipitate is widely known as pyrolysis lignin. The pyrolysis liquids are highly corrosive due to the presence of organic acids derived primarily from the hemicellulose content of the feedstock. Bio-oil is miscible with polar solvents such as methanol, acetone, etc., but totally immiscible with petroleum-derived fuels.

### **2.9.3. Corrosion of Containers**

Bio-oil is very acidic (pH value of less than 3) and contains significant amounts of water and metal ions. If any part of the pyrolysis reactor is fabricated from a metal other than stainless steel, significant concentrations of the metal could be found in the bio-oil. These metals are most probably leached from the pyrolysis reactor or peripheral installations. Aluminum and, to a lesser degree, copper can be corroded by bio-oil, whereas SS 316 is not affected.

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