



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Pyrolysis

The word “Pyrolysis” is defined as the breakdown of a macromolecule by heat under the absence of O₂ atmosphere. Characteristic of pyrolysis of a macro material depends on the energy source during the input heat. During pyrolysis, the covalent bonds of macromolecule are broken into simpler smaller molecules by thermal process. Even in the presence of air, macromolecule is pyrolyzed and the pyrolysis products are the products that participate in the combustion reaction. However, the pyrolysis is the breakdown of any covalent bonds and flammable and combustible gases and liquids are covalently bonding compound. As already mentioned, liquid in the biomass does not burn (Probstein and Hick, 1985).

Pyrolysis of biomass is a two-step process. First, the energy source is exposed to the surface of the biomass, and the absorption of energy by the biomass causes the breakdown of bonds. First step of pyrolysis is generally called “primary pyrolysis”, which occur in the temperature range of 200-400°C. Therefore, the products are hydrocarbon derivatives from fed biomass, typically a long-chain molecule containing large amount of carbon-to-carbon, carbon-to-hydrogen, carbon-to-oxygen, and oxygen-to-hydrogen bonds. The major gaseous products obtained after primary pyrolysis are usually some of methane, ethylene, ethane, propylene, propane, C₄, AcH, CO, CO₂, methanol and water. The end of primary pyrolysis is occurs when the donatable hydrogens from hydroaromatic or aliphatic portion are depleted. The second step of pyrolysis is called “secondary pyrolysis”. This step presents in the temperature range from approximately 500-800°C. Main mechanism of secondary pyrolysis is crosslinking of macro-hydrocarbon molecule and char condensation. In addition, methane (from methyl groups), HCN (from ring nitrogen compounds), CO (from ether links), and H₂ (from ring condensation) are evolved during secondary pyrolysis. Figure 2.1 showed basic pyrolysis mechanism of cellulose (Vitrification International Technologies, Inc., 2002)

CELLULOSE, $(C_6H_{10}O_5)_n$
 where $n \sim 2,000-4,000$

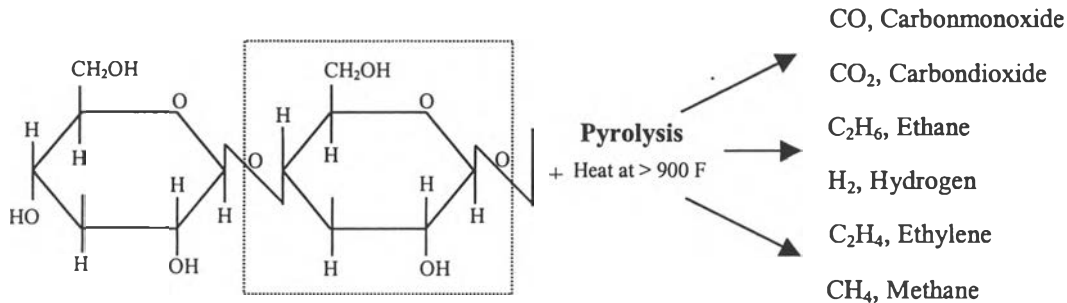


Figure 2.1 Schematic of the pyrolysis process (Vitrification International Technologies, Inc., 2002).

The broadly events of pyrolysis process can be summarized as following steps (Solomon *et al.*, 1992):

- Step 1: Disruption of hydrogen bonds,
- Step 2: Vaporization and transport of noncovalently bond “guest” molecule,
- Step 3: Low temperature crosslinking (for low rank coal),
- Step 4: Bridge breaking to fragment the macromolecular network,
- Step 5: Hydrogen utilization to stabilize free radicals,
- Step 6: Vaporization and gas phase transport of light fragments,
- Step 7: Moderate temperature crosslinking to resolidify the macromolecule network,
- Step 8: Decomposition of functional groups to produce light species,
- Step 9: High molecular of the macromolecular network by hydrogen elimination.

The main objective of pyrolysis is production of pyrolysis liquid or liquid oil from decomposition of organic material. Pyrolysis oil is obtained from converting of biomass solid into oil vapor before condensation into pyrolytic oil. Remain solid residue from the process is called “Char”, which consist of coke and ash content. In practice about 40-75 % of the (dry) biomass is converted into oil vapour. About 10-20 % of the biomass is converted into char (solid porous carbon particles) and 10-30 % is converted into an uncondensable gas. The simplest pyrolysis process used in industries is illustrated in Figure 2.2.

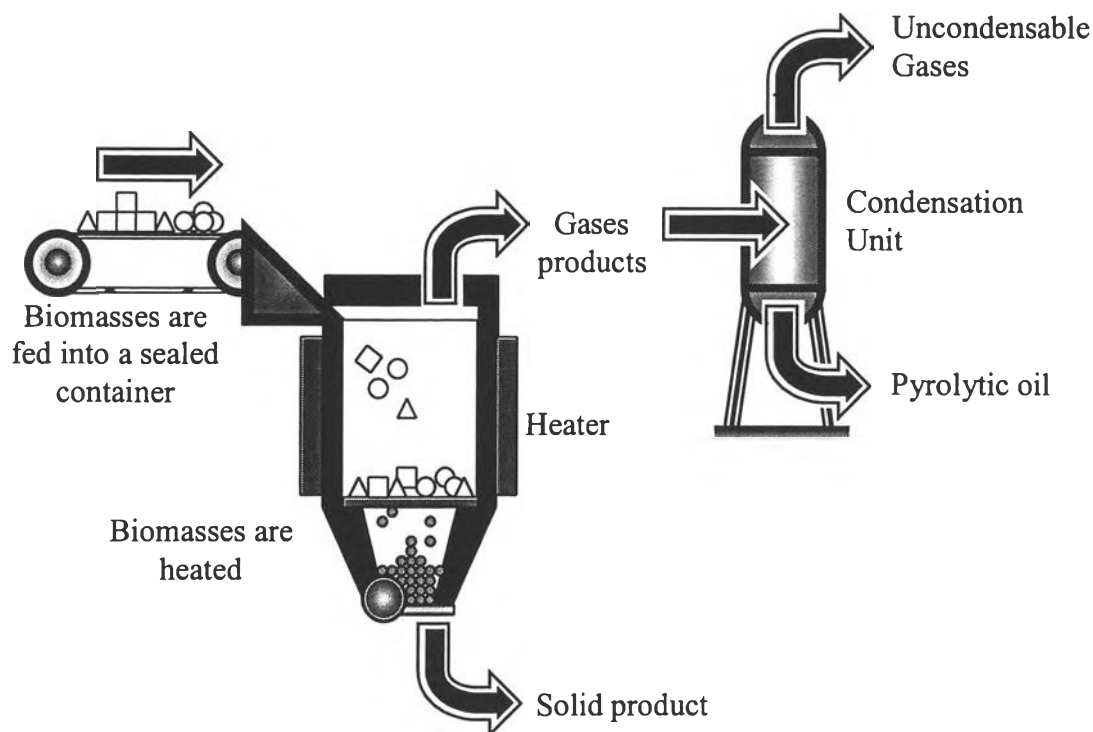


Figure 2.2 The simplest pyrolysis process.

Pyrolysis technology can generally be divided into two main types depending on difference operating condition and characteristic of the time required for heating the material. The pyrolysis technologies are defined as “slow” and “fast” pyrolysis which are mention as followed:

2.1.1 Slow Pyrolysis

The process is typically operated under the slow heating time and has generally taken place at low temperature, below 400°C, allowing local equilibrium reaction along the temperature path. Heat rate, which is transferred to solid materials, is not considered in slow pyrolysis. An important factor to specify the pyrolysis process in many industries is superficial velocity or SV (Reed *et al.*, 2003) of a gasifier which can be defined as

$$SV = \text{Gas Production Rate} / \text{Cross Sectional Area} = (m^3/s) / (m^2/s) = m/s$$

If the SV has low values, it causes the low pyrolysis condition. The products obtained from slow pyrolysis are almost solid, approximately 20-30 %, unburned tars, gaseous products with high hydrocarbon and tar content. At low SV the particles are heated slowly until the particles temperature goes to isothermal state that is the pyrolysis temperature. The reaction within solid material will be taken place very slowly (Reed *et al.*, 2003). Recently, the slow pyrolysis process is usually used to produce charcoal, activated carbon, carbon black, and food flavoring (The Ensyn Technology, 2000).

2.1.2 Fast Pyrolysis

Fast pyrolysis is a thermo chemical process operated under the fast heating rate. Contact time of heat transferred from the wall of the reactor to material matter is so fast. The process is negligible amount of reaction during the heat up period. Solid material is decomposed into the most volatile product or oil vapor around 40-75 %, which is further condensed by reducing the temperature to yield combustible liquid. The combustible liquid yields obtained from fast pyrolysis process are called pyrolysis liquid, bio-crude-oil, bio-oil, bio-fuel-oil, pyrolysis oil, etc. Term “bio” is referred to natural materials used to convert to valuable products such as wood, corn, etc. About 10 to 30 wt% of dry solid material is converted into a medium calorific value uncondensable gaseous products, such mainly as H₂, CO, CO₂, C₁-C₄, etc. and also around 10 to 20 wt% of dry solid material can be converted into solid porous carbon particles, which is called char. In generally, the water limitation of the process is around 15 wt% (Bridgwater, 1999).

2.2 Fast Pyrolysis

Fast pyrolysis is concerned an important renewable energy process, in which this process can produce the valuable product, bio-oil, gaseous, and solid char. Recently, fast pyrolysis technology grows very fast in Europe and other development countries and is believed this process will be the most important process in the future. Fast pyrolysis processes are operated under the main four types of reactor (Bridgwater, 1999):

- Fluid Beds Pyrolysis Reactor
- Ablative Pyrolysis Reactor
- Vacuum Pyrolysis Reactor
- Rotating Cone Pyrolysis Reactor

2.2.1 Fluid Beds Pyrolysis Reactor

Many industries are interested in fluid beds pyrolysis reactor because of ease to operation and ready scale up. The main advantage of using fluid bed is that this type of reactor has high heat transfer to the solid material and high efficiency to produce bio-oil. The process is illustrated in Figure 2.3. Before using this reactor, solid material will be dried and crash into small particle by drier and hammermill, respectively.

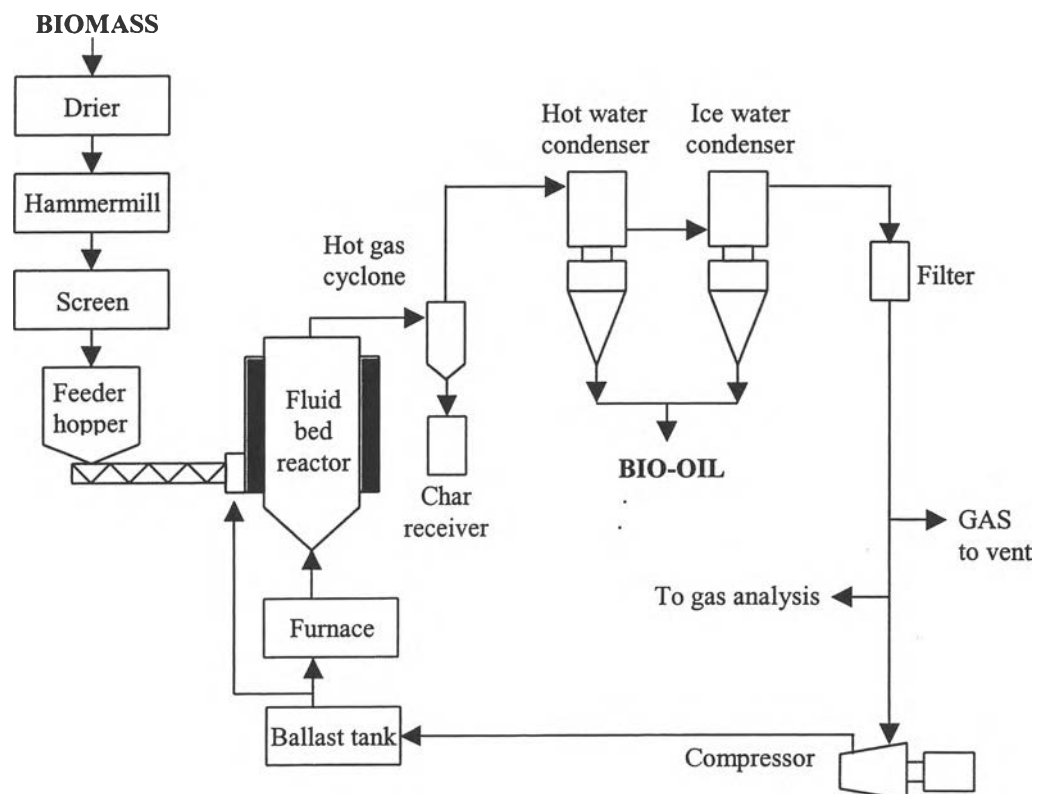


Figure 2.3 Diagram of fluidized bed pyrolysis process (Bridgwater and Peacocke, 2000).

If solid material is in wet form and big size the heat is loss to dry solid and difficult to spread to solid matter. This result will cause a decrease in efficiency of the process. The size of solid material will be separated by screen. Only small size can be passed to feeder hopper. Small solid particles are fed into fluid bed reactor consisting of inert refractory and coke particles. Cyclone is used to recover bed particular matter almost consisting of solid char particles. The solid char matters are then kept in char receiver. The overhead products after separating the solid char are quenched and recovered by condensers. The recovered liquid product by condenser is bio oil. Uncondensed gaseous products are recycled to ballast tank and used as furnace fuel. Two important commercial types of fluid bed reactor are bubbling and circulating fluid bed (Bridgwater and Peacocke, 2000).

2.2.2 Ablative Pyrolysis Reactor

Figure 2.4 presents the simplified schematic of ablative pyrolysis reactor.

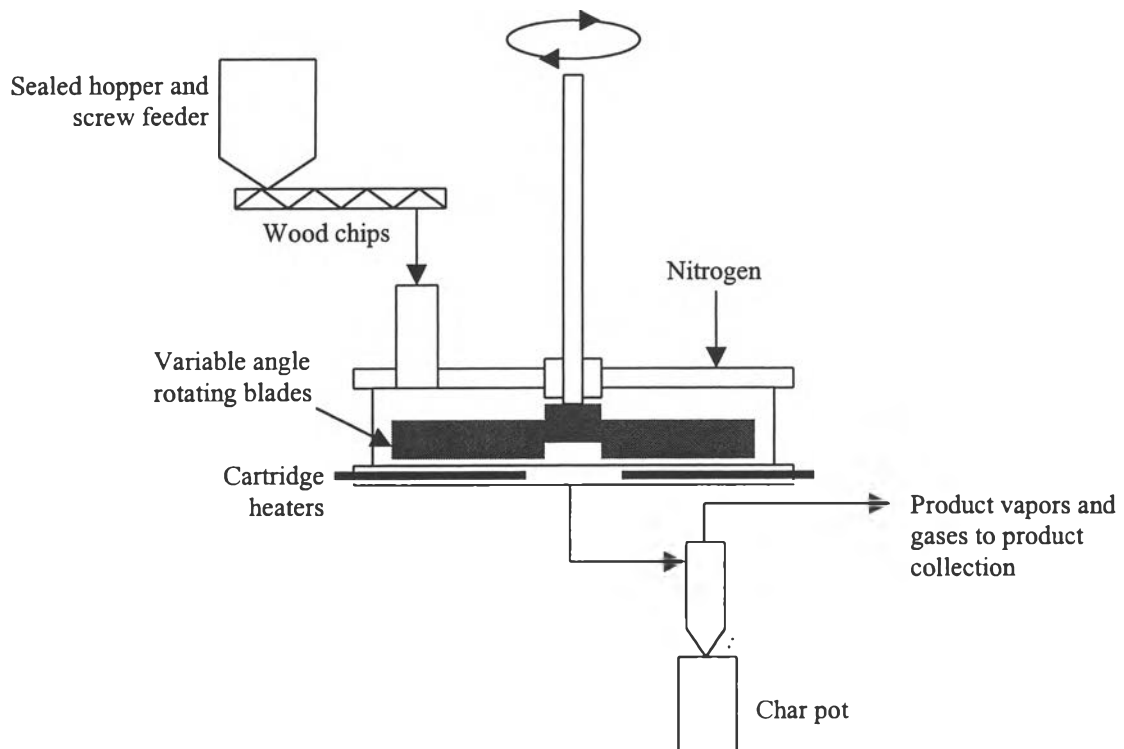


Figure 2.4 Simple schematic of ablative pyrolysis reactor (Bridgwater and Peacocke, 2000).

The main concept of ablative pyrolysis reactor is it can be employed for larger solid particles. The solid materials in general size are fed to reactor by screw feeder and pyrolyzed on the hot surface of reactor. Rotating blades are moved at high speed. During rotating blades are rotated, it generates a mechanical pressure on the particles. The particles, then, are pressed on heat plate cause the particles to pyrolyze into volatile vapor and gases. Gaseous products are continuously removed by nitrogen purged gas. The solid residues are dropped to the bottom reactor mixed with gaseous products. Solid-gases mixtures are then removed by cyclones before sending the gaseous and solid char products to other units. Recently, development for ablative reactor offers a more intensive and potentially compact reaction system.

2.2.3 Vacuum Pyrolysis Reactor

Vacuum pyrolysis reactor is controlled the condition by removing the vapors from pyrolysis reaction as soon as they are formed. Figure 2.5 shows The Pyroclycling™ vacuum pyrolysis process. The process is typically operated under a vacuum condition; a total pressures of 15 kPa.

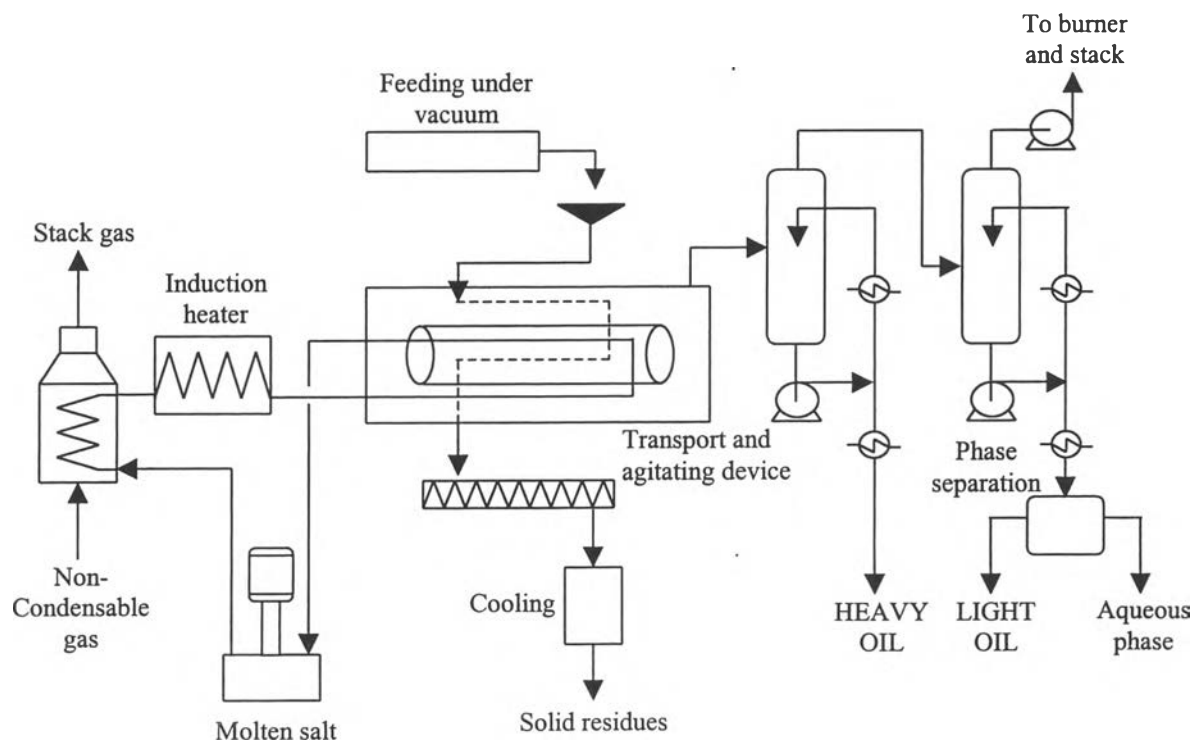


Figure 2.5 The Pyroclycling™ vacuum pyrolysis process (Bridgwater and Peacocke, 2000).

The feed materials after drying are moved on the metal horizontal conveyor plates and received heat from molten salts. Solid materials are changed chemical structures and produced gaseous products. Volatile vapors and gaseous products are rapidly removed by vacuum pumps and directly sent to condenser units to recover valuable products; heavy oil, light oil, and aqueous phase. The solid products are removed from reactor and quenched in cooling unit before keeping in solid receiver. The molten salts after giving the heat to solid materials are recycled to furnace. Heating rate used in this reactor after comparing with other types of reactor is so low. The only main variable of the process with effect to chemical reaction is due to the pressure of the system

2.2.4 Rotating Cone Pyrolysis Reactor

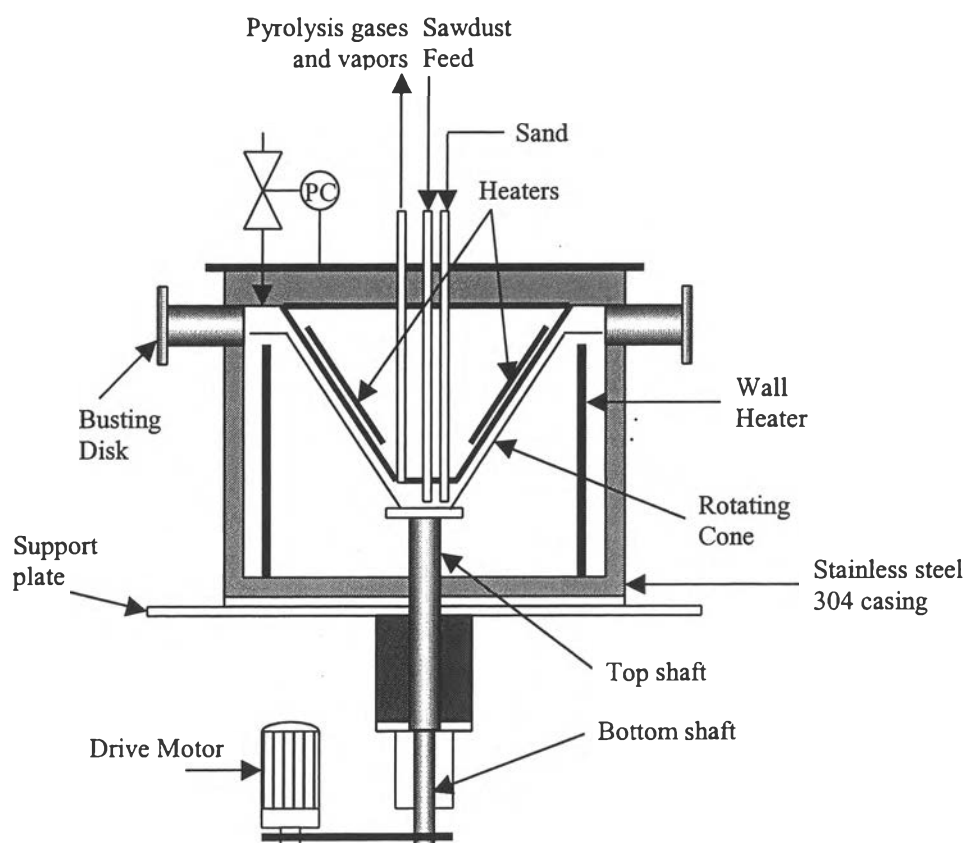


Figure 2.6 Rotating cone pyrolysis reactor (Bridgwater and Peacocke, 2000).

The rotating cone pyrolysis reactor is illustrated in Figure 2.6. The rotating cone is a new type of pyrolysis reactor technology, which was developed in Europe between 1989 and 1997 (Bridgwater and Peacocke, 2000). The aim of this reactor is achieving the pyrolysis efficiency by sliding solid material on the hot surface of rotating cone. The reactor is controlled under centrifugal force by means of the solid material are moved spiral upward along the hot surface. Unreacted solid materials are removed from the reactor automatically by centrifugal force. The outside of the cone reactor is contacted with sand and char mixture, which is received the heat from wall heater and transfer the heat to rotating cone. Centrifugal force increases the effect of heat transfer to solid materials by means of surface contraction. Liquid oils are collected after passing pyrolysis gases and vapors to condenser systems. An advantage of this system is it can reduce the small solid particles after pyrolysis before spreading out into air.

2.3 Pyrolysis Product from Fast Pyrolysis

Fast pyrolysis process is concerned to be the most important pyrolysis process in which not only the process can produce important product, bio-oil, which is the one of valuable energy source in the future but also it is economical process. This section will only present and discuss about important information of bio-oil.

2.3.1 Bio-oil

Bio-oil is liquid oil obtained after condensing volatile matter evolved during pyrolyzed solid material. Bio-oil is almost a dark brown to dark green liquid and a pungent smoky odor. The properties of bio-oil are depending upon the initial feed stock and the operation mode of fast pyrolysis. For example, hot vapor filtration mode will give bio-oil is appeared in translucent red-brown color form while if the process contained high nitrogen gas content, bio-oil can give it a dark green color.

Bio-oil contains varying contents of the mixture of oxygenated compounds containing various chemical functional groups with a wide-varying molecular weight distribution such as carbonyl, carboxyl, and phenolics.

Bio-oil sometime is called pyrolysis oil, bio-crude-oil, bio-fuel-oil, loquid smoke, pyroligous tar, pyroligneous acid, etc. Typically, bio-oil has heating value around 16 to 18 MJ·kg⁻¹. In another word, it has heating value nearly half of conventional fuel oil. The major problem of the present pyrolysis reactors are the quality and the stability of the produced oil, both are strongly affected by the char/ash content of the bio-oil. Besides the known problems concerning solid particles in the bio-oil, the char fines will catalyze the repolymerization reactions inside the oil resulting in a higher viscosity. The char can be removed by after treatment of the condensed products like filtering the oil. The disadvantage of this is that the alkali, concentrated in the char, will dissolve in the bio-oil because high acidity the oil (pH = 2-3). Another option to remove the char is hot gas cleaning of the oil vapor. For both options additional capital investments are required.

The following Table 2.1 and Table 2.2 list typical properties and characteristics of bio-oil from wood pyrolysis (Bridgwater, 1999) and properties and composition of Bio-oil from BioThermTM pilot plant (DynaMotive Energy Systems Coroperation, 2001), respectively.

2.3.2 Properties of Bio-oil

2.3.2.1 *Distillation*

From Table 2.1, the pyrolysis oil can not be completely recovered from the vapor phase. If the process tries to remove the water mixture or light fraction by heating the bio-oil to 100°C, char residue is produced around 50 wt% of bio-oil. In addition, primary and secondary products and water mixture obtained from distillation of bio-oil are not stable form.

The most suitable condition used to store the liquid product is at room temperature because chemically unstable composition solubilized within bio-oil will be changed more slowly at room temperature.

2.3.2.2 Density

The density of bio-oil is so high when compared with water. It is approximately $1.2 \text{ kg}\cdot\text{L}^{-1}$. This property can be concluded that bio-oil is difference from mineral oil.

2.3.2.3 Energy Content

Bio-oil has energy content around 42 % of fuel oil on weight basis and 61 % on volumetric basis, from Table 2.1, and has energy content around 40 % of diesel oil on weight basis and 50 % on volumetric basis, from Table 2.2.

Furthermore, the calorific value is a major deciding factor in the profitability of the process but it is not concerned here.

2.3.2.4 Kinematics Viscosity

The kinematics viscosity of bio-oil is high. It can vary in wide range of 25 to 1000 cSt. This property is the most important in many fuel applications such in case of the efficiency of atomization due to the characteristic of fuel to burn completely.

Table 2.1 Typical properties and characteristics of wood derived pyrolysis oil (Bridgwater, 1999)

No.	Physical properties	Typical Value
1	Moisture content, %	15.0-30.0
2	pH	2.5
3	Specific gravity	1.2
4	Elemental analysis, dry basis, %	
	C	56.4
	H	6.2
	O (by difference)	37.3
	N	0.1
	Ash	0.1
5	HHV as produced (depends on moisture) , MJ · kg ⁻¹	16.0-19.0
6	Viscosity (at 40°C and 25 % water), cp	40.0-100.0
7	Solids (char), %	0.5
8	Distillation	Max. 50% as liquid degrades

Table 2.2 The properties and composition of bio-oil produced from Bio Therm™ pilot plant, derived from three different biomass feedstocks (DynaMotive Energy Systems Corporation, 2001)

NO.	Biomass Feedstock	Bagasse	Pine/Spruce 53% wood + 47% bark	Pine/Spruce 100% wood
1	Moisture, %	2.1	3.5	2.4
2	Ash Content, %	2.9	2.6	0.42
Bio-oil Properties				
1	pH	2.6	2.4	2.3
2	Water Content, %	20.8	23.4	23.3
3	Lignin Content, %	23.5	24.9	24.7
4	Solid Content, %	<0.10	<0.10	<0.10
5	Ash Content, %	<0.02	<0.02	<0.02
6	Density, kg · L ⁻¹	1.20	1.19	1.20
7	Calorific Value, MJ · kg ⁻¹	15.4	16.4	16.6
8	Kinematic Viscosity			
	CS _t @20°C	57	78	73
	CS _t @80°C	4.0	4.4	4.3
Bio-oil composition, %				
1	Water	20.8	24.3	23.3
2	Lignin	23.5	24.9	24.7
3	Cellobiosan	-	1.9	2.3
4	Glyoxal	2.2	1.9	2.3
5	Hydroxyacetaldehyde	10.2	10.2	9.4
6	Levoglucosan	3.0	6.3	7.3
7	Formaldehyde	3.4	3.0	3.4
8	Formic acid	5.7	3.7	4.6
9	Acetic acid	6.6	4.2	4.5
10	Acetol	5.8	4.8	6.6

2.3.3 Application of Bio-oil

Bio-oil can be brought to apply and to substitute for diesel oil or fuel oil in many applications. In present year, the bio-oil acts as a clean fuel and has many advantages. For example, it is considered to be green house gas neutral. In another word, it can generate the CO₂ (complete combustion) in more credit than fuel oil. In the past, bio-oil has been known that it was not similar to petroleum derived oils. The reasons are that bio-oil has high oxygen content, which has important influence to nature of Bio-oil. The oxygen content gives bio-oil has hydrophilic nature rather than hydrophobic one so that it has poor miscibility with hydrocarbon solvents. Recently, there is successful a latest technology to mix bio-oil with diesel fuel (NO.2) by BDM ProcessTM of CANMET Energy Technology Center (CETC) (CANMET Energy Technology Centre, 2002). The blend oil is stable, non-corrosive, and easy to ignite according to ASTM and ISO standard test method. Moreover, blend oil product can be used to generate heat for boilers, turbine, and power generation stations. The properties of blend oil (Bio-oil/Diesel fuel (NO.2)) compared with diesel fuel are shown in Table 2.3.

2.4 Pyrolysis Factor

2.4.1 Solid Material Composition

The composition of solid material is an important factor used to determine the yield of volatile product during decomposition process takes place. Difference in composition of solid feed will give different composition of volatile matter. For example, when the process is controlled at slow heating rate and is pyrolyzed in N₂ atmosphere (500°C), coals are decomposed into 65 wt% gases and water and remained fractions (35 wt%) are tar and light oil. For oil shale pyrolyzed at the same condition, the volatile matter (gases and water) is produced about 20 wt% and 80 wt% of oil.

Table 2.3 Similarities between grade-2 diesel fuel and some bio-oil/diesel fuel (CANMET Energy Technology Centre, 2002)

NO.	Parameter	ASTM Test	Diesel Fuel (NO.2)	Bio-oil/Diesel Fuel Mixtures (wt%)			
				10	20	30	40
1	Flash Point, °C						
	• Open Cup	D-92	92	86	82	82	90
	• Closed Cup	D-93	68	71	74	72	75
2	Fire Point, °C	D-92	94	94	98	94	98
3	Combustion Heat, Cal · g ⁻¹	ISO-1928	10738	10274	9754	9253	8601
4	Pour Point, °C	D-97	-45	-48	N/A	-48	N/A
5	Cloud Point, °C	D-5773	-18	23	N/A	22	N/A
6	Corrosion (Cu, 3 h @100°C)	D-130	1b	1a	N/A	1a	N/A
7	Ash, %	D-482	0	0.02	N/A	0.13	N/A
8	Water & Sediment, %	D-1796	0	0.1	N/A	0.2	N/A

2.4.2 Pyrolysis Temperature

The pyrolysis temperature is a controlled variable which effect of both composition and volatile matter yeild. At differrent temperature will cause and reflect to differrent stage of pyrolysis process. In practice, studying TGA or cumulative mass loss and differential mass loss can do the effect of temperature.

In generally for solid material, such as coal, oil shale, and tar, there are three principle stages of pyrolysis. The first stage will begin from 100 to approximately 300°C. This stage refers to small amount of volatile matter evolved after heat transfer to solid matter. The volatile gaseous products mainly consist of oxide of carbon and water. Almost volatile matter will evolve in second stage in the

temperature of 300 to 450°C around 75 % of all volatile matter. The last stage refers to gasification process. This stage gaseous product is mainly char.

2.4.3 Heating Rate

Heating rate is the most important factor to control pyrolysis process. In order to get desired product, the operator must control the process with appropriated heating rate. The appropriated heating rate is called characteristic heating rate with depend on nature of solid matterial. Charateristic heating rate is related with charateristic heating time (T_H) and charateristic reaction time (T_R). From previous section, the heating rate is related with slow and fast pyrolysis pattern. If reaction time is so slow, the pyrolysis process will be slow pyrolysis. In contrast, the pyrolysis process will be fast pyrolysis. Further more, heating rate is an influent factor for both primary and secondary reaction. For coal pyrolysis, the characteristic of reaction time in second can be shown as $T_H > 10$ sec and $T_H < 0.1$ sec and $T_H \gg T_R$ and $T_H \ll T_R$ for slow and fast pyrolysis, respectively.

2.4.4 Solid Particle Size

The particle size may be related to heating rate in which larger particles will heat up more slowly than smaller one. In another word, heat is difficulty completely to spread out of solid particles so the average particle temperature will be lower and expected volatile yield is to be less.

2.4.5 Pressure

The meaning of pyrolysis is as same as the meaning of cracking. Cracking reaction is favors in high pressure so high pressure will decrease tar and oil fractions whereas will increase light hydrocarbon gases.

2.5 Definition of Thermal Analysis (TA)

The thermal analysis (TA), which investigates temperature measurements under controlled conditions, is applied and used to analyze physical properties of a substance. TA can be classified into many types such as proximate and ultimate

analyzes, thermogravimetry (TG), differential thermogravimetry (DTG), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and differential thermal analysis (DTA). The properties of a substance and TA methods are summarized in Table 2.4 (Hatakeyama, 1994).

Table 2.4 TA methods related to properties of a substance (Hatakeyama, 1994)

Property	TA method	Abbreviation
Mass	Thermogravimetry	TG
Difference temperature	Differential thermal analysis	DTA
Alternating temperature	Alternating current calorimetry	ACC
Enthalpy	Differential scanning calorimetry	DSC
Length, volume	Dilatometry	
Deformation	Thermomechanical analysis	TMA
	Dynamic mechanical analysis	DMA
Electric current	Thermostimulated current	TSC
Luminescence	Thermoluminescence	TL

Actually, the use of only a single thermal analysis technique might not provide sufficient information for a given system. For example, it is common to complement all TGA or DSC data with DTA. If one or more deformation products are mostly produced, TMA may prove useful in solving the problem at hand.

To study reaction mechanism and to determine the thermal stability of the sample in the pyrolysis processes, the recording of mass change is the best way to do. TGA is one method that can be applied. It involves the measurement of sample mass change as a function of temperature and/or time and is applied for the reaction, which has a lot of volatilization substance of the sample mass during the reaction. It can also be applied in the fields of metallurgy, ceramics, inorganic, polymers, biochemistry and so on.

TGA curves are normally plotted the relationship between the mass change (Δm), which can be expressed as percentage, and temperature (T) or time (t). Figure 2.7 presents the schematic of single stage and multiple stage of TGA curve.

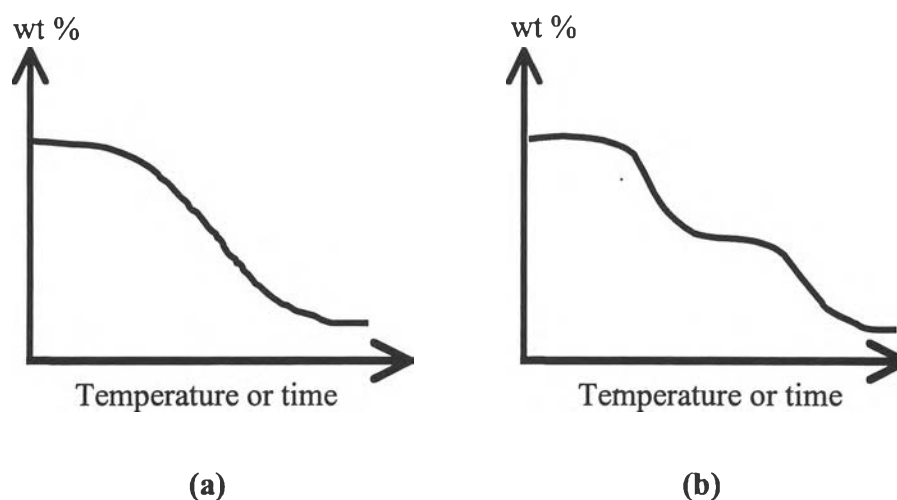


Figure 2.7 Schematic diagrams of single stage (a) and multiple stage (b) of TGA curve.

2.6 Kinetic Studying

2.6.1 Basic Theory of Kinetic Rate Equation

The rate of reaction can be expressed in terms of concentration of reacting substances or products formed. There are three basic ways a species may lose its chemical identity. One way is by **decomposition**, in which a molecule is broken down into smaller molecules, atoms, or atom fragments. A second way is by **combination** of two molecules or atoms and can combine with another molecule or atom. The third way is a species may lose its identity through **isomerization**. Although the molecule neither adds other molecules to itself nor breaks into smaller molecules, it still loses its identity through a change in configuration (Fogler, 1999).

Systems in which reaction occurs can be divided into two main classes, heterogeneous and homogeneous. In homogeneous systems, all reacting materials are found within a single phase and the rate of reaction can be determined by measuring isothermally the decrease in concentration of the reactant or the

increase in concentration of the product. The rate of reaction of component A, r_A , is given by

$$r_A = f(\text{state of the system}) = f(\text{pressure, temperature, composition}) \quad (2.1)$$

If the pressure can be determined, the reaction rate may be written in the new form of

$$r_A = f(\text{state of the system}) = f(\text{temperature, composition}) \quad (2.2)$$

In the basic form, the kinetic rate may be written as

$$\frac{dx}{dt} = -kf(x) \quad (2.3)$$

where k is the rate coefficient, x is the concentration of reactant, $f(x)$ is the function, which is presumed nature of the reaction process, and t is time during reaction. The rate coefficient, k , can be given by the Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2.4)$$

The unit of k is s^{-1} , A (frequency factor) is s^{-1} , E (Activation Energy) is $\text{kJ} \cdot \text{mol}^{-1}$, T (temperature of the sample) is K and R (gas constant) is $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Sometimes, A can be expressed as $A = A_n T^n$. From the reaction rate equation, the change in reactant concentration, x , with a function of time, t , at various temperature, T , A and E values can be determined by graphical method.

2.6.2 Kinetic Model for Pyrolysis System

Thermal analysis data are useful for both research and engineering applications. In the case of research scientists, thermal analysis can be used to identify the different reaction mechanisms, determine the kinetic parameter and

optimize the conditions favoring one reaction over the other. In the case of engineering applications, there are two basic methods to determine reaction rate kinetic parameters, isothermal and non-isothermal methods. The latter can also be called dynamic method (Siddhartha and Thomas, 1998).

In the isothermal methods, a sample is quickly brought to a predetermined temperature, where TA instrument shows the behavior of the pyrolysis system as a function of time while the non-isothermal method is used to record the response of the sample as it is scanned. Usually, the non-isothermal method is controlled under a constant rate and is preferred for studying reaction kinetic rate as the following reasons:

- 1) It is easy to interpret the results obtained from the system.
- 2) The reaction process can be followed over a wide temperature range.
- 3) Several reaction processes can be observed in a single experiment.
- 4) A number of methods of data evaluation are available.

Since 1960s, several mathematical methods have been developed to determine the kinetic parameters from the data obtained from TA analysis. In the present, the most worldwide experiment used to determine the kinetic parameters is thermal gravimetric analysis, TGA.

2.6.2.1 Coats and Redfern Method

Coat and Redfern (1964) firstly developed this method. The function $f(x)$ from equation (2.3) was expressed in the n^{th} order reaction form for a reaction $F(s) \rightarrow G(g) + S(s)$ where alphabet F, G and S are referred to feed, gas and solid, respectively. In this case, the kinetic rate equation can be written as

$$\frac{dx}{dt} = k(1-x)^n \quad (2.5)$$

or

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-x)^n \quad (2.6)$$

where x is the percent conversion of the solid matter or percent mass change during pyrolysis occur, k is the rate constant, A is Arrhenius parameter, E is the activation energy of reaction and T is temperature.

For constant heating rate condition, equation (2.6) can be written in the new form as follow:

$$\frac{dx}{dT} \cdot \frac{dT}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-x)^n \quad (2.7)$$

or

$$\frac{dx}{dT} = \frac{A \exp\left(-\frac{E}{RT}\right)}{dT/dt} (1-x)^n \quad (2.8)$$

Substituting this equation with $\Phi = \frac{dT}{dt}$ so the equation is

$$\frac{dx}{dT} = \frac{A \exp\left(-\frac{E}{RT}\right)}{\Phi} (1-x)^n \quad (2.9)$$

or

$$\frac{dx}{(1-x)^n} = \frac{A \exp\left(-\frac{E}{RT}\right)}{\Phi} dT \quad (2.10)$$

For the first order reaction, $n = 1$, the integration of equation (2.10) and rearranging give

$$-\log\left(\frac{1-x}{T^2}\right) = \frac{AR}{\Phi E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (2.11)$$

For $n \neq 1$, the solution is

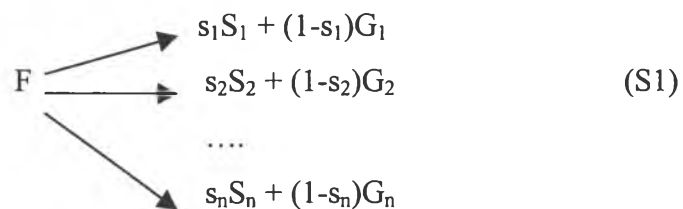
$$1 - \frac{(1-x)^{(1-n)}}{(1-n)} = \frac{AR}{\Phi E} \left(1 - \frac{2RT}{E} \right) \exp\left(-\frac{E}{RT} \right) \quad (2.12)$$

The general drawbacks of this method are commented by Conesa *et al.* (2001) including

- 1) the data obtained from TGA are very much manipulated,
- 2) the methods are only used for a single process,
- 3) the programmed temperature is usually used and
- 4) the methods can be used only one heating rate.

2.6.2.2 Distributed Activation Energy Model (DAE)

The Distributed Activation Energy model is a new developed kinetic model used for determining kinetic parameters of multi-step reaction such as parallel reactions. The mechanism equations of parallel reactions can be written in a general form by Conesa *et al.* (2001) as shown below:



Where s_1, s_2, \dots, s_n , S_1, S_2, \dots, S_n and G_1, G_2, \dots, G_n are solid yield coefficient for reaction steps, different kind of gas and liquid, respectively.

Figure 2.8 shows the weight loss (TGA) and differential thermal gravimetric (DTG) curves.

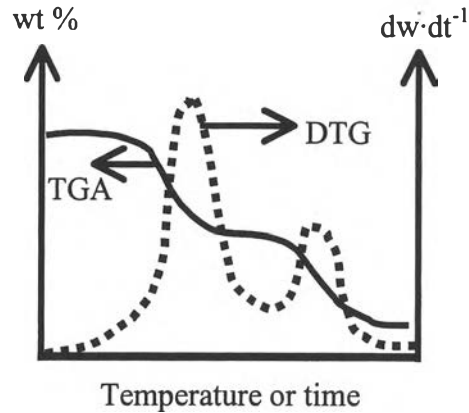


Figure 2.8 TGA (weigh loss) and DTG (differential thermal gravimetric) curve.

From Figure 2.8, it shows that this pyrolysis has two steps. DAE assumes that the distribution of reactivity caused by the reaction complexity can be represented by a set of independent and parallel reactions with their own values of A_i and E_i (Burnham *et al.*, 1995).

Alonso *et al.* (2001) proposed the reaction mechanisms of coal pyrolysis. They found that there are many reaction mechanism steps occurred during the coal pyrolysis. The DAE model was applied.

For the n^{th} order reaction, the basic kinetic equation is

$$\frac{dx}{dt} = k(1-x)^n \quad (2.3)$$

and

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2.4)$$

By applying the basic kinetic equation with parallel reactions, the reactivity equation can be written for the entire pyrolysis temperature range:

$$\frac{dx}{dt} = \sum_{i=1}^m \hat{f}_i \frac{dx_i}{dt} = \sum_{i=1}^m f_i k_i (1 - x_i)^n \quad (2.13)$$

From this equation, the subscript i refers to the different DTG peaks during the non-isothermal heating, x_i refers to the conversion degree of process i at time t , f_i refers to the mass fraction of release i on total mass release basis and k_i refers to kinetic rate constant of process i . Computer analysis programs can find all kinetic parameters.

There are many problems after solving kinetic parameters by this method. The problems commented by Conesa *et al.* (2001) are more kinetic constants must be solved, more than one differential equation must be integrated at the same time and the conditions could not be extrapolated.

2.7 Application and Related Works

Although study of pyrolysis has been carried out with a wide range of materials, not much has been reported on pyrolysis of oil sludge and API separator sludge. Here, only works related to pyrolysis of sludge will be provided.

Font *et al.* (2001) analyzed differences between pyrolysis and combustion of sewage sludge behaviors by TGA. The experiment was carried out at $15^\circ\text{C} \cdot \text{min}^{-1}$, showing that the behavior of pyrolysis was similar and different from combustion. The different behaviors between combustion and pyrolysis may be due to combustion has char forming and aerobic stabilization at the last part of heating while pyrolysis is only initial step before combustion take place. In addition, the experiment showed that main pyrolysis can be observed around 500°C . It was referred to no decomposition above this temperature.

Chang *et al.* (2000a) studied kinetics of oil sludge pyrolysis by TGA. The experiment was conducted under the nitrogen atmosphere in the temperature range of 380-1073 K and constant heating rates of 5.2, 12.8, and $21.8 \text{ K} \cdot \text{min}^{-1}$. The results showed that the pyrolytic reaction was significant at the temperature range of 450-800 K. In addition, two- and three-reaction model were developed and found that the three-reaction model gave the best fit. With the first reaction model, it was

concluded that the activation energy, reaction order, and frequency factor of the corresponding pyrolysis reaction for oil sludge were $78.22 \text{ kJ}\cdot\text{mol}^{-1}$, 2.92, and $9.48 \times 10^5 \text{ min}^{-1}$, respectively.

Major products from the oil sludge pyrolysis were also characterized by Chang *et al.* (2000b). The products could be divided into two major parts; gaseous and liquid products. The gaseous products (non-condensable gases) were CO_2 (50.88 wt%), HCs (Hydrocarbons, 25.23 wt%), H_2O (17.78 wt%) and CO (6.11 wt%). The main hydrocarbon gaseous products were low molecular weight paraffins and olefins, which were in the range of $\text{C}_1\text{-C}_2$ (51.61 wt% of HCs). The liquid products were close to diesel oil and contained significant amount of vacuum residue, 9.57 wt%.

Effects of inexpensive and non-harmful additives on the improvement of oil sludge pyrolysis were also studied by Chang *et al.* (2002). The groups of the additives are: (1) aluminum compounds consisting of Al, Al_2O_3 , and AlCl_3 and (2) iron compounds consisting of Fe, Fe_2O_3 , $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, FeCl_3 , and $\text{Fe}_2(\text{SO}_4)_3\cdot n\text{H}_2\text{O}$. The results showed that $\text{Fe}_2(\text{SO}_4)_3\cdot n\text{H}_2\text{O}$ was the most active additive and could enhance the reaction rate in the temperature range of 650-710 K. Above 720 K, the ratio of the reaction rates in the presence to absence of additives (R_{pa}) was less than 1. The mixed additive of $\text{Fe}_2(\text{SO}_4)_3\cdot n\text{H}_2\text{O}$ and Al gave the highest liquid yield of pyrolysis oil.

Schmidt and Kaminky (2001) carried out pyrolysis of oil sludge in fluidized bed reactors in both laboratory and pilot scales. Oil sludge could be pyrolyzed into oil and solid products at the temperature range between 460 and 650°C. The experiments showed that the amount of oil from the pyrolysis was approximately 70 to 84 %. It was found that oil was cracked into small and low boiling point compounds with the increase of pyrolysis temperature.

A bubbling fluidized bed incinerator was also used to investigate combustion of oil sludge. The combustion chamber was operated under bed temperature ranging from 700-800°C. The main flue gas emissions from the bed were 400-500 ppm. of CO and 98 ppm. of NO_x . The efficiency of the combustion chamber was around 77 % (Surjosatyo *et al* 1999).

2.8 Currently Analysis Method for Pyrolysis Products

The understanding of pyrolysis mechanism of solid material can be studied by analysis on quality and quantity of pyrolysis products consisted of semi-volatile or volatile compounds. There are many analysis methods to analyze products obtained from pyrolysis of many solid materials such as Fourier Transform Infrared Spectroscopy (FTIR), Mass Spectrometry (MS), Gas Chromatography (GC), Pyrolysis-GC, Pyrolysis-MS, or Pyrolysis-GC/MS. Recently, a highly sensitive technique to elucidate products of pyrolysis is Pyrolysis-GC/MS. Pyrolyzer is connected with GC and MS. Light volatile organic compounds from pyrolyzer are then analysis by GC and MS. This method can provide a fast and convenient to study the effect of temperature or heating rate on the decomposition products and generating at the same time. These following are exemplified researchers who analyzed pyrolysis products by Pyrolysis-GC/MS.

Francisco *et al.* (1991) used Pyrolysis-GC/MS method to provide information on the formation and degradation stages of charred residues from lignocellulosic biomass. They were found that charred residues after severe heating contain some concentrations of resistant plant structure components. The observation from intensity of isothermal heating could provide the order of alkyl compounds yield as follow phytadienes < fatty acids < alkanes < wax esters < sterols. Further more, Pyrolysis-GC/MS can be applied with many biochemical fields. For example, Alexis *et al.* (1994) studied primary and secondary pyrolysis products of 1-[(2'-Carboxy)pyrrolidinyl]-1-deoxy-D-fructose (Proline Amadori Compound). They found that the main products were 1-(1'-pyrrolidinyl)-2-propanone, 2-hydroxy-1-(1'-pyrrolidinyl)-1-buten-3-one, and 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one with acetic acid and pyrrolidine. In addition, they got many pyrolysis informations after running Pyrolysis-GC/MS, they could propose pyrolysis fragmentation mechanism of Proline Amadori Product.