



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Problem Statement

##### 2.1.1 Sewage Sludge

Sewage sludge may be used in term “biosolid”, the solid material that is produced during the treatment of water/wastewater at a treatment facility. Solid materials are removed from sewage during the wastewater treatment process. Consider the ultimate content of material, sewage sludge by definition may be considered as biomass (Yaman, 2004). In term of elemental composition, it consists mainly of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in less proportion.

Wastewater is a combination of the liquid- or water-carried wastes discharged from residential, institutional, commercial and industrial establishments together with ground water, surface water and storm water, as may be present (Werther and Ogada, 1999). Domestic sewage, produced in urban residences, institutions and businesses, is usually collected by pipes and channels called sanitary sewers, which lead to a central discharge point. In rural residences domestic sewage is often collected in a septic tank on the property. Industrial wastes, which consist of liquids produced in manufacturing processes, are sometimes collected in sanitary sewers, but the nature of many industrial wastes may make it dangerous or difficult to do so. Oftenly, industries dispose their own wastes. Storm sewage, which comes from rain and groundwater, is collected either in a storm sewer or, with domestic sewage and industrial wastes, in what is called a combined sewer

During treatment, bacteria and other microorganisms break components in the wastewater down into simpler and more stable forms of organic matter. Non-organic matter also settles into sludge. For instance, heavy metals and other toxic materials, including persistent organic pollutants, are commonly found in sewage sludge. Once solids are removed, they are treated in one of several ways. Most often, they are removed in a semi liquid mass referred to as sludge.

An amount of sewage sludge generated from wastewater treatment system seems to increase proportionally with the development of all sections in most countries. All indications suggest that the sludge production will continue to increase. Now or later, many cities of the world in both developed and developing countries have to find a suitable solution for the disposal of the expected large quantity of sewage sludge.

### 2.1.2 Sewage Sludge Disposal

The most common ways to deal with sewage sludge are dumping into the sea, landfill, incineration and utilization as agricultural fertilizer. These techniques however might not be the most suitable solutions since one may possibly cause subsequent problems and usually require secondary treatments (Pinto *et al.*, 1999).

#### 2.1.2.1 *Dumping into the Sea*

Dumping into the sea has been banned in most countries. The reason is related to the effect to marine environment. Dumped sludge can affect or even kill marine life (Chapman *et al.*, 1988) and maybe threatened beaches or coasts.

#### 2.1.2.2 *Landfill Disposal*

Landfill, also called sanitary landfill or secure landfill, requires a lot of space, adequate barriers or seals such as liners, leachate collection systems, and procedures to protect the public from exposure to the disposed wastes. Well-monitoring task is always considered necessary. All landfills must be constructed and operated in accordance to specific requirements related to location or sitting requirements, stability, protection of soil and water through, installation of liner and collection systems, storm water control, leachate and landfill gas management, and hazards management. A well-run landfill is a hygienic, inexpensive solution to waste disposal but poorly-run landfill can pollute both air and groundwater. A number of problems can occur during landfill operations. The consequences of these problems, depending on their nature and severity, vary from fatal accidents to minor infrastructure damage and from environmental pollution (e.g., releases of leachate to the underground soil bed and/or aquifer) to simple nuisance problems (e.g., dust, noise). Some local communities have also found the difficulty to locate new landfills because conflict with the people nearby.

### *2.1.2.3 Incineration*

Incineration is the complete oxidation of materials producing ash and hot flue gas. Via this process, materials are completely stabilized and their volumes are drastically reduced. It is intended to reduce the wastes' toxicity and other hazardous characteristics of hazardous substances. Most types of wastes generated can be burnt in an incinerator. The direct combustion is known to take advantage of materials heating value. The hot flue gas is allowed to use for heating purpose or steam production and subsequently power generation by means of steam turbine. On the other hand, the densities of most wastes are lower than that of conventional solid fuel like coal, leading to the economic limitation in transportation (Yaman, 2004).

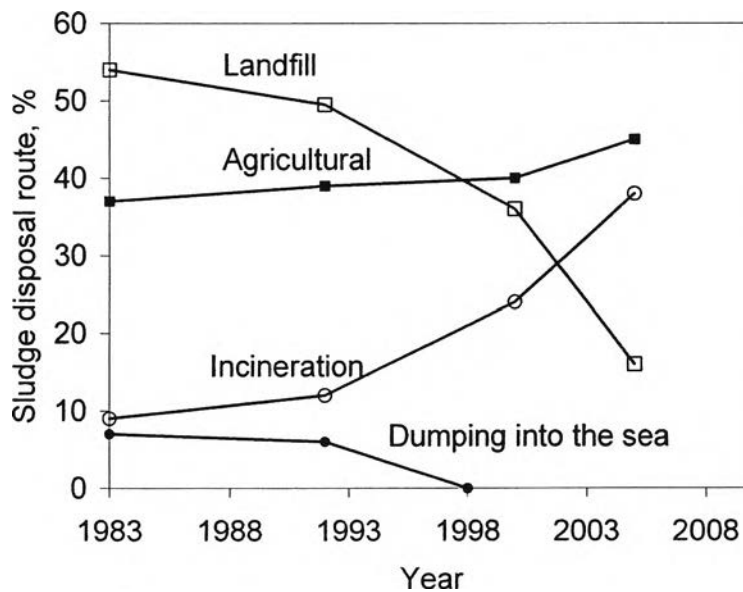
Incineration also creates several forms of waste such as the emission of unburned gases and metals in secondary products of combustion and leftover ash. The hazards associated with these emissions and incinerator wastes are the subject of controversy. The potential pollutants generated include acid gases, hydrogen chloride and sulfur dioxide, NO<sub>x</sub> (as nitric oxide and nitrogen dioxide) and carbon dioxide. Special kind organic pollutants such as dioxins and furans are also of concern. Thus, the implementation equipment for preventing particulate and gas pollutants is a must. The volume of solids or ash left after incineration is drastically decreased from original quantity. The ash is in turn more concentrated with pollutants than the original waste. The ash is often regulated as a hazardous waste itself and must be landfilled. Other factors also must be concerned such as high capital and operating expense. Once an incinerator is built, fuels are required for run. This provides a dis-incentive to reducing waste production and reusing waste products.

### *2.1.2.4 Use in Agricultural Works*

As one of most common sludge utilizations, sewage sludge was applied in an agricultural works as a fertilizer for soil conditioning. It is feasible to use stabilized sewage sludge-amended soil for planting as long as the application rate is controlled. However, it is important to note that stabilized chemically-modified sludge may not suitable for planting food crops because of the presence of a significant amount of heavy metals (Chu and Poon, 1999). Nonetheless, an extensive use of sewage sludge in all agricultural purpose can probably risk an

increase in the heavy metal concentration in the soil and underground water as well as in savior human health problems if pathogen presents.

An interesting example of sewage sludge disposal route here has drawn from European community (Figure 2.1). Despite the fact that landfill is currently the most widely used disposal outlet, almost all the countries recognize that this outlet will not be sustainable at current or projected levels far into the future due to increasing competition for landfill space, higher cost, more stringent environmental standards and the implementation of policies to promote recycling. As a result, landfill as a way of sludge disposal is expected to decrease. On the other hand, many countries recognize agricultural land as the major beneficial outlet for sludge. Concern over risks from heavy metals and organic contaminants in the sludge, and caution over the addition of nitrogen- and phosphorus-rich manure to land, will continue to be a major factor in limiting the use of sludge as fertilizer. Incineration is currently a minor method of sludge disposal, but it is anticipated that it will increase substantially in the future.



**Figure 2.1** Forecast sewage sludge disposal routes in European community (Hall and Dalimier, 1994).

Although sufficient information is not available concerning the trend in other countries, it may be expected that the role of incineration as a route for sludge disposal will increase. With the future of disposal through land-filling and recycling in agriculture constrained, and disposal to sea facing a ban, growing interest is now being directed towards utilization by incineration and thermal processes.

### 2.1.3 New Alternative to Sewage Sludge Utilization

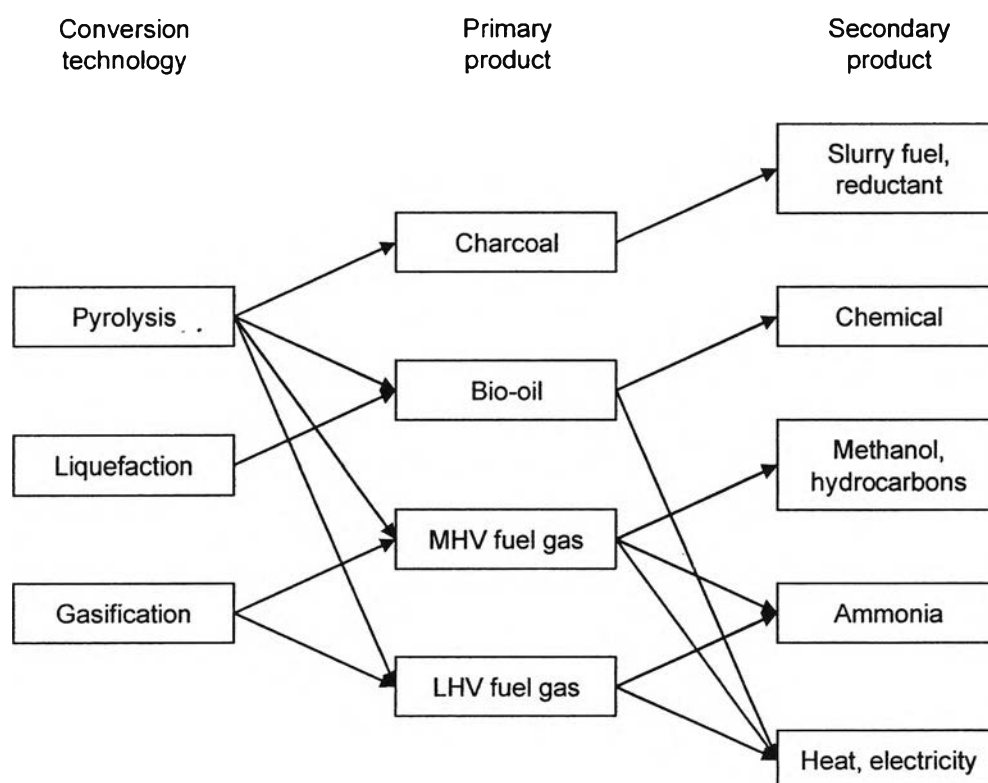
Nowadays, there are a number of new methods of thermal sludge utilization around the world, either being in a development stage or already implemented (Bien *et al.*, 2000). As alternative, thermal processes such as, gasification, liquefaction and pyrolysis has recently received a renew attention of a few research groups. It was considered that pyrolysis might be a solution to the problems of both secondary pollution and of large energy consumption.

## 2.2 Introduction to Thermal Conversion Process

It has been demonstrated that various kinds of waste, such as oil sludge, used plastics, agricultural wastes, scrap tire, coal, municipal solid wastes (MSW), and industrial solid wastes, including “sewage sludge”, can be transformed to energy or valuable chemicals. This has been attracting attention from the view points both of alternative energy by utilization of wastes replacing the fossil fuel and of sustainable waste stabilization. It is normally achieved by several routes including bioconversion and thermal conversion processes (Conesa *et al.*, 1998 and Inguanzo *et al.*, 2002). Bioconversion methods are based on the conversion of materials to alcohols or oxygenated products by biological activity. For, thermal conversion processes, three techniques are used in practice, pyrolysis, liquefaction and gasification. Each of these processes gives the different products in different proportions. These products can be classified as primary and secondary products (Figure 2.2). Three conversion processes are here of interest as individually described in the following:

### 2.2.1 Gasification

Gasification is the thermal degradation of carbonaceous materials in the presence of an externally supplied oxidizing agent (air, oxygen or steam). Main purpose of gasification is to produce low- or medium-heating value gas that convenient only for on-site use. The practical process was started for the application for biomass conversion in late 1870s (Hunt, 1983). The gasification process may occur after complete pyrolysis by slightly increase the temperature in the reactor. In this process, the external energy is needed only for start the operation. Adding a certain amount of oxidative agent such as air into the reactor allows the partial combustion in the reactor, resulting in a generation of heat and subsequently an increase the temperature of reactor. Then, the energy generated by its product combustion is adequate for self-operation



**Figure 2.2** Primary and secondary products from thermal conversion process.

### *2.2.1.1 Gasification Sub-process*

To reach a gasification condition, the carbonaceous materials undergo three processes:

#### 1) Pyrolysis of carbonaceous fuels

The pyrolysis (or devolatilization) process occurs as the carbonaceous particle heating up. Volatiles are released and char is produced. The process is depended on the properties of the material and determines the structure and composition of the char, which will then undergo gasification reactions.

#### 2) Combustion

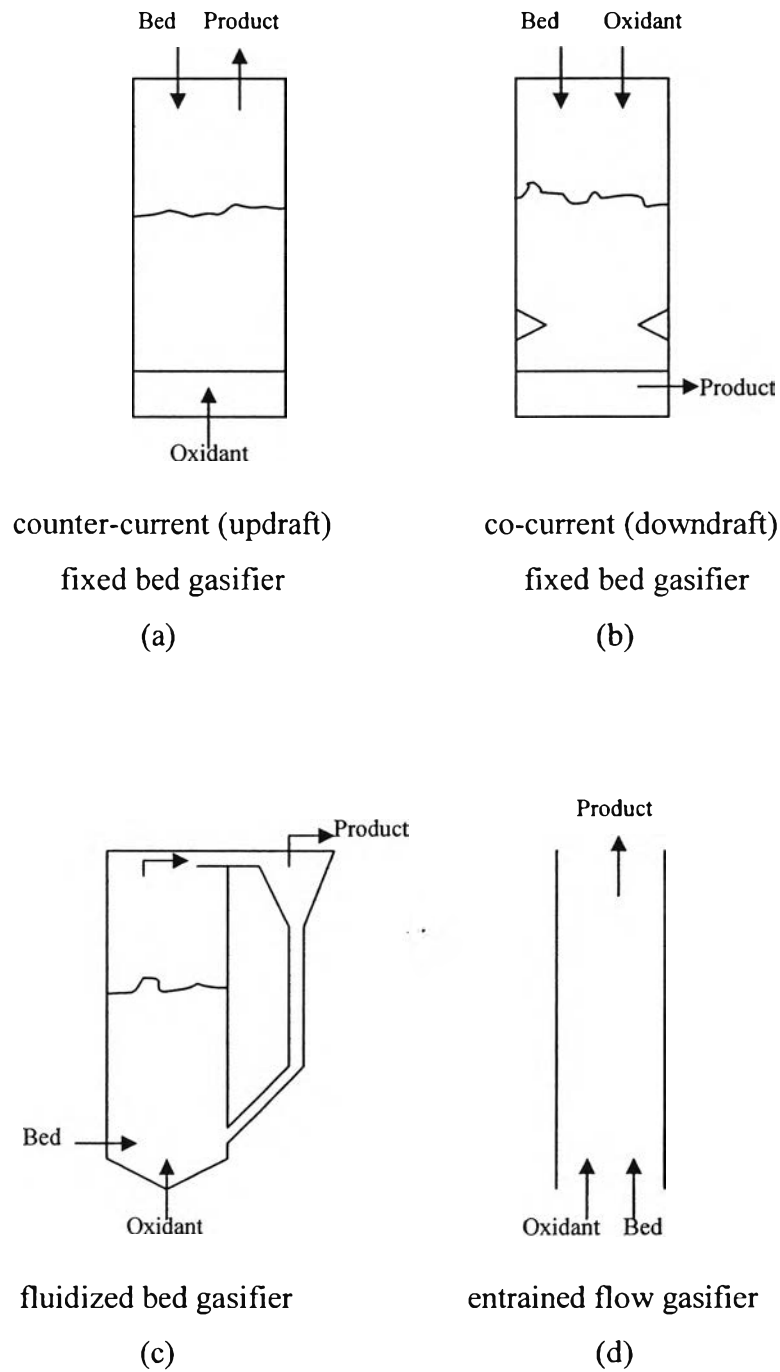
The combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. Pyrolysis and combustion are very rapid processes.

#### 3) Gasification of char

The gasification process occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen. The resulting gas is called producer gas or syngas (or wood gas when fueled by wood). It may be more efficiently converted to energy such as electricity than would be possible by direct combustion of the fuel. As the fuel is first combusted in a gas turbine, generated heat is used to produce steam to drive a steam turbine. Also, corrosive ash elements such as chloride and potassium may be refined out by the gasification process, allowing high temperature combustion of the gas from otherwise problematic fuels.

### *2.2.1.2 Gasification System*

Several types of gasifiers are currently available for commercial use: fixed bed, fluid bed and entrained flow reactors. Fixed bed is normally limited using for small-scale gasification. The different fixed bed types are often categorized by the direction of the gas flow through the reactor (upward or downward) or by the respective directions of the solid flow and gas stream (co-current or counter-current). Larger gasifiers are usually of the fluidized-bed or entrained-flow type (Stassen, 1995). Figure 2.3 shows four types of gasifiers. The following is an individual description:



**Figure 2.3** Typical type of gasification system.



### 1) The counter-current fixed bed ("up draft") gasifier

The counter-current fixed bed gasifier consists of a fixed bed of materials through which the "gasification agent" (steam, oxygen and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon in order to reach temperatures higher than the ash fusion temperature. The nature of the gasifier means that the material must have high mechanical strength and must be non-caking so that it will form a permeable bed. The throughput for this type of gasifier is relatively low. Thermal efficiency is high as the gas exit temperatures are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use or recycled to the reactor.

### 2) The co-current fixed bed ("down draft") gasifier

The co-current fixed bed ("down draft") gasifier is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the fuel (downwards, hence the name "down draft gasifier"). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in energy efficiency on level with the counter-current type. Since all tars must pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type.

### 3) The fluid bed gasifier

In this gasifier, the fuel is fluidized in oxygen (or air) and steam. The ash is removed dry or as heavy agglomerates that defluidized. The temperatures are relatively low in dry ash gasifiers, so the fuel must be highly reactive; low-grade coals are particularly suitable. The agglomerating gasifiers have slightly higher temperatures, and are suitable for higher rank coals. Fuel throughput is higher than for the fixed bed, but not as high as for the entrained flow gasifier. The conversion efficiency is rather low, so recycle or subsequent combustion of solids is necessary to increase conversion. Fluidized bed gasifiers are most useful for fuels

that form highly corrosive ash that would damage the walls of slagging gasifiers. Biomasses generally contain high levels of such ashes.

#### 4) Entrained flow reactor

In the entrained flow gasifier, a dry pulverized solid, an atomized liquid fuel or a fuel slurry is gasified with oxygen (much less frequent: air) in co-current flow. The gasification reactions take place in a dense cloud of very fine particles. The high temperatures and pressures also mean that a higher throughput can be achieved. However, thermal efficiency is somewhat lower as the gas must be cooled before it can be cleaned. The high temperatures also mean that tar and methane are not present in the product gas; however the oxygen requirement is higher than for the other types of gasifiers. All entrained flow gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as black fly ash slurry. Some materials can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However some entrained bed type of gasifiers do not possess a ceramic inner wall but have an inner water or steam cooled wall covered with partially solidified slag. These types of gasifiers do not suffer from corrosive slag. Some materials also have ashes with very high ash fusion temperatures. In this case mostly limestone is mixed to the fuel prior to gasification. Addition of a little limestone will usually suffice for the lowering the fusion temperatures. The fuel particles must be much smaller than for other types of gasifiers. This means the materials must be pulverised, which requires somewhat more energy than for the other types of gasifiers. By far the most energy consumption related to entrained bed gasification is not the milling of the fuel but the production of oxygen used for the gasification.

#### 2.2.2 Liquefaction

By liquefaction, the process employs the concept of catalytic conversion in which a suitable catalyst is used to add hydrogen to substances. Raw material is converted to the liquid product at low temperature (350 °C) and high pressure (300 atm). The major features of this process are (1) rapid heating, (2) short residence time, and (3) reactor effluent quenching (Speight, 1994). The pressure in the reactor is normally balanced by hydrogen partial pressure (Beenackers *et al.*,

1989). In order to achieve direct hydrogenation, the catalyst must be intimately contact with materials. Otherwise, the process is generally inefficient. The main product of liquefaction is a liquid hydrocarbon or oil that has low oxygen content. That means, the quality of this oil is higher than that from pyrolysis. The oil obtained from this process has heating value in range of 35-40 MJ/kg. However, disadvantages of this process include high cost and the difficulty in feeding raw material to high-pressure system and in product separation.

### 2.2.3 Pyrolysis

Pyrolysis is a thermal conversion of carbonaceous materials under an inert atmosphere, resulting in production of gas, liquid (bio-oil) and solid residue fractions. Relatively low temperature, 300-600 °C, are employed in pyrolysis compared to 800 - 1000 °C or even higher in gasification and incineration. The pyrolysis process has more advantages compared with the incineration process due to the economic, the energy utilization and releasing of heavy metal to natural resource (Lewis, 1975). The relative proportions and characteristics of the pyrolysis products highly depend on the pyrolysis methodology, the characteristics of material and reaction parameters. By this process, gas produced is combustible that is normally subjected to direct combustion to provide energy. The liquid, as a major product, contains several different chemicals in varying proportions. It can potentially be either directly used as fuel or extracted for some chemicals. The solid residue is typically composed of mostly stabilized carbon and inorganic compounds, which can be further utilized as a fuel or as an adsorbent or even safely goes directly to the disposal.

Various kinds of wastes are considered hydrocarbon-rich compounds. There are several ways to make use of the energy contained in such materials by either direct burning or relatively new method like pyrolysis. Compare to others, direct combustion is an old method, in which the material is completely transformed into heat, but with very low efficiency. Instead, the pyrolysis is attractive because solid wastes which are difficult and costly to manage, can be convert to liquid products. The liquid have advantages in transport, storage, combustion and flexibility

in production and marketing. It therefore does not require the waste be used at the site for energy production as in gasification or combustion (Piskorz *et al.*, 1986).

At present, the pyrolysis of waste materials such as plastics, cartons, municipal wastes has received a renewed attention due to the possibility of converting these wastes into useful energetic products or valuable chemicals (Conesa *et al.*, 2004). As focus in this study, more detailed discussion of this process is in the following section.

## 2.3 Pyrolysis of Sewage Sludge

### 2.3.1 Principal

Pyrolysis can be defined as a thermal decomposition of materials under a non-oxygen atmosphere. As the temperature elevated above 300 °C, the decomposition of high molecular weight organic molecules will take place. It is also important to note that some materials can be decomposed at somewhat lower temperature. This was proposed to be a depolymerization with breaking of the chemical bond of carbonaceous components. Breaking of high molecular weight organics results in production of smaller compounds, forming volatile or other products. This process is sometimes called “devolatilization”. The decomposition temperature of different groups of organic compound was reported by Shen and Zhang (2003) as given in Table 2.1.

**Table 2.1** Temperature ranges for different groups of compounds to decompose

Group of compounds decomposed	Temperature range (°C)
Moisture	up to 150
Carboxylic	150-600
Phenolic	300-600
Ether oxygen	up to 600
Cellulosic	up to 650
Oxygen containing compounds	150-900

However, the pyrolysis of materials, which are considered heterogeneous by nature with a wide variety of unknown components, is even not simple in practice. It is believed that many decomposition reactions are involved in the pyrolysis. Unfortunately, complex detail of each reaction is typically unknown and difficult to analyze. Nonetheless, there was also an attempt for an explanation in general. The detail on several processes which occur in certain temperatures has been reported in general by Bien *et al.* (2000), and they are represented in Table 2.2.

**Table 2.2** Several processes occur in temperature elevation of organics (Bien *et al.*, 2000)

Temperature (°C)	Detail of sub-process
250	Separating water CO <sub>2</sub> , depolymerization, first phase of separating sulfur compounds
340	Decomposition of aliphatic compounds, first phase of separating methane and other gas hydrocarbons
380	Low temperature gas carbonization
400	Decomposition of organic acids as well as organic nitrogen compounds
500	Alteration of bituminous substance into low temperature carbonized oil or pitch (tar)
600	Cracking of oil into short chain gas hydrocarbons and formation of aromatic compounds
>600	Olefin dimerization and formation of high boiling temperature aromatic compounds

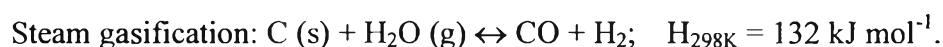
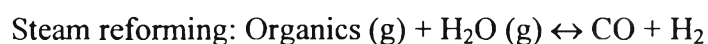
### 2.3.2 Pyrolysis Products and Applications

The typical pyrolysis products are in form of combustible gas, liquid or bio-oil and carbon-rich solid residue (char). Percentages of particular post pyrolysis products received during the process strongly depend on the process methodology, material characteristics and conditions used such as temperature and

heating rate. Especially, the product distribution strongly depends on operating temperature. As well known in general, use of higher pyrolysis temperature produces larger the fraction of gas product and smaller fraction of the solid residue, while the oil fraction was rarely changed regardless pyrolysis temperature (Bien *et al.*, 2000 and Inguanzo *et al.*, 2002). However, the effect of the heating rate is only important at low final pyrolysis temperatures. At temperatures higher than 650 °C, it is practically negligible. At low temperature, cracking reactions are favored by high heating rates. Thus lighter compounds are produced, which can be removed from the reactor, increasing in the liquid fraction. On the other hand, at temperatures above 650 °C the liquid fraction yield is rather constant. This suggests that all condensable compounds have already been released, so that the remaining volatiles correspond to non-condensable gases (Inguanzo *et al.*, 2002). The detail of each product is described below.

#### 2.3.2.1 Gas

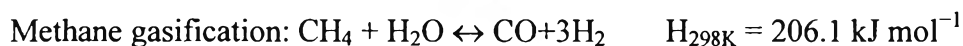
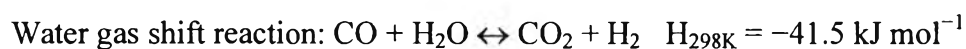
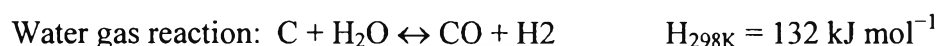
Gas may be called “uncondensed gas” since all volatile products are in form of vapor but part of volatile is condensed to form liquid. By pyrolysis, CO<sub>2</sub>, CO, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and C<sub>x</sub>H<sub>y</sub> (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>) are the main components in gas phase released during pyrolysis (Inguanzo *et al.*, 2002 and Shen and Zhang, 2003). Nitrous oxide (N<sub>2</sub>O) is also detected; however, the maximum volume percent is 131 ppm at 600 °C (Shen and Zhang, 2003). An increase in the pyrolysis temperature leads to a decrease in CO<sub>2</sub>, and to an increase in CO and H<sub>2</sub>. Whilst, the hydrocarbons CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> show a maximum in their yields at around 600 °C for CH<sub>4</sub> and 450 °C for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. However, hydrogen rich gas can be produced from pyrolysis of high moisture sludge by using a high heating rate and a low flow of carrier gas. This condition allows the steam reforming and steam gasification as follow (Domínguez *et al.*, 2006):



Indeed, the overall gas heating value is influenced by the evolution of the hydrocarbons present in the gas. The averaged pyrolysis gas heating value is in between 12.0 and 13.0 MJ·m<sup>-3</sup>, depending on the pyrolysis temperature and heating rate used. At certain conditions, maximum heating value of pyrolysis gas can be as high as 25.0 MJ·m<sup>-3</sup>. The optimization of the gas yield would be probably achieved aiming that gas fraction produced to be re-circulated and burned in order to produce energy supplied to the process or other applications.

### 2.3.2.2 Liquid or Bio-oil

Condensable vapors represent the liquid fraction of the pyrolysis products. This fraction can in turn be divided into an aqueous fraction which contains certain water- and hydro-soluble organic compounds, and an organic fraction containing other substances. The percentage of aqueous fraction obtained was lower than the original moisture content of the sewage sludges. This suggests that some of the water (about 15 wt%) is consumed during pyrolysis (Menéndez *et al.*, 2004). In fact, the yield of this fraction is slightly higher than the original moisture content of the sample up to temperatures of 600 °C due to the breaking of functional groups from the volatile matter (Morf *et al.*, 2002). However, the water yield decreases when the temperature increases. This is attributed to the following gasification reactions:



All these reactions were favored by the high temperatures at which the pyrolysis was carried out.

In an energy view point, the pyrolysis liquid has a heating value close to a conventional fuel oil (typically 16-18 MJ/kg) (Bridgewater and Peacocke, 2000). Some authors reported the quality of pyrolysis oils as high as 27 MJ/kg (Bien *et al.*, 2000). This oil has good commercial value as a fuel to power diesel engines. However, the properties of the oil, such as its bad odour, high

viscosity and its instability can be a disadvantage for marketing the oil. Nonetheless, it is possible to improve the characteristics of this oil. Like many other bio-fuel derived oils, it has high oxygen content that induces instability within the oil through polymerization reactions, which then increases the viscosity of the oil. Esterification of the pyrolysis oil with ethanol and sulfuric acid (as a catalyst) was found to improve the odour characteristics significantly. Moreover, this method not only improves the stability of the oil making it more suitable to be stored for long-term use, but also contributes to an increase in the heating value of the oil by up to 9% (Doshi *et al.*, 2005).

### 2.3.2.3 *Solid Residue*

In general, even as high as 850 °C, the sewage sludge pyrolysis is not likely completed. It seems that at high temperatures, devolatilization rate slows down. That means the volatile fraction is still remaining in the solid residue, leaving its functionalities and subsequent heating value. Principally, three methods can be used for the disposal of this residue; (1) incineration, alone or mixed with other fuels (2) landfill disposal and (3) used as cheap adsorbent of suitable pollutants prior applying either of the other two options.

From an energy point of view, solid carbonaceous residues from pyrolysis have relatively low heating values compared with those of other fuels or even of original sludge itself. The heating value of the pyrolyzed residue undergoes a slight decrease as the pyrolysis temperatures and the heating rate increase. Although the possibility of incineration cannot entirely be ruled out, the relatively low heating value along with the high concentration of heavy metals that these types of residue possess makes them unattractive for use in incineration (Werther and Ogada, 1999).

For landfill, concentrating of heavy metals presented in the final residue is considered the advantage (Kaminsky and Kummar, 1989 and Stambach *et al.*, 1989). In contrast to combustion ash, lixiviation of these metals is minor. Thus, the final use or disposal in landfill of this sludge is most secure. Apart from this advantage, pyrolysis offers the possibility of a high level of volume reduction. Thus, when disposing of the pyrolyzed residues through landfill, it is



important to consider the reduction in the volume of raw sewage sludge that can be attained by pyrolysis.

The third option, using the residue as an adsorbent in pollution control, is compatible with the two earlier options. It can be used firstly as an adsorbent and then burned. The relatively high amount of heteroatom, especially oxygen and nitrogen, signifies a solid organic fraction with abundant functionalities. The residue is therefore of a basic nature. However, the basicity increases as the pyrolysis temperature increases. This increase can be attributed to a loss of the acidic oxygen-containing surface groups of the organic fractions. It is well known that basic carbons are preferable for adsorbing acidic compounds such SO<sub>2</sub> or H<sub>2</sub>S and other pollutants like phenol and phenol-derivatives (Radovic *et al.*, 1997). Most of its porosity is due to macropores, while the meso- and micro-pore volumes are relatively low. The adsorption capacity of this solid is about of 25% that of commercial activated carbon for H<sub>2</sub>S adsorption (Max Lu and Lau, 1996). However, the textural properties can be improved by both chemical and physical activation. Further investigation is necessary as well.

#### 2.3.2.4 Applications

The combined pyrolysis process and its application can be schematically represented in Figure 2.4.

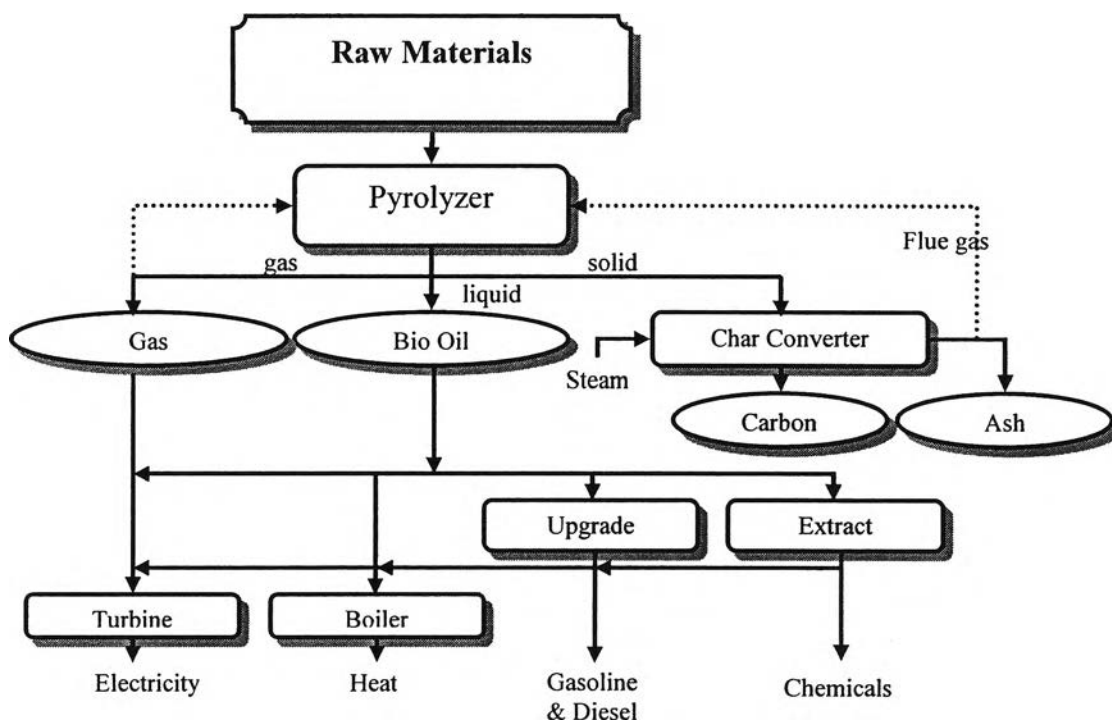
#### 2.3.3 Type of Pyrolysis Process

Pyrolysis process can be classified into flash, fast and conventional (or slow) pyrolysis according to the heating rate or residence time. The ranges of operating parameters for each type are in Table 2.3. The conventional pyrolysis consists of the slow, irreversible, thermal decomposition of organic components. Slow pyrolysis has traditionally been used for the production of charcoal. Indeed, the slow pyrolysis requires long residence time of feed inside the reactor to ensure that the fully cracking has occurred. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products (Klass, 1998). High yield of oil can be achieved under high heating rates (>1,000 °C/s) and short residence time (<1s). However, a high heat transfer rate can cause incomplete cracking of high molecular weight hydrocarbons. Therefore the feed particle sizes should be small enough in order to achieve a high heat transfer.

Generally, the fast pyrolysis is preferred because of the economic reason even though it gives products in lower quality.

### 2.3.4 Pyrolysis Reactors

To achieve a high yield and good product quality, different types of reactor have been developed. Type of reactor is an extremely important factor for quality of pyrolysis products. There are several types of reactor available for pyrolysis process, including top- and side- feed fixed bed, and fluidized bed reactors. These reactors are operated differently and give different product characteristics. Reactor selection and design are highly concerned to both product quality and quantity requirements. Process flexibility and safety are also concerning factors.



**Figure 2.4** Diagram of pyrolysis applications for converting materials into energetic product and valuable chemicals (Thipkhunthod *et al.*, 2002).

**Table 2.3** Operating parameters for pyrolysis process (Maschio *et al.*, 1992)

	Conventional Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Operating Temperature (°C)	300-700	600-1000	800-1,000
Heating rate (°C/s)	0.1-1	10-200	>1000
Solid residence time (s)	600-6000	0.5-5	<0.5
Particle size (mm)	5-50	<1	Dust

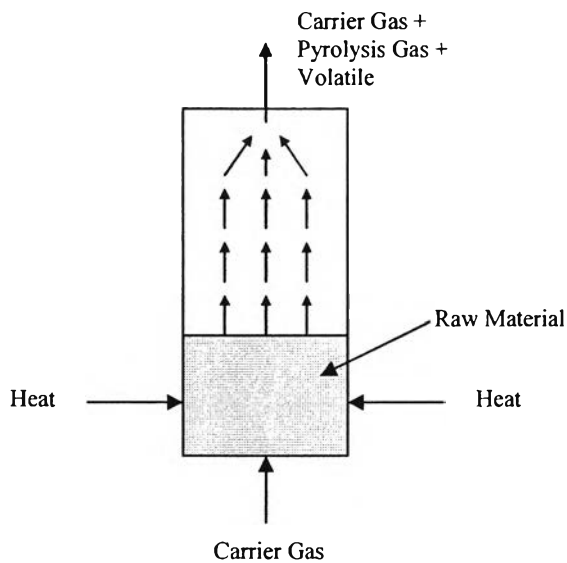
Type of pyrolysis reactor can be divided to three types, fixed bed, fluidized bed and other type. The detail of each type is discussed below (Bridgewater and Peacocke, 2000).

#### 2.3.4.1 Fixed Bed Reactor

In this type, carrier gas flows through stationary bed containing raw material in reactor. The reaction takes place after supplying heat to the reactor. Gas product and volatile are generated and flow out with the carrier gas as shown in Figure 2.5.

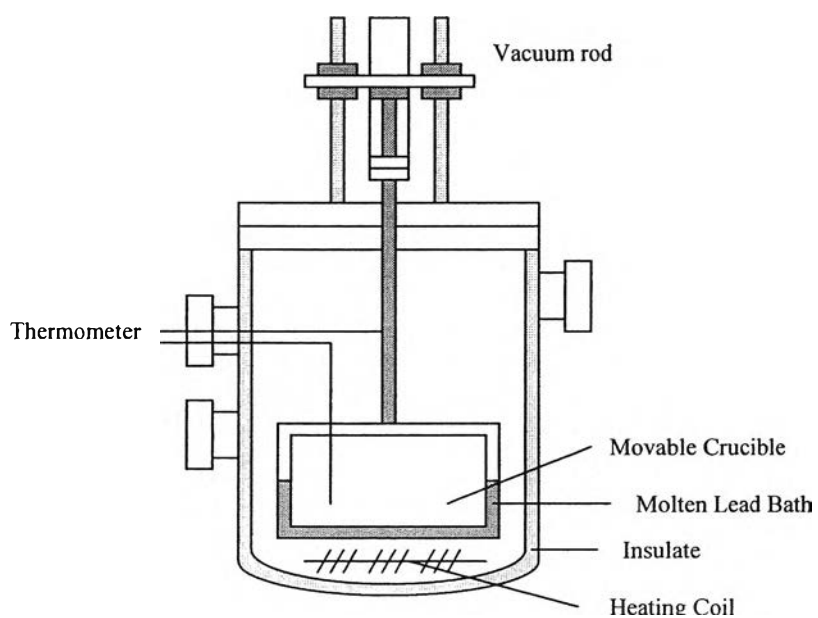
Fixed bed reactor can be also subdivided to either batch or continuous reactors. The first type is suitable for a lab scale study since it is easy to observe any parameter that affects to the pyrolysis reaction. In contrast, a continuous type reactor is suitable for pilot scale to study the effect of feed rate and for industrial scale to obtain a highest amount of product and shortest operating time.

There are several developments, designs, or even applications of a continuous fixed bed reactor. Roy *et al.*, (1994) proposed vacuum-fixed bed reactor for fast pyrolysis. It can be operated with low heating rate (normally over 1,000 °C/s) allowing the feed to have a longer time to absorb heat. Since the gas product has short residence time in the reactor, undesired reaction between gas products can be avoided. A vacuum pyrolysis reactor is shown in Figure 2.6.



**Figure 2.5** Fixed bed reactor.

However, fixed bed reactor is not extensively used because of many reasons such as high investment cost, large area requirement, and less product amount than fluidized bed.



**Figure 2.6** A vacuum fixed bed reactor.

### 2.3.4.2 Fluidized Bed Reactor

Fluidized bed reactor seems to be more suitable than fixed bed reactor because of the difficulty in operating a fixed bed reactor with severe conditions. In contrast, a fluidized bed reactor can give high heat transfer efficiency. With a high flow rate of carrier gas, the gas product can be taken off very fast from the reactor. A fluidized bed reactor is shown in Figure 2.7.

In a fluidized bed reactor, an inert gas (e.g. N<sub>2</sub>) at fluidizing state velocity flows through the bed (e.g. sand) from the bottom of the reactor. Raw material is fed at the side of the reactor and suddenly exchanges heat with the bed. The pyrolysis reaction exists at this zone. A gas product, mixture of gas generated and a small amount of char and bed particle, is taken off at the top of the reactor. Then, the product stream will enter a cyclone for solid separation. Finally, gas product is condensed while char particles will be fed back to the reactor.

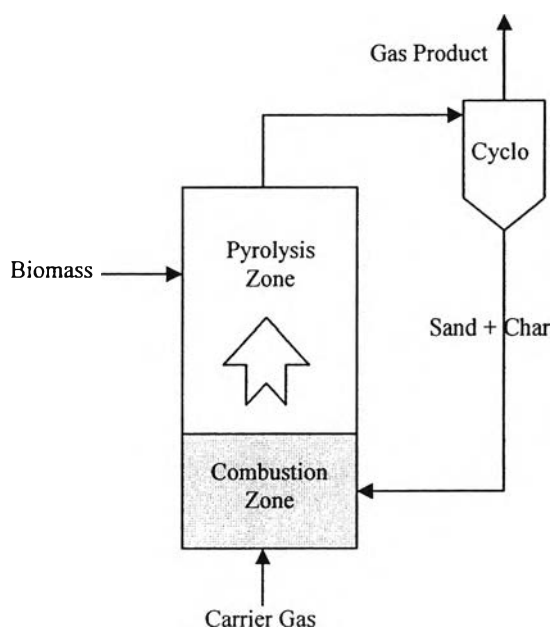


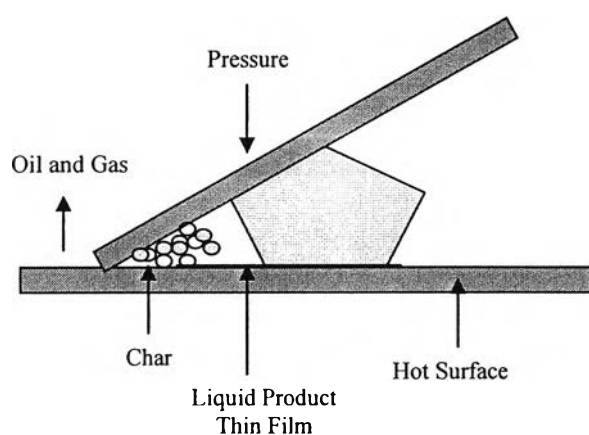
Figure 2.7 A fluidized bed reactor.

### 2.3.4.3 Other Reactor

There are many types of pyrolysis reactors other than fixed and fluidized bed reactors. These are three examples.

#### 1) Ablative Reactor

A meaning of ablative is almost the same as “melting” or “thermal corrosion”. In this reactor, biomass will contact with a hot surface under a fast pyrolysis condition. An ablative reactor is shown in Figure 2.8.



**Figure 2.8** An ablative reactor.

The basic principle of an ablative reactor is to use a rotating blade pressing raw material on a hot surface. Material contacting with a hot surface will be pyrolyzed converting to gas and char. From this concept, a practical ablative pyrolysis reactor was developed with an attempt to pyrolyzed a continuous feed.

#### 2) Pyrocycler

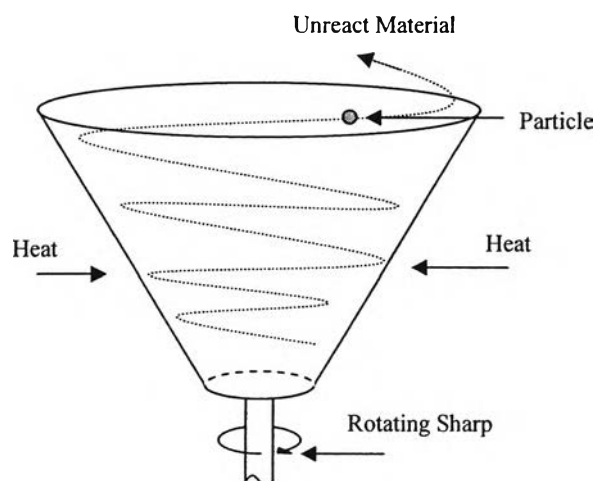
In this reactor, a thermal conversion of raw material is operated at a specific condition such as pressure, heating rate, and temperature to achieve the highest yield of product. Raw material will be dried and ground before entering to the pyrocycler in the vacuum condition. It will be heated by use melting salt holding at a specific temperature. The melting salt absorbs heat from uncondensed gas (from pyrolysis process) combustion. The temperature control system is also required to control the heat balance in the reactor.

The gas product is suddenly removed out of the reactor by the vacuum pump after it is generated. Then, the gas stream will directly enter a series of two condensers to separate the light and heavy fractions. Char is also cooled down.

### 3) Rotating Cone Reactor

The difference of this reactor from others is that it does not require a carrier gas. A rotating cone reactor is shown in Figure 2.9. Biomass is fed and heated at the top of the reactor. Heat and mass transfer simultaneously occur when the reactor is rotating. Raw material will rotate following the reactor and move up along the reactor wall. When it reaches to the top of the cone, it is totally converted to the char. Meanwhile, the gas and vapor will naturally move out at the top of the cone.

The advantage if this reactor is no carrier gas required. This can enhance to reduce the reactor size and the investment cost concerning to secondary oil collection. However, this process is under study and development stage. Many parts of the system are needed to clarify before practical use.



**Figure 2.9** A rotating cone reactor.

## 2.4 Review of Kinetics of Sewage Sludge Pyrolysis

Before pyrolysis can be used in practical operation, the development of a system for sewage sludge conversion to energy and derived chemicals however requires a fundamental knowledge or understanding of the thermal properties and reaction kinetics.

### 2.4.1 How to Study Solid Decomposition Kinetics

#### 2.4.1.1 *General*

In general, in order to investigate any reaction kinetics, the reaction was usually performed under a set of certain conditions whereas the information concerning to the reaction nature was monitored. The attained information was then interpreted normally with an assistance of the mathematical modeling, achieving all concerned kinetic parameters.

Likewise, pyrolysis reaction was studied with the same manner. As the pyrolysis mostly involves the solid state reaction by elevation of temperature, the method can be so-called “thermal analysis”. The methods are categorized into two groups either non-isothermal or isothermal systems used. Non-isothermal system that was extensively used is the Thermogravimetric Analysis (TGA), whereas the weight loss of material is monitored as a function of temperature (or time). The product output may be simultaneously detected, for instance, by connection with the FTIR spectrometer. This method is widely used for study the thermal decomposition of various materials. Although the method is quite simple and easy to perform, it gives lots of useful information.

The obtained data are useful for both research and engineering applications. In the case of research scientists, identification of different reaction mechanisms, determination of kinetic parameters and optimization of conditions to favor one reaction are necessary information that can be obtained. For engineering applications, thermal analysis data on specific temperatures at which various reactions occur, their reaction rates, and energy involved are valuable information for practical process design (Gaur and Reed, 1998).



#### 2.4.1.2 Performing Mathematics

In kinetic formulation of solid state reactions, it has been assumed that the isothermal homogeneous gas or liquid phase kinetic equation can be applied (Dickinson and Heal, 1999 and Conesa *et al.*, 2001). Therefore, for any single reaction, the decomposition kinetic expression is represented in the form of:

$$\frac{dw}{dt} = kf(w), \quad (2.1)$$

where,  $w$  is the mass of materials and  $k$  is a kinetic constant. Oftenly, it is useful to represent  $w$  in another form such as mass loss fraction,  $x$ . Hence,

$$\frac{dx}{dt} = kf(x). \quad (2.2)$$

The kinetic constant  $k$  is governed by the Arrhenius law:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2.3)$$

where,  $A$  is an exponential factor,  $E$  is an activation energy,  $R$  is a universal gas constant and  $T$  is an absolute temperature.

The specific form of  $f(x)$  represents the hypothetical model function, which indeed depends upon an assumption on a reaction mechanism. Many kinds of mechanisms have been found to control different kinetic mass loss processes, and the corresponding forms of the function  $f(x)$  as well as the derivations were frequently stated in literature. Table 2.4 shows the basic model functions usually employed for the kinetic study of solid state reactions. The application of the Arrhenius equation to the kinetics of solid state reactions and this empirical equation can represent the experimental rate data as function of temperature accurately for both homogeneous and heterogeneous reactions (Dickinson and Heal, 1999).

**Table 2.4** The kinetic model functions  $f(x)$  and corresponding  $g(x)$  usually employed for the solid state reactions (Liu *et al.*, 1999 and Conesa *et al.*, 2001)

Model	$g(x)$	$f(x)$
1. Reaction order		
- zeroth order	$x$	$1$
- first order	$-\ln(1-x)$	$1-x$
- second order	$(1-x)^{-1}$	$(1-x)^2$
- third order	$(1-x)^{-2}$	$(1-x)^3$
2. Phase boundary controlled reaction		
- two phase	$1-(1-x)^{1/2}$	$2(1-x)^{1/2}$
- three phase	$1-(1-x)^{1/3}$	$3(1-x)^{2/3}$
3. Diffusion		
- one-dimension	$x^2$	$1/2x$
- two-dimension	$(1-x)\ln(1-x)+x$	$[-\ln(1-x)]^{-1}$
- three-dimension	$[1-(1-x)^{1/3}]^2$	$3/2(1-x)^{2/3}[1-(1-x)^{1/3}]^{-1}$
- Ginstling-Brounshtein	$(1-2x/3)-(1-x)^{2/3}$	$3/2[(1-x)^{-1/3}-1]^{-1}$

Deriving kinetic parameters from TG data could be done by either differential or integral methods. The emphasis in these methods is on finding a way to plot the TGA data attained, which can provide a rapid visual assessment of the form of  $f(x)$  as well as prepare the kinetic parameters such as  $E$  and  $A$  (Liu *et al.*, 2002). The example of the mathematic analysis starts at combining Eq. (2.2) and (2.3), hence

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x). \quad (2.4)$$

By TGA experiment, the data is normally obtained by using a constant heating rate, defined as  $\beta = dT / dt$ . With some mathematical manipulation, Eq (2.4) becomes

$$\frac{dx}{f(x)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT. \quad (2.5)$$

Following an integral method, function  $g(x)$  is defined as:

$$g(x) = \int_0^x \frac{dx}{f(x)}, \text{ and thus} \quad (2.6)$$

$$g(x) = \int_{T_0}^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (2.7)$$

where  $T_0$  is the initial temperature. The integral has no exact solution. Therefore, an analytical approximation or numerical solution must be used to evaluate the integral. The approximation methods were collected in literature (Gaur and Reed, 1998). One of the most popular methods was proposed by Coats and Redfern (1964). The detail on Coat and Redfern derivation method is available in Appendix A. The function  $g(x)$  can be eventually obtained (Table 2.4) in correspondence with a model function,  $f(x)$ . The following equation can then be achieved:

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \quad (2.8)$$

The rate equation is now become an ordinary equation, which is ready for the interpretation of TGA data. The plot  $\ln\left[\frac{g(x)}{T^2}\right]$  against  $1/T$  should give a straight line of a slope of  $-E/R$ . The kinetic parameters such as A and E as well as order of reaction can be obtained after the correct model is applied.

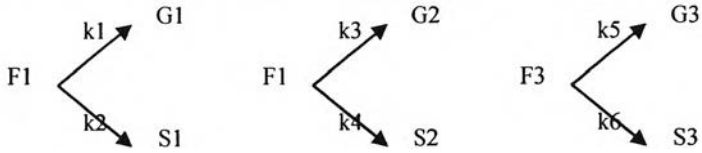
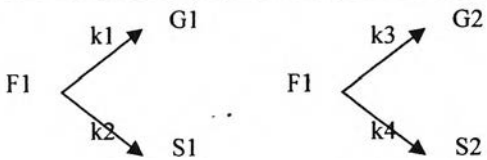
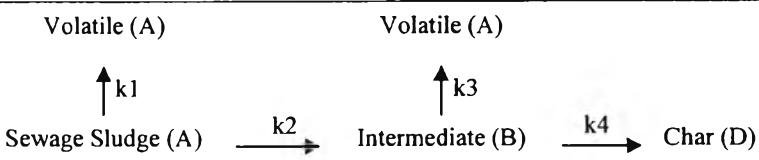
#### 2.4.2 Kinetic Model for Sewage Sludge Pyrolysis

For such highly heterogeneous materials with a wide variety of unknown components as sewage sludge, it is believed that many decomposition reactions are involved in the pyrolysis. Unfortunately, to analyze complex detail of each reaction is not an easy task. Nevertheless, there have been many attempts to

describe pyrolysis of sewage sludge with a suitable kinetic model by different authors (Conesa *et al.*, 1997, Chu *et al.*, 2000, Conesa *et al.*, 2001 and Chen and Jeyaseelan, 2001).

The pyrolysis process in general is too complex for the development of a realistic mechanistic kinetic model. Therefore, strongly simplified kinetic schemes involving “lumps” are used instead of single reaction. The kinetic modeling of sewage sludge pyrolysis documented in literature has been reported by several authors. The model has been reviewed and given in Table 2.5.

**Table 2.5** The kinetic models proposed for sewage sludge pyrolysis

Author	model
Conesa <i>et al.</i> , 1997	 <p style="text-align: center;">three parallel reaction model</p>
Chu <i>et al.</i> , 2000	 <p style="text-align: center;">two parallel reaction model</p>
Chen and Jeyaseelan, 2001	

The early study of sewage sludge pyrolysis kinetics was studied and the model proposed by Dumpelmann *et al.* (1991). In this study, the fluidized bed reactor was used and the kinetic model can be used to forecast the maximum weight loss. Conesa *et al.* (1997) have studied sewage sludge kinetics by using Thermogravimetric analysis. Possible models of sewage sludge thermal decomposition have been considered using different heating rates. The best model

considers three different organic fractions, each of them associated with a different thermal behavior. These three independent reactions occur in parallel. The model was validated with the TG data obtained for a non-digest and anaerobically digested sludge. One fraction has been assigned to non-biodegradable compounds. Meanwhile, the other two evolve biodegradable organic matter and dead bacteria. This model was supported by the study of primary gas evolution stage (Conesa *et al.*, 1998). It was claimed to correlate to three stages of gas evolution centered at ca. 250, 350 and 550 °C.

Chu *et al.* (2000) also examined the thermal pyrolysis characteristics of a polyelectrolyte flocculated activated sludge by means of TGA and observed two peaks in their TGA curves. Thus a kinetic scheme with two parallel reactions was proposed and found to fit.

With different experimental methods and equipments used, a different sewage sludge pyrolysis mechanism was proposed by Chen and Jeyaseelan (2001). In this proposal, the decomposition of sewage sludge is separated to three global stages. In the first stage, a slight mass loss occurs at ca 100-174 °C, which was speculated to be associated with the dehydration process. The second stage occurs up to ca 325 °C. This was suggested to be a primary responsible for the depolymerization of the carbonaceous components in sludge, resulting in a generation of gaseous product and intermediate fragments that further decompose in the third stage.

However, a simple kinetic model modified from previous one was adopted for engineering use because the complex detailed reaction scheme is difficult to analyze. Thus, kinetic evaluation of sewage sludge decomposition was accomplished by a simple parallel reaction model. According to the model, the total decomposition is resulted from sum of two reactions (1 and 2), each one corresponding to the decomposition of unknown constituent component groups occurring at low and high temperature. The equation describing the overall conversion rate, Arrhenius-type expression with nth-order, is

$$\frac{dx}{dt} = A_1 \exp\left(-\frac{E_1}{RT}\right)(1-x)^{n_1} + A_2 \exp\left(-\frac{E_2}{RT}\right)(1-x)^{n_2}, \quad (2.9)$$

There were not only different models proposed for sewage sludge pyrolysis among authors. The apparent kinetic parameters were also of controversial. As shown in Table 2.6, the values of kinetic parameters were collected for comparison. The values are varied and some of those are rarely occur in general chemical reaction. The physical meaning was limited in chemical sense. Since, the models are different; comparisons between authors also have to be done carefully.

**Table 2.6** The kinetic parameters of sewage sludge pyrolysis

Author	No. of reaction routes	E (kJ/mol)	n
Conesa <i>et al.</i> , (1997)	6	17.3 - 332.1	0.5 - 23.2
Chu <i>et al.</i> , (2000)	4	43.3 - 137.0	0.00 - 10.5
Chen and Jeyaseelan, (2001)	4	52.7 - 205.2	1

#### 2.4.3 Kinetics of Sewage Sludge Pyrolysis in Connection with Its Fractions

In the study of pyrolysis of heterogeneous material such as sewage sludge, it was also done in connection with the assumption of its unknown compositions. The most important compositions of sewage sludge would be probably comparable to that of natural mixture such as in wood.

The chemical structure and major organic components in biomass are extremely important to their chemical reaction. The major organic components of biomass can be classified as cellulose, hemicellulose and lignin (Klass, 1998). Other than these three main components, there is also a particular group of chemicals presented in biomass as a minor fraction called extractives. Chemical structures of all compounds listed above were exhibited in Figure 2.10.

#### 2.4.3.1 Cellulose

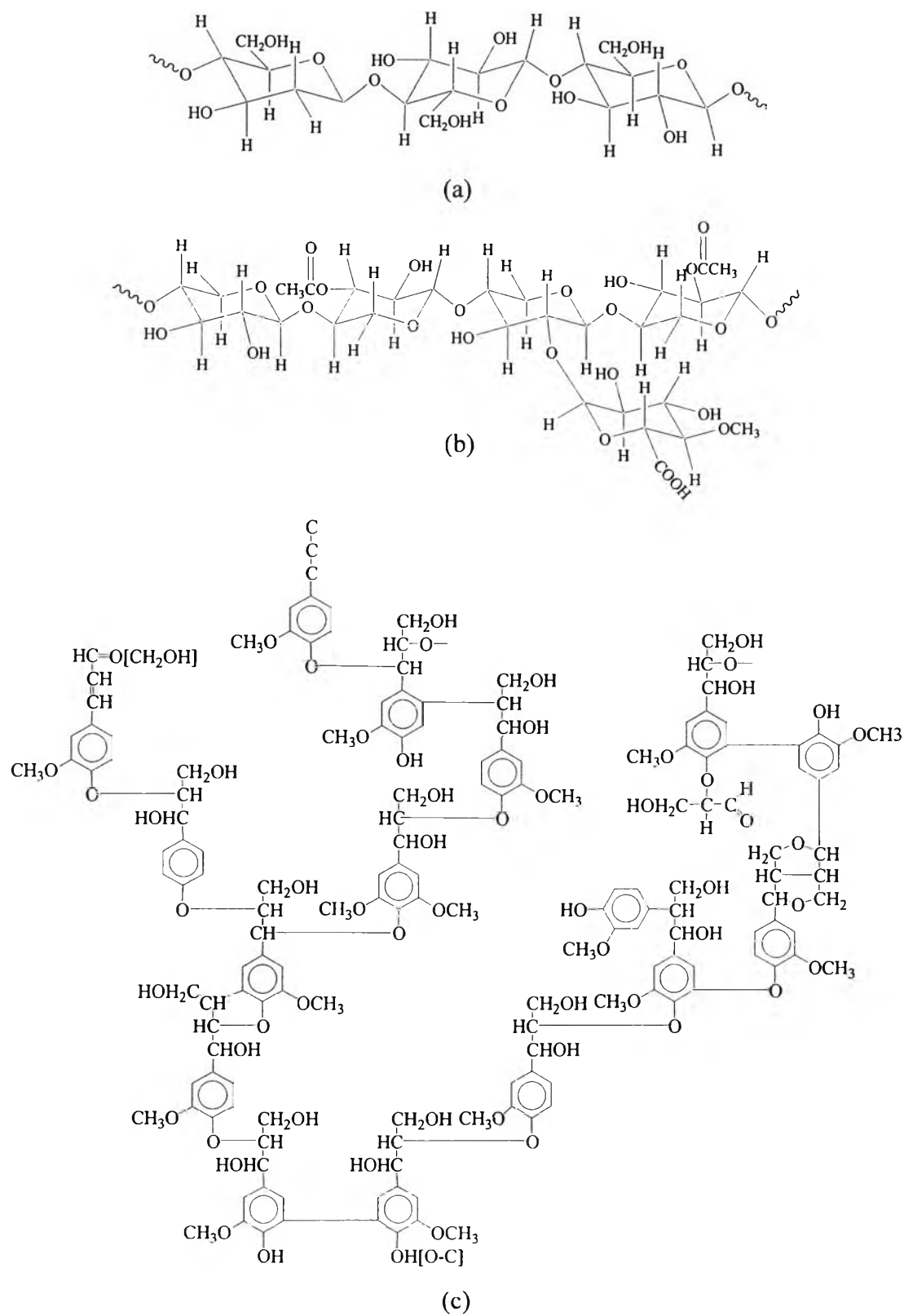
Alpha cellulose is a polysaccharide having the general formula  $(C_6H_{10}O_5)_n$  and an average molecular weight range of 300,000–500,000. Cotton is almost pure  $\alpha$ -cellulose, whereas wood cellulose, the raw material for the pulp and paper industry, always occurs in association with hemicellulose and lignins. Cellulose is insoluble in water, forms the skeletal structure of most terrestrial biomass and constitutes approximately 50% of the cell wall material. Starches are polysaccharides that have the general formula  $(C_6H_{10}O_5)_n$ . They are reserve sources of carbohydrate in some biomass and are also made up of some D-glucose units.

#### 2.4.3.2 Hemicellulose

Hemicelluloses are complex polysaccharides that take place in association with cellulose in the cell wall, but unlike cellulose, hemicelluloses are soluble in dilute alkali and consist of branched structures, which vary considerably among different woody and herbaceous biomass species. Many of them have the general formula  $(C_5H_8O_4)_n$ . Hemicelluloses usually carry 50–200 monomeric units and a few simple sugar residues. The most abundant one is xylan. The xylan exists in softwoods and hardwoods up to about 10% and 30% of the dry weight of the species, respectively.

#### 2.4.3.3 Lignin

The lignin is highly branched, substituted, mononuclear aromatic polymers in the cell walls of certain biomass, especially woody species, and is often bound to adjacent cellulose fibers to form a lignocellulosic complex. This complex or the lignin alone is often quite resistant to conversion by microbial systems and many chemical agents. The complex can be broken, and the lignin fraction separated, however, by treatment with strong sulfuric acid, in which the lignin is insoluble. The lignin contents on a dry basis in both softwoods and hardwoods generally range from 20% to 40% by weight and from 10% to 40% by weight in various herbaceous species, such as bagasse, corncobs, peanut shells, rice hulls and straws.



**Figure 2.10** Partial structure of a) Cellulose, b) Hemicellulose and c) Lignin (Peterson, 1983).



#### 2.4.3.4 Minors

The minor compound may be considered “lipids”. It actually refers to a collection of organic molecules of varying chemical composition, which are grouped on the basis of their solubility in non-polar solvents (Dennistion *et al.*, 2001). That is why it is so-called “extractives”. Lipids are commonly subdivided into four groups:

- 1) fatty acids – saturated or unsaturated long chain monocarboxylic acid,
- 2) glycerides – esters that contain the glycerol molecule and fatty acid,
- 3) non-glyceride lipids – lipids that are not derived from glycerol i.e. steroids and waxes, and
- 4) complex lipids – lipids that bonded with other type of molecules.

#### 2.4.4 Comments on the Kinetic Study by TGA

##### 2.4.4.1 *A Variation in Apparent Kinetic Parameters*

In the kinetic study of pyrolysis, at which many reactions are involved, the error normally arises. The data interpretation generally encounters major difficulties in distinguishing the weight versus temperature (or time) data to yield a complex reaction scheme. It is projected that an accurate determination of the kinetic parameters from TG data for a particular material would be useful in a practical process plant design. However, the existing kinetic parameters determined from this technique have almost never been applied because there was such a scattering in kinetic data that no one knew which set of data appropriately explains the reaction process (Gaur and Reed, 1998). The variation in apparent kinetic parameters reported among authors was also found even for the study of a certain compound such as cellulose, for instance, which has relatively fixed structure. The variation in these values can be attributed to the several reason including heating rate, method used for mathematical analysis and the instrumental errors coupled with sample impurity.

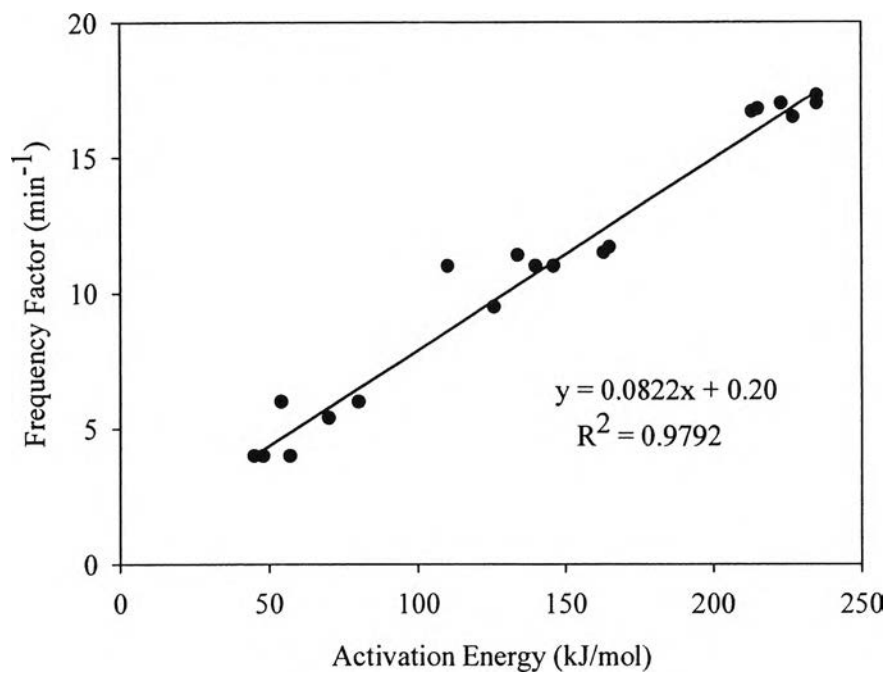
In particular determination of kinetic parameter, the apparent activation energy and pre-exponential factor are likely not independent (Gaur and Reed, 1998). The example has drawn from kinetics evaluation of cellulose decomposition which has a unit reaction order. An excellent correlation exists between frequency factor and the activation energy as represented in Figure 2.11. This is called the “compensation effect”.

The recommendation on controlling the error from study of pyrolysis kinetics by TGA experiments were reviewed by Conesa *et al.* (2001). The following things should be bear in mind:

- For the equipment, a thermocouple must be at right position. The temperature calibration is needed to maintain correct results.
- It is possible that different models can give the same level of the fit.
- Heat transfer equation may be needed.
- Various runs with different conditions should be performed. The reproducibility should be guaranteed.
- The method may be not valid for some processes.
- Modern TG can collect thousands of data points. A selection of data point for mathematical analysis should be done carefully.

#### 2.4.4.2 Application of Obtained Kinetic Data

The goal objective of a kinetic study is to design reactor to convert materials to chemicals or energy, in corresponding to the decomposition nature of those materials. Conesa *et al.* (2001) showed that the use of kinetic model from correctly obtained in TGA experiment allows the reactor to be designed. The model of the primary pyrolysis obtained from TGA must be accompanied with the study of conditions where the reactions is to be conducted i.e. heat transfer effect, secondary reaction, possible expansion of the gases and volatile. It was also demonstrated that in a study of secondary pyrolysis in an iso-thermal reactor, a primary reaction kinetic data can be obtained from TGA with a reasonable result.



**Figure 2.11** Compensation effect represents the excellent correlation between frequency factor and activation energy of cellulose decomposition (Guar and Reed, 1998).