



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Sewage Sludge: Formation, Treatment and Disposal

##### 2.1.1 Formation of Sewage Sludge

Sewage sludge is the solid material produced in the wastewater treatment process. Wastewater is a combination of the liquid- or water-carried wastes removed from residential, institutional, commercial and industrial establishments, together with ground water, surface water and storm water, as may be present (Chobanoglous, 1987). Domestic sewage, produced in urban residences, institutions and businesses, is usually collected by pipes and channels called sanitary sewers, later drained 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. Often, 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. Wastewater may contain certain undesirable components, including organic, inorganic and toxic substances, as well as pathogenic or disease-causing micro-organisms.

Sewage sludge originated from the wastewater treatment process is the residue from the primary (physical and/or chemical), the secondary (biological) and the tertiary (additional to secondary, often nutrient removal) treatment. The flow diagram of wastewater treatment processes are illustrated in Figure 2.1. In the mechanical stage, the incoming wastewater passes through racks and screens where coarse solids are removed, and then flow thru the grid chambers, where sand, gravel, cinders and other heavy solid materials are separated. In sedimentation tanks, readily settled solids and floating materials are removed. Around 50-70% of the suspended solids and 25-40% of the BOD<sub>5</sub> can be removed in this stage (Chobanolous, 1987). The materials removed from primary sludge, have 3-5 wt.% solids which consists of 30% inorganic and 70% organic matter (Werther and Ogada, 2000).

In the biological treatment phase, the coagulation and removal of the non-settled colloidal solids and the stabilization of the organic matter is accomplished biologically using a variety of micro-organisms, principally bacteria (McGhee, 1991). The micro-organisms convert the colloidal and dissolved carbonaceous organic matter into various gases and cell tissues. The cell tissues have a specific gravity slightly higher than that of water and can therefore be removed through sedimentation. The sludge removed at this stage is normally referred to as a secondary sludge.

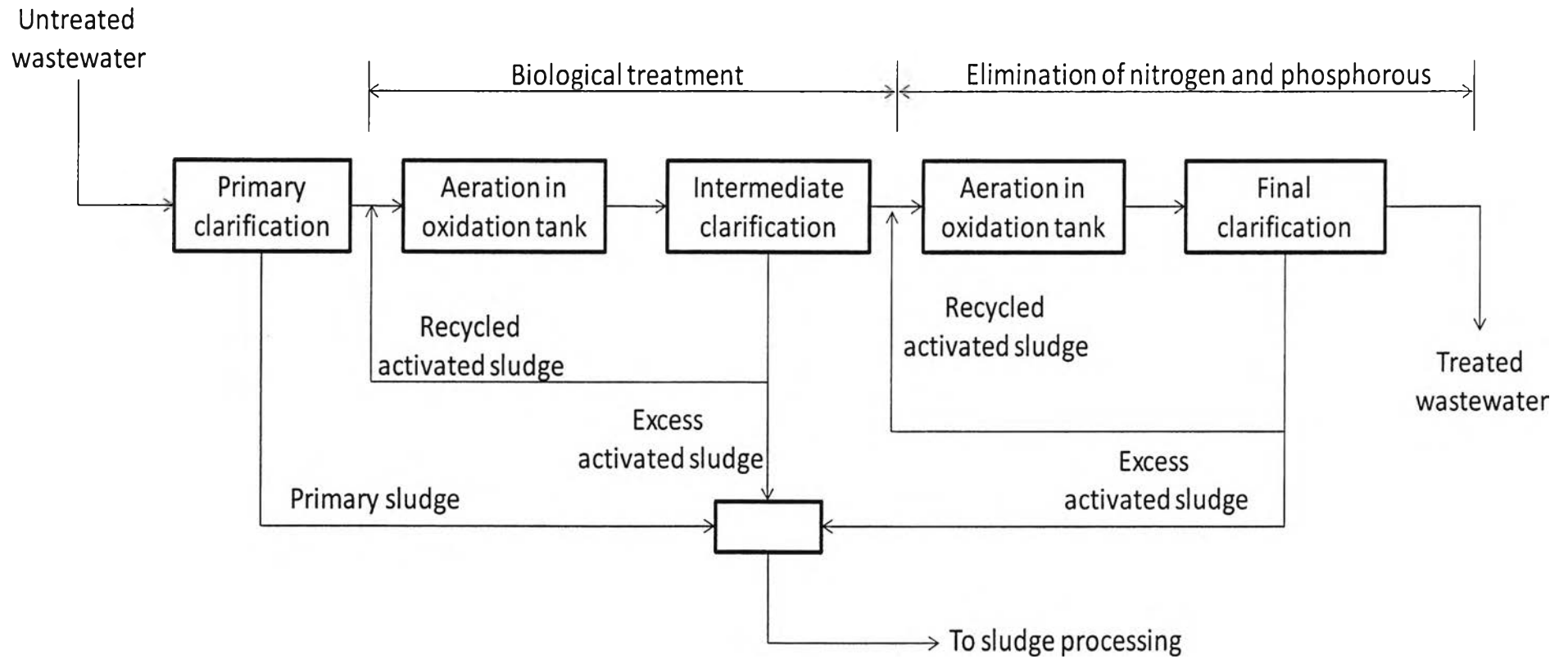
In the third treatment stage, the elimination of phosphorous and nitrogen takes place. Nitrogen elimination may be achieved by a two-stage process: nitrification and denitrification. Ammonia in the wastewater is first oxidized to nitrate (nitrification) and thereafter the nitrate is converted to free nitrogen (denitrification) before it is discharged (Mathias *et al.*, 1994). Denitrification is an important part of the nitrogen cycle, since through the release of the nitrogen to the atmosphere, the cycle is completed (Mathys, 1994). Phosphorous compounds can be eliminated through chemical precipitation using additives followed by the sedimentation of the sludge formed, or through biological treatment, where phosphorous compounds are incorporated in the cell tissues which are thereafter removed through sedimentation (Söter *et al.*, 1994). Nitrogen and phosphorous may be formed in this stage.

### 2.1.2 Sewage Sludge Compositions

A typical chemical composition and properties of untreated and digested sludge is reported in Table 2.1. The control of pH levels, alkalinity and organic acid content is important in the process of anaerobic digestion. Additionally, the content of heavy metals, pesticides and hydrocarbons should be determined when sewage sludge is incinerated or land filled. Lastly, the energy (thermal) content of sludge is significant when thermal processes (combustion, gasification, wet oxidation and pyrolysis,) are considered. The heavy metals are also present in a significantly amount in sludge.

Sewage sludge tends to accumulate heavy metals existing in the wastewater sludge treatment processes particularly in the physical-chemical treatment processes. Typical heavy metals containing in sewage sludge are zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr). These metals are principal elements restricting use of sludge for agricultural purposes (Hsiao and Lo, 1998). Their potential accumulation in human tissue and biomagnifications through the

food-chain create both human health and environmental concerns (Krogmann *et al.*, 1999). Concentrations of heavy metals in sewage sludge may vary widely, depending on the sludge origins. Typical metal concentrations are indicated in Table 2.2. The sources of sludge in a treatment plant vary according to the type of plant and its method operation. In order to treat and dispose of the sludge effectively, it is crucial to know the characteristics of the sludge that will be processed.



**Figure 2.1** A flow diagram of wastewater treatment plant (Werther and Ogada, 1999)

**Table 2.1** Typical chemical composition and properties of untreated/digested sludge (Metcalf and Eddy, 1991)

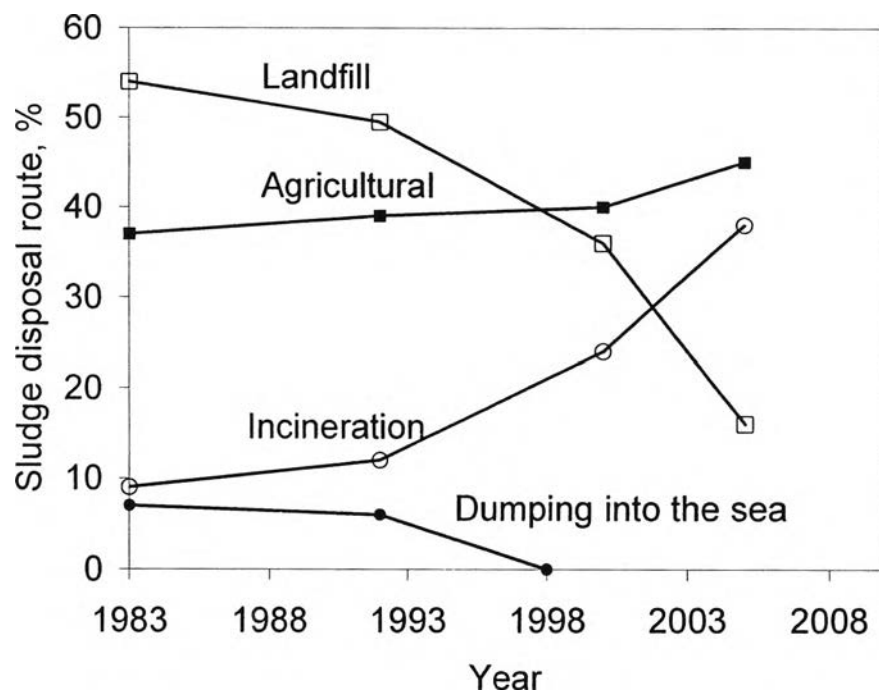
Item/sludge	Untreated primary		Digested primary		Activated range
	Range	Typical	Range	Typical	
Total dry solids (TS), %	2.0-8.0	5.0	6.0-12.0	10.0	0.83-1.16
Volatile solids (% of TS)	60-80	65	30-60	40	59-88
Grease and fats (% of TS)					
Ether soluble	6-30	-	5-20	18	-
Ether extract	7-35	-	-	-	5-12
Protein (% of TS)	20-30	25	15-20	18	32-41
Nitrogen (N, % of TS)	1.5-4	2.5	1.6-6.0	3.0	2.4-5.0
Phosphorous (P <sub>2</sub> O <sub>5</sub> , % of TS)	0.8-2.8	1.6	1.5-4.0	2.5	2.8-11.0
Potash (K <sub>2</sub> O, % of TS)	0-1	0.4	0.0-3.0	1.0	0.5-0.7
Cellulose (% of TS)	8.0-15.0	10.0	8.0-15.0	10.0	-
Iron (not as sulfide)	2.0-4.0	2.5	3.0-8.0	4.0	-
Silica (SiO <sub>2</sub> , % of TS)	15.0-20.0	-	10.0-20.0	-	-
Alkalinity (mg/l as CaCO <sub>3</sub> )	500-1,500	600	2,500-3,500		580-1,100
Organic acids (mg/l as Hac)	200-2,000	500	100-600	3,000	1,100-1,700
Energy content	10,000-12,500	11,000	4,000-6,000	200	8,000-10,000
pH	5.0-8.0	6.0	6.5-7.5	7.0	6.5-8.0

**Table 2.2** Typical metal content in wastewater sludge (Metcalf and Eddy, 1991; Hsiau and Lo, 1998)

Metal	Dry sludge (mg/kg)	
	Range	Median
Arsenic	1.1-230	10
Cadmium	1-3.410	10
Chromium	10-990,000	500
Cobalt	11.3-2490	30
Copper	84-17,000	800
Iron	1,000-154,000	17,000
Lead	13-26,000	500
Manganese	32-9,870	260
Mercury	0.6-56	6
Molybdenum	0.1-214	4
Nickel	2-5,300	80
Selenium	1.7-17.2	5
Tin	2.6-329	14
Zinc	101-49,000	1700

## 2.2 Sewage Sludge Treatment and Disposal in Practice

Figure 2.2 shows the sludge disposal routes in the European community. Despite the fact that landfilling is currently the most widely used disposal outlet, almost all the countries recognize that this outlet will not be sustainable at current or projection for landfill space, higher cost, more stringent environment standards and the implementation of policies to promote recycling. As a result, landfilling 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 phosphorous-rich manure to land will continue to be a major factor in limiting the use as fertilizer. Incineration is currently a minor method for sludge disposal, but it is anticipated that it will increase substantially in the future to cope with the increasing sludge product.



**Figure 2.2** Sludge disposal routes in the European Community up to 2005 (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 landfilling and recycling in agriculture constrained, and dumping to the sea facing a ban, growing interest is now being directed towards utilization by incineration and other thermal conversion processes.

Generally, the selection of the best disposal route for the sludge from a particular treatment plant should start by identifying the most secure and environmentally acceptable final destination for the specific sludge type, and this in turn would dictate the type of treatment required (Hall, 1992). Currently, the sludge disposal outlets which exist are recycling as fertilizer, land filling, dumping to the sea and incineration.

### 2.2.1 Application of Sewage Sludge as Fertilizers

Residues of treatment of municipal wastewater can be applied to the land to serve as a fertilizer and soil conditioner. Based on its content of nitrogen and phosphorous, communal sludge shows good fertilizer properties. Sludge recycling as fertilizer has several advantages which includes the return of the organic materials into the bio-cycle. Sludge also replaces the application of artificial fertilizers whose production also requires a lot of energy. The application of sludge in agriculture takes 60% of the sludge produced in France, 54% in Denmark, 50% in Spain, 44% in UK and 26% in USA (McGhee, 1991; Hall and Dalimier, 1994).

In the recent past, the application of sludge on agricultural land has met a lot of setbacks due to the presence of heavy metals in the sludge. Analyses of 6800 sludge samples have shown that the average content of heavy metals in municipal sludge is higher than the average for most farming soils (Poletschny, 1988). This implies that uncontrolled addition of sludge to the agricultural land may increase the concentration of heavy metals in the farm land. This could have an effect on the crop production due to uptake and also lead to the transfer of heavy metals to human beings through plants and animals (Poletschny, 1988). Therefore, the regulation on the use of sewage sludge as fertilizers should not exceed the limits of application. For example, Netherlands and Denmark have set very strict limits for metals in sludge applied to land due to the vulnerable shallow sand soils in these countries and also to the need for the land to take a large quantity of animal slurries (Davis, 1996).



### 2.2.2 Disposal of Sewage Sludge through Land Filling

Disposal of sewage sludge to sanitary landfill is the main sludge disposal method. In the U.S.A., 48% of the sludge produced in 1990 was deposited through land filling. For Greece, Luxembourg and Italy, 90, 88 and 85%, of the sludge are taken to landfill (McGhee, 1991).

However, the problem of land filling is the poor physical nature of the sludge resulting in handling and stability problems (Hall, 1992). It is desired that sludge for land filling should be well stabilized and dewatered to reduce the emission of odor, gas (*e.g.* CH<sub>4</sub>) and percolating water (Doedens, 1991). Because of the problems of stability, emissions of odor and gas, and pollution of the ground water, there is a trend towards establishing a minimum standard for the physical properties of the sludge for disposal in some countries in order to minimize these problems.

### 2.2.3 Dumping of Sewage Sludge into the Sea

Dumping into the sea has been banned in most countries. In Europe, there will be no more dumping of sludge into the ocean as from 31 December 1998, when the North Sea Conference Agreement comes into force. The reason is related to the effect to marine environment. Dumped sludge can affect or even kill marine life (Chapman *et al.*, 1988) and threaten beaches or coasts.

### 2.2.4 Disposal of Sewage Sludge through Incineration

Incineration is the complete oxidation of sludge to produce hot flue gas and ash. Via this process, sludge is completely stabilized and their volumes are drastically reduced which accounts for only 10% of the volume of mechanically dewatered sludge (Vesilind and Ramsey, 1996). It is intended to reduce the wastes' toxicity and other hazardous substances. Most types of wastes generated can be burnt in an incinerator. The direct combustion is known to take advantages of sludge heating value. Furthermore, the calorific value of sludge may be recovered (Römer, 1991). The hot flue gas is allowed to use for heating purposed 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).

The hazardous associated with the 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 of organic pollutants such as dioxins and furans are also of concern. Thus, the implementation equipment for preventing particulate and gas pollutants is a must. Techniques are now available to control gaseous emissions and incineration costs are becoming much more competitive with other disposal options, to the extent that incineration is now seen as the only solution to the increasing problems of other sludge disposal options (Hall, 1992). Already, incineration takes 24% of the sludge produced in Denmark, 20% in France, 15% in Belgium and 14% in Germany. In the USA and Japan, 25 and 55% of the sludge produced, respectively, is incinerated (Hall and Dalimier, 1994).

## **2.3 Production of Valuable Products from Sewage Sludge**

From the disposal methods presented earlier, the valuable products contained in the wastes are lost by destroying them without recovery. Nowadays, there are a number of methods of sludge conversion and utilization, either being in a development stage or already implemented (Bien *et al.*, 2000). As alternative, thermal processes such as, combustion, gasification, liquefaction and pyrolysis has recently received a renew attention of research groups. It was considered that pyrolysis might be a solution to the problems of both secondary pollution and of large energy consumption.

### 2.3.1 Thermochemical Conversion Processes for Sewage Sludge

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 point both of alternative energy by utilization 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. As summarized in Figure 2.3, thermal

conversion processes include direct combustion to provide heat, for steam production and hence electricity generation. Gasification also provides a fuel gas that can be combusted, generating heat, or used in an engine or turbine for electricity generation. The third alternative is the pyrolysis process that provides liquid fuel which can substitute fuel oil in any static heating or electricity generation application. The advantage of pyrolysis is that it can directly produce a liquid fuel, which is beneficial when resources are remote from where the energy is required since the liquid can be readily stored and transported. Charcoal is also produced from the pyrolysis process. For liquefaction, liquid fuel is produced which can be used in engine or turbine for electricity generation. A review of direct thermal liquefaction was produced by Elliot *et al.* 1993.

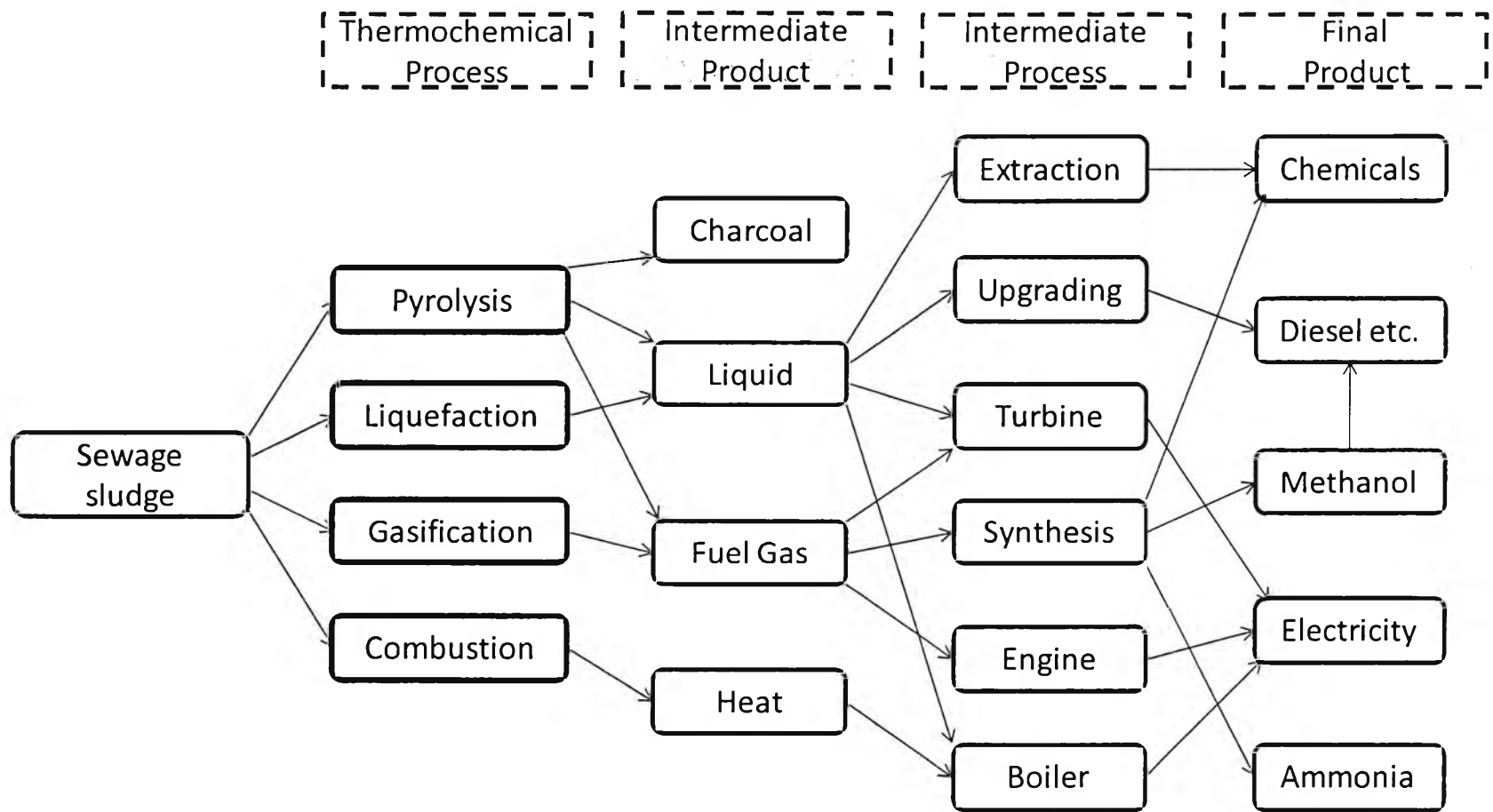


Figure 2.3 Thermochemical process and products for sewage sludge (modify from Bridgwater, 2000)

### *2.3.1.1 Combustion*

Combustion is the complete oxidation of sewage sludge resulting in the recovery of energy in the form of heat containing in the hot flue gas at the temperature around 800-1000°C. It is possible to practically burn only the material which contains moisture < 50%, unless the material is pre-dried. By this approach, the volume of sludge is reduced by 70 to 90%. The hot flue gas can be used for steam production and subsequently power generation by steam turbine.

Combustion mechanisms of sewage sludge consist of (i) drying, (ii) devolatilization (pyrolysis), (iii) release and combustion of the volatiles and (iv) sewage sludge char combustion.

#### (i) Drying

Sewage sludge is a complex of inorganic and organic matter bound together with a high percentage of water: 70-75% is free water, 20-25% floc water, and 1% each capillary and bound water (McGhee, 1991). Based on drying experiments in Figure 2.4, it was found that sewage sludge exhibits peculiar drying characteristics consisting of two falling rate periods (Lowe, 1995), unlike the classical drying curves which have only falling rate period. The sludge moisture has been characterized as free moisture will be removed during a constant drying rate period, floc water or interstitial moisture will be removed during the first falling rate period, the capillary water or surface water will be removed during the second falling rate of the drying curves, and bound water which is chemically bound and is not removable during the experiment (Lowe, 1995).

#### (ii) Devolatilization (or Pyrolysis)

Devolatilization means thermal decomposition of carbonaceous substances with subsequent release of the volatiles. It consists of a series of complex chemical reactions which leads to the decomposition and breakage of the organic matter and the separation of different components into individual gases. The devolatilization and drying of sewage sludge combustion appear to be a significant overlap during sludge combustion such that the two processes may be considered to take place parallel to each other. The main products of sludge pyrolysis are gas (volatile), char and oil. The quantities of these products are affected by the operation parameters. The resulting product is then combusted with the oxygen in the combustion chamber.

Typically devolatilization time is normally estimated from the release history of proximate volatile contents or by the degree of completion of the evolution of the volatiles (e.g. 95% of the evolution of the volatiles), or the flame ignition method (Borodulya *et al.*, 1995). Typical devolatilization times range between 10 and 100 sec for coal particles of 5-10 mm diameter (La Nauze, 1985) and 100-300 sec for wet sludge particles of diameter 4-20 mm, whereas 50 sec for pre-dried sludge of the same diameter (Wether *et al.*, 1995). More scientific information on sewage sludge pyrolysis are discussed in the next section.

#### (iii) Release and Combustion of Volatiles

The volatiles, which are produced during the devolatilization step, are subjected to react with oxygen resulting in the energy in the form of heat. This step is considered to be a very important step during the whole of sewage sludge combustion. The studies of the release and combustion of volatiles was carried out in a fluidized bed reactor and the model for coal combustion was applied for the release and combustion of volatile during sewage sludge combustion. It was found that the model for coal combustion can be applied for the release and combustion of the volatiles during the sewage sludge combustion process. Further reading can be found elsewhere (La Nauze, 1985; Bellgardt *et al.*, 1987; Hembach, 1992; Schoessler, 1993)

#### (iv) Sewage Sludge Char Combustion

Subsequent to the drying, devolatilization and combustion of volatiles, the remaining sludge char will continue to react with oxygen until it burn out. The burn-out time of char can be considerably longer than the devolatilization time. Agarwal and La Nauze, 1989 reported that the burn-out time of 10 mm diameter char (coal) particles under fluidized bed is typically 1000 sec while the devolatilization time is typically less than 100 sec. Therefore, the combustion of coal is controlled by the char combustion step. However, the situation is different for sewage sludge. First, due to the low fixed carbon of sewage sludge, the char burn-out time is less than or comparable to the time span for the release and combustion of the volatiles. Furthermore, for wet sludge the devolatilization time is even longer. Therefore, the significance of the char combustion step in sludge combustion is negligible. The measurement of the carbon load during the char combustion step in fluidized bed and compared the results with those obtained from coals of different ranks. The results showed that sewage sludge combustion is characterized by very low carbon load in the

bed (Table 2.3). Changing from sludge and lignite to bituminous coal, graphite coke and graphite, the reactivity of the fuels decreases in that order, so that lignite and sludge form the most reactive chars whereas the graphite is the least reactive.

Further information about the reactivity of the sludge char combustion can be obtained if characteristic combustion parameters are determined. Several conventional approaches are available for the determination of the kinetic parameters; one is based on the effective reaction rate constant (Section 2.6).

**Table 2.3** Comparison of the in-bed char carbon concentration from the sludge with those from coals (Ogada and Werther, 1996 )

Fuel type	Fixed carbon, %	O <sub>2</sub> in flue gas, %	Temperature, °C	Char carbon conc. in bed kg/m <sup>3</sup>
Sewage sludge	15	2.3	800	0.15
Valdarno lignite	46	2.2	850	1.4
Bituminous coal	60	2.3	850	27.4
Coke	81	3.1	850	126.4
Graphitized coke	87	1.9	850	374
Graphite	98	0.6	900	557

Based on the composition of sewage sludge, presented in earlier in Table 2.1 and 2.2, combustion of sludge may be seen as potential source of various pollutants and care must be taken during its disposal. The following sources of pollutants are important for public health (Johnson, 1994):

- Release of heavy metals.
- The handling of solid residues, e.g. bed and filter ash.
- Emissions of dioxins and furans, NO<sub>x</sub>, N<sub>2</sub>O, SO<sub>2</sub>, as HCl, HF and C<sub>x</sub>H<sub>y</sub>.

With this regard of sludge combustion, of greatest concern is the release of gaseous (e.g. NO<sub>x</sub>, SO<sub>x</sub>, HCl, HF and C<sub>x</sub>H<sub>y</sub>) and solid (e.g. fly ash) pollutants into the atmosphere. Furthermore, potential problems with raising temperature during combustion or even using gasification, the problem of heavy metals

still remains unsolved in the conventional multiple and fluidized bed furnaces (Johnson, 1994). As far as the emissions of mercury, dioxins and furans are concerned, these are controllable; characteristically, currently many large scale incinerators of sewage sludge function in such a way that stringent emission limits are met, using state-of-art technologies (Ogada and Werther, 1996). Despite of the noticeable content of sewage sludge in nitrogen, the conversion ratio of fuel N to NO<sub>x</sub> is less than 5%, and the total net emissions of NO<sub>x</sub> are in very low levels (Zhao *et al.*, 1994). From this aspect of view, the raising public concern of potential of adverse effects of sewage sludge combustion is generally unwarranted. Further reading can be found elsewhere (Werther and Ogada, 1999).

### 2.3.1.2 Gasification (McKendry, 2002)

Gasification is the conversion of biomass to a gaseous fuel by heating in a gasification medium such as air, oxygen or steam at the temperature > 800°C. Unlike combustion where oxidation is substantially complete in one process, gasification converts the intrinsic chemical energy of the carbon in the biomass into a combustible gas in two stages under stoichiometric amount of supplied oxygen. The gas produced can be standardized in its quality and is easier and more versatile to use than the original biomass e.g. it be used to power gas engines and gas turbines, or used as a chemical feedstock to produce liquid fuels.

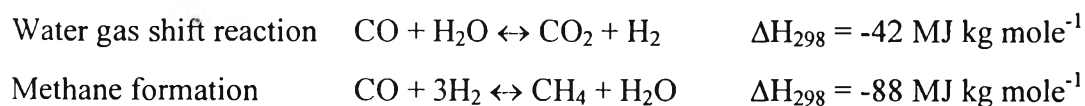
The reactions taking place in the gasifier are similar to the case of combustion and can be summarized as indicated below:

Partial oxidation	$C + \frac{1}{2} O_2 \leftrightarrow CO$	$\Delta H_{298} = -268 \text{ MJ kg mole}^{-1}$
Complete oxidation	$C + O_2 \leftrightarrow CO_2$	$\Delta H_{298} = -406 \text{ MJ kg mole}^{-1}$
Water gas reaction	$C + H_2O \leftrightarrow CO + H_2$	$\Delta H_{298} = +118 \text{ MJ kg mole}^{-1}$

The heat of reaction for the three processes shows that the greatest energy release is derived from the complete oxidation of carbon to carbon dioxide i.e. combustion, while the partial oxidation of carbon to carbon monoxide accounts for only about 65% of the energy released during complete oxidation. Unlike,



combustion that produces only a hot gas product, carbon monoxide, hydrogen and steam can undergo further reactions during gasification as followed:



The arrows indicate that the reactions are in equilibrium and can proceed in either direction, depending on the temperature, pressure and concentration of the reacting species. It follows that the product gas from gasification consists of a mixture of carbon monoxide, carbon dioxide, methane hydrogen and water vapor.

Three product gas qualities can be produced from gasification by varying the gasifying agent, the method of operation and the process operating conditions. The main gasifying agent is usually air but oxygen/steam gasification and hydrogenation are also used. Catalytic steam gasification is another mode of operation that influences both the overall performance and efficiency.

The three types of product gas have different calorific values (CV):

Low CV	4-6 MJ Nm <sup>-3</sup>	Using air and steam/air
Medium CV	12-18 MJ Nm <sup>-3</sup>	Using oxygen and steam
High CV	40 MJ Nm <sup>-3</sup>	Using hydrogen and hydrogenation

Low CV gas is used directly in combustion or as an engine fuel, while medium/high CV gases can be utilized as feedstock for subsequent conversion into basic chemicals, principally methane and methanol.

As the use of oxygen for gasification is expensive, air is normally used for processes up to about 50 MW<sub>th</sub>. The disadvantage is that nitrogen introduced with the air dilutes the products gas, giving gas with a net CV of 4-6 MJ Nm<sup>-3</sup> (compared with natural gas at 36 MJ Nm<sup>-3</sup>). Gasification with oxygen gives a gas with a net CV of 10-15 MJ Nm<sup>-3</sup> and with steam, 13-20 MJ Nm<sup>-3</sup>. It can be seen that while a range of product gas qualities can be produced, economic factors are a primary consideration of carbon with steam (the water gas reaction) is endothermic, requiring heat to be transferred at temperatures around 700°C, which is difficult to achieve.

Gasifiers self-sufficient in heat are termed auto-thermal and if they require heat, allothermal: auto-thermal processes are the most common. The overall efficiency of conversion of biomass to energy using gasification and pyrolysis is estimate as 75-80%.

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 2.4 shows four types of gasifiers. The following is an individual description:

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

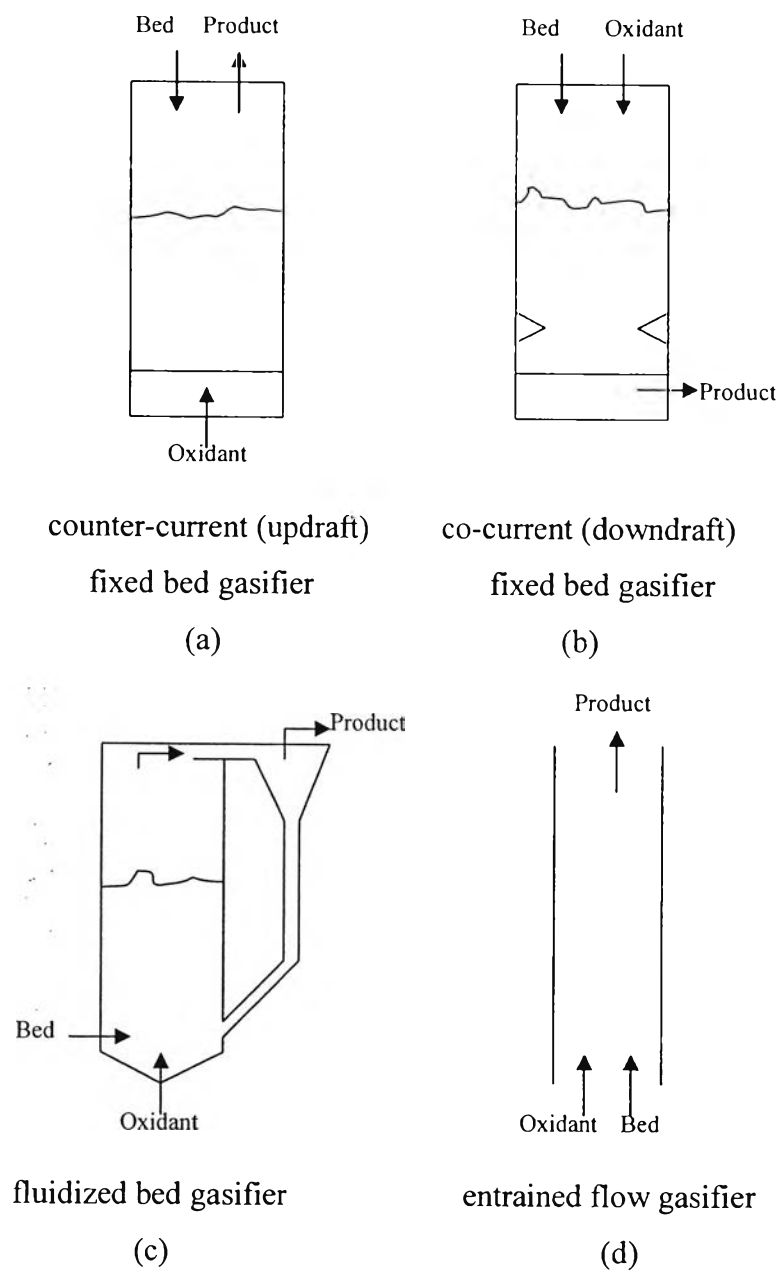
The counter-current fixed bed gasifier consists of a fixed bed of materials through which the "gasification agent" (steam, oxygen and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon 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.

(ii) 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.

(iii) 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.



**Figure 2.4** Typical type of gasification system.

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.

(iv) 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 pulverized, 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.

### 2.3.1.3 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. 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. This 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<sup>-1</sup>. However, disadvantages of this process include high cost and the difficulty in feeding raw material to high-pressure system and in product separation.

#### 2.3.1.4 Pyrolysis

Pyrolysis is a thermal conversion of carbonaceous materials under an inert atmosphere, He or N<sub>2</sub>, 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 combustion. The pyrolysis process has more advantages compared with the combustion process due to the economic, the energy utilization and releasing of heavy metal to natural resource. The distribution and characteristics of the pyrolysis products strongly depend on the pyrolysis reactor, the characteristics of raw 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.

Several kinds of wastes are considered hydrocarbon-rich compounds. There are several ways to extract 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. As focus in this study, more detailed discussion of this process is in the following section. Compare to the gasification and combustion processes, pyrolysis spend less energy to reach operating temperature. Therefore, pyrolysis is considered to be a promising solution to the problems of both secondary pollution and of large energy consumption. More details of pyrolysis are in the following section.

### 2.3.2 Biological Conversion Processes for Sewage Sludge

Instead of thermochemical technologies, conversion of biomass or sewage sludge to energy is undertaken using biological conversion technologies. Biochemical conversion technologies encompass two process options: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol).

#### 2.3.2.1 *Anaerobic Digestion (AD)*

AD is the conversion of organic material directly to a gas, termed biogas, a mixture of mainly methane and carbon dioxide with small quantities of other gases such as hydrogen sulphide. The biomass is converted by bacteria in an anaerobic environment, producing a gas with an energy content of about 20-40% of the lower heating value of the feedstock. AD is a commercially proven technology and is widely used for treating high moisture content organic wastes, i.e. 80-90% moisture. Biogas can be used directly in spark ignition gas engines and gas turbines and can be upgraded to higher quality i.e. natural gas quality, by the removal of CO<sub>2</sub>. Used as a fuel in spark ignition gas engines to produce electricity only, the overall conversion efficiency from biomass to electricity is about 10-16%. As with any power generation system using an internal combustion engine as the prime mover, waste heat from the engine oil and water-cooling system and the exhaust could be recovered using a combined heat and power system. A typical flow sheet for processing biomass using AD is shown in Figure 2.5.

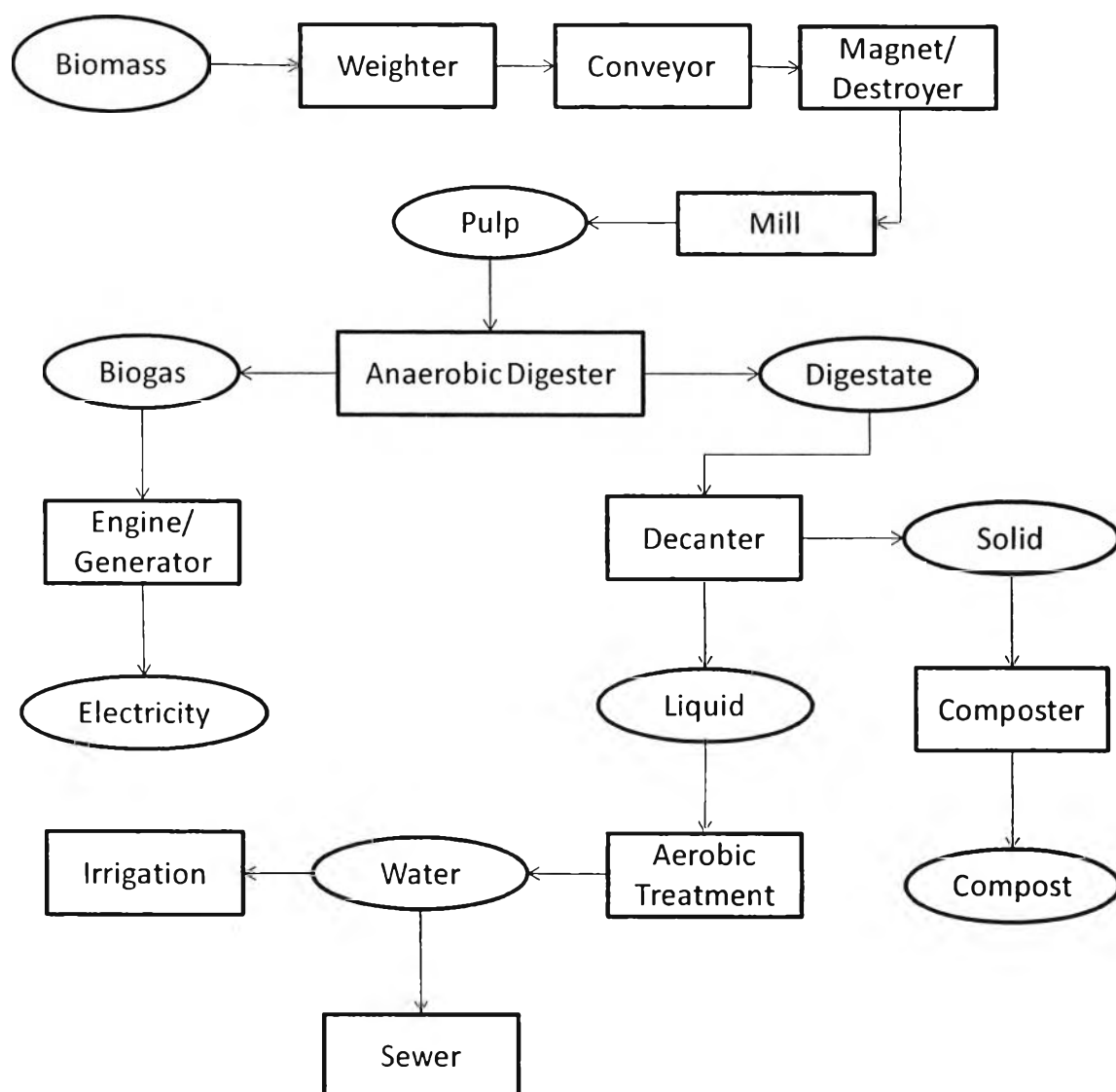
#### 2.3.2.2 *Fermentation*

Fermentation is used commercially on a large scale in various countries to produce ethanol from sugar crops (e.g. sugar cane, sugar beet) and starch

crops (e.g. maize, wheat). The biomass is ground down and the starch converted by enzymes to sugar, with yeast then converting the sugars to ethanol. Purification of ethanol by distillation is an energy-intensive step, with about 450 litres of ethanol being produced per ton of dry corn. The solid residue from the fermentation process can be used as cattle-feed and in the case of sugar cane, the bagasse can be used as a fuel for boilers or for subsequent gasification (Coombs, 1996)

The conversion of lignocellulosic biomass (such as wood and grasses) is more complex, due to the presence of longer-chain polysaccharide molecules and requires acid or enzymatic hydrolysis before the resulting sugars can be fermented to ethanol. Such hydrolysis techniques are currently at the pre-pilot stage.





**Figure 2.5** Flow sheet for the anaerobic digestion of biomass (McKendry, 2002)

## 2.4 Sewage Sludge Pyrolysis

### 2.4.1 Principle

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always the second step, after drying, in combustion and gasification processes. 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. Break 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 2.4. From the table it can be easily drawn, that at 525°C where the maximum oil yield is achieved, carboxylic and phenolic compounds are decomposed, suggesting that these are the substances of sludge that finally generate the oil.

**Table 2.4** Temperature ranges for different groups of compounds to decompose (Shen and Zhang, 2003)

Compounds	Temperature (°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

Pyrolysis processes are classified to flash, fast and conventional (or slow) pyrolysis according to the heating rate or vapour and/or solid residence time. Typical operating parameters for each modes of pyrolysis are summarized in Table 2.5. High liquid yield is achieved under high heating rates (>1,000°C/s) and short residence time (<1s) as in fast, or flash pyrolysis. Table 2.5 indicates the product distribution obtained from different modes of pyrolysis process compare to the gasification process. Lower

process temperature and longer residence times favor the production of char. High temperature and longer residence time increase the conversion of solid fuel to gas and moderate temperature and short residence time are optimum for producing liquids.

**Table 2.5** Typical operating parameters for pyrolysis processes (Maschio *et al.*, 1992)

Parameters	Modes	Slow Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
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

#### 2.4.2 Pyrolytic Yield

The major fractions that are formed after thermal degradation of the sewage sludge in an inert atmosphere or vacuum are the following:

1. The gaseous fraction; this non-condensable gas (NCG) contains mainly hydrogen, methane, carbon monoxide, carbon dioxide, and several gases in smaller concentrations.

2. The liquid fraction; this stream consists of oil and aqueous phase. Oil phase consists mainly of aromatic and oxygenated compounds. For aqueous phase contains substances such as acetic acid, acetone and methanol.

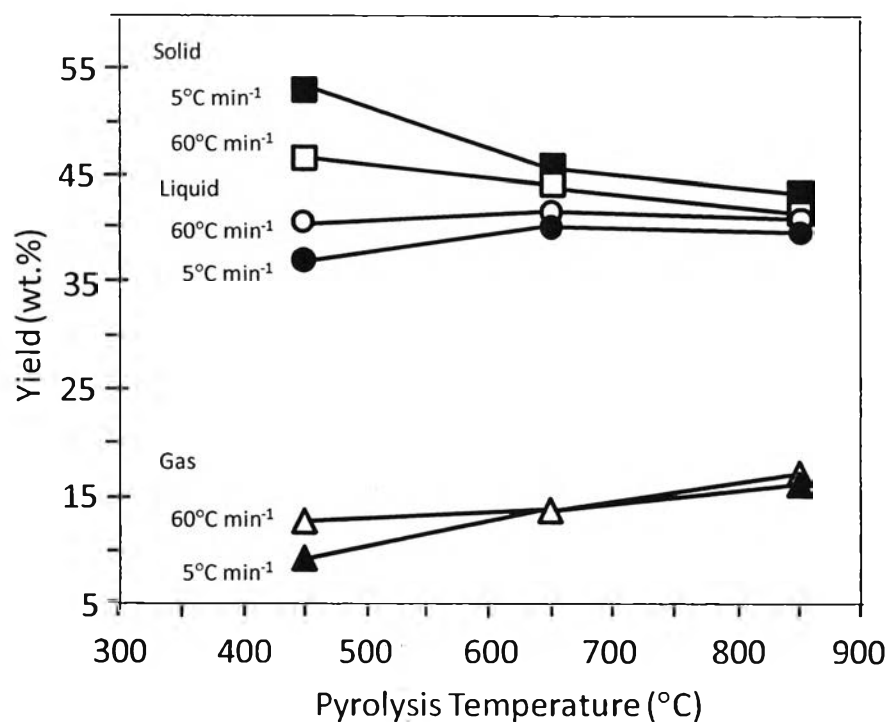
3. The solid fraction that consists mainly of carbon and inorganic compound with the small amount of metals.

Depend on the mode of pyrolysis, the pyrolysis product yields is varied as summarized in Table 2.6. Fast pyrolysis produces liquid product up to 75% while slow pyrolysis produces liquid product only 30%. Unlike pyrolysis, gasification produces gas product as a major fraction.

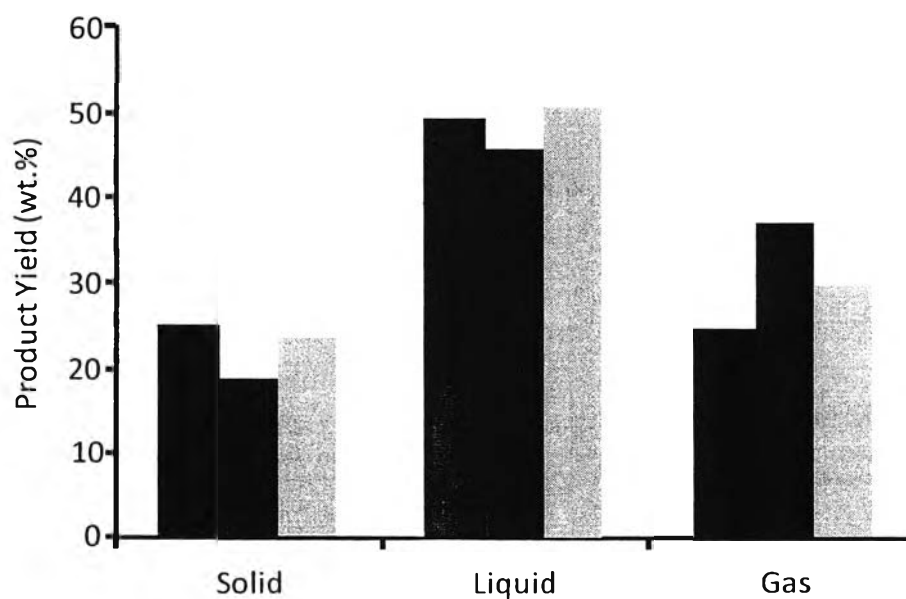
**Table 2.6** Typical product yields obtained from wood pyrolysis and gasification (Bridgwater, 2003)

Modes	Descriptions	Liquid (wt%)	Char (wt%)	Gas (wt%)
Fast Pyrolysis	Moderate temperature, short residence time	75	12	13
Slow Pyrolysis	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence time	5	10	85

Moreover, the product distribution strongly depends on pyrolysis process parameters such as temperature, heating rate, reactor residence time, pressure, turbulence, and also the chemical composition of the feedstock. For example, Figure 2.6 shows the evolution of the gas, liquid and solid product yields with the pyrolysis temperature and heating rate from the horizontal quartz reactor. An increasing in the final pyrolysis temperature gives rise to a decrease in the solid fraction and to an increase in the gas fraction. The liquid fraction, increases slightly (from 40 to 42 wt.%) when the end temperature is increased from 450 to 650°C, but remains more or less constant above 650°C. The effect of the heating rate is only important at low end temperature (i.e. 450°C). Thus, at this temperature the higher the heating rate, the more efficient the pyrolysis is, resulting in a higher production of liquids and gases and a decrease in solid residue. At temperatures higher than 650°C this effect is practically negligible (Inguanzo *et al.*, 2002).



**Figure 2.6** Variation of the yields of solid, liquid and gas products with the pyrolysis conditions (Inguanzo *et al.*, 2000)



**Figure 2.7** Product yields of sewage sludge pyrolysis samples: (■) S1 (■) S2 and (□) S3. (Fonts *et al.*, 2008)

Three types of sewage sludge samples were pyrolyzed at 550°C in fluidized bed reactor (Font *et al.*, 2008). As shown in Figure 2.7, the product yields of solid, liquid and gas are ca. 25, 48 and 32 wt.%, respectively regardless with the type of pyrolysis reactor.

### 2.4.3 Pyrolytic Products and Their Applications

#### 2.4.3.1 *Gas*

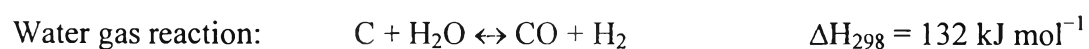
Gas product may be called “uncondensed gas” since all volatile products are vapour but some of volatile is condensed into liquid. By pyrolysis, CO<sub>2</sub>, CO, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and C<sub>x</sub>H<sub>y</sub> (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>) are the main components in gas product 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 (Domínguez *et al.*, 2006).

Indeed, the overall heating value of produced gas is influenced by the evolution of the hydrocarbons present in the gas. The averaged heating value of pyrolytic gas is in between 12.0 and 13.0 MJ Nm<sup>-3</sup>, depending on the pyrolysis process parameter (temperature and heating rate used). At certain conditions, maximum heating value of pyrolysis gas can be as high as 25.0 MJ Nm<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.

#### 2.4.3.2 *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. 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<sup>-1</sup>) (Bridgwater and Peacocke, 2000). Some authors reported the quality of pyrolysis oils as high as 27 MJ kg<sup>-1</sup> (Bien *et al.*, 2000). This oil has good commercial value as a fuel to power diesel engines. There are some important characteristics of liquid that are summarized in Table 2.7 and discussed briefly in Table 2.8. Moreover, the overview of compound classes and prominent representatives that found in bio-oil is shown in Table 2.9.

**Table 2.7** Typical properties of wood derived crude bio-oil

Physical property	Typical value	Characteristics
Moisture content	15-30%	-Liquid fuel
pH	2.5	-Ready substitution for
Specific gravity	1.20	conventional fuels in many
Elemental analysis		static applications such as
C	55-58%	boilers, engines, turbines
H	5.5-7.0%	-Heating value of 17 MJ
O	35-40%	kg <sup>-1</sup> at 25% wt. water, is
Ash	0-0.2%	about 40% that of fuel
HHV as produced	16-19 MJ kg <sup>-1</sup>	oil/diesel
Viscosity [at 40°C and 25%		-Does not mix with
water]	40-100 cP	hydrocarbon fuels
Solids [char]	1%	-Quality needs definition
Vacuum distillation residue	Up to 50%	for each application



**Table 2.8** Typical properties and characteristics of wood derived crude bio-oil

Appearance	Pyrolysis oil typically is a dark brown free flowing liquid. Depending upon the initial feedstock and the mode of fast pyrolysis, the colour can be almost black through dark red-brown to dark green, being influenced by the presence of micro-carbon in the liquid and by the chemical composition. Hot vapour filtration gives a more translucent red-brown appearance due to the absence of char. High nitrogen contents in the liquid can give it a dark green tinge
Odour	The liquid has a distinctive odor-an acrid smoky smell, which can irritate the eyes if exposed for a prolonged period to the liquids. The cause of this smell is due to the low molecular weight aldehydes and acids. The liquid contains several hundred different chemicals in widely varying proportions, ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides
Miscibility	The liquid contains varying quantities of water which forms a stable single phase mixture, ranging from about 15 wt.% to an upper limit of about 30-50 wt.% water, depending on how it was produced and subsequently collected. Pyrolysis liquids can tolerate the addition of some water, but there is a limit to the amount of water, which can be added to the liquid before phase separation occurs, in other words the liquid cannot be dissolved in water. It is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels
Density	The density of the liquid is very high at around 1.2 kg/litre compared to light fuel oil at around 0.85 kg/litre. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications on the design and specification of equipment such as pumps
Viscosity	The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 100 cSt [measured at 40°C] or more depending on the feedstock, the water content of the oil, the amount of light ends that have been collected and the extent to which the oil has aged.
Distillation	Pyrolysis liquids cannot be completely vaporized once they have been recovered from the vapour phase. If the liquid is heated to 100°C or more to try to remove water or distil off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt.% of the original liquid and some distillate containing volatile organic compounds and water. The liquid is, therefore, chemically unstable, and the instability increases with heating, so it is preferable to store the liquid at room temperature. These changes do also occur at room temperature, but much more slowly and can be accommodated in a commercial application
Aging of pyrolysis liquid	The complexity and nature of bio-oil causes some unusual behavior, specifically that the following properties tend to change with time: viscosity increase, volatile decrease and phase separation and deposition of gums can occur.

**Table 2.9** An overview compound classes and some representative in pyrolytic liquid (Morf, 2001)

Compound class	Representatives	Formula
Acids	Acetic acid	$C_2H_4O_2$
	Propionic acid	$C_2H_6O_2$
	Butanoic acid	$C_4H_8O_2$
Sugars	Levoglucosan	$C_6H_{10}O_5$
	Fructose	$C_6H_{12}O_5$
	Cellobiosan	$C_{12}H_{20}O_6$
Ketones	Acetol	$C_3H_6O_2$
	Cyclopentanone	$C_5H_8O$
	2-Methyl-2-cyclopenten-1-one	$C_6H_8O$
Phenols, Cresols	Phenol	$C_6H_6O$
	o, m, p-Cresol	$C_7H_8O$
	x, y-Dimethylphenol	$C_8H_{10}O$
	2-Ethylphenol	$C_8H_{10}O$
Guaiacols	Guaiacol	$C_7H_8O_2$
	4-Methylguaiacol	$C_8H_{10}O_2$
	4-Ethylguaiacol	$C_9H_{12}O_2$
Furans	Furan	$C_4H_4O$
	Furfural	$C_5H_4O$
	5-Methylfurfural	$C_6H_6O_2$
BTX	Benzene	$C_6H_6$
	Toluene	$C_7H_8$
	o, m, p-Xylene	$C_8H_{10}$
Polyaromatic	Naphthalene	$C_{10}H_8$
Hydrocarbons (PAH)	Anthracene	$C_{14}H_{10}$
	Benzo [a] pyrene	$C_{20}H_{12}$
	Coronene	$C_{24}H_{12}$

The presence of the several compound classes has different effects on the bio-oil properties. Bio-oil with a dominating content of oxygenates is highly reactive. These will alter the some properties of the bio-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).

Beside the esterification of bio-oil, the catalytic deoxygenation is considered to be the promising way in order to upgrade the crude bio-oil for using as a fuel replacing the fossil fuel. The catalytic deoxygenation will discuss in detail in section 2.6.

#### 2.4.3.3 Solid Residue

In general, even as high as 850°C, the sewage sludge pyrolysis is not likely completed (Inguzano *et al.*, 2001). 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) combustion, 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.

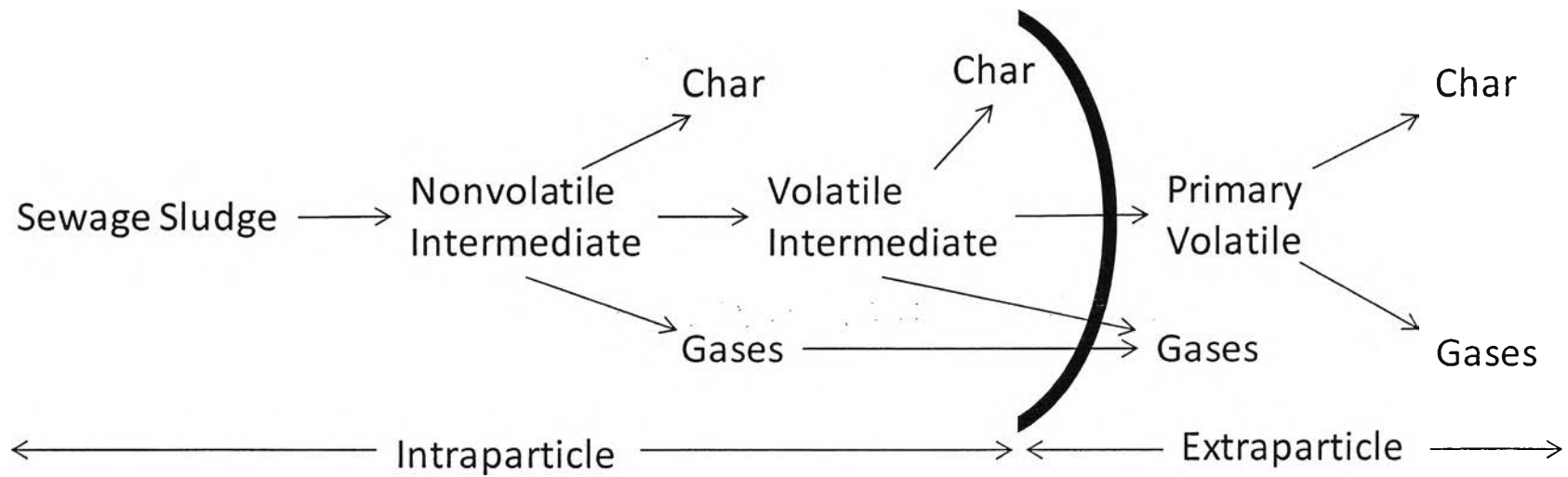
From an energy point of view, solid carbonaceous residues from pyrolysis have relatively low heating values compared with those of other fuels or even of original sludge itself (Inguzano *et al.*, 2002). The heating value of the pyrolyzed residue undergoes a slight decrease as the pyrolysis temperatures and the heating rate increase. Although the possibility of combustion 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 combustion (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 the 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 (Lu and Lau, 1996). However, the textural properties can be improved by both chemical and physical activation. The application of sewage sludge char as adsorbent will be reviewed in next section. An example of using sewage sludge as adsorbent for textile dye will be illustrated in this work.

#### 2.4.4 Pyrolysis Mechanism

This section will give more details about the pyrolysis product formation. Figure 2.8 shows the intraparticle and extraparticle pyrolysis product formation and conversion.



**Figure 2.8** Intraparticle and extraparticle pyrolytic product formation and conversion (Modified from Morf, 2001).

Under heating, sewage sludge will be converted into nonvolatile intermediate and then decomposed to char, volatile intermediate and gases within the particle. The volatile intermediate will react further to form the primary volatile, char and gases (primary reaction). After their evolution from the solid phase, the primary volatile are subjected to the secondary reaction, which alter both mass and composition of volatile, and converted to secondary volatile, char and gases. It should be noted that in the literature, the distinction between “pyrolysis” and “secondary reaction” is not always made. This is because it is possible to conduct pyrolysis experiments yielding primary products that have not undergone secondary reactions to some extent. Thus the term “pyrolysis” is also used for decomposition reactions of primary volatiles in the gas phase. Both the processes pyrolysis and secondary reactions are discussed by means of a literature review of important studies in these fields in the following sections.

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 2.10.

**Table 2.10** 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

#### 2.4.5 Pyrolysis Kinetics

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. Often, 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 2.11 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 2.11** 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:

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

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

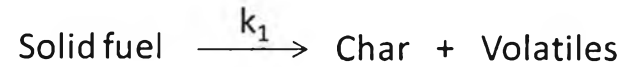
where  $T_0$  is the initial temperature. The integral has no exact solution. Therefore, an analytical approximation or numerical solution must be used to evaluate the integral. The approximation methods were collected in literature (Gaur and Reed, 1998). One of the most popular methods was proposed by Coats and Redfern (1964). The function  $g(x)$  can be eventually obtained (Table 2.11) in correspondence with a model function,  $f(x)$ . The following equation can then be achieved:

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

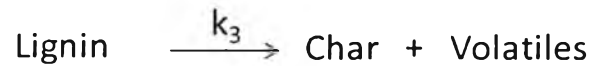
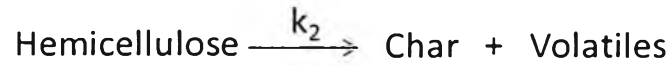
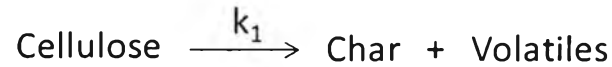
The rate equation is now become an ordinary equation, which is ready for the interpretation of TGA data. The plot  $\ln\left[\frac{g(x)}{T^2}\right]$  against  $1/T$  should give a straight line of a slope of  $-E/R$ . The kinetic parameters such as A and E as well as order of reaction can be obtained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

The kinetic modeling of pyrolysis documented in literature has been reviewed by several authors, for example Di Blasi, 1993 and Grønli, 1996. The pyrolysis process is too complex for the development of realistic mechanistic kinetic models of pyrolysis. Therefore, strongly simplified kinetic schemes involving product classes (“lumps”) instead of single species are used. An overview of widely used kinetic schemes for pyrolysis models is given in Figure 2.9

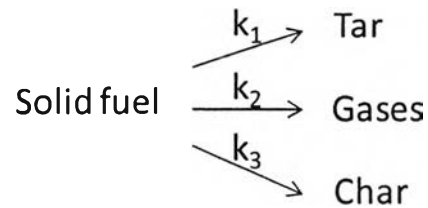
Global one-step reaction



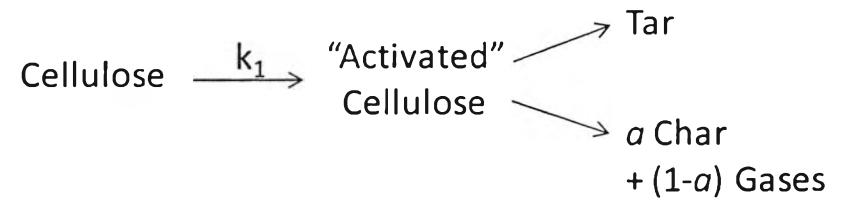
Parallel reactions



Competitive reactions



"Broido-Shafizadeh"-model  
(Bradbury et al., 1979)



Model by Di Blasi and Russo, 1994

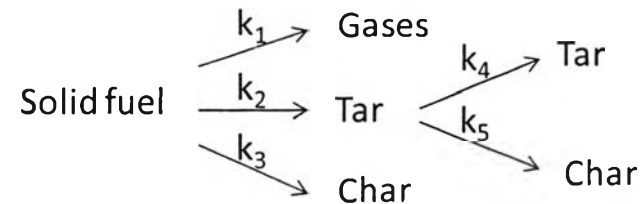


Figure 2.9 Kinetic models for pyrolysis (Morf, 2001)

In the global one-step model, the decomposition of the fuel into “volatiles” (no distinction between gases and tar is made) is described in one first-order reaction. The main drawback of this very simple approach is that it does not provide any information about the product yield distribution.

Multi-step, competitive reaction schemes are proposed in many different forms. The “Broido-Shafizadeh”-model (Bradbury *et al.*, 1979 modified a model proposed by Broido, 1979) was one of the first of this kind. Its kinetic parameters are given in Table 2.12. The necessity of the intermediate step to form active cellulose has been subject of discussions.

The newer models account for secondary reaction by one or even two competitive reaction steps. In the model by Di Blasi and Russo, 1994, the pyrolytic liquid cracking reaction parameters (Table 2.12) were based on data by Liden *et al.*, 1988, whereas the parameters for the char forming reaction were assumed.

**Table 2.12** Reaction rate constants for pyrolysis (Bradbury *et al.*, 1979)

Reaction	A [s <sup>-1</sup> ]	E <sub>a</sub> [kJ mol <sup>-1</sup> ]
1	2.83×10 <sup>19</sup>	242.8
2	3.17×10 <sup>14</sup>	198.0
3	1.32×10 <sup>10</sup>	150.7

## 2.5 Pyrolysis Reactor

The most widely used of pyrolysis reactor type can be categorized into three types, fixed bed, fluidized bed and other type. The detail of each type is discussed below (Bridgewater and Peacocke, 2000).

### 2.5.1 Fixed Bed Reactor

Carrier gas flows through stationary bed containing raw material in the reactor. The reaction takes place after supplying heat to the reactor and the temperature of material is at the given temperature resulting in the volatile product. The generated volatile flows out by the aid of the carrier gas as shown in Figure 2.10.

Fixed bed reactor can be also subdivided to either batch or continuous reactors. The first type is practical 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.

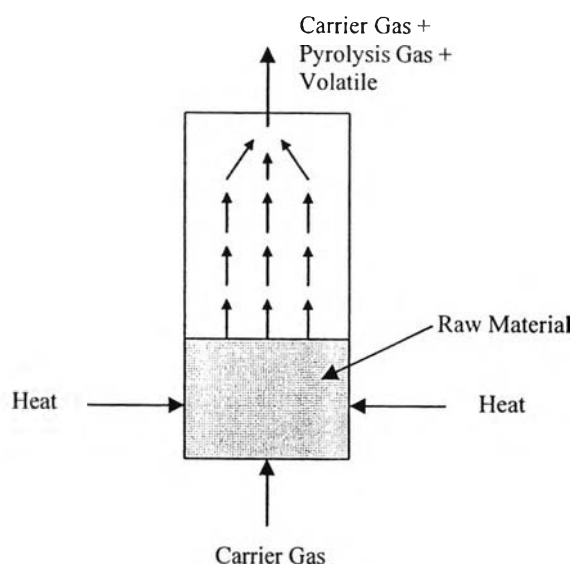
There are several developments, designs, or even applications of a continuous fixed bed reactor. Roy *et al.*, (1994) proposed vacuum-fixed bed reactor for fast pyrolysis. It can be operated with low heating rate (normally over 1,000 °C/s) allowing the feed to have a longer time to absorb heat. Since 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 2.11.

However, fixed bed reactor is not extensively used for commercial scale. This is because of many reasons not only the operating difficulties but also the investment cost including comparable higher energy cost, larger area for construction, and less productivity than fluidized bed.

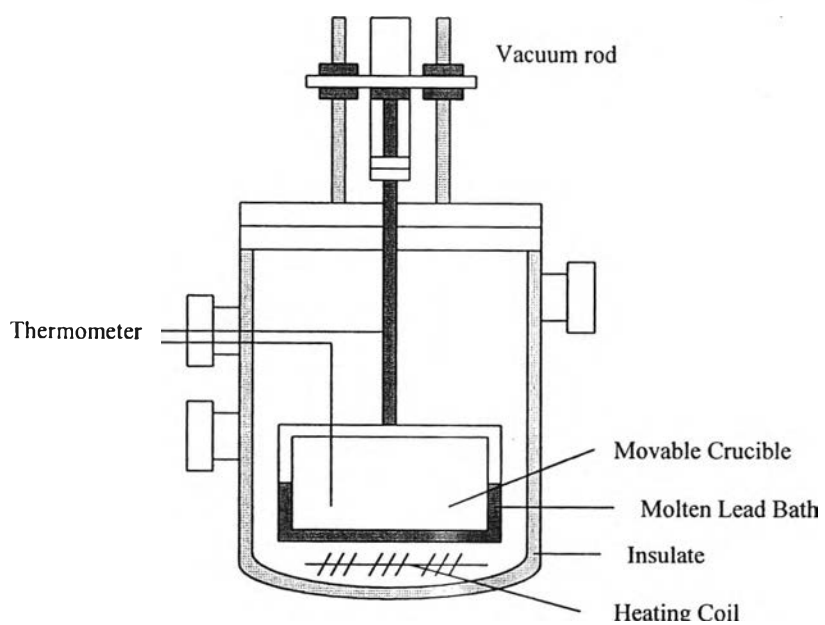
### 2.5.2 Fluidized Bed Reactor

Fluidized bed reactor is more practical than the fixed bed reactor because the difficulty in operating a fixed bed reactor under severe conditions. In contrary, a fluidized bed reactor can give high heat transfer efficiency. With 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 2.12.

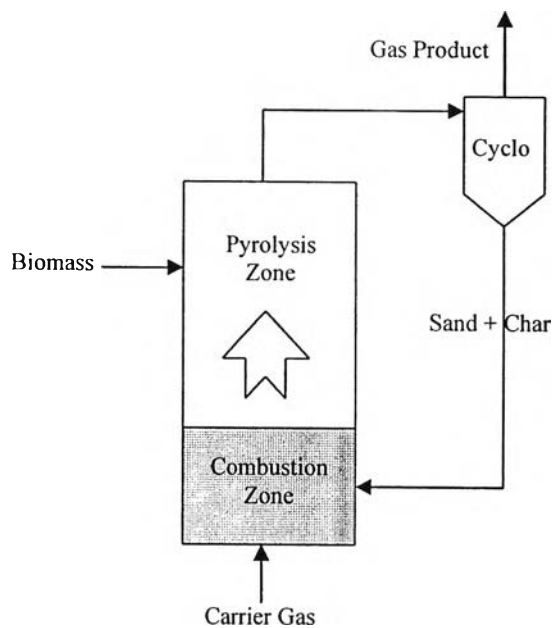
In a fluidized bed reactor, an inert gas (e.g. He or N<sub>2</sub>) at fluidizing state velocity flows through the bed (e.g. sand) from the bottom of the reactor. Raw material is fed at the side of the reactor and suddenly exchange heat with bed. The pyrolysis reaction exists at this zone. A gas product, mixture of gas generated and 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 particle will be fed back to the reactor.



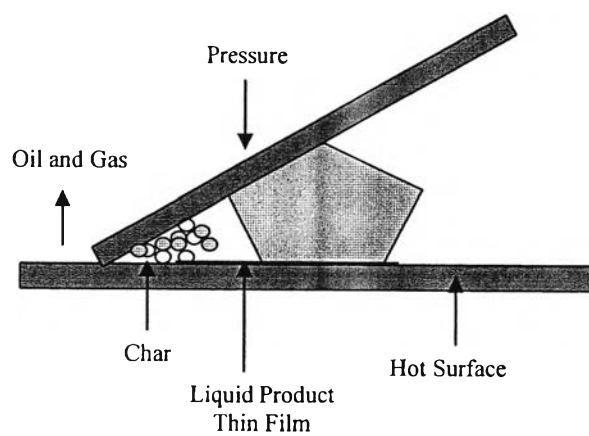
**Figure 2.10** Fixed bed reactor.



**Figure 2.11** A vacuum fixed bed reactor.



**Figure 2.12** A fluidized bed reactor.



**Figure 2.13** An ablative reactor.

### 2.5.3 Other Reactors

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 2.13.

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 pyrolyze a continuous feed.

#### 2) Pyrocycler

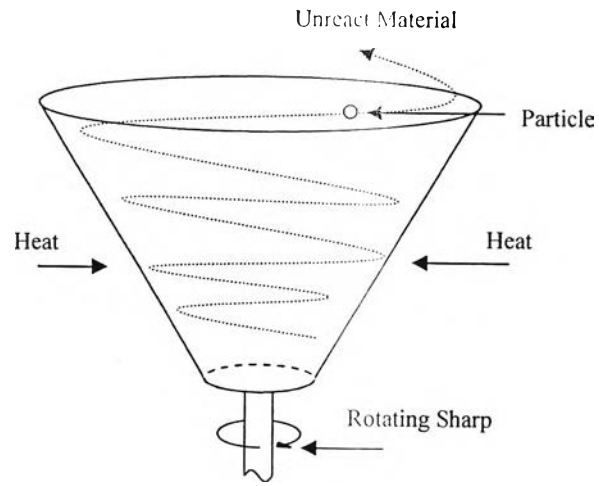
In this reactor, a thermal conversion of raw material is operated at a specific condition such as pressure, heating rate, and temperature to achieve the highest yield of product. Raw material will be dried and ground before entering to the pyrocycler in the vacuum condition. It will be heated by use 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 2.14. 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.





**Figure 2.14** A rotating cone reactor.

## 2.6 Upgrading of Pyrolytic Liquid

Bio-oils are multi-component mixtures of different size molecular derived from pyrolysis of biomass. Therefore, the elemental composition of bio-oil and petroleum derived fuel is different, and the basic data are shown in Table 2.13.

**Table 2.13** Typical properties of wood pyrolysis bio-oil and of heavy fuel oil (Oasmaa and Czernik, 1999)

Physical property	Bio-oil	Heavy fuel oil
Moisture content (wt.%)	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition (wt.%)		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (at 50°C) (cP)	40-100	180
Solids (wt.%)	0.2-1	1
Distillation residue (wt.%)	Up to 50	1

Bio-oil has a content of water as high as 15-30 wt.% derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. The presence of water lowers the heating value and flame temperature, but on the other hand, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine. The better performance and better ignition of oil derived from its lower water content and lower molecular weight (Shihadeh and Hochgreb, 2002)

The oxygen content of bio-oil is usually 35-40% (Oasmaa and Czernik, 1999; Scholze and Meier, 2001), distributed in more than 300 compounds depending on the

resource of biomass and severity of the pyrolytic processes (temperature, residence time and heating rate). The presence of oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content leads to the lower energy density than the conventional fuel by 50% and immiscibility with hydrocarbon fuels also. In addition, the strong acidity (pH value of 2-3) of bio-oils makes them extremely unstable. Because of their complex compositions, bio-oils show a wide range of boiling point temperature. During the distillation, the slow heating induces the polymerization of some reactive components, and bio-oils start boiling below 100°C, while stopping at 250-280°C, leaving 35-50 wt.% as solid residue. Therefore, bio-oils cannot be used in the instance of complete evaporation before combustion.

Wang *et al.*, 2004 analyzed the compositions of bio-oils from *F. mandshurica* pyrolysis by gas chromatography-mass spectroscopy (GC-MS) and illustrated the similarities of the main contents that is the fragments, such as furfural, dimethyl phenol, 2-methoxy-4-methyl phenol, eugenol, cedrol, furanone, etc., are a large proportion in every bio-oil. Most of the components identified, are the phenols with ketones and aldehydes groups attached, and nearly all the functional groups showed the extensive existence of oxygen. On the other hand, the analysis proved that the abundant aldehydes and ketones make bio-oils especially and highly hydrated, which leads to the water being difficult to eliminate. Unlike bio-oil from woody biomass, bio-oil derived from sewage sludge contain mainly of long chain hydrocarbon of carboxylic acid (Jindarom *et al.*, 2007). From the deleterious properties of bio-oil, the upgrading process by reducing the oxygen content is required before its application. The recent upgrading techniques are summarized in Table 2.14 and described as follows.

**Table 2.14** Summary for bio-oil upgrading methods

Method	Product	Pro/Con
Hydrodeoxygenation	Low oxygen content liquid fuels	Complicated process equipment Severe process conditions Superior techniques High cost of investment
Catalytic cracking of pyrolysis liquid	Low oxygen content liquid fuels	Cheaper than Hydrodeoxygenation technique
Emulsification	Bio-oil emulsion	Poor quality of derived liquid The simplest way to utilize liquid bio-oil Corrosive to engine and subassemblies
Steam reforming	Hydrogen or syngas	Low cost of chemicals used Complicated process equipment Severe process conditions Superior techniques
Extraction	Fine chemicals	High cost of investment High cost of chemicals/solvents used Need developing reliable low cost of separation and refining techniques

### 2.6.1 Hydrodeoxygenation

The hydro-process is performed in hydrogen providing solvents activated by the catalyses of Co-Mo, Ni-Mo and their oxides or loaded on  $\text{Al}_2\text{O}_3$  under pressurized conditions of hydrogen and/or CO. Oxygen is removed as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and then the energy density is elevated. The volatile from fast pyrolysis of eucalyptus in a two stage reactor was upgraded by hydrodeoxygenation. Hydrocracking without catalysts was operated in the first stage, and catalytic hydrotreatment was operative in the second stage with lower temperature and the same pressure compared with the first stage. The analysis indicated that the deactivation of the catalyst did not result from carbon deposition. Instead, the embodiments of volatile components blocked the activated sites in the zeolites catalyst (Pindoria *et al.*, 1997, Pindoria *et al.*, 1998)

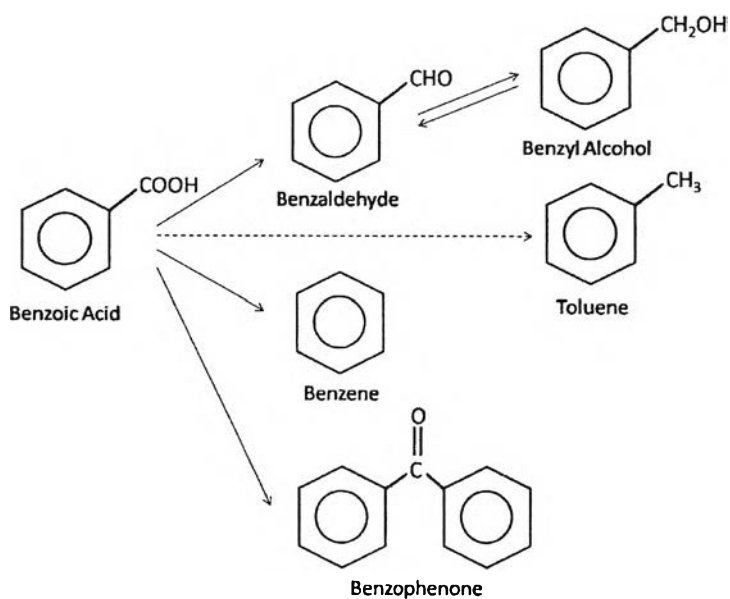
Senol *et al.*, 2005 eliminated oxygen in carboxylic groups with model compounds of methyl heptanoate and methyl hexanoate on sulphided  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$  in a flow reactor to discern the reaction schemes. Aliphatic methyl esters produced hydrocarbons via three main pathways: the first pathway gave alcohols followed by dehydration to hydrocarbons. The de-esterification yielded an alcohol and a carboxylic acid in the second pathway. Carboxylic acid was further converted to hydrocarbons either directly or with an alcohol intermediate.

Elloit and Neuenschwander, 1996 examined the hydrocatalytic reactions of bio-oils from NREL, UF (Union Electrica Fenosa) and RPT3 (Ensyn Technologies, Inc.) in a continuous in the downflow configuration compared to the upflow one. The conversion was doubled on  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$  compared to the  $\text{CoMo}/\text{spinel}$  at elevated temperature.

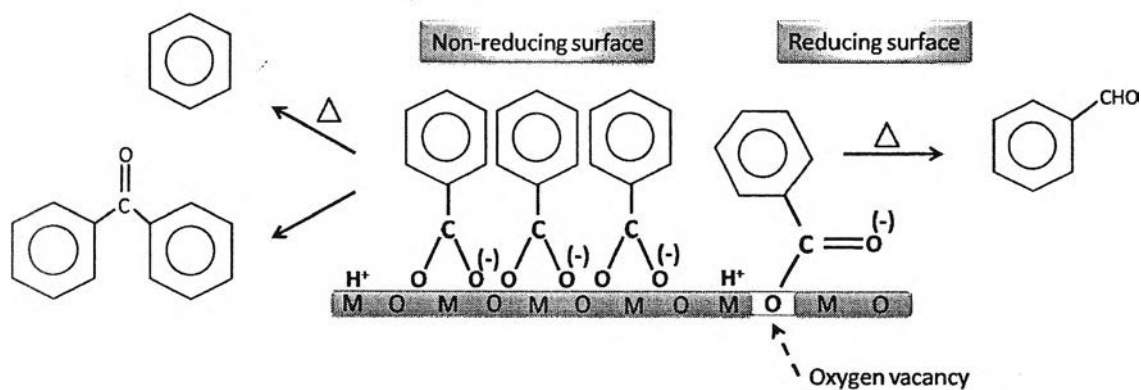
The deoxygenation of acetic acid (Parida *et al.*, 1999) and benzoic acid (de Lange *et al.*, 2001; de Lange *et al.*, 2002) has been studied over the several types of the metal-oxide catalysts. A great number of metal-oxides were tested and the correlation between reducibility and catalytic behavior was found (Sakata *et al.*, 1999).  $\text{CeO}_2$ ,  $\text{ZnO}$  and  $\text{ZrO}_2$  exhibit a good catalytic performance and highly selective reduction of benzoic acid to benzaldehyde, especially  $\text{CeO}_2$  (Sakata *et al.*, 1998). The reaction network for benzoic acid deoxygenation can be drawn schematically as shown in Figure 2.15. Under the presence of the oxygen vacancies, firstly, benzoic acid is deoxygenated to benzaldehyde and subsequently benzaldehyde is deoxygenated to toluene or benzoic acid reacts through to toluene directly. Under no oxygen vacancies,

the reactions toward benzene and benzaldehyde can take place. Details for the deoxygenation reaction model of adsorbed benzoic acid over both non-reducible and reducible catalysts are also shown in Figure 2.16.

Moreover,  $\text{ZrO}_2$  was found to promote the decarboxylation of stearic acid resulting in  $\text{C}_{16}$ -hydrocarbons and  $\text{CO}_2$  under the supercritical water (SCW). The addition of KOH into  $\text{ZrO}_2$  was found to promote the decarboxylation of stearic acid to  $\text{C}_{17}$ -hydrocarbons and  $\text{CO}_2$  (Watanabe *et al.*, 2006). Recently, the addition of Zr atom into the  $\text{CeO}_2$  lattice can increase the thermal stability and reducibility of the catalysts and it might be expected to increase the deoxygenation activity (González-Velasco *et al.*, 2000; Pengpanich *et al.*, 2002).



**Figure 2.15** The reaction network for the deoxygenation reaction of benzoic acid (de Lange *et al.*, 2002)



**Figure 2.16** The deoxygenation reaction model of benzoic acid over both non-reducible and reducible catalysts (de Lange *et al.*, 2001)

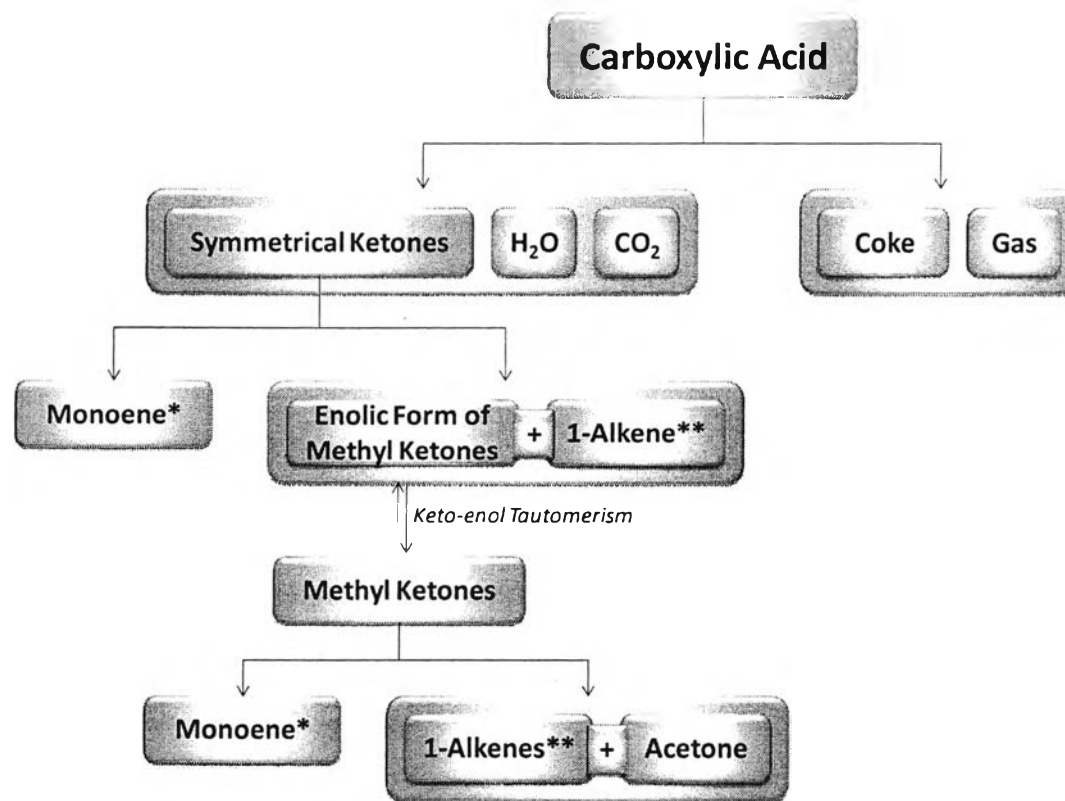
### 2.6.2 Catalytic Cracking of Pyrolysis Vapors

Oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygen as H<sub>2</sub>O, CO<sub>2</sub> or CO. Nokkosmaki *et al.*, 2000 proved ZnO to be a mild catalyst on the composition and stability of bio-oils in the conversion of pyrolysis vapor, and the liquid yields were not found to be substantially reduced. Despite the indicated deactivation of the catalyst, the improvement in the stability of the ZnO treated oil was clearly observed.

The upgrading of pyrolysis oils over acidic catalysts of HZSM-5 has been studied. The results showed that HZSM-5 capable to deoxygenate the pyrolysis oils derived from fast pyrolysis system (Demirbas *et al.*, 1998). However, HZSM-5 catalyzes many reactions such as deoxygenation, decarboxylation and decarbonylation reactions. In addition, they also promote cracking, oligomerization, alkylation, isomerization, cyclization and aromatization reactions at the same time. As a consequence of the catalytic process, not only a board distribution of oil compositions was obtained but also severe coking was found to be a serious problem.

The catalytic conversion of carboxylic acids over activated alumina has been studied (Vitolo *et al.*, 2001). The results showed that the carboxylic acids produced symmetrical ketones, water and CO<sub>2</sub> and symmetrical ketones were further degraded to methyl ketones and alphaolefins (and parafins) with two fewer carbon atoms. The obtained methyl ketones will also be further degraded to alkenes presumably via a  $\gamma$ -hydrogen transfer mechanism. The reaction path way is illustrated in Figure 2.17.





- The monoene derived from the symmetrical ketones and the monoene derived from the methyl ketones are not identical.
- The 1-alkenes derived from both ketones are identical.

Figure 2.17 Overview of the pathway for the deoxygenation of a carboxylic acid (Leung *et al.*, 1995)

Depending on the carbon number of feedstocks, the symmetrical ketones were the main composition in the liquid derived from C<sub>4</sub> acids whereas the alkenes were main composition in the liquid derived from C<sub>12</sub> acids. Moreover, coke formation on the catalysts' surface was found to be the serious problem. Amount of coke was increased as a function of the carbon number of acids from 10.3 wt.% (for C<sub>4</sub> acids) to 25.6 wt.% (for C<sub>12</sub> acids).

Guo *et al.*, 2003 reviewed various catalysts used in bio-oil upgrading in detail and believed that although catalytic cracking is a predominant technique, the catalyst with good performance of high conversion and little coking tendency is demanding much effort.

### 2.6.3 Emulsification

The simplest way to use bio-oil as a transport fuel seems to be combine it with Diesel directly. Although the bio-oils are immiscible with hydrocarbons, they can be emulsified by the aid of a surfactant. Chiaramonti *et al.*, (2003) prepared emulsified bio-oil by the ratios of 25, 50 and 75 wt.% and found the emulsions were more stable than the original ones. The higher the bio-oil content, the higher the viscosity of the emulsion. The optimal range of emulsifier to provide acceptable viscosity was between 0.5% and 2.0%. In particular, the effect of the long term use of emulsions on the stainless steel engine and its subassemblies should be estimated.

Ikura *et al.*, 2003 obtained light fractions of bio-oil by centrifugation and emulsified them in No. 2 Diesel by CANMET surfactant with ratios of 10, 20 and 30% separately. The cost of producing stable emulsions were 2.6 cents/L for 10% emulsion, 3.4 cents/L for 20% emulsion and 4.1 cents/L for 30% emulsion separately. The bio-oil was determined to have a cetane number of 5.6, which will decrease by 0.4 for each 10% concentration augmentation. The viscosity of 10-20 wt.% emulsions was much lower than that of pure bio-oil, and their corrosiveness was about half of pure bio-oil alone.

### 2.6.4 Steam Reforming

Hydrogen is a clean energy resource and very important in the chemical industry and the rising focus on reforming the water fraction of bio-oil looks promising. Production of hydrogen from reforming bio-oil was investigated by NREL (Wang *et al.*,

1997; Wang *et al.*, 1998) extensively, including the reactions in a fixed bed or a fluidized bed and studies of the reforming mechanisms on model compounds. The fixed bed used in the conventional reforming of natural gas or naphtha is not suitable in the lignin derived fraction of bio-oil because of its tendency to decompose thermally and form carbon deposits on the upper layer of the catalyst and in the reactor freeboard.

Czernik *et al.*, 2002 obtained hydrogen in a fluidized bed reactor from the carbohydrate derived fraction of wood pyrolysis oil with a yield of about 80% of theoretical, which corresponds to approximately 6 kg of hydrogen from 100 kg of wood used for pyrolysis. Commercial nickel catalysts showed good activity in processing biomass derived liquids and was readily regenerated (20 min to 2 h) by steam or CO<sub>2</sub> gasification after deactivation, which occurred during reforming. The commercial catalysts, designed for fixed bed applications, were susceptible to attrition in the fluidized bed. Consequently, they were entrained at a rate of 5%/day. The development of a fluidized catalyst that has both high activity and mechanical strength at the conditions of the steam reforming process is needed and is being pursued.

Takanabe *et al.*, 2004 completely convert acetic acid the model compound, by steam reforming over Pt/ZrO<sub>2</sub> catalysts and found a hydrogen yield close to thermodynamic equilibrium. Analysis showed that Pt was essential for the steam reforming to proceed, and ZrO<sub>2</sub> was needed to activate the steam, which was also active for oligomers precursor formation under the conditions investigated. The results illustrated that steam reforming took place at the Pt-ZrO<sub>2</sub> boundary, and that deactivation occurred when this boundary is blocked by oligomers.

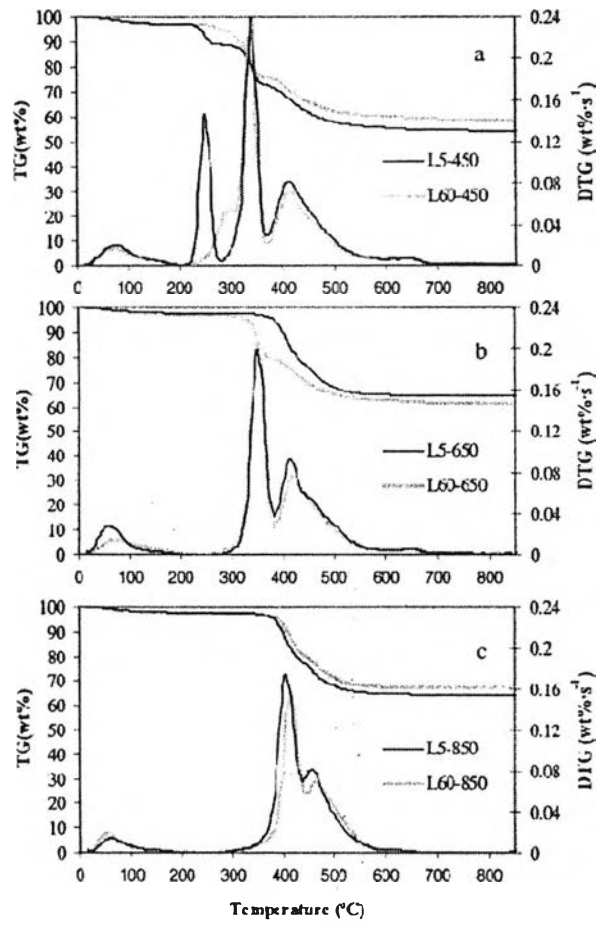
### 2.6.5 Extraction

Hundreds of the components of bio-oil are determined, and reclaiming one or more kinds of small and valuable chemicals arouses great interests among scholars and businessmen. There are many substances that can be extracted from bio-oil, such as phenols used in the resins industry, volatile organic acids in formation of de-icers, levoglucosan, hydroxyacetaldehyde and some additives applied in the pharmaceutical, fiber synthesizing or fertilizing industry and flavoring agent in food products (Bridgwater and Peacocke, 2000; Bridgwater *et al.*, 1999). Commercialization of special chemicals from bio-oils requires more devotion to developing reliable low cost separation and refining techniques.

## 2.7 Sewage Sludge Chars Combustion

Although the combustion of coals has been studied and commercialized, the differences in the combustion profile is expected. Unlike coals, biomass and waste materials comprise of complex constituents and vary in their amount. Focusing on the sewage sludge, the sewage sludge combustion technology was studied (Werther and Ogada, 1999). In combustion processes, two important stages are always present in the solid phase (Conesa *et al.*, 1998; Spliethoff and Hein, 1998). The first stage is the pyrolysis stage (essentially promoted by thermal mechanisms) followed by a char combustion stage. Pyrolysis and combustion stage may be sequential or contemporary, depending on the feature of the process considered (Conesa *et al.*, 1998). Therefore, the individual study of pyrolysis process has been studied in many literatures (Font *et al.*, 2005; Gomez-Rico *et al.*, 2005; Scott *et al.*, 2006; Thipkhunthod *et al.*, 2006) but there is limited information about sewage sludge char combustion.

Thermogravimetry (TG) has a number of advantages for routine char reactivity measurements. Although the details vary, these are all based on continuous weight loss measurements for a combusting char sample held in a temperature-controlled furnace. The derivative of the weight loss or weight loss rate (DTG) with adequate sensitivity and accuracy is commercially available. Figure 2.18 and Table 2.15 show example for the temperature programmed combustion of sewage sludge char and characteristic temperatures and burn-out time derived from the DTG curves (Inguanzo *et al.*, 2001). The analysis of TG and DTG curves may be useful for optimizing activation or burning the carbonaceous material in air. For instance, as the pyrolysis temperature increases, the temperature of the beginning of the reaction ( $T_v$ ) shifts to higher values and the temperature of the end of the reaction ( $T_e$ ) to lower ones.



**Figure 2.18** Example of TG and DTG profile of sewage sludge char combustion (a) L5-450 and L60-450, (b) L5-650 and L60-650, (c) L5-850 and L60-850 (LX-Y, where X represent the heating rate and Y represent the pyrolysis temperature (Inguanzo *et al.*, 2001))

**Table 2.15** Characteristic temperatures of the sewage sludge char combustion reactivity and burn-out time derived from DTG curves

Sample	$T_v$ (°C)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$T_{m3}$ (°C)	$T_e$ (°C)	$T_b$ (s)
L5-450	225	249	341	411	63	1730
L60-450	245	296	337	414	62	1640
L5-650	302	-	351	415	585	1120
L60-650	292	-	351	421	587	1160
L5-850	333	-	404	455	573	946
L60-850	338	-	415	464	573	926

In consequence, the burn-out time ( $t_b$ ) decreases with the pyrolysis temperature at which the materials are obtained. On the other hand,  $T_m$ , temperature at the maximum is taken as a measure of combustibility or reactivity. Thus, the lower the maximum peak temperature the more reactive a material can be considered to be.