CHAPTER V
PYROLYTIC CHARACTERISTICS OF SEWAGE SLUDGE

5.1 Abstract

In this study, a number of different sewage sludge including sludge samples from industrial and hospital wastewater treatment plants were characterized for pyrolysis behavior by means of thermogravimetric analysis up to 800 °C. According to the thermogravimetric results, five different types of mass loss behaviors were observed depending on the nature of the sludge used. Typical main decomposition steps occurred between 250 and 550 °C although some still decomposed at higher temperatures. The first group (Types I, II and III) was identified by main decomposition at approximately 300 °C and possible second reaction at higher temperature. Differences in the behavior may be due to different components in the sludge both quantitatively and qualitatively. The second group (Types IV and V), which rarely found, has unusual properties. DTG peaks were found at 293, 388 and 481 °C for Type IV and 255 and 397 °C for Type V. Kinetics of sludge decomposition can be described by either pseudo single or multi-component overall models (PSOM or PMOM). The activation energy of the first reaction, corresponding to the main pyrolysis typically at 300 °C, was rather constant (between 68 and 77 kJ mol^{-1}) while those of second and third reactions were varied in the range of 85–185 kJ mol^{-1}. The typical order of pyrolysis reaction was in the range of 1.1–2.1. The pyrolysis gases were composed of both saturated and unsaturated light hydrocarbons, carbon dioxide, ethanol and chloromethane. Most products, however, evolve at a quite similar temperature regardless of the sludge type.

5.2 Introduction

Sewage sludge is generated and collected from several parts of wastewater treatment system in both community and industrial sections. All indications suggest that sludge production will continue to increase, and a suitable solution for the

disposal of the expected large quantity of sludge would be needed (Werther and Ogada, 1999). The most common methods to handle the problem are incineration, agricultural use, and landfill disposal. However, the problem is not totally solved because one may cause subsequent problems and require secondary treatment. A promising way for sewage sludge disposal that has been widely studied is the thermal application such as pyrolysis. Pyrolysis has been considered as an alternative to the problems of both secondary pollution in thermal processing and of large energy consumption.

Development for sewage sludge conversion to energy and chemicals by pyrolysis process requires better understanding of its thermal properties and reaction kinetics. For highly heterogeneous materials with a wide variety of unknown components such as sewage sludge, it is believed that many decomposition reactions involve in the pyrolysis. Moreover, complex details of each reaction are generally unknown and difficult to analyze. There have been many attempts to describe pyrolysis of sewage sludge with suitable kinetic models by different authors (Conesa *et al.*, 1997, 1998; Chu *et al.*, 2000; Chen *et al.*, 2001; Conesa *et al.*, 2001; Chao *et al.*, 2002). The models usually inherit their own assumptions and supported data. Nonetheless, any evaluation of complex reaction scheme may not be accomplished due to limitation in a number of samples.

In this work, with an extensive number of samples, kinetics of the sludge pyrolysis was investigated by means of thermogravimetric analysis.

5.3 Materials and Methods

5.3.1 Sample Preparation

Samples used in this study were collected from 20 sources comprising municipal, hospital, and industrial wastewater treatment plants located in Bangkok, Thailand and its vicinity. The sample collection was repeated monthly over a two-year period, resulting in exceeding a total number of 210 samples. The sample collecting method was in accordance with the standard method (ASTM D346-90, 1999). The samples were naturally dried for 1–2 d and ground by a ball mill. The fraction of 150–250 μm in particle size was selected for further study.

Physical and chemical properties of sludge samples were given in Table 5.1. On the whole, a broad range of sludge characteristics was observed. The lower and higher volatile matter limits of the samples are 17 and 60 wt%, corresponding to ash contents of 80 and 31 wt%, respectively, in dry basis. The samples contain only a small fraction of fixed carbon, with an average of 5 wt%. Typical heating values of the samples varied from 2.6 to 16.3 MJ kg^{-1}.

Small differences between the sludge characteristics from the same source were also found. Most samples in this work, however, have lower volatile matter (higher ash) and heating values than those reported in the literature (Dogru *et al.*, 2000; Menéndez *et al.*, 2001; Shen *et al.*, 2001; Inguanzo *et al.*, 2002; Otero *et al.*, 2002; Folgueras *et al.*, 2003).

Table 5.1 Properties of sludge samples used in this study

Property	Average
Proximate analysis (wt%)[*]	
- Moisture	5.2±1.1
- Volatile matter	42.6±4.9
- Ash	52.8±5.7
- Fixed carbon	4.6±1.1
Ultimate Analysis (wt%)[*]	
- Carbon content	21.1±3.2
- Hydrogen content	3.4±0.4
- Nitrogen content	3.2±0.6
- Sulfur content	1.1±0.3
- Oxygen content	18.4±2.2
Heating value	9.9±1.6

[*] Dry basis except moisture is in air-dried basis

5.3.2 Pyrolysis experiment

The samples were pyrolized using a TG7 Perkin–Elmer thermogravimetric analyzer. A sample weight of approximately 10 mg was used for each experiment under non-isothermal conditions. The sample was heated up from ambient temperature to 105 °C and held until its weight was constant in which free moisture was removed out. Then, the sample was further heated to 800 °C with a heating rate of 20 °C min^{-1}. The experiments were carried out under the nitrogen flow of 20 ml min^{-1}. Some samples were randomly selected for repeating the experiment to ensure the reproducibility, which was found to be very consistent. The effect of heating rate was also studied between 5 and 20 °C min^{-1}. The thermogravimetric and differential thermogravimetric (TG–DTG) data were used to characterize the pyrolysis behavior of the sludge samples as well as to provide estimates of their kinetic parameters.

5.3.3 Product Gas Evolution

Evolution of various gases produced from the sludge pyrolysis was analyzed by coupled temperature programmed pyrolysis/mass spectroscopy (TPP/MS). A mass spectrometer (Blazers OmnistarTM) was directly connected to a temperature programmed pyrolyzer (TPDRO 1100, ThermoFinnigan). A sample weight of approximately 10 mg was placed in a quartz tube. The sample was heated in a nitrogen flow from room temperature to 800 °C with a heating rate of 10 °C min^{-1} and held for 10 min. Evolved gases of m/z of less than 60 were monitored during the heat up. The ion intensities were normalized to the sample in order to minimize errors caused by a shift in the mass spectrometer sensitivity.

5.4 Thermogravimetric Results

5.4.1 Thermal Decomposition Behavior of Sewage Sludge

Typical DTG curves for the sludge pyrolysis are shown in Figure 5.1 and the DTG characteristics were given in Table 5.2. It should be noted that the pyrolysis reaction occurred within 600 °C. For most samples, a small fraction of mass loss occurred as indicated by a DTG peak in the temperature range of 120-180

°C. The mass loss in this region corresponds to the vaporization of sorbed water in the sludge, called dehydration or drying process (Chen and Jeyaseelan 2001; Calvo *et al.*, 2004). Its magnitude depends on the nature of individual sludge, typically varying from 5 to 10% of the total mass loss. A main decomposition step was normally observed at higher temperature. Five different types of DTG patterns were observed in this study. They were designated as Types I - V as shown in Figure 5.1. All five behavior types were distinguished as the following descriptions.

Type I: the main decomposition or pyrolysis step starts slowly after dehydration and more sharply after 200 °C. The decomposition profile presents the main DTG peak at 299 °C and ceases at the temperature of ca. 550 °C. Overall decomposition (excluding dehydration) is accounted to be a single step with the magnitude of more than 80% of the total mass loss.
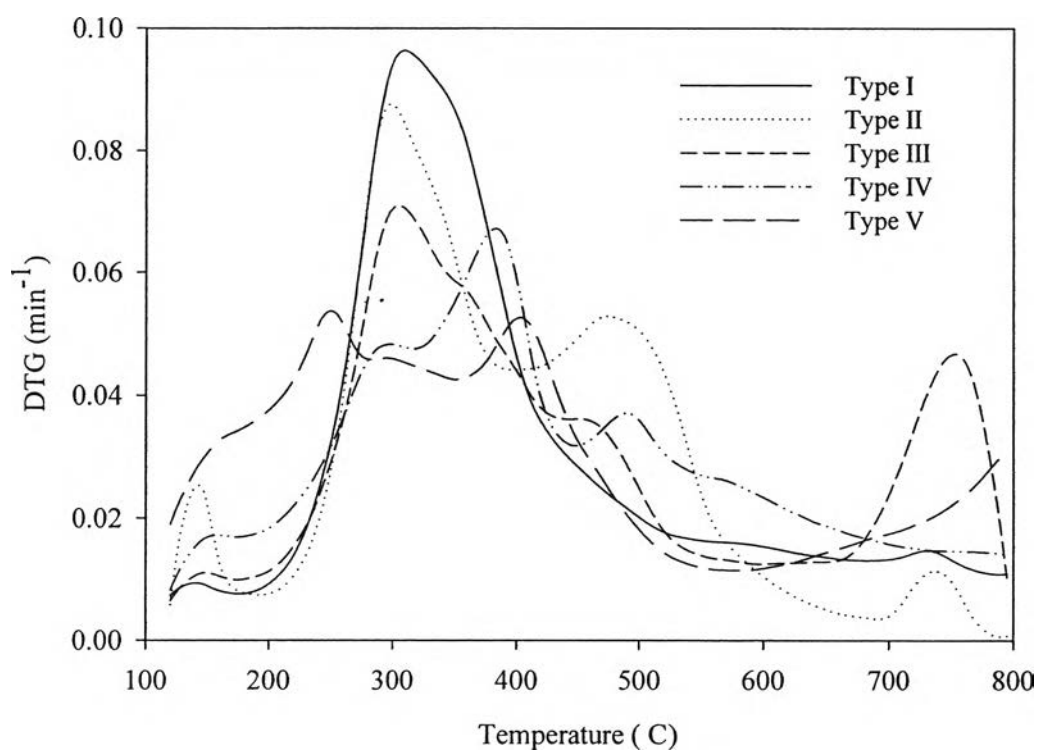
Figure 5.1 DTG profile of sewage sludge decomposition (heating rate of 20 °C min^{-1}).

Table 5.2 DTG peak temperature and height in accordance with the sludge decomposition (excluding dehydration)

Type	Peak temperature	Corresponding peak height
I	299±1	0.21±0.02
II	292±2, 488±11	0.20±0.03, 0.11±0.02
III	301±2, 458±7, 755±8	0.17±0.03, 0.07±0.01, 0.10±0.02
IV	293±1, 388±7, 481±5	0.10±0.01, 0.14±0.01, 0.08±0.01
V	255±3, 397±6	0.10±0.01, 0.08±0.01

Type II: the sludge has an almost similar behavior as Type I up to 400 °C. The DTG curve presents the peak at 292 °C. At higher temperature, the mass loss presents a distinguished DTG peak at 488 °C. These two steps account for approximately 50 and 30% of the total mass loss, respectively. This, in turns, may refer to the two distinguished composition groups in the sludge.

Type III: a main decomposition takes place at 301 °C and next decomposition centered at 458 °C. These two steps were thought to be the same as Type II. However, for this type, another sharp peak occurs at the temperature higher than 700 °C. This region is accounted to be 15-20% of the total mass loss. The decomposition at such a high temperature is due to the degradation of calcium carbonate (Caballero *et al.*, 1997).

The equilibrium between calcium carbonate and calcium oxide is shown as follow (Menendez *et al.*, 2004):

$$CaCO_3 \leftrightarrow CaO + CO_2, \qquad H_{298K} = 178 \text{ kJ mol}^{-1}$$

The catalytic effect of calcium oxide in the pyrolysis of carbonaceous materials was studied in a previous work, where it was concluded that CaO catalyses secondary cracking reactions of volatiles, causing an increase in the gas fraction at the expense of the oil fraction and an increase in the production of H_2. Moreover,

CaO has been used as an adsorbent of carbon dioxide in new H_2 production methods during coal gasification.

On the other hand, in the presence of water CO equilibrates with CO_2 in the water gas shift reaction, which means that the decrease in CO_2 gives rise to a reduction of CO in the pyrolysis gas.

Type IV: the decomposition takes place in three steps. Like other types, the first step at 293 °C takes place but as a shoulder. The main decomposition step occurs at 388 °C as the highest peak. At higher temperature, another shoulder was observed at 481 °C and overall decomposition ceases at 600 °C.

Type V: a mass loss in drying step is higher than those of other types, corresponding to high moisture in proximate analysis (Table 5.3). Other than the drying step, the decomposition can be clearly separated into two steps. The former occurs at 255 °C, which is lower than usual case. The later occurs at 397 °C with an almost similar magnitude to the first peak and stops at 550 °C.

In general, small variances in DTG characteristics such as peak height and temperature are possible due to the variation of samples (Table 5.2). It was also noticed that most sludge samples behave as Types I, II and III as the samples in these three types exceeds 90% of the total samples. Such thermograms also have been reported by many literatures (Caballero *et al.*, 1997; Chen and Jeyaseelan, 2001; Tian *et al.*, 2002; Calvo *et al.*, 2004). In addition to the common case, Types IV and V as minor have only been observed in this work.

5.4.2 Effect of Heating Rate

Although it was not reported here, it was observed that all thermograms were generally shifted to higher temperatures when the heating rate is increased from 5 to 20 °C min^{-1}. However, overall decomposition behaviors (DTG patterns) do not significantly change for all sludge types. With the same trend, DTG peak heights were increased. This fact is also true for other materials, for instance, biomass or cellulosic materials, API sludge and plastics (Dubdub and Tiong, 2001; Punnaruttanakun *et al.*, 2003).

5.4.3 Relationship between Decomposition Behavior and Characteristics

The characteristics of the sludge that represent each decomposition type were reported in Table 5.3. The behavior type was reported in the orders of increasing ash content and of lowering volatile matter, heating value, carbon and oxygen contents and C/O ratio. It was observed that Types I, II and III are not highly different in both proximate and ultimate analyses. For example, the volatile matter are 47, 43 and 42 wt%, C/H ratios are 6.39, 6.34 and 6.64 and C/O ratios are 1.37, 1.21 and 1.13 for Types I, II and III, respectively. This might be the reason why these three types have quite similar decomposition behaviors. Coincidence that these three types having a main decomposition step at approximately 300 °C, which almost constant, is however comparable to premature coal (Speight, 1994). The difference in these three types is the second decomposition pronounced at higher temperature (approximately 450 °C). This peak is believed to owe to the decomposition of higher molecular weight or more complex molecules (Gascía-Pèrez *et al.*, 2001; Sørum *et al.*, 2001).

The properties of other two sludge types (IV and V) are considerably different from the others. C/H ratio of Type IV was found to be lower (reported at 5.12) than that of Types I, II and III. Notably, the characteristic of Type V sludge is highly different from the others. It has drastically low volatile matter, 24 wt%, as well as C/H and C/O ratios at 4.18 and 0.81. This may be due to the fact that this type of the sludge contains significant amount of inorganic substances or ash content, which is uncommonly found in most organic solids. As such manner, the property of material such as its heating value is unpredictable (Thipkhunthod *et al.*, 2005).

Table 5.3 Properties of sludge samples (indicated in average) corresponding to each sludge type[*]

Type	Proximate Analysis[**]				HHV	Ultimate analysis						
	M	V	A	FC	(MJ kg^{-1})	C	H	N	S	O	C/H	C/O
I	5.3±0.9	47.0±3.8	47.7±4.4	5.3±1.0	11.5±1.1	24.5±2.3	3.8±0.3	3.9±0.3	1.0±0.1	19.1±2.1	6.39±0.1	1.37±0.3
II	4.1±1.1	43.2±3.9	51.3±4.6	5.5±1.0	10.4±1.2	22.0±2.3	3.5±0.3	3.4±0.3	0.8±0.2	18.9±2.1	6.34±0.1	1.21±0.2
III	4.4±1.0	42.4±4.9	54.4±5.5	3.2±1.0	8.9±1.4	20.5±3.2	3.1±0.5	2.7±0.5	1.2±0.3	18.1±1.7	6.64±0.1	1.13±0.1
IV	4.9±0.7	37.3±0.6	59.6±1.0	3.0±0.6	8.5±0.2	17.3±0.2	3.4±0.2	1.7±0.1	1.9±0.2	16.1±1.1	5.12±0.2	1.09±0.1
V	8.5±1.3	24.0±1.1	73.5±1.0	2.5±0.4	3.6±0.4	9.3±0.5	2.3±0.5	1.5±0.1	1.6±0.4	11.8±0.9	4.18±0.3	0.81±0.1

[*] dry basis except for moisture in air-dried basis

[**] M, V, A, FC and HHV are moisture, volatile matter, ash, fixed carbon and high heating value

Table 5.4 The DTG peak temperature and C/H ratio of various materials

Materials	Temperature (°C) at presence of DTG peak	C/H ratio
Micro algae[1]	330-360	-
Cellulosic material[2,3,4]		
Xylan	298	-
Cellulose	350	-
Lignin	350	-
Leather[4]	342	-
Wool[4]	339	-
Composted sludge[5]	250, 400	-
API separator sludge[6]	250, 440	-
Asphalt[7]	350, 474	7.85-8.44
Petroleum residue[2]	450	8.27
Scrap tire[4,8]	400, 450	11.24
Various plastics[9]		
PS	413	11.73
PP	456	6.28
LDPE	472	6.04
HDPE	479	6.62
PVC	294, 316, 455	7.81

[1]Peng et al. (2001); [2]Gascía-Pèrez et al. (2001); [3]Grønli et al. (2002); [4]Heikkinen et al. (2004); [5]Pietro and Paola (2004); [6]Punnaruttanakun et al. (2003); [7]Gong et al. (2003); [8]Chen et al. (2001); [9]Sørum et al. (2001).

$$\frac{dx}{dT} = \begin{cases} \dfrac{w_{10} - w_{1\infty}}{w_{10} - w_{1\infty}} \dfrac{dx_1}{dT} & w_{10} < w < w_{1\infty} \\[2mm] \dfrac{w_{20} - w_{2\infty}}{w_{10} - w_{2\infty}} \dfrac{dx_2}{dT} & w_{20} < w < w_{2\infty} \end{cases} \quad , \text{and} \qquad (5.1)$$

$$\begin{cases} \dfrac{dx_1}{dT} = \dfrac{A_1}{\beta} e^{-E/RT} f_1(x_1) & w_{10} < w < w_{1\infty} \\[2mm] \dfrac{dx_2}{dT} = \dfrac{A_2}{\beta} e^{-E/RT} f_2(x_2) & w_{20} < w < w_{2\infty} \end{cases} \qquad (5.2)$$

where subscripts 1, 2 correspond to the pseudo components 1 and 2 and subscripts 0, ∞ correspond to the initial and final mass percentages, respectively. The analogy to these two equations is considered when single and more than two pseudo components involve.

The kinetics for any single pyrolysis reaction can be represented by the following rate equation:

$$\frac{dx}{dt} = kf(x), \qquad (5.3)$$

where x is the mass loss fraction. Constant k obeys Arrhenius correlation:

$$k = Ae^{-E/RT}, \qquad (5.4)$$

where A is the frequency factor; E is the activation energy; R is the universal gas constant and T is the absolute temperature. With some mathematic manipulation, Eq. (5.3) is converted to

$$\frac{dx}{dT} = \frac{A}{\beta} \exp(-E/RT) f(x), \qquad (5.5)$$

where β is the heating rate. The specific form of $f(x)$ represents the hypothetical model of the reaction mechanism or 'model function', which may be presented here in the form of an n-th order of reaction:

$$f(x) = (1-x)^n ,$$

$$(5.6)$$

where n is the order of reaction. However, Eq. (5.5) is in a suitable form for the application with constant heating rate TG-DTG data. An integral form of Eq. (5.5) is normally written as:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_o}^T e^{-E/RT} dT .$$

$$(5.7)$$

Following Coats and Redfern approximation method (Coats and Redfern, 1964), Eq. (5.7) hence becomes:

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

$$(5.8)$$

$$\text{where } g(x) = \begin{cases} -\ln(1-x) & n = 1 \\ \dfrac{1-(1-x)^{1-n}}{1-n} & n \neq 1 \end{cases} .$$

$$(5.9)$$

To obtain the kinetic parameters, the TG-DTG information was used. A non-linear regression scheme was used in fitting Eqs. (5.8) and (5.9) or other suitable forms with respect to each sludge type and experimental data. The analysis was done in the temperature range between 180 and 600 °C depending upon the characteristics of DTG patterns for each type.

The obtained kinetic parameters are summarized in Table 5.5. It should be noted that the difference between the models is a number of reactions, which is in accordance with the DTG profile. A common model for sludge pyrolysis is the PBSM as represented Types II, III and V behaviors. It was found that the activation

energy of the first reaction (main reaction) is almost similar for different types of sludge (ca. 60.8-76.7 kJ mol^{-1}). This reaction represents the main decomposition step of the sludge occurring at 300 °C especially for Types I, II, III and even IV (not main decomposition step for Type IV). For the second reaction, the activation energy is also comparable for Types II, III and IV (136.1, 123.0 and 142.0 kJ mol^{-1}, respectively) whilst that of Type V is 85.4 kJ mol^{-1}, which is less than the other types. For the third reaction, only for Type IV, the activation energy is reported at 131.8 kJ kg^{-1}. Notably, the third reaction only accounts for 5% of the overall fractions. The orders of all reactions were found in the range of 1.1 to 1.8. Any difference that distinguishes sludge to each type would be resulted from the second and third reactions.

There have been a number of sewage sludge pyrolysis kinetic models reported in the literature (Conesa *et al.*, 1997; Chu *et al.*, 2000; Chen and Jeyaseelan, 2001; Chao *et al.*, 2002). However, the values of kinetic parameters were varied depending on the assumptions made. Due to the different models used, the values may not be comparable. Any discussion should be done individually. Conesa *et al.* (1997) and Chu *et al.* (2000) studied the sewage sludge pyrolysis by means of TGA and reported global kinetics by three and two reaction schemes, respectively. The activation energies reported are typical (in the range of 17-332 and 43-137 kJ mol^{-1}, respectively) but the reaction order is somewhat as high as 10, which rarely occurs in general chemical reactions. Chen and Jeyaseelan (2001) on the other hand took the four consecutive first order reactions constrain and reported the activation in the same range (53-205 kJ mol^{-1}). The first order reaction model with a transition state theory was also purposed by Chao *et al.*, (2002), with reported high activation energy of 295 kJ mol^{-1}. In the present study, the proposed models were found to well fit with the TGA behaviors. The activation energy of particular reactions was in agreement with those reported in the literature. The modeling also allows reaction order to be independently varied. Typical orders of reaction were found between 1.1 and 1.8, reasonable for most chemical reactions.

Table 5.5 Kinetic parameters resulting from different models [*]

| Type	Model	Reaction I		Reaction II		Reaction III	
		E	n	E	n	E	n
I	PSOM	60.8	1.8				
II	PBSM	64.5	1.3	136.1	1.5		
III	PBSM	70.4	1.3	123.0	1.6		
IV	PMOM	76.7	1.1	142.0	1.5	131.8	1.3
V	PBSM	73.2	1.6	85.4	1.8		

[*] E = activation energy (kJ mol^{-1}), n = order of reaction

5.6 Product Gas Evolution

The detected products from TPP/MS analysis are listed in Table 5.6, which also represent corresponding compounds formed during pyrolysis of sewage sludge. Figure 5.2 shows the typical evolution profiles of various gas products during the decomposition of sewage sludge. Although the gases are not quantified, the amount of each gas is observed to be different as indicated by the height of MS signals.
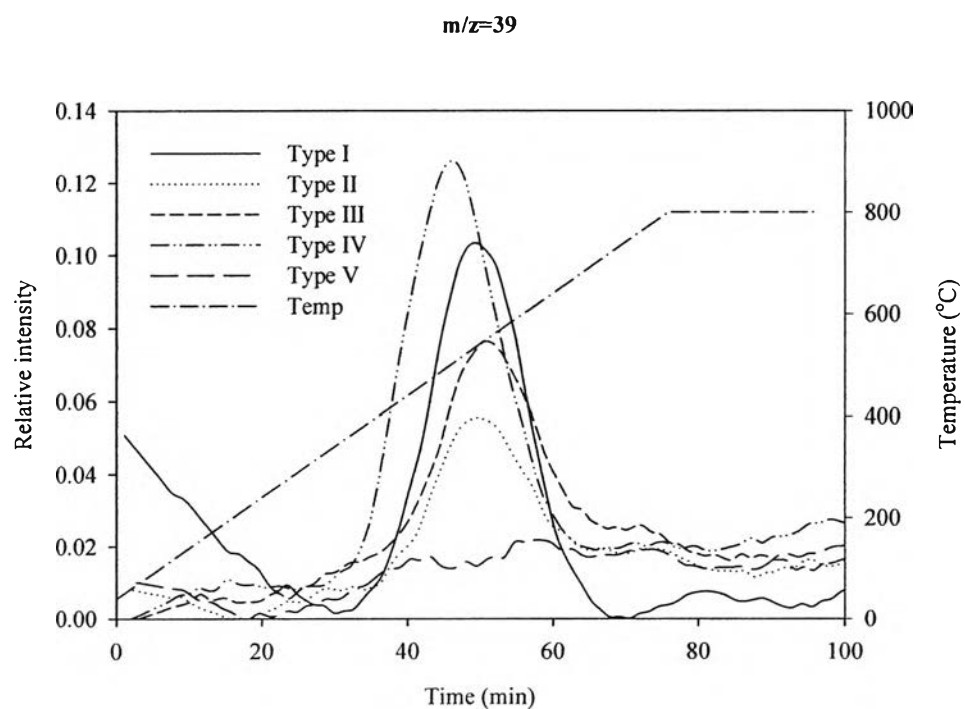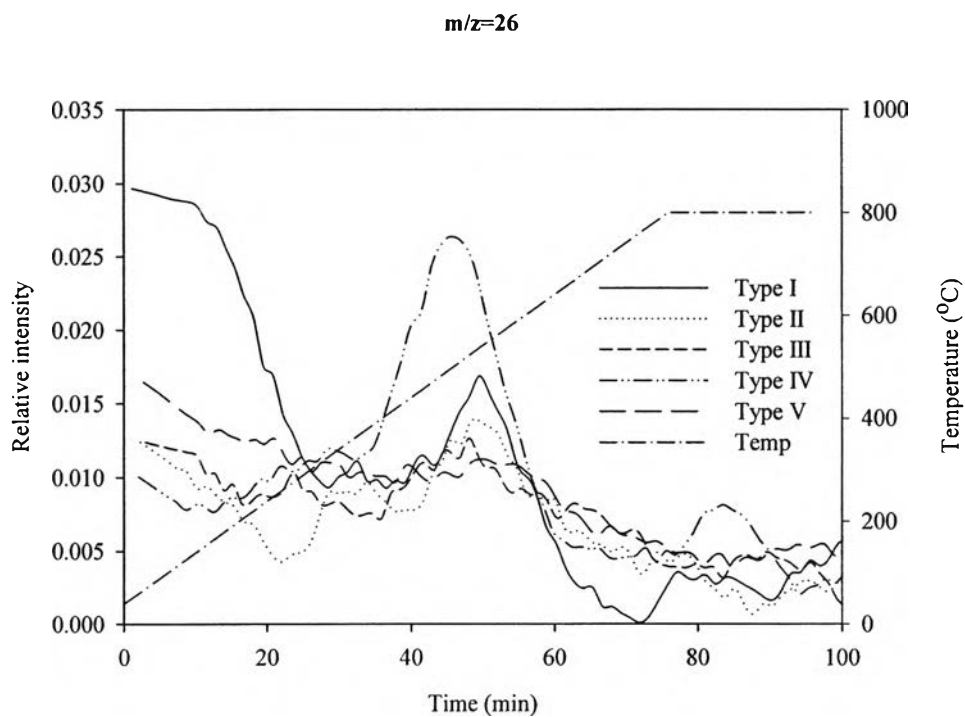
Table 5.6 Suggested identification of mass spectra from MS (Conesa *et al.*, 1998)

m/z	Ion	Name
2	H_2^+	Hydrogen
15	CH_3^+	Methane
26	HCN^+, $C_2H_2^+$	HCN, Ethylene
39	$C_3H_3^+$	Propylene
43	$C_3H_7^+$	Propane
44	CO_2^+	Carbon dioxide
45	CH_3CHOH^+	Ethanol
50	CH_3Cl^+	Chloromethane
55	$C_4H_7^+$	Butane

m/z=2

(a)

m/z=15

(b)
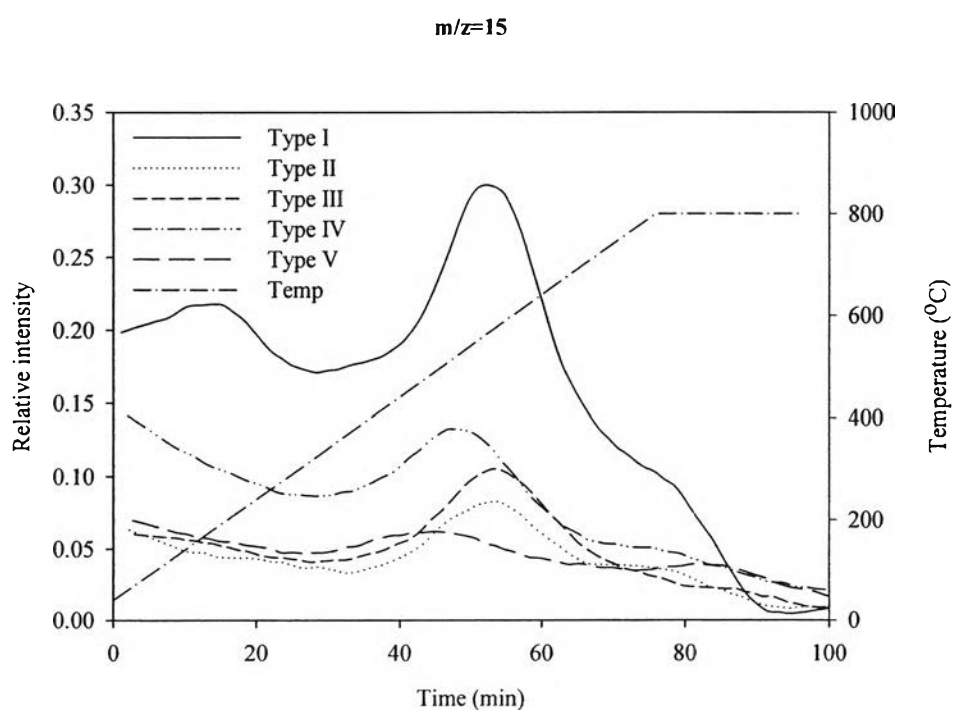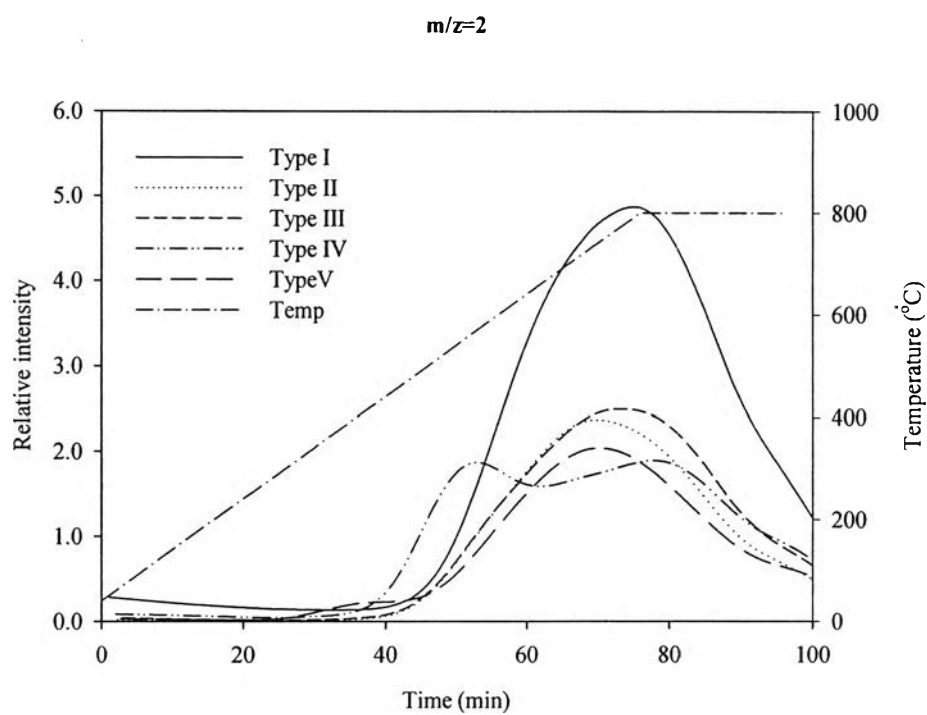
Figure 5.2 Mass spectra represented the gas evolved from sewage sludge pyrolysis.

m/z=26

(c)

m/z=39

(d)

Figure 5.2 (cont'd) Mass spectra represented the gas evolved from sewage sludge

pyrolysis.

m/z=43

(e)

m/z=44

(f)

Figure 5.2 (cont'd) Mass spectra represented the gas evolved from sewage sludge pyrolysis.

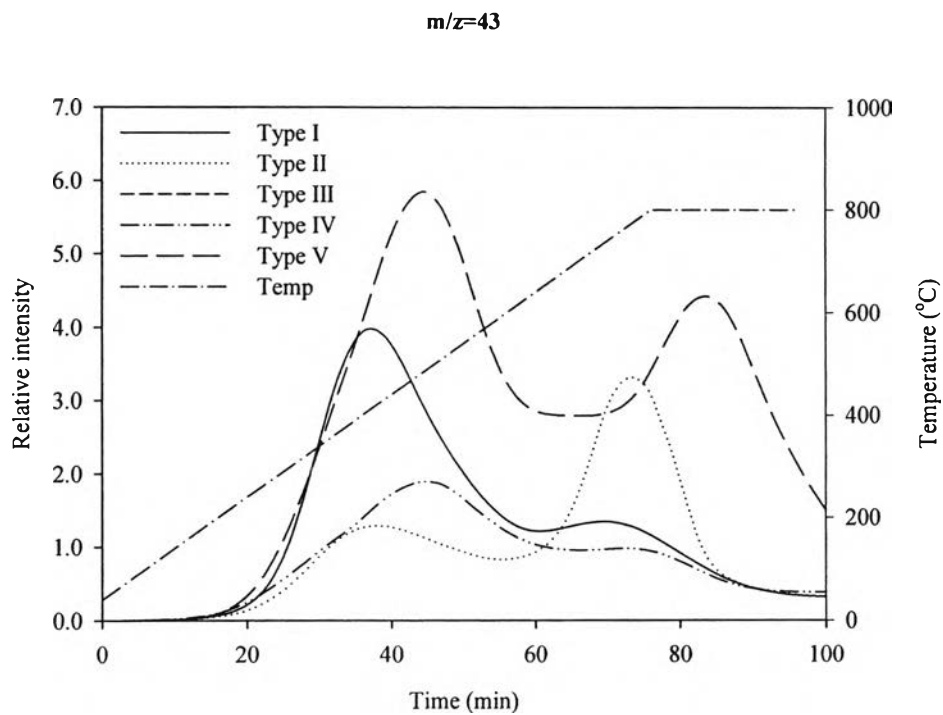91

m/z=45

(g)

m/z=50

(h)

Figure 5.2 (cont'd) Mass spectra represented the gas evolved from sewage sludge
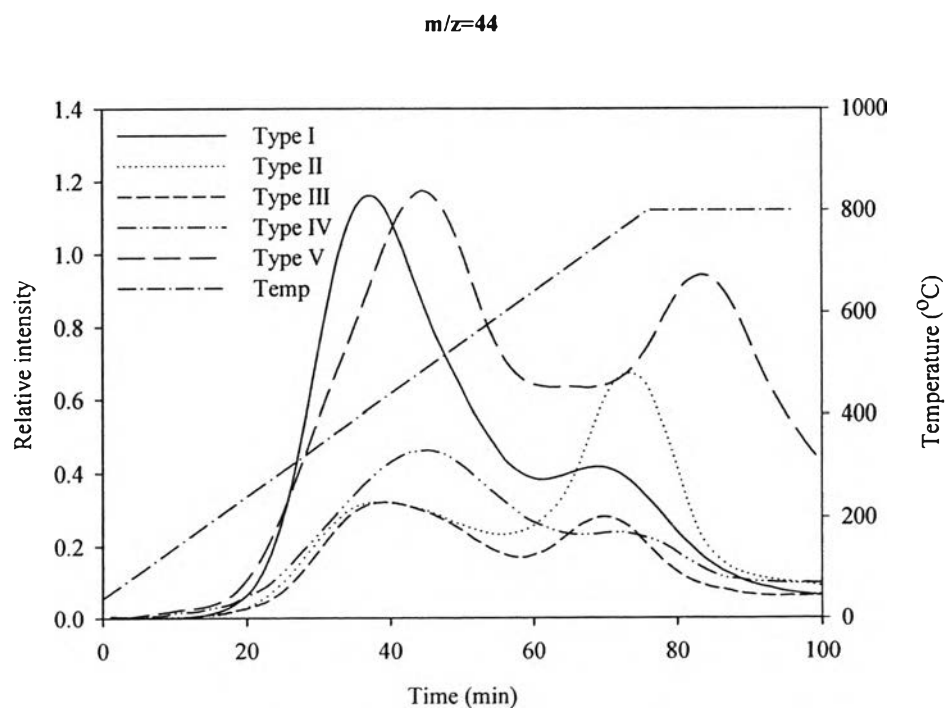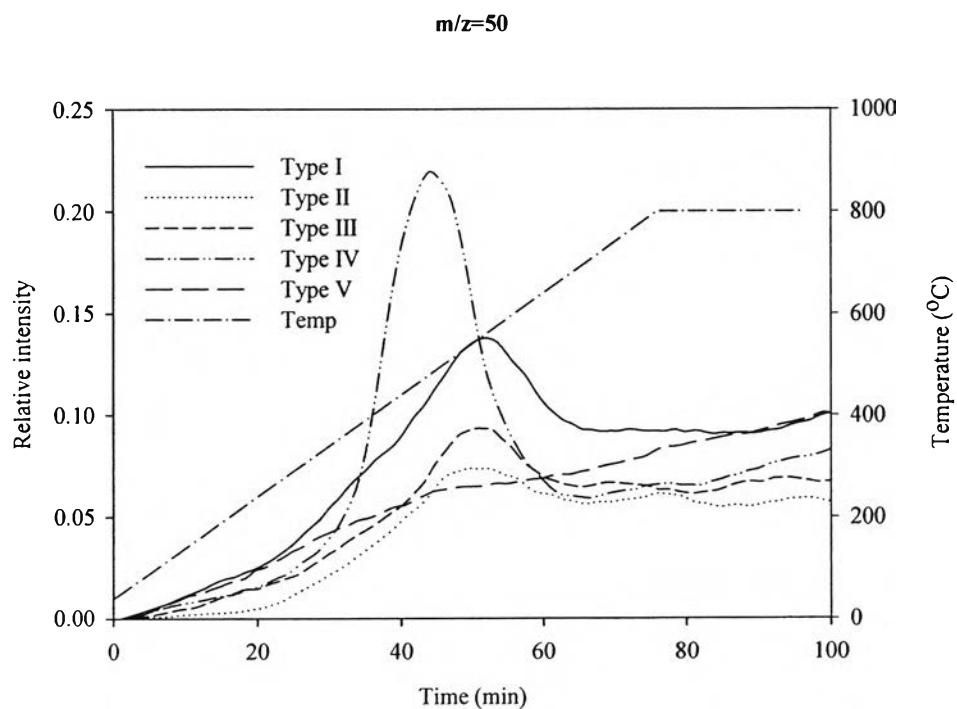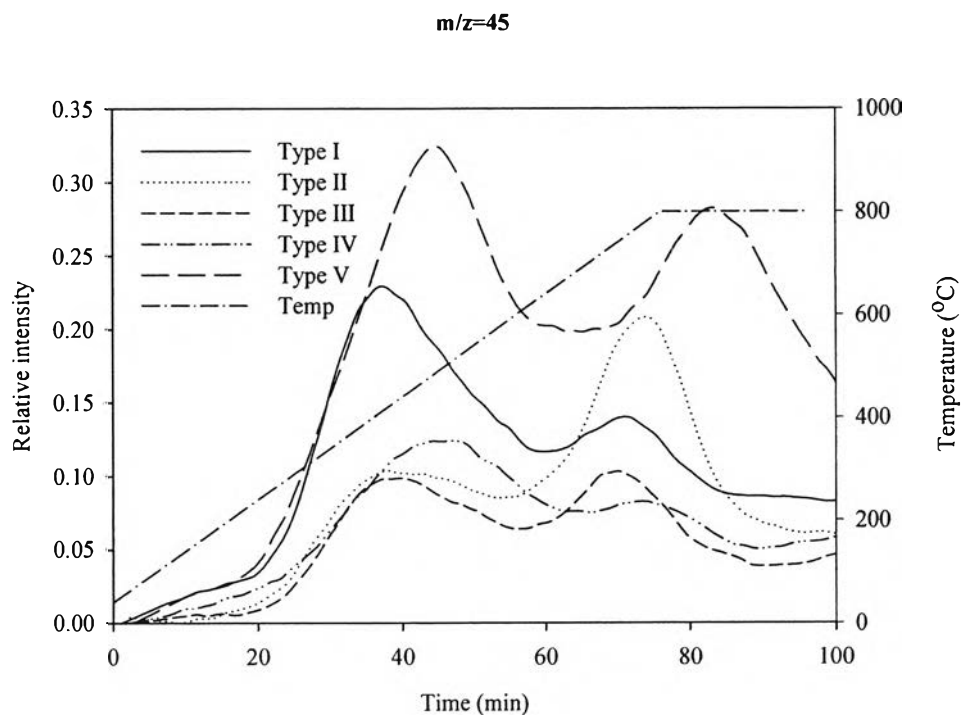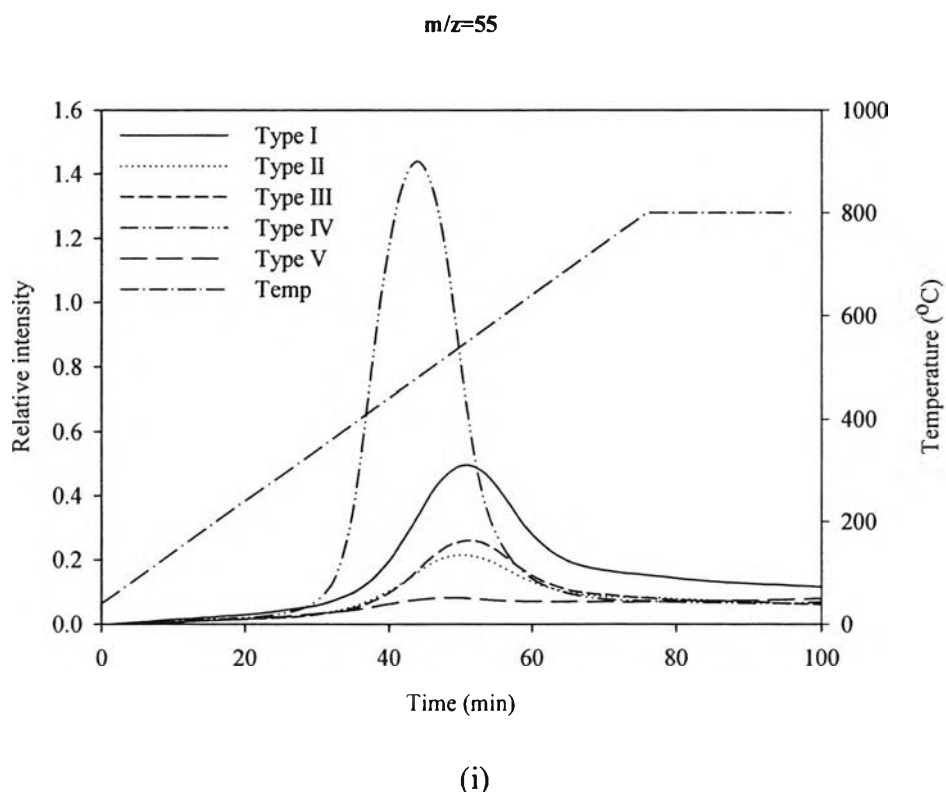
pyrolysis.

m/z=55

(i)

Figure 5.2 (cont'd) Mass spectra represented the gas evolved from sewage sludge pyrolysis.

The evolution of gas can be divided into three zones according to MS peaks at 350, 500 and 750 °C leading to three classified groups of gas products. Hydrogen evolution starts at 500 °C and reaches the highest point at ca 750 °C. The second group comprises methane, ethylene, propylene, chloromethane and butane (m/z = 15, 26, 39, 50 and 55) as shown in Figs. 5.2b, c, d, h and i, respectively. The products in this group evolved from a single step at 500 °C. The third group comprises propane, carbon dioxide and ethanol (m/z = 43, 44 and 45) as shown in Figs. 2e, f and g, respectively. These products evolved from all three steps at 350, 500 and 750 °C.

It is apparent that most gases evolve at a similar temperature regardless of sludge type. Nonetheless, there are differences in quantity and a small temperature shift may be possible depending on the nature of sludge. For the special case, Type V has main mass loss at 250 °C but has very little effect on the gas evolution profile. The absence of gas profile might be due to larger mass number of the precut at this

range. At 750 °C, although the decomposition of sludge at this temperature is very small (except Type III), the gas evolution also occurs at such high temperature for all sludges. It is possible that these gases come from either secondary gas phase reaction or liquid decomposition.

Only detected gases were discussed although other gases were also produced. The evolved gas was analyzed based on the recommended MS spectra identification listed in Table 5.6. Other sorts of gas may be detected and may be different from some literatures. One should take care of the application of the data reported both in this study and literatures. Conesa *et al.* (1998) reported a three-stage process for sewage sludge pyrolysis centered at 250, 350 and 450 °C due to three organic fractions namely non- and biodegradable organic matters and dead bacteria (Conesa *et al.*, 1997). Instead of focusing on the sludge contents, Chen and Jeyaseelan (2001) proposed a different mechanism by a two-decomposition reaction scheme. The first reaction is primary decomposition resulting in generation of some gaseous products and intermediates decomposed at second stage. The product evolved was also slightly different from each other and from this work due to the sludge heterogeneity or even equipment used and its sensitivity.

The kinetic model proposed for sewage sludge pyrolysis (PSOM, PBSM and PMOM) correlated to different fractions decomposed at different temperatures. For example, the common type is the PBSM model, which corresponds to the two reaction scheme. Overall, the evolutions of gas are not so much different regardless the sludge types. The differences are only peak height and possibility of temperature shift. The gas evolution is just the confirmation of the stages of reaction. Although the sewage sludge pyrolysis kinetics is different among the original source, the gaseous products are qualitatively the same.

5.7 Conclusions

The extensive study on the kinetics of sewage sludge pyrolysis was done by Thermogravimetric Analysis. According to the TG-DTG patterns, five different pyrolysis behaviors were categorized. For more detail, the decomposition of sewage

sludge start with vaporization of moisture at slightly above 100 °C. The main pyrolysis step occurs between 250 and 600 °C, which distinguish the behavior type for different sludges. Some samples also decompose at the temperature of more than 700 °C, whereas the calcium carbonate was degraded. Differences in the behavior may be due to different components in the sewage sludge both quantitatively and qualitatively. The second group (Types IV and V), which rarely found, has unusual properties. DTG peaks were found at 293, 388 and 481 °C for Type IV and 255 and 397 °C for Type V. Increasing heating rate from 5 to 20 °C min^{-1} can shift TG-DTG to higher temperature at which the overall curve patterns were not affected.

The kinetics of sewage sludge pyrolysis can be represented in form of either Pseudo single-, bi- or multi-component overall model. That means, the overall reaction can be modeled by a combination of single pseudo component decompositions. The activation energy of the first reaction, corresponding to the main pyrolysis typically at 300 °C, was rather constant (between 60.8 and 76.7 kJ mol^{-1}) whilst those of the second and third (as only in Type IV) reactions were varied in the range of 85.4–142.0 kJ mol^{-1}. A difference in the pyrolysis kinetics was laid on the second or third reactions. Typical order of the pyrolysis reaction was in the range of 1.1–1.8. However, the detail on each reaction was not figured out. The model is useful in application with the satisfied results.

Most gases evolve at a quite similar temperature regardless of the sludge type. Their evolution behaviors confirm the stages of thermal decomposition and kinetics. The pyrolysis gases comprised both saturated and unsaturated light hydrocarbons, carbon dioxide, ethanol and chloromethane.

5.8 Acknowledgements

5.9 References

Caballero, J.A., Font, R., Marcilla, A. and Conesa, J.A. (1997) Characterization of sewage sludges by primary and secondary pyrolysis. Journal of Analytical and Applied Pyrolysis, 40–41, 433–450.

Calvo, L.F., Otero, M., Jenkins, B.M., García, A.I. and Morán, A. (2004) Heating process characteristics and kinetics of sewage sludge in different atmospheres. Thermochimica Acta, 409(2), 127–135.

Chao, C.G., Chiang, H.L. and Chen, C.Y. (2002) Pyrolytic kinetics of sludge from a petrochemical factory wastewater treatment plant-a transition state theory approach. Chemosphere, 49(4), 431–437.

Chen, X. and Jeyaseelan, S. (2001) Study of sewage sludge pyrolysis mechanism and mathematical modeling. Journal of Environmental Engineering, 127(7), 585–593.

Chen, J.H., Chen, K.S. and Tong, L.Y. (2001) On the pyrolysis of scrap automotive tires. Journal of Hazardous Materials, 84(1), 43–55.

Chu, C.P., Lee, D.J. and Chang, C.Y. (2000) Thermogravimetric analysis of activated sludge flocculated with polyelectrolyte. Journal of Environmental Engineering, 126(12), 1082–1087.

Coats, A.W. and Redfern, J.P. (1964) Kinetic parameters from thermogravimetric data. Nature, 201, 68–69.

Conesa, J.A., Marcilla, A., Prats, D. and Rodroguez-Pastor, M. (1997) Kinetic study of the pyrolysis of sewage sludge. Waste Management Research, 15(3), 293–305.

Conesa, J.A., Marcilla, A., Moral, R., Moreno-Caselles, J. and Perez-Espinosa, A. (1998) Evolution of gases in the primary pyrolysis of different sewage sludges. Thermochimica Acta, 313(1), 63–73.

Conesa, J.A., Marcilla, A., Caballero, J.A. and Font, R. (2001) Comments on the validity and utility of the different methods for kinetic analysis of thermogravimetric data. J. Anal. Appl. Pyrol. 58–59, 617–633.

Dogru, M., Midilli, A. and Howarth, C.R. (2000) Gasification of sewage sludge using a throated downdraft gasifier and uncertainty analysis. Fuel Processing Technology, 75(1), 55–82.

Dubdub, I.J.M. and Tiong, N.P. (2001, September) Recycling of plastic wastes: comprehensive kinetic pyrolysis study of PVC and PET polymers using TGA. Proceedings of 6th World Congress of Chemical Engineer, Melbourne, Australia.

Folgueras, M.B., Díaz, R.M., Xiberta, J. and Prieto, I. (2003) Thermogravimetry analysis of coal and sewage sludge. Fuel, 82(15-17), 2051–2055.

Gascía-Pèrez, M., Chaala, A., Yang, J. and Roy, C. (2001) Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: Thermogravimetric analysis. Fuel, 80(9), 1245–1258.

Gong, J.S., Fu, W.B. and Zhong, B.J. (2003) A study on the pyrolysis of asphalt. Fuel, 82(1), 49–52.

Grønli, M.G., Várhegyi, G. and Blasi, C.D. (2002) Thermogravimetric analysis and devolatilization kinetics of wood. Industrial and Engineering Chemistry Research, 41(17), 4201–4208.

Heikkinen, J.M., Hordijk, J.C., Jong, W.D. and Spliethoff, H. (2004) Thermogravimetry as a tool to classify waste components to be used for energy generation. Journal of Analytical and Applied Pyrolysis, 71(2), 883–900.

Inguanzo, M., Domínguez, A., Menéndez, J.A., Blanco, C.G. and Pis, J.J. (2002) On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. Journal of Analytical and Applied Pyrolysis, 63(1), 209–222.

Liu, N.A., Fan, W., Dobashi, R. and Huang, L. (2002) Kinetic modeling of thermal decomposition of natural cellulosic materials in air atmosphere. Journal of Analytical and Applied Pyrolysis, 63(2), 303–325.

Menéndez, J.A., Domínguez, A., Inguanzo, M. and Pis, J.J. (2001) Microwave pyrolysis of sewage sludge: analysis of gas fraction. Journal of Analytical and Applied Pyrolysis, 71(2), 657–667.

Otero, M., Díez, C., Calvo, L.F., Garcia, A.I. and Morán, A. (2002) Analysis of the co-combustion of sewage sludge and coal by TG–MS. Biomass Bioenergy, 22(4), 319–329.

Peng, W., Wu, Q., Tu, P. and Zhao, N. (2001) Pyrolytic characteristics of microalgae as renewable energy source determined by thermogravimetric analysis. Bioresource Technology, 80(1), 1–7.

Pietro, M. and Paola, C. (2004) Thermal analysis for the evaluation of the organic matters evolution during municipal solid waste aerobic composting process. Thermochimica Acta, 413(1-2), 209–214.

Punnaruttanakun, P., Meeyoo, V., Kalambaheti, C., Rangsanvigit, P., Rirksomboon and T., Kitiyanan, B. (2003) Pyrolysis of API separator sludge. Journal of Analytical and Applied Pyrolysis, 68–69, 547–560.

Shen, L., Vuthaluru, H.B., Yan, H.-M. and Zhang, D.K. (2001, September) Pyrolysis of putrescible garbage and sewage sludge mixtures in the OFS process. Proceedings of 6th World Congress of Chemical Engineer, Melbourne, Australia.

Sørum, L., Grønli, M.G. and Hustad, J.E. (2001) Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel, 80(9), 1217–1227.

Speight, J.G. (1994) Coal Technology Theory and Application. New York: Marcel-Dekker.

Thipkhunthod, P., Meeyoo, V., Rangsunvigit, P., Kitiyanan, B., Siemanond, K. and Rirksomboon, T. (2005) Predicting the heating value of sewage sludges in Thailand from proximate and ultimate analyses. Fuel, 84(7-8), 849–857.

Tian, F.J., Li, B.Q., Chen, Y. and Li, C.Z. (2002) Formation of NOx precursors during the pyrolysis of coal and biomass. Part V. Pyrolysis of a sewage sludge. Fuel, 81(17), 2203–2208.

Werther, J. and Ogada, T. (1999) Sewage sludge combustion. Progress in Energy and Combustion Science, 25(1), 55–116.