CHAPTER VI
DESCRIBING SEWAGE SLUDGE PYROLYSIS KINETICS
BY A COMBINATION OF BIOMASS FRACTIONS DECOMPOSITION

6.1 Abstract

The sewage sludge is considered to be highly heterogeneous and comprising a mixture of various compounds. The characterization was performed in order to follow their compositions according to biomass fractions. The analytical method used was a sequence of ethanol-toluene extraction and digestion by hot water and sulfuric acid, achieving the fractionation of extractives, water- and acid-insoluble materials and lignin contents, respectively. Pyrolysis behavior was studied by Thermogravimetric Analysis run on original sludge and its extracted/digested residues. Typical main decomposition occurred in the range of 250-600 °C. The decomposition mechanism was more obviously elucidated when extracted and digested residues were tested. According to DTG data, the kinetic modeling was performed using a combination of four reactions, each reaction contributed by an individual compound. The apparent activation energies were found at ca. 82, 121, 64 and 121 kJ mol^{-1}. The first three values were comparable to that of biomass species decomposition, namely hemicellulose, cellulose and lignin, respectively. The first compound may be also explained by a complex protein presented in bacteria. Another reaction, however, was categorized into extractives such as lipids, waxes or oils. Instead of 1.0 as realized in biomass species, reaction order of sludge component decomposition was somewhat deviated from 1.0 (between 0.91 and 1.63). This indicated some properties of sludge constituents that deviate from natural biomass fractions. The hypothesis was also confirmed by FTIR run on original and extracted/digested sludges which indicate the closely analogy to those biomass species.

6.2 Introduction

Pyrolysis is considered as an alternative method to sewage sludge treatment as well as to convert this kind of waste to produce energy and more valuable chemical feed stocks [1]. The sludge, by nature, is highly heterogeneous and considered a mixture of various compounds, both organic and inorganic. It was though that sludge from different source would have different compositions both qualitatively and quantitatively, hence the variety in terms of the energy potential and pyrolysis properties [2-3]. However, practical design of pyrolysis process of either mixture or pure material inevitably requires an understanding in the decomposition kinetics. Overall pyrolysis behavior of the mixture was oftenly found to be a combination of it components' behavior. By the popular method to study the decomposition kinetics like thermogravimetric analysis (TGA), the calculated differential thermogravimetric (DTG) curve can be represented by a sum of the individual parent components' behavior and satisfied the following equation:

$$\left(\frac{d\alpha}{dt}\right)_{sum} = \sum_{i}^{N} c_i \left(\frac{d\alpha}{dt}\right)_i , i = 1, 2, 3 \ldots N \tag{1}$$

where $\left(d\alpha/dt\right)_{sum}$ and $\left(d\alpha/dt\right)_i$ represent weight loss rate of mixture and that of parent material; c_i represents a contribution of partial reaction to overall process (sometimes means the fraction of individual component); and N represents a number of reaction contributed by an individual component, respectively.

Number of reaction can be varied depending upon a typical number of components. For example, natural blend such as wood has three main components namely hemicellulose, cellulose and lignin. This corresponds to three reaction scheme [4-5]. The common tire is made of several rubbers such as natural rubber, styrene-butadiene rubber and butadiene rubber (with additives) and its decomposition can be modeled by a linear combination of three reactions without interaction between rubbers [6]. The number of reaction can be as high as eight reactions such as

in biomass blended with coal, three as found in wood and five unknown components in coal [5].

In the same way, since the sludge was though to be the mixture of several organics, the overall decomposition kinetics should be possibly described in the same manner. In this work, different sludges were directly fractionated according to the biomass analysis standard. The pyrolysis behaviors of the original sludge and fractionated residues were tested and correlated to possible sludge compositions. The overall decomposition kinetics was proposed to be a combination of the decompositions of each fraction.

6.3 Experimental

In previous report [3], the extensive number of sewage sludge samples was surveyed for their pyrolysis behaviors, and five types of DTG patterns were found. In this study, five different sludge samples were selected as representatives covering all those five sludge types. The detailed information was described in our previous paper [3]. The sample compositions were analyzed following series of ASTM standards, D1107 and D1106, respectively. The first standard is to extract the ethanol-toluene soluble contents. The extraction was performed for 8 hours in a Soxhlet apparatus at which the solvent was kept briskly boiling that provides with 4-6 siphoning per hour. The latter analysis is the determination of acid insoluble lignin in samples and the soluble substance was considered cellulose. The sample was initially digested by hot water (approximately 100 °C) for three hours. This step is in the same analysis standard but here separated for observation. Then, sample was digested by 72% sulfuric acid for two hours prior to diluting to 3% concentration and boiling for three hours. Overall analysis scheme was given in Figure 6.1. Abbreviations namely RS, ES, WDS and ADS referred as raw, extracted, water-digested and acid-digested sludge, respectively, are used throughout this chapter.
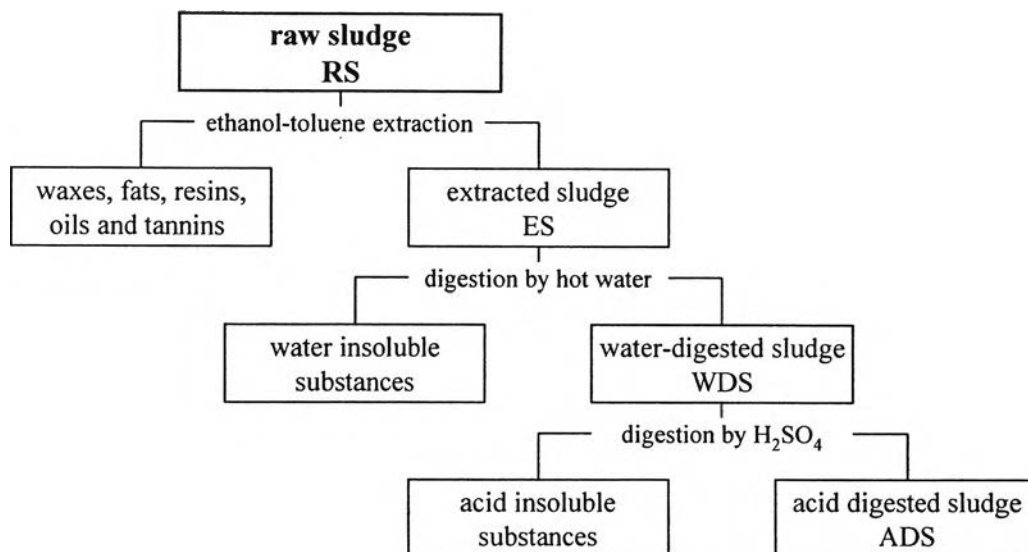
Figure 6.1 Sewage sludge analysis scheme.

Original sludge and extracted/digested residues were characterized by Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra were observed in range 500-4000 cm^{-1} using NEXUS 670 ThermoNicolet spectrometer. The standard conditions used were 32 scans (estimated 68 s), sample gain of 1, mirror velocity of 0.6329 and spectral resolution of 4 cm^{-1}. The spectra were subtracted from background daily measured on dried KBr pellet standard. The relative absorbance was considered since the sample weight was uncontrolled. Pyrolysis experiments were performed using Thermogravimetric Analysis (TGA) under nitrogen flow of 60 ml min^{-1} with heating rate of 20 °C min^{-1}. The initial sample weight was controlled approximately at 10 mg for each run. The weight loss data were observed in the range of 120 – 800 °C.

6.4 Results and Discussion

6.4.1 Sludge Characteristics

The proximate and ultimate analyses of samples used in this study as well as heating values are shown in Table 6.1. Volatile matters in sewage sludge typically are varied from 26 to 52 wt%, which corresponding to heating values of 3.4-12.2 MJ kg^{-1}. The sludge contains ash content in between 43 and 71 wt%, and

only small fraction of fixed carbon (<7 wt%). The ultimate composition of the sludge S1-S3 is comparable to that of lignocellulosic materials (roughly 47 wt% of C and O and 6 wt% of H [4]) but slightly lower oxygen and higher nitrogen contents. Properties of S4 and S5 are, however, quite different from others in the way of lowering fuel quality, low volatile matters and heating value. Since these two sludges were not of interest, further discussion of these sludges may be ignored [3].

6.4.2 FTIR Analysis

Figure 6.2 shows the IR spectra obtained from original sludges, extracted and digested residues. The functional groups of sludge content were analyzed based on the identification of FTIR spectra in Table 6.2. The functional characteristics of the sludge were qualitatively similar among the samples but different amplitude except only sludge S5. This also provides evidence of comparability between quality of the sludge and of natural lignocellulosic material components namely extractives, cellulose or lignin. Unfortunately, to distinguish these chemicals by IR spectra is not an easy task because their functionalities are quite similar. The FTIR analysis therefore can be done only based on the difference in their absorption intensities.

Table 6.1 Physical properties of sewage sludge[a]

Sample	M	Proximate analysis			Ultimate analysis					HHV
		V	A	F	C	H	N	S	O[b]	(MJ kg⁻¹)
S1	7.5	52.4	43.4	4.2	48.4	7.4	7.4	1.2	35.5	12.2
S2	3.2	50.1	43.5	6.4	46.8	7.2	7.0	2.9	36.2	12.2
S2	4.3	46.7	50.3	3.0	47.0	6.6	5.6	5.6	35.3	10.3
S4	4.2	42.1	53.9	4.0	42.5	7.3	3.9	3.5	42.7	10.2
S5	7.6	25.9	71.4	2.7	27.6	6.5	4.7	7.6	53.7	3.4

[a] M is moisture (wt%, air-dried basis); V, A and F are volatile matter, ash and fixed carbon (wt%, dry basis); C, H, N, S and O are Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen (wt%, dry and ash-free basis)
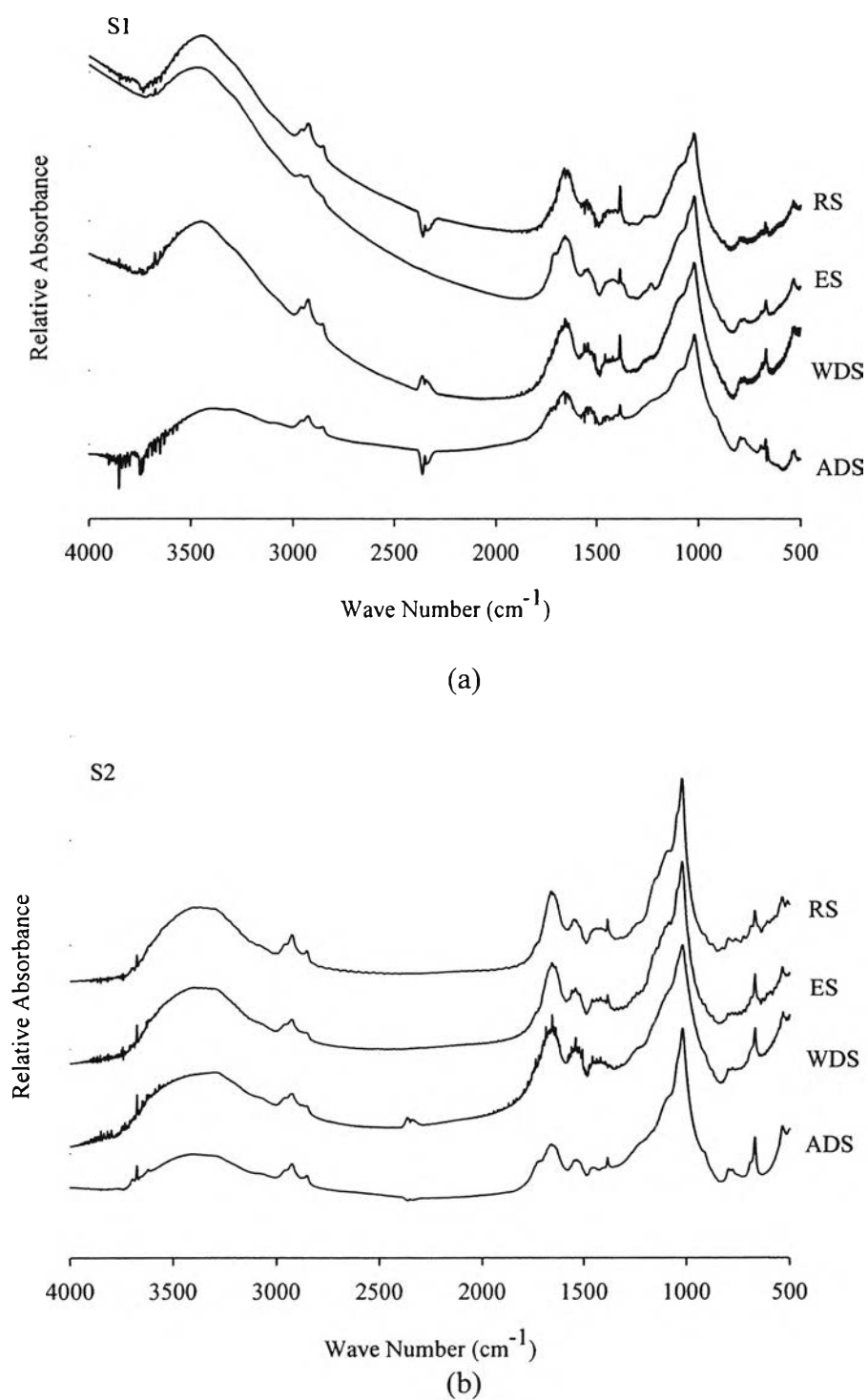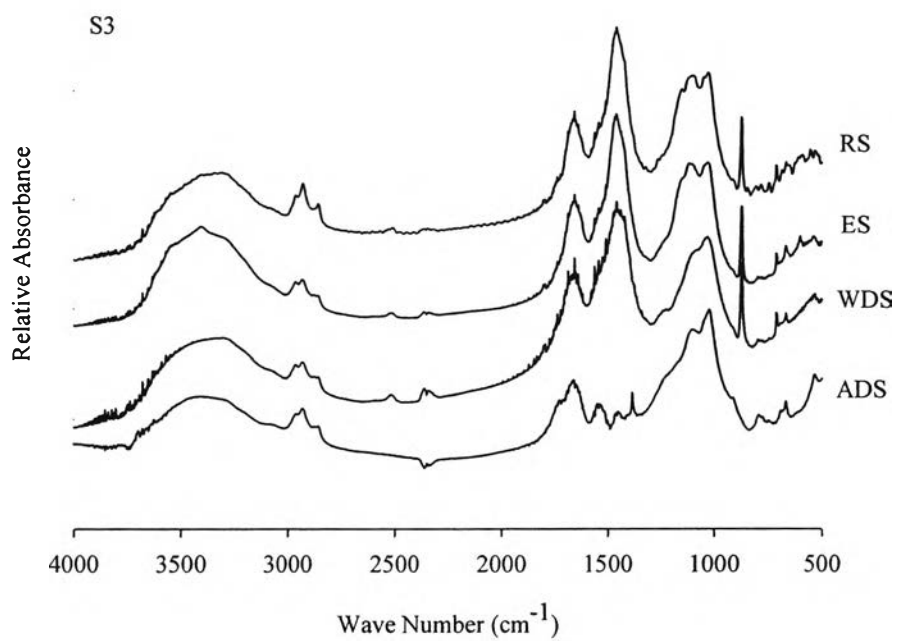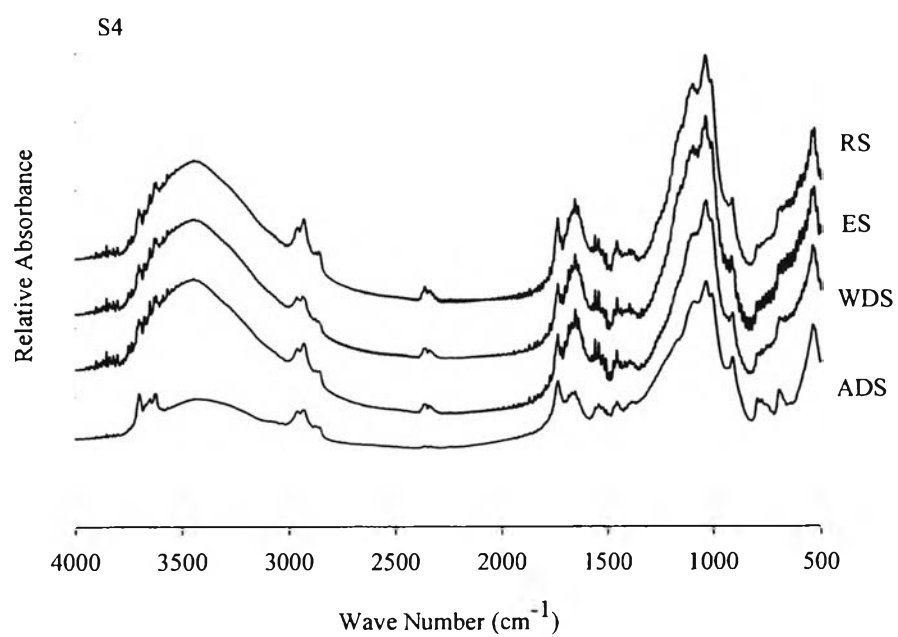
[b] calculated by mass balance

Figure 6.2 FTIR spectra on samples and their extracted, water-digested, acid-digested residues.

(c)

(d)

Figure 6.2 (cont'd) FTIR spectra on samples and their extracted, water-digested, acid-digested residues.
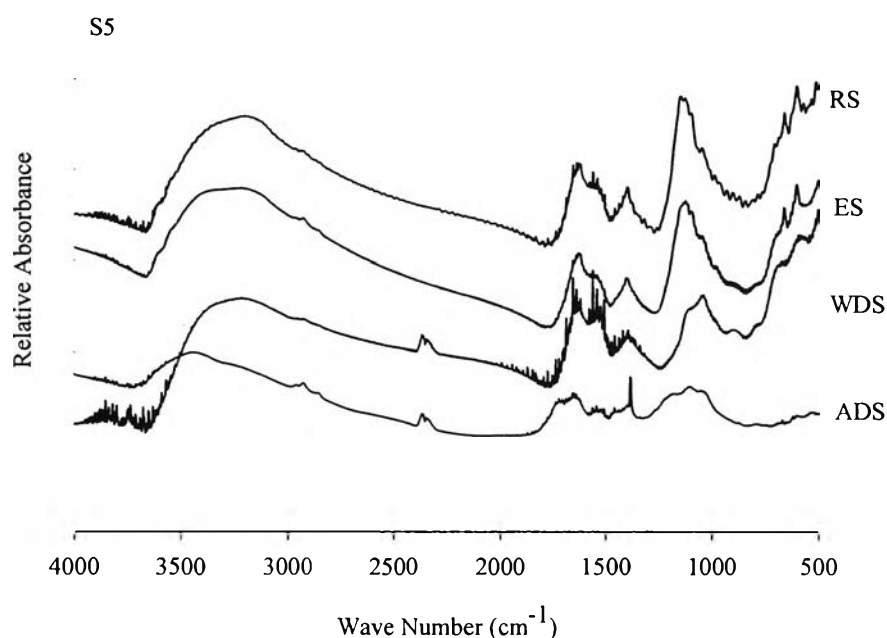
Figure 6.2 (cont'd) FTIR spectra on samples and their extracted, water-digested, acid-digested residues.

Table 6.2 The identification of IR spectra observed on sludge and extracted/digested samples [7-11]

Wave number	Functional group
Broad band 3100-3600 cm^{-1}	O-H vibration of carboxylic and alcoholic groups H-bonded N-H groups
Peaks between 2800-3000 cm^{-1}	Aliphatic C-H stretching
Peak at 1720 cm^{-1}	C=O stretching of COOH and ketonic and carbonyls
Band at 1640 cm^{-1}	C=C in aromatics structures
Band at 1300-1500 cm^{-1}	Aliphatic C-H deformation
Peak at 1400 cm^{-1}	C-H and OH of COOH
Peaks between 1000-1100 cm^{-1}	C-O stretching of carbohydrate and alcohol functions and reflect the occurrence of polysaccharides or cellulose

The lower absorption band at 2800-3000 and 1400 cm^{-1} of extracted residue indicates the loss of aliphatic carbon and carboxylic group. The standard method suggests these extractives to be waxes, fats, resins or oils. Water-digested residue has rather similar IR spectra compared to extracted residue. This might be due to the fact that the water-soluble compounds such as starch and its complex may not present in sludge. These compounds, however, do not persist for extended periods since they are readily attacked by soil microbes and utilized for energy or synthesis purposes [12]. The presence of these compounds may relate to the extended period of the sludge processing. The remaining strong band at 1030 cm^{-1} and a broad band centered at 3400 cm^{-1} contributing to C-O bonding and OH group were supposed to be cellulose structure belonging. These groups are significantly loss in acid digestion step, which also indicated in the standard. The remaining weak band at 1590-1700 cm^{-1} contributing aromatic carbon vibration indicates the unique lignin characteristic [10].

Although it was not intended, inorganic substances were possibly washed by a strong acid [13]. In the case of the sludge, inorganic content was possibly leached out. This makes several inorganic absorption bands disappear for acid digestion residue. This effect was pronounced especially for sludge S3 and S5.

6.4.3 Thermal Decomposition

The weight loss (TG curve) and derivative weight loss (DTG curve) for all five samples as well as their extracted and digested residues are exhibited in Figure 6.3. For most original sludges, first decomposition state is at slightly higher than 100 °C, which corresponds to vaporization of moisture and do not involve pyrolysis. The major weight loss occur in range of 250-600 °C, with maximum weight loss at approximately 300 °C for S1-S3, 450 °C for S4 and 250 and 400 °C (two peaks with the same amplitude) for S5. The weight loss at higher temperature (>700 °C) was observed as the degradation of inorganic content such as calcium carbonate [14]. The similar DTG characteristics were also found in the literature except for S4 and S5 that only found in our study [14-17]. However, the decomposition mechanism was more obviously elucidated when extraction and digestion residues were tested.

Visual observations from the TG-DTG of original and extracted/digested sludges, the fractions of sludge are generally disappeared. For S1-S3, the sludges seem to generate at least three decomposition peaks or shoulders (approximately 300, 350 and 450 °C). The DTG peaks at 300 and 450 °C of extracted sludge are lower than the original ones especially for sludge S2. It seems that the DTG peaks at 300 and 350 of sludge S1 and S3 are slightly lower after extraction but overall pattern looks the same. This may not be a change in reaction mechanism but a lowering reactivity. The water-digestion does not create a significant change in DTG profile of all samples. The acid-digested residue is highly different from original sludge. The DTG peak at 300 °C is obviously lower for S1-S4. For only sludge S5, overall decomposition can be separated to two steps as DTG peaks presented at approximately 250 and 400 °C. There is no significant difference in DTG profile was observed between original, extracted and water-digested sludge S5. After acid-digestion, the peak at 450 °C was completely disappeared.

As mentioned, there is a possibility of washing inorganic content by a strong acid. As a result, the disappearance of DTG peak in accordance with the degradation of inorganic at high temperature was observed. This was especially found in sludge S3 at which the DTG peak at >700 °C was disappeared. Furthermore, it is possible that other inorganics was also leached even though they may not present DTG peak in the experimental condition. Mathematically, several DTG peaks (other than inorganic decomposition) of the acid-washed sludge were substantially higher. This can be observed especially in case of sludges S3, S4 and S5.
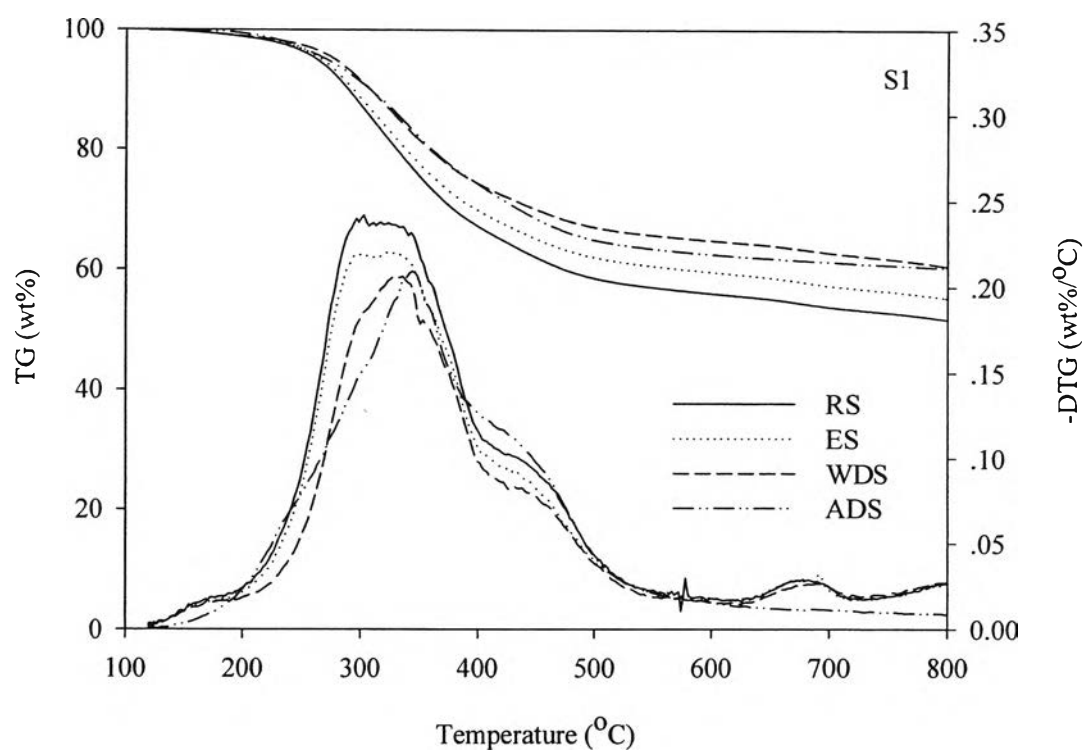
(a)
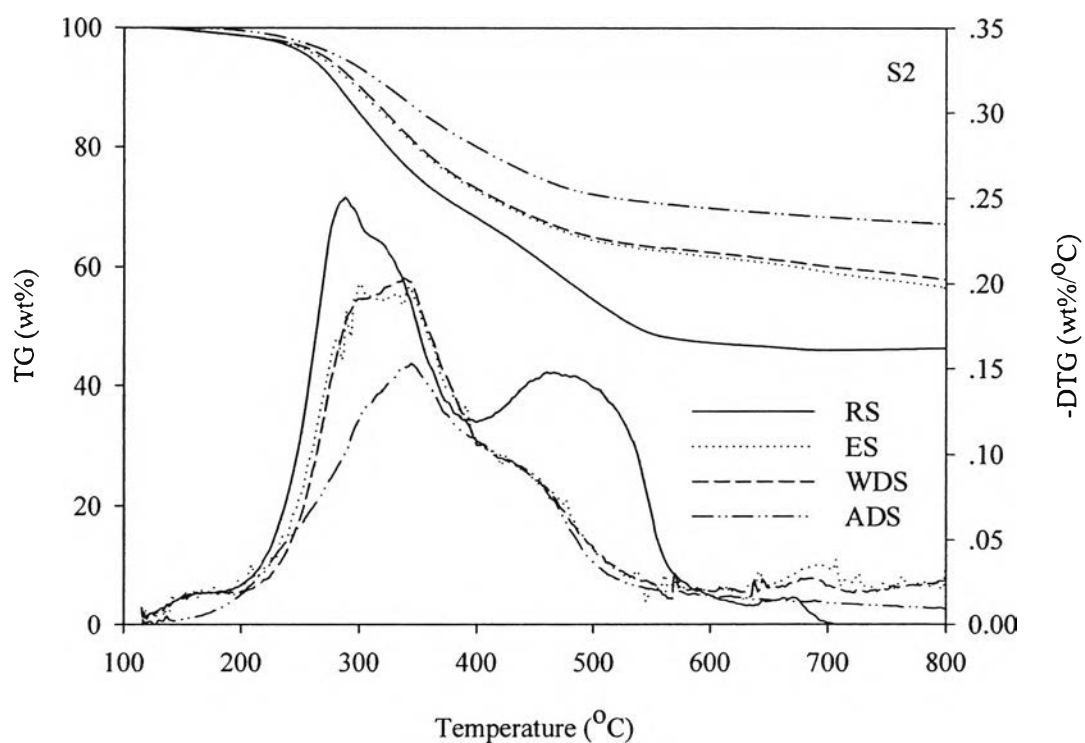
(b)

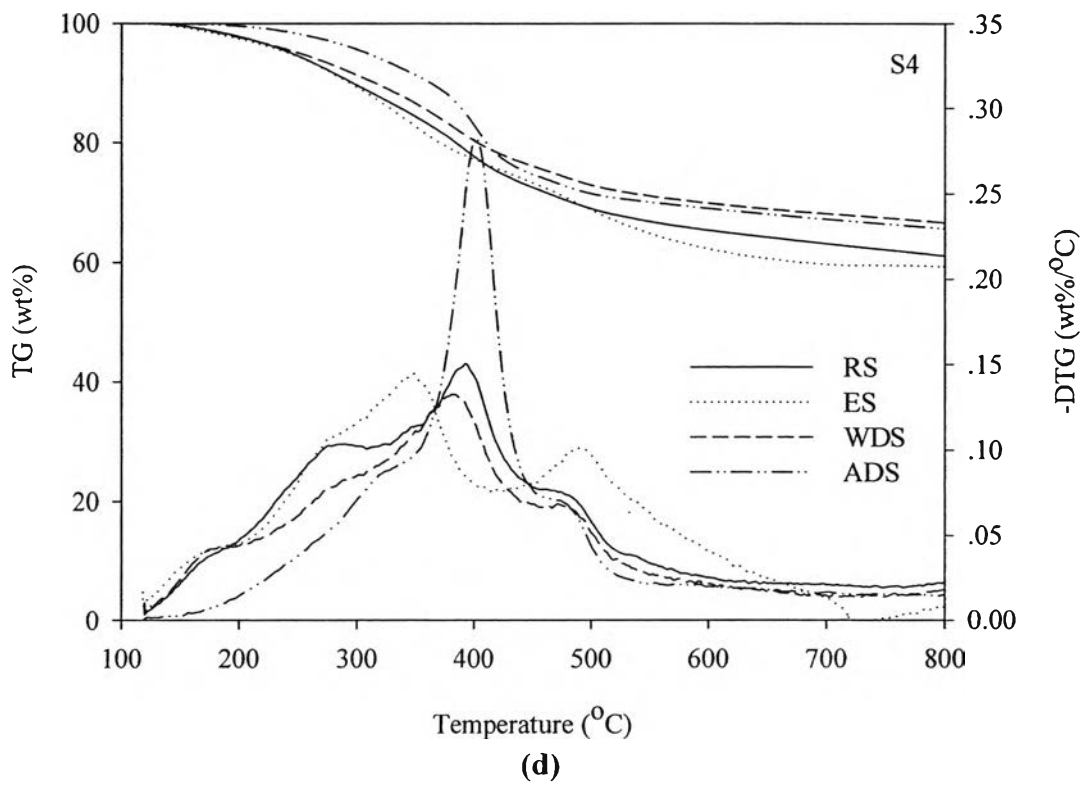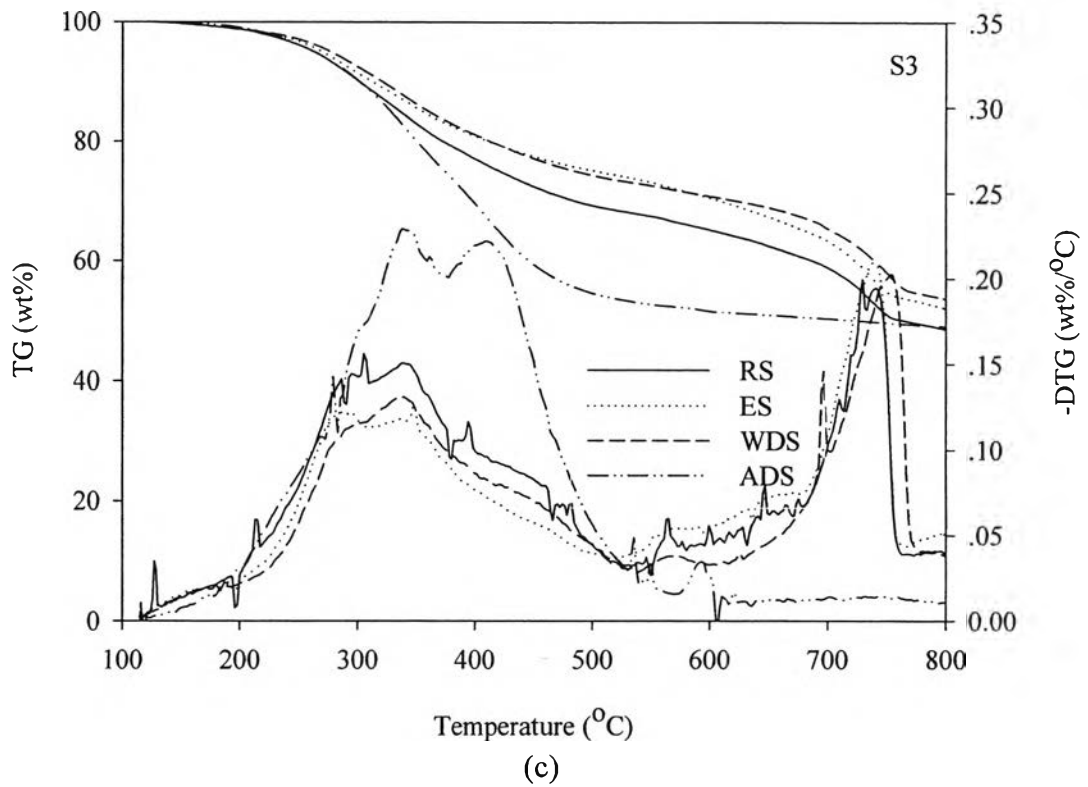**Figure 6.3** TG-DTG analyses of five different sewage sludge samples.

(c)

(d)

Figure 6.3 (cont'd) TG-DTG analyses of five different sewage sludge samples.
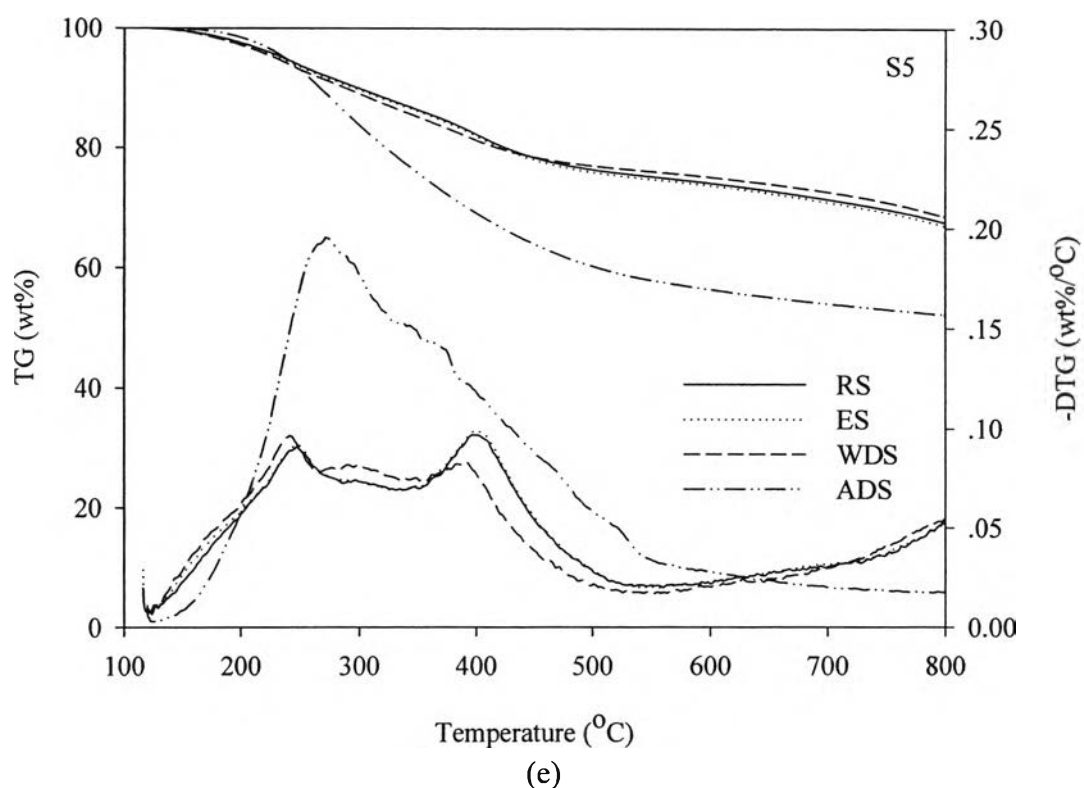
Figure 6.3 (cont'd) TG-DTG analyses of five different sewage sludge samples.

6.4.4 Kinetic Studies

In general, the kinetic evaluation of biomass decomposition is normally approached by the independent parallel, first-order reaction model. The overall rate equation can be described as Eq. (1). This well-known model is currently considered realistic for most biomass species and the detail can be mostly found in literature [4-5, 18]. However, for the sewage sludge, an individual decomposition reaction here was modeled according to nth-order of reaction scheme in order to observe the possible deviation of reaction order from value of 1.0 if there is any. The detailed descriptions of the model and numerical treatment method were described elsewhere [6].

It is the fact that the better fit can be obtained by using more reaction number. To optimize number of reaction, two indicators, an objective function (OF) and coefficient of determination (r^2), were considered coupled with visual assessments of DTG plots. OF was defined as a sum of squared error between experimental and calculated DTG data points. The selection criteria used was a

minimum reaction number that give a reasonable fit between experimental and predicted DTG curves.

Here, sludge S2 and its residues were selected as an example. The overall decomposition of the sewage sludge was found to be a combination of four reactions in parallel (excluding water vaporization). The apparent kinetic parameters and the comparison between calculated and experimental DTG curves were shown in Table 6.3 and Figure 6.4, respectively. The calculated DTG curve is in agreement with the experimental data as indicated by very low OF and high r^2. However, most part of the predicted curve is lower than experimental. This indicated that the model, although acceptable, is not very good.

For sludge S2, the order of pyrolysis reaction was found in range of 0.91-1.63. The average activation energy of pyrolysis reaction was ca. 82±4.3, 121±0.6, 64±4.2 and 121 kJ mol^{-1} for reaction one to four, respectively. According to Eq. (1), one may say that the value c represents the weight fraction of the corresponding compound. However, considered the mathematical analysis method used in this study, regression analysis, the parameters were allowed to vary arbitrarily until the objective function was satisfied. The values of c and pre-exponential factor may not independent. Therefore, it may not be very good to conclude that c represented the weight fraction in our case. One should take very good care in an interpretation the value of c.

Table 6.3 The apparent kinetic parameters of sludge S2 and its extracted/digested residues achieved by four parallel reaction scheme [a]

| Reaction	Kinetic parameter	Sample			
		RS	ES	WDS	ADS
1st	c	0.16	0.08	0.07	0.04
	ln A [b]	25.7	23.7	23.7	20.7
	E (kJ mol^{-1})	91.9	82.6	82.5	71.0
	n	1.03	1.20	1.18	1.23
2nd	c	0.15	0.11	0.10	
	ln A [b]	29.7	29.3	29.3	
	E (kJ mol^{-1})	119.4	121.1	121.1	
	n	1.53	1.63	1.60	
3th	c	0.18	0.06	0.06	0.04
	ln A [b]	18.1	15.7	15.7	15.7
	E (kJ mol^{-1})	76.4	60.1	60.0	58.9
	n	1.04	0.92	0.95	0.91
4rd	c	0.41			
	ln A [b]	22.8			
	E (kJ mol^{-1})	120.6			
	n	0.92			
	OF [c]	0.3720	0.1193	0.1129	0.2800
	r^2	0.9853	0.9892	0.9862	0.9860

[a] RS, ES, WDS and ADS refer to raw, extracted, water-digest and acid-digested sludge, respectively.

[b] Unit of pre-exponential factor, is depended upon the order of reaction, n.

[c] OF refers to an objective function.
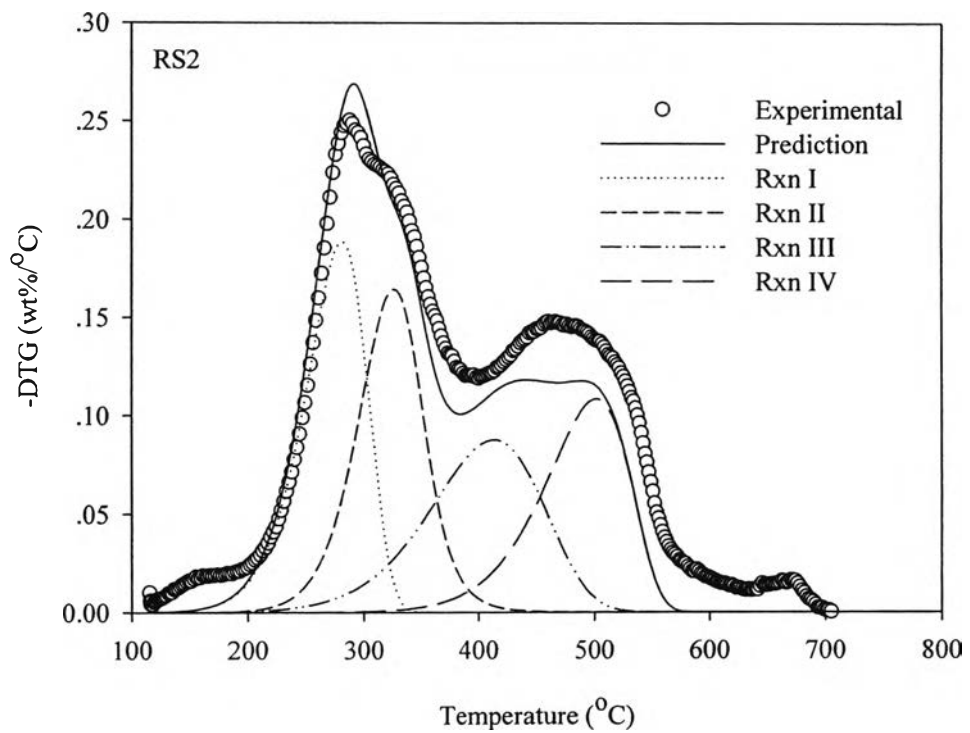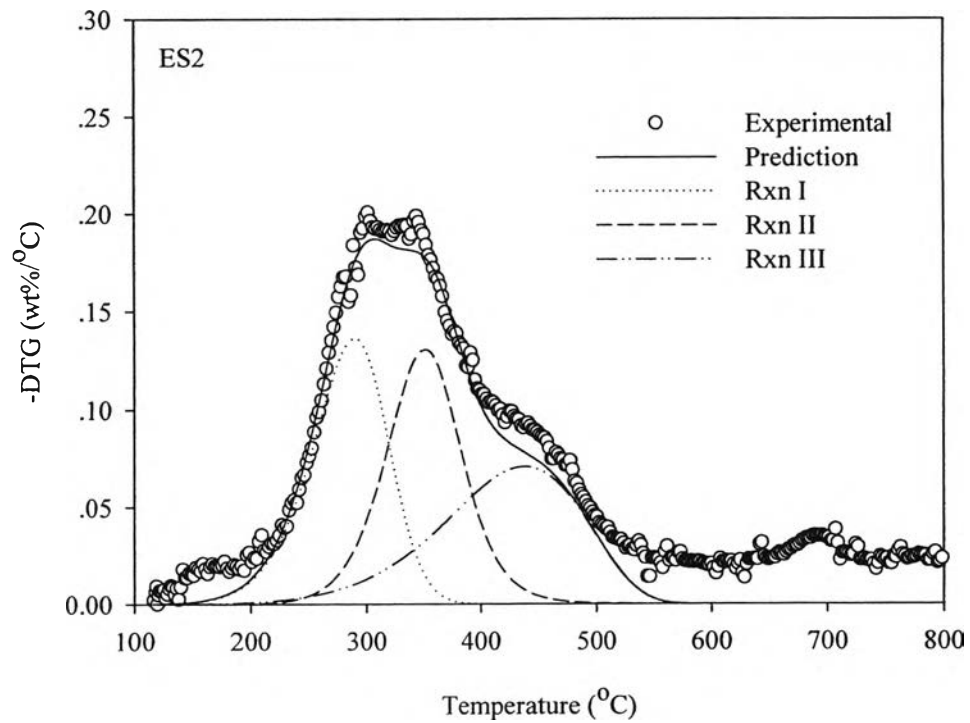
Figure 6.4 A comparison between experimental and predicted DTGs of sludge S2 and its extracted, water-digested and acid-digested residues.
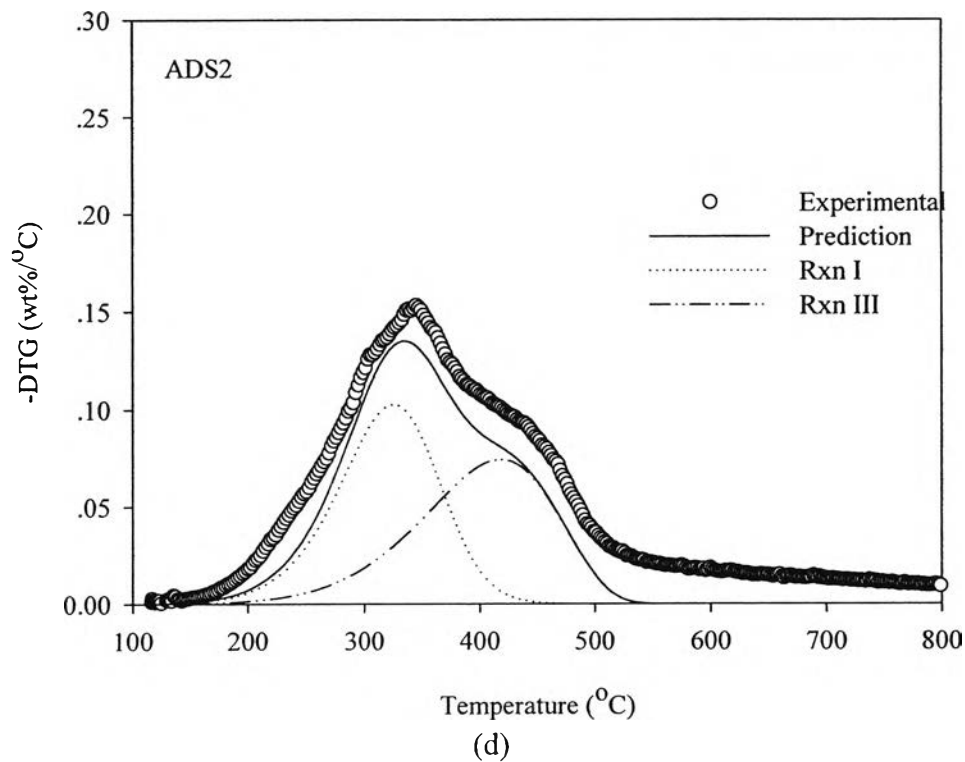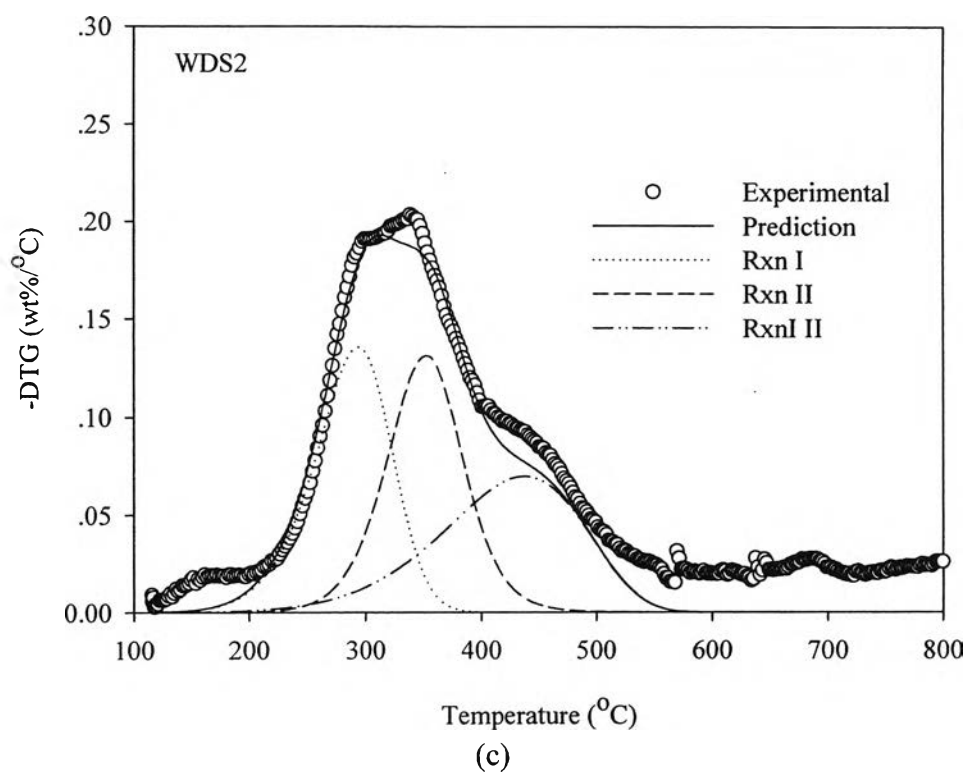
(c)

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Figure 6.4 (cont'd) A comparison between experimental and predicted DTGs of sludge S2 and its extracted, water-digested and acid-digested residues.

By varying heating rate at 5, 10 and 20 °C/min, the results did not show a significant change in DTG pattern for all samples [3]. Also, the apparent kinetics parameters were not significantly deviated from those reported in Table 6.3. The standard error of individual parameter was within 7%, while that of r^2 was even less than 1%.

The similar manner and closed kinetic parameters were found for other samples except S5. According to the very low fuel quality that was not of interest, analysis of sludge S5 may be ignored. The activation energies of other samples pyrolysis were found in range of 81-90, 115-250, 57-61 and 125-148 kJ mol^{-1} for reaction one to four, respectively. Meanwhile, the order of reactions was found in narrow range between 0.89 and 1.55.

Considered between the apparent kinetic parameters achieved in this study and reported ones for biomass species from literature; it is possible to compare the first three compounds to the hemicellulose, cellulose and lignin, respectively. The activation energy reported in literature for those compounds decomposition reactions were in ranges of 82-156, 124-284 and 19-65 kJ mol^{-1}, respectively [4-5]. The varieties of activation energies of these material decompositions, however, depend upon several factors such as the type of wood and particle size [5]. These values should be comparable to values of 82, 121 and 64 kJ mol^{-1} for first three reactions, respectively.

It is the fact that carbohydrates such as cellulose and hemicellulose are normally dissolved in a strong acid. However, the first compound was still remaining after acid digestion (Figure 6.4d). This compound is thought to be protein presented in a complex form, which indeed tolerate in acid solution. The presence of the dead bacteria in the sludge was proposed by some authors [19-20]. The bacteria cell wall was chemically composed of complex polysaccharide, consisting of sugars and peptides [21]. This wall complex makes bacteria tolerate in a savior environment. Inner cell may be composed of other compounds such as carbohydrate and fats. The carbohydrate and fats may be categorized into cellulose and extractive species, respectively. In conclusion, since it is not easy to identify the exact compound, our first reaction was proposed as decomposition of protein according to the dead cell. The decomposition of protein can be demonstrated by study of meat

and bone meal pyrolysis. The decomposition temperature of this material is in range of 300-400 °C [22-23]. This also corresponds to our result at which the first compound was decomposed in the same temperature range. The presence of protein constituent was also confirmed by the presence of remaining N-H spectra at 3100-3600 cm^{-1} in Figure 6.2.

The fourth compound was categorized into ethanol-toluene extractives such as lipids waxes, oils etc. as indicated by the standard. This compound is hardly comparable to the material found in literature. The data are rarely available and more studies may be needed. The fourth compound was, however, obviously presented in only sludge S2, while rarely found in other samples.

All reaction orders were found somewhat deviating from a unity. This may be explained in several ways including natures of sludge components that slightly deviate from natural biomass species, interaction between sludge components, many compounds inside the fraction or even mathematical errors.

Such analogy study in this paper was done based upon TGA data, apparent kinetic parameters achieved from the TG-DTG analysis and FTIR run on samples only. The proposed compounds were probably not the exactly biomass species, but at least have closed properties.

6.5 Conclusions

The three evidences, TG-DTG analysis, FTIR spectroscopy and kinetic study, were proved to elucidate the sewage sludge pyrolysis by four decomposition reactions, each possibly contributed from an individual compound. The apparent activation energies of sewage sludge constituent decomposition reactions were ca. 82, 121, 64 and 121 kJ mol^{-1}. First three were comparable to those of biomass species such as hemicellulose, cellulose and lignin. The first compound was also possibly explained by complex protein presented in bacteria. The remaining reaction, however, was probably contributed by extractive compound such as lipids, waxes and oil or even unknown. The reaction orders were found in between 0.91-1.63, indicating the nature of sludge that somewhat deviated from biomass species. The results also showed the closely analogy between DTG curve of individual sludge

constituents and those of biomass species. The FTIR spectra of raw sludge and extracted/digested residues also confirmed this proposal. The biomass species including the complex protein of bacteria cell wall might be based compositions of sewage sludge, which effluent to its pyrolysis property.

6.6 Acknowledgements

6.7 References

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