CHAPTER IV

PREDICTING THE HEATING VALUE OF SEWAGE SLUDGES IN THAILAND FROM PROXIMATE AND ULTIMATE ANALYSES

4.1 Abstract

There have been various methods used for determining a heating value of solid fuel such as coal, biomass and municipal solid waste (MSW) either by experiment using a bomb calorimeter or by modeling based on its compositions. This work proposes another aspect in developing models to predict the heating value of sewage sludge from its proximate and ultimate analyses data. The extensive number of samples was collected from different wastewater treatment plants in Bangkok and in the vicinity and was then analyzed for their heating values, proximate and ultimate analyses. Based upon proximate and ultimate analyses, the heating value models were proposed. The best results show coefficients of determination (R^2) of 0.899 and 0.905 for the models based on the proximate and ultimate analyses, respectively. The heating values examined from the models were in good agreement with that attained by experiment. The application of the created models was appreciable for the sewage sludge with ash content up to 50% (db).

4.2 Introduction

The concept of converting waste to energy has drawn a lot of attention from the community. It has been demonstrated that wastes such as municipal solid waste (MSW), plastics, agricultural waste and sewage sludge can be transformed to energy or valuable chemicals. It is normally achieved by several routes including bioconversion, incineration or thermochemical conversion processes [1, 2].

It has been reported that the amount of sewage sludge generated from wastewater treatment plants seems to increase proportionally with the industrial development in most countries [1–3]. It normally contains undesirable components such as organic, inorganic, toxic substances as well as pathogenic or disease-caused microorganisms.

Traditionally, it was disposed by depositing in the ground, utilization in agricultural works, dumping into the sea and incineration. With the future of disposal through the first three methods facing a ban, a growing interest is now being directed towards incineration and other thermal sludge disposal processes [3]. These methods are found to benefit the concept of waste-to-energy. For such thermal applications, what a crucial property of material has to be met is its energy content or heating value. It is used, as the priority, for evaluating the potential of sewage sludge.

The heating value of materials, even solid, liquid or gas, can be determined experimentally by a bomb calorimeter or calculated from their compositions or some properties using a mathematical model. There have been many models proposed for predicting heating value of many types of materials with various compositions [4–18]. Nonetheless, there have been only few works contributed to sewage sludge. The objective of this study was to develop correlations between heating value and sewage sludge characteristics (proximate or ultimate analysis) for sewage sludges produced in Thailand.

4.3 Literature Review

Regarding the empirical approaches, there are three types of models that are normally used to predict heating values based on the following analyses [10]:

- Physical or chemical compositions
- Proximate analysis
- Ultimate analysis

The first two analyses are common when dealing with MSW and lignocellulosic materials or biomass while models based on ultimate analysis have been derived mostly for coals and liquid fuels [13]. The physical or chemical composition analysis is based on the level of different components of the solid matrix, for instance plastics, paper and garbage in MSW or lignin, cellulose and hemicellulose in biomass, etc. The proximate analysis typically involves determination of moisture, volatile matter, fixed carbon and ash contents whereas the ultimate analysis includes an assessment of the levels of carbon, hydrogen, oxygen, nitrogen and sulfur contents.

For most models, from simple to complex forms, a combination of proximate or ultimate analysis data is generally considered. Table 4.1 summarizes the practical model patterns used to predict the energy content of materials namely MSW, coal, refuse and biomass [4–8, 10, 13–17]. The expressions may have either variable or fixed constants. For the former type, they were simply assumed to be the result of a linear combination of variables with a set of constants, i.e. Eqs. (4.1)–(4.23). The method of regression analysis is generally used to accomplish the most suitable values of these constants. All constants in the equations may change arbitrarily resulted from the regression analysis. They may vary upon the kind or original source of materials. For the latter type, Eqs. (4.35)–(4.39) were derived using thermochemical concept. The total heating value was determined from heat released by the combustion reactions in correspondence to the amount of each component [17]. The equations are generally preferable for particular materials such as MSW and coal [4, 5, 7, 14, 16, 17]. It is also possible to use combined forms of those two types of equations, Eqs. (4.24)–(4.34). More detailed explanations on the basic assumptions for each expression were described elsewhere [4–8, 10, 13–17]. To select an appropriate form of heating value model equation, the error, simplicity, liability or even versatility were considered.

Other than those compositions, there are some heating value models based on other properties of the materials e.g. sponification and iodine values for predicting the heating value of oils, density and viscosity for predicting the heating value of liquid fuels [9, 11, 12, 18].

In this work, only models based on the proximate and ultimate analyses were focused. The model equations presented in Table 4.1 were analyzed with the aim to find the most appropriate form of equation for predicting heating value of sewage sludge.

Table 4.1 Summary of models used for predicting the heating value of various types of materials based on their proximate and ultimate analyses

No.	Equation*	Application	Unit	Basis**	original
Eq (4.1)	$HHV = a - bM$	Refuse	kJ/kg	adb.	
Eq (4.2)	$HHV = aF + b$	Biomass	kJ/kg	db.	
Eq (4.3)	$HHV = aV + b$	MSW	kJ/kg	db.	
Eq (4.4)	$HHV = aV + bF$	Coal/refuse	kJ/kg	daf.	Goutal
Eq (4.5)	$HHV = aV + bF$	Biomass	kJ/kg	db.	
Eq (4.6)	$HHV = a(V + F) + b$	Biomass	kJ/kg	db.	Jimenez
Eq (4.7)	$HHV = aV + bF + c$	MSW	kJ/kg	db.	
Eq (4.8)	$HHV = aV - bM$	Refuse	kJ/kg	adb.	Liu
Eq (4.9)	$HHV = aV - bM + c$	Refuse	kJ/kg	adb.	Bento
Eq (4.10)	$HHV = a(V + F) - bM$	MSW	kJ/kg	adb.	
Eq (4.11)	$HHV = a(V + F) - bM + c$	Refuse	kJ/kg	adb.	Bento
Eq (4.12)	$HHV = aV + bF - cM$	MSW	kJ/kg	adb.	
Eq (4.13)	$HHV = aV + bF - cM + d$	MSW	kJ/kg	adb.	

* *HHV* = higher heating value, a, b, c, ... = arbitrary constants, V = volatile matter, F = fixed carbon, M = moisture, C = carbon content, H = hydrogen content, N = nitrogen content, S = sulfur content, O = oxygen content, A = ash content

** adb. = air-dried basis, db. = dry basis, daf. = dry and ash-free basis

Table 4.1 (cont'd) Summary of models used for predicting the heating value of various types of materials based on their proximate and ultimate analyses

No.	Equation*	Application	Unit	Basis**	original
Eq (4.14)	$HHV = aC + b$	Biomass	kJ/kg	db.	Tillman
Eq (4.15)	$HHV = aC + bH + cO$	Biomass	kJ/kg	db.	Ruyter
Eq (4.16)	$HHV = aC + bH + cO + dS$	Coal/refuse	kJ/kg	db.	Mott & Spooner
Eq (4.17)	$HHV = aC + bH + cO + d$	Biomass/refuse	kJ/kg	db.	Jenkins
Eq (4.18)	$HHV = aC + bH + cO + dN + e$	MSW	kJ/kg	db.	
Eq (4.19)	$HHV = aC + bH + cN + dS + eO + f$	Biomass	kJ/kg	db.	Francis
Eq (4.20)	$HHV = aC + bH + cS + dO + eN + fA + g$	Coal	kJ/kg	db.	
Eq (4.21)	$HHV = aC + bH + cS + dO + eN + fA$	Coal	kJ/kg	db.	
Eq (4.22)	$HHV = aC + bH + cS + d(O + N) + eA + f$	Coal	kJ/kg	db.	
Eq (4.23)	$HHV = aC + bH + cS + d(O + N) + eA$	Coal/refuse	kJ/kg	db.	
Eq (4.24)	$HHV = aC + bH + c(O2/(1 - A/100)) + d(1 - A/100)$	Coal	kJ/kg	db.	
Eq (4.25)	$HHV = aC + bH + cO + d(O2/(1 - A/100)) + eS$	Coal	kJ/kg	db.	
Eq (4.26)	$HHV = a[C/H] + b(O + N) + cA$	Coal	kJ/kg	db.	
Eq (4.27)	$HHV = 328C + 1{,}419H + 92.8S$	Coal	kJ/kg	db.	
Eq (4.28)	$HHV = 328C + 1{,}419H + 92.8S - a(O + N) + bA + c$	Coal	kJ/kg	db.	

Table 4.1 (cont'd) Summary of models used for predicting the heating value of various types of materials based on their proximate and ultimate analyses

No.	Equation*	Application	Unit	Basis**	Original
Eq (4.29)	$HHV = a(328C + 1{,}419H + 92.8S) + b(O + N) + cA$	Coal	kJ/kg	db.	
Eq (4.30)	$HHV = a(328C + 1{,}419H) + 92.8S - 23.8N + bO + cA$	Coal	kJ/kg	db.	
Eq (4.31)	$HHV = [a(H/(1 - A/100)) + b]\ [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	
Eq (4.32)	$HHV = [a(O/(1 - A/100)) + b]\ [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	
Eq (4.33)	$HHV = [a(C/(1 - A/100)) + b]\ [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	
Eq (4.34)	$HHV = [a(C/(1 - A/100)) + b(H/(1 - A/100))$ $+ c((O + N)/(1 - A/100)) + d(S/(1 - A/100)) + e]$ $[C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	
Eq (4.35)	$HHV = [33.5C + 142.3H - 15.4O - 14.5N] \times 10\text{-}2$	Biomass	MJ/kg	daf.	
Eq (4.36)	$HHV = 81C + 342.5(H - O/8) + 22.5S$	Coal/MSW	kcal/kg	daf.	Dulong
Eq (4.37)	$HHV = 81(C - 3O/8) + 171O/8 + 342.5(H - O/16) + 25S$	Coal/MSW	kcal/kg	daf.	Steuer
Eq (4.38)	$HHV = 81(C - 3O/8) + 342.5H + 22.55S + 171O/4$	Coal/MSW	kcal/kg	daf.	Scheurer-Kestner
Eq (4.39)	$HHV = 370.8C + 1{,}112.4H - 139.1O + 317.8N + 139.1S$	MSW	kJ/kg	db.	

4.4 Materials and Methods

4.4.1 Sample Preparation

Sewage sludge samples used in this study were collected from 20 different wastewater treatment plants (WWTPs) in Bangkok and vicinity in accordance with the standard method, ASTM D346-90. The sample sources include municipal, hospital and industrial WWTPs. The sample collection was carried out monthly over a 2-year period. The total number of collected samples exceeded 219 samples. The samples were naturally dried under sunlight for 1–2 days prior to characterization.

4.4.2 Sample Characterization

Sewage sludge characteristics were analyzed according to ASTM D3172-89. This technique provides proximate analysis of the sludge, namely moisture, volatile matter, fixed carbon and ash contents. Ultimate analysis, ASTM D3176-89, was also done for all samples providing weight percentage of carbon, hydrogen, nitrogen, sulfur and oxygen (by subtraction) elements. The heating values of samples used were attained in accordance with ASTM D2015.

4.4.3 Heating Value Models

Model patterns listed in Table 4.1 were fit with the experimental data by regression analysis using all sample data points. The method of least square, minimizing the error squared, was used to evaluate the adjustable parameters for each expression [19]. To select the most appropriate correlation, the coefficient of determination (R^2) was mainly considered.

Models with the highest R^2 were used to calculate the heating value and compared with the data obtained from the experiments. The validation of the selected models was observed by an error analysis. The absolute and bias errors were considered. These quantities are defined as:

$$\%\text{absolute error} = \left|\frac{HHV_c - HHV}{HHV}\right| \times 100\%$$

$$\%\text{bias error} = \left(\frac{HHV_c - HHV}{HHV}\right) \times 100\%$$

where HHV_c and HHV are heating values of each data point from calculation and experiment, respectively. Furthermore, the validity of the models was also confirmed by applying to other sludge.

4.5 Results and Discussion

4.5.1 Sewage Sludge Characteristics

Table 4.2 shows the averages of sample characteristics comparing among different sources. The results show a wide range of the sewage sludge characteristics. The compositions of sewage sludge are mainly volatile matter and ash contents with the averages of 42.4 and 53.2%and can be as high as 60.2 and 80.3%, respectively. However, the sewage sludge contains only a small amount of fixed carbon, maximum 11.8%. The characteristics of the community sludge seem to cover an entire possible range. For example, their heating values are from less than 4 MJ/kg to as high as almost 14 MJ/kg. However, those of hospital and industrial sludge samples are between the average values to that on the high side. The characteristics of some other sludge samples were also collected from the literatures for comparison and given in Table 4.3. It was observed that the heating values of the samples in this study are lower than those reported in literatures corresponding to the lower volatile matter and higher ash content.

Simple correlations between the heating value of the samples and its proximate and ultimate analyses data were also investigated using plots exhibited in Figs. 4.1 and 4.2.

Table 4.2 Characteristics of sewage sludge from different sources (average for each source) *

ID**	M	Proximate Analysis			Ultimate Analysis				Ratio		HHV MJ/kg
		V	A	F	C	H	N	S	C/H	C/O	
C1	6.1	53.0	38.4	8.6	31.1	4.2	3.3	1.1	7.45	1.31	13.9
C2	5.1	51.2	42.0	6.7	27.5	4.1	4.0	1.1	6.72	1.18	13.2
C3	5.4	50.0	43.0	7.0	26.4	4.1	4.3	0.9	6.46	1.13	12.6
C4	6.4	47.6	48.4	4.0	23.9	3.9	3.8	1.3	6.08	1.10	11.0
C5	3.7	42.2	51.8	6.0	20.9	3.4	3.3	0.9	6.20	0.97	10.1
C6	4.1	34.5	61.8	3.7	18.0	2.9	2.3	0.8	6.21	1.08	9.4
C7	3.4	39.0	56.0	5.0	19.5	3.2	3.1	0.8	6.13	1.03	8.7
C8	3.9	33.3	63.5	3.2	14.5	2.6	2.6	1.2	5.51	0.82	6.9
C9	3.7	32.9	64.0	3.1	15.3	2.5	2.3	0.5	6.05	0.87	6.5
C10	3.2	30.6	67.6	1.8	12.7	2.0	1.8	0.6	6.34	0.74	5.7
C11	4.4	24.8	72.9	2.2	10.6	2.0	1.6	0.4	5.38	0.69	4.3
C12	8.9	23.4	74.2	2.4	9.0	2.2	1.5	1.6	4.06	0.50	3.5
H1	6.6	55.5	39.4	5.1	26.7	4.0	4.3	0.7	6.60	1.01	13.3
H2	5.6	52.6	40.6	6.8	29.6	4.6	5.0	1.0	6.52	1.60	12.8
H3	4.6	47.7	45.9	6.5	25.5	3.9	4.2	1.0	6.61	1.19	12.4
H4	6.9	50.4	45.7	3.9	25.0	3.8	3.7	0.8	6.62	1.04	11.1
H5	4.6	36.6	60.2	3.2	19.0	3.0	2.7	1.2	6.42	1.21	8.2
I1	5.2	54.5	42.3	3.2	25.1	4.0	3.8	0.9	6.29	0.97	10.9
I2	5.0	45.6	51.6	2.8	22.6	3.2	2.9	2.0	7.01	1.13	9.9
I3	4.7	38.2	58.8	3.0	18.3	3.4	1.8	1.8	5.36	1.00	9.0

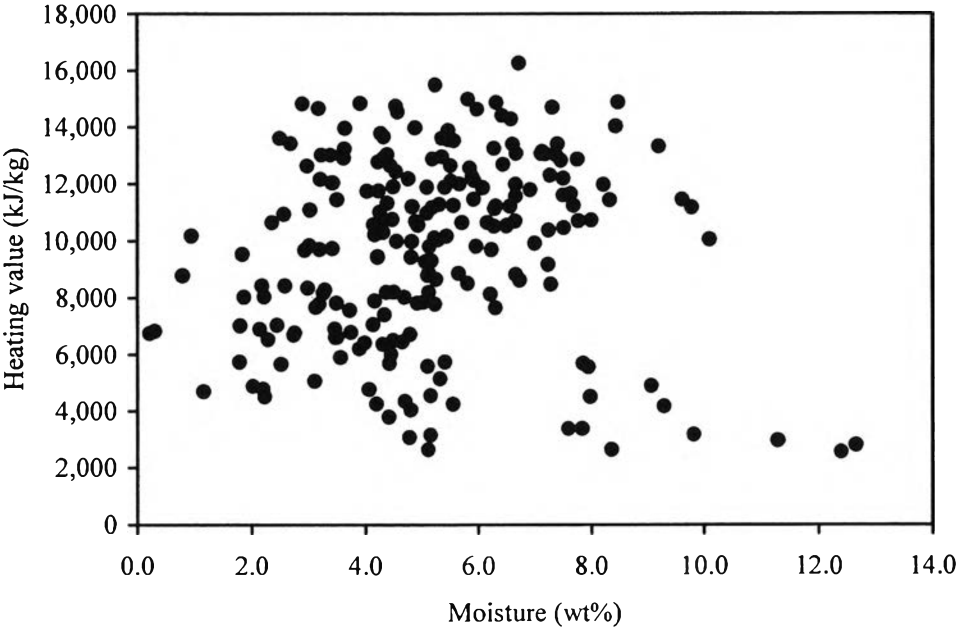
* reported in wt% dry basis except moisture in air-dried basis

** C, H and I indicated community, hospital and industrial sludges, respectively

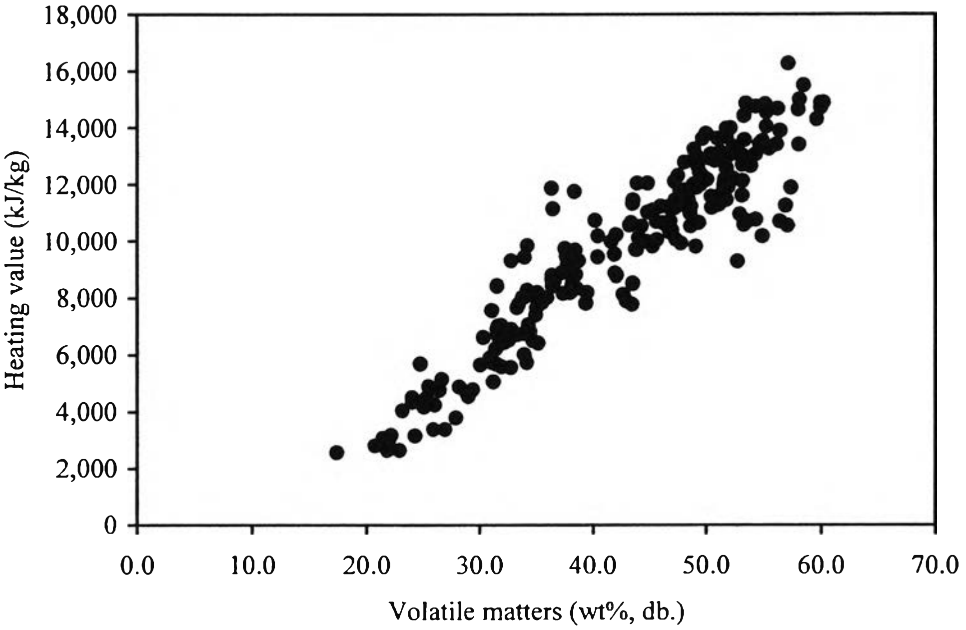
Table 4.3 Characteristics of some other sludge samples collected from literatures [2, 20-24]*

ID	M	Proximate Analysis			Ultimate Analysis				Ratio		HHV
		V	A	F	C	H	N	S	C/H	C/O	MJ/kg
S1	5.2	60.7	29.5	9.8	35.7	5.2	3.5	0.7	6.87	1.41	16.6
S2	5.0	72.5	16.0	11.5	45.9	6.3	5.1	0.6	7.29	1.71	20.9
S3	11.8	60.6	26.6	12.8	39.5	6.2	3.9	1.5	6.38	1.55	17.1
S4	4.3	59.3	31.0	9.7	38.1	5.2	4.5	0.9	7.33	1.88	16.8
S5	3.9	58.5	30.8	10.7	38.3	5.1	3.7	0.7	7.48	1.79	16.6
S6	8.5	50.8	43.3	5.9	30.1	4.1	3.8	0.9	7.31	1.69	13.3
S7	78.1	60.7	36.9	2.4	37.3	5.8	5.5	0.8	6.43	2.72	16.6
S8	-	55.9	40.3	3.8	29.0	4.4	3.2	0.5	6.56	1.28	12.8
S9	-	49.6	44.0	6.4	25.5	3.7	2.4	0.6	6.88	1.07	12.6
S10	-	71.0	21.2	7.8	40.0	6.0	7.0	0.7	6.69	1.59	18.4

* dry basis accept moisture in air-dried basis

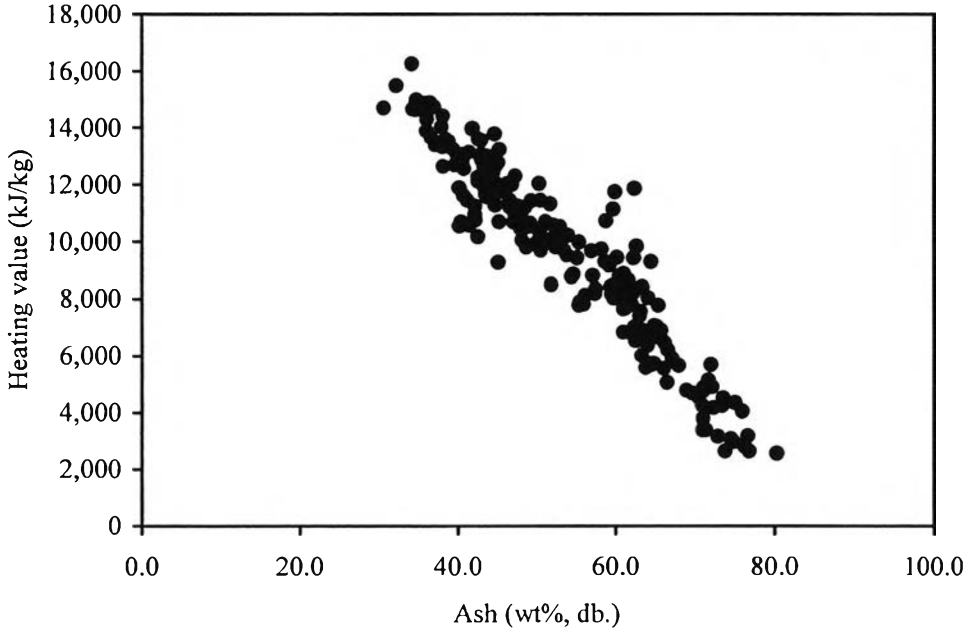


(a)



(b)

Figure 4.1 Correlation between the heating value of sewage sludge and its proximate analysis.



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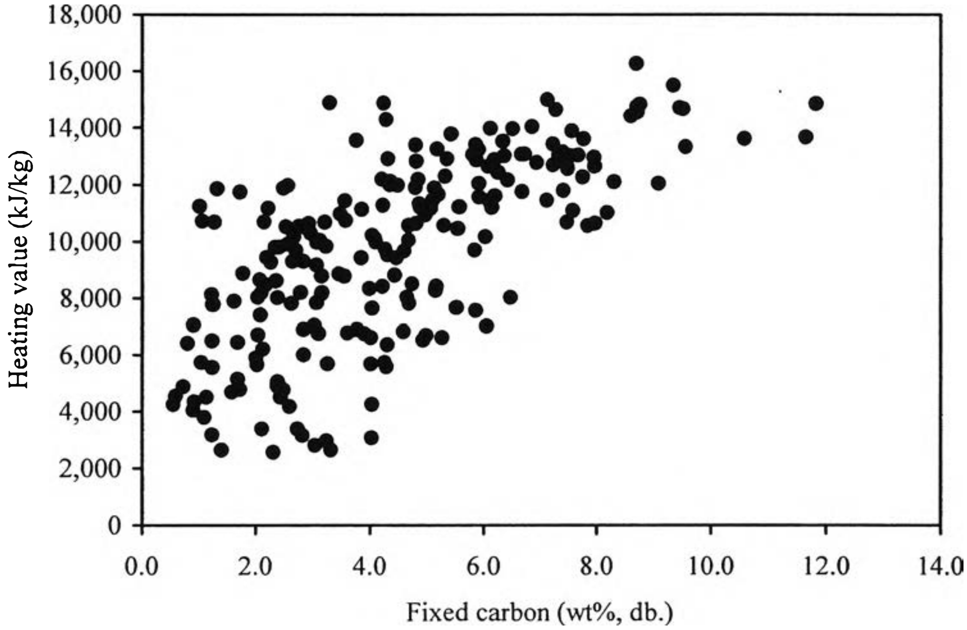
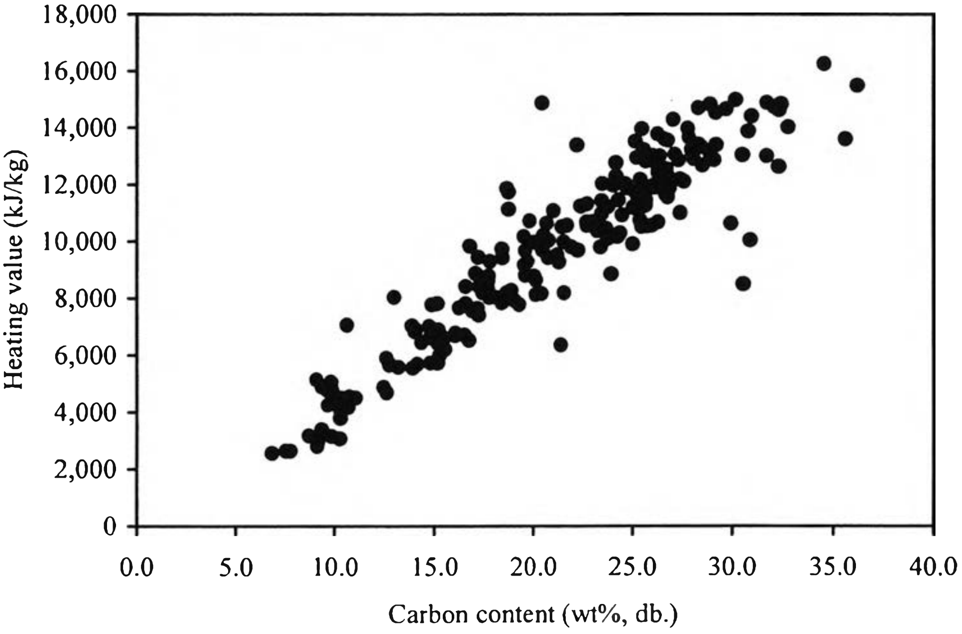
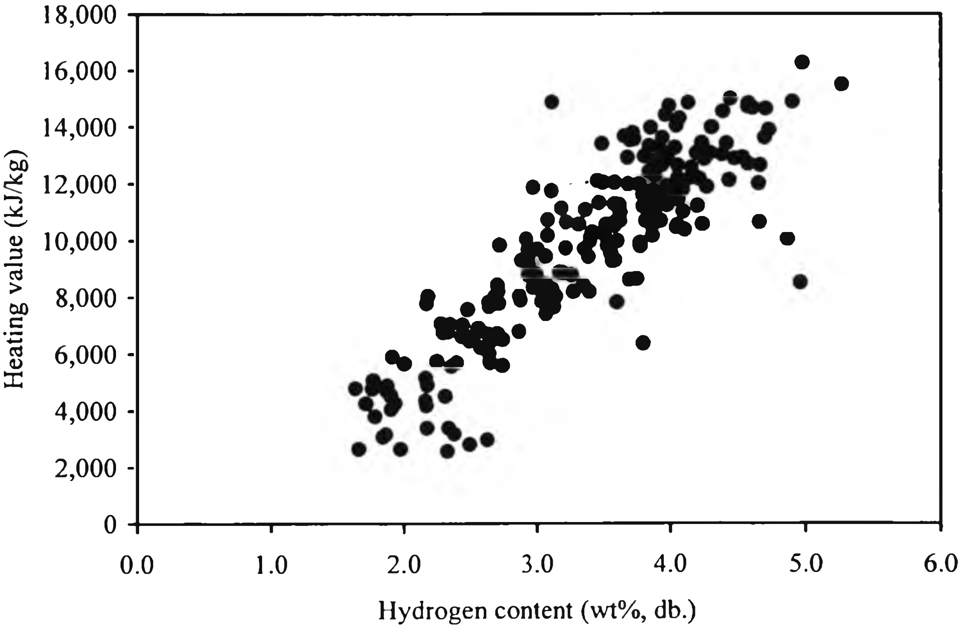


(d)

Figure 4.1 (cont'd) Correlation between the heating value of sewage sludge and its proximate analysis.

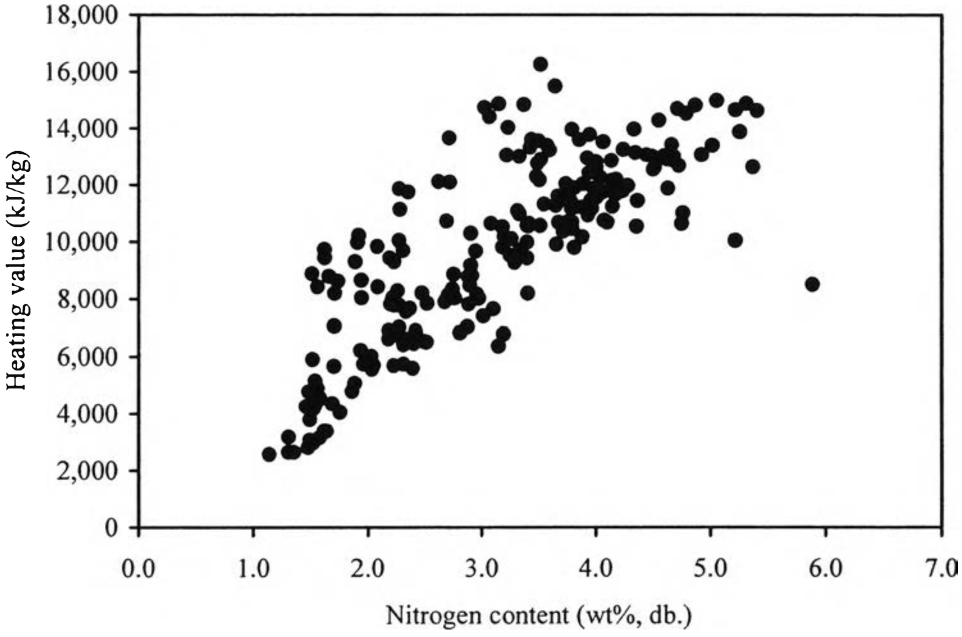


(a)

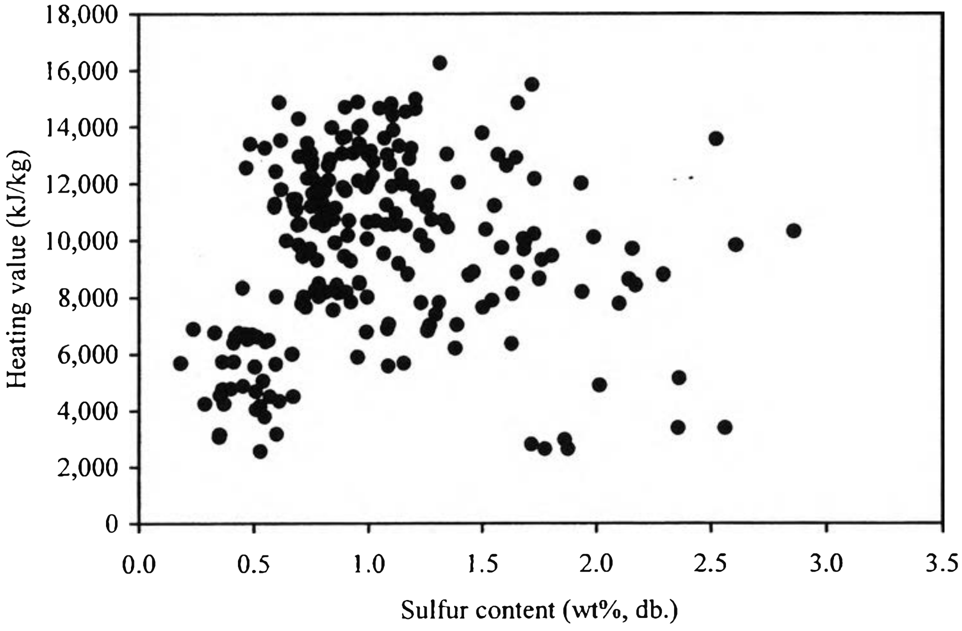


(b)

Figure 4.2 Correlation between the heating value of sewage sludge and its ultimate analysis.

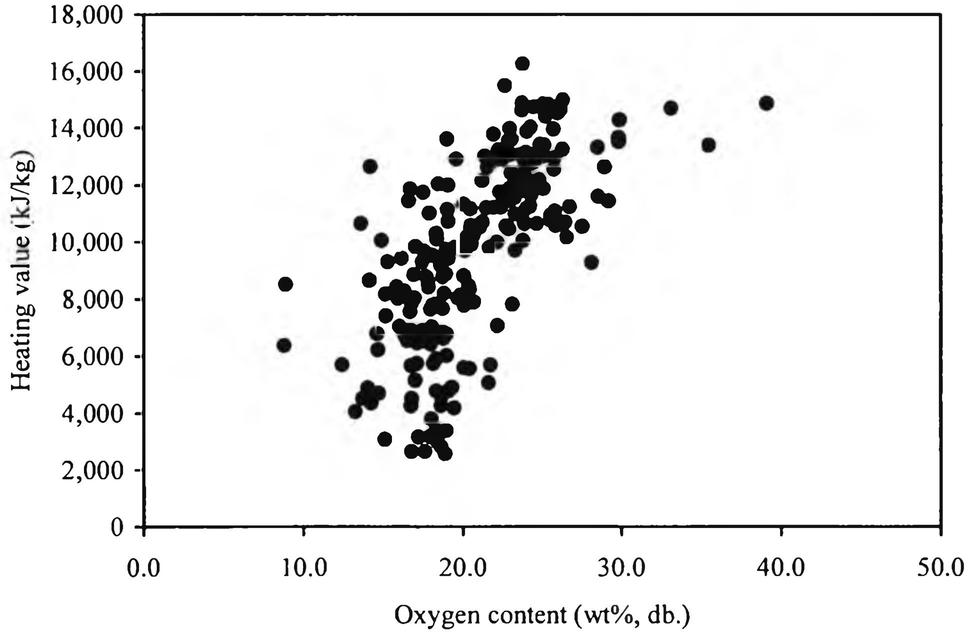


(c)



(d)

Figure 4.2 (cont'd) Correlation between the heating value of sewage sludge and its ultimate analysis.



(e)

Figure 4.2 (cont'd) Correlation between the heating value of sewage sludge and its ultimate analysis.

For proximate analysis, the heating value shows a poor correlation to moisture content (Fig. 4.1a). It is clear that samples that have higher volatile matter and lower ash content would reasonably contain higher heating value (Fig. 4.1b and c). The volatile matter would be the main component that contributes the heating value of the sewage sludge. Meanwhile, the correlation is not quite clear in the case of fixed carbon (Fig. 4.1d). For ultimate analysis, the carbon, hydrogen, and nitrogen contents seem to positively contribute to the heating value (Fig. 4.2a–c), whereas sulfur and oxygen contents give poor correlations to the heating value (Fig. 4.2d and e).

4.5.2 Heating Value Models

From the regression analysis, all adjustable parameters in each model were obtained. A list of models with the coefficients of determination (R^2) of more than 0.880 is compiled in Table 4.4. For most models, they give almost the same coefficient. The values are in narrow ranges, 0.881–0.901 and 0.883–0.905 for models based on proximate and ultimate analyses, respectively.

With the reasonably high R^2 of the models in Table 4.4, they should be applicable with an acceptable result. Nonetheless, a practical model should be in a simple form to avoid the complication in further mathematical analysis. So, simplicity of the model was also taken into account in addition to R^2 from the regression analysis. Most models in Table 4.4 are a linear combination of variables except only Eqs. (4.24) and (4.25).

For models based on the proximate analysis, the best fit was achieved by Eqs. (4.11) and (4.13) with the R^2 of 0.901. According to the models, the volatile matter and fixed carbon contribute positively to the resulting heating value whereas the moisture content more or less has the negative effect. However, for practical applications, it is important to note that the moisture content rarely presents in the expression except for only some applications such as refuse and MSW in which the moisture contents can be as high as 50% [16, 18]. Depending on the method or even the conditions of preparation, the final moisture content can be arbitrarily varied. Eventually, it may cause a significant error in heating value determination by using mathematical models. The explanation is confirmed by considering the moisture content in the sludge, which shows a poor correlation to its heating value (Fig. 4.1a). Therefore, in order to eliminate the effect of moisture on the determination of heating value, the term M should not be present in the equation, leading to Eq. (4.7). From the regression analysis, it gives R^2 of 0.899. This shows an acceptable level of correlation, which is not much different from that of Eq. (4.13). To sum up, the best universal correlation to represent the heating value of sewage sludge in terms of proximate analysis data would be Eq. (4.7).

Table 4.4 Models prediction the heating value of sewage sludge achieved from regression analysis and relative error generated when applying to the experimental data

No.	Equation*	R^2	% Relative Error				
			Avg. abs.	Avg. bias	Min	Max	Stdev
	Models based on proximate analysis						
Eq (4.6)	$HHV = 259.83(V+F) - 2454.76$	0.899	9.1	2.1	-38.7	66.6	10.5
Eq (4.7)	$HHV = 255.75V + 283.88F - 2386.38$	0.899	9.1	2.1	-38.3	64.5	10.3
Eq (4.11)	$HHV^{\Delta} = 278.07(V + F) - 50.44M - 2875.52$	0.901	8.9	1.8	-38.8	64.1	9.8
Eq (4.12)	$HHV^{\Delta} = 219.98V + 327.44F - 68.39M$	0.881	11.4	4.9	-37.3	99.4	13.5
Eq (4.13)	$HHV^{\Delta} = 276.04V + 289.70F - 51.45M - 2847.53$	0.901	8.9	1.8	-39.1	65.5	9.9

* dry basis and unit of kJ/kg unless otherwise stated

$^{\Delta}$ air-dried basis

Table 4.4 (cont'd) Models prediction the heating value of sewage sludge achieved from regression analysis and relative error generated when applying to the experimental data

No.	Equation*	R^2	% Relative Error				
			Avg. abs.	Avg. bias	Min	Max	Stdev
	Models based on ultimate analysis						
Eq (4.15)	$HHV = 491.2C - 911.9H + 117.7O$	0.891	10.8	-3.9	-66.9	29.1	11.6
Eq (4.16)	$HHV = 492.5C - 926.0H + 117.6O + 19.3S$	0.891	10.8	-3.9	-66.7	29.1	11.6
Eq (4.17)	$HHV = 414.8C - 184.1H + 178.9O - 2159.5$	0.904	9.3	-2.1	-60.2	32.5	10.2
Eq (4.18)	$HHV = 425.9C - 69.8H + 181.7O - 180.5N - 2277.0$	0.904	9.3	-2.1	-62.1	32.0	10.2
Eq (4.19)	$HHV = 430.2C - 186.7H - 127.4N + 178.6S + 184.2O - 2379.9$	0.905	9.3	-2.1	-64.8	32.4	10.4
Eq (4.20)	$HHV = 406.4C - 210.6H + 154.7S + 160.3O - 151.3N - 23.8A + .0034$	0.905	9.3	-2.1	-64.8	32.4	10.4
Eq (4.21)	$HHV = 406.4C - 210.5H + 154.8S + 160.4O - 151.2N - 23.8A$	0.905	9.3	-2.1	-64.8	32.4	10.4
Eq (4.22)	$HHV = 395.9C - 447.1H + 255.5S + 154.3\ (O + N) - 18.1A - 21.7$	0.903	9.3	-2.1	-63.0	33.3	10.6
Eq (4.23)	$HHV = 395.6C - 446.0H + 254.5S + 154.0\ (O + N) - 21.9A$	0.903	9.3	-2.1	-63.0	33.3	10.6
Eq (4.24)	$HHV = 134.3C - 1{,}502.1H - 2.7\ (O2/(1-A/100)) + 29{,}132.8\ (1 - A/100)$	0.893	10.4	-3.6	-67.4	30.1	11.5
Eq (4.25)	$HHV = 279.8C - 849.1H + 724.9O - 9.2(O2/(1 - A/100)) - 118.5S$	0.902	9.6	-3.1	-61.4	32.0	9.7
Eq (4.28)	$HHV = 328C + 1{,}419H + 92.8S + 276.7\ (O + N) + 110.4A - 14{,}278.3$	0.883	10.2	-2.4	-89.4	34.0	13.4
Eq (4.29)	$HHV = 661.0\ (0.328C + 1.419H + 0.0928S) + 146.5\ (O + N) - 31.4A$	0.890	9.9	-2.4	-87.8	34.1	13.2
Eq (4.30)	$HHV = 683.8\ (0.328C + 1.419H) + 0.0928S - 0.0238N + 154.6O - 33.1A$	0.892	9.9	-2.4	-89.9	34.0	13.4

Fig. 4.3 shows the plots between heating values from experiment and calculation by Eq. (4.7). The results show fairly small discrepancies between the calculated and experimental values. For models based on the ultimate analysis, Eqs. (4.19)–(4.21) give the same highest R^2 of 0.905. All models are a linear combination of ultimate analysis data. Three models give the same coefficients even though they have somewhat different numbers of variables. However, they have the same contexts in the parameters contributing to the heating value. That is, the carbon, sulfur and oxygen contents contribute positively to the heating value while the hydrogen, nitrogen and ash contents have negative effects. The difference between Eqs. (4.20) and (4.21) is only whether it has the residual constants or not. However, it was proved to have no significant effect on the final heating value calculation. Results from Eq. (4.19) are comparable to that from Eqs. (4.20) and (4.21). As these equations are in a simple linear combination of variable form, these three equations were selected as the best model from the ultimate analysis data. Fig. 4.4 exhibits the plots between the heating values from the experiment and calculation by Eq. (4.19) (Eqs. (4.20) and (4.21) give a similar result).

4.5.3 Validation of the Models

The validation of the models was discussed in two aspects, the error of the models and its application. For error analysis purpose, the statistical approach was taken. This information was used to indicate the performance of the models based upon the following criteria [16]:

- the average absolute and bias errors should be or close to zero,
- the range should be smallest, and
- the standard deviation should be smallest.

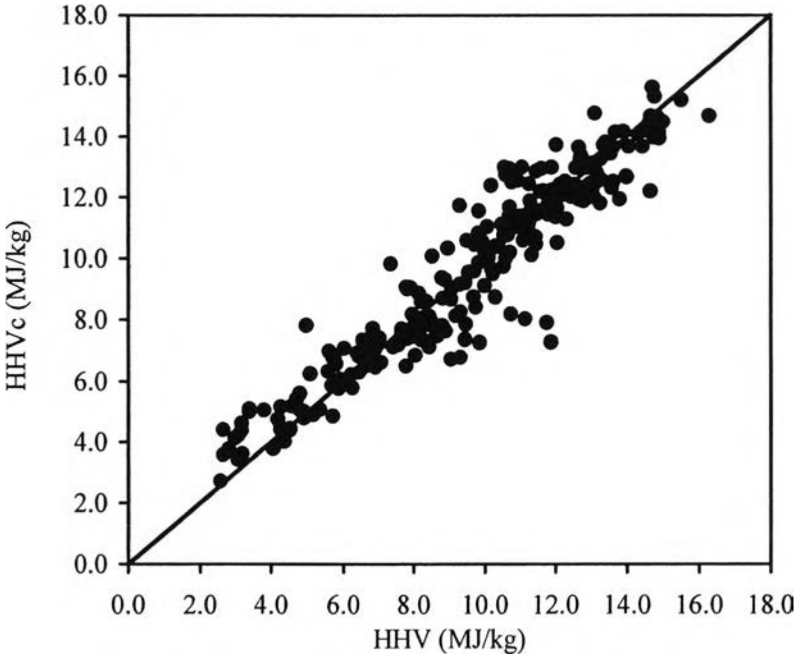


Figure 4.3 Comparison between the heating values of sewage sludge calculated from Eq (4.7) and experimental value.

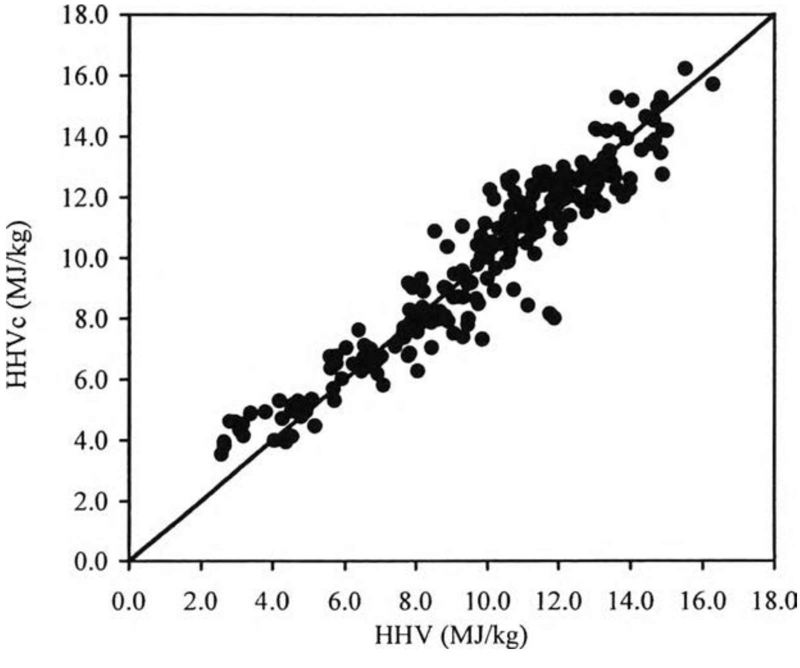


Figure 4.4 Comparison between the heating values of sewage sludge calculated from Eq (4.19) and experimental value.

The results of statistical evaluations are given in Table 4.4. For most models, they show small discrepancies bet ween the calculated and experimental values. The averages and standard deviations of error are 11.4 and 13.5%, respectively. Nonetheless, there are some calculated data points showing big difference from the experimental values, which can be noticed from the high range of error. Even for Eqs. (4.7) and (4.19), the absolute error can be as high as 65%. To explain the cause of error from the models, let's consider the plots between the bias error and ash content of sewage sludge. As shown in Figs. 4.5 and 4.6, the plots indicate the increase in the error with the higher ash content in the sewage sludge. Similarly, this trend was also observed for other models. It infers that ash components would have a significant effect on the error in the determination of heating value.

On the other hand, this confirms the inapplicability of some equations for sewage sludge, especially popular expressions such as Dulong, Steuer, and Scheurer-Kestner equations. In such models, the organic materials were presumed to combust with oxygen gas and yield certain compounds such as CO_2 and H_2O. Heat released (or heating value) is then determined by thermochemical and stoichiometric calculations. These equations are generally useful in most cases [4, 5, 7, 9, 14, 16, 17]. However, they may not be applicable for the case of sewage sludge. Although it is not reported here, using such equations usually overestimates the heating value of sewage sludge [14]. It is possibly due to complex sorption of organic contents on ash components. The combustion heat may compensate for breaking this kind of sorption bonding, resulting in lower final heating value. The net heating value is eventually decreased.

However, for a certain application such as incineration, pyrolysis and gasification as focused in this work, the characteristics of the materials are also necessarily considered r ather than only their heating value. Here, the proximate analysis plays an important role in the sludge evaluation. Normally, the more volatile matter or the less ash content, the more heating value. It is not beneficial to deal with sludge containing high ash content or low heating value. Therefore, after the observation from this study, the limitation of the model may be mentioned because of two reasons:

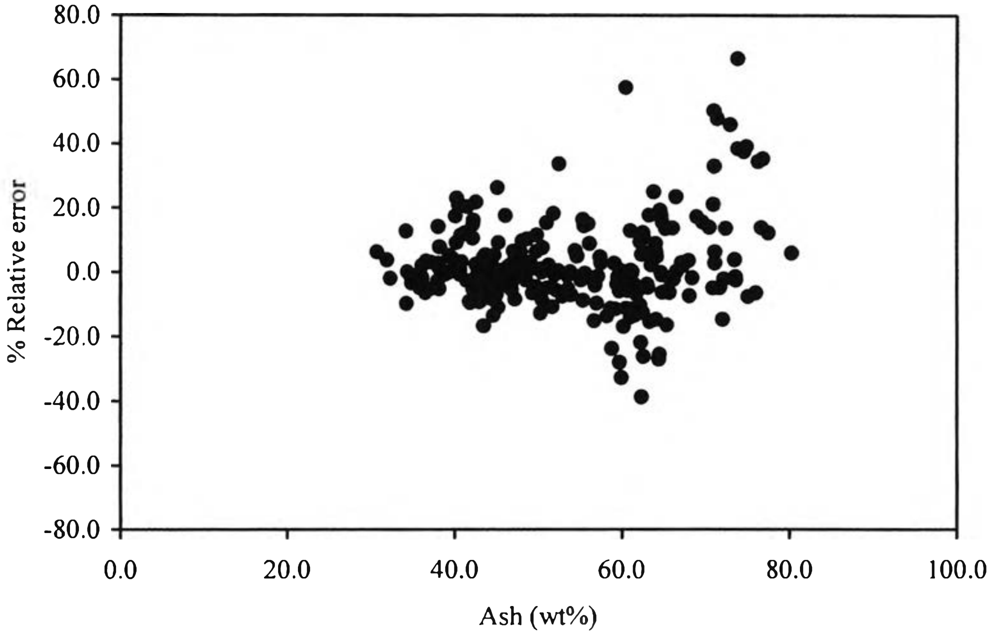


Figure 4.5 The error raised when predicting the heating value of sewage sludge from it proximate analysis respects to its ash content.

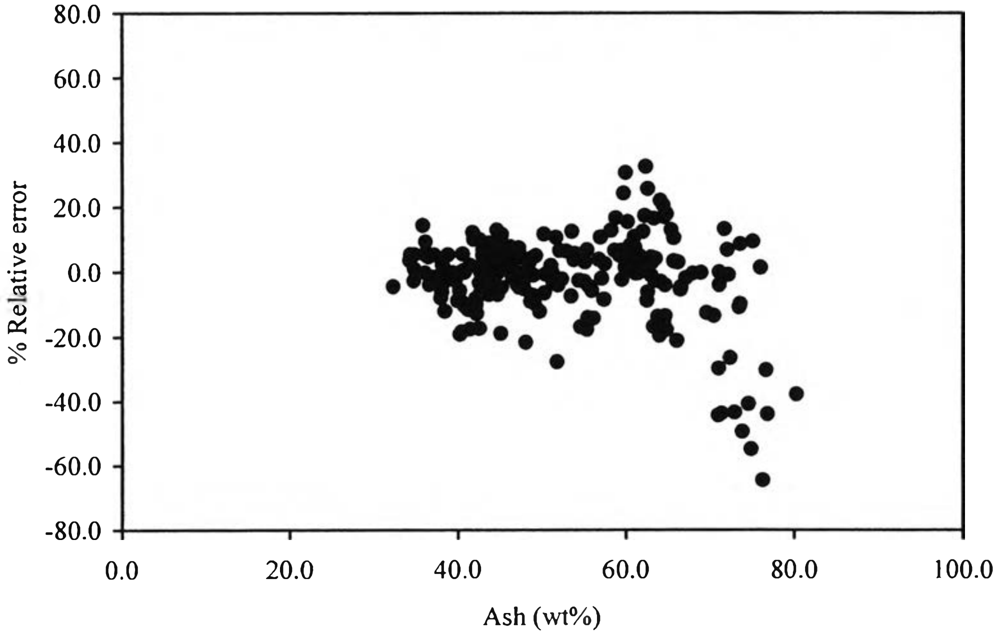


Figure 4.6 The error raised when predicting the heating value of sewage sludge from it ultimate analysis respects to its ash content.

- the error arises when models are applied to high ash content sludge, which also contain low heating value, and
- it is unlikely to deal with sewage sludge samples with low heating value as they are not attractive for underlined applications.

As seen in Figs. 4.5 and 4.6, it is reasonable to limit the application of the model for samples having the ash content less than 50%. The selected models then were reanalyzed with this specific range of data. From Eqs. (4.7) and (4.19), the averages of the absolute error were reduced to 5.9 and 6.4%, respectively. In addition, the averages of bias error were 1.2 and 1.1% for both equations. Other statistical values are also improved.

Table 4.5 Calculated heating values of sewage sludge from literatures*

Sample	Experimental heating value	Eq (4.7)		Eq (4.19)	
		Heating value	%error	Heating value	%error
S1	16.6	15.9	-3.9	16.4	-1.2
S2	20.9	19.4	-7.1	20.6	-1.4
S3	17.1	16.7	-2.3	17.9	4.4
S4	16.8	15.5	-7.4	16.4	-2.4
S5	16.6	15.6	-5.7	16.7	1.0
S6	13.3	12.3	-8.0	12.8	-4.4
S7	16.6	13.8	-16.8	14.5	-12.4
S8	12.8	13.0	1.6	13.1	2.4
S9	12.6	12.1	-4.1	12.1	-4.5
S10	18.4	18.0	-2.5	17.5	-4.9

* kJ/kg

Finally, the validity of the heating value models was also proved by applying to some other sludge samples. The results are given in Table 4.5. This sludge has slightly higher heating value than those of the samples in this study. The models also give good result in the determination of heating value even though its characteristics are sometimes outside the range used in this study. The models can be extrapolated to predict the heating value of the sludge with the higher heating value than that of sample used in this study.

4.6 Conclusions

With the extensive number of sample data point, the models predicting the heating value of sewage sludge based on the proximate and ultimate analyses were created. The calculated heating values using the selected correlations show good agreement with experimental values. The error analysis confirmed the validity and applicability of the models to sewage sludge data both in this work and literatures. The application of models however limited to sewage sludge with the ash content of less than 50%. In the case of proximate analysis, such a simple procedure may have a particular interest in contexts where relatively sophisticated equipments for experimental determination of heating values or ultimate analysis are not available. Nonetheless, the ultimate analysis data is required for some applications. This allows the model based on ultimate analysis to work instead.

4.7 Acknowledgements

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