

Sewage Sludge Heating Value Prediction through Proximate and Ultimate Analyses

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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. An extensive number of samples were 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 the proximate and ultimate analyses, models were proposed. The best correlations show coefficients of determination (R^2) of 0.8993 and 0.9050 for the models based on the proximate and ultimate analyses, respectively. The heating values obtained from the models were in good agreement with that from experiment. The application of the selected models was appreciable for the sewage sludge with ash content up to 50% (db.).

Keywords: Sewage Sludge, Heating Value, Proximate Analysis, Ultimate Analysis.

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 increases proportionally with the industrial development in most countries [1-3]. The sludge normally contains undesirable components such as organic, inorganic, toxic substances as well as pathogenic or disease-caused microorganisms. It has been 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 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 either 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 values of many types of materials with various compositions [4-18]. Nonetheless, only few works involve sewage sludge. The objective of this study was to develop correlations between heating value and sewage sludge characteristics (proximate or ultimate analyses) for sewage sludges produced in Thailand

Literature Survey

Regarding the empirical approach, 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 SW and 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 lignocellulose in biomass etc. The proximate analysis typically involves determination of moisture, volatile matters, fixed carbon and ash contents whereas the ultimate analysis includes an assessment of the levels of carbon, hydrogen, oxygen, nitrogen and sulfur contents.

Table 1 summarizes models used to predict the heating value of materials namely MSW, coal, refuse and biomass [4-8, 10, 13-17]. They were simply assumed to be the result of a linear combination of variables with a set of constants, i.e. Eqs (1)-(23). The method of regression analysis is generally used to obtain 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. Eqs (35)-(39), however, 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 preferred 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 (24)-(34). More details 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 generally considered.

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

In this work, models based on the proximate and ultimate analyses were focused. The model equations listed in Table 1 were analyzed with the aim to find the most appropriate form of equation for predicting heating value of sewage sludge.

Materials and Methods

Sample Preparation

Sewage sludge samples used in this study were collected from different wastewater treatment plants (WWTP) in Bangkok and its vicinity following ASTM D346-90. A total number of samples exceed 200 samples from 20 different

Table 1 Summary of empirical models used for predicting the heating value of various types of materials

No.	Equation*	Application	Unit	Basis [∇]	Ref.	Original
<i>Models based on Proximate Analysis</i>						
Eq(1)	$HV = a - bM$	Refuse	kJ/kg	adb.	[7]	Goutal
Eq(2)	$HV = aF + b$	Biomass	kJ/kg	db.	[8]	
Eq(3)	$HV = aV + b$	MSW	kJ/kg	db.	[16]	
Eq(4)	$HV = aV + bF$	Coal/refuse	kJ/kg	daf.	[8]	Jimenez
Eq(5)	$HV = aV + bF$	Biomass	kJ/kg	db.	[13]	
Eq(6)	$HV = a(V + F) + b$	Biomass	kJ/kg	db.	[13]	
Eq(7)	$HV = aV + bF + c$	MSW	kJ/kg	db.	[16]	Liu
Eq(8)	$HV = aV - bM$	Refuse	kJ/kg	adb.	[16]	
Eq(9)	$HV = aV - bM + c$	Refuse	kJ/kg	adb.	[16]	
Eq(10)	$HV = a(V + F) - bM$	MSW	kJ/kg	adb.	[10]	Bento
Eq(11)	$HV = a(V + F) - bM + c$	Refuse	kJ/kg	adb.	[10]	
Eq(12)	$HV = aV + bF - cM$	MSW	kJ/kg	adb.	[10]	
Eq(13)	$HV = aV + bF - cM + d$	MSW	kJ/kg	adb.	[10]	
<i>Models based on Ultimate Analysis</i>						
Eq(14)	$HV = aC + b$	Biomass	kJ/kg	db.	[14]	Tillman
Eq(15)	$HV = aC + bH + cO$	Biomass	kJ/kg	db.	[15]	Ruyter
Eq(16)	$HV = aC + bH + cO + dS$	Coal/refuse	kJ/kg	db.	[16]	Mott & Spooner
Eq(17)	$HV = aC + bH + cO + d$	Biomass/refuse	kJ/kg	db.	[7, 14]	Jenkins
Eq(18)	$HV = aC + bH + cO + dN + e$	MSW	kJ/kg	db.	[16]	Francis
Eq(19)	$HV = aC + bH + cN + dS + eO + f$	Biomass	kJ/kg	db.	[13]	
Eq(20)	$HV = aC + bH + cS + dO + eN + fA + g$	Coal	kJ/kg	db.	[14]	
Eq(21)	$HV = aC + bH + cS + dO + eN + fA$	Coal	kJ/kg	db.	[14]	Francis
Eq(22)	$HV = aC + bH + cS + d(O + N) + eA + f$	Coal	kJ/kg	db.	[14]	
Eq(23)	$HV = aC + bH + cS + d(O + N) + eA$	Coal/refuse	kJ/kg	db.	[14, 16]	
Eq(24)	$HV = aC + bH + c(O^2/(1 - A/100)) + d(1 - A/100)$	Coal	kJ/kg	db.	[14]	Francis
Eq(25)	$HV = aC + bH + cO + d(O^2/(1 - A/100)) + eS$	Coal	kJ/kg	db.	[14]	
Eq(26)	$HV = a[C/H] + b(O + N) + cA$	Coal	kJ/kg	db.	[14]	
Eq(27)	$HV = 328C + 1,419H + 92.8S$	Coal	kJ/kg	db.	[14]	Francis
Eq(28)	$HV = 328C + 1,419H + 92.8S - a(O + N) + bA + c$	Coal	kJ/kg	db.	[14]	
Eq(29)	$HV = a(328C + 1,419H + 92.8S) + b(O + N) + cA$	Coal	kJ/kg	db.	[14]	
Eq(30)	$HV = a(328C + 1,419H) + 92.8S - 23.8N + bO + cA$	Coal	kJ/kg	db.	[14]	Francis
Eq(31)	$HV = [a(H/(1 - A/100)) + b] [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	[14]	
Eq(32)	$HV = [a(O/(1 - A/100)) + b] [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	[14]	
Eq(33)	$HV = [a(C/(1 - A/100)) + b] [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	[14]	Francis
Eq(34)	$HV = [a(C/(1 - A/100)) + b(H/(1 - A/100)) + c((O + N)/(1 - A/100)) + d(S/(1 - A/100)) + e] [C/3 + H - (O - S/8)]$	Coal	kJ/kg	db.	[14]	
Eq(35)	$HV = 335C + 1,423H - 15.4O + 14.5N$	Biomass	kJ/kg	daf.	[8]	Dulong
Eq(36)	$HV = 81C + 342.5(H - O/8) + 22.5S$	Coal/MSW	kcal/kg	daf.	[4-5, 7, 14-16]	
Eq(37)	$HV = 81(C - 3O/8) + 171O/8 + 342.5(H - O/16) + 25S$	Coal/MSW	kcal/kg	daf.	[5, 7, 16]	
Eq(38)	$HV = 81(C - 3O/8) + 342.5H + 22.5S + 171O/4$	Coal/MSW	kcal/kg	daf.	[5, 7, 16]	Scheurer-Kestner
Eq(39)	$HV = 357.8C + 1,135.7H - 84.5O + 59.4N + 111.9S$	MSW	kJ/kg	db.	[17]	

* a, b, c, ... = arbitrary constants, V = volatile matters, F = fixed carbon, M = moisture, C = carbon content, H = hydrogen content, N = nitrogen content, S = sulfur content, O = oxygen content, A = ash content (all in percentage)

[∇] adb. = airdried basis, db. = dry basis, daf. = dry and ash free basis

sources comprising 12 municipal, 5 hospital and 3 industrial WWTPs. The samples were naturally dried under sunlight for 1-2 days prior to characterization.

Sample Characterization

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

Heating Value Models

Models listed in Table 1 were fit to the experimental data by regression analysis using all sample data points. The method of least square 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:

$$\begin{aligned}\% \text{absolute error} &= \left| \frac{HV_c - HV}{HV} \right| \times 100\% \\ \% \text{bias error} &= \left(\frac{HV_c - HV}{HV} \right) \times 100\%\end{aligned}$$

where HV_c and HV 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 from literatures.

Results and Discussion

Sewage Sludge Characteristics

Table 2 shows the characteristics of sewage sludge samples used in this work. The results show a wide range of the sewage sludge characteristics. The compositions of sewage sludge are mainly volatile matters and ash contents, averages of 42.35 and 53.23% and can be as high as 60.19 and 80.27%, respectively. However, the sewage sludge contains only a small amount of fixed carbon, maximum 11.82%. The characteristics of some other sludge samples were also collected from literatures for comparison. 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 matters and higher ash contents.

Heating Value Models

From the regression analysis, all adjustable parameters in each model were obtained. Table 3 shows a list of models with the coefficients of determination (R^2) higher than 0.8800. The R^2 can be as high as 0.9012 and 0.9050 for models based on proximate and ultimate analyses, respectively. With the reasonably high R^2 of all models listed in Table 3, 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

Table 2 The characteristics of sewage sludge from different sources (C, H, I and S indicate sample from community, hospital, industrial and literature, respectively)

Sludge ID	Proximate analysis (wt%)				Ultimate analysis (wt%)					Heating value (kJ/kg)
	M	V*	A*	F*	C*	H*	N*	S*	O*	
C1	6.11	53.01	38.38	8.61	31.11	4.19	3.27	1.14	24.25	13,920
C2	5.06	51.24	42.03	6.73	27.53	4.10	4.02	1.14	23.30	13,176
C3	5.35	49.98	43.03	6.99	26.35	4.08	4.26	0.91	23.68	12,558
C4	6.38	47.58	48.37	4.05	23.85	3.93	3.82	1.34	21.79	11,022
C5	3.69	42.25	51.79	5.96	20.85	3.36	3.28	0.93	21.72	10,139
C6	4.11	34.46	61.83	3.70	18.00	2.91	2.26	0.81	16.73	9,408
C7	3.42	38.98	56.01	5.01	19.53	3.19	3.05	0.75	19.37	8,716
C8	3.91	33.26	63.50	3.24	14.51	2.64	2.58	1.15	18.11	6,853
C9	3.70	32.86	64.04	3.10	15.28	2.53	2.34	0.45	17.74	6,489
C10	3.20	30.56	67.60	1.83	12.66	1.98	1.84	0.59	17.49	5,719
C11	4.39	24.83	72.93	2.24	10.56	1.96	1.64	0.40	15.71	4,270
C12	8.89	23.42	74.21	2.37	9.00	2.23	1.46	1.57	18.17	3,528
H1	6.62	55.47	39.39	5.14	26.68	4.04	4.30	0.70	27.50	13,341
H2	5.63	52.57	40.60	6.84	29.62	4.55	5.01	0.99	21.54	12,772
H3	4.56	47.68	45.86	6.47	25.45	3.85	4.20	1.02	21.70	12,392
H4	6.92	50.42	45.72	3.86	24.97	3.77	3.65	0.78	24.26	11,144
H5	4.60	36.62	60.19	3.19	18.98	2.97	2.69	1.21	16.75	8,214
I1	5.22	54.49	42.28	3.23	25.14	4.00	3.82	0.88	26.10	10,920
I2	5.03	45.56	51.63	2.81	22.60	3.23	2.85	2.03	20.26	9,917
I3	4.72	38.15	58.80	3.05	18.32	3.42	1.77	1.80	18.66	9,006
S1 [2]	5.20	60.70	29.50	9.80	35.70	5.20	3.50	0.70	25.40	16,558
S2 [20]	5.00	72.53	16.00	11.47	45.91	6.30	5.12	0.56	26.91	20,900
S3 [21]	11.75	60.60	26.64	12.77	39.48	6.19	3.93	1.45	25.46	17,140
S4 [22]	4.30	59.30	31.00	9.70	38.10	5.20	4.51	0.91	20.28	16,774
S5 [22]	3.90	58.50	30.80	10.70	38.30	5.12	3.69	0.72	21.37	16,564
S6 [22]	8.50	50.80	43.30	5.90	30.10	4.12	3.79	0.85	17.84	13,343
S7 [23]	78.10	60.70	36.90	2.40	37.30	5.80	5.50	0.80	13.70	16,611
S8 [24]	-	55.90	40.30	3.80	28.98	4.42	3.22	0.48	22.60	12,790
S9 [24]	-	49.60	44.00	6.40	25.47	3.70	2.43	0.56	23.84	12,640
S10 [24]	-	71.00	21.30	7.80	39.95	5.97	7.00	0.65	25.13	18,440

* dry basis

Table 3 Models with complete parameters achieved from regression analysis and statistical values

No.	Equation*	R ²	Avg. %error		Stdev.
			Abs.	Bias	
Models based on proximate analysis					
Eq(6)	$HV = 259.83(V+F) - 2454.76$	0.8991	9.05	2.03	10.30
Eq(7)	$HV = 255.75V + 283.88F - 2386.38$	0.8993	9.08	2.07	10.45
Eq(11)	$HV^d = 278.07(V + F) - 50.44M - 2875.52$	0.9011	8.88	1.82	9.78
Eq(12)	$HV^d = 219.98V + 327.44F - 68.39M$	0.8810	11.39	4.88	13.54
Eq(13)	$HV^d = 276.04V + 289.70F - 51.45M - 2847.53$	0.9012	8.91	1.84	9.86
Models based on ultimate analysis					
Eq(15)	$HV = 491.2C - 911.9H + 117.7O$	0.8906	10.82	-3.88	11.60
Eq(16)	$HV = 492.5C - 926.0H + 117.6O + 19.3S$	0.8906	10.82	-3.89	11.63
Eq(17)	$HV = 414.8C - 184.1H + 178.9O - 2159.5$	0.9035	9.31	-2.12	10.16
Eq(18)	$HV = 425.9C - 69.8H + 181.7O - 180.5N - 2277.0$	0.9044	9.30	-2.12	10.17
Eq(19)	$HV = 430.2C - 186.7H - 127.4N + 178.6S + 184.2O - 2379.9$	0.9050	9.26	-2.12	10.44
Eq(20)	$HV = 406.4C - 210.6H + 154.7S + 160.3O - 151.3N - 23.8A + .0034$	0.9050	9.26	-2.12	10.44
Eq(21)	$HV = 406.4C - 210.5H + 154.8S + 160.4O - 151.2N - 23.8A$	0.9050	9.26	-2.12	10.44
Eq(22)	$HV = 395.9C - 447.1H + 255.5S + 154.3(O + N) - 18.1A - 21.7$	0.9028	9.25	-2.14	10.63
Eq(23)	$HV = 395.6C - 446.0H + 254.5S + 154.0(O + N) - 21.9A$	0.9028	9.26	-2.14	10.62
Eq(24)	$HV = 134.3C - 1,502.1H - 2.7(O^2/(1-A/100)) + 29,132.8(1 - A/100)$	0.8926	10.36	-3.62	11.45
Eq(25)	$HV = 279.8C - 849.1H + 724.9O - 9.2(O^2/(1 - A/100)) - 118.5S$	0.9024	9.55	-3.07	9.69
Eq(28)	$HV = 328C + 1,419H + 92.8S + 276.7(O + N) + 110.4A - 14,278.3$	0.8830	10.15	-2.39	13.40
Eq(29)	$HV = 661.0(0.328C + 1.419H + 0.0928S) + 146.5(O + N) - 31.4A$	0.8898	9.91	-2.43	13.21
Eq(30)	$HV = 683.8(0.328C + 1.419H) + 0.0928S - 0.0238N + 154.6O - 33.1A$	0.8921	9.89	-2.44	13.38

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

^d air-dried basis

For models based on the ultimate analysis, Eqs (19), (20) and 21) give the same highest R² of 0.9050. 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 (20) and (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 (19) are comparable to that from Eqs (20) and (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. 1 (b) exhibits the plots between the heating values from the experiment and prediction by Eq (19) (Eqs (20) and (21) give a similar result).

Validation of the Models

The validation of the models was discussed in two aspects, the error of the models and their applications. 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 standard deviation should be small.

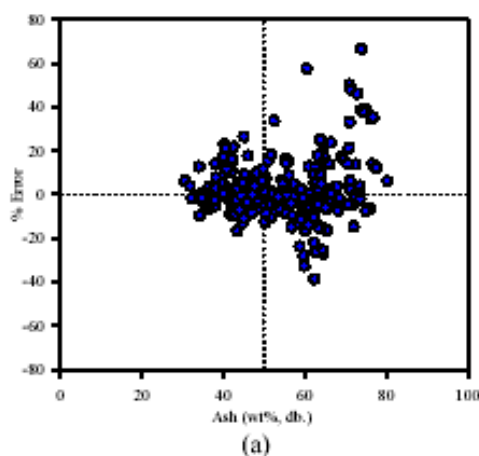
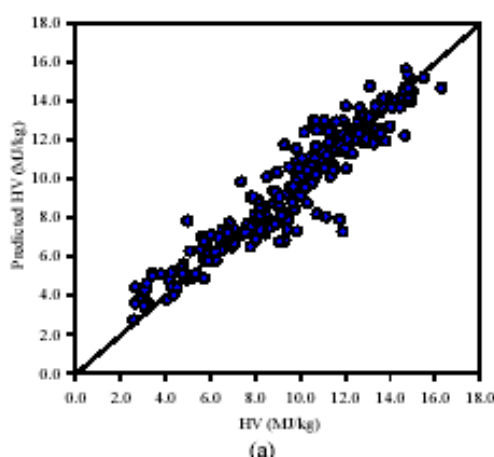
The results of statistical evaluations are given in Table 3. For most models, they show small differences between the calculated and experimental values. Nonetheless, there are some calculated data points showing big differences from the experimental values. Even for Eqs (7) and (19), the absolute error can be as high as 65%. To explain the cause of error from the

models, consider the plots between the bias error and ash content of sewage sludge. As shown in Fig. 2, the plots indicate the increase in the error with the higher ash content in the sewage sludge. Similarly, this trend can also be 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 the 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 sewage sludge. Although it is not reported here, using such equations 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 lower than calculated one.

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 rather than only their heating value. Here, the proximate analysis plays an important role in the sludge evaluation. Normally, the more volatile matters or the less ash content, the more heating value. It is not beneficial to deal with sludge containing such high ash content or low heating value. Therefore, after the observation from this study, the limitation of the model may be stated because of two reasons:

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



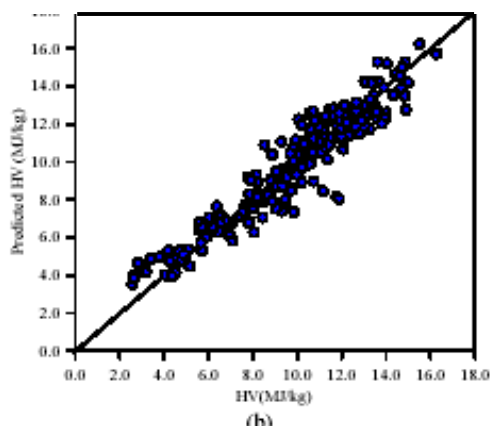


Fig. 1 Comparison between heating values of sewage sludge and the predicted one from (a) Eq. 7 and (b) Eq. 19.

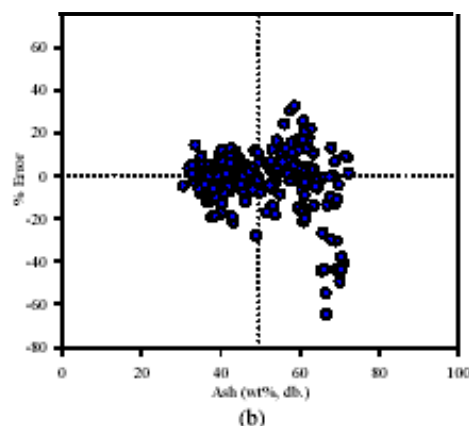


Fig. 2 Plot between % error and ash content in sludge when applying (a) Eq. 7 and (b) Eq. 19.

As seen in Fig. 2, it is reasonable to limit the application of the model for samples having the ash content less than ca. 50%. The selected models then were reanalyzed with this specific range of data. Table 4 shows the error analysis resulting from applying Eqs (7) and (19) to the sample within the ash content of less Than 50%. The averages of the absolute error are reduced to 5.86% and 6.40% for both equations, respectively. Other Statistical values namely average percentage of bias error and standard deviation were also improved.

Table 4 average percentages of error and standard deviation from applying selected model to the sludge containing ash of less than 50%

Model	Avg. %error		Stdev.
	Abs.	Bias	
Eq(7)	5.86	1.22	5.92
Eq(19)	6.40	-1.07	5.19

Finally, the validity of the heating value models was also proved by applying to some other sludge samples. The results are given in Table 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.

Table 5 Heating values of sewage sludge from literatures compared to the calculated values

Sludge	HV (kJ/kg)	Eq 7		Eq 19	
		HV _c (kJ/kg)	%error	HV _c	%error
S1	16,558	15,919	-3.9	16,365	-1.2
S2	20,900	19,419	-7.1	20,598	-1.4
S3	17,140	16,737	-2.3	17,896	4.4
S4	16,774	15,533	-7.4	16,363	-2.4
S5	16,564	15,612	-5.7	16,735	1.0
S6	13,343	12,280	-8.0	12,755	-4.4
S7	16,611	13,819	-16.8	14,549	-12.4
S8	12,790	12,988	1.6	13,100	2.4
S9	12,640	12,115	-4.1	12,068	-4.5
S10	18,440	17,986	-2.5	17,545	-4.9

Conclusion

With the extensive numbers of sample data point, the models predicting the heating value of sewage sludge based on the proximate and ultimate analyses were developed. 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 is, however, limited to sewage sludge with the ash content of less than 50%.

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