EVALUATION OF DATA ON HIGHER HEATING VALUES AND ELEMENTAL ANALYSIS FOR REFUSE-DERIVED FUELS

T. J. BUCKLEY AND E. S. DOMALSKI
Chemical Thermodynamics Division
National Bureau of Standards
Gaithersburg, Maryland

Discussion by

Richard C. Hittinger
Environmental Science Services
Providence, Rhode Island

This paper by Mr. Buckley and Mr. Domalski relied on information collected during an ASTM round robin testing program conducted during 1978 and 1979. It is, therefore, dependent on data which is nine years old and data which was not collected as part of this study. This is a significant limitation, and must be identified as such. Such changes as improvements in the analytical methods available and possible real changes in the waste stream composition would make it highly desirable for this procedure to be verified with newer data on elemental composition and calorific content of wastes.

However, this significant limitation does not reduce the importance of the comparison made in this paper between calorimeter measured HHV and HHV predicted using various formulas. With the problems recently in the Resource Recovery industry due to inaccurate prediction of HHV, the importance of knowing HHV of solid waste accurately and of understanding compositional changes that may affect HHV becomes even more obvious. This paper suggests a method of calculating HHV that could not only be used as a substitute for direct measurement of HHV, but also could help one predict the effect of changes in waste stream composition on HHV. Because of this, it is important to get these hypotheses as discussed in this paper before the scientific and engineering community for critical review.

One further concern, however, with the data set reviewed here is the constancy of elemental composition amongst the five round robin groups. The compositional analyses shown on Table 2 of the paper indicate virtually no significant difference among the five sample groups for carbon, hydrogen or oxygen. The higher heating value on a dry basis (HHV2) shown on Table 2 appears to be on the high end of the expected range and very consistent between the five sample groups. In comparison, dry HHV values given by Churney et al. 1986 ranging from 15.4 to 16.1 MJ/kg for processed MSW. If this ability to predict HHV from the elemental composition is to be proven useful in the Resource Recovery industry, this procedure must be tested with materials that demonstrate the extremes of variability in elemental composition and calorimeter determined HHV.

Discussion by

H. Gregor Rigo
Rigo & Rigo Associates, Inc.
Berea, Ohio

The authors rightly point out the need for a reasonably reliable algorithm to determine when a laboratory analysis is likely to contain errors and both heating value and ultimate analysis data are available.

This paper analyzes a number of available equations and concludes that the Dulong and IGT formulas are the best ones to use. Unfortunately, this conclusion is based on the false assumption that 149 valid data sets have been analyzed.

The data are really from free samples that have been analyzed repeatedly. The experiment run was the equivalent of going to a brick yard, selecting 3 bricks (the inter-lab tests are a finely ground and mixed subsample of the round robin sample, hence one of the original "bricks") and measuring the first one 16 times, the second 66 times, and the third 67 times. This is not the same thing as making three trips to the brick yard and selecting, at random, and measuring 16 bricks on the first trip, 66 the second and 67 the third.

The first brickyard experiment includes three independent samples with repeated measurements. The second brickyard experiment has 149 independent samples that one could argue are "blocked" by a trip to the brickyard.

Because of the need for a data checking tool, I have compared the IGT and Dulong equations along with the Wilson,[1] Boie and Vondracek[2] equations to reported laboratory results for 170 MSW and RDF analyses and in a separate evaluation to 66 waste component (i.e., dirt, grass, wood, paper, plastics, rubber, leather, garbage, etc.) analyses. Figure 1 is a scatterplot of MSW and RDF laboratory HHV versus the IGT equation predicted HHV. Clearly, the IGT equation shows a high bias and an increasing slope. On the other hand, Fig. 2 is for the Vondracek equation and is typical of the plats for the other equations. Here, the data does not display any appreciable bias and the slope is nearly 1.

The results of our review of the various equations for the two data sets are summarized in Table HGR 1. From a regression between the laboratory and calculated heating values, estimates of the squared correlation coefficient, intercept and slope are developed along with the standard error of the estimate (this is the RMS error between the predicted and actual data points for each lab/calculated pair). To be a perfect predictor, the intercept and standard error should be zero and the slope and correlation coefficient one. The laboratory RMS error from the authors' paper is about 410 Btu/lb (0.46 MJ/kg).

From the data analysis in Table HGR 1, the IGT equation has the largest intercept and slope for both the MSW/RDF and waste components data. The Dulong equation has the largest standard error and is statistically significantly less accurate than the Boie and Vondracek equations, which are statistically equivalent.

Based on the available information, the IGT and Dulong equations should not be used to determine the internal consistency of waste analyses. Rather, the Boie or Vondracek equations should be used to determine if the bomb calorimeter and ultimate analysis based estimates are within about 10% of each other.

A checker using an equation to calculate HHV must realize, however, that failure to pass this validity screen does not mean that an individual result is wrong. Rather, it points to sets of analyses that should be checked for obvious sources of laboratory error. If no laboratory errors can be found, the need for replicated analyses is identified. Additional lab tests are needed to prove whether the suspect results are happenstance or the sample really produces unexpected results.

Discussion by

Roger S. Hecklinger
Velzy/Weston
Armonk, New York

The thesis that higher heating value of refuse derived fuel can be calculated from elemental analysis to the same degree of accuracy as experimental measurement in a bomb calorimeter is certainly intriguing. The data presented seem to bear out the validity of the thesis. The purpose of this discussion is to fuss with the data a little bit and to propose a way to make this knowledge useful.

The authors compared measured higher heating values with data calculated from five different formulas, that have been developed for varying reasons, to calculate higher heating value from an elemental analysis. They point out that the Dulong formula and the Institute of Gas Technology formula give the best agree-

---

[1] Dry-Basis HHV = 14,096 C_{ORG} + 55,750 (H-O/8) + 3982 S − 6382 C_{INORG} − 4274 (0/2) + 1040 N—where C_{ORG} is the dry basis organic carbon content, C_{INORG} is the dry basis inorganic carbon content and all other weight fractions are on a dry basis.

[2] As-Fired Btu/lb = C (160.5 − 0.112 C_1) + 486 (H-O/10) + 45 S—where C_1 is the carbon content on a MAF basis and all other parameters are as-fired weight percents.

SCATTERGRAM OF (DOWN) IGT INSTITUTE OF GAS TECH HHV (ACROSS) HHL LAB HHV

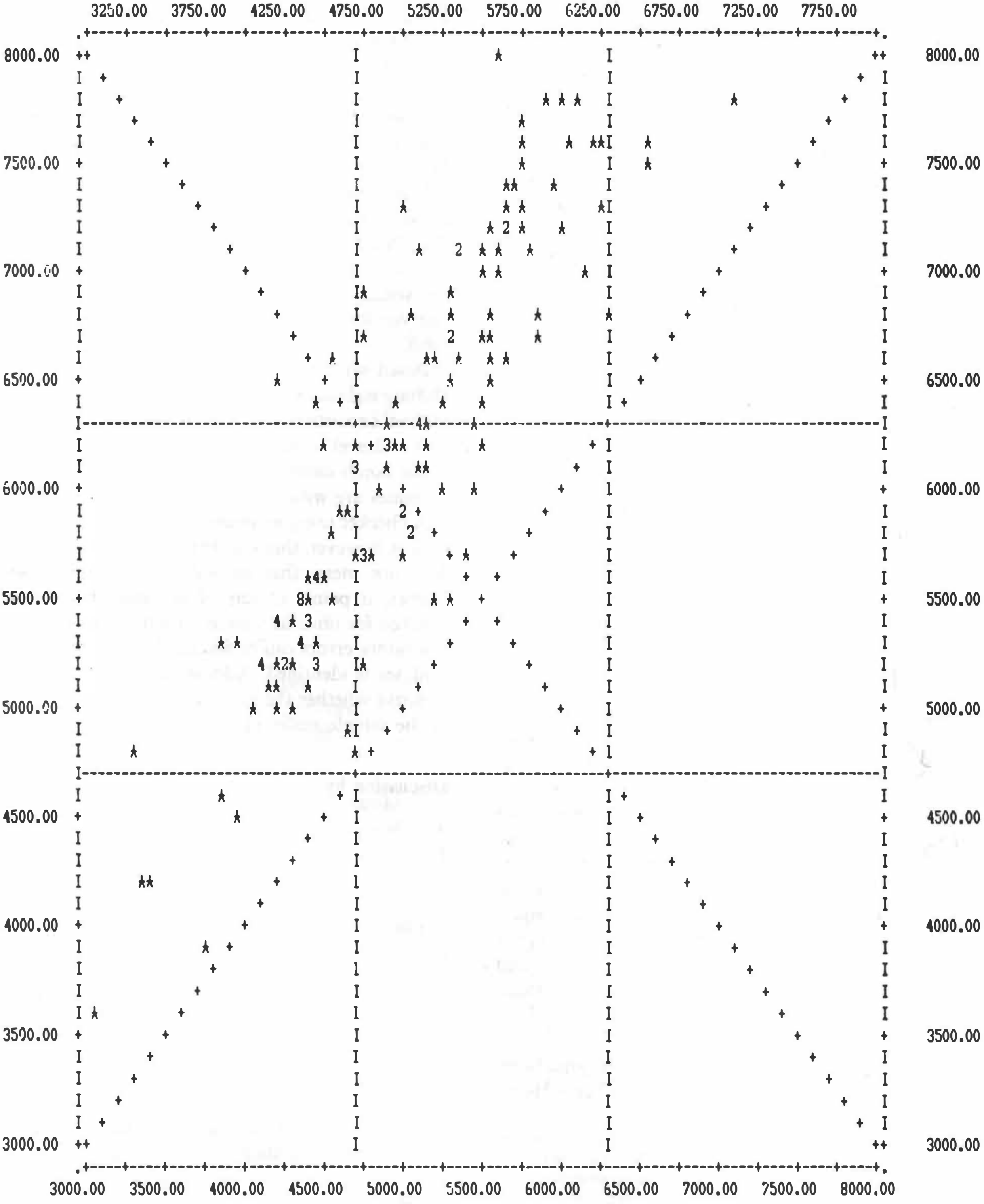

FIGURE 1

SCATTERGRAM OF (DOWN) HHV VONDRACEK HHV (ACROSS) HHL LAB HHV

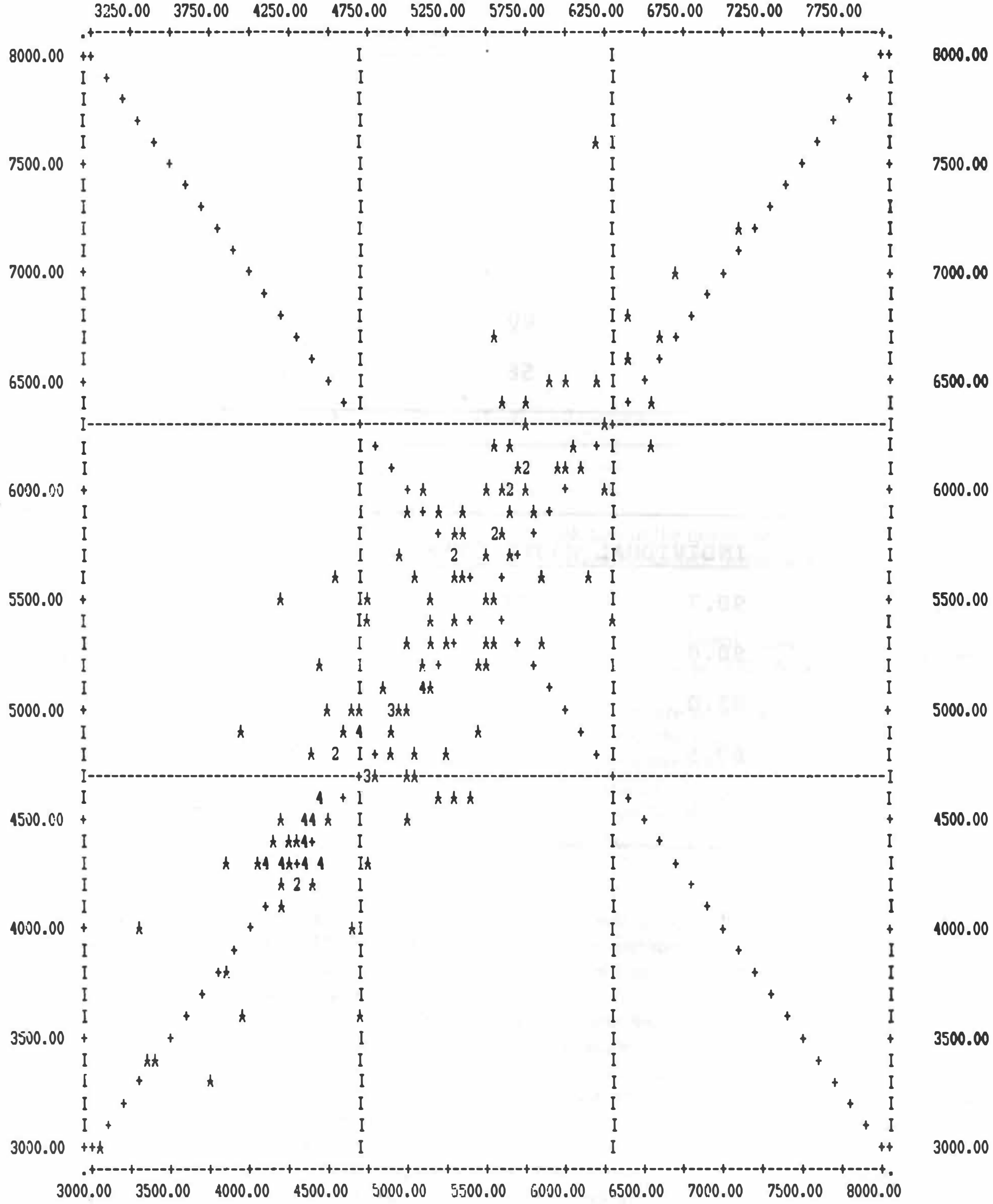

FIGURE 2

TABLE HGR 1 COMPARISON OF 170 BOMB CALORIMETER AND CALCULATED RESULTS FOR MSW AND RDF DATA AND 66 SETS OF DATA FOR WASTE COMPONENTS

MSW & RDF ANALYSES

FORMULA	R^2 (%)	INTERCEPT	SLOPE	STD ERROR (Btu/lb)
IGT	79.2	550	1.128	408
BOIE	78.6	56	1.006	382
DULONG	73.7	-162	0.997	423
WILSON	76.8	-200	1.030	414
VONDRACEK	79.5	58	1.015	383
INDIVIDUAL WASTE COMPONENT ANALYSES				
IGT	90.7	672	1.154	1006
BOIE	90.0	190	1.034	1015
DULONG	83.0	68	0.990	1216
WILSON	87.5	-53	1.062	1148
VONDRACEK	90.5	198	1.037	988

ment with the experimental heating values. They further point out that minor components of the elemental analysis, namely nitrogen, sulfur and chlorine, are of little significance.

As it turns out, if the minor components are included with oxygen in the elemental analysis, the calculations for the Dulong formula and the International Gas Institute formula would be in closer correlation with the experimental values than when minor components are included in the calculation.

The authors also point out that the Tillman formula, which only requires percentage of carbon for the calculation, gives low values relative to the experimental value. This is true, but the low values are consistently low, which suggests that the low values are a bias rather than an error. If the Tillman formula is modified to MJ/kg = 0.413 c, the correlation between calculated value and experimental value is closer than for any of the formula results tabulated on Table 4. (See Table RSH 1.)

What are the implications? If this relationship is real, then one can determine the heating value of refuse-derived-fuel if percent carbon is known. Other elemental determinations do not have to be made.

How can it be that carbon alone can be used to represent the entire combustible fraction of refuse-derived-fuel? If one determines HHV3 (moisture and ash free heating value) from the HHV2 in Table 2 by dividing HHV2 times 100 by 100 minus percent ash, one finds that HHV3 for all five "round robins" is

TABLE RSH 1

	ROUND ROBIN				
	1	2	2 I	3	3 I
HHV2, MJ/kg	17.4±1.5	18.5±0.7	17.7±0.5	17.4±1.1	17.1±0.5
TILLMAN ERROR, MJ/kg	-0.6	-0.7	-0.8	-0.6	-0.5
HHV2 / %C, MJ/kg	0.411	0.414	0.418	0.411	0.410
HHV3, MJ/kg	22.3	21.7	22.1	22.2	21.9

22.0 ± 0.3 MJ/kg (9450 ± 150 Btu/lb). In other words, HHV3 is apparently very consistent for refuse-derived-fuel. (See Table RSH 1.) Since carbon is the preponderant combustible element, it would seem that the relationship of carbon to the other combustible elements (largely hydrogen) should also be relatively consistent. Therefore it just may be practical to determine higher heating value by knowing percentage of carbon. More data should be examined.

Customary laboratory practice is to perform bomb calorimeter tests on 1 g laboratory samples and to perform carbon and hydrogen analyses on 0.2 g laboratory samples (apparently the National Bureau of Standards uses an instrument that works on 0.002–0.004 g samples); so it is inherently more difficult to have a representative sample for carbon analysis than for bomb calorimetry. It also happens that the cost of a bomb analysis is less than the cost, in some if not most laboratories, for a carbon and hydrogen analysis. (Traditionally, carbon and hydrogen are analyzed in the same procedure; and it should be pointed out that the sample sizes and test equipment used for bomb calorimetry and carbon and hydrogen analysis were developed for coal analyses.)

Perhaps it would be a worthwhile undertaking for the National Bureau of Standards to develop apparatus to measure carbon content of a larger, say 25–30 g (1 oz), sample that could be performed in the laboratory for less cost than a bomb calorimeter test. If this can be done, then the only task left to us would be to find the solution to the primal problem of obtaining a truly representative sample in the first place.

Discussion by

Floyd Hasselriis
Forest Hills, New York

The authors are to be commended for carrying out and presenting the results of their investigation of the relationship between elemental composition and heating value determined by calorimeter, using the precise science of the National Bureau of Standards.

As a member of the Laboratory Advisory Committee of the ASTM Committee E-38-01 (Energy) in 1978, I had the pleasure of following the Round Robin tests, described by the authors, of refuse-derived fuel samples, and the discussions of sources of error and lack of agreement between laboratories as these problems were worked out.

At the same time, I have observed within the waste-to-energy industry many inconsistencies between heating values determined by calorimeter and those calculated from elemental analysis. The question "which method gives the correct answer" has been elusive. Dr. Domalski even investigated the heating value of metal oxidation and the effect of sulfates in an effort to understand these inconsistencies, and resorted to extremely fine grinding and mixing to overcome non-uniformities and nonrepresentative samples. These efforts resulted in the high precision needed to make comparisons between heating values obtained by calorimetry and elemental analysis.

In order to use the exceptional data base of the RDF Round Robin tests, the authors have had to study the data in detail, so that rather than reject inconsistent data, they tried to determine the reason for the inconsistencies, and make the corrections. Small errors were allowed, but data with large errors were dropped from further analysis: "outliers were defined as values which did not lie within roughly plus or minus 2.5 standard deviations (98% confidence level) of the component's mean value."

The authors point out that in the first round of testing, half of the tests had to be discarded, and for the second and third rounds over half of the tests were self-consistent. This attests to the difficulties in measuring heating value even from individual samples which are obtained from a single sample, ground and mixed carefully. It was difficult to determine whether differences derived from variations in the RDF itself or from laboratory procedures, and easy to blame the RDF. However, the various laboratories closely agreed on the analyses of RDF taken from plants in different parts of the country, in spite of substantial differences in composition. The main discrepancy was the moisture determination, since moisture is lost during handling and milling.

One source of inconsistencies has been the determination of oxygen by difference, since the reported oxygen has considerable leverage on the resulting calculated heating value. According to the authors, this is overcome by requiring the total mass percent to add up to exactly 100. This accountability check uncovered errors related to neglecting chlorine and failing to deal with moisture properly.

The major contributor to the total error was found to be hydrogen, due to its high heating value.

The conclusion that the uncertainty of the higher heating value calculated by formula is not much different from that measured by bomb calorimetry is of major importance. The selection of the Dulong and IGT formulas as the most accurate will encourage their use as standards. The finding that the Boie formula has a slightly higher error does not invalidate data obtained from use of this formula.

A major value to the use of the Dulong or IGT formulas is their use as a check on the calorimeter data, or vice-versa. In my opinion, such a check should be required before a laboratory's data be accepted. What do the authors think about this?

Another reason for preferring the Dulong formula (or the IGT, which considers ash, which may or may not be significant), is their use of coefficients which are essentially the same as the individual heating values of carbon and hydrogen. When this is done, then the calculation of oxygen requirements for complete combustion, as used by combustion system designers, will be consistent, and especially consistent with the heating value.

I have encountered difficulties in trying to use data from sorting analyses of MSW to determine heating value, and comparing it with parallel measurements of heating value. By critical analysis, which identifies non-representative factors or other outliers, a consistent set of numbers can be collected which will achieve agreement between the knowledge of the elemental analysis of the sorted components, and their consistent heating values.

Outside of the sources of error described by the authors, it must be recognized that obtaining representative samples of MSW is much more difficult. The major factor in as-received heating value is moisture, which is difficult to retain during sorting procedures. In addition to the errors due to unintended air-drying, daily and seasonal variations take place which cannot readily be evaluated. Due to this problem, the heating values determined in MSW analyses carried out in order to plan waste-to-energy projects are likely to be seriously in error. The only way to know the heating value of MSW is to use the boiler as a calorimeter during performance tests and throughout the course of the entire year, after the plant is in operation.

I have one serious question: many published versions of the Dulong equation, such as that presented in B&W's "Steam" show the oxygen as one-eighth of the hydrogen, as "a correction for the hydrogen already combined in the fuel to form water vapor." The Dulong equation offered by the authors has a coefficient of about 9.8, and in the IGT and Boie equations it is 10.5. My own correlations indicate that the factor of 8 gives a plus error of about 5%, whereas the authors' variant reduces the overestimate to about 3%. Is this the "fudge factor" which can be used to make the calculated data agree with calorimeter data? Should this factor be further considered? In calculating the oxygen required for combustion, should the same factor be used for consistency?

I want to express my personal gratitude to Donald Walter of the Biofuels and Municipal Waste Technology Division of the U.S. Department of Energy for funding this most urgent project which has brought a fundamental answer to such a basic question.

AUTHORS' REPLY

We thank the authors of the written discussions for their support of this study. We are pleased to see that the resource recovery industry has a use and a need for formulas which can predict the heating values of RDF from elemental analysis. We are also thankful for the constructive criticism of this initial study and will try to incorporate some of the comments to produce a calculation procedure which is useful to the resource recovery industry.

The comments from the discussion authors will be answered separately.

To Mr. R. C. Hittinger

In paragraph one of the discussion, Mr. Hittinger mentions that a significant limitation exists with using 9-year old data, and that more recent data should have been collected as part of this study. No new data were collected as a part of this study. Only the measurements made in the original Round Robin study were used, even though some data were not reported earlier. Mr. Hittinger also states that it is highly desirable for the procedure to be repeated with newer data on elemental composition and calorific content of wastes obtained using newer analytical techniques. We agree that such a repeat of the Round Robin tests would be desirable and expect that better agreement between calculated and measured heating values may be possible.

In paragraph two, Mr. Hittinger mentions that the HHV calculations can be used as a substitute for measured heating values and also that they allow one to predict heating values of waste streams as its composition changes. While there is no substitute for bomb calorimetric measurements when calculated heating values are suspect, the idea of using heating value formulas for prediction purposes is a good application of our findings.

In the last paragraph of Mr. Hittinger's discussion, he notes that the test data used did not have much variation in elemental composition. This is certainly a fact for the Round Robin test samples used in this evaluation. The need to demonstrate the formula's ability to predict higher heating values with extremes in composition variability is certainly true if one is to apply these formulas to waste streams other than "typical" RDF from MSW. We plan to perform an evaluation of calculated and measured heating values on individual components of RDF in a future study. While the ability of a formula such as the IGT equation (which was obtained by an empirical fit of composition and heating value data) to work for extreme compositions may be a valid concern, formulas based on thermodynamic arguments, such as the Dulong formula, should be able to accommodate extremes in composition.

To Dr. H. Gregor Rigo

In paragraph two of Dr. Rigo's discussion, he states that our conclusions should be based on three Round Robin samples analyzed with duplicates (inter-lab results) for two of the samples and not on the assumption of 149 valid data sets. We did just that. The 149 valid data sets mentioned by Dr. Rigo were not considered independent measurements, but rather used to quantify the uncertainty in the measured values for the samples used in each of the Round Robin tests. Our conclusions are based on the average values and their uncertainties for three Round Robin and two inter-lab tests. We acknowledge that the Round Robin data come from three RDF samples which were analyzed repeatedly. The repetitions were needed to test "within-lab" and "between-lab" agreement and establish that RDF could be characterized by ASTM methods similar to those for coal. Without their repetition, precision limits for the ASTM methods for RDF would not have emerged.

In paragraph eight of his discussion, Dr. Rigo states that the Dulong and IGT equations are not the best to use for calculating higher heating values. According to his analysis, the Boie or Vondracek equations should be used. We thank Dr. Rigo for pointing out a better equation for calculating heating values. Due to the large number of formulas in the literature for calculation heating values of everything but RDF, we made no attempt to find the "best" equation, but rather used some equations which have been useful for other fuels. We have no problem with using an equation such as that of Vondracek which fits the data better. We thank Dr. Rigo for pointing us to a better formula and will investigate it further in our next study.

Dr. Rigo states that the calculated heating values should agree to within 10% of the bomb calorimetry results. We believe that the Dulong and Vondracek formulas do even better but may not be realized due to problems in obtaining identical (or representative) samples needed for the bomb and ultimate analysis measurements.

To Mr. Roger S. Hecklinger

In paragraph four of Mr. Hecklinger's discussion, the use of a modified version of the Tillman formula to calculate heating values from carbon content measurements is proposed. We agree that it is certainly possible to use carbon as a means of calculating higher heating values, since carbon is the major combustible fraction on a mass basis. However, this method is prone to produce errors when the composition of the RDF changes from the fuel mix used to derive the carbon coefficient. Since any formula is apt to be applied to other than typical municipal waste streams, a modified Tillman formula would not work well for extreme variations in composition. We prefer a formula which uses the major elemental components and ash of a fuel to calculate its heating value.

In paragraph six, the consistency of HHV3 between the Round Robins is used to support the proposal of using only carbon as the determining heating value of RDF from MSW. Our determination of empirical formulas support the proposal that the relationship between the elements is constant for MSW. But as stated in the previous paragraph, a modified Tillman formula would severely limit its usefulness when the composition changes.

In paragraph seven, Mr. Hecklinger mentions the fact that smaller sample sizes are used for carbon and hydrogen measurements than for bomb calorimetry results. He states that this creates a more severe problem in making a representative sample for carbon and hydrogen measurements. The preparation of small representative samples of a heterogeneous material such as MSW is certainly a problem in analyzing its composition. We are not in position to debate which is more cost effective to obtain higher heating values, bomb calorimetric measurements or ultimate analysis. However, in cases where the elemental analysis is needed anyway, or a bomb calorimeter is not available, the calculation of heating values should be an acceptable way of obtaining it. (The National Bureau of Standards does have analytical instruments which use 2 to 4 mg samples; however, the instrument mentioned in our paper was used on coal samples and was cited to illustrate that there is a capability for determining the elemental composition of very small samples when the particle size is in the 80–150 μm range.)

Mr. Hecklinger's suggestion of NBS developing a method for determining carbon content of 25–30 g (1 oz) samples of MSW would certainly help in overcoming some sampling problems while providing a measurement which could be used for calculating heating values. However, NBS does not have any authorization or funding in MSW or resource recovery to pay for such a project. We are dependent on other agency money to support such work and currently have no funds for the project. Also, as Mr. Hecklinger points out, one is still left with the problem of obtaining representative samples from a pile of MSW in the first place.

To Mr. Floyd Hasselriis

Mr. Hasselriis' suggestion of requiring the agreement of calculated heating values with measured values is a useful application of a heating value formula. However, we feel that it is premature to mandate to test laboratories and require that calculated and measured heating values agree. We do feel that a significant disagreement between the ultimate analysis and bomb calorimetric heating values should cause one or both to be suspect. We agree with Dr. Rigo's comments at the end of his discussion on what one should do when calculated and measured values disagree. They are, check for obvious sources of error and repeat measurements if necessary.

Mr. Hasselriis questions the source of our oxygen coefficient in the Dulong formula in the next to last paragraph in his discussion. The oxygen coefficient used was not altered in any way but taken directly from the literature reference. The difference between the ideal 1/8 value for oxygen bound in water and the coefficient in the Dulong formula is to account for the fact that all the oxygen in a sample is not bound in the form of water but also found in other chemical binding states, such as, in alcohols, ketones, and ethers. We feel that the oxygen coefficient should be considered further for a heating value formula derived especially for MSW as a fuel. The oxygen coefficient should be adjusted based on thermodynamic arguments and the relative amount of the different chemical bonding states of oxygen found in a sample and not used as a "fudge factor" just to make the data agree.

Determining the amount of oxygen required for combustion has been proposed as one method of determining the heat of combustion of a sample, as pointed out by Mr. Hasselriis. We do not have the background to comment on the significance of the oxygen coefficient in the Dulong formula and the coefficient used in the oxygen required heating value calculation. We refer the interested reader to an article by C. Huggett [1] for further information on the subject.

REFERENCE

[1] Huggett, C. "Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements." *Fire Water* 4 (1980): 61-65.