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Determination of the Calorific Value of Refuse-Derived-Fuels by Large-Bomb Calorimetry Summary of the 1978 Fiscal Year Results

D. R. Kirklin, E. S. Domalski and D. J. Mitchell

Chemical Thermodynamics Division
and the
Thermal Processes Division
National Bureau of Standards
Washington, D.C. 20234

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Prepared for
U.S. Department of Energy
Office of the Assistant Secretary
Conservation and Solar Applications
Division of Building and Community Systems
Urban Waste and Municipal Systems Branch
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and

U.S. Environmental Protection Agency
Municipal Environmental Research Laboratory
Solid and Hazardous Waste Research Division
Cincinnati, OH 45268
DETERMINATION OF THE CALORIFIC VALUE OF REFUSE-DERIVED-FUELS BY LARGE-BOMB CALORIMETRY

SUMMARY OF THE 1978 FISCAL YEAR RESULTS

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An oxygen bomb calorimeter which can accommodate a 25 gram sample of refuse or a refuse-derived-fuel (RDF) has been designed and constructed at the National Bureau of Standards for the purpose of studying the effects of sample processing on the measured calorific value of such material. This large calorimeter is an enlarged and modified version of a conventional-size calorimeter also in use at NBS. The large calorimeter can handle samples ten times larger than the conventional-size calorimeter and therefore can be used to investigate RDF samples with either minimal or no processing. Calorimetric results are presented for calorific value measurements carried out on d(densified)-RDF in both calorimetric systems. Moisture- and ash-free (MAF) calorific values were obtained in the large calorimeter from six randomly chosen unprocessed RDF samples and had a mean value of 24.99 MJ·kg⁻¹ (10 742 Btu·lb⁻¹). Another randomly-chosen sample of unprocessed RDF was subjected to extensive processing to obtain a "homogeneous" analysis sample for use in the conventional-size calorimeter. Individual measurements in the conventional size calorimeter on each of ten "homogeneous" sub-samples gave a mean calorific value of 24.99 MJ·kg⁻¹ (10 743 Btu·lb⁻¹). The results of this investigation indicate that the calorific value of d-RDF is unaffected by the sample processing technique used at NBS.
INTRODUCTION

The Resource Conservation and Recovery Act of 1976, PL 94-580, identifies solid waste as a potential source of oil, gas, or solid fuel which can be converted into energy and mandates that the Department of Commerce provide accurate specifications for recovered materials. The National Bureau of Standards will furnish guidelines, as indicated in this Act, for the development of specifications which pertain to the physical and chemical properties, and characteristics of recovered materials with a view toward their replacing virgin materials for various applications.

The heating (or calorific) value of a fuel is perhaps its most significant property. Heating values are used extensively to evaluate the commercial potential of fuels and also to evaluate the performance of incinerators and refuse-fired boilers. The E-38 Committee on Resource Recovery of the American Society of Testing Materials (ASTM) is interested in the development of standard methods of test required for the establishment of refuse-derived-fuels (RDF) as an article of commerce. The American Society of Mechanical Engineers (ASME) Performance Test Code 33 Committee is interested in a method to evaluate the performance of large incinerators and boilers. A laboratory measurement procedure giving representative and reproducible heating values is necessary to equip commercial laboratories to certify accurately the energy content of RDF and also to evaluate the compliance of large incinerators and refuse-fired boilers with their contract performance specifications.
A method must be established for the precise and accurate measurement of the heating value of refuse and RDF to evaluate adequately their merit as fuels. Therefore, the National Bureau of Standards has entered into a collaborative research agreement with the U.S. Environmental Protection Agency and the U.S. Department of Energy to establish the procedures necessary to determine the calorific value of refuse and RDF by bomb calorimetry.

Refuse consists of combustible and non-combustible materials. Unfortunately, heating values are determined on small portions of refuse and considerable processing is necessary to obtain values representative of the original collection of refuse. The first step of producing a refuse-derived-fuel (RDF) is to remove the large non-combustible materials. The remaining materials are then reduced to 15 cm (6in) particle size or smaller and with the aid of air classifiers, the light combustible fraction is separated from the heavy non-combustibles. This air classified, combustible fraction of refuse is then reduced to a smaller particle size to produce a more homogeneous material.

The objectives of this project are to determine the optimum particle size of samples for combustion measurements and to establish whether a conventional-size (2.5 gram capacity) calorimeter or a larger (25 gram capacity) calorimeter will provide more representative calorific values of RDF. This report which summarizes work carried out during fiscal year 1978 provides a response to both objectives from the results obtained for a Teledyne National RDF sample using a conventional-size (2.5 gram
capacity) bomb calorimeter and a recently constructed large (25 gram capacity) bomb calorimeter. This report presents data that indicate calorific values of unprocessed d-RDF (2.5 cm or 1 inch particle size before densification) are identical to those of RDF processed to 0.2 cm particle size.

**EXPERIMENTAL**

**Materials**

1. **Benzoic Acid.** NBS Standard Reference Material 39i, certified energy of combustion of \(26 \ 434 \pm 3 \ J \cdot g^{-1}\) at standard bomb conditions, was used to calibrate the conventional-size calorimeter. All samples were drawn from the same bottle. Fisher Scientific Company's certified benzoic acid with an energy of combustion of \(26 \ 437 \pm 3 \ J \cdot g^{-1}\) was utilized for the large calorimeter under standard bomb conditions.

2. **Oxygen.** Ultra High Purity (UHP) grade of oxygen was supplied by Matheson Gas Products. This oxygen is certified by the manufacturer to contain combustible impurities not exceeding 0.002 percent and total impurities of less than 0.05 percent.

3. **d-RDF.** In February 1977, a 20 kg (44 pound) sample of extruded, d(densified)-RDF pellets was received from Teledyne National. This laboratory sample was from the Baltimore County Resource Recovery Plant located in Cockeysville, Maryland. The collection of extruded pellets was contained in a plastic bag enclosed in a cardboard box. The Teledyne National pellets are cylindrical in shape, with a diameter of 2.5 cm (1 inch) and are broken-off lengths of about 2.5 to 7.5 cm (1 to 3 inches).

*The materials and equipment are specified to clarify the experimental procedure, however, in no way does this imply an NBS endorsement of these materials and equipment.*
Sample Preparation

1. **Sample Requirements.** It is necessary that any set of analysis samples prepared from a gross field sample of refuse or RDF be representative of the composition of the field sample and be unaffected by the laboratory techniques utilized to produce these analysis samples. It is assumed that the milling and blending of the gross field sample produces a homogeneous product and the variational parameter which must be measured and controlled is the moisture content. This study shows that analysis samples equilibrated in a constant-humidity container at the average relative humidity of the bomb-calorimetric laboratory increases the precision of the measurements. The temperature and relative humidity of this laboratory are maintained at $295 \pm 2$ K and $45 \pm 10$ percent, respectively.

2. **Small Calorimeter Samples.** A random group of extruded Teledyne National pellets was removed from the field sample of RDF. The preparation from these pellets of RDF samples for the conventional-size calorimeter has already been described [1] and is also provided below: The pellets were ground in a Quaker City Mill (Model 4) to a particle size of less than 1.3 cm (0.5 inch). The particles were then milled to pass a 2 mm (10 mesh) screen in a Wylie Micro-Mill. The ground sample was riffled and then thoroughly blended in a vee blender.

The ground material was then pressed into pellets with a pressure of approximately 221 MPa (32 000 psi). Each pellet weighed approximately 2.2 grams. These pellets were dried to constant weight at 105 °C in a drying oven. The samples were then placed in the constant-humidity atmosphere for a minimum of 48 hours and moisture equilibration checked by successive weighings.
3. **Large Calorimeter Samples.** Extruded RDF pellets were utilized in the large calorimeter with no further processing by NBS laboratories. The long extruded pellets were broken into pieces weighing between 20 and 25 grams and placed in the constant-humidity atmosphere.

Figure 1 shows the size of a benzoic acid pellet for the large calorimeter, pellets for both the small and large calorimeters, and the unprocessed RDF sample as-received from Teledyne National. These as-received extruded RDF pellets appear heterogeneous while the milled and blended RDF pellets have a more homogeneous appearance.

**Calorimetric Apparatus**

1. **Large Isoperibol Bomb Calorimeter.** The design of the large "isoperibol" (isothermal-jacket) calorimeter which will accommodate the large combustion bomb, described in the following section, is similar to that of Coops et al. [2,3] and Gundry et al. [4], and is shown in Figure 2.

The calorimeter is constructed entirely of stainless steel. It consists of a cylindrical calorimeter vessel (25.4 cm diam., 45.7 cm height (10 inch diam., 18 inch height)) in which three rods support a concentric cylindrical shield (20.3 cm diam., 30.5 cm height (8 inch diam., 12 inch height)). The calorimeter lid supports a stirrer assembly and a shield cover. The shield, shield cover, and stirrer assembly facilitate the flow of water in the calorimeter so that water is moving (downward) in the space between the bomb and shield, and (upward) between the shield and wall of the calorimeter vessel. The combustion bomb is supported by a foot which has been welded to the bottom of the vessel to insure that the bomb will be positioned in the same manner in the calorimeter for each experiment. The calorimeter vessel contains 19 liters of water for
each calorimetric measurement and is housed in a submarine vessel which has a cover. The submarine cover is fastened to the vessel with six bolts and has four vertical ports for: (1) fuse circuit leads, (2) a calorimeter heater, (3) a central stirrer assembly and, (4) quartz thermometer leads. The frequency of oscillation of a temperature-sensitive quartz crystal is used to determine the calorimeter temperature. The NBS standard frequencies of 10 and 100 kHz are utilized. The entire calorimeter system (bomb, calorimeter vessel, and submarine compartment) is immersed in a constant temperature water bath maintained at 30° ± 0.03°C. The overall volume of the bath is 280 liters and holds 235 liters of water with the calorimeter system immersed in it.

2. Large Combustion Bomb. The combustion bomb which accommodates a 25 gram sample of RDF was purchased from the Parr Instrument Company and is shown schematically in Figure 3. The bomb has an overall height of 35 cm (13.75 in) and has a mass of 13.8 kg (30.5 lb) when assembled; the internal and external volumes of the bomb are 1.85 and 3.62 liters, respectively. A platinum crucible (\(\approx 50 \text{ cm}^3\)) was used in the calibration experiments with benzoic acid and a stainless steel crucible (\(\approx 50 \text{ cm}^3\)) was used in the combustion experiments with RDF. The bomb body has a wall thickness of 0.953 cm (0.375 in) and an outer diameter of 11.4 cm (4.5 in).

A photograph of the small and the large combustion bombs is shown in Figure 4. Figure 5 is a photograph of the large calorimeter viewed from the top. It shows the large bomb immersed in the calorimeter vessel with the submarine lid and calorimeter cover (inverted to display the stirrer and shield cover).
Calorimetric Procedure

Bomb-calorimetric techniques are well established and are described in detail elsewhere [5,6], but a brief description of the method used in this work follows. In the thermochemical investigations, the heat evolved by complete oxidation of a measured amount of RDF is compared with the heat evolved by a measured amount of a selected standard reaction, using a fixed calorimeter system with a specific temperature rise. The standard reaction is the combustion of benzoic acid under standard bomb conditions producing a temperature rise of 3 and 5 degrees in the small and large calorimeters, respectively. The energy equivalent of the calorimeter is the amount of energy produced by the standard reaction and its accompanying side reactions divided by the corrected temperature rise. The corrected temperature rise is derived from the observed temperature rise by subtracting the contributions due to stirring energy and thermal leakage.

Multiplication of the energy equivalent of the calorimeter (obtained from the calibration experiments) by the corrected temperature rise (measured in the RDF combustion experiment) gives the total energy produced in the RDF combustion experiment. This total energy is then corrected for known side reactions and divided by the mass of the RDF sample to produce the gross calorific value. In a typical RDF experiment, a moisture equilibrated RDF pellet is weighed in a tared stainless-steel crucible. The crucible and sample are supported inside the bomb. The sample is in contact with a 10 cm length of 0.127 mm (.005 in) diameter iron fuse wire. The bomb also contains 10 cm$^3$ of H$_2$O to
dissolve certain gaseous products of combustion and maintain an atmosphere that is saturated with water. The sealed bomb is then charged with high-purity oxygen at a pressure of 4.1 MPa (40.8 atm). The bomb is lowered into the water-filled calorimeter and the covered calorimeter then submerged in the constant temperature water bath (30°C). The calorimeter system is then heated to slightly below 25 °C, and frequent measurement of temperature and time is begun. Figure 6 is an example of a time-temperature curve for a typical bomb-calorimetric experiment (see ref. 5, chap. 3 for more detail). The temperature is measured during the period before the sample is ignited ("fore period", line ab in Figure 6), during the reaction period immediately after the sample is ignited ("reaction period", line be in Figure 6), and during the period after the reaction is complete ("after period", line eh in Figure 6). The difference between the first point in the after-period and the last point in the fore-period gives the observed temperature rise. The slopes with respect to time of the temperature-time curve during the fore- and after-periods allow one to calculate the portion of the temperature rise due to stirring energy and thermal leakage. The submerged calorimeter must be stirred at a constant rate to obtain a uniform and meaningful temperature vs. time curve. A preliminary experiment was performed to determine the amount of RDF sample necessary to produce about the same temperature rise in the calorimeters as that produced in our calibration reaction with benzoic acid, (a three and five Kelvin temperature rise in the small and large calorimeter, respectively).
DISCUSSION AND RESULTS

Calibration Experiments

It is necessary to determine in preliminary calibrations the energy equivalent for both the large and conventional-size calorimeter systems. The results of these calibration experiments are presented in Table I. Experiments number 1046 through 1050 were performed in the conventional-size calorimeter and 2006, 2010 and 2011 were performed in the large calorimeter. In a calibration experiment, one accounts for all energy supplied to the calorimeter system and measures the resulting temperature rise. The identifiers in rows 4 through 10 of column 1 of Table I are the different sources of energy in a typical calorimetric experiment. A comparison of the small- and large-calorimeter entries will point out some of the differences between the two calorimeters. \( \Delta U_{c}^{o}, t_h \) is the energy of combustion of benzoic acid at the specified reference temperature, \( t_h \). The small calorimeter is referenced to 28 °C and the large calorimeter is referenced to 30 °C. The heat of combustion of the calorimetric standard, benzoic acid, is known to approximately one part in ten thousand. From the mass of benzoic acid, shown in row 3, \( m_{BA} \), the energy supplied by combustion of benzoic acid can be calculated and is presented in row 4, \( q_{BA} \). Row 5 shows the electrical energy that was supplied to ignite the sample, \( q_{-ign} \). The platinum fuse wire of the small calorimeter is heated electrically to its melting point to ignite the samples. The molten platinum fuse solidifies and therefore supplies no detectable energy to the small calorimeter. In the large calorimeter an iron fuse wire was used. The electrical energy necessary to melt the iron fuse wire must be accounted for, but in addition, the molten iron
reacts to produce iron oxides. The quantity of iron fuse wire burned and the energy of combustion of the iron fuse wire are used to calculate the energy supplied by the combustion of iron, $q_{\text{Fe}}$. Some of the nitrogen impurities in the oxygen are converted to nitrogen oxides which react with water to form nitric acid. The quantity of nitric acid produced is measured and from its energy of formation, $q_{\text{HNO}_3}$ is calculated. In high-precision combustion calorimetry, it has become standard practice to apply corrections proposed by Washburn [7] that produce calorimetric data referenced to a standard set of conditions. These corrections to standard states for the isothermal bomb process at 28 °C and unit fugacity are known as Washburn Corrections and are presented as $q_{\text{wc}}$. The small calorimeter is designed to operate between 25 °C and 28 °C while the large calorimeter operates between 25 °C and 30 °C. In actual practice, the final temperature of our experimental reaction is not exactly 28 °C or 30 °C and therefore, a small correction must be applied to the calorimetric data for high precision work and is shown as $q_{T_f \text{ corr.}}$ in Table I. Due to the limited quantity of oxygen in the large bomb, combustion is incomplete and a few tenths of a milligram of carbon residue were found in the combustion crucible. The energy of combustion of benzoic acid assumes complete combustion and therefore a small correction for unburned carbon, $q_{C \text{ corr.}}$, was included in the energy summation. The algebraic sum of the energies in rows 4 through 10 from various sources yields the total energy supplied to the calorimeter, $Q_{\text{Total}}$, corrected to 28 or 30 °C.

Some additional discussion is warranted in regards to the unburned carbon residue. Stoichiometrically, 2 grams of oxygen are required for
the combustion of 1 gram of benzoic acid. Normally, 10 grams of oxygen are used for each gram of benzoic acid to insure complete combustion in the conventional-size bomb. It has been found in practice that 6.5 g of O₂ per gram of benzoic acid is the minimum requirement for complete combustion in the present design of bomb calorimeters. The large bomb, utilizing a 16.3 gram benzoic acid sample and 4.1 MPa (40 atm) of oxygen contains about 100 grams of O₂. This is on the borderline of the minimum amount of oxygen necessary for complete combustion in bomb calorimetry. However, in our experiments the total correction for unburned carbon is usually less than 40 joules for a 400 000 joule experiment (1 part/10 000) and even if completely neglected, the error thereby introduced would be acceptable for precision combustion calorimetry of benzoic acid. The correction for unburned carbon, q-C corr', is given in Table 1 for the large calorimeter data.

The corrected temperature rise of the calorimeter, ∆T-corr, is calculated and divided into the total energy supplied to the calorimeter, Q-total, to yield the energy equivalent, E_cal, of the calorimeter. The mass of water introduced into the bomb, the crucible and the sample may change from experiment to experiment. The product of the mass of these materials and their specific heats are subtracted from the energy equivalent of the calorimeter and the energy equivalent of the "empty" calorimeter, E_s1', is obtained.

The important parameters to compare between the two calorimeters are the energy equivalents and the total energy capacities of the two calorimeters. The energy equivalent of the small calorimeter is 14 555 joules per Kelvin while that of the large calorimeter is 86 162 joules
per Kelvin. The product of the energy equivalent and the specified temperature rise gives the total energy capacity. The large calorimeter has a total energy capacity of 430,810 joules compared to 43,665 joules of the small calorimeter. Therefore, a sample which has a mass ten times larger and less particle size reduction can be used in the large calorimeter. This is extremely important since the calorific value of a solid fuel can now be determined with only minimal processing and the possibility of chemical changes imposed upon the refuse or RDF analysis sample as a result of size reduction, can now be investigated quantitatively.

**RDF Combustion Experiment**

In a calorimetric experiment, the corrected temperature rise of the calorimeter multiplied by the mean energy equivalent of the empty calorimeter plus its contents yields the total energy supplied to the calorimeter.

A correction is subtracted for the formation of sulfuric acid from the small amount of sulfur (\%0.1\%) contained in the d-RDF sample. Of the six energy correction types contained in rows 5 through 10 of table I, neither the Washburn correction nor the carbon corrections are applied. The Washburn correction (used in high-precision calorimetry) cannot be applied since the actual reactants and products in the RDF experiments are unknown. In addition, complete combustion was assumed in the RDF experiments. The total energy measured, minus the algebraic sum of all corrections yielded the energy of combustion of the analysis sample. The calorific value of each RDF sample is simply the energy of combustion per unit of mass (weighed in air).
Table II presents the calorific values obtained on several analysis samples of an RDF from Teledyne National. The values presented from the conventional-size calorimeter were obtained on samples which were subjected to considerable processing as outlined in the experimental section earlier. The values determined in the large calorimeter were obtained on the as-received densified RDF with no further processing.

Table II presents moisture- and ash-free (MAF) calorific values obtained from these two types of calorimetric samples. Typical RDF samples have a moisture- and ash-free calorific value of between 20.93 and 23.23 MJ·kg\(^{-1}\) (9000 and 10000 Btu·lb\(^{-1}\)). The Teledyne National samples studied are obviously atypical and exhibit an unusually high heating value.

Ten experiments in the small calorimeter on "homogeneous" RDF yielded a mean calorific value of 24.99 MJ·kg\(^{-1}\) (10,743 Btu·lb\(^{-1}\)) and a standard deviation of a measurement of 0.80 percent while six experiments on as-received RDF samples with no further processing yielded a mean calorific value of 24.99 MJ·kg\(^{-1}\) (10,742 Btu·lb\(^{-1}\)) and a standard deviation of 2.54 percent in the large calorimeter. The agreement of these mean calorific values is significant when one considers the radically different treatment of the two samples.

The range of calorific values is much larger on the large, unprocessed samples than on the small, processed ones. Calorific values were dispersed over the range from 24.51 to 25.20 MJ·kg\(^{-1}\) (10,539 to 10,835 Btu·lb\(^{-1}\)) for the small calorimeter samples while a range of 24.39 to 26.09 MJ·kg\(^{-1}\) (10,485 to 11,216 Btu·lb\(^{-1}\)) was observed for the large calorimeter samples. As expected, these results suggest that the unprocessed
samples are more heterogeneous and that the calorific values would scatter widely. A closer look at the heating values obtained in the large calorimeter reveals that five of the six values are close together and that one value, 26.09 MJ·kg⁻¹ (11 216 Btu·lb⁻¹), lies further from the mean. The 26.09 MJ·kg⁻¹ (11 216 Btu·lb⁻¹) value is 1.7 standard deviations from the mean and cannot be traced to any instrumental malfunctions. Therefore, it is included as part of the sample population.

If the high calorific value were to be omitted, the mean calorific value would be 10 647 Btu·lb⁻¹ which is less than one percent from the mean obtained when 11 216 Btu·lb⁻¹ is included. This omission would change the standard deviation from 2.54 percent to 1.51 percent.

Several things could account for the spread of calorific values from the large calorimeter. In addition to the sampling problems associated with RDF, the moisture and ash contents are very important parameters. Table III contains the moisture and ash contents used to calculate the moisture- and ash-free results from the as-determined calorimetric data which are presented in Table II. We attribute the fluctuations in the moisture content of analysis samples 1052, 1053 and 1054, to the relative humidity changes of the room. Therefore, sample 1056 through 1062 were equilibrated in a constant humidity atmosphere and all had virtually the same moisture content. Water was absorbed or evaporated from the samples during the weighing process but always at a rate which was not readily reflected in the corresponding calorific value. This was accomplished by maintaining the constant humidity container at the average relative humidity of the room (≈45 percent).
One reason for the good precision of the small calorimeter results is that the moisture was virtually constant for all analysis samples and was determined on the calorimetric analysis sample directly. This was not true for the large calorimeter analysis samples. With the small analysis samples, 48 hours were sufficient for equilibration, but the as-received extruded pellets for the large calorimeter had approximately 13 percent moisture and equilibrated very slowly in our constant humidity atmosphere. Since equilibrated analysis samples of the same size have the same moisture content, we feel that separate moisture experiments would give an average moisture value indicative of all the equilibrated RDF analysis samples. Two experiments were carried out on several extruded pellet fragments each weighing about 5 grams, and yielded moisture contents of 5.71 and 5.92 percent. Two experiments were performed on extruded pellets of approximately the same size (\( \sim 25 \) grams) as the combustion samples and yielded moisture contents of 6.82 and 6.30 percent. We feel that none of the extruded pellets had equilibrated completely and that the equilibration was very slow and largely dependent upon the size of extruded pellets chosen for equilibration. The moisture measurements were done on different days during the period that the calorimetric experiments were being performed. We feel that the moisture measurements on extruded pellets of approximately the same size (\( \sim 25 \) grams) as our calorimetric analysis samples were more representative of the calorimetric samples used in the combustion experiments. We, therefore, used an average moisture of 6.56 percent to calculate calorific values on a moisture-free basis. The uncertainty of the actual moisture of each calorimetric sample may be part of the cause for the larger range of heating values measured in the large calorimeter.
Our earlier experiences in determining MAF heating values of RDF indicated that the precision can be enhanced by determining the ash content from the combustion bomb residue for each sample burned. For the small calorimeter samples, the percent standard deviation of a measurement is less than one percent. The bomb combustion residue method is especially applicable to the "unprocessed" large calorimeter samples because of the heterogeneity of these samples. The lower precision obtained with these "unprocessed" samples is probably caused by their heterogeneity and not by variability of their ash content.
CONCLUSION

We have designed and constructed a bomb calorimeter which is capable of handling a sample with ten times the mass of that handled in our conventional-size bomb calorimeter. Variance in the calorific value of RDF samples because of sampling or preparation procedures (e.g., size reduction) can be determined from heat measurements in this large calorimeter. This isoperibol (isothermal-jacket) calorimeter is an enlarged and modified version of our conventional-size calorimeter with the same basic principles of operation. The large calorimeter has been calibrated and exhibits a precision better than one part in ten thousand. It can be considered a precise calorimeter like our conventional-size one. However, the internal volume (1.85 liters) of the bomb can contain only the minimum amount of oxygen usually required for complete combustion of solid samples with ten times the mass of conventional 2.5 gram samples (4.1 MPa of oxygen for a 25 gram RDF sample).

One objective of this research project is to decide whether or not the calorific value of refuse is altered by the amount of particle size reduction and if so, whether there is an optimum size. From a limited number of experiments in both the large and small calorimeters, we found that the calorific value of a given sample of Teledyne National RDF was unaffected by particle size reduction in our laboratories. As-received, extruded RDF pellets were found to have the same mean calorific value as pellets prepared from 2 mm (10 mesh) particles which were obtained by the milling of as-received, extruded RDF pellets followed by several riffling and blending operations.

Our calorific values, which were measured in two different bomb calorimeter, suggests that either system is applicable to processed
RDF samples. However, a considerable amount of time and effort can be saved with the 25 gram capacity calorimeter since the larger sample size requires less sample processing.

The precision (standard deviation) of calorific value measurements on pellets prepared from 2 mm particles was three times better than that obtained with pellets where no processing was done in our laboratory. The reason for this difference in precision is not known but we suspect that it is the result of a greater heterogeneity of the unprocessed sample and the variance in the moisture content of our analysis samples. We believe that more precise moisture data can be obtained if as-received, extruded RDF pellets are equilibrated in a constant humidity atmosphere and for each calorimetric sample, a moisture sample also is selected. If the calorimetric and moisture samples have the same history and are weighed soon after each other, then the moisture contents should be comparable. In addition, it is worth noting that the moisture content of pellets of identical size prepared from 2 mm (10 mesh) particles was found to be the same after the pellets were air-dried and equilibrated at constant humidity.

We found that the measurements of the ash content of RDF by conventional dry-ashing techniques yields a range of values for "homogeneous," milled and blended 2 mm (10 mesh) particles of RDF. We suggest that the non-combustible fraction of RDF clings to the fibrous RDF particles and is not evenly distributed by the blending process. Therefore, we adopted a procedure of determining the ash from the combustion residue remaining in the bomb which is a characteristic of the actual combustion sample.
In summary, it appears that the calorific value of the Teledyne National RDF is unaffected by the particle size reduction procedures carried out in our laboratory. Also, to obtain good precision, one must correct the measured calorific value for ash residue remaining in the combustion bomb after an experiment. To avoid any sample processing for the large calorimeter experiments, a "twin" moisture-determination pellet must be selected and its moisture content measured while it still may reasonably be expected to have the same moisture content as the calorimetric sample. One can draw the general inference from the calorimetric results that processing of a sample, which has been extruded from minus 1.9 cm (0.75 inch) pieces of RDF, down to a particle size below 0.2 cm (0.08 inch), can be effected without changes in chemical composition or representativeness.

The processing carried out at NBS on the RDF samples represents only a small portion of the processing necessary to prepare calorimetric samples from municipal solid waste (MSW). Our results show no change in the calorific values as a consequence of NBS processing on d-RDF. Resource recovery facilities (e.g. Teledyne National) start out with MSW (i.e. raw refuse) and process it into an RDF. We have no assessment of the possible changes in the calorific value which could take place as a result of the processing by the RDF manufacturer.

Determination of calorific values of MSW which have received minimal or no processing requires large samples. Experts in resource recovery intuitively feel that kilogram-size samples (1-25 kg) may approach the kind of sampling representation desired for a large array of MSW.
Kilogram-size samples which have minimal processing (i.e., to minus 6 inch material) would be desirable. Statistical studies must be performed on MSW to establish the actual size of sample which is truly representative.

Conventional bomb calorimetry is limited to gram-size samples which have experienced considerable processing (i.e. particle size reduction). Since representative calorific values of MSW will probably require kilogram-size samples which have received minimal processing, a combustion calorimeter which can accommodate such large samples must be developed. Therefore, our future research efforts will be directed toward statistical studies needed to derive a representative sample from MSW and the development of a kilogram-capacity combustion calorimeter.
REFERENCES


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<tr>
<td>$q_{-BA}/J$</td>
<td>43202.35</td>
<td>43102.68</td>
<td>43581.45</td>
<td>43291.81</td>
<td>43314.57</td>
<td>396143.48</td>
<td>429785.98</td>
<td>430236.69</td>
</tr>
<tr>
<td>$q_{-ign}/J$</td>
<td>1.08</td>
<td>1.72</td>
<td>0.94</td>
<td>1.19</td>
<td>1.01</td>
<td>2.19</td>
<td>1.59</td>
<td>1.92</td>
</tr>
<tr>
<td>$q_{-Fe}/J$</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>56.05</td>
<td>38.80</td>
<td>38.82</td>
</tr>
<tr>
<td>$q_{-HNO_3}/J$</td>
<td>6.80</td>
<td>5.90</td>
<td>5.77</td>
<td>5.20</td>
<td>5.30</td>
<td>183.43</td>
<td>57.87</td>
<td>57.87</td>
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<tr>
<td>$q_{-wc}/J$</td>
<td>37.13</td>
<td>34.59</td>
<td>34.96</td>
<td>34.85</td>
<td>34.80</td>
<td>383.16</td>
<td>510.15</td>
<td>510.78</td>
</tr>
<tr>
<td>$q_{-T_f\text{corr}}/J$</td>
<td>.02</td>
<td>.04</td>
<td>-.02</td>
<td>.03</td>
<td>.02</td>
<td>5.84</td>
<td>-.98</td>
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<tr>
<td>$q_{-C_{corr}}/J$</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>-101.60</td>
<td>-29.50</td>
<td>-19.66</td>
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<tr>
<td>$Q_{-Total}/J$</td>
<td>43247.38</td>
<td>43144.93</td>
<td>43623.10</td>
<td>43333.08</td>
<td>43355.70</td>
<td>396672.54</td>
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<td>$\Delta T_{corr}/K$</td>
<td>2.969681</td>
<td>2.963055</td>
<td>2.995277</td>
<td>2.976097</td>
<td>2.977749</td>
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<td>$E_{-cal.}/J \cdot K^{-1}$</td>
<td>14562.97</td>
<td>14560.96</td>
<td>14563.96</td>
<td>14560.37</td>
<td>14559.89</td>
<td>86197.61</td>
<td>86206.56</td>
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<td>6.87</td>
<td>6.89</td>
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<td>6.88</td>
<td>31.78</td>
<td>49.88</td>
<td>49.89</td>
</tr>
<tr>
<td>$E_{-si}/J \cdot K^{-1}$</td>
<td>14556.10</td>
<td>14554.09</td>
<td>14557.07</td>
<td>14553.49</td>
<td>14553.01</td>
<td>86165.83</td>
<td>86156.68</td>
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<td>$E_{-si\text{ mean}}/J \cdot K^{-1}$</td>
<td>14554.75</td>
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<td></td>
<td></td>
<td>86162.31</td>
</tr>
<tr>
<td>Std. Dev. $/J \cdot K^{-1}$</td>
<td>1.72(0.012%)</td>
<td></td>
<td></td>
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<td></td>
<td>5.00(0.0058%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Dev. Mean $/J \cdot K^{-1}$</td>
<td>0.78(0.0053%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.89(0.0034%)</td>
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</tr>
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</table>
Table II. MAF Calorific Values in MJ$\cdot$kg$^{-1}$ (Btu$\cdot$lb$^{-1}$) of Teledyne National RDF

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Small Calorimeter</th>
<th></th>
<th>Large Calorimeter</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>$Q_v$</td>
<td></td>
<td>$Q_v$</td>
<td></td>
</tr>
<tr>
<td>1052</td>
<td>24.95</td>
<td></td>
<td>25.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10726)</td>
<td></td>
<td>(10866)</td>
<td></td>
</tr>
<tr>
<td>1053</td>
<td>24.51</td>
<td></td>
<td>26.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10539)</td>
<td></td>
<td>(11216)</td>
<td></td>
</tr>
<tr>
<td>1054</td>
<td>25.01</td>
<td></td>
<td>24.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10752)</td>
<td></td>
<td>(10732)</td>
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<td>24.78</td>
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<tr>
<td></td>
<td>(10656)</td>
<td></td>
<td>(10501)</td>
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<tr>
<td>1057</td>
<td>25.06</td>
<td></td>
<td>24.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10776)</td>
<td></td>
<td>(10650)</td>
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<tr>
<td>1058</td>
<td>25.06</td>
<td></td>
<td>24.39</td>
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<td></td>
<td>(10776)</td>
<td></td>
<td>(10485)</td>
<td></td>
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<tr>
<td>1059</td>
<td>25.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10835)</td>
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<td></td>
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<tr>
<td>1060</td>
<td>25.12</td>
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<tr>
<td></td>
<td>(10799)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1061</td>
<td>25.09</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>(10788)</td>
<td></td>
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<tr>
<td>1062</td>
<td>25.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10781)</td>
<td></td>
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</table>

Range (10539-10835) (10485-11216)
Mean (10743) (10742)
Std. Dev. (86) (273)
%Std. Dev. 0.80% 2.54%
Table III. Moisture and Ash Contents of RDF Samples

<table>
<thead>
<tr>
<th>Small Calorimeter Samples</th>
<th>Large Calorimeter Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt. No.</td>
<td>% Moisture</td>
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<tr>
<td>1052</td>
<td>3.74\textsuperscript{a}</td>
</tr>
<tr>
<td>1053</td>
<td>4.15\textsuperscript{a}</td>
</tr>
<tr>
<td>1054</td>
<td>3.75\textsuperscript{a}</td>
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<tr>
<td>1056</td>
<td>3.89</td>
</tr>
<tr>
<td>1057</td>
<td>3.82</td>
</tr>
<tr>
<td>1058</td>
<td>3.85</td>
</tr>
<tr>
<td>1059</td>
<td>3.88</td>
</tr>
<tr>
<td>1060</td>
<td>3.96</td>
</tr>
<tr>
<td>1061</td>
<td>3.93</td>
</tr>
<tr>
<td>1062</td>
<td>3.88</td>
</tr>
</tbody>
</table>

\textsuperscript{a} These samples were not equilibrated in a constant-humidity atmosphere prior to weighing.

\textsuperscript{b} All percent by weight
Pellets of benzoic acid (left), processed RDF (middle), and unprocessed densified RDF (right)

Figure 1.
25-gram-capacity Bomb Calorimeter

A, pulley to stirrer motor; B, one of four stacks attached to the submarine lid to accommodate (1) fuse circuit, (2) heater, (3) temperature sensor, and (4) stirrer, C, submarine lid; D, submarine flange with "O" ring; E, calorimeter vessel lid; F, stirrer shaft; G, shield cover; H, stirrer; I, calorimeter vessel supports; J, shield; K, combustion bomb; L, submarine vessel; M, calorimeter vessel; N, bomb foot.

Figure 2. 26
Inner Arrangement of Large Combustion Bomb

A Grounded Electrode  G Bomb Head  M Fuse Attachment Hook
B Valve  H Bomb Body  N Ring Holder
C Split Ring  I Handle  O Ring Support
D Compression Ring  J Gas Inlet Tube  P Sample Pellet
E Drop Band  K Ungrounded Electrode  Q Crucible
F Buna-N O-Ring  L Fuse

Figure 3. 27
Small and large combustion bombs

Figure 4.
Large calorimeter system (A view from the top)

Figure 5.
Time-temperature curve for a bomb calorimeter experiment.

$t_i$, initial time of an experiment; $t_b$, time at which main reaction period begins, commenced by ignition of sample; $t_x$, mid-time determined graphically to calculate the cooling correction; $t_e$, time at which main reaction period ends; $t_f$, final time of an experiment; $\theta_i$, initial temperature of an experiment; $\theta_f$, final temperature of an experiment; $\theta_j$, jacket temperature (i.e., temperature of water bath); $\theta_{\infty}$, convergence temperature (i.e., temperature which the calorimeter would attain in an infinite time if $\theta_j$ and the rate of stirring remain constant.

Figure 6.
TITLE AND SUBTITLE
Determination of the Calorific Value of Refuse-Derived Fuels by Large-Bomb Calorimetry
Summary of the 1978 Fiscal Year Results

AUTHOR(S)
D. R. Kirklin, E. S. Domalski and D. J. Mitchell

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WASHINGTON, DC 20234

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U.S. Environmental Protection Agency, Solid and Hazardous Waste Res. Div., 26 W. St. Clair St., Cincinnati, OH 45268

SUPPLEMENTARY NOTES
Funding shared equally by sponsors.

ABSTRACT
An oxygen bomb calorimeter which can accommodate a 25 gram sample of refuse or a refuse-derived-fuel (RDF) has been designed and constructed at the National Bureau of Standards for the purpose of studying the effects of sample processing on the measured calorific value of such material. This large calorimeter is an enlarged and modified version of a conventional-size calorimeter also in use at NBS. The large calorimeter can handle samples ten times larger than the conventional-size calorimeter and therefore can be used to investigate RDF samples with either minimal or no processing. Calorimetric results are presented for calorific value measurements carried out on hydrogen-RDF in both calorimetric systems. Moisture- and ash-free (MAF) calorific values were obtained in the large calorimeter from six randomly chosen unprocessed RDF samples and had a mean value of 24.99 MJ·kg⁻¹ (10 742 Btu·lb⁻¹). Another randomly-chosen sample of unprocessed RDF was subjected to extensive processing to obtain a "homogeneous" analysis sample for use in the conventional-size calorimeter. Individual measurements in the conventional size calorimeter on each of ten "homogeneous" subsamples gave a mean calorific value of 24.99 MJ·kg⁻¹ (10 743 Btu·lb⁻¹). The result of this investigation indicate that the calorific value of d-RDF is unaffected by the sample processing technique used at NBS.

KEY WORDS
Bomb Calorimetry; 25 gram capacity bomb calorimeter; gross calorific values; refuse-derived-fuels; sample characterization; sample processing effects.

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