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400 Commonwealth Drive, Warrendale, PA 15096-0001

SURFACE VEHICLE INFORMATION REPORT

Submitted for recognition as an American National Standard

SAE J1498

REV.
FEB1998

Issued 1987-05
Revised 1998-02

Superseding J1498 MAY90

Heating Value of Fuels

1. ***Scope***—The heating value or heat of combustion is a measure of the energy available from the fuel. The fraction or percentage of the heat of combustion that is converted to useful work is a measure of the thermal efficiency of an engine. Thus, a knowledge of the heat of combustion of the fuel is basic to the engineering of automotive engines. This SAE Information Report provides information on the standardized procedures for determining the heat of combustion of fuels that may be used for automotive engines.

2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein. Unless otherwise indicated, the latest version of SAE publications shall apply.

2.1.1 SAE PUBLICATIONS—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE J313—Diesel Fuels
SAE TSB 003—Rules for SAE Use of SI (Metric) Units

2.1.2 OTHER PUBLICATIONS

1. J. M. Sturtevant, "Calorimetry", Chapter VII, Vol. I, Part V of "Physical Methods of Chemistry", Edited by A. Weissberger and B. W. Rossiter, Wiley-Interscience, New York, NY, 1971.
2. ASTM Methods cited throughout the text are available in the latest volume of the Annual Book of ASTM Standards as shown as follows. These volumes are available from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

Method	Volume
D 86	05.01
D 240	05.01
D 1018	05.01
D 1405	05.01
D 1826	05.05
D 1945	05.05
D 1946	05.05
D 2015	05.05
D 2163	05.01
D 2421	05.01

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D 2650	05.02
D 3286	05.05
D 3338	05.02
D 3588	05.05
D 3701	05.02
D 4529	05.02
D 4809	05.03
D 4868	05.03
E 380	14.02
E 711	11.04

3. F.D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimental, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", pp. 445–463, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, PA, 1953.
4. ASTM Data Series Publication DS4B, "Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds", ASTM, West Conshohocken, PA, 1991.
5. "Reference Data for Hydrocarbons and Petro-Sulfur Compounds", Phillips Petroleum Company Bulletin No. 521, Bartlesville, Oklahoma.
6. R. C. Wilhoit and B. J. Zwolinski, "Physical and Thermodynamic Properties of Aliphatic Alcohols", Journal of Physical and Chemical Reference Data, Vol. 2, Supplement No. 1, 1973, American Chemical Society and the American Institute of Physics.
7. E. S. Domalski, "Selected Values of Heats of Combustion and Heats of Formation of Organic Compounds Containing the Elements of C, H, N, O, P, and S", Journal of Physical and Chemical Reference Data, Vol. 1, No. 2, pp. 221–278, 1972, American Chemical Society and the American Institute of Physics.
8. "Technical Data Book - Petroleum Refinery", 3rd Edition, American Petroleum Institute, Washington, DC, 1977.
9. J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, 1970.

3. Measurement Of Heat Of Combustion—Heats of combustion can be determined to high precision by burning a known amount of the sample completely in pure oxygen in a calibrated calorimeter. The heat of combustion is the product of the temperature rise and the total heat capacity of the calorimeter and its contents. For precision measurements, corrections are applied for energy added to initiate combustion and for the energy involved in the formation of extraneous products such as nitric acid and sulfuric acid.

Calorimeters of various types have been developed to obtain heats of combustion of gases, liquids, or solids to various levels of precision (Reference 1). For evaluation of fundamental thermodynamic properties, precision of calorimetric measurements of the highest order is required since the results are obtained as small differences in large quantities. For heats of combustion of fuel mixtures, lower precisions are usually sufficient for many purposes and less sophisticated techniques are usually used.

Heats of combustion or calorific values of gaseous fuels are usually measured in flame calorimeters in which the sample and oxygen react at constant pressure. Heats of combustion of solid and liquid fuels are usually measured in bomb calorimeters at constant volume.

4. Units Of Measurement—In the SI system of measurement, the heat of combustion is expressed in joules per kilogram. For materials generally used as fuels, the heat of combustion is of such magnitude that it is customarily expressed in terms of a multiple of the basic unit, namely in megajoules per kilogram, MJ/kg. Where the molecular weight is known as in pure compounds, it is sometimes expressed in terms of megajoules per mole, MJ/mole.

A large body of literature is available - and still accumulating - in terms of other, non-SI units such as calories per gram or British Thermal Units (Btu) per pound. The following factors can be used in converting these other units to SI units as in Table 1:

TABLE 1—UNITS OF MEASUREMENT

To Convert From	To	Multiply by
Calorie (International Table)	Joule (J)	4.186 800
British Thermal Unit (IT)	Joule (J)	1055.056
Calorie/Gram	Megajoules/kilogram (MJ/kg)	0.004 186 800
Btu/pound	Megajoules/kilogram (MJ/kg)	0.002 326 000
Pound (Avoirdupois)	Kilogram (kg)	0.453 592 4
Btu/cubic foot	Megajoules/cubic meter (MJ/m^3)	0.037 258 95

SAE TSB 003 and ASTM E 380 list conversion factors for units other than those included here. In any conversions, the number of digits retained should not exceed that implied by the precision of the original quantity.

Many fuels are sold by volume. Heating values are, therefore, frequently expressed in terms of heat units on a volume basis. Thus, the heating values of gaseous fuels are given in terms of heat units per cubic foot or per cubic meter and those of liquid fuels are frequently given in terms of heat units per gallon or per liter. These terms can be computed to a mass basis using the density in appropriate units at the appropriate temperature and pressure.

5. Types of Heating Values—Four types of heating values may be defined according to the assumed state of water as a combustion product (gaseous or liquid) and according to the nature of the assumed combustion process (constant volume or constant pressure). Gross (liquid water) and net (gaseous water) heating values differ by the heat of vaporization of the water in the combustion product mixture. Constant volume and constant pressure heating values differ by the heat equivalent of the work represented by the volume change at constant pressure caused by the change in the number of moles during combustion. Numerical differences between constant volume and constant pressure combustion are small and normally neglected for fuels. Tables of heating values usually list gross and net values at constant pressure.

ASTM D 4809 defines the gross heat of combustion, Q_g, as follows:

"The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25 °C."

ASTM D 4809 also defines the net heat of combustion, Q_n, as:

"The net heat of combustion at constant pressure of a liquid or a solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen at a constant pressure of 0.101 MPa (1 atm), the products of combustion being carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of the fuel and the oxygen and the final temperature of the products of combustion at 25 °C."

These two types are interrelated by Equation 1:

$$Q_n \text{ (net, 25 °C)} = Q_g \text{ (gross, 25 °C)} - 0.2122 \times H \qquad \text{(Eq. 1)}$$

where:

Q_n (net, 25 °C) = net heat of combustion at constant pressure, MJ/kg
Q_g (gross, 25 °C) = gross heat of combustion at constant volume, MJ/kg
H = mass % hydrogen in sample.

NOTE—The percentage of hydrogen in the sample may be determined in accord with ASTM D 1018 or with ASTM D 3701 (IP 338).

The net heat of combustion is also known as the "lower heating value, (LVH)". It is the value customarily used in calculating thermal efficiency of engines since the exhaust gases are emitted at nearly the same pressure as that of the air and fuel supplied to the inlet system and since they contain water in the uncondensed or vapor state.

6. ***Standard Conditions—***Whenever heats of combustion are reported, the temperature, pressure, and physical state (solid, liquid, gas) of the reactants and products should be included. By international convention, a standard state of 25 °C and 1 atm pressure is currently in use. It should be noted that in the change to the SI system of measurement, the standard state pressure is being changed to 1 bar, which is 100 kPa, instead of 1 at which is 101.3250 kPa. Few data are yet available at 1 bar pressure. This change will have negligible effect on the practical heating value of fuels.

Many data in the technical literature are given at temperatures other than the standard reference temperature of 25 °C. These can be converted to 25 °C (77 °F) by correcting for the difference between the total heat capacity of the products of the combustion and the total heat capacity of the reactants at constant pressure. ASTM DS 4B, p. 62 (Reference 4) provides the details of such corrections when the heat capacities are known. ASTM D 2382 provides a series of empirical correction factors that can be used for petroleum fuels when the heat capacities are unknown. Equation 2 applies to such corrections:

$$Q_g \text{ (gross, 25 °C)} = Q_g \text{ (gross, t °C)} + A \text{ (t °C} - \text{25 °C)} \qquad \text{(Eq. 2)}$$

where:

A = correction factor

Although heating values of gaseous fuels are usually expressed in terms of heating units per cubic foot, the amount of gas contained in a cubic foot has not been completely standardized throughout the gas industry. In ASTM D 1826, the standard cubic foot is regarded to be the quantity of gas that will fill one cubic foot at a standard pressure of 14.73 psia (71.92 kg/m^2) and a standard temperature of 60 °F (15.56 °C) when in equilibrium with water.

7. ***Heating Values of Pure Compounds—***The heats of combustion of pure compounds, particularly hydrocarbons, have been measured with great precision because of their significance in elucidating structures and the chemical, physical, and thermodynamic properties of organic molecules. Major compilations of such data have been published (References 2 to 9) showing centimeter-gram-second metric and/or U.S. inch-pound units at standard state conditions of 25 °C and 1 atm pressure.

8. ***Heating Values of Mixtures—***Heating values of mixtures of nonpolar liquids and gases, which do not react, are generally additive for practical purposes and can be computed from the known amounts and heating values of each component. When any of the components are polar liquids, solids, or gases that interact with each other, the heats of combustion may no longer be additive and, therefore, should be measured calorimetrically.

If water is present in the fuel as is frequently the case with such fuels as oxygenated fuels and coals, the total net heating value of the wet fuel will be lower than that of dry fuel. In this case, some of the heat of burning the fuel will be spent in evaporating the water present with the fuel.

9. ***Standardized Methods for Measuring Heating Values*—**A variety of methods for measuring or estimating the heating values of fuels have been standardized by technical societies. The methods published by ASTM include statements of precision which are included here as guides to the usefulness of the method in proposed applications. A statement on precision, i.e., repeatability and reproducibility, provides information on the degree of mutual agreement between individual measurements while a statement on accuracy provides information on the agreement of the measurements with an accepted reference value. In general, 95% of the measurements can be expected to lie within the precision limits stated in the method when conducted properly. However, readers are cautioned to examine each of the methods for full information including the range of materials included in the interlaboratory comparison on which the method is based.

It should also be noted that the precision of the methods for computing heats of combustion from measured values of other properties such as aniline point and gravity are dependent upon the precision of these measured values rather than on the computation process.

9.1 **Gaseous Fuels—**The heat of combustion of a gaseous fuel can be measured directly or can be calculated from the composition of the mixture and the heats of combustion of its individual constituents provided that there is no chemical reaction between the constituents.

ASTM D 1826 is a standardized procedure for measuring the heat of combustion of gases in the natural gas range of 900 to 1200 Btu/standard ft^3 with a precision of 0.3 to 0.5%. In this procedure, the test gas is burned in a stream of air and the temperature rise of the air stream is measured. The water is condensed to the liquid state and the gross heat of combustion is obtained.

ASTM D 3588 is applicable to all common types of utility gaseous fuels for which suitable methods of analysis are available. This includes dry natural gas, reformed gas, oil gas (both high and low Btu), propane-air, carbureted water gas, and coke oven and retort coal gas. The calorific values are calculated from the molar composition and the respective ideal gas values for the components. These values must then be converted to the real gas basis by means of compressibility summation factors which are listed in ASTM D 3588 for most of the lower molecular weight hydrocarbons and gaseous nonhydrocarbons.

The following ASTM documents are helpful in determining the molar composition of the gaseous fuels:

a. ASTM D 1945—Method for Analysis of Natural Gas by Gas Chromatography
b. ASTM D 1946—Method for Analysis of Reformed Gas by Gas Chromatography
c. ASTM D 2163 (IP 264)—Method for Analysis of Liquefied Petroleum (LP) Gases and Propane Concentrates by Gas Chromatography
d. ASTM D 2421—Test Method for Interconversion of Analysis of C_5 and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Weight Basis
e. ASTM D 2650—Test Method for Chemical Composition of Gases by Mass Spectrometry

9.2 **Liquid Fuels—**Heats of combustion of liquid fuels and solid fuels as well, are usually measured in a bomb calorimeter equipped with either an isothermal or an adiabatic type jacket.

a. ASTM D 240 describes a method which is particularly applicable to hydrocarbons of both low and high volatility. The precision of this method is as follows:

   1. Repeatability—0.13 MJ/kg (55 Btu/lb)
   2. Reproducibility—0.40 MJ/kg (175 Btu/lb)

b. ASTM D 4809 was designed specifically for use with aviation turbine fuels but is also directly applicable to such fuels as gasolines, kerosenes, No. 1 and 2 fuel oil, No. 1D and 2D diesel fuel and No. 0-GT, 1-GT, and 2-GT gas turbine fuels. The precision of the method varies with the type of fuel and can be summarized in Table 2:

TABLE 2—ASTM D 4809 TEST METHOD PRECISION

	Gross Heat of Combustion MJ/kg	Gross Heat of Combustion Btu/1b	Net Heat of Combustion MJ/kg	Net Heat of Combustion Btu/lb
Repeatability:				
All Fuels	0.097	42	0.096	41
Nonvolatile Fuels	0.096	41	0.099	43
Volatile Fuels	0.100	43	0.091	39
Reproducibility:				
All Fuels	0.228	98	0.324	139
Nonvolatile Fuels	0.239	103	0.234	101
Volatile Fuels	0.207	89	0.450	193

9.3 Solid Fuels—ASTM has standardized three procedures for the determination of the gross heating value of solid fuels:

1. ASTM D 2015—Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter
2. ASTM D 3286—Test Method for Gross Calorific Value of Solid Fuel by the Isothermal-Jacket Bomb Calorimeter
3. ASTM E 711—Test Method for Gross Calorific Value of Refuse-Derived Fuel (RDF-3) by the Bomb Calorimeter

The precision of these three methods is listed in Table 3:

TABLE 3—TEST METHOD PRECISION

	Repeatability MJ/kg	Repeatability Btu/lb	Reproducibility MJ/kg	Reproducibility Btu/lb
ASTM D 2015	0.116	50(1)	0.233	100(1)
ASTM D 3286	0.116	50	0.233	100
ASTM E 711	not determined	not determined	not determined	not determined

1. Dry basis

9.4 Heterogeneous Fuels—Heterogeneous fuels such as emulsions of diesel fuel and water, microemulsions of vegetable oils and alcohols, and slurries of coals in liquids have received some attention as possible fuels for automotive engines. However, no calorimetric methods for measuring the heats of combustion of such fuels have yet been standardized by ASTM. It is expected that ASTM D 4809 can be used for such measurements, possibly in modified form, but no estimate of precision can be given. Special care is required to ensure that the sample taken for such measurements is representative of the fuel ingested into the engine.

When water is present as in a fuel/water emulsion or as moisture associated with the fuels such as coals, alcohols, and esters, some of the net heat of combustion of the dry fuel will be spent in evaporating the water.

10. *Empirical Methods For Estimating Heats Of Combustion*—Several empirical methods have been developed for estimating the heat of combustion where experimental measurements are unavailable or cannot be made conveniently and where estimates may be satisfactory. Such empirical estimates are based on observed correlations between accurately measured properties and the heats of combustion of representative samples of compounds or fuels typical of a particular class of fuels. The correlations may change when the composition of the class of fuel changes as a result of changes in crude oil supply and in refinery practice. The estimates may be in error by large amounts even within the same class of fuels as well as with fuels of other classes. Some automotive fuels now contain oxygenated compounds to help meet mandates requirements for the control of atmospheric carbon monoxide and ozone, to enhance octane level, and to augment the total fuel supply. The oxygen in such fuels adds to the mass and volume of these fuels without adding to the heat of combustion. Thus, the heat of combustion per unit mass and unit volume will be lowered in proportion to the mass percent oxygen. Also, some oxygenated fuels have an increased propensity to absorb atmospheric moisture which will reduce the heat of combustion as well. However, to date experimental methods for estimating the heat of combustion of such fuels has not been standardized and therefore direct measurement is advisable. Whenever possible, heats of combustion should be measured.

ASTM D 1405 (IP 193) and ASTM D 4529 provide estimates of the heat of combustion of certain aviation fuels. These fuels include aviation gasolines, aircraft turbine, and jet engine fuels of limited boiling ranges and compositions. They are liquid hydrocarbons derived from normal refining processes and conventional crude oils. Both methods are based upon an empirical relationship between aniline point, density, sulfur content, and heat of combustion for fuels of these types. When values of densities, aniline points, and sulfur are obtained in replicate determination on a fuel sample, they may show some variation; consequently, heats of combustion estimated from them using the empirical relationship may also vary. For a given fuel, estimates (95% confidence) are considered suspect if duplicate results obtained by the same operator differ by more than 0.012 MJ/kg or if results submitted by each of two laboratories differ by more than 0.035 MJ/kg.

ASTM D 3338 provides a correlation between the net heat of combustion and gravity, aromatic content, and average volatility of aviation gasolines, aircraft turbine, and jet engine fuels. When a second set of measured values of aromatic content, gravity, and distillation data are used to obtain estimates from the empirical relationship of this method, the estimates are considered suspect if duplicate results obtained by the same operator differ by more than 0.021 MJ/kg (or 9 Btu/lb) or if results submitted by each of two laboratories differ by more than 0.046 MJ/kg (or 20 Btu/lb).

D 4868 covers the estimation of heating values from density, sulfur, water, and ash content. It is applicable to a variety of petroleum fuels derived by normal refining processes from conventional crude oil and which have densities in the range of 750 to 1000 kg/m^3. It is not applicable to pure hydrocarbons or fuels of high aromatic content. The precision for the fuels used in the development of this method is:

a. Repeatability—0.05 MJ/kg
b. Reproducibility—0.15 MJ/kg

A variety of other nonstandardized correlations for hydrocarbon fuels have been published. SAE J313 shows several correlations for diesel fuels that have been developed for relating

a. Gravity, aniline point, and heat of combustion
b. Density, mid-boiling point, and heat of combustion
c. 50 and 90% recovery temperatures from the ASTM D 86 distillation, API gravity, cetane number, viscosity, cloud point, and net heating value

No estimate of precision is available for these methods.

11. Notes

11.1 Marginal Indicia—The change bar (l) located in the left margin is for the convenience of the user in locating areas where technical revisions have been made to the previous issue of the report. An (R) symbol to the left of the document title indicates a complete revision of the report.

PREPARED BY THE FUELS AND LUBRICANTS TECHNICAL COMMITTEE 7—FUELS