BRITISH STANDARD

BS 7420:1991

Guide for

Determination of calorific values of solid, liquid and gaseous fuels (including definitions)

Committees responsible for this British Standard

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British Coal Corporation
British Gas plc
Department of Energy (Gas and Oil Measurement Branch)
Institute of Petroleum
Institution of Chemical Engineers
Institution of Gas Engineers
University College London

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Contents

Foreword

This British Standard has been prepared under the direction of the Refrigeration, Heating and Air Conditioning Standards Policy Committee, and represents a revision of BS 526.

BS 526 was first published in 1933. It was revised and updated in 1961, but was withdrawn in 1987.

However, the content of BS 526 has since been found still to be needed, being referred to in a number of other British Standards, and accordingly BS 7420 has been produced to provide up-to-date technical information, and to incorporate SI units.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 6, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

0 Introduction

The amount of heat which would be released by complete combustion of unit quantity of a fuel under specified conditions is termed the calorific value of that fuel for those conditions. This may be determined directly by calorimetry or indirectly by inferential methods.

The most useful basic expression of calorific value is often considered to be the heat released by complete combustion of a unit quantity of the fuel at a defined pressure and a specified reference temperature. The products of combustion are returned to the specified reference temperature and the water formed or liberated during combustion is in the liquid phase, sulphur from the fuel is converted to sulphur dioxide, and nitrogen from the fuel either is converted into oxides of nitrogen or remains as nitrogen gas, depending upon the type of fuel.

Complete combustion is achievable with gaseous fuels at atmospheric pressure but solid and liquid fuels require higher pressures. Since the heat released at higher pressure differs from that which would be obtained with complete combustion at atmospheric pressure, the conditions for solid and liquid fuels need to be defined in such a way that this difference can be evaluated and kept small enough to be ignored in most circumstances.

It should be noted that the term “calorific value” is the legal and contractual term used in common practice by the solid fuel and gas industries, whereas the oil industry uses the alternative term “heat of combustion”.

1 Scope

This British Standard gives guidance on the determination of calorific values of solid, liquid and gaseous fuels. It includes definitions of different calorific values calculated on the basis of either constant pressure or constant volume, and with the water produced present either in the liquid or the vapour phase. The standard gives conditions for the experimental determination of calorific values and presents details of how to interconvert numerical values of differently defined calorific values.

It is sometimes necessary to convert a calorific value determined for a known set of specified conditions to the corresponding calorific value for a different set of conditions, and this standard gives guidance on calculations by means of which this may be achieved.

NOTE 1 The titles of the standards publications referred to in this standard are listed on the inside back cover.

NOTE 2 Details of the other publications referred to in this standard are listed in the bibliography in Appendix A.

2 General

This British Standard gives definitions of four calorific values:

a) gross calorific value at constant pressure;

b) net calorific value at constant pressure;

c) gross calorific value at constant volume;

d) net calorific value at constant volume.

The word “gross” signifies that the water formed or liberated during the combustion is in the liquid phase; “net” signifies that the water formed or liberated during the combustion is in the vapour phase.

For each type of fuel, a particular calorific value which can be obtained as the result of experimental determination is regarded as basic; the other three calorific values, which are calculated from it, are regarded as derived quantities. For the purposes of this standard, the basic calorific value for solid and liquid fuels is the gross calorific value at constant volume, and for gaseous fuels it is the gross calorific value at constant pressure.

This standard describes the conditions for the experimental determination of the basic value and the methods by which the derived values may be calculated from the basic value. Fuels cannot be compared precisely unless their calorific values are referred to the same conditions; for example calorific values of solid and liquid fuels should be converted to the corresponding values at a pressure of 101.325 kPa when they are to be compared with those of gaseous fuels. Methods for conversion of calorific values to a different pressure basis are given by Washburn (1933) and Rossini (1956).

The definitions of calorific value given in clause **3** take into account the basis on which the quantity of fuel is measured, namely, mass for solid and liquid fuels, and volume for gaseous fuels; they also take into account the conditions under which the fuels can be burned completely.

3 Definitions

For the purposes of this British Standard the following definitions apply.

3.1
gross calorific value at constant volume of a solid or liquid fuel

the amount of heat liberated per unit quantity of fuel burned in oxygen in a bomb calorimeter under standard conditions (see note 2) in such a way that the materials remaining after combustion (corrections having been made [see **5.2**)] consist of ash; the gases oxygen, carbon dioxide, sulphur dioxide and nitrogen; and liquid water in equilibrium with its vapour, and assumed to be saturated with carbon dioxide, and possibly also containing dissolved hydrogen chloride, plus oxides of nitrogen and sulphur, as acids

NOTE 1 Known in thermodynamics as the "specific energy of combustion".

NOTE 2 The international thermochemical reference temperature is 25 °C. This temperature was chosen because the change in the specific heat capacity of water over the range 20 °C to 30 °C is small. It is desirable that the reference temperature be close to the temperature at which determinations are made to ensure that corrections, which are empirical, are sufficiently accurate; 25 °C satisfies this requirement.

Although calorific values with reference temperature 0 °C are sometimes used, e.g. for heat balances, this is not to be recommended if it involves a large empirical adjustment of the observed calorific value.

3.2
gross calorific value at constant pressure of a solid or liquid fuel

the amount of heat liberated per unit quantity of fuel burned in oxygen at constant pressure in such a way that the heat released is equal to the sum of the gross calorific value at constant volume and the work which would have been done by the atmosphere under isothermal conditions, had the pressure remained constant

NOTE Known in thermodynamics as the "specific enthalpy of combustion".

3.3
net calorific value at constant volume of a solid or liquid fuel

the amount of heat liberated per unit quantity of fuel burned in oxygen in a bomb calorimeter under standard conditions (see **3.1** note 2) in such a way that the materials remaining after combustion [corrections having been made (see **5.2**)] consist of ash and the gases oxygen, carbon dioxide, sulphur dioxide and nitrogen, plus water vapour

3.4
net calorific value at constant pressure of a solid or liquid fuel

the amount of heat liberated per unit quantity of fuel burned in oxygen at constant pressure in such a way that the heat released is equal to the sum of the net calorific value of the fuel at constant volume and the work which would have been done by the atmosphere under isothermal conditions, had the pressure remained constant

3.5
gross calorific value at constant pressure of a gaseous fuel

the amount of heat liberated per unit volume of fuel burned in oxygen in such a way that the materials remaining after combustion consist of the gases carbon dioxide, sulphur dioxide, oxygen and nitrogen, plus liquid water. The reactants and the materials remaining after combustion are all measured under the standard conditions, given in the UK Gas Act (1986)[1], which are 15 °C and 101.325 kPa

3.6
gross calorific value at constant volume of a gaseous fuel

the amount of heat liberated per unit volume of fuel burned in oxygen in such a way that the materials remaining after combustion consist of the gases carbon dioxide, sulphur dioxide, oxygen, and nitrogen, plus liquid water. The reactants are measured at 15 °C and at 101.325 kPa with the materials remaining after combustion occupying the same total volume at 15 °C

3.7
net calorific value at constant pressure of a gaseous fuel

the amount of heat liberated per unit volume of fuel burned in oxygen in such a way that the materials remaining after combustion consist of the gases carbon dioxide, sulphur dioxide, oxygen and nitrogen, plus water vapour. The reactants and the materials remaining after combustion are all measured at 15 °C and 101.325 kPa

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[1] Available from HMSO, 49 High Holborn, London WC1, for personal callers, or by post from HMSO, P.O. Box 276, London SW8 5DT.

3.8
net calorific value at constant volume of a gaseous fuel

the amount of heat liberated per unit volume of fuel burned in oxygen in such a way that the materials remaining after combustion consist of the gases carbon dioxide, sulphur dioxide, oxygen and nitrogen, plus water vapour. The reactants are measured at 15 °C and 101.325 kPa with the products of combustion occupying the same total volume at 15 °C

4 Symbols

For the purposes of this British Standard the following symbols apply.

T	absolute temperature
R	molar gas constant
L	molar enthalpy of vaporization of water at 25 °C and constant pressure
$\overline{H}$	percentage by mass of hydrogen in the fuel
$\overline{O}$	percentage by mass of oxygen in the fuel
$\overline{W}$	percentage by mass of water in the fuel
M_H	relative molecular mass of hydrogen
M_O	relative molecular mass of oxygen
M_W	relative molecular mass of water
$Q_{gr,p}$	gross calorific value at constant pressure
$Q_{gr,v}$	gross calorific value at constant volume
$Q_{net,p}$	net calorific value at constant pressure
$Q_{net,v}$	net calorific value at constant volume

Other symbols are defined in the text where they occur.

5 Determination of calorific values of solid and liquid fuels

5.1 General

The only satisfactory method for the determination of the calorific value of solid and liquid fuels is that in which a sample of the fuel is burned in oxygen under pressure in a bomb calorimeter immersed in water, the temperature rise of which is measured; this is called the “oxygen-bomb” method. The gross calorific value of the fuel at constant volume is determined by this method. It is suitable for both solid and liquid fuels but the very high rate of combustion of some liquid fuels necessitates certain differences in procedures between solid and liquid fuels. It is essential that the particular conditions under which any calorific value has been determined be defined, where possible, by reference to the standard test method adopted for the determination (see **5.2**).

The three derived calorific values may be calculated from the gross calorific value at constant volume if the composition of the fuel is known. When the fuel is burned in the bomb calorimeter, the work which would be done by the atmosphere on the products if unit quantity of the fuel were burned at constant pressure may be calculated and added to the gross calorific value at constant volume to obtain the gross calorific value at constant pressure. Likewise, the enthalpy of vaporization of the water formed by the combustion of unit quantity of the fuel may be calculated and subtracted from the gross calorific value at either constant volume or constant pressure to obtain the corresponding net calorific value.

5.2 Standard test methods for the determination of gross calorific value at constant volume of a solid or liquid fuel

Standard test methods for determining gross calorific value at constant volume are given in BS 1016-5 for solid fuels and BS 2000-12 for liquid fuels which include procedures to correct for the formation of sulphuric and nitric acids during the test.

NOTE For a discussion of the effect of chlorine, see Barker et al. (1955).

5.3 Calculation of gross calorific value at constant pressure of a solid or liquid fuel

Let $\overline{H}$ and $\overline{O}$ be the percentages (m/m) of hydrogen and oxygen in the fuel (see note) on the basis (e.g. as-received, air-dried) to which the determined value, $Q_{gr,v}$, refers. Then the work done by the atmosphere when unit quantity of the fuel is burned at constant pressure to give liquid water is:

$$0.01RT\left(\frac{0.5\overline{H}}{M_H} - \frac{\overline{O}}{M_O}\right)$$

This expression is equal to $Q_{gr,p} - Q_{gr,v}$.

Thus, at a reference temperature of 25 °C, and with suitable rounding of the above expression, $Q_{gr,p}$ may be calculated from the expression:

$$(Q_{gr,p} - Q_{gr,v}) = (0.006\overline{H} - 0.0008\overline{O})\ \text{MJ/kg} \qquad (1)$$

NOTE $\overline{H}$ and $\overline{O}$ refer to hydrogen and oxygen in the fuel substance only, and specifically exclude the hydrogen and oxygen present in the moisture and in the mineral matter associated with the fuel. For practical purposes, values of $\overline{H}$ and $\overline{O}$ may be derived by multiplying the dry mineral-matter-free hydrogen and dry mineral-matter-free oxygen contents by:

$$\frac{100 - (Y + Z)}{100}$$

where Y and Z are the percentages of moisture and mineral matter, respectively, in the fuel on the basis to which $Q_{gr,v}$ refers. For further explanation of calculation to different bases, see BS 1016-16.

5.4 Calculation of net calorific value at constant pressure of a solid or liquid fuel

Let $\overline{W}$ be the percentage (m/m) of water contained in the fuel, including the combined water of the mineral matter (see note), on the basis (e.g. as received, air-dried), to which the gross calorific value refers. Then the quantity to be subtracted from $Q_{\text{gr,v}}$ is:

$$0.01L\left(\frac{\overline{H}}{M_{\text{H}}}+\frac{\overline{W}}{M_{\text{W}}}\right) - 0.01RT\left(\frac{0.5\overline{H}}{M_{\text{H}}}-\frac{\overline{O}}{M_{\text{O}}}\right)$$

Thus, at a reference temperature of 25 °C, and with suitable rounding of the above expression, $Q_{\text{net,p}}$ may be calculated from the expression:

$$(Q_{\text{net,p}} - Q_{\text{gr,v}}) = -(0.212\overline{H} + 0.024\overline{W} + + 0.0008\overline{O})\ \text{MJ/kg} \qquad (2)$$

NOTE $\overline{W}$ is equal to Y plus the combined water of the mineral matter. The combined water of the mineral matter may be assumed to be equal to one-tenth of the ash for coal, and to be zero for coke. (For further explanation of "mineral matter" see BS 1016-16).

5.5 Calculation of net calorific value at constant volume of a solid or liquid fuel

The quantity to be subtracted from $Q_{\text{gr,v}}$ is:

$$0.01\,(L - RT)\left(\frac{\overline{H}}{M_{\text{H}}}+\frac{\overline{W}}{M_{\text{W}}}\right)$$

Thus, at a reference temperature of 25 °C, and with suitable rounding of the above expression $Q_{\text{net,v}}$ may be calculated from the expression:

$$(Q_{\text{net,v}} - Q_{\text{gr,v}}) = -(0.206\overline{H} + 0.023\overline{W})\ \text{MJ/kg} \qquad (3)$$

6 Determination of calorific values of gaseous fuels

6.1 General

The gross calorific value of a gaseous fuel at constant pressure may be determined by a variety of methods. These methods include: continuous recording calorimetry, either direct (see ASTM D 1826-88) or inferential (see ASTM D 4891-89); non-recording direct combustion calorimetry, [see BS 3804-1 and Cowan and Humphreys (1986)]; calculation from a molar composition analysis (see ISO 6976), the latter usually being made by gas chromatography (see ISO 6974). The determination of gross calorific value at constant volume in a bomb-type calorimeter is rarely undertaken.

Continuous recording calorimeters operate at atmospheric pressure and usually in a room with temperature control. The calorific value reported is usually derived from a comparison between the records for the gas under test and a standard gas. The latter is often pure methane, the calorific value of which is known at the appropriate reference conditions. The sensitivity of the instrument is usually predetermined by use of at least two other gases of known calorific value (often simple methane-ethane-nitrogen mixtures) which closely "span" the calorific value of the gas under test. A calorific value thus determined differs imperceptibly from the true calorific value at constant pressure. The relevant reference conditions are as given in **3.5**.

Non-recording (discrete sample) combustion calorimeters operate under similar ambient conditions. Calibration may be by electrical power dissipation or by combustion of an accepted standard gas of known calorific value, such as pure methane. Instruments of a water-flow type do not require an "energy-equivalent" calibration.

Gas chromatography based systems also require standard calibration gases, but in this case several complex multicomponent mixtures containing known proportions of at least the main components in the gas under test are needed; preferably these should be prepared gravimetrically.

6.2 Standard test methods for the determination of gross calorific value at constant pressure of a gaseous fuel

The only British Standard test method for the determination of the gross calorific value at constant pressure of a gaseous fuel, is BS 3804-1. This method is now obsolescent and has been largely superseded in usage by methods such as the others listed in **6.1**.

The publications referred to in **6.1** alone, however, are often insufficient to define the detailed procedures and operating conditions necessary for an optimally accurate determination. For commercial instrumentation, the instrument manufacturer's instruction manual should also be consulted, together with any other procedural instructions, such as those contained in the British Gas Analytical Methods numbers 2.1.2 to 2.1.7 and 2.1.9. See also British Gas Engineering Standard BGC/PS/INQ2.

6.3 Calculation of gross calorific value at constant volume of a gaseous fuel

Suppose the composition by mole fractions, X_1, X_2 etc. of the gas mixture is expressed as:

$$X_1(\mathrm{N_2}) + X_2(\mathrm{CO_2}) + X_3(\mathrm{H_2S}) + X_4(\mathrm{H_2}) + \\ + X_5(\mathrm{CH_4}) + X_6(\mathrm{C_2H_6}) + X_7(\mathrm{C_3H_8}) + \dots = 1 \quad (4)$$

where $X_1(\mathrm{N_2})$ is the mole fraction of N_2 and so on, and the extension to components not specifically mentioned is obvious.

This composition may be re-expressed in terms of a single pseudo-component $\mathrm{C_aH_bO_cN_dS_e}$, where:

$$a = X_2 + X_5 + 2X_6 + 3X_7 + \dots$$
$$b = 2X_3 + 2X_4 + 4X_5 + 6X_6 + 8X_7 + \dots$$
$$c = 2X_2$$
$$d = 2X_1$$
$$e = X_3$$

The stoichiometric combustion equation for this pseudo-component is:

$$\mathrm{C_aH_bO_cN_dS_e} + A\mathrm{O_2} = D\mathrm{CO_2} + \\ + E\mathrm{H_2O} + F\mathrm{SO_2} + G\mathrm{N_2} \quad (5)$$

where:

$A = a + (b/4) - (c/2) + e$

$D = a$

$E = b/2$

$F = e$

$G = d/2$

The gross calorific value at constant volume, $Q_{\mathrm{gr,v}}$ may then be calculated from the expression:

$$(Q_{\mathrm{gr,v}} - Q_{\mathrm{gr,p}}) = -0.10\ V_{\mathrm{gr}}\ \mathrm{MJ/m^3}$$

where

$V_{\mathrm{gr}} = (A + 1) - (D + F + G)$

Since V_{gr} is always a small positive number, the gross calorific value at constant volume is always smaller than the gross calorific value at constant pressure by a small amount.

6.4 Calculation of net calorific value at constant pressure of a gaseous fuel

The net calorific value at constant pressure, $Q_{\mathrm{net,p}}$, is calculated from the expression:

$$(Q_{\mathrm{net,p}} - Q_{\mathrm{gr,p}}) = -1.88E\ \mathrm{MJ/m^3} \quad (7)$$

where E is as defined in **6.3**.

The computation of E may be carried out only if the gas composition is known with sufficient accuracy. If this is not the case it is reasonable, at least for natural gases consisting mainly of methane, to take the net calorific value as 10 % lower than the gross calorific value.

6.5 Calculation of net calorific value at constant volume of a gaseous fuel

The net calorific value at constant volume, $Q_{\mathrm{net,v}}$, is calculated from the expression:

$$(Q_{\mathrm{net,v}} - Q_{\mathrm{net,p}}) = -0.10\ V_{\mathrm{net}}\ \mathrm{MJ/m^3} \quad (8)$$

where

$V_{\mathrm{net}} = (A + 1) - (D + E + F + G)$.

and A, D, E, F and G are as defined in **6.3**.

In general, V_{net} is a small number. For pure methane $V_{\mathrm{net}} = 0$; consequently, for typical natural gases, the net calorific value at constant volume can be taken as approximately equal to the net calorific value at constant pressure.

Appendix A Bibliography

BARKER, J.E., MOTT, R.A., and THOMAS, W.C., 1955, *Fuel*, **34**, 303.

BRITISH GAS ANALYTICAL METHODS[2)]

2.1.2 Boys non-recording calorimeter (revised 1977)
2.1.3 Fairweather calorimeter (revised 1976)
2.1.4 LRS calorimeter (issued 1985)
2.1.5 Sigma calorimeter (issued 1973)
2.1.6 Thomas calorimeter (issued 1977)
2.1.7 Union calorimeter (issued 1973)
2.1.9 Cutler-Hammer calorimeter (issued 1980)

COWAN, P. and HUMPHREYS, A.E., 1986, The British Gas reference calorimeter. *Proc. Int. Congress Gas Quality* (G.J. VAN ROSSUM ed.) Groningen, April 1986, Amsterdam: Elsevier.

ROSSINI, F.D. (ed.), 1956, *Experimental thermochemistry*, (chapter 6), New York: Interscience Publications.

WASHBURN, E.W., 1933 *J. Res. National Bureau of Standards*, **10**, 525.

[2)] Available from the Editor, British Gas Analytical Methods, British Gas plc, Plant Operations Department, Brick Kiln Street, Coventry Road, Hinckley, Leicestershire LE 10 ONA.

Publication(s) referred to

BS 1016, *Methods for analysis and testing of coal and coke.*

BS 1016-5, *Gross calorific value of coal and coke.*

BS 1016-16, *Methods for reporting results.*

BS 2000, *Methods of test for petroleum and its products.*

BS 2000-12, *Heat of combustion of liquid hydrocarbon fuels.*

BS 3804, *Methods for the determination of the calorific value of fuel gases.*

BS 3804-1, *Non-recording methods.*

ISO 6974, *Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C8 — Gas chromatographic method.*

ISO 6976, *Natural gas — Calculation of calorific value, density and relative density*[3].

ASTM D 1826-88, *Test method for calorific value of gases in natural gas range by continuous recording calorimeter.*

ASTM D 4891-89, *Test method for heating value of gases in natural gas range by stoichiometric combustion.*

BGC/PS/INQ2, British Gas Engineering Standard — General specification for calorimeter rooms (1985)[4].

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[3] Revised version in preparation.

[4] Available from British Gas plc, Standards Department, National Westminster House, 326 High Holborn, London WC1V 7PT.

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