BRITISH STANDARD

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Generation and analysis of toxic gases in fire — Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires

ICS 13.220.01

British Standards

National foreword

This British Standard reproduces verbatim ISO 19703:2005 and implements it as the UK national standard.

The UK participation in its preparation was entrusted to Technical Committee FSH/16, Hazards to life from fire, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Generation and analysis of toxic gases in fire — Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires

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Foreword

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ISO 19703 was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

Introduction

It is the view of committees ISO TC92/SC3 (Fire threat to people and the environment), ISO TC92/SC4 (Fire safety engineering), and IEC TC89 (Fire hazard testing) that commercial products should not be regulated solely on the basis of the toxic potency of the effluent produced when the product is combusted in a bench-scale test apparatus (physical fire model). Rather, the information that characterizes the toxic potency of the effluent should be used in a fire risk or hazard assessment that includes the other factors that contribute to determining the magnitude and impact of the effluent. The characterization of (a) the apparatus used to generate the effluent and (b) the effluent itself must thus be in a form usable in such a fire safety assessment.

As described in ISO/TS 13571, the time to incapacitation in a fire is determined by the integrated exposure of a person to the fire effluent components. The toxic species concentrations depend on both the yields originally generated and the successive dilution in air. The former are commonly obtained using a bench-scale apparatus (in which a specimen from a commercial product is burned) or a real-scale fire test of the commercial product. These yields, expressed as the mass of effluent component per mass of fuel consumed, are then inserted into a fluid mechanical model that estimates the transport and dilution of the effluent throughout the building as the fire evolves.

For the engineering analysis to produce accurate results, the yield data must come from an apparatus that has been demonstrated to produce yields comparable to those produced when the full product is burned. In addition to depending on the chemical composition, conformation and physical properties of the test specimen, toxic-product yields are sensitive to the combustion conditions in the apparatus. Thus, one means of increasing the likelihood that the yields from a bench-scale apparatus will be accurate is to operate it under combustion conditions similar to those expected when the real product burns. The important conditions include whether the fuel is flaming or non-flaming, the degree of flame extension, the fuel/air equivalence ratio, and the thermal environment. Similarly, these parameters should be known for a real-scale fire test.

The yields of toxic gases, the combustion efficiency and the equivalence ratio are likely to be sensitive to the manner in which the test specimen is sampled from the whole commercial product. There may be difficulty or alternative ways of obtaining of a proper test specimen. That is not the subject of this document, which presumes that a specimen has been selected for study and characterizes the combustion conditions and the yields of effluent species for that specimen.

For those experimental fires in which time-resolved data are available, the methods in this International Standard can be used to produce either instantaneous or averaged values. The application may be influenced by changes in the chemistry of the test specimen during combustion. For those fire tests limited to producing time-averaged gas concentrations, the calculated values produced by the methods in this International Standard are limited to being averages as well. In real fires, combustion conditions, the fuel chemistry and the composition of fire effluent from many common materials and products vary continuously during the course of the fire. Thus, how well the average yields obtained using these methods correspond to the yields in a given real fire has much to do with the stage of the fire, the pace of fire development and the chemical nature of the materials and products exposed.

This International Standard provides definitions and equations for the calculation of toxic product yields and the fire conditions under which they have been derived in terms of equivalence ratio and combustion efficiency. Sample calculations for practical cases are provided.

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Generation and analysis of toxic gases in fire — Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires

1 Scope

This International Standard provides definitions and equations for the calculation of toxic product yields and the fire conditions under which they have been derived in terms of equivalence ratio and combustion efficiency. Sample calculations for practical cases are provided. The methods can be used to produce either instantaneous or averaged values for those experimental fires in which time-resolved data are available.

This International Standard is intended to provide guidance to fire researchers for

- appropriate experimental fire data to be recorded,
- calculating average yields of gases and smoke in fire effluents in fire tests and fire-like combustion in reduced scale apparatus
- characterizing burning behaviour in experimental fires in terms of equivalence ratio and combustion efficiency using oxygen consumption and product generation data.

This International Standard does not provide guidance on the operating procedure of any particular piece of apparatus or interpretation of data obtained therein (e.g. toxicological significance of results).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurements, methods and results — Part 1: General principles and definitions*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurements, methods and results — Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method*

ISO/TR 9122-1:1989, *Toxicity testing of fire effluents — Part 1: General*

ISO/TR 9122-4:1993, *Toxicity testing of fire effluents — Part 4: The fire model (furnaces and combustion apparatus used in small-scale testing)*

ISO/TS 13571, *Life-threatening components of fire — Guidelines for the estimation of time available for escape using fire data*

ISO/IEC 13943:2000, *Fire safety — Vocabulary*

ISO/TR 19701:—[1)], *Analytical methods for fire effluents*

BIPM/IEC/IFCC/ISO/IUPAC/IUPAP/OIML, *International vocabulary of basic and general terms in metrology (VIM), 1993*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943:2000 and the following apply.

3.1
atomic mass
⟨of an element⟩ value proportional to the mass of its atom relative to carbon (isotope ^{12}C) that is assigned the value of 12,00 containing 1 mole of carbon atoms

3.2
combustion efficiency
ratio of the heat released in a combustion reaction to the theoretical heat of complete combustion

NOTE 1 Combustion efficiency can be calculated only for cases where complete combustion can be defined.

NOTE 2 Combustion efficiency can also be expressed as a percentage.

3.3
empirical formula
chemical formula of a substance in which the relative numbers of atoms of each type are given

NOTE Typically, the number for one type of atom is chosen, to be an integer (usually C or O), e.g. a particular sample might be represented as $C_6H_{8,9}O_{4,1}N_{0,3}Cl_{0,01}$.

3.4
equivalence ratio
ϕ
actual fuel-to-air mass ratio divided by the stoichiometric fuel-to-air mass ratio for that fuel

NOTE 1 For $\phi < 1$, as in small or well-ventilated fires, the fuel/air mixture is said to be fuel lean and complete combustion (i.e., to CO_2 and H_2O) will dominate. For $\phi = 1$, the mixture is stoichiometric. For $\phi > 1$, as in ventilation-controlled fires, the mixture is fuel rich and relatively high concentrations of pyrolysis and incomplete combustion gases will result.

NOTE 2 Standard, dry air contains 20,95 % oxygen by volume. In practice, the oxygen concentration in entrained air can vary, requiring correction in the calculation of ϕ to a standard, dry air basis. In this International Standard, fuel-to-oxygen ratios, rather than fuel/air ratios, are used for the equivalence ratio calculations.

NOTE 3 For gaseous fuels, an alternative expression of the equivalence ratio can be based on the fuel-to-air volume ratio.

3.5
mass loss concentration
mass of a test specimen consumed during combustion per unit chamber volume (closed system) or per total volume of air passing through an open system

NOTE 1 Mass loss concentration is typically expressed in units of grams per cubic metre.

NOTE 2 For an open system, the definition assumes that the mass is dispersed in the air flow uniformly over time.

1) To be published.

3.6
mass concentration of gas
mass of gas per unit volume

NOTE 1 The mass concentration of a gas can be derived from the measured volume fraction and its molar mass, or measured directly.

NOTE 2 Mass concentration is typically expressed in units of grams per cubic metre.

3.7
mass concentration of particles
mass of solid and liquid aerosol particles per unit volume

NOTE Mass concentration of particles is typically expressed in units of grams per cubic metre.

3.8
molar mass
mass of 1 mole

NOTE Molar mass is normally expressed in units of grams per mole.

3.9
net heat of combustion
enthalpy, per unit mass of fuel consumed, generated in complete combustion with the water produced being in the gaseous state

NOTE Net heat of combustion is typically expressed in units of kilojoules per gram or megajoules per kilogram.

3.10
notional yield
stoichiometric yield
maximum possible mass of a combustion product generated during combustion, per unit mass of test specimen consumed

NOTE Notional yield is typically expressed in units of grams per gram or kilograms per kilogram.

3.11
recovery of element
⟨in a specified combustion product⟩ degree of conversion of an element in the test specimen to a corresponding gas, i.e. a ratio of the actual yield to notional yield of the gas containing that element

3.12
stoichiomeric mixture
mixture of fuel and oxidizer which has the correct composition to produce only the products of complete combustion

3.13
stoichiometric oxygen demand
stoichiometric oxygen-to-fuel mass ratio
amount of oxygen needed by a material for complete combustion

NOTE Stoichiometric oxygen demand is typically expressed in units of grams per gram or kilograms per kilogram.

3.14
uncertainty of measurement
parameter associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the measurand

NOTE The description and propagation of uncertainty in measurements is described in GUM[20].

3.15
yield
mass of a combustion product generated during combustion per unit mass of test specimen consumed

NOTE Yield is typically expressed in units of grams per gram or kilograms per kilogram.

4 Symbols and abbreviated terms

Symbol	Quantity	Typical units
A	extinction area of smoke	square metre
$A_{\sigma f}$ or A_{SEA}	specific extinction area of smoke per unit mass of material burned	square metres per gram or square metres per kilogram
D_{MO}	mass optical density ($\log_{10}$ analogue of SEA)	cubic metres per gram or cubic metres per kilogram
$F_{R,E}$	recovery fraction of element E in gas containing E	dimensionless
ΔH_{act}	measured heat release in a combustion	kilojoules per gram
ΔH_c	net heat or enthalpy generated in complete combustion	kilojoules per gram
I / I_o	fraction of light transmitted through smoke	dimensionless
L	is the light path through the smoke	metre
$m_{A,E}$	atomic mass of the element E	gram
m_E	mass of element E per unit mass of material	dimensionless
$m_{E,per}$	mass of element E in the material, as percentage	percent
m_{fuel}	mass of fuel	gram
m_{gas}	total mass of the gas of interest	gram
$m_{m.loss}$	total mass loss of material	gram
$\dot{m}_{m,loss}$	material mass loss rate	grams per minute
$m_{O2.act}$	actual mass of oxygen available for combustion	gram
$\dot{m}_{O2,act}$	actual mass flow rate of oxygen available for combustion	grams per minute
$m_{O2.stoich}$	stoichiometric mass of oxygen required for complete combustion	gram
m_{part}	total mass of particles	gram
m_s	mass concentration of smoke	grams per cubic metre
M_{gas}	molar mass of the gas of interest	grams per mole
M_{poly}	molar mass of the polymer unit	gram
n_E	number of atoms of element E in the gas	dimensionless
$n_{E.poly}$	number of atoms of element E in the polymer unit	dimensionless
P_{amb}	ambient pressure	kilopascal
P_{std}	standard pressure	101,3 kPa
T_C	temperature of the gas of interest at the point of measurement	degree Celsius
V_{eff}	total volume of fire effluent in cubic metres	cubic metre
$\dot{V}_{air}$	volume air flow rate	cubic metres per minute
$w_{O2,cons}$	measured mass fraction of oxygen consumed	dimensionless
$w_{O2,der}$	derived mass fraction of oxygen consumed	dimensionless

$w_{\text{Oex poly}}$	mass fraction of oxygen in polymer that contributes to the formation of oxygen-containing products	dimensionless
w_{Ogases}	mass fraction of oxygen consumed in the form of the major oxygen-containing products ($w_{\text{OCO2}} + w_{\text{OCO}} + w_{\text{OH2O}}$)	dimensionless
w_{Opoly}	mass fraction of oxygen in the polymer	dimensionless
Y_{gas}	measured mass yield of gas of interest	dimensionless
Y_{part}	measured mass yield of smoke particles	dimensionless
α	linear decadic absorption coefficient (or optical density)	inverse metre
α_{k}	light extinction coefficient	inverse metre
χ	combustion efficiency ratio	dimensionless
χ_{cox}	combustion efficiency ratio calculated from the generation efficiency of carbon in the fuel to oxides of carbon	dimensionless
χ_{ox}	combustion efficiency ratio calculated from oxygen depletion	dimensionless
χ_{prod}	combustion efficiency ratio calculated from the oxygen in the major combustion products	dimensionless
ϕ	equivalence ratio	dimensionless
η	generation efficiency for oxides of carbon	dimensionless
φ_{gas}	volume concentration of the gas of interest	volume per volume, percent, [parts per million (ppm) deprecated]
φ_{O2}	volume fraction oxygen in the air supply (0,209 5 for dry air)	dimensionless
ρ_{gas}	mass concentration of the gas of interest	grams per cubic metre
$\rho_{\text{m.loss}}$	mass loss concentration of the material	grams per cubic metre
$\rho_{\text{part.}}$	mass concentration of the smoke particles	grams per cubic metre
σ_{α}	mass specific extinction coefficient	square metres per gram or square metres per kilogram
Ψ_{gas}	notional mass yield of gas of interest	dimensionless
Ψ_{O}	stoichiometric mass oxygen-to-fuel ratio (stoichiometric oxygen demand)	dimensionless

5 Appropriate input data required for calculations

5.1 Data handling

5.1.1 Uncertainty

In calculating the fire parameters described in this document, it is essential to take into account the uncertainty or error associated with each component, and to combine them in the correct manner[1]. Uncertainty is derived from accuracy (how close the measured value is to the true value) and precision (how well the values agree with each other). There will be uncertainties relating to physically measured parameters (e.g. mass loss, gas concentrations etc.).

Assuming all errors to be independent, the total error, δq, is obtained by summing the squares of the errors in accordance with the general Equation (1):

$$\delta q = \sqrt{\left(\frac{\delta q}{\delta a}\delta a\right)^2 + \ldots + \left(\frac{\delta q}{\delta z}\delta z\right)^2} \quad (1)$$

In other words, evaluate the error caused by each of the individual measurements, and then combine them by taking the root of the sum of the squares.

In empirically derived equations, uncertainties in “constant” values should be treated similarly to measurement uncertainties. If a constant is truly constant, i.e. has negligible uncertainty, then it can be neglected.

5.1.2 Significant figures and rounding off

When recording and reporting data, it is also important to handle significant figures properly. The general approach is to carry one digit beyond the last certain one. When rounding off, the typical rule is to round up when the figure to be dropped is 5 or more and round down when it is less than 5.

5.2 Test specimen information

5.2.1 Composition

Information should be given where possible on the combustible fraction, organic and inorganic combustible components, inert components, elemental composition, empirical formula, and molecular or formula weight

The combustible in a fire experiment of any scale is often a single, homogenous material, perhaps with dispersed additives. In this case, the molecular formula of the material should be provided. Commercial products, however, are generally non-homogeneous combinations of materials, with each component containing one or more polymers and possibly multiple additives. For complex materials representative of commercial products, the yields, effective heats of combustion, etc. will vary with time as the various components become involved. For some of the following (global) calculations, a simplification is the use of an empirical formula for the composite.

5.2.2 Net heat of combustion

The net heat of combustion for combustible components may be required for some of the calculations (e.g. combustion efficiency).

5.3 Fire conditions

5.3.1 Apparatus

Give the name of the apparatus with a brief description of mode of operation (e.g., flow-through steady state, calorimeter, closed chamber system, etc.). Refer to the appropriate standard or other reference relating to the procedure.

5.3.1 Set-up procedure

The fire conditions are generally apparatus-dependent, and largely dictated by the set-up procedure for the particular apparatus. The following information is required:

a) test specimen details, its mass, dimensions and orientation of the combustible;

b) thermal environment in terms of the temperature (expressed in degrees Celsius) and/or irradiance (expressed in kilowatts per square metre) to which test specimen is subjected;

   NOTE The temperature distribution and the radiation field in a test are frequently not uniform and as a result are rarely well documented. Sufficient information about the thermal and radiative conditions is needed that another person can reproduce the results using the same apparatus, compare the results with results for the same specimen tested in another apparatus, etc.

c) oxygen concentration in the air supply (volume percent or volume fraction);

d) volume of chamber or air flow. For a closed system, give the air volume (expressed in litres or cubic metres), and for an open system, give the air flow (expressed in litres per minute or in cubic metres per metre), and the dynamics of the flow. In both cases, give information on the atmospheric mixing conditions and the degree of homogeneity of the fire effluent.

5.4 Data collection

5.4.1 Data acquisition

Time-resolved data or time-integrated data may be acquired. The method of data acquisition will be specified in the test protocol.

5.4.2 Measured data and observations

Most of the following data parameters will be required in order to calculate yields, equivalence ratios and combustion efficiencies in experimental fires. The units applied to data will be usually dictated by the operational procedure associated with a particular piece of apparatus. A number of typical units are suggested below:

a) mass loss of the test specimen, derived by measuring the test specimen mass before and after test to give overall mass loss (expressed in milligrams, grams or kilograms) or mass loss fraction (expressed in mass percent, grams per gram or kilograms per kilogram), or by measuring the specimen mass throughout a test to give mass loss rate (expressed in milligrams per second, grams per minute, or kilograms per minute);

b) gas and vapour concentrations and oxygen depletion [expressed in volume percent, volume fraction, microlitres per litre, milligrams per litre, or milligrams per cubic metre (parts per million is deprecated)];

c) smoke particulate concentration (expressed in milligrams per litre or milligrams per cubic metre) and smoke obscuration (expressed in optical density per metre or square metres per kilogram);

d) heat release (expressed in kilojoules per gram), used to calculate combustion efficiency, forms part of the protocol for some apparatuses;

e) combustion mode, time to ignition (expressed in minutes or seconds) and whether the specimen flames or not throughout the test.

6 Calculation of yields of fire gases and smoke, stoichiometric oxygen demand, and recovery of key elements

6.1 Calculation of measured yields from fire gas concentration data

In experimental fires, the mass yield, Y_{gas}, of a gas can be calculated from the measured mass concentration of the gas of interest and the mass loss concentration of the material, or from the total mass of gas generated and the total mass loss of material in accordance with Equation (2); see Notes 1, 2, and 3):

$$Y_{\text{gas}} = \frac{\rho_{\text{gas}}}{\rho_{\text{m.loss}}} \qquad (2)$$

where

ρ_{gas} is the mass concentration, expressed in grams per cubic metre, of the gas ;

$\rho_{\text{m.loss}}$ is the mass loss concentration, expressed in grams per cubic metre, of the material.

Alternatively, the expression can be written as given in Equation (3):

$$Y_{\text{gas}} = \frac{m_{\text{gas}}}{m_{\text{m.loss}}} \tag{3}$$

where

m_{gas} is the total mass, expressed in grams, of the gas;

$m_{\text{m.loss}}$ is the total material mass loss, expressed in grams.

NOTE 1 These calculations can be derived from instantaneous data or from data which assumes (a) that the gases are uniformly dispersed in a certain volume and (b) that this volume is the same one in which the lost sample mass is (evenly) dispersed. If the dispersion is not uniform, the equations still work if the lost mass and the gas in question are dispersed equivalently. If a combustion gas is prone to surface losses within the apparatus, the apparent yield will depend on where the concentration is being measured.

NOTE 2 In flow-through devices, the total effluent is generally well mixed at some distance downstream. For closed-box combustion systems, it is not necessarily so, especially if there are large molecular weight differences and large thermal gradients. If multiple fuels are involved, only some averaged combined yield could be calculated.

NOTE 3 In setting up these calculations, it is important to keep track of the uncertainty. There will be uncertainties relating to lost sample mass, fluctuations in the measured concentration, etc. The calculated yield needs to take account of and combine these, enabling a sound basis for comparing yields under different combustion conditions, comparing yields from different materials, etc.

Whilst concentrations of the specific gas are most often measured in volume units, the mass loss from a solid will almost always be in mass units, since the molecular weight of the effluent is difficult to determine. Equations (4) and (5) show how to convert the volume fraction concentrations of a gas to its mass concentration:

$$\rho_{\text{gas}} = \varphi_{\text{gas}} \times \frac{M_{\text{gas}}}{22{,}414} \times \frac{273{,}16}{(273{,}16 + T_{\text{C}})} \times \frac{P_{\text{amb}}}{101{,}3} \times 10^{-3} \tag{4}$$

where

φ_{gas} is the concentration, expressed as microlitres per litre, of the gas;

M_{gas} is the molar mass, expressed in grams per mole, of the gas;

T_{C} is the temperature, expressed in degrees Celsius, of the gas at the point of measurement;

P_{amb} is the ambient pressure, expressed in kilopascals;

273,16 is standard temperature, expressed in kelvins;

101,3 is standard pressure, expressed in kilopascals;

22,414 is the volume, expressed in cubic metres, occupied by the molar mass of the gas at standard temperature and pressure.

Thus, for fire effluent at 20 °C and standard pressure, Equation (4) simplifies to Equation (5):

$$\rho_{\text{gas}} = \varphi_{\text{gas}} \times \frac{M_{\text{gas}}}{24{,}055} \times 10^{-3} \tag{5}$$

EXAMPLE The calculations for a well ventilated fire atmosphere where mass loss concentration of the material is 25 g·m $^{-3}$, and carbon monoxide (CO) concentration is 0,125 0 volume % at 20 °C are shown in Equations (6) and (7):

$$\rho_{CO} = 0{,}125\,0 \times \frac{28{,}01}{24{,}055} \times 10 = 1{,}456 \quad (6)$$

$$Y_{CO} = 1{,}456/25 = 0{,}058\,2 \quad (7)$$

where

ρ_{CO} is the mass concentration, expressed in grams per cubic metre, of CO;

Y_{CO} is the mass yield, expressed in grams of CO per gram material;

28,01 is the molar mass, expressed in grams, of CO.

The atomic mass, molar mass and gas concentration conversion factors for the major fire gases are listed in Tables 1 and 2.

Table 1 — Atomic mass of key fire gas elements[2]

Element	Symbol	Atomic mass[a]
Carbon	C	12,011
Hydrogen	H	1,0079
Oxygen	O	15,999
Nitrogen	N	14,007
Chlorine	Cl	35,453
Bromine	Br	79,904
Fluorine	F	18,998
Sulfur	S	32,065
Phosphorus	P	30,973
Antimony	Sb	121,76

[a] Atomic mass values rounded to five significant figures

Table 2 — Molar masses of common fire gases and volume/mass concentration conversion factors

Gas or vapour	Formula	Molar mass[a] $g \cdot mol^{-1}$	Gas concentration conversion factors (at 20 °C and 101,3 kPa)	
			(µl/l)[b] to $g \cdot m^{-3}$	$g \cdot m^{-3}$ to (volume % × 10^4)[b]
Carbon dioxide[c]	CO_2	44,01	$1,830 \times 10^{-3}$	$0,546 \times 10^{3}$
Carbon monoxide[c]	CO	28,01	$1,164 \times 10^{-3}$	$0,859 \times 10^{3}$
Hydrogen cyanide	HCN	27,02	$1,124 \times 10^{-3}$	$0,890 \times 10^{3}$
Nitrogen dioxide	NO_2	46,01	$1,913 \times 10^{-3}$	$0,523 \times 10^{3}$
Nitrous oxide	N_2O	44,01	$1,831 \times 10^{-3}$	$0,546 \times 10^{3}$
Nitric oxide	NO	30,01	$1,248 \times 10^{-3}$	$0,801 \times 10^{3}$
Ammonia	NH_3	17,03	$0,708 \times 10^{-3}$	$1,413 \times 10^{3}$
Hydrogen chloride	HCl	36,46	$1,516 \times 10^{-3}$	$0,660 \times 10^{3}$
Hydrogen bromide	HBr	80,91	$3,364 \times 10^{-3}$	$0,297 \times 10^{3}$
Hydrogen fluoride	HF	20,01	$0,832 \times 10^{-3}$	$1,202 \times 10^{3}$
Hydrogen sulfide	H_2S	34,08	$1,417 \times 10^{-3}$	$0,706 \times 10^{3}$
Sulfur dioxide	SO_2	64,06	$2,663 \times 10^{-3}$	$0,376 \times 10^{3}$
Water	H_2O	18,01	$0,749 \times 10^{-3}$	$1,335 \times 10^{3}$
Phosphoric acid	H_3PO_4	97,99	$4,074 \times 10^{-3}$	$0,245 \times 10^{3}$
Acrolein	C_3H_4O	56,06	$2,331 \times 10^{-3}$	$0,429 \times 10^{3}$
Formaldehyde	CH_2O	30,03	$1,248 \times 10^{-3}$	$0,801 \times 10^{3}$
Oxygen	O_2	32,00	$1,331 \times 10^{-3}$	$0,751 \times 10^{3}$
Oxygen depletion	O_2	32,00	See note d.	

[a] Molar mass values are rounded to two decimal places.

[b] Conversion factors:
ppm = volume % × 10^4
ppm = volume fraction × 10^6

[c] CO_2/CO volume ratio equals the CO_2/CO mass ratio divided by 1,571.

[d] The (initial volume fraction minus the measured volume fraction) × 1 331 = $g \cdot m^{-3}$.

The volume fraction in totally dry air is 0,209 5 and this is appropriate for dry air supplies. Room air is generally lower in oxygen due to the presence of water vapour. At room temperature and 100 % relative humidity, water is present at a volume fraction of around 0,03.

NOTE: Example calculation:

0,100 0 volume % CO = 0,100 0 × 1,164 10 = 1,164 $g \cdot m^{-3}$.

6.2 Calculation of notional gas yields

6.2.1 General

The notional yields of gases and vapours are a measure of the maximum theoretical combustion product yields. They are based on the composition of the material and are entirely material-dependent. Two primary methods for calculating notional yields are described in 6.2.2 and 6.2.3.

6.2.2 From the elemental composition

Provided the elemental composition of the base material is known (e.g. by elemental analysis), the maximum possible (notional) yield, Ψ_{gas}, of fire gas corresponding to each specified element, E, is calculated in accordance with Equations (8) and (9):

$$\Psi_{gas} = m_{E} \times \frac{M_{gas}}{n_{E} \times m_{A,E}} \qquad (8)$$

where

m_{E} is the mass, expressed in grams, of element E per unit mass, expressed in grams, of material;

n_{E} is the number of atoms of element E in the gas;

$m_{A,E}$ is the atomic mass, expressed in grams, of the element E.

or

$$\Psi_{gas} = m_{E,per} \times \frac{M_{gas} \times 10^{-2}}{n_{E} \times m_{A,E}} \qquad (9)$$

where $m_{E,per}$ is the mass of element E in the material, expressed as percent.

EXAMPLE The notional yield, Ψ_{CO}, of CO from cellulose is calculated as shown in Equation (10):

$$\Psi_{CO} = 44,5 \times \frac{28,01 \times 10^{-2}}{1 \times 12,011} = 1,038 \qquad (10)$$

where

Ψ_{CO} is expressed in grams of CO per gram of material;

44,5 is the mass, expressed as percent, of carbon in the cellulose;

28,01 is the molar mass, expressed in grams per mole, of CO;

12,011 is the atomic mass, expressed in grams, of carbon.

Factors for calculating notional gas yields from the elemental composition are given in Table 3.

6.2.3 From the empirical formula

If the empirical formula of the material is known, the notional yield, Ψ_{gas}, can be calculated from Equation (11):

$$\Psi_{gas} = \frac{n_{E.poly}}{n_{E}} \times \frac{M_{gas}}{M_{poly}} \qquad (11)$$

where

$n_{E.poly}$ is the number of atoms of element E in the polymer unit;

M_{poly} is the molar mass, expressed in grams, of the polymer unit.

EXAMPLE The notional yield, Ψ_{CO2}, of carbon dioxide (CO_2) from polypropylene with the empirical formula (C_3H_6) is calculated as shown in Equation (12):

$$\Psi_{CO2} = \frac{1}{3} \times \frac{44,01}{42,03} = 3,142 \qquad (12)$$

where

Ψ_{CO2} is expressed in grams of CO_2 per gram of polymer;

1 is the number of atoms of carbon in CO_2;

3 is the number of atoms of carbon in the polymer unit;

44,01 is the molar mass, expressed in grams per mole, of CO_2;

42,03 is the molar mass, expressed in grams, of the polymer unit.

NOTE The notional yield of a gas that contains more than one element from the fuel molecule will be determined by the least prevalent element (other than oxygen). Thus the notional yield of HCN will most often be determined by the nitrogen content of the fuel. However, for a product gas like formaldehyde, it could be either the carbon or hydrogen fraction that provides the criterion, depending on the fuel composition.

Table 3 — Factors for calculating notional gas yields from the elemental composition of material

Gas or vapour		**Notional yield of gas or vapour** Ψ_{gas} mass fraction of base material	
Formula	**Molar mass** g·mol-1	**Element E inbase material** %	**Factor**[a]
CO_2	44,01	carbon	$3,664 \times 10^{-2}$
CO	28,01	carbon	$2,332 \times 10^{-2}$
H_2O	18,02	hydrogen	$8,939 \times 10^{-2}$
HCN	27,02	nitrogen	$1,929 \times 10^{-2}$
NO_2	46,01	nitrogen	$3,284 \times 10^{-2}$
N_2O	44,01	nitrogen	$1,571 \times 10^{-2}$
NO	30,01	nitrogen	$2,142 \times 10^{-2}$
NH_3	17,03	nitrogen	$1,216 \times 10^{-2}$
HCl	36,46	chlorine	$1,028 \times 10^{-2}$
HBr	80,92	bromine	$1,013 \times 10^{-2}$
HF	20,01	fluorine	$1,053 \times 10^{-2}$
H_2S	34,08	sulfur	$1,063 \times 10^{-2}$
H_3PO_4	97,98	phosphorus	$3,163 \times 10^{-2}$
SO_2	64,06	sulfur	$1,998 \times 10^{-2}$
Acrolein (C_3H_4O)	56,06	carbon	$1,556 \times 10^{-2}$
Formaldehyde (CH_2O)	30,03	carbon	$2,500 \times 10^{-2}$

[a] Factor derived from Equation (9), and rounded to four significant figures.

6.3 Calculation of recovery of elements in key products

The recovery of an element in a key combustion product (alternatively the degree of conversion of an element in the test specimen to a corresponding gas or efficiency yield of the element) can be calculated from the measured yield, Y_{gas}, of the gas of interest relative to its notional yield, Ψ_{gas}. For a material containing element E, this corresponds to Equation (13):

$$R_E = Y_{gas} / \Psi_{gas} \tag{13}$$

where

Y_{gas} is derived from Equations (2) to (7);

Ψ_{gas} is derived from Equations (8) to (12);

R_E is the recovery fraction of element E in gas containing E.

6.4 Calculation of stoichiometric oxygen demand

6.4.1 General

Stoichiometric oxygen demand (or oxygen-to-fuel ratio) is the amount of oxygen needed by a material for complete combustion. Its derivation is somewhat more complex than notional gas yields, and can be calculated by three primary methods as described in 6.4.2 to 6.4.4:

6.4.2 From the chemical equation for complete combustion

6.4.2.1 For fuel containing C, H, O, for complete combustion to carbon dioxide and water

For the complete combustion of fuels containing C, H, O, the products will only consist of CO_2 and gaseous H_2O. For fuels which contain oxygen, the requirement of oxygen from air for complete combustion is less than for fuels which do not contain oxygen. For a polymer with the general formula $C_aH_bO_c$, Equations (14) to (16) apply:

$$C_aH_bO_c + zO_2 \rightarrow aCO_2 + b/2\ H_2O \tag{14}$$

and

$$z = \frac{2a + (b/2) - c}{2} \tag{15}$$

where

z is the (stoichiometric) number of moles of O_2 required for complete combustion of the polymer,

a is the number of atoms of carbon in the polymer;

b is the number of atoms of hydrogen in the polymer;

c is the number of atoms of oxygen in the polymer.

The stoichiometric mass oxygen required for complete combustion is then calculated from Equation (16):

$$\Psi_O = \frac{z \times 32,00}{M_{poly}} \tag{16}$$

where

Ψ_O is the stoichiometric oxygen demand, expressed in grams per gram the polymer;

32,00 is the molar mass, expressed in grams per mole, of oxygen.

EXAMPLE The stoichiometric combustion equation for polymethyl methacrylate (PMMA) is given in Equations (17) and (18):

$$C_{1,0}H_{1,6}O_{0,4} + 1,20\ O_2 \rightarrow CO_2 + 0,80\ H_2O \tag{17}$$

$$\Psi_O = \frac{1,20 \times 32,00}{20,02} = 1,918 \tag{18}$$

where

1,0 is the number of atoms of carbon in the polymer;

1,6 is the number of atoms of hydrogen in the polymer;

0,4 is the number of atoms of oxygen in the polymer;

1,20 is the (stoichiometric) number of moles of O_2 required for complete combustion of PMMA;

1,918 is the calculated stoichiometric oxygen demand, expressed in grams of O_2 per gram of PMMA.

6.4.2.2 For fuels containing hetero-elements

For the complete combustion of fuels containing (organically-bound) elements in addition to C, H and O, it is assumed that nitrogen generates gaseous N_2, halogens generate gaseous acid gases (HCl, HBr etc) and sulfur generates gaseous SO_2.

Combustion equations for this type of test material are more complex because, for example, hydrogen from the material is used to form acid gases as well as water, and sulfur consumes oxygen to form SO_2. For a halogenated material with the general formula of $C_aH_bO_cN_dCl_eBr_fF_gS_h$, the equation for stoichiometric oxygen demand is as follows:

$$z = \frac{2a + 2h - c + (b - e - f - g)/2}{2} \tag{19}$$

where

z is the (stoichiometric) number of moles of O_2 required for complete combustion of the polymer;

a is the number of atoms of carbon in the polymer;

b is the number of atoms of hydrogen in the polymer;

c is the number of atoms of oxygen in the polymer;

d is the number of atoms of nitrogen in the polymer;

e is the number of atoms of chlorine in the polymer;

f is the number of atoms of bromine in the polymer;

g is the number of atoms of fluorine in the polymer;

h is the number of atoms of sulphur in the polymer.

EXAMPLE The stoichiometric combustion equation for unplasticized polyvinyl chloride (C_2H_3Cl) is given by Equations (20) to (23):

$$C_aH_bCl_e + zO_2 \rightarrow aCO_2 + (b - e) / 2H_2O + eHCl \tag{20}$$

The number of moles of O_2 is calculated by substituting the appropriate values into Equation (19) as given in Equation (21):

$$z = \frac{2a - c + (b - e)/2}{2} = \frac{4 - 0 + (3 - 1)/2}{2} = 2{,}5 \tag{21}$$

Equation (20) can be written as Equation (21):

$$C_2H_3Cl + 2{,}5\ O_2 \rightarrow 2CO_2 + H_2O + HCl \tag{22}$$

and

$$\Psi_O = \frac{2{,}5 \times 32{,}00}{62{,}5} = 1{,}280 \tag{23}$$

where

2,5 is the (stoichiometric) number of moles of O_2 required for complete combustion of UPVC;

62,5 is the molar mass, expressed in grams per mole, of UPVC;

1,280 is the calculated stoichiometric oxygen demand, expressed in grams O_2 per gram of UPVC.

6.4.3 From the net heat of combustion ΔH_c

It has been empirically determined that when a material burns, for every gram of oxygen consumed, the heat released is approximately 13,1 $kJ \cdot g^{-1}$, (accurate to ± 5 %)[3]. Thus, if the net heat, ΔH_c, generated in complete combustion is known (e.g., as measured by bomb calorimetry), the stoichiometric oxygen demand can be calculated as given in Equation (24):

$$\Psi_O = \Delta H_c / 13{,}1 \tag{24}$$

EXAMPLE The calculation for polystyrene is shown in Equation (25):

$$\Psi_O = 39{,}2 / 13{,}1 = 2{,}99 \tag{25}$$

where

ΔH_c is the net heat or enthalpy per unit mass of fuel consumed, generated in complete combustion with the water produced being in the gaseous state;

39,2 is the net heat, expressed as kilojoules per gram, of complete combustion for polystyrene;

2,99 is the calculated stoichiometric oxygen demand, expressed in grams O_2 per gram of polystyrene.

NOTE From its chemical composition, Ψ_O for polystyrene is 3,07 $g \cdot g^{-1}$.

6.4.4 From the carbon content of the material

There is a less accurate correlation between the carbon content and stoichiometric oxygen demand of polymeric materials empirically derived from the carbon content where the correlation coefficient, R^2, is 0,933, as shown in Equation (26):

$$\Psi_{O,poly} = (m_{C,per} \times 0{,}038\ 7) - 0{,}3399 \tag{26}$$

where

$m_{C,per}$ is the mass fraction, expressed as a percentage, of carbon in the material;

0,0387 and 0,3399 are empirically-derived mathematical coefficients.

EXAMPLE The calculation of the carbon content for polymethyl methacrylate is given in Equation (27):

$$\Psi_O = (60{,}0 \times 0{,}038\,7) - 0{,}339\,9 = 1{,}98 \quad (27)$$

where

60,0 is the mass fraction, expressed as a percentage, of carbon in PMMA;

1,98 is the calculated stoichiometric oxygen demand, expressed in grams O_2 per gram of PMMA.

NOTE From its chemical composition, Ψ_O for PMMA is 1,918 $g \cdot g^{-1}$.

The step-wise procedures for calculating notional gas yields and stoichiometric oxygen demand for a polymer containing C, O, H, and X and for polyamide using chemical equation methods are summarized in Table 4.

Three methods for calculating stoichiometric oxygen demand for selected polymers are compared in Table 5.

Notional gas yields and stoichiometric oxygen demand derived for a number of common polymers are listed in Tables 6, 7 and 8.

Table 4 — Example calculations for notional gas yields and stoichiometric oxygen demand for a polymer containing C, O, H, X, and for polyamide using chemical equation methods

Polymer	Contains C, H, O, X	Polyamide
Empirical formula	$C_aH_bO_cX_d$	$C_{12}H_{22}O_2N_2$ $(C_1H_{1,83}O_{0,17}N_{0,17})$[b]
Molar mass of polymer M_{poly}, grams	$(12 \times a) + (1 \times b) + (16 \times c) + (m_{A,E} \times d)$[a]	$(12 \times 12) + (1 \times 22) + (16 \times 2) + (14 \times 2) = 226$ (= 18,83 relative to each C atom)
Notional yield CO_2 Ψ_{CO2}, grams per gram	$a/1 \times 44 / M_{poly}$	$12 \times 44 / 226 = 2{,}336$ $g \cdot g^{-1}$
Notional yield CO Ψ_{CO}, grams per gram	$a/1 \times 28 / M_{poly}$	$12 \times 28 / 226 = 1{,}487$ $g \cdot g^{-1}$
Notional yield H_2O Ψ_{H2O}, grams per gram	$b/2 \times 18 / M_{poly}$	$22/2 \times 18 / 226 = 0{,}876$ $g \cdot g^{-1}$
Stoichiometric oxygen demand, z moles O_2[c]	$(2a + b/2 - c) / 2$	$(24 + 11 - 2) / 2 = 16{,}5$ mol
Stoichiometric oxygen demand of polymer $\Psi_{O,poly}$, grams per gram	z mol $\times 32 / M_{poly}$	$16{,}5 \times 32 / 226 = 2{,}336$ $g \cdot g^{-1}$

[a] $m_{A,E}$ is the atomic mass, expressed in grams, of the element E.

[b] Empirical formula re-based to one carbon atom.

[c] This assumes that nitrogen in the material is converted to N_2. In practice a small proportion will be converted to nitrogen products containing hydrogen or oxygen. The error is considered to be small.

Table 5 — Examples of stoichiometric oxygen demand derived by three methods

Generic polymer types	Empirical formula	ΔH_c[a,b,c] kJ·g^{-1}	Carbon content of polymer %	Stoichiometric oxygen demand of polymer Ψ_O g·g^{-1}		
				From elemental composition	From ΔH_c[d]	From carbon content[e]
Polyethylene	C_2H_4	43,1 to 43,6	85,7	3,420	3,29 to 3,32	2,98
Polystyrene	C_8H_8	39,2 to 39,9	92,3	3,080	2,99 to 3,05	3,23
Polymethylmethacrylate	$C_5H_8O_2$	24,9 to 25,2	60,0	1,920	1,90 to 1,92	1,98
Polycarbonate	$C_{16}H_{14}O_3$	29,7 to 29,8	75,4	2,260	2,27	2,58
Polyethylene terephthalate	$C_{10}H_8O_4$	21,3 to 22,0	62,5	1,665	1,63 to 1,68	2,08
Polyester, unsaturated	$C_{5,77}H_{6,25}O_{1,63}$	20,3 to 28,5	68,2	2,051	1,55 to 2,18	2,30
Polyvinyl chloride	C_2H_3Cl	16,4 to 16,9	38,4	1,280	1,25 to 1,29	1,15
Polytetrafluoroethylene	C_2F_4	6,2 to 5,00	24,0	0,640	0,473	0,59
Polyacrylonitrile	C_3H_3N	30,8 to 31,0	67,9	2,270	2,35 to 2,37	2,29
Polyamide	$C_6H_{11}NO$	29,5 to 30,8	63,7	2,330	2,25 to 2,35	2,13
Polyurethane foam, rigid	$C_{6,3}H_{7,1}NO_{2,1}$	~27 to 22,7	66,2	2,100	2,06 to 1,73	2,22
Polyurethane foam, flexible	—	23,2 to 31,6	—	—	1,77 to 2,41	—
Wool	—	20,7 to 26,6	—	—	1,58 to 2,03	—
Cellulosics (e.g., pinewood)	$CH_{1,7}O_{0,83}$	16,0 to 20,4	44,5	1,197	1,22 to 1,56	1,38

a Reference[4].

b Reference[5].

c Reference[6].

d Calculation uses 13,1 as a divisor[3].

e From empirical correlation derived from data given in References[4], [5], [6]; see Equation (26) where $\Psi_O = (m_{C,per} \times 0{,}038\,7) - 0{,}339\,9$ and $R^2 = 0{,}933$.

Table 6 — Notional gas yields and stoichiometric oxygen demand for common polymers containing C, H, O, in the structure

Material	Empirical formula	C %	Ψ_O[a] $g \cdot g^{-1}$	Notional gas yields[b]	
				Ψ_{CO2} $g \cdot g^{-1}$	Ψ_{CO} $g \cdot g^{-1}$
Polyethylene	CH_2	85,7	3,421	3,140	2,000
Polypropylene	CH_2	85,7	3,421	3,140	2,000
Polystyrene	CH	92,3	3,070	3,380	2,150
Polymethyl methacrylate	$CH_{1,6}O_{0,40}$	60,0	1,920	2,200	1,400
Cellulose	$CH_{1,7}O_{0,83}$	44,5	1,197	1,630	1,040
Viscose	$CH_{1,7}O_{0,83}$	44,5	1,197	1,630	1,040
Polyester[c]	$CH_{1,4}O_{0,22}$	70,9	2,340	2,600	1,650
Polyethylene terephthalate	$CH_{0.80}O_{0,40}$	62,5	1,667	2,292	1,458
Polycarbonate	$CH_{0.88}O_{0,19}$	75,4	2,260	2,760	1,760

a Stoichiometric oxygen demand, Ψ_O, (used to calculate the equivalence ratio, ϕ) has been calculated from the chemical composition of the polymer and the equation for complete combustion.

EXAMPLE 1 Stoichiometric oxygen demand for complete combustion of polyethylene:

$CH_2 + 1,5\ O_2 = CO_2 + H_2O$

$14,03\ g + 48,00\ g \rightarrow 48,00 / 14,03$

$\Psi_O = 3,421\ g \cdot g^{-1}$.

EXAMPLE 2 Stoichiometric oxygen demand for complete combustion of polyester:

$CH_{1,4}O_{0,22} + 1,24 O_2 = CO_2 + 0,7\ H_2O$

$16,92\ g + 39,70\ g \rightarrow 39,70 / 16,92$

$\Psi_O = 2,346\ g \cdot g^{-1}$.

b Notional gas yields, expressed in grams per gram: $\Psi_{CO2} = \%C \times 3,67 \times 10^{-2}$
$\Psi_{CO} = \%C \times 2,33 \times 10^{-2}$.

c The values given in the table are examples only, and not necessarily characteristic of the whole family of polymers.

Table 7 — Notional gas yields and stoichiometric oxygen demand for common polymers containing C, H, O, N in the structure

Material	Empirical formula[a]	C %	N %	Ψ_O[b] $g \cdot g^{-1}$	Notional gas yields[d]			
					Ψ_{CO2} $g \cdot g^{-1}$	Ψ_{CO} $g \cdot g^{-1}$	Ψ_{HCN} $g \cdot g^{-1}$	Ψ_{NO2} $g \cdot g^{-1}$
Poly acrylonitrile PAN	$CHN_{0,33}$	68,1	26,4	2,270	2,500	1,590	0,510	0,870
Polyamide	$CH_{1,8}O_{0,17}N_{0,17}$	63,7	12,6	2,330	2,330	1,480	0,240	0,415
Polyurethane foam, flexible	$CH_{1,8}O_{0,35}N_{0,06}$	59,3	4,2	2,010	2,170	1,380	0,080	0,140
Polyurethane foam, rigid	$CH_{1,2}O_{0,22}N_{0,10}$	66,2	7,7	2,100	2,430	1,545	0,150	0,250
Polyisocyanurate foam, rigid	$CH_{1,0}O_{0,19}N_{0,11}$	68,2	8,8	2,100	2,430	1,545	0,171	0,286
Aramid fibres	$CH_{0,71}O_{0,14}N_{0,14}$	71,0	11,8	2,094	2,600	1,650	0,230	0,390
Wool[c]	$CH_{1,62}O_{0,38}N_{0,27}S_{0,03}$	49,1	N = 15,5 S = 3,9 O = 24,9	1,590	1,800	1,145	0,290	0,490

[a] The values given in the table are examples only, and not necessarily characteristic of the whole family of polymers.

[b] Stoichiometric oxygen demand, Ψ_O, (used to calculate equivalence ratio, ϕ) has been calculated from the chemical composition of the polymer and the equation for complete combustion.

[c] Approximate values for wool.

[d] Notional gas yields:

$$\Psi_{CO2} = \%C \times 3,67 \times 10^{-2}$$

$$\Psi_{CO} = \%C \times 2,33 \times 10^{-2}$$

$$\Psi_{HCN} = \%N \times 1,93 \times 10^{-2}$$

$$\Psi_{NO2} = \%N \times 3,29 \times 10^{-2}$$

Table 8 — Notional gas yields and stoichiometric oxygen demand for common polymers containing C, H, O, X in the structure[a]

Material	Empirical formula	C %	Cl %	F %	Ψ_O[b] $g \cdot g^{-1}$	Notional yields[f]			
						Ψ_{CO2} $g \cdot g^{-1}$	Ψ_{CO} $g \cdot g^{-1}$	Ψ_{HCl} $g \cdot g^{-1}$	Ψ_{HF} $g \cdot g^{-1}$
Polyvinyl chloride (PVC)	$CH_{1,5}Cl_{0,50}$	38,4	56,7	—	1,280	1,410	0,895	0,585	—
Polyvinyl chloride plasticized	$CH_{1,5}Cl_{0,50}$ + 50 % DOP[c]	56	28	—	1,917[c]	2,060	1,300	0,290	—
Poly tetra fluoro-ethylene (PTFE)	CF_2	24,0	—	75	0,64[d] 0,32[e]	0,880	0,560	—	0,750

a The stoichiometric number of moles of oxygen required for complete combustion of halogenated polymers is as follows; see Equation (19):

$$z = \frac{2a - c + (b - e - f - g)/2}{2}$$

The general formula for the polymer is $C_aH_bO_cN_dCl_eBr_fF_g$.

b Stoichiometric oxygen demand, Ψ_O, (used to calculate equivalence ratio, ϕ) has been calculated from the chemical composition of the polymer and the equation for complete combustion.

c The formula for dioctylphthalate (DOP) is $C_{24}H_{36}O_4$; $\Psi_{DOP} = 2,553\ g \cdot g^{-1}$.

d Oxygen demand assumes no H_2O in the reaction, i.e. $CF_2 + O_2 \rightarrow CO_2 + F_2$.

e Oxygen demand assumes H_2O in the reaction, i.e. $CF_2 + ½O_2 + (H_2O) \rightarrow CO_2 + 2HF$.

f Notional gas yields: $\Psi_{CO2} = \%C \times 3,67 \times 10^{-2}$

$\Psi_{CO} = \%C \times 2,33 \times 10^{-2}$

$\Psi_{HCN} = \%N \times 1,93 \times 10^{-2}$

$\Psi_{NO2} = \%N \times 3,29 \times 10^{-2}$

6.5 Calculation of smoke yields

6.5.1 General

Smoke is an aerosol consisting of liquid droplets, solid particles and two-phase combinations of the two. It can be measured as a function of its gravimetric properties (the mass of smoke particles), of its light obscuring properties or a mixture of the two[7, 8].

6.5.2 Smoke yields based on mass of smoke particulates

Gravimetric methods give mass of particles for each gram of mass loss of material. Most systems use simple filter-based sampling devices, whilst other methods are more sophisticated and can characterize the smoke by fractionating the particles into different sizes.

The yield of smoke as particles can be calculated from its mass concentration (grams per cubic metre) and the mass loss concentration of the material (grams per cubic metre), or from the total mass of particles generated and the total mass loss of material as given in Equation (28):

$$Y_{\text{part}} = \frac{\rho_{\text{part}}}{\rho_{\text{m.loss}}} \tag{28}$$

where

Y_{part} is the measured mass yield, expressed in grams per gram of material, of smoke particles;

ρ_{part} is the mass concentration, expressed in grams per cubic metre, of the smoke particles;

$\rho_{\text{m.loss}}$ is the mass loss concentration, expressed in grams per cubic metre, of the material.

Alternatively, the relationship can be written as given in Equation (29):

$$Y_{\text{part}} = \frac{m_{\text{part}}}{m_{\text{m.loss}}} \tag{29}$$

where

m_{part} is the total mass, expressed in grams, of particles;

$m_{\text{m.loss}}$ is the total material mass loss, expressed in grams.

6.5.3 Smoke yields based on light obscuring properties

Smoke can also be quantified in terms of its extinction coefficient, α_{k}, derived from Bouguer's law [Equations (30) and (31)] which describe the attenuation of monochromatic light by smoke:

$$I/I_0 = \mathrm{e}^{-(\alpha_{\text{k}} L)} \tag{30}$$

$$\alpha_{\text{k}} = \frac{1}{L} \times \ln\left(I_0/I\right) \tag{31}$$

where

α_{k} is the light extinction coefficient, expressed as inverse metres;

I_0 is the intensity of incident light;

I is the intensity of transmitted light (at the detector);

L is the length, expressed in metres, of the light path through the smoke.

Correlations have been established between visibility in smoke and its extinction coefficient such that their product is a constant, but the value of the constant depends on the contrast and illumination of the target being viewed.

In some studies, base-10 logarithms are used to calculate the optical density per unit light path length, α, formally designated the linear decadic absorption coefficient, as shown in Equations (32) and (33):

$$\alpha = \frac{1}{L} \times \log_{10}\left(I_0/I\right) \tag{32}$$

$$\alpha \times 2{,}303 = \alpha_k \tag{33}$$

where

α is the linear decadic absorption coefficient (optical density), expressed as inverse metres;

2,303 is the base-10 logarithm conversion factor to give the extinction coefficient, α_k, in Equation (31).

The extinction area, A, of the smoke is the total effective cross-sectional area of all the smoke particles, and this is related to the volume, V, of the chamber in which it is contained as given in Equations (34) and (35):

$$A = \alpha_k \times V \tag{34}$$

or

$$A = 2{,}303 \times \alpha \times V \tag{35}$$

where

A is the extinction area, expressed in square metres, of the smoke;

V is the volume, expressed in cubic metres, of the chamber in which the smoke is contained.

The specific extinction area ($A_{\sigma f}$ or A_{SEA}) is a normalized parameter relating the extinction area of smoke to the mass of material burned by Equation (36):

$$A_{\sigma f} = A / m_{m,loss} \text{ or } A_{SEA} = A / m_{m,loss} \tag{36}$$

where $A_{\sigma f}$ or A_{SEA} is the extinction area, expressed in square metres, of smoke per kilogram of material burned.

The relationships in Equation (36) can also be expressed as Equation (37):

$$A_{\sigma f} = \alpha_k \times V_{eff} / m_{m,loss} \text{ or } A_{SEA} = \alpha_k \times V_{eff} / m_{m,loss} \tag{37}$$

where V_{eff} is the total volume, expressed in cubic metres, of effluent.

The relationships in Equation (37) can also be expressed as Equation (38):

$$A_{\sigma f} = \alpha_k / \rho_{m,loss} \text{ or } A_{SEA} = \alpha_k / \rho_{m,loss} \tag{38}$$

A parameter known as the mass optical density (D_{MO}) is the $\log_{10}$ analogue, and usually refers to mass in grams rather than kilograms. The specific extinction areas ($A_{\sigma f}$ or A_{SEA}) can be converted to values based on $\log_e$ and kilograms as given in Equation (39):

$$A_{\sigma f} = D_{MO} \times 2{,}303 \times 1\,000 \text{ or } A_{SEA} = D_{MO} \times 2{,}303 \times 1\,000 \tag{39}$$

Various other derivations have been used in the literature. They are given in more detail in references[7],[8],[9].

6.5.4 Relationship between mass measurement and light obscuration

Both large and bench-scale test procedures tend to monitor the optical/obscurational properties of smoke. However, the mass concentration of smoke is sometimes useful (e.g. for input to field and zone computational models). A relationship between optical properties and mass concentration has been developed for post-flame generated smoke for a wide range of fuels under well-ventilated conditions[8]. Bouguer's law again is the basis, relating the ratio of the transmitted and incident intensities to the mass concentration, m_s, of the smoke, the path length, L, through the smoke, and the specific mass extinction coefficient, $\sigma_{m,\alpha}$, using Equation (40):

$$I/I_0 = \exp(-\sigma_{m\alpha}, m_s, L) \tag{40}$$

The estimated mean value for $\sigma_{m,\alpha}$was 8,7 m^2·g^{-1} with an expanded uncertainty (at the 95 % confidence interval) of 1,1 m^2·g^{-1}.

NOTE The value of 8,7 becomes 10 when corrected from He-Ne laser light to visible light[8] and it depends on the smoke produced being primarily carbonaceous soot. The value is stated to be smaller and more variable for smoke generated under smouldering or pyrolytic conditions as a result of the low light absorption of this type of smoke and variability in smoke droplet size.

Soot yields have been shown to double ± 50 % during under-ventilated burning of polymeric fuels in a small-scale apparatus[8].

7 Calculation of equivalence ratio

7.1 General

The equivalence ratio, ϕ, is defined as the actual fuel-to-air mass ratio divided by the stoichiometric fuel-to-air mass ratio, in accordance with Equation (41). In this International Standard, fuel-to-oxygen ratios are used rather than fuel-to-air ratios:

$$\phi = \frac{(m_{\text{fuel}}/m_{\text{O2.act}})}{(m_{\text{fuel}}/m_{\text{O2.stoich}})} \tag{41}$$

where

m_{fuel} is the mass, expressed in grams, of fuel;

$m_{\text{O2.act}}$ is the actual mass, expressed in grams, of oxygen available for combustion;

$m_{\text{O2.stoich}}$ is the stoichiometric mass, expressed in grams, of oxygen required for complete combustion.

Equation (41) rearranges to Equations (42) and (43):

$$\phi = (m_{\text{fuel}}/m_{\text{O2.act}}) \times (m_{\text{fuel}}/m_{\text{O2.stoich}}) \tag{42}$$

$$\phi = (m_{\text{fuel}}/m_{\text{O2.act}}) \times \Psi_{\text{O}} \tag{43}$$

where Ψ_{O} is the oxygen-to-fuel ratio for stoichiometric combustion ($m_{\text{O2.stoich}}/m_{\text{fuel}}$), also referred to as the stoichiometric oxygen demand.

Equation (44) applies for systems which measure mass loss rate:

$$\phi = (\dot{m}_{\text{m.loss}}/\dot{m}_{\text{O2.act}}) \times \Psi_{\text{O}} \tag{44}$$

where

$\dot{m}_{\text{m.loss}}$ is the material mass loss rate, expressed in grams per minute;

$\dot{m}_{\text{O2.act}}$ is the actual mass flow rate, expressed in grams per minute of oxygen available for combustion.

and where the mass flow rate of oxygen is calculated from Equation (45):

$$\dot{m}_{\text{O2.act}} = \dot{V}_{\text{air}} \times \varphi_{\text{O2}} \times 1\,331 \quad (45)$$

where

$\dot{V}_{\text{air}}$ is the volume air flow rate, expressed in cubic metres per minute;

φ_{O2} is the volume, expressed as the volume fraction, of oxygen in the air supply (0,209 5 for dry air);

1 331 is the factor to convert the volume, expressed in cubic metres per minute, of oxygen to mass, expressed in grams, of oxygen at 20 °C.

Alternatively, for systems that measure mass loss concentration, Equation (46) applies:

$$\phi = \left(\rho_{\text{m.loss}} / \rho_{\text{O2.act}}\right) \times \Psi_{\text{O}} \quad (46)$$

where

$\rho_{\text{m.loss}}$ is the material mass loss concentration, expressed in grams per cubic metre;

$\rho_{\text{O2.act}}$ is the actual mass concentration, expressed in grams per cubic metre, of oxygen available for combustion, calculated from $\varphi_{\text{O2}} \times 1\,331$.

For fuel lean mixtures (small or well-ventilated fires) $\phi < 1$.

For stoichiometric mixtures $\phi = 1$.

For fuel rich mixtures (ventilation-controlled fires) $\phi > 1$.

NOTE In all fires, ranging from real-scale test fires to the burning of test specimens in bench-scale apparatus, both spatial and temporal variations in equivalence ratio occur. Any measurement of equivalence ratio (or any other fire parameter), therefore, represents the results of some degree of averaging. This has been expressed in terms of a “global” equivalence ratio[10]. The relationships between local transient equivalence ratios and global equivalence ratio estimates depend upon the extent of averaging within the system. The concept was originally developed to represent equivalence ratio measurements in the upper layer of enclosure fires over limited time periods, but has been extended to encompass the total fuel mass loss over the whole fire duration and the total air mass passing into the combustion zone. While combustion products yields are determined by the local availability of oxygen and fuel, the needed detailed measurements are rarely performed and there is no general algorithm for combining the local yields of a gas into an overall yield for the full test specimen.

7.2 Derivation of ϕ for flow-through, steady-state experimental systems

For experimental fires where rates of air supply (oxygen) and mass loss rate (fuel) are controlled (e.g., flow-through, steady-state systems such as a moving-tube furnace), determining a global equivalence ratio is relatively straightforward, provided the specimen combusts steadily and leaves no residue, or leaves a residue of similar chemical composition to the initial specimen. Examples of tube furnace devices are described in a DIN 53436, Parts 1 to 3[11] and BS 7990[12]. Examples of the calculation in this type of apparatus are given in Table 9.

Table 9 — Example calculations of equivalence ratio for a tube furnace for a hydrocarbon polymer and a cellulosic polymer

Characteristic	Desired ventilation condition	
	Well ventilated flaming	Ventilation-controlled flaming
Apparatus settings		
Fuel mass loss rate (nominal grams per minute)	1,000	1,000
Primary air flow, (cubic metres per minute)	0,018 0	0,004 0
Primary air flow, (litres per minute)	18,0	4,0
Oxygen supply (cubic metres per minute)[a]	(0,209 5 × 0,018 0 × 1 331) = 5,019	(0,209 5 × 0,004 0 × 1 331) = 1,112
Fuel-to-oxygen mass ratio: (m_{fuel} / $m_{O2.act}$)	1,00 0/5,019 = 0,199	1,00 0/1,112 = 0,899
Stoichiometric oxygen demand, Ψ_O		
Hydrocarbon polymer[b]	3,422	3,422
Cellulosic polymer[c]	1,198	1,198
Equivalence ratio, $\phi = (m_{fuel} / m_{O2.act}) \times \Psi_O$		
Hydrocarbon polymer[b]	0,199 × 3,422 = 0,68	0,899 × 3,422 = 3,08
Cellulosic polymer[c]	0,199 × 1,198 = 0,24	0,899 × 1,198 = 1,08
Actual ventilation conditions		
Hydrocarbon polymer[b]	well-ventilated	ventilation-controlled
Cellulosic polymer[c]	well-ventilated	stoichiometric

[a] The oxygen fraction will be lower than 0,209 5 if room air is used.

[b] Hydrocarbon polymer (empirical formula, CH_2; Ψ_O = 3,422).

[c] Cellulosic polymer (empirical formula, $C_6H_{10}O_5$; Ψ_O = 1,198).

NOTE 1 The table highlights the strong influence of polymer type on the value of ϕ (and consequent ventilation condition) for a fixed air flow and mass loss rate.

NOTE 2 In tube furnaces, the mass loss of specimen is not monitored continuously (although it can be estimated from the concentrations of combustion products). Thus, in these systems one generally obtains an average global equivalence ratio for the test. Furthermore, since the oxygen is depleted at the downstream portion of the specimen, the systems do not measure a local equivalence ratio. For a uniform specimen that burns or pyrolyzes evenly, this may equate to the instantaneous value of ϕ. For a non-uniform specimen, or one that burns in stages, or one that leaves a residue that is different from the initial specimen, this might not be the case. The example above is for determining the average value.

NOTE 3 For some bench-scale non-steady state flow-through systems, where the fuel-to-air ratio varies rapidly during the test, the fire type and/or model cannot usually be described in terms of equivalence ratio. However, in a room fire test, it can be possible to characterize a portion of the test by a time-averaged global equivalence ratio, as is done in Note 2.

7.3 Derivation of ϕ for flow-through, calorimeter experimental systems

There is a family of devices in which the air flow is metered and constant and the specimen mass is monitored continuously. When the sample mass loss rate is steady, as might be experienced with a thermoplastic material or a liquid fuel, the equivalence ratio is also steady and the analysis in 7.1 applies. When the mass loss varies during a test (as in case of most furnishing or internal finish products), a time-dependent form of Equation (43) is used, where the mass loss during a time interval determines the global equivalence ratio for that interval. The implementation and accuracy of oxygen control may thus be fairly easy or difficult according to the type of fire calorimeter used.

Examples of this type of device are the fire propagation apparatus (FPA)[13],[14] used in two American standards (ASTM E 2058[15] and NFPA 287[16]) and the ventilation-controlled cone calorimeter[17].

NOTE 1 Calculation of the global equivalence ratio in the conventional ISO 5660[18] device is more complex. Some of the exhaust air flow passes the test specimen and is entrained in the fire plume; some of the exhaust air flow may be entrained downstream of the combustion zone. Thus the use of the total exhaust flow in Equation (43) will result in an artificially low value of ϕ. However, since the standard air flow always results in highly over-ventilated combustion, this device should not be used for determining toxic product yields except possibly for the smallest of real-scale fires.

NOTE 2 For some bench-scale non-steady state flow through systems, where the fuel-to-air ratio varies rapidly during the test, the fire type and/or model cannot usually be described in terms of equivalence ratio. However, in a room fire test, it can be possible to characterize a portion of the test by a time-averaged global equivalence ratio, as is done in the Note in 7.1.

7.4 Derivation of ϕ for closed chamber systems

For a closed cabinet apparatus, an instantaneous global equivalence ratio can be only calculated from the sample mass loss rate (or the cumulative concentrations of carbonaceous by-products, mainly CO_2 and CO) and the oxygen concentration in the chamber, provided the oxygen depletion is small and the air is well mixed. Generally with these types of apparatus however, the sample mass is not monitored, there is a significant decrease in oxygen concentration, and the mixing of the chamber gases may not be sufficient to create a homogeneous atmosphere during the test. Thus, determination of the instantaneous equivalence ratio is not possible, and one must determine an average global equivalence ratio based on the overall mass loss and oxygen depletion.

The operator should be aware that the yields of toxic products are likely to be highest when there is significant vitiation in the vicinity of the test specimen. Thus, the average global equivalence ratio may not be indicative of the toxicologically most important fraction of the specimen combustion.

7.5 Derivation of ϕ in room fire tests

When the air inflow and the mass of the test specimen(s) are monitored continuously, Equation (44) is used to determine a time-varying global equivalence ratio. Note, however, that all the incoming air does not necessarily approach the combustion zone. Thus, as with ISO 5660[18], the determined equivalence ratio values may not relate directly to those in a more closely controlled bench-scale device.

One approach is to calculate ϕ from Equation (46) using measurements of the total fuel and air derived from the composition of fire effluent samples (in terms of the oxides of carbon, soot, hydrocarbons and oxygen content).

8 Calculation of combustion efficiency

8.1 General

Combustion efficiency, χ, can be defined as the ratio of the heat released in a combustion reaction to the theoretical heat of complete combustion.

In a perfectly efficient combustor, the atoms in the fuel would be converted to the thermodynamically most stable by-products (carbon to carbon dioxide, hydrogen to water, nitrogen to nitrogen gas, etc.) and the heat released would equal the enthalpy of reaction. However, this rarely happens in accidental fires and the processes are less than 100 % efficient.

This is partially due to considerable variations in local fuel and oxidizer concentrations in the immediate vicinity of diffusion flames, so that combustion efficiency tends to be less than predicted by stoichiometry, even under well-ventilated (low-ϕ) conditions. Under vitiated (high-ϕ) conditions, where the rate of oxygen supply is less than the rate of fuel supply, then combustion efficiency is further reduced. Furthermore, a material may burn inefficiently because of its chemical structure, or because it is flame-retarded in some way.

Combustion efficiency is generally reported as a global value, averaged over the full burning time. (This can be misleading when considering toxicological implications, since most of the impact will result from periods when the combustion efficiency is low).

There are different (but interrelated) ways of defining combustion efficiency. It can be based on

a) the fraction of possible heat that is released,

b) the fraction of the maximum oxygen consumption that occurs,

c) the fraction of the maximum oxides of carbon that are formed.

The first of these is most important in calculating thermal hazard, the latter two in characterizing the toxicity of the fire atmosphere. The three methods of calculation are described in 8.2 to 8.4 and summarized in Table 10. Worked examples are given in Table 11.

NOTE When experimental data are used to calculate combustion efficiency values, they are subject to experimental variations, and can, therefore generate values greater than 1.

8.2 Heat release efficiency

The formula for heat release efficiency is given in Equation (47):

$$\chi = \Delta H_{\mathrm{act}}/\Delta H_{\mathrm{c}} \qquad (47)$$

where

χ is the combustion efficiency, expressed as a ratio or as a percent;

ΔH_{c} is the net heat of combustion, expressed in kilojoules per gram, and defined as the enthalpy, per unit mass of fuel consumed, generated in complete combustion with the water produced being in the gaseous state;

ΔH_{act} is the actual measured heat release, expressed in kilojoules per gram, of the combustion.

NOTE Enthalpy and heat release can be used interchangeably since the burning process is usually at constant pressure and does not perform any mechanical work.

The enthalpy (net heat) of **complete** combustion of a sample may be determined in an oxygen bomb calorimeter. The measurement of the **actual** heat release in a test apparatus is more complex. The heat released warms the ambient gases, heats some or all of the apparatus itself, and may radiate a significant fraction to the external world. Thus a true calorimetric measurement is extremely difficult and unlikely to be accurate.

Research leading to the development of the cone calorimeter showed that the heat release per mole of oxygen consumed during burning of organic materials is independent of the fuel composition (within 5 %). Thus, for systems where the total amount of oxygen is known, the numerator of the equation can be determined from oxygen concentration measurements. (Note that in a flow-through apparatus, both the flow of air/oxygen and the change in oxygen concentration must be measured. In a closed system, only the latter is needed, but it is important to take care that the final value is taken after the chamber atmosphere has equilibrated).

8.3 Oxygen consumption efficiency

8.3.1 General

This ratio, χ_{ox}, can be determined either directly from the change in oxygen concentration or indirectly from the appearance of oxygen in combustion products. Each requires knowing the empirical formula of the test sample, which might not be available, so that the measured gas data can be compared with the stoichiometric data. χ_{ox} can differ from χ because

a) as noted above, the heat release per mole of oxygen consumed during burning is a function of fuel composition, and

b) different combustion conditions may produce the same global thermal efficiency, but produce different oxygenated product yield distributions.

In doing calculations based on the empirical formula of the sample, a typical assumption is that the empirical formula of the mass lost during burning is the same as that of the original product. This will not be the case for layered products or those composed of a mixture of components. The calculation will also be inaccurate to the extent that there is a solid residue, particularly a carbonaceous residue.

8.3.2 Oxygen depletion method

This method calculates combustion efficiency by direct measurement of oxygen depletion in the fire atmosphere and calculating the mass fraction of oxygen consumed as given in Equation (48):

$$\chi_{ox.dep} = w_{O2.cons} / \Psi_O \qquad (48)$$

where

$\chi_{ox.dep}$ is the combustion efficiency ratio calculated from oxygen depletion;

$w_{O2.cons}$ is the measured mass fraction, in grams per gram, of oxygen consumed.

8.3.3 Oxygen-in-products method

8.3.3.1 General

This is an indirect method where the total amount of combined oxygen contained the major oxygen-containing combustion products (CO_2, CO and H_2O) is calculated, and the amount of oxygen contributed from the base polymer or fuel is subtracted to give a derived mass fraction of oxygen consumed

$$\chi_{ox.prod} = w_{O2.der} / \Psi_O \qquad (49)$$

where

$\chi_{ox.prod}$ is the combustion efficiency calculated from the oxygen contained in the major combustion products;

$w_{O2.der}$ is a derived mass fraction, expressed in grams per gram, of oxygen consumed;

$$w_{O2.der} = w_{Ogases} - w_{Oex.poly} \qquad (50)$$

where

w_{Ogases} is the measured mass fraction of oxygen consumed per unit mass of polymer in the form of the major oxygen-containing products ($w_{O,CO2} + w_{O,CO} + w_{O,H2O}$);

$w_{Oex.poly}$ is the mass fraction of oxygen in the burned polymer (fuel) that contributes to the oxygen-containing products.

8.3.3.2 Oxygen in CO_2, CO and H_2O (w_{Ogases})

This procedure calculates and then sums the oxygen content in the major products.

Step 1 is to calculate the yields of CO_2, CO and H_2O, in accordance with Equations (51) to (53), from the measured gas concentrations, the corresponding factors to convert from parts per million (deprecated unit) to grams per cubic metre for each gas (Table 2), and fuel mass loss concentration ($\rho_{m.loss}$):

$$Y_{CO2} = (\varphi_{CO2} \times 1{,}830 \times 10^{-3}) / \rho_{m.loss} \quad (51)$$

$$Y_{CO} = (\varphi_{CO} \times 1{,}164 \times 10^{-3}) / \rho_{m.loss} \quad (52)$$

$$Y_{H2O} = (\varphi_{H2O} \times 0{,}749 \times 10^{-3}) / \rho_{m.loss} \quad (53)$$

where

Y is the yield, expressed as a mass fraction, for each product gas;

φ is the concentration, expressed as microlitres per litre [equal to parts per million (ppm), a deprecated unit], of each product gas.

1,830, 1,164 and 0,749 are the factors to convert from microlitres per litre [equal to parts per million (ppm), a deprecated unit] to grams per cubic metre for each gas (see Table 2).

Step 2 is to calculate the amount of oxygen contained in the products as calculated from Equations (51) to (53), and sum them as given in Equations (54) to (56):

$$w_{O,CO2} = Y_{CO2} \times 32/44 \quad (54)$$

$$w_{O,CO} = Y_{CO} \times 16/28 \quad (55)$$

$$w_{O,H2O} = Y_{H2O} \times 16/18 \quad (56)$$

where

32/44 is the mass ratio of “O” in CO_2;

16/28 is the mass ratio of “O” in CO;

16/18 is the mass ratio of “O” in H_2O.

NOTE If H_2O is not measured, an assumed yield can be derived from the following combustion reactions:

$C_aH_bO_c + O \rightarrow aCO_2 + b/2H_2O$ (+ minor unburnt C-H-O products)

and $C_aH_bO_c + O \rightarrow aCO + b/2H_2O$ (+ minor unburnt C-H-O products)

Thus, for a polymer with the formula $C_aH_bO_c$, a moles CO_2 or CO are equivalent to $b/2$ moles H_2O. Therefore, 1 mole CO_2 or CO is equivalent to $b/2a$ moles H_2O, and 0.100 volume % (equal to 1 000 ppm; deprecated unit) of (CO_2 + CO) is equivalent to (0.100 × $b/2a$) volume % H_2O [equal to (1 000 × $b/2a$) ppm (deprecated unit) H_2O].

8.3.3.3 Contribution from “O” in polymer ($w_{O,ex.poly}$)

This component of the calculation takes account of “O” in the polymer and assumes its contribution to combustion is in the same proportion as the carbon conversion to CO_2 and CO in accordance with Equations (57) and (58):

$$w_{O,ex.poly} = w_{O,poly} \times \chi_{cox} \quad (57)$$

where

$w_{O,poly}$ is the actual mass fraction of oxygen in the polymer;

χ_{cox} is the generation efficiency of carbon in the fuel to oxides of carbon (see 8.2.3).

Finally, the combustion efficiency ratio can be determined as given in Equation (58):

$$\chi_{ox,prod} = \frac{(w_{O,CO2} + w_{O,CO} + w_{O,H2O}) - w_{O,poly}}{\Psi_O} \tag{58}$$

8.4 Oxides of carbon method

This method of calculation is based on the generation efficiencies of CO_2 and CO. Although not as robust theoretically as the direct and indirect oxygen consumption methods above, it may be a useful alternative under some circumstances.

The hypothesis is that the fully oxidized molecule CO_2 contributes **all** its generation efficiency to the combustion process whilst the partially oxidized molecule CO only contributes **half** its generation efficiency.

$$\chi_{cox} = \eta_{CO2} + \eta_{CO} / 2 \tag{59}$$

where η is the generation efficiency yield, expressed as a fraction, for each oxide of carbon.

NOTE Efficiency yields can be calculated using the recovery equations in 6.3

Table 10 — Summary of the three methods for calculating combustion efficiency for polymers[a]

Parameters determined			Method of derivation
Type	**Symbol**	**Units**	
Stoichiometric O_2 demand	Ψ_O	mass fraction (grams per gram)	stoichiometric oxygen-to-fuel mass ratio
Stoichiometric yield CO_2	Ψ_{CO2}	mass fraction (grams per gram)	from %C in polymer × 3,67 × 10^{-2}, or from empirical formula
Stoichiometric yield CO	Ψ_{CO}	mass fraction (grams per gram)	from %C in polymer × 2,33 × 10^{-2}, or from empirical formula
Stoichiometric yield H_2O	Ψ_{H2O}	mass fraction (grams per gram)	from %H in polymer × 9,00 × 10^{-2}, or from empirical formula
Oxygen in polymer	—	mass fraction (grams per gram)	from %O in polymer × 10^{-2} (converts mass % to fraction) from atoms O in polymer × 16 / molar mass polymer
Mass loss concentration	$\rho_{m.loss}$	grams per cubic metre	derived from mass loss and air flow rate or volume
Oxygen consumption method, $w_{O,2.cons}$			
O_2 in fire atmosphere	—	volume fraction	measured concentration, in percent or as a fraction
O_2 used from atmosphere	—	grams per cubic metre	(inflow O_2 volume fraction − measured volume fraction) × 1 331
O_2 consumed by polymer	—	mass fraction (grams per gram)	O_2 used (grams per cubic metre) / mass loss concentration (grams per cubic metre)
Combustion efficiency	$\chi_{ox.dep}$	dimensionless	O_2 consumed (grams per gram) / stoichiometric O_2 demand (grams per gram)

Table 10 (*continued*)

Parameters determined			Method of derivation
Type	Symbol	Units	
Oxygen in products method, $w_{O,2.der}$			
CO_2 in test		(microlitres per litre)[b]	measured concentration (microlitres per litre)
CO_2 yield	Y_{CO2}	mass fraction (grams per gram polymer)	CO_2 (microlitres per litre)[b] × 1,831 × 10^{-3} / mass loss concentration (grams per cubic metre)[b]
CO in test		(microlitres per litre)[b]	measured concentration (microlitres per litre)
CO yield	Y_{CO}	mass fraction (grams per gram polymer)	CO (microlitres per litre)[b] × 1,164 × 10^{-3} / mass loss concentration (grams per cubic metre)
Assumed H_2O in test		(microlitres per litre)[b]	[CO_2 (microlitres per litre)[b] + CO (microlitres per litre)[b]] × $b/2a$
Assumed H_2O yield	Y_{H2O}	mass fraction (grams per gram polymer)	H_2O (microlitres per litre)[b] × 0,749 × 10^{-3} / mass loss concentration (grams per cubic metre)
Oxygen in CO_2	$w_{O,CO2}$	grams per gram polymer	Y_{CO2} × 32,00 / 44,01 Equation (60)
Oxygen in CO	$w_{O,CO}$	grams per gram polymer	Y_{CO} × 16,00 / 28,01 Equation (61)
Oxygen in H_2O	$w_{O,H2O}$	derived grams per gram polymer	Y_{H2O} × 16,00 / 18,01 Equation (62)
Oxygen in $CO_x + H_2O$	—	—	Σ Equations (60)+(61)+(62)
Efficiency C → CO_x	χ_{cox}	—	(efficiency CO_2 yield) + (efficiency CO yield)
Oxygen contribution from polymer	—	mass fraction	"O" in base polymer (grams per gram) × efficiency C → CO_x
Oxygen consumed from air	—	mass fraction	("O" in $CO_x + H_2O$) − ("O" contribution from polymer)
Combustion efficiency	$\chi_{ox.prod}$	—	oxygen from air (grams per gram) / stoichiometric demand (grams per gram)
Oxides of carbon method			
Efficiency CO_2 yield	—	η_{CO2}	CO_2 yield (grams per gram) / stoichiometric CO_2 yield (grams per gram)
Efficiency CO yield	—	η_{CO}	CO yield (grams per gram) / stoichiometric CO yield (grams per gram)
Combustion efficiency	—	χ_{cox}	efficiency CO_2 yield + (efficiency CO yield) / 2

[a] The polymer has the general formula $C_aH_bO_cX_d$ and a molar mass polymer, M_{poly}, expressed in grams per mole, calculated from the expression $(a \times 12) + (b \times 1) + (c \times 16) + (d \times m_{A,E})$.

[b] Microlitres per litre = parts per million (ppm), a deprecated unit.

Table 11 — Examples of combustion efficiency calculations by the three methods[11],[19],a

Characteristic			Material					
			Untreated cotton fabric		**FR cotton fabric (Proban)**		**Untreated wool yarn**	
Empirical formula:			$C H_{1,67} O_{0,83}$		$C H_{1,67} O_{0,83}$		$CH_{1,62} O_{0,38} N_{0,27} S_{0,03}$	
Molar mass polymer	M_{poly}	grams per mole	26,95		26,95		24,44	
Stoichiometric O_2 demand	Ψ_{O}	grams per gram	1,197	—	1,197	—	1,591	—
Stoichiometric yield CO_2	Ψ_{CO2}	grams per gram	1,633	—	1,633	—	1,800	—
Stoichiometric yield CO	Ψ_{CO}	grams per gram	1,039	—	1,039	—	1,146	—
Stoichiometric yield H_2O	Ψ_{H2O}	grams per gram	0,558	—	0,558	—	0,597	—
Oxygen in polymer	—	mass fraction (grams per gram)	0,493	—	0,493	—	0,249	—
Test no. [19]			T156	T66	T18	T68	T238	T259
Conditions: (°C, fl/nf)			400 nf	700 fl	400 nf	700 nf	400 nf	700 fl
Mass loss concentration	$\rho_{m.loss}$	grams per cubic metre	18,7	19,0	14,6	16,9	10,7	16,2
Oxygen consumption method, $w_{O,2.cons}$								
O_2 volume fraction in test atmosphere	—	—	0,199	0,191	0,201	0,197	0,208	0,196
O_2 used from atmosphere	—	grams per cubic metre	13,3	23,9	10,6	16,0	1,33	17,3
O_2 consumed by polymer	—	mass fraction	0,711	1,260	0,729	0,944	0,124	1,067
Combustion efficiency	$\chi_{ox.dep}$	—	0,594	1,052	0,609	0,789	0,078	0,671

Table 11 (*continued*)

Characteristic			Material					
			Untreated cotton fabric		FR cotton fabric (Proban)		Untreated wool yarn	
Oxygen in products method								
CO_2 in test	—	(microlitres per litre)[b]	8 170	17 600	6 400	8 000	1 550	10 400
CO_2 yield	Y_{CO2}	grams per gram polymer	0,800	1,696	0,803	0,866	0,265	1,175
CO in test	—	(microlitres per litre)[b]	3 650	625	2 825	8 750	265	4 500
CO yield	Y_{CO}	grams per gram polymer	0,227	0,038	0,225	0,603	0,029	0,323
Assumed H_2O in test	—	(microlitres per litre)[b]	9 870	15 218	7 703	13 986	1 470	12 069
Assumed H_2O yield	Y_{H2O}	grams per gram polymer	0,395	0,600	0,395	0,620	0,103	0,558
Oxygen in CO_2	$w_{O,CO2}$	grams per gram polymer	0,582	1,233	0,584	0,630	0,193	0,854
Oxygen in CO	$w_{O,CO}$	grams per gram polymer	0,130	0,022	0,129	0,344	0,016	0,185
Oxygen in H_2O	$w_{O,H2O}$	derived grams per gram polymer	0,351	0,533	0,351	0,551	0,092	0,496
Oxygen in $CO_x + H_2O$	—	grams per gram polymer	1,063	1,788	1,064	1,525	0,301	1,535
Efficiency $C \rightarrow CO_x$	χ_{cox}	—	70,9	107,7	70,9	111,2	17,3	93,5
Oxygen contribution from polymer	—	mass fraction	0,350	0,531	0,349	0,547	0,043	0,233
Oxygen consumed from air	—	mass fraction	0,720	1,267	0,714	0,978	0,258	1,303
Combustion efficiency	$\chi_{ox.prod}$	—	0,599	1,057	0,600	0,821	0,162	0,819
Oxides of carbon method								
Efficiency CO_2 yield	η_{CO2}	—	0,48,8	1,038	0,492	0,530	0,147	0,653
Efficiency CO yield	η_{CO}	—	0,219	0,037	0,217	0,290	0,025	0,282
Combustion efficiency	χ_{cox}	—	0,588	1,057	0,601	0,820	0,160	0,794

fl flaming

nf non-flaming

a The experimental apparatus is the tube furnace (flow through, steady state system)[11].

b Microlitres per litre = parts per million (ppm), a deprecated unit.

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