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

Production et analyse des gaz toxiques dans le feu — Calcul des taux de production des espèces, des rapports d'équivalence et de l'efficacité de combustion dans les feux expérimentaux

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

This second edition cancels and replaces the first edition (ISO 19703:2005), clauses of which have been editorially revised.

Introduction

It is the view of committees ISO TC 92/SC 3, ISO TC 92/SC 4, and IEC TC 89 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. It is intended that the characterization of

a) the apparatus used to generate the effluent, and

b) the effluent itself

be in a form usable in such a fire safety assessment.

As described in ISO 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 which estimates the rate of fuel consumption, transport and dilution of the effluent throughout the building as the fire evolves.

For the engineering analysis to produce accurate results, it is preferred that the yield data 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 are accurate is to operate it under combustion conditions similar to those expected when the real product burns. As described in ISO 19706, 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 can be difficulty or alternative ways of obtaining a proper test specimen. That is not the subject of this International Standard, 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 can 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.

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 13943, *Fire safety — Vocabulary*

3 Terms and definitions

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

3.1
mass concentration of gas
mass of gas per unit volume

NOTE 1 The mass concentration of a gas can be derived directly 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.

3.2
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.

3.3
molar mass

mass of 1 mole

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

3.4
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

3.5
relative atomic mass

average mass of one atom of an element divided by one twelfth of the mass of one atom of carbon (isotope ^{12}C)

3.6
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.

3.7
uncertainty of measurement

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

NOTE The description and propagation of uncertainty in measurements are described in ISO/IEC Guide 98-3[24].

3.8
expanded uncertainty

quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

NOTE Adapted from ISO/IEC Guide 98-3:2008, 2.3.5.

4 Symbols and units

Table 1 — Symbols

Symbol	Quantity	Typical unit
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 ($\lg_{10}$ analogue of A_{SEA})	cubic metres per gram or cubic metres per kilogram
$F_{\mathrm{R,E}}$	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 of combustion or enthalpy generated in complete combustion	kilojoules per gram
I/I_{o}	fraction of light transmitted through smoke	dimensionless
L	is the length of the light path through the smoke	metre
$m_{\mathrm{A,E}}$	relative atomic mass of the element E	dimensionless
m_{E}	mass fraction of element E in the material	dimensionless
$m_{\mathrm{E,per}}$	mass of element E in the material	percent
m_{fuel}	mass of fuel	gram
m_{gas}	total mass of the gas of interest	gram
$m_{\mathrm{m,loss}}$	total mass loss of material	gram
$\dot{m}_{\mathrm{m,loss}}$	material mass loss rate	grams per minute
$m_{\mathrm{O_2,act}}$	actual mass of oxygen available for combustion	gram
$\dot{m}_{\mathrm{O_2,act}}$	actual mass flow of oxygen available for combustion	grams per minute
$m_{\mathrm{O_2,stoich}}$	stoichiometric mass of oxygen required for complete combustion	gram
m_{part}	total mass of particles	gram
m_{s}	mass concentration of smoke - Reference [8]	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 one molecule of gas	dimensionless
$n_{\mathrm{E,poly}}$	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	cubic metre
$\dot{V}_{\mathrm{air}}$	volume air flow	cubic metres per minute
$w_{\mathrm{O_2,cons}}$	measured mass fraction of oxygen consumed per unit mass of fuel	dimensionless
$w_{\mathrm{O_2,der}}$	derived mass fraction of oxygen consumed per unit mass of fuel	dimensionless
$w_{\mathrm{Oex,poly}}$	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 ($w_{\mathrm{O,CO_2}} + w_{\mathrm{O,CO}} + w_{\mathrm{O,H_2O}}$)	dimensionless
$w_{\mathrm{O,poly}}$	mass fraction of oxygen in the polymer	dimensionless
Y_{gas}	measured mass yield of gas of interest	dimensionless

Table 1 (*continued*)

Symbol	Quantity	Typical unit
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_{O_2}	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 fraction in percent, [parts per million (ppm) deprecated]
φ_{O_2}	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
ρ_{part}	mass concentration of the smoke particles	grams per cubic metre
$\sigma_{\text{m},\alpha}$	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 International Standard, the uncertainty or error associated with each component shall be taken into account and they shall be combined 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 are uncertainties relating to physically measured parameters (e.g. mass loss and gas concentrations).

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):

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

In other words, evaluate the error caused by each of the individual measurements, 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, it can be neglected.

5.1.2 Significant figures and rounding off

When recording and reporting data, significant figures should be handled 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. 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 can 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 and closed chamber system). Refer to the appropriate standard or other reference relating to the procedure.

5.3.2 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 shall be 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 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 intended to allow another person to 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 minute) 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 should be specified in the test protocol.

5.4.2 Measured data and observations

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

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);

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):

$$Y_{\text{gas}} = \frac{\rho_{\text{gas}}}{\rho_{\text{m,loss}}} \tag{2}$$

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 by 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 that the gases are uniformly dispersed in a certain volume and 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 depends 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 can be calculated.

NOTE 3 In setting up these calculations, uncertainties relating to lost sample mass, fluctuations in the measured concentration, etc. occur.

The uncertainty should be monitored. The calculated yield should take account of and combine these, enabling a sound basis for comparing yields under different combustion conditions, comparing yields from different materials and so on.

Whilst concentrations of the specific gas are most often measured in volume units, the mass loss from a solid are almost always in mass units, since the molar mass of the effluent is difficult to determine. Equations (4) and (5) show how to convert the volume concentration 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 the standard temperature, expressed in Kelvins;
101,3	is the standard pressure, expressed in kilopascals;
22,414	is the volume, expressed in litres, 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):

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

$$Y_{\text{CO}} = 1{,}456/25 = 0{,}058\,2 \tag{7}$$

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 relative atomic mass, molar mass and gas concentration conversion factors for the major fire gases are listed in Tables 2 and 3.

Table 2 — Relative atomic mass of key fire gas elements[2]

Element	Symbol	Relative 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] Relative atomic mass values rounded to five significant figures.

Table 3 — 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)	
			To convert µl/l[b] to $g \cdot m^{-3}$, multiply by:	To convert $g \cdot m^{-3}$ to µl/l[b], multiply by:
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].	

NOTE Example calculation:

$0,100\ 0$ volume % CO = $0,100\ 0 \times 1,164$ x10 = $1,164\ g \cdot m^{-3}$.

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

[b] Conversion factors: µl/l = volume % × 10^{4}

µl/l = volume fraction × 10^{6}

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

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

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.

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):

$$\Psi_{gas} = m_E \times \frac{M_{gas}}{n_E \times m_{A,E}} \tag{8}$$

where

m_E is the mass fraction of element E in the material;

n_E is the number of atoms of element E in one molecule of the gas;

$m_{A,E}$ is the relative atomic mass of the element E.

or

$$\Psi_{gas} = m_{E,per} \times \frac{M_{gas} \times 10^{-2}}{n_E \times m_{A,E}} \tag{9}$$

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 given by Equation (10):

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

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 relative atomic mass, expressed in grams, of carbon.

Factors for calculating notional gas yields from the elemental composition and derived from the term $\frac{M_{gas} \times 10^{-2}}{n_E \times m_{A,E}}$ in Equation (9), are given in Table 4.

Table 4 — Factors for calculating notional gas yields from the elemental composition of material

Gas or vapour		Element E considered in base material[a]	Factor[b]
Formula	Molar mass g·mol-1		
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] Percent composition of element E in material ($m_{\mathrm{E,per}}$) used to calculate Ψ_{gas} [see Equation (9)].

[b] Factor for each gas derived from the $\frac{M_{\mathrm{gas}} \times 10^{-2}}{n_{\mathrm{E}} \times m_{\mathrm{A,E}}}$ term in Equation (9) and rounded to four significant figures.

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):

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

where

$n_{\mathrm{E,poly}}$ is the number of atoms of element E in the empirical formula;

M_{poly} is the molar mass, expressed in grams, of the empirical formula.

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

$$\Psi_{CO_2} = \frac{3}{1} \times \frac{44{,}01}{42{,}03} = 3{,}142 \qquad (12)$$

where

Ψ_{CO_2} 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 is determined by the least prevalent element (other than oxygen). Thus, the notional yield of HCN can be most often determined by the nitrogen content of the fuel. However, for a product gas like formaldehyde, it can be either the carbon or hydrogen fraction that provides the criterion, depending on the fuel composition.

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):

$$F_{R,E} = Y_{gas} / \Psi_{gas} \qquad (13)$$

where

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

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

$F_{R,E}$ 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 fuels containing C, H, O, for complete combustion to carbon dioxide and water

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

$$C_aH_bO_c + zO_2 \rightarrow aCO_2 + b/2\ H_2O \qquad (14)$$

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 one mole of $C_aH_bO_c$;

a is the number of atoms of carbon in $C_aH_bO_c$;

b is the number of atoms of hydrogen in $C_aH_bO_c$;

c is the number of atoms of oxygen in $C_aH_bO_c$.

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

$$\Psi_{\text{O}} = \frac{z \times 32{,}00}{M_{\text{poly}}} \tag{16}$$

where

Ψ_{O} is the stoichiometric oxygen demand, expressed in grams per gram of 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 by Equations (17) and (18):

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

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

where

1,0 is the number of atoms of carbon in $C_{1,0}H_{1,6}O_{0,4}$;

1,6 is the number of atoms of hydrogen in $C_{1,0}H_{1,6}O_{0,4}$;

0,4 is the number of atoms of oxygen in $C_{1,0}H_{1,6}O_{0,4}$;

1,20 is the (stoichiometric) number of moles of O_2 required for complete combustion of one mole of $C_{1,0}H_{1,6}O_{0,4}$;

1,918 is the calculated stoichiometric oxygen demand, expressed in grams of oxygen 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 given by Equation (19):

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

where

z is the (stoichiometric) number of moles of O_2 required for complete combustion of one mole of $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

a is the number of atoms of carbon in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

b is the number of atoms of hydrogen in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

c is the number of atoms of oxygen in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

d is the number of atoms of nitrogen in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

e is the number of atoms of chlorine in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

f is the number of atoms of bromine in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

g is the number of atoms of fluorine in $C_aH_bO_cN_dCl_eBr_fF_gS_h$;

h is the number of atoms of sulphur in $C_aH_bO_cN_dCl_eBr_fF_gS_h$.

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 by Equation (21):

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

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 one mole of $C_aH_bCl_e$;

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

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

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·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 by Equation (24):

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

where

ΔH_c	is the net heat or enthalpy per unit mass of fuel consumed, generated in complete combustion. It assumes that any water produced is in the gaseous state;

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

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

where

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 of oxygen per gram of polystyrene.

NOTE From its chemical composition, Ψ_O for polystyrene is 3,07 g·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):

$$\Psi_{O,poly} = (m_{C,per} \times 0{,}038\,7) - 0{,}339\,9 \tag{26}$$

where

$m_{C,per}$	is the mass fraction, expressed as a percentage, of carbon in the material;
0,038 7 and 0,339 9	are empirically-derived mathematical coefficients.

EXAMPLE The calculation for polymethyl methacrylate is given by Equation (27):

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

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·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 5.

Three methods for calculating stoichiometric oxygen demand for selected polymers are compared in Table 6.

Notional gas yields and stoichiometric oxygen demand derived for a number of common polymers are listed in Tables 7, 8 and 9.

Table 5 — 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	$(12 \times a) + (1 \times b) + (16 \times c) + (m_{A,X} \times d)^a$	$(12 \times 12) + (1 \times 22) + (16 \times 2) + (14 \times 2) = 226$ (= 18,83 relative to each C atom)
Notional yield CO_2 Ψ_{CO_2}, 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_{H_2O}, 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] $m_{A,X}$ is the relative atomic mass, expressed in grams, of the element X.

[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 is converted to nitrogen products containing hydrogen or oxygen. The error is considered to be small.

Table 6 — Examples of stoichiometric oxygen demand derived by three methods

Generic polymer type	Empirical formula	ΔH_{c}[abc] kJ·g^{-1}	Carbon content of polymer %	Stoichiometric oxygen demand of polymer, $\Psi_{\text{O,poly}}$ 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] and [6]; see Equation (26) where $\Psi_{\text{O,poly}} = (m_{\text{C,per}} \times 0{,}038\,7) - 0{,}339\,9$ and $R^2 = 0{,}933$.

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

Material	Empirical formula	C	Ψ_O[a]	Notional gas yields[b]	
		%	g·g^{-1}	Ψ_{CO_2} g·g^{-1}	Ψ_{CO} g·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
Polymethylmethacrylate	$CH_{1,6}O_{0,40}$	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→48,00/14,03;

$\Psi_O = 3,421$ g·g^{-1}.

EXAMPLE 2 Stoichiometric oxygen demand for complete combustion of polyester:

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

16,92 g + 39,70 g→39,70/16,92;

$\Psi_O = 2,346$ g·g^{-1}.

[b] Notional gas yields, expressed in grams per gram: $\Psi_{CO_2} = \%C \times 3,67 \times 10^{-2}$; $\Psi_{CO} = \%C \times 2,33 \times 10^{-2}$.

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

Table 8 — 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]	Notional gas yields[d]			
		%	%	$g \cdot g^{-1}$	Ψ_{CO_2} $g \cdot g^{-1}$	Ψ_{CO} $g \cdot g^{-1}$	Ψ_{HCN} $g \cdot g^{-1}$	Ψ_{NO_2} $g \cdot g^{-1}$
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 this table are examples only and not necessarily characteristic of the whole family of polymers.

[b] Stoichiometric oxygen demand, $\Psi_{O,}$ (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:

$\Psi_{CO_2} = \%C \times 3{,}67 \times 10^{-2}$;

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

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

$\Psi_{NO_2} = \%N \times 3{,}29 \times 10^{-2}$.

Table 9 — 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_{CO_2} $g \cdot g^{-1}$	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 fluoroethylene (PTFE)	CF_2	24,0	—	75	0,64[d] 0,32[e]	0,880	0,560	—	0,790

[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: $\Psi_{CO_2} = \%C \times 3{,}67 \times 10^{-2}$;

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

$\Psi_{HCl} = \%Cl \times 1{,}03 \times 10^{-2}$;

$\Psi_{HF} = \%F \times 1{,}05 \times 10^{-2}$ (assumes H_2O in the reaction as in table footnote e).

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 by Equation (28):

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

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

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

$$Y_{\mathrm{part}} = \frac{m_{\mathrm{part}}}{m_{\mathrm{m,loss}}} \tag{29}$$

where

m_{part}	is the total mass, expressed in grams, of particles;
$m_{\mathrm{m,loss}}$	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 describes the attenuation of monochromatic light by smoke:

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

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

where

α_{k}	is the light extinction coefficient, expressed as inverse metres;
I_{o}	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 given by Equations (32) and (33):

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

$$\alpha \times 2{,}303 = \alpha_{\mathrm{k}} \tag{33}$$

where

α	is the linear decadic absorption coefficient (optical density), expressed as inverse metres;
2,303	is the base-10 logarithm conversion factor that gives 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 by Equations (34) and (35):

$$A = \alpha_\mathrm{k} \times V \tag{34}$$

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

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

where $A_{\sigma\mathrm{f}}$ 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):

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

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):

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

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 ($A_{\sigma\mathrm{f}}$ or A_SEA) can be converted to values based on $\log_\mathrm{e}$ and kilograms as given by Equation (39):

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

Various other derivations are used in the literature. They are given in more detail in References [7], [8] and [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]. Again, Bouguer's law 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, $\sigma_{\mathrm{m},\alpha}$, using Equation (40):

$$I/I_\mathrm{o} = \exp(-\sigma_{\mathrm{m},\alpha} \times m_\mathrm{s} \times L) \tag{40}$$

The estimated mean value for $\sigma_{\mathrm{m},\alpha}$ is 8,7 $\mathrm{m}^2 \cdot \mathrm{g}^{-1}$ with an expanded uncertainty[24] (at the 95 % confidence interval) of 1,1 $\mathrm{m}^2 \cdot \mathrm{g}^{-1}$.

NOTE The value of 8,7 $m^2 \cdot g^{-1}$ becomes 10 $m^2 \cdot g^{-1}$ 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 obtained during under-ventilated burning of polymeric fuels in a small-scale apparatus have been shown to be higher than those under well-ventilated conditions by a factor of approximately 2 ± 0,5[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:

$$\phi = \frac{\left(m_{\text{fuel}} / m_{\text{O}_2,\text{act}}\right)}{\left(m_{\text{fuel}} / m_{\text{O}_2,\text{stoich}}\right)} \tag{41}$$

where

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

$m_{\text{O}_2,\text{act}}$ is the actual mass, expressed in grams, of oxygen available for combustion;

$m_{\text{O}_2,\text{stoich}}$ is the stoichiometric mass, expressed in grams, of oxygen required for complete combustion.

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

$$\phi = \left(m_{\text{fuel}} / m_{\text{O}_2,\text{act}}\right) \times \left(m_{\text{O}_2,\text{stoich}} / m_{\text{fuel}}\right) \tag{42}$$

$$\phi = \left(m_{\text{fuel}} / m_{\text{O}_2,\text{act}}\right) \times \Psi_{\text{O}} \tag{43}$$

where Ψ_{O} is the oxygen-to-fuel ratio for stoichiometric combustion ($m_{\text{O}_2,\text{stoich}}/m_{\text{fuel}}$), also referred to as the stoichiometric oxygen demand.

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

$$\phi = \left(\dot{m}_{\text{m,loss}} / \dot{m}_{\text{O}_2,\text{act}}\right) \times \Psi_{\text{O}} \tag{44}$$

where

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

$\dot{m}_{\text{O}_2,\text{act}}$ is the actual mass flow, expressed in grams per minute, of oxygen available for combustion.

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

$$\dot{m}_{\text{O}_2,\text{act}} = \dot{V}_{\text{air}} \times \varphi_{\text{O}_2} \times 1\,331 \tag{45}$$

where

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

φ_{O_2} 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, of oxygen to mass, expressed in grams, of oxygen at 20 °C.

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

$$\phi = \left(\rho_{\text{m,loss}} / \rho_{O_2,\text{act}}\right) \times \Psi_O \tag{46}$$

where

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

$\rho_{O_2,\text{act}}$ is the actual mass concentration, expressed in grams per cubic metre, of oxygen available for combustion, calculated from $\varphi_{O_2} \times 1\ 331$.

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 necessary 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 and 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 DIN 53436-1[11], DIN 53436-2[12], DIN 53436-3[13], BS 7990[14] and ISO/TS 19700[25]. Examples of the calculation in this type of apparatus are given in Table 10.

Table 10 — 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 setting		
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: $(m_{\text{fuel}}/m_{\text{O}_2,\text{act}})$	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, $\phi = (m_{\text{fuel}}/m_{\text{O}_2,\text{act}}) \times \Psi_{\text{O}}$		
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 condition		
Hydrocarbon polymer[b]	well-ventilated	ventilation-controlled
Cellulosic polymer[c]	well-ventilated	stoichiometric

NOTE 1 This 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 can 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 described in Note 2 of this table.

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

[b] Hydrocarbon polymer (empirical formula, CH_2; $\Psi_{\text{O}} = 3{,}422$).

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

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 can be experienced with a thermoplastic material or liquid fuel, the equivalence ratio is also steady and the analysis in 7.1 applies. When the mass loss varies during a test (as is the 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 can 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)[15][16] used in two American standards (ASTM E 2058[17] and NFPA 287[18]) and the ventilation-controlled cone calorimeter[19].

NOTE 1 Calculation of the global equivalence ratio in the conventional ISO 5660-1[20] 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 can be entrained downstream of the combustion zone. Thus, the use of the total exhaust flow in Equation (43) results in an artificially low value of ϕ. However, since the standard air flow always results in highly over-ventilated combustion, it is not intended that this device 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 described 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 only be 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 it is possible for the mixing of the chamber gases to not be sufficient to create a homogeneous atmosphere during the test. Thus, determination of the instantaneous equivalence ratio is not possible and one shall 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 change when significant vitiation occurs in the vicinity of the flames above the test specimen, with large increases in several important toxic products. Thus, it is possible for the average global equivalence ratio to 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. However, all of the incoming air does not necessarily approach the combustion zone. Thus, as with ISO 5660-1[20], it is possible for the determined equivalence ratio values to 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, such 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 can 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 results 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, or

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 methods for b) and c) summarized in Table 11. Worked examples are given in Table 12.

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 by Equation (47):

$$\chi = \Delta H_{\text{act}}/\Delta H_{\text{c}} \tag{47}$$

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 can 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 can 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 during burning is approximately 13,1 kilojoules per gram of oxygen consumed (±5%) for most organic materials. Thus, for systems where the total amount of oxygen is known, ΔH_{c} can be determined from oxygen concentration measurements. (In a flow-through apparatus, both the flow of air/oxygen and the change in oxygen concentration shall 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_{O_2}, 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, such that the measured gas data can be compared with the stoichiometric data. χ_{O_2} 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 can produce the same global thermal efficiency, but produce different oxygenated product yield distributions.

In carrying out 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 is not the case for layered products or those composed of a mixture of components. The calculation also tends to 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 by Equation (48):

$$\chi_{O_2} = w_{O_2,\text{cons}} / \Psi_O \tag{48}$$

where

χ_{O_2} is the combustion efficiency ratio calculated from oxygen depletion;

$w_{O_2,\text{cons}}$ is the measured mass fraction of oxygen consumed per unit mass of fuel;

Ψ_O is the stoichiometric mass fraction (i.e. stoichiometric mass oxygen-to-fuel ratio or stoichiometric oxygen demand).

8.3.3 Oxygen-in-products method

8.3.3.1 General

This is an indirect method where the total amount of combined oxygen in 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:

$$\chi_{\text{prod}} = w_{O_2,\text{der}} / \Psi_O \tag{49}$$

where

χ_{prod} is the combustion efficiency calculated from the oxygen contained in the major combustion products;

$w_{O_2,\text{der}}$ is a derived mass fraction of oxygen consumed per unit mass of fuel:

$$w_{O_2,\text{der}} = w_{\text{Ogases}} - w_{\text{Oex,poly}} \tag{50}$$

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 ($w_{\mathrm{O,CO_2}} + w_{\mathrm{O,CO}} + w_{\mathrm{O,H_2O}}$);

$w_{\mathrm{Oex,poly}}$ 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 microlitres per litre to grams per cubic metre for each gas (Table 3) and fuel mass loss concentration ($\rho_{\mathrm{m,loss}}$):

$$Y_{\mathrm{CO_2}} = (\varphi_{\mathrm{CO_2}} \times 1{,}830 \times 10^{-3}\ \mathrm{g \cdot m^{-3}})/\rho_{\mathrm{m,loss}} \tag{51}$$

$$Y_{\mathrm{CO}} = (\varphi_{\mathrm{CO}} \times 1{,}164 \times 10^{-3}\ \mathrm{g \cdot m^{-3}})/\rho_{\mathrm{m,loss}} \tag{52}$$

$$Y_{\mathrm{H_2O}} = (\varphi_{\mathrm{H_2O}} \times 0{,}749 \times 10^{-3}\ \mathrm{g \cdot m^{-3}})/\rho_{\mathrm{m,loss}} \tag{53}$$

where

Y	is the yield, expressed as a mass fraction, for each product gas;
φ	is the concentration, expressed as microlitres per litre, of each product gas.
1,830, 1,164 and 0,749	are the factors to convert from microlitres per litre to grams per cubic metre for each gas (see Table 3).

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 by Equations (54) to (56):

$$w_{\mathrm{O,CO_2}} = Y_{\mathrm{CO_2}} \times 32/44 \tag{54}$$

$$w_{\mathrm{O,CO}} = Y_{\mathrm{CO}} \times 16/28 \tag{55}$$

$$w_{\mathrm{O,H_2O}} = Y_{\mathrm{H_2O}} \times 16/18 \tag{56}$$

where

32/44	is the mass ratio of oxygen in CO_2;
16/28	is the mass ratio of oxygen in CO;
16/18	is the mass ratio of oxygen in H_2O.

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

$$C_aH_bO_c + O \rightarrow aCO_2 + b/2H_2O \quad \text{and} \quad C_aH_bO_c + O \rightarrow aCO + b/2H_2O.$$

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 µl/l) of (CO_2 + CO) is equivalent to (0.100 × $b/2a$) volume % H_2O [equal to (1 000 × $b/2a$) µl/l H_2O].

8.3.3.3 Contribution from oxygen in polymer ($w_{\text{Oex,poly}}$)

This component of the calculation takes account of oxygen 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):

$$w_{\text{Oex,poly}} = w_{\text{O,poly}} \times \chi_{\text{cox}} \tag{57}$$

where

$w_{\text{O,poly}}$ 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 8.4).

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

$$\chi_{\text{prod}} = \frac{(w_{\text{O,CO}_2} + w_{\text{O,CO}} + w_{\text{O,H}_2\text{O}}) - w_{\text{O,poly}}}{\Psi_{\text{O}}} \tag{58}$$

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 can 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.

$$\chi_{\text{cox}} = \eta_{\text{CO}_2} + \eta_{\text{CO}}/2 \tag{59}$$

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 11 — Summary of three methods for calculating combustion efficiency for polymers[a]

Parameters determined			Method of derivation
Type	Symbol	Unit	
Stoichiometric O_2 demand	Ψ_{O}	mass fraction (grams per gram)	stoichiometric oxygen-to-fuel mass ratio
Stoichiometric yield CO_2	Ψ_{CO_2}	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	$\Psi_{\text{H}_2\text{O}}$	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	$\rho_{\text{m,loss}}$	grams per cubic metre	derived from mass loss and air flow or volume

Table 11 (*continued*)

Parameters determined			Method of derivation
Type	**Symbol**	**Unit**	
Oxygen depletion 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	χ_{O_2}	dimensionless	O_2 consumed (grams per gram)/stoichimetric O_2 demand (grams per gram)
Oxygen in products method, $w_{O_2,der}$			
CO_2 in test		microlitres per litre	measured concentration (microlitres per litre)
CO_2 yield	Y_{CO_2}	mass fraction (grams per gram polymer)	CO_2 (microlitres per litre) × 1,831 × 10^{-3}/mass loss concentration (grams per cubic metre)
CO in test		microlitres per litre	measured concentration (microlitres per litre)
CO yield	Y_{CO}	mass fraction (grams per gram polymer)	CO (microlitres per litre) × 1,164 × 10^{-3}/mass loss concentration (grams per cubic metre)
Assumed H_2O in test		microlitres per litre	[CO_2 (microlitres per litre) + CO (microlitres per litre)] × $b/2a$
Assumed H_2O yield	Y_{H_2O}	mass fraction (grams per gram polymer)	H_2O (microlitres per litre) × 0,749 × 10^{-3}/mass loss concentration (grams per cubic metre)
Oxygen in CO_2	w_{O,CO_2}	grams per gram polymer	$Y_{CO_2} \times 32,00/44,01$ Equation (54)
Oxygen in CO	$w_{O,CO}$	grams per gram polymer	$Y_{CO} \times 16,00/28,01$ Equation (55)
Oxygen in H_2O	w_{O,H_2O}	derived grams per gram polymer	$Y_{H_2O} \times 16,00/18,01$ Equation (56)
Oxygen in $CO_x + H_2O$	—	—	Σ Equations (54)+(55)+(56)
Efficiency C → CO_x	χ_{cox}	—	(efficiency CO_2 yield) + (efficiency CO yield)
Oxygen contribution from polymer	—	mass fraction	oxygen in base polymer (grams per gram) × efficiency C → CO_x
Oxygen consumed from air	—	mass fraction	(oxygen in $CO_x + H_2O$) − (contribution of oxygen from polymer)
Combustion efficiency	χ_{prod}	—	oxygen from air (grams per gram)/stoichiometric demand (grams per gram)
Oxides of carbon method			
Efficiency CO_2 yield	η_{CO_2}	—	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 $(a \times 12) + (b \times 1) + (c \times 16) + (d \times m_{A,X})$.

Table 12 — Examples of combustion efficiency calculations by three methods[11][12][13][21][a]

Characteristic			**Material**					
			Untreated cotton fabric		**FR cotton fabric**		**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 of the empirical formula	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_{CO_2}	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_{H_2O}	grams per gram	0,558	—	0,558	—	0,597	—
Mass fraction of oxygen in the material	—	grams per gram	0,493	—	0,493	—	0,249	—
Test no. [21]			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 depletion 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	χ_{O_2}	—	0,594	1,052	0,609	0,789	0,078	0,671

Table 12 (*continued*)

Characteristic			**Material**					
			Untreated cotton fabric		**FR cotton fabric**		**Untreated wool yarn**	
Oxygen in products method								
CO_2 in test	—	micro litres per litre	8 170	17 600	6 400	8 000	1 550	10 400
CO_2 yield	Y_{CO_2}	grams per gram polymer	0,800	1,696	0,803	0,866	0,265	1,175
CO in test	—	micro litres per litre	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	—	micro litres per litre	9 870	15 218	7 703	13 986	1 470	12 069
Assumed H_2O yield	Y_{H_2O}	grams per gram polymer	0,395	0,600	0,395	0,620	0,103	0,558
Oxygen in CO_2	w_{O,CO_2}	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,H_2O}	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	χ_{prod}	—	0,599	1,057	0,600	0,821	0,162	0,819
Oxides of carbon method								
Efficiency CO_2 yield	η_{CO_2}	—	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].

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