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Heat release rate in diffusion flames

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Abstract

The dependence of heat release rate on fuel- and environment-based parameters is discussed. The parameters are the combustion efficiency and its convective and radiative components, net heat of complete combustion and heat of gasification, molecular weight of the gasified fuel, equivalence ratio, external and flame heat flux, and surface re-radiation loss.

The combustion efficiency of fuels with saturated carbon–hydrogen–oxygen bonds is close to 95% (60% convective, 35% radiative). Increase in bond unsaturation, removal of O atoms and introduction of N and S atoms reduce the combustion efficiency to 88% (50% convective and 38% radiative). Further increase in the bond unsaturation and introduction of benzene rings reduce the combustion efficiency to 72% (32% convective, 40% radiative). Introduction of large numbers of halogen atoms to saturated or unsaturated compounds with or without benzene rings reduces the combustion efficiency to 35%.

Keywords: Combustion efficiency; Convective and radiative components; Heat release rate calorimetry; Saturated and unsaturated bonds

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List of symbols, abbreviations, and acronyms

a_T	mass coefficient for the net heat of complete combustion in MJ kg^{-1}
b_T	molar coefficient for the net heat of complete combustion in MJ mol^{-1}
C_p	specific heat in MJ kg^{-1} K^{-1}
CDG	carbon dioxide generation calorimetry
G_j	mass generation rate of product j in kg s^{-1}
GTR	gas temperature rise calorimetry
ΔH_i	heat of combustion per unit mass of fuel in MJ kg^{-1}

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ΔH_{CO}	heat of complete combustion of CO in MJ kg^{-1}
ΔH_g	heat of gasification of the fuel in MJ kg^{-1}
ΔH^*_{CO}	net heat of complete combustion per unit mass of CO generated in MJ kg^{-1}
$\Delta H^*_{CO_2}$	net heat of complete combustion per unit mass of CO_2 generated in MJ kg^{-1}
ΔH^*_O	net heat of complete combustion per unit mass of oxygen consumed in MJ kg^{-1}
HRP	heat release parameter $(\Delta H_T/\Delta H_g)$
$\dot{m}_a$	mass flow rate of air in kg s^{-1}
$\dot{m}_f$	mass gasification rate of the fuel in kg s^{-1}
OC	oxygen consumption calorimetry
$\dot{q}''_e$	external heat flux in kW m^{-2}
$\dot{q}''_{fl}$	flame heat flux in kW m^{-2}
$\dot{q}''_{rr}$	surface re-radiation loss in kW m^{-2}
$\dot{Q}_i$	heat release rate in kW $(\dot{m}\Delta H_i)$
S	mass air-to-fuel stoichiometric ratio
$\dot{W}$	total mass flow rate of the fire product–air mixture in kg s^{-1}
W_f	total mass of materials gasified in kg
W_j	total mass of product j generated in kg
y_j	yield of product j in kg kg^{-1} (W_j/W_f)
Y_O	mass fraction of oxygen

Greek

α	ventilation correlation coefficient for the equivalence ratio
Φ	equivalence ratio $(S\dot{m}_f/\dot{m}_a)$
χ	efficiency $[\Delta H_i/\Delta H_T]$
Ψ_j	stoichiometric yield for the maximum conversion of fuel to product j

Subscripts

a	air or ambient
ch	chemical
con	convective
e	external
f	fuel
fl	flame
i	chemical, convective, radiative
j	fire product
rad	radiation
rr	surface re-radiation
T	complete combustion (net)
v	ventilation-controlled fire
∞	well ventilated

Superscripts

	per unit time in s^{-1}
$''$	per unit area in m^{-2}

Chemical structures and abbreviations

Alkane	hydrocarbon with single bonds between carbon and hydrogen atoms
Alkene	hydrocarbon with double bonds between carbon and hydrogen atoms
Alkyne	hydrocarbon with triple bonds between carbon and hydrogen atoms
Aliphatic	hydrocarbon without the benzene ring in the structure
Arene	hydrocarbon with aliphatic and aromatic structures
Aromatic	hydrocarbon with benzene ring in the structure
CTFE	chlorotrifluoroethylene (Kel-F)
Diene	hydrocarbons with two bonds between carbon and hydrogen atoms
DSC	differential scanning calorimetry
ECTFE	ethylene–chlorotrifluoroethylene (Halar)
ETFE	ethylenetetrafluoroethylene (Tefzel)
FMRC	Factory Mutual Research Corporation
FRS	flame radiation scaling
FEP	fluorinated polyethylene–polypropylene (Teflon)
NIST	National Institute of Standards and Technology
OSU	Ohio State University
PE	polyethylene
PFA	perfluoroalkoxy (Teflon)
PMMA	polymethylmethacrylate
PP	polypropylene
PS	polystyrene
PVF	polyvinyl fluoride (Tedlar)
PVF_2	polyvinylidene fluoride (Kynar)
PVC	polyvinylchloride
TFE	tetrafluoroethylene (Teflon)

1. Introduction

Heat release rate is the rate with which energy is generated in chemical reactions in the combustion of gasified material (fuel) and oxygen from air. The actual rate of generation of energy is defined as the chemical heat release rate [1]. Chemical heat release rate has a convective and a radiative component, defined, respectively, as the convective and radiative heat release rate. Chemical heat release rate is determined from the generation rate of products, such as CO_2 (*carbon dioxide generation, CDG*, calorimetry [1]) and from the consumption rate of reactants, such as O_2 (*oxygen consumption, OC*, calorimetry [1, 2]).

The convective heat release rate is determined from the increase in the gas temperature above ambient (*gas temperature rise*, *GTR*, calorimetry [1,3]). Radiative heat release rate is determined by the difference between the chemical and convective heat release rates as the heat losses are negligibly small [1].

In addition to the measurements for CDG, OC, and GTR calorimetries, other measurements made include [1–3]:

(1) net heat of complete combustion of the fuel;
(2) time to ignition;
(3) mass gasification rate of the fuel;
(4) generation rates of the products;
(5) optical transmission through the products;
(6) corrosion rate of a metal exposed to the products;
(7) flame height;
(8) flame propagation rate; and
(9) flame extinction.

In the experiments, several variables are used [1–3]:

(1) velocity and oxygen concentration of co-flowing air;
(2) external heat flux;
(3) flame heat flux;
(4) ventilation; and
(5) fuel configuration (horizontal and vertical slabs, cylinders, and rolls, liquid pools and sprays, boxes, etc.).

In this paper, the effects of fuel- and environment-based parameters on heat release rate are discussed. The fuel-based parameters considered are:

(1) heat of combustion and combustion efficiency and the convective and radiative components;
(2) molar coefficient for the net heat of complete combustion;
(3) molecular weight of the gasified species;
(4) heat of gasification (specific heat, heats of melting, decomposition, charring, vaporization, etc., and temperature associated with these processes);
(5) flame heat flux; and
(6) surface re-radiation. The environment-based parameters considered are:

(1) equivalence ratio; and
(2) external and flame heat flux.

2. Heat release rate calorimetry

Heat release rate calorimetry is used to determine chemical, convective, and radiative heat release rates. Several apparatuses have been designed. The most widely used apparatuses are:

(1) the flammability apparatus shown in Fig. 1 (designed by the Factory Mutual Research Corporation, FMRC) [1],

(2) the cone calorimeter (designed by the National Institute of Standards and Technology, NIST) [2], and

(3) the heat release rate apparatus (designed by the Ohio State University, OSU) [3].

2.1. Chemical heat release rate

Chemical heat release rate is determined from measurements of the mass generation rates of CO_2 and CO (CDG calorimetry) and from the mass consumption rate of O_2 (OC calorimetry). The chemical heat release rate determined from the CDG calorimetry is equal to the chemical heat release rate determined from the OC calorimetry because of the conservation of energy and mass.

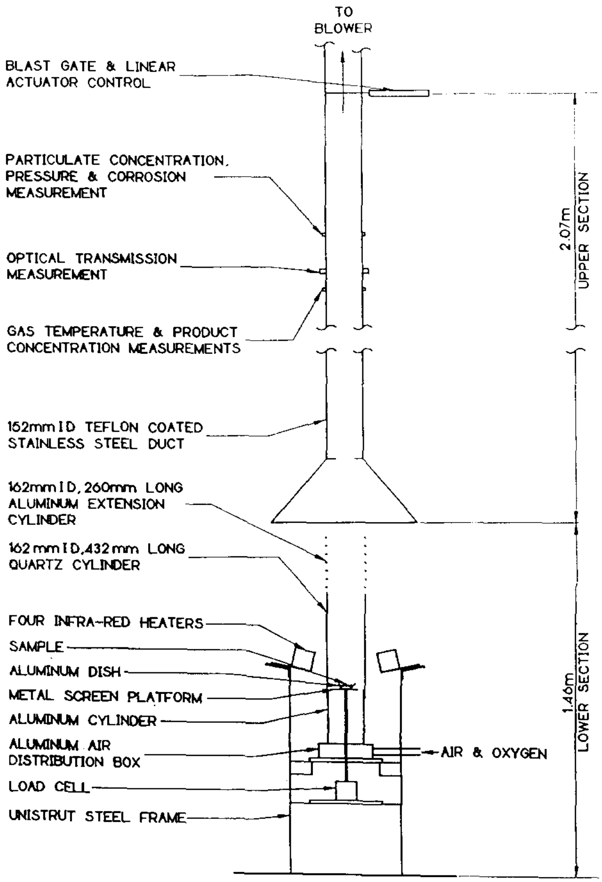

Fig. 1. The flammability apparatus (50 kW peak heat release rate, PKRR) designed by the Factory Mutual Research Corporation.

In the flammability apparatus at FMRC, both CDG and OC calorimetries are used for checks and balances and for providing accurate data.

2.1.1. The CDG calorimetry

Expressions used in the CDG calorimetry for the determination of the chemical heat release rate are [1]:

$$\dot{Q}''_{\mathrm{ch}} = \Delta H^{*}_{\mathrm{CO_2}} \dot{G}''_{\mathrm{CO_2}} + \Delta H^{*}_{\mathrm{CO}} \dot{G}''_{\mathrm{CO}} \tag{1}$$

$$\Delta H^{*}_{\mathrm{CO_2}} = \Delta H_T / \Psi_{\mathrm{CO_2}} \tag{2}$$

$$\Delta H^{*}_{\mathrm{CO}} = (\Delta H_T - \Delta H_{\mathrm{CO}} \Psi_{\mathrm{CO}}) / \Psi_{\mathrm{CO}} \tag{3}$$

2.1.2. The OC calorimetry

Expressions used in the OC calorimetry for the determination of the chemical heat release rate are [1,2]:

$$\dot{Q}''_{\mathrm{ch}} = \Delta H^{*}_{\mathrm{O}} \dot{C}''_{\mathrm{O}} \tag{4}$$

$$\Delta H^{*}_{\mathrm{O}} = \Delta H_T / \Psi_{\mathrm{O}} \tag{5}$$

where $\dot{Q}''_{\mathrm{ch}}$ is the chemical heat release rate in kW m^{-2}, ΔH_T is the net heat of complete combustion per unit mass of fuel gasified in MJ kg^{-1}, $\Delta H^{*}_{\mathrm{CO_2}}$, $\Delta H^{*}_{\mathrm{CO}}$, and $\Delta H^{*}_{\mathrm{O}}$ are the net heat of complete combustion per unit mass of CO_2 and CO generated and oxygen consumed, respectively, in MJ kg^{-1}, $\Psi_{\mathrm{CO_2}}$ and Ψ_{CO} are the stoichiometric yields of CO_2 and CO, respectively, in kg kg^{-1}, Ψ_{O} is the mass-oxygen-to-fuel stoichiometric ratio in kg kg^{-1}, $\dot{G}''_{\mathrm{CO_2}}$ and $\dot{G}''_{\mathrm{CO}}$ are the generation rates of CO_2 and CO, respectively, in kg m^{-2} s^{-1} and $\dot{C}''_{\mathrm{O}}$ is the mass consumption rate of oxygen in kg m^{-2} s^{-1}.

In the experiments, $\dot{G}''_{\mathrm{CO_2}}$, $\dot{G}''_{\mathrm{CO}}$ and $\dot{C}''_{\mathrm{O}}$ values are measured; actual or average values of $\Delta H^{*}_{\mathrm{CO_2}}$, $\Delta H^{*}_{\mathrm{CO}}$, and $\Delta H^{*}_{\mathrm{O}}$ are used. The average values used are: $\Delta H^{*}_{\mathrm{CO_2}} = 13.3$ kJ g^{-1} ± 11%, $\Delta H^{*}_{\mathrm{CO}} = 11.1$ kJ g^{-1} ± 18%, and $\Delta H^{*}_{\mathrm{O}} = 12.8$ kJ g^{-1} ± 7% [1]. The use of average values of $\Delta H^{*}_{\mathrm{CO_2}}$, $\Delta H^{*}_{\mathrm{CO}}$, and $\Delta H^{*}_{\mathrm{O}}$ gives only approximate heat release rates, whereas the use of actual values gives accurate rates. Chemical heat release rate is determined mostly in the flammability apparatus at FMRC (both CDG and OC calorimetries are used) and in the cone calorimeter (only OC calorimetry is used).

Figs. 2 to 4 show the experimental data from the flammability apparatus at FMRC, where actual values of $\Delta H^{*}_{\mathrm{CO_2}}$, $\Delta H^{*}_{\mathrm{CO}}$, and $\Delta H^{*}_{\mathrm{O}}$ have been used. Fig. 2 shows the chemical heat release rate for the well-ventilated combustion of a single slab of polypropylene (PP) exposed to 50 kW m^{-2} of external heat. Figs. 3 and 4 show the chemical heat release rates for the well-ventilated combustion of four slabs of polystyrene (PS) and polymethylmethacrylate (PMMA) respectively, exposed to 50 kW m^{-2} of external heat flux.

PP melts and burns as a liquid pool with the entire liquid boiling (Fig. 2). PS also burns as a liquid pool, but with only surface boiling (Fig. 3). PMMA burns as a solid slab with a thin layer of liquid at the surface. The chemical heat release rates in Figs. 2 to 4 determined from the CDG and OC calorimetries are, as expected, in excellent agreement.

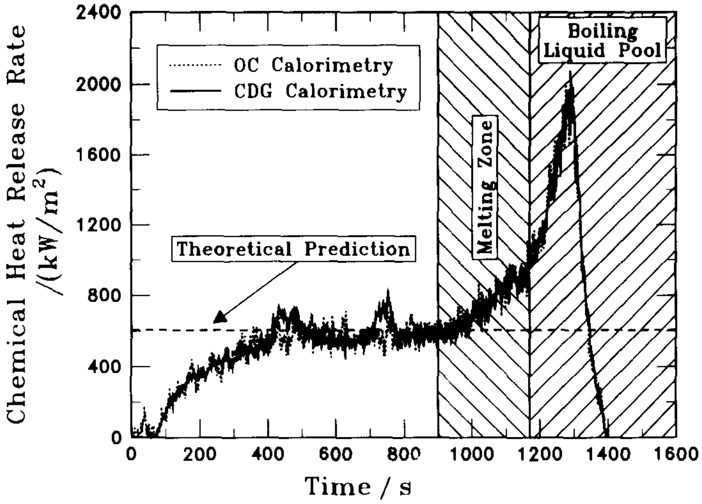

Fig. 2. Chemical heat release rate for a single 100 mm diameter and 25 mm thick polypropylene (PP) horizontal slab burning at an external heat flux exposure of 50 kW m^{-2} under well ventilated conditions in the flammability apparatus (50 kW PKRR) at FMRC.

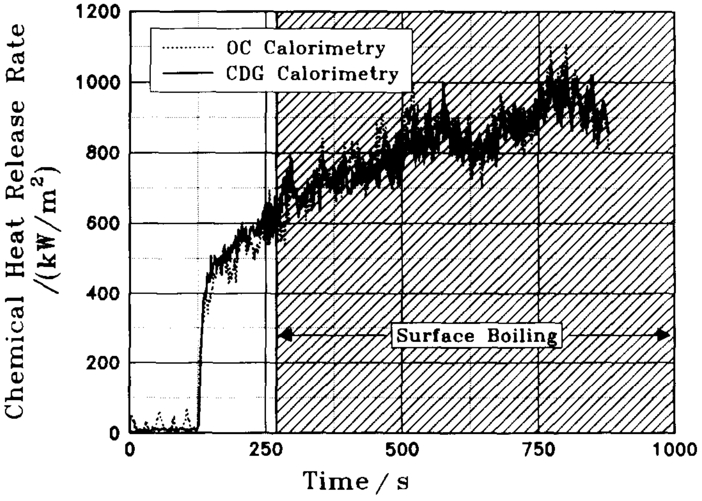

Fig. 3. Chemical heat release rates for four 91 mm diameter and 25 mm thick polystyrene (PS) horizontal slabs burning at an external heat flux exposure of 50 kW m^{-2} under well ventilated conditions in the flammability apparatus (500 kW PKRR) at FMRC.

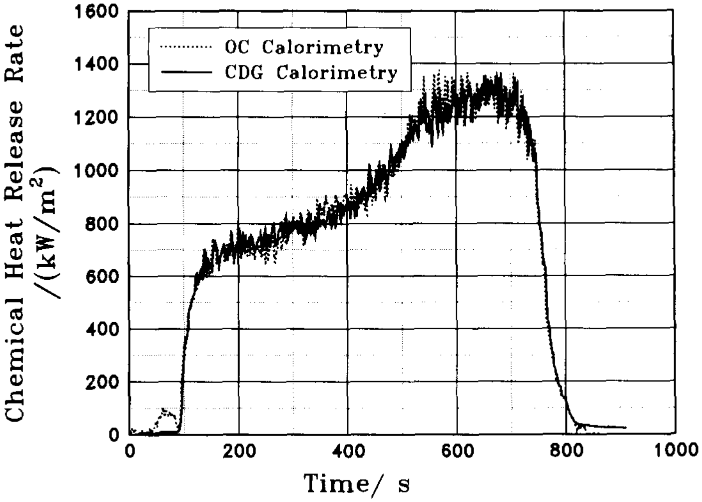

Fig. 4. Chemical heat release rates for four 91 mm diameter and 25 mm thick polymethylmethacrylate (PMMA) horizontal slabs burning at an external heat flux exposure of 50 kW m^{-2} under well ventilated conditions in the 500 kW scale flammability apparatus (larger version of the 50 kW scale apparatus).

2.2. *Convective heat release rate: the GTR calorimetry*

The following relationship is used in the GTR calorimetry for the determination of the convective heat release rate [1,3]:

$$\dot{Q}''_{\mathrm{con}} = \frac{\dot{W} C_p (T_g - T_a)}{A} \tag{6}$$

where $\dot{Q}''_{\mathrm{con}}$ is the convective heat release rate in kWm^{-2}, C_p is the specific heat at the gas temperature in MJ kg^{-1} K^{-1}, T_g is the gas temperature in K, T_a is ambient temperature in K, $\dot{W}$ is the total mass flow rate of the product–air mixture in kg s^{-1}, and A is the total surface area of the burning fuel in m^2.

In the experiments, $T_g - T_a$ and $\dot{W}$ values are measured; specific heat value of air from the literature as a function of temperature is used because the products are highly diluted by air. Convective heat release rate is determined in the flammability apparatus at FMRC [1] and the OSU apparatus [3].

3. Factors affecting heat release rate

Heat release rate is directly proportional to the mass gasification rate of the fuel:

$$\dot{Q}''_{\mathrm{i}} = \Delta H_{\mathrm{i}} \dot{m}''_{\mathrm{f}} \tag{7}$$

where ΔH_{i} is the heat of combustion in MJ kg^{-1}, subscript i represents chemical, convective, or radiative, and $\dot{m}''_{\mathrm{f}}$ is the mass gasification rate of the fuel in kg m^{-2} s^{-1}, expressed as:

$$\dot{m}''_{\mathrm{f}} = \dot{q}''_{\mathrm{e}} + \dot{q}''_{\mathrm{ff}} - \dot{q}_{\mathrm{rr}}/\Delta H_{\mathrm{g}} \tag{8}$$

where $\dot{q}''_{\mathrm{e}}$ is the external heat flux in kW m^{-2}, $\dot{q}''_{\mathrm{ff}}$ is the flame heat flux received by the burning fuel in kW m^{-2}, $\dot{q}''_{\mathrm{rr}}$ is the surface re-radiation loss in kW m^{-2}, and ΔH_{g} is the heat of gasification in MJ kg^{-1}.

In diffusion flames, chemical, convective, and radiative heat of combustion is always less than the net heat of complete combustion as combustion remains incomplete. Thus combustion efficiency and its convective and radiative components are expressed as:

$$\chi_{\mathrm{i}} = \Delta H_{\mathrm{i}}/\Delta H_{T} \tag{9}$$

where χ_{i} is the combustion efficiency or its convective or radiative component. From Eqs. (7) to (9):

$$\dot{Q}''_{\mathrm{i}} = \chi_{\mathrm{i}}(\Delta H_{T}/\Delta H_{\mathrm{g}})(\dot{q}''_{e} + \dot{q}''_{\mathrm{ff}} - \dot{q}''_{\mathrm{rr}}) \tag{10}$$

where $\chi_{\mathrm{i}}(\Delta H_{T}/\Delta H_{\mathrm{g}})$ is defined as the *heat release parameter* (*HRP*) in MJ MJ^{-1}. Heat release rate thus depends on the combustion efficiency, heat of combustion, heat of gasification, external and flame heat flux, and surface re-radiation loss.

3.1. Heat release rate and heat of gasification

Eq. (10) shows that the heat release rate is inversely proportional to the heat of gasification, which is the energy required to gasify unit mass of fuel originally at ambient temperature [4]:

$$\Delta H_{\mathrm{g}} = \int_{T_{\mathrm{a}}}^{T_{\mathrm{k}}} C_{p,\mathrm{s}}\,\mathrm{d}T + \Delta H_{\mathrm{k}} + \int_{T_{\mathrm{k}}}^{T_{\mathrm{v}}} C_{p,\mathrm{k}}\,\mathrm{d}T + \Delta H_{\mathrm{v}} \tag{11}$$

where ΔH_{k} is the heat of melting, decomposition, crosslinking, etc., in MJ kg^{-1}, ΔH_{v} is the heat of vaporization in MJ kg^{-1}, $C_{p,\mathrm{s}}$ and $C_{p,\mathrm{k}}$ are the specific heats of the fuel in the solid and molten, charred, decomposed or other state in MJ kg^{-1} K^{-1}, respectively, T_{a} is the ambient temperature in K, T_{k} is the temperature of melting, decomposition, charring etc., in K, and T_{v} is the vaporization temperature in K. For crosslinking polymers, $\Delta H_{\mathrm{k}} \gg \Delta H_{\mathrm{v}}$.

Fig. 5 shows plots of heat of gasification versus molecular weight for alkanes (aliphatic saturated hydrocarbons) and poly(dimethylsiloxanes) (PDMS), where heat of gasification is calculated from Eq. (11), using specific heat, boiling point and heat of vaporization of the liquids from Refs. [5] and [6], assuming an ambient temperature of 293 K. The data satisfy the following relationships in the molecular weight range of 30 to 250 × 10^{-3} kg mol^{-1} for alkanes and 162 to 458 × 10^{-3} kg mol^{-1} for PDMS.

Alkanes

$$\Delta H_{\mathrm{g}} = -3.72 \times 10^{-6} M^{2} + 0.0042M + 0.164 \tag{12}$$

PDMS

$$\Delta H_{\mathrm{g}} = -4.45 \times 10^{-7} M^{2} + 0.0009M + 0.222 \tag{13}$$

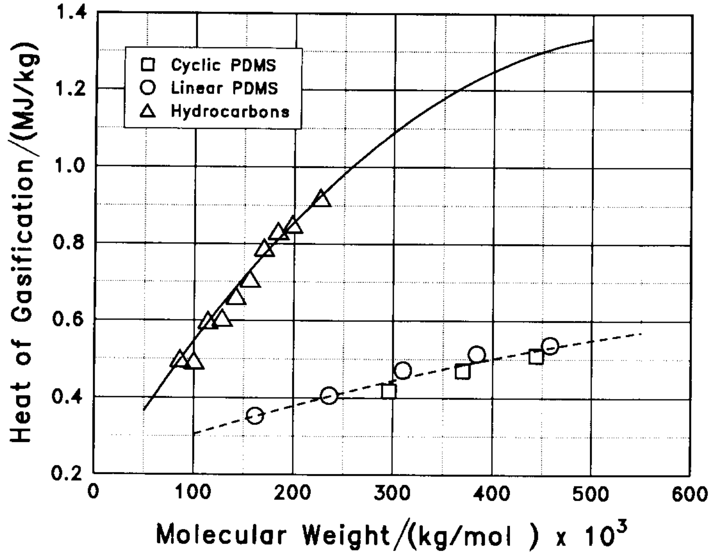

Fig. 5. Heat of gasification versus the molecular weight of saturated aliphatic hydrocarbons (alkanes) and poly(dimethylsiloxane)s. Heat of gasification is calculated from the specific heat boiling point, and heat of vaporization of liquids assuming ambient temperature to be 293 K. Property data for hydrocarbons are taken from Ref. [5] and for poly(dimethylsiloxane)s from Ref. [6].

where M is the molecular weight in g mol^{-1}. The heat of gasification increases with molecular weight and is higher for the alkanes than it is for the PDMS. Thus under similar heat flux exposure and geometrical conditions, the mass gasification rate for PDMS would be higher than for the alkanes.

The heat of gasification is quantified by *differential scanning calorimetry* (*DSC*), and *mass pyrolysis calorimetry* (*MPC*). In the DSC technique, measurements of specific heat, heats of melting, vaporization, decomposition, etc., are made under an inert atmosphere and data are used to obtain the heat of gasification numerically from Eq. (11).

In the MPC technique, heat of gasification is quantified globally by measuring the mass gasification rate of the fuel as a function of external heat flux in the presence of co-flowing nitrogen and a nitrogen–10% oxygen mixture in the flammability apparatus at FMRC [4]. Mass gasification rate data are used to obtain the heat of gasification numerically from Eq. (8), where flame heat flux is zero. The external heat flux value at which there is no measurable mass gasification rate for 15 min of heat flux exposure is taken as the value of the surface re-radiation loss. The heat of gasification and surface re-radiation loss values obtained from the MPC technique in the flammability apparatus at FMRC have been reported in the literature [1, 4].

The heats of gasification from the DSC and MPC techniques show good agreement. For example, the heat of gasification, in MJ kg^{-1}, of low density polyethylene (PE), high density PE, polypropylene (PP), polyoxymethylene, polymethylmethacrylate

(PMMA), and polystyrene (PS), respectively, are 1.9, 2.2, 2.0, 2.4, 1.6, and 1.8 from DSC and 1.8, 2.3, 2.0, 2.4, 1.6, and 1.7 from MPC.

Since heat of gasification is determined in an inert environment, if a fuel crosslinks in the presence of oxygen, experiments with nitrogen and nitrogen–10% oxygen mixture in the DSC technique as is done in the MPC technique would delineate the cross-linking effects.

3.2. Heat release rate and external and flame heat flux and surface re-radiation loss

Eq. (10) shows that heat release rate would increase with increase in the external and flame heat flux and decrease in the surface re-radiation loss. Flame heat flux increases with increase in the surface area of the burning fuel. A simulation technique has been developed at FMRC to quantify flame heat flux expected in the large-scale combustion of fuels using the laboratory-scale experiments in the flammability apparatus [1, 7, 8]. The technique is called the *flame radiation scaling* (*FRS*) technique [1, 7, 8]. The FRS technique utilizes the concept that flame radiative heat flux from small diffusion flames increases as oxygen mass fraction, Y_O, is increased [8]. For $Y_O \geq 0.30$, flame heat flux reaches an asymptotic limit comparable to the asymptotic flame heat flux limit in the large-scale combustion of fuels [1, 7, 8].

In the FRS technique, the simulation of large-scale flame heat flux conditions in the laboratory-scale experiments is performed by increasing the Y_O values in the co-flowing air. The mass gasification rate of the fuel is measured as a function of Y_O value. Flame heat flux is calculated from the mass gasification rate (Eq. 8), using known values of the heat of gasification and surface re-radiation loss [1, 7, 8]. The flame heat flux obtained from the FRS technique shows good agreement with the flame heat flux obtained by the direct measurements in the large-scale combustion experiments [1, 7, 8].

The flame heat flux for the large-scale combustion of fuels varies from about 22 to 77 kW m^{-2}, dependent primarily on the molecular weight of the gasified fuel [1, 7, 8]. For example, for liquids, which vaporize as low molecular weight species, flame heat flux is in the range of about 22 to 44 kW m^{-2}, whereas for polymers, which vaporize as high molecular weight species, it increases substantially to the range of about 49 to 75 kW m^{-2} [1, 7, 8].

3.3. Heat release rate and net heat of complete combustion

Eq. (10) shows that heat release rate is directly proportional to the net heat of complete combustion, which is an inverse function of the molecular weight [9, 10]:

$$\Delta H_T = a_T + \frac{b_T}{M} \tag{14}$$

where a_T is the mass coefficient for the net heat of complete combustion in MJ kg^{-1} and b_T is the molar coefficient for the net heat of complete combustion in MJ mol^{-1}. The values of a_T and b_T derived from the literature for over 100 fuels [9, 10] are listed in Table 1.

Table 1
Coefficients for the net heat of complete combustion, combustion efficiency and its convective and radiative components for the well ventilated combustion of fuels[a]

Chemical structure	a_T	b_T	χ_{ch}	χ_{con}	χ_{rad}
Fuels containing carbon and hydrogen					
Normal alkanes	43.6	0.104	0.91	0.62	0.30
Branched alkanes	43.6	0.101	0.89	0.58	0.32
Cyclic alkanes	41.3	0.209	0.86	0.51	0.35
Alkenes	43.3	0.131	0.87	0.53	0.35
Alkynes	43.7	0.107	0.80	0.42	0.38
Acetylene	43.7	0.107	0.77	0.39	0.38
1,3-Butadiene	42.8	0.097	0.75	0.35	0.41
Arenes	37.4	0.211	0.72	0.30	0.42
Fuels containing carbon, hydrogen, and oxygen					
Aliphatic esters	43.8	−1.750	0.98	0.62	0.35
Aliphatic alcohols	45.4	−0.813	0.91	0.63	0.28
Methyl alcohol	45.4	−0.813	0.96	0.81	0.15
Aliphatic ketones	45.0	−0.888	0.94	0.68	0.27
Various aromatics	39.4	−0.732	0.73	0.33	0.40
Fuels containing carbon, hydrogen and nitrogen					
Aliphatics	44.0	−0.441	0.89	0.56	0.34
Aromatics	42.3	−0.795	0.74	0.34	0.40
Fuels containing carbon, hydrogen, and sulfur					
Aliphatics	39.0	−0.706	0.89	0.53	0.36
Aromatics	41.3	−0.793	0.72	0.32	0.40

[a] data taken from Refs. [9] and [10]. a_T is in MJ kg^{-1} and b_T is in MJ mol^{-1}. Hydrocarbons with a benzene ring in the structure are defined as *aromatics* and without the benzene ring as *aliphatics*. Hydrocarbons with *single*, *double*, or *triple* bonds between carbon and hydrogen atoms are respectively defined as *alkanes*, *alkenes*, or *alkynes*. Hydrocarbons with mixed aliphatic and aromatic structures are defined as *arenes*.

The values in Table 1 show that a_T has lower sensitivity than b_T to changes in the chemical structures of the fuels. The average value of a_T is 42.6 ± 2.2 MJ kg^{-1}. The b_T values are positive for fuels containing carbon and hydrogen and become negative on introduction of oxygen, nitrogen, and sulfur atoms into the structure.

Eq. (14) shows that the net heat of complete combustion of fuels which gasify as low molecular weight species depends on both a_T and b_T values, but would be approximately equal to a_T for fuels which gasify as high molecular weight species. From Eqs. (10) and (14):

$$\dot{Q}_{\mathrm{i}}'' \simeq (\chi_{\mathrm{i}}/\Delta H_{\mathrm{g}})(43 + b_T/M)(\dot{q}_{\mathrm{e}}'' + \dot{q}_{\mathrm{f}}'' - \dot{q}_{\mathrm{rr}}'') \tag{15}$$

Thus, heat release rate would depend on the molecular weight of the gasified species and the molar coefficient of the net heat of complete combustion. Under similar conditions or values of heat flux exposure, geometry, heat of gasification and combustion efficiency, heat release rate from the fuels containing carbon and hydrogen would be higher than from fuels containing carbon, hydrogen, and oxygen or nitrogen or sulfur as b_T becomes negative.

For fuels which gasify as low molecular weight species, b_T/M is important but flame heat flux is lower, whereas for fuels which gasify as higher molecular weight species, b_T/M is less important but flame heat flux is higher.

3.4. Heat release rate and combustion efficiency

According to Eq. (15), heat release rate is directly proportional to the combustion efficiency. Data for the combustion efficiency and its convective and radiative components for the well ventilated combustion of fuels, based on the experimental data for over 100 fuels, measured in the flammability apparatus at FMRC [1, 4–10], are listed in Tables 1 and 2. In Table 1, data are listed according to the generic nature of the fuel and in Table 2, data are for the halogenated polymers.

Data in Tables 1 and 2 show that combustion efficiency varies from 0.98 for fuels containing aliphatic carbon, hydrogen, and oxygen to 0.35 for the highly halogenated fuels. Combustion efficiency and its convective component have similar dependencies

Table 2
Well ventilated combustion properties of polymers containing carbon, hydrogen, and halogen or carbon, hydrogen, silicon and oxygen[a]

Polymer	Formula	$M \times 10^3$ (monomer)	S	ΔH_T	χ_{ch}	χ_{con}	χ_{rad}
Chloropolymers							
PE + 0% chlorine	CH_2	14	14.7	43.6	0.84	0.47	0.37
PE + 25% chlorine	$CH_{1.9}Cl_{0.13}$	19	11.0	31.6	0.72	0.32	0.40
PE + 36% chlorine	$CH_{1.8}Cl_{0.22}$	22	9.3	26.3	0.40	0.24	0.16
PE + 42% chlorine	$CH_{1.8}Cl_{0.29}$	24	8.3	22.2	0.38	0.22	0.16
PE + 48% chlorine	$CH_{1.7}Cl_{0.36}$	26	7.4	20.6	0.35	0.19	0.16
PVC	$CH_{1.5}Cl_{0.50}$	31	6.1	16.4	0.35	0.19	0.16
Fluoropolymers							
PVF (Tedlar®)	$CH_{1.5}F_{0.50}$	23	7.5	13.5	0.38		–
PVF_2 (Kynar®)	CHF	32	4.3	13.3	0.39	–	
ETFE (Tefzel®)	$CH_{1.0}F_{0.99}$	32	4.3	12.6	0.43	–	–
ECTFE (Halar®)	$CHF_{0.75}Cl_{0.25}$	36	3.8	12.0	0.38	–	–
PFA (Teflon®)	$CF_{1.7}O_{0.01}$	44	3.1	5.0	0.35	–	
FEP (Teflon®)	$CF_{1.8}$	46	3.0	4.8	0.35	–	
TFE (Teflon®)	CF_2	50	2.7	6.2	0.35	–	–
CTFE (Kel-F®)	$CF_{1.5}Cl_{0.50}$	58	2.4	6.5	0.35	–	
Poly(dimethylsiloxanes) (PDMS)							
PDMS	$CH_{1.3}O_{0.23}Si_{0.18}$	22	8.5	21.7	0.50	–	–

[a] data taken from Ref. [1]; M is in kg mol^{-1}; S: mass air-to-fuel ratio stoichiometry in kg kg^{-1}.

on the chemical structure of the fuel, the radiative component, however, has an opposite dependency. Combustion efficiency and its convective component for hydrocarbon fuels decrease and the radiative component increases with increase in bond unsaturation (single, double, and triple), introduction of the benzene ring, or nitrogen, sulfur, and halogenated atoms into the fuel structure. The combustion efficiency of halogenated fuels decreases with increased amounts of halogen atoms in the structure.

The average combustion efficiency and its convective and radiative components for saturated aliphatic fuels containing carbon, hydrogen and oxygen are about 0.95, 0.60, and 0.35, respectively. The average values change to about 0.88, 0.50, and 0.38 for unsaturated and nitrogen- and sulfur-containing structures. The combustion efficiency and its convective and radiative components are about 0.72, 0.32, and 0.40 for all the fuels with aromatic and highly unsaturated aliphatic structures. These average values can be used in Eq. (15) for the approximate heat release rate calculations for the well ventilated combustion of fuels.

The combustion efficiency and its convective and radiative components depend not only on the chemical structure of the fuel but also on the ventilation.

3.5. *Heat release rate and ventilation*

Ventilation is the amount of air available for combustion relative to the amount of fuel and is expressed as the *equivalence ratio* [11]:

$$\Phi = S\dot{m}_{\mathrm{f}}/\dot{m}_{\mathrm{a}} \tag{16}$$

where Φ is the equivalence ratio, S is the mass air-to-fuel stoichiometric ratio in kg kg^{-1}, and $\dot{m}_{\mathrm{a}}$ is the mass flow rate of air in kg s^{-1}.

For nonhalogenated fuels, $\Phi < 1.0$ for well ventilated flaming combustion, $\Phi > 1.0$ for ventilation-controlled flaming combustion; flaming combustion changes to nonflaming combustion for $\Phi \geq 3.5$, and for $1.0 \geq \Phi \leq 3.5$, combustion is in a transition state [11]. For highly halogenated fuels, there is a rapid decrease in the combustion efficiency for Φ values between 0.5 and 0.6, where combustion is well ventilated.

The data for the combustion efficiency and its convective component versus the equivalence ratio are shown in Figs. 6 and 7 for the nonhalogenated fuels and in Fig. 8 for the well ventilated combustion of PVC. The efficiencies are normalized by the efficiencies for the well ventilated combustion of fuels. The data in the figures are taken from Ref. [11]. Flaming, transition, and nonflaming regions are identified in the figures. Efficiency is very sensitive to changes in the equivalence ratio in the transition region. Flame is extinguished when combustion efficiency ratio is reduced below 0.40. The experimental data in Figs. 6 and 7 provide the following correlations [11]:

Nonhalogenated fuels

$$\chi_{\mathrm{i,v}} = \chi_{\mathrm{i},\infty}\left[1 - \frac{1.0}{\exp(2.5\Phi^{-\alpha})}\right] \tag{17}$$

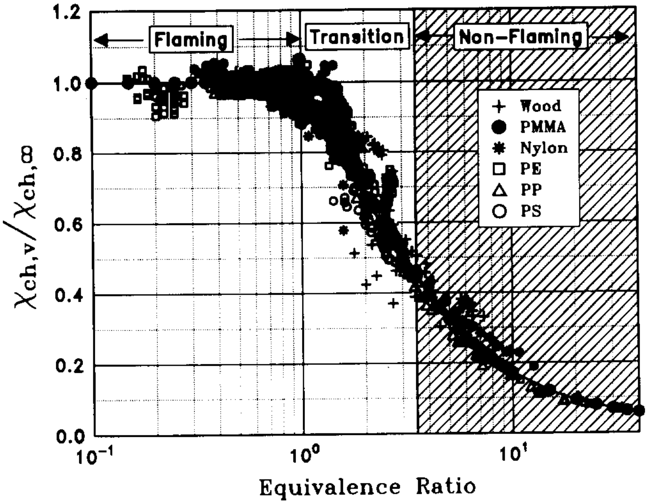

Fig. 6. Ratio of the combustion efficiency for ventilation-controlled combustion to the efficiency for well ventilated combustion for nonhalogenated polymers versus the equivalence ratio. Data are taken from Ref. [11].

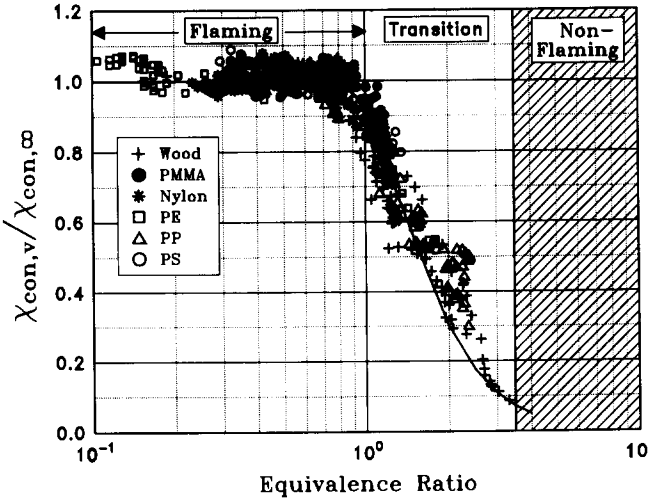

Fig. 7. Ratio of the convective component of the combustion efficiency for ventilation-controlled combustion to the efficiency for well ventilated combustion for nonhalogenated polymers versus the equivalence ratio. Data are taken from Ref. [11].

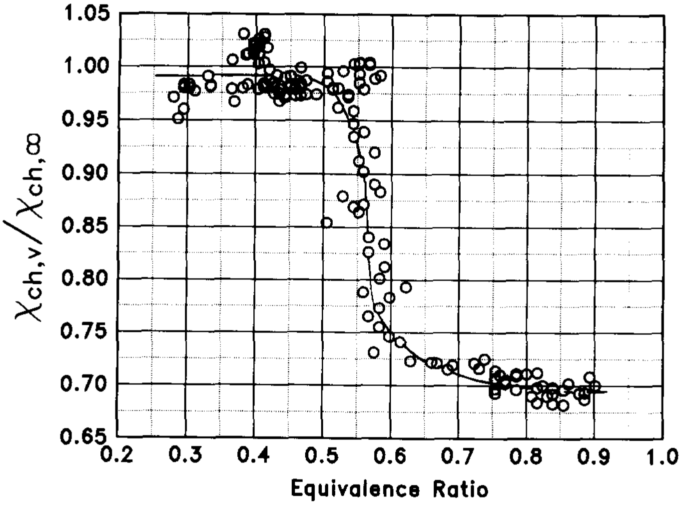

Fig. 8. Ratio of the combustion efficiency for ventilation-controlled combustion to the efficiency for well ventilated combustion for poly(vinylchloride) versus the equivalence ratio. Data were measured in the flammability apparatus.

Halogenated fuels

$$\chi_{ch,v} = \chi_{ch,\infty}\left[1 - \frac{0.30}{\exp(0.001\Phi^{-11})}\right] \tag{18}$$

where $\chi_{i,v}$ is the combustion efficiency or its convective component for ventilation-controlled combustion, $\chi_{i,\infty}$ is the combustion efficiency or its convective component for well ventilated combustion, and α is the ventilation correlation coefficient. For nonhalogenated fuels, $\alpha = 1.2$ for the combustion efficiency and $\alpha = 2.8$ for the convective component of the combustion efficiency. From conservation of energy without heat losses:

$$\chi_{rad} = \chi_{ch} - \chi_{con} \tag{19}$$

which is used for the calculation of the radiative component of the combustion efficiency. The values calculated in this fashion are shown in Fig. 9 for the non-halogenated polymers. The $\chi_{rad,v}$ values increase with equivalence ratio whereas $\chi_{ch,v}$ and $\chi_{con,v}$ decrease. All values decrease as the flame extinction limit approaches.

4. Heat release rate and fuel- and environment-based parameters

Various effects of fuel- and environment-based parameters on heat release rate discussed previously can be expressed by a single relationship (from Eqs. (15) and (17)):

$$\dot{Q}''_{i,v} = \chi_{i,\infty}\left[1 - \frac{1.0}{\exp(2.5\Phi^{-\alpha})}\right]\left[\frac{43 + (b_T/M)}{\Delta H_g}\right][\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}] \tag{20}$$

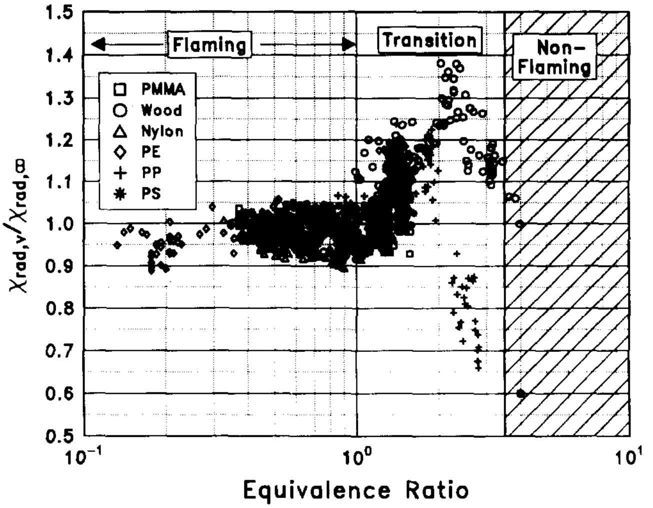

Fig. 9. Ratio of the radiative component of the combustion efficiency for ventilation-controlled combustion to the efficiency for well ventilated combustion for nonhalogenated polymers versus the equivalence ratio. Data are taken from Ref. [11].

4.1. Combustion efficiency and its convective and radiative components

The effect of the combustion efficiency and its components on the heat release rate can be predicted using literature data [1] (examples in Tables 1 and 2) as well as quantified experimentally by measuring the heat release rate for fuels with varying degrees of combustion efficiency.

4.2. Molar coefficient for the net heat of complete combustion, molecular weight of gasified fuel, and heat of gasification

The effects of these parameters on the heat release rate can be predicted (Table 1) and quantified by measuring the heat release rates for fuels with various modes of gasification such as low to high molecular weight hydrocarbons and polymers.

4.3. External and flame heat flux and surface re-radiation loss

The effect of external and flame heat flux and surface re-radiation loss on heat release rate can be predicted for many fuels using literature data [1] (examples in Table 3) and can be measured experimentally by using the flame radiation scaling (FRS) technique and radiant heaters.

4.4. Ventilation correlation coefficient

The effect of ventilation can be calculated and determined experimentally by measuring the heat release rate at various equivalence ratios.

Table 3
Combustion properties of well ventilated diffusion flames[a]

Fuel	HRP[b]	χ_{ch}	$M \times 10^3$/ (kg mol^{-1})[c]	ΔH_T (MJ kg^{-1})	ΔH_g (MJ kg^{-1})	$\dot{q}''_{rr}$ (k Wm^{-2})	$\dot{q}''_f$ (k Wm^{-2})
Liquids							
Hexane	83	0.93	86	44.8	0.50	0.50	37
Heptane	75	0.92	100	44.6	0.55	0.63	37
Dodecane	52	0.91	170	44.2	0.77	2.8	30
Kerosene	47	0.91	198	44.1	0.85	3.0	29
Solid polymers							
PP	19	0.84	28	43.6	2.0	15	61
PE	17	0.85	42	43.4	2.3	15	67
PS	16	0.76	104	39.2	1.7	13	75
PMMA	15	0.96	100	25.2	1.6	11	60
POM	6	0.94	30	15.4	2.4	13	50
ETFE	6	0.43	32	12.6	0.9	27	50
PVC	3	0.35	31	16.4	1.7	10	50
FEP	2	0.35	46	4.8	2.4	38	52

[a] data from Ref. [1].
[b] HRP is the heat release parameter obtained from the slope of the heat release rate versus external heat flux relationship or calculated from the ratio of the chemical heat of combustion to the heat of gasification.
[c] M is the molecular weight of the monomer.

5. Conclusions

(1) The actual rate of generation of energy in a diffusion flame is defined as the chemical heat release rate, which has a convective and a radiative component. Chemical heat release rate is determined from the measurements of the generation rates of the products (CO_2 and CO; *carbon dioxide generation calorimetry*) and the consumption rates of the reactants (O_2; *oxygen consumption calorimetry*). The convective heat release rate is determined from the measurements of gas temperature rise above ambient and total mass flow rate of the product–air mixture (*gas temperature rise calorimetry*).

(2) Heat release rate depends on the combustion efficiency and its convective and radiative components, net heat of complete combustion, heat of gasification, molecular weight of the gasified fuel, equivalence ratio, external and flame heat flux, and surface re-radiation loss.

(3) In a diffusion flame, combustion always remains incomplete. For well ventilated combustion, combustion efficiency of aliphatic fuels containing carbon, hydrogen and oxygen is close to 95%, where the convective and radiative components are 60 and 35%, respectively. Bond unsaturation, absence of oxygen, and the presence of nitrogen and sulfur in the fuel structure reduce the combustion efficiency to 88%, and convective and radiative components to 50 and 38%, respectively. Aliphatic fuels with

a high extent of unsaturation and benzene rings in the fuel structure have a combustion efficiency of 72% with convective and radiative components of 32 and 40%, respectively. The highly halogenated fuels have a combustion efficiency of 35%.

(4) Chemical and convective heat release rates decrease with decrease in ventilation, primarily because of decreases in the combustion efficiency and its convective component. The radiative heat release rate increases because of the increase in the radiative component of the combustion as ventilation is decreased. Flame is extinguished under highly under-ventilated conditions when the combustion efficiency decreases to below 40% of its value for well ventilation combustion.

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