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Material flammability, combustion, toxicity and fire hazard in transportation

Indrek S. Wichman*

Department of Mechanical Engineering, Michigan State University, East Lansing, MI 48824-1226, USA

Received 30 October 2001; accepted 4 March 2003

Abstract

Many materials used in transportation vehicles are combustible, often dramatically so. These materials may include gases, liquids and solids. They are sometimes employed in order to increase fuel efficiency, reduce manufacturing cost or meet other market demands such as durability or appearance. Extensive research has been conducted on such materials both with and without the expressed intent of applying the results directly to transportation.

Combustion and fire research, considered generally, are much broader than (and in fact encompass), the specific applications to transportation issues discussed here. Much if not most of fire and combustion research, therefore, has a direct bearing on transportation. This review ties together disparate subjects of fundamental fire and combustion research that have relevance to transportation fire. The goal is to provide a technical overview of the combustion literature related to, but not exclusively concerned with or focused on, transportation fire safety.

Although they are not a large percentage of transportation-related fatalities, fires can be costly in human and economic terms. In the United States, post-collision fires occur in 1–5% of fatal motor vehicle accidents, while approximately 20% of air traffic fatalities are attributed to fire. This review addresses scientific and technical engineering issues in the fields of fire initiation; fire spread; products of combustion and their toxicity; and practical fire prevention in vehicles and other modes of transportation.
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Keywords: Material flammability; Combustion; Transportation

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* Corresponding author. Tel.: +1-517-355-5131; fax: +1-517-353-1750.
E-mail address: wichman@egr.msu.edu (I.S. Wichman).

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1. Introduction

In the past, the vehicles used for transportation were constructed almost exclusively of wood and metal. The general fire behavior of these materials, for example whether or not they readily burn, was common knowledge, and alternative materials were limited both in their availability and in their use.

With time and technological advancement, larger numbers of potentially combustible materials have been used in transportation vehicles. The precise reasons are many, although two prominent design considerations have been (1) mass reduction, resulting in increased fuel efficiency, and (2) reduced manufacturing costs. Numerous complicated physical processes occur during the combustion of materials frequently used in transportation: these include, but are not limited to dripping and running of liquefied surface layer during burning; by-products of combustion; loss of material integrity and desirable physical performance properties; production of lightweight, combustible, decomposition gases; and flame spread to nearby combustible materials.

This review was prepared in accordance with an agreement between General Motors (GM) and the US Department of Transportation. The document outlining this research agreement is described in the settlement agreement between the United States Department of Transportation and the General Motors Corporation dated March 7, 1995. Part of the research program established by this agreement required a literature search of articles related to transpor-

tation fire and materials flammability. Of the more than 1000 articles culled from research journals by GM engineers, approximately 150 were abstracted at Michigan State University (MSU). To avoid copyright infringement, copyrighted abstracts were not included in the Transportation Fire Safety (TFS) Bibliography developed by LaDue [1]. Original abstracts for the approximately 150 selected articles were written by me and included in the GM TFS Bibliography. The present article is, in part, a topically organized and condensed version of these abstracted articles. Nevertheless, in addition to the works abstracted in the TFS bibliography, numerous additional works are described and discussed when they shed light on the particular subjects discussed. These additions were carried out at my discretion without significant input from GM.

The intent in this review is to provide a systematic examination of the combustion, flammability and toxicity features of materials associated with transportation and transportation fires. The reader is assumed to have sufficient scientific or engineering background to understand the technical content of this review. The background discussions found in each subsection are meant to outline relevant fundamental concepts and methods in each research field.

1.1. Fire safety

Three means are employed for addressing the problem of fire safety in vehicles and other modes of transportation.

Nomenclature		ΔH_c	enthalpy of combustion per mole (e/mol)
B	pre-exponential factor $((\text{mol/L}^3)^{-(n-1)} \text{t}^{-1})$	λ_g	gas phase thermal conductivity (e/L t K)
c_{pg}	specific heat per unit mass (of gas) (e/m K)	λ_s	solid phase thermal conductivity (e/L t K)
c_{ps}	specific heat per unit mass (of solid) (e/m K)	ρ	density (m/L ³)
C_i	concentration of species i (mol/L ³)	<i>Acronyms</i>	
E	activation energy (e/mol)	ABS	acrylonitrile–butadiene–styrene
h	heat loss coefficient (e/L ³ t K)	APB	ammonium pentaborate
k	rate constant, $k = R \exp(-E/RT)$ $((\text{mol/L}^3)^{-(n-1)} \text{t}^{-1})$	ATF	automatic transmission fluid
l	material thickness (L)	ASTM	American Society for Testing and Materials
l_q	distance from flame tip to fuel surface (L)	BART	Bay Area Rapid Transit System
\dot{m}''	mass flux of fuel from surface of decomposing fuel (m/L ² t)	CB	cement block
\dot{m}_{ig}''	mass flux at ignition (m/L ² t)	CFD	computational fluid dynamics
\dot{q}''	heat flux (e/L ² t)	CN	cyanide
\dot{Q}	heating rate (e/t)	CP	chloroparaffins
R	universal gas constant (e/mol K)	CWSS	cabin water spray system
S	surface area (L ²)	DIMS	direct inlet mass spectrometry
t_{ig}	ignition time (t)	DMMP	dimethyl phosphate
T_f	flame temperature (K)	DOT	Department of Transportation
T_{ig}	ignition temperature (K)	DSC	differential scanning calorimetry
T_v	surface gasification or 'vaporization' temperature (K)	DTA	differential thermal analysis
T_∞	ambient temperature (K)	EHOC	effective heat of combustion
V	velocity (L/t)	EP	epoxy
V_f	velocity of flame spread (L/t)	EU	European Union
V_g	velocity of gas flow (L/t)	EVA	ethylene-vinyl-acetate
V	volume (L ³)	FAA	Federal Aviation Administration
w	width of material (L)	FHA	fire hardening assessment
x_f	flame tip position (in wind-aided flame spread) (L)	FINN	finnacryl
x_p	pyrolysis front position (wind-aided flame spread) (L)	FMRC	Factory Mutual Research Corporation
Y_o	oxidizer mass fraction	FR	fire retardant
		FRA	Federal Railway Administration
		GB	gypsum board
		GC	gas chromatography
		GC–MS	gas chromatographic mass spectrometry
		GM	general motors
		HC	hydrocarbon
		HCL	hydrogen chloride
		HCN	hydrogen cyanide
		HDPE	high density polyethylene
		HR	heat release
		HR	high resistance
		HVAC	heating, ventilation, and air conditioning
		IPS or ImpPS	impact polystyrene
		IR	infra-red
		ISO	International Standards Organization
		LDPE	low density PE
		LDV	laser Doppler velocimetry
		LIFT	lateral ignition and flame spread test
		LOI	limiting oxygen index
		LSF	low smoke and fume
		MAR	marinite
		N	nylon
		NBS	National Bureau of Standards
<i>Subscripts</i>			
c	combustion		
f	flame		
g	gas		
ig	at ignition		
O	oxidizer		
s	solid		
∞	ambient		
<i>Greek symbols</i>			
α	thermal diffusivity, $\alpha = \lambda/\rho c_p$ (L ² /t)		
δ	heated segment of solid fuel in the plane of flame travel (L)		
Δh	enthalpy difference (e/m)		
Δh_c	enthalpy of combustion per unit mass (e/m)		

NHTSA	National Highway and Transportation Safety Administration	PP	polypropylene
NIST	National Institute for Standards and Technology	PRHR	peak rate of heat release
NT	Nord Test	PS	polystyrene
NYCTA	New York City Transit Administration	PU	polyurethane
OSU	Ohio State University	PVC	poly vinyl chloride
PA	polyamide	PX	perspex
PA-6	polycapolactum	RHR	rate of heat release
PA-7	polyoenantholactum	RUF	rigid urethane foam
PA-8	polycapylolactum	TC	thermocouple
PA-11	rislin	TFS	transportation fire safety (Bibliography compiled at GM)
PAR	policy accident report	TGA	thermogravimetric analysis
PC	polycarbonate	THR	total heat release
PE	polyethylene	TPRHR	time to peak RHR
PET	polyethylene terephthalate	TTI	time to ignition
PEU	polyether urethane	UFF	urea formaldehyde foam
PH	phenolic resin	UMTA	urban mass transit authority
PMMA	polymethylmethacrylate ('plexiglass')	VE	vinylester
POM	polyacetyl	W	wood

These are fire prevention, fire minimization and fire suppression.

In *fire prevention*, the choice of materials and minimization of potential ignition sources are of principal concern. Also important, if combustibles are used, are geometrical placement, orientation, and choice of the materials. The objective is to prevent ignition. For example, a tube constructed of a flammable material can safely carry premixed combustible gases when its inner diameter is smaller than the quench distance [2]. Provided that the external environment surrounding the tube is not itself hot. Despite their apparent simplicity, tube-quenching studies [3] may be especially relevant for fire safety in complex systems laden with potentially combustible liquid and gas-vapor fuels.

In *fire minimization*, one might employ fire resistant materials in locations where fire is believed likely to propagate. As in prevention, the choice of materials may vary. The geometrical configuration may be altered to reduce oxygen crossflow, for example, or the radiative view factor directed towards other, possibly non-combustible, surfaces, or the materials may be treated with additives to reduce their flammability. Additives may also be employed to reduce the toxicity of combustion by-products.

In *fire suppression*, one seeks to extinguish fire once it has begun. The location of the suppressant stream is important, as are the suppressant delivery rate, its chemical structure, the intensity and location of the fire and its exposure to the environment, all of which can alter the suppression effectiveness. Fire suppression is important in forms of transportation where large volumes of highly volatile fuel are stored near physically combustible surrounding materials.

The scientific and technical questions raised in all aspects of fire prevention, fire minimization and fire suppression are distilled into three research categories, namely (1) fire initiation, (2) fire growth, and (3) fire chemistry. All aspects of fire prevention, minimization or suppression can be discussed in terms of (1)–(3). In each of these research categories, it is helpful to picture the specific question under study in terms of an actual, physical model problem, or a set of model problems whose mutual similarities exceed their differences. The model problem may form the basis for a rational, interpretable technical engineering test.

1.1.1. Fire initiation

Fire initiation occurs when ignition yields self-sustained combustion, such as a propagating flame in a gas or a spreading flame over a liquid or a solid. Initiation is influenced by geometry (position and placement of materials), airflow, type and duration and placement of ignition source, ambient temperature, temperature of ignition source, and heat flux from the ignition source. For liquids and solids, the simplest case of fire initiation is the one-dimensional, transient exposure of a material to a heat flux or a high temperature. Fire initiation may thus be visualized as a one-dimensional, semi-infinite slab of material subjected to thermal insult. We note that fire above a liquid or solid requires gasification of the condensed-fuel phase because the flame is commonly situated in the gas. Exceptions such as combustion in unusual solids (e.g. propellants) and smolder fronts are not considered in this review. Pure gas-phase initiation occurs when a combustible gaseous mixture of fuel and oxidizer has been formed and ignited. The process of flame and fire

initiation is complicated, and one must realize that in nearly all applications, nearby surfaces are strongly involved and cannot be ignored. Indeed, the concept of pure gas phase initiation may be an unrealistic and counterproductive engineering-science simplification. A simple fire initiation configuration with relevance to real-world fire initiation involves a sample material placed horizontally, say, and then subjected to a constant heat flux in the presence of a nearby ‘pilot’ flame that provides the ignition source.

A model apparatus now commonly employed for fire initiation testing is the cone calorimeter [4–6]. It is the most widely used device for static material flammability tests although other methods are used, like the French ‘*épiradiateur*.’ The cone calorimeter will be extensively discussed in Section 2.

1.1.2. Fire growth

The incipient flame kernel may propagate (in the gas, as in SI engines or vapor-filled fuel tanks, for example) or spread (over a liquid or solid fuel). The expansion of the flame is referred to as fire growth, although some qualifications are necessary. A small O (1–10 cm) flame is seldom referred to as ‘fire’. A large conflagration is never referred to as a ‘flame’, but instead as a fire. However, a fire may consist of individual flames.¹ Thus, the words flame and fire are commonly and ordinarily associated with scale. The former is an element of the latter, never vice versa. We refer to ‘fire growth’ in this review because fire safety analysis requires that we deal at a minimum with human-scale conflagrations, not laboratory-scale flames.

Fire growth is therefore a multi-dimensional process involving airflow, products of combustion, flame and surface radiation, and other physical phenomena. It is useful to visualize fire growth as a partially burning surface with fire spreading from the burned (involved) region to the unburned (virgin) region. In wind-aided fire spread the gas flow assists spread (e.g. upward fire spread over a wall) whereas the gas flow opposes spread in wind-opposed spread (e.g. downward fire spread over a wall). These two model configurations have in common the advancement, or spread, of the fire front from one location to the next. However, they are almost completely different processes because wind-aided spread is intrinsically distinct from wind-opposed spread.

The model apparatus associated with fire spread either upward, downward or sideways is the LIFT (Lateral Ignition and Flame Spread Test) apparatus, devised by Quintiere [7]. Test devices like the LIFT apparatus make *dynamic* fire measurements because they examine the *propagation of a flame front*. In the cone calorimeter the flame does not move, hence it is referred to as a *static* test even though the burning sample surface is consumed. This consumption can be

compensated by supplying new fuel at the same rate, in which case the Cone test would truly be static.

1.1.3. Fire chemistry

Fire chemistry differs from ordinary chemistry in the more specialized sense of referring (generally) to hydrocarbon fuel oxidation. Fire chemistry also differs from laboratory chemistry in the fact that in real fires, unlike small-scale laboratory flames, the reactants and products of combustion convect and diffuse into the surroundings. In addition, reactants and products of combustion can also mix. These real-world complications can produce differences from laboratory experimental studies in which fire toxins and other products of combustion are examined in idealized homogeneous chemical calorimeters or similar scientific apparatuses. In fires, the transport of these substances is generally transient, three-dimensional and highly dependent on geometry and flow patterns. The following quotation reiterates the importance of flow and transport in fire [8]: “...During the (last 25 years) it (has become) clear that while chemists had done excellent chemistry, this had little to do with fire. For most, but not all fire processes, chemical kinetics is essentially infinitely fast. The rate-controlling steps in the fire are the dynamic processes which mix, heat, and ignite the fuel and air.” We add that the rate is also affected by processes that transport the products of combustion. In this review the only aspects of fire chemistry that are considered are those occurring after the principal heat releasing reactions are finished. Combustion toxicity, for example, deals with the consequences of the formation of ‘slow’ chemical species that linger and cause harm due to their very nature and concentration as chemical species, not because they release heat.

The chemical bomb calorimeter and other standard chemical diagnostics are used for chemical testing [9]. It has been recognized, however, that species movement or transport by convection and diffusion are also important processes, as textbooks in combustion amply illustrate [10].

1.1.4. Summary

Fire initiation, fire growth and fire chemistry are relevant in different stages of transportation fires and the aspects of transportation fires can be discussed in terms of these three categories of fire processes. If no fire is to be permitted, growth and chemistry need not be discussed: initiation is the most important steps. If initiation cannot be absolutely prevented, growth and chemistry must be carefully examined. If initiation and growth are possible, the chemical production and transport of species (chiefly products of combustion) are important. All articles in this review deal with one or another of these stages of fire.

1.2. Discussion

This review is organized as follows. In Section 2 we examine fire initiation, subdivided into flammability and

¹ A very small flame is called a ‘flamelet’ in turbulent combustion. A flame may consist of many flamelets.

ignition studies and testing based on the rate of heat release (RHR), cone calorimetry, and diagnostic methods for material degradation and combustion. In Section 3 we examine fire growth, subdivided into sections focused on fire and flame spread and the influences of external variables such as ambient temperature and oxygen delivery rate, among others. In Section 4 we consider fire chemistry. The principal focus is on products of combustion, with emphasis on toxins. The subcategories are products of combustion, toxicity, smoke, retardants, and inhibition. In Section 5 some practical studies related to transportation fires and commonly used combustible materials like polyurethane (PU) are addressed. A brief conclusion section is provided.

2. Fire initiation

Fire initiation is defined as the onset by ignition of self-sustained combustion. Thus, gas-phase ignition must generally occur before fire initiation is possible because solid-phase combustion of the kind observed in propellants, for example, seldom occurs in transportation: ignition of a gas, liquid or solid is therefore usually a gas-phase process.

Combustion, whether intended (as in an engine cylinder) or unintended (as in an accidental fire) is defined as an exothermic (heat releasing) chemical reaction between a fuel and an oxidant. Most combustion reactions in transportation involve hydrocarbon (HC) fuels with air as the ordinary oxidant. The HC fuel may be in any phase: gas, liquid, solid or any combination of the three (e.g. melting plastics, sprays with liquid droplets and fuel vapors, burning solids with liquid melt layers underneath gaseous flames). Some of the possible ignition mechanisms are thermal radiation, electrical spark, adjacent flame, and conductive heating. The most common ignition mechanism in transportation is likely the spark plug in IC engines: gas turbine engines employ a pilot flame. Any or all of these mechanisms are possible in fire, singly and in combination. In an unplanned or accidental fire it is often a confluence of events that may lead to ignition. Quantities employed to describe ignition include time to ignition, ignition temperature, ignition heat flux, ignition mass flux of volatiles from a heated liquid or solid surface.

2.1. Ignition of gases, liquids and solids

2.1.1. Gases

Ignition will occur when a volume of gas reaches a temperature sufficiently high that self-sustaining exothermic chemical reaction can prevail against heat losses by conduction, convection and radiation to the surroundings. In the simplest case of a stationary, homogeneous, fixed volume V of gas, ignition is a balance between rate of heat generation by chemical reaction and rate of heat loss by conduction or radiation. If the gas temperature is sufficiently high, the former will exceed the latter, leading to ‘thermal

runaway’ or ignition [11, pp. 284–291, pp. 576–581,12]. As combustion proceeds, the burning gas volume will extinguish when the reactant in shortest supply (the ‘limiting’ reactant [12]) is finally consumed. A representative graph of the ignition event, including eventual extinction, is shown in Fig. 1. Note the rapid rise of temperature at ignition. Thermal runaway (a rapid rise of temperature of the order of 10^3 °C in a short time interval of the order of 1 ms) is followed by a temperature plateau of steady combustion. A simple global or ‘lumped’ equation illustrating this balance is

$$\rho c_V V \frac{dT}{dt} = \dot{Q}_{\text{gen}} - \dot{Q}_{\text{loss}}. \quad (2.1)$$

If the heat generated in the volume V is greater than the heat lost, the temperature will rise, and vice versa. The global chemical heat generation term is of the form $\dot{Q}_{\text{gen}} = |\Delta H_c| V B C_R^n \exp(-E/RT)$, which increases exponentially with temperature (T) rise and decreases algebraically with decrease of reactant concentration, C_R . Here, n is the order of the chemical reaction, $|\Delta H_c|$ is the chemical heat release per mole of reactant R , B is the pre-exponential factor (units $t^{-1}(\text{concentration})^{-(n-1)}$) and E is the activation energy for the reaction. The heat loss term depends algebraically (not exponentially) upon temperature, and is often represented in the form $\dot{Q}_{\text{loss}} = hS(T - T_0)$, where S is the surface area of the volume of gas and h is a ‘heat-loss coefficient’ [9,11, pp. 579–580, 13]. Such models with lumped parameters are useful for characterizing the complex phenomena of ignition. The principal assumption in such lumped models is that transport is infinitely fast and all gradients of T, C_R are instantaneously leveled in the region under examination. Needless to say, such ideal conditions are not met in ordinary practice, hence Eq. (2.1) is simply a model that is used to characterize the general features of ignition problems. The goal is to produce reasonable order-of-magnitude estimates and functional dependencies.

The analysis of the most simplified version of Eq. (2.1), with $C_R = \text{constant}$ (i.e. no reactant depletion!), $V = \text{constant}$, $S = \text{constant}$, $h = \text{constant}$ is straightforward. Consider a plot of the two heating terms as functions of temperature, see Fig. 2. Shown is a single \dot{Q}_{gen} and four \dot{Q}_{loss} terms, each with a different hS value. The \dot{Q}_{gen} term can also be changed by varying, for example, $|\Delta H_c|$, C_R , B or E . For low temperatures the term \dot{Q}_{gen} is larger than \dot{Q}_{loss} . Depending on the value of h , however, the loss term may subsequently: (1) never intersect the generation term; (2) intersect (touch) it at one point; (3) intersect it at two points.² Case (1) is always explosive, case (3) is explosive only when $T > T_2$. The intersections defined by the locations T_1, T_2 are the stationary solutions of Eq. (2.1),

² The real case in which reactant depletion finally diminishes the generation term is not examined here. The extension can be found in the literature [13].

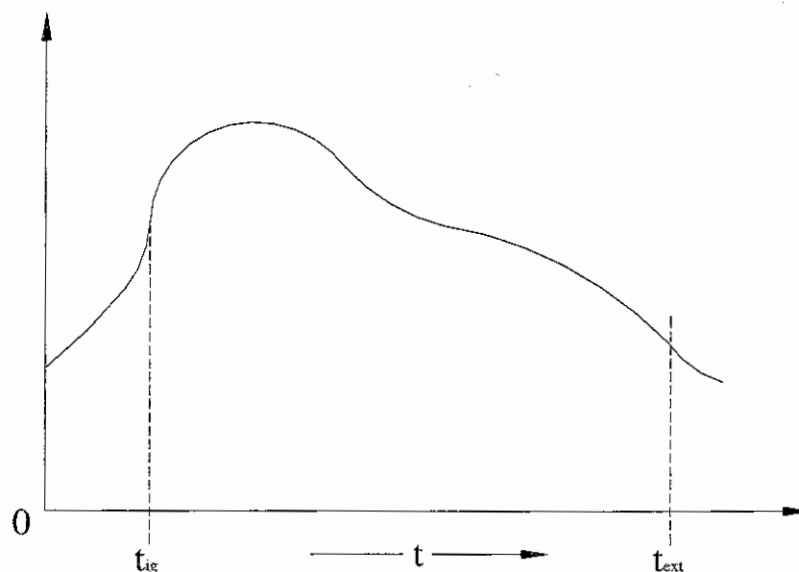


Fig. 1. Temporal plot of temperature in a combustion calorimeter. The ignition and extinction points are indicated. The leveling after ignition is produced by reactant depletion (which is not included in the simplified presentation given here).

where $dT/dt = 0$. Point 2 is unstable whereas point 1 is stable, meaning that a small perturbation of the solution for T at point 1 returns to that point. The division between always explosive and possibly non-explosive behavior occurs for curve (2). At this so-called 'critical' condition, it is easily shown that the Semenov number Se is given by

$$Se = \frac{1}{e} = \frac{\text{(chemical rate of heat release)}}{\text{rate of heat loss to surroundings}} \quad (2.2)$$

$$= \frac{|\Delta H_C| (k C_R^n V)}{h (RT_0^2/E) S},$$

$$k = B e^{-E/RT_0}$$

When $Se < 1/e$, the mixture is in regime (1), explosive; when $Se > 1/e$, the mixture is in regime (3), which is potentially non-explosive between points 1 and 2 (bounded by T_1 and T_2). Se is the ratio of heat generation rate to heat loss rate, so a physical interpretation of the criterion $Se \leq e^{-1}$ is possible. Se is increased by increasing S/V : of all common geometric shapes the sphere has the largest value of S/V . It is increased by increasing the heat loss coefficient h , and by decreasing the chemical reaction rate (by decreasing B or increasing E , or both).

It is also possible to examine the differential equation in order to determine the time to ignition, t_{ig} . When ignition is approached, the generation of heat by chemical reaction exceeds the heat losses. The continual thermal energy feedback produces a sharp rise in the heating rate, or rate of temperature increase. Consequently, in the lowest approximation the time to ignition is determined as the time at

which the $T(t)$ vs. t slope becomes infinite. The result is

$$t_{ig} = \frac{\rho C_V (RT_0^2/E)}{|\Delta H_C| k C_R^n}, \quad k = B e^{-E/RT_0} \quad (2.3)$$

which provides the parametric proportionalities for gas-phase ignition of combustible mixtures. The dependence upon all parameters except E and T_0 is algebraic, and therefore not highly sensitive, whereas the dependence in E and T_0 is exponential, and therefore extremely sensitive. The primary function of a spark, for example, is to raise the local temperature, thereby decreasing exponentially the time to ignition. For example, with $E \approx 30 \text{ kcal/mol} = 126 \text{ kJ/mol}$ we see that increasing T_0 from 500 to 1000 K decreases the ignition time by the factor $e^{-15} = 3 \times 10^{-7}$, whereas increasing T_0 from 1000 to 1200 K decreases it by $e^{-2.5} = 8 \times 10^{-2}$.

Consequently the ignition of a combustible gas mixture can be understood as a balance between heat generation by chemical reaction and heat loss by conduction, convection, and radiation. The volume of gas to be ignited must be sufficiently large (with characteristic linear dimension approximately comparable to flame thickness [11]), the ignition temperature must be sufficiently high (greater than or equal to T_2 in Fig. 2), and reactant depletion cannot be an important limitation in the early stage of ignition. These concepts are useful for understanding ignition of flame over liquid and solid fuels, since ignition nearly always occurs in the gas.

Several limitations cloud this idealized picture of ignition. One of these is that the heated gas volume V must be approximately at least as wide as the characteristic flame thickness during combustion. If the heated volume is

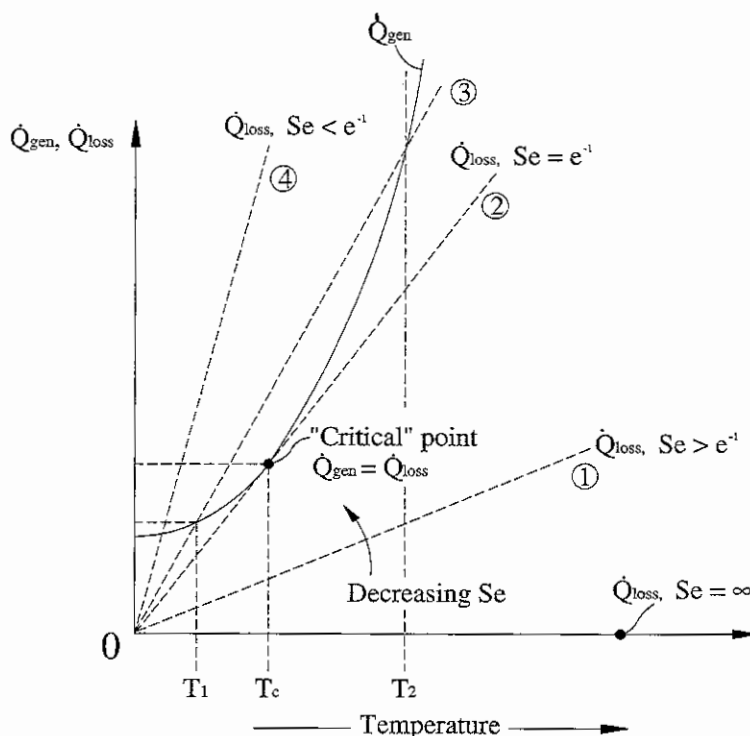


Fig. 2. Idealized plot of \dot{Q}_{gen} and \dot{Q}_{loss} versus temperature. Reactant depletion is neglected, else the diminishment of C_R^2 would cause \dot{Q}_{gen} to decrease. A leveling off should also occur (without reactant depletion) as $T \rightarrow \infty$ since $\exp(-E/RT)$ approaches unity in that limit. This 'leveling-off' region can be considered as being to the right (on the graph) of the region shown. When $Se = e^{-1}$, the curves for \dot{Q}_{loss} and \dot{Q}_{gen} touch at only one point. Curves resembling '1' are always explosive, whereas curves resembling '4' are non-explosive.

smaller, the heat losses to the surroundings are large enough to self-quench the incipient reaction, regardless of temperature [3,10,11, pp. 268–271]. Another limitation is that real gases undergo thermal expansion when they are heated. Therefore, the volume of gas being heated changes during heating unless ignition occurs in a constant volume bomb calorimeter. The constant volume bomb calorimeter, used in practice to measure the heat release of various fuels in oxidizing environments, is a commonly used ignition device, whose operation is described in Ref. [14] and whose uses in ASTM testing are listed.³ Another means of ignition keeps pressure, not volume, constant, so the gas volume changes during heating. It is difficult to conduct systematic ignition experiments because

³ Many ASTM tests use the bomb calorimeter. From the ASTM website (www.astm.org) one finds the following tests related to transportation: D4809-95 (Heat of Combustion of Liquid Hydrocarbon Fuels); D-4368-90 (Heat of Combustion of Burner/Diesel Fuels); D6446-99 (Net Heat of Combustion—Specific Energy—of Aviation Fuels); D6227-99 (Standard Specification for Grade 82 Unleaded Aviation Gasoline); D6202-00a (Evaluation of Automotive Engine Oils on the Fuel Economy of Passenger Cars and Light-Duty Trucks in VIA Spark Ignition Engine); D5862-99a (Evaluation of Engine Oils in Two-Stroke Cycle Turbo-Supercharged 6V92TA Diesel Engine).

the buoyancy-induced flow caused by the rising heated gases adds fluid-dynamic complexity to ignition. Thermal expansion and buoyancy introduce flows that are difficult physically to quantify and experimentally to reproduce. For this reason, many gas ignition measurements are conducted in the constant-volume bomb calorimeter. These data are of limited value, however, because fire initiation generally occurs at constant pressure, not constant volume. Other complications include crossflows, concentration gradients, multi-stage ignition [15], oscillatory ignition, heat losses to non-simple nearby surfaces, gas mixtures containing particulates, and additional processes too numerous to mention in this review. The interested reader may consult books and articles and symposia proceedings devoted to the subject of ignition.⁴

In the initiation of fire over liquid and solid fuels, ignition into flame occurs in the gas. The condensed phase must be gasified to produce a combustible gaseous mixture of fuel vapor and oxidant (air), usually above or near the gasifying condensed material. The mass flow rate of volatile products

⁴ See, e.g. volumes of the Combustion Symposia (International) in which whole sections are devoted to ignition in numerous practical problems. Also, the Fire Safety Science Proceedings contains discussions of ignition relevant to fire.

of condensed phase pyrolysis or gasification must, in general, be sufficient to produce what may simplistically be referred to as the *lower flammable limit* of the fuel/oxidizer mixture. This mixture can be ignited by an external (pilot) source. Numerous complications arise, however. Among these are spatially inhomogeneous temperatures and reactant concentrations, heat losses from gas to condensed phase, flows in both phases, influences of buoyancy. For all of these real-world reasons, the ‘lower flammability limit’ referred to previously is usually an unmet and unrealized idealization, and as such is unable to properly characterize the actual condition of the gas at ignition. In other words, it is not the flammability of the mixture itself, rather it is a combination of conditions met by the mixture and the surroundings that permits ignition to occur. Self-ignition is generally not relevant to many applications in fire. Piloted ignition tests are more common [16,17]. In such ignition tests, a small ‘pilot’ flame is placed at or near the condensed phase surface (where the fuel vapor and air are most nearly well mixed) for a fixed time interval, then it is withdrawn. Ignition occurs when combustion is sustained without the pilot flame.

2.1.2. Liquids

In order to ‘ignite a liquid fuel,’ the liquid must be sufficiently heated for a flammable fuel vapor/air mixture to form above the liquid phase. As for pure gases, two limits of flammability or ignitability are employed. These limits are the lean limit (where the vapor-phase mixture is fuel-lean) and the rich limit (where the vapor-phase mixture is fuel-rich). Sustained ignition, or flaming, is attained when the fuel production rate from the vaporizing liquid fuel can generate a flame whose heat release rate is large enough to overcome heat losses to the liquid, the ambient gas and any nearby walls or surfaces. Three common measures of liquid fuel flammability form the bases for liquid flammability tests. These are the closed-cup flash point, the open-cup flash point and the theoretical flash point. The *closed-cup flash point*, which is measured in a closed, uniformly heated vessel, is the temperature at which the vapor pressure of the liquid fuel rises to the lower limit of flammability of the fuel vapor in air (or other oxidizer). The *flash point* is the fuel liquid surface temperature at which the fuel vapor above the liquid will ignite into flame in the presence of a pilot flame. In the open-cup flash point test the vessel is open to the ambient atmosphere.

The closed cup flash point test overlooks the important role of concentration and temperature gradients in the gas mixture and possibly the liquid fuel. It is a homogeneous measure, which provides a thermodynamic ignitability criterion ideally independent of the actual surroundings.

The open-cup flash point test accounts for gas phase gradients of concentration. These can be altered by buoyancy (natural convection) and forced convection, as well as the constituents of the prevailing gas mixture (air, diluted air, oxygen, ...) If the pilot flame is very small, ignition can

depend upon pilot location, whether too far from the surface for significant diffusion of fuel or too close to the surface (i.e. within the flame quenching distance). The optimum pilot location may differ for each fuel, for it may depend upon fuel density, specific heat and conductivity and other properties. Additionally, ignition depends upon the liquid fuel in-depth temperature, not merely on the (higher) temperature of the heated surface layer. Consequently, inhomogeneity and transient evolution may alter ignitability in the flash point test [16,17].

2.1.3. Solids

To describe the flammability of specific combustible materials in the simplest possible burning configuration (the burning slab) one attempts to answer the question “How does the heated surface ignite into flame?” Four explanations have been put forth. Two are based on attainment of a critical surface temperature or a minimum volatile mass flux into the adjacent gas. The remaining two explanations require a minimum oxygen concentration and a minimum external heat flux. Complications arise because these four criteria are closely related and may depend upon other, external variables. The surface temperature and mass flux depend on the oxygen mass fraction and heat flux, and the surface mass flux may be a function of the surface temperature, and the influence of the air velocity and velocity field may need to be quantified. The flow field is one of the ‘external’ factors whose influence is difficult to quantify. The incident heat flux is the most primitive flammability ‘property’. The practical measure of interest is the time to ignition. Most tests specify the oxygen concentration and the ‘applied’ heat flux.

Heated gaseous fuels and warm air, mixed to the correct proportions, can self-ignite. In many fires thermal radiation from nearby flames, or a nearby layer of hot product gases, or hot walls in close proximity to the surface are the primary reasons why as-yet-unburned materials ignite into flame. This ignition may be spontaneous (self-ignition) or piloted. The most rigorous test of flammability exposes the heated sample to a pilot flame. The two kinds of pilot flames are continuous and intermittent. Unless a gas flow is present, the continuous pilot may alter the energetics of the flammability test, bathing the sample in an additional stream of heat. Hence, the intermittent pilot is often preferred. The intermittency interval should be a mere fraction of the characteristic sample heat-up time, which is measured as the quotient of the square of the sample thickness and its thermal diffusivity, $t_{\text{heat-up}} \approx L^2/\alpha$, $\alpha = \lambda/\rho c$. In the limit as the intermittency level approaches the sample heat-up time there really is no intermittency and heating is in fact continuous. Since a knowledge of the influences of the heat flux is crucial, the conditions at the rear of the heated sample (Fig. 3) are important, because the overall energy balance can be influenced by this region. If the sample is ‘thick’, the conditions at the rear face do not influence

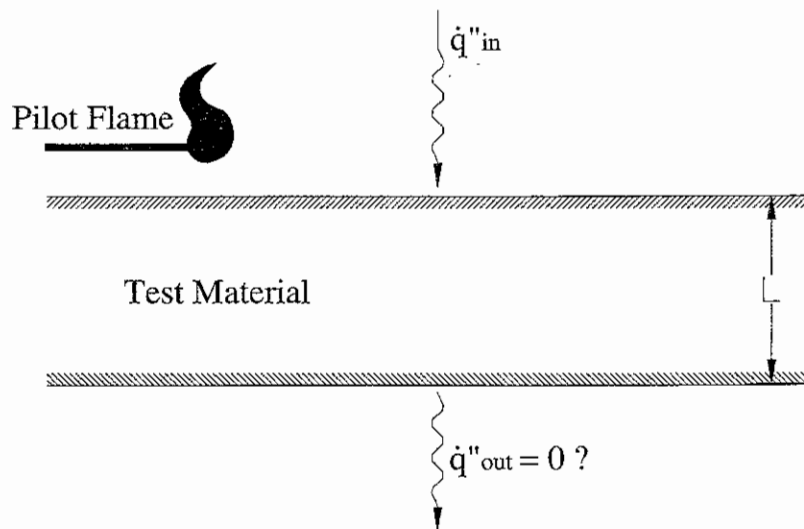


Fig. 3. Piloted ignition of a combustible solid subjected to heat flux q''_n . The location of the pilot may alter ignition. The thickness of the solid may be important if heat losses occur from the back.

burning. If, however, the sample is 'thin', the conditions at the rear face of the sample must be carefully controlled. Here, thick and thin mean 'thermally thick' and 'thermally thin'. A material is thermally thick if, during the course of the entire flammability test, its rear face does not detect the thermal insult received at its front face. It is thermally thin when the thermal response of the front and rear faces occurs simultaneously.

Experimental data are always interpreted through a theoretical explanation. Consider Mikkola and Wichman [18] and Atreya and Abu-Zaid [19], in which an explanation is provided for the differences in the dependence of the critical incident heat flux for thermally thick and thin materials. For incident heat fluxes below the critical heat flux, the heated surface will not undergo piloted ignition even if the surface is indefinitely heated. Above the critical heat flux, piloted ignition is possible. The explanation of Mikkola and Wichman [18] rested on the formulation of a simple model which consists essentially of an energy equation in the heated solid integrated over the heated volume. Thus, we have

$$t_{ig} = \rho_s c_s l (T_{ig} - T_\infty) / \dot{q}'' \quad (2.4)$$

for piloted ignition of a thin sample of thickness l and

$$t_{ig} = \frac{\pi}{4} \rho_s c_s \lambda_s (T_{ig} - T_\infty)^2 / \dot{q}'' 2 \quad (2.5)$$

for piloted ignition of a thick sample. Here, t_{ig} is the time to ignition of the material, which is subjected over this time period to the net heat flux \dot{q}'' . Eqs. (2.4) and (2.5) do not explicitly contain heat losses, which are therefore included in \dot{q}'' . The solid density, specific heat and thermal conductivity are ρ_s , c_s , λ_s , respectively. The ambient

temperature of the surroundings is T_∞ , and T_{ig} denotes the temperature of the solid at the moment of ignition. Experimental data plotted in this manner fall accurately onto straight lines confirming both the qualitative and quantitative accuracy of the theory. The critical heat flux is obtained by the extrapolation of these lines to $t_{ig} = \infty$, as shown in Fig. 4a and b. The extrapolation to $t_{ig} = \infty$ is not permitted by this simple model, however. A more detailed examination of this limit is found in Ref. [19], which demonstrates the inaccuracy of the extrapolation while explaining limiting ($t_{ig} \rightarrow \infty$) ignition heat fluxes in terms of convective gas flow. The lines shown in the figures actually curve near the point $t_{ig} = \infty$, where the correlations of Eqs. (2.4) and (2.5) break down.

We notice from Eqs. (2.4) and (2.5) that the equations relate ignition time, external heat flux and attainment of critical surface temperature. If, in addition to the fuel surface: (1) the narrow nearby gas region is also heated to T_{ig} ; (2) the concentration of the constituents (including the gaseous oxidizer) renders this heated layer of gas ignitable and combustible; and (3) the mass gasification rate is sufficiently high, then a self-sustaining flame may be produced over the heated, pyrolyzing, combustible surface. Transition from ignition to flaming will then occur, resulting in fire initiation.

2.2. Flammability and ignition

In this section we first describe basic features of flammability and ignition of real materials by describing a complicated, real example of ignition in Section 2.2.1. Then in Section 2.2.2 we discuss the TFS Bibliography references on flammability and ignition.

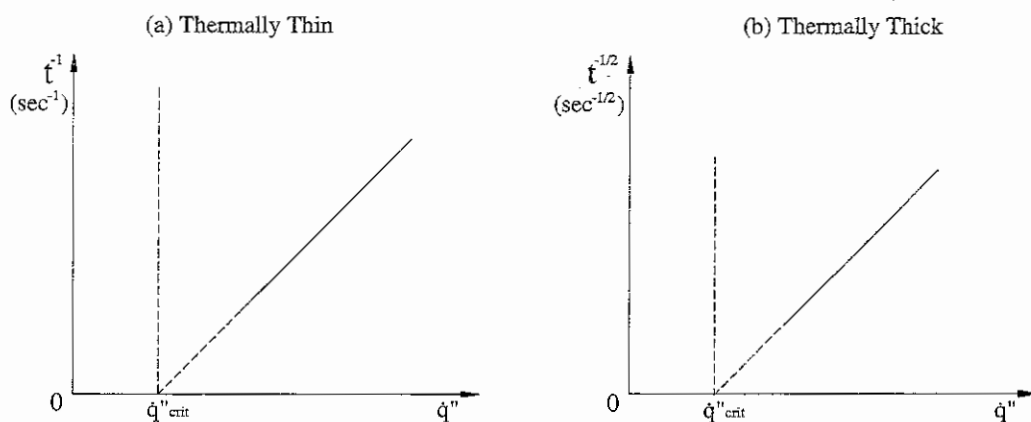


Fig. 4. Plots of \dot{q}'' versus t^{-1} (thin fuels (a)) and $t^{-1/2}$ (thick fuels (b)), showing the near-linear dependence as predicted by the ignition equations. As $t \rightarrow \infty$, the predictions break down, and mechanisms that have been neglected become important.

2.2.1. Fundamentals of flammability and ignition (an example)

Many experimental methods have been developed for investigating ease of ignition and material flammability. Generally the fuel sample, whether in a vertical or horizontal position, is exposed to external radiation in the presence of a pilot flame. The time required to initiate sustained flaming is measured along with the sample surface temperature [20] (AW). These data are correlated to produce an empirical ignition criterion. Several empirical criteria have been proposed, among them: critical surface temperature T_{ig} at ignition (Eqs. (2.4) and (2.5)); critical fuel mass flux \dot{m}''_{ig} [21]; critical mean solid temperature [22]; and, for cellulosic or charring materials, critical char depth [23]). According to AW, “the critical fuel mass flux at ignition seems to be physically the most correct, but surface temperature has proved to be the most useful, since it can be conveniently related to the fire spread rate.”

As noted in AW, these four ignition criteria are indirect measures all of which are presumed closely related to ignition. The actual ignition process requires first that the heated solid fuel chemically decompose, resulting in the injection of fuel gases to the surrounding air. The fuel gases then mix with the surrounding air to produce a flammable mixture that is ignited by the nearby pilot flame. To achieve sustained ignition, the fuel production rate from the decomposing condensed fuel must be sufficient to produce a flame whose heat release rate is large enough to overcome heat losses to the surface and the surroundings.

A full computational description of piloted ignition requires a transient, multi-dimensional model for the simultaneous processes of solid-phase thermochemical decomposition and gas-phase mixing and combustion [AW]. Limited progress toward such computational models has been made [24,25]. The “absence of such comprehensive models has necessitated the various attempts to develop

the (empirical) ignition criteria” [AW] that were outlined at the beginning of Section 2.1.3.

In order to establish ideas, we presently examine the history, from inception of heating to ignition,⁵ of heated red oak as shown in Fig. 5 (AW). In the initial heating stage, the fuel responds as predicted by heat conduction analysis. The temperature rise for the thermally thick sample shows a $t^{1/2}$ time dependence. Near to but preceding the ignition time, flashes of unsustained flaming occur in both the vertical and horizontal sample configurations. When the external heat flux is low ($\dot{q}'' \sim 0$ (0.1 kW/m²)), a sufficient elapse of time occurs between flashes for the sample surface to thermally equilibrate with the externally applied radiant flux. Between flashes the surface temperature resumes its previous monotonic, steady increase. The surface temperature at the commencement of sustained flaming is lower than the momentary maximum flash temperature. The flashes occur because the pyrolysis of the sample produces combustible fuel vapors of insufficient quantity for sustained, continuous burning. In addition, because the surface temperature is lower than required for full burning, heat losses to the surface from the flashes prevent sustained ignition from being achieved during the flashes. From Fig. 5 we see that sustained flaming occurs when the surface temperature produced by external heating rises to a critical value of approximately 650 K. As observed by AW: “The contributions of the gas phase exothermicity must not be included in the determination of this critical value (of the surface temperature). Furthermore, the total heat contribution to the solid (from the) flashes (which is proportional to the area

⁵ Atreya [35] and Wichman [20] focused on cellulosic fuels but many noncellulosics—which are also polymeric long-chain HC fuels—show the same pattern of behavior. Sustained flaming by piloted ignition occurs when surface temperatures are of the order of 700 K and deviations are usually not more than 10–20%. See the data in Appendix F of Ref. [9].

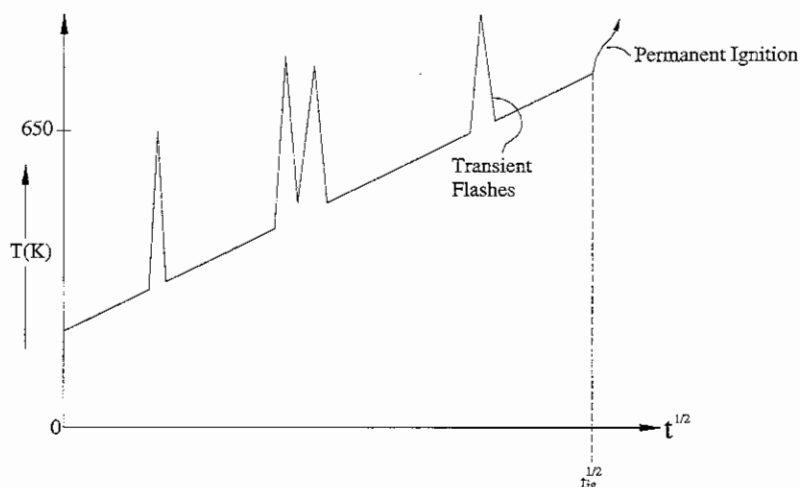


Fig. 5. Surface temperature versus time history for a sample of red oak subjected to $\dot{q}'' = 1.9 \text{ W/cm}^2$. Sustained ignition occurs at $t = 750 \text{ s}$, $T_{ig} = 372 \text{ }^\circ\text{C} = 645 \text{ K}$, even though temperatures at flashes exceed T_{ig} .

under the peaks) is small compared to that (from the external flux). Thus, it may be concluded that although the heat lost by the flame to the solid at the instant of ignition is significant (and may cause thermal quenching, resulting in a flash) its contribution to the enthalpy rise of the solid is negligible and, consequently, the critical conditions for ignition are achieved primarily by the (external heat flux).” AW provides formulas that relate the sample surface temperature at ignition to the critical mass flux at ignition for various external heat fluxes. The theoretical model developed in AW incorporates all four ignition criteria described at the beginning of Section 2.1.3.

2.2.2. Flammability and ignition literature review

The focus of most of the works discussed here is on the flammability and ignition of solids and liquids. As discussed, numerous ignition criteria have been used by various researchers, one or another according to preference. As also discussed, an actual ignition criterion is much harder to develop and it requires careful consideration and analysis. It is far simpler to revert to a standard definition, which singles out one of the main physical processes. Thus, Hilado and Clark [26,27], Settle [28], Clark [29], Thompson and Drysdale [30] and Thompson et al. [31] employ the critical temperature as the sole ignition criterion, while Richard et al. [32] and Drysdale and Thompson [33] employ the critical mass flux and Yang et al. [34] employ the limited oxygen index (LOI: ASTM D-2863) test. None of these works consider the critical heat flux for ignition.

The critical temperature of ignition T_{ig} is the most common quantitative measure of material flammability, as described in Chapter 4 of the book by Quintiere [17]. In Ref. [26], a discussion is provided of pre-1972 methods for obtaining the autoignition temperature (i.e. no pilot flame) via four methods. These include the Arrhenius and Semenov

equations, normalization of T_{ig} according to ignition delay time, t_{ig} , and, for liquids, by injecting a liquid sample into a heated flash in the presence of air and then measuring the lowest temperature at which ignition occurs. This is defined as the ‘flash’ temperature. Tests show a decrease of T_{ig} and t_{ig} as the flash volume increases, presumably due to a reduced surface-to-volume ratio. The reduced surface-to-volume ratio decreases heat losses from the flask.

Hilado and Clark [26] found the largest discrepancies in T_{ig} data between combustion engine studies and fire safety studies. They suggested the adoption and use of normalized T_{ig} values. The normalization was to be achieved by grouping into categories of similar ignition times, such as 1, 10 or 100 s, so that ‘unintentional bias due to differences in apparatus volume and ignition delay time’ may be eliminated. Hilado and Clark [27] subsequently compiled T_{ig} values for over 300 liquefied organic chemicals. Their list provides the lowest reported T_{ig} value using the glass flask apparatus discussed in Ref. [26], which amounts to ASTM D 2155 where a metered sample is injected into a heated $200 \text{ }^\circ\text{C}$ glass flask containing air. Fire-protection groups also commonly report lowest values, for obvious reasons. An approximate analytical relation between T_{ig} and t_{ig} is provided, along with the Arrhenius equation describing the influence of temperature on reaction rate. The equation takes the form $\log(t) = (A/T) + B$, where A and B are constants, t is the ignition-delay time and T is the temperature. This equation is obtained directly from the Semenov equation, Eq. (2.3). The article also discusses numerous test methods that were developed by organizations such as ASTM, the National Bureau of Standards, The US Naval Research Laboratory and various corporations and universities.

In contrast to Refs. [26,27], the work of Settle [28] employed a small, horizontal, electrically heated

stainless-steel plate to examine T_{ig} for the instantaneous (non-piloted) ignition of nylon, viscose, acrylic, polypropylene (PP) and wool. The plate temperature was fixed, the sample and plate touched for 2 s, then the plate was lowered and its temperature rose by 25 °C until ignition occurred upon subsequent two-second contact. The maximum temperatures for non-ignition lay between 650 °C (for nylon, viscose) and 750 °C (for wool). The minimum T_{ig} ranged from 675 °C (nylon, viscose) to 760 °C (wool). On an absolute temperature scale, the relative difference between these ignition temperatures is lower than 10%. Methods of measuring ignition temperature and autoignitability generally no longer employ direct contact between test sample and heat source because of the complexities associated with the direct contact test configuration. Direct contact is also problematic because of the complicated nature of the heat and mass transfer processes that take place when a material is heated: it changes phase, releases volatile vapors and internally degrades. The conductivity of the heater plate, the formation of a liquidous melt, the duration of contact, the accessibility of oxidizer to the heated surface are difficult to account for, describe, rationally specify, or calculate, respectively. These or other phenomena may account for the fact that constant ignition temperatures are nearly 300 K higher than those measured using non-contact techniques (see footnote 5).

Subsequent work has emphasized radiant heating, which mirrors more accurately the situation in many real fires. Clark [29] studied the ignition of solid polymers using a radiant heater and a pilot in the form of a periodically discharged Tesla coil. Samples, whose sizes ranged from $5 \times 5 \times 4 \text{ mm}^3$ to $20 \times 20 \times 17 \text{ mm}^3$ (last dimension is depth), included plexiglass (PMMA), polyethylene (PE), polycarbonate (PC), and red oak. Some of these materials melt under heating. Some, such as oak, PC, and PE form char. PMMA was the only material that did neither char nor self-extinguish following ignition. The smooth-burning characteristics of PMMA are well known and form the basis for its common use as a test material [36]. It was not clear from Ref. [29] why small (25 mm^2) samples were harder to ignite than large (400 mm^2) samples, although edge losses are a possible explanation for this phenomenon. For small samples the ratio of the edge area to the sample surface area can become large. In Ref. [30], times to ignition (t_{ig}) and T_{ig} were measured for six thermoplastics using a conical radiant heater. The plastics were perspex (PX), finnacryl (FINN), polyacetyl (POM), PE, PP and polystyrene (PS). The external radiant flux varied from 10 to 40 kW/m^2 . The data 'show too much scatter to reveal any pronounced trend' except for PMMA, 'which showed a decrease in T_{ig} at the lowest heat flux used.' Below 20 mm^2 surface area, however, T_{ig} became a function of the irradiated area. The sample surface temperature was monitored using thermocouples. PS had the highest T_{ig} of 370 °C (643 K) at a heat flux of 19 kW/m^2 . The time to ignition at this heat flux was little over a minute, $t_{ig} = 67 \text{ s}$. The authors found between PX and POM that the latter had

the lower T_{ig} but the higher t_{ig} . This seeming paradox was explained though the influence of higher thermal inertia (product of density, specific heat and thermal conductivity, $\rho c \lambda$, see Eq. (2.5)) of POM. The results for t_{ig} were much more sensitive to the flux level, leading to the call for a 'better understanding of the interrelationship between the spectral characteristics of the source and the absorption characteristics of the target polymer.'

A similar experiment was carried out in Ref. [31], although this latter study employs an International Standards Organization (ISO) apparatus. The ignition was piloted. It was found that significant temperature increases of the heated sample surface up to 15 K occurred following pilot flame applications near T_{ig} . As the external heat flux increased, the value of t_{ig} decreased. The two test heat fluxes used were approximately 12 kW/m^2 (ranging from 10 to 15 kW/m^2) to 50 kW/m^2 . The t_{ig} values averaged approximately 1400 s at the former and 44 s for the latter heat flux. An increase of the external heat flux by a factor of four decreased the time to ignition by a factor of 30. The authors concluded that the critical surface temperature for piloted ignition was a 'suitable for use in engineering predictions of piloted ignition of solids' because qualitative and quantitative agreement was obtained from the ISO tests and tests using another apparatus (the EU test). Interestingly, the authors also concluded that the spectral radiant properties of the solids are important in determining the ignition behavior: for the same incident heat flux, for example, 'radiation from the hot layer in a compartment fire will cause ignition significantly faster than from a diffusion flame.'

One of the measures of material flammability is critical mass flux at ignition \dot{m}_{ig}'' , see Section 2.1.3. An advantage of this measure is high accuracy using precise weight-measurement techniques such as TGA [20]. As discussed in Section 2.1.3, Ref. 3 of Ref. [20] and in Refs. [26–31] the surface temperature and the heat flux are also important even though most of these studies use only one criterion, namely the temperature. The study of Ref. [33], though focused primarily on critical mass fluxes at flash point [17] for radiant fluxes between 13 and 33 kW/m^2 , demonstrated that convective heat transfer at the surface must be included in a complete ignition analysis. Recall from Ref. [19] that convection was especially important as the external flux decreased and the time to ignition increased. Indicative of the fact that they believed mass flux cannot be the sole criterion for sustained ignition, Drysdale and Thompson [33] examined flame-retarded PP and PS, finding the following: (1) flame retarded PP and PS could only be ignited for heat fluxes between 25 and 33 kW/m^2 (unlike the non-retarded PP and PS, which could be ignited between 3 and 25 kW/m^2). (2) The critical mass flux at ignition decreased as the radiant intensity decreased. (3) The fire point appeared to be sensitive to surface boundary conditions and sample configuration.

The results of Drysdale and Thompson [33] show that flammability is dependent on the chemical nature of the evolved decomposition gases, and that flammability can be altered with chemical additives or suppressants. Similar conclusions are made by Nyden et al. [37] and Nyden and Brown [38]. These works examined the flammability of honeycomb composites, which are used in interior cabin compartments of commercial aircraft. The phenol–formaldehyde resin was found to alter flammability. The authors examined many resins, which differed in relative amounts of phenol and formaldehyde. The flammabilities of resins synthesized in excess phenol were lower than those synthesized in excess formaldehyde.

Practical materials whose flammability has been scrutinized include various fluids [39,40] and electrical cables [41,42]. In Ref. [39] a general theory is developed for the prediction of closed-cup flash points of mixtures of flammable and non-flammable liquids. Experimental values of flash points of pure liquids are available. For example, Ref. [40] contains data for 22 physical properties of automatic transmission fluid (ATF) including composition, viscosity, thermal conductivity, volumetric thermal expansion, heat capacity, specific gravity, density, bulk modulus, boiling range, gas solubility, shear resistance, surface tension, electrical resistivity, heat of vaporization, flash point and fire point. As described in Section 2.1.2, the flash point is the lowest liquid surface temperature at which the fuel vapor will ignite in air in the presence of an open flame. For typical ATFs, the flash point is approximately 200 °C. The fire point, at which sustained combustion occurred, was approximately 210 °C. In Ref. [39], the flammability of two types of mixtures was studied. In the first, all components were separately flammable. In the second, some components were non-flammable. These non-flammable additives suppress flammability through vapor-phase inhibition. Thus, consistent with results for solid flammability [33,37,38], combustible fluid flammability can be altered by additives.

The flammability of materials used for the insulation and sheathing of electrical cables was studied by Matheson et al. [41] and Tewarson et al. [42]. In the former, various fire retardant (FR) and low smoke and fume (LSF) materials were examined. The fire parameters considered were flammability temperature, oxygen index, and hydrogen chloride (HCL) emission. It was found that the addition of fire retardant (e.g. fire-retarded PVC) could produce higher HCL emissions. The work of Tewarson et al. [42] examined 31 wire and cable samples, which were ranked according to seven parameters, among them ignition and flame spread, electrical failure, fire product corrosivity, generation of fuel vapors, heat, gaseous compounds and light obscuration.

The several conclusions of this subsection include: T_{ig} varies relatively little across tests and heating methods, generally under 10% for absolute temperatures, making it a suitable ignition criterion for solid ignition; t_{ig} is a sensitive quantity, varying across orders of magnitude according to Eq. (2.3); radiant spectral properties of the materials are

important and dictate that the levels of absorption may be very different depending on the type of emitter; ignition also depends on the type and nature of the emitted pyrolysis and decomposition gases, and ignitability can thus be altered by the addition of certain additives and suppressants; the flammability of many commonly used liquids has been thoroughly studied, showing that ignition temperatures are usually lower (around 570 K) than for solids (around 700 K); the formation of a vapor phase is an important aspect of ignition, both for liquids and solids, and means are available for suppressing both the amount of vapor formed and its chemical reactivity; somewhat negatively, the addition of fire retardant could in some cases produce increased HCL emission levels. Correlations of the data are extremely helpful, and for use correlations given in the form $\log(\dot{t}) = (A/T) + B$ appear to be useful for engineering practice, although as shown in Ref. [20] the actual correlations are much more detailed and sophisticated. Insufficient knowledge of detailed surface physics prevents replacing empirical engineering correlations with numerical model simulations, although key parameters appear to be radiant absorption, degradation chemistry, emission of degradation products into the surrounding gas, and the properties of the vapor molecules, including the collective radiant transfer properties.

2.3. Rate of heat release (RHR): the cone calorimeter and other diagnostic devices

In this section we first describe the principal features of devices used to measure material flammability and ignition. According to Babrauskas [43], two principal testing strategies are deployed: The first creates a test exposure, usually of a small scale, that directly mimics the expected actual exposure. The second is a controlled but simple exposure condition that can be modeled and described scientifically. A substantially lower emphasis is placed in the latter on simulating actual burning conditions than in the former, hence the controlled exposures usually now involve radiant heat sources, which can be accurately monitored, unlike convective heating. Principal focus is placed on the cone calorimeter. Then in Section 2.3.2 the various uses of the cone calorimeter are described in some detail.

2.3.1. Background and principles of the cone calorimeter

As it became ever more necessary to quantify the flammability of materials, methods were devised that could measure flammability parameters. These tests include the oxygen index (OI) test, pyrolysis and thermal analysis, and gas analysis, as described in Ref. [44]. In the OI test [ASTM D2863-77] the material being tested is burned in a 'candle-like flame and the oxygen concentration of the ambient air is reduced to the limit where the flame just (barely) exists.' The measured oxygen concentration is the OI of the tested material. According to Elomaa et al. [44], the "benefits of the method are... simplicity, ease of execution, small

demand of material, and good reproducibility.” The principal use of the OI test is as a research and development tool for new flame-retardant fabrics and plastics, chiefly because the test is not considered acceptable for fire hazard assessment. The ASTM standard states: “...this test should not be used for the description or appraisal of the fire hazard of materials, products or systems under actual fire conditions” [44]. Pyrolysis and thermal analysis involves the rapid heating of small, presumably homogeneous, material samples to a specified ‘pyrolysis’ temperature, then the application of various chemical and other diagnostic techniques to examine their pyrolysis products, rate of weight loss, decomposition kinetics, and other quantities of technical interest. An inherent limitation of this method is the impossibility of achieving the test temperature without proceeding through all lower temperatures at a certain rate: this rate can influence subsequent measurements, as examination of the equations of decomposition kinetics clearly demonstrates [45]. As stated in Ref. [44], the pyrolysis of polymers has been ‘often’ studied by thermo-analytical methods, the most common being thermogravimetry (TG), which is “... (routinely) used for determination of the (polymer) degradation temperatures and the formations of char.” Numerous methods are used for analyzing the gaseous by-products of combustion and pyrolysis. Also the report ISO/TR 9122-3 [46] provides “suitable methods for the analysis of gases and vapors in fire effluents.” The principal method for numerous gases (CO, CO₂, O₂, CN, HCl, NO_x) is gas chromatography. Other methods (FTIR: Fourier Transform infrared), GC-MS (gas chromatography-mass spectrometry) are also discussed in Ref. [44] including numerous references to their particular uses.

Experimental diagnostics in ignition and flammability testing have increasingly placed principal emphasis on rate of heat release (RHR). The following quotation from Babrauskas and Peacock [47] is therefore apt: “Perhaps the most important quantity related to fire is the energy release rate (because it) represents the size of the fire and its potential for damage.” It may be defined as $\dot{Q} = \dot{m}'' A \Delta h_c$ where \dot{m}'' is the mass flux from the burning surface, A is its surface area and Δh_c is the ‘effective heat of combustion’ per unit mass [17]. The function \dot{Q} is also commonly referred to as RHR.

The importance of RHR in fire is discussed in Refs. [47, 48]. The former authors explain in detail why RHR characterizes the flammability and fire hazard of combustible materials. Many years before, Tewarson [48] had pointed out that although fire deaths are primarily caused by emitted toxic gases, RHR is the best predictor of the subsequent fire hazard. The logical ordering of fire hazard is thus a local ignition, with a RHR sufficient to sustain fire, which, in turn, produces toxic gases. Without fire sustenance by RHR, no toxins are produced. Additionally, Tewarson [48] provided a definition of the heat of combustion. The complete (or theoretical) heat of combustion is an inaccurate measure of Δh_c because complete combustion is generally

not attained in real fires. Tewarson [48] therefore discusses means for defining realistic estimates of heats of combustion. Quintiere [17] provides a concise, precise means for determining RHR. Noting that the oxygen consumption calorimeter ‘works on the principle that the heat of combustion per unit mass of oxygen consumed is nearly a constant (13 kJ/g) for a wide range of ordinary (hydrocarbon) fuel compounds,’ a simple calculation of RHR by the principle of oxygen consumption proceeds as follows. The object being burned is placed in a flow-through chamber. The incoming air has oxygen mass fraction 0.233, the exhaust has oxygen mass fraction $Y_{O_2,ex} < 0.233$. The incoming mass flow rate is \dot{m}_{in} , the exiting mass flow rate is \dot{m}_{ex} . The oxygen consumed in the fire is $(0.233\dot{m}_{in} - Y_{O_2,ex}\dot{m}_{ex})$. Multiplication by the constant 13 kJ/g heat release per unit mass of oxygen gives the RHR. Shown in Table 1 are values of the heats of combustion per unit mass of oxygen consumed for numerous pure hydrocarbon fuels. RHR can be measured during the course of a flammability test. Typically, it is initially low, then rapidly rises because of fire growth and spread, then slowly decays as fire burnout is approached.

Although flame spread is a complicated dynamic process involving flow and transport, limited attempts have been made to relate ignition time and fire RHR to the actual flame spread rate over a surface [49]. This subject deserves much more attention than it has received since it asks a fundamental question: to what degree can one-dimensional overall measurements be applied to a transient,

Table 1

The heat release per kilogram of O₂ is calculated from the stoichiometric reaction $C_nH_m + \alpha O_2 \rightarrow nCO_2 + (m/2)H_2O$. The O-atom balance gives $\alpha = n + m/4$ as the entry in the fourth column. The quantity in the fifth column is obtained from the quantity in the third column after multiplying it by 10^{-3} MJ/KJ and then dividing by 32α kg O₂/kmole fuel. Note the near constancy of the heat release normalized per kg of oxidiser, and note also that certain unsaturated hydrocarbons can deviate, though not by much more than $\pm 15\%$ from the average value of ~ 14 MJ/kg O₂

Hydro-carbon fuel	Chemical symbol	Heat of combustion per mole of fuel ΔH_c /kJ/kmole fuel)	Stoichiometric coefficient α	Heat of combustion per kg of O ₂ / ΔH_{CO_x} (MJ/kg O ₂)
Methane	CH ₄	890,360	2	13.91
Ethane	C ₂ H ₆	1,559,900	3.5	13.93
<i>n</i> -Butane	C ₄ H ₁₀	2,877,100	6.5	13.93
<i>n</i> -Hexane	C ₆ H ₁₄	4,194,800	9.5	13.80
<i>n</i> -Octane	C ₈ H ₁₈	5,512,200	12.5	13.78
Toluene	C ₇ H ₈	3,947,900	9	13.61
Benzene	C ₆ H ₆	3,301,500	7.5	13.76
Acetylene	C ₂ H ₂	1,299,600	2.5	16.25
Ethylene	C ₂ H ₄	1,410,970	3	14.70
Propylene	C ₃ H ₆	2,058,500	4.5	14.30

three-dimensional process? This question has lain in the background of nearly all investigations using the cone calorimeter, and led in the late 1970s and early 1980s to the rapid development of devices for measuring material flammability for evaluating fire hazard. Among them was the furniture calorimeter [50,51]. In the former article, the influences of fabric type, padding type (cotton, PU foam, etc.) and frame types were assessed. The advantages of furniture calorimeter testing over conventional room-fire testing are primarily a lesser ability to specify fire growth in a vague, undefined region (such as a 'room') as compared with a well-defined, single object (such a piece of furniture, whose flammability properties can be nominally measured). In the latter article, the analysis of a large number of tests demonstrated that for most specimens a good approximation to the graph of RHR as function of time is a suitably drawn triangle. Methods for generating triangular RHR vs. time curves, which are used for fire protection engineering hazard determinations, were developed.

The furniture calorimeter, however, suffered from the same vagueness with respect to individual items of furniture as did the room fire with respect its contents. This ambiguity resulted in the subsequent development of the individual *material* calorimeter, which measured the flammability of a single, individual, isolated substance. Although numerous calorimeters were designed, including

models from France (the *épiradiateur*) and other countries of Europe, the Ohio State University (OSU) calorimeter (ASTM E906), and the cone calorimeter (ASTM E 1354 and ISO 5660, among other listings), only the latter has become a universally accepted testing device.

The cone calorimeter, developed by Babrauskas [4,5] consists of a cone-shaped array of electrically heated radiant coils that impose a known heat flux up to approximately 100 kW/m^2 on a small sample of material in the vicinity of a nearby pilot flame. The apparatus is usually horizontal, enabling the capture, by the heater cone and attached flow pipe of the decomposition off-gases, see Fig. 6. Nevertheless, the cone calorimeter can also be oriented vertically. The cone calorimeter can measure [52] rate of heat release, peak rate of heat release, time to peak rate of heat release, total heat released after a specified time interval, time to ignition, smoke production rate, chemical composition of product gases (and toxic gas production), mass loss rate during burning, as well as time to ignition, heat flux at ignition and all other parameters related to fire initiation and discussed in Section 2.1.3. Certain conditions are encountered in practice that are difficult for the cone calorimeter and other diagnostic devices to examine. Among these are ignition and flammability for weakly reacting materials, conditions of low or fluctuating

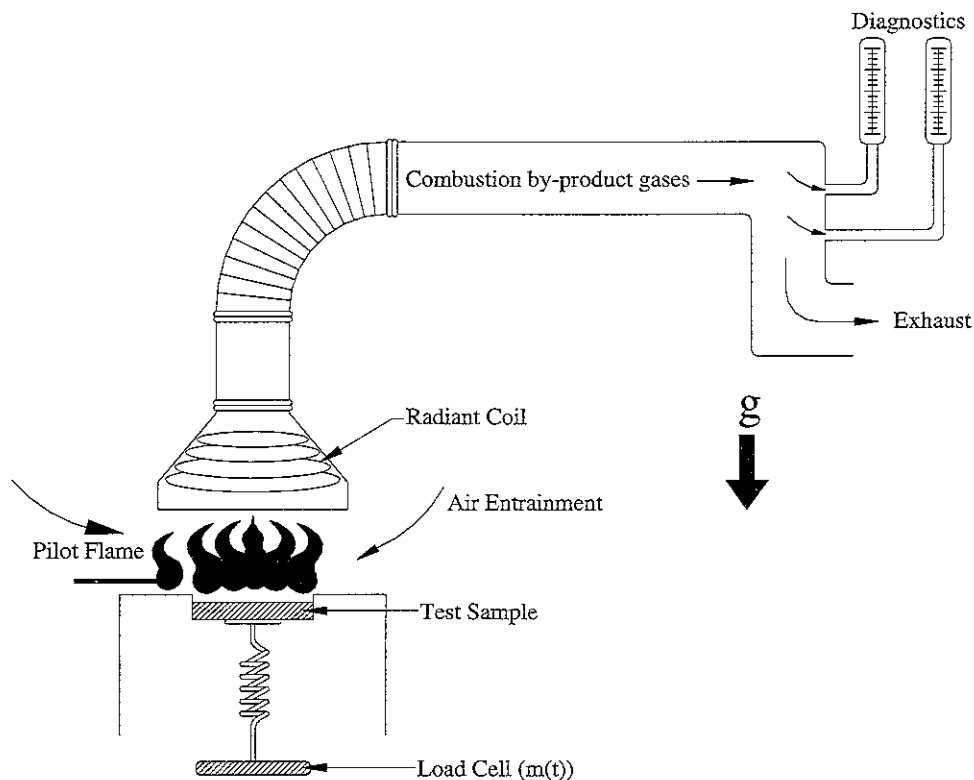


Fig. 6. Diagram of the cone calorimeter showing the heater cone, the heated horizontal sample, the gas collection system and the load cell used to measure sample weight.

oxygen concentration, and variable material thickness and composition. Thermally thin materials also appear to be limited in the cone calorimeter, unless means can be developed to eliminate the heat losses associated with the sample holder. Under some of these conditions the materials may gasify vigorously, but ignition cannot be sustained. Flammability is also altered where the absence of buoyant flow produces conditions favorable or unfavorable to ignition [53]. In other words, in cases where buoyant flow is absent (as in outer space) the cone calorimeter may provide inaccurate measures of flammability, requiring the development of other more representative test methods that account for the influences of buoyancy more systematically. Despite these qualifiers, however, according to Babrauskas [43], the cone calorimeter is currently 'the most common apparatus used in laboratories worldwide for measuring the radiant ignitability of materials.'

2.3.2. Practical uses of the cone calorimeter and other fire diagnostic devices

The cone calorimeter 'was inspired by the earlier...ISO 5657 test,' [43] which was developed around 1970, and which differed from the cone calorimeter in certain minor details, such as sample size and use of a 'dipping duck' pilot ignition process, in which a propane gas flame is periodically lowered every 4 s into the vicinity of the sample surface. The similarities and differences between the two devices are presented in tabular form in Ref. [43]. According to the latter, the differences in ignition data 'are no more than the scatter of the data.' The cone calorimeter has been described as 'The most versatile instrument available for small-scale fire hazard assessment under conditions of uniform, adjustable irradiance levels...which allows the simultaneous determination of a number of parameters and utilizes the oxygen consumption principle' [54].

In its development stages, the cone calorimeter was quite extensively compared with other bench-scale test methods, and also with some large-scale tests. Babrauskas [55] studied low-flammability wall lining materials representative of aircraft cabin walls. The cone calorimeter, the FMRC flammability apparatus and the flame height apparatus gave similar results. The OSU calorimeter results were typically half these three methods. Babrauskas [55] examined techniques for predicting full-scale performance from bench-scale tests. Babrauskas et al. [56] addressed the issues of sample preparation and mounting. It is believed that edge flow and heat transfer produced by sample edge frames may alter flammability measurements. Thus, one phenomenon that the cone calorimeter wishes to avoid, namely two-dimensional lateral cross-sample flow, nevertheless apparently enters into consideration. Babrauskas et al. [56] showed that insulated edge frames produce measurements that are more consistent and 'slightly closer to expected true values.' For routine fire testing, the authors

do not advocate the use of an edge frame unless the sample presents 'special difficulties, such as due to intumescence.' When an edge frame is used (e.g. a steel frame), the effective exposure area is reduced, providing near-constant conditions away from the frame. In other words, the uniformly heated area for flammability testing is smaller with the edge frame.

The cone calorimeter has been used to examine many kinds of materials. These include fabrics and PU foams [57–61,63], polymeric materials including PVCs, PE, PP, acrylonitrile–butadiene–styrene and polyphenylene oxide/PS, polyethimide, polyethersulfone, polycarbonate, polyether ethylketone, polyphenyleneoxide, high impact PS, polybutylene terephthalate, and PVC [62], polymer composite materials containing combustible reinforcing fibers and combustible matrix resins, e.g. extended-chain PE, and aramid fiber-reinforced composites containing epoxy (EP), vinylester (VE) and phenolic (PH) matrix resins [54]. In Refs. [57,59] the influences of melamine content on PU foam flammability were quantified. The peak rate of heat release (PRHR) of the PU foam was significantly reduced with the melamine additive [57], with an average reduction of 37 kW/m² for every 10 pphp. Melamine addition greatly decreased the rate of burning and the smoke yield. Chlorinated phosphate fire retardant produced results similar to melamine in RHR reduction, but was opposite in smoke yield. Much of the information is presented in convenient graphical form. Results were obtained by Vanspeybroeck et al. [59] for three commercial PU foams and cotton, polyester and polypropylene. The three foams tested were (1) not modified, (2) melamine filled, (3) highly melamine filled. Tests measured the effective heat of combustion (EHOC), total heat release (THR), time to ignition (TTI), PRHR, and time to peak rate of heat release (TPRHR). The sample dimensions were 10 × 10 × 2.5 cm³, the exposure heat flux was 25 kW/m². Vanspeybroeck et al. [63] measured the relative contributions of fabric and foam to fire-hazard parameters. The EHOC of the individual foams and fabrics was determined with a flux of 25 kW/m². The high-resilience (HR) PU foam had the highest EHOC. PP had the highest EHOC of the fabrics tested. As shown in Ref. [58], measurements of large heat release were associated with large sample densities. The work of Vanspeybroeck et al. [60] adds comparisons of cone calorimeter results with those of the Nordtest NT 032 calorimeter (NT032). The empirical trends of the two devices were similar, but quantitative correlations were not developed in this work. These investigators concluded that post-ignition performance of the materials was determined mostly by the fabric, whereas ignition characteristics were determined by foam and fabric. This appears to make sense because during ignition, which is a go/no-go event, a *limit* condition is encountered, in which heat losses often play a major role. Thus, the interior to the fabric, or the 'backing' or 'substrate' represented by the foam under the fabric appears to play a large role in the ignition regime. Once open

burning is achieved, the importance of the backing wanes by comparison.

Costa et al. [61] compare the combustion behavior of some polymeric materials in the cone calorimeter with behaviors in some 'traditional' tests that have been widely used to assess fire retardancy, such as the oxygen index (OI), glow wire, rate of combustion and an ASTM D 1929 ignition test. These authors believe that the evaluation of relative material fire hazard can vary greatly with the evaluation method, but that the cone calorimeter has 'high potential' for providing mechanistic insight into the combustion of organic materials.

Measurements for the composite materials of Brown et al. [54] showed that the combination of two combustible components in a single composite material produced a complicated RHR behavior. The maximum RHR for the individual components may not be representative of the RHR for the entire composite. For most tests TTI appeared to correlate with the component having the higher ignitability. Phenolic composites had superior fire performance, as demonstrated by their propensity for char formation. The authors measured TTI, RHR, time to reach maximum RHR, Δh_c , smoke density, CO and CO₂, and sample mass loss. The smoke density 'is measured by the decrease in transmitted light intensity of a helium–neon laser beam photometer, and expressed in terms of a specific extinction area (SEA) with units $m^2 kg^{-1}$.' It was observed that in many cases the RHR does not diminish to zero asymptotically but that the asymptote after long heating times is constant. This behavior coincided with a lower rate of mass loss and an increase in Δh_c , 'which is consistent with char formation in the latter stages of combustion.' The authors also state that 'it is significant that smoke is observed (for the Aramid/Epoxy composite) well before ignition' indicating that the release of volatile vapors into the gas phase is an important preliminary step. They also state that when the charring regime is attained for the phenolic and aramid components, the SEA decreases to zero, i.e. the smoke vanishes. In this case, volatiles are sealed off from the gas. Finally, the authors conclude that a RHR averaged over the first 180 s is 'the most appropriate variable for predicting full-scale fire properties' because the overall average RHR has the disadvantage of an arbitrary choice of an endpoint for data collection. These observations are singled out for this particular study because of their apparent universality and because they were made in the context of a rigorous examination of a specific, increasingly important class of materials, namely composites. Additional bench-scale cone calorimeter tests on composites were conducted by Brown et al. [64].

Cleary and Quintiere [65] attempted to 'more completely characterize foamed plastic flammability' by subjecting 10 foamed plastics to cone calorimeter and Lateral Ignition and Flame Spread Tests (LIFT). The flammability parameters obtained from these apparatuses describe the dynamic flame spread properties found from the LIFT tests in addition to

the static parameters of the cone calorimeter. The word 'dynamic' is interpreted here as implying a transient spreading process, in which previously unburned material is heated and pyrolyzed and consumed by the flame, whereas 'static' implies no such spread of flame to unburned surface. To a laboratory observer, little or no change is evident in the static test, whereas significant visible changes are evident in the 'dynamic' test.

A large number of cone calorimeter tests was conducted on 28 materials classified as thermoplastics, thermosets, textiles and cellulose [66]. The results showed a dependence of ignition on method of exposure to the heat source, and on the thickness of the samples. The authors pointed out that mean and peak values alone did not fully represent material RHR. As discussed in Ref. [17], the width of the RHR curves, or more accurately, the area under the RHR curves, is a measure of the quantity of fuel burned. The authors also described various smoke tests using the SEA method proposed by in theoretical terms by Babrauskas and Mulholland [67]. The actual development of quantitative means for making smoke production measurements and species evolution measurements using the cone calorimeter is described in Ref. [68]. The smoke measurements are made by the SEA method described previously. In order to measure gas chemical species, gas samples are extracted from the exhaust line. Smoke production measurements and toxic species production measurements are needed for toxicity determinations to compare fire-retarded and non-retarded materials [58–60,63]. As pointed out by Scudamore et al. [66], however, in order to use the cone calorimeter for toxicity measurements, variation of the oxygen concentration in the atmosphere and the ventilation stream is necessary.

A fundamental discussion of the use of the cone calorimeter in conjunction with other diagnostic methods (TGA and DSC) for studying charring on ethylene-vinyl-acetate (EVA) copolymers and polyethylenes (HDPE and LDPE) both with and without phosphorous-containing additives was carried out by Wang et al. [69]. The cone calorimeter was used to determine RHR. Oxygen was found to play an important role in material thermal degradation in agreement with previous OI testing.

The cone calorimeter has proven itself to be an extremely useful device for measuring flammability properties of a wide class of materials. It provides many important indicators of fire hazard, perhaps none more important than RHR. Nevertheless, parameters such as PRHR, TPRHR, TTI, SEA, Δh_c , smoke density, CO and CO₂ species mass fractions, and sample mass loss and mass loss rate are also important indicators of expected fire performance in an ignition-like mode and in full scale (non-spread) burning. Direct evidence for this assertion is found in the large number of articles in which these quantities are measured, categorized, compared, and tabulated. Indirect evidence, perhaps even more compelling, is found in the fact that the cone calorimeter is almost universally used in fire

hazard assessment tests in any industry that produces materials susceptible to or used in fields where fire safety is a concern: in short, it has become an industry standard. Certain limitations to the cone calorimeter, however, cannot be ignored. One of these is the difficulty of assessing the behavior of thermally thin materials, as discussed by Vanspeybroeck et al. [60], where it was determined for fabrics that post-ignition performance was determined mostly by the fabric, whereas ignition characteristics are determined by the supporting foam and fabric. This indicates that for thermally thin materials it is difficult to separate the influences of the material and its ‘backing’ or ‘substrate.’ Another difficulty, briefly mentioned in this section, is that various important properties that are needed to predict flame spread rates cannot be obtained from a cone calorimeter type apparatus [70,71]. In order to predict spread rates, and thus evaluate what in many cases is an important fire hazard variable, different tests are needed. Among these flame spread tests are the LIFT apparatus of Quintiere [7], the Fire Tunnel apparatus of Wichman et al. [72], and the Downward Spread Test of Delichatsios [71, 73]. As discussed in Ref. [71], important limitations are found in the LIFT, which the other two devices largely avoid.

3. Fire spread

The objective of fire-spread studies is to address the question ‘How fast does the flame (or fire) spread over the sample surface?’ The rate of fire spread has obvious fire safety implications, and (as discussed) it cannot be measured through static tests such as the cone calorimeter. Sections 3.1 and 3.2 describe the principles of fire spread over liquid and solid fuels, respectively. Section 3.3 discusses the various applications of these principles in transportation.

3.1. Fire spread over liquid fuels

Spread over liquids in fire safety applications can be preceded by a fuel spill, hence the liquid layer over which flame spreads may be thin. Regardless whether or not the liquid fuel is thin or thick, however, during flame spread a gradient of surface tension is formed at the surface given by $d\sigma/dx = (d\sigma/dT)(dT/dx) = \gamma dT/dx$, where $\gamma = d\sigma/dT$ is the surface tension temperature coefficient. In front of the advancing flame, the temperature gradient, dT/dx , is negative. Similarly, as temperature increases, the surface tension decreases, so that $\gamma = d\sigma/dT$ is negative. Consequently, the gradient of surface tension $d\sigma/dx$ is positive, indicating that the cold surface in front of the flame ‘pulls’ hot surface toward it thereby explaining the experimentally observed movement of liquid in the same direction as the flame spread [74–76]. This surface-tension driven mechanism of flame spread with accompanying liquid phase motion, which obviously cannot occur for solid fuels, is an important reason why flame spread over liquids is ordinarily at least one to two orders of magnitude faster than flame spread over solids. Another reason flame spread over liquids is faster is that flame enthalpy is employed only to heat and vaporize a layer of fluid, whereas for solids the ‘gasification’ of the surface requires the transmission to the condensed phase of a much greater percentage of the flame heat release. For the latter, some solid materials must both liquefy and then vaporize, requiring the supplying by the flame of both liquefaction and vaporization enthalpies.

Research on flame spread over liquids has demonstrated that if the liquid fuel layer is ‘deep enough,’ a complicated convective flow pattern can be established in the liquid. The flow involves a vortical inflow from below, followed by a surface flow toward the cooler upstream, see Fig. 7. Such flows can be visualized in ordinary candle flames by observing the circular motion of ash and contaminant

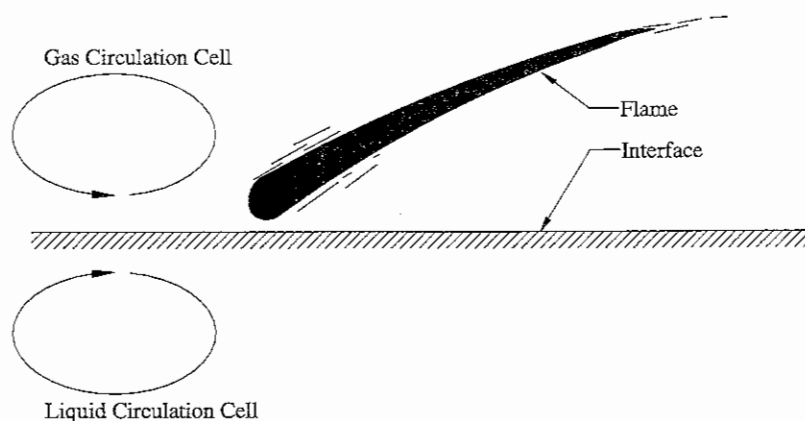


Fig. 7. Flame spread over a liquid fuel showing the characteristic pre-flame circulation cell and the gas-phase circulation cell produced by the interfacial no-slip condition. The flame spreads to the left.

particulates in the melted wax layer. In support of the notion that flame spread over liquids and solids is fundamentally different, Ross and Sotos [77] show that the solid-phase model of Ref. [78], with appropriately chosen parameters for liquid fuels, still under-predicts the liquid fuel flame spread rate. They conclude that the under-prediction is owed to convection primarily, not the fluids' thermophysical properties such as conductivity, specific heat, density, and most importantly gasification enthalpy.

The liquid thermocapillary flow may influence the flow of gas near the flame leading edge, with the no-slip condition possibly producing a corresponding gas-phase 'recirculation cell' [79]. The latter is thought to have an important influence on the mechanism of pulsating flame spread, whereby the flame front slows down and speeds up at a regular frequency. Coupled liquid and gas-phase convection are viewed in Refs. [80–82] as the controlling mechanisms of pulsation, but the work of Garcia-Ybarra et al. [83] suggests that the liquid phase alone is responsible for the pulsation. Other research, by contrast, speculates that the gas phase is the source of the oscillations: the detailed, transient, 3D computational work of Cai et al. [84], which includes the influences of the liquid pool container side walls, states that 'the mechanism of flame pulsations is due to the formation of a gas-phase recirculation zone resulting from the balance of the forced flow, thermal expansion, buoyancy (if it occurs), and thermo-capillary surface tension in the liquid fuel. This recirculation transports fuel vapor

upstream from below an initially slow-moving flame until it builds a sizable premixed fuel–air mixture in front of the flame.' They also assert that the pulsation frequency depends on the air–fuel temperature T_0 and gravity level g , since a higher T_0 yields a higher pulsation frequency f , whereas lower g reduces f .

Although flame spread over liquids is conceptually easy to explain, it is dynamically more complicated than flame spread over solid fuels because of the associated liquid motion. Much research has been carried out in this field, as computed by described in an exhaustive review by Ross [80]. Basic research sponsored by NASA [85,86] has demonstrated that fuel pool size (especially width) strongly influences the flame spread across the surface, see Fig. 8. When the pool width is greater than a minimum value, fingering spread can occur, in which certain portions of the flame spread faster than others, leading to a corrugated spreading flame front that occurs in numerous other configurations also, including smolder fronts [87,88] and large-scale wildfire fronts [89,90], though possibly for different reasons.

Because of the complicated nature of the surface-tension-driven surface flow, the in-depth vortical flow, the complicated buoyancy-induced gas flow pattern, and the unstable fingering spread, analytical correlations of flame spread over liquids are few. To quote Ross [80]: "...the subject of most recent research, convective motion couples both gas and liquid phase in unique ways and greatly

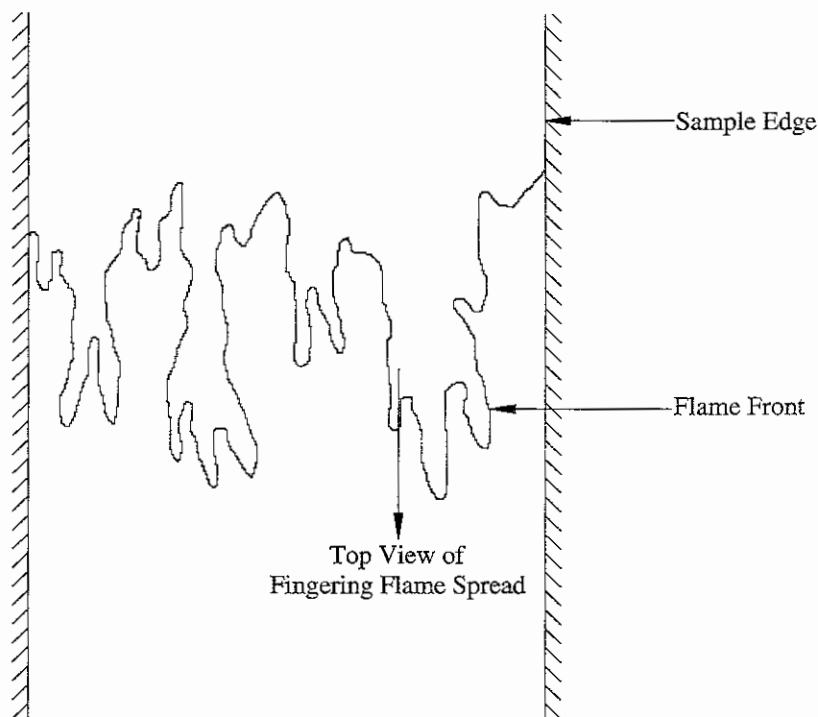


Fig. 8. Top view of the development of an irregular flame front in liquid fuel flame spread. The flame is spreading in the direction indicated by the arrow.

complicates analysis, numerical models, and experimentation.” Some of these difficulties can be eliminated by conducting experiments in fuel-soaked beds of sand or glass beads or other granular materials [91], in which case, for better or worse, spread partly resembles that over solid fuels.

3.2. Theory of fire spread over liquid and solid fuels

Some of the basic features of ignition and flame spread for liquid fuels are described here. An important quantity is the ‘flash’ temperature, defined by Ross [80] as “...the pool temperature at which the equilibrium vapor pressure yields an interfacial (gas-side) fuel concentration equal to that of the lean-limit concentration for a premixed gaseous fuel–air system.” Generally, when the liquid pool temperature is below T_{flash} , the flame, once ignited, will spread across the fuel at a measurable rate, but when the pool temperature is above T_{flash} , the flame ‘flashes’ across the surface at a rate characteristic of pure gas-phase premixed combustion. The latter condition is more easily predicted and described than the former. Regrettably, however, as pointed out by Ross [80] the quantity T_{flash} is ‘not a unique property of a liquid fuel... (but is instead an artifact) of the experimental apparatus...’ Much empirical support is available for this assertion. The interested reader is referred to Ross [80] for more detailed discussions. The regimes of flame spread are characterized as (1) pseudo-uniform subflash, (2) pulsating subflash (fast–slow, sometimes forward–backward), (3) uniform near-flash, (4) uniform superflash. In (1), (3), (4) constant spread rates may be observed, but in (2) the spread rate is transient. Of these four spread regimes (1) and (2) contain the most liquid-phase physics. Regime (2) is difficult to describe without including significant detail, as in the detailed 3D numerical models discussed above [84 and references therein] so its treatment is foregone in this introductory review. Some features of regime (1) are examined instead.

In regime (1) the operational hypothesis is that the flame spread rate V is of the same order of magnitude as the interface velocity V_i , hence estimates of V_i may

suffice to predict V [80]. Because V_i is produced by buoyant convection and thermocapillary flow, these mechanisms introduce the scale parameters Grashof number Gr , Marangoni number Ma , Reynolds number Re and Rayleigh number Ra . The focus here is on the thermocapillary flow, in which motion of the surface is caused by a balance of surface tension with the gas and liquid shear stresses, $d\sigma/dx = \mu_l(\partial u_l/\partial y)_s - \mu_g(\partial u_g/\partial y)_s$, where u_l and u_g are liquid and gas streamwise velocities, and subscript ‘s’ denotes the surface. Now write $d\sigma/dx = \gamma dT/dx$ and ignore the gas-phase shear in comparison with liquid-phase shear to find $\gamma dT/dx \approx \mu_l(\partial u_l/\partial y)_s$, then scale coordinate x with the distance over which the surface temperature varies by the amount ΔT , coordinate y with its depth h , velocity u with the thermocapillary flow velocity $V_\sigma \approx V_i$, and the temperature with the difference ΔT between heated and cold temperature. Thus,

$$V_i \sim \frac{h}{\mu L} \gamma \Delta T. \tag{3.1}$$

In the case that a boundary layer flow develops, the scale h is replaced by the scale $LRe^{-1/2}$, where L is now the physical scale and $LRe^{-1/2}$ is the scale for the thickness of the thermocapillary layer. Here $Re = V_i L/\nu$. Substitution into Eq. (3.1) gives, after rearrangement,

$$V_i \sim \left[\frac{\gamma^2 \Delta T^2}{\mu^2} \frac{\nu}{L} \right]^{1/3} = \left[\frac{\gamma^2 \Delta T^2}{\rho \mu L} \right]^{1/3}, \tag{3.2}$$

where we used $\nu = \mu/\rho$. The flame spread rate increases with $(\gamma \Delta T)^{2/3}$, whereas increases in liquid density, viscosity and characteristic temperature gradient length (L) diminish V_i according to the $-1/3$ power. Although this model is not expected to be very accurate, it allows estimates to be made and observed trends to be explained.

Switching now to solid fuels, research in flame spread over solids has provided two separate spread configurations. One configuration is wind-opposed flame spread. Here the oxidizer flow opposes the spreading flame.

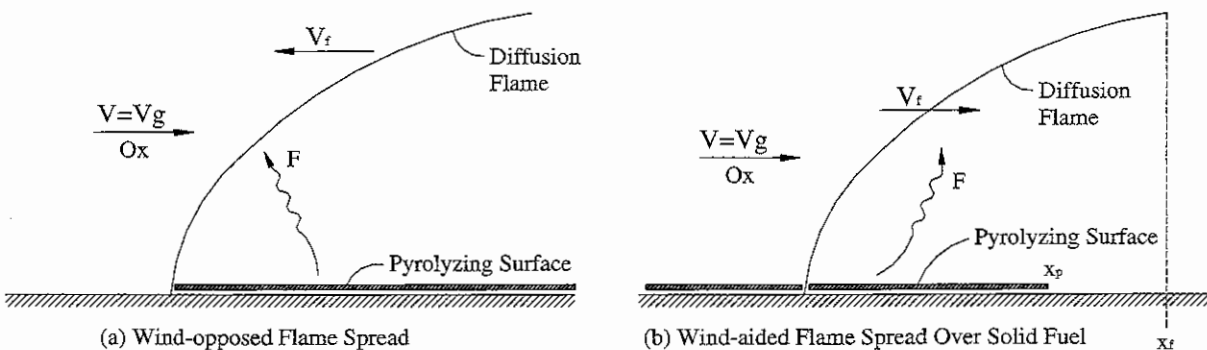


Fig. 9. Diagrams showing wind opposed (a) and wind-aided (b) flame spread. The burnt or burning surface is indicated by the thick wavy black lines.

Examples are vertically downward flame spread against a buoyantly induced opposed flow and lateral flame spread across a horizontal surface in an initially quiescent environment, see Fig. 9a. For the latter, buoyancy induces an inflow of oxidizer. The second fundamental configuration of flame spread over solid fuels is wind-aided flame spread. Here the oxidizer flow assists the spreading flame by flowing in the same direction. An example of wind-aided flame spread is vertically upward flame spread, see Fig. 9b. Under most conditions, wind-aided flame spread is at least an order of magnitude faster than wind-opposed flame spread. It is also more difficult to predict because acceleration is an inherent feature of wind-aided flame spread.

It is convenient to view flame spread over solids (and in some cases liquids) as a sequence of piloted ignitions. Here the advancing flame acts as its own pilot, and various notions arising in the study of fire initiation discussed in Section 2 can be carried over directly to fire spread. In order to motivate this hypothesis, consider the equation of flame spread proposed by Williams [92], $\rho_s VA \Delta h = \dot{Q}$, where ρ_s is the fuel density, V is the flame spread rate, $A = wl$ is the fuel cross-sectional area (width \times depth), $\Delta h = c_{ps}(T_v - T_\infty)$ is the mass-based enthalpy difference between the ambient (T_∞) and gasifying (T_v) fuel slab, and \dot{Q} is the heat transfer rate from the flame to the surface, see Fig. 10. The heating rate can be rewritten, in terms of the flame heat flux (q''), and the characteristic flame tip extent (δ), and its lateral width (w), as $\dot{Q} = q'' \delta w$, whereupon $V = q'' \delta / \rho_s c_{ps} l (T_v - T_\infty)$. The quantity $\rho_s c_{ps} l (T_v - T_\infty) / q''$ can be interpreted with the support of Eq. (2.4) as the ignition time. Thus, in its general form the equation of flame spread is

$$V = \delta / t_{ig}, \quad (3.3)$$

where V and δ retain their previous definitions and t_{ig} is the characteristic time to piloted ignition. For a thermally thin solid fuel, whose entire sample cross-section is simultaneously heated to the gasification temperature T_v , Eq. (3.3) gives

$$V = \frac{q'' \delta}{\rho_s c_{ps} l (T_v - T_\infty)}$$

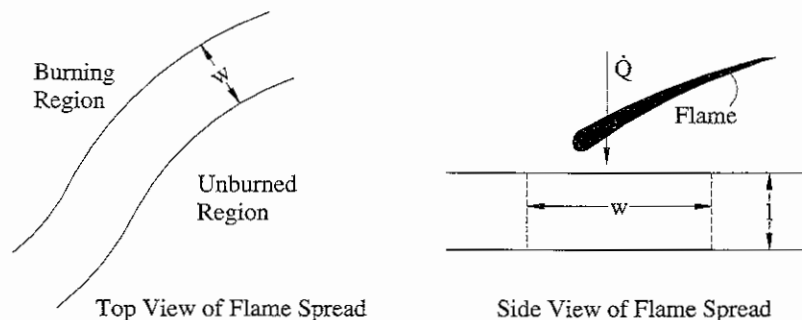


Fig. 10. A schematic diagram representing the fundamental equation of flame spread. The flame front is the line shown. Flame spread occurs in a direction locally perpendicular to this line.

The relevant points to notice from this simple equation are the following. The flame spread rate V is proportional to the flame heat flux and is inversely proportional to the material density, specific heat, thickness and gasification temperature.

If we write the heat flux from the flame to the surface as $\lambda_g(T_f - T_v)/l_q$, where T_f is the flame temperature, λ_g is the gas thermal conductivity, and l_q is the distance from the flame tip to the fuel surface, we obtain the flame spread equation for a thin fuel

$$V = \frac{\lambda_g}{\rho_s c_{ps} l} \left(\frac{T_f - T_v}{T_v - T_\infty} \right), \quad (3.4)$$

where $l_q \approx \delta$ was assumed. For thermally thick fuels, on the other hand, the relevant solid sample heated area thickness is not the sample thickness l but rather a characteristic heated layer depth, $\delta \approx \sqrt{\alpha_s t_{ig}}$, where $\alpha_s = \lambda_s / \rho_s c_{ps}$ and t_{ig} is the time from inception of heating to ignition. With t_{ig} given by Eq. (2.5) we obtain by substitution into Eq. (2.3) the result $V = \delta (q'')^2 / [\rho_s c_{ps} (T_v - T_\infty)^2]$. When we write $q'' \approx \lambda_g(T_f - T_v)/l_q$, where the flame quenching distance l_q is approximately equal to the characteristic extent of the flame tip, δ , we obtain

$$V = V_g \frac{\rho_g c_{pg} \lambda_g}{\rho_s c_{ps} \lambda_s} \left(\frac{T_f - T_v}{T_v - T_\infty} \right)^2. \quad (3.5)$$

Here we used $\delta \approx l_q \approx \lambda_g / \rho_g c_{pg} V_g$ for the characteristic gas-phase conduction length and the streamwise extent of surface heating under the flame tip. We have defined V_g is the opposed oxidizer velocity (see Fig. 9a). Equation (3.5) describes the functional dependencies for wind-opposed flame spread over thermally thick solid fuels. Its range of applicability and its limitations are extensively discussed by Wichman [36]. Fig. 11a and b shows diagrams of the thermally thick and thin configurations.

Despite the success of these models in providing flame spread formulas when spread is considered to consist of a series of ignitions, the simple fact is that actual flame spread is strongly influenced, if not actually controlled, by the oxidizer inflow rate, which is ordinarily not measured in an ignition test such as the cone calorimeter. Thus, relating the above formulas, which generally depend on the oxidizer

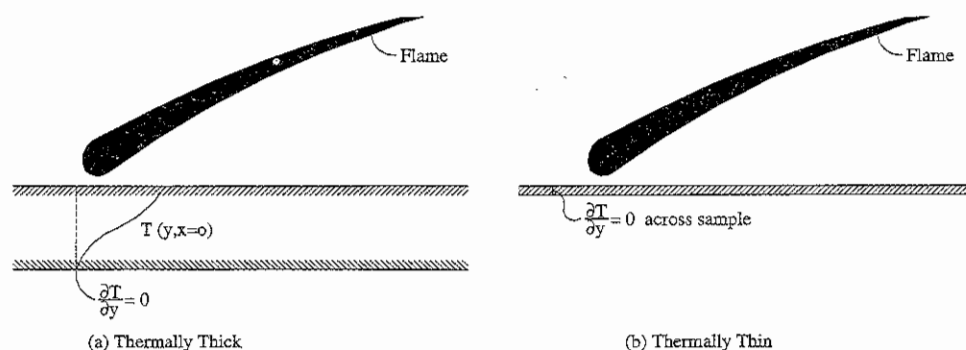


Fig. 11. Diagrams showing the temperature fields under the spreading flame for thick (a) and thin (b) fuels. For the thick fuel a distribution of temperatures is found ranging from the surface value to the ambient value at the back face. For a thermally thick sample the back face temperature should remain constant for the duration of the test. For the thin sample (b), the top and lower surfaces have nearly identical temperatures, thus the solid temperature is a function only of position along the sample axis.

inflow, to pure static material ignition data, is not possible [70,71].

Results can also be derived for the case of wind-aided flame spread. Because of its greater complexity, much less is known about this form of flame spread. A simple model derived by Thomas [93] demonstrates the essence of wind-aided flame spread. If the overhanging flame of Fig. 9b imparts a constant heat flux to the surface beneath it, we may define the time to ignition as $t_{ig} = (x_f - x_p)/V$, where V is the mean flame front speed as it traverses the distance $x_f(t) - x_p(t)$. If the flame front accelerates, the preceding expression overestimates t_{ig} because V is in fact slightly larger. We define $V = dx_p/dt$ to obtain the fundamental equation of wind-aided flame spread

$$\frac{dx_p}{dt} = \frac{x_f - x_p}{t_{ig}} \quad (3.6)$$

For thin fuels we use Eq. (2.4) for t_{ig} . For thick fuels Eq. (2.5) is used for t_{ig} . Eq. (3.6) suggests the possibility of: (i) accelerated spread, for example when $x_f - x_p$ is constant. (ii) Asymptotic approach to zero spread rate when x_p approaches x_f . In practice, correlations for x_f are devised and examined a posteriori in the light of various modeling approximations. The general approach has been to fit the model to the experimental results. We refer the interested reader to the research literature, where many such simplified calculations have been made [93–101].

It is necessary for the reader to understand that the preceding models describe two-dimensional flame spread across flat, homogeneous combustible surfaces. Real flame spread is almost never two-dimensional nor are combustible materials necessarily homogeneous or flat, especially in applications related to transportation. Multi-dimensional flame spread occurs over objects in complicated geometric arrangements, such as cables in confined spaces or in venting and air transmission ducts connecting separate regions. The preceding formulas offer guidance and provide generally accurate proportionalities to material properties

and characteristic temperature differences. Caution is necessary when simplified correlations are adapted to complicated real-life problems of transportation. Nevertheless, it appears that considerations of material flame spread processes, as outlined here, can provide a valuable guide to making rational decisions on the use and placement of potentially combustible materials.

3.3. Fire and flame spread over materials

A review of wind-opposed flame spread containing a discussion of flame spread from an analytical, conceptual and historical viewpoint is provided by Wichman [36]. The earliest researchers in flame spread quickly understood that certain polymeric materials possessed burning behaviors that rendered them suitable for repeatable and accurate scientific testing. PMMA (polymethylmethacrylate), for example, has been described [36] as an ‘ideal vaporizing solid’ whose decomposition in a fire can accurately be explained by simple, accurate models. Many of the distinctions made in flame spread research originated in the PhD thesis of DeRis [78], which contains detailed discussions of (1) The ‘vaporizing solid’. (2) Thermally thick and thin solid fuels. (3) Externally imposed (background) heat fluxes. (4) Flame-tip attachment and flame-tip structure. As demonstrated in the review of Wichman [36], subsequent works on flame spread have focused their efforts on at least one of the features originally described by DeRis [78].

One of the most commonly discussed features of DeRis’ model is the surface ‘vaporization’ or gasification-temperature, previously referred to as T_{ig} or T_v . Most solids do not gasify at a fixed temperature T_v , rather T_v varies with ambient oxidizer fraction, external heat flux, and other variables such as gas pressure. Thus, for a solid, in contrast with a liquid, no single, unique gasification temperature exists. However, many polymeric materials have a nearly invariant gasification temperature, as demonstrated by

Flint and Magill [102] for polycarbonate, for which $T_v \cong 580\text{ °C} = 850\text{ K}$. As discussed in Section 2.2.1 (footnote 5), the piloted ignition temperatures for many combustible hydrocarbon fuels vary less than 10–20% on an absolute temperature scale, hence the designation of a representative T_v is a reasonable theoretical modeling approximation.

Another feature of DeRis' theory amounted to making the distinction between thermally thick and thin flame spread. Wichman [36] showed that this distinction was not clearly made before DeRis published his PhD thesis (1968). This matter is still an open question, however, and means for resolving it are still not completely apparent. For example, under some conditions certain physically thin materials can still display thickness-dependent responses [103] that make it difficult to classify them as thermally thin. In this case, the temperature between front and back faces can vary appreciably, and if the solid decomposes as, for example, cellulose (which degrades to a char) the composition and thus the thermo-physical properties of the sample can be different between the front and rear of the sample.

Numerous experimental investigators examined flame spread over varying fuel-bed thicknesses. Hirano and Tazawa [104], for example, conducted an experimental study to examine the influences of fuel thickness on downward flame spread over thin solid-fuel sheets. Four different paper thicknesses were used, the air-flow rate opposing the flame spread was varied, and particle tracing techniques along with thermocouple (TC) measurements were used to diagnose the spread behavior. Measurements showed that the spread rate decreased as the sample thickness increased (consistent with Eq. (3.4)). The gas velocity profile in the vicinity of the flame tip and the gas temperature in the preheat zone were nearly independent of the sample thickness. Although the spread rate decreases, the mass-burning rate increases with increasing l . This was believed to be caused, in part, by forward heat transfer from the flame to the unburned material though the solid. A perhaps more important explanation is the solid-phase temperature gradient normal to the paper surface. This gradient will 'drive' the volatile mass flux from the paper surface into the gas. This discussion of fuel mass burning rate and spread rate points to the fact that they are quantitatively different subjects, which should be considered with appropriate caution. Flame spread rate is relatively easily measured, whereas the mass burning rate is not easily measured (unless static tests such as the cone calorimeter are used).

Another study by Hirano et al. [105] examined opposed flow flame spread over thick and thin sheets of PMMA. For $l < 0.2\text{ cm}$, they found $V \propto l^{-1}$ as predicted by Eq. (3.4). The authors suggested that for thin samples the heat flux from the flame into the preheat zone in front of the flame tip was larger than the flux to the pyrolyzing surface behind the flame tip, whereas the reverse occurs for thermally thick ($l > 2\text{ cm}$) fuels. These measurements suggest that the heat

flux near the flame leading edge has a complicated structure that must yet be carefully elucidated.

A simplified model of flame spread developed by Quintiere [7] incorporated the radiation term and led to the subsequent development at NBS (now NIST) of the LIFT apparatus discussed in Section 2.3.2. This test couples the ignitability criteria described for the cone calorimeter (and similar devices) in Section 2.3.2 with the subsequent evaluation of radiantly assisted creeping flame spread. Parameters defined in an analytical correlation for transient heat conduction to a semi-infinite solid are measured in the LIFT apparatus, which employs a radiant panel inclined at an acute angle to the sample surface. Flame spread rates and ignition events can be measured as functions of incident radiation and exposure time. The flame may spread both laterally and upward, the lateral rate being slower than the upward rate. The flame spread data are correlated for varying exposure conditions by plotting the inverse square root of the flame spread rate over thick materials against a product of the heat flux and a time function. The work of Harkleroad et al. [106] contains test and analysis results for six materials representative of aircraft (interior panels, carpeting, seat cushions) and buildings (plywood, PMMA, rigid foam). A detailed study of ignition and flame spread over two composites was conducted using the LIFT apparatus by Ohlemiller and Dolan [107]. One composite was a honeycomb panel, the other a composite armor. The ignition behavior of all materials was correlated by a simple predictive model. As already discussed, however, limitations with the LIFT and LIFT correlations have been examined in detail by Delichatsios [70,71]. The reader is referred to these references for extensive consideration of LIFT limitations and potential LIFT improvements.

Another feature of the spreading flame discussed by DeRis, namely the flame tip structure, is not yet resolved. Accurate measurements of gas velocity, temperature and concentration fields are needed, as are well-constructed theoretical models of flame tip structure. The information and insight provided by careful experiment and theory can lead to interpretable numerical simulations. An important step in describing the gas-phase flow structure was made with the introduction of laser-Doppler velocimetry (LDV) methods of measurement described by Fernandez-Pello [108]. Other sophisticated diagnostic methods have since been used to measure features of the spreading flame, see the rather extensive review of Fernandez-Pello and Hirano [109].

An area of great practical concern for flame spread involves flame spread along with wires and cables. Fires can begin in confined spaces near wiring and cable lines, hence this form of flame spread should be examined. A review of the literature on fire tests for wire and cable has been published by Babrauskas et al. [110]. Comparisons are made to British and other international standards for such materials. Approximately 300 references are compiled in this article. The scientific study of flame spread in

cylindrical geometries is, however, not highly developed. Except for some dimensional correlations and scaling arguments, the literature on the basic mechanisms of this form of flame spread is scant [111]. One important difference between cylindrical and planar spread is the presence in the former of ‘side relief’ for the flowing gases. The thermal expansion may produce a secondary flow in the circumferential direction along the cylinder or rod. Such a lateral flow is not possible for strictly two-dimensional planar flame spread.

Several other important physical variables can strongly influence the rate of flame spread. Among these variables are sample; ambient gas temperature; oxygen concentration in the ambient gas; regression of pyrolyzing surface; char formation at the pyrolyzing surface; fire retardant additions; and geometrical shape of the sample. As shown in Eqs. (3.4) and (3.5) the ambient temperature T_∞ can strongly influence V . As $T_\infty \rightarrow T_v$, the flame speed approaches infinity, which is flashover. Brauman [112] performed a study that included variations of sample temperature for various polymers, although other influences were also studied, such as enhanced heat losses, additives, and char formation. An indication of what might happen as the ambient gas temperature is raised is provided in Ref. [113], where PE, PP and PS samples were pyrolyzed in quiescent hot air at varied temperatures. To the knowledge of the author of this review, no studies of the influence of ambient air (or, more generally, oxidizer) temperature have been carried out for the flame spread problem. The influences of oxidant gas composition also enter Eqs. (3.4) and (3.5) through the enthalpy ratio, this time though T_f , the flame temperature. As the oxidizer mass fraction Y_O is increased, T_f dramatically increases [36,114–116].

Brown et al. [117] conducted a detailed and fundamental material fire spread evaluation for US Navy shipboard structures and installations. In addition to carrying out the various tests, criteria for ranking the tested materials are described, data from non-standard tests of fire performance are discussed, a review of data and results for selected tests is provided, and recommendations are made for test developments and for the future direction of the US Navy’s fire spread evaluation of composite materials. No such systematic test procedure appears to be available, hence the fire spread/hazard evaluation of composite materials is still an open subject of research.

Another fundamental question concerns quantifying the influences of fire retardant chemicals on flame spread. Babrauskas et al. [118] studied the influences of fire retardants on total fire hazard (not flame spread). They employed the cone calorimeter, NBS furniture calorimeter and NBS toxicity tests. In all categories except overall smoke production, the chemically treated samples performed better than the non-treated samples. In particular, reduced burning rates were obtained without increased combustion by-product toxicity. Systematic studies of the influences of

retardants specifically on flame spread have not been conducted, to the knowledge of the author of this review.

Flame heat fluxes to nearby surfaces have been analyzed and described. This is an important practical problem because in most real fires numerous surfaces are simultaneously burning and transmitting radiant and convective heat fluxes to each other. Quintiere and Cleary [119] produce simple dimensionless correlations that require empirical support. These correlations can become extremely useful, if further developed, but they require accurate experimental measurements. A literature search was conducted by Babrauskas [120] to determine how much is known about the heat fluxes from flame to surface in opposed-flow spread. There were few reported studies, and among those the reported data varied widely, even for similar materials under similar spread conditions. Interestingly, no data were found for the geometry of the LIFT test (ASTM 1321). This was considered surprising because LIFT is one of the few flame-spread tests for which a theory is systematically applied to the data. The LIFT theory, however, employs an empirical formula for the ‘driving force’ for flame spread and does not explicitly quantify the heat flux. Thus, it is necessary to experimentally measure flame heat fluxes in LIFT and in other geometries. Questions abound, such as whether the heat fluxes are total, whether significant fractions are lost to the environment, whether the lost heat is lost primarily by radiation, and so on. Delichatsios [70,71,121] wrote a series of articles on this subject. In the latter article, a version of the LIFT is proposed that combines features of the cone calorimeter and downward flame spread tests: specifically, the flame spread test sample is cylindrical, mounted vertically in a larger cylinder consisting of radiant heater coils, with the exhaust effluent exiting vertically as in the cone calorimeter.

Various other features of flame spread must be well understood, particularly as materials and their uses become more sophisticated. The Army, for example, is interested in assessing composites for performance of armored combat vehicles under conditions that may lead to fire. The study of Tewarson [122] describes a fire hardening assessment (FHA) methodology applied to five composites. Four separate tests were conducted for ignition, combustion, fire spread, and extinction. These data were used to establish the critical heat flux, thermal response parameter, fire propagation index, heat release rate, product generation parameter, smoke damage parameter, corrosion index, and flame extinction parameter.

Numerous simplified versions of Eqs. (3.4) and (3.5) have been deduced based on the Y_O -response of V . For example, $V \propto Y_O^b$ should give $b \sim 1$ for thin fuels and $b \sim 2$ for thick fuels because $T_f \propto Y_O$. Initial experimental work on flame spread [36,109] was founded on such correlations, which are used to ascertain the influences of finite-rate chemistry [123]. If the pure heat-transfer dependence b is known, the difference, a , between $V \propto Y_O^{b+a}$ and $V \propto Y_O^b$

can be determined and ascribed to finite chemistry. A fundamental discussion of the influences of oxygen concentration in the ambient oxidizing gas on the pyrolysis and combustion of various polymers (PP, PE) is found in Ref. [124]. In the absence of flame spread and dynamic flow mechanisms, polymer combustion is found to have a single degree of freedom, namely Y_O . This determines the fuel consumption rate at the flame and the fuel production rate through surface gasification. The exothermic heat flux from the flame must be sufficient to balance the endothermic degradation and volatilization of the polymer.

Finally, the influences of charring on flame spread have been examined. Questions have been raised concerning radiant heat losses from charred surfaces and whether the losses are sufficient to produce a slowdown of the flame spread rate. Radiant extinction appears to be possible for charring materials, see the numerical and theoretical work of Bhattacharjee and Altenkirch [125] and Bhattacharjee et al. [126]. Experimental work and limited comparisons are available, especially in the microgravity limit [127]. A plausible theoretical explanation, which proposes the use of a revised Damköhler number correlation including radiant heat losses has been advanced in Ref. [36] (Sections 4.4.1–4.4.3). This proposed correlation is based on the results of Bhattacharjee and Altenkirch [125] and Bhattacharjee et al. [126]. West et al. [128] conducted a detailed numerical examination of flame spread with heat losses, including comparisons to theoretical predictions. This numerical study showed that fuel surface radiation from thermally thick fuels is always important and can never be neglected, unlike for thin fuels. Essentially, the reason for this is that the ratio of conduction to radiation transfer ahead of the flame front is of order unity over nearly the entire range of airflow velocities into the flame front. Energy losses from the surface can produce extinction if they are sufficiently large. In many polymers, char formation is not a dominant consideration. However, certain polymers produce a char or carbonized surface layer, as described in Ref. [129]. Optical methods including reflected and refracted light along with X-rays, were used to study char formation on heated PS, PVC-powder, PVC-plasticized and polyamide (PA). Polarized light was used to detect the dependence of optical properties on direction. The degree of anisotropy increased with the intensity of thermal degradation (i.e. rapidity of heating) and the amount of carbonization.

4. Fire chemistry

The objective of fire chemistry studies is to describe the details of chemical reactions responsible for propagating the reaction, releasing thermal energy, forming combustion products and diffusing and convecting these product gases to certain 'sites of action.' An important distinction must be made between reactant species, which usually disappear

quickly and release great quantities of heat as they are consumed, and product species, with which the engineer must deal with both during and after the heat-releasing stages of the fire. As Emmons [8] noted, "For most, but not all fire processes, chemical kinetics is essentially infinitely fast. The rate-controlling steps in the fire are the dynamic processes which mix, heat, and ignite the fuel and air." This statement is certainly true for most *reactant* species, however many combustion *product* species are 'slow' and therefore 'linger' for long periods of time. In transportation fire research it is therefore fitting and proper to emphasize the production and subsequent fate of the product gases, which may be toxicants.⁶ Consequently, much fire and fire safety research focuses on combustion by-products because (1) these may contain toxicants and (2) the decay of these by-products to final or ultimate products (usually CO_2 and H_2O) is much slower than the nearly instantaneous heat releasing reactions.

Perhaps the single most important toxicant in fire research is carbon monoxide (CO), which is a product of almost all hydrocarbon combustion processes. CO toxicity is a vital consideration in structural fires, where occupants may be subjected to long-term exposures of the order of several hours. For example, approximately two-thirds of all fire-related deaths are attributable to CO poisoning [130]. Transportation fires, however, usually occur over considerably shorter times scales so that unless the CO levels are high, times of exposure will be insufficient to produce the longer term toxic results found in buildings. Thus, we expect in transportation that events are relatively rapid, therefore toxicity studies must account for all of the compounds released, particularly those with the capacity to act over shorter time scales.

The field of fire and flame chemistry, with principal emphasis on rates of individual reactions and energy release for individual elementary reaction steps and their relation to entire reaction mechanisms, has a large and burgeoning research literature with many reviews and articles of technical interest [131–135]. Much was learned in the decade from the mid-1980s to the mid-1990s about detailed HC reaction mechanisms, particularly for lower-order HC fuels such as methane, ethane, propane and other saturated HCs. We shall not review this literature because, as indicated, our principal interest in transportation fire safety is to quantify the types of combustion by-products produced in fire and their potential toxicological effect. The details of the reaction mechanisms (important individual reaction steps, individual reaction rates) are not as relevant presently as the number, concentration, nature and influence of the combustion by-products. Nevertheless, in more detailed investigations the influence of chemical formation rates on

⁶ Defined as toxic compounds that are somehow produced, e.g. by a chemical reaction or in material thermal degradation, in contrast to toxins, which appear naturally.

the ultimate concentrations of combustion by-products must be examined.

This section describes three principal areas of fire chemistry. These are products of combustion, toxicity, and smoke and retardants. Overlap clearly occurs in these categories (e.g. the analysis of combustion products of fire-inhibited combustibles).

4.1. Products of thermal decomposition and combustion

The release of products of thermal decomposition and combustion for materials used in transportation occurs over a range of temperatures, ranging from relatively low ($0(300\text{ }^\circ\text{C})$) for smoldering and initial thermal degradation of thermoplastic materials to relatively high ($0(1500\text{ }^\circ\text{C})$) for gas-phase combustion and open flaming. The former range of low temperatures characterizes the thermal breakdown of the material and perhaps the smoldering stage of combustion undergone by many materials. This temperature range, however, is associated with long time scales and implies low-level largely undetected fires. The latter range of high temperatures is more characteristically and vividly associated in the imagination with transportation fires: an accident involving a car or train or other large vehicle followed—inevitably in the Hollywood version—by a massive explosion and fireball. On the one hand, in this much shorter time scale the chemical product species that produce a harmful toxic effect may be less important than the disastrous effects of the heat release such as burns. On the other hand, if the high-temperature toxicant is very effective, perhaps only a very short time is needed for feeling its full effect. In either case it is clear that the range of temperatures and conditions in which transportation fires can occur is wide and no set range of conditions applies to all cases. It proves helpful in a review, however, to distinguish between low and high temperature product formation processes.

In order for a possibly lethal event to occur in a prolonged low-temperature thermal degradation process or in smoldering [130], active flaming is not necessary [16,17]. The low-temperature smoldering and moderate-temperature thermal decomposition of most HCs releases gaseous volatiles and toxicants [136]. For example, at approximately $300\text{ }^\circ\text{C}$ cellulosic materials such as wood and paper readily decompose [137], emitting CO and other potential toxicants. These toxicants often linger for long time periods because at such low temperatures they react slowly to form additional (or ultimate) products such as CO_2 and H_2O .

In high-temperature gas-phase combustion of even the simplest hydrocarbon (HC) fuel, methane, the final products CO_2 and H_2O do not appear instantaneously upon disappearance of the reactants CH_4 and O_2 as implied by the global formula $\text{CH}_4 + 2(\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2$ that describes stoichiometric methane oxidation in air. In actuality, the reactants CH_4 and O_2 quickly form a set of intermediate compounds,

which subsequently combine to form the final products CO_2 , H_2O when the surrounding gas temperature is sufficiently high. An important intermediate is CO, which is slowly oxidized to CO_2 after it has been produced by the decomposition of the reactants. Thus, the oxidation of a HC fuel generally proceeds in two or more stages. These stages can be *qualitatively*⁷ represented as a rapid production of CO from the parent fuel (the ‘essentially infinitely fast’ reaction described by Emmons [8]) followed by a slow oxidation of the CO to the final product CO_2 . A qualitative rendering of the previous 1-step global methane oxidation reaction is to divide it into two steps. The first step is the very fast oxidation of CH_4 to CO and H_2O , viz. $\text{CH}_4 + 1.5(\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO} + 2\text{H}_2\text{O} + 5.64\text{N}_2$. The second step is the slow oxidation of the intermediate CO to CO_2 via $\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$. It has been forcefully argued that it is impossible to reduce the methane oxidation sequence to fewer than three ‘global’ reactions. A four-step methane reduced chemistry sequence, which has successfully modeled aspects of combustion such as laminar premixed flame speeds and flame quenching, contains the steps (1) $\text{CH}_4 + 2\text{H} + \text{H}_2\text{O} \rightarrow \text{CO} + 4\text{H}_2$; (2) $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$; (3) $2\text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ and (4) $\text{O}_2 + 3\text{H}_2 \rightarrow 2\text{H} + 2\text{H}_2\text{O}$. The latter two steps describe the formation of H_2O (and are common to all hydrocarbon oxidation reduced schemes) whereas the former two steps are concerned with the consumption of the particular carbon-containing species, in this case CH_4 . We note from this scheme also that the methane oxidation contains CO as an intermediate, and that the second reaction is generally much slower than the first. CO oxidation chemistry, which is very sensitive to trace amounts of impurities, moisture and other influences, is discussed in detail by Yetter et al. [134] and Rightly [138]. For the purposes of this review it suffices to observe that CO is a potentially highly toxic gas whereas CO_2 is relatively non-toxic by comparison.

Toxicity measures depend upon both the location of their application and the time of toxicant application. The spatial location of both the source and the target are important because combustion products are not static and therefore move under the influence of mass diffusion and convection, both forced and natural. Similarly, the time of exposure is crucial to the target, but is also important for delivery: toxicant production rates can vary in time even if the source that produces them is spatially homogeneous.

Heavy HC fuels and non-stoichiometric HC oxidation produce large numbers of potential toxins. The analysis of intermediate products of combustion and toxins has been enhanced by the advent of new and sophisticated chemical diagnostic methods (e.g. FTIR spectrometry, gas chromatography/mass spectrometry (GC-MS)). GC-MS was used to examine the thermal decomposition products of HDPE

⁷ As discussed in Refs. [131–135] the oxidation of any hydrocarbon fuel proceeds through long, intricate reaction mechanisms containing up to 10^3 elementary reaction steps.

[139]. The samples were exposed for 20 min to relatively low pre-combustion temperatures of 375 °C. The decomposition products included propane, ethane, butane, propylene, ethylene and 1-hexane, with propane as the most abundant volatile product. At sufficiently high gas temperatures, such volatile gases may begin reacting with the available O₂ to form products of combustion such as CO, CO₂ and H₂O. The 375 °C = 650 K temperature is lower, we note, than the usual ignition temperature for solid combustibles (Section 2.2.2). Morimoto et al. [140] examined various polymers (PE, PS, nylon 66, PU, etc.) for their degradation products in two gas atmospheres, one hot but inert (all N₂), the other hot but oxidizing (air). The heated gas temperature ranged between 700 and 800 °C, sufficient for the air to ignite a flame and to produce flaming combustion. The main gaseous HCs produced in flaming were CH₄, C₂H₆ and C₂H₂. Hydrogen cyanide (HCN) was produced by all N-containing compounds and also for all polymers tested in the N₂ flows. Ammonia was produced from flaming combustion only for nylon 66 and polyacrylamide, but in N₂ it was produced in all cases except for PU. Compounds containing sulfur produced SO₂ in the gaseous products. These studies confirm the general truth that low-temperature pyrolysis and degradation produce a variety of heavier degradation products whereas high temperature degradation, as for example in the presence of a flame, produces lighter degradation products. The low-temperature products are often referred to as 'volatiles' because they can subsequently easily be ignited by a suitable heat source and they are generally heat-releasing reactants. To the author's knowledge, relatively few studies have examined the full range of degradation products for familiar materials under heating.

One work that attempts this is by Chien and Kiang [141] who examine the oxidative pyrolysis of PP, finding that the pyrolyzed polymer liberates oxygenated compounds that undergo subsequent oxidation by the gas-phase flame. These authors begin by noting there has been 'surprisingly little fundamental study of high temperature oxidations' of polymers in the stages between polymer surface and flame. They note, in addition, that 'there does not seem to be any thorough study of polypropylene oxidation above 200 °C.' TGA was used to show that polymer degradation begins at 200 °C and ends at 400 °C. The pyrolysis is called 'oxidative' because pyrolysis occurs in the presence of oxygen in the circumambient gas. As the amount of O₂ in the gas increased, the yields of acetaldehyde, acetone, butanol, and water all decrease, whereas in their place 'the yield of CO₂ increases rapidly.' This trend especially increases for %O₂ greater than 60%. The dominant and ultimate oxidation products for all %O₂ are CO₂ and H₂O but the predominant secondary oxidation products are CO and CH₃OH, which arise from formaldehyde and acetaldehyde. The oxidative pyrolysis of PP showed first-order kinetics in the narrow range between 240 and 289 °C. The authors wrote a simple Lindemann-like kinetic mechanism

which, using the steady-state approximation for the intermediate hydroperoxide (ROOH), was able to provide a first-order expression for the overall kinetics. We note that PP is a 'versatile polymer' that does not melt below 160 °C and is often used to make indoor-outdoor carpeting since it does not absorb water [142].

Thermoplastic polyamides form a large sector of the adhesives industry and thus may be utilized in the various transportation industries. Related compounds such as adhesives, printing inks, and reactants for epoxies are formed from a dimer acid (a polymerized fatty acid). Nylons are polyamides are not, however, made from dimer acids. Thermoplastic polyamides can vary from semi-solids with low molecular weight to solids of high molecular weight; polyamide adhesives can adhere to metals, glass, cellulosic substrates and many plastics; and these adhesives often have good impact resistance, thermal stability and flexibility [143]. The thermal decomposition of the polyamides polycaprolactum (PA-6), polyoentanholactam (PA-7), polycaprylolactam (PA-8) and rislin (PA-11) in 510, 610 and 770 °C atmospheres for heating rates of 15 °C/min was examined by Michal et al. [144]. As for Tsuchiya and Sumi [139], weight loss began at $T = 200$ °C. The polyamides began to decompose at $T = 400$ °C: major decomposition was completed by $T = 500$ °C. Approximately 80% of the volatiles were produced between 400 and 500 °C. The most toxic products were the nitriles, such as acrylonitrile and acetonitrile, which comprised up to 'half of the total volatile products' of thermooxidative degradation. Other main products of thermo-oxidation were long-chain nitriles, alkanes and olefins. The decomposition gases formed from these polyamides are dense, which according to the authors 'can be regarded as a warning signal of the dangerous nature of the pyrolysis and thermooxidative products of polyamides'.

Polyethylene, polypropylene, polystyrene and polyamides were examined by Mitera and Michal [145]. They studied flaming and non-flaming combustion of these thermoplastics using two different combustion chambers. One, the 'CAB 4.5' simulated the combustion of large samples in a small space while the other, the 'CAB 650' modeled the opposite: the stage of fire in which a flow of air over the burning material is employed. The higher-temperature flaming combustion in CAB 650 produced more CO₂ and more aromatic HCs. For PS, flaming combustion produced a complicated mixture of monomers, dimers and trimers in contrast to the non-flaming CAB 4.5 test. This study drew attention to the difference between the pre-burning degradation stage and the actively burning post-degradation stage, showing that flaming combustion produced greater quantities of products although overall proportions of the species remained similar. The authors also showed that for flaming combustion in the CAB 650, PS produced a more complicated mixture of monomers, dimers and trimers than in non-flaming degradation (i.e. the CAB 4.5). The authors concluded that the CAB 650 test was

a useful supplement to the CAB 4.5 for determining individual toxic substances, optical smoke density, and chemical evaluation of polymers in possible fire environments.

Grand [146] used the University of Pittsburgh Toxicity Test Apparatus to examine PP, PS, Douglas fir and cotton for the evolution of CO and CO₂. Consistent with previous discussions, CO evolved in higher concentrations when conditions inside the test device led to active flaming, and thus higher rates of decomposition of the material. CO and CO₂ measurements were also performed by Brauman [147] and Michal [148]. For PP, mixed polyester (PMPS), and polystyrene, Brauman [147] showed that increased CO formation was accompanied by smoke formation and that the flame retardant Sb₂O₃ increased CO and decreased CO₂ levels during combustion. The tests were not static but employed vertical sample rods that were radiantly heated in a 10 l/min air crossflow. Enhanced radiant fluxes produced accelerated rates of decomposition. Michal [148] demonstrated, as have several of the preceding studies, that CO production is sensitive to the gas-mixture oxygen content. An added complication in real fires is that combustion temperatures vary significantly from the beginning to the end of the fire. As the temperature increases, so does the CO content in the intermediate combustion products of polymeric materials. A measure of the sensitivity of the CO measurements of Michal [148] was the experimental reproducibility, which varied with respect to the chemical diagnostic technique used.

PU foams, which are commonly used in transportation, have been studied for their degradation and potential toxicity. Comeford [149] developed a flash-fire cell test method for PU foams in which samples are pyrolyzed in air while measurements are made for the time of onset of a flash fire and pyrolysis gases are simultaneously withdrawn for analysis. Comparisons were made for various PU foams and other polymers of potential interest to the aircraft industry. Einhorn et al. [150,151] examined the thermal degradation of 'model' rigid PU foams to determine the influence of chemical structure, fire-retardant structure and fire-retardant chemistry in order to 'gain insight into the burning mechanism of the rigid-urethane foam and fire retardancy by studying the products of degradation of both fire-retarded and non-fire-retarded model rigid-urethane foams.' The retardants used were tris(2,3-dibromopropyl)phosphate and tris(2,3-dichloropropyl)phosphate in concentrations ranging from 4 to 16% by weight. The LOI was determined for foams with different retardant levels. As the temperature of pyrolysis was increased, the quantity of light volatile gases increased. The major product at 500 and 1000 °C was CO₂, whose concentration depended more on pyrolysis temperature than retardant concentration. The pyrolysis products of the non-fire-retarded foams depended very strongly on the pyrolysis temperature. The basic degradation mechanism was unchanged with addition of retardant. The retardant did not influence the breakage of the urethane bond

(which would lead to the formation of CO₂). Unretarded PU lost 100% weight at 620 °C, whereas 8%-concentration retarded PU remained charlike at 800 °C. Retardant type had little influence on charring, since either retardant produced nearly the same TGA sample weight loss thermal decomposition curves (Figs. 14 and 15 of the article). Interestingly, the fire retardant catalyzed reactions leading to the formation of light and 'noxious' gases. At low heating rates a large portion of the retardant volatilized, whereas at high heating rates it caused the formation of light gases.

In Ref. [150] model urethane foams were examined for combustion products and polymeric structural changes using thermoanalysis, direct-probe analysis, and residue/volatile analysis. Pyrolysis consisted of heating and then igniting foams in He at 500, 750 and 1000 °C. The degradation process was divided into two distinct stages, a char-formation stage (250–400 °C) and a char-degradation stage (400–700 °C). The former stage was independent of heating rate. The latter stage occurred via slow thermal degradation and chain unzipping of the high-molecular-weight molecules, and an increase of degradation temperature appeared not to affect the urethane foam degradation mechanism, since the major reaction was still the breakage of the urethane bond, which released the CO₂. The main reaction occurring in this latter stage of heating produced predominantly CO₂ and H₂O indicating that the dominant reaction was oxidation of the char. The degradation products during the char-erosion stage were NO, CO₂, H₂O and benzene (in air), showing that the charring stage, for these model foams, produces few toxicants. A kinetic model with rate parameters was also derived.

Rotival et al. [152] examined small 100–200 mg thermoplastic samples heated at 5 °C/min in a 30 ml/min. airflow using TGA and gas analysis techniques. The thermal decomposition of PP, PU and PP/PU mixtures produced very low mass percentages of aldehydes–ketones, HCN, and isocyanates relative to CO and CO₂. The gases emitted from PP/PU mixtures differed from emissions for individual PP and PU samples. The mass percentages of CO and CO₂ were functions of temperature, O₂-level, and sample decomposition rate (i.e. weight loss).

PVC [(C₂H₃Cl)_n] is an important polymeric material in common use. PVC flame resistance can be attributed to the release upon heating of the Cl atom, which inhibits flaming combustion. However, a chemical pathway is formed for the production of the toxicant HCl. Boettner et al. [153], Zinn et al. [154], and Statheropoulos [155] studied the decomposition products of primarily PVC under external heating. Boettner et al. [153] used DTA and TGA along with IR and mass spectroscopy to identify pyrolysis products. The results showed that (1) endothermic peaks caused by the release of Cl occurred between 300 and 600 °C; (2) weight loss rate varied with temperature and was most rapid below 280 and above 510 °C; (3) different PVCs had different volatile products; (4) CO, CO₂, and HCl evolution was largely independent of airflow variation; (5) HCl production

appeared to be independent of sample heating rate. The study of Zinn et al. [154] examined 11 PVC samples of varying compositions (and also seven PP samples) under non-flaming conditions for smoke particle size distribution, total smoke particulate mass generated, smoke mean particle diameter, smoke optical density, and sample weight loss. The smoke characteristics are altered for PVC and PP by the different chemical additives. Statheropoulos [155] used direct-inlet mass spectrometry (DIMS) to study and identify PVC degradation products in 30 min constant-temperature tests. At low temperatures of 160 and 180 °C the volatiles (defined as HCl and the aromatic HCs) were 100% HCl. At 200 and 220 °C they were 96% HCl and 4% aromatics. At 240 and 280 °C a change occurred. A rapid evolution of HCl and aromatics occurred in the first minute of degradation, followed by a decreasing evolution rate thereafter. These studies state that the formation of HCl upon PVC degradation is an experimental fact, and that various sophisticated diagnostic methods can be used to make accurate measurements of its rate of evolution under thermal insult.

The decay of the combustion by-product HCl is itself a question of fire science. Galloway et al. [156] studied HCl decomposition in a 3L chamber, varying humidity, temperature, HCl concentration, and wall materials (PMMA, ceiling tile (CT), marinate (MAR), gypsum board (GB), cement block (CB), etc.) The research supports the assertion that HCl reacts rapidly with surfaces leading to peak HCl fire concentrations much lower than predicted from equilibrium chemical analysis. Almost all of the surface materials tested readily consume HCl, for which evidence is provided by progressively decreased consumption rates in repeat experiments with the same material. This study, in addition to demonstrating the uptake of HCl by nearby surfaces that may be present in transportation fires, demonstrates the importance of mass transport on toxicant behavior: according to these experiments, this particular toxicant appears to have a propensity for removing itself from the carrier gas.

Finally, Fardell et al. [157] conducted a 'fingerprint' sampling and analysis to study the chemical nature of fires of wood, PP, PMMA, and PS foam, using a 24 m³ compartment-corridor fire-test rig. Gas samples of 250 ml were extracted during various stages of the fire and analyzed using gas chromatography and mass spectrometry. It was found that the combustion products were similar for all fuels used, but their concentrations varied widely. CO concentrations were usually higher than the total concentrations for all the other compounds at the same point in the fire. After CO, the most toxic substance measured was acrolein. The acrolein concentrations were low: CO was still the dominant toxic product even when the acrolein concentration exceeded the lethal limit of 10 ppm.

These studies of thermoplastic materials commonly used in transportation suggest that, for nearly all materials studied, a large difference is found in products of material

degradation when temperatures are low and when they are high, as in a flaming environment. In low temperatures the degradation products appear to be heavier, including species such as methane, ethane, acetylene, HCN, acetaldehyde, butenol, acetone, and many others. At higher temperatures the formation of CO seems to dominate the intermediate product stage, and if the supply of oxidizer is sufficient and the temperature is sufficiently high the ultimate oxidation of the CO to CO₂ proceeds as expected. Nitrogen-containing compounds produce nitrogen-containing products, just as Cl-containing materials (PVC) produce Cl-containing products (like HCl). What are needed, apparently, are chemical rate formulas and rate parameters that allow the type and quantity of these species to be calculated in both pre-flaming and flaming environments. The overall mechanism of material breakdown followed by eventual oxidation to CO₂ and H₂O is understood, but the intermediate species distributions, their concentrations during degradation and subsequent combustion, cannot, it appears, yet be calculated. If mechanisms such as these are ultimately to be used in anything more than a descriptive and prescriptive manner, calculating the species concentration field evolution must become possible.

4.1.1. A case study: the sunshine mine

We study an example that illustrates many of the principles discussed to this point of the review, namely the Sunshine Mine (Idaho) fire of May 2, 1972, which killed 91 men. Wilde [158], whose study was commissioned by a legal firm investigating the fire, undertook to simulate the actual mine fire conditions in a large tunnel that is 200 m long, has a 1:30 rise/run ratio, a cross-sectional area of 4.25 m² (max height of 2.2 m), a width of 1.67 m, and a curved semi-circular ceiling. The main test section was approximately 25 m long. It was ventilated by a fan giving an air-speed of 4.9 m/s. The inside of the tunnel was lined with either polyurethane (two tests) or plywood (two tests). Ignition of the wall materials was achieved using wood cribs (about 100 kg), which were set afire in approximately the middle of the test section, providing a maximum of about 100 kW. At ignition, a door that separated the ignition 'pilot' flame and the test tunnel was opened both to the upwind and downwind sides of the test section. Measured quantities included O₂, CO and CO₂ concentrations, fume temperature, and flame speed using gas analysis, TCs at various tunnel locations, and visual camera measurements, respectively. For the PU tests, the igniting flame caused the heated foam 'to emit a grayish white vapor which formed a cloud in the upper levels of the tunnel.' When this cloud ignited, the fire very rapidly propagated downwind through the tunnel at speeds around 2 m/s and completely filled the tunnel with intense flames. The fire spread upwind O(100) times more slowly at approximately 0.02 m/s. These results show the necessity of piloted ignition, the phenomenon of vapor release from surfaces before they fully ignite, the stratification of the hot vapor layer in the upper section of

the tunnel, and the rapid rate of spread of flames through the stratified mixture. Each of these phenomena can be explained in fundamental, science-of-engineering terms. The rapid propagation of fire through combustible mixtures in the ceiling fire arrangement is particularly to be noted. The measurement by Wilde [158] of the transient species concentrations also supports fundamental observations made in this review. As the fire progressed, measured O_2 fell from the initial 23% (by volume) in air to $\sim 1.5\%$ (by volume). CO reached a maximum at that same instant. The CO_2 level attained its maximum value slightly later when CO was decreasing. Therefore, combustion of the fuel and air initially gives products that include large quantities of CO, which is subsequently oxidized to CO_2 . The measurements clearly show that the CO% falls as the $CO_2\%$ rises. The toxic effect consisted of the very rapid buildup of 'fumes' consisting of these oxides of carbon (CO and CO_2) coupled with the indicated severe oxygen depletion. The author speculated that the depletion of oxidizer, the formation of toxic fire fumes, and the high temperature of these fumes 'could each have proved fatal almost instantaneously to anyone caught directly in them.' Foam fires are of short duration because of their high burn rate. There was no discussion in Ref. [158] of other toxicants such as HCN, which would have shown up as trace quantities. The author states, however, that the fume toxicity cannot be ascribed to CO, CO_2 and O_2 depletion alone. The trends described for the PU foam case were repeated, though much less dramatically. For the wood wall cases the fire-spread rate was much slower, about 0.02 m/s downwind and about 10X slower upwind. Finally, consistent with Eq. (2.5) the importance of $\rho_s c_s \lambda_s$ was reiterated. A low value produces a high rate of temperature rise at the surface and vice versa. Wilde [158] notes that "If, in addition to heating up rapidly, a material decomposes at low temperature to yield gases and vapors which ignite easily, it is likely to be defined as highly flammable."

The elongated tube-like shape of the test tunnel, the rapid buildup of a combustible ceiling gas/vapor layer, the dramatic speed of combustion, the depletion of the oxygen, the rapid heat release and temperature rise, and the shear force of their combined effect appears to make this simulated mine shaft study quite relevant to transportation fire safety analyses.

4.2. Toxicity

This subject is vast and the number of articles reviewed is large. Hence, we subdivide this section as follows: After an initial discussion of the basic scope and nature of toxicity analysis, with specific emphasis on the general subject of fire and combustion gas toxicity, we discuss PVC toxicity in Section 4.2.1. This discussion is an extension and specialization of Section 4.1. In Section 4.2.2 we discuss polymer decomposition and toxicity, including polymers considered generally, as well as specific polymers such as

ABS and polymers that contain nitrogen. In Section 4.2.3 we consider the broad class of PU foam toxicity. Finally, Section 4.2.4 provides a summary of several reviewed articles describing toxicity of fire-retarded materials, practical materials and foams, and the influences of physical variables, such as heating rate, on toxicity.

Chemical research on fire toxicity and fire retardant chemistry usually involves the withdrawal, for chemical analysis, of very small, presumably homogeneous samples of gas or material. Since toxicology is the study of the harmful effects of chemicals on living organisms, properly homosapiens, it focuses on the amount of chemical that reaches a site in the organism as well as the ability of the chemical to initiate a harmful effect at that site. The 'target' site (e.g. the liver) may not be identical with the initial application site of the toxicant (e.g. the bloodstream). This is known as intrinsic toxicity of the substance. It is commonly observed that the concentration of chemicals at the internal site of action is proportional to the intensity of the observed toxic effect. Because the amount of chemical at the internal site of action (e.g. lung tissue) depends upon the quantity of chemical presented to the organism (e.g. its concentration in air), exposure of the organism to the toxic substance is an important consideration in predicting the intensity of the toxic effect. It is not the only consideration, however. Another important issue in chemical toxicity is the chemical's fate inside the organism prior to reaching its internal site of toxic action. Toxicologists in their research generally concentrate on the variables controlling chemical toxicity *in the organism itself*. The type of chemical and the degree of exposure of the organism (e.g. concentration, exposure time) are typical variables in toxicological experiments. In summary, most toxicological research focuses on quantifying the response of the *organism* to received chemical insult⁸ and does not as often address the environment in which and through which that toxicant is delivered. Ethical concerns associated with human experimentation have led to the practice of using surrogate test species (e.g. rats, mice, monkeys) to help characterize the potential health hazard associated with exposure to toxicants such as combustion by-products.

Nearly all substances can be considered toxic, for example, O_2 is toxic when concentrations are high and times of exposure are long.⁹ Such qualifiers, though important, cannot change the fact that it is not the toxicity of compounds like O_2 and air that causes concern, rather it is a limited, specific subset of compounds that causes the majority of injuries, incapacitations, and deaths. This review

⁸ The author is indebted to Professor L.J. Fisher, Director of the Michigan State University Environmental Toxicology Institute and Professor of Pharmacological Toxicology for this definition of toxicological research.

⁹ The famous quote of Paracelsus (1493–1541) embodies this viewpoint: 'All substances are poisons: there is none which is not a poison. The right dose differentiates a poison from a remedy.'

focuses on this subset of compounds, some of which were already discussed in Section 4.1.

Active (non-smoldering) fires in transportation typically exhibit times scales in the range of minutes to tens of minutes, unlike building fires where time scales range from tens of minutes to tens of hours. Overlap occurs, of course, for very large vehicles like warships and passenger ships, whose fire scenarios may resemble buildings more than automobile accidents, but generally (even in the case of ships) the emphasis is on immediate detection and rapid extinguishment. The time scales also become large for smoldering and thermal degradation events. Generally, therefore, the time scales associated with transportation fire safety should be an order of magnitude smaller than those associated with building fire safety, particularly as the size scale of the vehicle diminishes.

Real fires occur in regions where inhomogeneities produced by flow and diffusive transport can influence the nature and concentration of combustion by-products. The products of degradation or combustion are often hot and light so buoyancy can carry them away from their location of origin rendering concentration fields of the chemical by-products of combustion both transient and inhomogeneous (see, e.g. the case study of Section 4.1.1). In an ordinary room fire, for example, the gases are stratified in the lowest approximation into a hot gas layer in the upper part of the room, where the average temperature is $O(1000\text{ K})$, and a cold gas layer in the lower part of the room, where the temperature is much closer to 300 K . Firemen are taught in their training programs to understand this fact, and to respond appropriately. The non-homogeneity of a concentration field is known to have a dramatic influence on its flow behavior (particularly since density and pressure gradients are involved) and the combustion behavior (if, for example, the concentration of reactants depends on the location). Although there has been some research on product gas movement and dispersion in the context of fire hazard, there has not appeared a systematic emphasis on this subject analogous to research on flame propagation and fuel degradation chemistry.

Since toxicants can be oxidized or transported in fires away from their place of origin by forced or free convection, the determination of 'toxic hazard' in terms of actual room or external fire conditions is difficult. It is far easier to produce a homogeneous test environment for laboratory animals that are forced to inhale the gases that later appear in their bloodstream and vital organs. The decay and change of these measures is relatively slow, and animals exposed to known concentrations of specific combustion by-products in homogeneous testing environments can provide accurate information on toxic effects (for the animals). Extrapolation to the response of humans to similar homogeneous dosage levels is both common and controversial [159], thus the advent of the descriptor 'selective toxicity' as a measure of the differential response between different types of animals [160]. Recent research has shown that the toxicant uptake

differs between humans and surrogate species such as rats and monkeys. The transport of the by-products of combustion in non-homogeneous environments and in the nasal and other passages of the animal species themselves is thus as important, if not determining, part of their ultimate toxic influence.

Two approaches to the transport of potentially toxic combustion by-products have been followed in the research literature. In one approach, the movement of the products through the large-scale atmosphere is described with flow models that seek to predict downstream effluent concentrations. The objective is to determine which regions downwind of the source will be most severely subjected to the products. In the other approach, the host is 'exposed' to the toxicant, but the actual passage of the chemical from its entry into the nasal passage to the lung surface is carefully examined and modeled. Thus, Nikula et al. [161] demonstrated that for equal exposures "...relatively more particulate material was retained in monkey than in rat lungs..." for all groups tested. Their results, in which rats showed significantly more inflammatory and other responses in their nasal passages '...suggest that intrapulmonary particle retention patterns and tissue reactions in rats may not be predictive of retention patterns and tissue responses in primates exposed to poorly soluble particles...' Kimbell and colleagues [162,163] have employed computational fluid dynamics (CFD) methods to model inspiratory nasal airflow in rats and monkeys with the objective of determining whether nasal flow geometry and associated differences in flow patterns may be partly responsible for these differences of inhaled gas uptake. Kepler et al. [162] determine that "...uptake simulations...compared with published observations...indicated a strong correspondence between airflow-dependent transport patterns and local lesion sites." Additional details of the CFD simulations are provided by Subramanian et al. [163] and references cited therein. These authors state that "this model can be used to reduce uncertainty in human health risk assessment for inhaled materials." The research generally questions the appropriateness of employing certain animal species (e.g. rats) in the assessment of toxicological influences on other species (e.g. monkeys). The differences between rats and monkeys suggest that toxicity assessments for primates may require revised approaches.

Toxicological measurements often include such quantities as times to incapacitation, staggering, convulsions, collapse and death. According to Eaton and Klaassen [160] "simply recording a death is not an adequate means of conducting a lethality study of a new substance," rather "a careful, disciplined, detailed observation of the intact animal extending from the time of administration of the toxicant to the death of the animal." Respiratory rates and other vital organ responses (e.g. heart rate) may in some cases be recorded to determine the pre-death influences of chemical toxins. Histological examinations of possible abnormalities in the animal's major tissues and organs can yield additional

information about the nature of the toxic response mechanism. Tissue damage and toxin concentrations can be systematically examined, leading to the accumulation of 'specific information about the events leading to the lethal effect, the target organs involved, and often a suggestion about the possible mechanism of toxicity at a relatively fundamental level' [160]. For example, the study by Farrar and Galsten [164] assessed toxicity from material combustion using various 'toxicological endpoints.' Two of the endpoints were incapacitation and death (lethality). Others included 'post-exposure complications' and 'leg-flexion avoidance response,' which is a response to various combustion products.

Specific types of observed response can sometimes be used to help identify the specific toxicant to which the test subject was exposed. Farrar and Galsten [164] state that the exposure period (a crucial variable that must be recorded in such toxicity tests) alone is insufficient for determining which toxins were present, and that histological examination was necessary to determine all of the toxins. In their research on Long-Evans rats exposed (head only) to the decomposition products (flaming and non-flaming) of Douglas fir, phenolic foam, urea formaldehyde foam (UF) and flexible PU foam, the material comparison was based on the following five measures: (1) potency of combustion product atmospheres, (2) animal observation, (3) blood analysis, (4) gross pathology, (5) atmospheric analysis. For (1), the EC_{50} (concentration of chemical in air causing incapacitation in 50% of the exposed rats) and LC_{50} (lethal concentration = concentration of chemical in air causing death in 50% of the exposed rats) values were highest and approximately the same for Douglas fir and PU foam. Under non-flaming conditions phenolic foam had higher EC_{50} and LC_{50} values than UF, vice versa under flaming conditions. A higher LC_{50} value means simply that the dose (usually measured in units of moles of dose per kilograms of animal body weight, i.e. mole/kg) that causes 50% lethality is higher, or the substance is comparatively safer. See, e.g. Ref. [160] for an excellent description of this particular dose-response evaluation method, where many of its limitations are discussed. Specifically, they note that it is generally 'only necessary to characterize the LD_{50} (lethal dose) (or LC_{50}) within an order of magnitude range such as 5–50 mg/kg.' Greater differences between these four materials of their incapacitating effects were determined by the leg-flexion avoidance response than EC_{50} and LC_{50} . A concentration-response diagram (their Fig. 1) showed that incapacitation caused by non-flaming products was greater in UF followed (in order) by phenolic foam, PU and Douglas fir. Large differences between materials were observed in the COHb levels at time of incapacitation, with the highest value for phenolic foam followed by Douglas fir, PU and UF. The authors state for phenolic foam that the 'most valuable piece of information was the determination of COHb levels...clearly implicating CO as the intoxicating agent under the conditions of

the experiment.' The authors determined that the incapacitating effects of UF foam, however, could be attributed to HCN, not CO. For PU the situation was complicated by the 'wide range of incapacitation times and low atmospheric levels of CO and HCN at incapacitating doses.' The authors stressed the importance of lethality assessment, particularly the 'degree of involvement of CO in exposure deaths' in order to 'preclude the involvement of additional toxicants.' They conclude that 'a multi-component test is required to detect the toxicity of an acknowledged multi-component insult.'

Herpel [165] examined the toxicity of 35 building materials using Wilson rats. Cessation of respiration was employed to measure time of death from exposure to products of decomposition for materials falling in the general categories of woods, synthetic polymers, and textiles. Three different combustion temperatures were used. Histological examinations included measurements of COHb levels. The author divides animal toxicological evaluation into two groups: (1) simple methods using death, incapacitation, or both as endpoints, (2) more elaborate methods using many physiological parameters (e.g. electrocardiograms) and behavioral characteristics. Methods for type (1) 'seem preferable in relation to the problem of acute toxicity' whereas (2) seems 'more appropriate in assessing long-term' permanent damage in survivors. This particular research gave priority to acute toxicity. The author concludes (1) '...toxicity results are extremely dependent on test conditions, thus giving the general impression that any combustible material will become dangerous because of toxicity when placed in its own critical condition.' (2) Determining whether or not a material produces an 'unusual' toxic environment (as required by an ISO Technical Committee in 1976 to study 'toxic hazards in fire') is possible using present tests, but additional tests are necessary. (3) Present (circa 1980) 'state-of-the-art' research 'does not permit...establishing...well-founded toxicity safety regulation for materials in buildings.'

Herpel and Vandervelde [166] developed toxicity indices to express mortality rates as a function of time of exposure. Twenty materials, including plastics, textiles, and wood species were tested at 600 °C. The proposed mortality index penalizes materials that produce earlier deaths when compared with materials that give high mortality rates later in the experiments, meaning that early mortality is weighted less than late mortality. This may be important in building fires (which the authors mention in their article), but for transportation fires it may be valuable to weight early mortality more than late mortality. Nevertheless, these authors have suggested a means for carrying out the weighting process.

Hilado et al. [167] showed that for numerous polymeric combustibles the influences of pyrolysis gases on toxic response could be quantified. The responses of the freely moving mice were visually observed and they were recorded over the entire test time, with specific attention paid to

staggering, convulsions, collapse and finally death. Each of these measures is carefully defined, and the time is recorded of the first instance of such response. The authors used different test conditions to simulate different fire situations, with the intent of simulating pre-flashover conditions in a developing fire, e.g. 200–800 °C rising temperature at 40 °C/min with no forced airflow. Various post-flashover conditions were also simulated. Here the temperature was fixed and a cross-flow of air was employed for all cases. The specific gaseous toxicants arising as either pyrolysis products or combustion products were CO, HCl, HF, HCN, NO₂, SO₂ and NH₃. The authors state that “In contrast to the 8 h and longer exposures considered in evaluating long-term toxicity in the occupational environment, exposure periods of less than 1 h, preferably 30 min or less, are more relevant to fire situations because the time available for escape and rescue is often measured in minutes.” The authors further assert: “Specific toxicant test data under the latter conditions, however, are meager relative to data under longer-term exposures.” As noted in this review that the time scales associated with transportation are perhaps even one order of magnitude shorter than for homes and buildings. It was shown for tests at fixed temperatures 300, 350, 400, 450, 500, 600 and 800 °C for a PE polymer that generally (with only one exception at 350 °C, caused apparently by the release of acrolein) the animal response times decreased with increasing temperature.

The subject of fire-gas toxicity has been examined from the standpoint of fire research and not simply as a branch of Toxicology or Chemistry in the works of Babrauskas et al. [168], Gann and Levin [169], Babrauskas [170], Babrauskas et al. [171], Babrauskas [172]. We shall discuss these articles in chronological order. In Ref. [168] the authors discuss a ‘new approach’ to fire toxicity evaluations of fire hazard, emphasizing the comprehensive nature of the role of physical features of the fire, the building, the rate of smoke production, the rate of smoke loss (e.g. from windows), and occupant susceptibility. According to the authors, only when all of these criteria are properly accounted for does a complete fire hazard have logical meaning. We may compare these physics/engineering-based criteria to constrained, head-only toxicity tests on mice and rats relying on chemically based measures of toxicity. The work of Gann and Levin [169] summarizes the previous methods of measuring toxic potency while emphasizing numerous issues that require study. According to this work “...direct comparison of only toxic potency values is not a valid means of determining the fire safety of materials and is not sufficient for evaluation of fire hazard.” Babrauskas [170] describes experimental techniques for the measurement of heat, smoke, and toxic gas release from real fires. The need for minimizing apparatus dependence is discussed, as are differences between the data obtained from large-scale fire tests and bench-scale tests. In Ref. [171] the NIST group determined that the proper subject of smoke and fume

inhalation deaths is the *post-flashover fire*. In addition, the authors discuss criteria for useful bench-scale toxic potency measurements, their validation with respect to actual fires, computational methods for correcting CO levels obtained in real-scale post-flashover fires, and methods for interpreting chemical data using the ‘N-Gas Model’ of Babrauskas [170]. Much of this work is summarized in Ref. [172] in the form of a model that amounts to a fire hazard analysis using available test data. Examples of the use of the test data on various products can be obtained from the National Bureau of Standards Toxicity Test and from the cone calorimeter. The method described here represents an attempt to ‘place in correct context...the toxic potency and burning rate variables.’ In terms of human hazard one cannot discuss ‘toxic hazard’ when the rate of removal of toxins (by buoyancy-induced flows or forced flows) is comparable to their rate of production. In other words, the first step of the toxic mechanism, delivery of the toxicant [173], must be carefully assessed before venturing into detailed evaluations of neurophysiological biochemical response.

These works demonstrate that a characterization of toxicity on the basis of qualitative and quantitative chemical analysis is not only inadequate but may be misleading if applied without an understanding of the larger problem of which it is part. The implications for transportation are clear: without knowledge of the specific conditions including characteristic exposure times, temperature distributions, concentration distributions and movements, ventilation flows and air and oxygen delivery conditions, extrapolations of toxicity in terms of simple head-fixed toxicity tests or small-scale homogeneous chemical tests is, at best, questionable.

4.2.1. PVC and fire-gas toxicity

For toxicants whose dose–response relationships are well characterized (e.g. CO, HCN, HCl) it is not always necessary to perform animal experiments to characterize the toxic hazard associated with known concentrations of the toxicant of interest. In such instances, toxicity evaluation can be performed using measured toxicant concentrations and known dose–response relationships. Such is the case for many but not all of the following reviewed studies.

A compendium of the toxicity of individual gases such as CO, CO₂, reduced O₂, HCN and two, three and four-gas combinations of these gases was compiled for data taken using Fisher 344 rats exposed for 30 min, observed over at least 14 days [174]. The Center for Fire Research at NIST has developed a model to predict the toxicity of these compounds acting alone and in combination. Except for CO₂, the toxicity of mixtures of these gases appears to be additive. The synergistic and additive effects of toxic gases was apparent over nearly all times of exposure from 5 to 60 min. Most sublethal concentrations of individual gases were lethal in combination, as has been extensively discussed by Eaton and Klaassen [160] among others. Briefly, the superposition of effect resulting from two or

more toxicants is not always linear, in fact some toxicants may actually cancel one-another's responses. In some cases, however, they are additive as, apparently, in Levin et al.'s [174] study.

The articles by Barrow et al. [175], Murrell [176] and Huggett and Levin [177] studied specifically the toxicity of PVC degradation products. Barrow et al. [175] tested live Swiss-Webster mice exposed for 3–5 min in the head-only configuration. The sensory irritation response (change in respiratory rate) was measured and compared with similar experiments using HCl. The PVC products were more potent sensory irritants than HCl. Murrell [176] measured the degradation products of PVC combustion and pyrolysis (kiln temperatures ranging from 10 to 1000 °C in an air or N₂ flow of 100 ml/min) using gas chromatography (GC) and GC–mass spectrometry (GC–MS). High yields of HCl were measured, along with smaller yields of benzene, toluene, xylene, indene, and naphthalene. A toxicity table was constructed, which listed the toxicant concentration products of degradation. Their anticipated influences on humans were discussed and the duration of exposure to the (potentially) toxic compounds was assessed. HCl was found to be the most (potentially) toxic compound. It was followed by chloromethane and HCN. Huggett and Levin [177] have performed the valuable service of compiling the PVC thermal degradation literature over 1969–1984 (in English only). The complications entailed in such a compilation were extensively discussed, and they directed attention to the facts that (1) Pure PVC is almost never the sole material tested in such experiments as it is always mixed with various quantities of plasticizers and additives that 'improve their properties.' (2) Methods of thermal decomposition vary widely between studies, especially given the different thermal and atmospheric conditions. (3) The type and condition and time of exposure and other factors associated with the test animals are extremely variable. (4) A 'plethora of methods for measuring responses have been employed,' including the use of different endpoints and often non-comparable units. Generally, the pyrolysis of PVC homopolymer reveals poor thermal stability even at 100 °C, with HCl production rapidly increasing with rising temperature. Dehydrochlorination in air and nitrogen had activation energies of 151 and 174 kJ/mol, respectively. Approximately 70 compounds have been identified but among these HCl is the principal toxicant. It is both a sensory and pulmonary irritant. At 500 °C, fire retarded PVC is more toxic than non-fire retarded PVC: toxicities were approximately equal in the 600–700 °C range.

4.2.2. Polymer decomposition and toxicity

We first discuss chronologically the types of toxic compounds produced by polymer decomposition, then we consider ABS decomposition, and nitrogen-containing polymer degradation and toxicity.

The study of Wagner [178] presages some of the later work such as Babrauskas et al. [168], Babramskar et al.

[171], and Babrauskas [170,172]. They determined that additives, which may impart desirable mechanical and thermal properties to polymeric products also generate toxins when these materials are pyrolyzed under thermal insult. Thus, it was thought to be simpler and more systematic to examine virgin plastics with fixed and known amounts of specific additives, in order to simulate actual materials. A need was mentioned for a long-term program to study the synergistic effects of the various toxins produced when materials degrade under heating. Stark [179] examines PVC and flexible PU foams along with other materials, including cellulose. The PVC results are consistent with the later work of Murrell [176] and Huggett and Levin [177]. Both PVC and PU can produce lethal concentrations of toxic gases. PU smoke production increased with fire retardant for foams burned in the open; it decreased when burned in a compartment.

Michal et al. [180] examined PE and isotactic PP, which are used in automobile parts, insulations, piping, and industrial production. Small 50 mg samples were tested in air and analyzed using GC and GC–MS. PE thermo-oxidation produced aldehydes (48.2%), ketones (2.8%), olefins (25%), and paraffins (11.9%). For PP, the principal products were methylalkylketones (57.4%). For temperatures up to 800 °C an increase of atmospheric O₂ increased the smoke production. The authors concluded that combustion and pyrolysis of PE and PP did not result in the production of 'markedly toxic' compounds, although small amounts of toxic gases did arise, e.g. acrylic acid for PE, crotonaldehyde for PP. The smoke had a high optical density and thus was 'rich in solids.' Significantly, CO was not measured by these authors. The products of PE pyrolysis were listed in a table, whose columns include 71 combustion, pyrolysis and thermo-oxidation by-products, their 'toxicological comparison' by the Marhold danger index, critical concentration for shock exposure, and the physiological danger (e.g. irritation, nausea, narcotic effect). Another similar table containing 55 combustion by-products was constructed for PP. The degree of actual danger according to Marhold employs the following numerical comparison scale: 9 = HCN, H₂S; 8 = CO; 7 = phosgene; 5 = Cl; 4 = ethylene oxide, carbon disulphide; 3 = sulfur dioxide; 2 = ammonia; 1 = methane. Note that CO, which was not measured, is the second-most dangerous compound on this scale.

The study of Hilado and Cumming [181] used two toxicity test methods separately on two groups of animals (Swiss albino male mice, Sprague–Dawley male rats). The compounds tested were polycarbonate, PE, PS, and ABS polymers. A general toxicity measure used time to incapacitation or death. The results of the tests were inconsistent. Nevertheless, Hilado and Cumming [181] showed that fixed-temperature testing yielded the 'more rapid incapacitation and death.' According to the authors, the rising-temperature testing, 'involves the time period before the sample reaches its particular decomposition

temperature, and provides an advantage to more thermally stable materials because they evolve toxicants later in the test.' The authors conclude that relative material toxicity rankings are 'highly dependent on the test conditions and on the choice of incapacitation or death as the criterion of toxicity.'

A review of publications in English through 1984 on PE products of decomposition, and their toxicity, appeared in Ref. [182]. The principal influences on PE degradation are temperature and oxygen availability of the surroundings. The amounts of saturated and unsaturated HCs produced rise as the oxygen content of the atmosphere rises. Toxicity was evaluated by forming a correlation of animal response time with product concentration level. Generally, oxidative PE degradation produced fewer toxins than non-oxidative degradation. CO was the 'predominant toxicant'. Acrolein, produced in non-flaming (non-oxidative) degradation, was the next most significant toxicant. Non-flaming combustion 'favored the production of acrolein and other irritant gases,' whereas flaming combustion 'favored the production of CO₂, hydrocarbons, and aromatics.' In general, the authors state that 'polyethylenes are more toxic in the non-flaming mode than in the flaming (mode).' Consistent with our discussion of toxic hazard assessment in real-fire conditions, which include spatially and temporally variable concentration fields, convection, buoyancy, and large temperature variations, these authors state that "The only available comparative study of full-scale versus bench-scale experiments suggests that small-scale testing may produce toxicity results which overestimate those found under full-scale testing." Consistent with Michal et al. [180], PE was considered relatively ordinary with respect to toxicant production under fire conditions. To compare [180]: "The products (of PE, excluding CO) do not contain a markedly toxic component," [182]: "...the toxicity of the combustion products (of PE) are not highly or unusually toxic."

Another summary of the literature on the thermal decomposition of various commercial and industrial grade plastics is found in Ref. [183]. The seven most predominant synthetic materials identified by the authors were ABS, nylons, polyesters, PE, PS, PVCs and rigid PUs. Over 400 decomposition products are produced in their degradation. Oxygen-containing polymers, such as nylons, polyesters, and PU, produce CO and CO₂, whereas ABSs, PUs, nylons and PVCs with nitrogen additives produce nitrogen-containing compounds like HCN. The conclusion was that the decomposition products of these seven polymers were 'not unusually toxic' when compared with the toxicity of other natural and synthetic materials.

Morikawa [184] examines the toxicity of numerous polymeric compounds such as PE, PP, PMMA, nylon-6, PAN, PU and hemlock spruce wood. Toxicants analyzed were CO, HCN, HCl, acrolein, formaldehyde, and NO_x. As a general rule, the author's total toxicity index, C_i/C_{if} (C_i = concentration of component i , C_{if} = lethal value at 5–10 min exposure), increases with degree of completeness of

combustion. Of the three fire hazard threats, toxicity, oxygen deficiency and heat, the most important threat (compared on the basis of a total toxicity index) was stated to be toxicity followed by heat and oxygen deficiency. The author employed small-scale tests in his research.

Finally, Larsen et al. [185] examined the toxic effect of 11 substrate plastics with and without various metallic coatings on unrestrained male NIH Swiss mice subject to 30 min exposure. The 'most toxic materials' belonged to the ABS family, and uncoated PE (note the contrast with Michal et al. [180] and Paabo and Levin [182]). In the animals that died with exposure, the materials that produced the most toxic product gases also produced the most severe lung damage. In most cases, toxicity correlated with amount of CO and CO₂ produced. Comparison tests with restrained mice showed that the lethality index LC₅₀ was 'significantly greater for unrestrained mice.'

Rutkowski and Levin [186] reviewed the literature of ABS degradation and toxicity. ABS decomposition had been studied in both inert and oxidative atmospheres, and in various temperature ranges. Toxicity was evaluated using the following fire test methods: NBS (National Bureau of Standards, now NIST), UM (Univ. of Michigan), PITT (Univ. of Pittsburgh), DIN 53436 (West Germany) and USF (Univ. of San Francisco). The general results showed that CO and HCN were the principal toxicants. Overall ABS toxicity was found in this review to be comparable to materials such as Douglas fir.

Sumi and Tsuchiya [187] examined exclusively nitrogen-containing polymers. The materials examined included acrylic fiber (AF), nylon-6 (N), wood (W), urea-formaldehyde foam (UFF), and rigid urethane foam (RUF). Decomposition gases were analyzed for CO, CO₂, and HCN. A toxicity index similar to the Morikawa [184] index but extended to 30 min exposure showed that the toxicity of HCN was up to 55 times greater than that due to CO for AF, five times greater for N, eight times greater for W, 26 times greater for UFF and identical for RUF.

4.2.3. PU foam toxicity

PU foam toxicity is addressed in this section. The earliest studies [188–190] were concerned primarily with determining whether or not toxins of sufficient quantity were generated by PU thermal decomposition. Hilado and Schneider [188] and Hartung et al. [189] showed that the decomposition products were indeed toxic, but that unusual toxic gases were not produced in real-fire conditions. Herrington [190] used the Ohio State University Heat Release Apparatus to measure the levels of CO, HCN and unburned hydrocarbons released. Different ventilation rates were found to alter the toxicant generation rates. Subsequent studies [191–196] distinguished between rigid and flexible PU foams, and quantified the earlier work. When animals were used [192,193,196] the LC₅₀ test protocol was employed. Hartzell [195] did not use the LC₅₀, instead he examined

the irritant capability. The principal toxicants released were CO and HCN [192–196]. Prager et al. [196] concluded that death in the test rats occurred from CO inhalation, while HCN had no significant effect. This contrasted with Levin et al. [191] in which it was asserted that deaths could not be attributed to either CO or HCN alone. The work of Levin et al. [192] suggests an additive effect for CO and HCN. This work was followed up [193] in an attempt to simulate ‘real PU fires’ in which the combustion stage is preceded by a longer interval of smoldering. Paabo and Levin [194], essentially a rigid-PU literature review, concluded that (1) Rigid PU foam toxicity was essentially not dependent on the specific foam type; (2) Flaming PU was 2–3 times more toxic than non-flaming PU; (3) Addition of flame retardants did not significantly alter combustion product toxicity. Hartzell [195] added that in the case of both flaming and non-flaming combustion for rigid and flexible PU, the smoke toxicity levels were ‘average’, whereas for the flaming combustion of rigid PU the smoke toxicity was ‘slightly higher than average.’ Thus, in flaming combustion, rigid PU smoke appears to be more toxic than flexible PU smoke. Prager et al. [196] showed that under ‘developing fire conditions’ the acute toxicity of flexible PU was lower than that of flame-retarded cotton, wool, wood, and other upholstery materials.

Research discussed previously (Sections 2.3.2, 3.3 and 4.1) suggests that the products of combustion released into the gas are greatly reduced when a char layer forms on the PU. Charring and its promotion therefore appear to have fire-safety value.

4.2.4. Toxicity of fire-retarded materials; toxicity of foams and fabrics; influences of heating rates on toxicity

The toxicity of fire-retarded and unretarded materials was examined by Herpol [197] and Petajan et al. [198]. Herpol [197] examined samples of 35 materials including woods, synthetics, and textiles, which were burned for 30 min at 500, 600 and 700 °C with effluents analyzed for CO, CO₂; in addition, O₂ and COHb determinations were made on the test animals. The only parameter that was changed was temperature. The author concluded that ‘...(flame retardant effect on) toxicity has been proven to be variable depending both on the original material and on the applied treatment.’ Also, ‘...this...suggests that predicting toxic characteristics of a material without submitting it to a series of tests in different conditions is impossible.’ Thus, the authors demonstrate that it appears difficult to state general trends, even though some materials showed improved ignitability resistance (with enhanced toxicity) when treated with fire retardants.

The research of Petajan et al. [198] compared fire-retarded and non-retarded materials. Among these was PU foam, which was fire-retarded with *O-O*-diethyl-*N,N*-bis-(2-hydroxyethyl)-aminomethyl phosphate. Exposure to untreated PU combustion by-products produced mild

to moderate COHb level elevations, whereas treated PU combustion by-products produced seizures whose severity and frequency in Long–Evans rats increased with exposure time. The authors postulated that seizures were caused by bicyclic phosphate formed during the thermal decomposition of the fire retardant. Only very small quantities were needed to produce seizures. Because such compounds are usually not detected by conventional gas analysis techniques, the authors concluded that toxicity tests must employ chemical analytical methods coupled with biological tests.

The toxicity of foams and fabrics of common commercial use were examined by Hilado and Cumming [199], Braun and Levin [200], and Hilado [201]. Hilado and Cumming [199] examined 270 materials under conditions of gradually rising, then fixed, temperature to simulate a developing fire. Wool, silk, and polyester fabrics were the most toxic. The relative material rankings were unchanged despite changes in test conditions and test material. Braun and Levin [202] examined aliphatic polyamides (nylons). The results were compared to earlier research on other materials, showing that the combustion products of nylon were less toxic than cotton and rayon, although the toxicity of nylon combustion by-products was approximately the same as for most other polymeric materials. In Ref. [200] the same authors examined polyesters, finding that temperature and atmosphere were the principal influences on toxicity. The LC₅₀ values for flame-retarded polyester combustion by-products were in the same general ranges as those for commercial materials and non-flame-retarded polyesters. Assorted fabrics and flexible PU foams with and without flame retardant additives were examined by Hilado [201] to ascertain the relationship between heating rate and relative toxicity. There were no consistent observed trends between samples characterized by varying flame retardants, foam densities, and heating rates. The relative toxicities of tested materials’ combustion by-products were, in decreasing order, PVC, wool, Nomex, and urethanes.

Hilado et al. [203,204] also examined the influences of heating rate on the release rates of potentially toxic combustion by-products. Hilado et al. [203] showed that some materials (PE and PC polycarbonate) released more toxic gases at ‘intermediate’ (600 °C) than ‘high’ (800 °C) temperatures. Perhaps some of the toxicants are oxidized at higher temperatures. Some materials such as ABS appeared insensitive to different heating schemes. Hilado et al. [204] conducted two series of tests, one constant at 800 °C, the other starting at 200 °C and incremented by 40 °C/min. until 800 °C. Greater quantities of toxic gases were produced under fixed temperature conditions. This result contradicts Hilado [201] where there was no apparent trend with variable heating rate. Here the heating rate is varied between two plausible limiting cases (a successive ramp-up and an impulsive one-step ramp) with the latter apparently producing more toxicants.

4.3. Smoke and retardants

One method of reducing fire hazard is to add chemicals to the test material in order to render the products of thermal decomposition as innocuous as possible. The fire retardancy literature review [1] considered test materials composed of fire-retarded synthetic polymers. Most of this review addresses the measured influences of fire retardants such as halogens (e.g. chlorine, fluorine or bromine), intumescent, and phosphorous, on the fire performance of various materials, such as PU foams, polyolefins, and chloroparaffins.

The studies of Guyot et al. [205], Smith [206] and Purser [207] address PVC 'smoke performance.'. Guyot et al. [205] examined additives for their effect on smoke production. They determined that certain additives: (1) Resisted char residue volatilization; (2) Decreased benzene emissions, which reduced smoking; (3) Increased flammability and smoke production through their mutual synergism (plasticizer additives). Smith [206] compared PVC smoke production with smoke production from other common materials. A smoke parameter evaluation demonstrated that PVC occupies the low end of the smoke spectrum, only above PC. This behavior was attributed to the low RHR of PVC. Hirschler and Purser [207] examined the irritancies of numerous PVC compounds common in wire coatings. The degree of irritancy was greater than could be accounted for by the relatively low HCl quantities detected. The authors postulated that the incremental irritancy was caused by 'free radicals.'

Methods of fire retardance in common polymeric substances include chemical addition of various retardant substances during processing. These retardants are intended to reduce the tendency to burning, smoking, and toxicant volatile production. One such group of five elements are the halogens (fluorine, chlorine, bromine, iodine, astatine). The work of Brauman and colleagues in the mid 1970s discussed "substrate interactions in degrading Sb_2O_3 -halogen systems and the general mode of action of Sb_2O_3 -halogen fire retardance. In Sb_2O_3 -chlorinated wax (CW) combinations, the major volatile products are the known flame inhibitors Sb_2Cl_3 and some HCl, along with H_2O , which chemically and possibly physically inhibit the flame." Brauman et al. [208] examined the following additives to the polymers PE, PP, PS, Impact PS (ImpPS), PVC and other compound mixtures: Sb_2O_3 : a chlorinated wax (CW) containing 71.91% Cl; Dechlorane Plus 25 (an adduct of perchlorocyclopentadiene and cyclooctadiene); antimony oxychloride; Sb_2Cl_3 ; carbon black. Burning rates were studied in three configurations: the driven rod, a high thermal mass puddle, and a low thermal mass puddle. When the compound materials charred at lower temperatures, their burning rates decreased. But when 'the temperature is sufficiently high...the rate of fuel production can become sufficient to sustain combustion, even if some char is formed.' For some materials the rate of flame spread

decreased (PP, PS, ImpPS). The 'general effect of Sb_2O_3 -halogen fire retardance...(depended)...on (whether the process being measured was) ignition, fire spread, burning, extinction, or smoke generation.' The 'results confirm' that 'added Sb_2O_3 -chlorine...promotes extinction and limits fire spread.' For burning and ignition, ' Sb_2O_3 -chlorine can have a beneficial or detrimental effect, depending on...test conditions and sample types.' They concluded that under some conditions ' Sb_2O_3 -chlorine can...promote fuel (volatile) production...' and that 'If the environment is hot enough... Sb_2O_3 -CW will react with most polymers...to promote (their) decomposition, often resulting in increased weight loss or fuel production.' Thus, the fire retardants described here appear to be more effective at lower temperatures.

The work of Harris et al. [209] used the cone calorimeter to demonstrate that various non-halogenated compounds were more effective than halogenated compounds at fire retardancy. They reduced the amount of mass consumed, as well as PRHR, THR, ELOC, and the amount of smoke. The halogenated retardants, by contrast, increased smoke production and CO yield, and produced the acid-gas irritants HCl and HBr.

Another group of materials used for fire retardance is intumescent materials. Their mechanism of action is entirely different from that of chemical fire retardant additives described above. Upon heating, intumescent materials form internal gas bubbles and swell, thereby restricting outward mass transport from the interior of the heated material. Certain intumescent also form external carbon layers (i.e. char) at the surface to inhibit subsequent surface decomposition. Ballisteri et al. [210] demonstrated, however, that an intumescent PC was not self-extinguishing. The review of intumescent provided by Camino et al. [211] discusses desirable and undesirable properties of intumescent materials. Among the latter is an exothermic intumescent reaction. This limits the value of the additive compound. The tendency to form char in a surface layer is a positive feature, for it acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing further in-depth pyrolysis to volatile combustibles. This preventative mechanism may extinguish the flame by decreasing the supply of fuel volatiles for gas-phase combustion. The authors concluded that the effectiveness of various intumescent-promoting additives was 'inadequate' to justify their general use.

Myers et al. [212] examine the use of ammonium pentaborate (APB) for PUs, finding it an effective additive for providing a thermal barrier, although its drawbacks are its lack of high-temperature stability and water solubility. However, these were considered minor compared with its advantages.

Another class of flame retardants is chloroparaffins (CP) [213–216]. Camino and Costa [213] demonstrated that CP inhibited oxygen use during combustion. The authors state that "in addition to the flame poisoning effect

of HCl evolved by the CP, the solid phase effect...result(s) in a less flammable fuel being supplied by the thermal degradation of PP burning in mixtures with CP." In other words, the volatiles produced and provided to the flame also contribute to the flame retardation effect of the CP additive. The HCl 'poisons' the combustion reaction sequence by suppressing the branching step $H + O_2 \rightarrow OH + O$. The authors employed an oxygen index (OI) defined as the percentage of oxidant in an O_2-N_2 mixture that sustained the flame over molded rod specimens over 30 s, and they noted generally that saturated HCs such as methane, ethane, propane, etc. have higher OI than unsaturated HCs such as ethylene, propylene, etc. Their experiments suggest that the CP additive causes a higher production of the saturated HCs in the volatile products. Since these require more O_2 for their consumption, the fire retardant effect is enhanced. A companion study by Camino et al. [214] suggested that under some conditions the PP-CP compounds produced greater quantities of volatiles, some of which were highly reactive at room temperature. The 'competition' pathways between two volatilization mechanisms of PP (one to light HCs formed by chain end radicals, the other to longer chain fragments formed by radical scission) are 'shifted in the presence of the CP,' forming primarily through the second mechanism. Thus, although a smaller quantity of light HC volatiles (modified in composition) is produced in the thermally degraded PP-CP blend, an increase in the quantity of high boiling point chain fragments is measured, 'possibly due to interactions between the evolving HCs and the charring CP.' A similar pair of companion studies was later published by the same authors for CP-PE combinations [215,216], though in the former they also examine CP-PP and CP-PS combinations as well. The CP-PP blend was the only combination that produced a gas-phase 'flame poisoning' flame-retardant response. However, consistent with the mechanism described by Camino and Costa [213] a condensed-phase influence of CP was observed for PE, PP and PS. This suggested that chlorinated additives might possibly produce a condensed phase method of fire suppression that is more effective than gas-flame poisoning. Costa and Camino [216] examined the thermal degradation modifications of CP-PE mixtures. For the CP-PE mixture, 90% of the total weight loss was by CP volatilization, which rendered the PE insoluble. Since the gas-phase retardancy of CP in PE was poor, its primary influence was to act as a heat sink for the gas-phase flame. This additional heat loss from the flame could weaken or perhaps extinguish it.

The fire retardant influences of phosphorus (P) additives on various synthetic polymers is described by Brauman [217], where it is determined that P-additives work in both condensed and gaseous phases to decrease combustion. These P-additive retardants are acid precursors, which act

primarily in the condensed phase to decrease heat evolution, fuel production, and also increase charring.

Flame retardance was also examined for various standard commercially common materials such as PU foams [218–221] and polyolefins [222,223]. Benbow and Cullis [218] review the (then) three most common PU foam flame-resistant treatments. These are (1) Inorganic salts like calcium and magnesium ammonium phosphate, which form a 'protective coating...during burning and thus a barrier between...flame and...fuel-source'; (2) Alteration of the PU structure, such as by forming a 'nonburning rigid foam...'; (3) Organic flame retardants containing P, Cl, Br, or halogens. They focus on (3), suggesting that possible mechanisms causing retardance include: (1) phosphoric acid formation, which prevents normal fuel species formation in the degraded PU, (2) volatilization of nonhalogenated P-esters to 'blanket' the reaction, (3) catalysis of depolymerization leading to dripping and running with heat loss from the combustion zone, (4) volatilization of halogenated P-esters to yield hydrogen halides, an effective group of 'flame poisons.' Three additional reasons were presented why tris(2,3-dibromopropyl) phosphate and tris(2-chloroethyl) phosphate are more effective than suggested by (4) above: (1) catalysis of surface charring, (2) flame retardant action of phosphoric acid [217], (3) chemical incorporation of P and halogen into the PU structure. In general, this article demonstrates that PU flame retardance can be significantly altered by chemical additives, in agreement with Bonsignore and Levandusky [220] and McBrayer [221]. Hílado and Damant [219] treated various PUs with retardants (antimony trioxide/PVC, brominated organophosphate). The flame retardants hindered ignition, produced acceptable smoke densities, resisted flame spread, and produced fewer toxic gases. Similar results were obtained by Bonsignore and Levandusky [220] using hydrated aluminum in rigid HDPU (high density). Some samples also added calcium carbonate and dimethyl phosphate (DMMP). It was found that smoking decreased, flame resistance increased, aluminum trihydrate outperformed calcium carbonate, and DMMP accentuated flame resistance and smoke decline. Finally, McBrayer [221] demonstrated that the improvements in PU flame retardancy obtained by treatments with various commercial compounds (FIREMASTER LVT-238, PHOSOGARD 2XC20, THERMOLIN 101, BROMINEX 257) were only slightly degraded by accelerated aging. Most of the PU foams showed almost no reduction of their capacity for fire retardancy with accelerated aging.

Polyolefin flame retardance is described by Handa et al. [222] and Rychla and Rychla [223]. The retarded PP behavior depends upon the retardant's reactivity with Sb_2O_3 at high temperature, coupled with the interaction between Br release and thermal degradation [222]. Also, the formation of HBr produced lower burning rates at higher temperatures. The latter study shows that for flame retarded polyolefins,

ignition delay and the ignition temperature decreased relative to unretarded samples. Their theoretical model supported this conclusion.

It is difficult to distinguish between inhibition, suppression, and flame retardancy. Some clarification occurs when inhibition or suppression is defined with reference solely to gas-phase reduction of flaming [224]. This suggests the possibility of injection of flame inhibitors or suppressants from sources distinct from the decomposing fuel source itself. A reliable distinction is the following: in fire retardancy the flame above the material that feeds it must be weakened by the evolution of chemical additives in the material itself, whereas flame inhibition or suppression incorporates external sources of fire retardant which do not necessarily originate in or near the material closest to the fire.

The GM/DOT literature search did not address inhibition and suppression in detail. Two publications describing fire suppression in engine nacelle fires in aircraft have appeared [225]. These publications are extensive (over 400 pages) and provide detailed compilations of previous and currently active research on the problem of fire suppression in confined geometries. Also, inhibition flame chemistry is described in detail, as are numerous technical and technological aspects of such fires.

5. Vehicle fires

This section is divided into separate discussions of references for four types of vehicles. These are (1) buses, (2) railway and subway cars, (3) aircraft cabins, and (4) automobiles, light trucks and heavy trucks.

5.1. Buses

In one of the earliest studies of school bus fire safety conducted at the National Bureau of Standards (NBS, now NIST) in the mid-1970s, it was determined from three full-scale tests and small-scale laboratory tests that a variety of ignition mechanisms are possible [226]. These ignitions all originate at or near the seats, arising from (1) paper trash on a seat, (2) newspaper under a seat, (3) lighter fluid on the seat. Fire growth and spread in the bus occurs mostly through involvement of the seat cushioning, spreading from seat to seat with little apparent involvement of other interior materials. Additionally, within a few minutes after seat cushion (urethane) ignition, dense smoke filled the bus and greatly reduced the visibility. The study suggested that the burning characteristics of individual seats has the greatest influence on the burning of the bus interior. Thus, flammability and fire-retardant studies of seat materials seems warranted.

The study of Braun et al. [227] examined six seat assemblies using small scale tests (cone calorimeter, LIFT,

and NBS Toxicity Protocol). Large-scale tests (Furniture Calorimeter) were additionally conducted on single seat assemblies. Full-scale tests were performed on a simulated 2.44 m wide \times 2.13 m high \times 8.23 m long bus enclosure with three seat assemblies. The ignition sources were 50 and 100 kW (large scale) and 100 kW (full scale) burners. The small-scale tests could not predict the full-scale fire behavior. Based on the full-scale tests, a general full-scale test protocol for seat assembly evaluation was developed. It combines testing in an enclosure with an analysis that determines the time at which burning becomes 'untenable.' The procedure describes conditions for toxicity testing, and procedures for instrumentation and material orientation are explained.

A report summarizing and updating school bus safety activities at NHTSA is provided in a USDOT report on School bus safety [228]. This report describes congressional mandates and NHTSAs actions to improve school bus safety, including human behavior and motor vehicle safety performance.

5.2. Railway and subway cars

A Metrorail subway car mock-up interior was ignited and smoke density, heat flux, temperature and gaseous products were examined [229]. The interior materials were primarily plasticized PVC, acrylic PVC, and PU. Ignition was achieved [226] by lighting a newspaper or paper bag on a seat, or a newspaper against a wall. Presumably, the mode of ignition was not an important variable. Some trials subjected three Wistar rats to the fire in order to measure toxicity effects. CO and CO₂ production rates were measured as a function of temperature. Other experimental data indicate that: (1) HCl concentration was below the detectable 50 ppm limit, (2) HCN was present due to PU and the acrylonitrile in PVC, (3) PU combustion caused loss of balance of the rats in rotating cages, apparently from their elevated CO and HCN exposures as inferred from their CO and HCN blood levels.

An assessment of the San Francisco Bay Area Rapid Transit (BART) subway cars was made by Braun [230]. Upon analysis of the car's interior and exterior design, five recommendations were made that, once implemented, might improve passenger safety by diminishing fire hazard. Among these suggestions were urethane seat assembly upgrading and development of a fire detection system appropriate to rapid rail transit vehicles.

Rakaczky [231] provided a literature review of the flammability characteristics of materials either in use, or potentially in use, in rail passenger cars. Characteristics of interest included the main fire safety measures described in this review, including toxicological influences of combustion products. The information thus compiled was meant to assist the Federal Railway Administration (FRA) and the DOT in establishing rail passenger car material flammability safety standards. Miniszewski et al. [232] studied

the feasibility and cost effectiveness of the use of heat/smoke/fire sensors and automotive extinguishing systems in rail transit vehicles. The major rail transit lines were surveyed for their fire experience, the available hardware was surveyed, and placement and cost effectiveness were described. A testing program was outlined.

Since rail transport in Europe is more extensive than in North America, Kaminski [233] surveyed fire research and fire practical experience for European railways, including a summary of causes of fire, fire characteristics and European fire protection strategies. Test methods for various railcar materials were described, techniques for smoke emission measurement are outlined, and ignitability and surface flame spread were described. The British full-scale 'Phoenix' test facility was described. Detailed drawings of the facilities and test apparatuses were provided in the report. A discussion of transit undercar fire detection and suppression is found in Ref. [234]. Electrical cable fires may originate in the undercar area, after which rapid and dangerous upward spread of smoke and flame may occur. This report includes results of a laboratory test program using an instrumented motor control-group box for a New York City Transit Authority (NYCTA) transit car. A report was provided by the FRA's [235] updated guidelines on performance of materials (flammability, smoke emission, etc.) in new or rebuilt rail passenger cars. These guidelines are similar to the Urban Mass Transportation Administration (UMTA) recommendations to the rapid transit industry.

Peacock et al. [236] present a comparison of approaches used in the United States, Germany and France for assessing the influences of vehicle design, material selection, detection/suppression systems, and emergency egress on fire safety. They suggest that science-oriented fire policy dictates the rational use of fire hazard and fire risk assessment methods, which are supported by measurements based on RHR.

A recent area of emphasis in the transportation industry is the construction and use of large-scale wind tunnels in the automotive and aerospace industries. For example, Aiolos Engineering Corporation designed and managed the construction of the Ford Environmental Test Laboratory (ETL) in Dunton, UK. The facility contains an altitude/climatic wind tunnel, a climatic wind tunnel, a cold start and drive test cell, and an altitude/climatic chamber. The test sections (where the vehicle is placed and tested) are capable of simulating driving environment ranging from arctic to tropical conditions, and from the low to high altitudes. The test sections are large enough to accommodate cars, light trucks and four-wheel drive vehicles. Wind tunnels can, in principle, be built to accommodate buses and railroad cars, although the author is not aware of any such facilities. It is also not clear whether such large-scale facilities can be used for burn tests or the simulation of fire ignition and spread. The closest facility of which the author is aware is the full-scale building fire simulator being constructed at the University of Waterloo. In this facility, a full-scale two-story house can be

equipped (fire-loaded) and then burned inside a second, larger facility through which a controlled flow is passed. Instrumentation is used to track the fire progress. Facilities such as these are costly, thus they require a commitment to their financing and use.

5.3. Aircraft cabins

Aircraft cabin fire research has been sponsored by the FAA and NASA. The problem of aircraft fire safety is complicated by the absence of easy egress. In this feature, aircraft safety has much in common with submarine fire safety, ship fire safety and spacecraft fire safety. The latter three vehicle types are not considered in this review. Haley et al. [237] examined the development of fire resistant aircraft interior materials. The thermoplastics that can be considered in the design must be suitable for compression molding, injection molding and thermoforming. The promotion of 'pilot plant polymers' by various chemical companies was encouraged. Preliminary toxicity data were gathered by the NASA Ames Research Center. Dokko and Ramohalli [238] described the thermochemical modeling of aircraft cabin fire safety. The research was directed mostly to the performance of carpets and seat cushions with the objective of predicting burning rate as a function of material property values, geometry, and heat flux. It was determined that (1) condensed phase degradation of the polymeric material is the rate-limiting step of the overall process (Sections 2.2 and 3.2); and (2) diffusion and mixing of the pyrolysis products with air is the rate-limiting step of vapor phase combustion (Section 3.2). (3) Certain materials like carpet cannot burn on their own but require augmentation by an external radiation source or another burning surface. Global zone models for aircraft cabin fires occurring in flight or crash were developed by Delichatsios [239]. Simple-to-use expressions were derived for wall burning, flame heights and flame spread rates. Material properties controlling flammability were identified. Radiation and charring were discussed, as well as gas flows along aircraft ceilings.

More recent work on aircraft fire safety has focused on practical means of addressing specific, often perception-driven issues related to fire safety.¹⁰ Reynolds and Porter [240] and Garner [241] examined the CWSS (cabin water

¹⁰ We excerpt the following quote from NASA TM-1999-209198 'Microgravity Combustion Research: 1999 Program and Results,' Friedman, R., Gokoglu, S.A., and Urban, D.L. (Eds.): 'An immediate concern of aircraft fire safety is that of the hazards of the onboard aviation fuel. Two fire scenarios are possible: in flight tank fires and post-crash spilled-fuel fires. These are very rare fire events, but they are extremely feared and well publicized when they do occur.' For the first scenario, research 'contemplated or in progress includes...' studies of 'fuel flammability properties, such as minimum ignition energy, flammability limits, and flash point, as functions of fuel properties and aircraft tank designs and dynamic conditions.' Research proposed for the second scenario 'includes basic studies of so-called 'fire-safe' fuels...'

spray system) proposed to increase passenger evacuation and survival time following an accident. Disadvantages of CWSS were described in the former study including potential evacuation delays, ‘common cause failure’ in redundant fire safety systems, physiological problems for passengers, high cost of refurbishment following inadvertent discharge, and potential to negatively influence other safety systems. The latter study addressed the physiological damage that may occur to the respiratory system, with the goal of estimating the risk posed by a ‘more hazardous cabin environment by activation of CWSS.’ The activation of CWSS can potentially produce a small volume within the aircraft cabin that would experience an increase in heat content, which could result in ‘thermal injury’ to the respiratory systems of nearby passengers. Tapscott [242] summarized various fire suppressants, their properties, and their applicability in aircraft. Certain classes of agents were recommended for use in test protocol development. A similar study was carried out by Reinfurt [243] on Halon replacement in aircraft fire suppression.

5.4. Motor vehicles

Studies dealing with motor vehicle fires as a whole vehicle in a systematic, scientific manner are largely absent in the available public literature. The motor vehicle fires that are of most interest because of the potential for enhancing injuries are post-crash fires. It is generally easy for occupants to exit a vehicle in the event of a non-crash fire. In the US approximately 1250 annual crash fatalities involve fire. In these accidents, the fire is not necessarily the cause of fatality. The percentage of fatal car accidents involving fire is approximately 2% of all fatal car crashes.

The Federal Motor Vehicle Fire Safety Standard 301 Fuel System Integrity test (FMVSS301) has been used as a benchmark for evaluating automotive safety by Reinfurt [243], Flora and O’Day [244] and Parsons [245]. Of the 50 states covered by this Federal Standard, only the data from certain individual states could be statistically analyzed in each study (e.g. only Illinois and Michigan in Ref. [244], only five states in Ref. [245] with primary emphasis on Michigan). The FMVSS301, according to Parsons [245], is “a death and injury reduction Standard which includes requirements on the limits of leakage from the fuel tank, filler pipes, and fuel tank connections during and after 30 mph frontal barrier crashes.”

Flora and O’Day [244] examined police accident data to estimate the influence of FMVSS301 in real crashes. Passenger car and light truck fire rates were estimated as 1.5 and 2.4 per thousand crashes. The Standard appeared to produce reductions in fuel leakage from crashed vehicles. Parsons [245] stated that FMVSS301 has (1) ‘significantly reduced post-crash fires’ in car crashes, (2) the reduction in (1) has resulted in ‘400 fewer fatalities and 520 fewer serious injuries’ in the United States per year, and (3) the Standard

has increased the annual consumer vehicle cost by \$850 annually.

Tesmer [246] carried out a more detailed statistical study of fire occurrence in fatal and less serious crashes. Particularly helpful to this study was the fact that the Michigan policy accident report (PAR) collected data on fuel leaks, which were used to estimate the statistical relationship between fires and fuel leaks. The work of Mowrer et al. [247] indicates that even though truck fires are rare, they are often lethal, especially for heavy trucks. The study addresses various physical and chemical aspects of truck fires and discusses the breach vulnerability of various truck fuel components. Berkowitz [248] concluded that motor vehicles have remained in operation longer and have been driven further than previous estimates had indicated. This may influence their fire performance.

As explained in Section 1, the GM research program on fire safety of automobiles included simultaneous research efforts in numerous disciplines. These included occupant crash dynamics; biological response (e.g. head and neck injuries); numerical simulation of crash, heating, and burning; heat generation underhood and its transmission to the passenger compartment; ignition of materials; chemical composition of common vehicle materials; and so on. This research, which spanned the five years between 1995 and 2000, has been assembled at the NHTSA (Department of transportation, DOT) website, at <http://dms.dot.gov>. The ‘GM Docket’ is found by entering ‘simple search’ and then typing the last four numerical reference digits of the docket, namely 3588. The GM Docket contains 200 articles, letters and reports written during this 5-year research project. Attention is focused in the following discussion on articles 1, 70, 77, 104, 119, 158, 178, 179, 182, 184, 189, 190, 191, 193, and 199 of the docket. These articles deal directly with fire hazard and fire-related research.

The studies of Shields et al. [249] and Scheibe et al. [250] presented case studies from vehicle fire investigations of actual crash incidents involving automobiles, pickup trucks, vans and sport utility vehicles (SUVs). The case study method was chosen in this study because of the difficulty of isolating the precise conditions that produced the fires. Case studies illustrate the variety and complexity of the problem by inviting the reader to synthesize the information available for individual events without attempting yet to generalize it to all events. One of the main difficulties in these two studies is the necessary reliance on ‘eye-witnesses’ for determining a substantial number of the measured parameters. Shields et al. [249] and Scheibe et al. [250] recognize that the few (approximately 21) cases they analyze are insufficient for a comprehensive overview, stating that ‘databases containing thousands’ of cases are more appropriate to make conclusions regarding trends. The data presented ‘include a wide variety of post-collision ignition times, fluid system breaches, ignition source availability, impact types and impact severity.’ Three crash fires are examined in detail by Scheibe et al. [249].

Data for the 21 field investigations are compiled in an appendix. These data categorize the vehicle type; impact description (e.g. frontal impact with tree, frontal with rear of a pickup truck, etc.); most likely ignition source (e.g. gasoline, coolant/electrical spark, hot manifold surface, power steering fluid, mechanical spark, transmission fluid, shorted power distribution box); estimated time to ignition and time to interior in minutes (ranging from ignition at 1 min to fully engulfed by fire at 10 min); initial fire location (e.g. engine compartment, rear end, exhaust system, pool fire under car, passenger compartment, rear end); reported injuries (lacerations, bruising, concussion, burns, death); assistance in egress (yes, no, unnecessary (fatal)). Despite the authors' description of a 'wide variety' of ignition and burn times, what stands out from these data (if they are at all representative) is that a time scale of $O(10 \text{ min})$ often already characterizes a fully involved full-scale fire. Ignition usually occurs under 5 min. Thus, the characteristic time for ignition events in such accidents is of the order of minutes, and by times of $O(10 \text{ min})$ the fire is fully engaged: consideration of ignition are no longer either applicable or relevant. The *fire scenario* is thus, in chronological order: a collision; possible incapacitation (if only temporary) of the occupant or occupants, including injuries and vehicle geometry changes that make egress difficult or impossible; a rapid ignition on the order of minutes; full-scale flaming and flame/fire spread with the distinct possibility of burns and serious post-crash thermal injury in under approximately 10 min from the crash. This is different from the building fire scenario, where time scales can range over hours from incipient smolder to final and ultimate fire break-out. Scheibe et al. [249] concluded that coolant, oils and gasoline, all liquid combustibles, had the potential to initiate fire, and that electrical system damage 'provides a potential source of both fuel and ignition.' Discussions similar to those of Scheibe et al. [249] are found in the article by Shields et al. [249], although this report provides more background information (such as the background for the databases used and data collection details). The authors note the difficulty of recreating vehicle fire scenarios in the laboratory, noting that 'small differences in the crash configuration can make significant differences in the propensity to burn.'

One of the major efforts of the GM program was to examine the flammability of the various materials in vehicles. The report by Tewarson [251] examined the flammability of plastic vehicle components and parts, by subjecting them to ignition and burn tests in the factory mutual research corporation flammability apparatus, which resembles a large cone calorimeter. The measured quantities were critical heat flux (CHF) (below which ignition did not occur), thermal response parameter (TRP) (an indicator of ignition delay that relates the time to ignition to the net heat flux [252,253], the fire propagation index (FPI) (which measured the fire propagation behavior), and the yields of CO, CO₂, and smoke. This particular part of the GM project

was carried out by examining components and parts of a Dodge Caravan under the following rationale: current (late 1990s) 'market segment leaders' were always examined, these being passenger vans (Dodge Caravan), SUVs (Ford Explorer), front-wheel drive vehicles (Honda Accord) and rear-wheel drive vehicles (Chevrolet Camaro). The components and parts included headliner materials, instrument panels, resonators, air ducts, steering column boot, brake fluid reservoir, wheel well cover, windshield wiper tray, HVAC unit, headlight components, battery casing and cover, bulkhead insulation, and so on. The materials from which these components are made are standard thermoplastics (ABS, Nylon, PC, PE, PET, PEU, PP, PVC, etc.).¹¹ The tests were performed under a 'natural air flow condition' in which buoyancy was not suppressed nor was there a forced imposed flow. The parameters were measured and also calculated from property values, and then compared in several tables. Ignition temperatures were also tabulated and compared with literature values. Tewarson [251] concluded: 'The CHF values of the... components and parts of the 1996 Dodge Caravan... are comparable to the values for ordinary plastics.' The TRP values were about 30% larger than calculated values based on thermal property measurements made by GM researchers [254]. The FPI showed that of the 15 parts tested, 12 'were expected' to show either steady or accelerating fire propagation, whereas only three were expected to show decelerating fire propagation rates beyond the ignition location.

Santrock [255] examined the thermophysical properties of engine compartment fluids (other than gasoline). The data can potentially facilitate ignition calculations of the type carried out by Tewarson [251] for solid polymers. These fluids included *used and unused* motor oil, synthetic motor oil, transmission fluid, power steering fluid, brake fluid, engine coolant; and *unused* windshield washer fluid and gear lubricant. GC-MS was used to analyze the components of these fluids, and boiling ranges were determined using ASTM D 2887-01. The liquid heat capacities were also measured, by using ASTM D 2890-92. A total of 52 fluids were analyzed (for example, 22 of these fluids were either synthetic or non-synthetic motor oils in varying conditions).

Subsequent to these GC-MS tests, Santrock and Kononen [256] performed ignition tests on essentially the same set of 52 fluids (some were eliminated and others were added). Fluid ignition was achieved by pouring them onto heated solid surfaces. The minimum temperatures required

¹¹ A study by Santrock [267] used several diagnostic techniques to identify the base polymers from which automotive parts such as body front ends, cooling and radiator systems, engine air intakes, instrument panels, windshields, gauges and controls, HVAC systems, doors, seats, carpets, roofs, rear quarters, and rear bumpers are made. The automobile examined was a 1997 Ford Explorer (a market segment leader). All of the polymers identified [267], or apparently minor variants thereof, have been discussed in this review either in sections on ignition tests, flame spread, toxicity or suppression.

to self-ignite the resulting fluid vapors were measured. The heated surfaces consisted of a cast iron crucible and a cast iron hemisphere. For the crucible three temperature regimes were observed. In the lowest range, ignition never occurred, so that $P(i)_{\text{observed}} = 0$ for each of these tests, where $P(i)$ is the probability of observing ignition. For the highest range, $P(i)_{\text{observed}} = 1$ and ignition always occurred. In the intermediate temperature range, $0 < P(i)_{\text{observed}} < 1$. The authors examined these ignition tests using a type of statistical regression analysis commonly referred to as 'probit' analysis. In probit analysis the log-normal or Gaussian distribution serves as the 'link' function, analogous with examinations of toxicity data [159] that lead to definitions such as LC_{50} and LD_{50} . The ignition probit analysis determines, for example (subject to the hypothesized mathematical relationship) the temperature at which 50% of the samples ignite, or the probability $P(i)$ of ignition at a particular test temperature. The data showing the highest 0% response and lowest 100% response were presented, and various graphs were provided of the calculated (probit) and measured ignition probabilities $P(i)$ versus T . Variations in ignition temperature were observed for the two surfaces used (the crucible was convex upward, the hemisphere convex downward), which produced different residence times of the fluids (for the convex-downward hemisphere the fluid had a tendency to roll off the surface) along with different buoyant flow patterns near the surface. In some cases for the hemisphere a cross-flow was applied. For a 2.2 m/s cross-flow (hemisphere geometry) ignition was not achieved for power steering fluid with a surface temperature of 650 °C even though at zero cross-flow it ignited with $P(i) = 1$ at 370 °C.

Full-automobile tests were conducted as part of the GM/DOT research agreement. Several vehicles that were crash-tested were subsequently fire-tested at the Factory Mutual Research Corporation's full-scale fire test facility. Ignition sources were varied in each test (e.g. underhood, gasoline pool fire ignition).

The report by Santrock [257] describes a full-scale vehicle fire test for a 1997 Chevrolet Camaro. These tests were conducted in order to (1) determine the principal fire paths and flame-spread time-lines into the passenger compartment. (2) Identify the components that burn and measure the thermal environments around those components. (3) Measure temperatures, heat fluxes, gas concentrations in the passenger compartment. For the Camaro, gasoline apparently consistent with a ruptured tank was flowed onto the surface under the vehicle for approximately half a minute before it was ignited, depositing approximately 16 l. The vapor above the pool was ignited with a torch. Within 10–20 s of ignition flames had entered the passenger compartment. Three pathways were observed: (1) Crash-induced 'seam-openings'; (2) Gaps produced by crash damage (between door and door-frame); (3) Floor panel drain hole. Thus, fire spreads into the compartment through either designed openings and conduits

or openings produced by the crash. After 45 s, no flames were visible in the passenger compartment (i.e. the compartment was nearly smoke-filled). It was determined by comparing CO/CO₂ production ratios that in its initial stages the gasoline fire was under-ventilated, but that after approximately 60 s well-ventilated conditions were attained. At this time, the gasoline burning stage appears to have ended and other combustible materials had begun to ignite. Measurements suggest that the passenger compartment combustibles were ignited between 140 and 160 s post-ignition. It was speculated that the flame plume extending away from the vehicle produced a higher entrained flow and therefore increased the combustion efficiency (i.e. the ventilation). The heat release appeared to correlate with ventilation. In addition to these direct fire propagation measurements, two models of toxicity were examined using the data. These models were BURNSIM [258] and Purser's model [259]. Both of these models examine exposure risk to 'hot air, reduced oxygen, CO, CO₂, HCN, HCl, HF, HBr, acrolein, and NO₂.' BURNSIM also evaluates the potential damage to exposed human skin without factoring in 'variations in skin thickness,... presence of facial or head hair,... clothing,... (or)...skin pigmentation.' According to Santrock [257] 'the accuracy of the estimated skin temperature profiles in humans...obtained using BURNSIM has not been determined.' Relatively high heat fluxes (~30 kW/m², which are fire-level) were recorded inside the passenger compartment. Both models utilize a 'Fractional Effective Dose' for Incapacitation (i.e. FED(I)) and Lethality (FED(L)), although the measured results 'cannot be used to predict precisely when the gas concentrations... would have resulted in incapacitating narcosis or death for a vehicle occupant' [255]. Both models assume that humans respond the same as laboratory animals, and none of the model predictions of the FAA or Purser model (except for CO₂ exposure) 'have been validated for humans' [257]. Furthermore, the FED methodology assumes the toxic effects are additive, i.e. $FED_{\text{total}} = \sum (FED)_i$, where $I = (\text{CO}_2, \text{CO}, \text{HCl}, \text{HCN}, \text{O}_2)$. When $FED_{\text{total}} = 1$, 50% of the exposed population is assumed to experience incapacitating narcosis; lethality occurs in 50% of subjects when $FED_{\text{total}} \geq 1$. Values in this range were obtained for the tests after approximately 200 s from ignition. Santrock [257] notes, however, that 'the effect of the trauma caused by the crash on the occupant's tolerance to these toxic gases is impossible to quantify.' It would seem to be a reasonable goal, in future analyses of human response to trauma and subsequent fire, to assess the coupled set of responses. The limited time of safe egress would appear to make such studies essential.

A battery of similar full-scale vehicle fire tests for different vehicles (market standards) with different ignition source locations was conducted for a front-end impact 1996 Dodge Caravan [260], a front-end impact 1997 Camaro (steel pole impact at 55 mph, offset from centerline by 1') [261], a 1998 Ford Explorer underbody fire [262] and

a front-wheel drive vehicle test [263]. The interested reader is invited to examine this literature.

An important consideration in the propagation of vehicle fires is the potentially ameliorating effect that may be possible with fire-retarded materials. Such materials, used in strategic locations like necessary and unavoidable conduits (e.g. for HVAC or the ‘floor drain hole’ referred to above), might conceivably slow the fire in its spread from outside to inside the cabin. Given the rather rapid spread rates, even perhaps a small improvement might constitute a noteworthy achievement. Ohlemiller and Shields [264] determined in direct-fire tests involving a 2.4 and 6 kW heat source in configurations modeling (if only very approximately) those of an engine compartment that the tested materials showed the same ‘observed physical behavior.’ The fire-retarded PP was ‘distinctly less flammable’ than the non-retarded PP, although Nylon resins showed ‘more complex’ behavior. Tests that examine exposure to full fire, however, are different from developing-fire tests and transient flame spread tests, where the nature of the material may not be as important as the manner in which the growing fire seeks to provide oxygen for itself.¹² In Ref. [265] the author evaluates the use of plastic resins containing fire retardant chemicals in the HVAC modules of a fire-tested 1999 Chevrolet Camaro. The retardant treated vehicle was compared with a ‘control’ vehicle that contained a non-fire retarded HVAC module. The fires were underhood and spread to the passenger compartment (cabin). The author found that the use of fire-retarded plastics ‘did not affect the rate of flame spread from the engine compartment to the passenger compartment during these tests.’ This suggests (to the author of this review) that the underhood fires are under-ventilated and use the conduits as a means for consuming fresh air from the passenger compartment, not as a means for consuming additional combustible HVAC ducting materials. Thus, model studies of connected vehicle compartments may provide important information on the propagation of medium-scale fires between adjacent medium-scale compartments.

Finally, we review a detailed numerical computation of the spread of fire from outside the passenger compartment into the passenger compartment [266]. The numerical simulation was intended to describe the hazards of both heat and toxicant gases in a numerical model of a post-crash fire in a minivan. The CFD model includes the turbulence controlled eddy break up model, conjugate heat transfer, radiant heat transfer, gas radiation, and buoyancy-driven airflow. The BURNSIM [258] model is used to simulate the passenger skin response. This model computes the depth (and hence the severity) of the burns produced by radiant and convective heating of the subject’s skin. This model is intended as a complement to the full-scale vehicle fire tests

¹² The hypothesis based on ‘final cause’ [268] is that a flame or fire will spread in such a manner that optimizes its consumption, under prevailing conditions, of the available oxidizer.

conducted by Santrock [260]: the model uses the full-scale experiments as ‘validation data’ but according to the authors ‘cannot exactly reproduce the experimental results.’ Experimental heat release data measured during an actual vehicle fire test served to calibrate the model combustion parameters and set the fuel input rate to mimic the experimental heat release rate curve. The model combustion products consisted only of CO, CO₂, soot and heat. The purpose of this model was primarily ‘to provide insight, not predictions of future behavior.’ In the simulations, the passenger compartment was modeled in its deformed state after the descriptions provided in previous crash tests. The fuel was metered into the compartment at a fixed rate: the metered fuel combined with oxidizer to form the compartment fire combustion process. The fire was well ventilated. The fire did not spread to other materials in the cabin and increasing the fuel metered into the cabin was the only means of enhancing fire growth. This appears to be a major shortcoming of the model, since experiments make it abundantly clear that numerous internal surfaces ignite readily to flame. Incapacitating conditions were reached between approximately 1–4 min, depending on the venting rate and heat production rate, which could be enhanced by metering more fuel or by preventing the issuance of the heated gases from upper-level vents (such as slightly opened windows, for example). Burn injuries were computed from a simplified burn simulation model that does not include effects of skin pigmentation, skin thickness, superficial hair, the flushing response and the cooling effect of perspiration. In addition, the skin was uncovered by clothing. The thermal insult to the skin surface produced a ‘response’ in the layers simulating the skin. A drawback of the model appears to be over-prediction, by nearly a factor of two, of the incident radiation. Nevertheless, the model indicated that hazardous conditions could readily be achieved when fuel supply rates produced compartment or cabin fires of magnitudes similar to those of experiments. The time scale was of the order of minutes.

6. Conclusions

This review has examined the selected literature of material flammability with focus on technical issues relevant to transportation-related fires. The review has been topically organized into technical subjects arising in fire progression. These include fire initiation, fire spread, and fire chemistry. Each of these subfields is broad and multifaceted, and contains numerous areas of overlap with the others. The necessity of having agreed-upon testing methods is apparent in each subfield. Tests to measure flammability properties have been developed, for example, the cone calorimeter. Other tests that measure flame spread rates and dynamic flame spread properties have also been devised but their utility and accuracy are lower than the cone

calorimeter. Tests for toxicity are varied and numerous so the literature of toxicology is vast and enormous, but a toxicity test that also accounts for fire hazard is not presently available. Measuring concentrations and specifying LC₅₀ indices in homogeneous test cells will not suffice to determine the actual threat posed by the tested chemical in an actual transportation fire. The toxicant must act in a certain, often restricted, time interval, which requires consideration of its transport and possible chemical reaction (and therefore consumption) by other present chemical species. Finally, full-scale testing for transportation is expensive and technically challenging although facilities are being constructed that have the capability for making useful technical measurements. If such tests are not carried out the assurance of fire safety can never be complete.

Acknowledgements

This research was supported by General Motors, under an agreement between GM and the US Department of Transportation. The author gratefully acknowledges the assistance of B. Mackie, M. Franklin, D. Rege, S. Hammerschmidt, N. Von Sprecken, and S. Tanaya, as well as the extensive, detailed, and helpful comments and criticisms of the PECS referees.

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